

Careful investigation of vanadium dioxide synthesis: physico-chemical properties, elemental doping and film applications

Shian Guan

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Par Shian GUAN

Etude de la synthèse de dioxyde de vanadium : propriétés physico-chimiques, dopages élémentaire et applications sous forme de films

Sous la direction de : Aline ROUGIER et Manuel GAUDON (Co-Encadrant : Nicolas PENIN)

A Soutenir le 20 décembre 2019

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Résumé

Etat de l'art. Le dioxyde de vanadium (VO₂) est un matériau prometteur pour son utilisation en tant que film pour fenêtres intelligentes économes en énergie en raison de sa transition réversible métalisolant à 68°C. Cette transition est accompagnée par d'importantes modifications des propriétés optiques avec passage d'un état transparent à basse température à un état plus opaque (absorbeur/réflecteur) à haute température, notamment sur le domaine de longueur d'ondes du proche infrarouge. D'un point de vue cristallographique, la transition implique une transformation de deux phases cristallines: la phase monoclinique (M) et la phase rutile (R).

Les différentes formes cristallines du dioxyde de vanadium sont représentées dans la Figure R1 cidessous.



Figure. R1 (a) et (b) deux représentations schématiques différentes de la structure cristalline de VO_2 (M) (gauche) et VO_2 (R) (droite) c). Paramètres de maille de VO_2 (phases R et M) à partir des calculs DFT et des affinements de diffractogrammes de rayons X.

Les verrous technologiques limitant l'utilisation commerciale de ces oxydes sont leur température de transition élevée, leur couleur jaune indésirable (film) et leur faible stabilité thermique et chimique. Plus important encore, il n'existe toujours pas de méthode reproductible et peu coûteuse pour la synthèse des particules de $VO_2(M)$.

Chapitre 2. Deux méthodes de synthèse de poudre de VO_2 sont proposées dans ce travail. Dans la première méthode, des poudres de VO_2 (M) à cristallinité ajustée ont été préparées par un traitement thermique en deux étapes: une décomposition rapide du VEG (vanadyl-glycolate) préalablement obtenu par précipitation en milieu polyol, conduisant à la formation de cristaux de VO_2 de qualité cristalline médiocre, suivie d'un traitement de post-recuit à des températures plus élevées sous vide dynamique afin que la cristallinité augmente et atteigne finalement 100% après recuit à 700°C. Il est extrêmement important dans ce procédé de bien contrôler notamment la durée de traitement de la première étape du précurseur (vanadyl glycolate), car la transformation de l'oxyde obtenu en phases sur-oxydées comprenant un mélange de V⁴⁺ et de V⁵⁺ est rapide.

Il est aussi possible par décomposition du VEG d'obtenir des oxydes V_2O_3 ou V_2O_5 selon l'atmosphère de traitement. Le schéma global de cette première voie de synthèse est présenté ci-dessous (**Figure R2**).



Figure R2. Illustration de la première voie de synthèse de VO_2 (ou V_2O_3 ou V_2O_5) par décomposition maitrisée sous différentes atmosphères de vanadyl glycolate (VEG) obtenu en milieu polyol.

Les composés obtenus après traitement thermique final ont été caractérisés tant d'un point de vue morphologique (**Figure R3**) que structural (**Figure R4**). Des particules de tailles variables et de degré de cristallinité pouvant être ajusté à 100% peuvent être obtenues, par notre méthode de synthèse (par ailleurs de bas coût et facile à mettre en œuvre).



Figure R3. Images TEM et SEM des particules de $VO_2(M)$ telles que préparées synthétisées avec les conditions (a) VOx-3min: 300 °C pendant 3 min dans l'air par décomposition du VEG; (b) S-500: traitement post-recuit de VOx-3min à 500 °C pendant 5 h en atmosphère sans oxygène; (c) S-700: post-recuit de VOx-3min à 700 °C pendant 5 h en atmosphère sans oxygène. (d) Distribution granulométrique des particules de VO₂ synthétisées. (e) Illustration schématique de l'évolution morphologique des particules VO₂. (A et B désignent deux types d'octaèdre déformé)



Figure R4. Affinements Rietveld typiques pour (a) VOx-3min; b) S-500; c) S-700; (d) Comparaison du pic XRD à $2\theta = 27,95^{\circ}$ d'orientation (011) pour VO₂ (M); (e) et pourcentage en poids correspondant de chaque composant : amorphe, VO₂ (M) ou autres phases constituant le composé caractérisé.

Chapitre 3. La deuxième méthode, appelée méthode de carbo-réduction thermique, repose sur le rôle réducteur du carbone. Dans ce travail, la suie (carbone) est choisie pour effectuer une réduction directe d'un oxyde précurseur V_2O_5 élaboré préalablement et de taille de cristallite nanométrique. La comparaison de procédé de réduction effectué sous vide scellé et vide dynamique permet une meilleure compréhension du mécanisme de réduction (**Figure R5**).

Dans le système sous vide statique, le gaz CO généré en début du procédé de réduction de l'oxyde de vanadium continue d'opérer comme un réducteur, ce qui conduit à la formation de V_2O_3 . A contrario, dans le système sous vide dynamique, le gaz CO est rapidement éjecté, ce qui évite de prolonger la réduction des oxydes de vanadium et garantit la formation de VO₂ uniquement (**Figure R6**).



Figure R5. Les différentes voies de synthèse pour la préparation de VO_2 ou V_2O_3 à partir de la réduction de nano- V_2O_5 par le carbone. (b) Système de vide scellé (SVS): le tube de verre est scellé après avoir été mis sous vide; (c) Système de vide dynamique (DVS): le tube de verre est maintenu sous vide pendant tout le rocessus de recuit.



Figure R6. Illustration schématique des réactions possibles se produisant dans le SVS: système de vide scellé et dans le DVS: système de vide dynamique.

La taille moyenne des particules de VO₂ obtenues varie de 5,3 μ m à 415 nm selon la température et la durée du recuit opérées (**Figure R7**). De plus, les ions métalliques Al³⁺, Ti⁴⁺ et Nb⁵⁺ peuvent être dopés avec succès au sein des oxydes VO₂. Le dopage par les ions Nb⁵⁺ conduit à une diminution de la température de transition la plus efficace (cette température pouvant alors être ajustée autour de la température ambiante, 25°C).



Figure R7. Images SEM des particules VO₂ (M) synthétisées: échantillons DVS-700 et) DVS-1000. En encart est reportée la distribution granulométrique correspondante.

Chapitre 4. Les effets du dopage en Nb sur les propriétés des oxydes VO₂, sous tous leurs aspects : morphologie, distorsion des cristaux, stabilité thermique, capacité calorifique, résistivité électrique et susceptibilité magnétique ont été pleinement étudiés (**Figure R8**).

Plus en détails, pour révéler le rôle de la distorsion de la maille cristalline lors de la transition de phase (M/R), les distances de V-V et V-O, l'angle de V-O-V ont été soigneusement extraits des caractérisations structurales ; cette étude montrant que la diminution des écarts structuraux entre les phases M et R avec le dopage en Nb peut expliquer la baisse des températures de transition (**Tableau R1** et **Tableau R2**).



Figure R8. (a) Courbes DSC montrant la capacité thermique, (b) les courbes de résistivité et (c) la susceptibilité magnétique des échantillons VO_2 et VO_2 dopé au Nb (10% -NbVO₂-700A) en fonction de la température. (d) Résumé des températures de transition et de la largeur de la boucle d'hystérésis mesurée entre les modes de chauffage et de refroidissement extraits des analyses DSC, résistivité et VSM.

Tableau R1. Paramètres extraits des affinements Rietveld sur les formes monocliniques: longueurs des liaisons VO et distance des angles des liaisons VO dans la phase M pour des échantillons de VO₂ dopés à 0% -, 5% - et 10% de Nb et évaluation quantitative de la distorsion du site octaédrique dans la comparaison avec le site octaédrique de la phase R.

			0%Ref	0%	5%	10%
			R phase	M phase	M phase	M phase
	Apical	11	1.9330	2.0489	2.0116	2.0245
		12	1.9330	1.7579	1.7760	1.7551
V O longth	Length change (M/R _{ref})	ΔI/IR	0	10.86%	9.08%	10.13%
(Å)		L1	1.9216	1.8459	2.0503	2.0315
(**)	Equatorial	L2	1.9216	2.0240	1.9078	1.9397
		L3	1.9216	2.0626	1.8637	1.8941
		L4	1.9216	1.8726	2.0210	2.0428
	Length change (M/R _{ref})	ΔL/LR	0	10.21%	9.01%	8.68%
		α1	180	171.482	171.451	172.624
V-O-V angle		α2	180	169.556	169.678	169.226
(°)		α3	180	168.453	168.954	168.884
	Angle change (M/R _{ref})	Δα/αR	0	9.86%	9.65%	9.53%

Tableau R2. Distances V-V et distorsion de la longueur d'appariement V-V (en considérant une amplitude d'appariement nulle ou nulle pour la phase R) dans la phase M pour un échantillon VO_2 dopé avec 0%, 5% et 10% Nb.

Sample	Phase	d1 (Å)	d ₂ (Å)	d_1/d_2	$R_{ref} \rightarrow M$	$\Delta d/d_R$
					$\Delta d = [(d_1 - d_R)^2 + (d_2 - d_R)^2]^{0.5}$	
0%	М	3.1632	2.6242	1.205	0.3855	13.51%
5%	М	3.1523	2.6399	1.194	0.3675	12.88%
10%	М	3.1181	2.6885	1.160	0.3121	10.94%
$0\%_{Ref}$	R	2.8528	2.8528	1.000	0	0

Enfin, une étude approfondie des propriétés magnétiques est aussi présentée, notamment en se concentrant sur les impacts de la concentration en dopant et de la taille des particules (Figure R9).



Figure R9. Susceptibilité magnétique en fonction de la température: (a) des composés VO_2 non dopé 5% -Nb VO_2 et 10% Nb VO_2 obtenus après recuit à 700°C – 10 heures ; (b) VO_2 de morphologies différentes car obtenus après recuit à 700°C – 1 heure (700A), 700°C – 10 heures (700B) ou à 1000°C (1000A). L'inset montre le tracé des ajustements (lignes rouges) effectués sur les susceptibilités expérimentales dans le domaine des hautes températures.

Chapitre 5. La mise en forme en film mince à base de VO₂ a été entreprise avec la volonté de conserver un bon compromis entre la transmittance lumineuse (T_{lum}) et la capacité de modulation de l'énergie solaire (ΔT_{sol}) de ces films. Par dip-coating, des films VO₂ à « structure en îlots », avec une

couleur grise, ont été fabriqués en suivant notre stratégie de carbo-réduction. Un surfactant : PVP, est utilisé à la fois comme stabilisant de surface et agent réducteur.



Figure R10. Représentation schématique du protocole de préparation du film VO_2 synthétisé à partir du film V_2O_5 @ PVP; (b). Diffractogrammes de rayons X du substrat de quartz, d'un film V_2O_5 @ PVP sur quartz et d'un film VO_2 sur quartz. Images MEB de films VO_2 (c) vue de surface et (d) vue en coupe). (e-f) Spectres EDS correspondant du point A et du point B indiqué dans l'image MEB.

Pour moduler le taux de recouvrement par les îlots fonctionnels (VO₂) de la surface des substrats transparents (ici, du quartz), trois paramètres d'élaboration ont été modifiés: (i) la concentration de la suspension de $V_2O_5@PVP$ utilisée pour le dépôt; (ii) l'épaisseur de couche de film de $V_2O_5@PVP$ avant le recuit; et (iii) le nombre de couches de VO₂ en pouvant aussi, dans ce dernier cas, moduler les températures de recuit intermédiaires entre deux couches successives. Le paramétrage du procédé ainsi que les différentes morphologies atteintes sont résumées dans les **Figures R11** et **R12**.



Figure R11. Schéma des deux méthodes utilisées pour augmenter le recouvrement de surface; (a) augmenter le nombre de couches de film V_2O_5 @ PVP avant un seul recuit final; (b) répéter plusieurs fois le processus complet dépôt par spin-coating // recuit intermédiaire entre deux dépôts.



Figure R12. Micrographies MEB de films obtenus selon le nombre de dépôt ou le type de méthode de dépôt utilisée tel que décrit en Figure R10.

Chapitre 6. Enfin, la force motrice à l'origine de la transition de phase des oxydes de type VO_2 n'est toujours pas claire : certains auteurs proposent pour cette transition une origine structurale (modèle de Peierls), d'autres énoncent que la transition procède d'une corrélation complexe électron-électron (modèle de Mott).

Nous avons, dans une dernière partie, également exposé notre point de vue sur cette transition métalisolant des oxydes VO₂. Dans la limite d'une approche géométrique simple, mais avec une approche originale, les principales forces motrices impliquées dans la transition MIT de VO₂ ont été évaluées. Notre approche basée sur le modèle de valence de liaison, modèle bien établi, nous a permis de montrer que la transition de phase provenait certainement d'une maximisation de l'énergie réticulaire par maximisation du volume de la phase car cette dilatation est alors associée à une diminution des répulsions électrostatiques anions-anions et cations-cations : autrement dit, la forme allotropique la plus stable est celle présentant pour une température donnée le volume de maille unitaire le plus important. En effet, pour la phase rutile, l'effet de la distorsion tétragonale sur les volumes de maille notamment, a ouvert cette hypothèse (**Figure R13**).



Figue R13. Effet de la distorsion tétragonale c/a sur le potentiel électrostatique (énergie de la $1^{\text{ère}}$ sphère) (a); sur le volume unitaire (b) et sur les longueurs caractéristiques des arêtes des octaèdres de vanadium l 'et l' '(c).

De plus, ceci semble être validé par le suivi des évolutions de volume de maille unitaire en fonction de la température enregistrée par diffraction des rayons X *in situ* (rayonnement synchrotron). (Comme le montrent les **Figures R14** et **R15**).



Figure R14. Diagramme de diffraction synchrotron sur la plage de températures de 5°C à 105°C montrant la transition réversible entre les structures monoclinique (P21 / c) et rutile (P42 / mnm) lors du chauffage et du refroidissement (a). Affinement spectral des données enregistrées à 5°C (b) et 105°C (c). Le profil « différence » et les réflexions hkl des cellules unitaires sont présentés ci-dessous sous la forme d'une ligne bleue et de graduations vertes respectivement. La région d'exclusion 2 θ (environ 8 - 9 °) est indiquée par des points de données gris clair.



Figure R15. (a) Fraction (% en poids) de la phase monoclinique en fonction de la température de chauffage et de refroidissement, (b) Volume de cellule unitaire VO_2 (par unité de formule Z) en fonction de la température de chauffage et de refroidissement autour de la température de transition monoclinique-rutile.

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General introduction

Vanadium dioxide (VO₂) is a promising material for energy-saving smart windows due to its reversible metal-to-insulator transition (MIT) near room temperature (68°C), which is associated to large changes in optical properties. This thermally induced transition is reversible and accompanied by a structure transformation from high-temperature rutile (R) phase to a low-temperature monoclinic (M) phase. The latter corresponds to a low temperature transparent state whereas the former constitutes a reflecting/absorbing state at high temperature in the near-infrared region. Phase transition, imbues the VO₂-based window with the ability to regulate solar heat flux by responding to temperature.

Although investigations on VO_2 smart windows have been carried on since the 1980s on a worldwide scale, commercial utilization has not yet been achieved. The current issues are the high transition temperature, unpopular yellow color (film) and poor thermal and chemical stability. Most importantly, there is still a lack of a reproducible and low-cost method for VO_2 particles synthesis, which could guarantee the obtained particles are monodisperse, nano-size, and with high-crystallinity.

In addition, a fierce debate over the driving forces of the phase transition has persisted for several decades, with respect to whether the electron-electron correlation is strong enough to localize the electrons (Mott model) or whether structural distortions alone induce the insulating phase (Peierls Model). More studies are needed for a better understanding of the origin of the VO_2 (M/R) phase transition.

In chapter I, we present the state-of-the art of VO_2 researches, including the mechanism of VO_2 phase transitions, various VO_2 powder synthesis methods, film preparation, and elemental doping studies.

In chapter II, a method of VO_2 synthesis with tuned crystallinity is proposed and presented through a two-step thermal treatment: a first-thermolysis step under air followed by a post-annealing under oxygen-free atmosphere. The crystallinity of three different VO_2 powders is estimated with the help of XRD analyses.

In chapter III, a carbo-thermal reduction method is introduced for VO_2 synthesis, which is inspired by the reducing role of carbon in first synthesis method. The comparison of the results obtained using a dynamic or a sealed vacuum system associated with an accurate control of the carbon contents is studied for a better understanding of the reductive mechanism. Besides, large quantity of VO_2 powder could be prepared through this method. The preparation of VO_2 -based pellets using SPS technique concludes this chapter.

In chapter IV, some element doping, such as Al^{3+} , Ti^{4+} and Nb^{5+} ions are explored through the carbothermal reduction method. Especially the doping effects of Nb^{5+} on VO_2 from all aspects, including the morphology, the crystal distortion, the thermal stability, the heat capacity, the resistivity and the magnetic susceptibility, are deeply investigated.

In chapter V, taking advantage of the reductive strategy, a zero-dimensional island structure VO₂based film (gray color) is fabricated successfully. The shaping process is described in detail. Here PVP is used as the same time as a surface stabilizer and a reducer, PVP layer is coated on V₂O₅ NPs surfaces. Using spin-coating for V₂O₅@PVP suspensions, followed with an annealing treatment, films with variable thicknesses and surface coverage densities are prepared.

In chapter VI, we specifically discuss the mechanism of the metal-insulator transition (MIT) of VO_2 . Within the limit of a simple geometrical approach, an evaluation of the main driving forces involved in the MIT transition of VO_2 is proposed.

Chapter I: State-of-the-art and objectives



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1. Thermochromic materials devoted to smart windows

1.1.Energy consumption

World-wide energy consumption is continuously increasing. A significant amount of energy is consumed for maintaining thermal comfort in buildings. The global buildings sector consumes nearly 30% the world's total energy consumption (including 22% residential and 8% non-residential), and this figure is anticipated to increase steadily. Besides, on average most of the heat lost in a home occurs through the walls (35%), roofs (15%), floors (15%), and windows & doors (25%) mainly due to insufficient insulation, low quality materials and aging effects. [1] Central heating and air conditioning are the main energy consumer in buildings, which have been estimated to account for around 30% of all anthropogenic CO_2 emissions. [1-3] The functional windows. based on thermochromic/electrochromic/photochromic films are developed to replace the traditional window (Figure 1).



Chpt. I-Figure 1 (a). *Traditional window (left) and functional window (right); (b). Average main losses that occur in a typical house/building.* [1]

The solar radiation provides light and heat for the Earth and energy for photosynthesis. The three relevant bands, or ranges, along the solar radiation spectrum are ultraviolet (300-400 nm), visible (400-700 nm), and near-infrared (NIR, 700-2500 nm). Near-infrared radiation makes up 52% of the total energy of the solar radiation while visible light provides 43% and ultraviolet radiation. Even if UV photons are the most energetic, they represent only 5% of the total solar radiation. (**Figure 2**)



Chpt. I-Figure 2. Solar radiation spectrum from 200-2500 nm.

One efficient way to reduce building energy consumption is to modify the solar radiation input or blackbody radiation output through a functional coating on windows. Developing energy-efficient coating materials, which can sense and response to external stimuli as well as spontaneously regulate energy is an irresistible trend. Windows are known as one of the most energy-inefficient components of buildings, and energy-efficient smart windows can reduce air-conditioning load to save energy as they are capable of modulating the solar radiation that passes through the windows of buildings. Smart windows represent an important technology for increasing indoor comfort and reducing electrical consumption in the automotive and building sectors.

To modulate the visible light (400-700 nm), electrochromic window (ECW) are today commercially available (**Figure 3a**). Electrochromism is known as a modulation of the optical properties under an applied voltage. In the electrochromic window design (**Figure 3b**), the window can be described as an electrochemical cell in which two electrochromic materials on conducting glass panes are separated by an electrolyte. In the bleached state, both the working and the counter electrodes are transparent to solar radiation, allowing heat and natural light to enter the room. While in the colored state, the window limits the amount of heat and natural light that enters the room. These two switching modes enable the window to operate at different weather conditions, which is helpful for energy savings and comfort.



Chpt. I-Figure 3. (a) Design of electrochromic window; (b) Schematic of the electrochromic device *(ECW).*

1.2. Thermochromic material : VO₂

The use of thermochromic materials, of which optical properties are modulated by the temperature, is another self-regulated solution. Thermochromic windows are highly promising for their smart regulation of indoor solar transmission (700-2500 nm) automatically based on their transmittance-modulation abilities together with the relatively simple structure, facile fabrication, and low cost. The optical modification is usually associated with a structural phase transition. As a typical thermochromic material, vanadium dioxide (VO₂) has been attracting extensive attention. VO₂ smart windows are an important category in energy-saving smart window applications. For large-scale deposition to fabricate thermochromic glass, a thermochromic VO₂ thin film is usually directly grown or coated on conventional glass. Films are produced by various physical deposition or chemical decomposition processes. Recently, wafer-scale growth of VO₂ thin films has been realized by Zhang *et al*, [4] they successfully obtained a three-inch wafer with excellent uniformity.

As for its study in the academic area, we used Scopus to show the development of the research on VO₂ over the past decades. And VO₂ was firstly reported by Morin in 1959. [1] Scopus being one of the world's largest abstract and citation database of peer-reviewed literatures. In Scopus, we searched for

the academic paper with the words "VO₂", "Thermochromic", "VO₂+Film" and "VO₂+doping" within its title, abstract, or keywords. As a functional material, the study on VO₂ has been conducted comprehensively, including its physical-chemical properties, the phase transition mechanism, high quality powder synthesis, the preparation of various types of films and elemental doping for tailoring the transition temperature. The results are shown in **Figure 4**. Basically, the histograms reveal a sharp growth trend in the latest 10 years. More and more researchers show great interest in VO₂ study due to its outstanding properties and potential application in the energy-saving fields.



Chpt. I-Figure 4. Number of published paper with terms of (a) " VO_2 ", (b) " VO_2 +Synthesis", (c) " VO_2 +Film" and (d) " VO_2 +doping" over the last 50 years; Source: Scopus database.

1.3.Optical Performance

Among the issues concerning VO₂-based thermochromic windows, optical performance is the most important, because it directly determines the energy-conservation efficiency of the windows. The optical performance of a VO₂-based thermochromic window can be mainly characterized in terms of its luminous transmittance (T_{lum}, 380-780 nm), solar-energy modulation ability (ΔT_{sol} , 240-2500 nm, the difference in solar-energy transmittance below and beyond the phase transition temperature). These quantities are calculated as follows:

$$T_{lum/sol} = \int \varphi_{lum/sol}(\lambda) T(\lambda) \, d_{\lambda} / \int \varphi_{lum/sol}(\lambda) \, d_{\lambda}$$
$$\Delta T_{sol} = T_{sol}(T < T_c) - T_{sol}(T > T_c)$$

where $T(\lambda)$ represents the transmittance at wavelength λ , φ_{lum} is the standard luminous efficiency function for vision (380-780 nm), and φ_{sol} is the solar irradiance spectrum at air mass 1.5 (corresponding to the sun standing 37° above the horizon). The higher T_{lum} can save lighting while higher ΔT_{sol} determines the energy-conservation efficiency of VO₂-based thermochromic windows.

However, T_{lum} and ΔT_{sol} have a trade-off relationship (globally, higher is the T_{lum} and lower is the ΔT_{sol}), [5, 41] as shown in **Figure 5**, and it is difficult to improve both of them to acceptable values. For example, the ΔT_{sol} could be improved by increasing the film thickness, while the T_{lum} will be deteriorated. Therefore, most recent studies on thermochromic devices have been focusing on the attempts to optimize both T_{lum} and ΔT_{sol} at the same time.



Chpt. I-Figure 5. Optical performances of VO_2 *films prepared by different methods.* [41] *The results for composite films were deduced from numerical calculations.* [5]

The optical constants, including refractive index (n) and extinction coefficient (k), are quite useful for comprehensive studying on the T_{lum} and solar transmittance modulation ΔT_{sol} for VO₂ based films, such as thin films or composites. Taking advantage of the knowledge of the optical constants, the film's transmittance can be simulated by changing particle size or film thickness.

2. Mechanism of VO₂ transitions (MIT)

 VO_2 undergoes a first order metal-insulator phase transition (MIT) at critical temperature of T_c = 68°C, which is accompanied by a reversible structure transformation from low-temperature insulator phase (Monoclinic phase, shorted as M phase) to high-temperature metal phase (Rutile phase, shorted as R phase). The M-R transition is depicted in **Figure 6a**.

As illustrated in **Figure 6b**, the high temperature $VO_2(R)$ has a tetragonal rutile structure with V^{4+} ions occupying the corner and center positions of each unit-cell, and each V^{4+} is surrounded by six O^{2-} . The closest V-V distance is 2.85 Å in chains along the c-axis. Four of the six oxygen atoms in the VO_6 octahedra are located closer to the vanadium atom, and the V-O bond distances are 1.92 and 1.93 Å, respectively. [4]

During the phase transition, the crystal structure of VO_2 (M) is a distorted rutile structure, and the vanadium atoms move along the V-V direction, resulting in the pairing and tilting of VO_6 octahedra in this direction. The atoms number in one VO_2 (M) unit cell is 12 (Z=2, with Z the number of VO_2 oxide unit), which is doubled as compared with the 6 atoms in one VO_2 (R) unit cell (Z=4). Two different V-V distances of 3.19 and 2.60 Å between the nearest vanadium atoms form the zigzag atom chains (**Figure 6b**). [2]



Chpt. I-Figure 6. (a) and (b) two different schematic representations of the crystal structure of VO_2 (M) (*left*) and VO_2 (R) (*right*), with V ions green balls; O ions red balls. [2] (c). Lattice parameters for VO_2 (R and M phases) from DFT Calculations and XRD Refinement. [9]

Housel *et al* [9] reported the lattice parameters for VO₂ (M/R) from density functional theory (DFT) calculations as well as XRD refinement (**Figure 6c**). Below 68°C, it shows a low-temperature insulating M phase (Space group: P21/c, a_M = 5.75 Å, b_M = 4.53 Å, c_M = 5.38 Å, b= 122.6°). When the temperature is above 68°C, this insulating phase transforms to the high temperature metallic phase, which displays a tetragonal structure (Space group: P42/nm, a_R = b_R = 4.55 Å, c_R = 2.85 Å).

There are many techniques to show the phase transition between VO₂ (M) and VO₂ (R). Among them, XRD is commonly used. **Figure 7a** reported synchrotron powder X-ray diffraction data collected at room temperature and in the temperature range of 48-75°C. **Figure 7b** displays that the VO₂ (M/R) transition is observed clearly by a peak shift from 4.24° to 4.22°, which corresponds to the (011) and (110) planes for VO₂ (M) and VO₂ (R), respectively. In addition, Rietveld refinement was used to identify and quantify the phase concentrations at each temperature. **Figure 7c** reveals that the weight percentages of M and R phase as a function of increasing temperature. VO₂ (M) is the primary phase at room temperature, while there is a mixture of VO₂ (M) (75.5%) and VO₂ (R) (19.8%) phase at 66°C, and the weight percent of VO₂ (R) increases to 93.9% at 75°C. The transition is even better visualized by the *in situ* X-ray powder diffraction patterns in **Figure 7d**.



Chpt. I-Figure 7. (a) X-ray diffraction patterns of VO_2 as a function of temperature. (b) Highlighted two-theta range demonstrating peak shift associated with M to R transition. (c) Weight fractions of $VO_2(M)$ and $VO_2(R)$ as a function of temperature. (d). Temperature-dependent in situ X-ray powder diffraction patterns of VO_2 shown from 4-4.45°. [9]

2.1.Peierls model and Mott model

The mechanism of the MIT phase transition in VO_2 (M/R) has been extensively investigated. However, a complete understanding of the driving forces and the transition mechanism remains elusive. There is still no model about the MIT that can explain all experiment results, a fierce debate over the driving force has persisted for several decades, with respect to lattice distortion driven (Peierls model) or the electron-electron correlation driven (Mott model) transition. Recent theoretical treatments suggested a partial resolution to the controversy with an intermediate description in terms of "Mott-assisted Peierls" or "Peierls-Mott" pictures.

Goodenough has attributed the mechanism of the MIT to the anti-ferroelectric V zig-zig distortion with the assistance of V dimerization. The phase transition could be interpreted as resulting from a strong interaction of electrons and phonons. Thus the behavior of VO₂ is often described as Peierls transition. Baum *et al.* [13] found that the transition from the insulating phase to the metallic phase initially involves the expansion of the primary V-V bond with local displacements, followed by long-range shear rearrangements, revealing a structural pathway and non-concerted transformation mechanism. Besides, Wentzcovitch *et al.* [11] revealed a distorted monoclinic ground state to be in good agreement with the experimental findings and a nearly open gap with respect to charge excitations. Cavalleri *et al* [12] found that the initiation of the metallic phase formation was prompted by hole photo-doping into the valence band of the insulator phase, the phase transition could be retarded with respect to hole injection and exhibits a bottleneck timescale.

However, the transition also presents some aspects of Mott-like instability, namely, the electronphonon coupling does not appear sufficient to describe the entire mechanism of the MIT phase transition.

Meantime, a number of phenomena, such as anomalously low conductivity and other unusual properties of the metallic phase, have suggested that the MIT phase transition involves strong electronelectron correlations. [14] These include the anomalously low conductivity and other properties of the metal, the fact that band structure calculations fail to yield the insulator bandgap, the existence of an intermediate M2 structure, which can be stabilized by stress or doping, that is insulating in spite of having undimerized vanadium chains, and the dependence on excitation power in optical experiments, which indicates sensitivity to excited carrier density. The alternative Mott picture ascribes the presence of a band gap in $VO_2(M)$ to strong electron-electron correlations, and the results of several experiments, indicating that if the thermally, optically or gate-voltage-induced excitation of carriers reaches a threshold, the metallic phase could develop even without a phase transformation. [10]

Recently, the cooperation of these two mechanisms (Peierls model and Mott model) is also put forward to explain the MIT transition. Yuan *et al.* [15] reported measurements and calculations of the VO₂ phase transition and suggested that it might be both electronically and structurally driven. Photo induced insulator-metal transition in VO₂ and the related transient and multi-time-scale structural dynamics upon photoexcitation are explained within a unified framework. Holes created by photoexcitation weaken the V-V bonds and eventually break V-V dimers in the M1 phase of VO₂ when the laser fluence reaches a critical value. The breaking of the V-V bonds in turn leads to an immediate electronic phase transition from an insulating to a metallic state while the crystal lattice remains monoclinic in shape.

2.2. Theoretical description

To fully describe the phase-transition process of VO₂ (M/R), Goodenough *et al* [16] gave the first theoretical description based on crystal field theory in 1971. In brief and as shown in **Figure 8a** and **8b**. In VO₂ (R), a wide π bond and a narrow π^* anti-bond are formed between the V⁴⁺ and O²⁻ orbitals, and a d_{//} nonbond is formed between adjacent V⁴⁺ orbitals along the crystallographic c axis. Although the energy band of VO₂ (R) is approximately 2.5 eV, the unfilled π^* and d_{//} bands partially overlap, and the Fermi level falls at the point where the π^* and d_{//} bands overlap, giving it metallic characteristics. The density of states at E_F is formed form a mixture of the d_{//} orbitals and anti-bonding π^* orbitals. [17]

When the temperature decreases, or after the MIT, the dimerization of the V ions in VO₂ (M) causes splitting of the $d_{//}$ band to filled bonding and empty antibonding states $d_{//}^*$. Meanwhile, the π^* orbitals move to higher energies due to the antiferroelectric zigzag-type displacement of the vanadium atoms. To be more specific, the oxygen atoms stay essentially at their original positions and the vanadium atom shifts lead to an increased metal-oxygen bonding, and this causes an energetic upshift of the π^* bands. Meanwhile, it also opens up a gap between this band and the lowest occupied $d_{//}$ states. The band gap of around 0.7 eV is formed between the π^* and $d_{//}$ bonds, leading to the formation of an insulating phase.



Chpt. I-Figure 8. Schematic of electronic band structure of a) $VO_2(R)$ and b) $VO_2(M)$ based on crystal-field model. [17]

3. VO₂ powder synthesis method

The vanadium has many oxidation states, such as V^0 , V^{2+} , V^{3+} , V^{4+} and V^{5+} , causing the formation of nonstoichiometric vanadium oxides with variable oxygen contents, as shown in **Figure 9a**. Vanadium oxides include V₂O₃, V₃O₅, V₄O₇, V₅O₉, V₆O₁₃, VO₂ and V₂O₅, in which the atom ratio of oxygen to vanadium varies from 1.5 to 2.5. Besides, vanadium dioxide (VO₂) is a complex binary compound with different polymorph. More than ten kinds of crystalline phases in the system have been reported, such as VO₂ (M), VO₂ (R), VO₂ (B), VO₂ (A) and VO₂ (D). The complexity of multi-valence and the phase diagram about the vanadium-oxygen system makes the synthesis of VO₂ (M) difficult.



Chpt. I-Figure 9. (a). The V_2O_3 - V_2O_5 phase diagram; (b). XRD patterns of VO_2 thin films before and after air annealing at 100, 200 and 300°C for 2 h. [91]

Even if a relatively pure VO₂ (M) is prepared, it can be easily further oxidized to upper oxidation state vanadium oxides or hydroxides, especially in the presence of moisture. [91] As we can see in **Figure 9b**, during annealing in air at 300°C, the VO₂ film becomes over-oxidized. This instability leads to serious durability problems in practical applications. One solution involves the formation of VO₂ in an inert oxide shell, which is used to separate VO₂ from oxygen. This method has been certified to be useful to some degree, but the process to prepare a core-shell structure is not easy to control. Furthermore, this treatment step leads to the aggregation of well-dispersed nanoparticles, making them difficult to use. Increasing the crystallinity of VO₂ is also effective, but this method cannot completely address the problem. Increasing temperature and time would be quite helpful, but the particles size would also increase accordingly. Unfortunately, large particle size is unfavourable for their dispersion into suspensions, and will drastically reduce the possibility to achieve transparent film (the scattering efficiency is passively correlated to the particle size). More investigations are needed.

To prepare VO₂ (M) powders, a variety of approaches has been explored and summarized in **Figure 10**. These methods can be gathered into three categories: (i) solid phase reaction, (ii) gas phase reaction and (iii) liquid phase reactions. Also, the methods can be divided in two different classes: the preparation routes with the aim to prepare directly the V⁴⁺ oxide from various reacting raw precursors in adequate conditions (temperature, total pressure and oxygen partial pressure), or the ones for which an additional redox process to transform V⁵⁺ (reduction) intermediate or V³⁺ (oxidation) intermediate is the key step of the synthesis process.



Chpt. I-Figure 10. Summary of the preparation methods of VO₂ Particles. [94]

(i) The solid phase reaction includes pure solid state synthesis, thermolysis of precursor and thermal reduction from an upper oxidation state vanadium oxide. The advantage of these reactions is massive production and low cost. However, some disadvantages exist, such as impurity of the product, rigid experimental conditions, poor stability of the product and the aggregations of the particles. Usually, micro scale VO₂ particles can be synthesized with frequently irregular size and shape.

(ii) The gas phase reactions include physical vapor deposition (PVD) and chemical vapor deposition (CVD). The former method can be used to prepare the rod shape VO_2 , and the size can be controlled precisely. The latter method can be used to prepare nano-wire shape VO_2 with high crystallinity. However, it is low yield and the VO_2 film is greatly influenced by the substrates. Solid and gas phase reaction have long been regarded as the exclusive strategies to obtain VO_2 particles. The experimental conditions of solid or gas phase reactions frequently require precisely scaled inert gas atmospheres, rigidly controlled temperatures, post-treatment, and long synthesis time.

