



# Oxydes métalliques et ionosilices templatés avec de la cellulose pour des applications dans l'énergie

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# THÈSE POUR OBTENIR LE GRADE DE DOCTEUR DE L'UNIVERSITÉ DE MONTPELLIER

En Chimie et Physico-Chimie des Matériaux

École doctorale Sciences Chimiques Balard

Unité de recherche : Institut Charles Gerhardt de Montpellier

## Cellulose shaped metal oxides and ionosilicas for energy applications

Présentée par Aurélien HENRY  
Le 24 novembre 2017

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## **Présentation du manuscrit**

Cette thèse débute par un chapitre introductif, dont l'objectif est de rappeler l'état de l'art concernant d'une part les diverses utilisations de la cellulose en chimie, et d'autre part les problématiques du stockage de l'énergie – en particulier concernant les batteries Li-ion et Na-ion. La présentation des méthodes de synthèse et des modes opératoires fait suite dans un deuxième chapitre. Le troisième chapitre est une synthèse en français de l'ensemble des résultats sur la minéralisation de la cellulose qui sont présentés en détail dans les articles scientifiques (en anglais) ; il inclura également quelques résultats non publiés. Ainsi, le quatrième chapitre rassemble les publications issues de ce travail de recherche. Un cinquième chapitre présente brièvement les investigations portant sur les ionosilices.

## **I – Introduction**

Le travail de recherche qui est exposé ici vise à explorer de nouvelles voies de synthèse de matériaux en développant l'utilisation des bio-ressources et en intégrant les problématiques d'un domaine d'application crucial pour le développement de notre société : le stockage de l'énergie. Au préalable nous aurons présenté quelques aspects de l'utilisation de la cellulose, essentiellement pour la préparation de matériaux. Nous terminerons en expliquant comment, au croisement de ces problématiques, il nous a semblé possible de proposer une voie originale et nouvelle de préparation de matériaux pour le stockage de l'énergie.

### **I.1 - De la cellulose à la conception de matériaux**

#### **I.1.1 - Source, composition et structure**

La cellulose, le polymère naturel le plus abondant sur terre, est produite par l'exploitation de la biomasse (agriculture ou exploitation forestière). Sa structure linéaire est constituée d'un enchaînement d'unités D-anhydroglucopyranose (AGU) reliées entre elles par des liaisons glycosidiques  $\beta$ -(1-4), le motif de répétition étant un dimère appelé cellobiose. Les fibres élémentaires ( $\approx$  1.5 à 3.5 nm), comprenant des parties cristallines et des parties amorphes, sont agrégées en microfibrilles ( $\approx$  5 à 50 nm), formant elles-mêmes les fibres de cellulose ( $\approx$  20  $\mu\text{m}$ ) (Fig. 1). L'origine de la cellulose influe sur la taille de ces fibrilles (modifiant ainsi les propriétés mécaniques et la réactivité), leur taux de cristallinité (impactant alors la solubilité et le module d'Young) ou encore la présence d'impuretés. On distingue les différents types de cellulose en fonction de la structure cristalline mettant en jeu les interactions faibles par liaisons H intra- ou intermoléculaire.

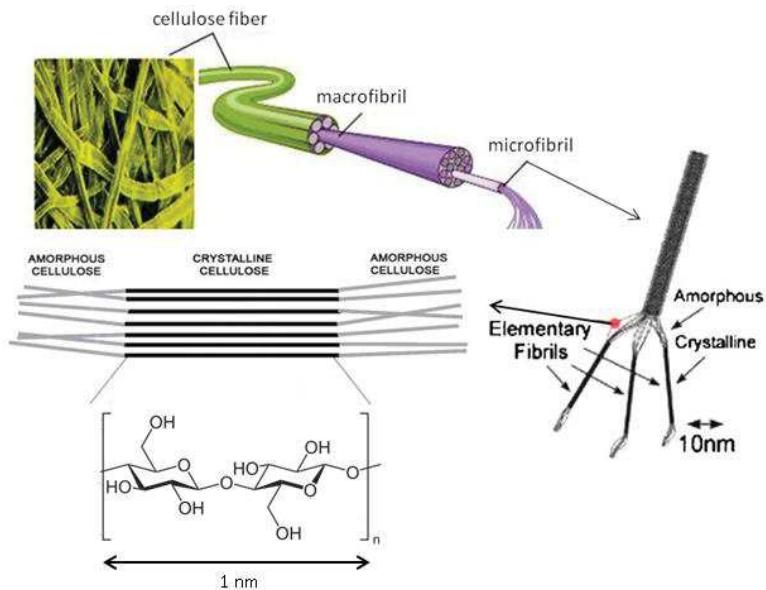


Fig. I.1 : Structure de la cellulose<sup>1-2</sup>

Cette structure cristalline, dont certains profils de diffraction sont présentés dans la Fig. I.2, peut varier de manière assez significative selon l'organisme qui la produit et peut être modulée par des processus chimiques ; elle détermine également une part importante des propriétés de la cellulose. On peut ainsi distinguer quatre types de cellulose, classés à la fois en fonction de leur méthode de préparation et de leur structure.

Au sein de la cellulose native – non traitée, isolée par broyage mécanique – peuvent être distingués deux allomorphes en proportions variables selon l'espèce dont elle est extraite : il s'agit des formes  $I_\alpha$  et  $I_\beta$  de la cellulose. La forme  $I_\alpha$  est majoritaire dans la cellulose provenant d'algues ou de bactéries, tandis que la forme  $I_\beta$  est présente en proportion plus importante dans le bois et le coton. La différence entre ces deux allomorphes est inhérente au mécanisme physiologique de la production de cellulose par les cellules. Tous les échantillons de cellulose utilisés dans cette thèse sont des échantillons de cellulose native (un mélange de cellulose  $I_\alpha$  et  $I_\beta$ ).

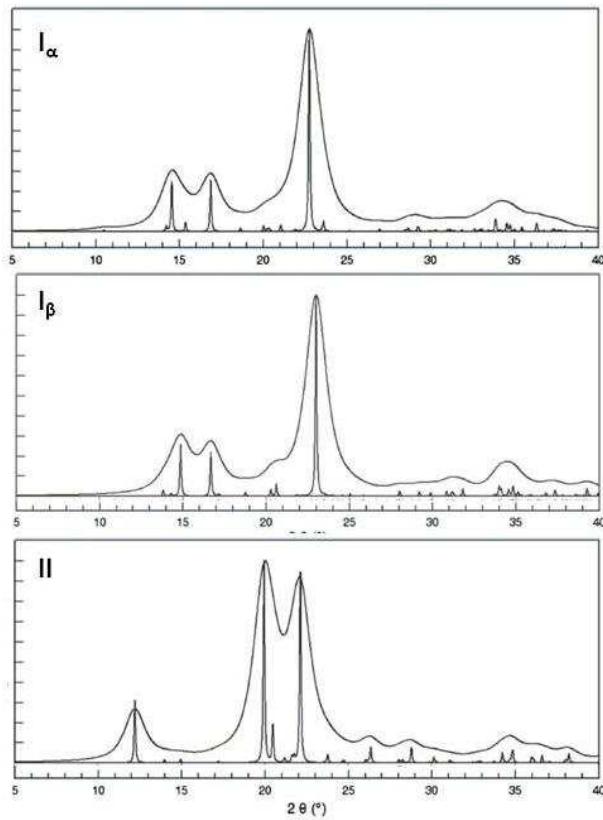


Fig. I.2 : Diffractogrammes simulés des celluloses  $I_\alpha$ ,  $I_\beta$  et  $II^3$

La cellulose de type II est désignée sous le nom de cellulose régénérée ; elle est obtenue par mercerisation ou dissolution-représécitation de la cellulose native. Il s'agit d'un traitement irréversible, qui permet cependant d'éliminer les impuretés potentiellement présentes dans la cellulose native. Les celluloses de type  $III_I$  et  $III_{II}$  sont obtenues à partir des celluloses I et II, respectivement, par traitement à l'ammoniac liquide. Cette étape est réversible, par immersion dans l'eau bouillante. Enfin, les celluloses  $IV_I$  et  $IV_{II}$  sont obtenues par traitement des celluloses  $III_I$  et  $III_{II}$  à chaud dans le glycérol. On peut retransformer la cellulose  $IV_I$  en cellulose I (ou de la cellulose  $IV_{II}$  en cellulose II) par une immersion dans une solution acide à ébullition. Ces méthodes de transformation sont résumées sur la Fig. I.3.

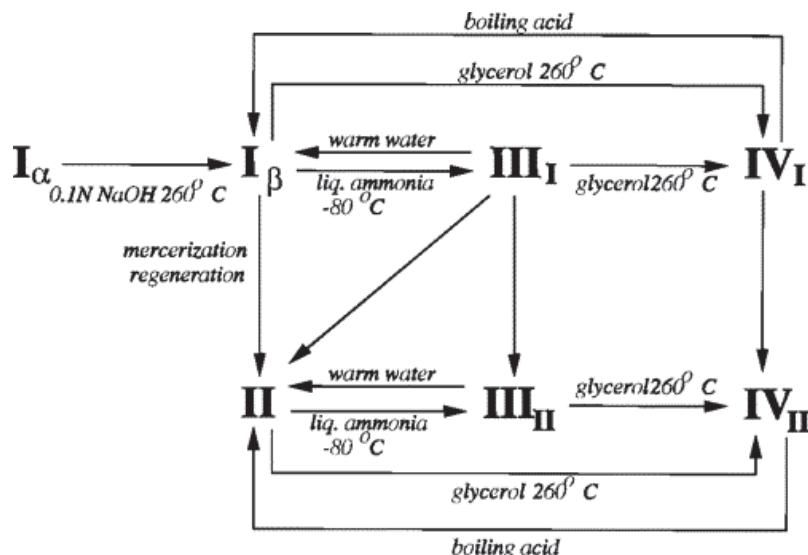


Fig. I.3 : Les différents allomorphes de cellulose et leurs voies de transformation<sup>4</sup>

D'autres traitements physico-chimiques peuvent également modifier les propriétés de la cellulose en conservant sa structure cristalline. Ainsi, un traitement en milieu acide contrôlé ( $H_2SO_4$  dilué) conduit à une hydrolyse préférentielle des parties amorphes libérant ainsi les parties cristallines, les nanocristaux de cellulose (CNC), de forme cylindrique ( $\approx 100 \times 5 \text{ nm}$ ) et hautement cristallins.

Dans le domaine des nanocelluloses, on trouve également la cellulose microfibrillée (MFC). Elle est obtenue par un traitement mécanique produisant la délamination partielle des fibres pour conduire à des fibres de taille sub-micrométrique ( $10 < \varnothing < 100 \text{ nm}$ ,  $1 < L < 10 \mu\text{m}$ )<sup>5</sup> constitutives des microfibrilles. Après un séchage par lyophilisation dans un mélange eau/*tert*-butanol (70/30 V:V), on obtient un aérogel dont les nanofibres sont relativement bien séparées les unes des autres. Un troisième type de nanocellulose, la cellulose bactérienne (BC) tient une place spécifique de par ses caractéristiques (grande pureté et morphologie) et son mode d'obtention. Résultant de l'activité de bactéries, la plus populaire étant *Acetobacter xylinum*, la cellulose bactérienne présente une taille et un diamètre de fibre très homogènes ( $20 < \varnothing < 60 \text{ nm}$ ,  $1 < L < 10 \mu\text{m}$ ).<sup>6</sup> Comme pour la MFC, les aérogels de BC nécessitent un procédé de lyophilisation utilisant l'eutectique eau/<sup>t</sup>BuOH.

A côté des nanocelluloses BC et MFC dont nous avons pu tester la réactivité, nous avons principalement utilisé le papier filtre sans cendres (FP), un produit commercial, standardisé et exempt de composés inorganiques qui pourraient interférer avec les traitements que nous envisagions (la quantité de cendre est de 0.002 % après calcination à 800 °C). Il présente des fibres bien plus massives que les nanocelluloses ( $5 < \varnothing < 50 \mu\text{m}$  et  $0.2 < L < 2 \text{ mm}$ ). Les résidus du papier après calcination représentent donc des quantités négligeables de cendres, qui n'influencent pas le résultat des analyses qualitatives. La Fig. I.4 permet de comparer les morphologies de ces trois types de celluloses.

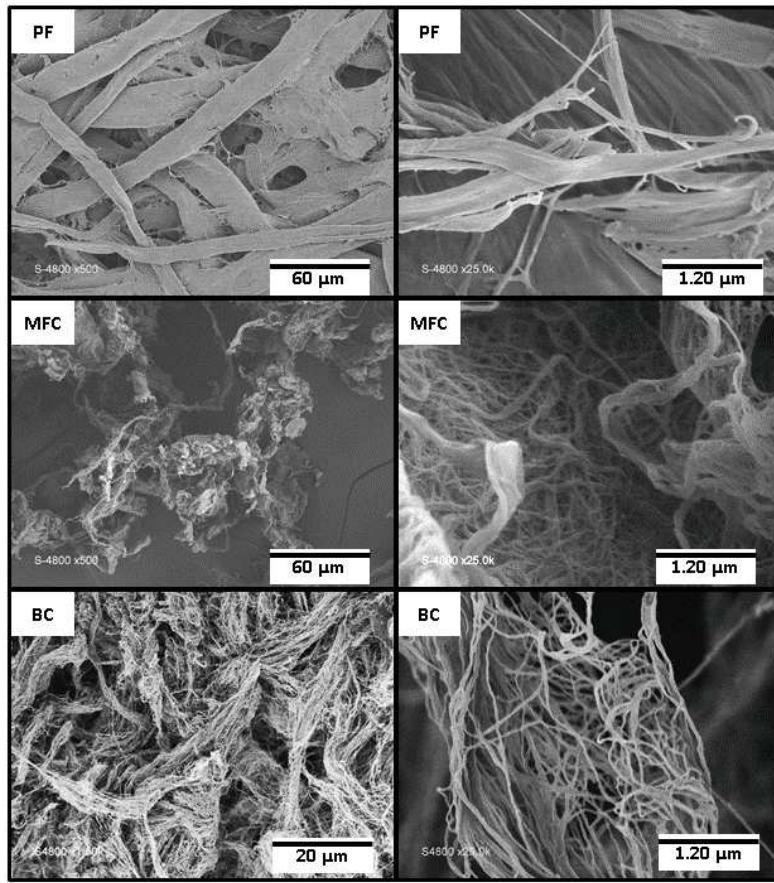


Fig. I.4 : Images MEB des celluloses utilisées dans cette thèse  
Papier filtre (PF), cellulose micro-fibrillée (MFC) et cellulose bactérienne (BC)

### I.1.2 – Quelques usages de la cellulose en chimie

Sans s'étendre sur les usages du bois, utilisé depuis des millénaires comme source d'énergie ou matériau de construction (isolant, emballage, composites, ...), la cellulose est un polymère dont l'utilisation est basée sur ses propriétés mécaniques, sa relative stabilité et son insolubilité dans la plupart des solvants classiques, et notamment l'eau. Dans des conditions douces de pH, la cellulose est relativement stable en milieux aqueux et cette stabilité est suffisamment élevée pour permettre son utilisation en filtration ou en chromatographie standard. Cependant, les fonctions chimiques et la structure de la cellulose présentent un très fort potentiel de transformation chimique qui a très tôt attiré les chimistes, dans la perspective de nouvelles applications, telles que cela est présenté sur la Fig. I.5.

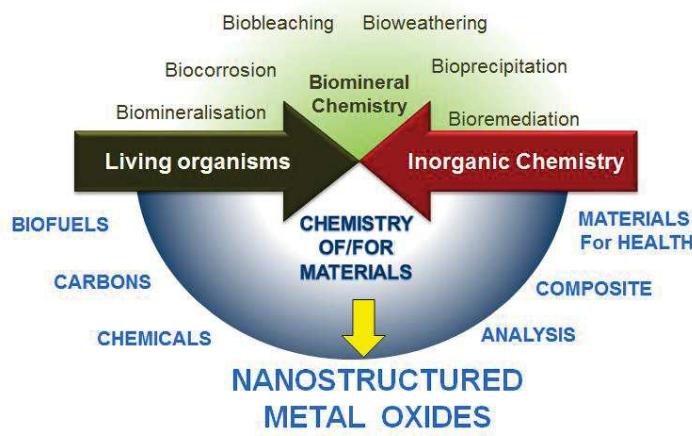


Fig. I.5 : Domaines de recherche comprenant l'utilisation de cellulose<sup>7</sup>

La conception de fibres textiles est un bon exemple des possibilités offertes par la cellulose. Le procédé viscose conduit à la fibre textile portant le même nom en passant par des intermédiaires xanthate ; la sulfuration des fonctions alcools  $\text{C}-\text{O}-\text{H} \rightleftharpoons \text{C}-\text{O}^-\text{Na}^+ + \text{CS}_2 \rightleftharpoons \text{C}-\text{O}-\text{CS}_2^- + \text{Na}^+$  produit ainsi un polyélectrolyte nommé viscose et ouvre la voie à la préparation de la rayone et des cellophanes (Fig. I.6).

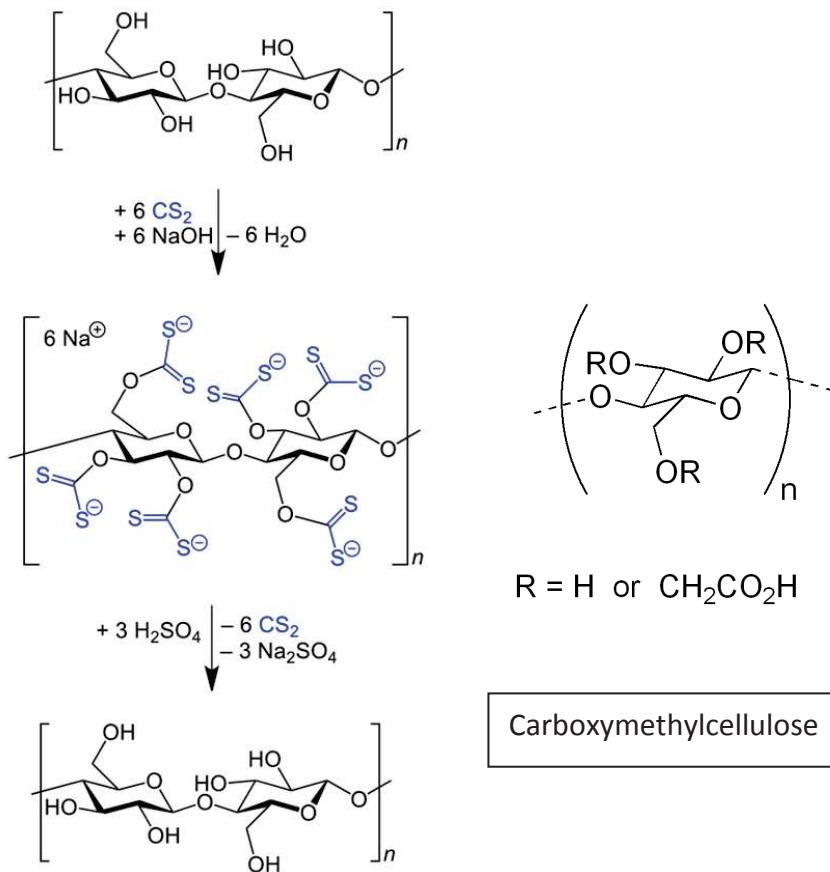


Fig. I.6 : Modification de la cellulose en viscose, puis traitement acide aboutissant à la fibre de rayone ;<sup>8</sup> formule chimique de la carboxymethylcellulose (CMC)

La carboxymethylcellulose (CMC) est un autre exemple de modification fonctionnelle simple : la réaction en milieu alcalin entre la cellulose et l'acide chloroacétique permet d'obtenir un matériau soluble dans l'eau aux multiples applications industrielles. La modification fonctionnelle peut ensuite servir de base pour développer une suite réactionnelle, la cellulose assurant les propriétés mécaniques du composé final.

Egalement basé sur la réactivité de la cellulose, le raffinage (ou bioraffinerie dans la littérature) est un autre aspect de la chimie de la cellulose. Ce domaine, en plein essor et extrêmement vaste, présente plusieurs liens avec le sujet de nos travaux car il mobilise certains aspects de la réactivité de la cellulose et utilise également des composés inorganiques. Le raffinage de la cellulose pour la production de synthons organiques vise la rupture des chaînes glycosidiques par hydrolyse conduisant à une dépolymérisation de la cellulose en unité sucre (glucose, fructose, ...), avec des rendements pouvant aller jusqu'à 74% en masse. Simultanément, le HMF (hydroxymethylfurfural) peut par exemple être obtenu par hydrolyse/déshydratation de la cellulose.<sup>9</sup> Pour catalyser ces processus, de nombreux dérivés des métaux de transition, notamment des oxydes, sont régulièrement rapportés dans la littérature, dont certains que nous retrouverons plus loin dans cette thèse.

Toujours à l'interface entre chimie inorganique et cellulose, on peut citer que cette dernière a été utilisée comme template (ou support) dans l'élaboration des oxydes métalliques par des procédés de chimie douce. Au tournant des années 1990, dans la mouvance des procédés sol-gel, sont apparus les premiers travaux visant à maîtriser la porosité (en terme de surface spécifique et de volume poreux), voire la structure cristalline de l'oxyde métallique par la présence de biopolymères tels que la cellulose. Dans la lignée des travaux sur les silices mésoporeuses utilisant un tensio-actif de synthèse, la cellulose a été utilisée comme un support de croissance sacrifiable et facilement éliminable par calcination.<sup>7</sup>

### **I.1.3 - La cellulose, précurseur de carbone**

L'oxydation thermique de la cellulose est une source de production d'énergie largement utilisée dans le monde.<sup>10</sup> On peut également traiter thermiquement la cellulose sous argon ou sous azote afin de former du carbone. Utilisée par l'Homme depuis la nuit des temps, pour la production de charbon de bois ou encore le durcissement des piques par un traitement thermique maîtrisé, cette transformation requiert un contrôle des conditions expérimentales, qui ne doivent surtout pas être oxydantes. Sur le principe, la transformation est une déshydratation qui s'opère, dans le cas idéal, sans changement du degré d'oxydation (DO) moyen du carbone. Le DO, initialement de 0 pour les fonctions majoritaires dans les carbohydrates ( $-\text{CH}(\text{OH})-$ ), est toujours de 0 pour les carbones d'un graphite ou du diamant. Les traitements thermiques non oxydatifs qui se sont développés récemment ont deux finalités, qui peuvent se rejoindre par certains aspects : d'une part la production d'huiles, de composés volatils et de gaz utilisables comme combustibles et plus facilement stockables que le bois ; d'autre part la formation de carbones pour des applications diverses (filtration/purification, électrochimie, catalyse, etc.).

La pyrolyse de la cellulose implique de chauffer à des températures importantes, de 750 à 1500 °C, pour parvenir à une carbonisation correcte. Ce traitement est très sensible aux conditions expérimentales : la modulation des différents paramètres que sont la température, la rampe (ou vitesse de montée en température) ou le débit de gaz permet de modifier les propriétés du matériau obtenu. Ainsi, il a été montré que la proportion des différents résidus (gaz, composés volatils, huiles) dépend principalement de la vitesse de chauffe, une pyrolyse lente favorisant la formation de composés solides alors que la pyrolyse rapide (rampe > 100 K.min<sup>-1</sup>) ou la pyrolyse flash (pyrolyse réalisée en quelques secondes) sont au contraire utilisées pour la production de composés liquides ou gazeux.<sup>11</sup> Le choix des conditions expérimentales est donc prépondérant : si les conditions de pyrolyse rapide ou flash sont en particulier adaptées à la synthèse de biofuel ou de syngaz, elles sont en revanche inadaptées pour la synthèse de matériaux carbonés solides.

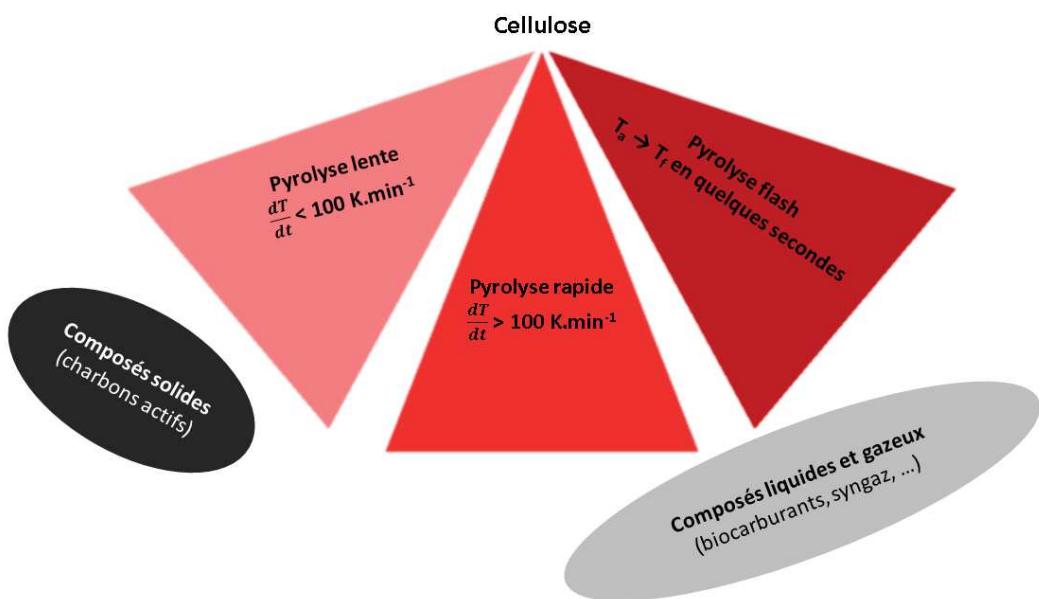


Fig. I.7 : Résumé des différents types de pyrolyse

Les études sur la pyrolyse lente se portent surtout sur la production de charbon actif, une poudre amorphe majoritairement composée de carbone et possédant une surface spécifique élevée – jusqu'à 2500 m<sup>2</sup>.g<sup>-1</sup>.<sup>12</sup> Pour obtenir des surfaces spécifiques aussi élevées, la pyrolyse de la cellulose doit être activée chimiquement (par l'ajout de réactifs tels que KOH, H<sub>3</sub>PO<sub>4</sub> ou ZnCl<sub>2</sub>) ou physiquement (par l'utilisation d'un flux de gaz, les plus utilisés étant H<sub>2</sub>O et CO<sub>2</sub>). Plus récemment, l'auto-activation de la cellulose par pyrolyse lente a été rapportée, le point-clé de cette étude étant le flux d'argon utilisé :<sup>13</sup> en diminuant le flux d'argon jusqu'à 10 cm<sup>3</sup>.min<sup>-1</sup>, la surface spécifique du charbon actif peut être augmentée. Les gaz émis par la dégradation de la cellulose semblent être responsables de l'activation dans ce dernier cas.

A côté de ces traitements thermiques « classiques », la dégradation thermique de la cellulose en présence d'eau est également un domaine très étudié. Initialement inspirées par le phénomène bien connu de « caramélisation » du sucre, les recherches ont d'abord porté sur l'évolution du glucose dans

des conditions de température et de pression similaires à celles utilisées pour les réactions hydrothermales de synthèse des oxydes métalliques et des zéolites. Ces expériences ont montré la possibilité de former des nanoparticules de carbone, ou « nanodots »,<sup>14</sup> particulièrement attractives pour leurs propriétés de photoluminescence ou leur surface spécifique élevée. Dans le prolongement logique de ces travaux, la dégradation de la cellulose par carbonisation hydrothermale<sup>15</sup> représente une voie alternative d'obtention de carbone. La cellulose est ici dégradée à une température plus basse que lors de la pyrolyse (<200 °C), mais sous pression. Menée en autoclave en suspension aqueuse, et selon des pH variables, cette technique conduit à des matériaux carbonés de différentes tailles et formes (monolithes, nanotubes, sphères creuses, ...).<sup>15</sup> Les matériaux carbonés obtenus par carbonisation hydrothermale ont une surface spécifique inférieure au charbon activé, mais leur fabrication est moins énergivore.<sup>16</sup> De plus, un pré-traitement de la cellulose ou l'ajout de réactifs dans l'eau permettent de moduler la morphologie ou la composition chimique du matériau obtenu. L'ovalbumine est par exemple utilisée pour contrôler la texture du matériau carboné et fournir des fonctions azotées (pyrroles et amines).<sup>16</sup>

## **I.2 - Le stockage de l'énergie**

### **I.2.1 – Du stockage de l'énergie aux batteries**

Le stockage de l'énergie est un enjeu important pour nos sociétés, et d'autant plus grand avec la transition énergétique engagée en France<sup>17</sup> et dans le monde.<sup>18</sup> On parle de stockage de l'énergie lorsque de l'énergie (le plus souvent électrique) fournie à un système peut être récupérée ultérieurement. Il existe différentes formes de stockage de l'énergie, chacune ayant ses caractéristiques propres. Notons que le seul stockage de matière combustible (pétrole, gaz) ne constitue pas un moyen de stockage de l'énergie, ces carburants étant des sources d'énergie primaire.<sup>19</sup> Le stockage gravitaire de l'énergie est notamment utilisé dans les stations de transfert d'énergie par pompage (ou STEP), systèmes combinant plusieurs bassins de rétention d'eau reliés par des systèmes de pompage (apport d'énergie) et de turbinage (récupération de l'énergie stockée). Le stockage inertiel de l'énergie est utilisé dans les volants d'inertie<sup>20</sup> pour stocker l'énergie grâce au moment d'inertie d'un axe en rotation. Le stockage thermique repose soit sur l'utilisation de matériaux ayant une grande résistance thermique (pour un stockage par chaleur sensible, on emmagasine de la chaleur par un changement de température),<sup>21</sup> soit sur le changement d'état du matériau de stockage (pour un stockage par chaleur latente, on emmagasine de la chaleur par changement d'état).<sup>22</sup> Enfin, le stockage électrochimique de l'énergie se divise en deux catégories : d'une part le stockage par accumulateurs (batteries, condensateurs) basé sur des réactions d'oxydo-réduction, et d'autre part la pile à combustible, qui utilise la réaction d'électrolyse de l'eau (l'énergie étant stockée sous forme d'hydrogène).<sup>23</sup>

Parmi les différentes formes de stockage de l'énergie, le stockage électrochimique par batteries (utilisant des réactions d'oxydoréduction réversibles) est le seul à pouvoir s'adapter à différentes échelles – depuis les dispositifs électroniques portables jusqu'à la régulation de réseaux nationaux.<sup>24</sup> En conséquence, les batteries connaissent une forte demande, appelée à s'amplifier avec l'augmentation du nombre de dispositifs électroniques (du smartphone jusqu'au véhicule électrique)

et le développement de sources d'énergie intermittentes (éolien et solaire). Les batteries commercialisées aujourd'hui sont principalement basées sur la technologie Lithium-ion, et la ressource mondiale en lithium est à la fois limitée et circonscrite à quelques pays.<sup>25</sup> L'éventualité de difficultés d'approvisionnement en lithium – ou d'une augmentation insoutenable des prix – a relancé l'intérêt pour d'autres technologies.

La principale alternative étudiée est l'utilisation d'autres ions que le lithium comme porteurs de charge : le sodium fait l'objet d'un intérêt accru ces cinq dernières années, et des études sur le magnésium ou le calcium existent également. Mais les systèmes utilisant ces ions, s'ils utilisent le même concept que les batteries lithium-ion, mettent en œuvre des mécanismes différents. Le développement de matériaux d'électrodes et d'électrolytes adaptés est donc nécessaire pour explorer ces voies et les connaissances acquises lors des recherches sur les systèmes Li-ion ne sont pas directement transposables pour la conception de ces nouveaux matériaux. En revanche, il est possible de s'appuyer sur l'expérience acquise quant à l'interprétation des courbes électrochimiques (pics de réaction d'oxydo-réduction (rédox) en cyclovoltamétrie, plateau d'insertion en galvanométrie) pour comprendre les phénomènes en jeu.

### **I.2.2 – Fonctionnement d'une batterie lithium-ion**

Une batterie lithium-ion (Li-ion) est un dispositif de stockage de l'énergie constitué d'une superposition d'accumulateurs. Son fonctionnement ne doit pas être confondu avec celui d'une pile chimique, même s'ils utilisent tous deux des réactions d'oxydo-réduction pour délivrer un courant électrique.

Une batterie Li-ion fonctionne grâce à la circulation des ions  $\text{Li}^+$ . Elle est constituée de deux électrodes déposées sur des collecteurs de courant et séparées par un séparateur. L'électrolyte, en contact avec les deux électrodes, est le milieu qui permet la circulation des ions. Dans la plupart des systèmes, l'électrolyte est une solution organique de sel de lithium ou de sodium ( $\text{LiPF}_6$  ou  $\text{NaClO}_4$ )<sup>26</sup> qui imprègne le séparateur et les électrodes. Des études portant sur des électrolytes alternatifs (liquides ioniques ou polyélectrolytes solides jouant également le rôle de séparateur)<sup>27</sup> existent, mais présentent un coût et des inconvénients spécifiques qui limitent leur développement.

Contrairement à une pile chimique, une batterie est rechargeable. Les électrodes doivent donc pouvoir stocker et relâcher les ions porteurs de charge, de façon réversible. Chaque électrode est alternativement le siège de réactions de réduction (quand le porteur de charge intègre l'électrode) et d'oxydation (quand le porteur de charge est libéré). D'un point de vue chimique, il est donc inexact de parler d'anode ou de cathode, chaque chacune se trouvant successivement dans l'une ou l'autre configuration. Il s'agit là d'un abus de langage, dérivé des piles chimiques, qui consiste à parler d'anode pour la borne négative du dispositif et de cathode pour la borne positive. Dans le cas d'une batterie, on préfèrera parler d'électrode négative et d'électrode positive.

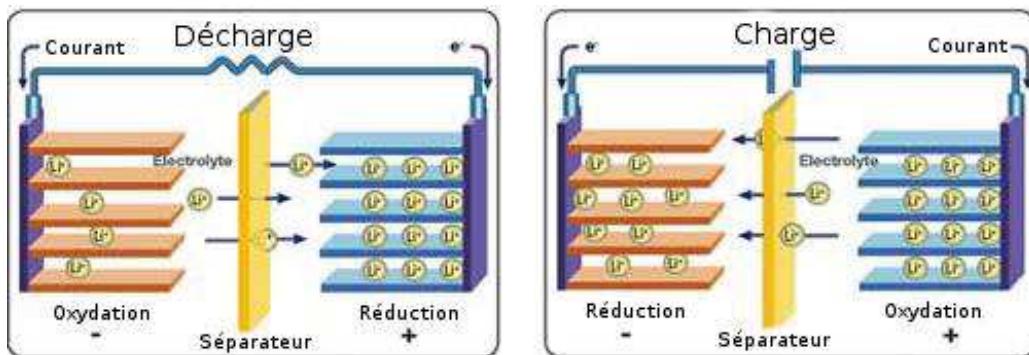


Fig. I.8 : Schéma de fonctionnement d'une batterie Lithium-ion<sup>28</sup>

Les performances des matériaux d'électrodes, qu'ils soient utilisés en électrode positive ou en électrode négative, sont évaluées en fonction de plusieurs critères, déterminés principalement par des mesures de cyclage galvanostatique. Pour ces mesures, effectuées en demi-pile (le matériau étudié formant une électrode, un disque de lithium formant l'autre), on impose un courant au système et on enregistre le potentiel entre deux bornes, avant de changer le signe du courant pour inverser le fonctionnement du système. L'intervalle entre ces deux potentiels est appelé la "fenêtre de travail" du système. La quantité de charges électriques échangées par les électrodes lors du fonctionnement de la batterie peut être quantifiée ; nommée "capacité", elle est exprimée en A.h. On la calcule en multipliant le courant imposé au système par le temps nécessaire pour passer de l'une des bornes de potentiel à l'autre (on parle de décharge si  $\Delta E < 0$  et de charge si  $\Delta E > 0$ ). Afin de comparer des électrodes différentes entre elles, on préfère utiliser la capacité spécifique, rapportée à la masse de matériau utilisée ; on l'exprime habituellement en mA.h.g<sup>-1</sup>. La Fig. I.9 montre deux représentations de la même mesure galvanostatique.

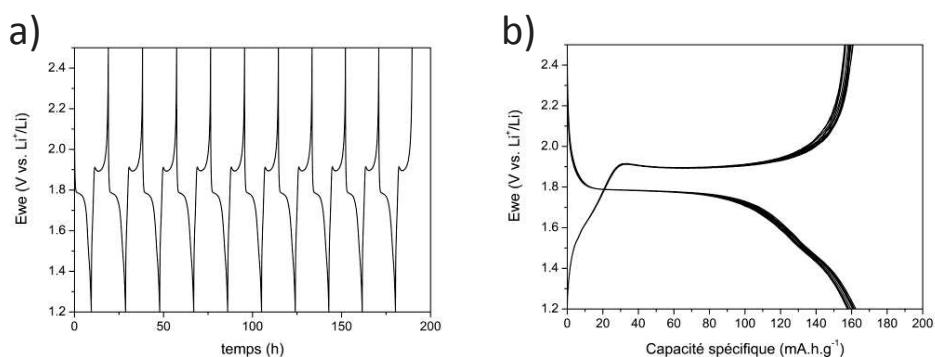


Fig. I.9 : Galvanogrammes d'une électrode de TiO<sub>2</sub> en fonction soit a) du temps, soit b) de la capacité spécifique

### I.2.3 - Les matériaux d'électrode

À l'intérieur de la batterie, le déplacement des charges électroniques est lié à celui des ions  $\text{Li}^+$ ; ceux-ci sont transférés d'une électrode à l'autre pendant le fonctionnement du système. Ce transfert, dont le support est l'électrolyte, aboutit au stockage réversible des  $\text{Li}^+$  dans les électrodes. Il existe pour cela plusieurs mécanismes différents, dont la compréhension nécessite de s'intéresser à la structure des matériaux d'électrode.

Dans les matériaux d'insertion – qui sont le plus souvent des oxydes métalliques ou des matériaux carbonés (le graphite en particulier) – les  $\text{Li}^+$  sont stockés dans les sites interstitiels des mailles cristallines. Il s'agit donc d'une insertion d'ions, sans modification de structure cristalline. On peut néanmoins observer une variation des paramètres de maille, due à la contraction engendrée par la réorganisation des orbitales moléculaires, ou un changement de groupe d'espace, lorsque l'occupation de certains sites interstitiels altère la symétrie du cristal, comme on le voit dans la Fig. I.10.

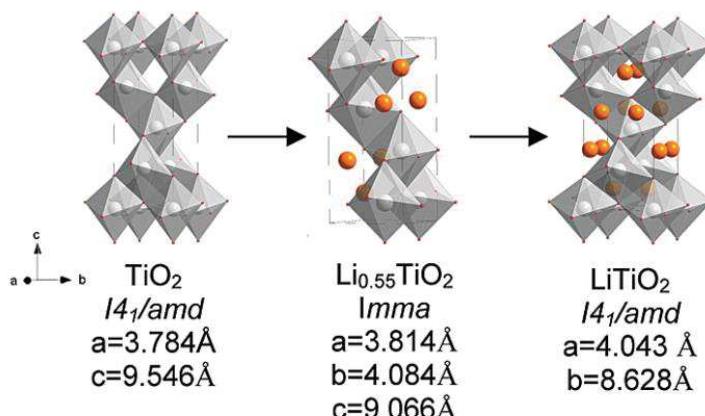


Fig. I.10 – Transition de phase lors de l'insertion du Li dans le  $\text{TiO}_2$  anatase  
(gris : Ti, rouge : O, orange : Li)<sup>29</sup>

Cette insertion passe par une réaction dite biphasique lorsqu'on passe d'une phase non lithiée à une phase lithiée. Cette transition est progressive au sein du matériau, les particules étant lithiées les unes après les autres. On observe donc la coexistence de deux phases cristallines, identifiable sur les galvanogrammes par un plateau dit "d'insertion", tel que présenté dans la Fig. I.11.

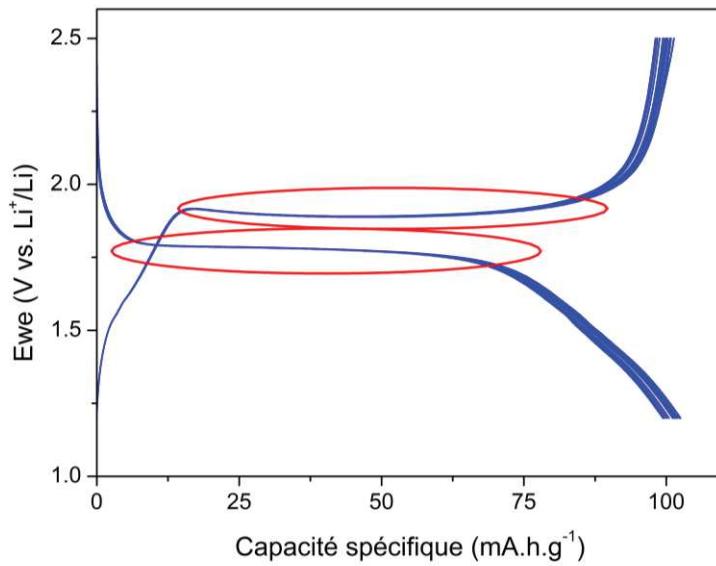


Fig. I.11 : Galvanogramme d'une électrode de  $\text{TiO}_2$  présentant un plateau d'insertion typique

Pour les composés d'insertion, on doit ainsi partir d'un matériau  $\text{MO}_n$  pour arriver à un  $\text{LiMO}_n$  si tous les sites sont occupés. On utilise alors la notation  $\text{Li}_x\text{MO}_n$  pour décrire l'état d'avancement du processus d'échange.

Il existe également des matériaux de conversion, dont le fonctionnement est moins intuitif : dans leur cas, le stockage des ions  $\text{Li}^+$  dans le matériau entraîne un changement important de sa structure. De plus, la réaction de conversion est une réaction rapide ; dans le cas de l'oxyde de fer  $\text{FeO}$ , par exemple, la réaction de conversion est  $\text{FeO} + 2 \text{Li}^+ + 2 \text{e}^- \rightleftharpoons \text{Li}_2\text{O} + \text{Fe}$ ,<sup>30</sup> et cette réaction a lieu dès les premiers instants de la conversion. Elle se produit cependant de façon hétérogène dans le matériau, si bien qu'il n'est pas possible de définir un ordre à grande échelle – donc, il n'y a pas de phase cristallographique identifiable – avant que la conversion ne soit totale pour l'ensemble du matériau. La structure des matériaux de conversion ne peut donc être définie qu'au début ou à la fin d'une (dé)charge.

Enfin, les matériaux dits “alliages” tels que l'étain ou l'antimoine procèdent à un stockage par une succession de changements de phases, formant successivement plusieurs alliages lithiés (Cf. Fig. I.12). En conséquence, on passe alors par une succession de réactions redox pour incorporer les  $\text{Li}^+$  au matériau. Ce mécanisme permet aux alliages d'incorporer plus d'ions  $\text{Li}^+$  que les autres types de matériaux d'électrode, et donc de développer des capacités spécifiques supérieures. Cependant, il occasionne aussi d'importantes variations du volume de l'électrode, ce qui soumet le système à des contraintes mécaniques à chaque cycle. Ce changement de volume est l'inconvénient majeur des alliages comme matériaux de batterie, qui freine leur développement malgré des performances supérieures à celles d'autres types de matériaux.

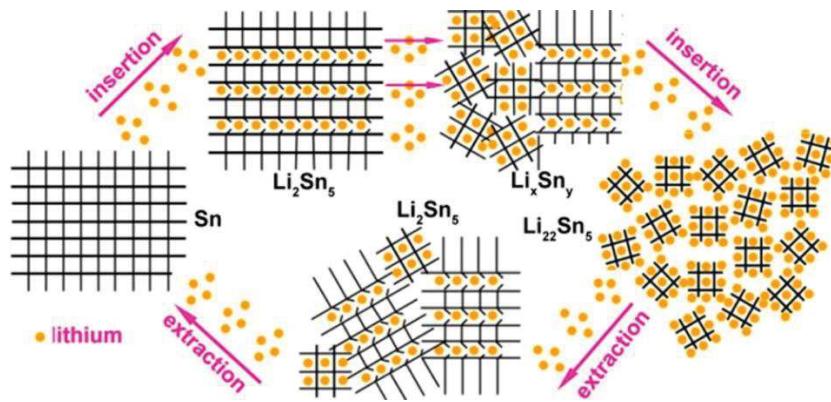


Fig. I.12 : Résumé du cycle de lithiation/délithiation de Sn. Les structures cristallines et les Li sont représentés par les matrices carrées et les points, respectivement<sup>31</sup>

C'est sur ces considérations de nature des phases cristallines qu'est basée la valeur "x", représentant la quantité de  $\text{Li}^+$  stocké par rapport à la quantité de matériau d'électrode. Il s'agit là de la même valeur que le  $\text{Li}_x\text{MO}_n$  évoqué pour les composés d'insertion mais, pour les alliages et les composés de conversion, il ne s'agit que d'un formalisme. En particulier, pour les matériaux de conversion, il n'existe pas de phase cristalline correspondant à cette notation. L'intérêt de cette notation est qu'elle permet de définir une capacité spécifique de référence pour chaque matériau, en fonction de la masse molaire de celui-ci. Nommée capacité théorique, sa valeur correspond au stockage d'une quantité définie de  $\text{Li}^+$  (qui dépend de la quantité maximale de lithium stockable par maille cristalline,  $\Delta x = 1$  pour  $\text{TiO}_2$ ) dans une mole d'un matériau actif de masse molaire connue.

$$Q_m = \frac{\Delta x \times F}{3.6 \times M_{ma}}$$

$Q_m$  capacité spécifique( $\text{mA.h.g}^{-1}$ ),  $\Delta x$  nombre d'électrons échangés,  $F$  constante de Faraday ( $\text{A.s.mol}^{-1}$ ),  $M_{ma}$  masse molaire du matériau actif ( $\text{g.mol}^{-1}$ )

Lors d'un cyclage galvanostatique, on choisit le courant appliqué à l'électrode étudiée d'après la capacité théorique du matériau qui la compose et la masse de matière active utilisée. On définit le régime de cyclage  $\frac{C}{N}$  comme le rapport entre la capacité théorique de l'électrode C et le nombre N d'heures nécessaire pour une (dé)charge complète. Pour déterminer le courant à appliquer à un régime de  $\frac{C}{N}$ , on applique donc l'équation  $I = \frac{C}{N}$ . Si le courant appliqué est caractéristique de l'électrode étudiée (puisque dépendant de la masse de matériau), le régime décrit seulement la cinétique étudiée. On utilise donc le régime pour décrire les conditions expérimentales afin de comparer des mesures entre elles.

Les galvanogrammes de la Fig. I.9 sont repris dans la Fig. I.13, au côté d'un graphe montrant le tracé selon x dans  $\text{Li}_x\text{TiO}_2$  (Fig. I.13-c). La Fig. I.13d représente les résultats d'une mesure galvanostatique effectuée à plusieurs régimes successifs. On cherche alors à comparer les capacités spécifiques aux

différents régimes, ainsi que la réversibilité du phénomène. Pour ce dernier point, on utilise l'efficacité coulombique, qui représente la proportion de charges restituées par rapport aux charges fournies. Exprimée en pourcentage, on la calcule par le rapport entre la capacité en oxydation et la capacité en réduction ( $\eta = \frac{C_{oxydation}}{C_{réduction}}$ ). Pour plus de clarté, les graphes des mesures en régime variable (ou C-rate) présentent seulement les capacités (en réduction et en oxydation) ainsi que l'efficacité coulombique, pour chaque cycle.

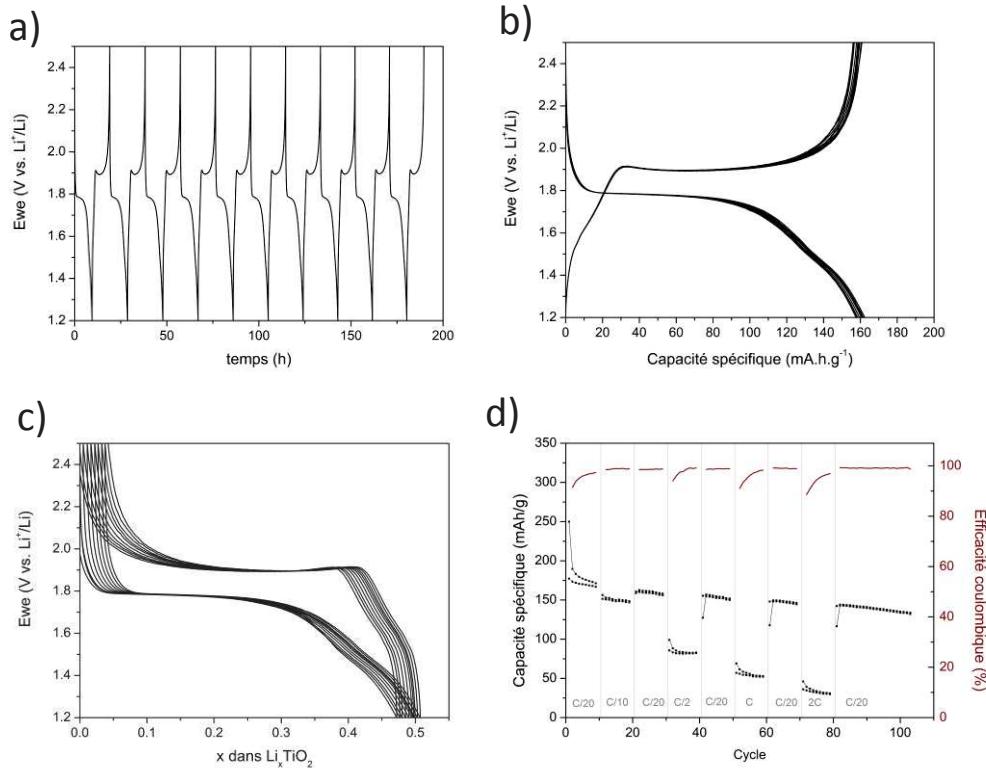


Fig. I.13 : Galvanogrammes d'une électrode de TiO<sub>2</sub> en fonction a) du temps, b) de la capacité spécifique et c) de x dans Li<sub>x</sub>TiO<sub>2</sub> ; d) capacité spécifique et rendement faradique en fonction du cycle

Malgré les récentes avancées dans le domaine des matériaux d'électrodes, plusieurs axes d'amélioration et/ou problèmes majeurs restent à étudier. Les performances des matériaux, dans leur ensemble, doivent être améliorées afin de répondre aux exigences futures : les capacités spécifiques des matériaux doivent être augmentées, une meilleure cyclabilité (i.e. l'aptitude du matériau à résister à un nombre important de cycles charge-décharge, sans perte d'efficacité coulombique) est nécessaire, tout comme l'efficacité en elle-même. Mais la recherche des performances n'est pas le seul aspect à prendre en compte. Les considérations de sécurité ont une place toujours plus importante dans un monde où les incidents sont très vite médiatisés, et la mise au point de procédés de production durable prend une importance à la fois sociale et économique. Enfin, la raréfaction attendue de la ressource en lithium encourage le développement de matériaux utilisables avec des métaux légers alternatifs.

## **Contexte et objectifs de cette thèse**

Dans le contexte général que nous venons d'exposer, nous avons initialement envisagé deux axes de travail, l'un sur la formation d'oxydes métalliques et de composites oxyde métallique/carbone par minéralisation de la cellulose, l'autre sur la préparation de polyélectrolytes par modification chimique de la cellulose dans des solutions de liquides ioniques. La seconde approche s'est révélée plus complexe et, si ses résultats présentent un fort potentiel, ils sont à ce jour trop incomplets et n'ont pu être finalisés sous forme de publication. Nous les présenterons brièvement en Annexe.

Concernant la formation d'oxydes métalliques et de composites oxyde métallique/carbone, les objectifs de cette thèse portaient sur l'approfondissement général des travaux menés précédemment, dans trois directions principales : montrer la possibilité de travailler avec des celluloses de taille nanométrique, montrer la généralisation de l'approche à la préparation d'autres oxydes métalliques, identifier les processus chimiques et physiques qui interviennent durant la minéralisation de la cellulose. Parallèlement, nous avons cherché à caractériser le comportement électrochimique des matériaux pour en montrer la pertinence et le potentiel.

Faisant suite aux travaux de R. Nair<sup>32-33</sup> et en parallèle avec ceux développés par S. Plumejeau dans le cadre de sa thèse portant sur des membranes photocatalytiques, nous avons exploré la minéralisation des celluloses sub-micrométriques MFC par TiCl<sub>4</sub>. Nous avons ainsi pu montrer la possibilité de préparer des matériaux d'électrode négative de batteries lithium-ion : des composites TiO<sub>2</sub>/C. Par ailleurs, toujours dans la perspective de matériaux d'électrode TiO<sub>2</sub>/C, nous avons montré l'effet d'une imprégnation du papier par l'urée, avec ses conséquences sur la morphologie du TiO<sub>2</sub> et sur les propriétés du carbone issu de la pyrolyse de la cellulose résiduelle. Toujours dans ce cas, des expériences complémentaires nous ont permis d'améliorer la compréhension du processus de minéralisation de la cellulose.

La minéralisation par Nb<sub>2</sub>Cl<sub>10</sub> a été le second exemple de minéralisation pour lequel nous avons développé l'étude jusqu'à la caractérisation des propriétés électrochimiques des composites Nb<sub>2</sub>O<sub>5</sub>/C comme matériaux d'électrode négative de supercapaciteurs. Nous avons enrichi notre étude par une comparaison entre des matériaux obtenus par minéralisation de trois types de cellulose : la cellulose issue du papier filtre, la cellulose microfibrillée et la cellulose bactérienne.

Enfin, de manière plus exploratoire, nous avons testé trois autres chlorures métalliques : FeCl<sub>3</sub>, VOCl<sub>3</sub> et WCl<sub>6</sub>; ces derniers étant choisis en fonction de leur structure mais aussi par rapport à l'oxyde métallique auquel ils donnent accès. Ceci nous a permis de mettre en évidence des morphologies originales mais également le rôle réducteur de la cellulose lors de la pyrolyse, donnant accès à des sous-oxydes dont certains présentent un fort potentiel en catalyse ou en électrochimie.

## **II - Modes opératoires et caractérisations**

### **II.1 - Procédé de synthèse**

Toutes les synthèses concernant la minéralisation de la cellulose s'appuient sur le même mode opératoire, dont plusieurs étapes peuvent être adaptées, certaines variations seront présentées. D'un point de vue général, la cellulose (ou le polysaccharide) est séchée à l'étuve à 80 °C pendant 24h avant d'être stocké dans une boite à gants sous argon (teneur en H<sub>2</sub>O < 10 ppm). A l'intérieur de la boite à gants, la cellulose est introduite dans un autoclave en acier muni d'une chemise en téflon, d'un volume interne de 80 mL, et on y rajoute le précurseur métallique et du solvant, généralement CH<sub>2</sub>Cl<sub>2</sub>. On peut effectuer cette synthèse sans solvant. Dans ce cas, le précurseur métallique est introduit en premier dans l'autoclave, et le polysaccharide est ajouté ensuite. Des morceaux de téflon intercalés entre les deux réactifs empêchent le contact avant le début du chauffage (et l'évaporation du précurseur métallique). L'autoclave est alors fermé hermétiquement, retiré de la boite à gants et placé dans une étuve pour une étape de chauffage variant de quelques heures à plusieurs jours. L'autoclave est ensuite ramené à température ambiante avant une étape de lavage au dichlorométhane, puis le matériau obtenu est séché.

**Choix du polysaccharide** : le polysaccharide le plus utilisé dans cette thèse a été la cellulose, sous forme de papier filtre standard (FT-3-101-090, papier filtre sans cendre de Sartorius – France), de cellulose microfibrillée (fournie par L. Heux, CERMAV Grenoble) ou de cellulose bactérienne (fournie par A. Foresti, Argentine). Des synthèses effectuées à partir d'amidon (Sigma-Aldrich 33615), de chitosan (Sigma-Aldrich 448877) et d'inuline (Sigma-Aldrich I2255) ont également été effectuées.

Le polysaccharide utilisé peut subir un pré-traitement avant d'être séché. Ceci est effectué par imprégnation de morceaux de papier filtre (1-2 cm<sup>2</sup>) dans une solution aqueuse d'urée à 10 % massique, pendant 24h, à température ambiante. Les morceaux sont ensuite retirés et laissés à sécher 12h à température ambiante, puis 3 jours à l'étuve à 80 °C avant d'être stockés en boite à gants.

**Choix du précurseur métallique** : différents précurseurs métalliques ont été utilisés pour étudier ce procédé. Les chlorures métalliques (FeCl<sub>3</sub>, Sigma-Aldrich 157746 ; NbCl<sub>5</sub>, Alfa Aesar 51108 ; SiCl<sub>4</sub>, Aldrich 289388; TiCl<sub>4</sub>, Sigma-Aldrich 208566 ; VOCl<sub>3</sub>, Aldrich 200891 ; WCl<sub>6</sub>, Aldrich 241911) ont montré les meilleurs rendements. D'autres précurseurs de titane ont été testés : TiF<sub>4</sub> (Aldrich 333239), Ti(O*i*Pr)<sub>4</sub> (Alfa Aesar 77115), TiBr<sub>4</sub> (Aldrich 307793).

**Etape de chauffage** : plusieurs températures et durées de chauffage ont été utilisées. Les températures utilisées étaient de 85 °C ou 150 °C dans le cas de FeCl<sub>3</sub>, NbCl<sub>5</sub>, VOCl<sub>3</sub>, WCl<sub>6</sub>, une température de 200 °C a également été testée dans le cas de TiF<sub>4</sub>. Les durées de chauffage s'échelonnaient de 3 à 30 jours, la durée habituelle étant de 3 jours. Des tests de cinétique à 24h et 48h ont été effectués.

**Ouverture des autoclaves** : lors de l'ouverture des autoclaves, le bouchon de téflon était rapidement remplacé par un septum pour éviter au maximum le contact avec l'humidité de l'air. Au moyen d'une seringue, le liquide contenu dans l'autoclave était retiré, puis le contenu de l'autoclave était lavé avec

du dichlorométhane anhydre (3 x 30 mL). Le septum était alors retiré et le produit de synthèse était lavé à l'air avec du dichlorométhane standard (3 x 30 mL) avant d'être séché.

Le lavage du produit de synthèse a également été effectué avec de l'eau distillée, directement après l'ouverture de l'autoclave. Dans ce cas, l'utilisation du septum et de la seringue n'était pas nécessaire.

Dans tous les cas, le matériau est alors laissé à l'air 12 heures puis séché en étuve à 80 °C pendant 24 h.

## **II.2 – Mesures electrochimiques**

**Préparation des électrodes** : toutes les électrodes étaient composées de matière active (le matériau à tester, 80 % massique), de noir d'acétylène (pour augmenter la conduction électronique dans l'électrode, 8 %) et de carboxymethylcellulose (utilisé comme liant, 12 %). Ces trois poudres étaient agitées dans une très faible quantité d'eau pour former une encre. L'encre était étalée sur un collecteur de courant en cuivre, avec une épaisseur uniforme de 150 µm. Après 12h de séchage à température ambiante, les électrodes étaient découpées à l'emporte-pièce au diamètre adéquat (15 mm pour les *coin cells*, 8 mm pour les *swagelok cells*) pour le montage des piles.

**Préparation des cellules** : les cellules étaient montées dans une boîte à gants sous atmosphère inerte ( $O_2 < 2 \text{ ppm}$ ,  $H_2O < 0.5 \text{ ppm}$ ).

Habituellement, les électrodes étaient montées dans des piles bouton CR2032. Des disques de lithium ou de sodium métalliques étaient utilisés à la fois comme contre-électrode et comme électrode de référence. Des morceaux de papier filtre Whatman 1001-047 étaient utilisés comme séparateurs. L'électrolyte utilisé pour les batteries au lithium était une solution de  $\text{LiPF}_6$  à 1 mol.L<sup>-1</sup> dans un mélange 1:1:3 en volume de *propylene carbonate* (PC), *ethylene carbonate* (EC) et *dimethyl carbonate* (DMC), avec 5 % de *fluoroethylene carbonate* et 1 % de *vinyl carbonate*. L'électrolyte utilisé pour les batteries au sodium était une solution de  $\text{NaClO}_4$  à 1 mol.L<sup>-1</sup> dans du *propylene carbonate*, avec 5 % de *fluoroethylene carbonate*.

Pour les mesures effectuées sur les oxydes de niobium, on a utilisé une cellule à trois électrodes. Un disque de lithium métallique était utilisé comme contre-électrode, un autre comme électrode de référence. Le même séparateur était utilisé pour le montage de cette cellule. L'électrolyte utilisé était une solution de  $\text{LiPF}_6$  à 1 mol.L<sup>-1</sup> dans un mélange 1:1:3 en volume de PC, EC et DMC.

**Cyclage galvanostatique** : les cellules ont été testées sur des appareils de mesure VMP (EC-Lab) et MPG-2 (BioLogic), dans une pièce à température contrôlée (26 °C). Une relaxe de 1h précédait systématiquement le début du cyclage. Le courant appliqué était calculé en fonction de la masse molaire et de la masse de matière active (dans le cas des composites, on considère la masse molaire de l'oxyde et la masse totale de composite). Pour les cyclages en régime variable, une ouverture du circuit (OCV en anglais) de dix secondes est appliquée à chaque changement de régime.

**Cyclovoltamétrie** : les mesures de cyclovoltamétrie ont été effectuées sur un VSP-300. Dans le cas des mesures avec plusieurs vitesses de balayage, un OCV de dix secondes était appliqué à chaque changement de vitesse de balayage.

**Spectroscopie d'impédance électrochimique** : les mesures de spectroscopie d'impédance électrochimique (EIS en anglais) ont été effectuées sur un appareil VSP (BioLogic), en utilisant des demi-piles CR2032. La modélisation des systèmes équivalents et les affinements correspondants ont été effectués avec le logiciel EC-Lab (version 10.44).

## **II.3 - Méthodes de caractérisation**

**Analyse thermogravimétrique** : les analyses thermogravimétriques ont été effectuées sur un appareil Netzsch Simultaneaus Thermal Analyser STA 409 PC Luxx, avec un débit de gaz de  $50 \text{ cm}^3.\text{min}^{-1}$ .

L'analyse thermogravimétrique (ou ATG) permet d'étudier les changements de masse d'un échantillon soumis à des modifications thermiques. L'échantillon, placé dans un creuset en alumine, est chauffé selon une rampe prédéterminée (de 1 à  $20 \text{ }^\circ\text{C}.\text{min}^{-1}$ ) et on mesure la masse de l'échantillon tout au long de l'analyse. On obtient une courbe représentant la variation de masse de l'échantillon en fonction de sa température ; on peut ainsi déterminer les températures de déshydratation, de décomposition ou de modification chimique, et ainsi en déduire la fraction d'eau et la présence d'éléments organiques ou inorganiques. Un balayage gazeux permet d'évacuer les gaz produits par la dégradation de l'échantillon. Ce balayage peut être constitué d'air (atmosphère oxydante), d'argon (atmosphère inerte), voire d'un mélange d'argon hydrogéné (atmosphère réductrice).

L'ATG peut être couplée à d'autres techniques d'analyses. Un spectromètre de masse ou un spectroscope infrarouge peuvent être positionnés en aval sur le système de balayage afin d'analyser les gaz produits lors du traitement thermique de l'échantillon, et ainsi de déterminer des mécanismes.

**Mesures de surface spécifique** : la surface spécifique des échantillons a été calculée par la méthode Brunauer, Emmett et Teller (BET) grâce aux données acquises sur un système Micromeretics Tristar, USA. Les isothermes d'adsorption d'azote ont été réalisées à 77 K. Les échantillons avaient été dégazés pendant au minimum 6 heures à  $110 \text{ }^\circ\text{C}$ .

Après avoir dégazé l'échantillon pour désorber toutes les molécules présentes sur sa surface, on réalise des mesures d'adsorption d'azote (où l'on mesure le volume d'azote adsorbé), à pressions relatives croissantes. Selon la pression considérée, l'azote peut remplir des pores de volume de plus en plus important. Une fois qu'on a atteint une pression relative  $P/P^0 = 1$ , on diminue la pression pour réaliser des mesures de désorption d'azote, à pressions relatives décroissantes. La surface spécifique est déterminée d'après les quantités adsorbées quand  $0.05 < P/P^0 < 0.3$ , en utilisant la méthode BET.

L'équation BJH permet de déterminer la distribution en taille des pores de l'échantillon.

Tous les calculs de porosité sont effectués sur la branche de désorption.

**Diffractomètre X** : les mesures de diffraction des rayons X ont été effectuées sur un diffractomètre PANalytical X-pert Pro utilisant un monochromateur et une source au cuivre. Les

identifications de phases cristallines ont été réalisées en utilisant le logiciel X'Pert Highscore. Le logiciel XFIT a été utilisé pour déterminer les largeurs à mi-hauteur utilisées dans l'équation de Debye-Scherrer.

La diffraction des rayons X a pour but de déterminer l'ordre à grande échelle dans l'échantillon. Le faisceau de rayons X émis par la source, possédant une longueur d'onde connue, est diffracté par le nuage électronique des atomes de l'échantillon ; les interférences des rayons diffusés sont alors alternativement destructives (disparition du rayon diffracté) ou constructives (augmentation de l'intensité du rayon diffracté). Si l'échantillon est amorphe, ses atomes n'ont pas d'ordre à grande échelle ; dans ce cas, il n'y a pas d'interférences constructives et on ne détecte pas de pics de diffractions. Si l'échantillon est cristallin, il possède un ordre à grande échelle. Dans ce cas, l'organisation des atomes en plans va générer des interférences constructives pour certains angles d'incidence, en fonction des distances séparant les plans de diffraction. On observe alors des pics de diffraction pour certains angles incidents, la valeur de l'angle permettant de calculer la distance entre deux plans homogènes (ayant la même organisation) successifs.

$$2d \sin \theta = n \cdot \lambda$$

$d$  : distance inter-réticulaire (entre deux plans de diffraction)

$\theta$  : angle de diffraction

$n$  : ordre de diffraction

$\lambda$  : longueur d'onde du faisceau incident

Le diffractogramme d'un échantillon représente l'intensité du faisceau diffracté en fonction de l'angle de diffraction. L'emplacement et l'intensité relative des pics de diffraction permettent de déterminer, le cas échéant, la maille cristalline de l'échantillon (et donc de procéder à une identification de phase dans le cas d'une phase connue). La largeur à mi-hauteur des pics de diffraction (*FWHM* pour *full-width at half maximum*) est utilisée dans la formule de Debye-Scherrer pour calculer la taille des cristallites, c'est-à-dire la taille des domaines cristallins continus.

**Microscope électronique à balayage/EDX** : les images MEB ont été enregistrées sur un microscope Hitachi S-4800 réglé sur une tension de 5 kV. Les analyses élémentaires par EDX ont été réalisées en utilisant le module d'EDX (Oxford Instruments) du MEB. Les échantillons ont été métallisés au platine avant les observations.

La résolution maximale d'un microscope optique est limitée par la longueur d'onde du faisceau utilisé. La microscopie électronique utilise donc un faisceau d'électrons plutôt que des photons pour obtenir des images de plus haute résolution. Dans un MEB, un faisceau d'électron est projeté sur l'échantillon à analyser. L'interaction entre l'échantillon et ce faisceau génère des électrons secondaires, de plus basse énergie, dont l'énergie dépend à la fois de la topographie de l'échantillon et de sa nature chimique. Un balayage de la surface de l'échantillon par le faisceau d'électrons permet donc de restituer une cartographie de sa surface.

**Microscope électronique à transmission** : les images MET ont été obtenues sur un microscope électronique JEOL 1200 EXII. Les échantillons étaient mis en suspension dans l'éthanol avant d'être déposés sur les grilles TEM.

Le MET est un microscope électronique dans lequel le faisceau d'électron traverse un échantillon de faible épaisseur. Dans ces conditions, on utilise le faisceau transmis pour obtenir une cartographie de l'échantillon. On peut également, dans le cas d'échantillons cristallins, détecter le faisceau diffracté pour obtenir des informations sur la structure cristalline de l'échantillon.

**Spectroscopie infrarouge** : les spectres IR ont été obtenus sur un spectromètre Spectrum 2 de PerkinElmer. L'acquisition a été effectuée au moyen du module d'ATR de l'appareil.

La spectroscopie infrarouge est basée sur l'excitation des liaisons intramoléculaires par un faisceau de lumière infrarouge. Lorsque l'énergie du faisceau correspond à une harmonique de l'énergie de la liaison, celle-ci entre en vibration. Une partie de l'énergie du faisceau est alors absorbée par l'échantillon, ce qui se traduit par une diminution de l'intensité de lumière transmise. En faisant varier la longueur d'onde du faisceau (donc son énergie), obtient le spectre IR de l'échantillon, qui présente des bandes d'absorption pour certaines longueurs d'onde. On peut alors déterminer quelles vibrations ont été provoquées par ces absorptions, et donc quelles liaisons chimiques sont présentes dans l'échantillon.