(iii) For the liquid phase reactions, a number of approaches have been reported over the past decade, such as the hydrothermal method, seeded growth method, precursors transformation method, and direct combustion method.

According to the vanadium valence state changes, the methods can also be described into intermediate phase transformations, reduction reaction and oxidation reaction.

 VO_2 has multiple polymorphic forms, including VO_2 (B), VO_2 (A), VO_2 (M), VO_2 (D), VO_2 (P) and so on. The intermediate phase transformation to VO_2 (M) sometime is a necessary step by appropriate thermal treatment with different annealing conditions such as temperature, time, atmosphere and pressure. Especially for the hydrothermal process, the obtained product is often a metastable or mixture phase, rather than the VO_2 (M). Thus a post annealing treatment is necessary to transform the intermediate phase to VO_2 (M) phase.

Redox reaction is another strategy to prepare VO₂ (M) particles, and V₂O₅ is usually the raw material. Namely, V₂O₅ can be reduced to VO₂ by supplementary reducing agents (*e.g.*, H₂C₂CO₄, amine, alcohols, and N₂H₄) in hydrothermal/solvothermal reactions or in a reductive atmosphere during high-temperature annealing. To resume, V^{5+} is the most stable state, and V^{3+} is also quite stable, while it is quite difficult to keep V^{4+} in air. Based on the vanadium oxidative changes during the synthesis, the VO₂ synthesis strategy can be grouped into three types: from a mixture of V^{5+} and V^{3+} to achieve V^{4+} oxide (solid state approach); from V^{4+} to V^{4+} , and redox reaction strategy, with reduction from V^{5+} to V^{4+} and oxidation from V^{3+} to V^{4+} . In the perspective of vanadium valence change, the specific synthesis methods will be discussed following this roadmap.

3.1.Solid state reaction

For the synthesis of VO₂, one strategy is using solid state reaction, starting from V₂O₃ and V₂O₅ precursors, as illustrated in **Eq. 1**. Stoichiometric mixtures of the precursors are intimately ground, pressed into pellets and sealed in evacuated silica tubes. The tubes are heated in a tubular furnace at the heating rate of 2 °C/min. After 2 days' reaction at 750°C, VO₂ powders can be prepared. Meanwhile, around 0.5 at% W, Nb and Cr elements can be doped into VO₂ *via* this strategy by mixing with WO₃, Nb₂O₅ and Cr₂O₃ under the same annealing condition. However, due to the long reaction time, especially for the Mo doping, it takes 6 days at 1000°C, this method draws less attentions for VO₂ synthesis. []

 $V_2O_5 + V_2O_3 \rightarrow 2VO_2$ Eq. 1

3.2. From V^{4+} to V^{4+}

Maintaining the V^{4+} in vanadium precursor and removing the organic part is the basic strategy. The precursors are usually prepared in advance through other methods. Many methods have been developed based on different precursors. In short, the methods can be grouped into: (i) combustion method, (ii) intermediate phase transformation and (iii) thermolysis of VEG precursor. In the third method, VEG precursor is shorted as vanadyl ethylene glycolate. It will be fully discussed, because this precursor is used in our own work.

3.2.1. Combustion method

Through the direct combustion of an ethanol solution containing VO(acac)₂ (ac= acetylacetonate) in a confined space (**Figure 11a**), VO₂ (M) particles can be synthesized successfully, as recently reported by Wu *et al.* [26] The confined space provided not only sufficient energy but also necessary reductive atmosphere (such as alcohol, aldehyde, H₂ and CO) to maintain the +4 valence state of vanadium, contributing to the formation of thermodynamically stable VO₂ (R). In this combustion process, the vanadium valence remains equal to be V⁴⁺.

The whole process is remarkably convenient, with short reaction time, and no need for any complex equipment or manipulations. Real-time thermal infrared images and synchrotron-radiation photoionization mass spectra clearly reveal the dual role of ethanol in the reaction system.



Chpt. I-Figure 11. (*a*). Direct confined-space combustion to give monoclinic VO₂ (*M*); (*b*). Schematic illustration of the temperature distribution for inner wall surface and the center of the beaker, measured by thermocouple detector; (*c*). Experimental, calculated, and standard XRD pattern of as-prepared VO₂. [26]

Figure 11b illustrates the temperature distribution (measured by thermocouple detector) for inner wall surface and the center of the beaker. Due to the presence of sufficient oxygen, the temperature at the open end of the beaker is usually higher than that at deeper points. The temperature on the inner beaker wall is lower than that of the central region due to significant thermal radiation of the glass wall. The temperature shows that ethanol combustion in confined space provides sufficient thermal energy to ensure formation of thermodynamically stable monoclinic phase of VO₂. XRD pattern of the synthetic product (**Figure 11c**) matches well with that of standard JCPDS card corresponding to monoclinic VO₂ (M).

Similar method was also used by Cao *et al* [35] to the precursor solution consisted of NH₄VO₃, C₂H₆O₂ and C₂H₅OH, and single crystal monoclinic VO₂ is synthesized without out impurity observed.

3.2.2. Intermediate phase transformation

As we discussed previously, VO₂ has multiple polymorphic forms, including VO₂ (B), VO₂ (A), VO₂ (D) and VO₂ (P), while only VO₂ (M/R) phase shows a significant thermochromic performance. Thus the metastable phases can be transformed to VO₂ (M) by appropriate thermal treatment with different annealing conditions such as temperature, time, atmosphere and pressure. The vanadium valence state V^{4+} is so unchanged during this transformation.

Among them, VO₂ (B) is the most common phase during hydrothermal, [29, 31, 32] and most studies on intermediate phase transformation focus on the fabrication of VO₂ (B) followed by the thermal treatment to transform VO₂ (B) into VO₂ (M) at elevated temperature. The reason is that the VO₂ (B) phase is the least thermodynamically favorable phase with the lowest formation energy among all VO₂ polymorphs, while the VO₂ (M) is the most thermodynamically favorable phase with the highest formation energy.

In addition to $VO_2(B)$, $VO_2(A)$ is also an intermediate phase for $VO_2(M)$ transformation. The phase evolution and crystal growth of VO_2 nanostructures against reaction time in a high-pressure were



systematically investigated. [30] The morphological evolution mechanism for VO_2 (B), VO_2 (A) and VO_2 (M) is illustrated in Figure 12a.

Chpt. I-Figure 12. (a). Schematic illustration of the morphological evolution mechanism for VO_2 (B), VO_2 (A) and VO_2 (M); (b). Schematic diagram of phase evolution route of VO_2 polymorphs; grey and red balls represent vanadium and oxygen atoms, respectively; (c). XRD patterns of the obtained samples obtained at 180°C for different reaction times (1 day to 7 days, named V1-V7) in diffraction angle range of (a) 10° to 40° and 40° to 60°. [30]

The corresponding scheme describing the "phase diagram" of the VO₂ polymorphs is also presented in **Figure 12b**. XRD patterns recorded to follow the phase evolution progress of vanadium dioxide against reaction time show that VO₂ (B) phase is obtained when the reaction time was controlled in 1 day (**Figure 12c**). XRD pattern also indicated that VO₂ (A) could also evolve besides the previous VO₂ (B) if the reaction time is elongated. Finally, the XRD patterns revealed that by further extending the reaction time, the VO₂ (B) phase would completely disappear and the diffraction intensity of VO₂ (M) phase would begin to gradually increase.

Besides, Liu *et al* [32] discovered a new metastable phase, $VO_2(D)$, and reported that $VO_2(M)$ could also be formed through the transformation from $VO_2(D)$ to $VO_2(M)$.

However, the intermediate phase transformation method has two weaknesses. One is that the $VO_2(M)$ particles usually present the belt-like or rod-like morphologies, which are unfavorable for dispersion in the aqueous solvent. The other one is that the transformation typically requires a high temperature (>400°C) and a long time to reach the full transformation of $VO_2(M)$ phase.

3.2.3. Thermolysis of VEG

Thermolysis of vanadium precursor is quite popular to prepare VO_2 (M). We would fully discuss the vanadyl ethylene glycolate (VEG) for VO2 (M) synthesis as a school-case example to well show the efficiency of this method. In this kind of precursor thermolysis, the vanadium valence state will be the same before and after the annealing process. Besides, VEG is also the precursor we are going to use for VO₂ synthesis, as shown in Chapter 2 and Chapter 3.

VEG (VC₂H₄O₃; 126.94 g/mol) can be prepared by reacting ethylene glycol (EG: $C_2H_6O_2$) and ammonium metavanadate (NH₄VO₃). EG is not only a well-known solvent used to prepare small metal particles, but also a cross-linking reagent coordinating to the central metal ion to form a metal glycolate further leading to subsequent oligomerization. Moreover, the coordination agent EG also plays a crucial role on the valence-state reduction of vanadium because of the reductive species deriving from the pyrolytic intermediate products in our reaction system. V⁵⁺ in NH₄VO₃ is reduced to V⁴⁺ in the VEG compound, as described in **Eq. 2**.

According to Zou *et al*, [18] the synthesis temperatures (120, 140 and 180°C) have little effect on the purity of VEG product (**Figure 13a**). After 2 h reaction under 160°C, VEG is prepared after a precipitate is produced by reacting NH_4VO_3 and EG. The obtained blue precipitate is filtered and washed three times with $C_2H_6O_2$, this blue precipitate exhibits a diffraction pattern with all the peaks corresponding to monoclinic phase VEG (space group: C2/c, a= 9.271, b=9.735, c=9.918 Å; b=106.118°; JCPDS NO.49-2497). In brief, the polyol route can be described by the equation:



Chpt. I-Figure 13. (a) XRD pattern of VEG synthesized from 120 to 180°C [18] and (b) its FTIR spectrum. [19]

The FTIR spectrum of the VEG is shown in **Figure 13b**. [19] The sharp absorption peaks at 550 and 1062 cm⁻¹ are attributed to the stretching vibrations of edge-sharing V-O and V=O, the peaks at 880 cm⁻¹ corresponds to the bending vibrations of V-O-V. The other two common peaks at about 1631 and 3437 cm⁻¹ in the samples are attributed to O-H stretching and H-O-H bending vibration modes of H₂O molecules. In addition, the peak at 1379 cm⁻¹ is related to -CH₂ bending vibration mode of trace organic molecules, which have not completely reacted during the solvent-thermal process. Thus the chemical formula of VEG is drawn inset in **Figure 13b**.

Once the VEG precursor is prepared, it is submitted to a post annealing process. The thermolysis of VEG usually leads to the preparation of VO_2 particles (**Eq. 3**). Various efforts have been done to study the annealing conditions, such as the annealing temperatures, annealing time and the atmosphere.

For the atmosphere of annealing, it is worth to mention that oxygen (O₂) is indispensable for the VO₂ preparation from VEG precursor. It has already been proved that V₂O₃ is obtained under inert atmosphere. [20] Among the various vanadium valences (+3, +4 and +5), V⁵⁺ is the most stable one, so the annealing temperature and time should be carefully controlled to avoid the formation of V⁵⁺ oxide.

The TG curve of VEG decomposition, shown in **Figure 14a**, describes a weight loss around 300°C of about 32.6%, which is consistent with the calculated weight loss (34.6%) based on the **Eq. 3**. The exothermic peak located at 253°C in the DSC curve corresponds to the pyrolysis of VEG. The small exothermic peak at 282°C can be attributed to the formation of V_2O_5 , which is accompanied by a small weight gain.

To choose the annealing temperatures, more detailed studies are carried out. As shown in **Figure 14b**, the variation in temperatures are recorded when VEG is heated at 180 °C in an oven full of air. It reveals that the real temperature inside the VEG sample, due from exothermic decomposition, can increase to a maximum value of 301 °C after about 23 min. Clearly, the local temperature value is much higher than the treatment temperature. It indicates that the exothermic decomposition reaction elevated the temperatures of the samples significantly and leads to a lack of control for such a process. The temperatures of the samples quickly dropped to below 300 °C from the maximum temperature after the decomposition reaction was completed. The thermolysis process lasts around 10 min. Besides, when the treatment temperatures increased from 180 °C to 300°C, the corresponding maximum temperature also increased nearly linearly from 300 to about 400°C, as shown in the inset of **Figure 14b**.



Chpt. I-Figure 14. (a). DSC-TG curves of VEG and (b) the variation in temperature of a VEG sample which decomposed at 180°C in an air atmosphere (inset: the highest temperature reached by samples during the decomposition of VEG at different treatment temperatures in an air atmosphere); (c) XRD patterns of VEG precursors synthesized at 160°C and VO₂ (M) synthesized by the thermolysis of VEG at 200°C; (d). Thermolysis of VEG for VO₂ preparation under different annealing temperatures and time. [18]
For example, reported by Zou *et al*, [18] the thermolysis of VEG conditions are set as 200°C for 30 min, and a black powder is obtained. Its XRD pattern (**Figure 14c**) matches that of the standard JCPDS card (N°. 43-1051) corresponding to VO₂ (M).

In fact, the annealing temperature and time for VO_2 preparation can be adjusted (**Figure 14d**). The annealing time basically follows the rules that a shorter time is needed when a higher annealing temperature is applied to the VEG. It takes 2 h for VO_2 synthesis when the annealing temperature is 170°C. It is shorted to 15 min when 240°C is applied.

Similar method was also used by H. Zhang *et al*, [19] they synthesized VO₂ (M) by combination of polyol synthesis precipitation of VEG precursor and pyrolysis process under air atmosphere. In their work, VEG was prepared by reacting NH₄VO₃ and $C_2H_6O_2$ under the condition of 160°C, and then the powder was heated in an oven at 180°C for 1 h for VO₂ preparation. During the thermolysis of VEG, higher V valence formed after a long time exothermal reaction. In order to eliminate or weaken the effect of energy surplus ion, the authors divided the pyrolysis process into two steps. The first pyrolysis step is fixed on 30 min, while the second pyrolysis time changes from 5 min to 30 min. However, no relatively purer and better crystallinity VO₂ (M) can be obtained using this route.

So one-step pyrolysis is chosen for VO₂ preparation. H. Zhang *et al* [19] studied the influences of annealing time on the product during the thermolysis of VEG and found that VEG starts its decomposition after 30 min at 180°C, as shown in **Figure 15**. High crystallinity and relatively pure VO₂ (M) is reported to be obtained after 1 h. However, traces of vanadium (V) oxides, such as V_2O_5 , V_6O_{13} , and V_3O_7 , are detected as impurities. The authors did not describe it as a surface oxidation, but rather as a partial energy surplus. The heat generated under the surface cannot dissipate at once in the pyrolysis process of VEG. This leads to trace of amounts of yellow V_2O_5 which could be observed at the bottom of the pyrolysis reactor.



Chpt. I-Figure 15. XRD patterns of powder prepared with one-step pyrolysis times ranging from 30 min to 60 min. [19]

In our group, Mjejri *et al* [21] also reported that well-crystallized VO₂ could be prepared by using a low-cost synthesis route based on the annealing of a single VEG precursor. The VEG was prepared *via* polyol synthesis by mixing the NH_4VO_3 as the vanadium source and EG as the template. After being heated under reflux at 160°C for 1 h with continuous stirring, a vanadyl glycolate (VEG) precipitate was obtained.

Chapter I: State-of-the-art and objectives

In this work, a higher annealing temperature than previous reports, equal to 500°C, was chosen for VEG decomposition, and vacuum ($PO_2\approx 2 \times 10^5$ Pa) was applied during the synthesis of VO₂, as illustrated in **Figure 16a**. The oxygen partial pressure was carefully controlled. It is believed that the crystallinity of prepared VO₂ powder will be highly increased thanks to higher treatment temperature than in previous studies. XRD pattern (**Figure 16b**) confirmed that the pure VO₂ was synthesized successfully. The corresponding TEM images are shown in **Figure 16c**. This route is ideal for the processing of very fine VO₂(M) powders having high purity, high crystallinity, excellent reproducibility, narrow particle size distribution, uniformity, and high reactivity.



Chpt. I-Figure 16. (a). Scheme of the polyol process used for the synthesis of vanadium pentoxide (V_2O_5) , vanadium dioxide (VO_2) , and vanadium sesquioxide (V_2O_3) powders obtained at 500°C post-treatment in air, post-treatment under vacuum, and under an Ar-H₂ atmosphere, respectively; (b). X-ray diffraction patterns of the as-synthesized VEG powders and V_2O_5 , VO_2 , and V_2O_3 ; (c). Corresponding TEM images. [21]

Besides, the VEG precursor is also a good precursor for the synthesis of V_2O_5 and V_2O_3 powders, through changing the atmosphere to air and 95% Ar/5% H₂ gas mixture, respectively. It should be mentioned that the experimental conditions are quite strict, which made it quite difficult to reproduce the preparation.

Towards to our work

In conclusion, VO_2 particles could be synthesized by pyrolysis of VEG in air at a relative lower temperature. It should be mentioned that the obtained VO_2 particles are easily aggregated, which is not beneficial for dispersion and film fabrication. Besides, the relatively lower synthesis temperature is unbeneficial to the VO_2 (M) crystallinity, and amorphous parts in the final product takes place.

In this work, to solve the mentioned difficulties, we propose a two-step (VEG decomposition and Post-annealing process) for VO₂ synthesis, through maintaining V⁴⁺ during the whole synthesis. After a short-time decomposition (~3 min) at 300°C, the VO₂ powder with large quantity of amorphous part is prepared. Then a post-annealing process is applied in a high temperature (500°C and 700°C) to increase its crystallinity and improve the performance. The crystallinity in each step is carefully calculated. The details of the optimization of this synthesis route are described in Chapter 2 of this manuscript.

3.3.Redox reaction strategy: From V⁵⁺ to V⁴⁺

Redox reaction is another effective strategy to prepare VO₂ (M) particles, while V₂O₅ is usually used as raw material. V₂O₅ can be reduced to VO₂ by supplementary reducing agents (*e.g.*, EtOH, H₂C₂CO₄, amine, alcohols, and N₂H₄) in hydrothermal/solvothermal reactions or in a reductive atmosphere during high-temperature annealing. The reducing agents and the synthesis methods are summarized in **Table**. **1**. As for the specific methods, they are hydrothermal method, solvothermal methods, gas reducing methods and electrochemical method. Only few solid reducing agents, allows leading to pure VO₂ compounds are reported.

Reducing agent	Vanadium	Method	Steps	Morpholoy	Ref
	precursor				
NH ₃	V_2O_5	Thermal reduction	1	Rhombohedral	[23]
N_2H_4	VOSO ₄	Hydrothermal method	1	Asterisk- shaped and microrod	[24]
Citric acid	V ₂ O ₅	Hydrothermal method	1	Spheres and fluffy	[28]
Li^+	V_2O_5	Electrochemical method	2		[25]
EtOH	V ₂ O ₅	Solvothermal reaction	2	Nanosheets or petaloid clusters	[22]
Oxalic acid	NH ₄ VO ₃	Hydrothermal- calcination method	2	Cucumber and nano- aggregates	[27]
Oxalic acid	V_2O_5	Hydrothermal- thermal treatment	2	nanowhiskers/ nanoneedles	[1]

Chpt. I-Table. 1. Redox reactions to prepare VO₂.

3.3.1. Hydrothermal method

As we have discussed, VO₂ has multiple polymorphic forms, including VO₂ (A), VO₂ (B) and VO₂ (D), and so on. The hydrothermal product is usually metastable phase or mixture phase, rather than the pure VO₂ (M) phase. The as-prepared metastable VO₂ phase can be transformed to VO₂ (M) by appropriate thermal treatment with different annealing conditions such as temperature, time, atmosphere and pressure. In another way, vanadium precursor V⁵⁺ can be reduced to VO₂ metastable phase through the hydrothermal method, a post-annealing treatment is necessary for the phase transformation to VO₂ (M) under appropriate conditions.

For example, Alie *et al* [31] reported on the isolation of VO₂ (M) particles by reducing V₂O₅ in the presence of oxalic acid (H₂C₂O₄). The molar ratio of the precursors plays a crucial role in fully reducing the vanadium to the desired V⁴⁺. The molar ratio between oxalic acid and V₂O₅ should be at least 2: 1 to fully reduce V⁵⁺ to V⁴⁺ (**Eq. 4**). VO₂ (A) phase is obtained using a 2: 1 molar ratio, by contrast, samples synthesized with a 3: 1 molar ratio yielded to VO₂ (M) phase. Besides, the synthesis temperature is also important as the VO₂ (B) phase would format at 160°C, and it can be fully converted to VO₂ (M) phase at 260°C.

$$V_2O_5 + 2H_2C_2O_4 \rightarrow 2VO_2 + 2H_2O + CO + 3CO_2 \dots Eq.4$$

Song *et al* [27] synthesized VO₂ (M) nanostructures of various shapes by a hydrothermal-calcination method. The VO₂ (D) polymorphs were also synthesized by reduction of NH₄VO₃ by H₂C₂O₄ under mild hydrothermal conditions. H₂C₂O₄ acts as the reducing agent in the first step. In the second step, the obtained VO₂ (D) was further calcined at 250-600°C for 3 h and transform to VO₂ (M). The reductive process could be described as **Eq. 5**, **Eq. 6** and **Eq. 7**. In order to describe the hydrothermal synthesis in greater details, *in situ* X-ray diffraction (XRD) experiment was conducted (**Figure 17a**).

$2NH_4^+ + 2VO_3^- + 4H_2C_2O_4 \to (NH_4)_2[(VO_2)(C_2O_4)]$	$(4)_{3} + 2CO_{2} + 4H_{2}O \dots Eq.5$
---	--

- $(NH_4)_2[(VO_2)(C_2O_4)_3] \rightarrow 2VOC_2O_4 + 2NH_3 + CO + CO_2 + H_2O \ldots \ldots \ldots \ldots \ldots \ldots \ldots Eq.\, 6$



Chpt. I-Figure 17. (a). Accumulated time-resolved in situ PXRD patterns (viewed down the intensity axis) collected during the synthesis at 200°C (λ = 0.7093 Å, solid content= 10 wt%); (b). XRD patterns images of the as-obtained VO₂ (D) and (c) VO₂ (M); (d) VO₂ (M) nano aggregates. [27]

The reaction mixture remained amorphous during the early stage of heating from room temperature to about 80°C. When temperature was further raised, bubbles were generated within the mixture, which were visible from the transparent capillary micro-reactor, suggesting intense reactions produced gases. The diffraction peaks belonging to VO₂ (D) appeared gradually and became stronger with increasing temperature and time. Once VO₂ (D) was formed (**Figure 17b**), VO₂ (M) was easily obtained by calcination of VO₂ (D) in vacuum. **Figure 17c** and **17d** presents the XRD patterns and SEM images of the as-obtained VO₂ (M) thermally treated at 550°C for 3 h.

Using same materials, Goncalves *et al* [1] also prepared VO₂ (M) based on a hydrothermal method assisted by microwave irradiation, using V₂O₅ and H₂C₂O₄ with 1: 1 molar ratio. This redox reaction leads to a change in the oxidation state of the vanadium cations from 5+ to 4+ as represented by Eq. 8. After 2 h stirring (mixed with WO₃), the solution displays a yellowish color (Figure 18a), after an additional microwave irradiation, the solution color changes to black powder and a supernatant blue

solution (Figure 18b). XRD confirmed that the black powder is the VO_2 (B). It means that V_2O_5 is successfully reduced to VO_2 .

$$V_2O_5 + H_2C_2O_4. H_2O \rightarrow 2VO_2(B) + 2CO_2 + 2H_2O \dots Eq.8$$

And then a thermal treatment was applied to transform the VO₂ (B) to VO₂ (M), as illustrated in **Eq.** 9. The DSC measurements were carried out to determine the required annealing temperature needed to obtain the expected VO₂ (M) phase (**Figure 18c**). The presence of exothermic peak at 357°C suggests the phase transition from VO₂ (B) to VO₂ (M), while the endothermic peak at 690°C is the melting point of some residual V₂O₅. After the *in-situ* annealing, the prepared VO₂ powder shows the phase transition VO₂ (M) to VO₂ (R), with an endothermic peak at 71.5°C (inset **Figure 18c**).



Chpt. I-Figure 18. Photography of the solutions prepared, before (a) and after (b) microwave irradiation; (c) DSC thermograms of as-prepared VO_2 (B) powder. The inset shows the VO_2 (M) powder after the in-situ annealing process. [1]

Son *et al.*, [24] reported hydrothermal synthesis and characterization of VO₂ (M) micro- and nanocrystals by hydrothermal treatment of hydrolyzed precipitate from V₂O₅ using N₂H₄ as a reducing agent. These authors established that the reaction conditions such as pH, temperature, and NaOH solution concentration could control the size and shape of the crystals from asterisk-shaped microcrystals to hexagon-shaped nanocrystals. Mutta *et al* [28] reported that the synthesis of VO₂ (M) *via* a hydrothermal process by reacting V₂O₅ and citric acid monohydrate in the steel autoclave with 250°C for 24 h. During the synthesis, citric acid was used as the reducing agent.

We can get a conclusion that hydrothermal method is the most common method to fabricate highquality VO₂ nanoparticles, and has its own advantages of large-scale synthesis and precise phase control of VO₂, and V₂O₅ and H₂C₂O₄ system is quite popular. It should be noticed that there are many parameters influencing the physicochemical properties of the powder synthesized by the hydrothermal methods. Among these parameters: the molar ratio of precursors, the hydrothermal temperature and the molar concentration of solution prior to synthesis, have the most significant effect on morphology and structure of the VO₂ powders.

3.3.2. Solvothermal method

 VO_2 (M) nanosheets and petaloid clusters can be also synthesized by solvothermal reaction and subsequent heat treatment of the mixture of commercial V_2O_5 powder and absolute alcohol (Et-OH) in a high-purity N_2 atmosphere, as reported by Liu *et al.* [22]

Here Et-OH acts as the reducing agent, and mixed with V_2O_5 powder. The autoclave with mixtures were sealed and maintained at 453K for 4 h. And then the obtained powder was calcined at 623 K under

high purity N_2 (99.999%) atmosphere to obtain blue-black crystalline VO_2 (M) powder. The process can be described in Eq. 10.

Two kinds of V_2O_5 were used in this work, commercial product and homemade one. Figure 19a and 19b shows typical XRD patterns of V_2O_5 and VO_2 , respectively. Figure 19c and 19d displays nanosheets and petaloid clusters of VO_2 (M). It reveals that the starting vanadium precursor has a big effect on the obtained VO_2 (M). A portion of ethanol, which served both as the reducing agent and the solvent, was oxidized to aldehyde. Thus, the total reaction of V_2O_5 and excess ethanol under the solvothermal condition could be expressed as follows:



Chpt. I-Figure 19. (a). XRD patterns of V_2O_5 : commercial product and homemade; (b). XRD patterns of VO_2 : with different morphologies: nanosheets and petaloid clusters; (c). HRTEM image of VO_2 nanosheets and (d) petaloid clusters. [22]

3.3.3. Gas reducing method

Some gas can be also used in the VO₂ synthesis as reducing agent. As illustrated by Qi *et al* [23], ammonia (NH₃) gas is used as one reducing agent for VO₂ preparation. The reduction of V₂O₅ in NH₃ gas leads to the direct synthesis of high-purity VO₂ (M). The container loaded with V₂O₅ was placed into a tube furnace. After the temperature reached 800 K, a mixture flow of NH₃ (5 ml/min) and N₂ (110 ml/min) was passed through the furnace. The XRD pattern of the sample matches well with VO₂ pure phase (**Figure 20a**) with no impurity peaks. The reaction equation could be expressed in **Eq. 11**:



Chpt. I-Figure 20. (a). X-ray diffraction pattern; (b). SEM image of the product VO₂. [23]

SEM results (Figure 20b) showed that the grain size distribution of the VO_2 microcrystal is in the range from several to several decade micrometers. The morphologies of the VO_2 particles are rhombohedral. The size of obtained VO_2 is quite large and uneven.

3.3.4. Electrochemical method

Electrochemical process is another way for VO₂ (M) synthesis by reducing vanadium precursor with V^{5+} to VO₂. Chen *et al.* [25] demonstrated a method to fabricate VO₂ particles through such process using V₂O₅ as cathode. An accurate control of the electrical discharging currents leads to the reduction of V⁵⁺ to V⁴⁺ allowing the successful synthesis of VO₂ particles. The author proposed three steps to describe the reduction: (i) electrochemical intercalation of Li⁺ and reduction of V⁵⁺ to V⁴⁺, (ii) ion exchange of Li⁺ with H⁺ by acid rinsing, and (iii) dehydration and VO₂ crystallization by annealing.

The process is shown in **Figure 21a**, and the electrochemical cell is presented in **Figure 21b**. It provides a new route to precisely control the reduction of layer-structured oxides. The process can also be summarized by the equations in **Figure 21c**.



Chpt. I-Figure 21. Schematic illustration of: (a) the three steps method; (b) structure of the device for electrochemical intercalation; (c). Corresponding equations. [25]

Towards our our work

In conclusion, the reduction strategy has been widely studied. More reductive agents are put forward. However, the redox reaction method has two weaknesses: the impurity of the as-prepared product and the toxicity of the intermediate compound: V_2O_5 . Besides, only few solid reductive agents are developed. The biggest challenge goes to the impurity problem due to the un-fully mixing. In another word, the valence state control is quite difficult due to the easy reduction of V^{5+} to V^{3+} directly in such reductive reaction.

As the solid reductive agent also shows many advantages, such as large-scale preparation and easy operation, we proposed a carbo-thermal reduction method for VO_2 synthesis. The V_2O_5 (homemade) is reduced to VO_2 successfully in the dynamic vacuum system. The synthesis mechanism is investigated by comparing the carbo-thermal reduction in dynamic vacuum and sealed vacuum system. The obtained VO_2 powder with various sizes shows good purity, high crystallinity and excellent thermal stability.

The carbo-thermal reduction processes developed during this thesis are detailed in the Chapter 3.

3.4. Redox reaction strategy: From V³⁺ to V⁴⁺

Oxidization from low valence vanadium oxides (V₂O₃) for VO₂ preparation is a more exotic synthesis strategy. By combining solution-phase hydrolysis and a thermal reduction process, a convenient route for the preparation of thermochromic VO₂ particles has been developed by Lu *et al.* [33] In their work, V₂O₅.xPy.yH₂O spheres were prepared by hydrolysis of vanadium isopropoxide VO(OiPr)₃ in acetone/pyridine/water solution. And then the V₂O₅.xPy.yH₂O powders were treated at 300°C for one hour to form crystalline V₂O₅, and reduced to V₂O₃ by heating in a tube furnace at 400°C for 2 hours under hydrogen flow (purity 99%, flow rate ~0.15 SCFH). Then the as-prepared V₂O₃ was converted to VO₂ at 400°C for 2 hours under N₂ atmosphere (purity 99.995%). [33] The detail process is also presented in **Figure 22**. It indicates that H₂ is not a perfect reducing agent for the preparation of VO₂, due to its strong reductivity. Using this method, the particle size can be easily tuned from tens to hundreds of nanometers.



Chpt. I-Figure 22. (a) Synthetic scheme for the vanadium oxide particles. (b) SEM images of (i) amorphous V_2O_5 .xPy.yH₂O, (ii) crystalline V_2O_5 , (iii) V_2O_3 and (iv) VO_2 (M) nanostructures. (c) The corresponding XRD patterns. [33]

3.5.Particle size control

Primary studies indicated that the thermochromic properties of VO_2 strongly depended on its size and morphology. In details, decreasing the VO_2 particle size can not only facilitate material processing but can also affect in a positive way the phase transition temperature and hysteresis properties.

One possibility to decrease the particle size and produce particles easy to disperse into a matrix involved mechanical ball-milling. Simply by milling a micro-sized commercial VO₂ powder, Liu *et al.* [34] prepare VO₂ nanoparticles with an average size of 20 nm. The weight percentage of commercial VO₂ powder was 23 wt%, and the organic solvent was dipropylene glycol methyl ether (DPM), the dispersing agent was Disperbyk 180 (4.5 wt%). The obtained dispersion was milled for 4 h in Dyno-Mill Research Lab WAB with the use of zirconia beads at the speed of 4200 rpm, followed by settling in the ambient condition for 2 days.

In the synthesis of VO₂, many experimental parameters including the reaction time, the temperature and the nature or morphology of the precursors, play a key role on the structure and purity of the vanadium oxide formed as well as on its morphology and size. Decreasing annealing temperature or the time could decrease the sintering effect, and then prevent the formation of large particles.

4. Film preparation

Several methods have been developed to fabricate VO_2 -based films. Based on films surface morphology, these VO_2 films can be grouped into two groups: (i) continuous films and (ii) discontinuous films.

Several chemical and physical technique have also been reported to prepare dense and continuous VO₂-films, including magnetron sputtering, [63-68] CVD, [69-70, 76] PVD, [71-73] Sol-gel, [41,72, 74,77, 86, 90] solution methods [75, 87, 82] and so on. Capon *et al* fabricated VO₂ film using magnetron sputtering, and their optical and electrical properties are fully discussed. [95] Vapor deposition is an efficient method for high quality VO₂-film fabrication. Depending on system configuration, there are several types of CVD systems such as atmospheric pressure CVD (APCVD), plasma enhanced CVD (PECVD), metal-organic CVD (MOCVD) and so forth. These techniques have been used to deposit VO₂ film as summarized by Long *et al*. [76] In addition, using sol-gel method, Liu *et al* [70] developed a VO₂ thin films deposited by aqueous medium followed by post annealing. The equipment required for the film deposition is usually complex and expensive. Solution-based deposition process is more cost effective, high-yielding, and flexible, but it always suffers from multiple-steps, lower purity, and small-scale production.

However, for the continuous film, the thickness needs to be increased to overcome the insufficient ΔT_{sol} but at the cost of depressing the T_{lum} . T_{lum} and ΔT_{sol} are usually limited and are unsatisfactory for practical use. Furthermore, it is required that for thermochromic application the phase transition temperature (T_c) has to be reduced through element doping. In most cases, the reduced T_c is always gained at the expense of lower T_{lum} and smaller ΔT_{sol} .

Two promising ways are investigated to tackle the trade-off relationship between T_{lum} and ΔT_{sol} : (i) multifunctional antireflection coatings; (ii) discontinuous films.

(i) For the design of multifunctional antireflection coatings (**Figure 23**), such as the $TiO_2/VO_2/TiO_2$ as well as $TiO_2/VO_2/TiO_2/VO_2/TiO_2$ [36] multilayer structures, which is found to be effective in achieving the simultaneous enhancements of T_{lum} and ΔT_{sol} . Magnetron sputtering is one of the most widely used methods for preparation of multilayer films. Compared to other physical methods like pulsed laser deposition (PLD), the competitive advantages of the sputtering process are remarkable homogeneity and compactness in products, promising scalability in large-scale substrates, and high efficiency in deposition. As far as we know, the best results, with a ΔT_{sol} of 15% and a T_{lum} of 50%, were achieved

by optically designing an optimized multilayered structured. [37] However, design such complicated film architecture results in several difficulties and a high cost of production.

(ii) In order to form discontinuous coatings, nano- and microscale engineering are proposed, including incorporating particles in a hosting transparent materials, tuning the porosity in the porous films, designing nanocomposites, creating grids. These discontinuous films include porous films, [51, 52, 58] photonic crystals structure, biomimetic surface reconstruction, [47, 48, 53, 54] gridded structure. [49, 55, 56] Based on the VO₂'s distribution on substrate and the film microstructure and morphology, the discontinuous films can be divided into three groups: three-dimensional, two-dimensional and zero-dimensional pattern's films (**Figure 23**). A summary of the different kinds of discontinuous film is given in the following part.



Chpt. I-Figure 23. Multifunctional antireflection coatings and different types of discontinuous film: three, two and zero-dimensional pattern.

4.1.Three-dimensional: Composite

The three-dimensional pattern is more often called composite structure. It is prepared by dispersing the particles in a dielectric host, such as polymers or metal oxides. Lot of experimental results and calculations [38-42] have shown that VO₂-based composite films have superior properties than the VO₂-based continuous solid films.

Usually, there are three requirements for the preparation of a VO₂-based composite film. (i) Ultrafine particles with size far smaller than the wavelength of visible light; (ii) Good dispersion in host to form a uniform and transparent coatings; (iii) High crystal quality of the VO₂ particles to achieve strong solar energy regulation ability.

In a composite film, VO_2 nanoparticles with fine crystallinity are dispersed in various hosting materials, for practical applications. Depending on whether they display distinct optical modulation during heating, the host materials can be classified as responsive or non-responsive matrixes,

(i) Responsive matrixes. As we shown in previous work, solar energy is dense in the visible range (43% of solar energy), but VO₂ cannot regulate in this region due to the limited difference of the optical constants in spectrum range of 400-800 nm between its rutile and monoclinic phases. Incorporating a responsive hosting material has been proved to be a promising way to overcome this limitation.

(ii) Non-responsive matrixes. Over the past decade, it has also been proved that VO₂-based nonresponsive composite can improve the thermochromic performances. Among these studies, the common used host materials are polyurethane (PU), Si-Al gel, polydimethylsiloxane (PDMS) and TiO₂. Long's group adopted a transparent Si-Al gel as the host material. [34] The VO₂ nanoparticles were well dispersed in the Si-Al gel, then the composite gel was coated on glass. Similar process, using PDMS polymeric matrix was employed Moot *et al.* [93] Inorganic hosting materials, such as TiO₂, were also explored. [43] The inorganic-inorganic composite coatings were fabricated successfully by two-step annealing of VO₂ nanoparticles in TiO₂ sol, for illustration.

But, the most widely studied host material remains PU. The VO_2 particles showed good dispersibility in aqueous solution containing PU, and embedding doped VO_2 nanoparticles into the PU matrix achieved superior thermochromic properties.

The incorporation of pure VO₂ nanocrystals with PU was achieved by Chen *et al.* [43] Firstly, crystalline VO₂ nanoparticles were prepared *via* a hydrothermal method. XRD results indicated that the precursor decomposition started at 150°C and completed at approximately 245°C (**Figure 24a**). The lowest formation temperature of VO₂ (M/R) was approximately 240°C. The obtained VO₂ particles average diameter was around 26 nm (**Figure 24b**). Then VO₂ nanoparticles were well dispersed in a PU matrix through the assistance of polyvinylpyrrolidone (PVP) forming a visible homogeneous film.

Cross sectional SEM (Figure 24c) and its partial enlargement image (Figure 24d) show that NPs were well-dispersed in the PU matrix. The VO₂ composite coatings are uniform, with an intrinsic yellowish green color (Figure 24e). They have huge infrared transmittance difference before and after phase transition, whereas the reflectance of the composite coating at 20°C and 100°C is independent with wavelength and remains below 8% (Figure 24f).



Chpt. I-Figure 24. (a). XRD of the nanoparticles synthesized at different temperatures. (b); SEM images of the VO_2 (M/R) prepared at 330°C. Insets show the size distribution (d=26 nm); (c). Cross sectional SEM of the PU & VO_2 composite coating and a partial enlargement image (d); (e) VO_2 composite photo; (f) Ttransmittance and reflectance difference before and after phase transition at 20 and 100 °C, the shadow is the spectral distribution of solar energy. [44]

Hence, the composite coatings based on the use of VO_2 nanoparticles can show wonderful optical performance. They displayed a much lower reflectance than the pure VO_2 coating on bare glass. The low reflectance, combined with the small size and high crystallinity of the VO_2 nanoparticles, revealed

a remarkable ΔT_{sol} of 22% and an acceptable T_{lum} of 45.6% at low temperature and 40.0% at high temperature, which is very close to the highest simulation results (ΔT_{sol} = 23.7%).

To improve their anti-oxidation and anti-acid abilities, a novel all-solution process that can be used to prepare transparent, stable and flexible VO₂-based composite films is put forward by Gao *et al.* [44] VO₂ nanoparticles were pretreated in a PVP aqueous solution to adsorb PVP onto the VO₂ surface. Second, the treated VO₂ particles were transferred into an ethanol solution with siloxane groups which form SiO₂ shells (**Figure 25a**). From EDS analysis, the formation of a VO₂-SiO₂ core-shells was shown (**Figure 25b**). Third, the VO₂-SiO₂ particles were further treated in an aqueous solution containing a trace amount of silane coupler. This treatment increased the dispersion of the particles in an aqueous solution containing PU. Finally, a VO₂-based composite film was prepared by casting the suspension on a PET flexible substrate (**Figure 25c** and **25d**).



Chpt. I-Figure 25. (a). TEM images of the silica-coated VO_2 particles after functionalization with PVP; (b). EDS spectrum of spot A and spot B pointed out in the image (a); (c). Preparation of the flexible composite films using $VO_2@SiO_2$ nanoparticles; (d). XRD patterns of the uncoated VO_2 and $VO_2@SiO_2$ nanoparticles after heat treatment at 300°C for 2 h in air and (b) the transmittance at 500 nm for the particles dispersed in an acidic solution for different time durations. [44]

The SiO₂ coating shell could serve as a barrier layer for oxygen diffusion, and it is expected to prevent the VO₂ from being oxidized to V₂O₅. This inference was confirmed by a comparative study of the uncoated and coated particles after annealing at 300°C in air for 2 h. As shown in **Figure 25d**, in addition to the diffraction peaks for VO₂ (M), V₂O₅ was also detected, making up approximately 62% of the uncoated sample, as estimated from the intensity of the main diffraction peaks associated with VO₂ and V₂O₅ structure. However, the V₂O₅ peaks were not observed for the VO₂@SiO₂ sample. Thus VO₂@SiO₂ structures effectively enhanced the anti-oxidation and acid-resisting properties of VO₂.

A comparative acid-corrosion experiment was carried out to investigate the anticorrosion properties of VO₂@SiO₂. Equal amounts of uncoated VO₂ and VO₂@SiO₂ were added to a hydrochloric acid solution (pH= 1). The slower increase of transmittance plot clearly shows that VO₂@SiO₂ was able to withstand the acidic treatment because of the protection of the SiO₂ shell (**Figure 25e**).

4.2.Two-dimensional patterned films

The introduction of air-filled nanopores, which are considered to be a secondary component in VO₂ films have been proved to be an effective method to improve the thermochromic performance (ΔT_{sol}), especially the T_{lum} .

The introduction of periodical patterned VO₂ can help achieve more favorable T_{lum} and ΔT_{sol} simultaneously. Ordered arrays of colloidal nanocrystals (NCs) represent an important class of metamaterials with tunable structures and properties. Two-dimensional (2D) patterned nanostructures [51], such as 2D ordered nanostructure arrays, surface-patterned nanostructures, and free-standing 2D patterned films, have attracted intensive interests due to the pattern-dependent properties. Here the properties of porous film and grid film, two typical two-dimensional VO₂ films, will be discussed.

4.2.1. Two-dimensional: Porous film

To prepare air-filled nanopores structured VO_2 film, many methods have been developed. These methods can basically be separated into three groups:

(i) Incorporating removable additive (pore formers), such as PVP, [46] cetyltrimethylammonium vanadate (CTAV), [53] cetyltrimethyl ammonium bromide (CTAB), [57] polyethylene glycol (PEG), [60] or SDS. [59]

(ii) Process control, such as freeze-drying [54] and sintering in CO₂ atmosphere [55].

(iii) Self-assembly methods, such as dual-phase transformation [56] and crystallographic orientation control.

Incorporating removable additives into the vanadium precursor has been demonstrated to be a facile way to fabricate porous films. Kang *et al.* [46] pioneered the preparation of VO₂-based porous films by a polymer-assisted deposition method. The image of the as-prepared VO₂ film is represented in **Figure 26**. The pores in the final films are formed from PVP degradation and combined with the shrinkage control of the gel films during high-temperature annealing. These air-filled pores had feature sizes much smaller than the visible wavelength lowering the optical constants (reflective index) without contributing to new significant scattering phenomenon, resulting in a high luminous transmittance.



Chpt. I-Figure 26. SEM image of VO_2 *films on quartz glass (a) on surface, and (b) the inset of part a is a cross-sectional SEM images. [46]*

Besides, using a dip-coating process, a micro-/nanosized hierarchical porous structure was also fabricated by Huang *et al.* [53] through the self-assembly of cetyltrimethylammonium vanadate (CTAV), which exhibited largely enhanced visible-light transmittance.

Instead of incorporating removable additives into the precursor, Long's group [54] achieved porous VO₂ films by controlling the drying procedure *via* a lyophilization method (freeze-drying). The powder precursors were dissolved in solution to form sol followed by gelation to form a more rigid structure, and the solution was dip-coated onto the fused silica substrates. The process is presented in **Figure 27a**, and the XRD patterns consist of a low intensity single peak at $2\theta \approx 28.0^{\circ}$ ascribed to the (011) plane of VO₂ (M) (**Figure 27b**).

The corresponding morphologies for the films obtained using different freeze-drying parameters are shown in **Figure 27c**. The calculated porosities vary from 2% up to 33%. This procedure can easily circumvent the collapsed pores induced by evaporation under atmospheric pressure.



Chpt. I-Figure 27. (a). Schematic flowchart for the synthesis of a control film via evaporation (ambient drying) and nanoporous film via lyophilization (freeze-drying); (b). XRD patterns of samples coated using different drying process; (c). and their corresponding SEM images. [54]

A spontaneous self-templating and assembly process during dual-phase transformation was successfully applied by Liu *et al.* [56] to prepare VO₂ porous structures. The formation of hydrous colloids was promoted by N_2H_4 but impeded by HCl. During the evaporation process, the promotional effect of N_2H_4 was enhanced, but the quenching effect of HCl was weakened, forming hydrous colloidal spheres from the homogeneous precursor. These spheres self-assembled into a close-packed structure at the colloid substrate interface when saturation was reached in the hydrous colloids. Thereafter, the hollow sphere structures developed at 300°C and then collapsed and crystallized to VO₂ during annealing at 500°C.

To be specific, this process can be divided into four steps: (i) The aqueous precursor was spin-coated on quartz substrate (**Figure 28a**). (ii) The precursor was spontaneously self-templated and assembled into hydrous sphere arrays after water evaporation in dry nitrogen. With evaporation of solvent, a large amount of hydrous colloids in microscale was formed (**Figure 28b**). (iii) The film was transferred to a preheated furnace at 300°C, leading to a rapid film solidification and resulting in a periodic structured framework. The hydrous colloids quickly dehydrated to VO(OH)₂ hollow spheres (**Figure 28c**). (iv)

These porous hollow spheres collapsed to honeycomb structures due to the weakened support strength, as shown in **Figure 28d**.



Chpt. I-Figure 28. (a-d) Formation mechanism of the highly ordered honeycomb-structured $VO_2(M)$ film inspired by the spontaneous self-template and assembly (SSTA) during the dual-phase transformation process; (e) Digital photo of a piece of ordered honeycomb-structured $VO_2(M)$ film with the dimensions of 25 mm × 20 mm; (f) Low magnification SEM image and a high magnification insert; (g) XRD patterns of the honeycomb-structured $VO_2(M)$ films with different thicknesses. [56]

Finally, the VO₂(M) film with highly ordered honeycomb microstructures are prepared. Figure 28e shows that the as-prepared VO₂ film is transparent with a pale bronze color. The microstructure has been investigated using scanning electron microscopy (SEM), as shown in Figure 28f, revealing the highly ordered honeycomb patterns. Figure 28g shows the XRD patterns of the VO₂ films with different thicknesses. The intensity of (011) plane of VO₂ (M), located at 2θ = 27.8°, is enhanced with increasing film thickness.

4.2.2. Two-dimensional: Grid film

Films based on grid-structured VO_2 have attracted increasing interest due to the great potential of structure-induced thermochromic enhancements, including but not limited to increased transmittance, antireflection. Up to now, there are several methods to prepare VO_2 films with grid structure. The methods are electrodeposition, [50] mesh printing, [68] nanosphere lithography [45] and modified nanosphere lithography. [61]

To fabricate such structure film, the electro-deposition method is used in Long's group. [50] The VO₂ nanoparticle coating is made from its aqueous dispersion without involving oxidation-reduction. Based on the ionic strength by electrical potential in the vicinity of the electrode surface, it caused the deposition. The concept is illustrated in **Figure 29a**. The optical images of the as-prepared VO₂ grid film are presented in **Figure 29b**. The mesh printing method, was reported by Lu *et al.* [68] to prepare micro-patterned VO₂/Si-Al gel composites by mounting a mesh above a glass substrate with controllable distance. The micro-patterned structure is able to favorably transmit visible light without sacrificing high near-infrared modulation.



Chpt. I-Figure 29. (*a*). Diagram of the concept of ionic strength induced electrodeposition; (*b*). Optical images of Cu grid/PET bare substrate and (*c*) VO₂ nanoparticles deposited on the conductive Cu grids. [50]

The preparation of grid films with periodicity in nanoscale is challenging. Colloidal lithography based on monolayer colloidal crystals (MCCs) is a facile, inexpensive, efficient, and flexible nanofabrication approach towards a wide variety of 2D patterned nanostructures with high controllability and reproducibility. Till now, the MCC-based colloidal lithography techniques have been successfully used for the controllable fabrication and assembly of a wide variety of 2D patterned nanostructures. [51]

For example, Xie's group [45] applied MCCs templates made of polystyrene (PS) nanospheres to prepare periodic porous VO₂ films. In their study, MCC templates consisting in closed-packed PS nanospheres were sequentially immersed vanadium precursor, then removed during annealing to leave the VO₂ nanonet structures. In the fabrication process of the periodic porous structure, PS spheres play a dual role as a hard structural template and a phase control material. The size of PS spheres is around 420 nm (Figure 30a). After removal of the PS spheres, a nearly semi-spherical hollow array with truncated tops as openings structure is obtained (Figure 30b). The authors also changed the precursor concentration to study the morphology evolution.



Chpt. I-Figure 30. SEM images of (a) MCC template, PS, with edge view inset; (b). Periodic ordered porous $VO_2(M)$ film. SEM images of morphology evolution of the $VO_2(M)$ film at different precursor concentrations: (c) nanoring array, 5 mmol/L; (d) nanonet array, 10 mmol/L; and (e) thicker nanonet array, 15 mmol/L; (f). Corresponding optical performances of the samples shown in (c)-(e). [45]

As we can see in **Figure 30c-30e**, the morphology of the obtained VO₂ films varies from a nanoring array and a nanonet array. Investigating the optical properties conclude that the lower space occupancy of VO₂ (M) is, the more visible light can be absorbed and the less near-infrared light can be switched, resulting in higher T_{lum} and ΔT_{sol} (**Figure 30f**).

Ke *et al.* [61] modified the nanosphere lithography method and produced diverse patterned VO₂ films with tunable periodicity and nanostructures, including nanoparticle, nanonet, and nanodome arrays. The fabrication process was flexible by controlling the plasma etching duration and precursor viscosity. The template with PS spheres be assembled in a hexagonally close-packed way, the inter distance between two adjacent PS spheres was controlled *via* Ar/O₂ plasma etching (PE). When the treatment lasts for 300 s, the size of PS spheres with a diameter of 640 nm is diminished (**Figure 31a**), while the sphere morphology is maintained.



Chpt. I-Figure 31. Effects of Synthesis Conditions on the Morphology Evolutiona. Route 1: Nanoparticle arrays are prepared via short PE duration and low viscosity precursor. Route 2: Nanodome arrays are produced, using high viscosity precursor that can stick on the tops of PS spheres. Route 3: Nanonet arrays are fabricated by controlling the interval space between adjacent spheres via prolonging PE duration; (b). SEM images of PS sphere MCC template after PE treatment of 300 s, and its original morphology as the inset. SEM images of patterned VO_2 films; (c). Nanoparticle; (d) nanodome; and (e). nanonet arrays prepared using 830 nm PS. [61]

After PE treatment of 300 s, the PS spheres are shown in **Figure 31b**. Inset shows the original morphology of PS spheres. The PE duration and precursor viscosity are carefully studied and controlled. It is found that when a short duration is applied, nanoparticle and nanodome arrays can be produced using low-viscosity and high-viscosity precursors (**Figure 31c** and **Figure 31d**), respectively. Nanonet arrays can be fabricated by prolonging the PE duration and using low-viscosity precursors. The produced 2D patterned VO₂ arrays are highly uniform (**Figure 31e**).

4.3.Zero-dimensional film

In this thesis, the zero-dimensional film is defined as the VO_2 with various shapes are separately and independently distributed on substrate surfaces. It looks like the islands in the sea. To prepare such morphology film, there are also some methods developed recently: acid-etching method, nanoimprinting method and one-step annealing process.

4.3.1. Zero Dimensional: Acid-etching method

An acid-etching top down method was proposed to tailor the VO_2 surface morphology from the continuous dense-packed surface to patterned structure, [52] as illustrated in **Figure 32a**. The proposed surface engineering methods represent a facile and cost-effective approach for enhancing thermochromic properties that could promote the application of VO_2 thin films in smart windows.



Chpt. I-Figure 32. (a). Schematic illustration of the surface engineering process through acid etching method; (b). Typical XRD for the VO₂ thin film prepared within this experiment. AFM images for VO₂ thin films starting from V_2O_5 - H_2O_2 precursor after HNO₃ etching for 0 min, 1 min and 2 min. The initial thickness for (c) and (d) are 500 nm/side and 100 nm/side. [52]

The XRD pattern in **Figure 32b** shows the characteristic (011) peak at $2\Theta \approx 28^{\circ}$ for monoclinic VO₂ indicating the formation of the VO₂ (M) phase. The broad XRD peak at $2\Theta \approx 20^{\circ}$ is ascribed to the signature of amorphous SiO₂ substrates. In **Figure 32c** and **32d**, the surface engineering *via* acid etching was performed on continuous VO₂ thin films with different film thickness (500 and 100 nm/side). Due to the different thermal mismatch response between the film and the substrate, the thick precursor film resulted in the normal dense-packed VO₂ film while the thinner one gave rise to the nano-grain array patterned continuous VO₂ film after annealing.

4.3.2. Zero Dimensional: Nanoimprinting method

Fabrication of subwavelength plasmonic building blocks from Au colloidal NCs has recently been demonstrated by nanoimprinting to achieve large-area, complex metamaterials. [62] Coupling this colloidal nanocrystal-based nanoimprinting technique with metallic VO_2 allows the preparation of switchable plasmonic VO_2 nanostructures.

The synthesis process is illustrated in **Figure 33a**. First, polymer resins are patterned by nanoimprint lithography using a nanostructured Si master designed in size and shape. Then, colloidal NCs are spin-coated on top of the patterned substrate, followed by lift-off of the polymer resins to deposit patterned VO_x thin films. Phase-change VO₂ nanostructures are then obtained after RTA of the patterned VO_x NC films. **Figure 33b-33c** shows SEM images of planar arrays of VO₂ nano-pillars and nano-wires.



Chpt. I-Figure 33. (a). Schematic of subwavelength VO_2 nanostructure fabrication using nanoimprint lithography; SEM images of VO_2 nanostructure arrays of (b) hexagonal lattice of nanopillars and (c) nanowires. [62]

4.3.3. Zero Dimensional: One-step annealing process

Independent island-structure VO₂ film is another type of discontinuous film, which has been reported by Long's group. [55] Based on the coating of V₂O₅-H₂O₂ precursor solution on fused silica substrates, high quality VO₂ films with various nanostructures. The key step creating the porosity is the annealing step of the precursor in CO₂ atmosphere, which is prepared by dissolving V₂O₅ in 30% H₂O₂. The annealing temperatures ranges in between 550-750°C. After boiling vigorously for a short time, a dark red sol was formed. The films deposited on fused silica substrates *via* spin coating were annealed at 350-750°C in a CO₂ gas flow, for structural characterization.

As shown in **Figure 34a**, the XRD results revealed that the valence reduction process in a CO_2 atmosphere could be roughly assumed to be $V_2O_5.2H_2O \rightarrow V_3O_7 \rightarrow VO_2$, and the major VO_2 (M) phase was obtained at 550°C.



Chpt. I-Figure 34. (a). The XRD results for the films grown on fused silica substrates at different annealing temperatures from 350 to 750 °C in CO_2 atmosphere; (b-d) The FESEM images for the films grown on fused silica substrates at different sintering temperatures (450, 550, 650 and 750°C). [55]

When the temperature was 550°C, an intriguingly interconnected nanoporous structure with elongated platelet VO_2 grains appeared (**Figure 34b**). As the temperature increased to 650 and 750 °C, the grains were isolated from each other, and zero dimensional island structures could be formed, and the island size and the island to island distance increased with temperature (**Figure 34c** and **Figure 34d**). The layer growth to island growth transition was mainly due to an increase in thermal stress with increasing growth temperature.

Towards to our work

It appears from the literature review, quite attractive to prepare zero dimensional VO₂ films with islandshape morphology. In this work, we also propose a new and simple method to fabricate island-structure VO₂ film using V₂O₅ nanoparticles as the vanadium source. The suspension is spinning coated in a quartz substrate. PVP, which is normally used as pore former, acts, in our strategy, as a surface stabilizer in the V₂O₅ suspension as well as a reducing agent during the annealing process. As it will be further described, V₂O₅ is reduced to VO₂ successfully. XRD pattern reveals a strong 011 peak of VO₂ (M), which indicates a highly crystallized structure thanks to the high temperature annealing (700°C). SEM images confirm the as-prepared VO₂ film morphology is island-structure dispersed on the substrate surface.

More details will be discussed in the Chapter 5.

4.4.Film color issue

Due to its strong absorption, especially in the blue part of the spectrum, VO_2 films typically demonstrates a brownish-yellow color (**Figure 35**). The color has limited effects on the visible transmittance, and color preference is closely related to cultural background. Generally, a colorless coating or coloration with light gray/blue is perceived as most favorable.

The brownish-yellow color of VO₂ would be acceptable, however, certain modifications are still required to tune the color. Although some simulations have suggested that doping may be an effective strategy to alter the color by shifting the adsorption edges (gap control), experimental results have shown that only limited changes can be achieved. Complexion with dyes or responsive matrix, either organic or inorganic, can modulate the original color of VO₂ at the expense of the ΔT_{sol} and T_{lum} of VO₂ films or transparency, which may not be desirable for some applications.



Chpt. I-Figure 35. Optical image and scheme image of the $VO_2(M)$ nanoparticle-based film.

5. Elemental doping

Since too high T_c is one of the long-lasting issues hindering the practical application of VO₂ in smart windows, metal ion doping is widely investigated to tailor the transition temperature (T_c), especially toward lower temperature. Elemental doping is a process that intentionally introduces other element(s)

into a pure material to modify its electrical or optical properties. Presently, more than 60 elements have been investigated as dopants for the VO_2 system either experimentally or theoretically (simulation models).

5.1.Doping strategy

The electronic phase transition in VO₂ is proposed to be accompanied by a (nearly) simultaneous structural phase transition between the VO₂(R) and VO₂(M) phase. It can be considered that to decrease the phase transition temperature, one has to produce a stabilization of the rutile phase to the detriment of the monoclinic one. On the opposite, a stabilization of the monoclinic form to the detriment of the rutile one, would induce an increase of the transition temperature, as illustrated in **Figure 36**.

Accordingly, the selection of the doping element is commonly based on two aspects: (i) increasing the carrier concentration with the effect to stabilize the metallic form (R) to the detriment of the insulating one (M) and so leading to a decrease of the transition temperature: this corresponds to the management of the phase transition temperature with a Mott approach; (ii) producing some defects, which deteriorate the ordered phase (M) (for illustration, fighting against V-V pairing) and so leading also to a decrease of the transition temperature: this corresponds to the management of the phase transition temperature.



Chpt. I-Figure 36. Scheme illustration of Mott approach and Peierls approach to tailor the transition temperature (T_c) through stabilizing the metallic form (R) or desstablizing the monoclinic form (M).

In the point view of Mott model, the element doping can increase the carrier concentration of VO_2 . When the doping element serves as the donor or acceptor in VO_2 , it injects its electrons or holes into the electronic structure of VO_2 , which increases the carrier concentration in the system. The increased carrier concentration could stabilize the high conductivity phase (rutile form) to the detriment of the insulating phase (monoclinic phase), thus decreasing the T_c. Depending on the valence of doping element, there are two ways to increase the carrier concentration.

(i) One way is to insert monovalence doping atoms into the interstitial sites of VO₂ (**Figure 37a**), such as hydrogen (H), lithium (Li) or sodium (Na). For instance, H is the lightest atom, which possesses one electron in its outermost orbital. When H atoms are doped into VO₂, it is found that the atoms are located at the interstitial sites and inject their electrons into the VO₂ system. The T_c can be reduced by 38 K/at% H. Explained by Cu *et al*, [78] the reduction in T_c is coupled with the changes in atomic and electronic structures, *i.e.*, the V-V chains feature the dimerization characteristics in H-doped VO₂ (R) and the V-O bonds become less ionic due to the formation of a typical H-O covalent bond.



Chpt. I-Figure 37. (*a*). The location of H atom at the tetrahedral (left) and octahedral (right) interstitial site in VO₂, where H, V, and O atoms are indicated by blue, gray, and red spheres, respectively; [78] (b). The location at which a W atom substitutes the V atom in VO₂. [79]

(ii) The other way to increase carrier concentration consist in the substitution of V sites with high-valence elements (**Figure 37b**). The typical elements are W, Nb, and Mo. For example, Zhang *et al* [79] calculated the substitution energy of W in VO₂ system. The negative value of the energies indicates that W can be doped into a VO₂ system easily. As a result, the reduction in T_c is calculated to be 27 K/ at% W and 18.6 K/ at% W depending on doping methods.

In the point view of Peierls model, introducing distortion into the atomic structure, especially along the V-V chain, can also assist the structural phase transition. To simplify, the introduction of a doping ion can induce as distortion in the rutile structure which decreases the re-organization to transform rutile into monoclinic form. Namely, if a dopant causes the V-V distances in $VO_2(R)$ to alternatively change thereby resembling that of $VO_2(M)$, the dopant will lower the T_c.

For example, Zhang *et al.* [80] reported that Be-doped VO₂(R) displays structural distortion around the Be atom, where the V-V chains present dimerization similar to those in VO₂(M). In detail, the short V–V distances in the Be-doped VO₂(M) range from 2.50 Å to 2.53 Å, quite close to the value of 2.52 Å in the pure VO₂(M). The structure of VO₂(R) are strikingly distorted by the doped Be with respect to that of VO₂(M). Finally, the authors predicated that the reduction of T_c in the Be-doped VO₂ is as large as 58 K/at% through first-principles calculations.

Indeed, the variations in the carrier concentration and structural distortion frequently occur together, as the doping element either occupies the interstitial sites or substitutes the lattice site of V or O atoms, leading to variations in both the electronic and atomic structures of VO₂.

Moreover, it was recently shown that the monoclinic VO_2 exhibit a complex phase transition diagram, involving not only the standard MIT between the monoclinic (M1) and rutile phase (R), but also possibly some other allotropic forms as triclinic (T) and a second monoclinic system (M2). Here it should be pointed out the M phase in this thesis refers to M1 phase. Doping with some elements could cause the formation of VO_2 (M2 or T). **Figure 38** shows a schematic diagram depicting mutual transformations of VO_2 phases as a function of composition and temperature.



Chpt. I-Figure 38. Schematics of temperature-composition phase diagram showing influence of doping and uniaxial stress along the [110] R crystallographic direction of the $V_{1-x}M_xO_{2+y}$ on the phase distribution. [81]

Substitution of V⁴⁺ with cations of higher oxidation state (*e.g.*, W⁶⁺, Nb ⁵⁺, and Mo⁶⁺) lowers the transition temperature, whereas dopants of lower oxidation states, such as Cr^{3+} , Al^{3+} , Fe^{3+} , or Ga^{3+} stabilize the M2 or T phases of VO₂ at room temperature. This behavior is in effect identical to reduction and oxidation of the V⁴⁺ ions, respectively, which is confirmed by studies of doped and undoped nonstoichiometric VO_{2+y}. The effect of application of uniaxial stress along the [110] direction of the R phase is similar to that of oxidation.

The effects of some doping elements on the MIT transition temperature are summarized in **Figure 39**. As simulated by Cui *et al*, [92] it seems K shows the highest doping efficiency, the d_{Tc}/d_x reaches 94 K/ at%.



Chpt. I-Figure 39. Elemental doping effects on the thermochromic performance of VO₂ thin films.

Actually, for all these doping elements showing a high doping efficiency, the T_c versus doping concentration is simulated, such as for H, Li, Na, K, Be and B. [91, 93, 106] As far as we know, none experimental results are reported. In terms of experimental results, the best doping elements are those with some certain higher valence cations. T_c can be experimentally adjusted to near room temperature by doping the materials with W, Mo and Nb or by the incorporation of fluorine (F) anions [82] into the VO₂ lattice.

5.2.W doping

Tungsten (W) is the most effective doping element to decrease the transition temperature. Based on previous researches, the reduction of T_c in the phase transition by around 20°C to 26°C per at% of W.

To unravel the MIT mechanism of VO_2 triggered by W doping, Tan *et al* [83] studied the atomic structure evolutions of W dopant and its role in tailoring the T_c of VO₂ MIT, using synchrotron radiation X-ray absorption spectroscopy combined with first-principles calculations. It is found that the local structure around W atom is intrinsically symmetric with a tetragonal-like structure, exhibiting a concentration-dependent evolution involving the initial distortion, further repulsion, and final stabilization due to the strong interaction between doped W atoms and VO₂ lattices across the MIT.

Among various synthesis routes, Zou *et al* [84] reported the preparation of $V_{1-x}W_xO_2$ powder wth tunable phase transition by a simple carbothermal reduction method. Based on calcination under carbonrich atmosphere (reductive atmosphere) of commercial V_2O_5 and $5(NH_4)_2O.12WO_3.5H_2O$ precursor, W can be introduced into VO₂ lattice successfully. **Figure 40a** represents the XRD patterns and enlarged part of XRD patterns of prepared $V_{1-x}W_xO_2$ solid solution powders. For the undoped sample, all peaks correspond to monoclinic VO₂ (M) while as early as the introduction of 0.01 doping content, the W-doped VO₂ exhibits the rutile structure. Besides, the enlarged part of XRD pattern (**Figure 40b**) shows the gradual shift of the main diffraction peak of the plane (110) of VO₂ (R), which indicates that the lattice constant increases with increasing W-doping content. As the atomic radius of W (2.02 Å) is larger than that of V (1.92 Å), the increase of lattice constant well agrees the W substitution on V of VO₂ (R) lattice.



Chpt. I-Figure 40. XRD patterns (*a*) and enlarged part of *XRD* patterns (*b*) of prepared $V_{1-x}W_xO_2$ solid solution powders. [97]

Besides, Song *et al* [85] found that using sodium tungstate (Na₂WO₄) as the dopant is efficient to make the doping V sub-lattice with W and so to lower the T_c . The authors believed that Na metal can be used as co-dopant for W-doped VO₂. With the co-doping of Na, W doping yields an extra depression in phase temperature of 6-12°C over that of 20-26°C per at% of W.

5.3.Nb doping

Substitutional niobium (Nb) atoms have also been found to depress the VO₂ transition temperature in bulk, thin films, and nanostructured samples. It is worth mentioning that the substitution with transition metals, such as Nb and W, depresses the VO₂ transition temperature but also reduces the difference in resistivity and reflectivity between the two phases. Especially, increasing Nb content beyond x = 0.05 results in a transition that occurs more gradually over a broad range of temperatures.

Reported by Piccirillo *et al*, [86] Nb-doped vanadium dioxide ($V_xNb_{1-x}O_2$) thin films were prepared by aerosol-assisted chemical vapour deposition (AACVD) of vanadyl (4+) acetonate and niobium (5+)

ethoxide in ethanol (**Figure 41**). A high Nb content up to 3.7 at% was introduced, and 2% of Nb in the film was shown to lower the transition temperature by 15°C.



Chpt. I-Figure 41. Schematic representation of AACVD experimental apparatus. [86]

Continuous hydrothermal flow synthesis (CHFS) [87] is another means to synthesize Nb-doped VO₂ nanoparticles. The schematic diagram is presented in **Figure 42a**. The X-ray diffraction patterns of the undoped and Nb-doped samples both matched the VO₂ (M) reference exclusively (**Figure 42b**). TEM images showed that nanoparticles in the size range of 30-40 nm were produced (**Figure 42c-42d**).



Chpt. I-Figure 42. (a). Schematic diagram of the continuous hydrothermal flow synthesis (CHFS) process used in the direct synthesis of VO_2 (M) nanoparticles; (b). XRD patterns of the VO_2 (M) and Nb- VO_2 (M) nanoparticles synthesised by CHFS; TEM images of (c) undoped VO_2 and (d) Nb-doped VO_2 .

CHFS has the advantage of being a direct, reproducible and scalable method. Unlike batch hydrothermal processes, CHFS is a continuous process, thus once a system is optimized it is possible to produce kg of material per hour. Previously, CHFS has been utilized to prepare VO_2 (M) and Nb-doped VO_2 (M) samples in a two-step process, in which the initial VO_2 product contained impurities and required post-synthesis annealing at 600°C to obtain phase pure VO_2 (M).

Barron *et al* [88] summarized T_c as a function of the Nb content from different literature articles. **Figure 43** mainly shows T_c decreased literally with increasing of Nb content. On the other hand, many studies report a minimum transition temperature between 35 and 50°C, suggesting that Nb may loses its efficiency beyond a critical concentration. Nonetheless, lacking the doping route, which could guarantee

the high Nb doping content keeping Nb-doped powder with a pure and homogeneous composition, could be also the reason of the absence of studies showing that the T_c can be lowered to 35°C.



Chpt. I-Figure 43. Temperature of the thermochromic transition as a function of Nb content in a $V_{1-x}Nb_xO_2$ combinatorial library. The linear fit at low Nb contents is extrapolated to higher Nb contents with a broken line. Transition temperatures from the literature for Nb-substituted VO₂ are included for comparison.

In Nb-doped VO₂ compounds, the oxidation states of vanadium (+4, +5) are also carefully studied by X-ray photoelectron spectroscopy (XPS). As illustrated in **Figure 44**, two oxidation states, V^{4+} and V^{5+} , at binding energies of 514.8 and 516.3 eV, co-exist.



Chpt. I-Figure 44. X-ray photoelectron spectroscopy (XPS) analysis of (a) undoped and (b) Nb (15%)VO₂ nanoparticles; [89] (c) Fitted XP spectra of the Nb-substituted VO₂ from select positions along the y-axis of the library film (x-position= 60 mm): (c1) V (2p) and the O (1s) spectral features were fitted to deconvolute the spectra. The raw data and the composite fit are offset for ease of viewing; (c2) The Nb (3d) region was fit with a background and the area under the curve was acquired. [88] XPS of the V $2p_{3/2}$ environments in the (d) undoped VO₂ and (e) Nb-VO₂ samples. [87]

According to previous study, [89] there is a significant change in the V⁴⁺: V⁵⁺ ratios upon Nb incorporation, resulting in an increase of V⁴⁺ ions in the doped samples. The authors believed that the Nb ions would presumably be incorporated initially in a reduced form and drive the reduction of V ions, favouring the content of V⁴⁺ ions at high Nb concentrations. The V⁴⁺: V⁵⁺ ratio (at%) changed from 17:

83 to 66: 34. Similar results are also reported. [88] As the Nb content increasing, the peak intensity at 514.8 eV, which corresponding to the V⁴⁺, keeps increasing. However, Malarde *et al* [87] reported contrast results. Nb doping did not cause any significant effect on the oxidation of the VO₂ powder, pure VO₂ and doped one shows the same V⁴⁺: V⁵⁺ ratio (*ca.* 33: 67) as we can see in **Figure 44d-44e**.