Le proche infrarouge va de 10 à 400 cm<sup>-1</sup> (soit des longueurs d'onde de 1000 µm à 25 µm), l'infrarouge moyen va de 400 à 4000 cm<sup>-1</sup> (soit 25 à 2.5 µm) et l'infrarouge lointain va de 4000 à 14000 cm<sup>-1</sup> (soit 2.5 à 0.7 µm).

**Spectroscopie Raman** : les spectres Raman ont été effectués sur des échantillons de poudre, au moyen d'un spectrophotomètre Horiba LabRAM ARAMIS, avec une longueur d'onde d'excitation de 633 nm.

La spectroscopie Raman est complémentaire de l'IR, puisqu'elle rend également compte des propriétés vibrationnelles des molécules du corps étudié, mais utilise des règles de sélection différentes. Cependant, l'intensité du rayonnement incident utilisé en Raman peut permettre un transfert d'énergie des photons au corps étudié ; l'énergie fournie via le faisceau incident (excitation) n'est alors pas entièrement restituée dans le faisceau diffusé. La variation d'énergie observée sur le photon nous renseigne alors sur les niveaux énergétiques de rotation et de vibration de la molécule étudiée.

### **Spectroscopie RMN :**

La spectroscopie RMN s'appuie sur le principe de la résonance magnétique nucléaire. Lorsque des noyaux atomiques de spin non nul sont placés dans un champ magnétique, une excitation par un rayonnement de fréquence appropriée (c'est-à-dire dont la longueur d'onde est calibrée sur la différence d'énergie entre les différents états de spin) provoque une absorption de l'énergie du rayonnement, suivie d'une libération d'énergie lors de la relaxation. En réglant la fréquence du rayonnement sur l'énergie d'un isotope spécifique, on sonde donc les noyaux de cet isotope présents dans l'échantillon étudié.

L'environnement local des noyaux sondés peut générer un champ magnétique interne, qui provoque un écrantage du rayonnement d'excitation. Dans ce cas, le rayonnement détecté lors de la relaxation possède une fréquence légèrement différente de celle du rayonnement initial. Cette différence de fréquence, appelée déplacement chimique, est caractéristique de l'environnement local de chaque

noyau sondé, et permet donc de déterminer la nature et la position de ses voisins. Il est donc nécessaire de calibrer le spectromètre avec une référence, un échantillon dont le déplacement chimique est connu.

La RMN en milieu solide (SS pour *solide state*), utilisée dans cette thèse, nécessite ainsi d'utiliser une référence externe ; un spectre est effectué sur cette référence, et sert de calibration pour le spectre de l'échantillon à analyser. De plus, afin de compenser l'anisotropie des échantillons en poudre, l'échantillon doit être mis en rotation autour d'un axe incliné à 54.74 ° par rapport au champ magnétique. Cet angle est appelé "angle magique", d'où l'acronyme *MAS* pour *magic angle spinning*.

### **III – Minéralisation de la cellulose**

Les travaux entrepris au cours de cette thèse s'appuient sur des études antérieures concernant la minéralisation de la cellulose. Il est donc important de rappeler les points qui semblaient acquis avant le début de cette thèse :<sup>34</sup>

- 1/ La minéralisation de la cellulose par  $TiCl_4$ , dont le mode opératoire a été décrit au chapitre II.1, conduit à la formation directe de  $TiO_2$  anatase possédant une morphologie différente de celle obtenue en sol-gel par templating de la cellulose.
- 2/ Les quantités de  $TiO_2$  produites sont trop importantes pour être dues à une réaction avec l'eau adsorbée par les fibres de cellulose. Par ailleurs, plusieurs méthodes de caractérisation (EDX, DRX, IR, Raman, RMN  $^{13}C$ ) montrent d'importantes modifications de la cellulose. Ces modifications suggèrent un changement de la structure et de la composition de la cellulose dès  $80^\circ C$  et après quelques heures de chauffage. Ceci a été interprété comme un processus de déshydratation de la cellulose libérant *in situ* de l'eau qui réagit avec le chlorure de titane.
- 3/ Les traitements thermiques post-synthétiques préservent la morphologie des cristaux. Une calcination permet ainsi d'obtenir un  $TiO_2$  débarrassé de tout résidu organique tandis qu'une pyrolyse conduit à un composite  $TiO_2/C$ .
- 4/ La présence de solvant n'est pas indispensable à la synthèse, dès lors que le chlorure métallique a une tension de vapeur suffisamment élevée dans les conditions expérimentales (température et pression dans l'autoclave). La réaction solide-gaz qui a lieu dans ce cas conduit également à la formation de  $TiO_2$  anatase, avec des propriétés similaires. On note que la morphologie est sensiblement différente de celle observée pour des réactions en présence de solvant.

Afin de développer cette approche, d'en montrer les avantages et les limites, nous avons réalisé un ensemble d'expériences qu'il est possible de regrouper en 4 grands thèmes : l'effet d'une pré-imprégnation de la cellulose, la généralisation à l'obtention d'autres oxydes métalliques, l'extension du procédé à l'utilisation de cellulose micro et nano-fibrillée (MFC et BC) et enfin la compréhension du processus de minéralisation. Les taux de conversion des synthèses sont calculés grâce aux résultats d'ATG sous air. On peut calculer un nombre de moles d'oxyde métallique formé (d'après le pourcentage de résidu en fin d'ATG) et un nombre de moles de polysaccharide (d'après le pourcentage de perte de masse). On détermine le taux de conversion du polysaccharide en oxyde métallique par la formule :

$$\eta = \frac{n_{oxyde}}{n_{oxyde} + n_{polysaccharide}}$$

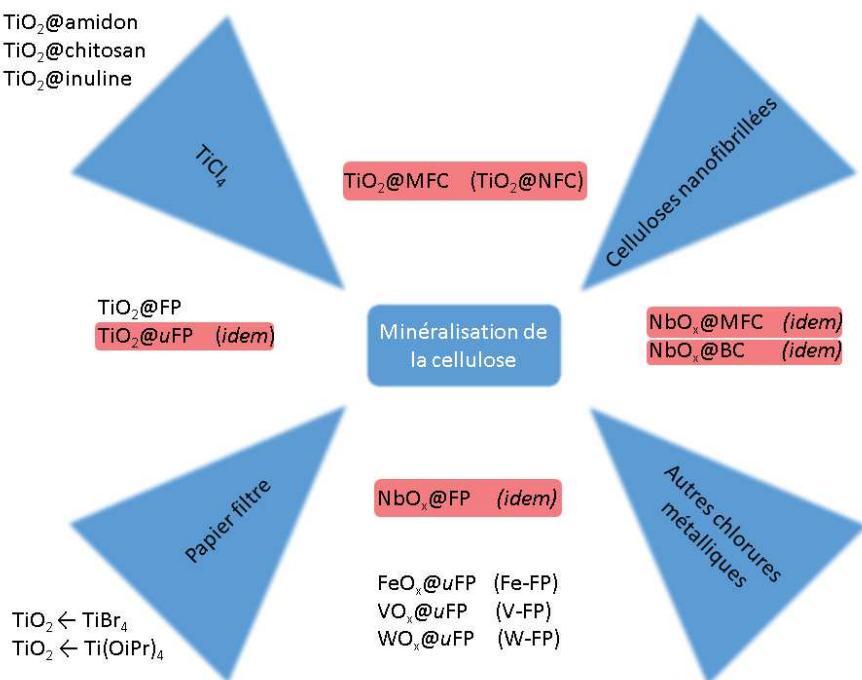


Schéma III.1 : Résumé des matériaux mentionnés dans cette thèse (de leurs nomenclatures dans les publications s'il y a lieu). En rouge, les matériaux évalués pour le stockage de l'énergie

### III.1 – Effet de l'imprégnation de la cellulose<sup>35</sup>

La cellulose est un support remarquable pour absorber des composés tant hydrophiles qu'hydrophobes. Dans la perspective de sa transformation par minéralisation, toutes sortes de composés pouvaient être envisagés pour explorer les conséquences de la présence d'une espèce absorbée sur la cellulose. Nous nous sommes intéressés à l'urée, celle-ci étant fréquemment décrite comme source d'azote pour l'obtention de TiO<sub>2</sub> dopés N notamment dans des procédés sol-gel ; nous avons procédé à une imprégnation par un simple trempage dans une solution d'urée suivie d'un séchage avant minéralisation (décrise au chapitre II.1). Rappelons que les interactions entre l'urée et la cellulose font toujours l'objet d'études,<sup>36</sup> certaines tendant à montrer une interaction de l'urée avec le réseau de liaisons hydrogènes de la cellulose.<sup>37</sup> Les résultats sont détaillés dans l'article reproduit au chapitre IV.1 ; on en mettra ici en lumière les points importants.

Tout d'abord, l'effet du pré-traitement à l'urée sur la fibre de cellulose semble se caractériser par une très légère modification de la structure fibrillaire externe de la cellulose. La formation de carbamates de celluloses est exclue par les analyses IR, mais les images MEB suggèrent une défibrillation partielle de la surface provoquée par la perturbation des liaisons hydrogène de la cellulose. Parallèlement, le profil de dégradation thermique obtenu par ATG montre un début de perte de masse à plus basse température (144 °C, contre 285 °C sans pré-traitement). L'ATG permet également de calculer le taux de conversion de TiO<sub>2</sub>{uFP}, qui est de 46 % (légèrement inférieure aux 53 % de TiO<sub>2</sub>).<sup>38</sup>

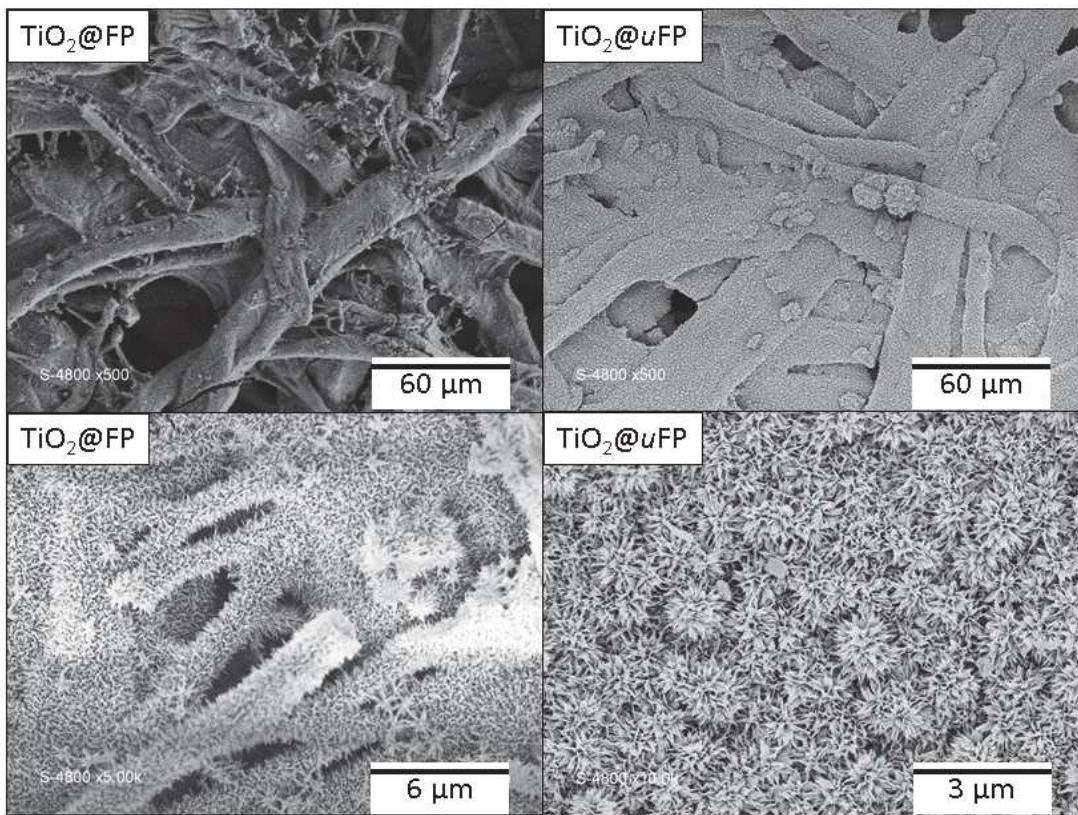


Fig. III.1 : Images MEB de  $\text{TiO}_2$  à partir de cellulose ( $\text{TiO}_2@\text{FP}$ ) et de cellulose pré-imprégnée à l'urée ( $\text{TiO}_2@\text{uFP}$ )

L'effet le plus spectaculaire de la pré-imprégnation est la modification de la morphologie des particules de  $\text{TiO}_2$  qui croissent à la surface des fibres, présentée sur la Fig. III.1. Une différence significative est visible lorsqu'on compare les images MEB de  $\text{TiO}_2$  obtenus par minéralisation de la cellulose, selon qu'ils ont été synthétisés à partir de cellulose pré-imprégnée ou non. De plus, il semble que l'imprégnation à l'urée conduise, après pyrolyse, à un composite  $\text{TiO}_2/\text{C}$  où le carbone contient une proportion non négligeable d'azote ( $\approx 2\text{-}3\%$  massique), ainsi qu'une quantité légèrement supérieure de domaines graphitiques. En revanche, le  $\text{TiO}_2$  obtenu (mentionné par la suite comme  $\text{TiO}_2@\text{uFP}$ ) ne présente pas de caractéristique pouvant attester d'un dopage à l'azote. Point important pour les propriétés électrochimiques, la calcination favorise la croissance des cristallites de  $\text{TiO}_2$  (pour une taille de 50 nm) alors que la pyrolyse la limite (10 nm). Ces dimensions, calculées d'après les diffractogrammes de la Fig. III.2, sont proches de celles observées avec une cellulose non imprégnée (respectivement 47 nm et 7 nm), il semble donc que le pré-traitement à l'urée n'ait pas d'influence à ce niveau.

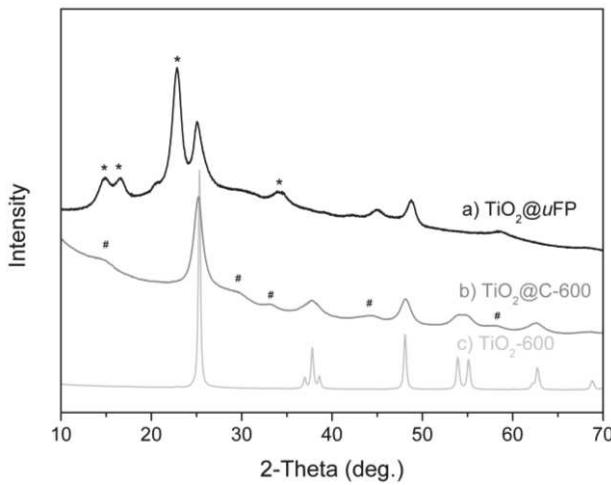


Fig. III.2 : Diffractogrammes de a)  $\text{TiO}_2@\text{uFP}$ , b)  $\text{TiO}_2@\text{C-600}$  et c)  $\text{TiO}_2\text{-600}$  ; \* et # indiquent les pics de diffraction des phases cristallines de cellulose (FP) et de  $\text{TiO}_2$  (B), respectivement

Les performances électrochimiques de ces matériaux ont été évaluées comme matériau actif d'anode de LIB et NIB. Sans entrer dans le détail des caractérisations électrochimiques, développées dans l'article présenté au chapitre IV.1, on constate l'influence de la taille des cristallites sur la capacité du matériau dans le cas des mesures en demi-pile Li-ion, avec la disparition du plateau d'insertion, un comportement bien connu pour les  $\text{TiO}_2$  nanocristallins (Cf. Fig. III-3).

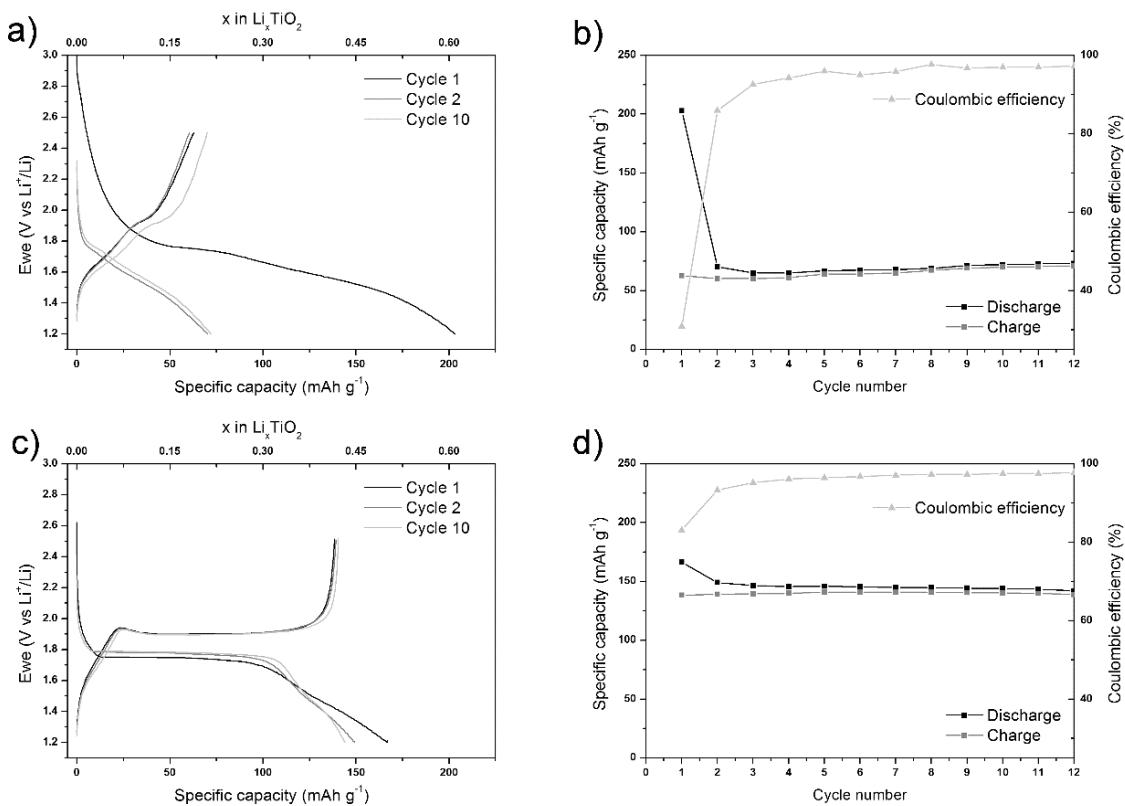


Fig. III.3 : a) Cyclage galvanostatique et b) courbe de cyclage charge/décharge pour des batteries  $\text{TiO}_2@\text{C-600}/\text{Li}$  cyclées à C/20 entre 2.5 et 1.2 V vs  $\text{Li}^+/\text{Li}$  ; c) cyclage galvanostatique et d) courbe de cyclage charge/décharge pour des batteries  $\text{TiO}_2\text{-600}/\text{Li}$  cyclées dans les mêmes conditions

Dans le cas des mesures effectuées en demi-pile Na-ion, présentées dans la Fig. III.4, l'effet majoritaire est à rechercher ailleurs ; en effet, l'ordre des capacités est ici inversé, le composite ayant une capacité ( $200 \text{ mA.h.g}^{-1}$ ) supérieure à celle du  $\text{TiO}_2$  ( $150 \text{ mA.h.g}^{-1}$ ). Comme il ne semble pas possible d'y voir l'effet de la taille des cristallites, cet écart de capacités serait attribuable à la présence de carbone issu de la pyrolyse de la cellulose. La présence de ce carbone, spécifique à ce composite et intimement lié à l'oxyde métallique, augmente la conductivité électronique du composite. Des mesures de spectroscopie d'impédance électrochimique (EIS) ont été effectuées sur  $\text{TiO}_2$  et  $\text{TiO}_2/\text{C}$  afin de comparer les résistances (et donc les conductivités) des deux matériaux. Le résultat est clair : la conductivité du composite est deux fois plus élevée que celle de l'oxyde.

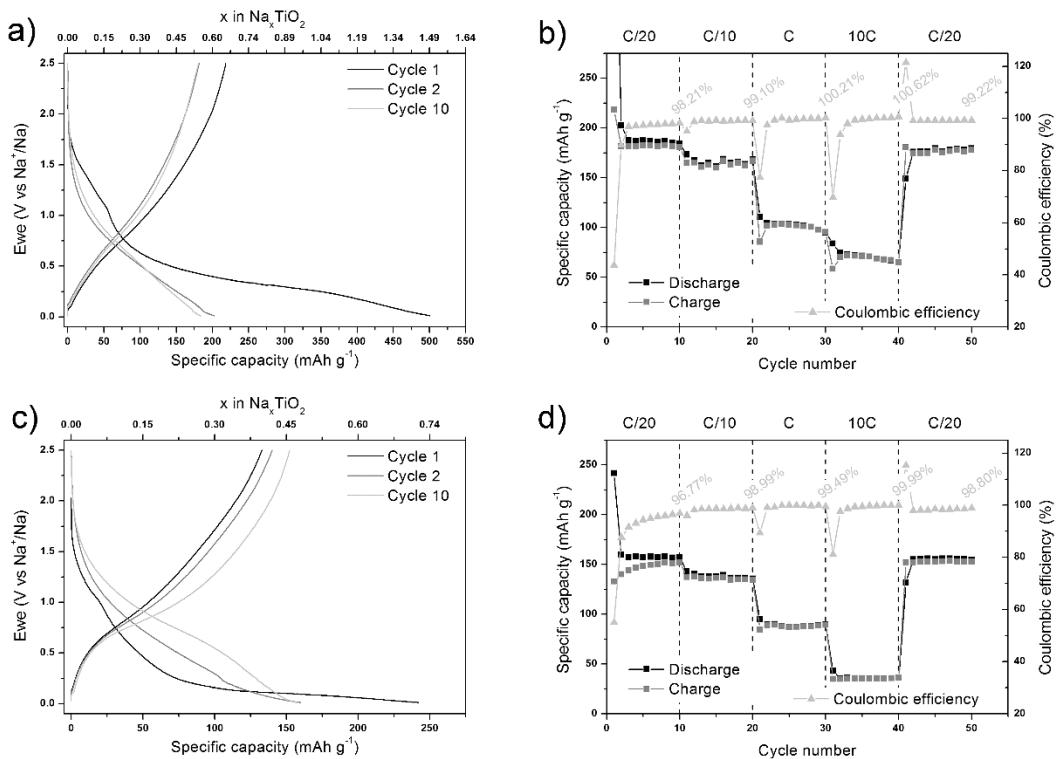


Fig. III.4 : a) Cyclage galvanostatique et b) courbe de cyclage charge/décharge pour des batteries  $\text{TiO}_2@C-600/\text{Na}$  cyclées à C/20, C/10, C, 10C et C/20 consécutivement, entre 2.5 and 0.01 V vs  $\text{Na}^+/\text{Na}$ . c) Cyclage galvanostatique et d) courbe de cyclage charge/décharge pour des batteries  $\text{TiO}_2-600/\text{Na}$  cyclées dans les mêmes conditions

Les résultats d'une minéralisation de cellulose pré-imprégnée par de l'urée, telle que décrite ci-dessus, suggèrent que le réseau de liaisons –H de la cellulose, ainsi que l'état de surface des fibres, pourraient avoir un rôle important dans le mécanisme réactionnel et la morphologie du matériau formé. Un autre type de pré-imprégnation avant minéralisation par  $\text{TiCl}_4$  a donc été testé dans les dernières semaines de cette thèse : l'imprégnation de la cellulose dans de l'huile de silicone, connue pour ses propriétés hydrophobes. Le choix de ce polymère repose sur différents arguments : d'une part la possibilité de minéraliser simultanément la cellulose et le polysiloxane, accédant ainsi à un  $\text{Si}_\epsilon\text{Ti}_{1-\epsilon}\text{O}_2$  ; d'autre part, la possibilité de venir écraser les liaisons hydrogène par la présence d'un polysiloxane ; enfin, si les polysiloxanes ne sont pas miscibles à l'eau, ils sont connus pour laisser passer la vapeur d'eau. On aurait donc une possibilité d'hydrolyser le  $\text{TiCl}_4$ , mais sans que celui-ci puisse "s'ancre" dans la

structure de la cellulose. La manipulation d'imprégnation est simplement réalisée par immersion du papier dans une solution à 10 wt. % d'huile de silicone dans le dichlorométhane pendant 1h, à  $T_{amb}$ . Le papier imprégné est ensuite séché à l'étuve pendant 24h, à 85 °C. La synthèse est effectuée en utilisant le procédé sans solvant, à 85 °C pendant 7 jours. Le résultat de cette synthèse est présenté ici à titre exploratoire, les caractérisations effectuées ayant été limitées par les délais d'analyse.

L'exploitation des données d'ATG révèle un taux de conversion (55 %) comparable aux synthèses sans pré-imprégnation (53 %) ou avec une pré-imprégnation à l'urée (46 %). Plus intéressant, les images MEB montrent la formation d'une croûte autour des fibres de cellulose (Fig. III.5 b, c et f), avec des excroissances cristallines de tailles et de formes régulières (Fig. III.5 b, c et e). Comme pour l'urée, nous constatons un effet important sur la morphologie de la couche d'oxyde qui couvre la surface des fibres de façon homogène. Les analyses n'étant pas complètes à ce jour, l'interprétation du phénomène est actuellement impossible. Mais les analyses déjà effectuées démontrent clairement la possibilité de moduler les morphologies obtenues en utilisant des pré-traitements différents pour la cellulose. De plus, le taux de conversion reste important, permettant ainsi d'envisager l'obtention de composites  $\text{TiO}_2/\text{C}$  possédant des proportions équilibrées de carbone et d'oxyde.

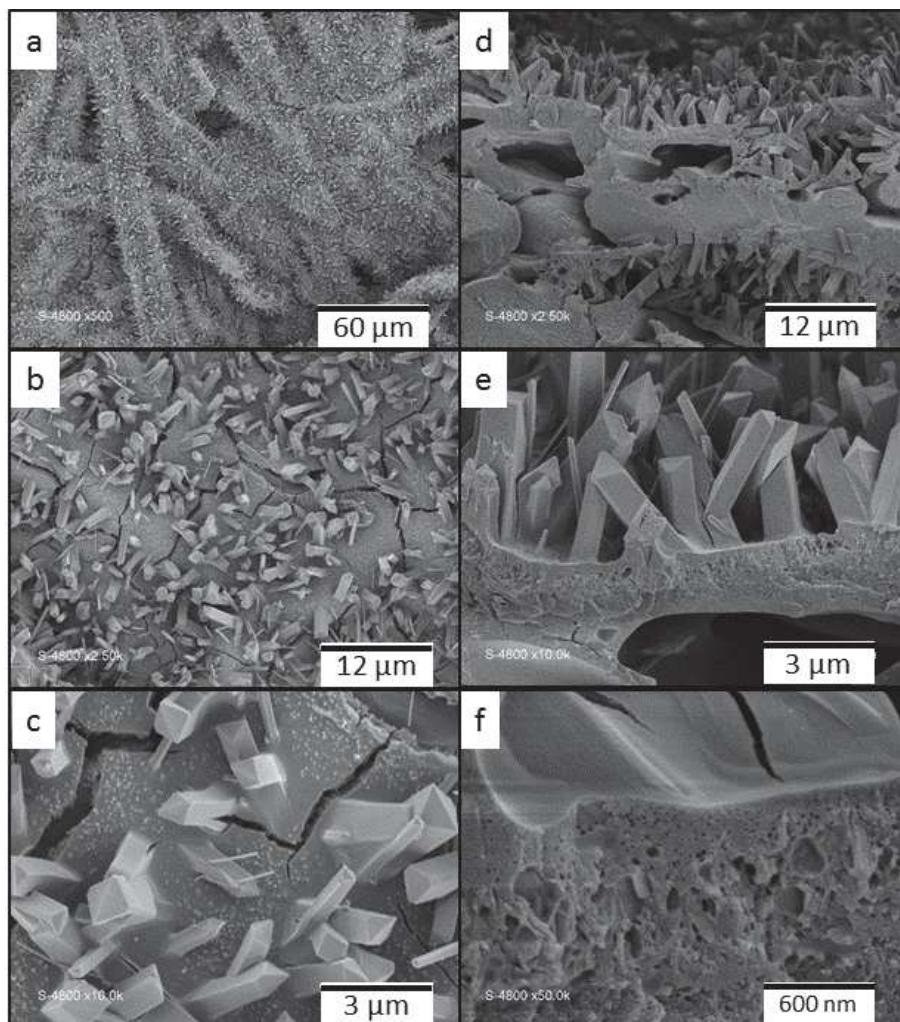


Fig. III.5 : Images MEB de  $\text{TiO}_2@oFP$  obtenus par minéralisation de cellulose pré-imprégnée dans l'huile de silicone. a, b, c) images de la surface d'un feuillet ; d, e, f) images d'une section de feuillet

D'autres types de pré-imprégnation sont envisagés : des polymères pouvant apporter des éléments chimiques (N, P, S, ...) comme dopant de l'oxyde ou du carbone, ou des sels et complexes métalliques pouvant être réduits pendant la pyrolyse et aboutir à des nanoparticules métalliques. L'adsorption de ces composés sur la cellulose peut également avoir d'autres conséquences : perturber le réseau des liaisons hydrogène, modifier les réactions chimiques pendant la minéralisation et ensuite pendant la pyrolyse, modifier l'état de surface de la cellulose sur laquelle s'opère la croissance des cristallites d'oxyde. Ces transformations peuvent conduire à des effets sur la nanostructuration des cristaux de TiO<sub>2</sub> et sur le carbone issu de la cellulose, et en conséquence sur les propriétés applicatives des matériaux.

### **III.2 – Extension du procédé de minéralisation de la cellulose à d'autres oxydes métalliques<sup>39</sup>**

Afin de montrer le potentiel que représente la minéralisation de la cellulose pour la synthèse d'oxydes métalliques et de leurs composites avec du carbone, nous avons testé la minéralisation avec d'autres chlorures métalliques. Des travaux concomitant ont montré qu'il était possible de procéder à cette minéralisation avec du TiCl<sub>4</sub> additionné à de faibles pourcentages molaires d'autres chlorures métalliques.<sup>40</sup> Les oxydes métalliques visés ont été choisis en fonction de leurs applications potentielles : V<sub>2</sub>O<sub>5</sub> et Fe<sub>2</sub>O<sub>3</sub> sont étudiés comme matériaux d'électrode de batterie Li-ion, WO<sub>3</sub> et Nb<sub>2</sub>O<sub>5</sub> comme matériaux d'électrode de supercapaciteur ou comme catalyseurs acides, fréquemment décrits dans le traitement de la biomasse. Deux études ont été mises en œuvre, l'une très prospective sur la synthèse de différents oxydes (de fer, de tungstène et de vanadium) à partir de cellulose pré-imprégnée à l'urée (Cf. article présenté au chapitre IV.2), l'autre sur la minéralisation par Nb<sub>2</sub>Cl<sub>10</sub>. Cette dernière synthèse a fait l'objet d'une étude plus poussée en comparant la minéralisation par Nb<sub>2</sub>Cl<sub>10</sub> de différents supports cellulosiques FP, MFC et BC (Cf. article présenté au chapitre IV.3).

Les minéralisations de la cellulose par du chlorure de fer (III) FeCl<sub>3</sub>, du chlorure de tungstène WCl<sub>6</sub> et de l'oxychlorure de vanadium VOCl<sub>3</sub> ont été réalisées avec du papier filtre pré-traité à l'urée. Compte tenu de la solubilité des précurseurs dans le dichlorométhane, la température de réaction a été portée à 150 °C. Les taux de conversion varient sensiblement : si VOCl<sub>3</sub> présente un taux de conversion de près de 49 %, les taux de conversion des deux autres chlorures sont plus faibles ; celui de FeCl<sub>3</sub> est de 37 %, celui de WCl<sub>6</sub> de 33 % (à comparer avec les 52 % de TiO<sub>2</sub>{uFP}). La minéralisation de la cellulose par Nb<sub>2</sub>Cl<sub>10</sub>, réalisée dans le cadre d'une autre étude, a utilisé du papier filtre non imprégné et des températures de traitement thermique différentes. Seuls les NbO<sub>x</sub><sup>38</sup> avec une température de réaction de 150 °C et non pyrolysés seront donc discutés ici.

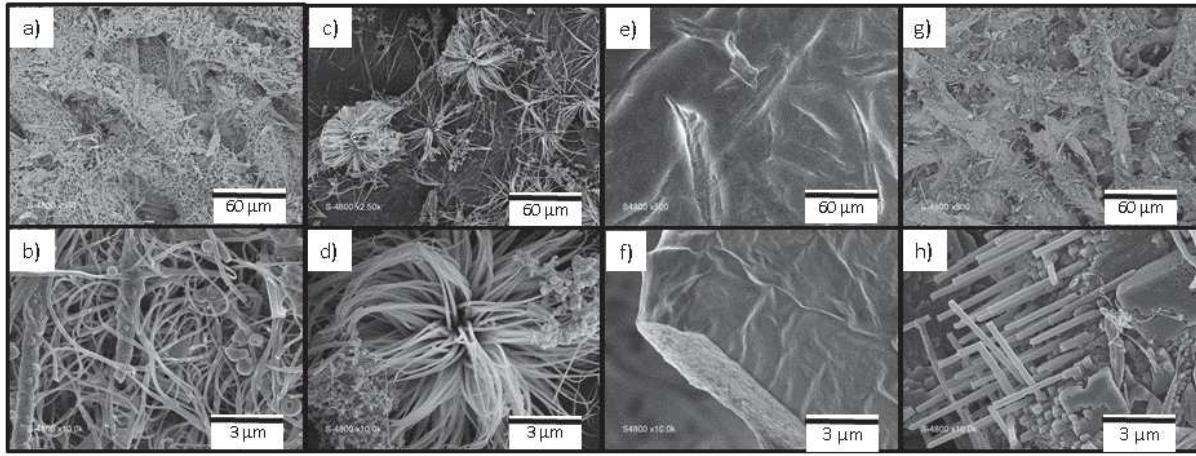


Fig. III.6 : Images MEB de a, b)  $\text{FeO}_x\{\text{uFP}\}$ , c, d)  $\text{NbO}_x^{38}$ , e, f)  $\text{VO}_x\{\text{uFP}\}$  et g, h)  $\text{WO}_x\{\text{uFP}\}$

Nous avons également noté que les morphologies observées diffèrent de manière importante selon le chlorure utilisé, et qu'elles sont, dans tous les cas, différentes de ce qui est rapporté dans la littérature concernant des procédés sol-gel de templating de la cellulose. Ainsi, les morphologies développées par les oxydes de vanadium (Fig. III.6 e et f) diffèrent fortement de celles des autres oxydes, présentant une gaine vitreuse et homogène autour des fibres de cellulose, bien que la DRX révèle un matériau cristallin. Après calcination, l'oxyde de vanadium forme des cristaux allongés (Fig. III.7), imbriqués en cylindres (autour de l'ancien emplacement de la fibre de cellulose). Après pyrolyse, les structures constituées de grains d'oxyde de vanadium ont clairement poussé à partir de points de germination situés sur la fibre de cellulose (Fig. III.8). Les images MEB des oxydes de fer, de niobium et de tungstène révèlent des morphologies plus originales, aussi bien avant qu'après traitement thermique.

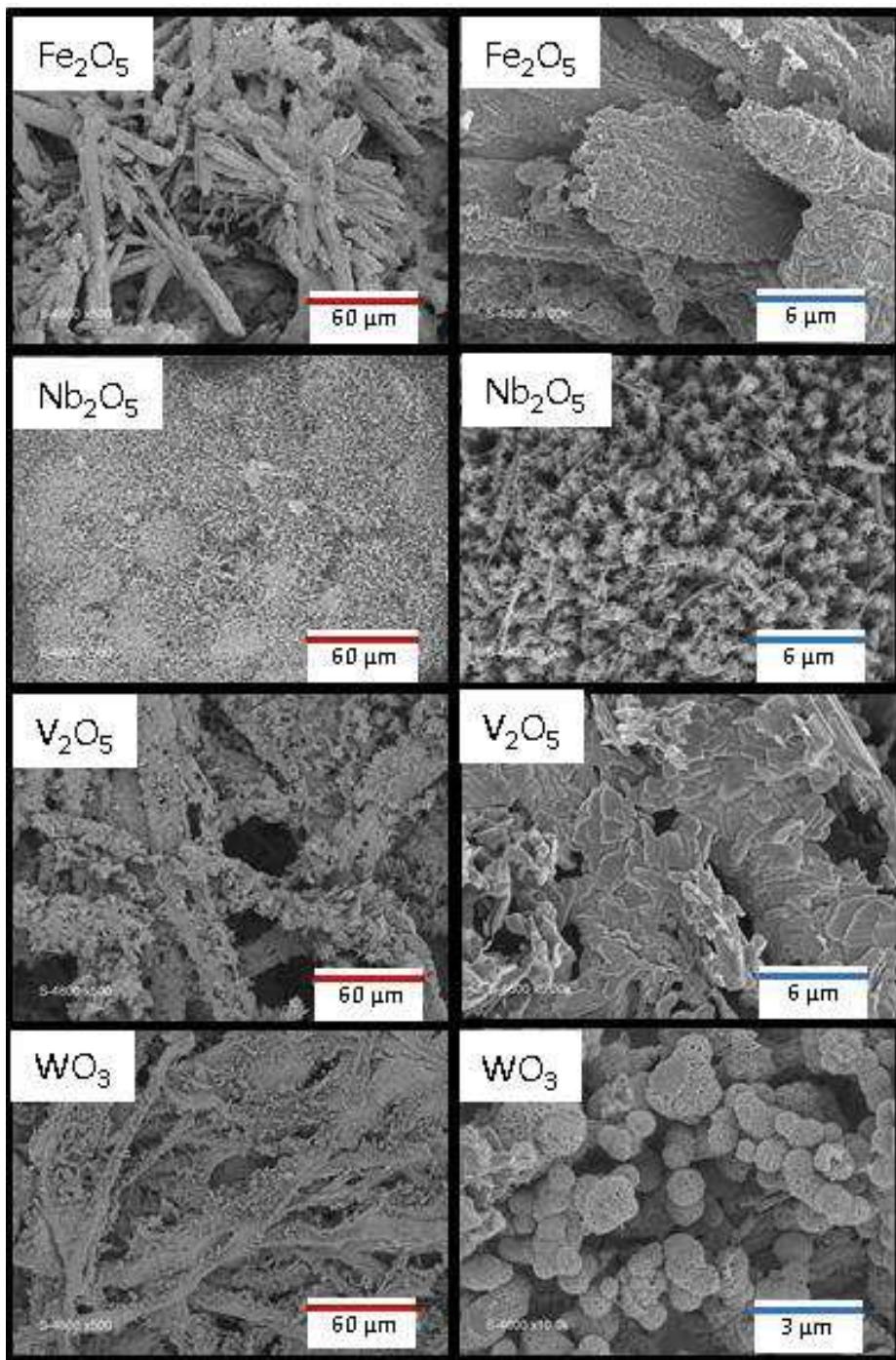


Fig. III.7 : Images MEB des oxydes de fer, de niobium, de vanadium et de tungstène après calcination

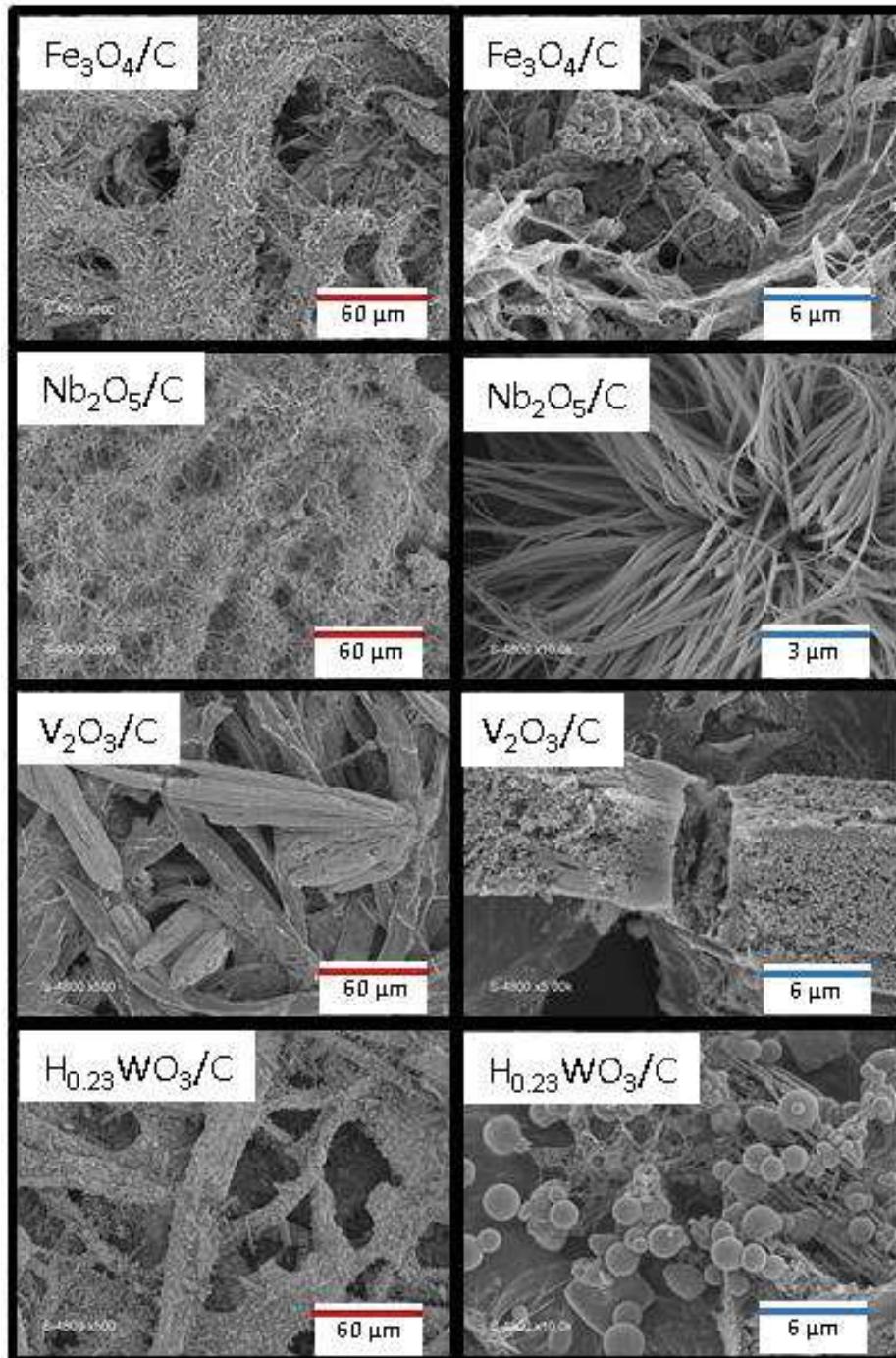


Fig. III.8 : Images MEB des composites oxyde métallique/carbone après pyrolyse

Avant traitement thermique, aucune phase cristalline correspondant à l'un des oxydes attendus n'est détectée par DRX, contrairement à ce qui était constaté lors de la minéralisation de la cellulose par  $\text{TiCl}_4$ . Après calcination (Fig. III.9), les oxydes attendus sont bien présents, respectivement  $\text{Fe}_2\text{O}_3$ ,  $\text{Nb}_2\text{O}_5$ ,  $\text{V}_2\text{O}_5$  et  $\text{WO}_3$ . Plus intéressant, la pyrolyse conduit à des composites  $\text{M}_x\text{O}_y/\text{C}$  où le métal présente un degré d'oxydation plus bas que celui du précurseur initial : Fe(II), V(III) et W(VI - x). Ainsi, pour  $\text{FeO}_x\{\text{uFP}\}$ , on identifie les phases  $\text{FeCl}_2(\text{H}_2\text{O})_2$  et  $(\text{NH}_4)\text{FeCl}_3$  avant pyrolyse et  $\text{Fe}_3\text{O}_4$  après pyrolyse ;  $\text{NbO}_x^{38}$  ne présente pas de phase cristalline avant traitement thermique ;  $\text{VO}_x\{\text{uFP}\}$ , dont le

diffractogramme n'est pas interprétable avant pyrolyse conduit à  $V_2O_3$  après pyrolyse ; enfin,  $WO_x\{uFP\}$ , qui ne présente aucune phase cristalline avant pyrolyse mène à un  $H_{0.23}WO_3$  peu cristallin par pyrolyse. De telles différences dans le degré d'oxydation des métaux n'avaient jusqu'ici été observées sur aucune de nos synthèses. Cette réduction semble se produire lors de la réaction de minéralisation de la cellulose, et non lors de la pyrolyse.

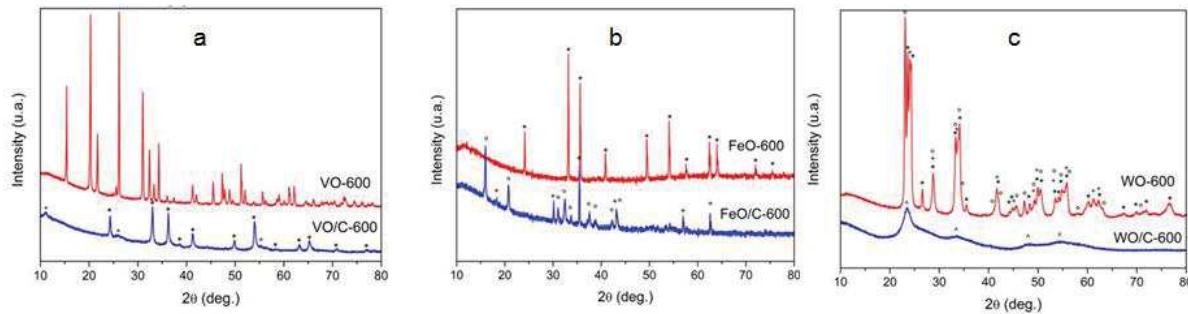


Fig. III.9 : Diffractogrammes de a)  $V_2O_5$  (VO-600) et  $V_2O_3/C$  (VO/C-600), b)  $Fe_2O_5$  (FeO-600) et  $Fe_2O_5/C$  (FeO/C-600), c)  $WO_3$  (WO-600) et  $H_{0.23}WO_3/C$  (WO/C-600)

Cette carbo-réduction gagnerait à être étudiée plus profondément, car son contrôle permettrait l'obtention de sous-oxydes métalliques tirant parti des avantages de la minéralisation de la cellulose (morphologie, présence de carbone intrinsèque). D'autre part, les différences observées sur les taux de conversion et les morphologies, en fonction du chlorure métallique, suggèrent que la réactivité varie d'un chlorure à l'autre. Comprendre les raisons de cette variation permettrait de connaître les conditions opératoires adaptées à chaque système. Une question se pose également : tous les chlorures métalliques sont-ils envisageables ? L'effet du chlorure métallique sur la structuration du carbone est un autre phénomène important à mieux comprendre. Ainsi, la déshydratation qui se produit lors de la minéralisation pose des questions sur le matériau carboné qui en résulte et son évolution ultérieure en pyrolyse.

### III.3 – La minéralisation de nanocelluloses<sup>41</sup>

De nombreuses applications nécessitent une grande surface spécifique afin de maximiser les surfaces par lesquelles s'opère la fonctionnalité des matériaux tels que la catalyse, l'absorption ou le stockage d'énergie. Dans cette optique, l'utilisation des nanocelluloses visait à augmenter la surface réactive du support cellulosique, augmenter sa réactivité et accéder à un assemblage nanométrique entre le carbone et l'oxyde dans le cas d'une pyrolyse. Dans ce dernier cas, la croissance de l'oxyde se faisant autour de la fibre de cellulose, on pourrait obtenir une structure nanofibrillée avec un cœur carboné et une coquille d'oxyde. En plus du papier filtre déjà mentionné, deux types de cellulose ont été utilisés : la cellulose micro-fibrillée (MFC) qui est un aérogel de cellulose séché par lyophilisation dans un mélange eau/<sup>t</sup>BuOH, et qui possède une surface spécifique de  $\sim 150 \text{ m}^2 \cdot \text{g}^{-1}$  ; la cellulose bactérienne (BC), qui est également un aérogel de cellulose, mais obtenue par lyophilisation classique, et possède

une faible surface spécifique. Deux études ont été réalisées dans cet objectif : la première, reproduite au chapitre IV.3, concerne la synthèse de composites oxyde de niobium/carbone à partir de papier filtre, de cellulose microfibrillée et de cellulose bactérienne. La seconde, présentée au chapitre IV.4, s'intéresse à la synthèse d'oxyde de titane à partir de cellulose microfibrillée.

La minéralisation par  $\text{Nb}_2\text{Cl}_{10}$  de FP a été comparée à celles de MFC et BC ( $T_{\text{chauffage}} = 85^\circ\text{C}$  dans les trois cas). En premier lieu, on observe d'importantes différences de taux de conversion en fonction du type de cellulose utilisé. Le meilleur taux de conversion est obtenu avec la cellulose micro-fibrillée (25 %) ; viennent ensuite le papier filtre, qui présente un taux de conversion de 20 % et enfin la cellulose bactérienne, avec un taux de conversion de 13 %. On constate également que les composites issus des MFC et BC ont une proportion en carbone plus faible que ceux obtenus à partir de FP ; leur réactivité est donc plus importante. On peut également noter la différence de taux de conversion entre  $\text{Nb}_2\text{O}_5$ ,<sup>38</sup> de 20 %, et celui de  $\text{TiO}_2$ ,<sup>38</sup> de 52 %. Comme on l'a vu au chapitre précédent, il semble que le taux de conversion soit fortement dépendant du chlorure métallique utilisé.

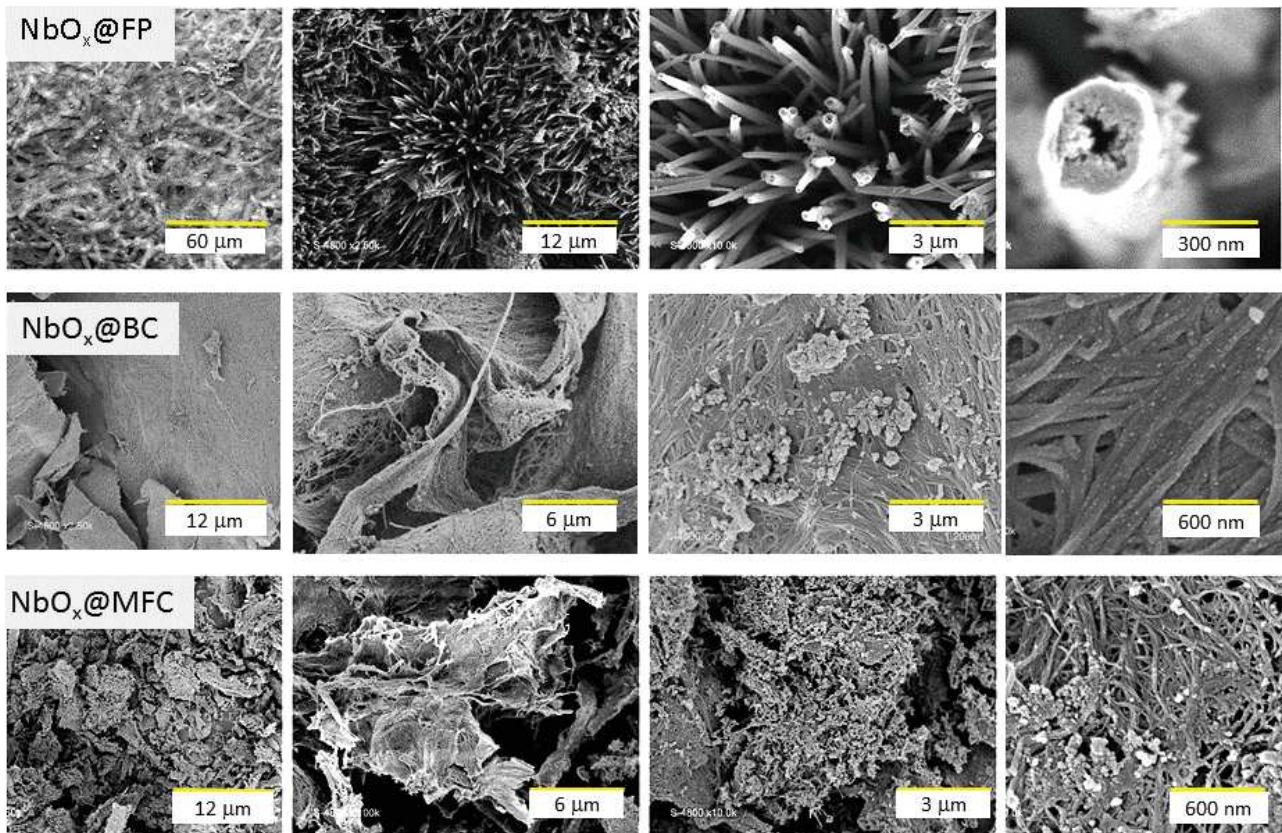


Fig. III.10 : Images MEB de  $\text{NbO}_x$ ,<sup>38</sup>  $\text{NbO}_x\{\text{MFC}\}$  et  $\text{NbO}_x\{\text{BC}\}$

Les images MEB de  $\text{NbO}_x$ ,<sup>38</sup> présentées dans la Fig. III.10, révèlent une morphologie proche de celle obtenue à  $150^\circ\text{C}$  (cf. chapitre III.2), alors que les images MEB de  $\text{NbO}_x\{\text{MFC}\}$  et  $\text{NbO}_x\{\text{BC}\}$  montrent la formation d'une couche d'oxyde autour des nanofibres de cellulose, avec la présence ponctuelles

d'agrégats de quelques dizaines de nanomètres. Après traitement pyrolyse, les aiguilles creuses de  $\text{NbO}_x$ <sup>38</sup> semblent s'être écroulées (Fig. III.11), tandis que les agrégats de  $\text{NbO}_x\{\text{MFC}\}$  et  $\text{NbO}_x\{\text{BC}\}$  ont grossi, des particules cristallines étant par ailleurs disséminées sur la surface des fibres.

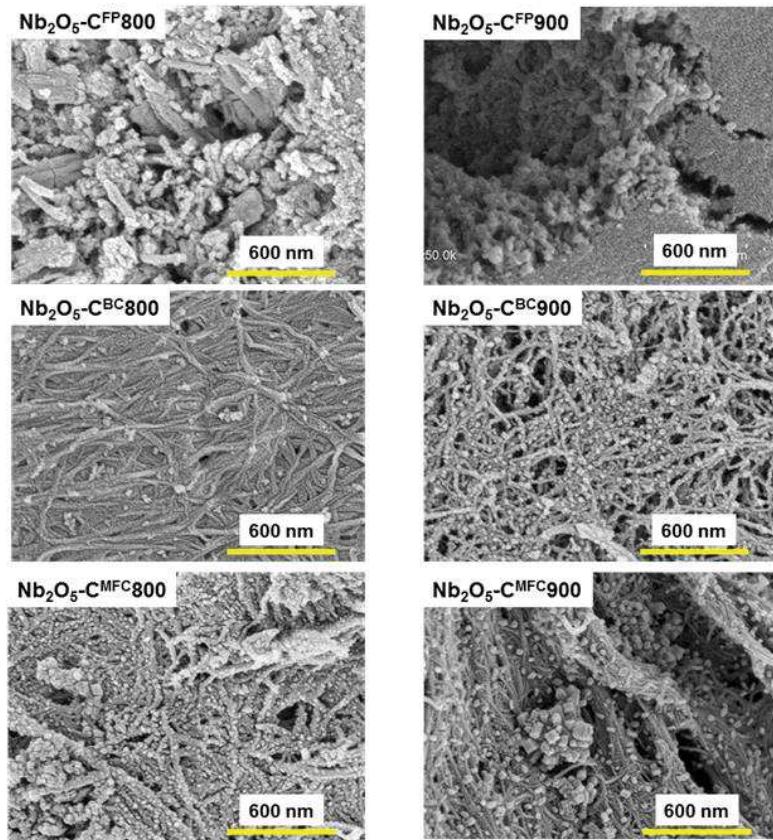


Fig. III.11 : Images MEB de  $\text{NbO}_x$ ,<sup>38</sup>  $\text{NbO}_x\{\text{MFC}\}$  et  $\text{NbO}_x\{\text{BC}\}$  après pyrolyse à 800 °C et 900 °C

Les composites  $\text{Nb}_2\text{O}_5/\text{C}$  ont été testés comme matériaux de supercapaciteurs. L'évaluation des trois matériaux révèle des performances intéressantes dans le cas de  $\text{Nb}_2\text{O}_5/\text{C}\{\text{MFC}\}$ , mais permet surtout, en comparant les trois matériaux, de déterminer les propriétés clés pour les capacités du matériau : la surface spécifique et la proportion de l'oxyde par rapport au carbone. Comme on le détaille en IV.3, on peut en effet constater que les capacités des matériaux sont corrélées à la fois avec la proportion oxyde/carbone et avec leurs porosités :  $\text{Nb}_2\text{O}_5/\text{C}\{\text{MFC}\}$  possède la surface spécifique la plus élevée – résultat de l'utilisation d'un aérogel de MFC – et les capacités les plus élevées.  $\text{Nb}_2\text{O}_5/\text{C}\{\text{BC}\}$  et  $\text{Nb}_2\text{O}_5/\text{C}$ ,<sup>38</sup> obtenus à partir de cellulosés faiblement poreuses, possèdent des surfaces spécifiques et des capacités plus faibles.

La seconde étude porte sur la synthèse de  $\text{TiO}_2$  ou de composite  $\text{TiO}_2/\text{C}$  par minéralisation de la nanocellulose. La caractérisation du  $\text{TiO}_2\{\text{MFC}\}$  montre, dans un premier temps, que le taux de conversion de la MFC (46 %) est comparable à celui du papier filtre. De manière inattendue, l'augmentation de la surface spécifique du support cellulosique ne permet pas d'augmenter sa

transformation, une observation à garder en mémoire dans la perspective de la compréhension du processus de minéralisation. En revanche, la surface spécifique des composites  $\text{TiO}_2/\text{C}$  issus de la pyrolyse est nettement supérieure :  $110 \text{ m}^2\cdot\text{g}^{-1}$  pour  $\text{TiO}_2/\text{C}\{\text{MFC}\}\text{-600}$  contre  $15 \text{ m}^2\cdot\text{g}^{-1}$  pour le  $\text{TiO}_2$ , ce phénomène étant également observé dans le cas de la minéralisation par  $\text{Nb}_2\text{Cl}_{10}$ .

La RMN SS du  $^{13}\text{C}$  nous fournit également des informations importantes sur la réactivité de la cellulose : en plus de confirmer la dégradation partielle de la cellulose (Fig. III.11, deux massifs marqués par des flèches vertes), elle nous apporte une indication sur la sélectivité de la réaction. En effet, l'analyse du spectre RMN permet de conclure à la forte diminution des fonctions alcools primaires du carbone C6 (indiquées par le trait gris dans la Fig. III.12).

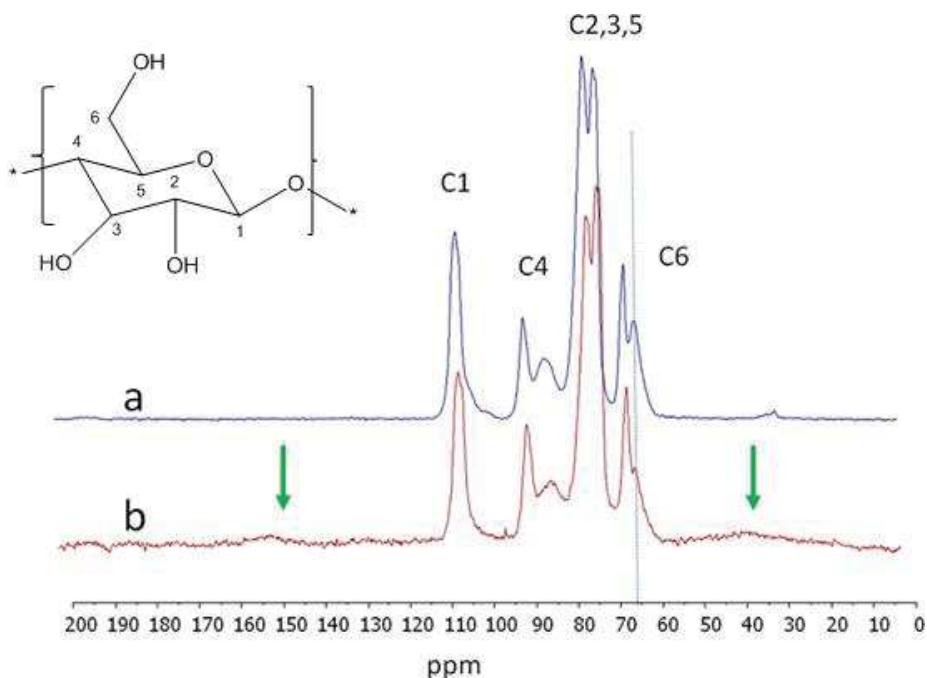


Fig. III.12 – RMN  $^{13}\text{C}$  solide de a) cellulose micro-fibrillée et b)  $\text{TiO}_2\{\text{MFC}\}$

De plus, on trouve ici une confirmation de la dégradation de la cellulose à une température relativement basse grâce à la présence de signaux larges typiques de la formation des "chars", un mélange de composés aromatiques et/ou insaturés, formés habituellement par une dégradation thermique à plus haute température.

La Fig. III.13 regroupe des images MEB et TEM, et montre clairement que la réPLICATION des fibres se fait parfaitement dans le cas de  $\text{TiO}_2\{\text{MFC}\}$  comme dans le cas de  $\text{TiO}_2$ ,<sup>38</sup> cette réPLICATION étant peu ou prou préservée après traitement thermique. Par ailleurs, des images à fort grossissement révèlent la formation de motifs semblables à des épines sur les fibrilles. Si les limites de grossissement du microscope ne permettent pas de pousser plus loin la précision des images, on peut toutefois supposer qu'il s'agit là d'excroissances cristallines ; on serait donc encore une fois face à une croissance du cristal vers l'extérieur de la fibre, et pas simplement sur la formation d'une couche d'oxyde enrobant la fibre. Cette même analyse semble confirmer une structure nanofibreuse cœur coquille  $\text{TiO}_2/\text{C}$  pour les composites après pyrolyse.

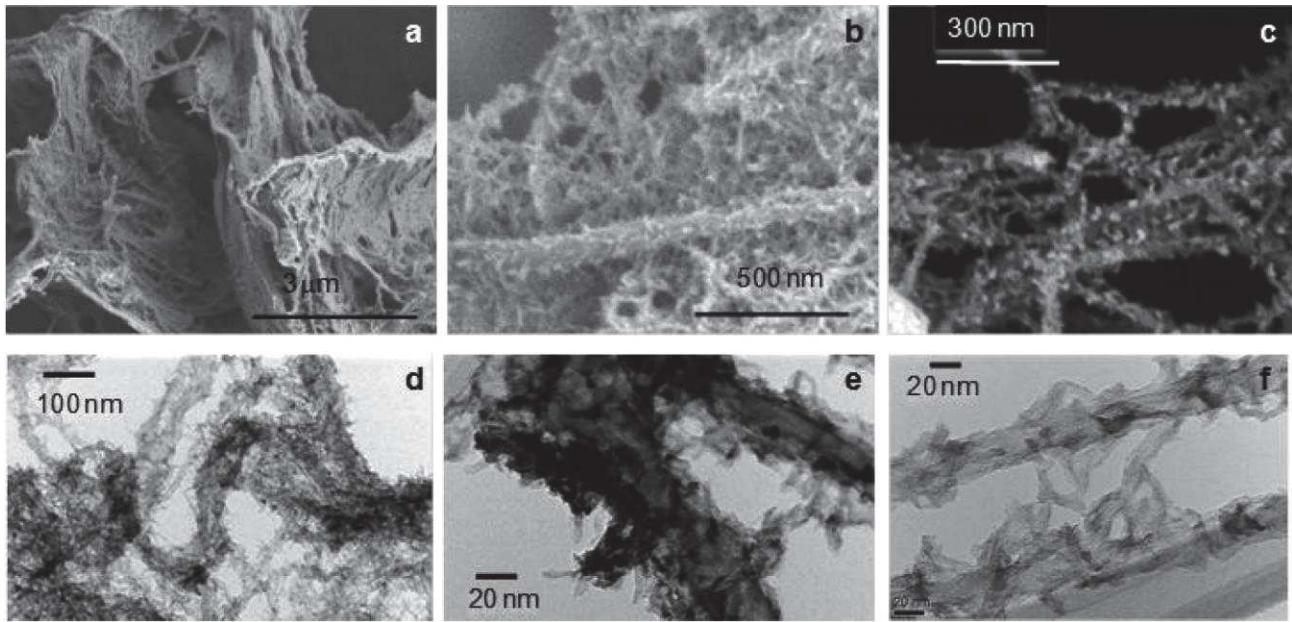


Fig. III.13 : Images de NFC (MEB, a) et  $\text{TiO}_2\{\text{MFC}\}$  (MEB, b-c ; TEM, d-f)

Le composite  $\text{TiO}_2/\text{C}$  issu de la pyrolyse de  $\text{TiO}_2\{\text{MFC}\}$  a fait l'objet de cyclages galvanostatiques afin de déterminer son potentiel comme matériau d'électrode de batterie Li-ion. On retrouve un comportement électrochimique typique des échantillons nanocristallins. Cependant, si les capacités initiales ( $\sim 130 \text{ mA.h.g}^{-1}$  réversibles) sont comparables à celles du composite issu de  $\text{TiO}_2\{\text{uFP}\}$ , elles subissent une décroissance continue au cours du cyclage. Dans le même temps, l'efficacité coulombique croît relativement lentement pour atteindre 96 %, une valeur considérée comme basse. Ces comportements sont attribués à la surface spécifique élevée du matériau, combinée à une quantité importante de résidus organiques. Ces deux éléments provoquent une dégradation de l'électrolyte tout au long du cyclage.

Ces deux études nous permettent de tirer une conclusion importante concernant la minéralisation de nanocelluloses : s'il est possible d'obtenir des assemblages d'oxydes métalliques aux échelles visées, la porosité du matériau obtenu est commandée par la structure de la cellulose utilisée, plus que par les dimensions de ses fibres. Ainsi, malgré la nanofibrillation de la cellulose bactérienne, sa structure en feuillet limite la porosité du composite synthétisé par rapport à la cellulose microfibrillée, qui forme un aérogel plus aéré.

En résumé, les travaux montrent que, dans l'ensemble, la minéralisation se déroule de façon similaire sur les nanocelluloses et sur le papier filtre. Il n'y a pas d'agglomération des fibres, l'oxyde se forme de manière homogène autour de la nanofibre de cellulose et ainsi, après calcination ou pyrolyse, on aboutit respectivement à un oxyde métallique de plus grande surface spécifique ou à une structure nanofibrillée oxyde métallique/C. On note que le taux de conversion n'est pas augmenté de manière significative par l'augmentation de la surface exposée par la cellulose. Enfin, nous constatons ici toute l'importance de la fabrication de ces celluloses micro et nanofibrillées, qui conditionne de manière importante leurs structures. Bien que produite à partir de cellulose bactérienne, un séchage par

lyophilisation simple, sans addition de  $t$ BuOH, conduit à des fibres partiellement agglomérées. À l'opposé, la lyophilisation de la MFC avec du  $t$ BuOH conduit à des fibres plus "aérées". Les développements de ces nanocelluloses passent donc par une maîtrise de leur élaboration. Cet enseignement devrait permettre d'optimiser les performances des matériaux synthétisés : dans le cas de  $Nb_2O_5/C$ , où une grande surface spécifique semble souhaitable, l'utilisation d'un aérogel de cellulose bactérienne avec des nanofibrilles nettement séparées serait probablement profitable ; au contraire, dans le cas de  $TiO_2/C$ , où la grande surface spécifique semble limiter la stabilité des performances, l'usage de cellulose bactérienne en feutre pourrait s'avérer intéressant.

### **III.4 - Compréhension du processus de minéralisation**

La compréhension de la transformation chimique durant le processus de minéralisation est un enjeu pour permettre le développement de cette approche et éventuellement l'ouvrir à d'autres procédés : accéder à d'autres oxydes, augmenter le taux de transformation, maîtriser la structure des composites. Comme nous avons commencé à le mentionner précédemment, différentes études nous ont permis d'affiner notre compréhension du processus de minéralisation. Nous tentons ici de les résumer en y adjoignant des expériences complémentaires.

Nos travaux se basent sur certains résultats de la chimie de la cellulose, notamment ceux portant sur son comportement en milieux aqueux. On sait ainsi que des conditions acides provoquent des transformations chimiques sur la cellulose, déshydratation et hydrolyse en particulier.<sup>16, 42</sup> De plus, la présence de sels métalliques est connue pour catalyser ces transformations – spécialement le processus de déshydratation. Par ailleurs, des travaux ont montré que certains oxydes métalliques ( $TiO_2$ ,  $WO_3$ ,  $Al_2O_3$  par exemple)<sup>43</sup> catalysent la déshydratation d'alcools simples – on peut donc imaginer que ce soit le cas pour la déshydratation des alcools de la cellulose. Enfin, on sait que la réactivité des chlorures métalliques sur les fonctions chimiques possédant des hydrogènes est à la fois rapide et quantitative.

Les conditions expérimentales que nous utilisons sont significativement différentes, mais peuvent être comparées aux travaux précédents. En premier lieu, la présence de chlorure métallique et de fonctions protiques de la cellulose – ou d'eau – doit entraîner la formation de HCl dans le milieu. On peut s'attendre à des réactions de déshydratation de la cellulose, activées par la présence de l'oxyde métallique ou de complexes métalliques. Enfin, des réactions de sol-gel non-hydrolytique ne sont pas à exclure.

On peut tirer plusieurs conclusions des expériences déjà évoquées. Tout d'abord, on peut éclaircir un point sur l'origine des oxygènes conduisant à la formation de l'oxyde : il n'est pas possible de sécher parfaitement la cellulose, mais la quantité d'eau absorbée ne représente, d'après certains auteurs, que ~5.5 wt%.<sup>44</sup> Des analyses ATG effectuées sur nos échantillons de cellulose permettent d'évaluer la désorption d'eau à ~2 wt%, dans nos conditions expérimentales. Dans l'hypothèse d'une réaction totale entre cette seule quantité d'eau et du chlorure de titane en excès, on atteindrait un taux de conversion de 8.5 %. Or, la minéralisation de FP par  $TiCl_4$  (en solution dans le dichlorométhane) présente un taux de conversion de 53 %, qui implique donc la présence d'une autre source d'oxygène.

D'autre part, on constate un important dégagement de HCl (dégagement gazeux à l'ouverture de l'autoclave, forte acidité du solvant retiré). D'après ce que l'on connaît de la réactivité des chlorures métalliques, on doit envisager une réaction entre  $\text{TiCl}_4$  et les alcools de la cellulose, au moins au début de la réaction. Par ailleurs, aucun sous-produit chloré n'a été identifié à ce jour (en dehors de HCl),<sup>32-33, 35, 39-41, 46</sup> or un mécanisme de sol-gel non-hydrolytique aurait dû produire des dérivés organochlorés. Simultanément, les analyses  $^{13}\text{C}$  RMN et IR montrent une modification profonde de la cellulose, pouvant indiquer une déshydratation de la cellulose. La source d'oxygène apparaît donc être l'eau produite par la déshydratation de la cellulose à pression et température modérées.

En revanche, on pouvait se poser la question du rôle du précurseur métallique, au-delà de sa réaction avec les alcools : un chlorure métallique (ou autre précurseurs engendrant une acidité) est-il indispensable, ou la présence d'oxyde métallique formé au contact de l'eau résiduelle est-elle suffisante pour catalyser la déshydratation ? Pour répondre à cette question, nous avons réalisé des expériences employant divers précurseurs d'oxyde de titane, en présence de solvant ou non. Trois précurseurs de  $\text{TiO}_2$  ont été testés :  $\text{TiBr}_4$  a été choisi car pouvant entraîner la formation de HBr, un acide fort ( $\text{pK}_a = -9$ ) et  $\text{Ti(OiPr)}_4$  a été retenu car son hydrolyse/condensation ne doit pas conduire à un dégagement d'acide. Enfin,  $\text{TiF}_4$  a été utilisé pour une synthèse sans solvant, son point de fusion élevé (377 °C, avec sublimation) permettant de vérifier l'importance d'un équilibre liquide-gaz (ou solide-gaz) à basse température.

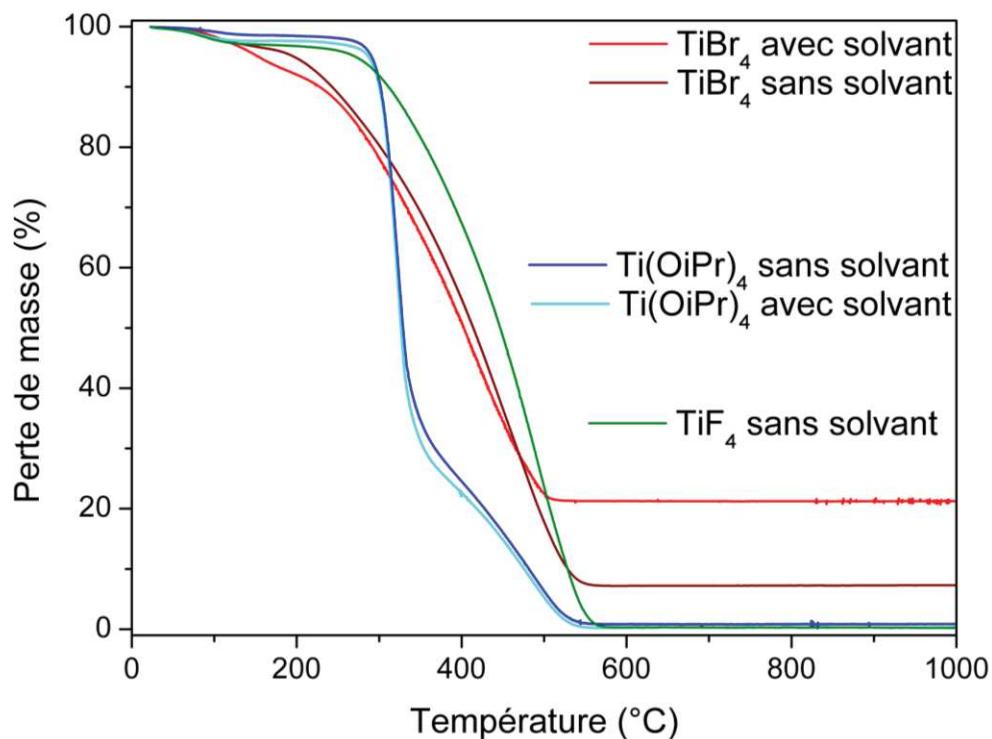


Fig. III.14 : ATG sous air des  $\text{TiO}_2@\text{FP}$  obtenus à partir de  $\text{TiBr}_4$  et de  $\text{Ti(OiPr)}_4$ , avec ou sans solvant

Avec l'utilisation de  $\text{TiCl}_4$  comme référence, la comparaison des taux de conversion, calculés à partir des ATG de la Fig. III.14, permet de confirmer la nécessité de conditions acides. En effet, si  $\text{TiCl}_4$  produit des taux de conversion de 53 % avec solvant et 52 % sans solvant, les taux de conversion résultant de

l'utilisation de  $\text{Ti(OiPr)}_4$  sont négligeables, et ceci avec ou sans présence de solvant. Il en va de même pour l'utilisation de  $\text{TiF}_4$ , qui ne produit pas de  $\text{TiO}_2$ . En revanche, les taux de conversion lors de l'utilisation de  $\text{TiBr}_4$  sont significatifs : la synthèse en présence de solvant a un taux de conversion de 35 %, et la synthèse sans solvant de 17 %, sans que l'une ou l'autre présente de morphologie particulière. A ce stade il faut mentionner la volatilité des précurseurs, particulièrement importante pour les réactions sans solvant, et leur solubilité, particulièrement importante pour des réactions en solution. Le chlorure de Titane (IV) est idéal car d'une part il présente un point d'ébullition de 136 °C à  $P_{\text{atm}}$  et, d'autre part, les quantités utilisées sont entièrement solubles dans le dichlorométhane. Les faibles taux de conversion obtenus pour  $\text{TiBr}_4$  peuvent être dus à son point d'ébullition élevé (230 °C), une faible tension de vapeur limitant la minéralisation sans solvant. Le cas de la minéralisation en présence de solvant peut s'expliquer par une solubilité plus faible dans le dichlorométhane et par une réactivité sur les fonctions protiques moins forte que celle de  $\text{TiCl}_4$ .

Une étude cinétique a été menée en utilisant le procédé sans solvant, avec des temps de chauffage de 24h, 60h et 96h (à 85 °C) ayant pour but d'observer la cinétique sur un temps court. La première information est apportée par les analyses thermogravimétriques : le taux de conversion augmente avec la durée de chauffage, passant de 25 % après 24h à 40 % après 96h. De plus, la diffraction des rayons X nous apprend que la phase cristalline  $\text{TiO}_2$  anatase est présente dès les premières 24h. Plus intéressantes, les images MEB révèlent que la morphologie des cristaux change sensiblement au cours du temps ; les fines aiguilles initialement formées (24h) semblent s'épaissir selon un seul axe, formant ainsi des lamelles (60h). Ce motif reste inchangé après 96h, mais on observe une densification de ces lamelles, surtout au plus près de la fibre, un phénomène déjà observé sur la première synthèse sans solvant (temps de chauffage 7 jours). Cette densification conforte l'idée d'une croissance depuis la fibre vers l'extérieur.

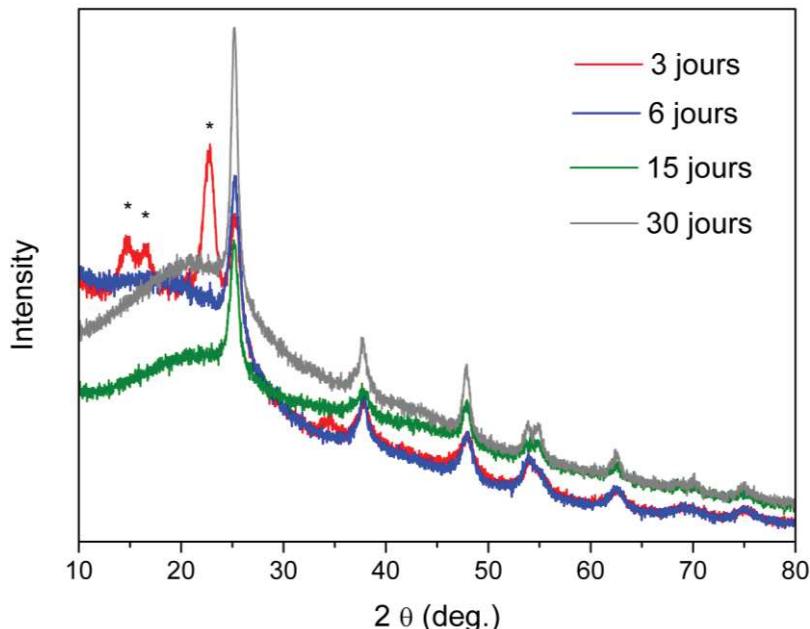


Fig. III.15 : Diffractogrammes des échantillons obtenus par minéralisation de la cellulose par  $\text{TiCl}_4$  (0.1  $\text{TiCl}_4$ ) après 3 jours, 6 jours, 15 jours et 30 jours de réaction. \* : pics de diffraction de la cellulose

Une seconde étude, menée avec des quantités de  $\text{TiCl}_4$  10 fois plus faibles, visait à démontrer l'importance de ce rapport Ti/cellulose. Toujours à 85 °C, les échantillons ont cette fois été chauffés 3 jours, 6 jours, 15 jours et 30 jours. Cette étude est difficilement interprétable : les images MEB montrent qu'une croûte d'aspect amorphe s'est formée autour des fibres, ce qui empêche toute observation sur le mode de croissance. On constate néanmoins, grâce à la diffraction des rayons X présentée dans la Fig. III.14, l'existence de domaines cristallins de  $\text{TiO}_2$  anatase, la taille des cristallites augmentant avec le temps de chauffage. La même analyse indique également une amorphisation complète de la cellulose à partir de 6 jours. Par ailleurs, les analyses ATG de la Fig. III.15 indiquent que le taux de conversion augmente jusqu'à se stabiliser à 18 % après 6 jours.

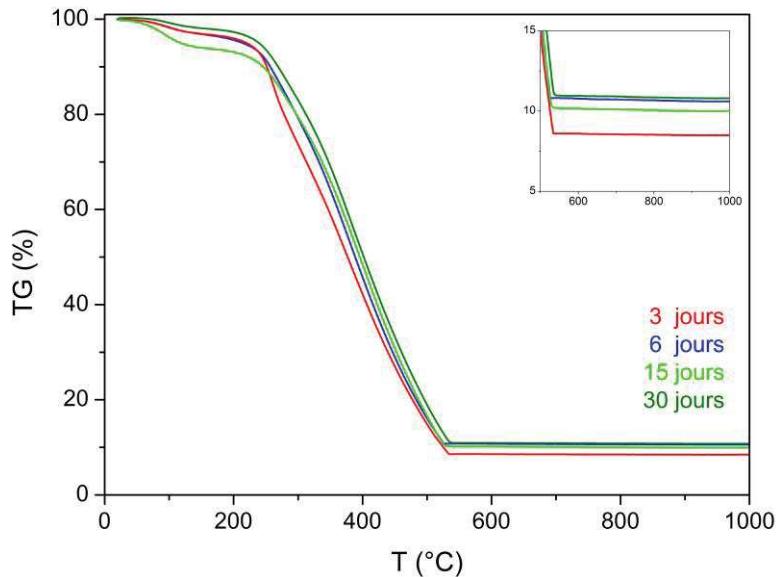
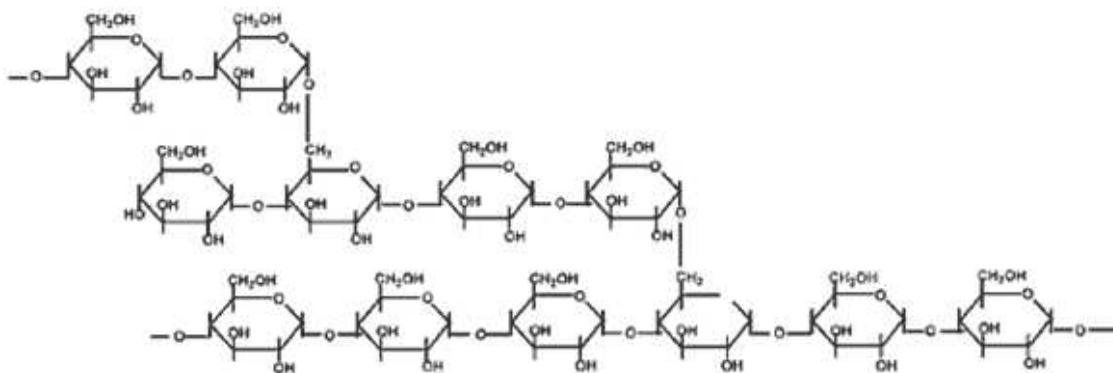
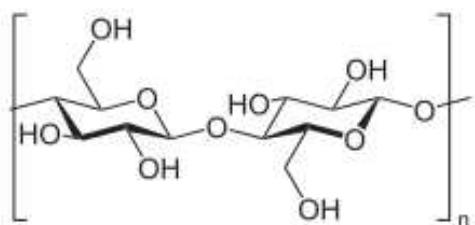


Fig. III.16 : ATG sous air de  $\text{TiO}_2$  obtenu par minéralisation de cellulose par  $\text{TiCl}_4$  pendant 3 jours, 6 jours, 15 jours et 30 jours

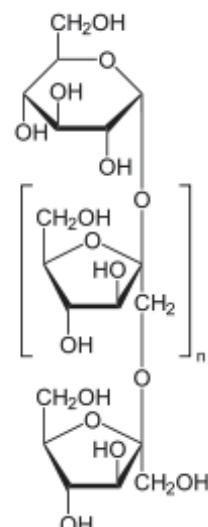
Enfin, des synthèses exploratoires ont été effectuées en utilisant d'autres polysaccharides que la cellulose, possédant une formule chimique proche (présentées dans la Fig. III.17) mais n'ayant pas la même structure fibreuse. On cherchait ainsi à montrer le potentiel d'autres polysaccharides tels que l'amidon et le chitosan ainsi qu'à vérifier l'importance de la structure fibrillaire de la cellulose. Par ailleurs, nous avons également testé l'inuline, en tenant compte de sa structure furanosique, dans l'idée que cette différence structurale (par rapport à la structure pyranosique des autres polysaccharides testés) pourrait nous renseigner sur l'évolution chimique du support.



amidon



cellulose



inuline

chitosan

Fig. III.17 : formules chimiques de la cellulose, du chitosan, de l'amidon et de l'inuline

La synthèse de l'inuline a été effectuée en présence de solvant, tandis celles de l'amidon et du chitosan utilisaient le procédé sans solvant ; le chauffage, à 85 °C, a duré 7 jours dans tous les cas. L'analyse des taux de conversion, calculés d'après les ATG présentées sur la Fig. III.18, montre des disparités importantes entre les différents polysaccharides. Le meilleur taux de conversion est obtenu avec l'inuline (65 %), suivie par l'amidon (52 %), le taux de conversion du chitosan étant beaucoup plus faible

(22 %). Dans les mêmes conditions, le taux de conversion de la cellulose était de 52 %. Le taux de conversion du chitosan, plus faible, peut être expliqué par le fait que ce polysaccharide a une proportion d'oxygène plus faible (37.8 wt%, contre 49.1 wt% pour l'inuline et 49.4 wt% pour l'amidon et la cellulose). De plus, les fonctions amine du chitosan peuvent neutraliser une partie du HCl dégagé, et donc limiter son effet catalytique. Concernant l'inuline, le début du profil d'ATG du produit de départ indique une perte de masse de ~10 % entre 120 et 180 °C, et montre un taux de conversion supérieur à celui des autres polysaccharides.

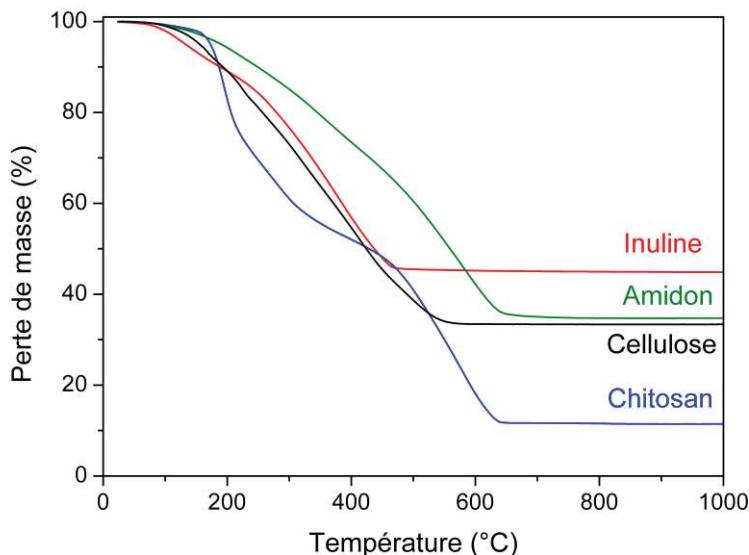


Fig. III.18 : ATG sous air de  $\text{TiO}_2$  synthétisé à partir d'inuline, d'amidon, de cellulose et de chitosan

Deuxièmement, la comparaison des images MEB de  $\text{TiO}_2^{38}$ ,  $\text{TiO}_2\{\text{chitosan}\}$ ,  $\text{TiO}_2\{\text{amidon}\}$  et  $\text{TiO}_2\{\text{inuline}\}$  (Cf. Fig. III.19) permet de constater des différences significatives. En particulier,  $\text{TiO}_2^{38}$  est le seul échantillon à présenter des morphologies en amas de feuillets (Fig. III.19 a et b), les trois autres matériaux présentant des morphologies en tapis d'aiguilles plus homogènes. Des quatre polysaccharides testés, la cellulose est le seul à présenter une structure fibrillaire : il est donc possible de penser que l'originalité des morphologies obtenues par minéralisation de la cellulose est liée à cette structure. Si des hypothèses peuvent être formulées sur les raisons de cette corrélation (réseau de liaisons hydrogène, processus de déshydratation thermique, accessibilité des fibres), de futurs travaux sont nécessaires pour les confirmer.

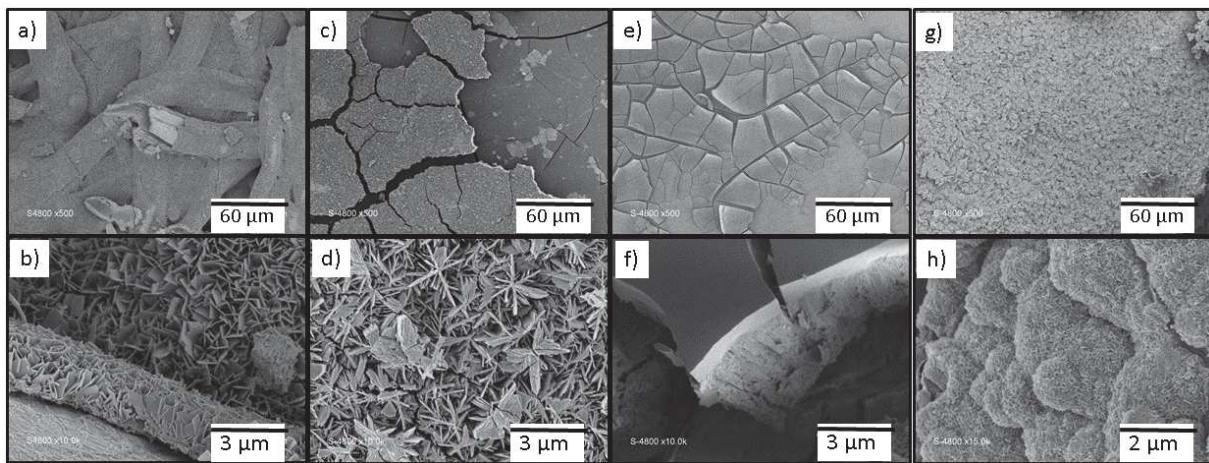


Fig. III.19 : Images MEB de  $\text{TiO}_2$  synthétisé à partir de a, b) cellulose, c, d) chitosan, e, f) amidon et g, h) inuline

Quoi qu'il en soit, cette dernière observation met en évidence l'originalité des morphologies obtenues par minéralisation de la cellulose, et invite à quelques remarques sur ce sujet. Tout d'abord, ces morphologies semblent dans leur ensemble croître depuis la fibre vers l'extérieur, à partir de points de germination plus ou moins concentrés. Bien que les morphologies observées soient fortement dépendantes du chlorure métallique, il semble qu'elles ne soient originales qu'avec la cellulose. De plus, on a vu au chapitre III.1 que le réseau des liaisons hydrogène a un lien avec la morphologie formée. Cependant, il nous est à ce jour impossible de prévoir ou même de comprendre la cause de cette croissance inédite.

## **Conclusions**

La minéralisation de la cellulose par des chlorures métalliques est un procédé original et d'une grande versatilité, produisant des morphologies inédites, qui posent des questions quant à leur formation. Initialement envisagé pour la synthèse d'oxyde de titane, nous avons pu montrer son potentiel pour la synthèse d'autres oxydes métalliques. Permettant de synthétiser aussi bien des oxydes métalliques purs que des composites oxyde métallique/carbone, elle a été appliquée avec succès à la fabrication d'oxydes de fer, de niobium, de titane, de tungstène et de vanadium. Le procédé est transposable à des celluloses de différentes dimensions, macro, micro ou nano, et on peut ainsi envisager son adaptation en fonction du domaine d'application visé.

Les oxydes métalliques, matériaux-cibles de ce procédé, sont en effet une famille de composés aux larges possibilités, dans des domaines où une morphologie spécifique peut avoir un grand intérêt. On a montré la pertinence de plusieurs composites,  $TiO_2/C$  et  $Nb_2O_5/C$  de différents types, comme matériaux d'électrode pour le stockage de l'énergie.

Les progrès effectués quant à la compréhension du mécanisme de la réaction permettent d'envisager des perspectives prometteuses : la synthèse d'oxydes métalliques (ou de composites) nanométriques, possédant des morphologies exceptionnelles, peut désormais être envisagée sans solvant, que ce soit pour les étapes de synthèse ou de lavage. De plus, l'exploration de l'imprégnation pré-synthèse devrait conduire à un meilleur contrôle de la morphologie ou à un contrôle des composés formés (sous-oxydes métalliques, dopage).



## **IV – Publications**

### **IV.1 – Synthesis of Titania@Carbon nanocomposite from urea-impregnated cellulose for efficient lithium and sodium batteries**

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*ChemSusChem* **2016**, 9 (3), 264-273

**Abstract:** Nanostructured TiO<sub>2</sub> and TiO<sub>2</sub>@C nanocomposites were prepared directly from urea-impregnated cellulose by a simple reaction/diffusion process and evaluated as negative electrode materials for Li and Na batteries. By direct treatment with TiCl<sub>4</sub> in anhydrous condition, the urea impregnation of cellulose impacts both the TiO<sub>2</sub> morphology and the carbon left by cellulose after pyrolysis. Hierarchical TiO<sub>2</sub> structures with flowers morphology grown from-and-at the surface of the cellulose fibers are obtained without any directing agent. The resulting TiO<sub>2</sub>/cellulose composite is then transformed either into pure TiO<sub>2</sub> flowers by calcination in air at 600 °C, or into TiO<sub>2</sub>@C nanocomposites by pyrolysis in argon at 600 °C. Electrochemical studies demonstrate that both samples can (de)insert lithium and sodium ions and are promising electrode materials.

## **Introduction**

In agreement with the necessity of producing new tailored materials for improved electrochemical energy storage devices by sustainable processes, increasing researches focus on the use of biopolymers for the production of metal oxide and metal oxide-carbon composites. Replication of polysaccharides such as cellulose, chitosan and chitin, agarose, starch, or carrageenan is well-documented in the case of TiO<sub>2</sub>,<sup>[1-3]</sup> a well-known metal oxide that shows interesting properties as negative electrode in electrochemical devices.<sup>[4-8]</sup> Bio-template of cellulose by TiO<sub>2</sub> was initially done starting from TiF<sub>4</sub>,<sup>[9]</sup> and then was developed for the formation of TiO<sub>2</sub> nanotubes by sol-gel process<sup>[10, 11]</sup> or ALD.<sup>[12, 13]</sup> We recently reported the mineralization in strictly anhydrous conditions of different cellulosic fibers: cotton,<sup>[14]</sup> filter paper (FP),<sup>[15]</sup> or nano-fibrillated cellulose.<sup>[16]</sup> In this new approach, cellulose is considered as a template but also as a reagent from which oxygen atoms are transferred to the metal center of a metal chloride.

This direct one-step process is a type of mineralization that avoids preparation of any metal oxide sol or the use of sophisticated ALD equipment. More importantly, differently from other processes, TiO<sub>2</sub> with unusual nanostructured morphology, such as urchins and carpets of needles is obtained. While there is still no consensus on real-life applications of TiO<sub>2</sub> among the Li-ion batteries (LIBs) community, numerous reports are nonetheless focused on the enhancement of its performances as anode of Li-ion systems.<sup>[17, 18]</sup> If we consider the encouraging capacities of TiO<sub>2</sub> in LIBs, the study of TiO<sub>2</sub> as an anode for Na-ion batteries (MABs) is quite logical.<sup>[19-67]</sup> Indeed post-LIB era recently started, emerging from the concerns about lithium greenness. As a candidate of choice for lithium replacement, sodium is a current research focus. While, to some extent, the knowledge about lithium-based cathodes can be transposed to their sodium-based counterparts,<sup>[68]</sup> such assumption is not true for anodes, hence the recent emulsion regarding anode materials for MABs.<sup>[69]</sup> In a recent review,<sup>[69]</sup> it is shown that only nanosized TiO<sub>2</sub> appears to be efficient as negative electrode for MABs, due to the shortening of migration length.

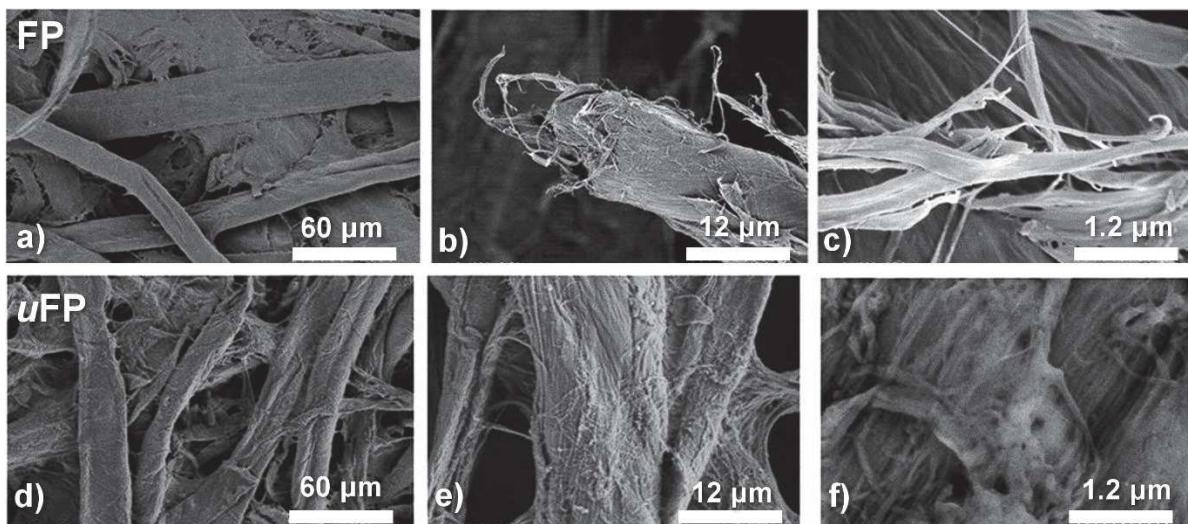


**Scheme 1.** Presentation of the concept, overall process and sample classification.

Here, we report a simple modification of the process which has remarkable effects on the morphology and on the properties of the final  $\text{TiO}_2$  and  $\text{TiO}_2@\text{C}$  compounds. As shown in Scheme 1, prior to treatment with  $\text{TiCl}_4$ , the filter paper is impregnated with an aqueous solution of urea. This treatment was investigated because urea is a versatile compound, especially in this situation. First it is frequently used as a nitrogen source, eventually leading to the N-doping of the  $\text{TiO}_2$ , which is expected to improve its conductivity properties.<sup>[70-72]</sup> Moreover, urea is an ideal dual-actor to dope carbons and to assist formation of nanosheet structures.<sup>[73, 74]</sup> Molecular dynamics simulations and NMR spectroscopy reveal that urea molecules close to a surface have a preferential orientation through hydrogen bonds to hydroxyl and hydroxymethyl groups located at the fibril surface.<sup>[75]</sup> Here, we evidence an important effect of urea adsorbed on paper prior its complete drying and mineralization with  $\text{TiCl}_4$  in anhydrous condition. Not only the morphology of the  $\text{TiO}_2$  is modified compared to urea-free process, but also the crystalline phase and the electrochemical behaviour of these materials that exhibit high potentialities as anode material for lithium and sodium ion batteries. We demonstrate here that *on-demand* nanotextured  $\text{TiO}_2$  works very well versus Na, which can be ascribed to the low diffusion barrier in this oxide,<sup>[76]</sup> as well as to the presence of a N-doped carbon core.

## Results and discussion

**Synthetic method. Urea-impregnated cellulose.** The preferred cellulose source used in our research was filter paper with a minimum content of 98 % of alpha-cellulose but the present methodology can easily be extended to other cellulose sources as already reported in the literature.<sup>[1, 15, 16]</sup> Figure 1 (a-c) displays the typical SEM images of the smooth fibres from cellulose filter paper (FP) with diameter of approximately 20  $\mu\text{m}$ . Urea impregnation was conducted by soaking FP into a 10 % aqueous solution of urea for one hour followed by 3 days of drying at 80 °C, yielding  $u\text{FP}$ . After such a process,  $u\text{FP}$  presents a modified surface with slightly degraded fibres (Figure 1d-f), suggesting that the microfibrillar outer structure of cellulose has been altered by urea at 80 °C, and no crystals of urea are detected at this stage.

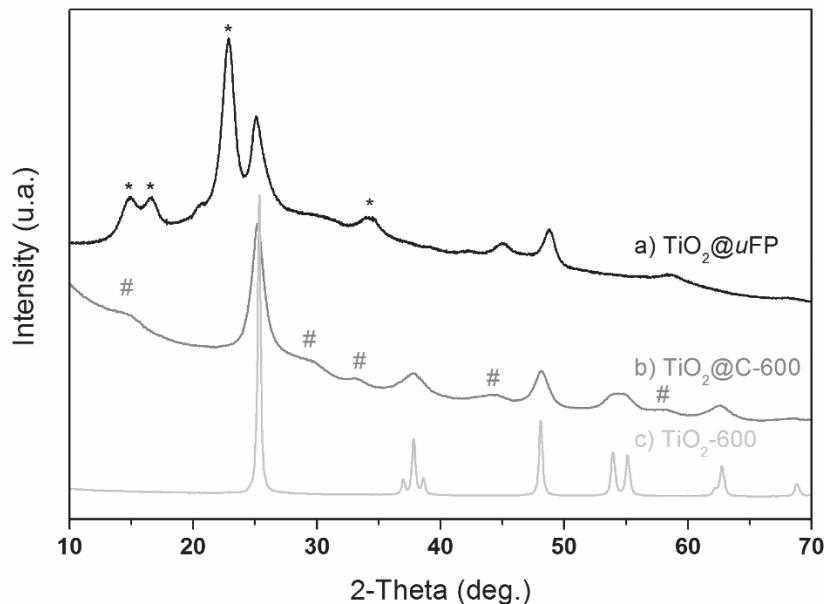


**Figure 1.** SEM images of filter papers before (top; *FP*) and after (bottom; *uFP*) impregnation in a 10 % aqueous solution of urea.

Cellulose is composed of microfibrils, each of which is an assembly of crystalline and semi-crystalline cellulose covered with amorphous nanofibrils of cellulose, and the microfibrils are held together by cross-linking.<sup>[77]</sup> A possible structural modification resulting from the urea impregnation is supported by infrared spectra in ATR mode of FP *uFP* (Figure S1) and agree with previous reports on the interactions between urea and cellulose.<sup>[75, 78]</sup> The appearance of new absorption bands in the IR spectrum of *uFP* in comparison with the one from FP clearly indicates that cellulose surface has been modified.<sup>[79-81]</sup> For instance, the bands in the 1600-1670 cm<sup>-1</sup> region should be assigned to the deformation vibrations of the NH<sub>2</sub> group, while weak to very weak peaks at 1715 and 783 cm<sup>-1</sup> belongs to the stretching and out-of-plane deformational vibrations of the carbonyl groups of urea. This allows us to conclude that urea is present at the cellulose surface, while changes in the structure of bands in the 3000-3500 cm<sup>-1</sup> region can be correlated with changes in inter- and intramolecular hydrogen bonding networks. Additionally, the low relative intensities of vibrational bands corresponding to carbonyl (783 cm<sup>-1</sup>) with respect to amine groups of the urea in the ATR-IR spectrum of *uFP* (Figure S1) indicates that NH<sub>2</sub> groups are more numerous than carbonyl, excluding any cellulose carbamate reaction.<sup>[79, 80]</sup> Moreover, decomposition of urea below its melting point (133 °C) into ammonia is unlikely.<sup>[82, 83]</sup> Comparison of XRPD patterns of FP and *uFP* showed weak signals of crystallized urea but no changes in the crystalline structure of cellulose, which suggests that either the reaction between urea and FP is extremely limited or occurs only in the amorphous domains of the microfibrils, keeping crystalline core unaffected (Figure S2). TG analyses under air further demonstrate the impact of urea (Figure S3). FP decomposes in three major steps: (i) water evaporation up to 285 °C, (ii) decomposition of hemicellulose and cellulose up to 350 °C, and (iii) oxidation of decomposition products up to 550 °C.<sup>[84]</sup> Decomposition of *uFP* occurs with slight but significant differences (Figure S3). Water evaporation is concomitant with urea decomposition up to 300 °C, and the inflection of TG curve at 144 °C may be characteristic of either the inception of urea pyrolysis or an earlier decomposition of cellulose/hemicellulose due to the action of urea and changes in the hydrogen bonding networks.<sup>[83, 85]</sup> Final decomposition step of *uFP* reaches a 100 %-weight loss at a temperature of 660 °C, which is almost 100 °C higher than for FP, thus indicating potential formation of nitrogen-doped carbonaceous oxidative products that degrade at higher temperature than undoped ones.<sup>[86]</sup>

**Mineralization process.** Mineralization of *uFP* was done by the solvothermal reaction of titanium tetrachloride and *uFP* in dichloromethane at 80 °C for 7 days. Mineralization can produce titanium dioxide by different possible reaction pathways: (i) a Ti-Cl alcoholysis, (ii) a Ti-Cl/C-O exchange, (iii) a hydrolysis with TiCl<sub>4</sub> water molecules of crystallization, and (iv) a possible intra- or inter-dehydration of cellulose.<sup>[15]</sup> Shape and mechanical consistence of TiO<sub>2</sub>@*uFP* hybrid material, after solvothermal treatment, is similar to the one of the starting *uFP*. While *uFP* is pure white, TiO<sub>2</sub>@*uFP* is dark brown.

The colour change suggests the formation of carbonaceous residues and supports the cellulose dehydration reaction during the mineralization at 80 °C.



**Figure 2.** X-ray diffraction patterns of  $\text{TiO}_2@\text{uFP}$  (a),  $\text{TiO}_2@\text{C-600}$  (b) and  $\text{TiO}_2\text{-600}$  (c); \* and # symbols indicates diffraction peaks of cellulose (FP) and  $\text{TiO}_2$  (B) phases, respectively.

Moreover, acidification of an aqueous solution containing  $\text{TiO}_2@\text{uFP}$  demonstrates the persistence of Ti-Cl bonds at this stage. XRPD measurement, as displayed on Figure 2a, confirms that, after mineralization, poorly crystalline anatase  $\text{TiO}_2$  is obtained, as shown by the presence of the main peaks at  $2\theta = 25.1^\circ$  and  $48.8^\circ$ , corresponding to  $(011)$  and  $(020)$   $hkl$  planes, respectively (ICSD #9855). Raman spectrum of  $\text{TiO}_2@\text{uFP}$  further confirms the presence of poorly crystalline anatase (Figure S4). Alongside anatase, cellulosic residue is still present, as shown by the peaks at  $2\theta = 14.9^\circ$ ,  $16.5^\circ$  and  $22.8^\circ$  that correspond to uFP XRD pattern (Figure S2). Whereas the dark brown colour of  $\text{TiO}_2@\text{uFP}$  may signify the formation carbonaceous species, not all the crystalline cellulose has been modified at this stage. The peak at  $2\theta = 20.6^\circ$  is currently attributed either to by-products, impurities, or modification of cellulosic domains. At the micrometre and nanometre scales, SEM images of  $\text{TiO}_2@\text{uFP}$  prior to any thermal treatment reveals a unique morphology of  $\text{TiO}_2$  flowers that cover homogeneously and continuously all the surface of cellulosic residue Figure 3. However, the closer to the surface of the cellulose, the denser is the  $\text{TiO}_2$  crust. Being significantly different from the urchins and carpets of needles reported when using a urea-free process,<sup>[15]</sup> this denser part evidences an important effect of the urea on the morphology of the oxide by this process, either through the modification of cellulose, and a potentially higher density of nuclei, or by its interaction with the growing  $\text{TiO}_2$  crystals. One of these flowers of  $\text{TiO}_2@\text{uFP}$  observed in TEM is shown in the Figure 4, and that confirms that these super-structures are made of elongated  $\text{TiO}_2$  nano-petals with approximately 200 nm in length and a width of 50 nm.

Thermal treatment of  $\text{TiO}_2@\text{uFP}$  under air or argon leads to TG curves similar in shape (Figure S5). The first weight loss of approximately 10 % in the range 25-225 °C might be attributed to urea decomposition and water evaporation, along with hydrolysis and condensation of residual Ti-Cl groups. The second weight loss (225-600 °C) is of approximately 35 % under argon, and this may correspond mostly to carbonization, alongside the condensation of hydroxyl groups linked to titanium and the crystallization of titanium dioxide. Under air conditions, the 60 % weight loss mainly corresponds to

the thermal oxidation of the cellulosic part of  $\text{TiO}_2@u\text{FP}$  that likely happens simultaneously with the crystal growth of  $\text{TiO}_2$ . The post-treatment temperature of 600 °C was chosen for all samples according to those TGA results, as no significant weight loss can be noticed above 600 °C.

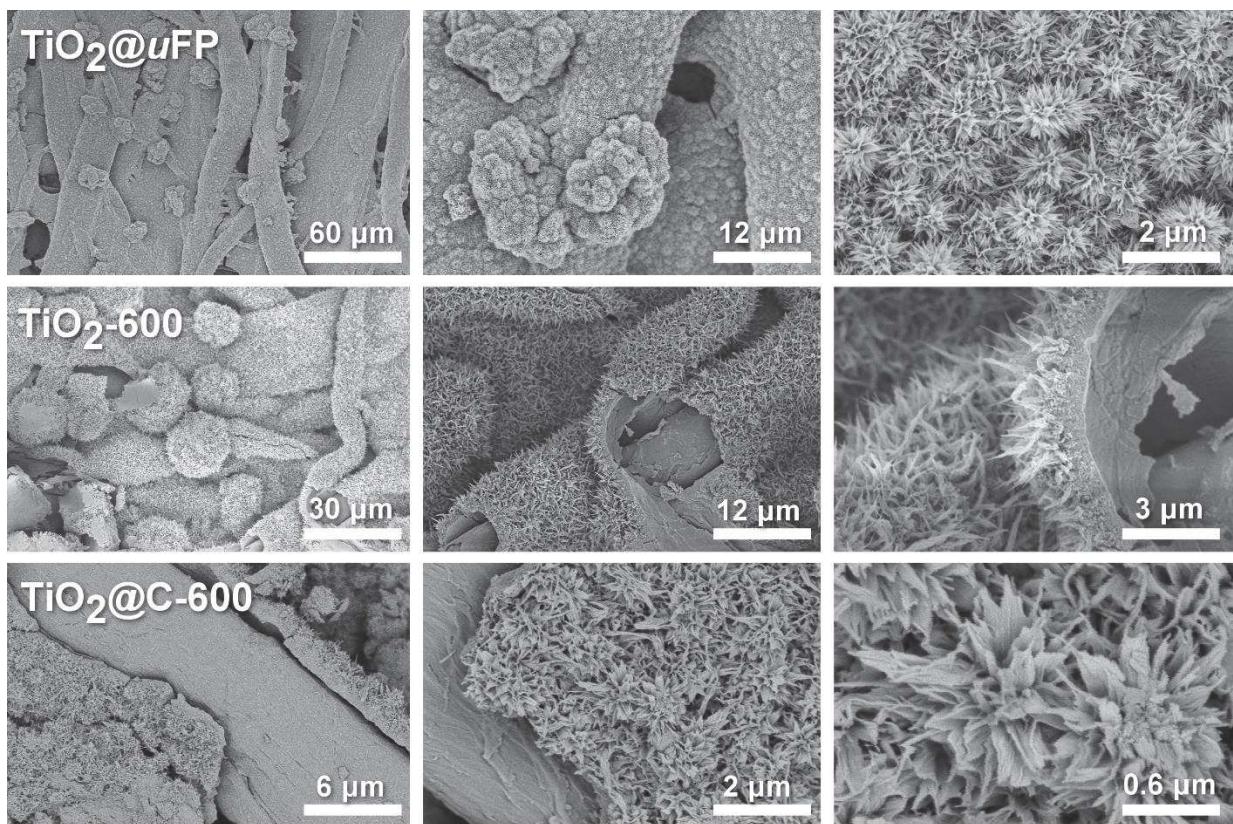
Combining TG analyses under air and argon, it can be assumed that  $\text{TiO}_2@C-600$  is a mixture of roughly 65 %  $\text{TiO}_2$  and 35 % amorphous carbon. Comparison with different  $\text{TiO}_2@C$  prepared by sol-gel impregnation shows that pyrolysis leads, in the present study, to a higher residue at higher temperature, while the amount of carbon and hydrogen is lower (C: 56.77; H: 2.12).<sup>[11]</sup>

**Table 1.** Elemental analyses of references and samples before and after thermal treatment.

| Samples                             | EDX      |      |      |      | Chemical determination |     |     |     |
|-------------------------------------|----------|------|------|------|------------------------|-----|-----|-----|
|                                     | C        | O    | Ti   | Cl   | C                      | H   | N   | O   |
| $\text{TiO}_2$                      | 3.9      | 48.6 | 47.3 | –    |                        |     |     |     |
| $\text{C}_6\text{H}_{10}\text{O}_5$ | 44.4     | 49.5 | –    | –    |                        |     |     |     |
| $u\text{FP}$                        |          |      |      |      | 39.7                   | 5.7 | 5.7 |     |
| $\text{TiO}_2@u\text{FP}$ fiber     | 67.5     | 25.9 | 0.6  | 6.0  |                        |     |     |     |
| $\text{TiO}_2@u\text{FP}$ crystals  | 13.6     | 46.2 | 45.0 | 11.7 | 25.8                   | 3.7 | 4.2 |     |
| $\text{TiO}_2@C600$ fiber           | 91.0     | 8.2  | 0.6  | 0.9  |                        |     |     |     |
| $\text{TiO}_2@C600$ crystals        | 27.433.9 | 38.6 | 0.1  |      | 36.4                   | 1.7 | 2.3 | 6.2 |
| $\text{TiO}_2-600$                  |          |      |      |      | 0.0                    | 0.6 | 0.0 |     |

From elemental analyses (**Erreur ! Source du renvoi introuvable.**), we can conclude that the cellulose effectively acts as a source of oxygen: for cellulosic domains of  $\text{TiO}_2@u\text{FP}$ , the atomic ratio carbon-oxygen (3-4 %) is three to four times higher than the theoretical one for cellulose (1.2). We also note that Ti-content is detected but very low in these domains (<1.5 wt%). Finally, chlorine is present in cellulosic and mineral domains of  $\text{TiO}_2@u\text{FP}$ , keeping in mind that on mineral domains data are less accurate due to their thinness.

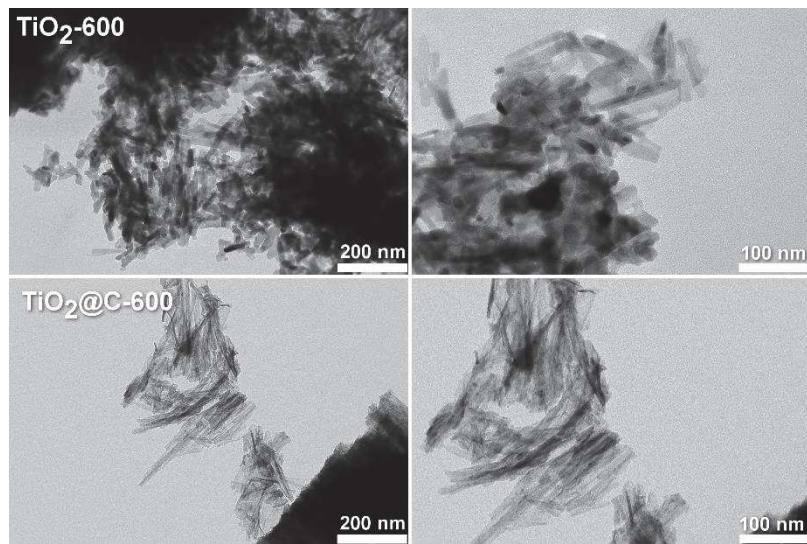
**Characterizations of  $\text{TiO}_2-600$  and  $\text{TiO}_2@C-600$ .** According to scheme 1, heat post-treatment of  $\text{TiO}_2@u\text{FP}$  was conducted under argon atmosphere in order to obtain titanium dioxide with a carbon framework resulting from the carbonization of the cellulosic residues. For such a purpose, heat treatment was conducted under argon atmosphere in order to carbonize the cellulosic residues. The flower-like morphology is preserved in  $\text{TiO}_2@C-600$  (Figure 3), SEM analysis revealing carbonaceous residues as well as  $\text{TiO}_2$  similar to initial  $\text{TiO}_2@u\text{FP}$ . When the latter is calcined under air, all carbonaceous species are removed (**Erreur ! Source du renvoi introuvable.**). SEM images of  $\text{TiO}_2-600$  nevertheless evidence a partial evolution of the morphology towards a more pronounced needle-like structure (Figure 3)). This latter fact is confirmed by TEM images, showing nanorods assembled into needles (Figure 4). Figure 2 shows XRPD patterns of  $\text{TiO}_2@u\text{FP}$  post-treated under argon (Figure 2b,  $\text{TiO}_2@C-600$ ) and under air (Figure 2c,  $\text{TiO}_2-600$ ). XRPD pattern of  $\text{TiO}_2@C-600$  confirms that the anatase polymorph, already present in  $\text{TiO}_2@u\text{FP}$ , is further crystallized compared to the initial pattern (Figure 2a), as shown by the intense peaks at  $2\theta = 25.2^\circ, 37.8^\circ, 48.1^\circ, 54.0^\circ, 54.8^\circ$ , and  $62.5^\circ$ , corresponding to (011), (004), (020), (015), (121) and (024)  $hkl$  planes, respectively (ICSD #9855).



**Figure 3.** SEM images of  $\text{TiO}_2@\text{uFP}$ ,  $\text{TiO}_2\text{-}600$ , and  $\text{TiO}_2@\text{C}\text{-}600$  showing the nanoflower structure of  $\text{TiO}_2$ .

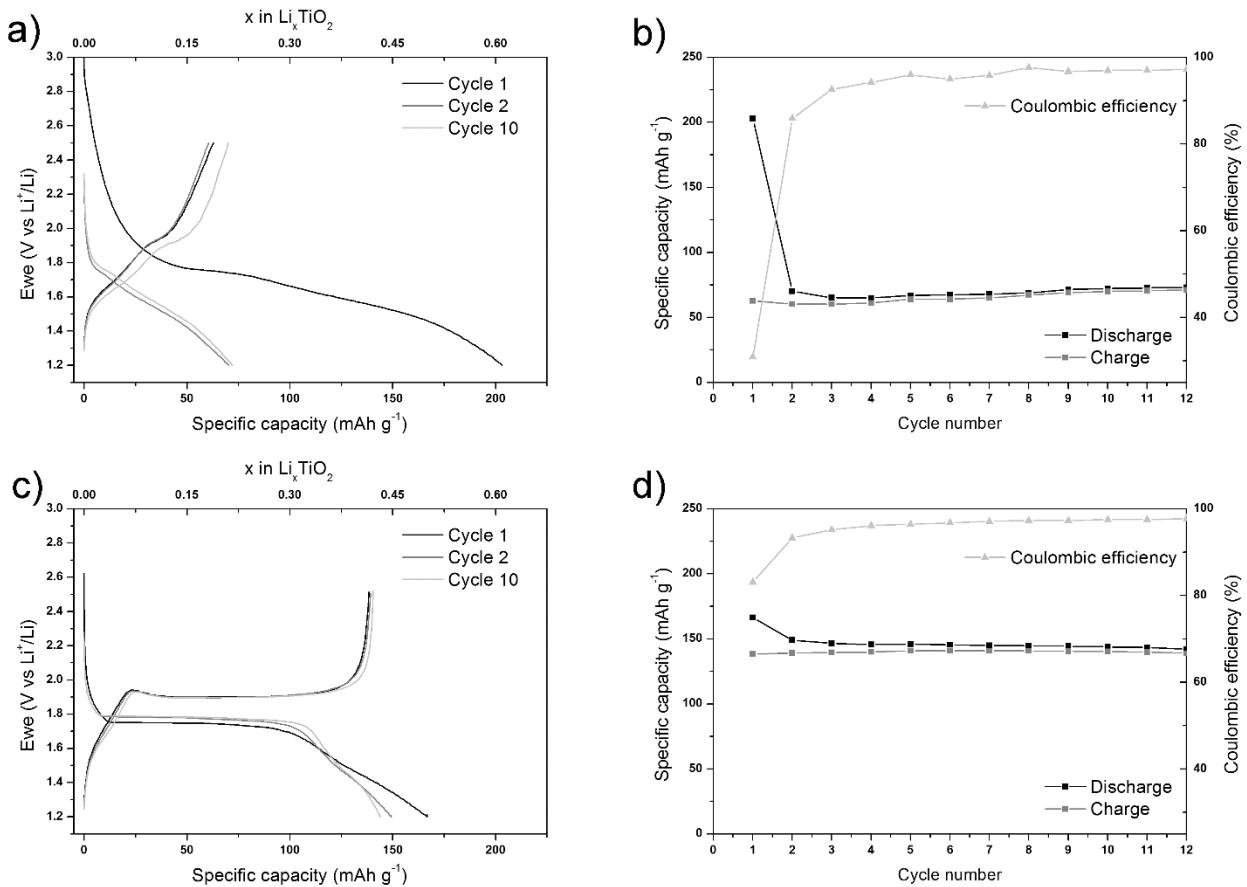
According to the Debye-Scherrer equation, crystallite size is larger in  $\text{TiO}_2\text{-}600$  than in  $\text{TiO}_2@\text{C}\text{-}600$  (average diameters of 50 and 10 nm, respectively), as a result of the carbon left by cellulose that prevents  $\text{TiO}_2$  crystal growth. No peak for crystalline graphite can be found at  $2\theta = 23.4^\circ$ ,  $43.5^\circ$ , corresponding to (002) and (100)  $hkl$  planes. Raman analysis confirms that anatase is the main phase (Figure S4), a careful analysis indicating slightly different values (153, 202, 391, 503 and  $629.5 \text{ cm}^{-1}$  for  $\text{TiO}_2@\text{C}\text{-}600$  and 142, 195, 395, 513 and  $638 \text{ cm}^{-1}$  for  $\text{TiO}_2\text{-}600$ ), a discrepancy that could result from crystallite size.<sup>[87]</sup> A set of diffraction peaks (Figure 2b) can be attributed to  $\text{TiO}_2$  (B) at  $2\theta = 15.2^\circ$ ,  $24.9^\circ$ ,  $28.6^\circ$ ,  $43.5^\circ$ ,  $48.5^\circ$ , and  $58.0^\circ$ , corresponding to (200), (110), (-111), (112), (020), and (-7-11)  $hkl$  planes, respectively (ICSD #171670). However, Raman spectrum of  $\text{TiO}_2@\text{C}\text{-}600$  does not clearly display the expected signals.<sup>[88]</sup> A distinctive feature of the present process, and the effect of urea pre-impregnation, is that  $\text{TiO}_2$  (B) has never been obtained neither from FP<sup>[15]</sup> nor from usual hydrolytic sol-gel templating of cellulose.

In the case of  $\text{TiO}_2@\text{C}\text{-}600$  (Figure S6a), two important broad signals attributed to 6-membered aromatic rings in graphitic materials are observed in Raman spectrum at  $1346 \text{ cm}^{-1}$  related to  $A_{1g}$  (D band, attributed to defect in graphite) and at  $1588 \text{ cm}^{-1}$  related to  $E_{2g}$  (G band, ascribed to  $sp^2$  hybridized carbon network).<sup>[89]</sup> A correlation length of graphitic domain in the range of 0.95-1.00 nm can be deduced from the  $I_D/I_G$  ratio (0.96). For a pure FP, with or without impregnation of urea, pyrolyzed at  $600^\circ\text{C}$  the  $I_D/I_G$  ratio is 0.90 to 0.95, respectively (Figure S6b). This difference could be ascribed to the presence of urea already reported in other work where urea is used in very high proportions.<sup>[73, 74]</sup>



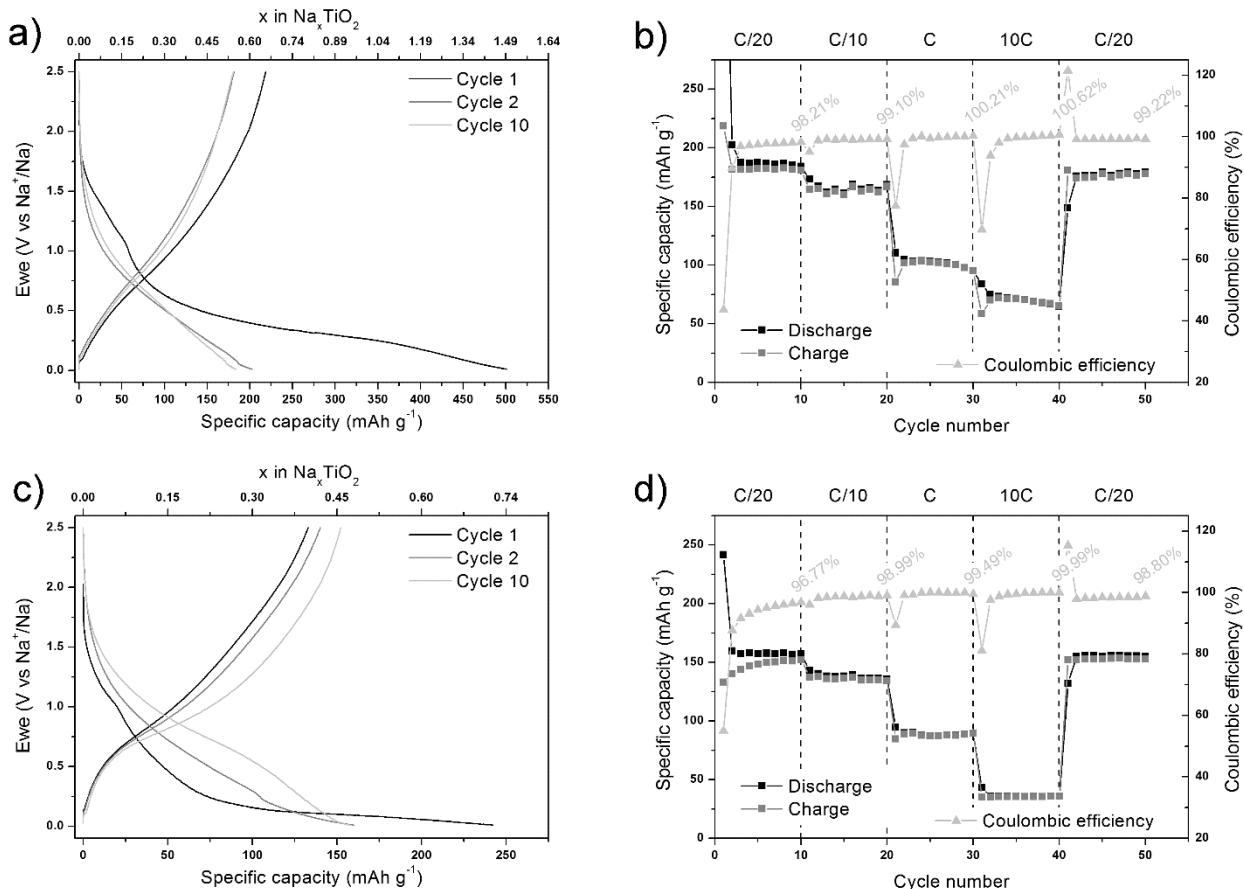
**Figure 4.** TEM images of  $\text{TiO}_2$ -600, and  $\text{TiO}_2@\text{C}$ -600 showing the carbonaceous and nanoflower structures of  $\text{TiO}_2$ .

Nitrogen adsorption measurements were performed on samples after thermal treatment, measurement on  $\text{TiO}_2@u\text{FP}$  was unsuccessful due to permanent desorption during conditioning (Figure S7). The specific surface area for  $\text{TiO}_2$ -600 is low  $14 \text{ m}^2 \text{ g}^{-1}$ , similar to the one reported without the urea pre-impregnation,<sup>[15]</sup> macro- and mesoporosity resulting essentially from inter-granular voids (data in tableau 1 and isotherms in SI 4). By comparison,  $\text{TiO}_2@\text{C}$ -600 is a mesoporous composite with a specific surface area of  $194 \text{ m}^2 \text{ g}^{-1}$  according to BET model; mesoporosity being mainly the fact of the carbon left by cellulose of  $\text{TiO}_2@u\text{FT}$ . The isotherm was identified as type IV with an H2-type hysteresis loop (IUPAC classification), supporting the mesoporous and macroporous nature (micropore volume:  $0.0640 \text{ cm}^3 \text{ g}^{-1}$  by the  $t$ -plot method) with a broad pore size distribution as evidenced by BJH method on desorption (Figure S8)



**Figure 5.** Galvanostatic voltage profiles (a) and charge-discharge cyclability curves (b) for  $\text{TiO}_2@\text{C-}600/\text{Li}$  cells cycled at C/20 between 2.5 and 1.2 V vs  $\text{Li}^+/\text{Li}$ . Galvanostatic voltage profiles (c) and charge-discharge cyclability curves (d) for  $\text{TiO}_2\text{-}600/\text{Li}$  cells cycled in the same conditions.

**Urea-impregnation effect on pyrolyzed cellulose.** As seen from SEM images,  $\text{TiO}_2@\text{C-}600$  is a composite of titanium dioxide nanocrystals attached to amorphous N-doped carbon fibers. The N-doped carbon fibers derived from cellulose were used to enhance the electrical conduction paths in  $\text{TiO}_2$  particles and improve kinetics of electron transfers during battery cycling. Doping with heteroatoms has been a successfully applied strategy to improve electrochemical reactivity and electrical conductivity of carbonaceous materials.<sup>[73, 90, 91]</sup> In the present study, *uFP* serves as N-doped carbon precursor. After pyrolysis under argon atmosphere, *uFP* gives rise to an amorphous *uFP-C600* compound, as evidenced by XRPD (Figure S2). Raman analysis confirms the graphitic nature of amorphous *uFP-C600* (Figure S6), and also emphasizes the fact that *uFP-C600* contains slightly more graphitic domains than the undoped pyrolysed FP-C600 carbonaceous sample. Indeed, the ratio of the intensity of the carbon *D* mode to that of the *G* peak is equal to 0.90 for undoped FP-C600, while its value equals 0.95 for *uFP-C600*. Global resistance of *uFP-C600*, as derived from impedance measurements, is lower than that of FP-C600 by more than one order of magnitude (Figure S9, Table S1). Raman spectrum of  $\text{TiO}_2@\text{C-}600$  displays the characteristic *D* and *G* modes of graphitized amorphous carbons (Figure S6a), with a  $I(D)/I(G)$  ratio close to 0.96, similar to the one of *uFP-C600* (Figure S6b). As a consequence of the N-doped carbon fibres network,  $\text{TiO}_2@\text{C-}600$  exhibits much lower interfacial resistance as well as charge transfer resistance compared to that of the carbon-free  $\text{TiO}_2\text{-}600$  anatase sample (Figure S10, Table S2). Such a behaviour could be attributed to better electrical contact and easier electron/ion transfer within the N-doped carbon fibre network of  $\text{TiO}_2@\text{C-}600$ . When impedance of  $\text{TiO}_2@\text{C-}600$  samples made from FP and *uFP* are compared, it is clearly evident that  $\text{TiO}_2@\text{C-}600$  containing N-doped carbon fibres exhibits an improved global conductivity (Figure S11, Table S3).



**Figure 6.** Galvanostatic voltage profiles (a) and charge-discharge cyclability curves (b) for TiO<sub>2</sub>@C-600/Na cells cycled at C/20, C/10, C, 10C, and C/20 consecutively between 2.5 and 0.01 V vs Na<sup>+</sup>/Na. Galvanostatic voltage profiles (c) and charge-discharge cyclability curves (d) for TiO<sub>2</sub>-600/Na cells cycled in the same conditions

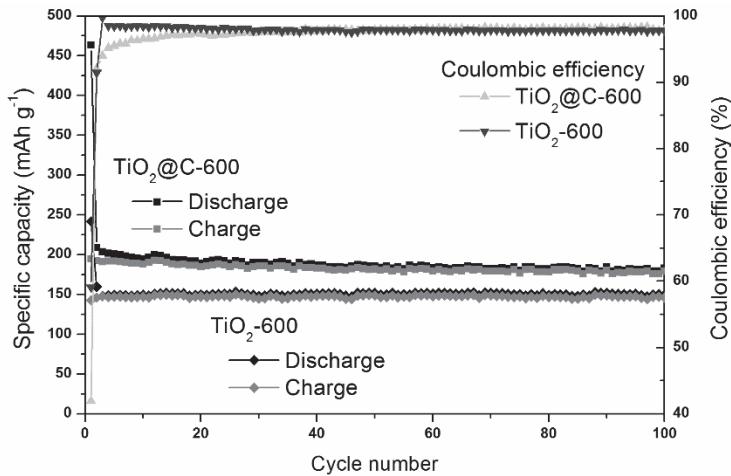
**Electrochemical investigation as Li-ion electrode.** First of all, TiO<sub>2</sub>@C-600 and TiO<sub>2</sub>-600 samples were tested as electrode of Li batteries in CR2032-type half-cells. The galvanostatic charge-discharge voltage profiles at a current of C/20 (where C is set at 335.6 mA h g<sup>-1</sup> for a 1-e<sup>-</sup> process) of the first, second, and tenth cycles for TiO<sub>2</sub>@C-600 and TiO<sub>2</sub>-600 *versus* Li metal between 2.5 and 1.2 V are shown in Figure 5. For TiO<sub>2</sub>@C-600, both discharge and charge curves displays a smooth slope with the absence of voltage plateau, a characteristic feature of nanosized TiO<sub>2</sub> particles.<sup>[92]</sup> The deinsertion of lithium measured upon the first charge leads to a rather low reversible capacity of 62.8 mA h g<sup>-1</sup>, a value that slowly increases upon the first tenth cycles to reach 70 mA h g<sup>-1</sup>. The large irreversible capacity on the first cycle may originate from the combined effect of both TiO<sub>2</sub> nanoparticle size and cellulose-derived carbon within the sample, which, in other words, could be explained by the formation of a passivation layer, so-called solid-electrolyte interface (SEI; Figure S12) For TiO<sub>2</sub>-600, galvanostatic curves display a clear voltage plateau for reduction and oxidation steps, in good accordance with the submicronic size of particles.<sup>[92]</sup> The irreversible capacity upon the first cycle is much smaller than for TiO<sub>2</sub>@C-600, with a reversible capacity of 140 mA h g<sup>-1</sup>. It is known that lithium insertion into TiO<sub>2</sub> shows three major storage mechanisms: (i) a rapid potential drop to ca. 1.7 V vs. Li<sup>+</sup>/Li characteristic of the formation of a solid-solution Li<sub>x</sub>TiO<sub>2</sub>, where x depends on particle size.<sup>[93]</sup> (ii) a two-phase reaction between the tetragonal Li<sub>x</sub>TiO<sub>2</sub> and the orthorhombic lithium titanate Li<sub>0.5±δ</sub>TiO<sub>2</sub> inducing a constant-voltage plateau around 1.7 V followed by (iii) another two-phase reaction up to 1 V towards rock-salt-type tetragonal LiTiO<sub>2</sub>.<sup>[94]</sup> The irreversibility of the latter mechanism is usually overcome through nanostructuration of the electrode

material, which induces a monophasic reversible pseudo-capacitive interfacial storage.<sup>[95]</sup> Below a certain size of the TiO<sub>2</sub> nanoparticles, the two phases at 1.7 V do not coexist and less lithium is required to give rise to the orthorhombic lithium titanate phase, hence the absence of voltage plateau.<sup>[93]</sup> Thus, the galvanostatic results presented on Figure 5 could be rationalized by taking into account the nanoscopic nature of TiO<sub>2</sub>@C-600 and the submicronic size of TiO<sub>2</sub>-600 crystals. In both cases, the coulombic efficiency reaches 97 %, a relatively low value indicating either electrolyte decomposition or the formation of solid-electrolyte interface (SEI) Li-based products.<sup>[96]</sup>

**Electrochemical investigation as Na-ion electrode.** TiO<sub>2</sub>@C-600 and TiO<sub>2</sub>-600 samples were tested as electrode in half-cells versus metallic sodium. Galvanostatic measurements are presented on Figure 6. Both materials display quite similar features that are shared with recently reported compounds: a shoulder at 1.0 V vs Na<sup>+</sup>/Na followed by a relatively flat plateau below 0.5 V for TiO<sub>2</sub>@C-600 and below 0.2 V for TiO<sub>2</sub>-600 on the first sodiation, while second and subsequent charge-discharge cycles do not display any well-defined capacity plateau (Figure 6a and c).<sup>[19, 46, 61]</sup> It could then be concluded that electrochemical processes occur very likely. As observed for Li-ion half-cells, the presence of intrinsic carbon residue has a strong influence on the electrochemical properties, yet the origin of such properties is still unclear. For the TiO<sub>2</sub>@C-600 sample, the irreversible capacity upon the first cycle is large (282.2 mA h g<sup>-1</sup>, 56.4 %). Such a value is remarkably lower (109 mA h g<sup>-1</sup>, 45.0 %) for TiO<sub>2</sub>-600 (Figure 6c). This might be due to the high surface area of TiO<sub>2</sub>@C-600 (194 m<sup>2</sup> g<sup>-1</sup>), or from the intrinsic carbon arising from the pyrolyzed cellulose, which irreversibly insert high amounts of Na on the first discharge (Figure S13). Reversible specific capacities of 180 and 150 mA h g<sup>-1</sup> are delivered upon desodiation for TiO<sub>2</sub>@C-600 and TiO<sub>2</sub>-600, respectively, when cycled at C/20. It should be reminded that capacities are based on the active material content, and for TiO<sub>2</sub>@C-600 there is a large amount of intrinsic carbon that decreases the resulting capacities. If the intrinsic carbon was ignored in the calculation, the specific capacities would be increased by a 53 % factor. In details, the influence of intrinsic carbon within TiO<sub>2</sub>@C-600 may also be noticed by comparing the first discharge of TiO<sub>2</sub>@C-600 and TiO<sub>2</sub>-600. The redox phenomenon observed at 1.0 V vs Na<sup>+</sup>/Na accounts for approximately 0.15 Na per TiO<sub>2</sub> (50 mAh g<sup>-1</sup>) for TiO<sub>2</sub>@C-600, and 0.07 Na per TiO<sub>2</sub> (25 mAh g<sup>-1</sup>) for TiO<sub>2</sub>-600. This sodium insertion reaction might occur at specific surface sites of titanium dioxide, and thus it may correlate with the samples surface area: the higher the surface area, the larger the amount of sodium inserted. It is noteworthy that this phenomenon might also depend on the electrode formulation, as it seems to be absent when the electrode is formulated without extrinsic carbon (Figure S14).