Hence, Nb-doping seems a promising solution to tune the T_c of VO₂ compound, but new studies need to be done in order to clarify some important key issue as the maximal doping concentration that can be reached and the effect of the Nb corporation on the vanadium oxidation state.

5.4.Al doping

The T_c can be reduced when donor is doped with higher-valence ions, and increased when acceptor is doped with lower-valence ions (Al³⁺, Cr³⁺, and Ga³⁺). In the study dealing with the increase of T_c by doping trivalent ions, the Al³⁺ dopant substitution gives rise to a phase diagram which displays three insulating phases: the monoclinic (M or M1), another monoclinic (M2) and a triclinic (T) phases. The M2 phase always emerges as an intermediate phase between the M1-R transition, and can only be stabilized at room temperature with sufficient Al/Cr-doping. Intriguingly, M2 phase is a Mott insulator, which can transform to a metallic M2 phase upon carrier injection (so with intermediate properties between R and M phases), showing potential applications in Mott field-effect transistor. Recent reports showed that M2-phase trivalent ions-doped VO₂ were more useful than M1-phase VO₂ for prospective microelectromechanical or optomechanical device applications, such as microcantilevers.

Wu *et al* [90] reported a new route to synthesize Al-doped VO₂ samples *via* a hydrothermal method followed by an annealing treatment. XRD patterns showed M1 and M2 phases of Al-doped VO₂ were successfully formed by controlling the Ar flux rates (**Figure 45a**). M2 phase was formed in the low Ar



Chpt. I-Figure 45. XRD patterns of the Al-doped VO_2 samples with different Al-doping concentrations, to form the crystal structure of (a) M1 phase and (b) M2 phase. In the top of both panels the corresponding structures of the two phases are shown.

flux rate (Figure 45b). The mechanism of the controllable phases of Al-doped VO_2 is related with the annealing treatment and the phase formation is considered to be sensitive to the oxygen partial pressure (oxygen content) in the annealing process.

Towards to our work

As we have developed a carbo-thermal reduction method for VO₂ synthesis using 700°C annealing for step in vacuum for 15 h. Element doping, namely W^{5+} , Nb^{5+} , Ti^{4+} and Al^{3+} , was experimentally tested through this new method.

Particular focus was put on doping with higher valence ions as the transition temperature can be tailored largely, so W^{5+} and Nb^{5+} were first tried.

Especially for the Nb doping, its impact on the physico-chemical properties of the $V_{1-x}Nb_xO_{2\pm\delta}$ oxide powder, focusing on the phase transition (*i.e.* heat capacity, resistivity and magnetic susceptibility variations through the transition), was carefully investigated. Furthermore, a deep investigation of the magnetic properties: impact of doping concentration and particle size on the susceptibility of the $V_{1-x}Nb_xO_{2\pm\delta}$ powder versus temperature, was carried out to highlight the doping effect.

The details are described in Chapters 3 and 4.

6. Reference

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Chapter II: Two-step synthesis of VO₂ (M) with tuned crystallinity

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Chapter II: Two-step synthesis of VO2 (M) with tuned crystallinity

1. Introduction

As a popular vanadium precursor, vanadyl ethylene glycolate (VEG) has been investigated through pyrolysis method to synthesize VO₂ (M) sub-micronic powder. [1, 2] In our group, Mjejri *et al.* reported the synthesis of VO₂ powder from a single polyol route by annealing the VEG directly under very low oxygen pressure ($\sim 10^{-5}$ Pa). [2] In order to eliminate or weaken the effect of energy surplus during VEG decomposition, Zhang *et al.* prepared VO₂ by dividing the VEG pyrolysis process into two steps. [3] Zou *et al.* obtained VO₂ powder *via* the thermolysis of VEG precursor in air atmosphere. [4] However, most of the studies in the literature focused on the thermochromic properties of synthesized VO₂ powders, while the decomposition of VEG and the quantification of crystalline VO₂ in powders synthesized with different annealing temperatures have not been yet investigated. This is a key issue as the occurrence of undesired amorphous VO₂ without any thermochromic properties would act drastically to the detriment of the smart optical/electrical effect of the as-prepared powders.

In this chapter, pure VO₂ (M) powder with high crystallinity through a two-step process (VEG decomposition and post-annealing treatment) was synthesized based on the improved polyol route reported by Mjejri *et al.* [2] Instead of annealing the vanadium precursor (VEG) directly in oxygen-free environment, the VEG is decomposed firstly in air, leading to the synthesis a relative pure VO₂ with poor crystallinity, further used as the starting material for the full-crystallization of VO₂ at higher temperatures in oxygen-free atmosphere. In summary, the decomposition process of VEG in the first step thermolysis, and the morphologies and crystallinity of obtained VO₂ powders from different conditions in the second step annealing are investigated, analyzed and discussed. Moreover, novel and particular microstructures for V₂O₃ and V₂O₅ compounds are also synthesized through this method changing the atmosphere of the second step annealing

2. Experimental

2.1.First step thermolysis for the VEG decomposition

Ammonium metavanadate (NH₄VO₃; 99.0%), ethylene glycol ($C_2H_6O_2$) were purchased from PROLABO and Sigma. 1.42 g NH₄VO₃ was mixed with around 125 ml $C_2H_6O_2$ in a 250 ml three-neck flask and heated to 160°C under vigorous stirring as reported. [2] The reaction time is 2 h after 30 min temperature increasing. The precipitate was collected by centrifugation, washed with ethanol three times, and dried overnight in oven at 80°C to remove excess of ethanol. Then the obtained vanadyl ethylene glycolate (VEG) precursor was heated in the furnace (air) at 300°C for durations from 1 to 90 min.

2.2.Post annealing treatment of poorly crystallized VO2 powder

The resulting powders from first step were further annealed in a nearly oxygen-free atmosphere (PO₂<10⁻⁴ bar) to enhance their crystallinity of VO₂ powders. After the decomposition of VEG for 3 minutes at 300°C, the powder (VO_x-3min) was chosen as the starting material for the post annealing for 5 h at temperatures of 500°C and 700°C in the second step, as illustrated by the **Scheme 1**. The annealing temperature was controlled by a temperature controller with a heating rate of about 10 °C/min. Furthermore, V₂O₃ and V₂O₅ with new and particular morphologies were prepared by annealing VO_x-3min powder under different conditions: 800°C for 0.5 h under Ar/H₂ atmosphere (95: 5 mol% ratio) for the preparation of vanadium sesquioxide (V₂O₃), and 600°C for 0.5 h under air for the preparation of vanadium pentoxide (V₂O₅).


Chpt. II-Scheme 1. Illustrations of the preparation of VO_2 , V_2O_3 and V_2O_5 .

3. Result and discussions

3.1. Synthesis of VEG

During its preparation of VEG with the polyol process, V^{5+} in NH₄VO₃ is reduced to V^{4+} by ethylene glycol (EG) with the consequent formation of vanadyl complex on the condition of 160°C for 2 h. EG is not only a well-known solvent used as the polyol method to prepare highly divided metal particles, but also a cross-linking reagent coordinating to the central metal ion to form a metal glycolate further leading to subsequent oligomerization. The detail process was recorded as shown in **Figure 1**. The color changes indicate the valence changes of vanadium before the temperature reaches to 160°C.



Chpt. II-Figure 1. Polyol process for VEG preparation in different stages.

3.2.Decomposition of VEG

To short the VEG decomposition time, referring to our own TGA measurements as well as the one reported with DSC data by Zhang *et al*, [3] the VEG precursor is annealed at 300°C in air. To select the

best annealing time, 1-5 min, 8 min and 90 min are tested in this work. And the XRD patterns results were shown in **Figure 2.** It can be observed that VEG gradually transformed into VO₂ and then V_2O_5 with annealing time. To be specific, the pyrolysis process can be separated in two stages.



Chpt. II-Figure 2. XRD patterns of samples synthesized by thermolysis of VEG precursor at 300°C in air with different annealing time (1-5 min, 8 min and 90 min). Corresponding PDF numbers provided at the bottom.

In the first stage (0-3 min), the VEG precursor starts to decompose and forms poorly crystallized VO₂ phase, as described as **Eq. 1**. The intensity of the peak at 2θ = 13.46° corresponding to a preferred (110) Miller orientation of the VEG compound decreases gradually during heating at 300°C in the first two minutes with simultaneous rising of VO₂ (M) peaks (the main peak being located at 2θ = 27.95°). Two phases VO₂ (M) as major phase and VO₂ (B) as minor one coexist after the heating treatment for 3 min, named as VO_x-3min sample while no more VEG peaks are detected.

$$2VO(OCH_2CH_2O) + 5O_2 \rightarrow 2VO_2 + 4H_2O + 4CO_2 \dots \dots Eq. 1$$

With continuous heating, V (V) containing phases start to emerge due to the further oxidation in the second stage (4-90 min), as shown in **Eq. 2**. XRD results show that traces of vanadium (V) oxide powders (V_2O_5 and V_6O_{13}) start to form at 4-5 min, also as a result of partial energy surplus due to the exothermic process of VEG decomposition. [3] After 8 min annealing, some new peaks (like $2\theta = 20.26^{\circ}$

and 26.26°) (Figure 2), which belong to V_2O_5 (space group: Pmmn, JCPDS No. 41-1426), appear and VO_2 coexists with V_2O_5 . Finally, VO_2 is entirely converted to V_2O_5 after VEG being heated for 90 min.

Figure 3a insets displays the photos of the VO_x obtained powders after decomposition of VEG precursor. For deeper comparison of the optical properties of the decomposition products, the reflection spectra are measured in the 200-2500 nm and in the UV-visible region (200 - 800 nm) as shown in **Figure 3b** and **3c**, respectively. Undecomposed VEG shows a bluish grey color, corresponding to a reflection of visible radiation at around 470 nm. The color changes to black after being heated for 3 min with a rather flat reflectance spectra of less than 5% in the visible region, corresponding to the color of VO₂ powder. After longer time heating, an orange color starts to emerge due to the presence of V₂O₅ phase. At 8 min, the orange mixes with the remaining black color from VO₂, and the color of the obtained powder becomes dark green (VO_x-8min) and the reflection gap shifts to higher wavelength (*i.e.* 560 nm). Finally, a completely orange color appears after 90 min, which indicates the full oxidation in V₂O₅, with a clear charge transfer band gap locates at about 600 nm. The color of each powder is consistent with the evolution of the phases previously detected by XRD data in **Figure 2**.



Chpt. II-Figure 3. (a) The reflection spectra of the VEG, VO_x -3min, VO_x -8min and VO_x -90min samples in the wavelength region of 300-2500 nm, insets show photos of the VEG and VO_x samples; and (c) their reflection spectra in the visible region of 200-800 nm.

The corresponding morphologies from low-magnification SEM (Figure 4) consist of elongated cuboids that remain basically unchanged after heating at 300°C for 90 min. Because of the large surface energy, these cuboids easily aggregate, forming spherical aggregates about 5 μ m size.

In order to gain further insight into the decomposition process of VEG, high resolution SEM is applied to VEG and VO_x-3min samples. As shown in **Figure 4a**, VEG nanostructures exhibit an elongated cuboid morphology and a typical length of several micrometers (~1.6 μ m) and an average length of ~350 nm (in its rectangular cross section). After 3 min heating in air and removal of the organic components (C and H), the cuboid shape remains, while the detailed morphology as cuboid surface changes from smooth to rough aspect (**Figure 4a** and **4b**). Combined with its TEM image (inset in **Figure 4b**), the structure of cuboid after decomposition could be seen more clearly and composed of numerous small particles, which can be attributed to the removal of organic part in the form of CO₂ and H₂O during the VEG annealing (**Eq. 1**), *i.e.* the small particles can be attributed to the appearance of the VO₂ crystallites.

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Chpt. II-Figure 4. SEM images of (a) VEG; and its decomposed products at 300 °C for different times: (b) VOx-3min (inset shows the evident porosity from its corresponding TEM), (c) VOx-8min and (d) VO_x -90min.

3.3.Post annealing treatment of VO_x-3min

3.3.1. Synthesis of VO₂

From the combination of the XRD data and morphology of decomposed products, the optimal time of heating VEG is around 3 min. The VO₂ powder (VO_x-3min) obtained from VEG decomposition is of relatively poor crystallinity due to the short heating time (3 min) at a rather low temperature (300°C), as confirmed by the wide XRD peaks (**Figure 2**).

Four samples with different decomposition times in the first step (VEG, VO_x-2min, VO_x-3min and VO_x-5min) were chosen for a higher temperature post annealing treatment. These samples were heat treated at 500°C for 5 h in an environment free of oxygen (PO₂<10⁻⁴ bar) in order to avoid VO₂ from being oxidized into V₂O₅.

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Chpt. II-Figure 5. (a) Carbon content of samples obtained through heating VEG with different times at 300 °C in air (1-5 min). (b) The XRD patterns of samples (S-0min, S-2min, S-3min and S-5min) synthesized after a post annealing treatment at 500 °C for 5h in oxygen-free atmosphere from VEG, VO_x -2min, VO_x -3min and VO_x -5min, respectively. (S-3min was also named as S-500 in the following).

As organic components, carbon materials are usually used as reducing agent, like hydrazine reported by Cao *et al*, [14] thus the carbon content of each sample is measured before annealing, and its evolution *vs* heating time is shown in **Figure 5a**. Overall, the carbon content decreases during the decomposition (**Eq. 1**). Thus a post annealing treatment at higher temperature for the VO_x-3min sample is necessary to prepare VO₂ powder with a higher crystallinity. During the second annealing step, it is found that the decomposition time for the VEG in the first step plays a critical role on the formation of VO₂.

The initial VEG contains around 12.42% of carbon. After a decomposition time of 2 min, 7.89% of carbon still existed in the VO_x-2min sample, which can be attributed to undecomposed VEG remaining in the powder. After the VEG being heated for 3 min (VO_x-3min), the carbon content decreases to 0.98%, indicating the nearly fully decomposition of the VEG. The residual carbon content remains unchanged for longer annealing times (VO_x-4min and VO_x-5min). The carbon content of most samples before and after annealing at 500 °C are gathered in **Table. 1**.

Table 1. Carbon content of samples before and after annealing at 500°C in the vacuum, measured from CHNS elementary analyzer.

Sample: Before annealing		Sample: After annealing		
VEG	12.42%	S-0min	3.11%	
VO _x -2min	7.89%	S-2min	1.86%	
VO _x -3min	0.98%	S-3min	0.24%	
VO _x -5min	1.14%	S-5min	0.10%	

The XRD patterns of post annealing samples are shown in **Figure 5b.** The 500°C post-annealing of VO_x-3min leads to the so-called S-3min sample. Pure V_2O_3 (S-0min) is obtained when VEG is annealed at 500°C in oxygen-free atmosphere, in agreement with previously reports showing that only V_2O_3 can

be obtained under inert atmospheres. [3, 4] Unexpectedly, the XRD of S-2min sample also shows a pure V_2O_3 phase (**Figure 6**). The lack of VO_2 peaks after post annealing treatment indicates that the V^{4+} is probably reduced to V^{3+} by reducing agents for the VO_x -2min sample that is in fact a combination of VEG and VO_2 (**Figure 2**) and that contains quite a lot of carbon (7.89%). The existence of carbon probably causes the reduction of VO_2 to V_2O_3 . When the VEG is heated for longer times (3 min and 5 min), the carbon content further decreases to a quite low level (0.98%) (**Figure 5a**), which might avoid the reduction for VO_2 to V_2O_3 . The XRD pattern of the S-3min and the S-5min samples showing mainly VO_2 (M) phase (**Figure 5b**) confirms our hypothesis that there is no V^{3+} after the post annealing treatment. However, in the S-3min sample especially in the S-5min sample, peaks of undesired V_6O_{13} phase, known as a V^{4+} and V^{5+} mixed valence oxide, [1, 11] are visible. Its presence probably results from excessive oxidation during the VEG decomposition in the first step (**Figure 2** and **Eq. 2**).



Chpt. II-Figure 6. Microstructure of V_2O_3 *particles* (*S*-2*min*) *obtained by post annealing* VO_x -2*min sample at* 500°C; (*a*) *SEM image;* (*b*) *TEM image;* (*c*) *HRTEM collected at the edge of a single particle and* (*d*) *its corresponding d-spacing of* 0.37 nm, *as indexed to* [012] *plane.*

To summarize, a relatively pure VO₂ phase (S-3min, called later S-500) with high crystallinity is synthesized by our two-step thermal process. Firstly, a thermolysis step allows the preparation of poorly crystallized VO₂ (VO_x-3min), by decomposing the VEG in a strict heating time (\sim 3 min). Organic part of undecomposed VEG remains in the powder when the heating time is shorter than 3 min, would



Chpt. II-Figure 7. (a) Rietveld refinement of X-ray diffraction pattern for VO_2 (M) (S-700) synthesized at 700°C for 5 h through post annealing of VO_x -3min powder. The observed and calculated intensities are represented by red crosses and the black solid line, respectively. The bottom blue line shows the fitting residual difference. The Bragg positions are represented by dark cyan ticks. (b) The refined structure of monoclinic VO_2 (M). The octahedron unit consists of one vanadium atom and six oxygen atoms, which are colored orange and red, respectively.

contribute to reduce the VO₂ to V_2O_3 in the follow-up post annealing treatment. On the contrary, V (V) coexists with V (IV) in the powder when the decomposition process is longer than 3 min. As V (V) is the most stable vanadium state, [11] it is difficult to remove once it is formed. Those results emphasize that the decomposition time for VEG in the first thermolysis needs to be controlled very accurately.

3.3.2. The crystal structure and morphology of the synthesized VO₂ samples

To study the influences of crystallized temperature on VO₂ powders, [5] VO_x-3min sample is chosen as starting material for another post annealing treatment at a higher temperature (700°C) in oxygen-free environment (S-700).

In an attempt to clarify structural analysis, XRD data was processed to software program Fullprof and the Rietveld structure refinement is shown in **Figure 7a** and **Table. 2.** With satisfactory convergence factors ($R_{Bragg} = 4.85$, $R_f = 4.2$), the diffraction pattern is refined as the monoclinic phase of VO₂ (M) (space group P2₁/C), with lattice parameters a = 5.7550(1) Å, b = 4.5291(7) Å, c = 5.3854(8) Å, and β = 122.6030(4) °. The corresponding structure deduced from unit cell parameters and V, O atomic positions extracted from Rietveld refinement is shown in **Figure 7b**. We confirm that the structure and atomic positions match with JCPDS data card 00-044-0252 from the reported structure of monoclinic VO₂. [12] No characteristic peaks of any other phases are detected, indicating that the sample is highly pure. Traces of V₂O₅ and V₆O₁₃, which were detected in the VO_x-3min powder before post annealing, are probably reduced to VO₂ during annealing at high temperature. [13] This reduction is helped by a mechanism of dilution of the minor phases into the VO₂ main phase in order to decrease the surface energies (co-sintering phenomenon).

Space group	P 1 21/c 1 (14) Monoclinic			
Cell parameters	a	b	С	β
	5.7550(1) Å	4.5291(7) Å	5.3854(8) Å	122.6030(4)°
Atom	Wyck position	Х	У	Z
V1	4e	0.2393(6)	0.408(2)	0.0266(6)
01	4e	0.095(2)	0.216(2)	0.198(2)
02	4e	0.408(2)	0.720(2)	0.308(2)

Table. 2. Lattice Parameters and Atomic Positions of VO₂ (M) (S-700).

The morphologies of VO₂ powders synthesized by VEG decomposition (VO_x-3min), and post annealing of VO_x-3min sample at 500°C (S-500) and 700°C (S-700) for 5 h, are displayed in **Figure 8**. The VO_x-3min sample shows a cuboid structure composed of uniform nanoparticles (**Figure 8a**). After post annealing at 500 °C, the elongated shape of the cuboids of VO₂ starts to break down and becomes a rod-like structure (**Figure 8b**) composed of larger nanoparticles. When the post annealing temperature is increased to 700°C, the rod-like structure is further broken down and the isolated VO₂ particles become more regular with clear grain boundaries (**Figure 8c**). To be more specific, the polyhedron (Octahedron deformation: *i.e.* A and B) shape indicates a crystallization through a preferred growth direction (111) ensuring the lowest surface energy.



Chpt. II-Figure 8. TEM and SEM images of the as-prepared VO_2 (M) particles synthesized with conditions (a) VO_x -3min: 300°C for 3 min in air through decomposition of VEG; (b) S-500: post annealing treatment of VO_x -3min at 500°C for 5 h in oxygen-free atmosphere; (c) S-700: post annealing of VO_x -3min at 700°C for 5 h in oxygen-free atmosphere.

Meanwhile, the corresponding particles size distribution (**Figure 9a**) shows that the size slightly increases from 32 nm to 46 nm after the post annealing at 500°C, and greatly increases to 745 nm when the temperature is 700°C. In literature reported by Xiao *et al*, [5] a large sintering effect was observed for vanadium dioxide particles in the same temperature ranges. Indeed, a similar large increase of VO₂ particle size is correlated to the huge endothermal peak at 675°C from DSC data. Those authors also discussed that the aggregation effect decreased drastically because of the low particles surface energy, and well-isolated VO₂ particles were observed, especially when the particle size was larger than 500 nm. The evolution of the morphology of our samples, is summarized in **Figure 9b**.



Chpt. II-Figure 9. (a) Size distribution of synthesized VO_2 particles (VO_x -3min, S-500 and S-700). (b) Schematic illustration of the morphological evolution for VO_2 particles. (A and B designate two kinds of deformed octahedron)

3.3.3. The crystallinity calculation of the synthesized VO₂ samples

To determine the nature and the proportion of the various components present in our three kinds of VO_2 powders, X-ray powder diffraction was used. The quantification analysis, using Rietveld refinement with Fullprof program, [6] was deduced from the scale factor of the different phases either amorphous or crystalline. [7]

An amount of calibration salt: lanthanum hexaboride (LaB₆), mixed as around10 wt.% with the three VO₂ samples (VO_x-3min, S-500 and S-700), is used as reference for calculation of the components proportions. The Rietveld refinement results are shown in **Figure 10a-c**, showing well-quality fit. The diffraction peaks at $2\theta = 27.95^{\circ}$ (**Figure 10d**), corresponding to the preferred (011) orientation of VO₂ (M), are thinner and of higher intensity for the annealed VO₂ powders (S-500 and S-700). The decrease of full width at half maximum (FWHM) from 0.554 ° to 0.292 ° and 0.162 ° after the post annealing treatment at 500°C and 700°C, confirm the trend of the increase in average crystallite size in agreement with the TEM and SEM results in **Figure 8**.



Chpt. II-Figure 10 Typical Rietveld refinements of XRD data from (a) VO_x -3min; (b) S-500; (c) S-700; (d) Comparison of XRD peak at $2\theta = 27.95^{\circ}$ preferred (011) orientation for VO_2 (M); (e) and the corresponding weight percentage of each component.

In addition to the larger crystallite sizes after being post annealed, the crystallinity of VO₂ particles also increases significantly. Deduced from the XRD patterns and analysis with Fullprof program (**Figure 10a-10c**), the weight percent of each component (including amorphous VO₂) in VO₂ powders is plotted in **Figure 10e.** The weight percent of crystalline VO₂ increases from 44% to 79% after post annealing at 500°C (S-500). Furthermore, it is of 100% when the post annealing temperature is increased to 700°C (S-700). It could be clearly observed that the proportion of crystallized VO₂ is improved clearly after post annealing in oxygen-free atmosphere. The enhanced crystallinity of VO₂ (M) should promote its thermochromic effect and make it more stable in the air environment.

It is well known that the first order phase transition of VO₂ (M) occurs at around 68°C with a large variation of latent heat. The DSC analysis of three synthesized VO₂ samples (VO_x-3min, S-500 and S-700) was measured using the same conditions (heating rate: 5°C/min, atmosphere: Ar, and in between - 30°C and 110°C) for both heating and cooling cycles (**Figure 11**). The endothermic and exothermic peaks during heating and cooling cycles are clearly visible. After post annealing, a more obvious phase transition of S-500 and S-700 samples comparing with the initial VO₂ (M) powder (VO_x-3min sample) is observed. To be more specific, the phase change enthalpy (Δ H) during the heating cycle increases from 3.824 J/g to 40.837 J/g and 43.656 J/g, which is considerably high, similar as the highest latent 43 J/g of the fine crystalline VO₂ nanoparticles reported by Chen *et al.* [8] and close to 51 J/g of bulk VO₂. The high latent could be attributed to the increase of crystalline VO₂ percentage in the powder. As for the two or three convoluted exothermic peaks detected in the cooling period probably result from a series of effects combination, including defects, lattice expansion, size effects and non-stoichiometry of synthesized VO₂ powders. [8]



Chpt. II-Figure 11. DSC curves of VO₂ samples of VO_x-3min (Inset shows its enlargement of DSC data), S-500 and S-700.

3.4. Synthesis of V₂O₃ and V₂O₅

In addition to the synthesis of VO₂ (M), this two-step thermolysis and annealing method is also suitable for the preparation of V₂O₃ and V₂O₅ using VO_x-3min as starting material under different conditions. The formation temperature of V₂O₃ and V₂O₅ is deduced from the thermogravimetric curve of VO_x-3min in **Figure 12a**, revealing that the sample mass is stable when VO_x-3min is annealed up to 800°C in Ar flow with 5% H₂ or up to 600°C in air.

XRD shows V_2O_3 and V_2O_5 are well obtained after annealing (**Figure 12b**). Interestingly, SEM results (**Figure 12c**) reveal that the V_2O_3 powder shows an urchin-like morphology with high specific surface area, which can be of great interest for the use of vanadium sesquioxide as battery materials, *i.e.* such morphology is able to provide a large number of active sites between the active materials and electrolytes. [9, 10] Moreover, the morphology of as-prepared V_2O_5 exhibits regular plates, which can be of a great advantage in terms of lithium storage property for the use as positive electrode in batteries or electrochemical layer. [11] Thanks to this new synthesis protocol, we are able to produce different morphologies, as V_2O_3 and V_2O_5 synthesized with this two-step thermolysis and annealing differ from the ones obtained by direct annealing of VEG as earlier reported. [2] Further investigations on their physical and chemical properties are under progress.



Chpt. II-Figure 12. (a) TG curves of VO_x -3min samples annealing under Ar/H_2 flow and air atmosphere, insets show the synthesis route of V_2O_3 and V_2O_5 from VO_x -3min; (b) XRD pattern of V_2O_3 and V_2O_5 samples after post annealing of VO_x -3min, and (c) its corresponding SEM images.

4. Conclusion

Herein, the decomposition of vanadyl ethylene glycolate (VEG), leading to VO₂ (M) particles with tunable crystallinity and morphology, through a two-step thermal treatment: a first-thermolysis step under air followed by a post-annealing under oxygen-free atmosphere, has been investigated. A careful control of the time and the temperature parameters for the VEG thermolysis (1st step) is required to obtain a pure VO₂ phase after the post-annealing (2nd step).

While the thermolysis step is performed with a strict time of 3 min at 300°C, a pure VO₂ (M) compound is synthesized with various crystallite sizes depending on the temperature of the postannealing treatment under oxygen-free atmosphere (500°C or 700°C). SEM & TEM observations show an increase in the crystallites size of the VO₂ (M) powders with temperature up to few microns for 700°C post-annealing temperature) while the crystallite shapes become regular polyhedrons. Moreover, thanks to XRD analyses (Rietveld refinements), the weight percent of the crystalline VO₂ (M) phase in the powders obtained after the 300°C thermolysis, after 500°C post-annealing or after 700°C post-annealing, is calculated. It increases from 44% to 79% reaching finally 100%. Hence, our synthesis protocol: a low cost and of easy implementation synthesis route, allows to obtain a pure and 100 % crystalline VO₂(M) phase using optimal conditions.

Even a full crystalline VO₂ is obtained after two step route, it should be pointed out that such short annealing time (\sim 3 min) is quite hard to control. The use of shorter (\sim 2 min) or longer time (5 min) than

~3 min of heating at 300°C for VEG decomposition, results, after the post-annealing, in the formation V^{3+} or V^{5+} compounds, respectively. As described in **Eq. 1**, the weight loss of the sample is around 65.3 wt% when all the VEG just finished decomposing, so the weight loss is used as an assisted tool to make sure the all the VEG decomposed without any V^{5+} oxides generated. Unfortunately, after many times experimental repeating, it is found that the annealing time is not so reliable to guarantee the weight loss is exact 65.3%, as illustrated in **Figure 13**. Thus a new simple method for VO₂ synthesis with high reproducibility is needed.



Chpt. II-Figure 13. Weight loss percentage of VEG sample during the decomposition process.

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1. Introduction

As described in Chapter 2, vanadyl ethylene glycolate (VEG) precursor was mainly used to synthesize VO_2 or V_2O_5 . In the post-annealing treatment, it was observed that carbon played a key role in the vanadium valence control during the transition of VO_2 (Amorphous) to VO_2 (Crystalline). Inspired by this observation, herein soot (carbon) is chosen for a direct reduction of nano V_2O_5 . The comparison of dynamic and sealed vacuum systems associated with an accurate control of the carbon content allows further understanding of the reductive mechanism. Highly crystallized VO_2 particles are successfully synthesized through this simple method showing nice physical properties. Besides, their morphologies and phase transition properties are also studied. Finally, VO_2 pellets are prepared from both conventional sintering and spark plasma sintering (SPS) process with the aim to propose a set of pellets with various relative densities between 50 and 100%.

In the literature, as for the reducing strategy for VO₂ synthesis, many reducing agents, including oxalic acid, diamide hydrochloride, or ethylene glycol, *etc.* were explored. Specifically, the reduction of pentavalent vanadium compounds (V_2O_5 or NH₄VO₃) as raw materials, always leading to a non-spherical (*i.e.* snowflake) shapes. [1-3] In addition, the use of reducing gas (*e.g.* H₂, CO, C₂H₄, and CO₂) is also reported. [4, 5] Nevertheless, disadvantages linked to the use of combustible gas, large energy consumption, toxicity, and cost production favor the utilization of a solid reducing agent. As far as we know, only few researches have focused on mixing directly in furnaces reducing solid agent with high valence vanadium compounds. [6]

2. Experimental

2.1. Materials and Synthesis

Soot (Carbon black, S. A. 75 m²/g; Bulk density: 80-120g/L), was purchased from Aldrich. All the chemicals reagents were used as obtained commercially without further purification. The VO₂ synthesis route is schematized in the **Figure 1a.** VEG was obtained through polyol process using NH₄VO₃ as vanadium soluble source, as described in Chapter 2. After being heated at 300°C for 90 minutes in air, nano V₂O₅ is prepared. Then various molar ratios of soot are mixed with the as-synthesized V₂O₅ (*i.e.* V₂O₅: C molar ratios =1: 0, 1: 0.5, 1: 1, 1: 2 and 1: 10), which are named as S-0, S-1, S-2, S-3 and S-4, respectively. The mixtures are further annealed at 500°C for 5 h in sealed vacuum system (SVS), as shown in **Figure 1b** (leading to SVS-1, SVS-2, SVS-3 and SVS-4 samples). SVS is designed by sealing the glass tube after being pumped to vacuum environment (~10⁻⁴ mbar). S-2 sample is further annealed to high temperatures (700°C and 1000°C) in this system (the impact of temperatures is studied between the as-called SVS-500, SVS-700, and SVS-1000).

As a comparison in **Figure 1c**, the dynamic vacuum system (DVS) is designed for pumping the glass tube during the whole annealing process. For this DVS system, only a V_2O_5 : C molar ratio =1: 1 is used (S-2 sample), and thermal treatments at 500°C, 700°C and 1000°C for 15 h are used (leading to DVS-500, DVS-700 and DVS-1000 samples, respectively). It should be mentioned that the two vacuum pressures are controlled the same (~10⁻⁴ mbar).



Chpt. III-Figure 1. (a) The different synthesis paths for the preparation of VO_2 or V_2O_3 from the reduction of nano- V_2O_5 by carbon. (b) Sealed vacuum system (SVS): glass tube is sealed after being pumped to vacuum environment; (c) Dynamic vacuum system (DVS): glass tube is pumped during the whole annealing process to maintain the vacuum environment.

3. Result and discussion

3.1.V2O5/Carbon ratio optimization through SVS process

According to previous study, [7] V_2O_3 powder can be obtained by annealing the VEG precursor directly in inert atmospheres or vacuum environment. V_2O_3 is synthesized when the VEG is annealed at 500°C for 5 h in sealed vacuum system, which is due to the reducibility of carbon from the VEG (VC₂H₄O₃). Meanwhile, VEG can also be used as vanadium precursor for preparing nano V_2O_5 when being heated at 300°C for 90 min in air (**Figure 2**). After the full decomposition, almost no carbon (0.32 wt%; measured by CHNS) remains in the V_2O_5 powder. Taking advantage of the reduction power of carbon and aiming at synthesizing VO₂, herein soot is used as a reducing solid agent starting from nano V_2O_5 .



Chpt. III-Figure 2. XRD patterns of (i) vanadyl ethylene glycolate (VEG) synthesized through polyol route, (ii) V_2O_3 synthesized by heating VEG at 500°C for 5 h in the sealed vacuum system (SVS), (iii) V_2O_5 obtained by heating VEG at 300°C for 90 min in air.

To control the vanadium valences changes from V (5+) to V (4+) or V (3+), the carbon content is carefully and precisely controlled. Various concentrations of soot (*i.e.* V₂O₅: carbon molar ratios = 1: 0, 1: 0.5, 1: 1, 1: 2 and 1: 10) are grinded with the as-synthesized V₂O₅. The morphology and microstructure of the mixture (S-2 sample) are shown in **Figure 3**.



Chpt. III-Figure 3. Left panel: TEM images of S-2 sample and the extracted particles distribution for V_2O_5 and carbon soot particles; Middle panel: TEM elemental mapping (V and C elements) showing the carbon-vanadium homogeneous distribution under the micron scale; Right panel: HRTEM images of (A) focus on one V_2O_5 nanoparticle and the corresponding d-spacing of 0.35 nm indexed to [201] plane, (B) focus on a soot particle showing a concentric layered architecture (onion like particle) and the corresponding spacing of 0.35 nm.

Two types of spherical particles co-exist. In A region, the darker ones with larger size are assigned to V_2O_5 , with a narrow size distribution around 65 nm. At high magnification, the corresponding d-

spacing of around 0.35 nm, can be indexed to [201] plane of orthorhombic V_2O_5 (S.G. Pmmn, JCPDS No. 41-1426). In B region, the agglomerated structure composed of smaller spherical primary particles (~35 nm) with a light color, are typical of the soot morphology. [10, 11] Focusing on one soot particle, an onion-like carbon nanostructures consisting of a continuous network of concentric, size-limited graphene layers is observed, while the characteristic nanostructure is visible with 0.35 nm d-spacing. Young-jin Ko et al also reported that this onion-like carbon could act as an electrocatalyst for $[VO]^{2+}/[VO_2]^+$ redox flow reaction. [11] The elemental mapping images show a uniform distribution under the micron scale of V and C components, which could guarantee the full reduction process during the annealing treatment.