TiO<sub>2</sub>@C-600 and TiO<sub>2</sub>-600 electrodes show interesting capacity retentions upon cycling at gradually increasing current rates Figure 6b and d). TiO<sub>2</sub>@C-600 displays a reversible capacity of 181 mA h g<sup>-1</sup> at C/20, and the value decreases up to 167, 95, and 65 mA h g<sup>-1</sup> at C/10, C and 10C, respectively. When cycled back at C/20, the reversible capacity equals its initial value of 180 mA h g<sup>-1</sup>. TiO<sub>2</sub>-600 possesses similar properties when cycled under the same current regimes (Figure 6d), with globally lower specific capacities. Those results are typical of carbon-supported materials versus carbon-free, and the specific capacities, and capacity retentions, obtained are in the top 25 % of reported results.<sup>[35, 37, 38, 46, 49]</sup>

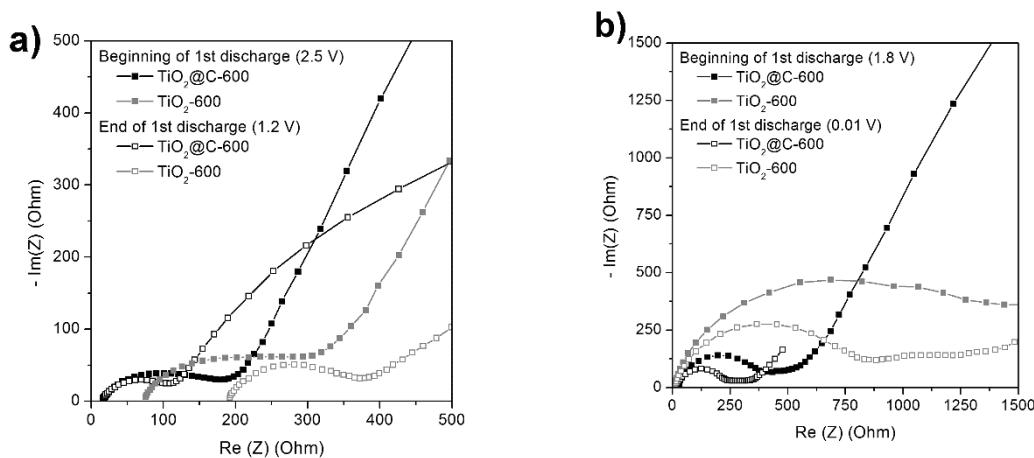
Both samples exhibit coulombic efficiencies around 97 % that increase with current rates. During the first cycles at C/20, coulombic efficiencies are close to 97 %, while they approach 99.9 % at C and 10C for TiO<sub>2</sub>@C-600 (Figure 6b) and TiO<sub>2</sub>-600 (Figure 6d). It should here be noticed that the coulombic efficiency is more rapidly stabilized in the case of TiO<sub>2</sub>-600. Again, the influence of intrinsic carbon is obvious: while both samples show similar electrochemical behaviors, TiO<sub>2</sub>@C-600 benefits from the cellulose-derived carbon that provides improved electron percolation, which makes the specific capacity higher than for TiO<sub>2</sub>-600.



**Figure 7.** Cycling performance curves of  $\text{TiO}_2@\text{C-600}$  and  $\text{TiO}_2\text{-600}$  materials in Na-ion half-cells at current densities of C/20.

As it can be observed from Figure 7, a highly remarkable stable capacity of about  $200 \text{ mA h g}^{-1}$  is obtained for  $\text{TiO}_2@\text{C-600}$  at a current density of C/20 for the first twenty cycles with a capacity loss of approximately  $10 \text{ mA h g}^{-1}$  after 100 cycles. For  $\text{TiO}_2\text{-600}$ , the specific capacity over hundred cycles is about  $150 \text{ mA h g}^{-1}$ , which  $50 \text{ mA h g}^{-1}$  lower than for the compound with intrinsic carbon. For both samples, the coulombic efficiency remains higher than 98%, a reasonable and promising value for the application of  $\text{TiO}_2$  as anode in sodium-ion full-cells. It is noteworthy that the conductive intrinsic carbon allows for a better electronic percolation within  $\text{TiO}_2@\text{C-600}$  compared with  $\text{TiO}_2\text{-600}$ , a fact that is translated into a better electrochemical activity, hence a better specific capacity.

In order to investigate the difference of electronic conductivity between  $\text{TiO}_2@\text{C-600}$  and  $\text{TiO}_2\text{-600}$ , EIS measurements were conducted at different depths-of-discharge during the first reduction. Figure 8, clearly shows that, whatever the state of charge and exchanged ion, the semicircular arc of the  $\text{TiO}_2\text{-600}$  curve is larger than the one of the  $\text{TiO}_2@\text{C-600}$ . It thus can be deduced that  $\text{TiO}_2\text{-600}$  electrode may be more resistive than the  $\text{TiO}_2@\text{C-600}$  one. The better conductivity of the latter may be related to the presence of intrinsic N-doped carbon stemming from cellulose pyrolysis. Indeed, the presence of carbon (confirmed earlier, *vide infra*) could increase the number of electron-conducting ways in the electrode. It should also be noted that, whatever the material or exchanged ion are, the resistivity decreases from the beginning to the end of the discharge, which implies that conductivity increases with the intercalation of a cation in the anode and the subsequent gradual reduction of the  $\text{Ti}^{4+}$  centres to  $\text{Ti}^{3+}$ .



**Figure 8.** Nyquist impedance plots of  $\text{TiO}_2$ -600 and  $\text{TiO}_2@\text{C}$ -600 electrodes in half-cells versus lithium (a) and sodium (b). Plots were obtained at the inception of lithiation (or sodiation) after 5 h relaxation time and at the end of the first discharge in potentiostatic mode.

## Conclusions

The mineralization method occurring at-and-with the cellulose fibre lead to the formation of hierarchical superstructure of  $\text{TiO}_2$ . In this report, we have established the possibility to modulate this process by the effect of an organic compound adsorbed onto the cellulosic fibres, urea in the present case. The composites obtained with or without carbonaceous residues display drastically different morphologies, with additionally an impact on their electrochemical properties.  $\text{TiO}_2$ -600 is micrometric anatase with conventional Li-insertion and low Na-insertion properties.  $\text{TiO}_2@\text{C}$ -600, on the other hand, is nano-sized anatase grown on top of N-doped carbonaceous residue with interesting Na-insertion properties and cyclability versus sodium. Such electrochemical behaviour may be rationalized by taking into account the crystal size of each compound, and the presence, or absence, of spinal carbon within the material. Impedance measurements demonstrated that the carbonaceous residue in  $\text{TiO}_2@\text{C}$ -600 lowers the global resistivity of the system by improving electrical contact and easier electron/ion transfer within the N-doped carbon fibre network.

## Experimental Section

**Chemicals.** Quantitative filter papers (FP) FT-3-101-090 from Sartorius France were used as cellulose source (98 % alpha-cellulose content min.). Titanium tetrachloride ( $\text{TiCl}_4$ , 99.9 %, Acros Organics) and urea (99+ %, Alfa Aesar) were used as supplied, without further purification. Dichloromethane (99 %, Sigma-Aldrich) was distilled over calcium hydride before use to obtain anhydrous dichloromethane (< 10 ppm  $\text{H}_2\text{O}$ ) used in this study.

**Preparation of urea-impregnated filter paper.** Filter papers were cut into 1-2 cm<sup>2</sup> pieces and submerged in a 10 wt% aqueous solution of urea for 24 h at room temperature. After impregnation, filter papers were removed from the solution, and let dry at room temperature for 12 h. Urea-impregnated filter papers were finally dried at 80 °C for three days and stored in a glove box, yielding urea-impregnated filter papers ( $u\text{FP}$ ; anal. found: C, 39.8; H, 5.7; N, 5.7).

**Mineralization of urea-impregnated filter paper.** In a glove box under inert atmosphere (< 2 ppm  $\text{H}_2\text{O}$ ), urea-impregnated filter papers (2.00 g, 12.09 mmol, assuming a 98 %-cellulose content), dichloromethane (30 mL), and  $\text{TiCl}_4$  (2.00 mL, 18.9 mmol) were placed into a Teflon-lined autoclave. After closing, the autoclave was placed in an oven at 80 °C for 7 days. When cooled down to room temperature, black urea-impregnated filter papers were washed dichloromethane (3 x 20 mL). Under air, the filter

papers were subsequently washed with standard dichloromethane ( $3 \times 20$  mL), and dried in an oven at  $80^\circ\text{C}$  for 24 h to yield  $\text{TiO}_2@\mu\text{FP}$  (anal. found: C, 25.8; H, 3.7; N, 4.2).

**Thermal treatment of  $\text{TiO}_2@\mu\text{FP}$ .** As-synthesized  $\text{TiO}_2@\mu\text{FP}$  samples were either calcined in air at  $600^\circ\text{C}$  for 1 h (heating rate  $5^\circ\text{C min}^{-1}$ ), yielding mesostructured  $\text{TiO}_2$ , namely  $\text{TiO}_2\text{-}600$  (anal. found: C, 0; H, 0.7; N, 0), or pyrolyzed under argon in the same conditions, yielding  $\text{TiO}_2@\text{C-}600$  (anal. found: C, 36.4; H, 1.7; N, 2.3). For comparison purposes, filter papers (FP) and urea-impregnated filter papers ( $\mu\text{FP}$ ) were submitted to similar thermal treatment under argon to give rise to FP-C600 and  $\mu\text{FP-C600}$  samples (under argon, after 1 h heating at  $600^\circ\text{C}$ , both FP and  $\mu\text{FP}$  samples displayed 87 % weight loss).

**Solid-state characterizations.** X-ray powder diffraction (XRPD) experiments were carried out on a PANalytical X-Pert Pro diffractometer equipped with a diffracted beam monochromator Cu K $\alpha$  source and an X'celerator linear detector. The total counting time was 9000 s, and the angle step was  $0.0390^\circ\cdot 2\theta$ . Raman spectra were measured on powder samples using a Horiba LabRAM ARAMIS spectrophotometer, with an excitation wavelength of 633 nm. Infrared spectra were collected on a Thermo Nicolet Avatar 320 FTIR fitted with an ATR module; each spectrum results from a 32-scan acquisition. Transmission electronic microscopy (TEM) images were recorded using a JEOL 1200 EXII electron microscopic and scanning electronic microscopy (SEM) images with a Hitachi S-4800 microscope (voltage 5 kV). Energy dispersive X-ray analysis (EDAX) was done using the EDAX attachment (Oxford Instruments) of the SEM system.  $\text{N}_2$ -physisorption isotherms were obtained at 77 K using Micromeritics Tristar, USA. The samples were outgassed for 12 h at  $150^\circ\text{C}$  under vacuum (2 Pa). The pore size distribution was calculated from the adsorption branch using the BJH method. Thermogravimetric analyses (TGA) were obtained using Netzsch Simultaneous Thermal Analyser STA 409 PC Luxx and Setaram Labsys TGA-DSC.

**Electrochemical characterizations.** Galvanostatic electrochemical characterizations were performed at room temperature on an MPG2 instrument from BioLogic by using CR2032-type coin cells. Electrochemical impedance spectroscopy (EIS) studies were done on a BioLogic VSP instrument, from 100 kHz to 1 mHz, with a 10 mV amplitude in potentiostatic mode. All electrodes were composed of the active material (about 80 wt%), acetylene black (8 wt%) and carboxymethylcellulose (12 wt%). After stirring in water, the mixture was tape casted uniformly at 150  $\mu\text{m}$  onto a copper current collector using a 3540 bird film applicator from Elcometer. Sodium or lithium metal disks were used both as reference and counter electrodes. The electrolytes used for NA and Li batteries were 1 M  $\text{NaClO}_4$  in propylene carbonate with 5 % fluoroethylene carbonate and 1 M  $\text{LiPF}_6$  in propylene carbonate, ethylene carbonate, and dimethyl carbonate (PC:EC:3DMC, 1:1:3 vol. %) with 5% fluoroethylene carbonate and 1% vinyl carbonate, respectively. Whatman glass fibers filters were used as the separator. The cells were assembled in an argon-filled glovebox. All capacities reported hereafter are calculated from the content of active material (80 wt%), which takes into account the intrinsic carbon of  $\text{TiO}_2@\text{C-}600$  for instance.

## Acknowledgements

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**Keywords:** Nanocomposite • Cellulose • Titania • Mineralization • Batteries

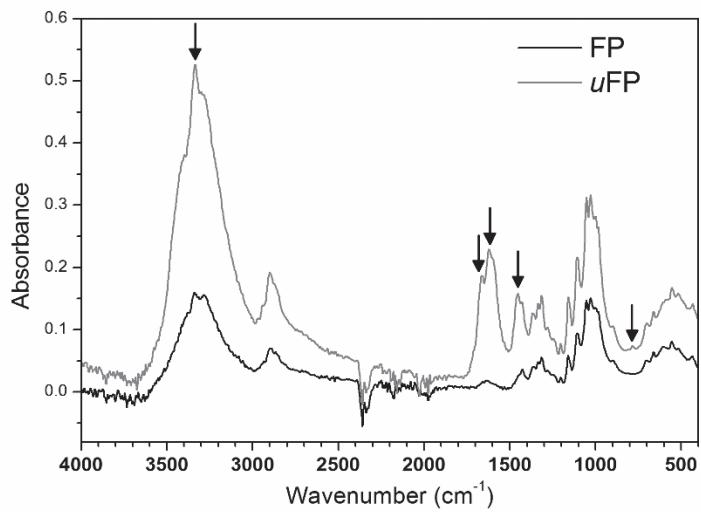
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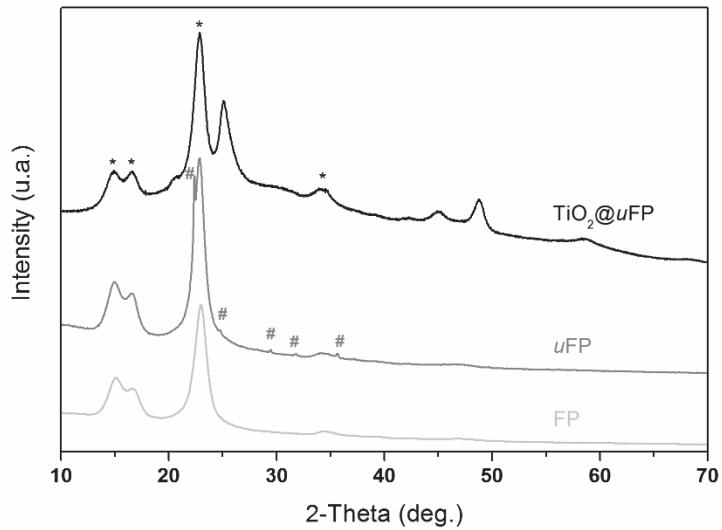
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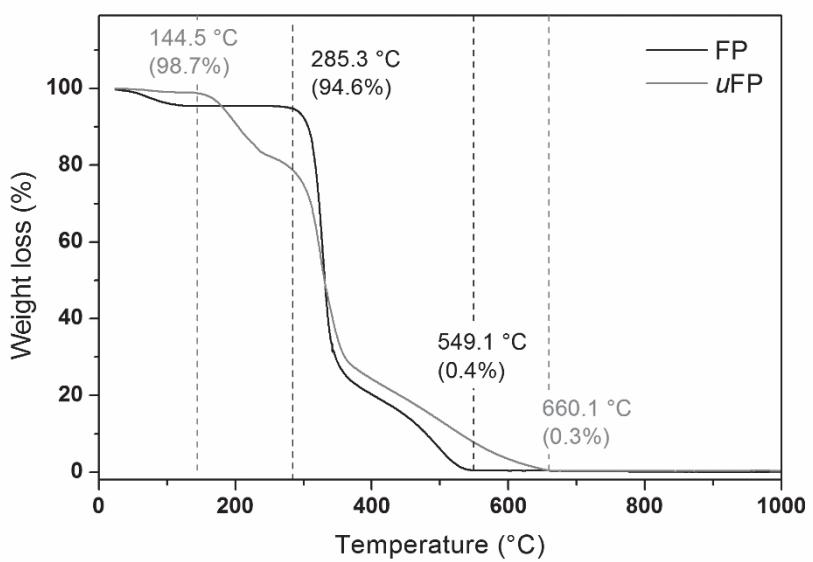
## Supporting information



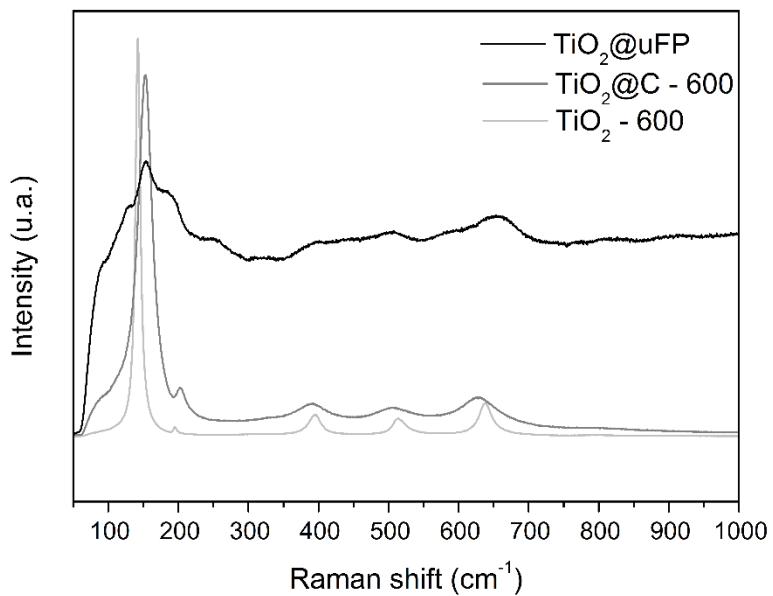
**Figure S9.** Infrared spectra in ATR mode of filter papers before (FP) and after (uFP) urea impregnation for 1 hr and subsequent drying at 80 °C for 3 days; black downward arrows indicate new vibrational bands that appeared after urea impregnation.



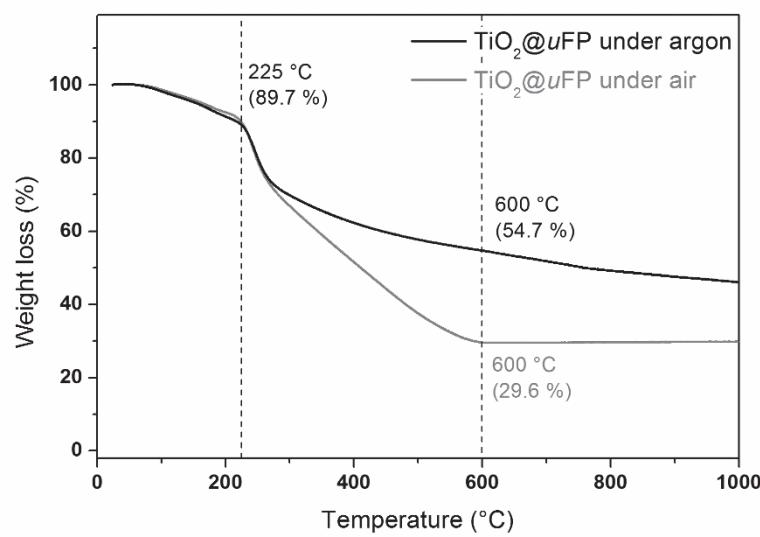
**Figure S10.** XRPD patterns of FP, uFP, and mineralized TiO<sub>2</sub>@uFP; \* symbols emphasize the peaks stemming from crystalline cellulose residues, while # symbols mark the presence of urea.



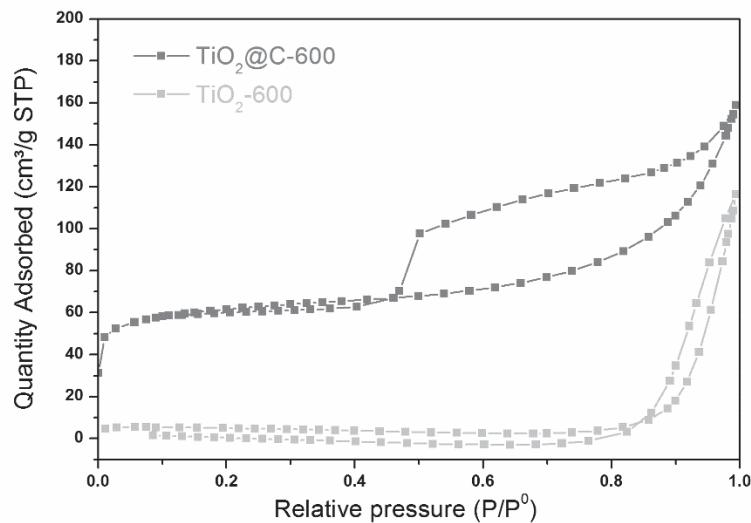
**Figure S11.** Thermogravimetric analysis of FP and uFP under flowing air up to 1000 °C at 5 °C min<sup>-1</sup>.



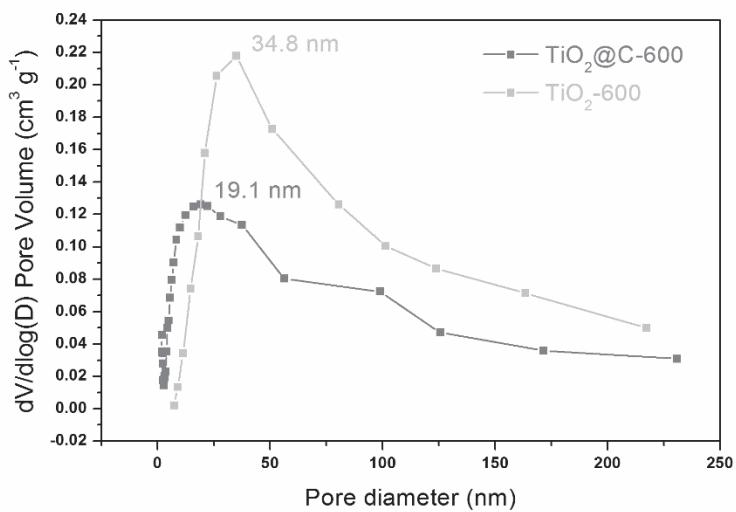
**Figure S12.** Raman spectra of TiO<sub>2</sub>@uFP, TiO<sub>2</sub>@C-600, and TiO<sub>2</sub>-600.



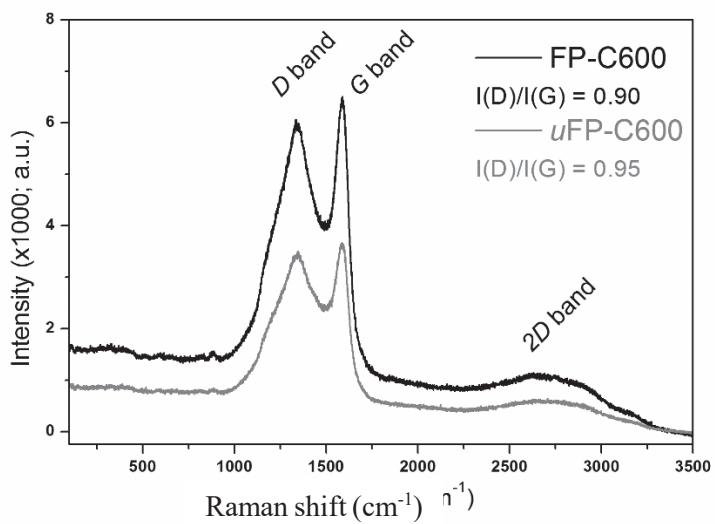
**Figure S13.** Thermogravimetric analysis of  $\text{TiO}_2@\text{uFP}$  under flowing air or argon up to 1000 °C at 5 °C min<sup>-1</sup>.



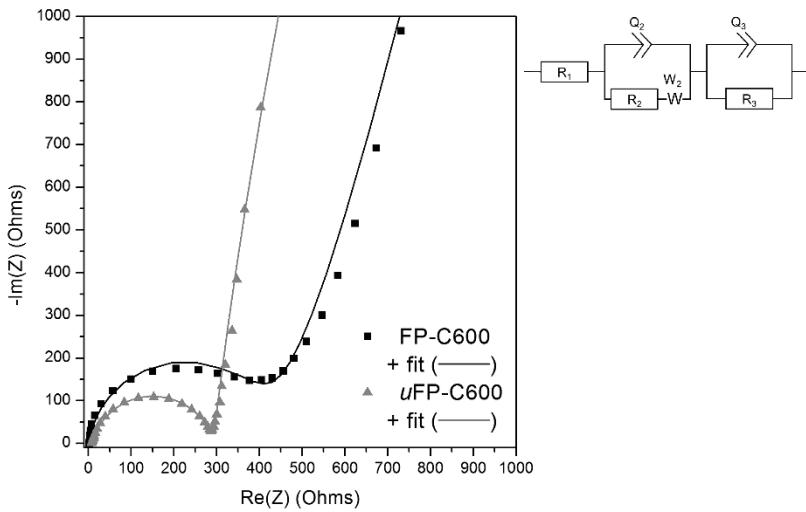
**Figure S14.** Nitrogen sorption measurements at 77 K for  $\text{TiO}_2\text{-}600$  and  $\text{TiO}_2@\text{C-}600$ .



**Figure S15.** Pore diameter of  $TiO_2$ -600 and  $TiO_2@C$ -600 samples according to the BJH method.



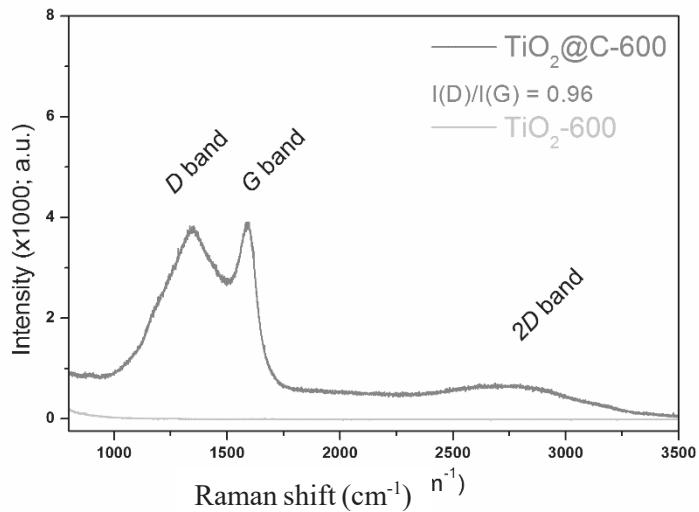
**Figure S16.** Raman spectra of FP and uFP pyrolysed at 600 °C for 1 h under argon. The  $I(D)/I(G)$  value is the ratio of the intensity of the D mode to that of the G mode.



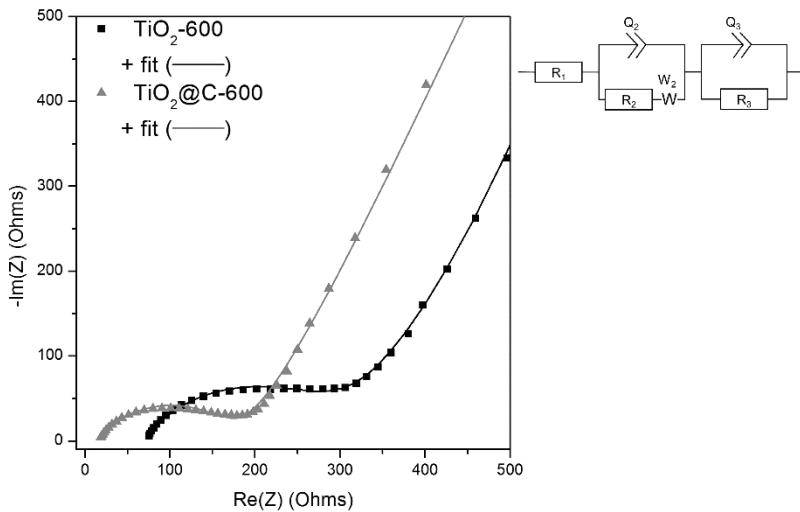
**Figure S17.** Complex impedance plots of FP-C600 and uFP-C600 electrodes in half-cells versus lithium. Plots were obtained in OCV mode after 5 h relaxation time before any lithiation. The equivalent circuit used for the analysis of the complex impedance plots is shown on the top right hand corner.

**Table S1.** Fitted resistance values from impedance plots of FP-C600 and uFP-C600 samples.

| Resistances | FP-C600        | uFP-C600       |
|-------------|----------------|----------------|
| R1          | 1.979 $\Omega$ | 7.424 $\Omega$ |
| R2          | 83492 $\Omega$ | 285.8 $\Omega$ |
| R3          | 396.6 $\Omega$ | 41.81 $\Omega$ |



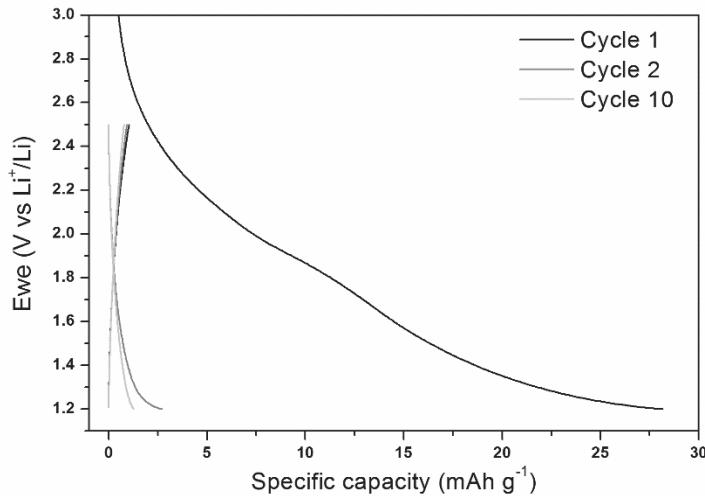
**Figure S18.** Raman spectra of  $TiO_2@C$ -600 and  $TiO_2$ -600.



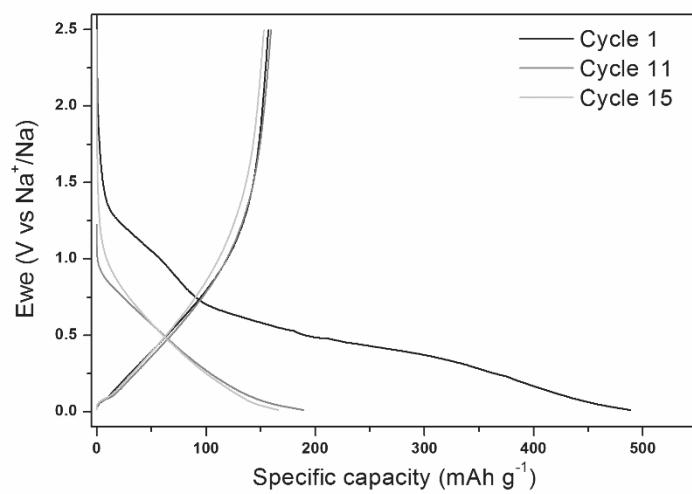
**Figure S19.** Complex impedance plots of  $\text{TiO}_2$ -600 and  $\text{TiO}_2@\text{C}$ -600 electrodes in half-cells versus lithium. Plots were obtained at the inception of lithiation after 5 h relaxation time. The equivalent circuit used for the analysis of the complex impedance plots is shown on the top right hand corner.

**Table S2.** Fitted resistance values from impedance plots of  $\text{TiO}_2$ -600 and  $\text{TiO}_2@\text{C}$ -600 samples.

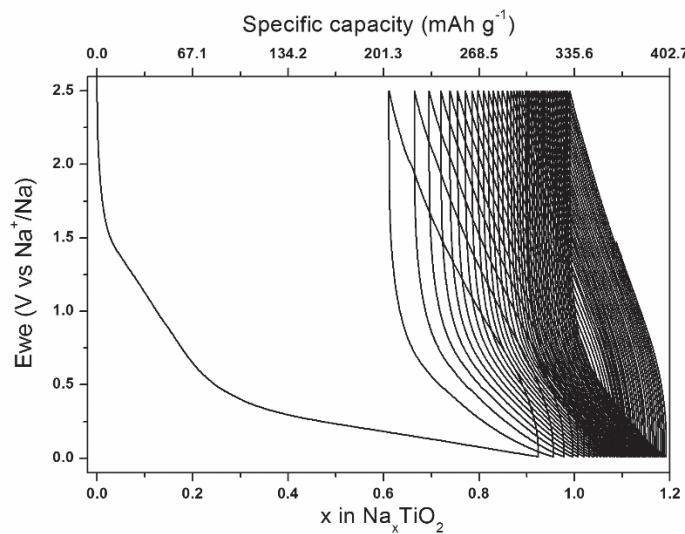
| Resistances | $\text{TiO}_2$ -600 | $\text{TiO}_2@\text{C}$ -600 |
|-------------|---------------------|------------------------------|
| R1          | $67.96 \Omega$      | $13.63 \Omega$               |
| R2          | $237 \Omega$        | $167.1 \Omega$               |
| R3          | $4104 \Omega$       | $1825 \Omega$                |



**Figure S20.** Galvanostatic voltage profile for uFP-C600/Li half-cell cycled between 2.5 and 1.2 V vs  $\text{Li}^+/\text{Li}$  with a current density of  $100 \text{ mA g}^{-1}$ .



**Figure S21.** Galvanostatic voltage profile for uFP-C600/Na half-cell cycled between 2.5 and 0.01 V vs  $\text{Na}^+/\text{Na}$  with a current density of 16.78  $\text{mA g}^{-1}$  (corresponding to C/20 for  $\text{TiO}_2$ ); here, uFP-C600:CB:PTFE ratio is 80:14:6.



**Figure S22.** Galvanostatic voltage profile for  $\text{TiO}_2@\text{C-600}/\text{Na}$  half-cell cycled between 2.5 and 0.01 V vs  $\text{Na}^+/\text{Na}$  with a current density of C/20. Electrode is formulated only with  $\text{TiO}_2@\text{C-600}$  and CMC binder; no carbon black was added.

## **IV.2 - Reductive mineralization of cellulose with vanadium, iron and tungsten chlorides: direct access to $M_xO_y$ metal oxides and $M_xO_y/C$ metal oxide/carbon composites**

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### **Abstract**

$M_xO_y$  and  $M_xO_y/C$  composites ( $M = V, Fe$  and  $W$ ) were obtained by mineralization of cellulose with several metal chlorides. Cellulose was used both as a templating agent and as an oxygen and a carbon source. Soluble chloride molecules ( $VOCl_3$  and  $WCl_6$ ) and a poorly soluble ionic chloride compound ( $FeCl_3$ ) were chosen as metal oxide precursors. In a first time, primary metal oxide/cellulose composites were obtained via a thermal treatment by reacting urea impregnated filter paper with the corresponding metal chlorides in an autoclave at  $150\text{ }^{\circ}\text{C}$  after 3 days. After either pyrolysis or calcination steps of these intermediate materials, interesting metal oxides with various morphologies were obtained ( $V_2O_5$ ,  $V_2O_3$ ,  $Fe_3O_4$ ,  $WO_3$ ,  $H_{0.23}WO_3$ ), composites ( $V_2O_3/C$ ) as well as carbides (hexagonal  $W_2C$  and  $WC$ ,  $Fe_3C$ ). This result highlights the reductive role that can play cellulose during the pyrolysis step that allows to tune the composition of  $M_xO_y/C$  composites. The materials were characterized by FTIR, Raman, TGA, XRD and SEM. This study highlights that cellulose can be used for a convenient preparation of a variety of highly demanded  $M_xO_y$  and  $M_xO_y/C$  composites with original shapes and morphologies.

### **Introduction**

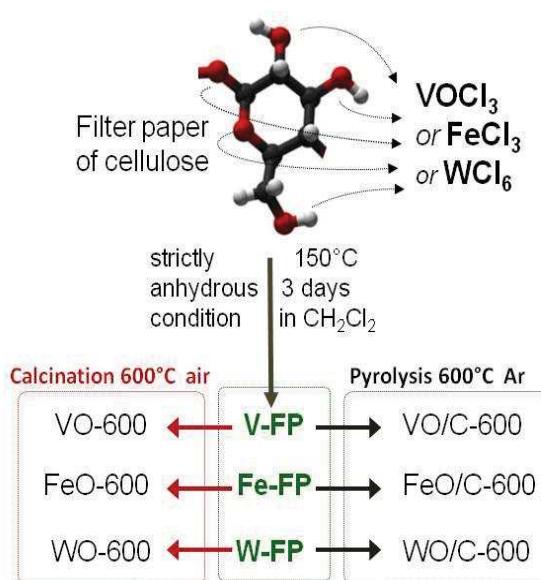
Anisotropic nanostructures of metal oxides, such as nanowires, nanorods, nanobelts, nanotubes and nanofibers, are stimulating great interest due to their potential performances in applications like catalysis, energy storage and sensing. Although their preparation can be achieved with industrial chemical compounds, increasing attention is currently paid to the use of lignocellulosic biomass as a renewable reagent that could be used to control porosity, morphology and particle size at the nanoscale. In addition to be the most abundant biopolymer on Earth, these biopolymers, and specially cellulose, have a well defined structure and can be prepared with reproducible specifications and in high purity. Thus, cellulose is more and more considered in the preparation of metal oxides, (Li & Huang, 2015; White, Brun, Budarin, Clark & Titirici, 2014) especially as template in hydrolytic Sol-Gel processes and, in fewer cases, by atomic layer deposition (ALD) and chemical vapour deposition (CVD). (Boury & Plumejeau, 2015)

The reaction of cellulose with metal-containing reagents is also of considerable importance for bio-refinery and the direct conversion into organic secondary building blocks or biofuels by a non-oxidative thermal treatment.(Huber, Iborra & Corma, 2006) The effect of inorganic salts on such processes is currently investigated, especially with alkaline and alkaline earth chlorides of such as sodium, potassium, magnesium or calcium chlorides.(Liu, Yu, Hayashi, Moghtaderi & Wu, 2014; Scheirs, Camino & Tumiatti, 2001; Yu, Liu & Wu, 2014)(Domvoglou, Ibbett, Wortmann & Taylor, 2009; Khelfa, Finqueneisel, Auber & Weber, 2008; Patwardhan, Satrio, Brown & Shanks, 2010) It has been shown that some of them, specially  $MgCl_2$  and  $CaCl_2$ , efficiently promote the dehydration/depolymerisation of cellulose as a result of the activation of the C-O bound in C-OH group or C-O- group of the acetal itself via the coordination of the  $M^{n+}$  cation.(Scheirs, Camino & Tumiatti, 2001) At 180°C, chain scission occurs, possibly with the formation of levoglucosan end-groups.(Domvoglou, Ibbett, Wortmann & Taylor, 2009) Under dry conditions, pyrolysis of cellulose in the presence of low concentration ( $5 \cdot 10^{-3} \text{ mol g}^{-1}$ ) of alkaline or alkaline-earth salts yields in a reduction of levoglucosan formation following the trends  $K^+ > Na^+ > Ca^{2+} > Mg^{2+}$  without clear evidence of the role of the cation.(Patwardhan, Satrio, Brown & Shanks, 2010) Transition metals have been less investigated, although  $NiCl_2$  and  $H_2PtCl_6$  display a significant effect on the thermolysis of cellulose, and “ $ZnCl_2$  has the most prominent effect by a catalytic role in all degradation mechanism occurring at lower temperature (between 60 and 70°C less than pure cellulose) leading to an increase in water and gas production at the expense of vapours” (Khelfa, Finqueneisel, Auber & Weber, 2008). For wood, a similar effect was reported (Di Blasi, Branca & Galgano, 2008) and other salts such as iron(III) and nickel(II) nitrates were reported to reduce the fraction of condensable organic compounds and to enhance the formation of gases like hydrogen (Bru, Blin, Julbe & Volle, 2007). However, compared to these inorganic salts, molecular transition metal chlorides such as  $TiCl_4$  are clearly different in their ability to react with the –OH function of cellulose that generates HCl vapour but also [M]-oxo complexes, both of them being active catalyst of reaction and isomerisation. Recently, a chromium salt(Kim et al., 2011; Zhang et al., 2015) and the super-acid system  $SO_4^{2-}/M_xO_y$ (Yang et al., 2015) have been reported for the production of 5-hydroxymethyl-2-furfural, an interesting intermediate in biorefinery.(Atanda et al., 2016; Atanda et al., 2015; Chareonlimkun, Champreda, Shotipruk & Laosiripojana, 2010; Kuo et al., 2014; Peng, Lin, Li & Yang, 2011)

We have previously reported the reaction of cellulose with  $TiCl_4$  under mild reaction conditions (85°C) and controlled atmosphere, with or without solvent (dichloromethane). We reported a significantly different reactivity of titanium(IV) chloride compared to the metal chlorides mentioned above. Instead of targeting

the decomposition of cellulose into small organic compounds, we introduced this approach as a new way to access  $\text{TiO}_2$  and  $\text{TiO}_2/\text{C}$  composites.(Henry et al., 2016; Henry et al., 2015; Plumejeau et al., 2016) We observed that cellulose was not only used as a template, but also as an oxygen-source through the *in situ* production of water leading to the formation of metal oxide. Cellulose was also used as C-source when the  $\text{TiO}_2/\text{cellulose}$  hybrid was pyrolyzed into a  $\text{TiO}_2/\text{C}$  composite. We have also evidenced a deep transformation of the cellulose, as shown by a decrease of the oxygen content and the formation of a carbonaceous residue. These transformations clearly indicate a dehydration of the cellulose, which is probably promoted by the highly acidic media and the strong Lewis acidic character of Ti-based species (see for example dehydration of carbohydrates promoted by Ti-pyrophosphate).(Benvenuti et al., 2000)

Herein, we report our results on the development of this synthesis pathway, expanding the reactivity of cellulose towards other metal chlorides, in particular  $\text{VOCl}_3$ ,  $\text{FeCl}_3$  and  $\text{WCl}_6$ . We show the scope of this strategy which appears to be a valuable way to access a variety of  $\text{M}_x\text{O}_y$  and  $\text{M}_x\text{O}_y/\text{C}$  composites. Furthermore, our study also offers an insight into the chemical transformation of cellulose with highly reactive metal chlorides. On the basis of our previous results obtained with titanium based species, we analyzed the formed samples in view of their morphologies and textures. Our concern was to investigate if the reaction allows to access materials with particular morphologies and shapes as already observed in the case of  $\text{TiO}_2$ .



**Scheme 1** General overview of the experiments and nomenclature of the sample

As illustrated in scheme 1, we report on the treatment of cellulose filter paper (FP) with  $\text{VOCl}_3$ ,  $\text{FeCl}_3$  and  $\text{WCl}_6$  leading to the corresponding hybrids M@FP (M = V, Fe, W). These intermediate materials were subsequently converted to the pure metal oxide MO-600 by calcination at 600°C or to the metal oxide/carbon composite MO/C-600 by pyrolysis at the same temperature under inert argon atmosphere. The three metal chlorides  $\text{VOCl}_3$ ,  $\text{FeCl}_3$  and  $\text{WCl}_6$  have been chosen considering that they yield oxides or oxides/carbon composites with interesting electrochemical, optical or catalytic properties that make them attractive for application in catalysis, sensing or energy storage. Additionally, they are abundant elements and particularly their corresponding chlorides are among the cheapest reagents industrially used. We also wanted to compare dichloromethane soluble reagents such as  $\text{VOCl}_3$  and  $\text{WCl}_6$  with a poorly soluble reagent,  $\text{FeCl}_3$ . In this situation, we investigated rather covalent chlorides ( $\text{VOCl}_3$  and  $\text{WCl}_6$ ) and compared them with a more ionic one,  $\text{FeCl}_3$ .

## Experimental section

**Chemicals.** Quantitative filter papers (FP) (FT-3-101-09, Sartorius, France) were used as cellulose source ( $\geq 98\%$  alpha-cellulose content, Vanadium(V) oxychloride (99%), tungsten(VI) chloride ( $\geq 99.9\%$ ), niobium(V) chloride (99%) and iron(III) chloride (97%) were purchased from Sigma-Aldrich and used as received. Dichloromethane (99%, Sigma-Aldrich) was distilled over calcium hydride before use (~10 ppm H<sub>2</sub>O). FP was first dried at 80°C at ambient pressure during 3 days before any uses. All manipulations with solvent and metal chloride were setup in the glovebox (<1 ppm H<sub>2</sub>O).

**Preparation of urea-impregnated filter paper (FP).** FP was cut into 1–2 cm<sup>2</sup> pieces and plunged in a 10 wt% aqueous solution of urea for 24 h at 20 °C and then dried at 80 °C for 3 days at ambient pressure before being stored in a glove-box. Elemental analysis found: C 39.8, H 5.7, N 5.7.

**Mineralization of filter paper.** In a general procedure, the FP is introduced into a Teflon-lined autoclave to which is then added dichloromethane (30 mL) and the corresponding metal chloride via a syringe; all quantities are given in Table 1. The autoclave is then placed in an oven at 150 °C for 3 days and then cooled down to room temperature. Removal of the liquid phase leaves black pieces of paper that are vigorously washed with dichloromethane (3 x 20 mL) at room temperature and then subsequently washed with standard dichloromethane (3 x 20 mL) at ambient atmosphere. Samples are then dried in an oven at 80 °C for 24h to give the corresponding hybrid samples: V-FP, Fe-FP and W-FP.

**Table 1:** composition of the samples

|       | Cellulose |                                       | Metal chloride |                          |
|-------|-----------|---------------------------------------|----------------|--------------------------|
|       | m (g)     | n (10 <sup>-3</sup> mol) <sup>a</sup> | m (g)          | n (10 <sup>-3</sup> mol) |
| V-FP  | 2.012     | 14.41                                 | 2.92 (1.6 mL)  | 16.85                    |
| Fe-FP | 2.022     | 12.47                                 | 2.675          | 16.49                    |
| W-FP  | 1.015     | 6.26                                  | 1.625          | 4.10                     |

<sup>a</sup> based on the molecular weight of glucose unit

**Thermal treatment.** Hybrid samples are calcined in air at 600 °C for 1h at a heating rate 5°C.min<sup>-1</sup>, yielding the metal oxides, or pyrolyzed under argon 600 °C for 1h at a heating rate 5°C.min<sup>-1</sup>, yielding the metal oxide/carbon composites. For nomenclature, see Scheme 1.

**Solid-state characterizations.** The X-ray powder diffraction (XRPD) patterns of the samples were recorded using a Philips X’Pert Pro diffractometer. Cristallite size was determined using Debye-Scherrer equation, considering, for each crystalline phase, the three most intense peaks. Full width at half maximum (FWHM) of the diffraction rays was determined using the Xfit program. Transmission electronic microscopy (TEM) images were recorded using JEOL 1200 EXII, and scanning electronic microscopy (SEM) images were obtained with an Hitachi S-4800. Energy dispersive X-ray analysis (EDX) was done using the EDAX attachment (Oxford Instruments) of the SEM system. N<sub>2</sub>-physisorption isotherms were obtained at 77K using Micrometrics Tristar apparatus. The samples were outgassed for 12h at 150 °C under reduced pressure (2 Pa). The pore distribution was calculated from the desorption branch using the BJH method. Thermogravimetric analyses (TGA) were obtained using a Netzsch Simultaneous Thermal Analyser STA 409 PC Luxx. Raman spectra were measured on powder samples using a Horiba LabRAM ARAMIS spectrophotometer with an excitation wavelength of 633 nm. Solid-state <sup>13</sup>C NMR measurements have been recorded using a VARIAN VNMRS300 spectrometer using a T3 MAS VARIAN probe with a 3.2 mm zirconia rotor. CP MAS experiment were carried out spinning at 6000 Hz, with a 3 ms contact time and a 5s recycling delay. The <sup>13</sup>C chemical shifts were referenced to TMS using the deshielded resonance of adamantane (38.5 ppm) as secondary reference.

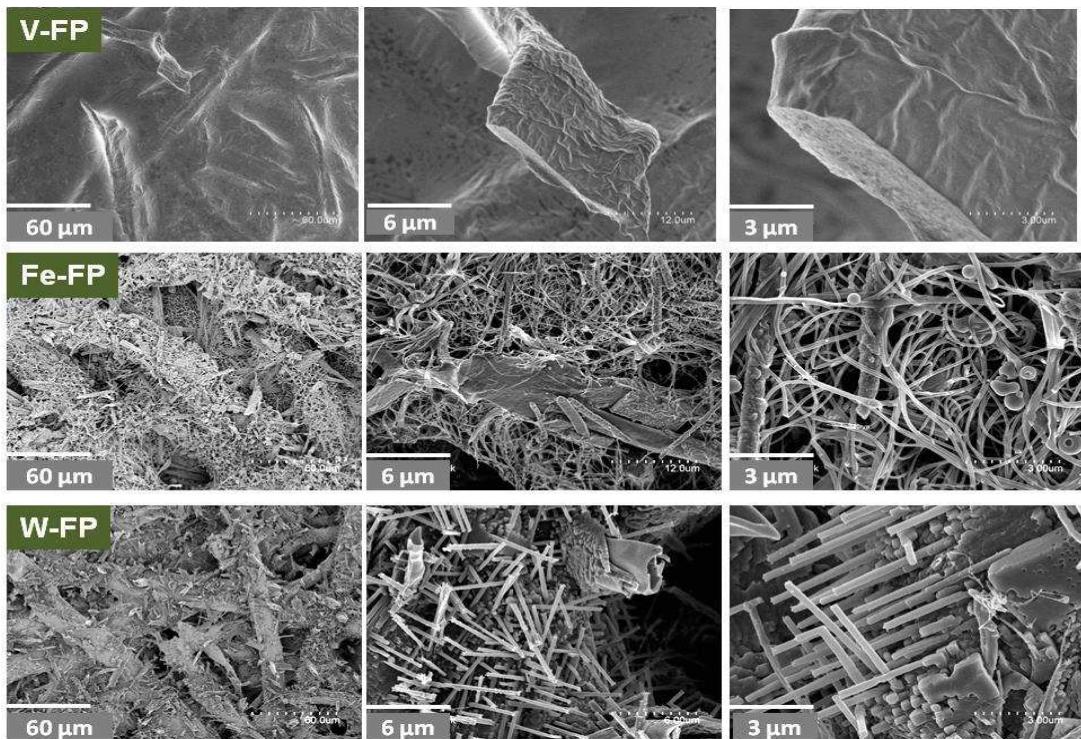
## Results and discussion

**Synthesis and characterization of the M<sub>x</sub>O<sub>y</sub>@FP sample.** FP was firstly impregnated with urea before the reaction with metal chlorides since we previously observed that this treatment was beneficial for the

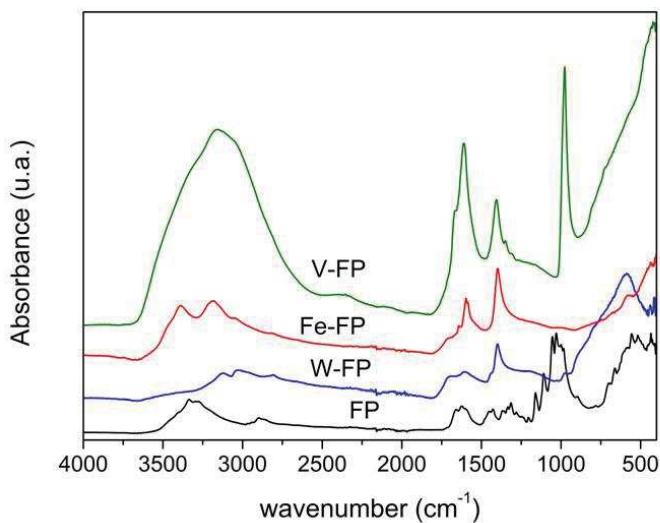
development of nano-flower morphology in the case of TiO<sub>2</sub>, possibly because through a slight defibrillation of the FP microfibers.(Henry et al., 2016)

In a second time, we performed reductive mineralisation reactions of FP with the corresponding metal chloride at 150 °C for 3 days. Considering our prior work on TiCl<sub>4</sub>, we have chosen a [C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>/metal chloride] molar ratio close to 1, since not all the O-containing functions of cellulose are expected to react.(Nair, Samdarshi & Boury, 2013) The recovered hybrids M-FP display shape and mechanical properties similar to those of the starting FP, except that they are black. No organic by-products could be detected in the CH<sub>2</sub>Cl<sub>2</sub> phase, only HCl vapour was identified.

SEM analysis of the sample reveals important differences of the mineralized samples with the starting FP as shown in Figure 1. The initial shape of the cellulose fibers can be identified in all cases at low magnification (x100). At higher magnification (x10K), deposits of new materials are observed in the three cases but with different features: a glassy and uniform deposit at the surface of the fiber in the case of V-FP, an entanglement of sub-micrometric fibers and particles for Fe-FP, and a crust around the cellulose fibers from which emerge sticks and particles with sub-micrometric diameter and several microns length for W-FP.

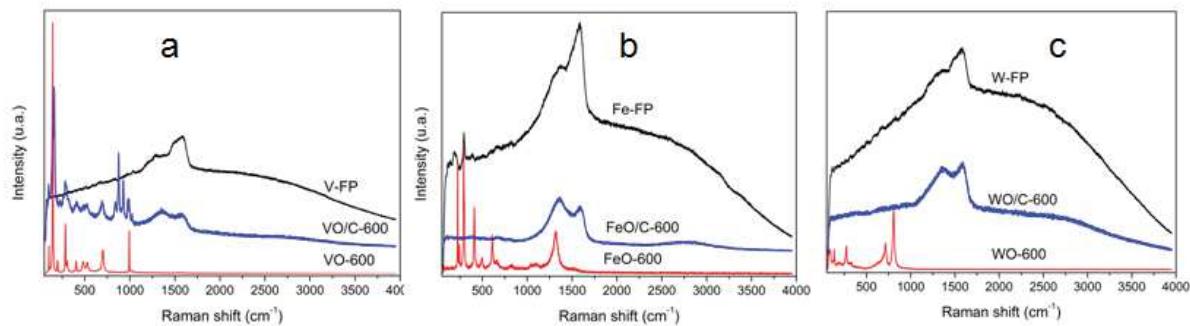


**Fig.1** SEM image at different magnification of hybrid samples V-FP, Fe-FP, W-FP



**Fig.2 2** Comparison of FT-IR spectra of the initial FP and the hybrid samples V-FP, Fe-FP, W-FP

Different analyses revealed the chemical transformations of the cellulose by comparison with the initial FP. The initial FTIR analysis (Figure 2) of unreacted FP display adsorption bands related to C-H bond ( $1330 \text{ cm}^{-1}$  CH rocking of the ring;  $2930 \text{ cm}^{-1}$   $\nu_{\text{a}}(\text{CH}_2)$ ;  $2860 \text{ cm}^{-1}$   $\nu_{\text{a}}(\text{CH}_2)$ ) and secondly band related to C-O bond ( $1146\text{--}1160 \text{ cm}^{-1}$   $\nu_{(\text{C-O-C} \& \text{CH})}$  deformation;  $1071\text{--}1067 \text{ cm}^{-1}$   $\nu_{(\text{C-O})}$ ;  $1046 \text{ cm}^{-1}$   $\nu_{(\text{C-O of carbohydrates C-OH})}$ ). (Movasaghi, Rehman & ur Rehman, 2008; Oh et al., 2005) The most important difference between FP and M-FP is the absence of bands related to C-H bond ( $1330 \text{ cm}^{-1}$ ;  $2930 \text{ cm}^{-1}$ ;  $2860 \text{ cm}^{-1}$ ) and the absence of the band related to C-O bond ( $1146\text{--}1160 \text{ cm}^{-1}$ ;  $1071\text{--}1067 \text{ cm}^{-1}$  and  $1046 \text{ cm}^{-1}$ ). These adsorption bands completely disappear in the spectra of the M@FP composites, which are dominated by strong bands characteristic for M-O (V-O stretching at  $996 \text{ cm}^{-1}$  and V=O vibration at  $1022 \text{ cm}^{-1}$ , W-O-W twisting at  $609 \text{ cm}^{-1}$ ), M-OH and M-Cl groups, as well as an absorption band at  $1600 \text{ cm}^{-1}$ , indicating the presence of water, and a band at  $1400 \text{ cm}^{-1}$  attributed at present to N-H bending. Such differences with the FT-IR spectrum of starting cellulose of FP are not observed when cellulose is used in Sol-Gel impregnation, ALD or CVD, for which bands related to the presence of cellulose are still present (see for example ref. (Sun, Yang & Wang, 2010)) All spectra are dominated by the intense absorption bands which can be ascribed to M-O-M bond at low wave numbers below  $1000 \text{ cm}^{-1}$  but more clearly by the M-OH and physisorbed water in the regions  $3400\text{--}3100 \text{ cm}^{-1}$  &  $1633 \text{ cm}^{-1}$ , the latter resulting of the contact between samples and air during the FTIR analysis.



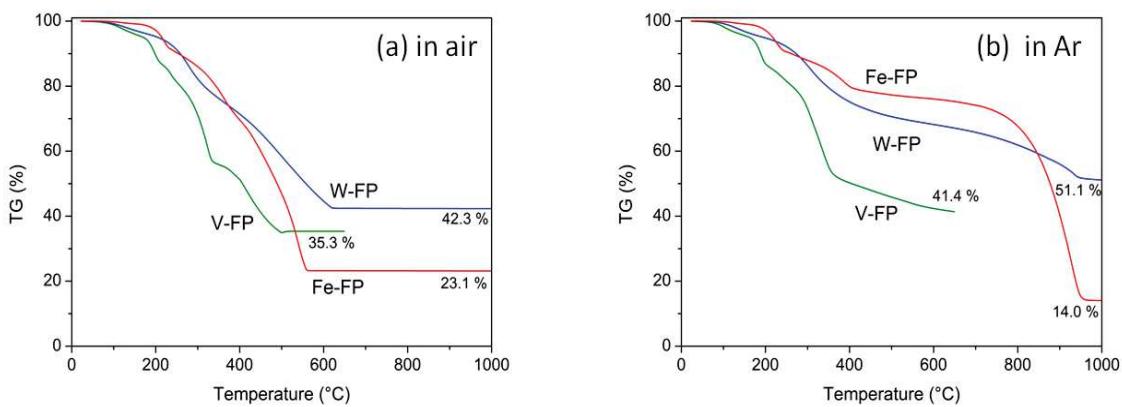
**Fig.3** Comparison of Raman spectra of starting hybrid samples V-FP, Fe-FP, W-FP, sample after calcination (VO-600, FeO-600, WO-600) or pyrolysis (VO/C-600, FeO/C-600, WO/C-600)

For all these samples and before any thermal treatment, despite the very large fluorescence observed in RAMAN spectroscopy (Figure 3) the usual broad band of carbon type materials can be clearly identified: D band  $\approx 1340\text{ cm}^{-1}$  (6-membered aromatic rings in graphitic materials related, attributed to defects in graphite) and a broad G band at  $\approx 1580\text{ cm}^{-1}$  (ascribed to the  $\text{sp}^2$  hybridized carbon network).(Ferrari & Robertson, 2000) More precisely maxima for the hybrid samples are: Fe-FP: 1373 et  $1582\text{ cm}^{-1}$ , V-FP:  $1583\text{ cm}^{-1}$  and a broad signal  $1291\text{--}1370\text{ cm}^{-1}$ ; W-FP:  $1361\text{ cm}^{-1}$  and  $1580\text{ cm}^{-1}$ . All the signals are very broad and probably include other contributions like  $D_2 \approx 1615\text{ cm}^{-1}$  (edges of graphitic crystallites),  $D_1 \approx 1360\text{ cm}^{-1}$  (in-plane breathing vibrations of  $\text{sp}^2$ -bonded carbon within structural defects),  $D_3 \approx 1500\text{--}1550\text{ cm}^{-1}$  (amorphous carbon phase) and  $D_4 \approx 1200\text{ cm}^{-1}$  ( $\text{sp}^2\text{--sp}^3$  bonds).(Ferrari & Robertson, 2000; Hoekstra et al., 2015) We also noted that the second-order Raman spectrum in the  $2100\text{--}3500\text{ cm}^{-1}$  region is not observed here, possibly due to high fluorescence.

The  $I(D)/I(G)$  ratio, shown to be inversely related to the crystalline thickness of graphitic materials,(Tuinstra & Koenig, 1970) is generally used here to estimate a correlation length of the graphitic domains. Although the value must be taken with precaution due to the high fluorescence, an  $I(D)/I(G)= 1\text{--}1.25\text{ nm}$  indicates a nanosized crystalline  $\text{sp}^2$ -hybridized carbon clusters embedded in a disordered matrix of both amorphous  $\text{sp}^3$ - and  $\text{sp}^2$ -hybridized carbon, for information a correlation length of  $1\text{--}1.25\text{ nm}$  was reported for cellulose pyrolyzed at  $500\text{--}600\text{ }^\circ\text{C}$ .(Hoekstra et al., 2015; Rhim et al., 2010) No metal-containing inorganic phase can be identified by such Raman analysis, due to the high fluorescence intensity of the material but also to the presence of a carbonaceous layer at the surface of the inorganic metal-containing phase. This was indeed previously observed when cellulose was reacted with  $\text{TiCl}_4$ .(Nair, Samdarshi & Boury, 2013; Plumejeau et al., 2016)

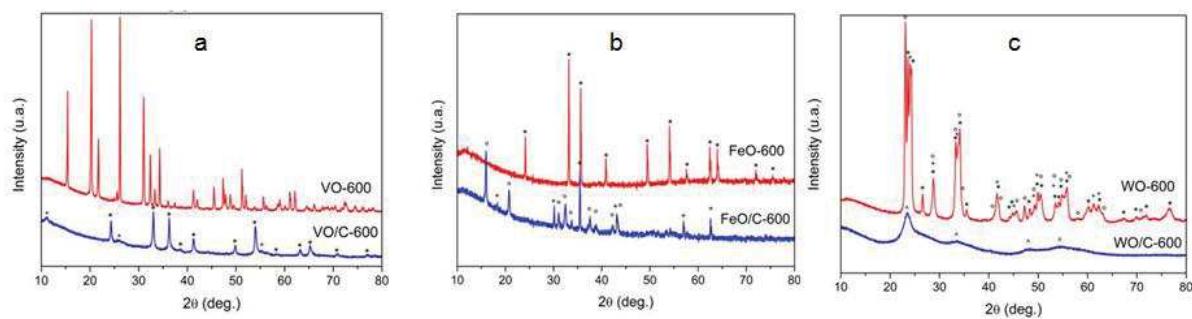
Some crystalline phases can be observed in some M-FP by X-ray analysis (Figure SI 1) but we first note the absence of the cellulose signal, confirming the deep structural modification. For Fe-FP,  $\text{FeCl}_2(\text{H}_2\text{O})_2$  and  $(\text{NH}_4)\text{FeCl}_3$  are identified and for W-FP,  $(\text{NH}_4)\text{Cl}$  is identified as a crystalline phase aside from what could be a poorly crystallised  $\text{HxWO}_3$ . However, for V-FP, the presence of  $\text{V}_4\text{O}_9$  is questionable as most of the more intense peaks cannot be attributed (using for example JCPDS files). Altogether these data evidence the decomposition of the urea leading to ammonia, a known process at this treatment temperature.(Schaber et al., 2004) More interestingly, it also evidence reduction processes with formation of Fe(II) from Fe(III) chloride and partial reduction in the case of Vanadium.

**Calcination of M-FP and characterisation of MO-600.** An oxidative thermal treatment of these hybrids at 600 °C is performed in order to crystallize the corresponding oxide and remove the cellulose. The MO-600 is obtained after calcination, this temperature has been chosen taking into account the TGA data in Figure 4(a). The latter shows that around 600 °C the weight loss is almost finished and corresponds to the combustion of cellulose (*cf.* Figure SI 2). The weight loss starts at similar temperature for all the samples and is lower than the 100 % weight loss of FP alone under these conditions.



**Fig. 4** TGA analyses under air and argon of V-FP, Fe-FP, W-FP

The obtained samples were characterized by X-ray diffraction (Figure 5a-c). In the case of vanadium oxide  $\text{V}_2\text{O}_5$  (orthorhombic, JCPDS no. 85-0601) is the only identified crystalline phase in VO-600 with an average crystallite size of  $\pm 54$  nm. In the case of FeO-600 (Figure 5b,  $\text{Fe}_2\text{O}_3$  (rhombohedral, JCPDS N° 86-2368) is the only identified crystalline phase with an average crystallite size of  $\pm 42$  nm. Finally, for WO-600 (Figure 5c), only  $\text{WO}_3$  is identified, also in different crystalline form, monoclinic 24-0747, monoclinic 87-2404 and tetragonal 89-1287) and with a different crystallite size of  $\varnothing = 46$  nm,  $\varnothing = 30$  nm and  $\varnothing = 23$  nm, respectively; this being given as estimation due to signal superposition.



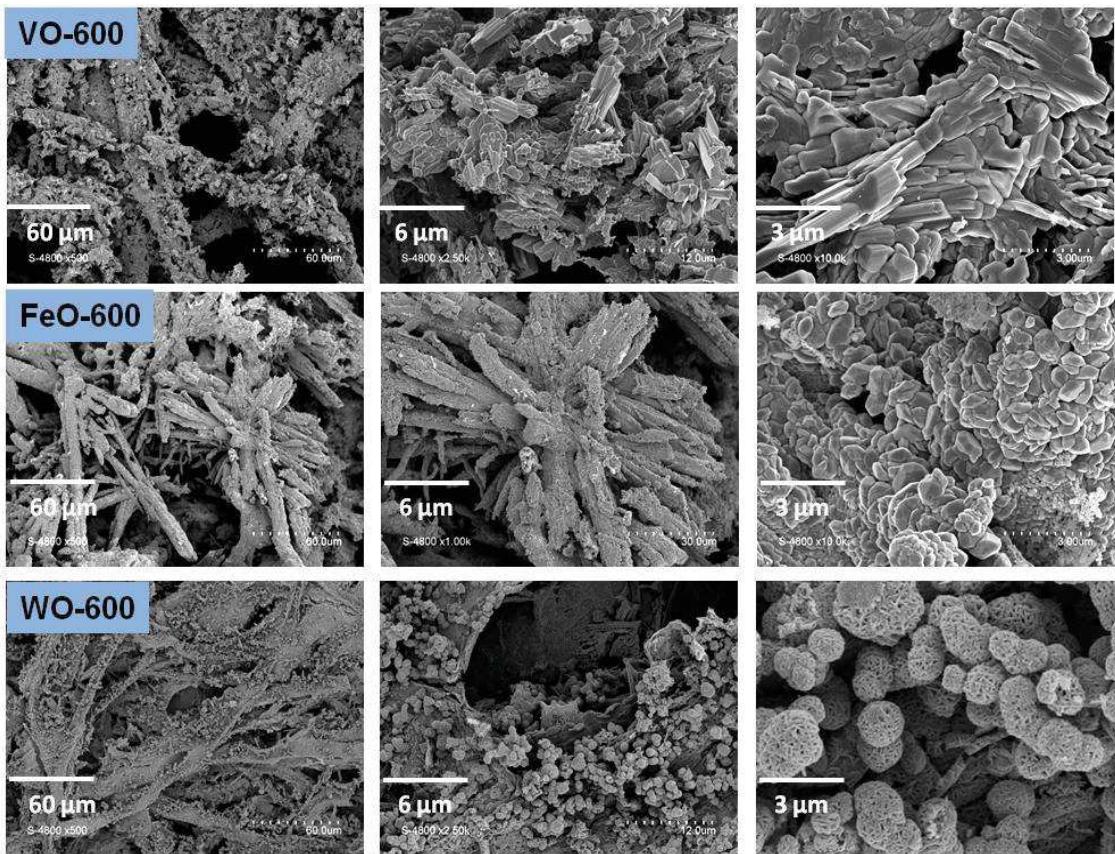
**Fig.5** X-ray powder diffraction spectra of a) VO-600 and VO/C-600, b)FeO-600 and FeO/C-600, c)X-ray powder diffraction spectra of WO-600 and WO/C-600

Assuming that 100 % of the inorganic phase is the one detected by X-ray diffraction and taking into account the ceramic yield in each cases, it can be determined a mole amount of M (M = V, Fe or W) per 100 g of M-FP hybrid: 0,38 mole of Vanadium in 100 g of V-FP sample (TGA yields 35 %),0,28 mole of Iron in 100 g of Fe-FP (TGA yields 23 %) and finally 0,18 mole of Tungsten in 100g of W-FP (TGA yields 42 %). Altogether, these data points out an order of reactivity, vanadium being the most reacted, followed by iron and tungsten.