The X-ray pattern of the SVS samples obtained after annealing at 500°C for 5 h in sealed vacuum system are gathered in **Figure 4**.



Chpt. III-Figure 4. XRD patterns of SVS samples synthesized by annealing of nano- V_2O_5 mixed with various carbon contents at 500°C for 5 h in sealed vacuum system. Corresponding PDF numbers provided at the bottom.

Without carbon, the X-ray pattern of SVS-0 indicates the crystallization of a pure V_2O_5 phase. After carbon addition, V_3O_7 phase appears in the SVS-1 sample, indicating that parts of V (5+) is reduced to V (4+) in this intermediate state between V_2O_5 and VO_2 . Further increase in carbon content leads to a relatively pure VO₂ (M1) phase for SVS-2, SVS-3 and SVS-4 samples, the main XRD peaks match with VO₂'s JCPDS data card 00-044-0252. Meanwhile, trace of undesired V_6O_{13} impurity is detectable (*i.e.* XRD peak located at 25°). Unexpectedly, the X-ray patterns are not further modified for a large increase in carbon content (*i.e.* comparing to SVS-2, SVS-3 and SVS-4). No additional peaks or intensity increase

of vanadium V (3+) compounds are being detected suggesting that V_6O_{13} trace does not result from an excessive carbon-reduction leading VO₂ to further V_6O_{13} transformation but more surely from a parasite reaction occurring at the beginning of the process. Even when a quite large quantity of carbon is added (*i.e.* SVS-4 sample, V_2O_5 : C=1: 10), VO₂ phase is prepared using this process. We assume that the relative low annealing temperature of 500°C probably limits the further reduction from V (4+) to V (3+).

Since carbon plays a critical role in the preparation of VO₂ powder and to conclude on the carboreduction mechanism, carbon weight fractions of SVS samples were measured before and after annealing (**Figure 5**). Herein, C: V₂O₅ molar ratios are converted in carbon wt %. For example, V₂O₅: C molar ratios =1: 1, which equals the carbon weight percentage is around 6.19 wt%. For SVS-1 sample, still 2.59 wt% of carbon remains in the powder from initial 3.21 wt%. Thus around 0.62 wt% is consumed during the reductive reaction, resulting in the formation of V₃O₇ (**Figure 4**). For the SVS-2 sample, the difference of carbon weight fraction during the annealing process is around 2.0%, and it remains unchanged for SVS-3 and SVS-4 samples, which indicates that excess of carbon in fact does not take part in the reductive reaction. The fractions of consumed carbon in the CHNS result well agree with the XRD results (**Figure 4**), revealing that excessive carbon is not used for further reduction of V (4+) to V (3+).



Chpt. III-Figure 5. Carbon wt. percentages of samples before and after annealing at 500°C in sealed vacuum system (SVS) for 5 h.

Moreover, these analyses show that even if 2 wt% of carbon is sufficient to transform V_2O_5 in VO_2 , a slight excess of carbon needs to be introduced in order to achieve the full reduction. For avoiding too much excess of carbon, S-2 sample is chosen for further investigation.

The morphology and microstructure of SVS-2 sample after being annealed at 500°C, are shown in **Figure 6**. Large VO₂ particles with clear boundaries, accompanied by some surrounding carbon soot nanoparticles, are observed. Specifically, in the A region, at the edge of one large crystallite, HRTEM image shows lattice fringes separated by 0.32 nm, which corresponds to [011] crystal plane of monoclinic VO₂ (M1). In the B region, the smaller particles correspond to unreacted carbon, showing the concentric network of graphene layers separated by 0.35 nm d-spacing. This analysis and so the VO₂ particles and carbon soot particle assignment are also confirmed by the elemental mapping image on the right of **Figure 6**.



Chpt. III-Figure 6. Left panel: HRTEM images of SVS-2 sample; Middle panel: TEM elemental mapping (V, O, and C elements) showing the only carbon occurrence inside the carbon soot in excess and its absence in VO₂ particles; Right panel: (A) focus on one VO₂ particle and the corresponding d-spacing of 0.32 nm indexed to [011] plane, (B) focus on a soot particle showing a concentric layered architecture (onion like particle) and the corresponding spacing of 0.35 nm.

3.2.A comparison of SVS and DVS processes:

During the annealing of V_2O_5 and soot in sealed vacuum system, an interesting phenomenon was noticed that V_2O_5 can only be reduced to VO_2 at 500°C (**Figure 4**), and V_6O_{13} impurity could not be removed totally, no matter how much carbon was added. Thus higher annealing temperatures (700°C and 1000°C) were applied to S-2 sample in both sealed vacuum and dynamic vacuum systems. The XRD pattern of the as-prepared samples are gathered in **Figure 7**.



Chpt. III-Figure 7. (a) XRD patterns of samples obtained from annealing treatment at 500°C, 700°C and 1000°C for (a) 5 h in the sealed vacuum system; (b) 15 h in dynamic vacuum system.

Using sealed vacuum system, the large decrease in VO₂ peaks intensities, such as for the main peak located at 2θ =27.95°, when the temperature increases from 500°C to 700°C, reveals that the VO₂ structure is partially destroyed, associated with an amorphisation. Indeed, the VO₂ peaks have completely disappeared at 1000°C being replaced by the ones of the V₂O₃ phase (S.G. R-3c, JCPDS No.

27-0940), suggesting the full reduction of V (4+) in V (3+) at this temperature. The obtained V_2O_3 is composed of few aggregated crystallites from a partial sintering phenomenon as shown by the electronic microscope images (**Figure 8**).

Interestingly, annealing in dynamic vacuum system leads to a different behavior as illustrated for the DVS sample series. Their XRD patterns are characteristic of a quite pure VO₂ (M1) phase after annealing at 700°C (DVS-700) and 1000°C (DVS-1000) in **Figure 7b**. All the peaks can be indeed indexed as VO₂ (M1) phase at the exception of the occurrence of low intense peaks (located $\approx 25^{\circ}$) potentially associated with some V₃O₇ impurity co-existing with the VO₂ powder obtained at 500°C.



Chpt. III-Figure 8. SEM images of V_2O_3 powder synthesized from V_2O_5 reduction by carbon at 1000°C for 5 h using the sealed vacuum system.

3.3.The reduction mechanism

Better understanding of the phase formation came from the measurements of the carbon content (**Figure 9**) in the different samples issued from SVS and DVS annealing treatments. Before annealing, S-2 sample contains around 6.19 wt% of carbon.



Chpt. III-Figure 9. Carbon wt. content of samples after annealing using two types of vacuum systems, namely sealed vacuum system (SVS) and dynamic vacuum system (DVS). (The dash line is the guideline standing for 6.19 wt% carbon in the mixed powder before annealing).

Surprisingly, after being annealed at 1000°C in the two vacuum systems, only little carbon left (0.16 and 0.15 wt%), indicating that almost all the carbon took part in the reductive process. Thus the method overcomes the disadvantage of the impurity in the VO₂ product, which usually exists in redox reaction methods. [12]

To explain the full mechanism in these two vacuum systems leading to different vanadium stoichiometries, two different scenari can be proposed depending on the vacuum system (Table 1).

In sealed vacuum system, two mechanisms may occur either CO (Eq. 1) or CO₂ (Eq. 2) can be formed leading to different carbon percentages. Based on Eq. 1, at least 11.66 wt% of carbon is required with CO forming. While only 6.19 wt% of carbon is needed if the reduction goes by generating CO₂. Similarly, in dynamic vacuum system, either CO (Eq. 3) or CO₂ (Eq. 4) can be produced, corresponding to 6.19 wt% of carbon or only 3.19 wt% of carbon consumption, respectively. The loss of 6.19 wt% of carbon as determined from CHNS data (Figure 9) after being annealed at 1000°C tends to favor Eq. 2 in sealed vacuum system (*i.e.* CO₂ formation) and Eq. 3 in dynamic vacuum system (*i.e.* CO formation).

Chpt. III-Table. 1. Possible equations taking place in sealed or dynamic vacuum systems, and the associated calculated carbon weight percentage needed considering stoichiometric proportion.

	Equations	$\frac{m(\mathcal{C})}{m(V_2O_5) + m(\mathcal{C})}$
SVS	$V_2O_5 + 2C \rightarrow V_2O_3 + 2CO \dots Eq. 1$	11.66%
	$V_2O_5 + C \rightarrow V_2O_3 + CO_2 \dots Eq. 2$	6.19%
DVS	$V_2O_5 + C \rightarrow 2VO_2 + CO \dots \dots Eq. 3$	6.19%
	$2V_2O_5 + C \rightarrow 4VO_2 + CO_2.\dots Eq.4$	3.19%

To be consistent with our calculation, a possible formation mechanism (**Figure 10**) is put forward. In sealed vacuum system, V_2O_5 is initially reduced to VO_2 by carbon at 500°C, generating CO gas at the same time. Since the glass tube is sealed, the CO gas cannot escape and further reacts with the new born VO_2 , until all the V (4+) is fully reduced to V (3+) at 1000°C, leading to the final formation of V_2O_3 sesquioxide. The whole process is illustrated in **Figure 10a**.



Chpt. III-Figure 10. Schematic illustration of possible reactions occurring in the SVS: sealed vacuum system and in the DVS: dynamic vacuum system.

On the contrary, in dynamic vacuum system, CO gas is removed out of the tube as soon as it is generated during the annealing process, preventing from any additional reduction of the new born VO₂, and corresponding to a reduction of V (5+) in V (4+) at 1000°C (Figure 10b).

At 700°C in sealed vacuum system, only around 3.58 wt% of carbon is consumed. It is probably due to the fact that CO gas also takes part in the reduction of V_2O_5 to VO_2 and VO_2 to V_2O_3 , explaining the poor crystallinity of VO_2 (SVS-700 in **Figure 7a**). As a comparison, almost all the carbon is consumed in dynamic vacuum system. In that case, CO gas is removed quickly preventing from any additional reduction, the carbon act as the only reducing agent, leading to the desired formation of a pure VO_2 dioxide.

To obtain pure VO₂ powder with high crystallinity, it is imperative to avoid the second reductive step of vanadium oxides linked to the oxidation of CO in CO₂ during the annealing treatment at high temperatures. Pure VO₂ (M1) particles can be synthesized in dynamic vacuum system at 700°C and 1000°C successfully, thanks to the extraction of the CO from the synthesis chamber.

3.4. Physical-chemical properties of the as-prepared VO₂ (M1) compounds

3.4.1. Crystal structure property

XRD patterns of the VO_2 compounds obtained using DVS treatments were refined using the Fullprof software program, to clarify the structural parameters of the as-obtained oxides: unit-cell parameters, atomic positioning, *etc.* The results are presented in **Figure 11**. The bottom blue line shows the fitting residual difference.



Chpt. III-Figure 11. Typical Rietveld refinements of XRD data for (a) DVS-700 sample; (b) DVS-1000 sample.

The crystal structure corresponding to the diffraction patterns well correspond to the monoclinic phase of VO₂ (M1 phase) (S.G. P2₁/C, JCPDS No. 44-0252), with standard lattice parameters and atomic positions (**Table. 2** and **Table. 3**).

Space group	P 1 21/c 1 (14) Monoclinic		
Cell parameters	s a	b	с	β
	5.7522(5) Å	4.5259(1) Å	5.3830(1) Å	122.6087(2) °
Atoms	Wyck position	х	У	Z
V1	4e	0.24048(0)	0.97887(0)	0.02785(0)
01	4e	0.10187(0)	0.20892(0)	0.20228(0)
O2	4e	0.40210(0)	0.70627(0)	0.30251(0)

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Chpt. III-Table. 3. Lattice parameters and atomic positions of DVS-1000 sample.

Space group	P 1 21/c 1 (14) Monoclinic			
Cell parameters	а	b	С	β
	5.7516(4) Å	4.5251(1) Å	5.3827(2) Å	122.6125(8) °
Atoms	Wyck position	Х	У	Z
V1	4e	0.23839(0)	0.98171(0)	0.02633(0)
01	4e	0.10311(0)	0.20925(0)	0.20715(0)
O2	4e	0.39813(0)	0.70770(0)	0.29400(0)
$R_{Bragg} = 9.85, R_f = 7.04$				

3.4.2. The morphology property

The morphologies and microstructures of DVS-700 and DVS-1000 samples are firstly investigated by SEM (Figure 12), the corresponding size distributions are added in the inset of Figure 12. Both powders show an isotropic shape. For the DVS-700, the size distribution, which is clearly a single-mode Gaussian distribution, is centered on 1.8 µm. The distribution width enlarges and the average size increases to 5.3 μm when the annealing treatment is 1000°C.



Figure 12. SEM images of the as-synthesized VO₂ (M1) particles: DVS-700 and) DVS-1000 samples. In inset is reported the corresponding particle size distribution.

High temperature will lead to a highly crystallized VO₂ (M1), which is more favorable because of its stability, while the particle size will also increase. To overcome such disadvantage, the time of the annealing treatment can be decreased allowing a good control of the average grain size. Indeed, the average size of the synthesized VO₂ particles is greatly decreased to 935 nm and 415 nm for an annealing temperature of 700°C when the annealing time is shortened to 2 h and 1 h, respectively (**Figure 13**). Xiao *et al* reported that it is known that the VO₂ particles are relatively uniform (in terms of shape and size distribution width) when an annealing temperature higher than 500°C is used. [13] For samples annealed at 700°C, the size of single particle is larger than 500 nm. This past research is in good agreement with our own experiments. Unlike the belt-like or rod-like VO₂ morphologies synthesized from intermediated phase transformation, [12] which are unfavorable for the dispersion in aqueous solvent, the obtaining of isotropic VO₂ particles with a narrow distribution width, is well adapted to their dispersion into suspension which could be used to elaborate homogeneous films from dip coating process.



Chpt. III-Figure 13. (a) *XRD* patterns, (b) *SEM* images and (c) particle size distribution of the $VO_2(M1)$ particles obtained by annealing at 700°C in the dynamic vacuum system for 2 h and 1 h.

More detailed structural information on the synthesized VO_2 powder is obtained from high resolution TEM. A focus was made especially for the DVS-700 sample as shown in Figure 14a.

The vanadium atomic columns are clearly visible and the V-V distance is extracted around 0.35 nm (Figure 14b-14c), which is fully consistent with the shortest V-V atomic distance in the VO₂ (M1) crystal structure (Figure 14d).



Chpt. III-Figure 14. (a) HRTEM image of VO_2 (M1) powder (DVS-700); (b) Enlargement of the HRTEM image showing V-V atomic distances and illustration of the perfect matching with the VO_2 crystal structure along [100] zone axis. (c) The crystal structure of monoclinic VO_2 (M1) from Diamond with same projection axis.

3.4.3. Thermal stability

 VO_2 is not the most thermodynamically stable oxide, after a long time's storage in air, a transformation to V_2O_5 usually occurs. A pure VO_2 film can be oxidized to V_2O_5 after being annealed at 300°C in air, [14] thus the chemical instability of VO_2 restricts its application. Besides forming a core-shell structure, a high crystallinity is the other strategy to enhance its anti-oxidation ability.

Firstly, the components proportion (including amorphous part) of VO₂ is calculated, using lanthanum hexaboride (LaB₆), mixed as 10 wt.% with the DVS-700 sample. The Rietveld refinement result is shown in **Figure 15a**, showing well-quality fit. Deduced from the XRD patterns and analysis with Fullprof program, the weight percent of crystalline VO₂ for DVS-700 is 100%. Secondly, its thermal stability is confirmed by annealing at 300°C in air for 2 h and 24 h. As shown in **Figure 15b**, only the VO₂ (M1) diffraction peaks are detected, revealing an excellent thermodynamically stability. The high crystallinity does prevent the VO₂ from being oxidized to V₂O₅ effectively, which avoids the complexity

of the core-shell structure and shows great advantages for its applications (*i.e.* thermochromic smart window).



Chpt. III-Figure 15. (a) Typical Rietveld refinements of XRD data from DVS-700 sample mixed with LaB₆; (b) XRD pattern of DVS-700 after annealing at 300°C in air for 2 h and 24 h.

3.4.4. Heat capacity and resistivity indicating the phase transition

The awaited phase transition between monoclinic phase (low temperature form) and rutile phase (high temperature form) for the as-prepared VO_2 compounds is investigated through its latent heat (thanks to DSC measurements) and the drastic change of electronic conductivity associated with this MIT phase transition (four probes measurements versus temperature on VO_2 pellets).

The DSC analysis is shown in **Figure 16a**. The endothermic and exothermic peaks during heating and cooling cycles are clearly visible, which shows a transition temperature of about 61°C in cooling mode and 70°C in heating mode, whatever the samples: DVS-700 or DV-S1000, *i.e.* with a hysteresis loop width of about 10°C. The phase change enthalpy (Δ H) during the heating cycle and cooling exhibited a considerably high value nearly 55 J/g, a bit larger than the value of 51 J/g for bulk VO₂ previously reported in literature. [15] The high enthalpy could be attributed to the well crystallized VO₂ (M1) obtained from the high annealing temperature. The ratio of Δ H_H and Δ H_C is 1.012 (54.259/53.612) for DSV-700 sample, and 1.016 (55.254/54.362) for DSV-1000 sample. The ratios are quite close to 1, which implies the excellent reversibility of the phase transition for these samples thanks to their good crystallinity.



Chpt. III-Figure 16. Phase transition behavior of synthesized $VO_2(M1)$ (DVS-700 and DVS-1000): (a) Their corresponding DSC curve; (b) Electrical resistance of the $VO_2(M1)$ pellets; the heating and cooling rate for all measurements is set as 5 °C /min.

Resistivity measurements on DVS-700 and DVS-1000 samples, reported in **Figure 16b**, show that the DVS-700 gets a change of resistivity of about 3 orders of magnitude between the insulating and the metallic forms whereas the DVS-1000 only show a jump of 2 orders of magnitude when the sample is cooled down. In agreement with DSC result, a 10°C hysteresis width is measured for both samples between cooling and heating modes. The M1-R transition is usually accompanied by a 3-6 orders of magnitude jump in conductivity. The typical curves for our samples are in substantial agreement with published results. [16] The DVS-1000 sample shows a poor transition behavior, probably because of the larger particle size (~ 5.3μ m) that makes difficult to prepare a quite dense pellet and can be at the origin of new cracks formation during the measurements; the observation of a higher resistivity of the DVS-1000 pellet whatever the temperature is and so the allotropic form in comparison with the DVS-700 pellet, tends to validate this interpretation.

4. Pellets preparation

Since the carbo-thermal reduction method for VO_2 powder synthesis is quite easy and reproducible, a large quantity of VO_2 powder (DVS-700) was easily prepared under the 15 h annealing at 700°C in the dynamic vacuum system, using multi-batch approach (about 0.5 g of powder per batch could be produced in our system). The purity of the powder is checked for each batch.

We used the VO_2 powder to prepare its pellets with high relative density for a further study. Indeed, VO_2 is an emerging material which can be used in infrared measurement devices, thanks to its charge of infrared emissivity through the phase transition. In a collaboration of our research team with Prime institute in Poitiers, ICMCB has in charge the preparation of dense VO_2 pellets with various porosity percentage, for exploration test of their infrared sensing abilities.

For the pellets preparation, two sintering methods are used: the conventional one and SPS. The difficulties lie in keeping the high purity of VO_2 compound during the sintering process aiming at increase in a control way the pellet's density. Indeed, the high temperature sintering in the vacuum system would possibly create oxygen vacancies in too high concentration inside the vanadium oxide network, and would so probably lead to the formation of V^{3+} associated with partial transformation of the VO_2 oxide in other crystal structures.

4.1.Sintering: phenomenological description

Sintering is a process of compacting and forming a solid mass of material by heat or pressure. The sintering of ceramic materials is the method involving consolidation of ceramic powder particles by heating the compacted pellet ("green compact") to a high temperature below the melting point, allowing atomic diffusion (surface or bulk atomic diffusions both taking place) in order to create particles neck at first and decrease drastically the ceramic porosity in a second time. The driving force of sintering process is the reduction of the surface energy of the particles caused by decreasing their vapour-solid interfaces. During the diffusion process, the pores, existing in the "green compact", diminish or even close up, resulting in densification of the part, improvement of its mechanical properties.

Usually, the sintering process consists of three stages [17]: (i) in the first stage (before sintering), called initial stage grains are contacted each other, grain boundary areas grow and grains start to merge; (ii) in the second stage, necks were formed between adjacent grains. There are small numbers of large grains instead of large number of small grains, and pores become smaller, and the grain merging is not completed. The grains will continue to grow in this stage; (iii) in the third stage, merging is completed. The grains are larger than calcined ceramic's grains. Small pores are formed and surface area is decreased. It is smaller than the surface area in the other two stage. The three stages are illustrated in **Figure 17**.



Chpt. III-Figure 17. Three stages of sintering process. [17]

Decrease of the porosity, caused by the sintering process, is determined by the level of the initial porosity of the "green" compact, sintering temperature and time. The sintering of pure oxide ceramics usually requires relatively long time and high temperature because the diffusion process in solid state occurs with a path length equivalent to the particle/pore sizes only just below the melting point. Sintering can be done using various methods as Conventional Sintering, Spark Plasma Sintering (SPS), Microwave Sintering etc.

4.2. SPS: theoretical description

Spark plasma sintering (SPS) is one sintering technique. The mechanism of the spark plasma sintering is still unclear therefore the process name pulsed electric current sintering (PECS) should be considered as more correct. However, the name SPS (spark plasma sintering) remains more common. The most accepted mechanism of the PECS is based on the micro-spark discharge in the gap between neighboring powder particles.

The main characteristic of SPS is that the pulsed or unpulsed current directly passes through the graphite die, as well as the powder compact (Figure 18). Joule heating is created and play a dominant role in the densification of powder compacts, which results in achieving near theoretical density at lower sintering temperature compared to conventional sintering techniques.



Chpt. III-Figure 18. Spark plasma sintering and the mechanism. [18]

The SPS process proceeds through three stages [18]:

(i) Plasma heating: the electrical discharge between powder particles results in localized and momentary heating of the particles surfaces up to several thousands of degrees. Since the micro-plasma discharges form uniformly throughout the sample volume the generated heat is also uniformly distributed. The particles surfaces are purified and activated due to the high temperature causing vaporization of the impurities concentrated on the particle surface. The purified surface layers of the particles melt and fuse to each other forming "necks" between the particles.

(ii) Joule heating: at this stage the pulsed DC electrical current flows from particle to particle through the necks connecting them. The joule heat is generated by the electrical current. The joule heat increases the diffusion of the atoms/molecules in the necks enhancing their growth. Localized character of heating and its uniform distribution allow rapid temperature rise and drop, which diminish coarsening (growth) of the material grains.

(iii) Plastic deformation: the heated material becomes softer and it exerts plastic deformation under the uniaxial force. Plastic deformation combined with diffusion result in the densification of the powder compact to over 99% of its theoretical density.

SPS process leads to several advantages in comparison with conventional sintering. Since no coarsening and grain growth are allowed to occur in SPS, high relative densities are reached in very short time and nano sized powders can be sintered without considerable grain growth which is not possible in conventional sintering process. Thus the use of SPS takes only a few minutes to complete a sintering process compared to conventional sintering which may take hours or even days for the same result. The heat generation is internal, in contrast to the conventional hot pressing, where the heat is provided by external heating elements. The general speed of the process ensures it has the potential of densifying powders with nanosize or nanostructure while avoiding coarsening which accompanies standard densification routes. All these advantages have made SPS a good method for preparation of ceramics based on nanoparticles.

4.3.Pellets obtained from conventional sintering

At first, conventional sintering method is used with two steps: pellet preparation and pellet annealing, as illustrated in Figure 19a. In the first step, the pellets are prepared by directly pressing the VO_2

powders under different pressures using laboratory manual press. During the pressing, the pressure is controlled as 1 ton and 3 tons and the pressing time lasts around 5 min. Finally, the pellets are named B1 and B3, respectively. All the pellet's diameters are 10 mm.

In the post-annealing process, the pellets are stored in a glass tube with a dynamic vacuum system. After 15 h annealing at 700 and 1000°C, the pellets are shown in **Figure 19b**. A color change from black to grey-blue is observed after the high temperature treatment (1000°C) for both B1-1000 and B3-1000 samples. The color of B1-700 and B3-700 pellets (annealed at 700°C) remains black. XRD pattern confirmed that all pellets are constituted of pure VO₂(M) phase. Thanks to the dynamic vacuum system, none over-oxidation or over-reduction occurs during the high temperature sintering process.



Chpt. III-Figure 19. VO₂-based pellet preparation: (a) schematic illustration: pellet preparation and pellet annealing; (b) photos of pellets before and after annealing; (c) XRD of pellets after annealing process; (d) the relative density of the as-obtained pellets.

The density of the as-prepared pellets is calculated from the mass divided by the volume, where the volume is calculated from the thickness and diameter. Then the relative density is estimated by dividing the pellet density by the VO₂ bulk density $(4.57g/cm^3)$. The sintering is all the more efficient than denser are the VO₂ pellets; *i.e.* with a relative density near 100%. The relative density of the pellets is illustrated in **Figure 20d**. Before annealing (for the green pellets), the relative densities are around 50%, which indicates single pressure without annealing process could not guarantee the high density. When the pressure is increased from 1 ton to 3 tons, there is a slight increase for the relative density from 49.22% to 55.94%. After annealing in the dynamic vacuum system at 1000°C and 700°C for 15 h, the relative density basically remains unchanged. The highest relative density is limited to 63.79% for the B3-700 sample. It is noticed that the higher temperature annealing leads to a lower relative density, probably due the occurrence of large and quite stable pores in the green pellets (inner-agglomerate porosity). Furthermore, as illustrated in **Figure 21**, the pellets obtained after the higher annealing treatments (B1-1000 for instance) are quite fragile and exhibit delamination (2D-cracks perpendicular to the axe of the

applied pressure), which indicating that a homogeneous sintering effect has not occurred during the annealing step.



Chpt. III-Figure 20. B1-1000 pellet, prepared by annealing the B1 pellet at 1000°C for 15 h in the dynamic vacuum system.

Using conventional sintering, pellets of high purity can be prepared. However, their relative density remains quite low with not much impact on the increase of the annealing treatment temperature. Even worse, the pellets are fragile, showing a delamination in different layers with poor mechanical properties (**Figure. 20**).

4.4.Pellets obtained from SPS

To further increase the relative density and prepare dense pellets, SPS technique was also conducted. Same VO₂ powders (DVS-700) were put into the graphite die, and the mass was fixed as around 0.5 g. The SPS conditions for each pellet preparation were controlled as 700°C and 1000°C, and the dwell time was fixed as 0 min (the treatment time is just composed of the heating and cooling ramps) and 10 min, respectively (**Figure 21a**). Here, the process was performance into the primary vacuum (around 10 Pa) to avoid redox reactions, and the atmosphere pressure was recorded during the whole process (**Figure 21b**). The pressures were similar for the four pellets preparation, and stayed in a low value range (7.5-17.5 Pa). After the SPS process, the obtained pellets were polished and shown in **Figure 21c**. The diameters of the pellets are around 10 mm, and the thickness is around 1.2 mm. As for the conventional sintering process, accurate relative densities were extracted from geometrical and mass measurements for each sample.

First, the purity of the pellets was checked through X-ray diffraction. As illustrated in **Figure 21d**, it reveals that the VO₂ structure can be maintained, as main phase, after annealing treatment at 700°C for 0 or 10 min and at 1000°C for 0 min. Nonetheless, the V⁴⁺ ions are partially (in minor quantity) reduced into V³⁺. For these three pellet samples, the major part is VO₂ phase, but with the presence as minor impurity VO_{1.87} oxides (within 75% of V⁴⁺ ions and 25% of V³⁺ ions). However, at 1000°C for 10 min, the pellet shows new phases V₂O₃ and V₃O₅ with disappearance of VO₂, which indicates a more advanced reductive process happening during SPS sintering process.



Chpt. III-Figure 21. SPS of VO_2 powders (DVS-700°C): (a) Annealing temperature and time; (b) the atmosphere pressure used in the SPS. (c) The photos; (d) XRD pattern and (e) relative density of the corresponding pellets.

Hence, using SPS sintering, the relative densities of the as-prepared pellets were also measured and calculated, **Figure 21e** illustrates two important key results. (i) Much higher values for the relative densities can be reached, and with relative densities which can be tuned from 73% to 96% depending on the SPS process parameters, in comparison with conventional sintering method. On this first hand, SPS offers a large benefit besides conventional sintering; (ii) However, associated to the sintering effect, performed in less controlled atmosphere condition, a partial reduction takes place and leads to a V³⁺-V⁴⁺ mixed oxides as impurities, especially while the SPS parameters (temperature and time) are increased to achieve very dense pellets.

As dense VO₂-based pellets were prepared with a relative good purity, the chracterization of their physical property, including the determination of their thermal conductivity and infrared sensing abilities with the group of J. Ordonnez at P Prime, is ongoing...

5. Conclusions

A method of synthesis of VO₂ (M1) powder by using soot to reduce our homemade nano-V₂O₅ oxide, is developed and investigated in this chapters. Two types of vacuum systems are designed and applied to study the mechanism of the reductive process. In the sealed glass system, two reducing steps are involved: carbon reduces V₂O₅ with CO gas generating simultaneously, the CO gas continues in a second step to reduce the new born VO₂, leading to the formation of V₂O₃ at 1000°C. As a comparison, the use of the dynamic vacuum system, while CO gas is removed directly in order to avoid the second step of the reductive process, guarantees the single formation of VO₂ at high annealing temperatures (700°C and 1000°C). The mechanism is confirmed by the carbon content measured before and after annealing. Hence, with the help of carbon, VO₂ (M1) powders with high crystallinity are synthesized successfully at 700°C (DVS-700) and 1000°C (DVS-1000). Their morphologies are compared through SEM, displaying the occurrence of particle sets with isotropic and narrow size distribution and with an

average particle size which can be easily controlled in a large range via the synthesis parameters: time and temperature of annealing, between 400 nm and more than 5 μ m. Both DSC and conductivity show the phase transition behavior and let open thermochromic applications.

Besides, VO_2 -based pellets were also prepared using both conventional sintering and SPS technique. While conventional sintering leads to pellets with poor relative density, the obtained pellets obtain from SPS process show a relative pure phase, and the relative density reaches to 91.29% when the VO_2 powder (DVS-700) was annealed under the condition of 1000°C for 0 min.

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Towards room-temperature thermochromism of VO₂ by Nb-doping: magnetic investigations. S. Guan, M. S. Basiège, O. Toulemonde, D. Denux, N. Penin, M. Gaudon*, A. Rougier, *Chem. Mater.*, In revision.



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1. Introduction

To tailor the T_c value, elemental doping is widely used as a conventional strategy, which involves the intentional incorporation of atoms or ions of suitable elements into the host lattice. Several studies, [1-14] have focused on the doping strategy to decrease VO₂ (M/R) transition temperature to nearer room temperature (RT). Based on the Mott model explanation, namely the correlation of electron-electron driven the MIT transition, there are two doping strategies to increase the carrier concentration and so decrease the Tc temperature: one is to insert monovalent doping atoms, such as H⁺,[1] Li⁺ and Na⁺,[2] and the other strategy is to substitute the V sites with high-valence elements, such as tungsten (W⁶⁺),[3-7] molybdenum (Mo⁶⁺),[8] and niobium (Nb⁵⁺).[9-15] The doping element either occupies the interstitial sites or substitutes the lattice V atom sites; it leads to variations in both the electronic and atomic structure of VO₂.

Some recent articles indicated that niobium would be even more efficient than tungsten if a greater doping fraction of the Nb content could be incorporated. [11] However, as far as we know, there has been only one report of a transition temperature less than 30°C for Nb-doped VO₂ oxide. [12] Most studies reported that the minimum T_c is between 30 and 50°C. [11,13-15] It is believed that there is still a lack of suitable synthesis methods for Nb-doped VO₂ which is able to guarantee the achievement of a sufficiently high Nb-doping content (3at%-5at%). Malarde *et al*, [9] used a continuous hydrothermal flow synthesis (CHNF) process to synthesize VO₂ and Nb-doped VO₂ nanoparticles (NPs), with particle sizes in the range of 50-200 nm. Pulsed laser deposition (PLD), [10] and aerosolassisted chemical vapour deposition (AACVD) methods, [11] are also reported to directly grow Nb-doped VO₂ films. Considering the high cost, low scale of production and/or complex equipment associated with these different strategies, a new chemical preparation method should be developed.

In this Chapter, Nb-doped VO₂ powders with controlled morphology (Nano-Particles: NPs) was prepared using the carbo-thermal reduction method, the as-prepared doped samples also provide perfect samples to investigate the doping effects from all several aspects, including the morphology, crystal distortion, thermal stability, heat capacity, resistivity and magnetic susceptibility.

In addition, W^{5+} , Ti^{4+} and Al^{3+} are also tried to introduce into VO_2 matrix using the carbo-thermal reduction method. Ti^{4+} ion, isovalent to V^{4+} can be introduced in VO_2 and no electron transfer occurs between Ti^{4+} and V^{4+} ions. For Al^{3+} doping, it is very meaningful to develop a controllable and reliable method of producing Al-doped VO_2 since it leads to the access of the M2 phase, which is an intermediate phase between the M1-R transition. [10, 11] As a Mott insulator, M2 phase can transform to a metallic phase upon carrier injection, showing potential applications in Mott field-effect transistor.

2. Experimental

2.1. Materials and synthesis

NH₄NbC₄O₉ was purchased from Aldrich Alta-Aesar, used as Nb source. For the Nb-doped VEG preparation, 125 ml ethylene glycol (EG) solution contained 1.42 g ammonium metavanadate (NH₄VO₃) and a certain amount of NH₄NbC₄O₉ (Nb/Nb+V=0%, 5 at%, 10 at% and 15 at%) were heated at 160°C for 2 h under refluxing conditions. The final product (Nb-VEG) was centrifuged and washed 3 times with ethanol, and dried overnight in an oven at 80°C. Then Nb-V₂O₅ was prepared by heating the Nb-VEG precursor at 300°C for 90 min in air. Finally, the as-prepared Nb-V₂O₅ was grinded with carbon in a mole ratio of 1: 1. The mixture was further annealed at 700°C for 15 h in a dynamic vacuum system (DVS), created by keeping pumping during the whole annealing process to maintain a vacuum environment (~10⁻⁴ mbar). According to the doping content and synthesis conditions (temperature and time), the sample names are listed in **Table 1**.

Sample	Doping perc	entage	Synthesis conditions
	Targeted	ICP	
VO ₂ -700A	0 at%		700°C+15 h
5%-NbVO ₂ -700A	5 at%	2.43 at%	700°C+15 h
10%-NbVO ₂ -700A	10 at%	5.77 at%	700°C+15 h
VO ₂ -700B	0 at%		700°C+1 h
VO ₂ -1000A	0 at%		1000°C+15 h

Chpt. IV-Table. 1. Sample list of VO₂ and Nb-doped VO₂ synthesized under different conditions.