The presence of these crystalline phases is confirmed by Raman (Figure 3) and FTIR spectroscopy (Figure SI 3). Raman spectrum of VO-600 exhibits characteristics bands for  $V_2O_5$  at 103, 145, 197, 284, 303, 405, 480, 527, 700 et 995  $\text{cm}^{-1}$ . (Souza Filho, Ferreira, Santos, Mendes Filho & Alves, 2004) The FTIR spectrum of VO-600 shows three bands: a band at 1010  $\text{cm}^{-1}$ , corresponding to V=O stretching vibrations, a band at 806  $\text{cm}^{-1}$  corresponding to V-O-V bending vibration and a broad band below 500  $\text{cm}^{-1}$ , attributed to V-O-V edge-sharing vibration.(Li, Sun, Yin, Ruan & Ai, 2013) The Raman spectrum of FeO-600, with its bands at 227, 245, 291, 411, 497, 611, 657, 817, 1047, 1099 and 1317  $\text{cm}^{-1}$ , is typical or  $\alpha\text{-Fe}_2\text{O}_3$  (hematite).(de Faria, Venâncio Silva & de Oliveira, 1997) The two bands of the FTIR spectrum, at 425 and 515  $\text{cm}^{-1}$ , are attributed to the Fe-O stretching vibration.(Apte, Naik, Sonawane, Kale & Baeg, 2007) Finally, the Raman spectrum of WO-600 shows several bands at 134, 182, 272, 327, 714 and 806  $\text{cm}^{-1}$ , corresponding to characteristic  $WO_3$  bands.(Siciliano et al., 2008) The FTIR spectrum of WO-600 presents only one broad band at 625  $\text{cm}^{-1}$  with a shoulder at 806  $\text{cm}^{-1}$  and it could be attributed to the W-O-W twisting (the shoulder corresponding to the W-O-W stretching).(Diaz-Reyes, Dorantes-Garcia, Perez-Benitez & Balderas-Lopez, 2008)

After having ascertained the elemental composition and the crystalline phase, we focused in the following on the determination of the morphology of the calcined samples. For this purpose, we recorded SEM images of the three samples VO-600, FeO-600 and WO-600. The templating effect of the cellulose is clearly observed in SEM images at low magnification (x500) shown in Figure 6. At higher magnification (x10K) 84

the usual morphology of elongated plaques for  $\text{V}_2\text{O}_5$  in VO-600 is easily identified, while faceted nanocrystal are observed for FeO-600 and essentially string balls in the case of WO-600. It is worth noting that all these morphologies do not impact the mechanical properties. These composites have poor mechanical properties and can easily be grinded to powders.



**Fig. 6** SEM image at different magnifications of calcined samples VO-600, FeO-600, WO-600

#### Pyrolysis of M-FP and characterisation of MO/C-600 samples.

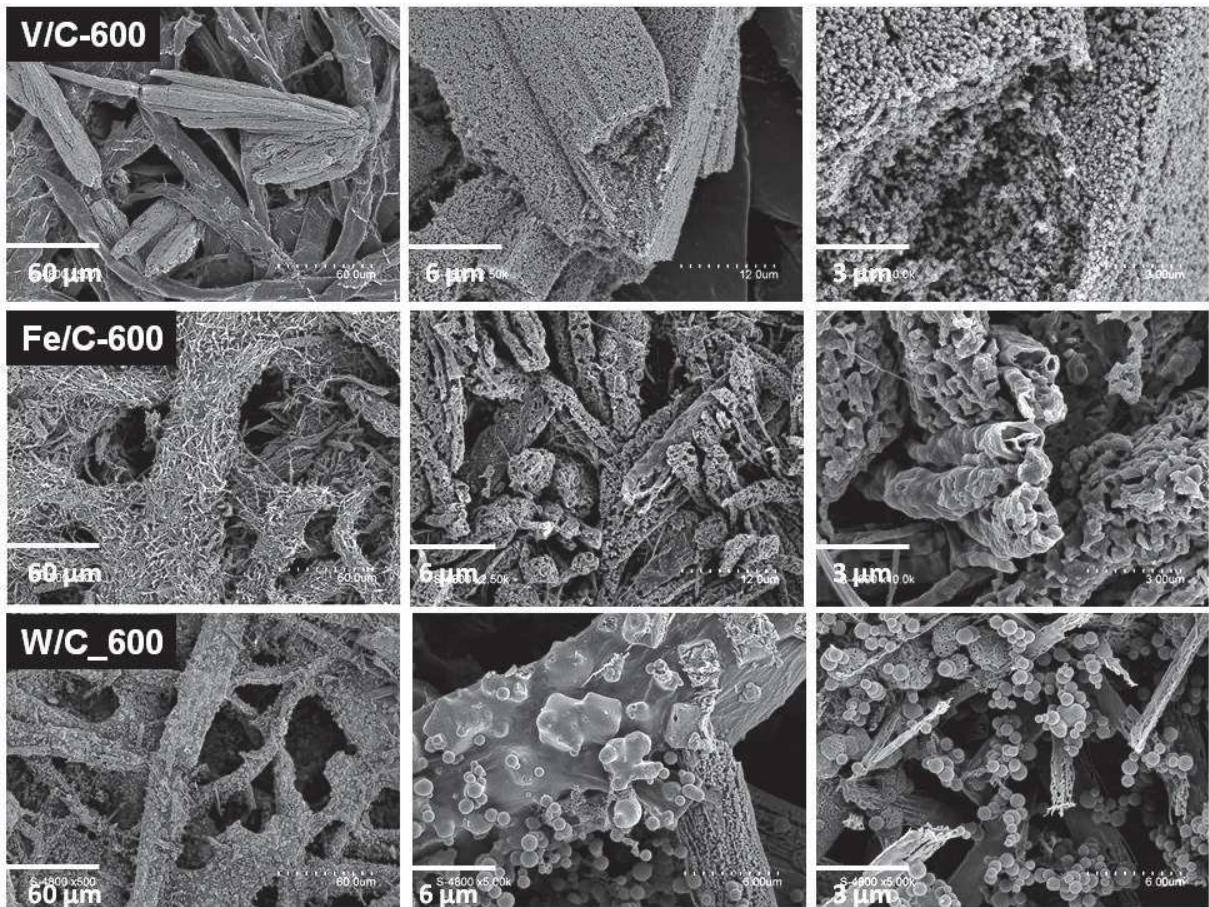
Quantitative pyrolysis was performed under argon up to 600°C, this temperature was chosen after considering the analysis of the TGA data of the M-FP samples in similar conditions (Figure 4b) and by considering that one of the oxides,  $\text{V}_2\text{O}_5$ , melts at 690 °C. It is clear that above this temperature, Fe-FP and W-FP still present important weight loss, probably due to carboreduction. It is also important to keep in mind that at 600°C, weight loss of FP is almost terminated and the char yield is 18-22%.

The inorganic phases identified by X-ray diffraction after pyrolysis samples are significantly different from those detected after calcination, this being ascribed to the role of cellulose and its carbonization. Indeed, for VO/C-600, only rhombohedral  $\text{V}_2\text{O}_3$  (JCPDS N° 85-1411) is observed with an average crystallite size

$\pm 41$  nm. Interestingly, no  $V_2O_5$  is detected (Figure 5a). A Raman spectroscopy analysis confirms this and a set of signals at 103, 145, 197, 284, 305, 405, 479, 527, 702 et 995  $cm^{-1}$  for VO/C-600 (Figure 3a) can be attributed to either  $V_2O_3$  but also suggests the presence of  $V_6O_{13}$ . (Armstrong, Osiak, Geaney, Glynn & O'Dwyer, 2014; Zhang et al., 2016) Concerning the carbon part of the material, from the D ( $1364\text{ cm}^{-1}$ ) and G ( $1584\text{ cm}^{-1}$ ) and because of the absence of fluorescence, a correlation length of 1.09 nm can be estimated from the ratio I(D)/I(G). For all the pyrolyzed samples, a low intensity and very broad signal corresponds to the second-order Raman spectrum in the  $2100\text{--}3500\text{ cm}^{-1}$  region to disordered carbon.

The formation of this V(III) oxide from the  $VOCl_3$  precursor is clearly the sign of a reduction process at low temperature. It can be noted that such  $V_2O_3/C$  composite was reported only very recently as a good candidate as anode material in Li-Ion batteries. (Li et al., 2016; Liu et al., 2016; Shi et al., 2015; Tang, Li, Ding & Zhang, 2016) As observed in Figure 7, a fiber-like structure can be identified at low magnification (x500), probably resulting from cellulose carbonization assembled with mineral particles of different shape. At higher magnification, these particles appear to be constituted of aggregated rounded-shape sub-nanometre particles with an average size of 100-200 nm. Inside the “paper”, the situation seems slightly different, as bundles of nanoneedles, closely associated with the carbonized fibers, can be observed (SI4).

Similar reduction occurs for Fe-FP since cubic  $Fe_3O_4$  cubic is detected as the oxide phase in FO/C-600 (Figure 5b) with an average crystallite size of  $\pm 60$  nm (JCPDS N° 75-1372) aside from a monoclinic Iron(II) chloride hydrate phase with an average crystallite size  $\pm 54$  nm (JCPDS N° 72-0268) that stems from the thermal decomposition of the  $(NH_4)FeCl_3$  identified before the pyrolysis step (the hydrate formation can be the result of a sample exposed to air moisture after pyrolysis). Both phenomena indicate a partial reduction of Iron(III) and only a partial transformation of the chloride into the oxide due to a incomplete reaction between  $FeCl_3$  and alcohol functions of cellulose. For FeO/C-600 D ( $1363\text{ cm}^{-1}$ ) and G ( $1592\text{ cm}^{-1}$ ) are observed and the I(D)/I(G) ratio can be calculated to 1.23 nm. Differently from VO/C-600, no metal-containing inorganic phase was detected in this case.



**Fig. 7** SEM image at different magnifications of pyrolyzed samples VO/C-600, FeO/C-600, WO/C-600

The SEM analyses (Figure 7) reveal a fibrous structure of the material resulting from a preservation of the templating effect of the cellulose. At higher magnification the inorganic material made covering the carbonized fiber seems to be constituted of inorganic particles assembled in tubular or elongated microparticles with inhomogeneous shape aside from nanometer size filament (see also figure SI5).

For Fe-FP, between 700 and 1000 °C, an important weight loss (see Figure 4) corresponding to a carboreduction process of the oxide. Indeed, X-ray powder analysis of samples pyrolyzed at 1000°C shows FeCl<sub>2</sub> rhombohedric : 8 nm (JCPDS N° 01-1106), Fe<sub>3</sub>C orthorhombic 35 nm (JCPDS N° 34-0001) and graphite 6 nm (JCPDS N° 41-1487) as crystalline phases (see Figure SI6).

The W-containing sample, WO/C-600 present in Raman the D ( $1369\text{ cm}^{-1}$ ) and G ( $1590\text{ cm}^{-1}$ ) bands from which the I(D)/I(G) ratio lead to an estimation of the correlation length = 0.87nm. A tentative attribution of the broad diffraction rays (Figure 5c) allowed us to identify H<sub>0.23</sub>WO<sub>3</sub> cubic (JCPDS 42-1260), a tungsten bronze that generally requires much more sophisticated processing.(Urretavizcaya, Tonus, Gaudin, Bobet

& Castro, 2007) As observed for FeO/C-600, SEM (Figure 7) reveals a fibrous structure of the material derived from the cellulose skeleton. However, at higher magnification (x10K), the particles covering the surface of the fibers are clearly heterogeneous in size and morphology. A weight loss between  $\approx 700 < T < \approx 950$  °C (Figure 4) is observed and can be ascribed to carboreduction process since hexagonal W<sub>2</sub>C 17 nm (JCPDS N° 35-0776) and hexagonal WC 13 nm (JCPDS N° 72-0097) are the only observed crystalline phases in sample pyrolyzed at 1000 °C (see Figure SI7). It represents a simple and interesting access to tungsten carbide at very low temperature compared to other recently reported synthetic strategies.(Jin, Liu, Li & Yang, 2011)

The chemistry behind this mineralization of cellulose when exposed to metal chlorides like VOCl<sub>3</sub>, FeCl<sub>3</sub> or WCl<sub>6</sub> is not fully clear at present. However, all the spectroscopy data confirm a significant modification of the cellulose composition and structure at least on its surface. They indicate a massive disappearance of oxygen concomitant with the formation of the corresponding metal oxide. The latter may be the result of the reaction of the metal chloride with residual water which may persist in the paper and estimated around 2 to 3% by TGA. This is not sufficient to explain the formation of 20% to 40% of the metal oxide. On the other hand, there is only one other source of oxygen in the system, those from the structure of cellulose. As we have already reported in our work on the treatment of cellulose by TiCl<sub>4</sub>, we propose that here also a process of dehydration of the cellulose takes place. This process is probably deeply different from that proposed for the action of the alkaline MCl and alkalin-earth MCl<sub>2</sub> chloride mentioned in the introduction. First because an important difference here is the presence of HCl which cannot be considered in the case of MCl or MCl<sub>2</sub> salt. Secondly because these latter doesn't exhibit a strong Lewis acidity like of V, W and Fe as cation or as metal-containing complexes. Thirdly, the way that they bound to O atom is also different to the one of the alkaline and alkaline-earth metal.

Aside from the chemistry of these transformations, the morphology of the oxide is also a very intriguing phenomenon but we must admit that we do not have at present any clear hypothesis on the role of cellulose on the morphology of the inorganic phase that forms at its surface.

## Conclusion

To conclude, our work demonstrates the versatility and efficiency of this mineralization of cellulose by metal chloride and is in agreement with a dehydration of the cellulose leading to an O-transfer from the cellulose to the metal. This is observed whatever is the metal chloride and without noticeable effect of its solubility in the solvent used here. Compared to other synthetic strategies, this approach presents three specificities: the simplicity and sustainability of the process performed in mild conditions with cheap reagents, the particular morphologies of the obtained metal oxides, and the close association of the oxide with the carbon in the case of a pyrolysis; the latter being improvable by the use of nanocellulose like nanocrystals and nanofibers. Above all, we point out the complexity of the role of cellulose that behaves as an oxygen source during the mineralization and, during the pyrolysis as carbon source as well as a reducing

agent of the metal-containing species leading to sub-oxides associated with a carbon phase. Applications of the metal oxides and the metal oxide/carbon composites in particular in energy storage are currently investigated in our group and will be reported in due course.

## Acknowledgements

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## Supporting information

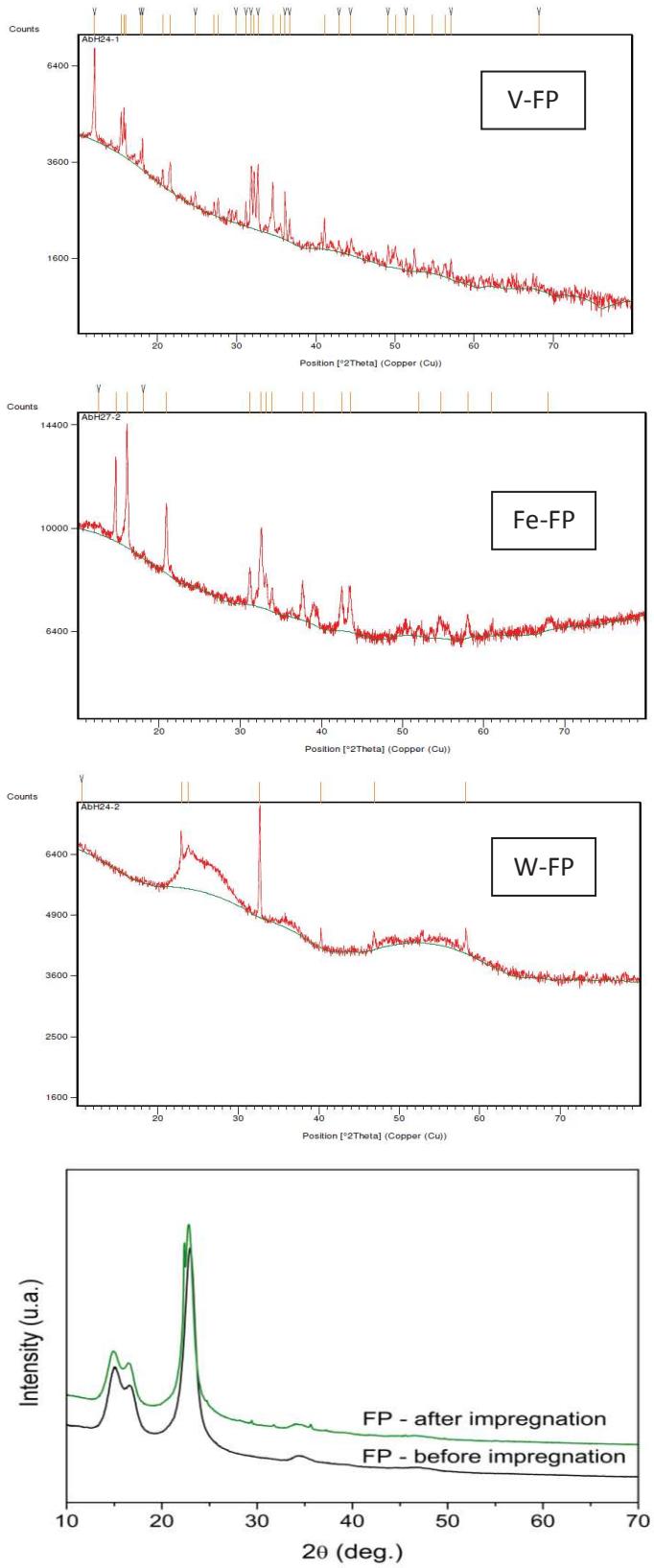


Figure SI 1: X-ray diffraction pattern of powder of hybrid material V-FP, Fe-FP, W-FP and FP

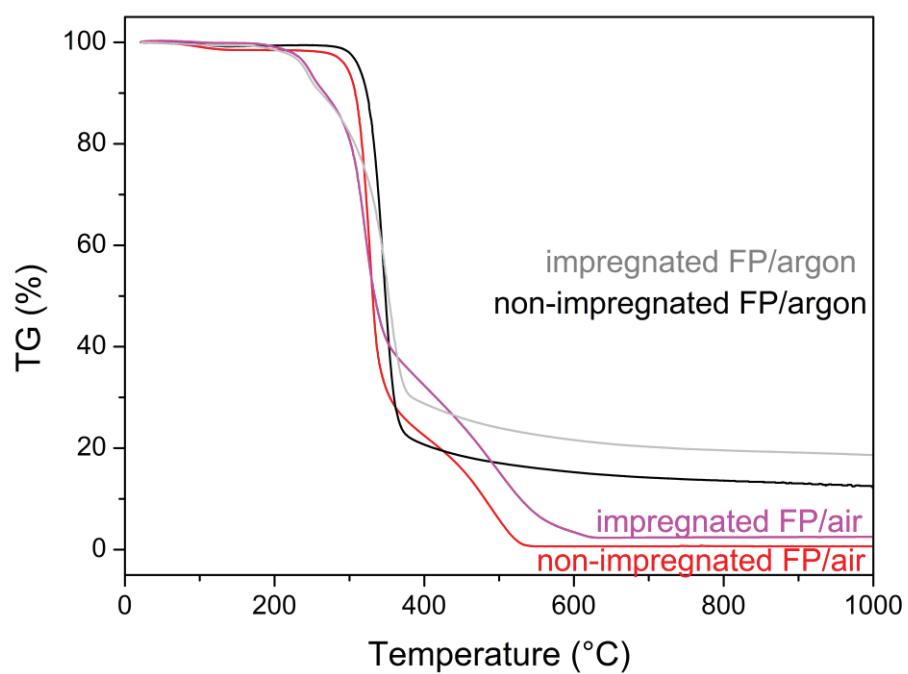


Figure SI 2: TGA analyses of FP in air and argon and of urea-impregnated FP in air and argon

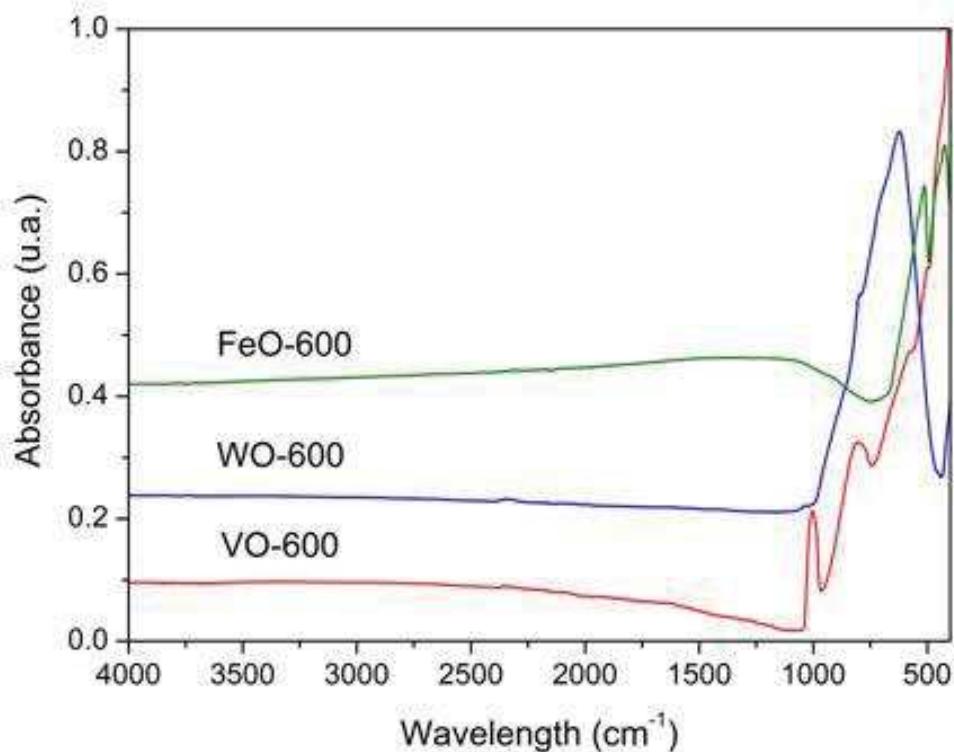


Figure SI 3: FTIR analysis of VO-600, FeO-600 and WO-600

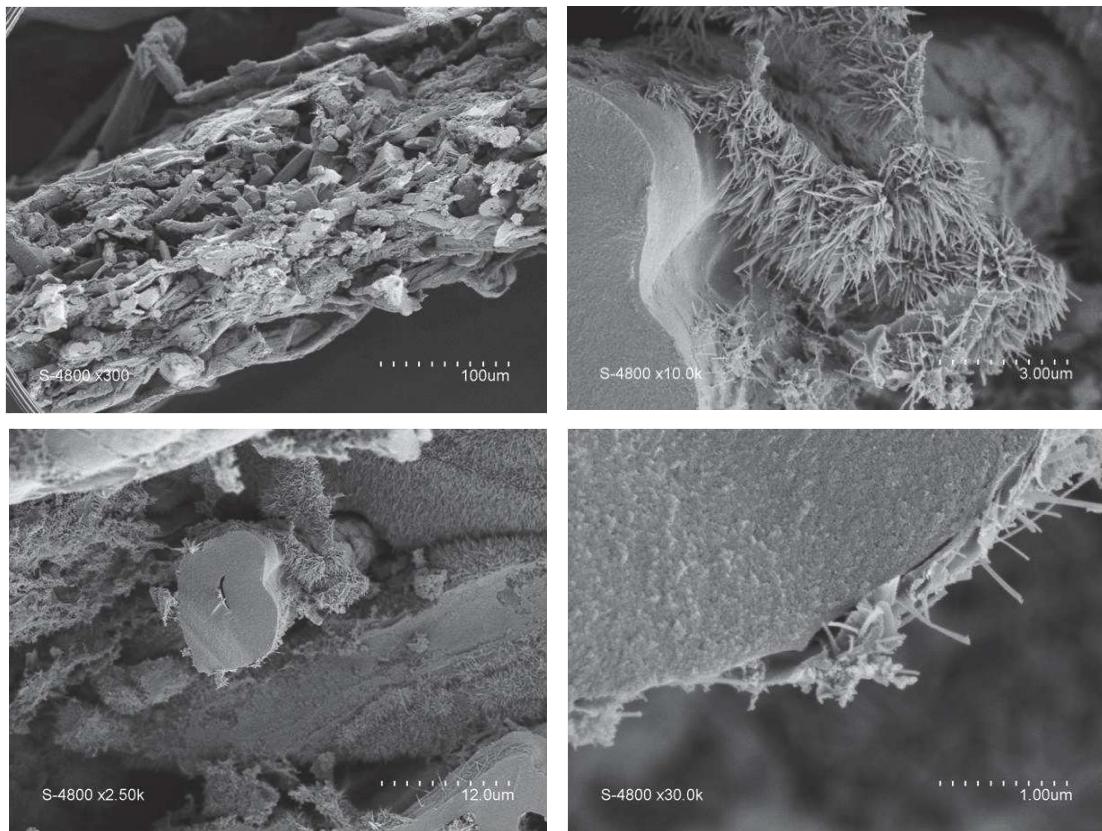


Figure SI 4: Additional SEM analysis of VO/C-600

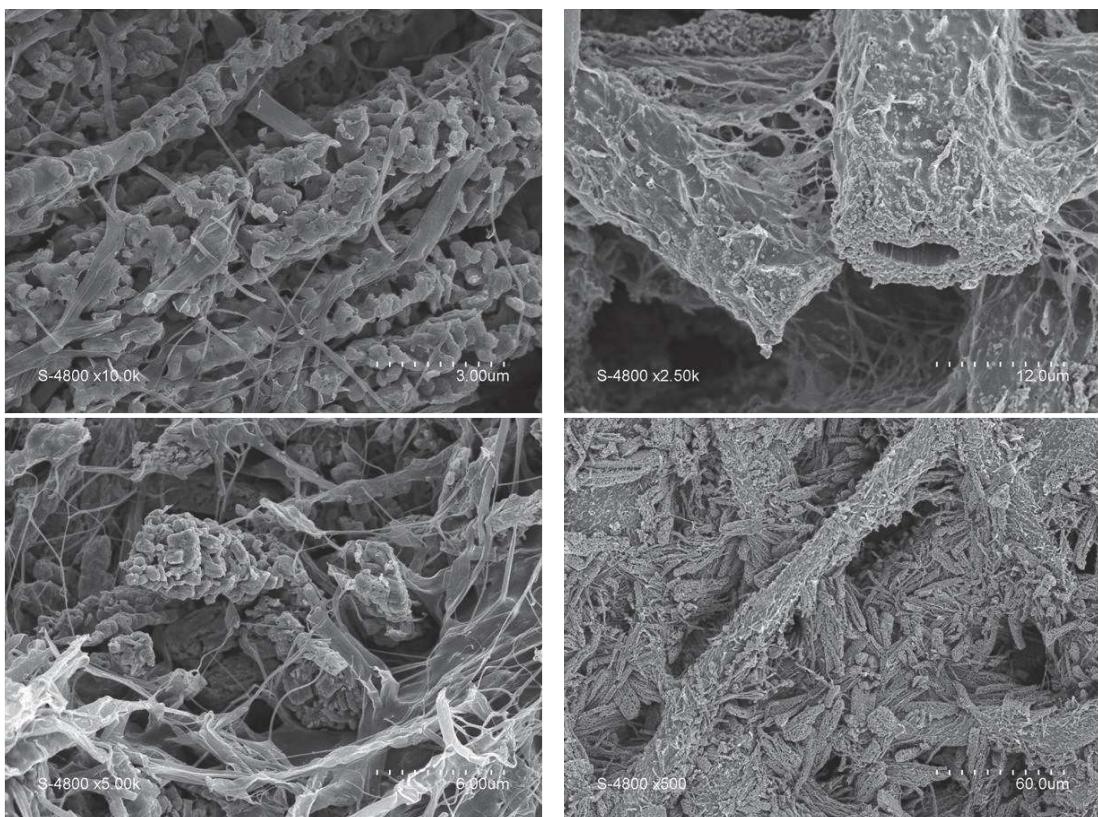


Figure SI 5: Additional SEM analysis of FeO/C-600

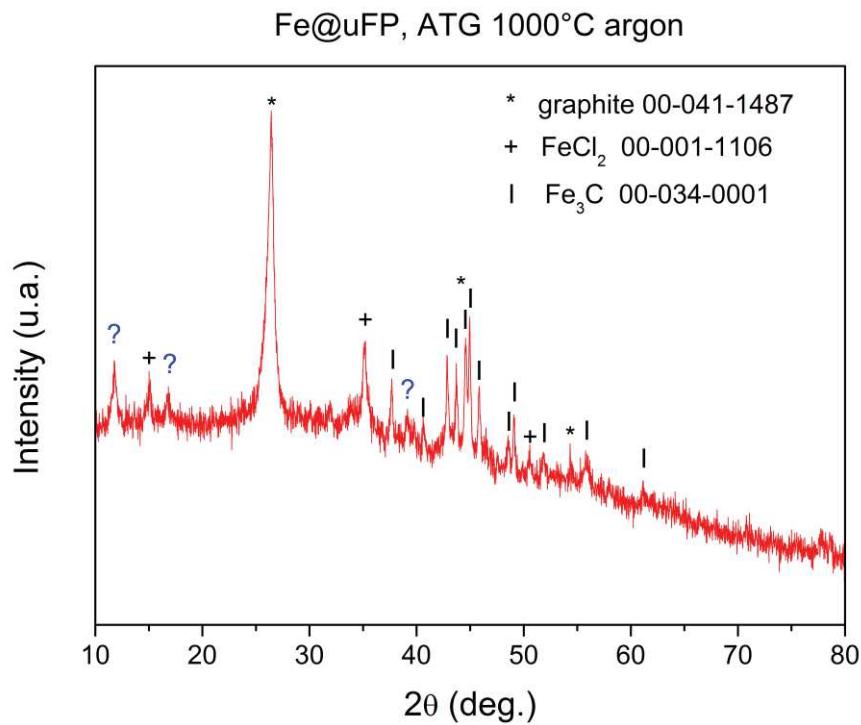


Figure SI 6: X-ray diffraction pattern of powder Fe/C obtain at 1000°C under argon

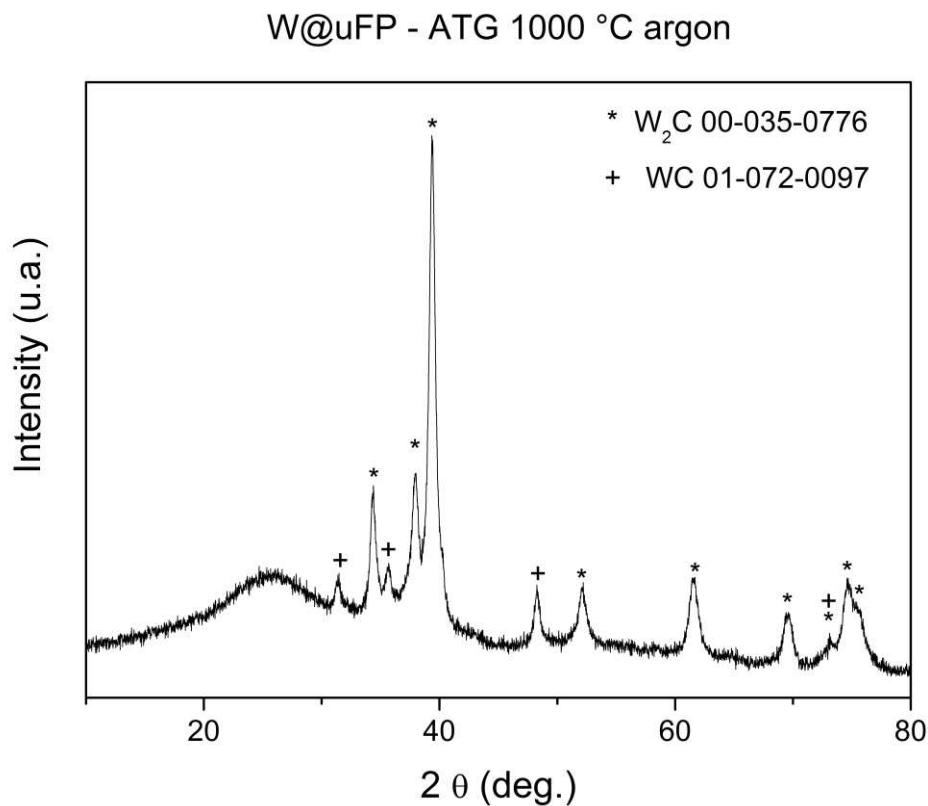


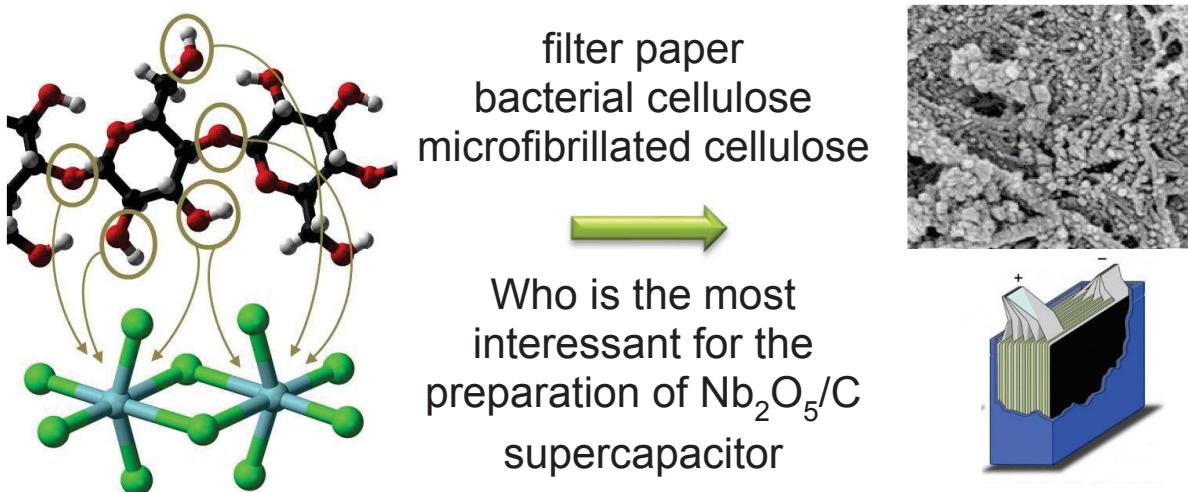
Figure SI 7: X-ray diffraction pattern of powder W/C obtain at 1000°C under argon



#### IV.3 – Fibrous bark/core Nb<sub>2</sub>O<sub>5</sub>/C composites by reductive mineralization using filter paper, microfibrillated and bacterial celluloses: comparison and application in hybrid supercapacitors.

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Under reporting



#### **Abstract**

New materials are required for energy storage and their elaboration from renewable biopolymer must be much more considered. Cellulose is one of the most attractive possible candidate, with a high potential due to its processability and reactivity. Both features were used in this study where cellulose is considered as an O- and a C-source for the elaboration of macro- micro- and nano-fibrous bark/core Nb<sub>2</sub>O<sub>5</sub>/C composites using either filter paper, microfibrillated or bacterial cellulose. Thanks to a new process of reductive mineralization of cellulose with Nb<sub>2</sub>Cl<sub>10</sub> in anhydrous conditions, the Nb<sub>2</sub>O<sub>5</sub>/C mass ratio can be adapted from 25 to 45% depending on the cellulosic fiber. Indeed, a difference of reactivity of cellulosic reagents toward Nb<sub>2</sub>O<sub>10</sub> is evidenced and connected to the crystallinity of the cellulose and accessible of the hydroxyl functions. The composites are characterized to show the chemical transformation of cellulose (FTIR, SS <sup>13</sup>C NMR XRPD), the assembly of the material (HRTEM, SEM), the Nb<sub>2</sub>O<sub>5</sub> polymorphs and the structure of the carbon part (XPRD, Raman, N<sub>2</sub> porosimetry). Extensive electrochemical characterizations of the C/Nb<sub>2</sub>O<sub>5</sub> composites have been performed in the 1.2-3 V vs Li<sup>+</sup>/Li potential range, using both cyclic voltammetry ranging from 0.5 to 500 mV.s<sup>-1</sup> and C-rate galvanostatic cycling from 1C to 1000C (1C

corresponding to a 100.82 mA.g<sup>-1</sup> current). High electrochemical performances are demonstrated in connection with the characteristics of the starting cellulosic reagents.

## Introduction

Energy storage materials such as battery and supercapacitor devices must now be designed at the nanoscale using green chemistry processes as much as possible.<sup>1</sup> This could also include very attractive semiconductor oxides like Nb<sub>2</sub>O<sub>5</sub> and its composites with potential electrochemistry applications, as well as in catalysis, photocatalysis, field emission, photovoltaics, photodetection, sensing and the elaboration of electrochromic materials.<sup>2-4</sup>

For energy storage, Bard et al. first demonstrated that Nb<sub>2</sub>O<sub>5</sub> exhibits lithium and proton insertion.<sup>5-6</sup> Compared to possible supercapacitor anode candidate materials, Nb<sub>2</sub>O<sub>5</sub> has a high theoretical capacity of ~200 mA h g<sup>-1</sup> (i.e. higher than Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> and TiO<sub>2</sub>, ~170 mA h g<sup>-1</sup>) which would be effective for improving the energy density. Moreover, unlike commercial Li-ion-capacitors made using graphite anodes, Nb<sub>2</sub>O<sub>5</sub>-based anodes work in a voltage range free of potential safety problems associated with electrolyte decomposition, resulting in a stable cycle life. Finally, the high-priced and inefficient prelithiation of anode materials necessary for high energy density with stable cycle performance are not required for Nb<sub>2</sub>O<sub>5</sub>-based anodes.<sup>7-10</sup> Fundamentally, the electrochemical performance is closely related to its crystal structure, which can be amorphous, pseudohexagonal (TT-), orthorhombic (T-), tetragonal (M-) or monoclinic (H-). Briefly, Nb<sub>2</sub>O<sub>5</sub> orthorhombic (T- Nb<sub>2</sub>O<sub>5</sub>) crystalline phase have been shown to perform better than pseudohexagonal (TT- Nb<sub>2</sub>O<sub>5</sub>) or amorphous phase.<sup>9-11</sup> The excellent capacity and rate performance of nanostructured T- Nb<sub>2</sub>O<sub>5</sub> have been attributed to the easy Li insertion along favored crystallographic pathways and open channels of interconnected NbO<sub>x</sub> sheets, leading to reduced energy barriers and improved local charge transfer in the structures.<sup>8-10, 12-13</sup>

The nanomorphology is the second key criterion according to Dunn et al.<sup>8, 10</sup> Like for other metal oxides, carbon has been assembled with niobium pentoxide with two aims. The first aim is to improve the poor electrical conductivity of Nb<sub>2</sub>O<sub>5</sub> ( $\pm 3 \cdot 10^{-6}$  S cm<sup>-1</sup>). This can be done by combining Nb<sub>2</sub>O<sub>5</sub> nanoparticles with conductive scaffolds of carbon nanotubes,<sup>14-16</sup> graphene,<sup>17</sup> reduced graphene oxide<sup>18</sup> or carbide-derived carbon.<sup>19-20</sup> Secondly, the sintering of Nb<sub>2</sub>O<sub>5</sub> nanoparticles is detrimental in reducing the specific surface area, which can occur during the thermal treatment that is necessary for T-Nb<sub>2</sub>O<sub>5</sub> formation (>600°C). To prevent this from occurring, a Ta-substitution was proposed to achieve a stabilized Nb<sub>2</sub>O<sub>5</sub>

polymorph.<sup>21</sup> However, wrapping nanoparticles in carbon appears to be the easiest way to prevent this phenomenon. Different approaches have been investigated to do this, such as polymer templated sol-gel processing of niobium oxide precursors in which the polymer (Igepal CO-520,<sup>22</sup> PEO-*b*-PS,<sup>23-26</sup>) is converted into carbon upon pyrolysis. In hydrothermal processes, resorcinol/formaldehyde,<sup>27</sup> sucrose<sup>28</sup> and glucose<sup>29</sup> have been used as a water soluble sources of carbon. Insoluble cellulose<sup>30-32</sup> or cellulose acetate<sup>33-34</sup> were the first sacrificial templates used to control Nb<sub>2</sub>O<sub>5</sub> particle growth. Cellulose has recently been the focus of renewed attention and, for example, insoluble nanocrystals were reported for use as a template for the development of Nb<sub>2</sub>O<sub>5</sub> composites prepared by a sol-gel route but in that case cellulose was not used a carbon-phase precursor.<sup>35</sup>

Our approach using cellulose for processing this kind of metal oxides and metal oxide/C composites is different. Recently we reported a new approach to limit solvent and reagent use, to work at low temperature while using the cheapest and greenest reagents. Here, cellulose provides the oxygen required for metal oxide formation, and serves also as a carbon precursor for the metal oxide/carbon composite, as illustrated in **Figure 1.**<sup>36-39</sup> By this inexpensive, simple and as green as possible process, we reported the mineralization of cellulose to obtain highly anisotropic morphologies like nanoplates, needles and flowers. Their formation is apparently linked to the reactivity of cellulose and similar morphology has never been reported when cellulose is combined with the sol-gel route to metal oxides. Moreover, in the case of TiO<sub>2</sub>/C, a deposit of a few nanometers of carbon on metal oxide nanoparticles was evidenced. All of these results prompted us to consider that this process could be a possible route to obtain Nb<sub>2</sub>O<sub>5</sub>/carbon nanocomposites.

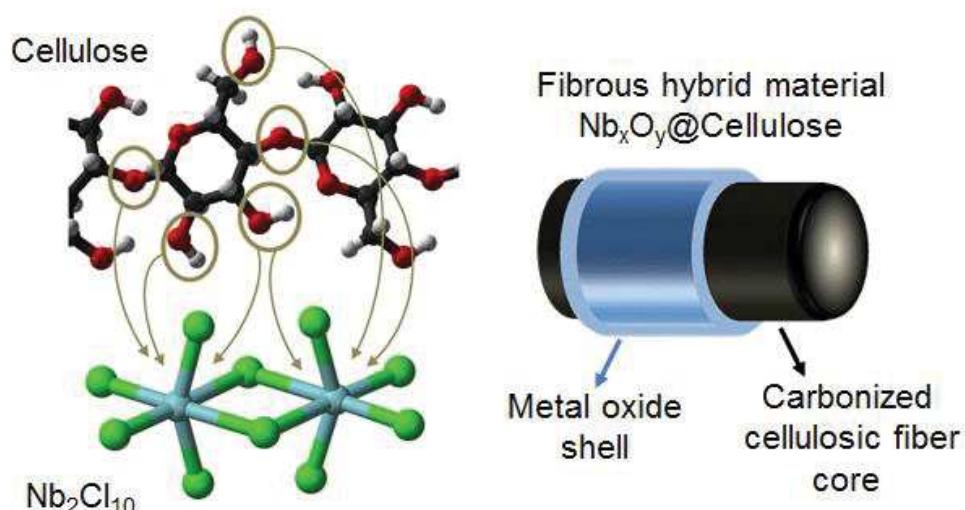


Figure 1. Illustration of the general concept of the cellulose mineralization process using niobium chloride in anhydrous conditions.

We thought it would be interesting to explore the possibility of preparing  $\text{Nb}_2\text{O}_5$  and especially  $\text{Nb}_2\text{O}_5/\text{C}$  nanocomposites by this route, while testing the effect of the cellulose morphology: large micrometric fibers of filter paper (FP), sub-micrometric fibers of micro-fibrillated cellulose (MFC) and nanometric fibers of bacterial cellulose (BC), as shown in Figure 2, which summarizes the overall approach.

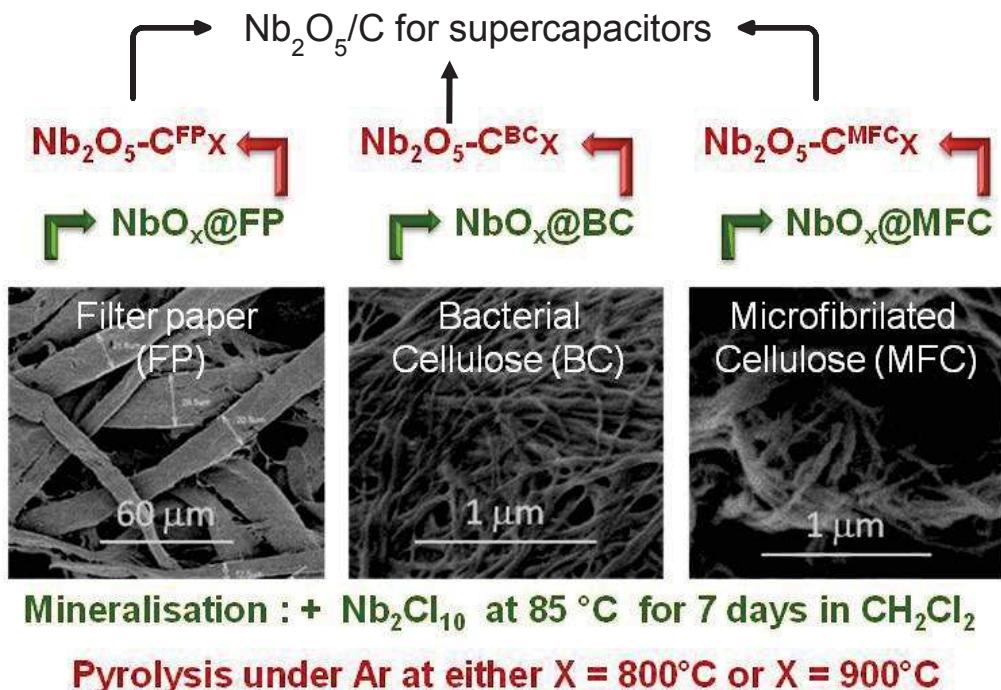


Figure 2. Material, processing conditions and nomenclature of the samples

## Results and discussion

**Mineralization of Cellulosic support by  $\text{Nb}_2\text{Cl}_{10}$  in anhydrous conditions.** Niobium(V) pentachloride was reacted with a 20% molar excess of insoluble cellulose in dichloromethane; either FP, BC and MCF, the latter being previously dried at  $80^\circ\text{C}$  to limit the amount of adsorbed water content to  $\approx 2\%$ . Otherwise, the reaction is performed in strictly anhydrous conditions by direct and simple mixing in dichloromethane for 7 days at  $85^\circ\text{C}$ . The recovered hybrid materials, either  $\text{NbO}_x@\text{FP}$ ,  $\text{NbO}_x@\text{BC}$  and  $\text{NbO}_x@\text{MFC}$  present shape and mechanical consistency like those of the starting cellulosic material, except the final color that was black (see Figure SI 1). For comparison, the same reaction was also performed at  $150^\circ\text{C}$  in the case of FP; all data are reported in Figure SI 2 (sample name  $\text{NbO}_x@\text{FP}^{150}$ ) and are sometime discussed below.

Analyzed by X-ray powder diffraction (XRPD), the starting cellulosic materials are all essentially native cellulose I and displays a crystal structure with typical diffraction peaks for the plane (002) at  $2\theta = 22.6$ , (101) at  $2\theta = 14.8^\circ$  and (101) at  $2\theta = 16.3^\circ$ .<sup>40</sup> Although they are broadened, these signals are observed in the corresponding hybrid samples before any thermal treatment (Figure 3). Consequently, at 85 °C, the crystal structure of cellulose seems partially preserved. However, when the same treatment is performed at 150°C, sample NbO<sub>x</sub>@FP<sup>150</sup>, these signals are not observed at all (see Figure SI 2), suggesting a massive transformation of cellulose, a distinctive point with previously reported works using hydrolytic approach.<sup>30-31, 33-35</sup> At that point, no niobium-containing inorganic crystalline phase could be identified at this point for these samples prepared at 85°C; however, when prepared at 150°C, NbO<sub>x</sub>@FP<sup>150</sup> exhibits slight peaks at 22.6, 23.7, 25.9, 31.9 and 47.6°, corresponding to an orthorhombic Nb<sub>3</sub>O<sub>7</sub>(OH) crystalline phase (ICSD 31-0928).

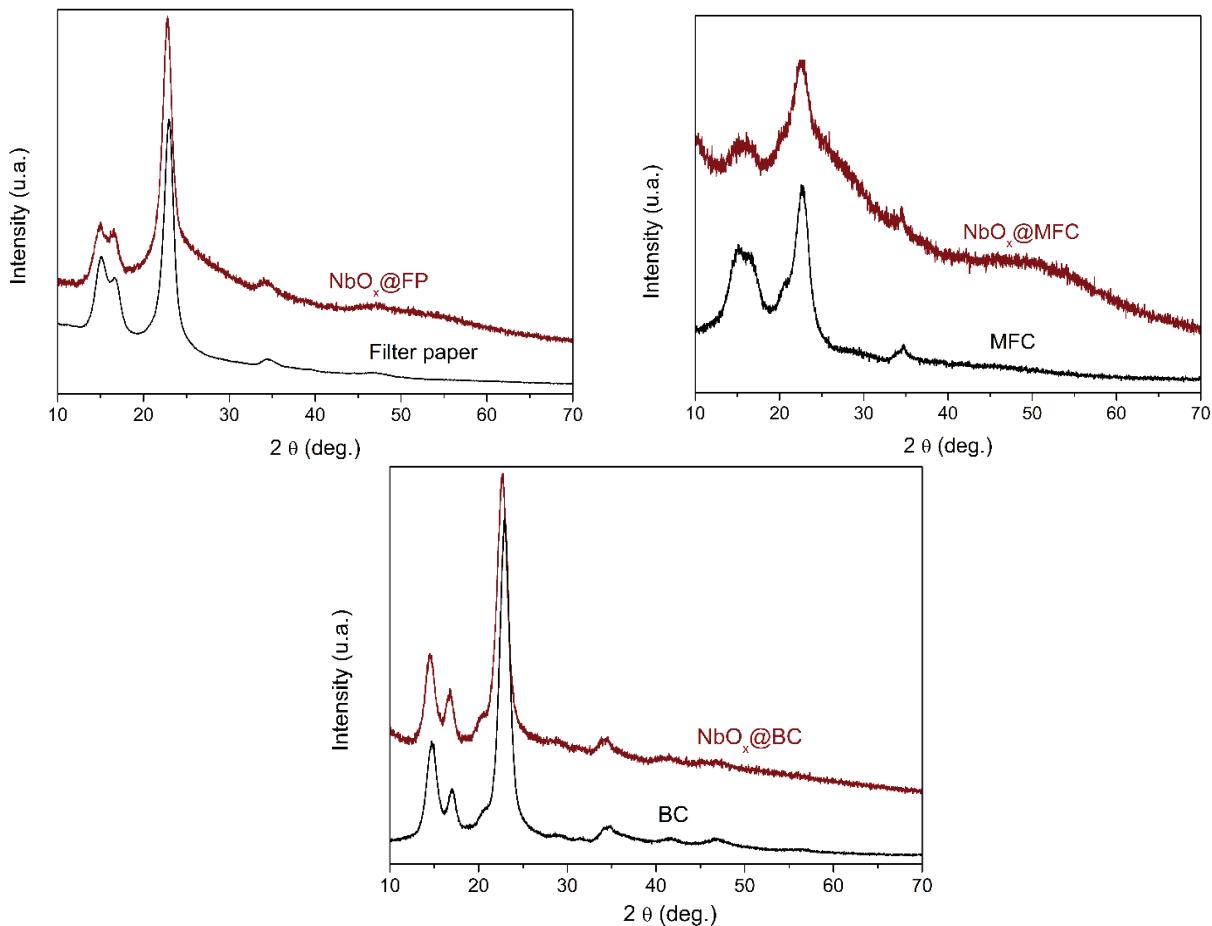


Figure 3. X-ray diffraction patterns of cellulosic material (FP, MCF and BC) and the corresponding hybrid materials resulting from the mineralization process, respectively NbO<sub>x</sub>@FP, NbO<sub>x</sub>@MCF and NbO<sub>x</sub>@BC.

An important evolution of cellulose during the process, at least at its surface, is evidenced specially for FP and MFC, by three important features observed by FTIR of the hybrids in Figure 4. Firstly, signals related to the pristine cellulose structure mostly disappeared ( $1330\text{ cm}^{-1}$  CH rocking of the ring;  $2930\text{ cm}^{-1}$  and  $2860\text{ cm}^{-1}$   $\nu_a$  CH<sub>2</sub>;  $1146\text{--}1160\text{ cm}^{-1}$   $\nu$ C-O-C & CH deformation;  $1071\text{--}1067\text{ cm}^{-1}$   $\nu$ C-O;  $1046\text{ cm}^{-1}$   $\nu$  C-O of C-OH). Secondly, an important absorption ascribed to Nb-OH and physisorbed water in the regions  $3400\text{--}31000\text{ cm}^{-1}$  &  $1600\text{--}1700\text{ cm}^{-1}$ , these groups being formed during the treatment or by hydrolysis of residual Nb-Cl by contact with air. Finally, a broad and intense absorption below  $1000\text{ cm}^{-1}$  including Nb=O stretching ( $953\text{ cm}^{-1}$   $880\text{ cm}^{-1}$ ), and Nb—O—Nb angular vibration ( $700$  and  $600\text{ cm}^{-1}$ ).<sup>41-43</sup> Nb-Cl bonds generally gives absorption at wavelength lower than  $500\text{ cm}^{-1}$ .<sup>44-45</sup> These evolutions observed for a treatment at  $85^\circ\text{C}$  are even obvious after a treatment at  $150^\circ\text{C}$  (see example FTIR spectrum of  $\text{NbO}_x@\text{FP}^{150}$  in Figure SI 2).

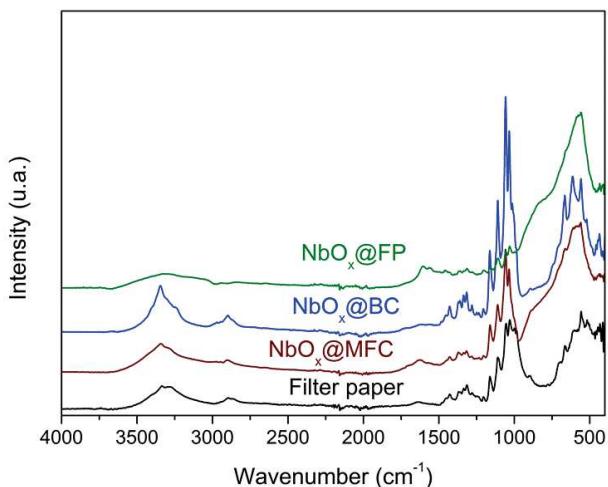


Figure 4. FTIR analyses of hybrid materials resulting from the mineralization process respectively  $\text{NbO}_x@\text{FP}$ ,  $\text{NbO}_x@\text{MCF}$ ,  $\text{NbO}_x@\text{BC}$  and the one of cellulose of FP as reference for a cellulosic material

At this stage, all samples exhibit an important fluorescence in Raman spectroscopy (Figure 5), meanwhile it is possible to detect the presence of broad signals in the region  $1300\text{ cm}^{-1}$  to  $1500\text{ cm}^{-1}$  especially for  $\text{NbO}_x@\text{FP}$ . If the mineralisation is performed at  $150^\circ\text{C}$  (see Figure SI 2) the usual band for disordered carbon material are observed for  $\text{NbO}_x@\text{FP}^{150}$ : D band  $\approx 1340\text{ cm}^{-1}$  (6-membered aromatic rings in graphitic materials related, attributed to defects in graphite) and a broad G band at  $\approx 1580\text{ cm}^{-1}$  (ascribed to the  $\text{sp}^2$  hybridized carbon network).<sup>46</sup> However, for these hybrid materials before any treatment, no second-order Raman spectrum in the  $2100\text{--}3500\text{ cm}^{-1}$  region is exploitable.

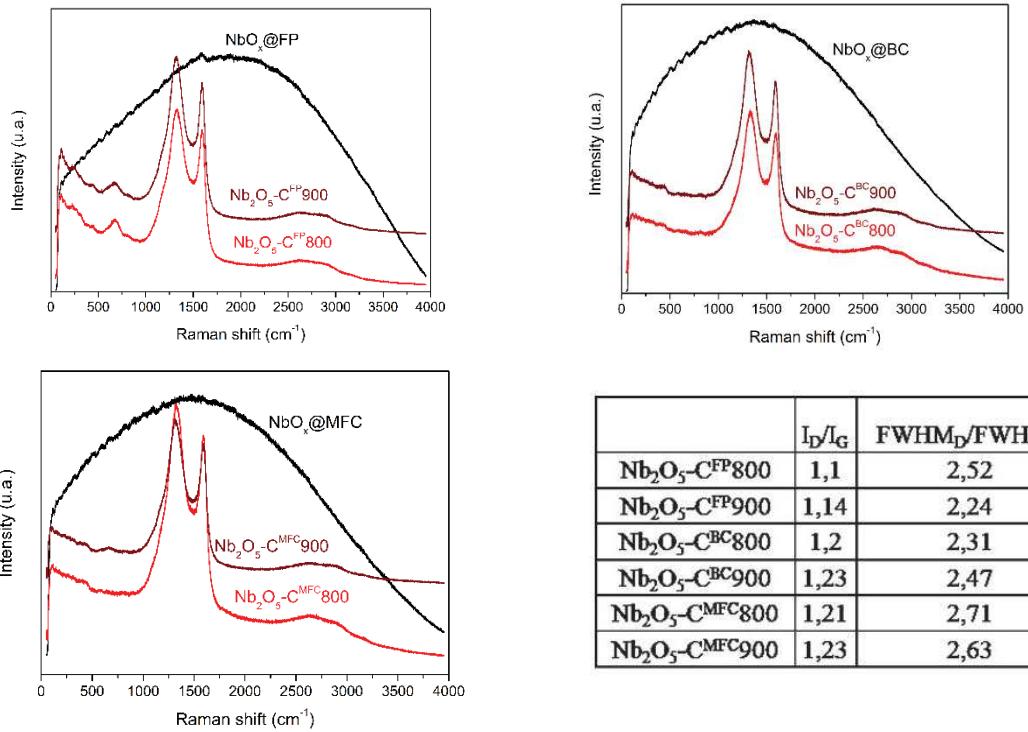


Figure 5. Raman of hybrid materials resulting from the mineralization process respectively NbO<sub>x</sub>@FP, NbO<sub>x</sub>@MCF, NbO<sub>x</sub>@BC and the I<sub>G</sub>/I<sub>D</sub> ratio and HWHM for the same sample

A last confirmation of the impact of the reaction on cellulose ultrastructure is provided by <sup>13</sup>C SS NMR of the samples, shown in Figure 6. For all the samples, the spectra displayed features typical of native cellulose that have been already abundantly described in the literature in terms of allomorphic ratio and crystallinity. Bacterial cellulose BC sample exhibit mainly I $\alpha$  phase and a high degree of crystallinity, whereas FP and MFC are predominantly I $\beta$ , with intermediate and lower crystallinity, respectively. A first conclusion is that the reaction seems to have partially preserved the integrity of the crystalline organization of the initial substrate, known to be sensitive to thermal or chemical transformation.

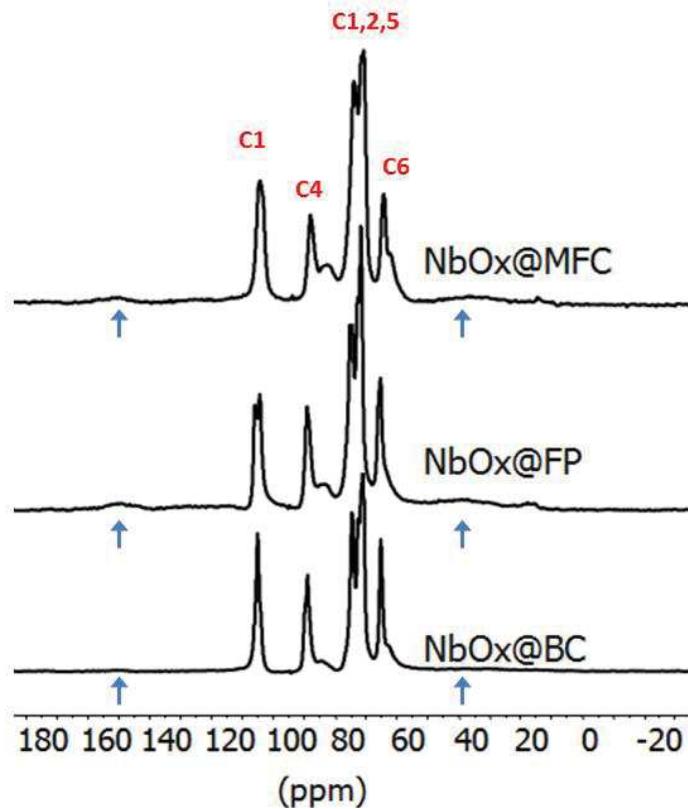


Figure 6.  $^{13}\text{C}$  SS NMR of hybrid materials resulting from the mineralization process respectively NbOx@FP, NbOx@MCF, NbOx@BC.

One interesting feature is that the two signals arising from the inner crystalline core and the disordered surface are separated in two distinct contributions for the C4 (engaged in the glycosidic bond) and C6 signals (the hydroxymethyl group pointing out of the sugar ring). To go further into details, we evaluated the degree of crystallinity of the samples by integrating the C4 signals from the crystalline (between 86 and 92 ppm) and the disordered contributions (between 80 and 86 ppm). The results give crystallinity indices of 0.57 for MFC, 0.65 for FP and 0.82 for BC. This in good agreement with the fact that the elementary nanocrystals are smaller in MFC, of intermediate size for FP and even bigger in BC, so that the surface to volume ratio is lower for bacterial cellulose.

The same calculation made on the C6 contributions can also give additional information on the amount of available hydroxyl at the surface. Strikingly, the same integration as the one performed for the C4 gave crystallinity indices of 0.64, 0.81 and 0.98 for MFC, FP and BC respectively. This last result strongly suggests that the hydroxymethyl exposed at the surface of the cellulose nanocrystals has been consumed by the reaction. This also suggests that the same reaction stopped at the surface and was unable to penetrate the cellulosic crystalline substrate as observed upon treatment with  $\text{TiCl}_4$ .<sup>36, 38, 47</sup> Such a topochemistry has already been observed in the case of TEMPO oxidation, or gas phase modification with bifunctional

moieties, for which the reaction is readily stopped at the surface of the cellulose nanocrystals<sup>48-49</sup> whereas in other situations the reagent can penetrate into the cellulose nanocrystal and destroy it.<sup>50</sup> Of lower intensity but clearly present, some very broad signals appear on both side of the spectrum, especially for MFC and FP samples. These peaks are very similar to what is obtained when cellulose is charring under harsh conditions, like elevated temperatures or in the presence of strong acids (Baccile, Rodrigues Alonso 2016). Indeed, for NbO<sub>x</sub>@FP<sup>150</sup> (see in Figure in SI2) the initial C1-C6 are no more present and signals now correspond more to furanic and arenes structures that are very similar to those obtained after dehydration of cellulose at elevated temperatures (i.e. > 300°C) with a furanic (F) to arene (A) ratio around 2,<sup>51</sup> or the char formation during the roasting process for T> 300°C.<sup>52</sup> This observation further supports that the mineralization process takes place at the expanse of the cellulose oxygen reservoir, leading to an unexpected dehydration process at low temperatures.

For NbO<sub>x</sub>@FP, NbO<sub>x</sub>@MCF, NbO<sub>x</sub>@BC integration of these contributions represents a molar fraction of 0.11, 0.08 and less than 0.02 for MFC, FP and BC respectively. This is in good agreement with the results obtained on the crystalline and disordered contributions, showing that the consumption of cellulose is directly proportional to the amount of hydroxyl exposed at the surface, and hence on the crystallinity of the sample.

By SEM analyses, images at low magnification (x50) reveals that the general appearance of the fibers-like structure of the starting cellulosic material is preserved in the three cases after mineralization (see Figure 7). However, there are noticeable differences at higher magnification (x10K and x100K) and for example NbO<sub>x</sub>@FP presents long and hollow needles (100-300 nm Ø, 2-6µm length) covering completely and densely the surface of the fibers. When performed at 150°C, sample NbO<sub>x</sub>@FP<sup>150</sup> exhibits another morphology: parquets of long filaments form anemones along the cellulose fibers (see Figure SI 3). This is not observed for NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC. For the latter, at higher magnification, the general appearance is a complete and dense covering of the fibers by nanocrystals, sometime forming aggregates on top of the fiber. We note that the process respects the fibrous structure of the cellulose in the sense that if the fibers are well separated, the mineralization leave them separated with a shell of inorganic material, but if they are aggregated, the shell produced by the mineralization is fused over them.

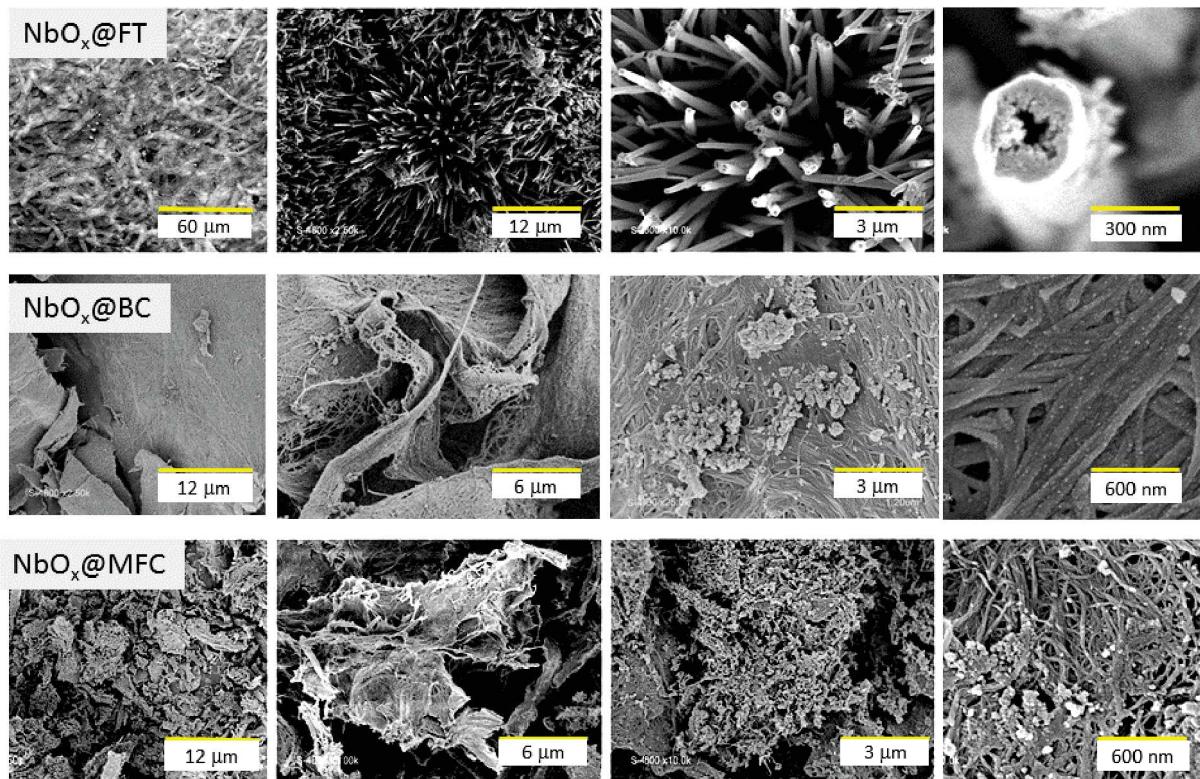


Figure 7. SEM images at different magnifications of hybrid materials resulting from the mineralization process respectively  $\text{NbO}_x@\text{FP}$ ,  $\text{NbO}_x@\text{MCF}$ ,  $\text{NbO}_x@\text{BC}$

**Preparation and structural characterization  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}\text{X}$ ,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}\text{X}$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}\text{X}$  ( $X=800$  or  $900$ )**. TGA analyses in air and in argon of the hybrids composite show weight losses starting in all cases around  $\approx 100^\circ\text{C}$ , much lower than the one of the pristine celluloses ( $180\text{-}200^\circ\text{C}$ ) (see in Figure SI 4). This can be ascribed to elimination of adsorbed volatile compound and elimination of HCl arising from condensation/hydrolysis of residual Nb-Cl and Nb-OH. In air, elimination of the carbonaceous residue by combustion is complete by  $450^\circ\text{C}$ ; yields are reported in Table 1. For a FP sample mineralized at  $150^\circ\text{C}$ , the TGA ceramic yield is higher and close to  $\approx 40\text{-}42\%$  (see TGA of  $\text{NbO}_x@\text{FP}^{150}$  in Figure SI 2). In good agreement with the SS-NMR results, the production of  $\text{NbO}_x$  is lower in the case of BC, as the number of hydroxyl groups available for the reaction is smaller for this more crystalline substrate. Indeed, these numbers are also in line with the char formation detected in the samples, BC, FP and MFC by order of importance, just as the  $\text{NbO}_x$  production.

Under argon, the weight loss due to carbonization of the cellulosic residue occurs up to  $1000^\circ\text{C}$ , although it results in higher yields. Combining these TGA yields under air and argon and assuming that carbon results

from the carbonization of cellulose, allows estimating the  $\text{Nb}_2\text{O}_5/\text{C}$  mass ratio of the different samples in table 1 and according to the calculation given in experimental part.

| Starting hybrid material   | Name of the sample<br>Yield at 1000°C under air <sup>a</sup><br>$\text{Nb}_2\text{O}_5/\text{C}$ (mass %) | Name of the sample<br>Yield at 800°C under argon <sup>a</sup><br>$\text{Nb}_2\text{O}_5/\text{C}$ (mass %) | Name of the sample<br>Yield at 900°C under argon <sup>a</sup><br>$\text{Nb}_2\text{O}_5/\text{C}$ (mass %) |
|----------------------------|---|--|--|
| <b>NbO<sub>x</sub>@FP</b>  | <b>Nb<sub>2</sub>O<sub>5</sub><sup>FP</sup></b><br>29,5 %<br>No carbon                                    | <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>800</b><br>55,4%<br>53,1/46,7                                 | <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>900</b><br>54,3%<br>54,3/45,6                                 |
|                            |   |  |  |
|                            |   |  |  |
| <b>NbO<sub>x</sub>@BC</b>  | <b>Nb<sub>2</sub>O<sub>5</sub><sup>BC</sup></b><br>19,5%<br>no carbon                                     | <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>800</b><br>29,9%<br>65,2/34,8                                 | <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>900</b><br>27,1%<br>72,0/28,0                                 |
|                            |   |  |  |
|                            |   |  |  |
| <b>NbO<sub>x</sub>@MFC</b> | <b>Nb<sub>2</sub>O<sub>5</sub><sup>MFC</sup></b><br>35,0 %<br>no carbon                                   | <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>800</b><br>48,3%<br>72,5/27,5                                | <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>900</b><br>45,8%<br>76,5/23,5                                |
|                            |   |  |  |
|                            |   |  |  |

a: determined by TGA analysis

**Table 1.** Yields of TGA under air and argon of NbO<sub>x</sub>@FP, NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC, name of the corresponding sample after thermal treatment and  $\text{Nb}_2\text{O}_5/\text{C}$  composition after TGA at 800 and 900°C.

According to these data, the cellulosic residue present in NbO<sub>x</sub>@FP leads to ~20% of C upon pyrolysis, which is twice the amount of carbon left by the pristine FP in similar conditions (~10%). This can be ascribed to the transformation of cellulose during the synthesis of the hybrid but also to a confinement of the cellulose by the metal oxide bark. Comparison of the sample shows that the proportion of carbon is the highest for samples prepared with FP (~45%) and the lowest is for samples prepared from MFC (~25%), the one for sample prepared from BC being in between around 30%. Interestingly, this process gives access to a proportion of carbon that is in-between the lowest one obtained with surfactant (Igepal® CO520 7 % of C<sup>22</sup> and PEO-PS 11% of C),<sup>23</sup> and the highest obtained with saccharides and resins (sucrose 59-87% of C<sup>28</sup> and resorcinol-formaldehyde:70-75 % of C<sup>27</sup>). We found some discrepancies between these data and those obtained by EDX analysis (see Figure SI 5), the reason being that EDX data must be considered along with the bark-core structure of the materials. Meanwhile, a mapping of the element confirms a complete and homogenous covering of C, O and Nb for all the sample, an example is given for Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>800 in Figure SI 5.

Altogether, the production of carbon in the three substrates is in line with the results shown by SS-NMR and TGA, showing a lower production of NbO<sub>x</sub> for the more crystalline substrate and higher rates for the

less crystalline, and hence more reactive substrates that exposed a higher number of hydroxyl groups. This allows to consider the tailoring of production of hybrid containing predictable amount of oxide, and hence a ratio of carbon/oxide that can be finely tuned.

Calcination in air at 1000 °C lead to crystallization and sintering resulting in submicrometric Nb<sub>2</sub>O<sub>5</sub> particles observed respectively in Nb<sub>2</sub>O<sub>5</sub><sup>FP</sup>, Nb<sub>2</sub>O<sub>5</sub><sup>BC</sup> and Nb<sub>2</sub>O<sub>5</sub><sup>MFC</sup> (see Figure SI 6), forming a more or less dense network, meanwhile it is still possible to detect the frame imposed by the cellulosic template. In the case of Nb<sub>2</sub>O<sub>5</sub><sup>FP</sup> and like for similar samples, two Nb<sub>2</sub>O<sub>5</sub> crystalline phases are present: a pseudo-hexagonal TT-Nb<sub>2</sub>O<sub>5</sub> (ICSD 28-0317) and a monoclinic M-Nb<sub>2</sub>O<sub>5</sub> phase (ICSD 30-0872) (see Figure SI 7).

Pyrolysis at 800°C and 900°C were performed to produce fibrous Nb<sub>2</sub>O<sub>5</sub>-C composites respectively Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>X, Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>X and Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>X (X = 800 or 900). These temperatures were chosen after an *in-situ* X-ray powder diffraction measurement from ambient temperature to 1100°C. SEM images at low magnification (x10K) evidence a partial preservation of the fibrous structure of the starting cellulosic support as shown in Figure 8. The same pictures show Nb<sub>2</sub>O<sub>5</sub> particles assembled at the surface of the carbon left by the carbonization of the cellulosic residue, this being even clearer at higher magnification x50K in Figure 9. For sample Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>X and Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>X, the assembly of Nb<sub>2</sub>O<sub>5</sub> nanocrystals and carbonaceous network is homogeneous at the nanoscale. For the sample prepared with FP, the situation is more contrasted, big pieces of carbonaceous residue being mixed with micro and sub-micrometer particles of niobium oxide.

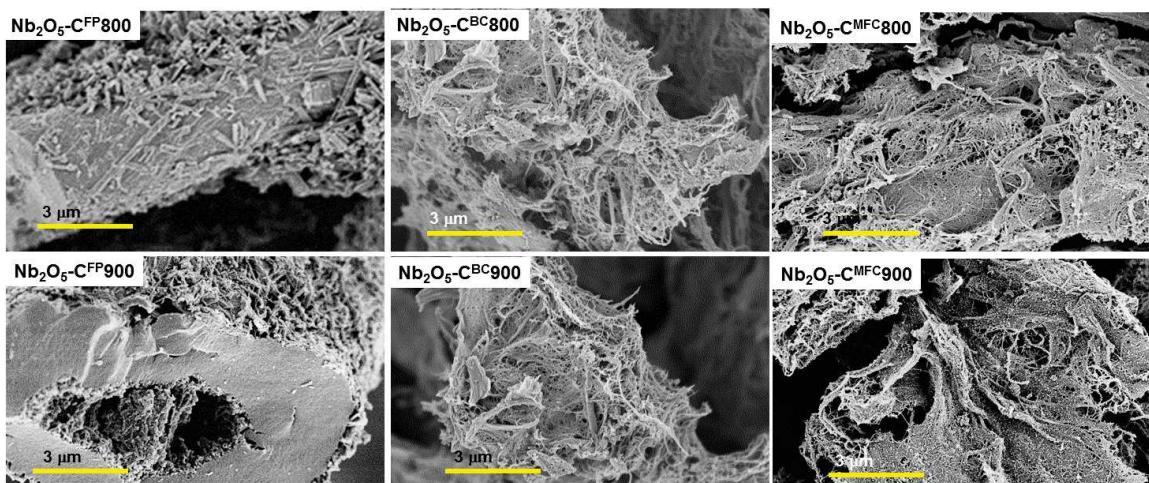


Figure 8. SEM images at magnifications x10K of Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>X, Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>X and Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>X (X = 800 or 900) resulting from the pyrolysis under argon of NbO<sub>x</sub>@FP, NbO<sub>x</sub>@MCF, NbO<sub>x</sub>@BC.

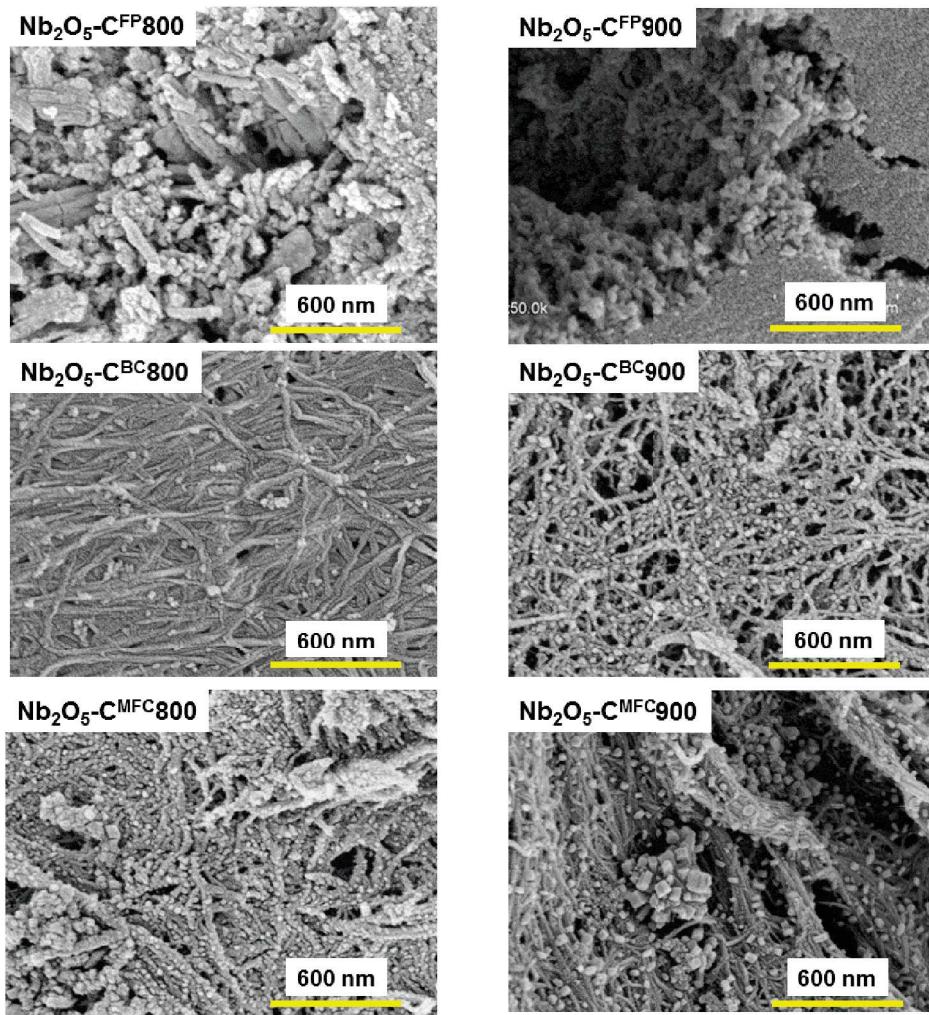


Figure 9. SEM images magnifications x50K of  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}\text{X}$ ,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}\text{X}$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}\text{X}$  ( $\text{X} = 800$  or  $900$ ) resulting from the pyrolysis under argon of  $\text{NbO}_x@\text{FP}$ ,  $\text{NbO}_x@\text{MCF}$ ,  $\text{NbO}_x@\text{BC}$ .

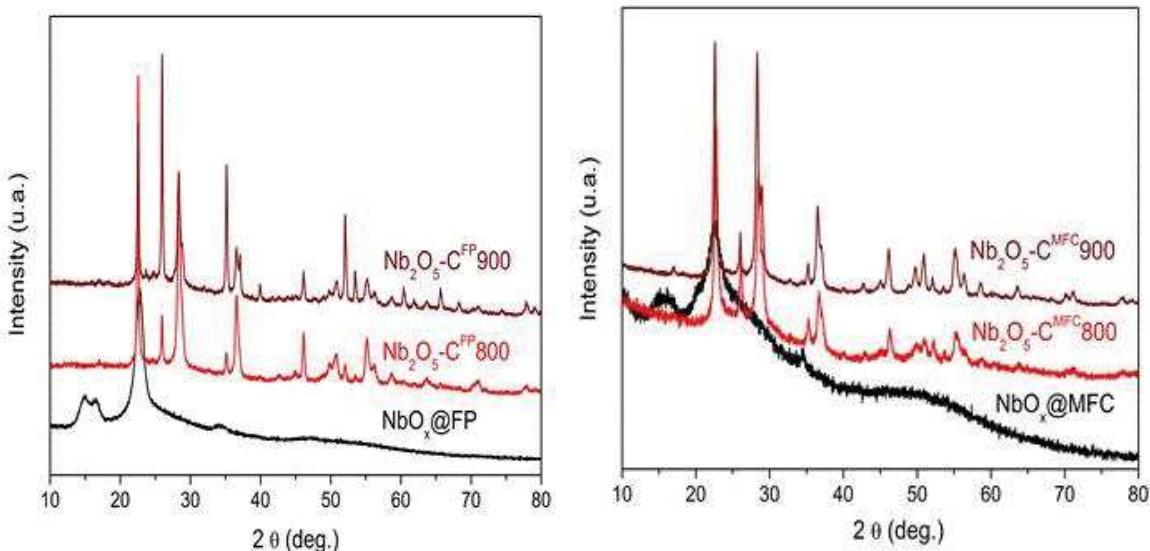
The Raman spectra of all the samples shown in Figure 5 exhibit the distinctive D band  $\approx 1340 \text{ cm}^{-1}$  (6-membered aromatic rings in graphitic materials related, attributed to defects in graphite) and G band at  $\approx 1580 \text{ cm}^{-1}$  (ascribed to the  $\text{sp}^2$  hybridized carbon network) of carbon.<sup>46</sup> All the signals are very broad and probably include other contributions like  $\text{D}_2 \approx 1615 \text{ cm}^{-1}$  (edges of graphitic crystallites),  $\text{D}_1 \approx 1360 \text{ cm}^{-1}$  (in-plane breathing vibrations of  $\text{sp}^2$ -bonded carbon within structural defects),  $\text{D}_3 \approx 1500\text{--}1550 \text{ cm}^{-1}$  (amorphous carbon phase) and  $\text{D}_4 \approx 1200 \text{ cm}^{-1}$  ( $\text{sp}^2\text{-sp}^3$  bonds).<sup>46, 53</sup> They are disordered carbon for which an estimation of the size of the graphic domain can be proposed on the basis of the  $I_G/I_D$  ratio, they are very close in all the case, in the range 1,1 – 13 nm.

An *in situ* X-ray powder diffraction measurement performed between ambient temperature and 1100°C of  $\text{NbO}_x@\text{FP}$  (see Figure SI 8) reveals that a heating up to 800°C and 900°C appears as the optimal conditions

to obtain T-Nb<sub>2</sub>O<sub>5</sub> without large crystallites. From the collected data, no hexagonal phase was detected and only orthorhombic phase was present. Additionally, a temperature of 700°C was found too low for the crystallization of the orthorhombic phase. XRPD measurements after bulk pyrolysis (Figure 10) reveal the evolution of the crystallinity of the samples during the thermal treatments, and show some similarities between the samples. Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>800 presents a mix of two phases: an orthorhombic T-Nb<sub>2</sub>O<sub>5</sub> (ICSD 30-0873,  $2\theta = 22.6, 28.4, 36.5, 46.1$  and  $55.2^\circ$ ) and a tetragonal NbO<sub>2</sub> (ICSD 76-0682,  $2\theta = 26.0, 35.2, 37.1, 40.0$  and  $52.0^\circ$ ), no quantitative ratio is proposed due to overlapping of signals. The T-Nb<sub>2</sub>O<sub>5</sub> phase seems to be the most present, even if it has smaller crystallites (30 nm) than the NbO<sub>2</sub> one (58 nm). The difference with Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>900 is representative of the behavior of the three types of materials: this second sample presents a slight change on the crystallite size (38 nm for T-Nb<sub>2</sub>O<sub>5</sub> and 56 nm for NbO<sub>2</sub>) and an increase of the relative content of the NbO<sub>2</sub> phase. There are also some traces of a monoclinic Nb<sub>12</sub>O<sub>29</sub>, at 23.7 and  $24.8^\circ$ .

Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>800 shows a lower signal to noise ratio possibly due to lower crystallization. The only crystalline phase detected is T-Nb<sub>2</sub>O<sub>5</sub>, which presents a crystallite size of 20 nm. The NbO<sub>2</sub> phase appears only in the Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>900, but with a relative content close to those of T-Nb<sub>2</sub>O<sub>5</sub>. Like for Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>900, the crystallite size of NbO<sub>2</sub> (35 nm) is larger than for T-Nb<sub>2</sub>O<sub>5</sub> (19 nm).

Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>800 presents also a mix of NbO<sub>2</sub> and Nb<sub>2</sub>O<sub>5</sub>, the latter being in major proportion. The crystallite sizes of the two phases are this time very close (25 and 24 nm, respectively). Surprisingly, the increase of relative content of the NbO<sub>2</sub> phase in Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>900 is less intense than for the other materials; Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>900 is more like Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>800, with T-Nb<sub>2</sub>O<sub>5</sub> in majority compared to NbO<sub>2</sub>, and close crystallite sizes (32 and 38 nm, respectively).



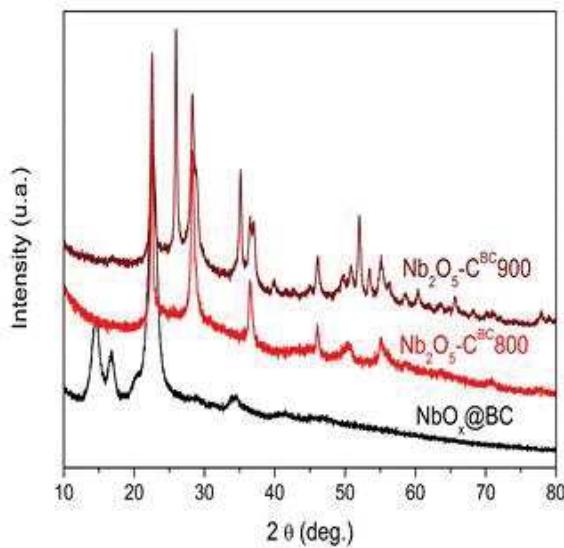


Figure 10. X-ray diffraction patterns of  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}\text{X}$ ,  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}\text{X}$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}\text{X}$  ( $\text{X} = 800$  or  $900$ ) resulting from the pyrolysis under argon of  $\text{NbO}_x@\text{FP}$ ,  $\text{NbO}_x@\text{MCF}$ ,  $\text{NbO}_x@\text{BC}$ .

According to textural data in Table 2 deduced from the nitrogen adsorption-desorption isotherms (see Figure SI9), samples before any thermal treatment exhibit low specific surface area and low porous volume. For BC and MFC, the values are especially lower compared to those of the starting materials and is probably the result of the  $\text{NbO}_x$  bark that covers and aggregates the micro- and nano-fibers. Inversely, for FP, the formation of nano- to micro- inorganic needles leads to an increase of the BET surface. The isotherms are intermediate between Type II (interparticle porosity) and type IV (mesoporous solids) of IUPAC classification. This is also the case for samples pyrolysed at  $800$  °C that are reported because they present the best electrochemical performances, as we will see below. For such, a high specific surface area and porous volume are determined and result from the pyrolytic decomposition of the cellulosic part. A broad pore size distribution is observed  $\text{Nb}_2\text{O}_5\text{-C}^{\text{FP}}800$  and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{BC}}800$ , extending from micro- to mesopores (up to 50nm) and even macropores for and  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}\text{X}$ . The sharp component at ca. 3-4 nm is an artefact related to the instability of the meniscus at  $P/P_0$  lower than 0.42,<sup>54</sup> and simply shows the presence of small mesopores (<4 nm). MCF is the cellulosic reagent that lead to the most porous material, a feature that is important to keep in mind when looking at the electrochemical properties reported below.

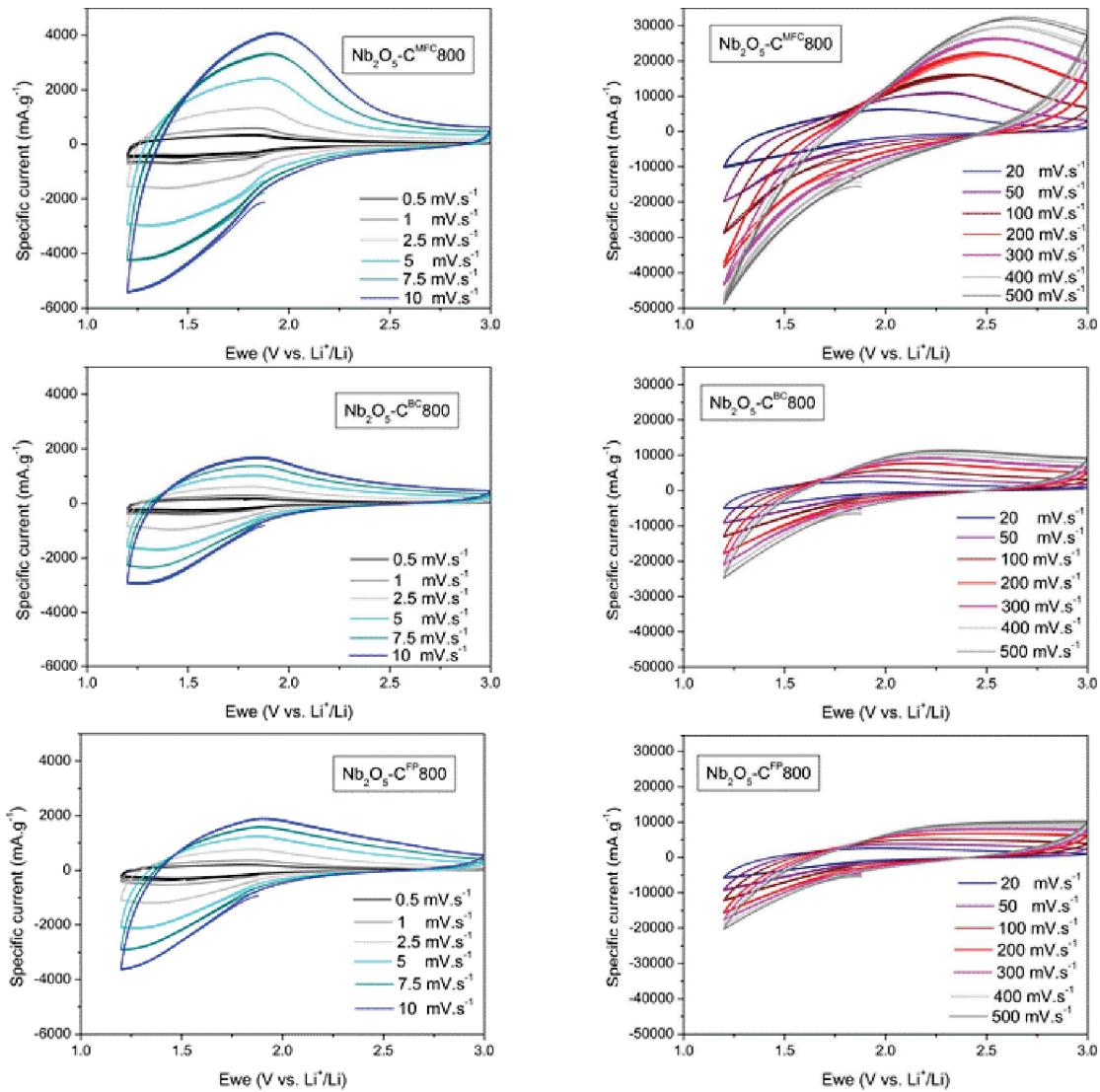
|   | $S_{BET}^a$<br>( $m^2 \cdot g^{-1}$ ) | $S_{Micro}$<br>( $m^2 \cdot g^{-1}$ ) | $S_{Meso}$<br>( $m^2 \cdot g^{-1}$ ) | $V_p^b$<br>( $cm^3 \cdot g^{-1}$ ) | $D_p$<br>(nm) |
|---|---------------------------------------|---------------------------------------|--------------------------------------|------------------------------------|---------------|
| <b>NbO<sub>x</sub>@FP</b>                             | 48,9                                  | 4,2                                   | 44,7                                 | 0,1764                             | 9,9           |
| <b>NbO<sub>x</sub>@BC</b>                             | 49,3                                  | 3,9                                   | 45,4                                 | 0,1902                             | 10,1          |
| <b>NbO<sub>x</sub>@MFC</b>                            | 69,4                                  | 6,8                                   | 62,6                                 | 0,3324                             | 15,8          |
| <b>Nb<sub>2</sub>O<sub>5</sub>-C800<sup>FP</sup></b>  | 192,6                                 | 49,5                                  | 143,1                                | 0,3902                             | 6,5           |
| <b>Nb<sub>2</sub>O<sub>5</sub>-C800<sup>BC</sup></b>  | 205,7                                 | 55,4                                  | 150,3                                | 0,3627                             | 6,8           |
| <b>Nb<sub>2</sub>O<sub>5</sub>-C800<sup>MFC</sup></b> | 372,3                                 | 258,5                                 | 113,8                                | 0,3592                             | 7,5           |

**Table 2.** Summary of textural data obtained from N<sub>2</sub> porosimetry for sample before and after thermal treatment; <sup>a</sup>specific surface area, <sup>b</sup>total pore volume; <sup>c</sup>BJH average pore diameter calculated from the desorption branch;

To summarize on the chemistry involved in the preparation of the materials, three major points appear. First, the chemistry behind this mineralization of cellulose when exposed to Nb<sub>2</sub>Cl<sub>10</sub> in anhydrous condition is clearly different from all previously reported preparation of Nb<sub>2</sub>O<sub>5</sub>/C composites, even using cellulose nanocrystals of saccharide like sucrose or glucose. All the spectroscopic data confirm a significant modification of the cellulose composition and structure at least on its surface. Niobium chloride can react with residual water estimated to ±2 to 3% by TGA but this is not sufficient to explain the formation of 20% to 40% of the metal oxide. The other O-source of the system is cellulose that can dehydrate leading to a partially carbonaceous residue prior any thermal treatment.<sup>39</sup> In this case, the comparison of FP, BC and MFC points out that the crystallinity of the cellulose is a key parameter in its reactivity with the metal chloride. Besides the chemistry of these transformations, the morphology of the oxide is also a very intriguing phenomenon for which there is no clear hypothesis at present.

**Electrochemical characterization of the Nb<sub>2</sub>O<sub>5</sub>/C composites.** A brief screening of the samples shows that the sample prepared by pyrolysis at 900°C displays lower performances than the one obtained at 800°C. This is in agreement with the phase composition of these materials and the higher content of hexagonal Nb<sub>2</sub>O<sub>5</sub> as shown in previous publications. Therefore, we present here only the electrochemical characterization of the sample prepared at 800°C. Nb<sub>2</sub>O<sub>5</sub>-C800<sup>FP</sup>, Nb<sub>2</sub>O<sub>5</sub>-C800<sup>BC</sup> and Nb<sub>2</sub>O<sub>5</sub>-C800<sup>MFC</sup> were tested as electrodes of Li-ion batteries using a Swagelok® three-electrode half-cell. For every composite,

two different experiments were successively performed. Cyclic voltammograms of  $\text{Nb}_2\text{O}_5$ -C800<sup>XX</sup>/Li cells at various scan rates (from 0.5 to 500 mV.s<sup>-1</sup>), shown in Figure 11, are the results of the first experiment. Both anodic and cathodic peaks are broad, but they flatten down as the sweep rate decreases. This is an expected behavior for this kind of intercalation materials. At high scan rate, diffusion of lithium ion is rate-limiting whereas at low scan rate, the current is surface controlled (*i.e.* no more diffusion limitation). However, Dunn et al. have already extensively studied electrochemical kinetics of  $\text{Nb}_2\text{O}_5$  and it is not the purpose of this paper to re-demonstrate all their findings. What is important herein is the comparison and the discussion about the three new synthesis methods that allowed preparing  $\text{Nb}_2\text{O}_5$ /carbon composites. The comparison of the three samples shows an important difference between the specific currents measured on the different materials.  $\text{Nb}_2\text{O}_5$ -C800<sup>MFC</sup> presents higher specific currents than the two others do. Moreover, if the peak shift is continuous for  $\text{Nb}_2\text{O}_5$ -C800<sup>MFC</sup>, we can see that, for the two other samples, the voltammogramms with a sweep rate higher than 200 mV.s<sup>-1</sup> are almost stackable, with a disappearance of the two peaks. It suggests that, beyond 200 mV.s<sup>-1</sup>, the sweep rate is too fast for exchanging  $\text{Li}^+$  between the electrodes on the investigated potential window.

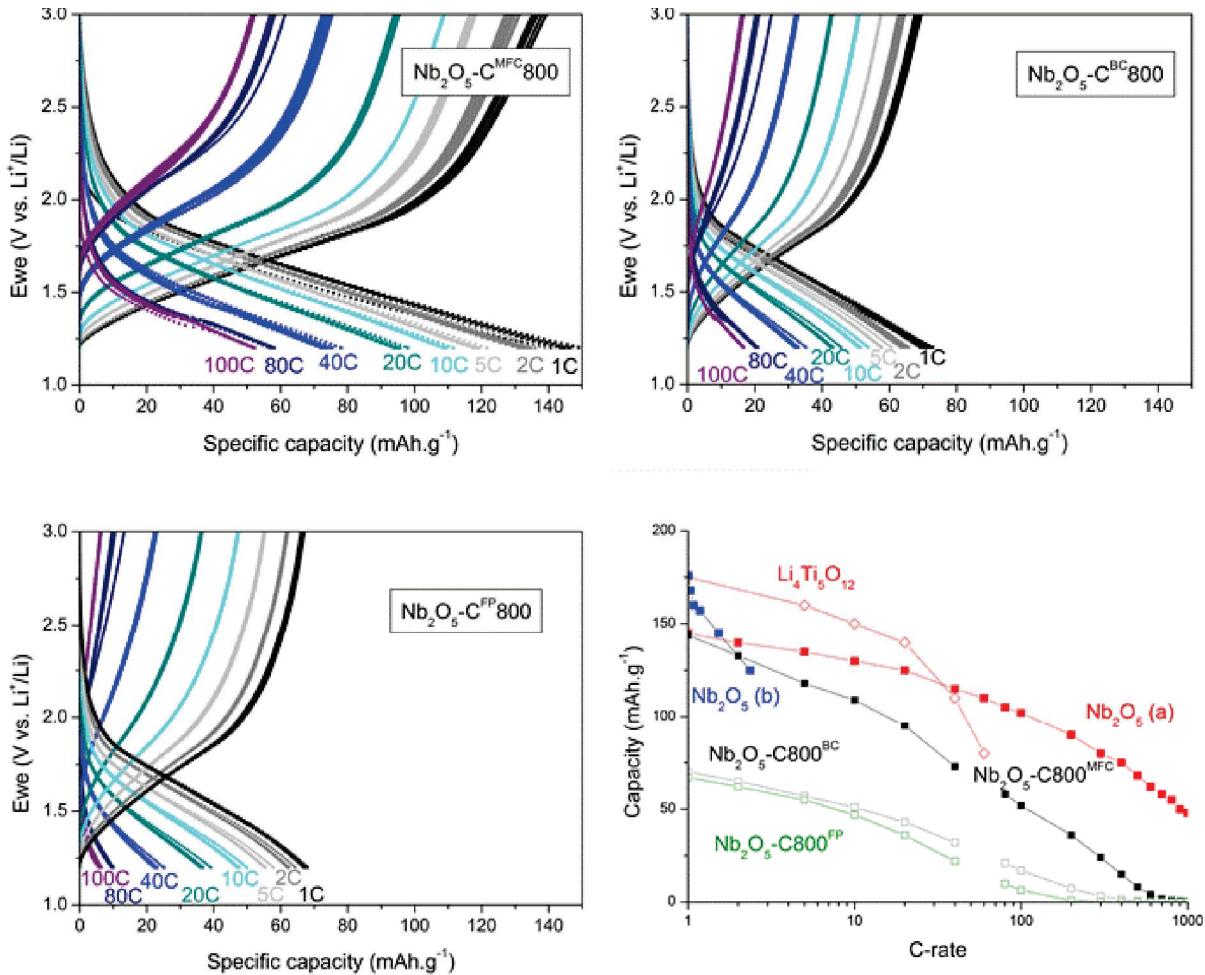


**Figure 11.** Cyclic voltammograms of a,b) Nb<sub>2</sub>O<sub>5</sub>-C800<sup>MFC</sup>, c,d) Nb<sub>2</sub>O<sub>5</sub>-C800<sup>BC</sup> and e,f) Nb<sub>2</sub>O<sub>5</sub>-C800<sup>FP</sup>

After performing cyclic voltammetry, C-rate galvanostatic cycling was performed on each sample. Figure 2a-c present the voltage profiles obtained upon charge/discharge at rates ranging from 1 to 100 C (where C is set at 100.83 mAh.g<sup>-1</sup> for 1 e<sup>-</sup>/h process), 10 cycles were recorded for each C-rate and are all shown. As we can see, the ten cycles are almost stackable, particularly at high rates. After 20 cycles, each electrode reaches a coulombic efficiency higher than 99 %. Similarly, to the cyclic voltammetry, an important difference of performances can be observed between Nb<sub>2</sub>O<sub>5</sub>-C800<sup>MFC</sup> and the two other samples; Nb<sub>2</sub>O<sub>5</sub>-C800<sup>MFC</sup> presents a reversible capacity of ~ 150 mAh.g<sup>-1</sup>, whereas Nb<sub>2</sub>O<sub>5</sub>-C800<sup>FP</sup> and Nb<sub>2</sub>O<sub>5</sub>-C800<sup>BC</sup> ones are close to 70 mAh.g<sup>-1</sup>. Another important feature is that the galvanostatic curves do not present any

insertion plateau, which is characteristic of nanosized insertion materials. In such systems, the specific area of the material is expected to have a great influence.

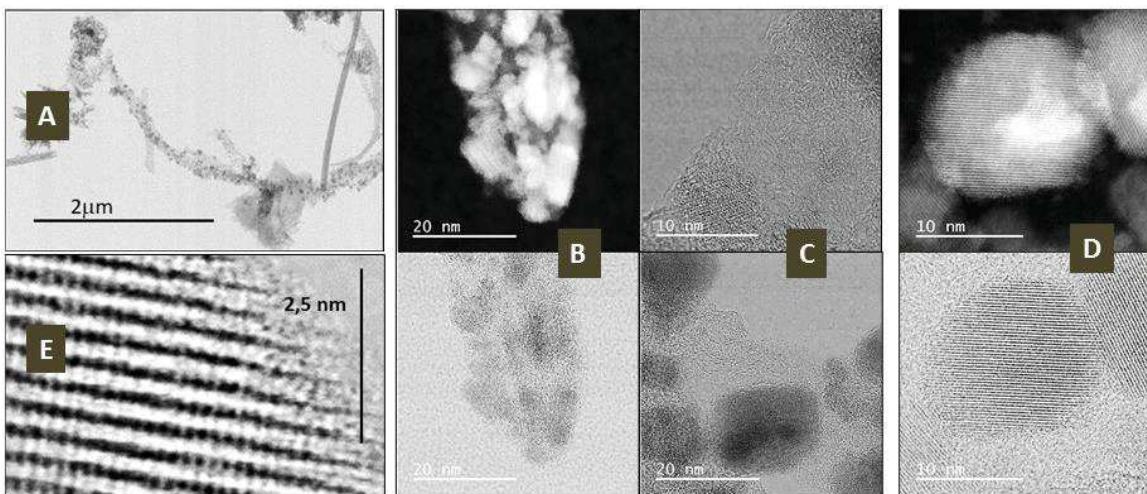
The specific capacity provided by  $\text{Nb}_2\text{O}_5\text{-C800}^{\text{FP}}$ ,  $\text{Nb}_2\text{O}_5\text{-C800}^{\text{BC}}$  and  $\text{Nb}_2\text{O}_5\text{-C800}^{\text{MFC}}$  according to the C-rate is presented in Figure 12. For clarity, each dot represents the capacity of the tenth discharge for the considered C-rate. As a comparison, values presented by Dunn et al.<sup>9</sup> are also given. First, the capacity decrease of our materials is more important than those reported by Dunn et al., what could be attributed to the presence of the less favorable  $\text{NbO}_2$  phase in our samples. Another notable feature is the difference of capacity between  $\text{Nb}_2\text{O}_5\text{-C800}^{\text{MFC}}$  and the two other samples. This difference is consistent to the gap of specific area between the samples. For a charging/discharging rate of 1C, the better material,  $\text{Nb}_2\text{O}_5\text{-C800}^{\text{MFC}}$ , exhibits a capacity of  $\sim 150 \text{ mAh.g}^{-1}$  and a specific area of  $370 \text{ m}^2.\text{g}^{-1}$ , to compare with the  $\sim 70 \text{ mAh.g}^{-1}$  and  $200 \text{ m}^2.\text{g}^{-1}$  of  $\text{Nb}_2\text{O}_5\text{-C800}^{\text{BC}}$ , the two samples having similar  $\text{Nb}_2\text{O}_5/\text{C}$  ratios (respectively 75 and 70 % of  $\text{Nb}_2\text{O}_5$ , in mass). The capacity of  $\text{Nb}_2\text{O}_5\text{-C800}^{\text{FP}}$  is  $\sim 67 \text{ mAh.g}^{-1}$ , attributed to the combination of a lower content in  $\text{Nb}_2\text{O}_5$  (55 %) and a higher specific area ( $245 \text{ m}^2.\text{g}^{-1}$ ) than  $\text{Nb}_2\text{O}_5\text{-C800}^{\text{BC}}$ . These results unambiguously demonstrate that our three composites possess the same intrinsic storage performances. However, as a very interesting finding, the  $\text{Nb}_2\text{O}_5\text{-C800}^{\text{MFC}}$  synthesis allowed to double the electrochemical surface of  $\text{Nb}_2\text{O}_5\text{-C}$  materials and thus to double their capacity.



**Figure 12.** C-rates of  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{MFC}}$ ,  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{BC}}$  and  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{FP}}$ ; comparison of the rate capacity of  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{MFC}}$ ,  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{BC}}$ ,  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{FP}}$  with  $T\text{-Nb}_2\text{O}_5$ , at various C-rates a/from Ref.<sup>9</sup> b/ from ref.<sup>55</sup> and c/ from ref.<sup>35</sup>

An HRETM analysis was performed on the most performant material  $\text{Nb}_2\text{O}_5\text{-C}^{\text{MFC}}800$  to better understand its nanostructure. At the lowest magnification, a micro- to nano-fibrillated structure is observed in agreement with MEB analysis as exemplified in Figure 13A. Some separated aggregates of inorganic nanoparticles are present but the major part of the material is made of nanoparticles of  $\text{Nb}_2\text{O}_5$  (20-50 nm) well dispersed along the carbonaceous fibrils (Figure 13B, C and D). This is confirmed by EDX analysis showing that, spotting on large zone ( $> 100$  nm) evidences the presence of C, Nb and O (see Figure SI 10). At higher magnifications, in small dark low-density zones ( $< 20$  nm) only C is detectable along with O, although with much lower intensity for this latter. At the opposite, high-density zones exhibit high intensity for rays of Nb and O, however, C rays is also clearly present although in lower intensity. This is in

agreement with the images that reveals a highly disordered and poorly graphitized carbon layer of few nanometres thickness  $\approx$ 1-5 nm covering the Nb<sub>2</sub>O<sub>5</sub> nanoparticles (Figure 13B, C, D and E).



**Figure 13.** HRTEM of Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>800 resulting from the pyrolysis under argon of NbO<sub>x</sub>@MFC

### Conclusion.

From the above set of results, we show a new aspect of the reactivity of cellulose, the latter being directly dehydrated with the cheapest and greenest niobium reagent, niobium(V) chloride, at low temperature. Therefore, the resulting Nb<sub>2</sub>O<sub>5</sub> and bark/shell Nb<sub>2</sub>O<sub>5</sub>/C composites can be prepared by a simple and up-scalable protocol. It is highlighted that all the cellulosic fibers are not equivalent, indeed comparison of filter paper, bacterial cellulose and microfibrillated cellulose shows that the latter is the best for elaborating a homogeneous and performant nanocomposite, thanks to its low crystallinity, small size and, consequently, the low proportion of carbon that is left after pyrolysis. In relation with that, performances as material for anode of supercapacitor are in the range of those prepared by much more sophisticated and expensive approaches like hydrothermal or polymer templated approach. Although the active material is the niobium oxide phase, a nanolayer encapsulating the nanocrystals, a porosity and a low proportion of carbon are key parameters adjustable through the choice of the cellulosic reagent. These results highlight the benefit of our approach to develop new enhanced architecture for energy storage applications from natural polysaccharides.

## Acknowledgments

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## Experimental part.

*Materials.* Niobium(V) Chloride ( $\text{Nb}_2\text{Cl}_{10}$ ), dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) are of analytical grad from Across (France). Dichloromethane was freshly distilled over  $\text{P}_2\text{O}_5$  before used. Filter paper FP-3-101-090 is from Sartorius (France). Aerogel of micro-fibrillated cellulose (MFC) was prepared by freeze-drying from tert-butanol solvent exchanged suspensions according to the procedure previously described.<sup>48</sup> Aerogel of bacterial cellulose (BC) were prepared according to a previously reported procedure then freeze dried from water solution.<sup>56</sup> All cellulosic materials were dried 3 days in an oven at 80°C just before use. All manipulations with  $\text{Nb}_2\text{Cl}_{10}$  and dried nanocellulose aerogel were performed in a glove box under argon atmosphere (<10 ppm of water).

*Instrumentation.* The X-ray powder diffraction (XRPD) patterns of the samples were recorded using a diffractometer (Philips X’Pert Pro, Netherlands). Raman spectra were obtained using Horiba LabRAM ARAMIS, Japan, with excitation wavelength of 633 nm. FT-IR were recorded on crushed powders with a Spectrum 2 (PerkinElmer) in ATR mode after 16 scans accumulated and analyzed. Transmission electronic microscopy (TEM) images were recorded using JEOL 1200 EXII, JEOL, Japan, and scanning electronic microscopy (SEM) images were obtained with a Hitachi S-4800, Canada. Energy dispersive X-ray analysis (EDAX) was done using the EDAX attachment (Oxford Instruments, UK) of the SEM system. N<sub>2</sub>-physisorption isotherms were obtained at 77 K using Micromeritics Tristar, USA. The samples were outgassed for 12 h at 150 °C under vacuum (2 Pa). The pore size distribution was calculated from the desorption branch using the BJH method. Thermogravimetric analyses (TGA) were obtained using Netzsch Simultaneous Thermal Analyzer STA 409 PC Luxx and Setaram Labsys TGA-DSC. Transmission electron microscopy images were acquired with a high voltage 200 kV JEOL JEM ARM 200F transmission electron microscope equipped with a STEM level and a spherical aberration corrector. STEM images were taken with high angle annular dark field (HAADF), EDX analyses were done with a JEOL CENTURIO detector and electron energy loss analyses were detected with a GATAN GIF QUANTUM.

All electrochemical characterizations were performed in Swagelok® cell at room temperature on an MPG2 instrument from BioLogic by using Teflon-made Swagelok® cell. All electrodes were composed of the active material (about 80 % by weight, w/w), acetylene black (8 % w/w, Y50A) and carboxymethylcellulose (12 % w/w, Sigma-Aldrich). After stirring in water, the mixture was spread uniformly at 150 $\mu$ m onto a copper current collector using a 3540 bird film applicator from Elecometer. Lithium metal disks were used as both reference and counter electrodes, and Whatman glass fibres filters were used as separator. The electrolyte was 1 M LiPF<sub>6</sub> in a 1:1:3 solution of ethylene carbonate, propylene carbonate and. All electrochemical analyses were done by taking into account the mass of the active material, the Nb<sub>2</sub>O<sub>5</sub>/C composite.

For galvanostatic measurements, the cells were cycled at various C rates from 1C to 1000C (1, 2, 5, 10, 20, 40, 80, 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1C corresponding to a 100.82 mA.g<sup>-1</sup> current).

For cyclic voltammetry, all cells were cycled at various scan rates ranging from 0.5 to 500 mV s<sup>-1</sup> (0.5, 1, 2.5, 5, 7.5, 10, 20, 50, 100, 200, 300, 400, and 500). All calculations based on cyclic voltammetry were done by using procedures described in the literature.<sup>5-6, 57</sup>

*Preparation of NbO<sub>x</sub>@FP, NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC.* In a glove box under inert atmosphere (< 2 ppm H<sub>2</sub>O), cellulose source (FP, MFC or BC), dichloromethane (30 mL), and Niobium(V) pentachloride were placed into a Teflon-lined autoclave, in quantities described in Table 1. After closing, the autoclave was placed in an oven at 85°C for 3 days. When cooled down to room temperature, black residue was washed with anhydrous dichloromethane (3 x 20 mL). In atmosphere, the residues were subsequently washed with standard dichloromethane (3 x 20 mL), and dried in an oven at 80 °C for 24 h to yield NbO<sub>x</sub>@FP, NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC, respectively.

Table 1: composition of the samples

|                       | Cellulose |                          | Niobium chloride |                          |
|-----------------------|-----------|--------------------------|------------------|--------------------------|
|                       | m (g)     | n (10 <sup>-3</sup> mol) | m (g)            | n (10 <sup>-3</sup> mol) |
| NbO <sub>x</sub> @FP  | 2.010     | 12.40                    | 2.669            | 9.88                     |
| NbO <sub>x</sub> @BC  | 0.505     | 3.11                     | 0.672            | 2.49                     |
| NbO <sub>x</sub> @MFC | 0.503     | 3.10                     | 0.673            | 2.49                     |

*Thermal treatments.* Hybrid materials were either calcined in air at 900 °C for 1 h (heating rate 5 °C.min<sup>-1</sup>) yielding niobium oxide called Nb<sub>2</sub>O<sub>5</sub>-900<sup>A</sup> where A is for FP or BC or MFC. Pyrolysis under argon was performed up to either 800 °C or 900 °C (for 1h, heating rate 5 °C.min<sup>-1</sup>), yielding the corresponding samples called Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>800, Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>900, Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>800, Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>900, Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>800 and Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>900, respectively.

*Evaluation of the composition of Nb<sub>2</sub>O<sub>5</sub>/C composites.* Based on TGA data, x is the yield under air and y is the yield under argon, then if z=y-x, z is the carbon resulting from the carbonization of cellulose. Consequently, a mass of y grams of Nb<sub>2</sub>O<sub>5</sub>/C composites includes z grams of C. For 100g of Nb<sub>2</sub>O<sub>5</sub>/C, the composition in weight percentage is given by (x\*100)/y = weight percentage of Nb<sub>2</sub>O<sub>5</sub> and (z\*100)/y = weight percentage of C.

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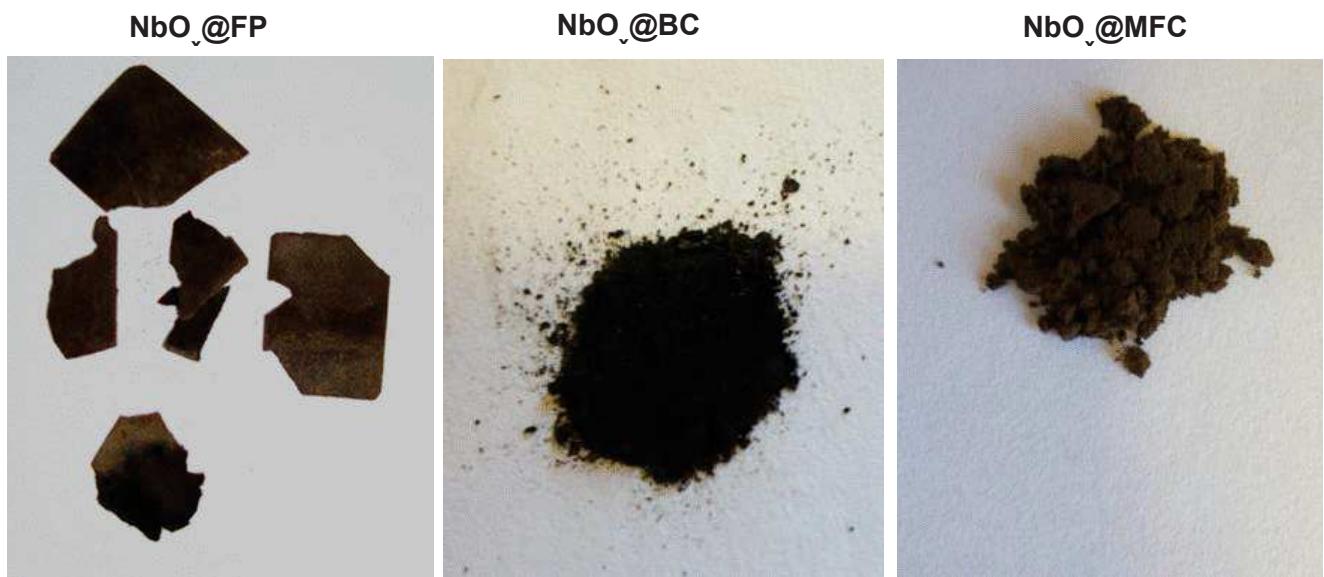
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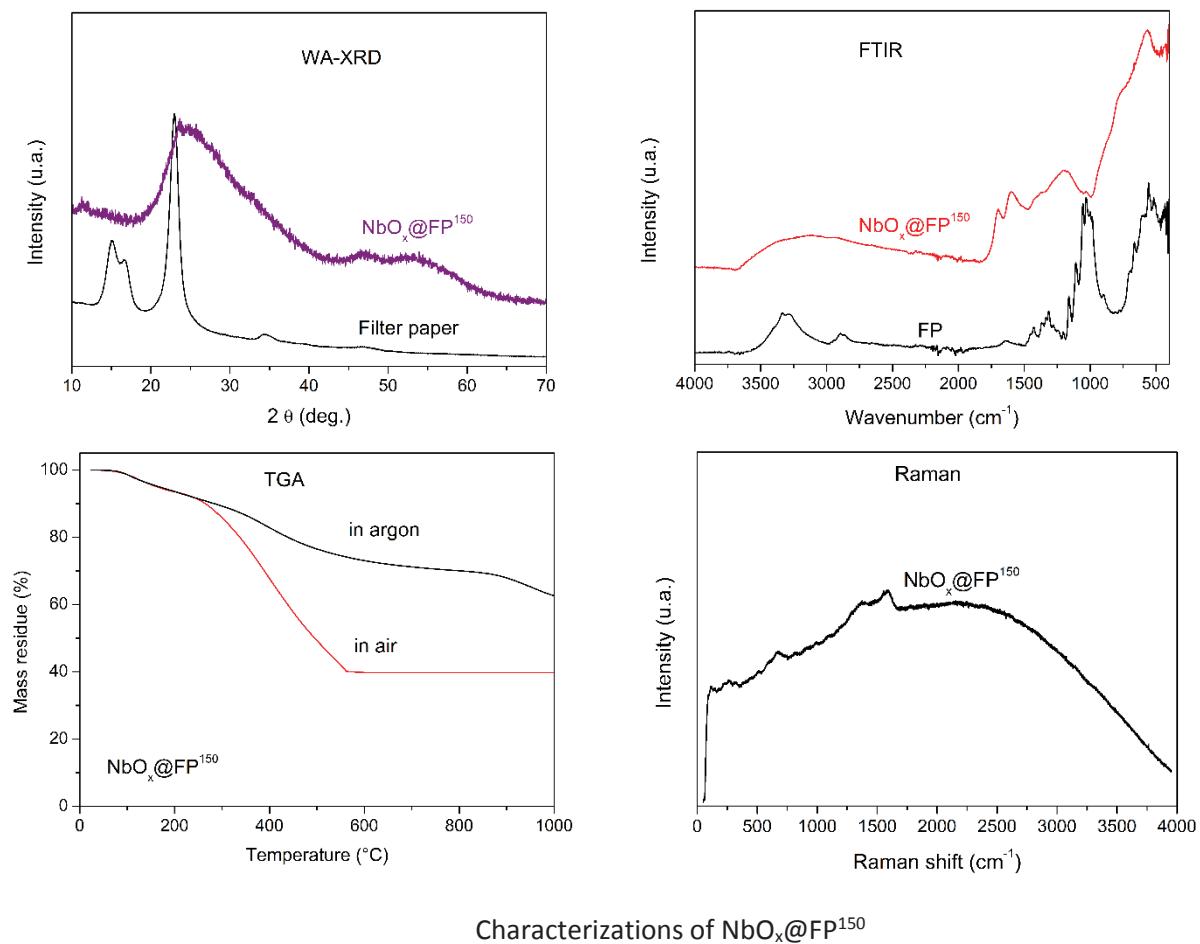
## Supporting information

Figure SI 1

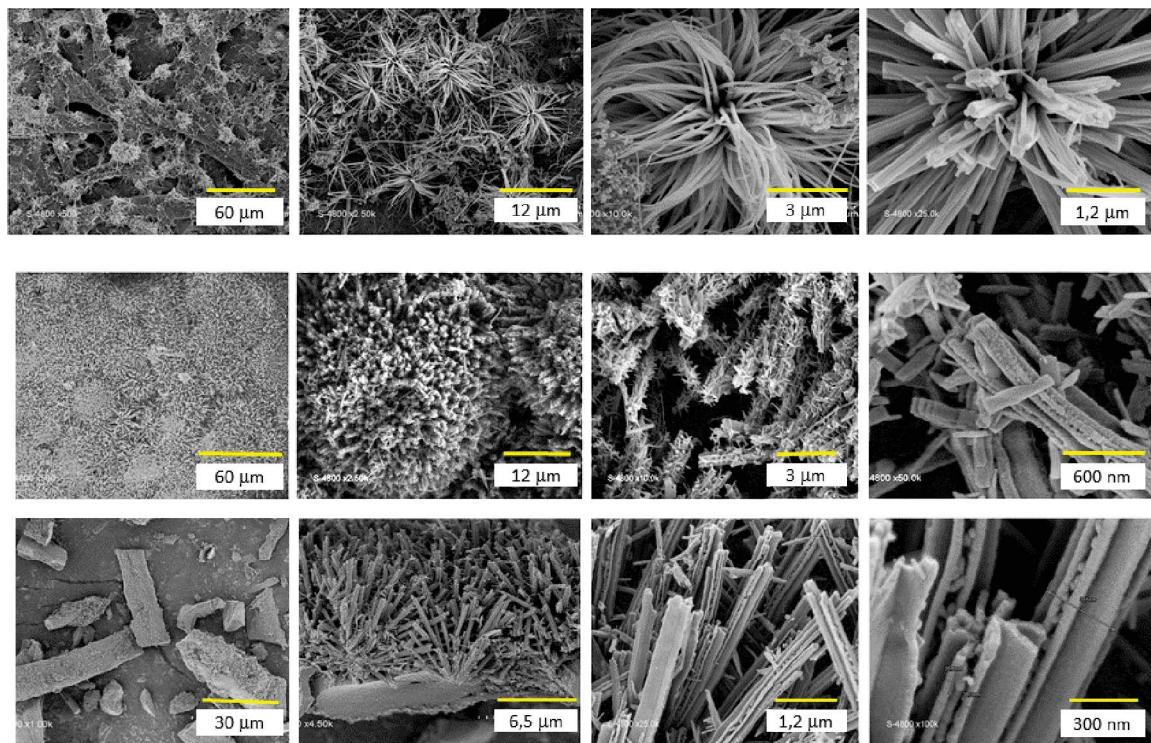


Images of NbO<sub>x</sub>@FP, NbO<sub>x</sub>@BC and NbO<sub>x</sub>@MFC

**Figure SI 2**

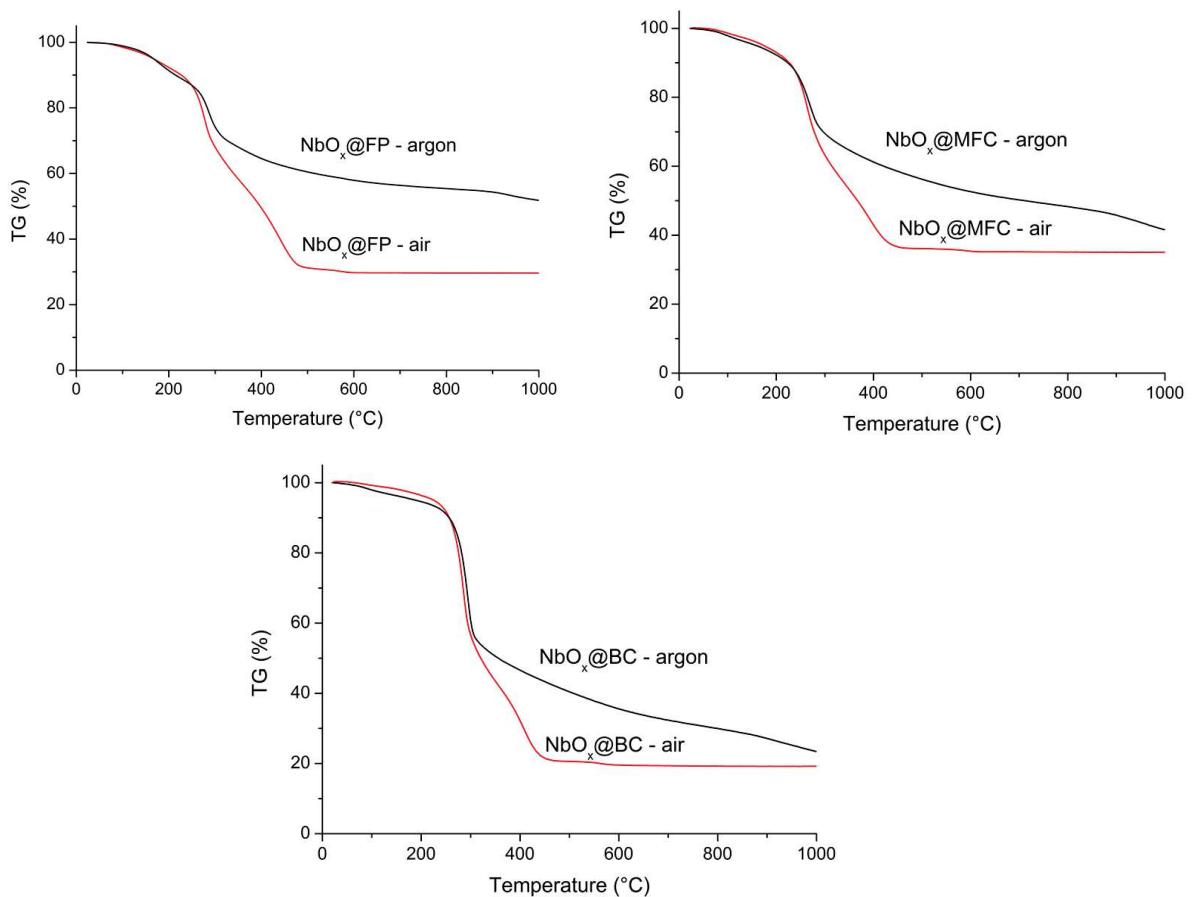


**Figure SI 3**



MEB images of NbO<sub>x</sub>@FP<sup>150</sup>

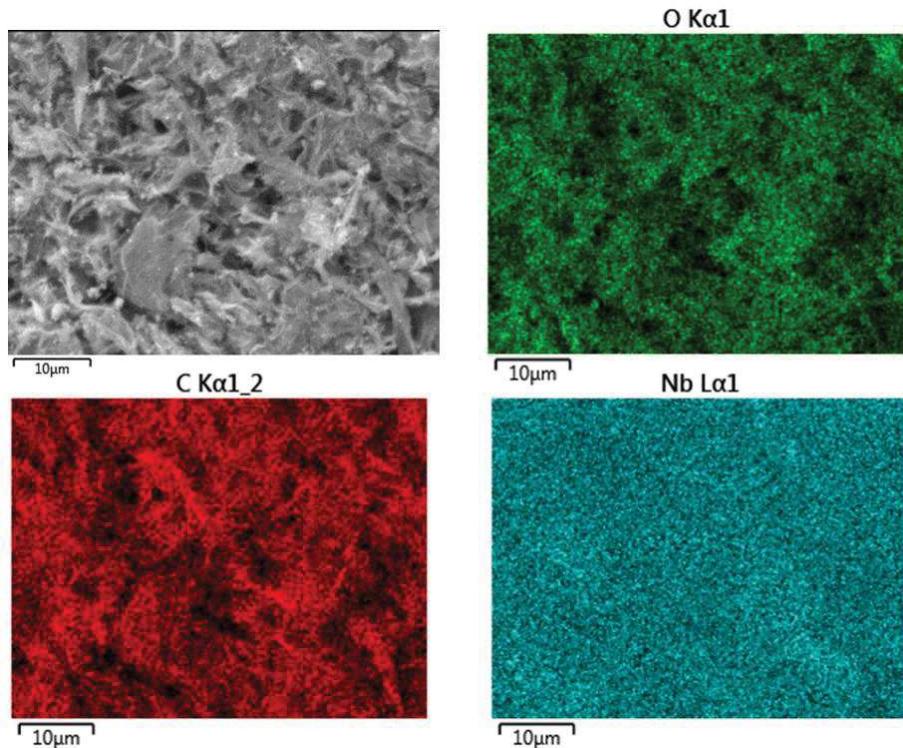
**Figure SI 4**



TGA of  $\text{NbO}_x$ @FP,  $\text{NbO}_x$ @MFC and  $\text{NbO}_x$ @BC

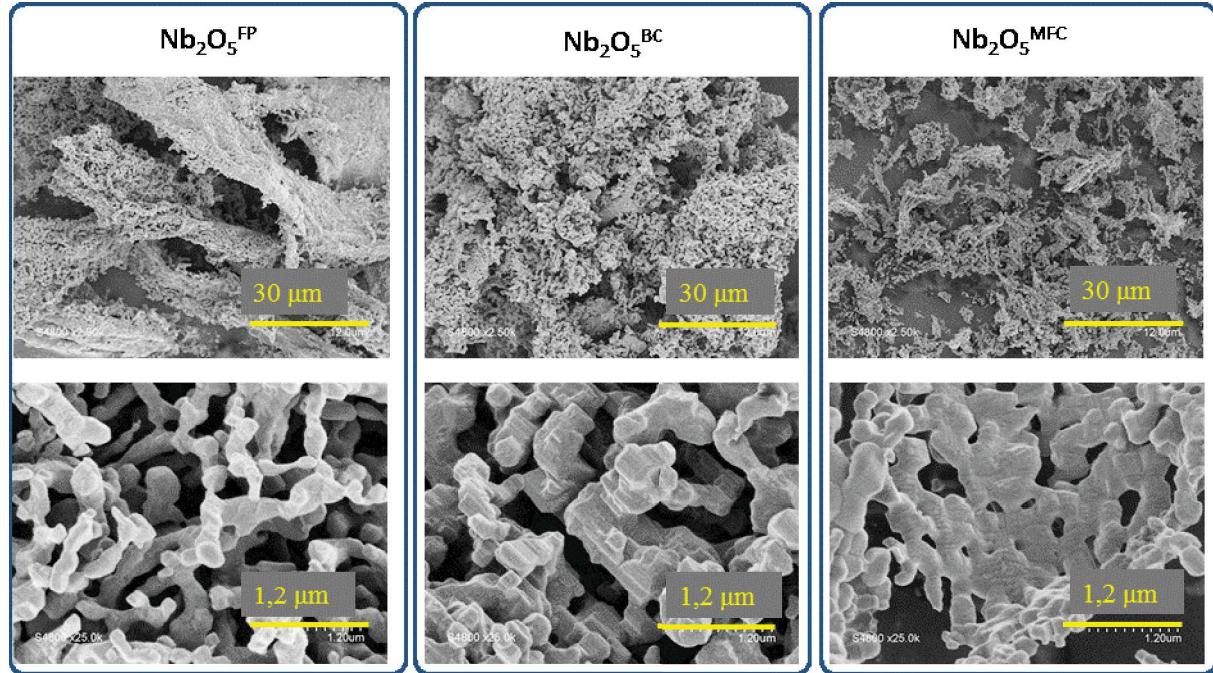
**Figure SI 5**

| Sample  | Mass % |      |      |     | Atomic % |      |     |     |
|---|--------|------|------|-----|----------|------|-----|-----|
|   | C      | O    | Nb   | Cl  | C        | O    | Nb  | Cl  |
| <b>NbOx@BC</b>  | 47,6   | 44,8 | 6,4  | 1,2 | 57,7     | 40,7 | 1   | 0,5 |
| <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>800</b>  | 68,2   | 13,4 | 18,4 |     | 84,6     | 12,5 | 2,9 |     |
| <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>BC</sup>900</b>  | 45,6   | 14,7 | 39,7 |     | 73,8     | 17,9 | 8,3 |     |
| <b>NbOx@FP</b>  | 31,7   | 36,2 | 28,7 | 3,5 | 49,7     | 42,7 | 5,8 | 1,8 |
| <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>800</b>  | 72,9   | 11,4 | 15,3 |     | 87,2     | 10,3 | 2,4 | -   |
| <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>FP</sup>900</b>  | 60,2   | 8,9  | 29,7 |     | 84,4     | 9,4  | 5,6 | -   |
| <b>NbOx@MFC</b>                                       | 41,3   | 27,3 | 28,2 | 3,2 | 61,7     | 30,9 | 5,7 | 1,7 |
| <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>800</b> | 46,4   | 14,6 | 38,9 |     | 74,4     | 17,5 | 8,1 |     |
| <b>Nb<sub>2</sub>O<sub>5</sub>-C<sup>MFC</sup>900</b> | 43,7   | 14,5 | 41,8 |     | 72       | 18,5 | 9,4 |     |



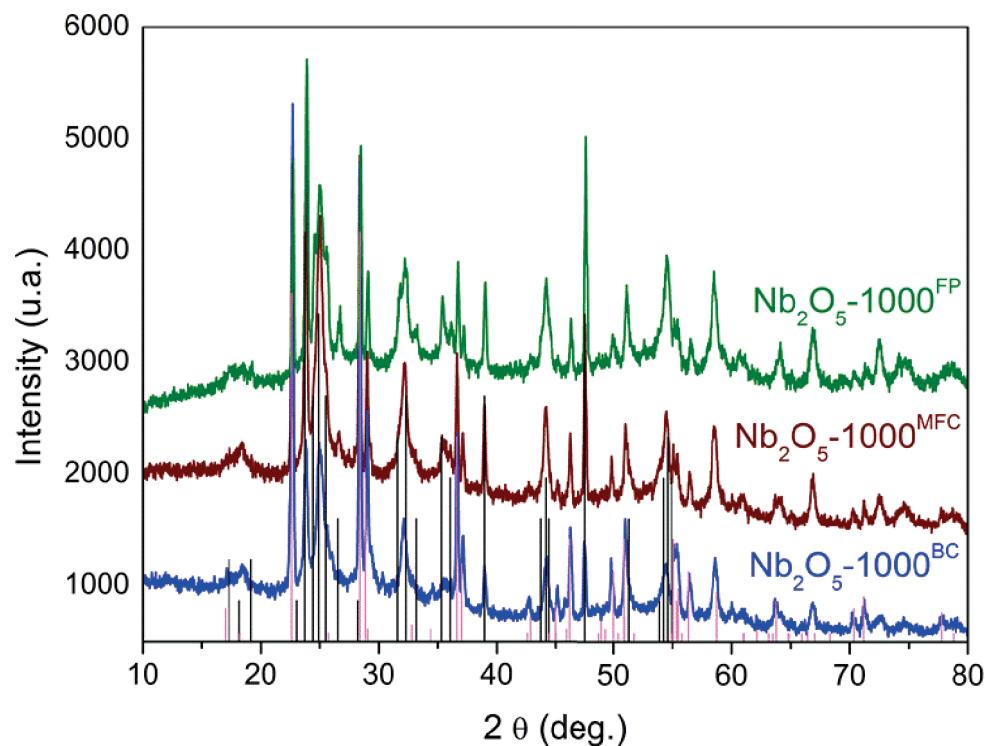
EDX analysis of NbO<sub>x</sub>@FP, NbO<sub>x</sub>@MFC and NbO<sub>x</sub>@BC