Nb-doped VO_2 powders were prepared from the corresponding Nb-doped VEG precursors, which were synthesized thanks to the stoichiometric addition of Nb precursor besides the NH₄VO₃ in polyol medium, respectively; the polyol suspension was heat-up to 160°C on a hot plate under reflux; the doped-precursor was then collected by centrifugation (stage 1). The coprecipitation occurring during the heating under reflux of the polyol starting suspension was visually followed (Figure 1). The complete dissolution of the ammonium metavanate and/or niobium chloride at room temperature is not achieved, the polyol allows a total dissolution of the raw-salts around 130°C during the temperature rise (in between 125°C: photography n°1 and 135°C: photography n°2); the dissolution is associated with a pale orange and hazy suspension to a clear solution with darker orange color. The precipitation of the Nbdoped VEG precursor then occurs at around 150°C, this precipitation being visibly conjugated to a reduction of V^{5+} ions (shift from a reddish suspension: photography n°3, to a suspension of particles with very dark purple color: photography n°4). The doped precursors were then annealed at 300°C for 90 min in air in order to prepare a nano- Nb-doped V_2O_5 oxide powder (second stage). After mixing with carbon black with a molar ratio of 1: 1, the mixtures were both annealed in dynamic vacuum system at 700°C or 1000°C for typically 15 h in order to prepare Nb-doped VO₂ powder with various crystallite sizes.



Chpt. IV-Figure 1. Photos illustrating the different steps of the Nb-doped VEG precipitation.

Likewise, Al-doped VO₂ (target composition of 10 at%) and Ti-doped VO₂ samples (target composition of 10 at%) were prepared from the corresponding M-doped VEG precursors and M-doped V₂O₅. M-doped VEGs were synthesized thanks to the stoichiometric addition of Al(O-*i*-Pr)₃ and TiOCl₂ besides the NH₄VO₃ in polyol medium, respectively. And M-doped V₂O₅ was prepared through the decomposition of M-doped VEGs at 300°C for 90 min in air. After M-doped V₂O₅ mixing with carbon

black with a molar ratio of 1: 1, the mixtures were both annealed in dynamic vacuum system (DVS) at 700°C for 15 h.

3. Results and Discussions

3.1.Nb doping

3.1.1. Physico-chemical properties of the $V_{1-x}Nb_xO_{2\pm\delta}$

The crystallographic properties of the Nb-doped vanadium have been studied at the different stages of the synthesis route (i: precursor stage, the Nb-VEG precursor synthesis; ii: V^{5+} stage, Nb-V₂O₅ synthesis *via* the annealing Nb-VEG under air atmosphere; iii: V^{4+} stage, the carbo-thermal reduction to reach the Nb-doped VO₂). The effect of the insertion of Nb into the precursor structure is significant and associated with a clear amorphization: the diffraction peak of the precursor series for Nb concentration from 0% up to 15% (targeted concentration) continuously enlarges versus the concentration (**Figure 2a**). This is already a strong indication of the actual introduction of Nb ions into the bulk structure of the precipitated precursor. For the 15 mol.%-doped VEG, the X-ray diffractogram no longer exhibits the characteristic peaks of the VEG precursor but, on the contrary, a single peak located on the 2-theta diffraction angle of 8.5° is observed (the origin of such diffraction peak cannot be clearly determined). Thus, the solubility limit (maximum content of niobium which can be incorporated into the VEG crystallographic network) seems to be reached between 10% and 15% in niobium.

After annealing at 300°C for 90 min under air, a visible evolution of the crystallinity of the Nb doped powders with the Nb content is observed as represented by the diffractogramms in **Figure 2b.** As shown in some of our previous studies, the annealing of the un-doped VEG leads to the obtention of pure V2O5 nanoparticles. [16, 17] The Nb-doped V₂O₅ type phases resulting from air annealing of the Nb-doped VEG precursors are more amorphous: the width of the diffraction peaks enlarges with the increase in the Nb content. Moreover, while the Nb ions is incorporated, a "reducing" effect is observed: V₃O₇ oxide, corresponding to a mixed V⁴⁺/V⁵⁺ oxidation states for vanadium ions, appears next to the V₂O₅ main phase for 5% and 10% Nb-doped samples; the V₃O₇ diffraction peak intensities increase versus the niobium concentration. The 15 mol.% Nb-doped sample exhibits a diffractogramm corresponding to an almost amorphous (only some remaining small diffraction peaks can be indexed in the V₃O₇ phase). Thus, as observed for the Nb-doped VEG precursors, for the Nb-doped V₂O₅ samples obtained after a first annealing treatment under air, a drastic change is observed for target niobium concentration.



Chpt. IV-Figure 2. X-ray diffraction patterns of (a) the Nb-doped VEG precursor and (b) the nano Nb-doped V_2O_5 for Nb target concentration ranging from 0 to 15mol.%.

between 10 and 15 mol.%. Subsequently, the following studies will only focus on the samples with a target niobium concentration in the range from 0 to 15 mol.%.

The Nb-doped V_2O_5 powders are then subjected to a carbo-thermal treatment according to the protocole developed previously in the laboratory to prepare un-doped VO₂ compounds (stage 3). [16] **Figure 3** displays the X-ray diffractograms of the series (with niobium target concentration from 0 to 15mol.%) issued from a similar carbo-thermal treatment (700°C-15 h), namely the samples VO₂-700A, 5%-, 10%- and 15%-NbVO₂-700A.



Chpt. IV-Figure 3. X-ray diffraction patterns of the Nb-doped VO_2 powders obtained from carbothermal treatment of the corresponding Nb-doped V_2O_5 intermediate oxides, for niobium concentration ranging from 0 to 15mol.%.

At first glance the similarities in the diffraction patterns of the VO₂-700A, 5%- and 10%-NbVO₂ - 700A compounds evidences that the effect of niobium introduction is far from obvious. Only the 15%-NbVO₂-700A exhibits a significantly different X-ray diffractogramm with the appearance of new peaks. However, a focus on the region of the (111) and (201) peaks indexed as from the VO₂ M monoclinic form, located respectively at 27° and 28°, and the (011) peak of the R rutile form (at about 27.5°), allows to determine the rutile/monoclinic ratio which increases greatly (rutile content increases whereas monoclinic content decreases) with the increase in the niobium concentration. Besides, the focus on this narrow angle domain (2 Θ between 26 and 29°) definitively shows that the 15%-NbVO₂-700A sample is not pure but contains some impurities, peaks well detected around 27.3° do not correspond to the rutile or the monoclinic form.

In conclusion, the 0%-, 5%-, 10%-NbVO₂-700A samples consist of the existence of the rutile and monoclinic phases (so these samples are with pure VO₂-type structures) of which proportion at room temperature is tunable from the niobium concentration.

The unit-cell parameters extracted from pattern matching of the rutile phase as well as the monoclinic phase when they are well detected in the X-ray powder patterns are reported in the **Table 2**.

The number of vanadium atoms in VO₂ (M) unit cell is doubled as compared with the one in VO₂ (R) unit cell, here z is defined as 1 for VO₂ (R), and 2 for VO₂ (M). For the M phase, the unit-cell volume increases from 59.03 Å³ to 59.22 Å³ and 59.43 Å³ after 5 at% and 10 at% doping, respectively. It should be mentioned that M and R phases coexist in the 10 at% Nb-doped VO₂ sample (**Figure 3b**), and the unit-cell volume of R phase shows a larger value of 59.58 Å³ comparing with the corresponding M phase

form. When Nb doping content reaches 15 at%, the R phase volume keeps increasing to 59.82 Å³. The summarized evolution of the unit-cell volume, relative to the number of form units (V/z), increases linearly with the niobium concentration, following a Vegard law. Furthermore, knowing that the radius of Nb⁵⁺ (6-coordination number) is 0.64 Å, Nb⁴⁺ = 0.68 Å while V⁴⁺ = 0.58 Å, without presuming of the niobium oxidation state, the increase of the unit-cell parameters versus the niobium concentration is well expected.

Chpt. IV-Table 2. Unit-cell parameters of the x% Nb-doped VO_2 oxides for M and/or R phase extracted from full-pattern matching.

x%-NbVO ₂ -70	0A	a (Å)	b (Å)	c (Å)	β (°)	Unit-cell volume/z (Å ³)
0%	М	5.75225(4)	4.52591(4)	5.38301(5)	122.6088(5)	59.03
5%	М	5.76206(8)	4.52985(7)	5.38650(8)	122.6118(6)	59.22
10%	М	5.7699(2)	4.5358(2)	5.3898(2)	122.576(3)	59.43
	R	4.5602(2)	4.5602(2)	2.8651(6)	90	59.58
15%	R	4.5619(4)	4.5619(4)	2.8742(6)	90	59.82

At this point, chemical titration from ICP measurements were performed on the, 5%- and 10%-NbVO₂-700A samples, *i.e.* for the two doped samples without any impurity detected by X-ray diffraction besides the VO₂ forms.

The effective concentration of niobium ions in the pure Nb-doped VO₂ samples, are 3 mol.% (2.43 mol.%) and 6 mol.% (5.77 mol.%) for target concentrations of 5 and 10 mol.% respectively, *i.e.* for the 5%- and 10%-NbVO₂-700A samples. The precipitation efficiency of vanadium and niobium ions during co-precipitation is therefore different, and whatever the target concentration, the precipitation of the doping ions (niobium) gets a yield of about 60%, only. This linear dependence between the target concentration (introduced in polyol medium) and efficient concentration really introduces in the precipitate well correlates the evolution of the unit-cell parameters versus the target niobium concentration in Nb-doped VO₂ compounds that follow a Vegard' law.

SEM micrograph illustrates the morphological evolution during Nb-doped VO₂ synthesis at the different stages (**Figure 4a-4c**) (Stage 1: 10% Nb-doped VEG precursor; Stage 2: Nb-doped V₂O₅ as intermediate compound; Stage 3: the rutile/monoclinic Nb-doped VO₂ mixture). Considering in first approximation the particles as spherical objects, the particle size distribution widths, for all the three kinds of vanadium compounds obtained after the 3 synthesis stages, are extracted from image treatment (**Figure 4d**).

The Nb doped VEG precursor is very isotropic in shape; spherical particles about the micron are observed with quite large distribution from 0.5 up to 1.75 microns around. Its morphology is quite different from the undoped VEG with an aggregation structure consisting of elongated cuboid.²² The Nb-doped V_2O_5 obtained after the intermediate air treatment exhibits similar morphology with exactly the same distribution width. This suggests that the VEG crystallites act like a template, during the decomposition process of the organic part when the temperature increases.



Chpt. IV-Figure 4. SEM images at two different magnitudes of the (a1, a2) 10%-Nb-doped VEG precursor, (b1, b2) the 10%-Nb doped V_2O_5 intermediate compound, (c1, c2) the 10%-Nb doped VO_2 final compound (following the synthesis stage 1, 2 and 3, respectively), and (d) their corresponding particle size distribution.

It has to be noticed that the spherical particles are now clearly polycrystalline: the spherical particle surfaces exhibit high roughness, and can be described as strawberry-like aggregates of smaller crystallites. On the opposite, the high temperature treatment under vacuum destroyed this "preliminary" morphology while the oxides convert from V_2O_5 to VO_2 . Quite isotropic but already faceted crystallites are observed for the as-prepared VO_2 monoclinic/rutile mixture, with a narrow distribution of size ranging from 0.4 to 0.8 micron.

Aiming at deeper structural characterization, Rietveld analyses were performed. The monoclinic and rutile unit cells are schematized in **Figure 5a**. The number of vanadium atoms in VO₂ (M) unit cell is 12, which is doubled the one of the 6 atoms for VO₂ (R) unit cell. Upon R to M transformation, two main additional distortions can be isolated and discussed separately:

(i) The octahedral site distortion of the $[VO_6]$ pattern unit is larger in M phase than in R phase. The vanadium atoms occupy the lattice point of the body-centered cubic structure and are located at the

centers of the titled VO₆ octahedra. Two of the six oxygen atoms in the VO₆ octahedra are located further to the vanadium atom with a V-O bond distance of 1.93 Å (L bond length), while the rest two oxygen atoms are located closer, and the V-O bond distances are 1.92 Å (l bond length). In VO₂ (M), due to the movement of vanadium atoms along the V-V direction, there is a slight change for the six V-O bond distances (L₁, L₂, L₃, L₄, l₁ and l₂ are different). Besides, the three angles of V-O-V (α_1 , α_2 and α_3) are 180° in R phase whereas these three angles can independently vary with significant amplitude from 180° in M phase, as illustrated in **Figure 5b**.

(ii) The vanadium cations sub-network is more distorted in M phase than in R phase. The vanadium atoms move along the V-V direction (axis of the edge-sharing octahedral chains) and four different twins can form; Thus, the most apparent difference between M and R phase lies in the lengths of the V-V bonds, as illustrated in **Figure 5c**. In the M phase, the V⁴⁺ ions distribute periodically in zigzag along the a_M axis, while in the R phase, a straight chain along the c_R axis are usually formed. The V-V distances are constant in R phase but alternatively varying within M phase: the dimerization results in two different V-V bond lengths: a longer inter-dimer length (d₁) and a short intra-dimer length (d₂), in contrast to equally spaced V-V bonds (d_R) as in the R phase.

The distortion of the octahedral sites in monoclinic form in comparison with the octahedral site in rutile form, as reference, remains similar whatever the niobium content (**Table. 3**). For different levels of Nb doping (0%, 5% and 10%), the length change of V-O bonds in apical and equatorial directions shows similar distortion between M and R phase. Around 10.02% difference ($\Delta l/l_R$) is observed in apical direction for these VO₂ samples. Meanwhile, about 9.3% difference ($\Delta L/L_R$) is calculated in the equatorial direction. Regarding the angle distortion of V-O-V between the M and R phase, the difference displays a similar difference ($\Delta \alpha/\alpha_R$) with a value of 9.68% for different Nb doping. In other word, the niobium to vanadium substitution has negligible impact on the octahedral site symmetry.

On the contrary, as gathered in **Table 4**, the longer V-V length (d₁) decreases while the shorter V-V length (d₂) increases versus the niobium introduction in monoclinic form. In other word, the ratio of d₁/d₂ shows a clear decrease trend, the ratio decreases from 1.205 to 1.194 and 1.160 after 5% and 10% Nb doping. In comparison, the ratio is 1 in R phase. Besides, the distortions between M and R phases are also carefully studied: the distortion can be defined and calculated by using $\Delta d = [(d_1-d_R)^2+(d_2-d_R)^2]^{0.5}$ relation, where d_R is the V-V distance in R phase (d_R=2.8583 Å), as reference, arbitrary fixed whatever the composition. Thus, the structural mismatches between the M and R phases decrease on the point of view of the spatial ordering of cationic subnetwork. For the pure VO₂, the Δd distortion shows a quite high value of 0.3855 Å, and decreases linearly as doping. In the range of 0% to 10% Nb-doping, the decrease of $\Delta d/d_R$ from 13.51% to 12.88% and 10.94% indicates the decrease of the mismatch between R and M phases. It further helps to interpret the impact of the Nb doping on both the transition temperature and the amplitude of the change in calorimetric, electrical and magnetic properties.

The influence of the doping on the V-V distance is clearly shown, especially for the short distance (d₂), which determined the formation of dimer. This distance slightly increases from 2.6242 to 2.6885 Å after 10% Nb doping. According to the coulomb's law, the longer vanadium atoms distance indicates a weaker coulomb interaction in the M phase. The weaker interaction of V-V in the dimer leads to an easier transition from M to R phase, and further decrease the transition temperature from 68 to 25°C after 10% Nb doping.



Chpt. IV-Figure 5. (a) Comparison of the monoclinic phase and rutile phase unit-cells; (b) $[VO_6]$ octahedron unit full description in terms of bond lengths and bond angles; (c) $(V^{4+}$ ion) metallic-center position along edge-sharing octahedral chains (illustration of zigzag chain of the M phase and straight chain in the R phase).

Chpt. IV-Table 3. From the atomic position extracted by Rietveld refinements on the monoclinic forms: *V-O* bond lengths and *V-O* bond angles distance in the *M* phase for 0%-, 5%- and 10% Nb-doped VO_2 samples and quantitative assessment of the octahedral site distortion in comparison to the octahedral site of the *R* phase.

			0%Ref	0%	5%	10%
			R phase	M phase	M phase	M phase
	Apical	l_1	1.9330	2.0489	2.0116	2.0245
		l_2	1.9330	1.7579	1.7760	1.7551
V-O	Length change (M/R _{ref})	$\Delta l/l_R$	0	10.86%	9.08%	10.13%
Length (Å)		L_1	1.9216	1.8459	2.0503	2.0315
(A)	Equatorial	L_2	1.9216	2.0240	1.9078	1.9397
		L_3	1.9216	2.0626	1.8637	1.8941
		L_4	1.9216	1.8726	2.0210	2.0428
	Length change (M/R _{ref})	$\Delta L/L_R$	0	10.21%	9.01%	8.68%
	-	α_1	180	171.482	171.451	172.624
V-O-V Angle (°)		α2	180	169.556	169.678	169.226
		α3	180	168.453	168.954	168.884
	Angle change (M/R _{ref})	$\Delta \alpha / \alpha_R$	0	9.86%	9.65%	9.53%

Sample	Phase	d ₁ (Å)	d ₂ (Å)	d_1/d_2	$R_{ref} \rightarrow M$	$\Delta d/d_R$
					$\Delta d = [(d_1 - d_R)^2 + (d_2 - d_R)^2]^{0.5} (\text{\AA})$	
0%	М	3.1632	2.6242	1.205	0.3855	13.51%
5%	М	3.1523	2.6399	1.194	0.3675	12.88%
10%	М	3.1181	2.6885	1.160	0.3121	10.94%
$0\%_{\text{Ref}}$	R	2.8528	2.8528	1.000	0	0

Chpt. IV-Table 4. *The V-V distance in the M phase for 0%, 5% and 10% Nb-doped VO*₂ *sample and the V-V pairing distortion (considering zero or no pairing amplitude for R phase).*

3.1.2. Comparison of the 0% and 10% Nb-doped VO₂

10%-NbVO₂-700A sample exhibits pure VO₂ type structure on the contrary to the 15% doped sample Moreover, the 10% sample corresponds to an equilibrated mixture of the monoclinic and rutile phases at room temperature, indicating the transition temperature (T_c) could be probably decreased to room temperature. On a room temperature application point of view, the 10%-NbVO₂-700A sample appears the most promising. Rietveld refinement of the diffractogramm, allows the calculation of the weight percent of monoclinic and rutile phases (**Figure 6**). At room temperature 10%-NbVO₂-700A consists of 54 wt% of monoclinic form and 46 wt% of rutile one (Inset **Figure 6**). So, the co-existence of nearly 50% of each VO₂ phase proves that the phase transition is really calibrated near the room temperature, as expected to open a use in large scale of such a compound as thermochromic film for smart windows. That is why we decided to investigate in the following discussion the difference in terms of calorimetric, electrical and magnetic properties.



Chpt. IV-Figure 6. X-ray diffraction pattern refinement of the 10%-NbVO₂-700A and extracted quantities for the VO₂ (R) and VO₂ (M) forms.

In order to get an idea of the oxidation state of both vanadium and niobium cations into the as-prepared 10%-NbVO₂-700A powder, TGA analyses were conducted on the undoped VO₂-700A powder under air aiming at producing the full oxidation of V^{4+} into V^{5+} cations (**Figure 7**).



Chpt. IV-Figure 7. TGA analyses under air atmosphere performed on the 10% - NbVO₂-700A and the VO_2 -700A samples. Relative proportion of V^{3+}/V^{4+} and V^{4+}/V^{5+} in both cases.

After the high temperature (600°C) TGA experiment, the powder color changes to orange, which is a typical V⁵⁺ color suggesting a full transformation to V₂O₅. After Nb doping, there is a slight improvement in thermal stability, the oxidation temperature increases from 450 to 480°C. For the undoped sample, the chemical formula changed from $VO_{2\pm\delta}$ to $VO_{2.5}$ during the TGA, the mass variation associated with the oxidation leads to calculate a δ =0.1 and further a V⁴⁺/V⁵⁺ content ratio equal to 4 (80 mol.%/20 mol.%). This result is in agreement with literature studies where it has been proved that V⁴⁺ and V^{5+} usually co-exist in undoped VO₂; [1, 9, 10] even if a pure VO₂ crystal is obtained, it can be reasonably assumed that surface oxygen over-stoichiometry leads to the occurrence of a significant proportion of V⁵⁺ ions. For the 10%-NbVO₂-700A sample, we consider the starting chemical formula $V_{1-x}Nb_xO_{2\pm\delta}$ with x value issued from the ICP titration equal to 5.77at%, and without presuming of the oxidation state of vanadium. In order to extract the vanadium average oxidation state: Nb is assumed with oxidation state +5, *i.e.* without any trace of Nb with oxidation state equal +4. With this hypothesis, the vanadium oxidation state is found to be 3.95, meaning nearly with all the vanadium ions (98 mol.%, exactly) with +4 oxidation state but also with traces of vanadium +3 (2 mol.%); this is coherent with a compensation of the aliovalent substitution of the V⁴⁺ from the Nb⁵⁺. Indeed, electroneutrality law engages the reduction of vanadium ions in order to compensate this aliovalent substitution. Hence, it can be concluded that in doped or undoped samples the largest quantity of vanadium species exhibits a +4 oxidation state. Also, TGA under oxidation atmosphere seems coherent with the consideration of +5 oxidation state for the niobium doping ion.

To further investigate the influence of the vanadium to niobium substitution on the first order transition of VO₂ (M/R), differential scanning calorimetry (DSC), resistivity and vibrating-sample magnetometer (VSM) *in situ* measurements versus temperatures were performed. As shown in **Figure 8a-8c**, a sudden transition occurs in both samples. The heat capacity, resistivity and magnetic susceptibility temperature dependences show for both samples a first-order transition exhibiting a clear hysteresis loop in between the heating and cooling processes. The transition temperatures (T_c) in heating and cooling cycle for the undoped and the 10%-Nb-doped VO₂ samples are gathered in **Figure 8d**.



Chpt. IV-Figure 8. (a) DSC curves showing the heat capacity, (b) resistivity curve and (c) magnetic susceptibility of un-doped VO₂ (VO₂-700A) and Nb-doped VO₂ (10%-NbVO₂-700A) versus temperature; (d) Summary of transition temperatures and the width of the hysteresis loop measured between heating and cooling modes extracted from DSC, resistivity and VSM analyses.

From pure VO₂, the T_c around 70°C greatly decreases to 25°C after Nb doping, being in good agreement with the occurrence of monoclinic/rutile mixture at room temperature as analyzed previously from X-ray diffraction patterns refinement. The widths of the hysteresis loop associated with this first order transition associated to the temperature mismatch in between the heating and cooling cycles measured by the different techniques, show a narrower transition width with Nb doping. On one hand, the impact on the transition temperature of doping ions inside VO₂ structures (as for Nb⁵⁺ ion doping) is intensively studied and discussed in literature, even if it remains the subject of controversies. [23, 24]

On the other hand, and more interestingly, the niobium doping is associated with a decrease of the hysteresis width as well as a decrease of the latent heat on the transition, a decrease of the amplitude mismatch in terms of electrical conductivity and magnetization values. For illustration, for the 10%-NbVO₂-700A, the latent heat as measured in the heating cycle is 33.42 J/g and, in the cooling cycle, is 33.39 J/g, which is expected to result from the combined contributions of the phonons and electrons coexisting within the phase transition. [25] The latent heat ratio 33.42/33.39=1.001, clearly demonstrates that the transition is perfectly reversible, while, as a comparison, the latent heat of the undoped VO₂ is 54.26 and 53.61 J/g in heating and cooling cycle respectively, which also displays an excellent reversibility with a latent heat ratio of 54.26/53.61=1.012. This is in good agreement with a smaller hysteresis in the case of Nb doped VO₂. Indeed, the latent heat and hysteresis width reductions are both linked to a decrease of the energetic barrier to cross through the first order phase transition, what can be put in regard of the structural mismatch between R and M phases versus doping.

More spectacularly, a deeper investigation was conducted on the electrical conductivity (σ) versus temperatures (on heating mode) of both undoped and doped samples (**Figure 9**). As the temperature increases, there is a sharp transition for both samples. The conductivity of the semiconducting state (low temperature) is enhanced significantly by the Nb substitution, while the one of the metallic state (high temperature) is reduced. The monoclinic pellet exhibits a semiconductor behavior, while the rutile pellet, reported to display a metallic behavior, shows here also a semiconducting behavior with a higher conductivity. The thermally activated conductivity exhibits the Arrhenius dependence, and In σ is a linear function of 1000/T in both sides of the transition from function: $\sigma = \sigma_{0*} \exp(E_a/kT)$. The high R-square (R²) value shows an excellent fitting. Assuming then that the slope is directly linked to the band

gap, the "activation energy" (E_a) can be calculated for both monoclinic and rutile forms for both samples. The calculated E_a is shown in inset of **Figure 9**. For the VO₂-700A sample, E_a is 0.387 and 0.113 eV for its monoclinic and rutile phase, and the corresponding E_a are 0.256 and 0.202 eV for 10%-NbVO₂-700A sample. Clearly, in terms of activation energies, the mismatch between two phases is nearly suppressed as Nb substitution is introduced into the VO₂ lattice. It is expected that the breaking of Peierls distortion and the weakening of electronic correlation within the V-V dimers would result in a decrease of the band gap (for M phase), leading to the decrease in T_c and increase of σ in the low temperature. Here the local V-V dimer distance, and especially the pairing strength, characterized previously as described in XRD part from the ratio between the long V-V length and the short V-V length (d₁/d₂) is slightly decreased from 1.205 for the undoped sample to 1.16 after 10%-Nb doping, hence it facilitates thermal activation of carriers and so, monoclinic to rutile phase transition.



Chpt. IV-Figure 9. Detailed study on the temperature dependence of the conductivity of un-doped and Nb-doped VO_2 samples (VO_2 -700A and 10%-Nb VO_2 -700A) along the phase transition, with large R^2 showing good fitting; And the activation energies (E_a) for both M and R forms are inserted.

Single crystals of VO₂ typically yield an E_a of 0.45 eV, doping with a valence greater than +4 will sharply lower this value. For example, the E_a of the M phase is decreased to 0.22 eV for W⁵⁺ doping and 0.1 eV for Mo⁶⁺ doping with a content of around 0.05-0.5 at%. [26] In fact, it is also reported that the E_a would be lowered after Al³⁺ doping. [27] Unexpectedly, above T_c, the electrical behavior of Nb-doped sample is not a metal. It seems that both R and M phases are both semiconducting phase, suggesting the electronic nature of the transition is different from the classic Mott metal-insulator transition, [28] or rather that the electronic conductivity is limited by the grain boundary conductivity.

All these observations converge towards: a decrease of the mismatch between M and R phases. This phenomenon is to be correlated to the previous discussions issued from our Rietveld analyses that have shown an accommodation of the structural transition while niobium is introduced in the crystallographic VO₂ network (accommodation which is due to the partial "de-pairing" of the V entities in dimers while Nb doping). Clearly, it reveals a correlation between the distortion of the V-V pairing caused by niobium doping and the decrease of the latent heat, the resistivity and the magnetization mismatches along the transition. It has to be noted that the latent heat is already known as to be made up from the accumulation of two contributions, one is from the lattice which results from the crystalline distortion, and the other one from the conduction electrons which results from the discontinuity in the carrier density. Our study shows that the decrease of the conductivity mismatch in between R and M phases as well as the decrease of the crystallographic mismatch associated to M and R transition are closely related; thus, structural considerations and electrical and magnetic properties through the phase transition seem actually entangled.

3.1.3. Impact of doping concentration and particle size on magnetic properties

The last part of our study focuses on the magnetic properties and their comparison on five selected samples: three first samples the VO₂-700A, 5%- and 10%-NbVO₂-700A allow a study of the impact of the niobium doping rate, between samples prepared using the same synthesis parameters; the sample VO₂-700A is to be compared with samples VO₂-700B and VO₂-1000A as for undoped samples the crystallite sizes vary thanks to different thermal treatments (the VO₂-700B sample, is annealed only 1 h at 700°C, while the VO₂-1000A sample is annealed 15 h at 1000°C). SEM images of the three latter samples are reported in **Figure 10**. The average crystallite sizes deduced from image treatments for the three samples are 0.4 um for the VO₂-700B, 1.8 um for the VO₂-700A and 5.3 um for the VO₂-1000A sample.



Chpt. IV-Figure 10. SEM images of (a) VO2-700B, (b) VO2-700A and (c) VO2-1000A compounds.

Figure 11 displays the magnetic susceptibility *vs*. T curve measured in the field of 15 000 Oe during cooling process for a wide range of temperature from 380K to 2K with SQUID magnetometer apparatus. For all the five samples, it can be clearly observed a clear magnetic susceptibility drop at the transition critical temperature T_c from rutile (high temperature) to the monoclinic (low temperature) form. The collected data can then be divided into High-T (T>T_c) and Low-T range (T<T_c). Above T_c , the plateau-like, with a roughly constant susceptibility in high temperature is associated to Pauli paramagnetism (PM) in relation with the high electronic conductivity of the rutile form as just underlined. To explain the Low-T susceptibility plateau, the formation of covalent V-V pairs was suggested. [29] After this stable value in the temperature range of 300-150K, the magnetic susceptibility shows a rapid increase below 150K, which was interpreted by the presence of traces of unpaired V⁴⁺ spins probably due to defaults (lattice defects) in the structure. [30] The curves as well as fits above and below T_c are reported in **Figure 11**.



Chpt. IV-Figure 11. Susceptibility versus temperature of the: (a) VO₂-700A, 5%-NbVO₂-700A and 10% NbVO₂-700A compounds; (b) VO₂-700A, VO₂-700B and VO₂-1000A compounds); Inset the plot of the fits (red lines) performed on the experimental susceptibilities in the high temperature, respectively.

First, we discuss the variation of the Pauli plateau values in High-T range for different samples. The fits of the Pauli magnetic part were made by refining two key variables: the Fermi energy (E_F^0) of the compound and the number of charge carriers per mol (N_p) using the following equations:

$$\chi_P = \chi_P^0 \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{E_F^0} \right)^2 \right] \dots \dots \dots Pauli PM$$
$$\chi_P^0 = N_P a \quad a = \frac{3\mu_B^2}{2E_F^0}$$

where $k_B=8.617\times10^{-5}$ eV/K is the Boltzmann constant and $\mu_B=5.788\times10^{-5}$ eV/K-Bohr magneton.

The plots of the different fits are added to experimental data in the inset of **Figure 11** and the different parameters calculated from the fits are gathered in **Table 5**. An ideal crystal of VO_2 should be diamagnetic if Van-Vleck's orbital paramagnetism is neglected.

$$\chi = \chi^0_{TIP} + \frac{C}{T - \Theta} \dots \dots Low - T \ range$$

Chpt. IV-Table 5. Pauli susceptibility (χ_P^0) , Fermi energy (E_F^0) , charge carrier concentration (N_P) and *R*-square of the fitting results (R^2) for the VO₂-700A, 5%-NbVO₂-700A and 10% NbVO₂-700A compounds; (ii) VO₂-700A, VO₂-700B and VO₂-1000A compounds.

Sample			χ^0_P	E_F^0	N _P	R ²
			$(\times 10^{-5} \text{ emu.mol}^{-1}.\text{Oe}^{-1})$	(meV)	(×10 ³)	
Doping	VO ₂ -700A	0%	59.46±0.11	108.79	12.9	0.9950
effect	5%-NbVO ₂ -700A	2.43%	71.80±0.15	105.94	15.1	0.9935
	10%-NbVO ₂ -700A	5.77%	78.58±0.18	101.33	15.8	0.9917
Size	VO ₂ -700B	0.5 um	66.41±0.11	120.40	15.9	0.9874
effect	VO ₂ -700A	1.8 um	59.46±0.11	108.79	12.9	0.9950
	VO ₂ -1000A	5.3 um	54.98±0.16	96.06	10.5	0.9838

Then below T_c, the low temperature parts of the susceptibility curves were also fitted considering in the monoclinic form the sum of (i) a Curie-Weiss law χ_{cw} due to traces of unpaired spins $\chi_{cw} = C/(T-\Theta)$ and (ii) a temperature-independent paramagnetism (χ_{TIP}^0) consist of Van-Vleck susceptibility and diamagnetic susceptibility to account for the magnetic susceptibility plateau. Other tests to fit our collected data considering a spin gap system due to V-V dimerization state with an antiferromagnetic interaction as proposed in literature, [22] were unsuccessfully giving Gap values in the range of 2 K. The temperature independent paramagnetic contribution susceptibility, Curie constant (C) and Curie-Weiss temperature (Θ) as well as correlation factors are reported in **Table 6**.

From the as so-obtained fitted parameters, the χ^0_{TIP} susceptibility value is positive meaning than the Van-Vleck's orbital paramagnetism cannot be neglected. Furthermore, it is more significantly impacted by the niobium substitution for vanadium; than by crystallites size and/or surface defects. The Curie constant C increases significantly with the niobium concentration and/or with the increase of the average crystallite size of the analyzed sample. The Θ Curie-Weiss temperatures remain near equal to zero whatever the sample indicating a very small strength between the magnetic species.

Chpt. IV-Table 6. Van-Vleck and diamagnetic susceptibility (χ^0_{TIP}) , Curie constant (C), Curie-Weiss temperature (Θ), and R-square of the fitting results (R^2) for the (i) VO₂-700A, 5%-NbVO₂-700A and 10% NbVO₂-700A compounds; (ii) VO₂-700A, VO₂-700B and VO₂-1000A compounds.

	Sample		χ^0_{TIP}	С	θ	R ²
			(×10 ⁻⁵ emu.mol ⁻ ¹ .Oe ⁻¹)	(10-3)		
Doping	VO ₂ -700A	0%	3.69±0.03	4.91±0.02	0.81±0.02	0.99991
effect	5%-NbVO2-700A	2.43%	7.16±0.12	15.26±0.07	-1.83 ± 0.02	0.99988
	10%-NbVO ₂ -700A	5.77%	9.91±0.48	33.39±0.30	-2.39±0.04	0.99947
Size	VO ₂ -700B	0.5 um	6.00±0.02	4.95±0.01	-2.75 ± 0.02	0.99983
effect	VO ₂ -700A	1.8 um	3.69±0.03	4.91±0.02	0.81±0.02	0.99991
	VO ₂ -1000A	5.3 um	4.10±0.07	10.62 ± 0.06	-2.15 ± 0.05	0.99963

The impact of the niobium concentration on the χ^0_{TIP} susceptibility can be expected from the different electronic configurations of the niobium ions and the vanadium ones, with a larger quantity of valence band electrons in niobium (the heavier atom) in comparison with vanadium (the lighter atom). Interestingly, Van-Vleck magnetic susceptibility has already been found to scale linearly with Nb dopant in BaTiO₃ diamagnetic matrices. [31] Our result suggests a possible counter charge balance introducing one V³⁺ for each Nb⁵⁺.

About the Curie constant, it exhibits for all the samples a very low value, confirming the d electrons trapping into homopolar bonds in relation with the dimer formation of largely the most of the vanadium (+4) ions in the monoclinic form, in good agreement with literature. [32] Hence, the reported Curie magnetism has definitively to be discussed as a "residual paramagnetism". This also explains why the Van-Vleck magnetism generally neglected in semi-conducting oxide with paramagnetic atoms, because of its relatively weak amplitude must be here taken into account. More interesting is the variation of the Curie constant with crystallite size and niobium concentration.

Reasonably, considering all the niobium ions with the +5 oxidation state, *i.e.* showing diamagnetic signal and a significant Van-Vleck magnetic susceptibility, the Curie residual paramagnetic can only result from un-paired V^{4+} ions and/or vanadium ions with low oxidation state (+3) as previously suggested. Un-paired vanadium ions can be located at the end of a V-V dimerization along the chain meaning at the crystal surface or in first-neighboring of Nb⁵⁺ ions. Hence, it can well explain the increase of the Curie constant with defects as Nb⁵⁺ ions act like "breaking points" along the chains formed by the edge-sharing octahedral sites. However, the increase of the Curie constant with the crystallite sizes appears illogical, on this point of view. Apparently, the predominant reason of this latter phenomenon is due to the occurrence of a small fraction of V³⁺ ions as it has been shown from TGA measurements (**Figure 7**). This V³⁺ fraction increase versus the thermal treatment temperature is expected since the temperature is always associated with a reductive effect. Finally, the constant value near 0 K for the Curie-Weiss temperatures can be interpreted in regard of the absence of long-range magnetic ordering between traces of unpaired V⁴⁺.