**Figure SI 6**



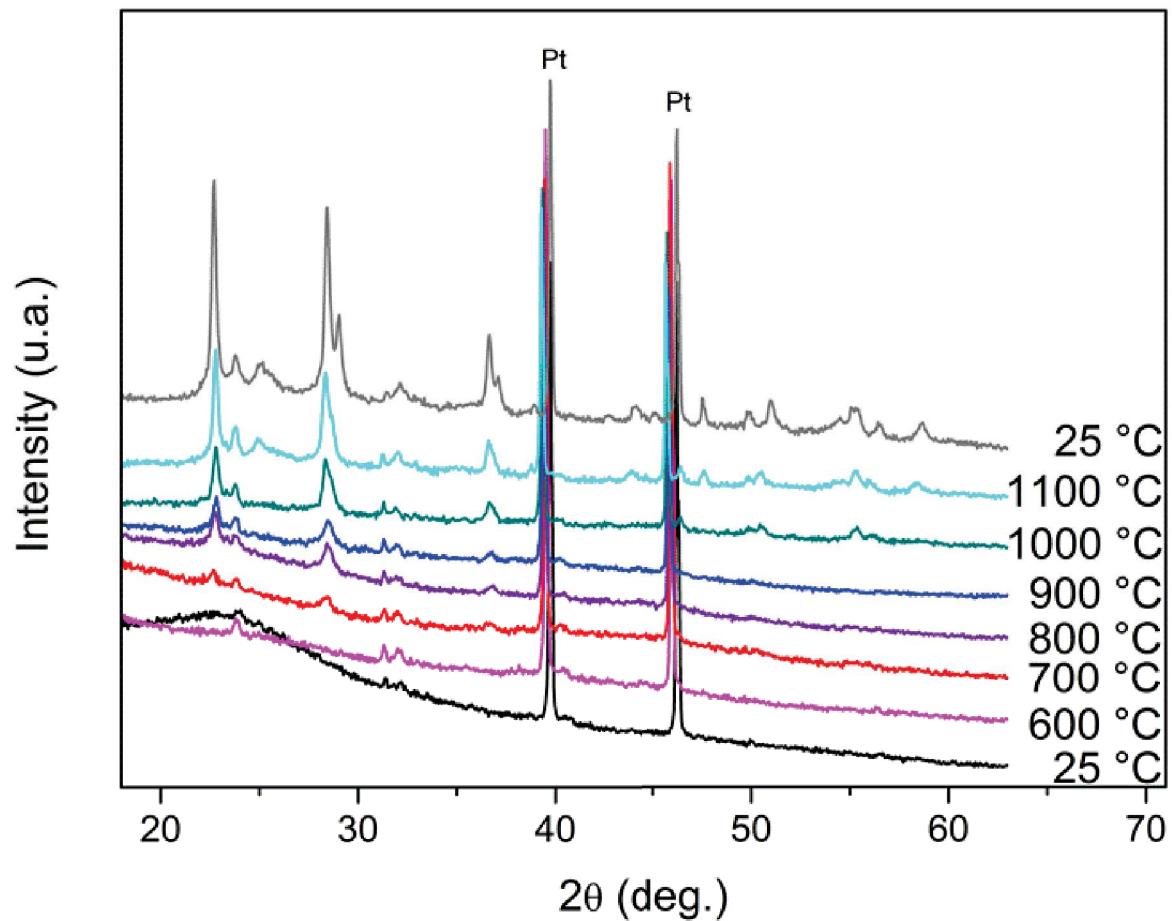
MEB images of  $\text{Nb}_2\text{O}_5^{\text{FP}}$ ,  $\text{Nb}_2\text{O}_5^{\text{BC}}$  and  $\text{Nb}_2\text{O}_5^{\text{MFC}}$ , obtained by calcination of  $\text{NbO}_x@\text{FP}$ ,  $\text{NbO}_x@\text{BC}$  and  $\text{NbO}_x@\text{MFC}$ , respectively

**Figure SI 7**



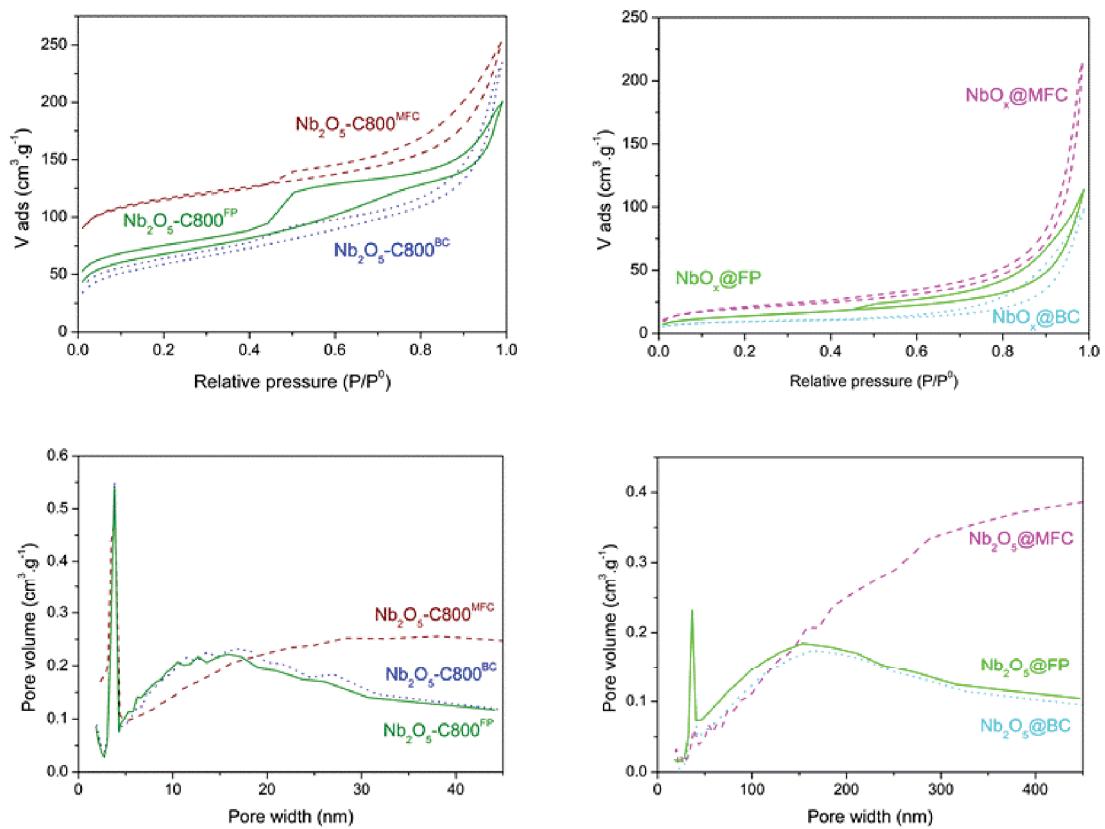
DRX of  $\text{Nb}_2\text{O}_5^{\text{FP}}$ ,  $\text{Nb}_2\text{O}_5^{\text{BC}}$  and  $\text{Nb}_2\text{O}_5^{\text{MFC}}$ , obtained by calcination of  $\text{NbO}_x$ @FP,  $\text{NbO}_x$ @BC and  $\text{NbO}_x$ @MFC, respectively

Figure SI 8



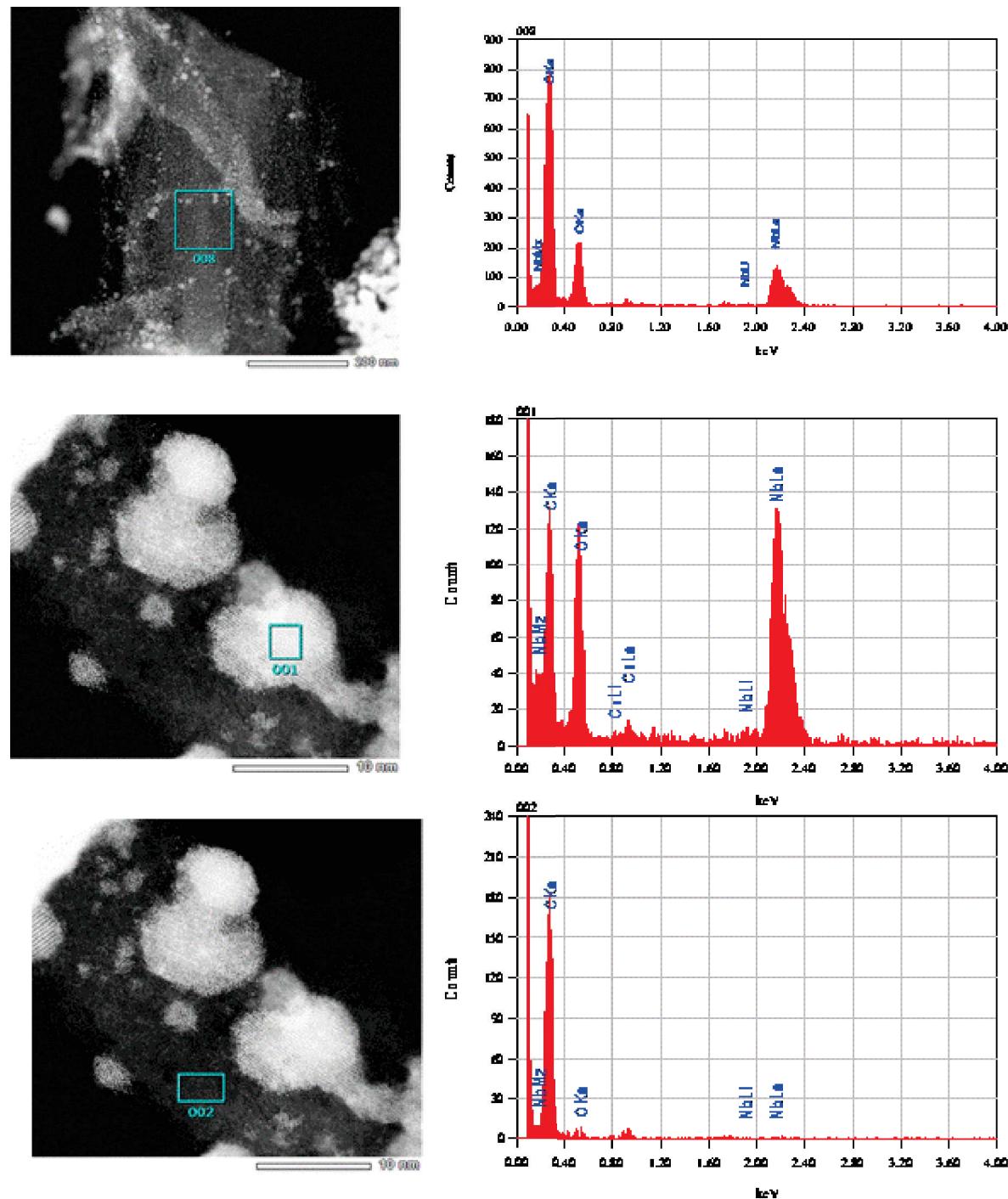
*In situ* X-ray powder diffraction measurement between ambient temperature and 1100 °C of  $\text{NbO}_x$ @FP

**Figure SI 9**



Nitrogen adsorption-desorption isotherms of  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{FP}}$ ,  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{BC}}$  and  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{MFC}}$ ; nitrogen adsorption-desorption isotherms of  $\text{NbO}_x\text{@FP}$ ,  $\text{NbO}_x\text{@BC}$  and  $\text{NbO}_x\text{@MFC}$ . Porous distribution of the same materials

**Figure SI 10**



EDX analysis on HRTEM-scanned samples of  $\text{Nb}_2\text{O}_5\text{-C}800^{\text{MFC}}$



## **IV.4 – Conversion of nanocellulose aerogel into TiO<sub>2</sub> and TiO<sub>2</sub>@C nanothorns by direct anhydrous mineralization with TiCl<sub>4</sub>. Evaluation of electrochemical properties in Li batteries**

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**ABSTRACT.** Nanostructured TiO<sub>2</sub> and TiO<sub>2</sub>@C nanocomposites were prepared by an original process combining biotemplating and mineralization of aerogels of nanofibrillated cellulose (NFC). A direct one step treatment of NFC with TiCl<sub>4</sub> in strictly anhydrous condition allows the formation of TiO<sub>2</sub> at the outmost part of the nanofibrils with preservation of their shape and size. Such TiO<sub>2</sub>@cellulose composite can be transformed either into TiO<sub>2</sub> nanotubes (TiO<sub>2</sub>-NT) by calcination in air at 600 °C and 900 °C, or into TiO<sub>2</sub>@C nanocomposites by pyrolysis in argon at 600 °C and 900 °C. A detailed characterization of these materials is reported here, as well as the evaluation of their performances as negative electrode materials for Li-ion batteries.

### **Introduction**

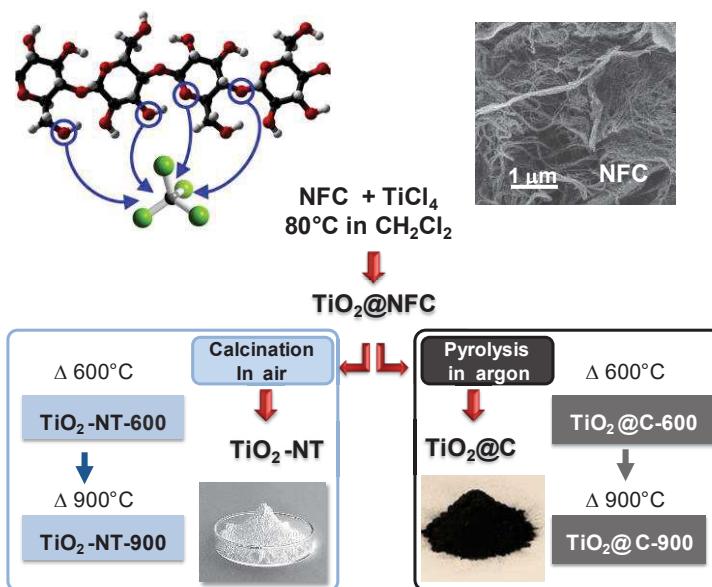
Metal oxides such as TiO<sub>2</sub> are highly demanded materials for new technologies. Their properties can be finely tailored by varying the porosity, crystallinity, morphology, doping, particle size and, last-but-not-least, their arrangement in hierarchical macro-, nano- and micro-scale structures. With increased emphasis on ‘green’ chemistry, interest in sustainable processes is aimed at minimizing the use of toxic chemicals, solvents, energy, etc. Accordingly, in the field of metal oxide synthesis, inorganic replication of biotemplates with polysaccharides (cellulose, chitosan and chitin, agarose, starch, carrageenan, etc.) has been actively explored.<sup>1, 2</sup>

We recently reported a completely new approach whereby cellulosic fibers are considered as a template and also as a reagent from which oxygen atoms are transferred to a metal atom of a metal chloride (Figure 1).<sup>3, 4</sup> This direct one-step process is a type of mineralization that avoids preparation of any metal oxide sol or the use of sophisticated ALD equipment. Moreover, it allows the formation of TiO<sub>2</sub> with unusual morphology, such as urchins and carpets of

needles, which has never been achieved by other processes. It is a solid/liquid process and it is noteworthy that the phenomena occurring at the interface of the cellulose fiber are determining for the all the characteristic of the material. In this sense, increasing the surface accessible to the reaction is likely to enhance the properties of such materials.

In this sense, nanocelluloses, such as bacterial cellulose (BC), cellulose nanocrystals (CNC), microfibrillated cellulose (MFC) and nanofibrillated cellulose (NFC), are sustainable, abundant, inexpensive and environmentally friendly nano-materials that exhibit interesting properties due to their nanometric scale.<sup>5,6</sup> They have been considered for uses in nanocomposites, as well as medical and life-science devices.<sup>7,8</sup> They also can serve as building blocks for the design of hierarchical materials, including aerogels<sup>9,10</sup>, emulsions,<sup>11</sup> but also nano-devices or templates with appropriate process or surface modification.<sup>7,8</sup>

They have thus been recently assessed as porogen building blocks for the synthesis of metal oxides which are generally obtained after thermal oxidation of this biotemplate.<sup>12,13</sup> This is especially true in the case of TiO<sub>2</sub>, a widely applied material in the field of photocatalysis,<sup>14</sup> which also showed interesting properties as negative electrode in electrochemical devices.<sup>15-19</sup> Such templating or replication of cellulosic fibers is generally performed by infiltration/deposition of a metal oxide sol, e.g. for TiO<sub>2</sub>,<sup>20-22</sup> but may be limited for precise replication of cellulosic nanostructures. ALD has been successfully used on NFC aerogels for this purpose, but NFC replication requires a sophisticated ALD process and high temperatures (190 °C) in the case of TiO<sub>2</sub>,<sup>23-25</sup> SiO<sub>2</sub> and HfO<sub>2</sub>.<sup>26</sup>



**Figure 1.** General overview of the process, nomenclature and preparation of TiO<sub>2</sub>-NT and TiO<sub>2</sub>@C samples by thermal treatment of the initial TiO<sub>2</sub>@NFC nanocomposite obtained by TiCl<sub>4</sub> treatment of NFC materials.

Following preliminary experiments with filter paper, we are now seeking ways to preserve the structure of NFC nanofibrils upon this mineralization and to form a new  $\text{TiO}_2@\text{NFC}$  nanocomposite. The starting material has been chosen as an aerogel obtained through freeze-drying of solvent-exchanged suspension in order to preserve the accessibility of the cellulosic surface,<sup>10</sup> leading to NFC with high specific surface area ( $\approx 100 \text{ m}^2 \text{ g}^{-1}$ ) The aim is to form a sheath of  $\text{TiO}_2$  grown with-and-on cellulose nanofibrils by its chemical reaction with titanium(IV) chloride. Thus, this  $\text{TiO}_2@\text{NFC}$  is potentially the precursor of two very attractive materials, either porous metal oxide nanotubes or tubular nanocomposites of carbon (inside) and metal oxide (outside), this being only dependent on the post-thermal treatment (Figure 2). In our case, thermal oxidation of cellulosic residue of  $\text{TiO}_2@\text{NFC}$  can lead to  $\text{TiO}_2$  with a porous inorganic nanotube morphology ( $\text{TiO}_2\text{-NT}$ ), such material being highly demanded solar cells,<sup>27</sup> photocatalyst, and negative electrode material for Li-ion batteries.<sup>14, 28-34</sup> On the other hand, thermal conversion of the cellulosic residue into carbon upon pyrolysis can lead to  $\text{TiO}_2@\text{C}$  nanocomposites, a route rarely explored in the field of bio-templating and that we report, to the best of our knowledge, for the first time. Such  $\text{TiO}_2@\text{C}$  nanocomposites can be prepared by a reductive thermal or hydrothermal process with bio-chemicals like furfural,<sup>35,</sup><sup>36</sup> and have potential applications in photocatalysis efficiency,<sup>37</sup> supercapacitors,<sup>38</sup> Li-ion batteries.<sup>39, 40</sup>

Even though the current commercial negative electrode material in Li-based systems is graphite, which is worldwide available and features good Li insertion properties, technological progress demands for faster, safer, lighter and higher capacity battery materials. Among other interesting candidates,  $\text{TiO}_2$  and lithium titanates show similar environmental benignancy and cost effectiveness to graphite, but have superior safety and rate capability, providing high charge and discharge rates.<sup>41</sup> Their working potential of about 1.5 V vs.  $\text{Li}^+/\text{Li}$  constitutes an intrinsic Li overcharge protection, impeding Li plating at high rates, while suiting the potential stability window of common organic electrolytes.<sup>42</sup> While the spinel  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  can be considered a reference material for lithium titanates in battery applications,<sup>43</sup> also pure  $\text{TiO}_2$  polymorphs such as anatase and  $\text{TiO}_2(\text{B})$  show promising Li insertion properties.<sup>44, 45</sup> Both polymorphs have a theoretical capacity of 336 mAh g<sup>-1</sup> corresponding to the insertion of one mole of lithium per mole of  $\text{TiO}_2$ . Such a capacity, however, is practically impossible to obtain without nanostructuring. In fact, using nanostructured  $\text{TiO}_2$  as active lithium insertion material not only offers the opportunity to overcome the low electron and ion conductivities imposed by bulk structure, but also enhance rate and cycling performance by increasing electrode-electrolyte contact area and surface to volume ratio.<sup>46, 47</sup> Such open structures permits higher diffusion rates due to surface diffusion as well as easy accessibility. In this paper, we present the mineralization/replication of nanofibrils of NFC into NT- $\text{TiO}_2$  and  $\text{TiO}_2@\text{C}$  that were characterized and assessed in the formulation of negative electrode materials for Li-ion batteries.

## Results and discussion

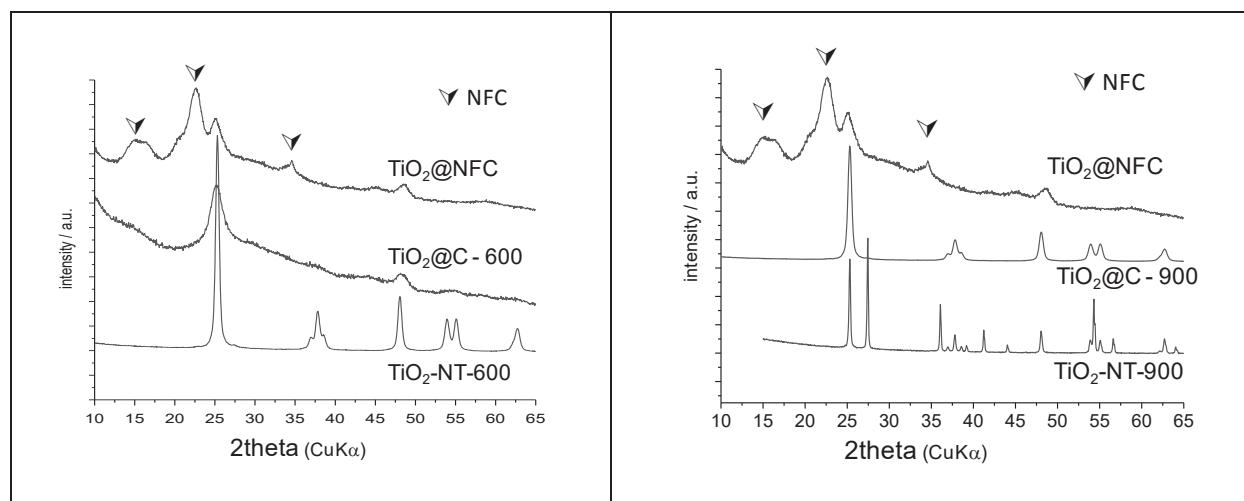
In strictly anhydrous conditions and using dried NFC aerogels, direct mineralization of the surface of the nanofibrils of NFC was achieved by treatment with  $\text{TiCl}_4$  at 80°C in autoclave under autogeneous pressure. These conditions are

similar to the non-hydrolytic process that has inspired this work; different reactions are assumed to occur during the treatment: a Ti-Cl alcoholysis with the primary and secondary alcohol group of cellulose, a Ti-Cl/C-O exchange like in non-hydrolytic sol-gel. It also cannot be excluded the reaction of  $\text{TiCl}_4$  with residual amount of water of crystallization.<sup>48</sup> Another possibility being the formation of water by dehydration, a process that generally occurs at temperature above 150 °C, but that could be activated by the presence of  $\text{TiCl}_4$  and acidic condition.



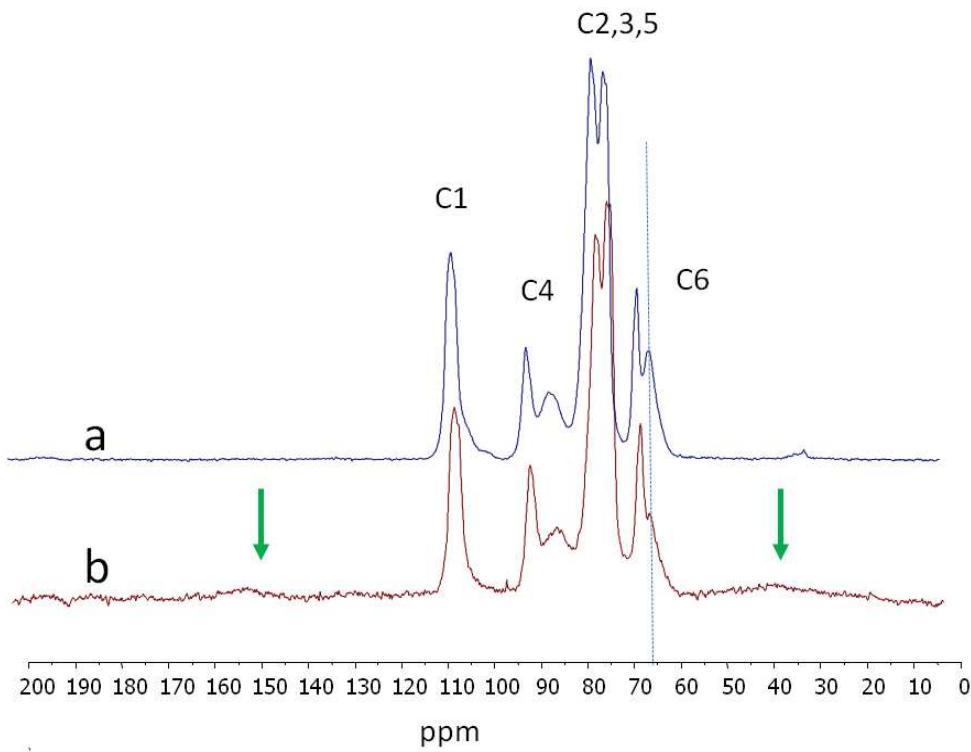
**Figure 2 .** Picture of the different materials at different stage of their preparation.

To the exception of the color, the  $\text{TiO}_2@\text{NFC}$  material recovered after mineralization and drying looks similar to the NFC aerogel: the centimeter scale, the shape, the mechanical consistency and flexibility of the initial NFC aerogel are mostly preserved. The black color of the  $\text{TiO}_2@\text{NFC}$  sample suggested at least a partial carbonization of fibrils, but  $\text{TiO}_2$  is already present as a poorly crystallized anatase phase evidenced by XRPD (crystallite size < 5 nm, Figure 3 and Table 2). Unreacted cellulose is evidenced by signals at 14-16°, 22.5° and 34.5°, similar to pristine NFC.



**Figure 3.** X-ray powder diffraction patterns of samples before and after thermal treatment in air or argon a either 600 °C or 900 °C.

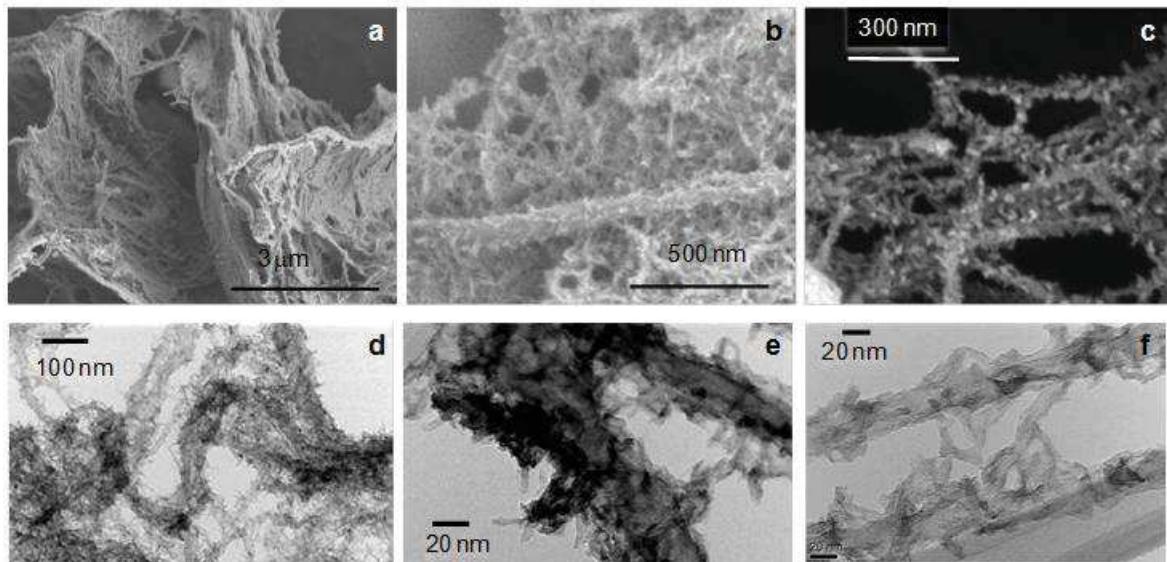
Therefore, the cellulosic residue before any thermal treatment is apparently a mix of “chemically carbonized” and pristine cellulose. No characterization of TiO<sub>2</sub>@NFC was possible by Raman due to extreme fluorescence phenomena.



**Figure 4.** Solid state NMR spectra of a) pristine nanocellulose and b) TiO<sub>2</sub>@NFC

Solid state NMR spectra obtained on TiO<sub>2</sub>@NFC are displayed in Figure 4 and shows interesting features. First, as indicated by the XRPD experiments, pristine cellulose is partially preserved during the process. More interestingly, two very broad signals around 150 ppm and 40 ppm (shown by arrows), typical of char formation,<sup>49</sup> indicate that part of the cellulose has been degraded. Even if the quantization could be rather delicate in the case of carbonization of cellulose, the overall contribution of degradation product can be estimated around 10%. Even strikingly, not only cellulose has preserved its crystalline structure, but also the decrease of the signal at 62 ppm (indicated by a dashed line) is a strong indication of a selective topochemistry of the reaction. Indeed, this signal has been identified as originating from the C6 hydroxymethyl group pointing out of the cellulosic surface, its crystalline analogs being located at 65 ppm. As already observed for surface restricted reaction on nanocellulose either oxidation,<sup>50</sup> or esterification,<sup>10</sup> the relative decrease of the surface signal is a very good marker of the substitution of the surface hydroxyls. In what they have been transformed is unfortunately impossible with <sup>13</sup>C CP-MAS experiments

At the nanometer scale, prior to any thermal treatment,  $\text{TiO}_2@\text{NFC}$  appear homogeneous and continuous, more or less aggregated, identical to NFC aerogel (SEM and TEM analysis Figure 5 and SI-4)). However, at high magnification, the fibrils look like nano-thorns, a distinctive feature associated with the presence of elongated inorganic nanoparticles. The presence of these is likely to be related to the formation of  $\text{TiO}_2$  needles and rods that we have described in a previous publication.<sup>3, 4</sup>



**Figure 5.** Images of NFC (SEM, a) and  $\text{TiO}_2@\text{NFC}$  (SEM, b-c; TEM, d- f)

By thermogravimetric analysis of  $\text{TiO}_2@\text{NFC}$  in air (see SI-1), a fast and important weight loss occurs above 150°C, attributed to carbonization followed by combustion that lead to a total weight loss of 65 to 70 % at 475-500°C (the weight loss of pristine NFC is approximately 98 % in air). Thus upon calcination at 600°C and 900 C,  $\text{TiO}_2\text{-NT-600}$  and  $\text{TiO}_2\text{-NT-900}$  are almost pure titanium dioxide, elemental analysis revealing a carbon content lower than 1 % (Table 1). Accordingly, the mass ratio in the starting  $\text{TiO}_2@\text{NFC}$  can be estimated to be 30-35 % of  $\text{TiO}_2$  plus 65-70 % of cellulosic residue.

In argon, the weight loss is slightly delayed but continues until 1000 °C. The final weight loss at this temperature is 35-40 % and must be compared to the 77 % weight loss of pure NFC in the same conditions. Therefore, an important proportion of carbon residue remains in  $\text{TiO}_2@\text{C-600}$  and  $\text{TiO}_2@\text{C-900}$ , approximately 37% and 32% respectively determined by elemental analysis (Table 1). Upon calcination in air, the weight loss the pyrolyzed samples is approximately 49% and 42%, indicating a possible under-estimation of the carbon content by elemental analysis of the sample after pyrolysis at 600°C and 900°C (Table 1).

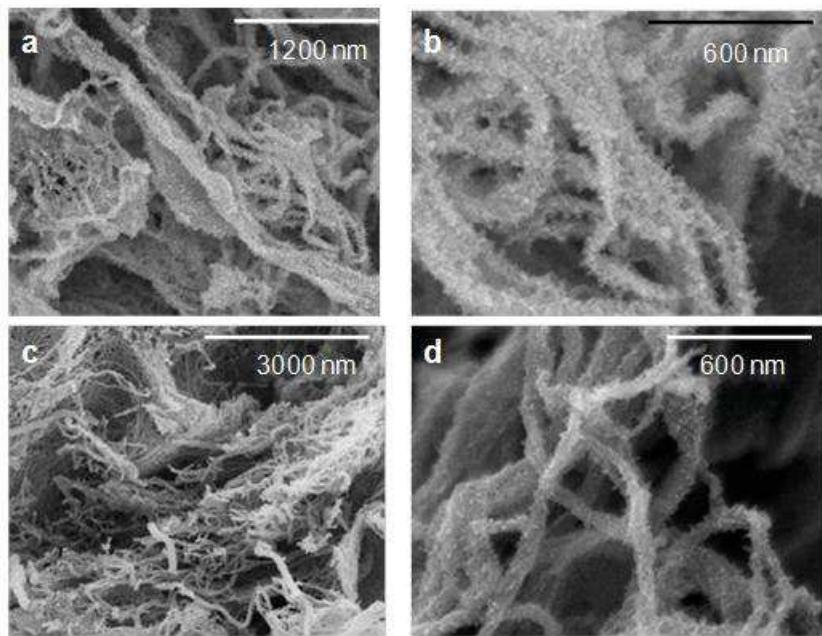
**Table 1:** Elemental composition of sample as determined by Chemical elemental analysis and EDX

| Sample                   | Chemical Elemental analysis<br>(weight % ) |      | EDX<br>(weight %) |       |       |       | Weight loss<br>(TGA until<br>1000 °C) |
|--------------------------|--|------|-------------------|-------|-------|-------|---------------------------------------|
|                          | C  | H    | Ti                | O     | C     | Cl    |                                       |
| TiO <sub>2</sub> @NFC    | 28.22                                      | 5.32 | 18.83             | 35.67 | 37.99 | 7.50  | 73.58 %                               |
| TiO <sub>2</sub> -NT-600 | 0.55                                       | 0.45 | 49.26             | 43.65 | 7.07  | 00.02 | 0 %                                   |
| TiO <sub>2</sub> -NT-900 | 0.06                                       | 0.08 | 56.55             | 41.82 | 1.53  | 0.00  | 0 %                                   |
| TiO <sub>2</sub> @C-600  | 37.70                                      | 1.61 | 28.44             | 28.98 | 41.25 | 1.34  | 49.06 %                               |
| TiO <sub>2</sub> @C-900  | 32.56                                      | 0.82 | 35.95             | 29.46 | 34.27 | 0.17  | 42.56 %                               |

After thermal treatment, anatase is the only crystallized phase at 600°C either under argon or air (Figure 3); rutile is only detected after calcination at 900°C (see SI-3). Carbonaceous residues produced and left upon pyrolysis limits the growing of the anatase crystallite (here < 20 nm, see SI-3) and prevent the anatase-to-rutile transformation.<sup>51</sup>

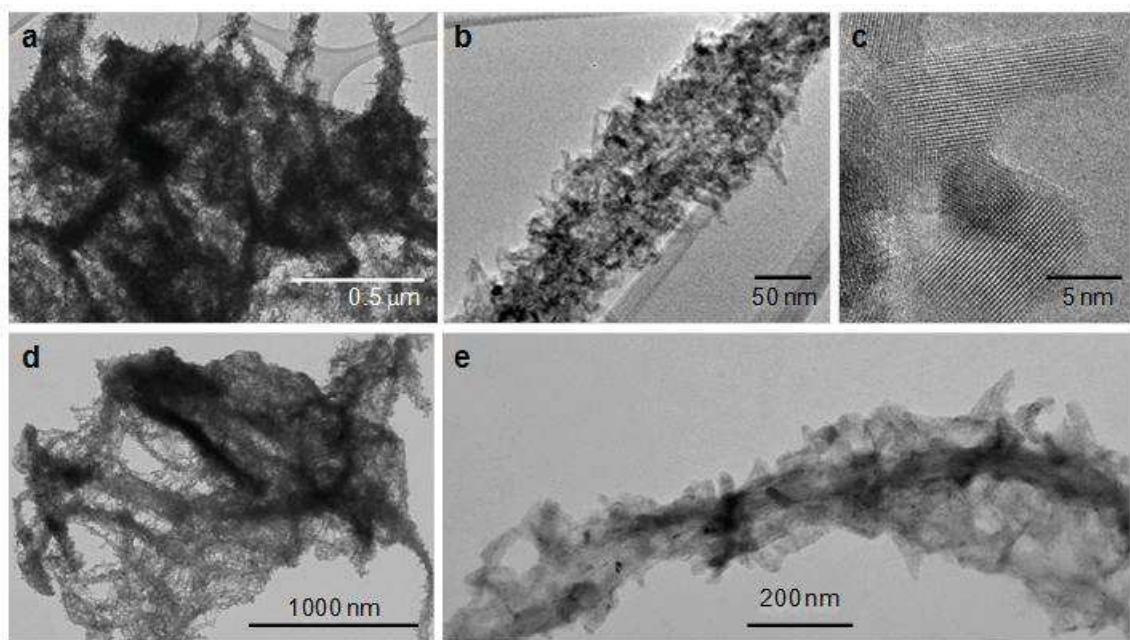
Anatase is also identified in calcined sample by Raman spectroscopy in all the samples (145, 196, 395, 516, 637 cm<sup>-1</sup>), rutile being only detected in TiO<sub>2</sub>-NT-900 (437, 613 cm<sup>-1</sup>) (see SI-2). On pyrolyzed samples TiO<sub>2</sub>@C-600 and TiO<sub>2</sub>@C-900, the same analysis shows important heterogeneity of the material resulting from the mixture of carbonaceous fibers and titania particles. Two broad signals attributed to 6-membered aromatic rings in graphitic materials are observed at 1350 and 1325 cm<sup>-1</sup> related to A<sub>1g</sub> (D band, attributed to defect in graphite) and at 1583-1593 cm<sup>-1</sup> related to E<sub>2g</sub> (G band, ascribed to sp<sup>2</sup> hybridized carbon network) (see SI-2).<sup>52</sup> Exploitation of these signals through the determination of the I<sub>D</sub>/I<sub>G</sub> ratio (I<sub>D</sub>/I<sub>G</sub> = 1 for TiO<sub>2</sub>@C-600 and I<sub>D</sub>/I<sub>G</sub> = 1.25 TiO<sub>2</sub>@C-900) lead to a correlation length of graphitic domain in the range of 1-1.25 nm.

In terms of morphology, the nanothorns-like structure is preserved upon thermal treatment, either pyrolysis or calcination, at 600 °C or 900 °C as shown on SEM images in Figure 6 and Figure 7.



**Figure 6** SEM images of TiO<sub>2</sub>-NT-600 (a and b) and TiO<sub>2</sub>@C-600 (c and d)

According to TEM and HRTEM analyses (Figure 7), the needles of the thorns are due to elongated nanoparticles of 10-20 nm associated with aggregated nanocrystal ( $5 < \text{size} < 30$  nm) having a more or less rounded shape (SI-5). No significant differences can be distinguished by TEM and SEM between on the one hand the sample calcined and on the other hand those pyrolysed. (SI-4) However, according to the important weight losses observed upon calcination we can conclude to the formation an hollow structure in the case of TiO<sub>2</sub>-NT-600 and TiO<sub>2</sub>-NT-900 with a good preservation of the imprint left by the NFC.



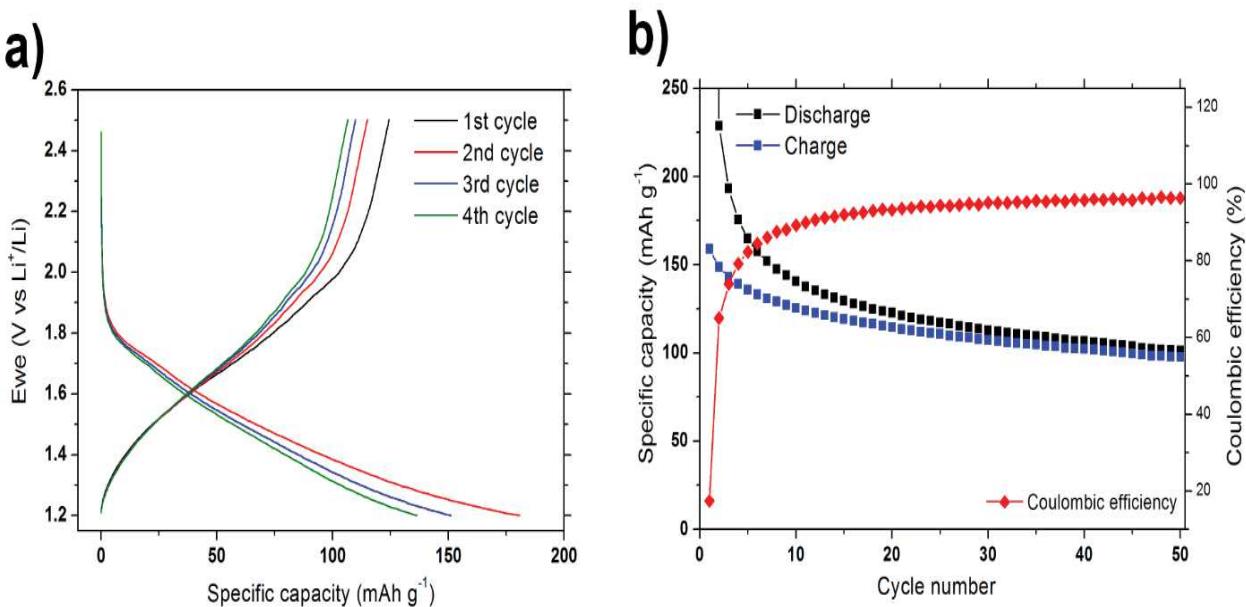
**Figure 7.** TEM images of  $\text{TiO}_2$ -NT-600 (a, b and c) and  $\text{TiO}_2$ @C-600 (d and e)

An evaluation of the texture of these materials by porosimetry measurements indicates an important effect of the thermal treatment (in SI Table 2). Compared to pyrolysis, calcination is detrimental in terms of specific surface area and leads to larger pores. As seen above, the presence of carbon during pyrolysis prevents the crystal growth. However, the data collected on the sample after pyrolysis is the sum of the texture of the carbon residue and the one of the oxide.

Biotemplating of cellulose with titania is known since the seminal work by Shimizu et al. using  $\text{TiF}_4$ ,<sup>53</sup> and then was developed for the formation of  $\text{TiO}_2$  nanotubes<sup>54</sup> or titania/carbon composite nanocomposite.<sup>55, 56</sup> This is also the case here, but additionally the process allows the formation of nanocrystal of  $\text{TiO}_2$  with an unexpected morphology. We emphasized that the situation is very different compare to previously reported biotemplating, first because no water is introduced to form the metal oxide, secondly because of the extremely low solubility of  $\text{TiO}_2$  in organic solvent ( $\text{CH}_2\text{Cl}_2$ ), and thirdly because the chemical process engaged the reactivity of the functionalities of cellulose. The unusual morphology of the  $\text{TiO}_2$  nanoparticles could be related to growth process occurring by reaction at-and-with the interface of the cellulose, the effect of the solvent could also play a role as it was demonstrated in the case of non-hydrolytic Sol-Gel.<sup>57, 58</sup>

Lithium insertion/deinsertion properties were evaluated vs. lithium metal at a C/20 current rate (where C is set at 335.6 mAh g<sup>-1</sup> for a 1 e<sup>-</sup>/hr process). The galvanostatic charge-discharge profiles of the first four cycles for  $\text{TiO}_2$  vs. Li between 2.5 and 1.2 V are displayed in Figure 8a. First of all, both discharge and charge curves show a smooth

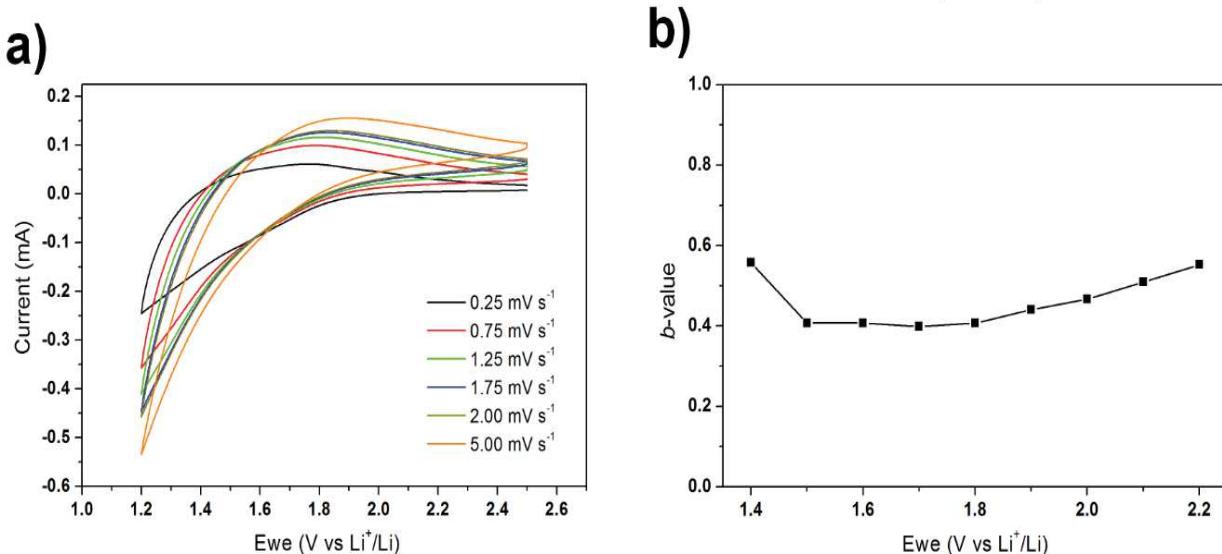
slope, with the absence of a voltage plateau. Due to the contribution of the nanocellulose-derived carbon (SI-6), a high irreversible insertion of Li is measured upon first discharge, with a reversible charge capacity of approximately  $125 \text{ mAh g}^{-1}$ . For clarity, we present only the further reversible cycling. The overall features of the galvanostatic curves are similar to the results obtained for other  $\text{TiO}_2$  nanoparticles.<sup>59</sup> The constant-voltage plateau, a two-phase region where the anatase and lithium titanate phases coexist during the  $\text{Li}^+$  insertion, is usually much shorter for the small particles than for the larger ones, and is even absent in certain cases.<sup>59, 60</sup> Indeed, lithium insertion into  $\text{TiO}_2$  shows three major storage mechanisms: (i) a rapid potential drop to ca. 1.7 V vs.  $\text{Li}^+/\text{Li}$  characteristic of the formation of a solid-solution  $\text{Li}_\epsilon\text{TiO}_2$ , where  $\epsilon$  depends on particle size.<sup>61</sup> (ii) a two-phase reaction between the tetragonal  $\text{Li}_\epsilon\text{TiO}_2$  and the orthorhombic lithium titanate  $\text{Li}_{0.5\pm\delta}\text{TiO}_2$  inducing a constant-voltage plateau around 1.7 V followed by (iii) another two-phase reaction up to 1 V towards rock-salt-type tetragonal  $\text{LiTiO}_2$ .<sup>62</sup> The irreversibility of the latter mechanism is usually overcome through nanostructuration of the electrode material, which induces a monophasic reversible pseudo-capacitive interfacial storage.<sup>60</sup> Nevertheless, below a certain size of the  $\text{TiO}_2$  nanoparticles, the two phases at 1.7 V do not coexist and less lithium is required to give rise to the orthorhombic lithium titanate phase, hence the absence of voltage plateau.<sup>61</sup> Thus, the galvanostatic results presented on Figure 8a could be understood by taking into account the nanoscopic nature of the  $\text{TiO}_2@\text{C-600}$  titanium dioxide sample.



**Figure 8.** Galvanostatic voltage profiles for  $\text{TiO}_2@\text{C-600}/\text{Li}$  cells cycled at C/20 between 2.5 and 1.2 V versus  $\text{Li}^+/\text{Li}$  (a); charge-discharge cyclability curves of  $\text{TiO}_2@\text{C-600}$  nanocrystals at C/20, and the corresponding coulombic efficiency (b).

As displayed in Figure 8b, a  $\text{TiO}_2@\text{C-600}/\text{Li}$  half-cell can sustain a specific capacity of more than  $125 \text{ mAh g}^{-1}$  at a current density of C/20 for tens of charge-discharge cycles between 2.5 and 1.2 V, before slowly decreasing towards  $100 \text{ mAh g}^{-1}$ . And as for the composition, the discharge capacity would correspond to the insertion of approximately 0.6 to 0.4  $\text{Li}^+$  ions for the first cycles, with only 0.3  $\text{Li}^+$  ions being reversibly inserted after 50 cycles. At the same time, the coulombic efficiency reaches 96 %, a relatively low value indicating detrimental lithium consumption during cycling. This might originate from the high surface area of  $\text{TiO}_2@\text{C-600}$  ( $271.8 \text{ m}^2 \text{ g}^{-1}$ , see Table 2 above), or from the intrinsic carbon arising from the pyrolyzed nanocellulose (SI-6), that would impact the electrochemical behaviour by continuously inducing either electrolyte decomposition or the formation of solid-electrolyte interface (SEI) Li-based products.<sup>63</sup>

Cyclic voltammograms of  $\text{TiO}_2@\text{C-600}/\text{Li}$  half-cells at various scan rates from  $0.25$  to  $5 \text{ mV s}^{-1}$  are presented in Figure 9a. In line with the previous galvanostatic results, a very broad band is observed in the range of  $1.2$ - $2.5$  V on the anodic curves during cycling at various rates. The maximum current response on the anodic curves is obtained between  $1.7$  and  $1.9$  V vs  $\text{Li}^+/\text{Li}$ , a value that is in good agreement with previous studies.<sup>16, 59, 63</sup> Nonetheless it is quite difficult to visually resolve the currents on the cathodic scans. This obviously indicates an emphasized pseudo-capacitive behaviour that could be well explained by either the nanometric size of the  $\text{TiO}_2@\text{C-600}$  material or the presence of amorphous  $\text{TiO}_2$  mixed along with the poorly crystallized anatase phase.<sup>6, 64</sup>



**Figure 9.** Cyclic voltammetry curves of  $\text{TiO}_2@\text{C-600}$  nanocrystals at various scan rates, from  $0.25$  to  $5.00 \text{ mV s}^{-1}$  (a); calculated *b*-values for a  $\text{TiO}_2@\text{C-600}$  electrode as a function of the anodic (lithium extraction) sweep (b).

As a way to go further into details in the understanding of Li-storage mechanism in nanocellulose-based  $\text{TiO}_2$  particles, the origin of the stored charge could be unravelled through the analysis of cyclic voltammetry curves. 145

Briefly, the total stored charge can be decomposed into the faradaic contribution from the  $\text{Li}^+$ -insertion process, the pseudo-capacitance surface effects and the non-faradaic contribution from the double layer effect. In order to distinguish between each contribution over the studied potential range, cyclic voltammetry data at various scan rates were analysed according to:<sup>63</sup>

$$i = a\nu^b$$

where the measured current  $i$  obeys a power law relationship with the scan rate  $\nu$ . This method has been successfully applied to  $\text{TiO}_2$  electrode materials versus lithium, where both  $a$  and  $b$  are adjustable parameters with  $b$ -values extracted from the slope of the fit of the  $\log i$  vs  $\log \nu$  plot.<sup>16,63</sup> For a capacitive response, the  $b$ -values would approach a value of 1.0, while a faradaic contribution would induce  $b$ -values close to 0.5.<sup>65</sup> The calculated  $b$ -values for a  $\text{TiO}_2@\text{C-600}/\text{Li}$  half-cell are shown in Figure 9b. At the peak potentials of 1.7-1.9 V for anodic processes, the  $b$ -values are close to 0.5. This shows that the currents arise primarily from the  $\text{Li}^+$  insertion into  $\text{TiO}_2$ . Nevertheless the  $b$ -values are close to 0.5 on the whole potential range, from 1.4 to 2.2 V for the anodic processes. Even though surprising at first, this result emphasizes that other faradaic contributions are to be taken into consideration. For instance, as underlined by the limited coulombic efficiency (Figure 7b), electrolyte decomposition would also contribute to the whole observed cell electrochemical mechanism.

## Conclusion

This study evidences the possibility to prepare nanofibrillated  $\text{TiO}_2$  or  $\text{TiO}_2@\text{C}$  structure by the direct mineralization of an NFC aerogels of high specific surface with  $\text{TiCl}_4$  in anhydrous condition. Different from ALD and Sol-Gel deposition, this nanoreplication of a biotemplate leads to unusual nano-thorns morphology for the replica. The thermal treatment applied after mineralization is a key step that allows the preparation of hollow nanostructure upon calcination or nano-assemblies upon pyrolysis. Such nanomaterials have potential for different application like in photocatalysis or electrochemical. Concerning the latter case even though the performance in term of specific capacity and rate capability in this preliminary study do not overtake the previous ones, this new synthesis approach by allowing the formation of  $\text{TiO}_2$  with unusual morphology, tunable porosity and  $\text{TiO}_2$ -carbon nanocomposites will undoubtedly bring interesting surface and conductivity properties to improve the performance of as-modified  $\text{TiO}_2$  electrode in LiB.

## Experimental part

Titanium(IV) chloride ( $\text{TiCl}_4$ ) and dichloromethane ( $\text{CH}_2\text{Cl}_2$ ) were purchased from Acros (France), all the other reagents were of analytical grade. Dichloromethane was freshly distilled over  $\text{P}_2\text{O}_5$  before used. Aerogel of nano-fibrillated cellulose (NFC) was prepared by freeze-drying from ter-butanol solvent exchanged suspensions according to the procedure previously described;<sup>10</sup> it was dried for 3 days in an oven at 80 °C just before use. All manipulations with  $\text{TiCl}_4$  and dried nanocellulose aerogel were performed in a glove box under nitrogen atmosphere (<10 ppm of water).

### *Instrumentation.*

The X-ray powder diffraction (XRPD) patterns of the samples were recorded using a diffractometer (Philips X'Pert Pro, Netherlands). Raman spectra were obtained using Horiba LabRAM ARAMIS, Japan, with excitation wavelength of 633nm. Transmission electronic microscopy (TEM) images were recorded using JEOL 1200 EXII, JEOL, Japan, and scanning electronic microscopy (SEM) images were obtained with an Hitachi S-4800, Canada. Energy dispersive X-ray analysis (EDAX) was done using the EDAX attachment (Oxford Instruments, UK) of the SEM system.  $\text{N}_2$ -physisorption isotherms were obtained at 77 K using Micromeritics Tristar, USA. The samples were outgassed for 12 h at 150 °C under vacuum (2 Pa). The pore size distribution was calculated from the desorption branch using the BJH method. Thermogravimetric analyses (TGA) were obtained using Netzsch Simultaneous Thermal Analyser STA 409 PC Luxx and Setaram Labsys TGA-DSC. All electrochemical characterizations were performed in coin cells at room temperature on an MPG2 instrument from BioLogic by using CR2032-type coin cells. All electrodes were composed of the active material (about 80 % by weight, w/w), acetylene black (8 % w/w, Y50A) and carboxymethylcellulose (12 % w/w, Sigma-Aldrich). After stirring in water, the mixture was spread uniformly at 150  $\mu\text{m}$  onto a copper current collector using a 3540 bird film applicator from Elecometer. Lithium metal disks were used both as reference and counter electrodes, and Whatman glass fibres filters were used as separator. The electrolyte was 1 M  $\text{LiPF}_6$  in a 1:1:3 solution of ethylene carbonate, propylene carbonate and dimethylcarbonate with 5 % fluoroethylene carbonate and 1 % vinylene carbonate. All electrochemical analyses were done by taking into account the mass of  $\text{TiO}_2$ . For galvanostatic measurements, the cells were cycled at C/20 between 2.5 and 1.2 V. For cyclic voltammetry, all cells were cycled at various scan rates ranging from 0.1 to 5 mV s<sup>-1</sup> (0.10, 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, 2.00, 3.00, 4.00, 5.00). All calculations based on cyclic voltammetry were done by using procedures described in the literature.<sup>16, 59, 63, 65</sup>

*Preparation of  $\text{TiO}_2@\text{NFC}$ .* In the Teflon liner of an autoclave, nanocellulose (0.60 g, 11.5 mmol assuming that NFC is 100% pure cellulose) is immersed in a solution of titanium tetrachloride (1.50 g, 4.56 mmol) in dichloromethane (30ml). The autoclave is then kept in an oven at 85 °C for 6 days. After cooling, the resulting black popcorn-like foam

is washed with dichloromethane (3x30 mL of anhydrous dichloromethane); the resultant solid ( $\approx 0.9$  g) is labeled as  $\text{TiO}_2@\text{NFC}$ .

#### *Preparation of calcined samples $\text{TiO}_2\text{-NT-600}$ and $\text{TiO}_2\text{-NT-900}$*

Part of  $\text{TiO}_2@\text{NFC}$  was calcined at 600 °C for 1 hr with a ramping rate of 5 °C min<sup>-1</sup> leading to the sample  $\text{TiO}_2\text{-NT-600}$ . Part of  $\text{TiO}_2@\text{NFC}$  was calcined at 900 °C for 15 min with a ramping rate of 10 °C min<sup>-1</sup> leading to the sample  $\text{TiO}_2\text{-NT-900}$ .

#### *Preparation of pyrolyse samples $\text{TiO}_2@\text{C-600}$ and $\text{TiO}_2@\text{C-900}$ .*

Part of  $\text{TiO}_2@\text{NFC}$  was pyrolyzed at 600 °C for 1 hr with a ramping rate of 5 °C min<sup>-1</sup> leading to the sample  $\text{TiO}_2@\text{C-600}$ . Part of  $\text{TiO}_2@\text{NFC}$  was pyrolysed at 900 °C for 15 min with a ramping rate of 10 °C min<sup>-1</sup> leading to the sample  $\text{TiO}_2@\text{C-900}$ .

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## Supporting Information

The reader will find in SI the TGA analysis of  $\text{TiO}_2@\text{NFC}$ , RAMAN spectrum of the samples after thermal treatment, Table 1 Porosimetry measurement of sample after thermal treatment, SEM images of NFC before any treatment and of  $\text{TiO}_2\text{-NT 900}$  and HRTEM image of elongated nano-crystal of  $\text{TiO}_2$  anatase in  $\text{TiO}_2\text{-NT900}$ . This material is available free of charge via the Internet at <http://pubs.acs.org>.

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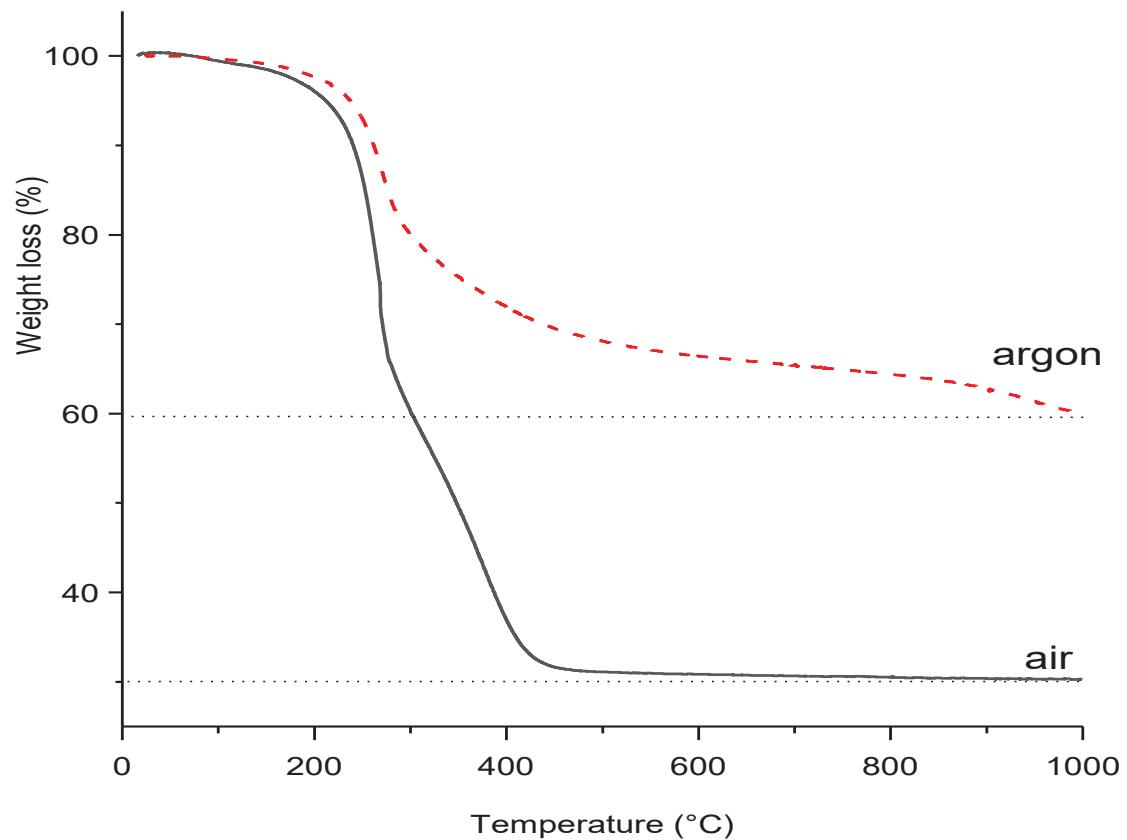
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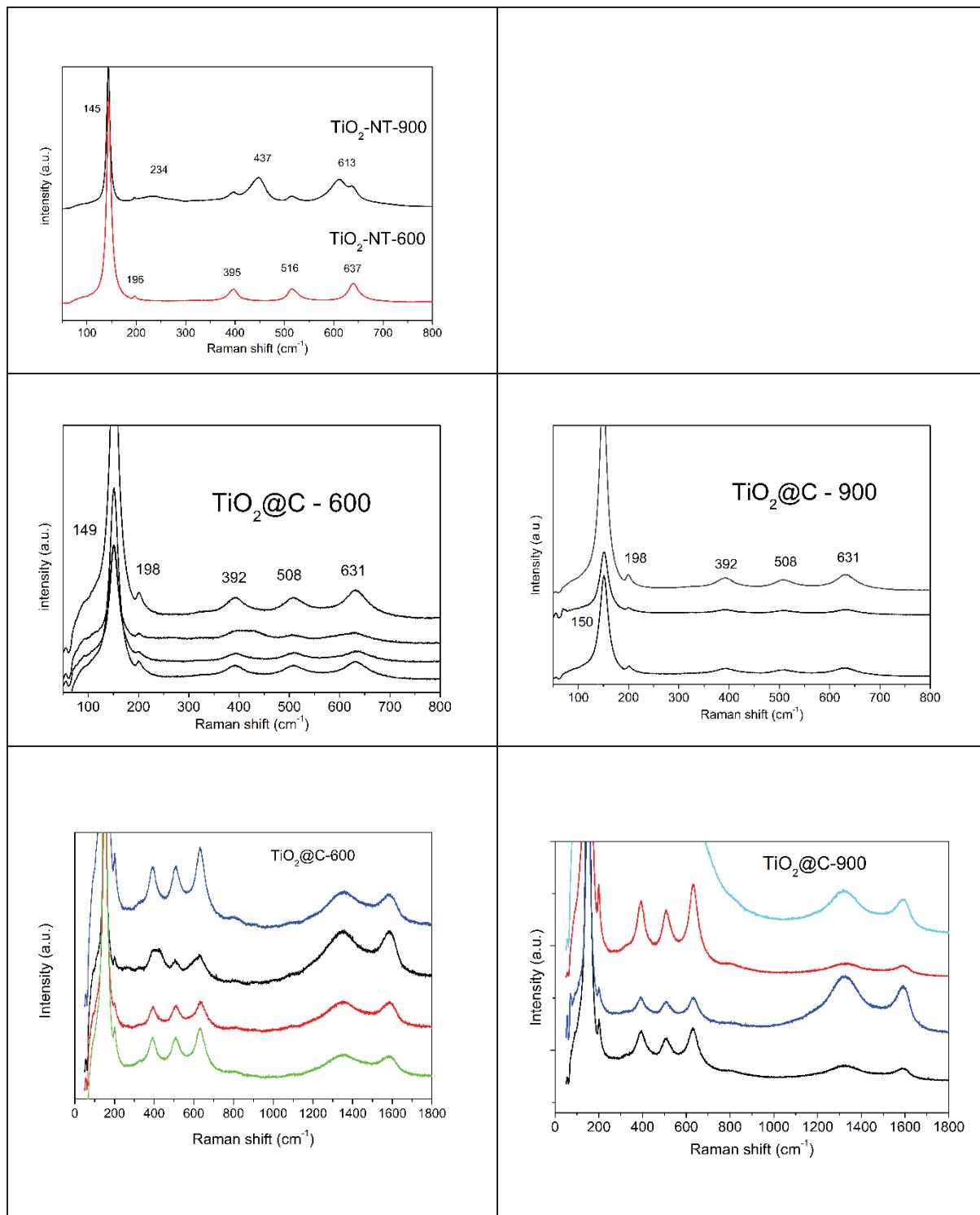
## Supporting information

Figure SI 1



TGA analysis of  $\text{TiO}_2@\text{NFC}$

**Figure SI 2**

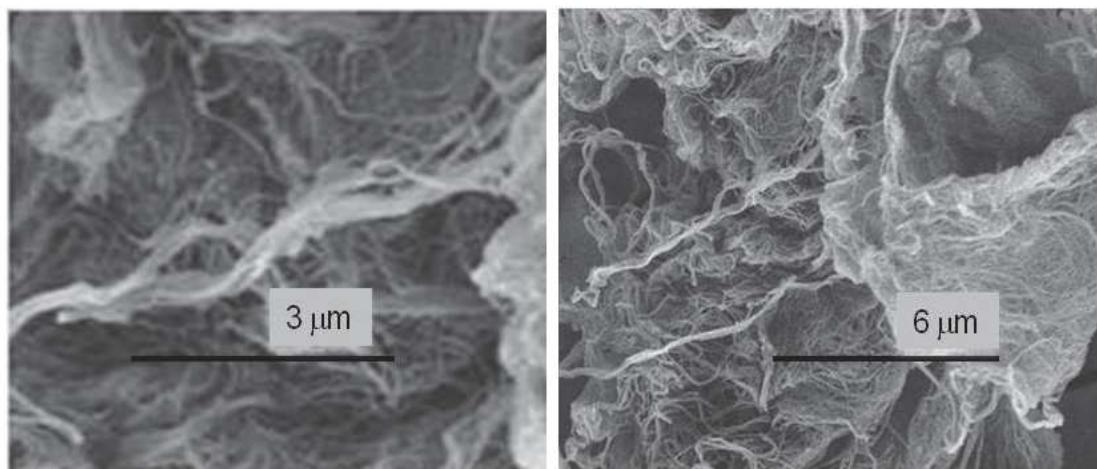


Raman spectra of the samples after thermal treatment

**Table SI 1** : porosimetry measurement of samples after thermal treatment

|                          | BET surface area<br>(m <sup>2</sup> g <sup>-1</sup> ) | Mean pore Ø<br>(nm) | Crystallite size by Debye-Scherrer<br>(nm) |
|--------------------------|---|---------------------|--|
| TiO <sub>2</sub> @NFC    | 49  | 18                  | < 5  |
| TiO <sub>2</sub> -NT-600 | 108   | 12                  | 12.3                                       |
| TiO <sub>2</sub> -NT-900 | < 5   |                     | A : 43.3<br>R : 55.3                       |
| TiO <sub>2</sub> @C-600  | 272   | 7                   | 11.0                                       |
| TiO <sub>2</sub> @C-900  | 438   | 5                   | 17.5                                       |

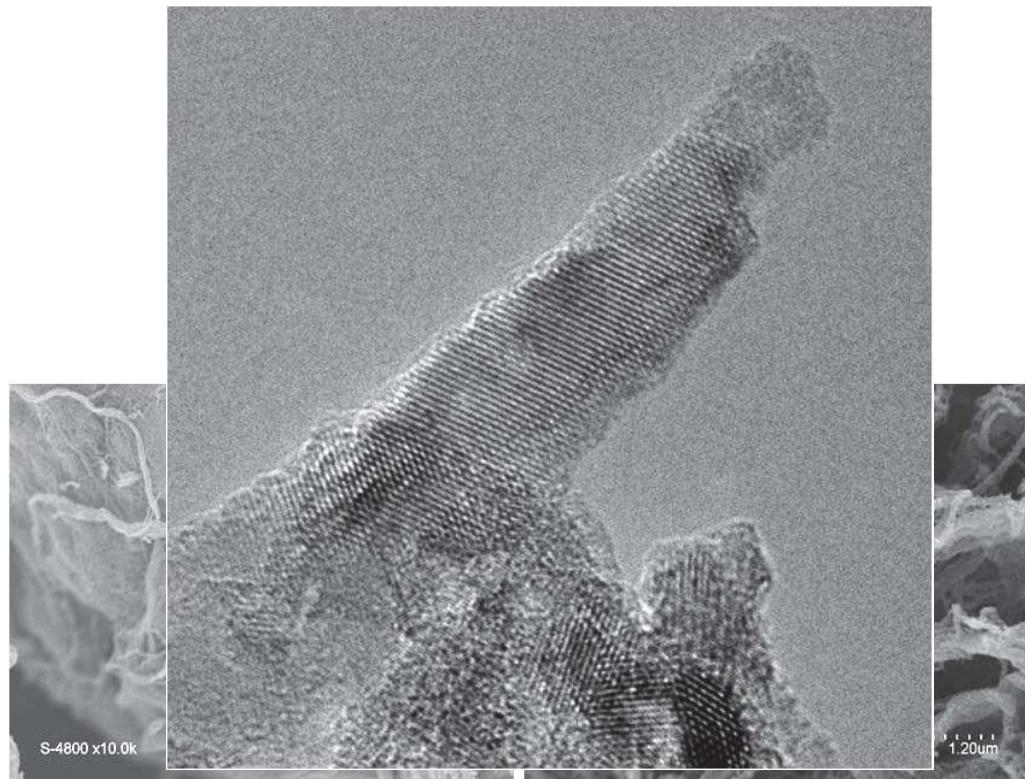
**Figure SI 3**



SEM images of NFC before any treatment

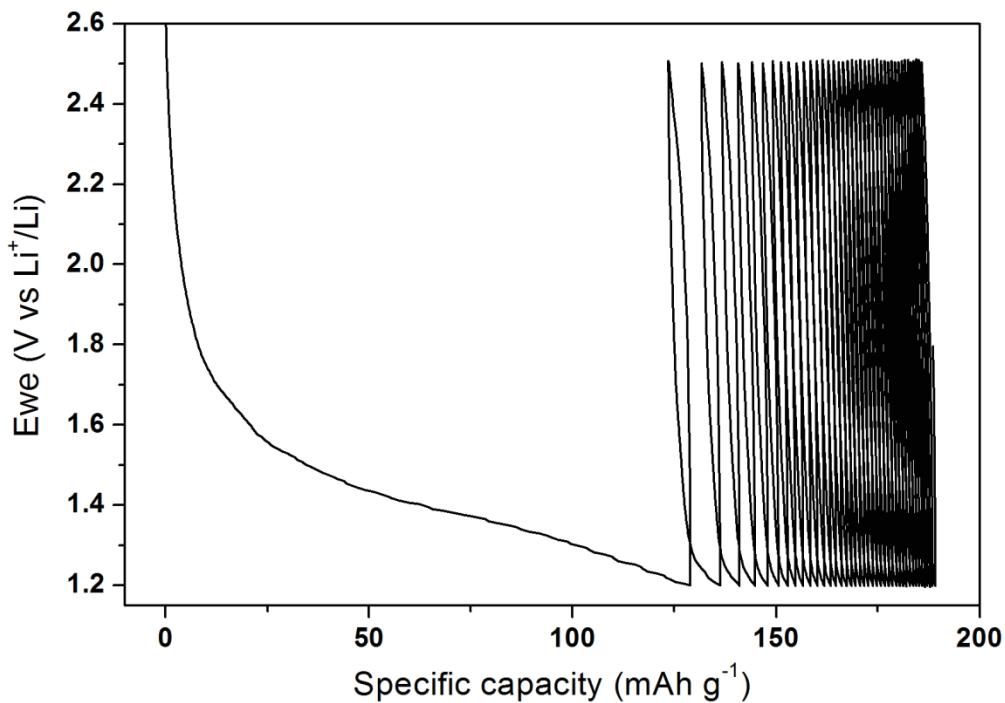
SEM images of TiO<sub>2</sub>-NT 900

**Figure SI 4**



HRTEM image of elongated nano-crystal of TiO<sub>2</sub> anatase in TiO<sub>2</sub>-NT900

**Figure SI 5**



Galvanostatic voltage profiles for a nanoCell@C600/Li half-cell cycled between 2.5 and 1.2 V vs Li<sup>+</sup>/Li with a current density of 20 mA.g<sup>-1</sup>.