As proposed by Goodenough, [29] in the rutile phase, a narrow π^* anti-bond is formed between the V⁴⁺ and O²⁻, and a d_{//} nonbond is formed between adjacent V⁴⁺ orbitals along the crystallographic c axis. The unfilled π^* and d_{//} bands partially overlap, the fermi level (E_F^0) falls at the point where π^* and d_{//} bands overlap, as illustrated in **Figure 12a**. During the phase transition R \rightarrow M, the π^* level is elevated and the d_{//} bond is split into d_{//}-bonding and d_{//}* anti-bonding due to V-V dimers formation.

Here the position of the E_F^0 respects to valence and or conduction bands depends on various parameters as the temperature, the effective masses of electrons and the number of free electrons. For the undoped VO₂, the Fermi energy is lying exactly at the middle of the energy bandgap at T=0 K. In order to maintain the number of particles (mass action law) and to fulfill the overall electrical charge neutrality (neutrality equation), the E_E^0 moves toward conduction band when Nb⁵⁺ (donor) is introduced, which gives additional electrons from the system. In our case, versus Nb doping concentration and particle size increase, the E_F^0 displays a clear decrease trend. Based on the squid measurement and the simulation, the number of near-free electron in R and M phases can be calculated based on the $\chi_P^0 = N_p a$ above T_c and $\chi^0_{TIP} = (N_p - 2N_{d0})a$ below T_c respectively, where N_p is the number of near-free electron in the R phase, N_{d0} is the number of dimers in the M phase and $a = 3\mu_B^2/2E_F^0$. Owing to that each dimer contains two electrons, the number of near-free electrons would change from Np to (N_p -2 N_{d0}) in the M phase, and (N_p-2N_{d0})/N_p is the percentage of unpaired V⁴⁺ ions. [22] The results are presented in Figure 12b. It can be seen that the major V⁴⁺ ions are paired into V-V dimers, ~94% V4+ are paired into dimers for the undoped VO₂. Due to the breaking of Peierls distortion as Nb substitution, the unpaired "free" V^{4+} ions percentage increased from ~6% to ~11% and ~15%. As for particle size increases, the unpaired V^{4+} ions percentages are ~9%, ~6% and ~7%, the size particle effect is not so clear. During the phase transition $R \rightarrow M$, as previously pointed out the V ions are shifted to form V-V pairs. The V-V pairs may trap all the available d electrons into homopolar bonds as suggested by Goodenough. [29]



Chpt. IV-Figure 12. (a) The band structures of VO₂ (M/R) depicted by molecular orbital diagrams; (b) Number of near-free electrons in M and R phases: doping effect: VO₂-700A, 5%-NbVO₂-700A, 10% NbVO₂-700A compounds, and size effect: VO₂-700A, VO₂-700B, VO₂-1000A compounds.

3.2.M-doped VO₂ with M= W, Ti or Al

Likewise, other popular doping elements for VO_2 were also gave a try, including W, Ti and Al. Firstly, W is used for the doping due to its clear effect on tailoring the T_c (see Chapter I). Unluckily, we failed to observe the W element in the W-doped VEG samples through ICP characterization. It may be not suitable for W doping *via* this method. And then we moved to Ti and Al doping.

10 mol% Al-doped VO₂ and Ti-doped VO₂ powders were prepared at 700°C for 5 h using the DVS system in order to be compared with the undoped DVS-700 sample. With the designed target composition of 10 at% doping, ICP-OES measurement shows the real doping content are 1.18 wt% and 4.37 wt% for Ti-VO₂ and Al-VO₂ sample.

X-ray diffraction pattern of the obtained powders are reported in **Figure 13a**. The Ti-doped VO₂ phase exhibits only peaks associated with the M1 monoclinic phase whereas M2 phase can be detected when

the vanadium is substituted with Al^{3+} dopant. Intriguing, M2 phase is a Mott insulator, which can transform to metallic M2 upon carrier injection, showing potential applications in Mott field-effect transistor. It has already been reported in literature, [33] that the introduction of aluminum inside the VO₂ crystal framework allows the stabilization of the M2 allotropic form. Thus, the synthesis process herein is able to provide a controllable and reliable method for producing M2 phase.

Figure 13 shows DSC curves of the two doped samples, which corresponding to the M1-R for transition for Ti-VO₂ and M1-M2-R multiple transition for Al-VO₂. The Ti-VO₂ shows unclear (non-significant) changes comparing with the pure VO₂ (DSV-700), in good correlation with literature reporting either a very slight decrease of the transition temperature versus Ti-doping, [34, 35] or a very slight increase of this temperature. [36, 37] Moreover, a careful comparison of the DSC curves of the undoped and Ti-doped samples indicates that (i) the enthalpies are non-significantly impacted, (ii) the hysteresis loop tends to slightly enlarge and especially, (iii) the temperature range on which occurs the transition for both cooling and heating modes becomes wider (the DSC peaks are larger, the transition becomes smoother) while Ti⁴⁺ ions are introduced in the VO₂ crystal network.

For Al-doping, the most interesting aspect is that the occurrence of a M1-M2-R multiple transition while Al^{3+} ions are introduced in VO₂ modifies the DSC peak from a single peak to a quite convoluted but clearly observable doublet, well illustrating the pathway through an intermediate phase, namely the M2 phase. Also, the phase change enthalpy (ΔH) decreases clearly after doping, which can be ascribed to the large local distortions inside the host monoclinic VO₂ matrix resulting from the aliovalent substitution of V⁴⁺ with Al³⁺ and/or by an "accommodation" of the phase transition from the occurrence of the intermediate allotropic form (M2 phase).



Chpt. IV-Figure 13. (a) XRD patterns of the Ti- VO_2 and Al- VO_2 , in comparison with DVS-700. (b) DSC curves of the corresponding doped VO_2 samples. For simplification, the target composition of 10 % is indicated.

4. Conclusion

In this Chapter, four doping elements (M= Nb, W, Ti and Al) were explored for the M-VO₂ compound synthesis with the carbo-thermal reduction method. More precisely, the process can be described as three stages, namely (i) M-VEG formation through the polyol process, (ii) oxidation to M-V₂O₅ in air annealing, (iii) reduction to M-VO₂ due to carbon black addition. This method provides the possibility for Nb, Ti and Al doping allowing the control of the phase transition parameters. Unluckily, we failed to dop W into VO₂ compound with this method.

More importantly, Nb content up to 5.77 at% was nicely achieved leading to a decrease in the transition temperature T_c , getting close to room temperature (~25°C). The influence of the Nb doping

on the thermochromic properties of Nb-doped VO₂ was investigated by differential scanning calorimetry (DSC), resistivity measurements and scarcely used vibrating-sample magnetometer (VSM) characterizations showing a strong dependency to the Nb content as well as the crystallite sizes. In particular, the input of the magnetic characterizations allows a significant step forward in the determination of the V/Nb cations distribution bringing crucial information for further consideration in the remaining debates on the origin of the driving force(s) behind the metal-insulator transition (MIT) of VO₂.

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Chapter V: VO₂-based films preparation



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5. R	eferences

1. Introduction

Designing improved energy-saving materials is an active research topic in materials science because of the increasing concerns related to energy consumption and sustainable development. As a representative thermochromic material, vanadium dioxide (VO₂) is a key material for smart windows that can respond to environmental temperature and modulate near infrared irradiation (NIR) by changing from a transparent state (M phase) at low temperature to a more reflective/absorptive state (R phase) at high temperature. The main difficulty besides such applications is to elaborate thin films combining sufficient transparency in the visible region and infrared absorption contast depensing on the M and R form. [1]

Over the past decade, many methods for preparing VO₂ NPs with fine crystallinity have been explored to prepare after their dispersion in various host materials, (glass or polymer matrices), composite films. Among them, polyurethane (PU) has been widely used and studied. Compared with a continuous film, VO₂ nanospheres in a dielectric matrix could accomplish to nearly double the theoretical ΔT_{sol} and T_{lum} based on nanothermochromic calculations using effective medium theories. [2] Chen *et al* [3] synthesized finely crystalline VO₂ NPs with average diameters of 26 nm, dispersed in PU matrix. The obtained composite coating showed an optimal optical performance.

Besides, as a transition metal, vanadium is a multivalent element and VO₂ (M) can be oxidized. For example, VO₂ film was oxidized to V₂O₅ after being annealed at 300°C in air. [5] This instability results in serious durability problems in practical applications, leading to the need for encapsulation process. To improve the stability of VO₂ NPs, Gao *et al* [4] reported a novel all-solution process to prepare a VO₂@SiO₂ core-shell structure nanocrystals, further integrated in PU; the SiO₂ shell can act as a protective layer to restrain oxygen diffusion and prevent thermodynamically unstable VO₂ being oxidized. Through the assistance of Polyvinypyrrolidone (PVP), VO₂ NPs were well dispersed.

However, due to VO_2 strong absorption, VO_2 films typically demonstrate a brownish-yellow color. The color preference is closely related to cultural background. Generally, a colorless coating or coloration with light gray/blue is most favorable.

As shown in the Chapter 1: state of the art, to enhance the performance of smart windows, nano- and microscale engineering methods are put forward, including incorporating particles, turning the porosity, designing nanocomposies, developing biomimetic patterns, creating grids, and applying multifunctional antireflection coatings. Among them, surface engineering is one of the most effective approaches. To design the 2D-patterned microstructures, several techniques [6] have been developed, such as photolithography, electron beam lithography, and colloidal lithography. For example, using polystyrene (PS) spheres in the monolayer colloidal crystal (MCC) template, Ke *et al.* [7] modified the nanosphere lithography method and produced diverse patterned VO₂ films with tunable periodicity and nanostructures, including nanoparticles, nanonet, and nanodome arrays. Two-dimensional photonic crystal is one of the most promising structures that demonstrates conspicuous structural color, and because it contains less VO₂ as compared to a 3D structure, static absorption in the VO₂ layer is minimized. Besides, the same team also demonstrated a 2D photonic crystal VO₂ film, which exhibit static visible light tunability and dynamic NIR modulation. [8] The films are prepared through a sol-gel infiltration method where the VO₂ is coated on the surface of silica nanosphere. However, these techniques usually suffer from low efficiency and high costs or the use of templates (masks or colloids).

To address the color concern and thermal stability problem, here we put forward a template-free surface-patterning method to prepare zero-dimensional and further developed into 2D-patterned monolayer VO_2 film, which shows visible homogeneous state with a gray/blue color.

In Chapters 2 and 3, carbon was reported as a perfect reducing agent for the VO₂ powder preparation through reducing the high valence oxide V_2O_5 . Dynamic vacuum system was applied, created by keeping pumping during the whole annealing process and allowing the CO gas removal as soon as its formation, thus preventing from the reduction down to V_2O_3 . In literature, as a bulky, non-toxic, nonionic polymer with functional groups (C=O, C-N and CH₂), PVP is mainly used as a surface stabilizer and reducing agent. It can dissolve in water and many non-aqueous liquids, as a result of the highly polar amide group in the ring and along its backbone. [10]

In this chapter, inspired by routes using the multifunctional PVP polymer, we propose a novel synthesis route to prepare a special morphology of VO₂ film with gray color. High temperature (700°C) annealing treatment is used to increase the crystallinity of VO₂, which is helpful to the film's thermal stability. For example, applications in energy efficient smart windows and solar cells for solar heat control. The preparation procedure is as follows. First, the obtained V₂O₅ NPs are pretreated in a PVP solution (CHCl₃) to absorb PVP on V₂O₅ surface (V₂O₅@PVP). Second, the V₂O₅@PVP films are prepared by spin-coating the suspension on a quartz substrate. Third, V₂O₅@PVP films are heated at 700°C for 15 h in a dynamic vacuum environment. Finally, the prepared discontinuous VO₂ films are characterized.

2. Experimental

2.1. Preparation of V2O5 nanoparticles (i.e. Chapter 3)

All reagents in experiments are analytical grade without further purification. V_2O_5 is be synthesized by heating the Vanadyl ethylene glycolate-VEG at 300°C for 90 min in air. [11] Then the obtained V_2O_5 is mixed with soot (Mole ratio 1: 1) and grinded fully in the ball milling at a speed of 400 rpm for 1 h. Nanoscale soot is used to destroy the rectangular structure for V_2O_5 NPs preparation. Then the mixture is annealed in air (500°C for 30 min) to remove the residual carbon.

2.2.Preparation of V2O5@PVP solution

First, the V₂O₅ NPs are pretreated with poly(vinylpyrrolidone) (PVP, MW= 40 000, Sigma-Aldrich) in CHCl₃ solution. In the PVP functionalization process, the suspensions are stirred vigorously for 1 h to ensure the fully PVP adsorption onto V₂O₅ NPs surface, and a yellow color and uniform suspension (V₂O₅@PVP) was formed. Different suspension samples are prepared under the conditions listed in **Table 1**. The PVP/V₂O₅ weight ratios and V₂O₅@PVP suspension concentrations are adjustable parameters in our synthesis process.

2.3.Fabrication of V2O5@PVP film and VO2 film

The prepared V₂O₅@PVP suspensions are dropped onto quartz substrates and spin-coated to form V₂O₅@PVP films. The spin-coating conditions are fixed to 1000 rpm for 30 s for all film preparations. In the next step, the obtained V₂O₅@PVP films are transferred into a dynamic vacuum system and are annealed at 700°C for 15 h (heating rate is 10°C /min) in a vacuum environment. The dynamic vacuum environment is created by keeping pumping during the whole annealing process. [11] Finally, homogeneous VO₂ films are prepared.

3. Results and discussion

3.1.Preparation of V₂O₅ NPs suspension

According to our previous studies (see chapters 2 and 3), pure V_2O_5 particles are easily prepared after heating the vanadyl ethylene glycolat (VEG) at 300°C in air for 90 min. The microstructure of the obtained V_2O_5 displays clusters composed of many rod-like (elongated cuboid-shape) structures (**Figure 1a**). However, this morphology is unfavorable for the dispersion in one organic solvent. So, preliminary preparation of V_2O_5 NPs with almost adequate microstructure is necessary. Since the rod-like V_2O_5 is composed of nanoparticles, ball-milling is used as effective way to destroy rectangular V_2O_5 . Nano size (~35 nm) soot is mixed with V_2O_5 in the mole ratio 1: 1. After the ball milling process, the residual carbon in V_2O_5 powder has to be removed. So a heat treatment is applied to the mixture at 500°C for 60 min in air. The carbon content, determined by CHNS, decreases from 6.37 wt% to 0.08 wt% after annealing, indicating that the carbon was almost totally removed. V_2O_5 NPs, with a size of around 185 nm, are successfully prepared (**Figure 1b**). It should be pointed out that the addition of soot is essential, ball-milling of pure V_2O_5 oxide without soot fails to produce nanoparticles with so adequate shape, on the opposite, in this case, no obvious changes occurred for V_2O_5 morphology.



Chpt. V-Figure 1. SEM micrograph of (a) rod-like V_2O_5 powder, synthesized from the 90 min VEG at 300°C; (b) V_2O_5 NPs, obtained via heating the mixture of rod-like V_2O_5 and soot, after a preliminary ball-milling step.

Although V_2O_5 NPs is prepared *via* ball-milling, it is still difficult to maintain real nano-sized oxides in a liquid medium due to the aggregation problem. This process involves the formation and growth of aggregates which are controlled by both interfacial chemical reactions and particle transport mechanisms. Aggregates up to several microns in size can be formed. Obviously, the formation of large size aggregates is unbeneficial to the achievement of a stable suspension.

In the absence of a surface stabilizer as PVP, the formation of continuous films is difficult. Besides, as an amphiphilic, non-ionic polymer, PVP polymer can also adsorb onto different metal oxides (such as kaolinite, titania, iron oxide, alumina, vanadium dioxide [4]), it can stabilize the NPs in water and many non-aqueous solvents. So PVP is used as a surface stabilizer to treat the V_2O_5 NPs to avoid the clusters formation (**Figure 2a**). Furthermore, the addition of PVP to the suspension enhances its wettability to the substrate, resulting in the formation of crack-free, uniform films. Chloroform (CHCl₃) is chosen as solvent for V_2O_5 suspension preparation, besides it is a good solvent for PVP. Additionally, its low boiling point (61.5°C) is also an advantage for film preparation through the use of spin-coating techniques in the following step. Indeed, low boiling point solvents for spin-coated suspensions allow the obtention of homogeneous thickness thanks to the fast gelification of the coated films.

Figure 2b shows the V₂O₅ particle size distributions in the suspensions with different PVP and V₂O₅ weight ratios. The particle size distributions in the suspensions are directly obtained from granulometric measurements. Without PVP addition (R=0), aggregates (\sim 2.2 um) are observed. After functionalization with PVP, the particle size decreases to around 160 nm, indicating that the PVP could act as an efficient surface stabilizer and could avoid the formation of clusters in this system. Furthermore, the size distribution in suspension is basically consistent with the V₂O₅ NPs average diameter (185 nm) extracted from SEM measurements (**Figure 1c**). Reasonably, it can be proposed that PVP acts as a protective shell on each single particle.



Chpt. V-Figure 2. (a) Scheme of the PVP treatment for the formation of V_2O_5 @PVP, (b) Particle size distribution in V_2O_5 @PVP suspension with different weight ratios, (c, d) TEM images of the V_2O_5 NPs before funciationlisation with PVP and (e, f) V_2O_5 NPs after functionalisation with PVP (V_2O_5 @PVP), $R(PVP/V_2O_5)=0.64$ (wt).

Thus, it can be assumed that a core-shell structure: $V_2O_5@PVP$, is formed in CHCl₃ suspension, PVP being coated on V_2O_5 NPs surface. To further investigate this microstructure, transmission electron microscopy (TEM) images were collected from V_2O_5 suspensions and $V_2O_5@PVP$ suspensions (R=0.64). Before PVP functionalization, **Figure 2c** reveal aggregates of V_2O_5 NPs. The aggregate size is in good agreement with the particle size distribution from granulometry, and even if **Figure 2d** shows the size of V_2O_5 particle is around 160 nm with a clear image of each single particle, necklace percolations are still visible.

In comparison, in **Figure 2e** and **2f** corresponding to the TEM images of the $V_2O_5@PVP$ (R=0.64) particles (*i.e.* after PVP functionalization), no clusters are observed. Furthermore, it has to be also noted that the particles display an unclear contour in **Figure 2e**, as surrounded by polymers. Moreover, this blurred contour cannot be improved through the adjustment of TEM instrument. Thus a polymer film is probably well coated on the V_2O_5 NPs surfaces. Further magnification show that V_2O_5 NPs are encapsulated by a layer structure, with a thickness of around 2.5 nm (**Figure 2f**). In combination with

the size decrease in suspensions (**Figure 2b**) and this latter observation, it can be concluded that the V_2O_5 particles are probably individually coated by PVP polymer layer. A core-shell structure is formed after PVP functionalization. Thus PVP serves as a surface stabilizer for V_2O_5 NPs, which could prevent the aggregation of NPs *via* the repulsive forces that arise from its hydrophobic carbon chains that extend into solvents and interact with each others (steric hindrance effect), it also helps to form a stable V_2O_5 suspension which can be easily spin-coated.

3.2.Preparation of V2O5@PVP and VO2 films

The PVP pretreatment favored the dispersion of V_2O_5 NPs in CHCl₃ solvent. The spin-coating technique is used to prepare V_2O_5 @PVP films. Two V_2O_5 suspensions (R=0 and 0.64) were spin-coated on quartz substrates. The SEM data of the V_2O_5 and V_2O_5 @PVP films are shown in **Figure 3**. Without the help of the PVP functionalization, the V_2O_5 film displays visiblemicroscale size aggregates (**Figure 3a**). With the use of PVP addition into V_2O_5 suspension, SEM images show the as-prepared films exhibit a relative smooth morphology (**Figure 3b**), well separated NPs are also visible and distributed on film surface. The obtained V_2O_5 @PVP films exhibit a bright-yellow color with a good uniformity. Hence, the V_2O_5 NPs are separated successfully with the help of PVP polymer. It indicates that the V_2O_5 @PVP film is beneficial to VO_2 film preparation in the next step.



Chpt. V-Figure 3. (a) SEM micrograph of V_2O_5 film and (b) V_2O_5 @PVP film, $R(PVP/V_2O_5) = 0.64$. The V_2O_5 concentration for the two suspensions is fixed to 40 g/L (C40).

In this work, PVP not only acts as a surface stabilizer in the V_2O_5 suspension, but it is also used as reducing agent leading to the transformation from the V_2O_5 film to VO_2 film during the film thermal annealing. In the previous part (Chapter 3), [11] we demonstrated that carbon could be used to reduce V_2O_5 to VO_2 when the mixtures were annealed in dynamic vacuum environment. As the PVP shell is perfectly coated on V_2O_5 NPs surface, thus the V_2O_5 would be perfectly and totally reduced to VO_2 , and then a uniform VO_2 film could be prepared.

Based on our calculations, the mole ratio of V_2O_5 and C [PVP] is 1: 7 when the R (PVP/ V_2O_5) is 0.64 (*wt*), while in the V_2O_5 powder reduction process, the mole ratio of V_2O_5 and Carbon is controlled as 1: 1. [9] So, it is believed that the content of PVP reducing agent (R=0.64) is largely enough to fully transform the V_2O_5 to VO_2 . The excess PVP polymer would be removed by the high annealing temperature treatment. The VO_2 film preparation is illustrated in **Figure 4a**.

The prepared V₂O₅@PVP films were annealed at a high temperature (700°C) to obtain highly crystalline VO₂ film. From our previous works on VO₂ powder synthesis (Chapt. 3), 700°C annealing temperature would guarantee the purity of VO₂ phase formation.



Chpt. V-Figure 4. (a) Schematic representation of the VO_2 film preparation synthesized from V_2O_5 @PVP film; (b). XRD patterns of the quartz substrate, V_2O_5 @PVP film on quartz and VO_2 film on quartz. (c) and (d) SEM images of VO_2 films on top view and cross-section view. (f) Corresponding EDS spectrum of the spot A and the spot B pointed out in the SEM image (e).

We fabricated the films on quartz glass, which is chosen as a substrate due to its ability of standing high annealing temperatures. The crystalline phases of the obtained films were determined by X-ray diffraction (XRD). The XRD patterns (**Figure 4b**) show that the quartz substrate is an amorphous type, no clear peaks are observed. When the quartz is annealed at 700°C, no obvious changes were detected, which means the high temperature (700°C) annealing has no effect on the quartz structure. After spin-coating the V₂O₅@PVP suspension (R=0.64), a bright yellow color film is formed on the substrate. The film is named as V₂O₅@PVP film, and the film shows a good uniformity. The yellow color indicates that the V₂O₅NPs are efficiently spin coated on the substrate, which is also confirmed by the weak V₂O₅ peaks detected in the XRD pattern.

Interestingly, after the high temperature annealing step, the film did not again show the intrinsic yellow-orange color of VO₂ (M), which is commonly reported in literature for VO₂-based composite films, but a light grey coloration. XRD patterns reveal two strong peaks located at 2Θ =27.8° and 57.5° that can be indexed as the (011) and (022) of the VO₂ (M) structure, without any noticeable minority phases, indicating the high purity of the as-prepared VO₂ film. We can conclude that V₂O₅ film are efficiently reduced to VO₂ film thanks to the use of PVP, acting as a carbon soruce associated to a

reductive effect. Besides, some reductive gases would also probably be released during the PVP degradation, which also assists the phase transformation from V_2O_5 to VO_2 . More details are needed to fully understand the PVP role in this system.

It should be pointed out that an important preferential orientation of VO₂ film, with the (011) zone axis perpendicularly aligned to the substrate surface, is observed. Indeed, only this crystallographic orientation is associated with XRD peaks of high intensity. In general, the degree of preferred crystallographic orientation in thin films is greater when the growth temperature is higher, due to the greater mobility of the growth species. When suing a well-chosen crystallized substrate, its influence of on the epitaxial growth of the VO₂ thin films has previously been reported. For example, Paik *et al* [13] reported nanocrystalline VO₂ films with a preferred orientation (011), synthesized through rapid thermal annealing transformation of the VO_x nanocrystals. Such preferential orientations are also observed in films deposited on fused quartz and c-cut sapphire. Reported by Sahana *et al*, [14] a strong (200) orientation for VO₂ film is observed for film deposition processes as metal-organic CVD; it can lead to a large drop resistance at M/R transition, associated with minimal temperature hysteresis.

Nevertheless, the observed crystallographic orientation appears surprising from the use of a noncrystalline substrate. Also, the observation of such a drastic orientation is also surprising in regard of the isotropic morphology of the vanadium oxide grains which exhibits isotropic shapes (**Figure 4c**).

3.3.Film morphology

The morphology of the prepared VO₂ films is of paramount importance to obtain the desired optical properties. As expected, the obtained VO₂ film displays zero-dimensional monolayer morphology with isolated islands structure distributed on substrate (**Figure 4c**). Specifically, the particles are a combination of elliptic-like shape and spherical shape. VO₂ crystals are formed as individual particles rather than as continuous films. Several experimental results and calculation indicate that discontinuous film, such as nanocomposite foils, nanoporous films, have superior properties, that can combine high luminous transmittance and high solar transmittance modulation, *i.e.* better properties than VO₂-thin and continuous solid films (such as single layer or multiple layers by RF). [15] For example, Wang *et al* [16] reported the use of surface engineering methods, including acid etching and self-patterning to enhance the thermochromic performances of VO₂ film in order to achieve film morphology as the one achieved in our work. It is found that the self-patterning-induced nanograin-array patterned VO₂ thin film exhibited much larger T_{lum} than dense-packed counterpart, which should be mainly ascribed to the antireflection effect. Introducing air as a secondary component into VO₂ (M) films is feasible alternative approach to achieve favorable T_{lum} and Δ T_{sol} simultaneously. [17] As reported recently, a nanoporous VO₂ film with reduced optical constants showed enhanced luminous transmittance. [18]

The cross-section SEM image of the VO₂ film (Figure 4d) confirms a thickness of around 1.5 um.

In the EDS spectra, only Si and O signals are detected at spot A, corresponding to the quartz substrate, while characteristic peaks of O, V, and Si are detected at spot B (**Figure 4e-4f**). So the EDS analyses confirm that the island-shape particles correspond to the VO_2 NPs.

The VO₂ surface coverage on the substrate determines the film thermochromic performances. Higher coverage (higher VO₂ content) will improve optical transmittance modulation ability (specifically in the NIR region), whereas it would get a negative effect besides its visible transparency. From the low surface coverage herein obtained, some further optimizations will have to be made to improve the substrate coverage by the functional VO₂ material.

According to our design (**Figure 4a**), the V_2O_5 @PVP suspension concentrations plays an important role on the concentration of V_2O_5 NPs distributed in V_2O_5 @PVP films, and further determined the VO₂ surface coverage that would be obtained after the reduction process. Thus, a series of V_2O_5 @PVP suspensions, in which the V_2O_5 concentrations were varied from 40 g/L to 20, 80 and 160 g/L, was

prepared. The PVP/V₂O₅ weight ratio was fixed as 0.64 for all samples, and the same spin-coating conditions were applied (1000 rpm for 30 s) to prepare V₂O₅@PVP films. The as-prepared V₂O₅@PVP films are transparent with a bright yellow color (**Figure 5**). Obviously, C160 sample is darkest in color because of its higher V₂O₅ content leading to the worst transparency whereas the one with the highest visible transparency is the C20 sample.

The theoretical V₂O₅@PVP film thickness, y_h , is linked to the kinematic viscosity, v, of the solution and the rotation rate, w, of the spin coater apparatus. [19]

$$y_h = 3.6(v/w)^{0.5}$$

Even the rotation rate is fixed to 1000 rpm, the increased of the $V_2O_5@PVP$ concentration could increase a bit the suspension's viscosity, and so the obtained film thickness, accordingly. The thicknesses are measured from profilometric measurements (thanks to a diamond sensor apparatus). The $V_2O_5@PVP$ film thickness increases from 1.0 um (C20) to 1.6 um (C40), 2.1 um (C80) and 4.6 um (C160). Here, it can be noticed that the thickness of the films increases in a softer way than the $V_2O_5@PVP$ concentration. At this step, it is presumed that the VO₂ surface density increases versus the $V_2O_5@PVP$ concentration.



Chpt. V-Figure 5. Photographs of V_2O_5 @PVP films, prepared through spin-coating with different V_2O_5 concentrations (20, 40, 80 and 160 g/L) in CHCl₃ suspension, named as C20, C40, C80 and C160, respectively. The corresponding VO_2 films after 700°C annealing in vacuum, are named as C20H, C40H, C80H and C160H, respectively.

After being annealed at 700°C, all V₂O₅@PVP films color changed to transparent dark gray or close to black, which indicates that V₂O₅ is reduced to VO₂ successfully. The films get acceptable visible transmittance with excellent uniformity.

To increase the surface coverage on substrate of the functional materials VO₂, and so to produce denser VO₂ films, two other strategies were applied other than increasing the concentration of V₂O₅@PVP suspension: namely, (i) increasing the number of V₂O₅@PVP layers before a single annealing (**Figure 6a**) or (ii) increasing the number of VO₂ film layers by repeating the spin-coating/annealing processes (*i.e.* performing intermediate annealing treatment between each new coating step) (**Figure 6b**). To be specific, for the first strategy, the V₂O₅@PVP film layers are set as 2 layers and 4 layers through spin-coating the suspension (C40), *i.e.* 2 or 4 successive coating are made

before annealing, and then after 700°C in the DVS, the obtained samples are named as C40-L2 and C40-L4. For the second strategy, between the successive spin-coating depositions from $V_2O_5@PVP$ suspension (C80), an annealing treatment is performed at 700°C; the obtained samples are named as C80-AT2 or C80-AT3 depending on the number of successive VO₂ layers (2 or 3 layers, respectively).



Chpt. V-Figure 6. Scheme of the two methods used to increase the surface coverage; (a) increasing the number of V_2O_5 @PVP layers before a single annealing; (b) repeating the spin-coating/annealing process several times.

It can be immediately noticed that the C80-AT2 and C80-AT3 films show a very dark gray/blue color because of its higher VO₂ content, and the visible transparency is degraded (*i.e.* darker black films) repeating the number of loops, as illustrated in **Figure 7**.



Chpt. V-Figure 7. Photographs of VO_2 films fabricated by repeating the spin-coating/annealing times (C80-AT2 and C80-AT3), the concentration of V_2O_5 @PVP suspension is 80 g/L.

3.4. The morphology and surface coverage rate of VO₂-based film

The top-view SEM micrographs reported in **Figure 8** confirms that, as expected, all the obtained VO_2 films still exhibit a zero-dimensional island-like structure. Two parameters are analyzed carefully, the VO_2 particle size (d) and the surface coverage (SC).

Chapter V: VO2-based films preparation



Chpt. V-Figure 8. SEM micrographs of the various as-prepared VO₂ films: C20H, C40H, C80H and C160H; L2 and L4; AT2 and AT3.

The surface coverages determined by image treatment of the SEM images (with Image J tool) are shown in **Figure 9**. The results basically fit our expectation. The surface coverage of VO₂ increases with the increase of the suspension concentration and the number of layers. Furthermore, to loop the full coating/annealing process with an intermediate heating between the cycles should lead to the most effective increase of the surface coverage. In rief, this last route to produce thicker and denser films is the most efficient, and the coverage can reach up to 65.8% for the C80-AT3 sample.

The surface coverage increases as the V₂O₅@PVP suspension concentration increases from 20 to 160 g/L. The surface coverage reaches 42.5% when the concentration is 80 g/L (C80). As the concentration increases to 160 g/L, the surface coverage only slightly increases, with a sacrifice of easy operation for spin-coating. Indeed, even if before annealing the spin-coating times increases to 4, it remains at 38.3%. As a comparison, through increasing the spin-coating/annealing cycles, the surface coverage is nearly twice for the C80-AT3 samples in comparison with the reference single layer made from the same suspension (C80). Consequently, the transparency of the VO₂ film is worsen for the C80-AT2 or C80-AT3 sample.



Chpt. V-Figure 9. Surface coverage of the VO₂ films.

The evolution of the VO₂ particle sizes is also investigated as presented in **Figure 10**. It can be reminded that the starting size of V_2O_5 NPs (precursor oxide) is around 200 nm. The particle size distributions of the VO₂ films, at least the ones obtained from a single deposition, are also centered on 200 nm. It can be explained considering that single V_2O_5 NPs are reduced by the PVP shell directly to form a new-born VO₂ particle, and the V_2O_5 size remains (VO₂ and V_2O_5 oxides being with quite similar densities). On the other hand, it is also believed that with the increase of the substrate coverage, partial

agglomeration is inevitable during the annealing process, leading to quite large size distribution width. As the V_2O_5 @PVP suspension concentration increases, it can be seen some large particles appear, especially for the C160 sample. For the C80-AT2 and in particular for C80-AT3 samples, the sintering effect is more obvious, the largest particle size distributions with micro-sized VO₂ particles are observed. On a macroscopic point of view, *i.e.* on the film homogeneity evaluation from simple human eyes investigation, the various particle distributions are without any effect. The particle size distribution should receive less consideration unless the formation of millimeter particles.



Chpt. V-Figure 10. Particle size distributions of the various as-prepared VO₂ films.

3.5.VO₂-based film phase transition

To evidence the phase transition, the as-prepared VO₂ film was characterized through *in situ* XRD at low temperature (25°C) and high temperature (90°C). Here cobalt K(α) radiation was used as X-ray source with the wavelength of 1.78901 nm. The evolution of the XRD patterns is shown in **Figure 11**. The inset of the figure reveals doublets that are better resolved. In the heating cycle from 25°C to 90°C, the orientation peak (011) at the angle of 32.5° shifts to a lower value, which could be ascribed to the phase transition R \rightarrow M or the thermal expansion. While for the peak at around 49.5°, no shift to a lower angle was observed, but the double peak of the M phase transforms into a single peak associated with the R phase (due to the increase of the crystal-unit symmetry). Most of the doublets appearing in the XRD pattern, can be attributed to K_{α 1} and K_{α 2} splitting. When the temperature cools back to 25°C, the VO₂ (M) phase is recovered. In short, the reversible VO₂ (M/R) phase transition can be clearly evidenced from XRD analyses versus temperature.


Chpt. V-Figure 11. X-ray diffraction patterns of the as-prepared VO_2 film at 25°C and 90°C in the heating cycle (25°C-a, 90°C-a), and at 25°C in the cooling cycling (25°C-r). Peak separation is greater at high diffraction angle values (see inset).

3.6.Thermal stability test

A zero-dimensional island structures VO₂ films were prepared at 700°C, with a strong preferred (011) orientation, in this part, its thermal stability is tested. As previous reported, [21] VO₂ can be oxidized into V₂O₅ easily in air, especially in the presence of moisture. For example, after 2 h annealing at 300°C in air, the VO₂ film was oxidized to V₂O₅. This thermal instability results in serious durability problems in practical applications. In our case, VO₂ (M) phase remains even after 24 h annealing at 300°C (**Figure 12**), indicating a great thermal stability improvement for the VO₂ film prepared using our method. This can be explained by the highly crystalline part of VO₂ growth on the substrate. Nevertheless, as the testing temperature increases to 400°C, V₂O₅ peaks are observed as illustrated in **Figure 12**. Even though, the experiment indicates a great improvement for the thermal stability, which could stand the 300°C test in air. Comparing with fabricating the VO₂-SiO₂ core-shell structure to protect VO₂ from being oxidized, [4] increasing the crystallinity of VO₂ is confirmed to be a more effectient and easy way to shape thermal-resistant VO₂ films.