#### **IV.5 – On the electrochemical encounter between sodium and mesoporous anatase TiO<sub>2</sub> as Na-ion electrode**

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*CrystEngComm*, 2016, **18**, 4431–4437

Mesoporous anatase titanium dioxide TiO<sub>2</sub> is prepared by an easily up-scalable synthesis protocol, using relatively inexpensive precursors. We demonstrate here that these submicronic anatase TiO<sub>2</sub> crystals show unexpected performances as electrode of Na-ion batteries (NaBs). They exhibit highly stable reversible specific capacities up to 200 mAhg<sup>-1</sup> and excellent cyclability at moderate current rates at an average potential of 1.0 V vs Na<sup>+</sup>/Na. While pseudocapacitance may appear to be the main process driving reactions between sodium ions and TiO<sub>2</sub> during the first discharge above 1 V vs Na<sup>+</sup>/Na, *operando* Raman and X-ray diffraction studies show that TiO<sub>2</sub> anatase structure is nearly entirely lost below 0.25 V vs Na<sup>+</sup>/Na. The subsequent cycling is based on amorphous sodium titanate materials.

#### **Introduction**

Titanium oxides are attractive anode energy materials owing to their versatile redox chemistry, relative abundance and nontoxic nature.<sup>1</sup> In lithium-ion batteries, they are able to deliver a theoretical capacity of 335.6 mAhg<sup>-1</sup> (i.e. one lithium per mole of TiO<sub>2</sub>), which makes it a relevant alternative to Li<sub>4</sub>Ti<sub>5</sub>O<sub>12</sub> that suffers from a limited, though stable, specific capacity of 175 mAhg<sup>-1</sup>.<sup>2</sup> For instance, anatase TiO<sub>2</sub> displays capacities of 160 to 270 mAhg<sup>-1</sup> (0.5 to 0.8 lithium ion in Li<sub>x</sub>TiO<sub>2</sub>) at an average voltage of 1.7 V vs Li<sup>+</sup>/Li.<sup>3</sup> While there is still no consensus on real-life applications of TiO<sub>2</sub> among the Li-ion batteries (LIBs)

community, numerous reports are nonetheless focused on the enhancement of its performances as anode of Li-ion systems.<sup>4</sup> Considering its encouraging capacities in LIBs, studying titanium dioxide as anode for NaBs seems to be quite logical.<sup>5, 6, 7-12, 13-16</sup> Indeed post-LIB era recently started, emerging from the concerns about lithium resources. As a candidate of choice for lithium replacement, sodium is a current research focus. While, to some extent, the knowledge about lithium-based cathodes can be transposed to their sodium-based counterparts,<sup>17</sup> such assumption is not true for anodes. Indeed, graphite does not intercalate sodium, hence the recent interest regarding anode materials for NaBs.<sup>18</sup> Other carbon morphologies have also been proposed for sodium storage at the anode, mostly hard carbons that, once heat treated at 1100 °C, can exhibit a sodiation capacity up to 300 mAh g<sup>-1</sup>.<sup>19</sup> Nevertheless, high irreversible capacities are a major roadblock, and titanium dioxide remains an alternative.

Different characteristics can be excerpted from the few reports on TiO<sub>2</sub>/Na published up to now: (i) the first discharge is drastically different from the subsequent cycles, (ii) capacities are limited to 150-200 mAh g<sup>-1</sup>, and (iii) the mechanism of Na-insertion cannot be rationalized by examining the lithium one. According to the literature, sodium ions interact only with the TiO<sub>2</sub> grain surface, and thus the surface area might be the key to improve properties.<sup>20</sup> Nevertheless few results tend to demonstrate that sodium may be incorporated within the TiO<sub>2</sub> structure.<sup>8, 21</sup> In a recent review,<sup>18</sup> it is shown that only nanosized TiO<sub>2</sub> appears to be efficient as negative electrode for NaBs, due to the shortening of migration length. However, we demonstrate here that submicronic TiO<sub>2</sub> works very well versus Na, and can even show specific capacity among the highest reported to date for this material, which can be ascribed to the low diffusion barrier in this oxide.<sup>21</sup> Moreover, *operando* study of the electrochemical behaviour of TiO<sub>2</sub> using Raman and XRD confirms the mechanism of the reaction between sodium and TiO<sub>2</sub> anatase recently proposed.<sup>15</sup>

## Experimental

### Synthetic procedures.

Titanium tetraisopropoxide (TTIP; Sigma-Aldrich), absolute ethanol and acetic acid (VWR Chemicals) were used as received. TTIP (0.032 mol) and glacial acetic acid (0.016 mol) were dissolved in 20 mL absolute ethanol and stirred for 12 hrs. Afterwards, the solution was added dropwise to 100 mL deionized water under vigorous stirring, and subsequently aged for 1 hr. The powder was isolated by centrifugation at 11'000 rpm for 15 min, vacuum dried overnight at 100 °C and calcined in air at 400 °C for 1 hr to yield mesoporous TiO<sub>2</sub> (TiO<sub>2</sub>-C400), results confirmed by chemical analysis (Tables S1 and S2, Figure S1).

### Materials and methods.

The thermal behaviour of the anatase precursor has been investigated by thermogravimetric analysis (TGA) under air on a Setaram LabSys instrument from 25 to 600 °C (5 °C·min<sup>-1</sup>). Raman spectra were obtained using a Horiba LabRAM ARAMIS spectrometer at 633 nm. X-ray diffraction (XRD) experiments have been carried out on a PANalytical Empyrean diffractometer (Cu K $\alpha$  source) on powder samples. Scanning electronic microscopy (SEM) was carried out on a Hitachi S4800 FE-SEM (voltage 5 kV). Transmission electron microscopy (TEM) images were recorded using a JEOL 1200 EXII electron microscope. Energy dispersive X-ray analysis (EDX) was done using the EDAX attachment (Oxford Instruments) of the SEM system. X-ray photoelectron spectroscopy (XPS) measurements have been carried out on a Thermo Electron ESCALAB 250, using a focused monochromatized Al K $\alpha$  radiation ( $h\nu = 1486.6$  eV). The analysed area of the samples was 400  $\mu\text{m}^2$ , and the binding energy scale was calibrated by the hydrocarbon C 1s peak at 285.0 eV. N<sub>2</sub> physisorption isotherms were collected at 77 K on a Micromeritics TriStar after a 2 hr-evacuation at 80 °C. Temperature-programmed desorption of NH<sub>3</sub> (TPD-NH<sub>3</sub>) was performed with a Micromeritics AutoChem 2910 instrument under helium flow (30 mL min<sup>-1</sup>) from 100 to 600 °C at a 10 °C min<sup>-1</sup> rate; the sample was initially evacuated for 2 hrs at 80 °C, then placed under ammonia gas for 1 hr at 100 °C. All electrochemical characterizations were performed in CR2032 coin cells at room temperature on an MPG2 instrument from BioLogic. All electrodes were composed of the active material

(80 wt.%), acetylene black (8 wt.%) and carboxymethylcellulose (12 wt.%), and prepared as follows: after stirring in water, the mixture was tape casted uniformly at 150 µm onto a copper current collector (17.5 µm, 99.9 %, GoodFellow) using a 3540 bird film applicator from Elcometer, and subsequently dried at room temperature. Electrodes were cut with a disk puncher (12 mm diameter). The chemical composition of the electrode is provided as supporting information (Tables S1 and S3, Figure S2). Sodium metal disks were used both as reference and counter electrodes. The electrolyte was 1 M NaClO<sub>4</sub> in propylene carbonate with 5 % fluoroethylene carbonate, and Whatman glass fibres filters were used as separator.

#### ***Operando* Raman and XRD measurements.**

Electrochemical measurements were conducted under *operando* conditions on a Raman spectrophotometer and on X-ray diffractometer (*vide infra*), with a dedicated electrochemical cell.<sup>22</sup> The cell was adapted with a beryllium window for XRD measurements,<sup>22</sup> and a with a quartz window for Raman spectroscopy,<sup>23</sup> as already reported. Electrode preparation was done by replacing carboxymethylcellulose with PTFE in order to obtain a self-supported film.

## **Results and discussion**

### **About titanium dioxide synthesis and characterization.**

Mesoporous anatase TiO<sub>2</sub> was prepared by a simple hydrolytic sol-gel method. TTIP and glacial acetic acid are mixed with ethanol. An esterification reaction takes place between the alcohol and the acid, slowly releasing water that leads to slow hydrolysis and to formation of hydroxide species, which can polymerize to yield Ti-O-Ti chains. This step ensures three-dimensional polymeric skeletons with close packing, a feature that is required for the formation of anatase nanocrystals.<sup>24</sup> The subsequent hydrolysis upon addition onto water under vigorous stirring gives rise to polycondensation of Ti-O-Ti networks. It finally yields closely packed first-order particles via a three-dimensionally developed gel skeleton (Figure S3). The control of aging time, hydrolysis rate, and calcination temperature is important to obtain high surface areas and narrow pore size distribution.<sup>25</sup> Figure 23 shows the TGA/DTA curves for the as-prepared sample. The first weight loss of approx. 30 % in the range 25-200 °C, centred on an endothermic peak at 120 °C, is attributed to the loss of solvent and adsorbed water. In the range 200-400 °C, there is a second weight loss of approx. 10 %, which may correspond to the condensation of hydroxyl groups linked to titanium. This second step happens simultaneously with the crystallization of amorphous TiO<sub>2</sub> that can be associated with an exothermic peak appearing around 322 °C. The calcination temperature of 400 °C has been chosen according to those TGA results, as no weight loss can be noticed above 400 °C.

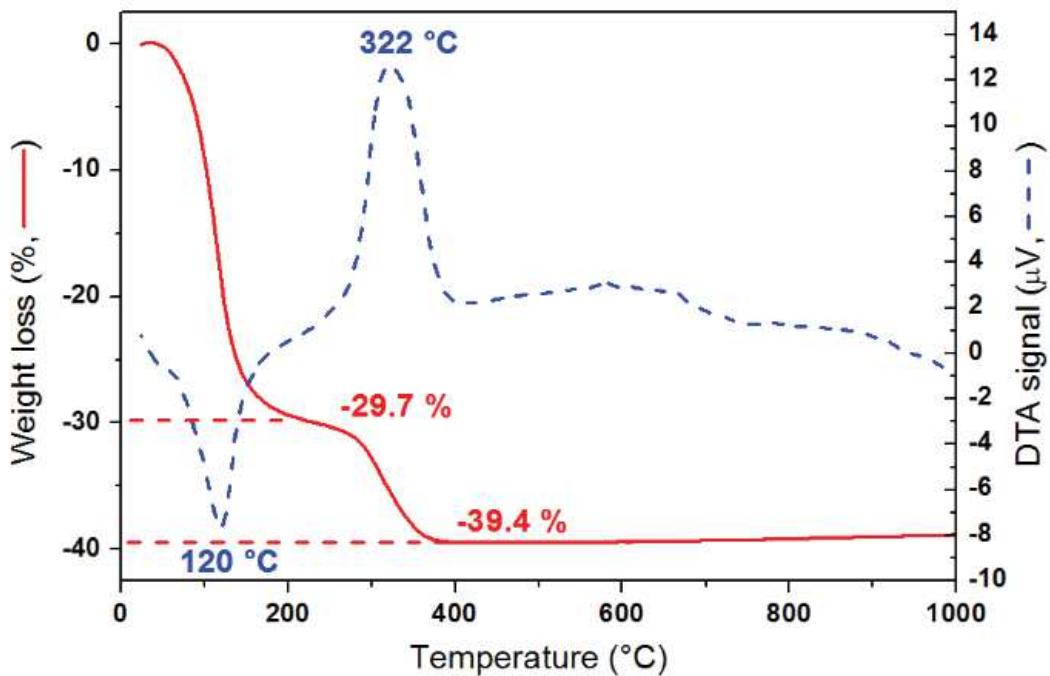


Figure 23. Thermogravimetric analysis of the as-prepared  $\text{TiO}_2$  powder precursor.

As displayed on Figure 24a, the Raman spectrum of  $\text{TiO}_2\text{-C}400$  is characteristic of the anatase phase.<sup>26</sup> XRD (Figure 24b) confirms that after calcination at 400 °C, the amorphous pristine material is converted to crystalline anatase  $\text{TiO}_2$ , as shown by the intense peaks at  $2\theta = 25.1^\circ, 37.8^\circ, 47.9^\circ, 54.0^\circ, 54.8^\circ$  and  $62.5^\circ$ , corresponding to (011), (004), (020), (015), (121) and (024)  $hkl$  planes, respectively (ICSD #9855). This result is supported by the profile refinement of the XRD data, in good agreement with the anatase phase (Figure S4, Table S4). Both Raman and XRD emphasize the absence of other crystalline impurities, a result further confirmed by EDX and XPS studies (Figure S1, Tables S1 and S2). The crystal size of  $\text{TiO}_2\text{-C}400$  is about 10 nm, from the Scherrer formula.

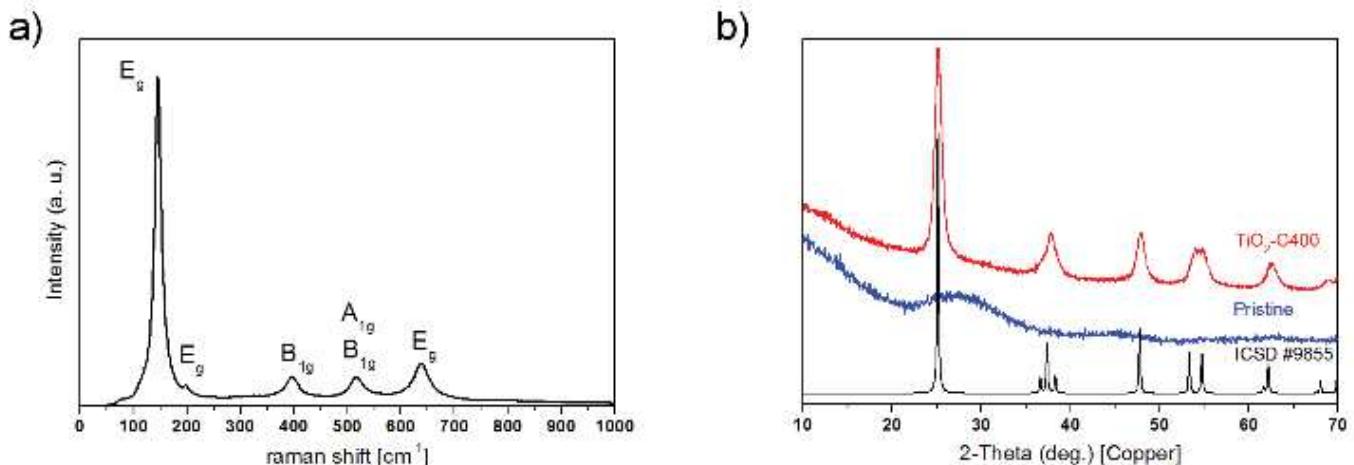


Figure 24. Raman spectrum of TiO<sub>2</sub>-C400 (a), and XRD patterns of the as-prepared precursor and TiO<sub>2</sub>-C400. The ICSD #9855 theoretical pattern is shown for comparison.

On the SEM image of TiO<sub>2</sub>-C400 (Figure 25a), the powder is composed of sponge-like aggregates, with various sizes from 50 to 400 nm, made up of self-assembled 10-nm nanoparticles, a result in good accordance with XRD. TEM image of the as-prepared sample evidences the non-crystalline nature of the product and shows closely packed first-order particles via a three-dimensionally developed gel skeleton, while TEM images of TiO<sub>2</sub>-C400 confirms results obtained by SEM in terms of size and morphology (Figure S3). The mesoporous architecture suggested by SEM and TEM is further confirmed by the N<sub>2</sub> sorption measurements. The representative isotherms and BJH pore size distribution of TiO<sub>2</sub>-C400 are presented in Figure 25b. The sorption curves present type H3 characteristics, and the hysteresis loop in the desorption isotherm between relative pressures P/P<sub>0</sub> of 0.45 and 0.9 are stemming from the condensation of the adsorbate within the framework-confined mesopores. The BET surface area is 97.6 m<sup>2</sup> g<sup>-1</sup>, with a narrow pore size of 4.0 nm.

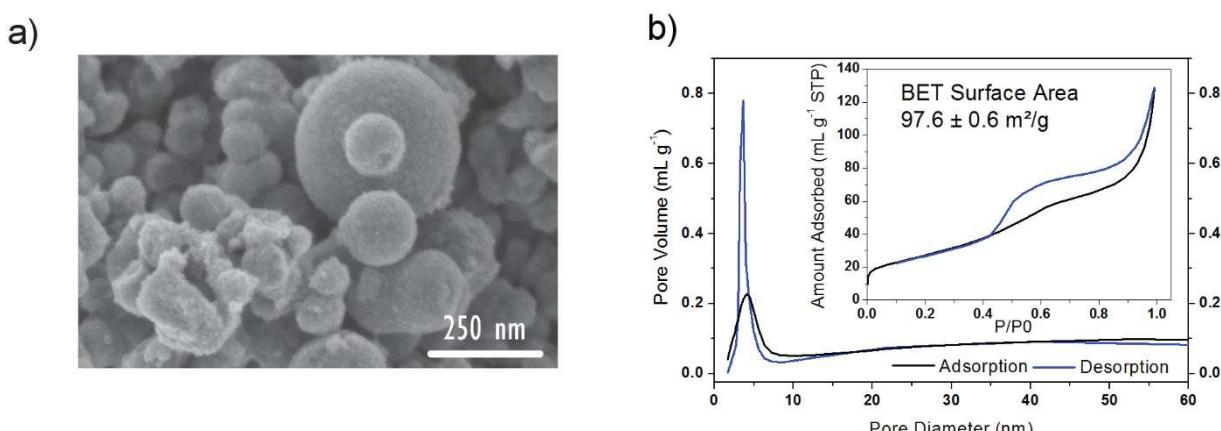


Figure 25. SEM images of TiO<sub>2</sub>-C400 (a) and BJH pore volume curves (b). The insert below displays the volume of adsorbed amount of N<sub>2</sub> as a function of the relative pressure.

#### About electrochemical properties.

Close inspection of the voltage profiles found in the recent literature seems to reveal that the sodium insertion process into anatase TiO<sub>2</sub> is drastically different from the well-known lithium one.<sup>5, 6, 7-11, 13, 14</sup> In most studies devoted to TiO<sub>2</sub>/Li, a limited 3.0-1.2 V vs Li<sup>+</sup>/Li potential window seems to be required for a reversibility of the lithium insertion mechanism. Briefly, used as an anode material in LIBs, it shows three

different major storage mechanism: (i) a rapid potential drop to ca. 1.7 V vs. Li<sup>+</sup>/Li characteristic of the formation of a solid-solution Li <sub>$\epsilon$</sub> TiO<sub>2</sub>, where  $\epsilon$  depends on particle size.<sup>27</sup> (ii) a two-phase reaction between the tetragonal Li <sub>$\epsilon$</sub> TiO<sub>2</sub> and the orthorhombic lithium titanate Li<sub>0.5± $\delta$</sub> TiO<sub>2</sub> inducing a constant-voltage plateau around 1.7 V followed by (iii) another two-phase reaction up to 1 V towards rock-salt-type tetragonal LiTiO<sub>2</sub>.<sup>28</sup> The irreversibility of the latter mechanism is usually overcome through nanostructuration of the electrode material, which induces a monophasic reversible pseudo-capacitive interfacial storage.<sup>3</sup> To identify the electrochemical mechanism without any kinetics constraint, a TiO<sub>2</sub>/Na half-cell was studied under galvanostatic intermittent titration conditions. Sodium was inserted for 1 hr at C/20 (where C is set at 335.6 mAhg<sup>-1</sup> for a 1-e<sup>-</sup>/h process) followed by 100 hrs of open-circuit relaxation. This process was continued until full sodiation occurred. The first discharge (Figure 26a) displays a plateau around 0.3 V, suggesting a two-phase reaction, and delivers a specific capacity of more than 400 mAhg<sup>-1</sup>, which is above the theoretical capacity of TiO<sub>2</sub> for a 1-e<sup>-</sup> process. The subsequent charge up to 2.5 V demonstrates, for the first time, that almost 1 Na<sup>+</sup> ion could be de-inserted out of the material.

The as-prepared nanocrystals of TiO<sub>2</sub>-C400 were tested as electrode (please refer to the experimental section for electrode preparation) of Na battery in coin cells. The galvanostatic charge-discharge profiles at a current rate of C/20 of the first, second, fifth and fiftieth cycles for TiO<sub>2</sub> versus Na between 2.5 and 0.01 V are shown in Figure 26b. First of all, the overall features of the galvanostatic curves are similar to the previous one obtained under GITT conditions, except that the reversible specific capacity is limited to 200 mAhg<sup>-1</sup>, compared with more than 300 mAhg<sup>-1</sup> in GITT. In details, the first discharge curve displays a shoulder at 1.0 V, accounting for approximately 0.06 Na per TiO<sub>2</sub> (20 mAhg<sup>-1</sup>), followed by a plateau around 0.25 V. The first insertion phenomenon at 1.0 V may be related with the capacitive interaction between sodium and the titanium surface sites. As derived from the TPD-NH<sub>3</sub> measurements, the surface of TiO<sub>2</sub>-C400 is covered with 0.06 mol of Ti<sup>4+</sup> acidic sites per mole of TiO<sub>2</sub>, acidic sites where sodium may preferentially react (Figure S5). This surface interaction is in good accordance with the electrochemical insertion of 0.06 Na ion per mole of TiO<sub>2</sub>. The subsequent sodium insertion, up to 0.01 V, leads to a specific capacity of 325 mAhg<sup>-1</sup>, close to the theoretical one, and suggests a two-phase reaction. The first cycle shows a coulombic efficiency of 63.5 %. Second and following charge-discharge cycles deliver a reversible specific capacity of 200 mAhg<sup>-1</sup> at an average voltage close to 0.85 V vs Na<sup>+</sup>/Na.

A TiO<sub>2</sub>-C400/Na half-cell can sustain a specific capacity of 200 mAhg<sup>-1</sup> at a current density of C/20 for 100 charge-discharge cycles between 2.5 and 0.01 V (Figure 26c). Interestingly, when cycled at the higher current density of C, the capacity is limited to 100 mAh g<sup>-1</sup> after the first discharge, then increases during the first fifty cycles and reaches 165 mAhg<sup>-1</sup>, a value close to the one obtained at C/20 (Figure 26c). The specific capacity obtained at C/20 is systematically resumed after being cycled at higher C/10, C and 2C rates (Figure 26d), and the specific capacity at 2C is still above 100 mAhg<sup>-1</sup>.

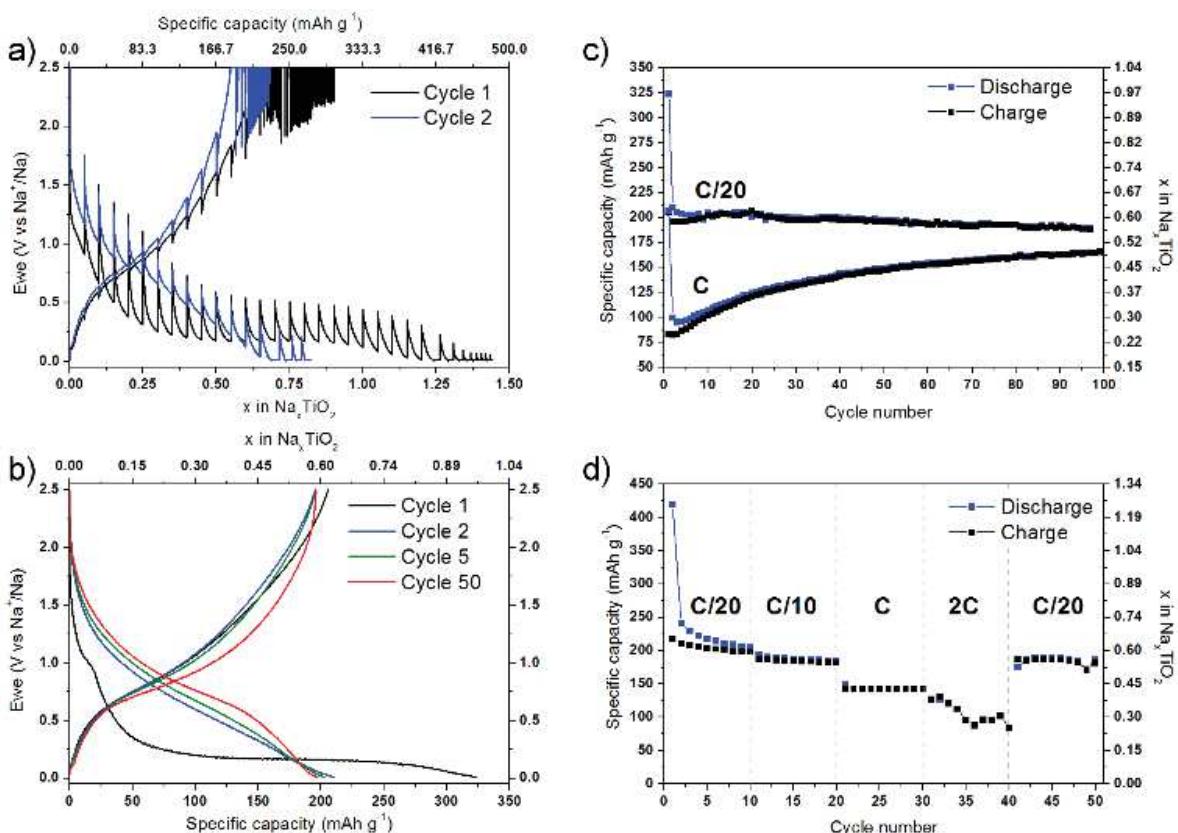


Figure 26. Galvanostatic intermittent titration technique (a), galvanostatic voltage profiles (b), charge-discharge cyclability at C and C/20 (c) for TiO<sub>2</sub>-C400, and at increasing current densities (d) for TiO<sub>2</sub>-C400.

#### About electrochemical mechanism.

In order to go further into details in the reaction mechanism of mesoporous anatase TiO<sub>2</sub> with Na ions, the first reduction (i.e. discharge) was investigated by *operando* Raman and XRD measurements (Figure 27). At the end of the open circuit relaxation, at a voltage higher than 2.0 V vs Na<sup>+</sup>/Na, the presence of the anatase phase is evidently displayed on the Raman spectrum (Figure 27a), from the peaks at 145, 398, 513, and 640 cm<sup>-1</sup>.<sup>26</sup> These clear features slowly disappear during the first discharge, and the Raman spectrum at the end of the reduction is characteristic of amorphous titanates. In particular, the Raman bands occurring in the region between 200 and 400 cm<sup>-1</sup> are overlapped to a broad spectral bump, which can be attributed to a density of vibrational states. The presence of this feature reflects the disordered nature of the nanostructures obtained under reducing conditions.<sup>29</sup> This result is even clearer when the electrode is kept at 0.01 V vs Na<sup>+</sup>/Na for 2 hr (Figure S6). In comparison with other reported data,<sup>15</sup> the *operando* conditions used in the present study allows for a detailed measurement, exempt from any relaxation. The broad peaks present at 277, 445, and 670 cm<sup>-1</sup> may be representative of the formation of a sodium titanate phase.<sup>29-31</sup> The band at 276 cm<sup>-1</sup> corresponds to the Na-Ti-O lattice modes of the Na<sub>2</sub>O-TiO<sub>2</sub> glass, and the peaks at 445 and 670 cm<sup>-1</sup> are attributed to Ti-O-Ti stretching bonds.<sup>30</sup> The peak centred on 217 cm<sup>-1</sup> may be related with the presence of sodium oxide Na<sub>2</sub>O,<sup>32</sup> a by-product of the electrochemical reduction of anatase TiO<sub>2</sub> versus sodium.

During *operando* XRD measurement, the intensity of the main *hkl* peak of anatase TiO<sub>2</sub>, namely (011), slowly decreases (Figure 27b). The fact that the anatase signature remains detectable during the galvanostatic discharge likely arises from inhomogeneous electrode reactions. Some parts of the TiO<sub>2</sub>-C400 formulated electrode may be left unchanged, while amorphisation occurs when sodium reacts with titanium dioxide under reducing conditions. This is further emphasized at the end of the second discharge; the anatase signal completely disappears (Figure S6).

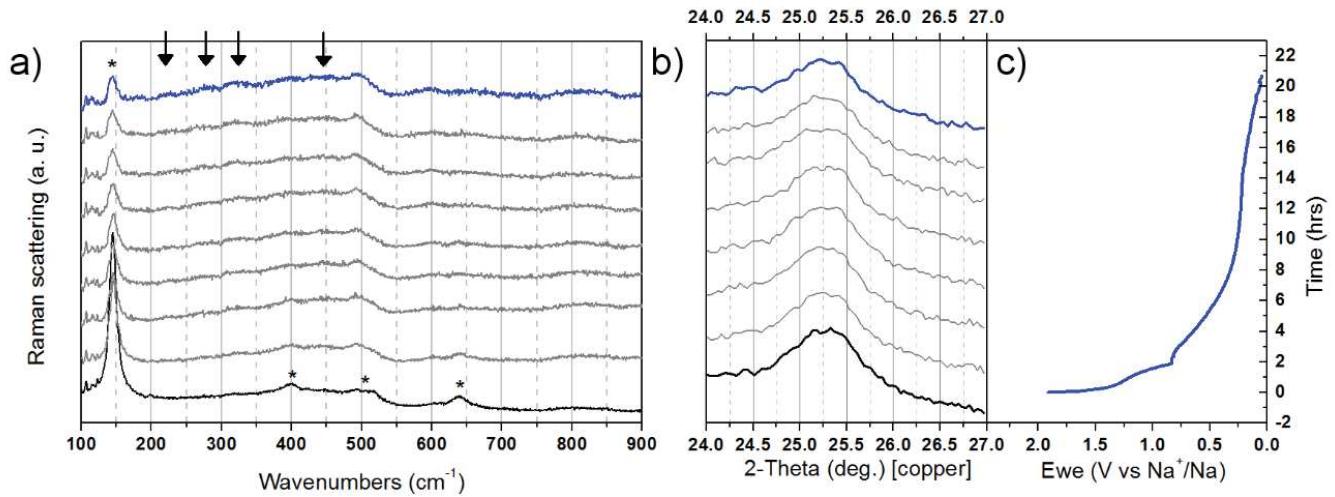


Figure 27. *Operando* Raman (a) and XRD (b) measurements under galvanostatic regime at C/20 rate of TiO<sub>2</sub>/Na cell. The star \* on the Raman spectra indicates the presence of anatase TiO<sub>2</sub>, and the arrows indicate specific regions (please refer to the text). The corresponding galvanostatic curve is displayed (c).

## Conclusions

Mesoporous anatase TiO<sub>2</sub> was prepared by a simple hydrolytic sol-gel technique and displays reversible specific capacities as high as 200 mAhg<sup>-1</sup> (0.6 Na in Na<sub>x</sub>TiO<sub>2</sub>) at a current density of C/20 and 165 mAhg<sup>-1</sup> at a C rate. As reported in Table 3, this mesoporous TiO<sub>2</sub>/Na cell presents high and interesting electrochemical performances among the best reported to date in terms of capacity, cyclability, and low irreversibility on the first cycle. Moreover, the working potential of this TiO<sub>2</sub>/Na half-cell is unlimited (2.5–0.01 V), while the TiO<sub>2</sub>/Li system is able to cycle only on a restricted 2.5–1.2 V potential window to avoid irreversible reduction processes on discharge at low potential. This unlimited potential window for TiO<sub>2</sub> in NaB guarantees a greater voltage of the full cell assembly. These performances are at least partly related to the surface properties, as suggested by other authors, and the mechanism behind sodium storage into anatase TiO<sub>2</sub> is hereby confirmed by means of *operando* experiments. The mechanism which takes place in NaB is far from the three steps mechanism in LiB.<sup>3</sup> Since long range atomic order is drastically modified, it seems essential to go towards local environment probes such as X-ray absorption spectroscopy or neutron PDF in order to unravel the sodium behaviour in contact with titanium dioxide at the local scale.

Table 3.  $\text{TiO}_2/\text{Na}$  properties excerpted from the recent literature.

| Ref.          | $S_{\text{BET}}$<br>( $\text{m}^2 \text{ g}^{-1}$ ) | Avg. Pore<br>diameter<br>(nm) | Crystal phase             | Crystal<br>size<br>(nm) | Specific<br>capacity<br>( $\text{mA h g}^{-1}$ ) | Current<br>rate<br>( $\text{mA g}^{-1}$ ) | Voltage<br>range (V<br>vs<br>$\text{Na}^+/\text{Na}$ ) |
|---------------|---|-------------------------------|---------------------------|-------------------------|--|---|--|
| 5             | 45.1  | -                             | Anatase                   | 30                      | 125  | 37  | 2.0-0.1 <sup>a</sup>                                   |
| 16            | 49.2  | -                             | Anatase + ?? <sup>b</sup> | 100                     | 230  | 50  | 2.9-0.1  |
| 13            | 74.9  | 2-10                          | Anatase                   | 10-15                   | 150  | 50  | 2.5-0.01   |
| This<br>study | 97.6  | 4.0                           | Anatase                   | 50-400                  | 200  | 16.8                                      | 2.5-0.01   |
|               |   |                               |                           |                         | 165  | 335.6                                     |  |
| 9             | 136.4   | 2.8                           | Anatase                   | 20-30                   | 155  | 33.5                                      | 2.0-0.01   |
| 11            | 153.3   | 2.20                          | Amorphous                 | -                       | 126  | 170                                       | 3.0-0.1  |
| 13            | 323.2   | <2                            | Anatase + C               | 10-15                   | 125  | 50  | 2.5-0.01   |
| 8             | -   | -                             | Anatase                   | 50-100                  | 180  | 168 <sup>c</sup>                          | 3.0-0.01   |
| 7             | -   | 92                            | Anatase                   | 18                      | 170  | 12.5                                      | 2.6-0.0  |
| 10            | -   | 25                            | Anatase + C               | 10-20                   | 135  | 50  | 3.0-0.01   |
| 14            | -   | -                             | Amorphous                 | -                       | 140  | 50  | 2.5-0.9  |

<sup>a</sup> First two cycles between 2.0 and 0.02 V; <sup>b</sup> the authors did not mention the presence of another phase;  
<sup>c</sup> first discharge at 10  $\text{mA g}^{-1}$

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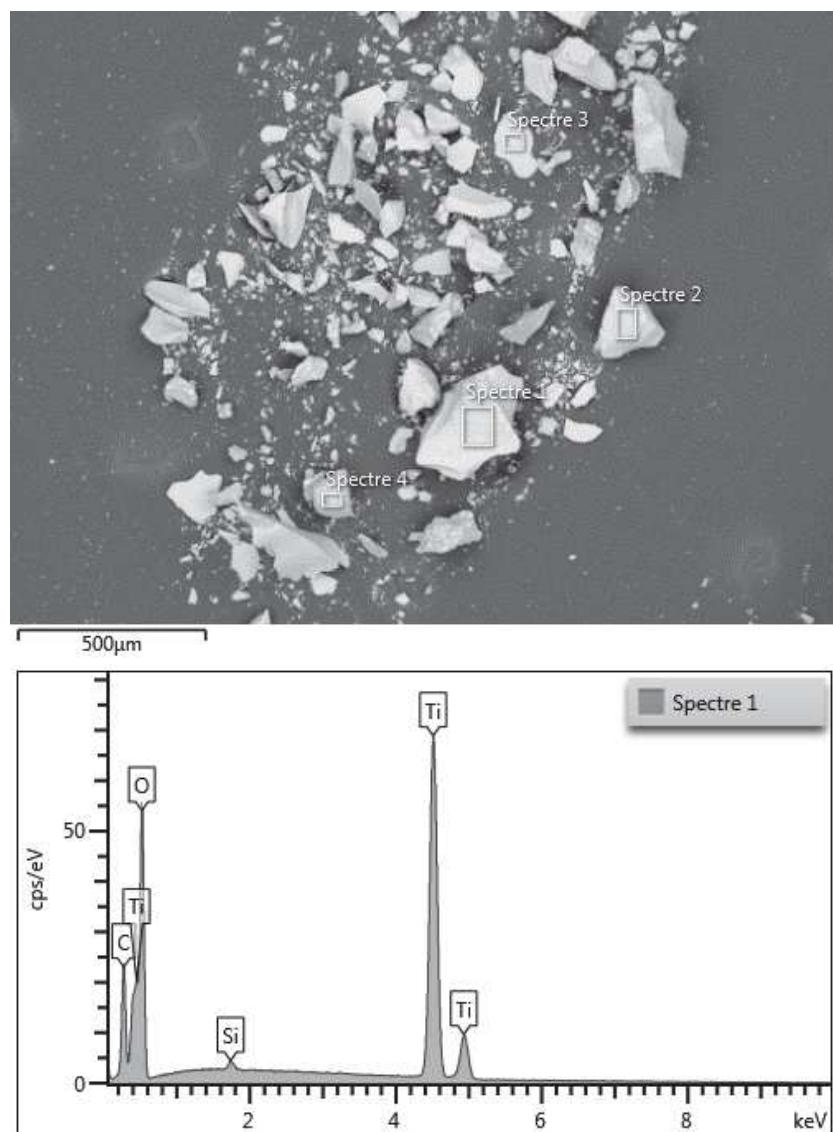
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## Supporting information

**Table S1.** XPS analysis results for both powder and electrode sample of sol-gel TiO<sub>2</sub>.

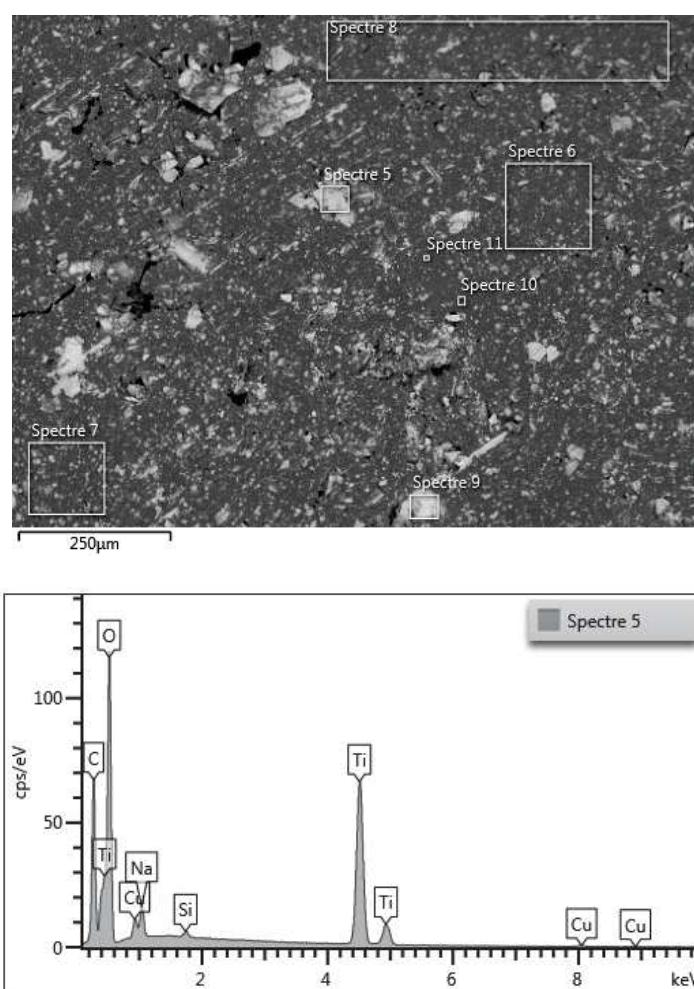
| Element | Powder at.% | Electrode at.% |
|---------|-------------|----------------|
| C 1s    | 33.39       | 51.02          |
| O 1s    | 47.86       | 35.49          |
| Ti 2p   | 18.74       | 0.34           |
| Na 1s   | 0.00        | 13.16          |
| Total:  | 100.00      | 100.00         |



**Figure S1.** SEM image and EDX spectrum of powder sample of sol-gel TiO<sub>2</sub>. The squares represent the areas studied by EDX.

**Table S2.** EDX results for powder sample of TiO<sub>2</sub>.

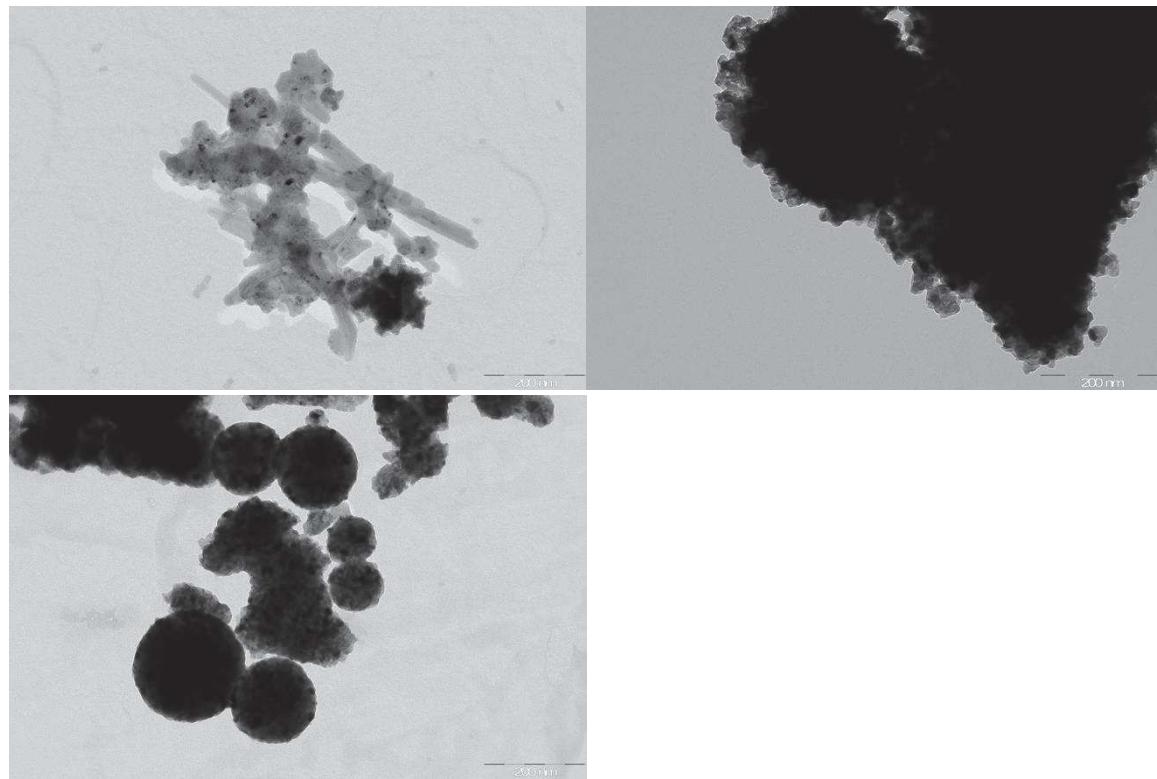
| Element | Wt.%   | At.%   |
|---------|--------|--------|
| O       | 36.93  | 63.59  |
| Si      | 0.32   | 0.31   |
| Ti      | 62.76  | 36.10  |
| Total:  | 100.00 | 100.00 |



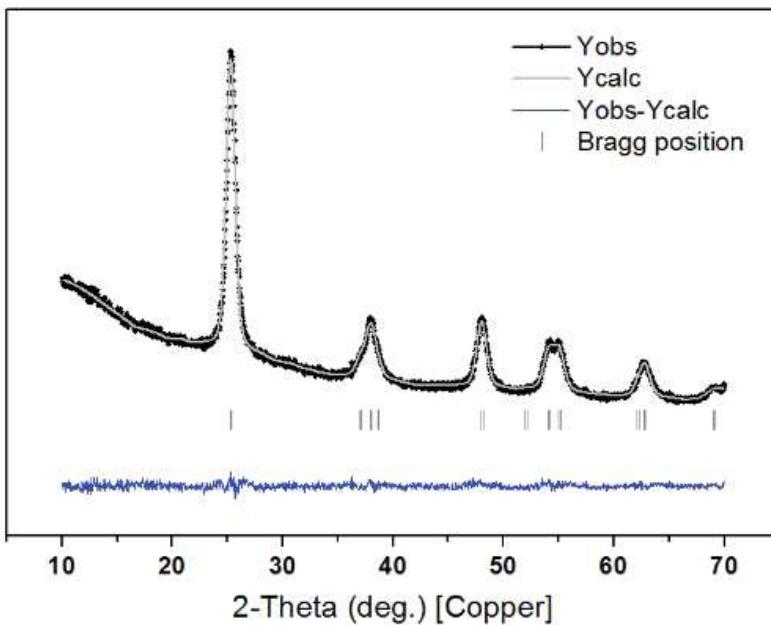
**Figure S2.** SEM image and EDX spectrum of an electrode sample of sol-gel TiO<sub>2</sub>. The squares represent the areas studied by EDX.

**Table S3.** EDX results for electrode sample of TiO<sub>2</sub>.

| Element | Wt.%   | At.%   |
|---------|--------|--------|
| O       | 46.91  | 71.91  |
| Na      | 2.25   | 2.40   |
| Si      | 0.33   | 0.29   |
| Ti      | 46.82  | 23.97  |
| Cu      | 3.68   | 1.42   |
| Total:  | 100.00 | 100.00 |



**Figure S3.** TEM images of sol-gel TiO<sub>2</sub> powder sample before (top image) and after calcination at 400 °C (middle and bottom images).



**Figure S4.** Profile matching result for the XRD pattern of TiO<sub>2</sub>-C400 (experimental points = black squares; simulated pattern = grey line; difference between experimental and simulated points = blue line; Bragg's peaks position = grey marks).

**Table S4.** Profile matching details for TiO<sub>2</sub>-C400.

```
=> Wavelengths: 1.54056 1.54439
==> RESULTS OF REFINEMENT:
-----&
=> Phase No. 1 TiO2 I 41/a m d
-----&
=> No. of reflections for pattern#: 1: 22/2
==> PROFILE PARAMETERS FOR PATTERN# 1
=> Cell parameters :
      3.78721 0.00051
      3.78721 0.00051
      9.47664 0.00146
      90.00000 0.00000
      90.00000 0.00000
      90.00000 0.00000
=> overall scale factor : 0.001000000 0.000000000
=> Eta(p-v) or m(p-vii) : 0.45731 0.00879
=> Overall tem. factor : 0.00000 0.00000
=> Halfwidth parameters : 1.61766 0.10051
      -0.00762 0.00000
      0.82914 0.01193
==> GLOBAL PARAMETERS FOR PATTERN# 1
=> Zero-point: 0.0000 0.0000
=> Cos( theta)-shift parameter : -0.0188 0.0045
=> Sin(2theta)-shift parameter : 0.0000 0.0000
==> RELIABILITY FACTORS WITH ALL NON-EXCLUDED POINTS FOR PATTERN: 1
=> Cycle: 4 => MaxCycle: 15
=> N-P+C: 2301
=> R-factors (not corrected for background) for Pattern: 1
=> Rp: 2.88 Rwp: 3.77 Rexp: 3.37 Chi2: 1.25 L.S. refinement
=> Conventional Rietveld R-factors for Pattern: 1
=> Rp: 16.4 Rwp: 12.1 Rexp: 10.82 Chi2: 1.25
=> Deviance: 0.287E+04 Dev* : 1.247
=> DW-Stat.: 1.0121 DW-exp: 1.8757
=> N-sigma of the GoF: 8.613
==> RELIABILITY FACTORS FOR POINTS WITH BRAGG CONTRIBUTIONS FOR PATTERN: 1
=> N-P+C: 2007
=> R-factors (not corrected for background) for Pattern: 1
=> Rp: 3.14 Rwp: 4.06 Rexp: 3.58 Chi2: 1.29 L.S. refinement
=> Conventional Rietveld R-factors for Pattern: 1
=> Rp: 13.9 Rwp: 11.5 Rexp: 10.12 Chi2: 1.29
=> Deviance: 0.257E+04 Dev* : 1.278
=> DW-Stat.: 1.1302 DW-exp: 1.8673
```

```

=> N-sigma of the GoF:          9.105
=> Global user-weighted Chi2 (Bragg contrib.):  1.44
-----
-----  

-----  

=> Phase: 1      TiO2  

=> Bragg R-factor: 0.217      Vol: 135.923( 0.033)  Fract(%): 0.00( 0.00)  

=> Rf-factor= 0.234      ATZ: 0.000      Brindley: 1.0000
-----  

-----  

-----  

-----  

-----  

=> ANALYSIS OF THE REFINEMENT FOR PATTERN # 1  -
-----  

-----  

-----  

=> GLOBAL INDICATORS:  

The first and last reflections appears at:  

2theta(degrees)/T.O.F(microsecs)/Energy(KeV) =>      25.305      68.973  

s (angstroms-1) => 0.2844 0.7351  

D (angstroms ) => 3.5167 1.3604  

sin(theta/lamb) => 0.1422 0.3675  

Q (angstroms-1) => 3.5734 9.2372  

The average FWHM is: 1.0928 Fwhm(av)/step = 42.0300  

=> Sum(Yiobs-Yical): -821.29 1679.91 -1109.78 196.34 <- Four regions  

Total -> -54.82  

Expected Rp (background uncorrected): 2.10 Observed-> 2.88  

Expected cRp(background corrected): 11.98 Observed-> 16.41  

-> Ratio Rp/Exp=cRp/cExp: 1.37  

Weighted Average Bragg R-factor: 0.22  

Weighted Average RF-factor: 0.23  

Reduced Chi-square : 1.29  

=> Total number of "independent" reflections: 11  

Effective number (account for resolution) of reflections:  

at level p=1.00 : 7.3  

at level p=0.50 : 11.0  

at level p=0.25 : 11.0  

A reflection contributes as x/(x+nearest), where "x"  

is the fraction of the total area of the current phase and  

"nearest" is the number of adjacent reflections verifying the formula:  

Postn-p*FWHM <= Postn(adjacent) <= Postn+p*FWHM  

"nearest" is weighted by the corresponding "x(s)"  

=>  

Number of global refined parameters: 1  

Number of profile refined parameters: 5  

Number of intensity-affecting refined parameters: 0  

(Preferred orientation belongs to this class)  

=> (Effective Number of reflections)/(Number of intensity parameters)= refni  

Ratio ( Optimistic view,p=0.25): 11.0  

Ratio ( Pessimistic view,p=1.00): 7.3  

Ratio ( Eclectic view,p=0.50): 11.0  

=> PHASE DEPENDENT INDICATORS:  

=> Positions and FWHM of the sharpest reflection  

Phase 2Theta/TOF FWHM Q DQ Delta Dd/d(%)  

1 25.30 0.9530 1.7867 0.06619 0.36394 3.705  

Q ,DQ(FWHM in Q-space) and Delta are given in 1/angstroms  

Delta is the expected step between consecutive reflections at Q  

Phase %Cont Nintdp Nprofpl Nref Enref(Effective)  

R:p=1 R:p=1/2 R:p=1/4  

1 100.00 0 5 11 7.33 11.00 11.00  

7.33 11.00 11.00  

Where:  

%Cont: percentage of the total integrated intensity (100x)  

Nintdp: Number of intensity-affecting refined parameters  

Nprofpl: Number of profile refined parameters  

Nref: Number "independent" contributing reflections  

Enref: Effective Number of reflections for each p-value  

R:p=1/n: Ratio Enref(Effective)/Nintdp  

=> ANALYSIS OF STANDARD DEVIATIONS  

Phase: 1 Degrees of freedom for p=1, 1/2, 1/4: 7.33 11.00 11.00  

Chi2 based on integrated intensities: 0.53 0.36 0.36  

Calculated with Scott's FORMULA : 79.55 53.36 53.36  

=> Standard deviations concern the PRECISION of parameters and  

represent ACCURACY only if there is no systematic errors  

A better estimate of the accuracy of structural parameters  

is obtained multiplying sigmas by the parameter SCOR  

-> SCOR = 1.8979 { Berar's FORMULA}  

-> SCOR = 6.4831 {Pawley's FORMULA}  

-> Application of modified Scott's FORMULA  

SCOR(p=1,1/2,1/4) = 0.6434 0.5253 0.5253  

SCOR(expected Si) = 7.8604 6.4382 6.4382  

Warning! Do not take into account Scott's SCOR  

These indicators are under test....  

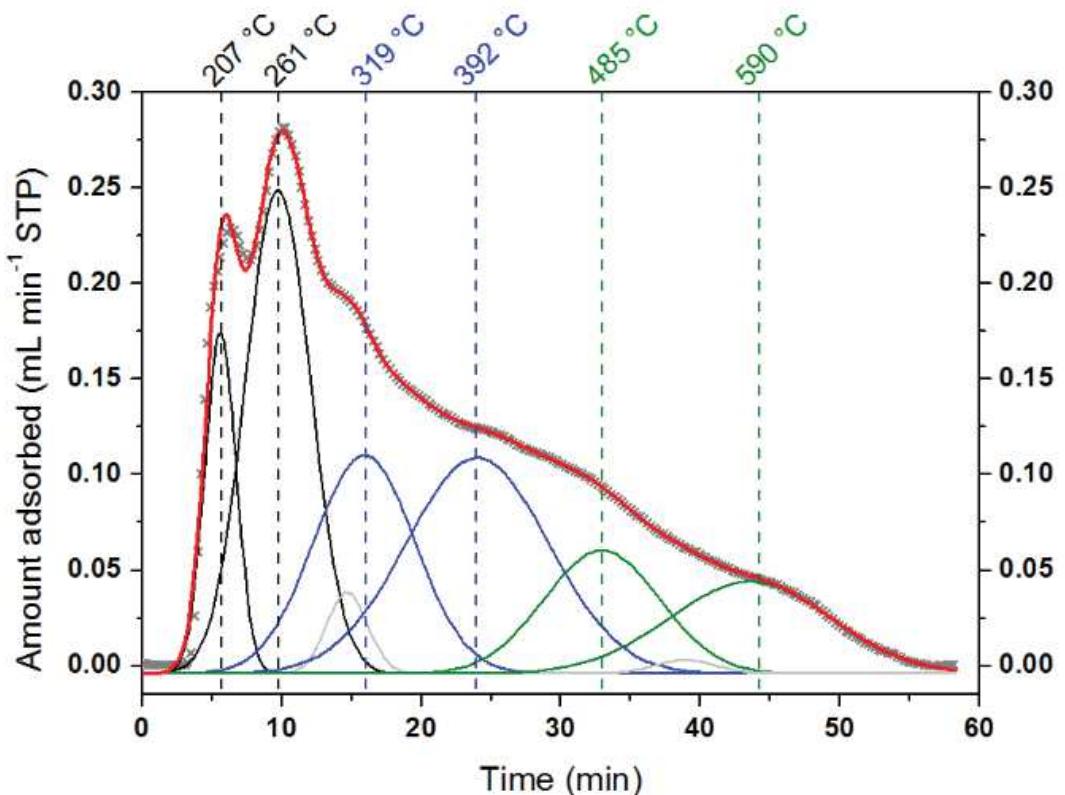
=> ANALYSIS OF CORRELATED PARAMETERS  

-> The parameter: 2 appears 2 times  

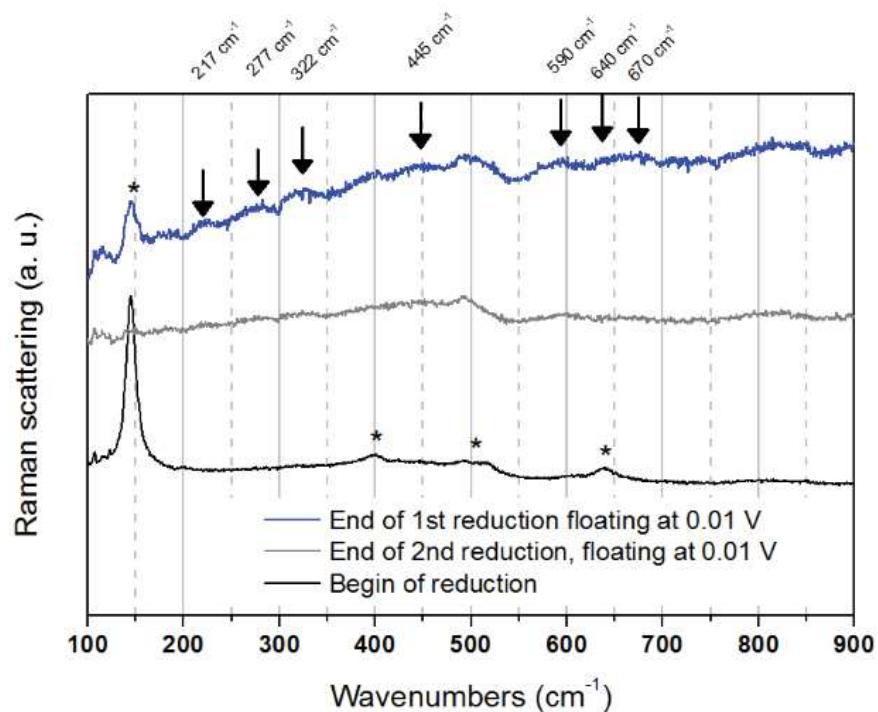
-> The number of correlated parameters is : 1  

=> Your refinement seems to be very good!

```



**Figure S5.** Temperature-programmed desorption of  $\text{NH}_3$  for  $\text{TiO}_2\text{-C}400$ .



**Figure S6.** *In situ* Raman spectra of  $\text{TiO}_2\text{-C}400$  at the beginning (black line), at the end of the 1<sup>st</sup> galvanostatic discharge (blue line), and at the end of the 2<sup>nd</sup> galvanostatic discharge (grey line). Each reduction is followed by a 2 hr floating at 0.01 V vs  $\text{Na}^+/\text{Na}$  (potentiostatic mode).

## V. Résumé des travaux portant sur la synthèse de composites polysaccharide/ionosilice

Les ionosilices sont une famille de silices porteuses de fonctions ioniques,<sup>47-48</sup> soit en surface du matériau sont incorporées dans sa structure, qui possèdent donc des propriétés de tri ionique. L'idée originelle de cette partie était de parvenir à un composite cellulose/ionosilice, dans lequel la cellulose aurait apporté une tenue mécanique et l'ionosilice des propriétés de conduction ionique pour le matériau. Les difficultés successives rencontrées en suivant cet objectif nous ont poussés à explorer trois approches différentes.



Schéma V.1 : Matériau envisagé *via* fonctionnalisation de la cellulose

La fonctionnalisation de la cellulose, premier axe envisagé, devait tirer parti du greffage de silice sur les fonctions alcools de la cellulose, qui a été rapporté dans des conditions douces.<sup>49</sup> L'idée était de procéder à un greffage de silice fonctionnalisée, puis de travailler sur les fonctions du greffon afin de parvenir au polyélectrolyte visé.

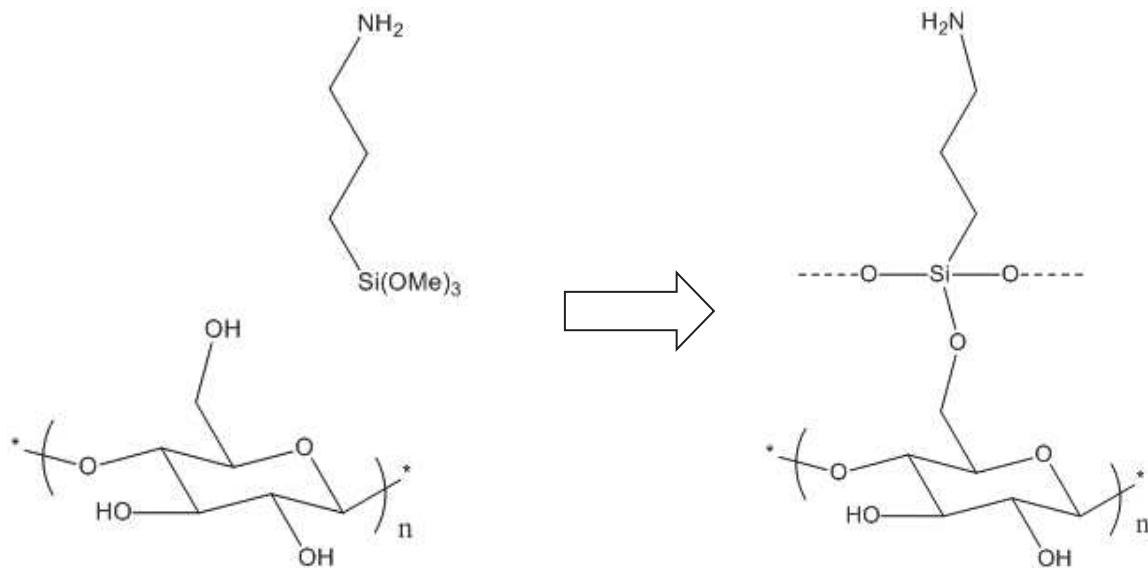


Fig. V.1 : Réaction visée pour la fonctionnalisation de la cellulose

Plusieurs précurseurs de silice ont été testés, sans qu'il soit possible de caractériser le matériau formé. En particulier, la caractérisation des liaisons chimiques formées entre la cellulose et l'architecture de  $\text{SiO}_2$ , ou encore la quantification du taux de greffage, ont été impossible à réaliser. Ces difficultés à représenter le résultat de nos expériences nous ont forcé à envisager d'autres méthodes pour obtenir un polyélectrolyte composite cellulose/ionosilice.



Schéma V.2 : Matériau envisagé *via* la silylation du chitosan

Dans un second temps, nous avons travaillé sur le chitosan, un polysaccharide issu de la déacetylation de la chitine. Le chitosan étant soluble dans les solutions aqueuses acides,<sup>50</sup> l'idée était d'utiliser des précurseurs de silice anioniques pouvant créer des liaisons ioniques avec les fonctions ammonium du chitosan pendant la polycondensation des siloxanes. On aurait ainsi obtenu un composite présentant un cœur de chitosan entouré par une coquille de silice, l'interface devant être fortement ionique.

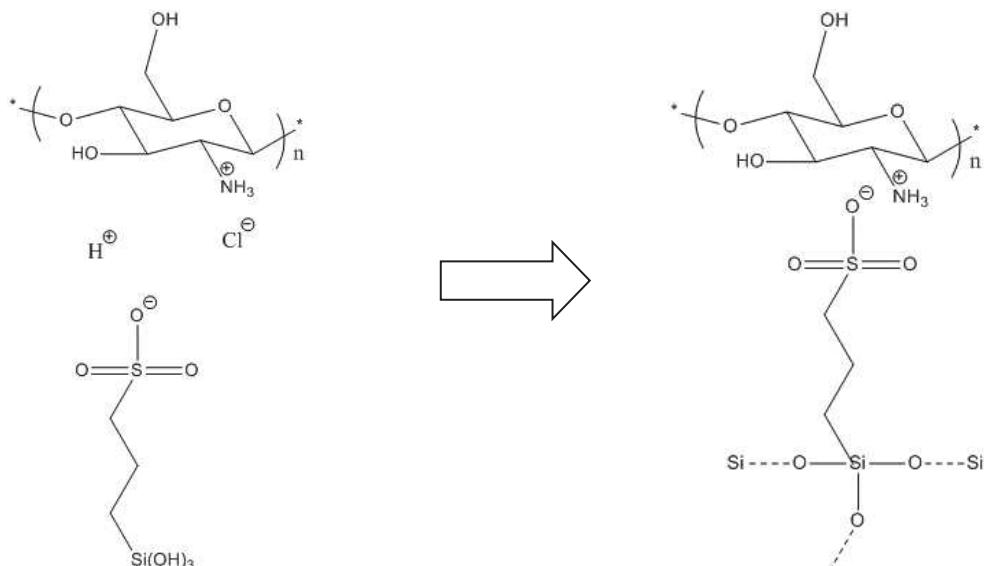


Fig. V.2 : Réaction visée pour la silylation du chitosan

La silylation a été tentée sur du chitosan et du chitosan guanylé, présentant chacun une fonction cationique différente. Ces expériences, en milieu multi-phasiques, ont conduit à des bruts réactionnels dans lesquels précurseurs et matériaux étaient difficiles à séparer et à purifier. La nécessité d'effectuer de nombreux tests pour espérer obtenir les matériaux recherchés, lors d'une longue période d'indisponibilité des équipements d'analyse, nous a contraint à mettre ces travaux en suspens.

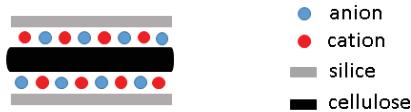


Schéma V.3 : Matériau envisagé *via* la synthèse de ionogel

Enfin, la troisième approche envisagée repose sur la dissolution de la cellulose dans un liquide ionique,<sup>51</sup> le chlorure de 1-butyl-3-methylimidazolium ( $BuMImCl$ ), suivie par l'assemblage des fibres dissoutes avec une matrice de silice. Si la dissolution de la cellulose dans  $BuMImCl$  est connue, la solution obtenue possède une viscosité importante, si bien que la préparation des ionogels demande un ajustement empirique des conditions expérimentales afin de parvenir à un système suffisamment fluide pour permettre une gélification homogène. La fin de la thèse est intervenue alors que ces ajustements étaient encore en cours, avant qu'un matériau valorisable n'ait été obtenu. Les manipulations réalisées semblaient cependant encourageantes, des matériaux gélifiés ayant été synthétisés.



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