Chpt. V-Figure 12. The X-ray diffraction patterns after thermal stability test of the as-prepared VO_2 film by annealing at 300°C in air for different time (0, 2 and 24 h), and 400°C for 24 h.

3.7. Optical property characterization

The transmittance in the range of 200-2500 nm was measured at 20 and 90°C (in situ transmittance measurements versus temperature). C80-AT1 (42.5%), C80-AT2 (61.8%), and C80-AT3 (65.8%) samples with different surface coverages were characterized under the same conditions. The results are presented in **Figure 13**.



Chpt. V-Figure 13. The recorded in-stiu transmittance in the range 200-2500 nm at 20 and 90°C for C80-AT1, C80-AT2 and C80-AT3 films.

A slight modulation of transmittance is observed in between low and high temperature, especially in near infrared region as expected. Nevertheless, the contrast in transmittance between the M and the R-phase (respectively at 20 and 90°C) remains quite poor: around 2% at 2500 nm for each film.

Besides, the transmittance at wavelength of 2500 nm was also recorded in the cooling and heating cycles in the range of 30-100°C. The temperature program was shown (red line) in **Figure 14** (for practical reasons, one starts the experiment with a cooling half cycle from 90°C and then, the heating half cycle is applied. The transmittance evolution vs temperature was then recorded and is shown in the same figure (blue line).

During first half cooling cycle, globally, there is a jump of about 2-3% around the cooling transition close to 45°C. During the half heating cycle, a sudden drop happens at around 85°C in the transmittance-time curve. It clearly illustrates a thermochromic phenomenon. In the high temperature (T>T_c), the VO₂ film exists as a rutile phase with a high transmittance in the infrared region, while in the low temperature (T<T_c), a phase transition occurs from rutile to monoclinic VO₂, then the film displays a low transmittance. Even if the transmittance contrast is quite low, the evolution of the heating and cooling half temperature to 45 and 85°C, respectively, *i.e.* with a hysteresis width of about 40°C, is in good agreement with our early results reported on VO₂ powder in the previous chapters.



Chpt. V-Figure 14. The in situ transmittance at 2500 nm recorded during cooling and heating of the VO_2 films (C80-AT1) in the range of 30-100°C.

4. Conclusion

A novel route to synthesize discontinuous VO₂ films is reported. V₂O₅ NPs are prepared with the help of soot, and further reduced to VO₂ by PVP polymer in the high temperature (700°C) annealing process. The obtained VO₂ film shows high crystallinity with preferred orientation (011). Moreover, the film morphology can be adjusted from zero-dimensional to 2D-patterned by changing the VO₂ surface coverage on substrate. Indeed, the surface coverage of the substrate (specific density of the VO₂ films) can be adjusted by tuning the deposition process parameters of the V₂O₅@PVP suspension as the number of coated layers before a single annealing treatment or by multiplying the number of full coating/annealing process cycles. Tuning such parameters offered an adequate path to tune the asprepared film morphology, and in particular, the VO₂ surface coverage can be improved.

The films well showa M to R phase transition with increasing the temperature, and the transition parameters have been successfully extracted from in situ transmittance investigations versus temperature. However, further morphological optimization should be performed since our films show very low

transmittance contrast in the near infrared region (about 2-3% transmittance contrast for the best prepared film).

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Chapter VI: M/R Phase Transition Study of VO₂

Geometric considerations of the monoclinic-rutile structural transition in VO₂. S. Guan, A. Rougier, M. R. Suchomel, N. Penin, K. Bodiang, M. Gaudon, *Dalton Trans.*, **2019**, 48, 9260-9265.



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1. Introduction

Two methods for VO_2 particles synthesis are developed and studied, namely through (i) VEG decomposition, followed by post-annealing and (ii) carbo-thermal reduction strategy. Besides, inspired by the reducing carbon reducing role, VO_2 -based film with a zero dimensional morphology was proposed. Simultaneously, the metal-insulator transition (MIT) is also investigated for a better understating of VO_2 (M/R) based on the well-established bond valence model through a simple geometrical approaChpt.

The origin of the driving force(s) behind the MIT of VO₂ has been the subject of controversy for decades. Structurally, the MIT transition at approximately 70 °C is accompanied by a change from a high-temperature tetragonal rutile structure (S.G. *P*42/*mnm*) to a low-temperature monoclinic (M) form (S.G. *P*21/*c*) characterized by a structural twist and V⁴⁺ cations shift along the rutile *c* axis to form V-V pairs (homopolar bonds) [1]. From a simplistic point of view considering the orthonormal referential constituted by the octahedral cage edges, the key aspect of the transition is an off-centring of vanadium ions along (111), with an antiferroelastic correlation. A crystal description of the transition was first reported by Goodenough *et al.* [2], associating the lattice distortion (pairing and tilting) in the VO₂ (M) phase with an increase of the antibonding 3*d* band above the Fermi level. Herein lies the controversial point; whether the phase transition originates from the crystal distortion and unit-cell doubling (Peierls mechanism), or from the opening of a correlation gap due to the presence of electron-electron correlations (Mott mechanism) [3].

Recent structural calculations (Peierls approach) based on density functional theory within the local density approximation tends to predict the monoclinic phase as the most stable [4-9]. In a complex structural approach, *i.e.* using the Buckingham potential to describe the short-range interaction (V-O and O-O bonds), a Morse potential for V-V interaction (at the origin of the octahedral chain distortion) and additional optimization techniques, Woodley [10] concludes that monoclinic and rutile free energies cross at nearly 300K, in favour of a Peierls transition. Cavalleri et al. [11] showed evidence of a structurally driven transition with the use of ultrafast pump-probe spectroscopy. Conversely, several authors argue for a Mott-driven transition [12-14] based on experimental parameters such as switching time using femto-laser sources [12,13] or by measuring the electromagnetic response of a VO₂ thin film by scattering scanning near-field infrared microscopy. [14] Current interpretations seem to propose a combination of both mechanisms simultaneously; meanwhile the appearance of new phases during the structural phase transition (well supported by nanoscale imaging techniques and/or optical/electronic spectroscopy) makes it increasingly critical to understand the true nature of this transition [15-19]. Despite the complex nature of previously reported theoretical structure calculations, a basic interpretation of the transition in terms of fundamental geometrical factors such as unit-cell volume and bond distances is often neglected in these studies. However, these parameters are linked to the thermal expansion and coulombic interactions of both VO₂ allotropic forms and are thus potential significant driving forces to consider near the boundary of the structural transition.

In this chapter, we describe here a new approach for evaluating the main driving forces involved in the MIT transition of VO_2 , within the limit of a simple geometrical approaChpt. This approach compares measured unit-cell parameters to basic calculations for the cell volume and electrostatic potential of the 1st and 2nd sphere anion/cation pairs in monoclinic and rutile structure types near the phase transition. Calculations are based on the well-established bond valence model, [20] and can be rapidly performed with a standard spreadsheet software package. The experimental temperature dependence of monoclinic and rutile phase unit-cell parameters near the transition temperature for this study were obtained from *in-situ* synchrotron powder diffraction measurements of VO_2 samples, the synthesis of which was previously reported. [21]

2. Calculation

Using Brown's bond valence model [20] to evaluate all atom positions in a structural unit cell with a basic set of geometric equations is a powerful tool which has been previously used with success to predict crystal structure anisotropy (as in Würtzite compounds [22]) or even multiple phase transitions (as in the BaTiO₃ perovskite [23]). In this type of an approach, atomic positions are typically relaxed to minimize the electrostatic potential between first neighbouring cations and anions pairs. The constraints of the Brown equations result in convergence towards a single solution, *i.e.* the valence of the vanadium ion deduced from the bond valence model must be kept equal to 4. For the binary ionic compound as VO₂, the Brown equation for each V-O pair relating bond lengths and bond valences (BV) is thus BV= exp [$(r_0 - d_{ij})/0.37$].

- $r_0 = 1.78$ Å (V-O bond empirical parameter given by Brown tables);
- $d_{ij} =$ V-O bond length in Å.

In the VO_2 crystal structure, as the vanadium cations occupies an octahedral coordination site, six bonds are summed up for the valence of the vanadium cations.

The initial step of this geometrical approach was to consider positional shifts of vanadium ions in the octahedral cages of the rutile (tetragonal) vs. monoclinic structures and to examine if V^{4+} decentring is associated with an increase of the surrounding 1st sphere coulombic interaction E (1st sphere) (*i. e.*, a stabilization effect) and thus connected to the transition between these polymorphic forms. The parameters used to describe the rutile structure are shown in **Figure 1***a* and 1*c*, the unit-cell parameters; *x*, describing the oxygen position at (x, x, 0); *l'*, the edge length of the octahedral cages along the octahedral chains; *l''*, the shared edge length of the octahedral chains; and h, the half-height of the octahedral cage (note that *h* is identical to the distance of apical V-O bonds, while the other 4 equivalent equatorial V-O bonds are noted as *r* in **Figure 1**). The equations linking these parameters are:

- $h = \sqrt{2.a.x}$; $l' = c; l'' = 2.\sqrt{2.(0.5 x)};$
- $\mathbf{r} = [(\frac{1}{2}.l')^2 + (\frac{1}{2}.l'')^2]^{\frac{1}{2}};$

•
$$V_{cell} = a^2.c$$

Considering an ionic approach, the first sphere potential is defined as E $(1^{st} \text{ sphere}) = K.(2/h + 4/r)$, where K is a constant.

A simplified geometric description of the pseudo-monoclinic VO₂ structure can be obtained by considering only V⁴⁺ decentring along [111] direction as oxygen site displacements in the distorted octahedral cages are negligible. This leads to the new set of equations: δ is the amplitude of the decentring in (111) direction; α is the angle of the [111] axis with respect to the equatorial plane of the octahedral cage;

• $h' = (h^2 + \delta^2 - 2.h.\delta''.\sin\alpha)^{\frac{1}{2}};$

•
$$h'' = (h^2 + \delta^2 + 2.h.\delta''.\sin\alpha)^{\frac{1}{2}};$$

•
$$r' = [(\frac{1}{2}l')^2 + (\frac{1}{2}l'')^2 + \delta^2 - \delta . l'.\cos\alpha]^{\frac{1}{2}};$$

- $r'' = [(\frac{1}{2}l')^2 + (\frac{1}{2}l'')^2 + \delta^2 + \delta . l'.\cos\alpha]^{\frac{1}{2}};$
- $l' = c; l'' = 2\sqrt{2(0.5 x)};$
- $V_{cell} = a^2. c;$



Chpt. VI-Figure 1: Rutile VO_2 structure with l' and l'' are the two edges lengths of the octahedral equatorial rectangle, h the half height of the octahedron, and oxygen in (x, x, 0) Wyckoff position. Vanadium octahedral sites and their associated parameters in rutile, monoclinic or "simulated" monoclinic structure: i.e. considering a rutile octahedral cage with a cation δ decentring in (111) direction. (r' and r'' represent two V-O bonds distance in the plane after V^{4+} decentring).

The first sphere potential becomes E (1st sphere) = K.(1/h' + 1/h'' + 2/r' + 2/r''). c, a and x as have been considered as variables in order to maximize (considering positive terms for crystal energies) the E (1st sphere) versus δ . From these calculation, E (1st sphere) and the optimised unit cell volume can be plotted versus cation decentering (**Figure 2**).

As shown in **Figure 2a**, the decrease of E (1st sphere) with δ shows that our ionic approach fails to explain the rutile to monoclinic phase transformation. With a higher absolute energy, the tetragonal environment appears most stable in these geometrical calculations, with any monoclinic-type decentring (δ) appears to reduce the overall energy. However, based on the same calculations, it is noted that the unit-cell volume is predicted to slightly increase with vanadium cation decentring (**Figure 2b**), suggesting that the transition may be eased by an expansion of the cell volume. This later result is somewhat unexpected, as crystal energies are normally to increase (stability increase) with crystal density (*i.e.* with shortening bond lengths).



Chpt. VI-Figure 2: Effect of the consideration of δ decentring amplitude in the simulated monoclinic structure on the electrostatic potential (1st sphere energy) (a) and the unit-cell volume (b).

In a second step, the origin of the tetragonal distortion is evaluated, *i.e.* the E (1st sphere) and unitcell volume of tetragonal phase are calculated versus the c/a ratio. The goal of this analysis is to probe why the VO_2 rutile phase does not exhibit cubic symmetry; a discussion that could in principle be extended to all rutile compounds typically exhibiting a tetragonal distortion. The isotropic point, defined by a c/a ratio equal to 0.586 (*i.e.* $\sqrt{2}$.($\sqrt{2}$ -1)), corresponds to a "cubic-rutile form". For the calculation, the c/a value is fixed while a and x are variables adjusted in order to minimize the E (1^{st} sphere). Regardless of the tetragonal distortion a stable minimum for the E (1st sphere) can be determined (Figure **3a**). Despite the tetragonal distortion of the unit-cell and consequently of the octahedral cages also, the six V-O bond lengths remain constant. Indeed, the distortion of the equatorial plane of the octahedral site can be followed via the evolution of the l'and l' parameters (Figure 3c), but this distortion occurs such as the r bond lengths remain equal to the h length, whatever the c/a ratio (fixed refined values for r = h = 1.930 Å). Thus, the tetragonal distortion from the cubic form of the rutile structure is apparently not due to a minimization of the E (1st sphere). In addition, it is noted that the plot of unit-cell volume versus c/a adopts a bell-shape curve with a maximum at approximately $c/a \approx 0.626$ (Figure 3b), in good agreement with experimental measured values for the rutile form of VO2. Moreover, by fixing ab initio the value of h to 1.930 Å, since no deviation of this parameter was found with varying c/a ratio, it is possible to treat all a, c (and so c/a) and x parameters as variables, and to perform a calculation in order to maximize the unit-cell volume. This optimization leads to a crystal defined by a c/a ratio of 0.626, with a = 5.754 Å, c = 2.870 Å, with characteristic octahedral lengths of l' = 2.87 Å, l'' = 2.57 Å and r = h = 1.93 Å.

Interestingly, these calculated lengths are very similar to the experimental parameters given in the literature for VO₂ (R) phase. [24-27] The stability of the rutile form is therefore strongly linked to a maximization of the cell volume while simultaneously maintaining the E (1st sphere). Indeed, the cell volume maximization is directly correlated to the minimization of the E (2nd sphere), *i.e.* the decrease of

the anion-anion or cation-cation coulombic repulsions. Moreover, these conclusions are supported by an additional calculation performed to minimize the E (2^{nd} sphere) using the set of shortest V-V and O-O bond lengths. In a manner analogous to that detailed above, the bond distances can be described as follows:

- 2 V-V bonds and 2 O-O bonds = 2.1';
- 8 V-V bonds = $[(h + \frac{1}{2}.1'')^2 + (\frac{1}{2}.1')^2]^{1/2};$
- 8 O-O bonds = $(h^2 + r^2)^{1/2} + 2.1$ ';
- 2 last O-O bonds = $[(2.x.a)^2 + (a 2.x.a)^2]^{1/2}$;

Then the E (2^{nd} sphere) minimization calculations are performed with a, c and x as variables, and h fixed to 1.93 Å (as above), the overall crystal parameters results are nearly identical to that found with the described cell volume maximization calculations.



Chpt. VI-Figure 3: Effect of the c/a tetragonal distortion on the electrostatic potential (1^{st} sphere energy) (a); the unit-cell volume (b) and the l' and l'' octahedral edges lengths (c).

Hence our basic geometric calculation clearly shows that by considering only a Peierls origin for the VO₂ phase transition, with a pure ionic bond approach, the tetragonal distortion of the rutile phase is well explained by an energy minimization. The tetragonal distortion allows the decrease of the crystal energy which can be approximated as $E(crystal) = E(1^{st} \text{ sphere}) - E(2^{nd} \text{ sphere})$. The originality of the system is that the tetragonal distortion does not impact of E(1st sphere); thus, the optimization of the electrostatic potential is governed by $E(2^{nd} \text{ sphere})$ associated with cell volume maximization. This

result on the driving forces of the tetragonal distortion origin has to be correlated to our first calculation showing that the monoclinic to rutile phase transition is not associated with an increase of the cationanion interaction potential (1st sphere maximization) but may be promoted by an increase in the unit cell volume (2nd sphere minimization).

3. Experimental results

Synthesis details of the VO₂ (M) powder, which showed minor trace of a V₃O₇ impurity, has been described previously [1]. The phase transition as a function of temperature was followed by *in-situ* powder diffraction. High-resolution synchrotron X-ray powder diffraction (HR-SPD) data of VO₂ have been recorded on both heating and cooling with 20 °C temperature steps between 280 and 380 °C using beamline 11-BM at the Advanced Photon Source (APS), Argonne National Laboratory. For each temperature scan, data were collected over a 0.5-35° 20 range with a 0.001° step size using a wavelength of $\lambda = 0.41417$ Å; the powder sample being sealed in a 0.8 mm diameter Kapton capillary and was spun at 60 Hz during data collection (**Figure 4a**). Determination of VO₂ unit cell parameters were performed by profile matching and cell fractions from Rietveld refinements using the TOPAS software package, as illustrated on the low (monoclinic) and the high (tetragonal) temperature forms recorded at 5°C (**Figure 4b**) and 105°C (**Figure 4c**), respectively.



Chpt. VI-Figure 4: Synchrotron powder diffraction pattern over the $5^{\circ}C \rightarrow 105^{\circ}C$ temperature range showing the reversible transition between monoclinic phase ($P2_1/c$) and rutile ($P4_2/mnm$) structures on heating and cooling (a). Profile fits of VO_2 HR-SPD data collected at $5^{\circ}C$ (b) and 105 °C (c), showing the observed (red points) and calculated (black line) intensities as a function of 2θ angle. The difference profile and unit cell hkl reflections are shown below as a blue line and green ticks, respectively. The exclude 2θ region (approximately 8- 9°) is indicated by light grey data points.

The evolution of the rutile and monoclinic phase fractions over the studied temperature range are summarized in **Figure 5a**. The unit-cell parameters of both rutile and monoclinic forms were refined, and normalized unit cell volumes *vs*. temperature are plotted to support the discussion (**Figure 5b**). The rutile to monoclinic phase transition is described by a hysteresis loop, centred on 65-70 °C with a width of about 20°C: it can be seen that at 65°C the percentage of rutile phase / monoclinic phase ratio in the heating mode is about the same than the one calculated at 45°C in the cooling mode. in good agreement with past studies [2, 12-19]. The evolution of both cell parameters versus temperature shows that the volumetric coefficients of thermal expansion for the two phases are significantly different. Using a simple linear slope fit of the low temperature (monoclinic) and high temperature (tetragonal) unit cell volumes, we can estimate the volumetric thermal expansion coefficients ($\alpha_{Vol.}$) using $\alpha_{Vol.} = (\Delta V/\Delta T)/V$,

where $\Delta V/\Delta T$ is simply the linear fit slope. For the low temperature (monoclinic) phase, $\alpha_{Vol.} = 20.3 \times 10^{-6}$ K⁻¹ and for high temperature (tetragonal) phase, $\alpha_{Vol.} = 37.2 \times 10^{-6}$ K⁻¹. Note that for ideal anisotropic materials, the $\alpha_{vol.}$ value is 3 times larger than the linear thermal expansion coefficient; these estimated volumetric thermal expansion coefficients are in good agreement with the range of VO₂ literature values [28].

The rutile form exhibits a higher α_{Vol} than the monoclinic one. On the transition temperature, the volume of the two phases is similar, *i.e.* the intersection point of the unit-cell evolution is located at the transition temperature. Consequently, due to the hysteresis phenomenon linked to the 1st order character of the phase transition, and due to the mismatch between the monoclinic thermal expansion coefficient (TEC) and the rutile TEC, both in cooling and heating modes, the transition is associated with a slight volume expansion. The volume expansion is experimentally with an amplitude of about 0.01 Å³ in cooling mode and about 0.02 Å³ in the heating mode, *i.e.* roughly 0.025% volume (or 0.3% of bond length variation). It is apparently a minor change, but it well governs the phase transition scheme is very different to most other 1st order transitions in crystalline solids for which the volume difference between the two crystalline forms around the transition is the main aspect (as in the textbook austenite-martensitic example [29-30] or for the AMO₄ phase transitions [31-33]). From these experiments, it appears that the driving force of the transition comes from this volume difference: a greater unit-cell volume leads to higher crystal structure stability.



Chpt. VI-Figure 2: (a) Phase fraction (weight %) of the monoclinic phase as a function of temperature on heating and cooling, (b) VO_2 unit cell volume (per formula unit Z) as a function of temperature on heating and cooling.

4. Conclusion

This work considers the advantage of simplistic geometric examination of the much studied VO_2 transition, in a marked contrast to the very complex literature debates on competing Peierls and Mott-type origins. From a solid-state chemistry point of view, there is often considerable benefit to interpret such transitions in terms of a structural origin and an optimization of electrostatic potentials. Through the positively correlated calculations and experimental data examined in this work, it is shown that the VO_2 rutile to monoclinic phase transition is likely the consequence of very short atomic shifts, leading to non-significant (at least non-dominant) changes on the charge interactions of the cations and anions in first neighbouring, however allowing a decrease of the 2nd sphere coulombic interactions.

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General conclusion and prospective

Vanadium dioxide: VO₂, is known for its thermochromic properties linked to a Metal-Insulator transition (MIT), associated with a structural transformation from low-temperature Monoclinic (M) to high-temperature Rutile (R) phase at 68°C. Due to the existence of vanadium with several oxidation states, V^{3+} , V^{4+} , V^{5+} , as well as the existence of several oxides with variuous stoichimometries, the synthesis of highly crystallized pure VO₂ (M) is still a challenge.

In this work, we proposed and developed two methods for the synthesis of highly crystallized VO₂. The first method can be shorted as VEG \rightarrow VO_{2(amorphous)} \rightarrow VO_{2(crystalline)}, VO₂ (M) powders with tuned crystallinity were prepared through a two-step thermal treatment: a first-thermolysis step under air followed by a post-annealing under oxygen-free atmosphere. The vanadyl ethylene glycolate (VEG) was first decomposed in air and a poor crystal VO₂ powder was prepared with a strict time of 3 min at 300°C. To enhance its crystallinity, the as-obtained VO_{2(amorphous)} was further annealed at higher temperatures in oxygen-free environment for a full-crystallization. The crystallinity was calculated carefully with the help of rietveld refinements of the X-ray diffraction patterns. It was found that the crystallinity increases from 44% for the VO_{2(amorphous)} precursor to 79% then finally 100% after 500 and 700°C post-annealing treatments. Meanwhile, the phase change enthalpy (Δ H) increased from 3.8 to 40.8 and 43.7 J/g.

As earlier mentioned, the VEG decomposition time (3 min) had to be controlled very accurately. The use of shorter or longer times than ~3 min of heating at 300°C resulted in the formation V (III) or V (V) compounds after the post-annealing treatment. Namely, carbon acted as a reducing agent on the formation of VO₂(M). Inspired by this finding, carbo-thermal reduction method was developed, shorted as VEG \rightarrow V₂O₅ \rightarrow VO₂. Herein soot (carbon) was chosen for a direct reduction of V₂O₅. The comparison of dynamic and sealed vacuum systems associated with an accurate control of the carbon contents allowed further understanding of the reductive mechanism. In the sealed glass system, two reducing steps were involved: carbon reduced V₂O₅ with CO gas generating simultaneously, the CO gas continued in a second step to reduce the new born VO₂, leading to the formation of V₂O₃ at 1000°C. As a comparison, the use of a homemade dynamic vacuum system, for which CO gas was directly removed in order to avoid the second step of the reductive process, guaranteed the single formation of VO_2 at high annealing temperatures (700 and 1000°C). The mechanism was confirmed by the measurement of the carbon content before and after annealing. The crystallite size distributions of VO₂ (M) were centered on 1.8 and 5.3 µm, respectively. Indeed, for anannealing temperature of 700°C, the average size of the synthesized VO₂ particles was further decreased to 935 nm or even 415 nm when the annealing time was shortened to 2 or 1 h.

In addition, Al^{3+} , Ti^{4+} and Nb^{5+} metal ions were introduced to VO₂ successfully with the carbo-thermal reduction method. The Ti-doped VO₂ compound exhibited only peaks associated with the M1 monoclinic phase whereas M2 phase was detected when the vanadium was substituted with Al^{3+} dopant. The addition of Nb⁵⁺ leds to the most efficient effect on decreasing the transition temperature (T_c). Various characterization methods including, DSC, resistivity and VSM showed that the T_c decreased to around 25°C after Nb doping (≈ 6 at%). Using magnetic measurement for pure and Nb-doped VO₂, the relationship between the crystal structure and the electronic property was carefully discussed. Moreover, doping effects of the Nb incorporation on the Nb-doped VO₂ from all aspects, including the morphology, the crystal distortion, the thermal stability, the heat capacity, the resistivity and the magnetic susceptibility were fully investigated.

By taking advantage of the reductive strategy, a zero-dimensional island structure VO₂-based film was fabricated successfully. In the synthesis, PVP was used as a surface stabilizer and reducing agent. V₂O₅ NPs were prepared through VEG decomposition and a ball-milling process. Then, using spincoating methods for V₂O₅@PVP suspension on a quartz substrate, followed with an annealing treatment in the dynamic vacuum system, VO₂ films with island structure and of gray color were fabricated, presenting an excellent thermal stability (300°C for 24 h in air). The film's phase transition (M/R) was observed through *in situ* XRD and spectrophotometer measurement at 25°C and 90°C. To increase the coverage of functional materials VO₂ on substrate, three elaboration parameters were changed: (i) the suspension concentration; (ii) the V₂O₅@PVP film layer thickness; and (iii) the number of VO₂ layers through repeating the spin-coating/annealing loop. Finally, a surface coverage of 61.8% was reached.

Till now, the driving force of the phase transition of VO_2 type oxides remains the subject of debates: some authors propose to explain this transition a distortional induced structural origin (Peierls model), while other state that the transition proceeds by a complex electron-electron correlation (Mott model). In the limits of a simple geometrical model, we described with a new approach, the main driving forces involved in the MIT transition of VO_2 . Our approach, based on the bond valence model, a wellestablished model, has allowed us to suggest that the phase transition is certainly consistent with a maximization of the lattice energy due to a maximization of the unit-cell volume of the VO_2 oxides (M and R), because this expansion is then associated with a decrease in anion-anion and cation-cation electrostatic repulsions: in other words, the most stable allotropic form is the one presenting for a given temperature the largest unit-cell volume. This seems to be validated by the experimental characterization of the unit-cell volume evolution versus the temperature, recorded by *in situ* X-ray diffraction.

Among the possible applications, thermochromic windows represent an important technology for increasing indoor comfort and reducing electrical consumption in the automotive and building sectors. A VO_2 film can respond to the environment by regulating the infrared transmittance. In the future, the development of flexible VO₂ foils by dispersing VO₂ nanoparticles into a matrix and coating of this VO₂-incorporated matrix onto a polymer would be a step forward in the realization of adaptive curtains for windows. As we have demonstrated the synthesis of highly crystallized VO₂ particles, VO₂-based composite film could be fabricated in the near future by exploring new hosting materials and substrates. In our study, the anti-oxidation ability was achieved through improving the crystallinity of VO₂, nevertheless oxidation to V2O5 was still observed after annealing at 400°C. This instability can result in durability problems in practical applications. Thus in the furture, other solutions should be developed for a further improvement of the thermal stability. Furthermore, in addition of thermal stability concern, there are also some other challenges that need to be addressed, such as the color issue of VO₂-based films. Indeed, the as-prepared VO_2 films fabricated via the reductive strategy showed an advantageous gray color, instead of the typical brownish-yellow color. As for the film morphology, the fabrication from $V_2O_5@PVP$ suspension needs to be further optimized to lead to a more uniform distribution. Other polymers or solvents for the suspension could be tried, including a modulation of the size of V₂O₅ NPs for suspension preparation. If we can find way to control the "island" size on VO2 based zerodimensional film, as well as the substrate surface coverage, to increase the film selectivity, *i.e.* maximizing the infrared absorption but keeping a high visible transparency. All these efforts would be benefit to the VO₂ film's thermochormic ability, and promote its large-scale application.

For the doping part, we have successfully proven that the carbo-thermal reduction method is an excicient route to dope the matrix with some elements, such as $(Nb^{5+}, Ti^{4+} \text{ and } Al^{3+})$ cations. Although we failed in doping W⁶⁺ into VO₂ lattice using this method, the exploration of W-doping is still attractive as it decreases the transition temperature close to room temoerature. The utilization of new precursors as W source would be the first trial. For future work, more doping elements could be explored and investigated in a similar way, we believe that it would be helpful for the understanding of phase transition of VO₂ (M/R).

Annex

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1. X-ray diffraction (XRD) analyses

X-ray diffraction (XRD) is a powerful characterization technique used in the analysis of crystalline solids that exhibit long range order. Indeed, the most common and preliminary analysis used in material/physics/chemistry. It is utilized for checking phase purity, and, in case of the occurance of several phases, a quantitative analysis of the phases (phase ratios) can be done. When impacted by a radiation (X-rays with wavelength about Å), a 3-dimensional array of atoms, molecules or ions, cause the light to be diffracted, as described by W. H. Bragg and W. L. Bragg in 1913. This behavior is summarized by the expression, $n\lambda = 2d\sin\theta$ (Bragg's Law) where λ is wavelength of radiation was used.

In this work, powder XRD patterns were first collected "as routine mode", on a PANalitycal X'pert PRO MPD diffractometer in Bragg-Brentano θ - θ geometry equipped with a secondary monochromator and X'Celerator multi-strip detector. Each measurement was made within an angular range of $2\theta = 8$ -80°. The Cu-K α radiation was generated at 45 KV and 40 mA (λ = 1.5418 Å). The samples were dispersed on sample holders made of aluminum alloy and flattened with a piece of glass. In addition, high resolution data (for Le Bail and Rietveld refinements) were collected on a PANalitycal Bragg-Brentano θ -2 θ geometry diffractometer equipped with a primary Ge (111) monochromator over an angular range of 2θ = 5-120° with a step of 0.02°. (CuK α ₁ = 1.54056 Å)

1.1.Bragg's Law

The hypothesis is to imagine Bragg's diffraction as a reflection of X-rays on the surface of imaginary "mirrors" formed by atomic planes in the crystal lattice (shown as horizontal lines containing scattering centers, that is, atoms shown as blue circles in **Figure 1a**). Due to the repetitive nature of the crystal, these planes would be separated by a constant distance d. It is illustrated in **Figure. 1b**. The two X-ray beams of wavelength (λ), arrive in phase onto the respective imaginary planes, with an angle of incidence θ , and form a wave front. In order to obtain a cooperative effect, after reflection both X-ray beams should still be in phase, a situation that will only happen if the difference of path traveled by the wave fronts corresponds with an integer number of wavelengths. Namely, the sum of the wave fronts segments corresponds to an integer (n) times the λ , and therefore expression is shown as n λ = 2dsin θ .



Chpt. VII-Figure 1. The Bragg's Law: scattering and diffraction.

1.2.The Powder Diffraction File Database

The Powder Diffraction File (PDF) is the primary reference for powder diffraction data for more than half a century. The file is a collection of about 65 000 reduced powder patterns stored as sets of d-I data along with the appropriate crystallographic, physical and experimental information, the d-spacing (d) determined from the angle of diffraction, and the intensity (I) experimentally measured under the best possible conditions for a phase-pure material. These data provide a "fingerprint" of the compound

because the *d*-spacing is fixed by the geometry of the crystal and the intensities are dependent on the elements and their arrangement in the crystal structure. Thus, the *d*-*I* data may be used for identification of unknown materials by locating matching *d*-*I* data in the PDF with the *d*-*I*'s obtained from the unknown. Identification is the most common use for the PDF, but the presence of considerable supporting information on each compound allows further characterization of the compound under study.

The increased use of computers for analysis of diffraction data and the increasing size of the file require greater accuracy of the reference information. Both improved instrumentation and more sophisticated analyses have placed more stringent requirements on how data are collected, reviewed and presented, particularly in computer-readable form.

The goal of the PDF is to provide the user with as much information as possible to assist in the identification of the compound. The identification of compounds is made by comparing the experimental XRD patterns to standards compiled by the Joint Committee on Powder Diffraction and Standards (JCPDF). Each individual data set contains, as a minimum, a list of the *d-I* pairs, the chemical formula, the mineral name if appropriate, a unique identification number (PDF), and a reference to the original source of the data. In addition to this information, supplemental data may include: the crystal unit cell and symmetry, Miller indices, physical constants, experimental details, and other comments such as preparation techniques and the chemical analysis. Here are some PDF numbers for the materials related to our work:

Formula	PDF Numbers	System	Space group
VO ₂ (M)	00-044-0252	Monoclinic	$P2_1/c$ (14)
VO ₂ (M2)	00-033-1441	Monoclinic	C2/m (12)
$VO_2(B)$	01-081-2392	Monoclinic	C2/m (12)
V_2O_5	00-041-1426	Orthorhombic	Pmmn (59)
V_2O_3	00-034-0187	Rhombo. H. axes	R-3c (167)
V ₆ O ₁₃	00-043-1050	Monoclinic	C2/m (12)
LaB_6	00-034-0427	Cubic	Pm-3m (221)

1.3.FullProf Refinement

Rietveld refinement of the XRD pattern is one of the crystallographic techniques that helps derive information such as crystal structure (unit-cell parameters accurate quantification), and local defects as vacancies, or interstitial sites occupanices from doping ions, etc. FullProf is a program for Rietveld analysis (structure profile refinement) of X-ray powder diffraction data collected as a function of the scattering variable T (2-theta or TOF). The program can be also used as a Profile Matching tool, without the knowledge of the structure (i.e. the program can be used with peak intensities that are free to be adjusted for the best fit between calculated and experimental patterns: La Bail fitting step).

Rietveld refinement is based on least square fitting using algorithm with crystallographic constraints. It is thereby necessary to provide close model for the program to provide us meaningful results. As part of best practice always first perform profile/Le Bail fitting to obtain lattice parameters, confirmation of symmetry and X-ray profiles (which depend on crystallite morphology). These parameters will be kept fixed and, in a second step, atomic positions will be introduced to perform the Rietveld refinement. The specific steps are presented in **Figure 2**.



Chpt. VII-Figure 2. Flowchart to follow for the analysis.

The crystallographic information about the phase/phases, such as space group, a, b, c, α , β and γ , and atomic/Wyckoff positions are then deduced. It is also used for qualitative analysis for calculation of the various phases weight percentage. The weight fraction can be obtained after the refinement of each phase. To be more specific, Si, LaB₆ and Al₂O₃ phases are usually as weight reference.

In this thesis, LaB₆ was used to evaculate the crystallinity of the obtained VO₂ (M) compound.

2. ICP

ICP, abbreviation for Inductively Coupled Plasma, is one method of optical emission spectrometry. When plasma energy is given to an analysis sample from outside, the component elements (atoms) are excited. When the excited atoms return to low energy position, emission rays (spectrum rays) are released and the photon wavelength of the emission rays are measured. The element type is determined based on the wavelength of the emission rays, and the content of each element is determined based on the rays' intensity. [1-3]

To generate plasma, first, argon gas is supplied to torch coil, and high frequency electric current is applied to the work coil at the tip of the torch tube. Using the electromagnetic field created in the torch tube by the high frequency current, argon gas is ionized and plasma is generated. This plasma has high electron density and temperature (10000K) and this energy is used in the excitation-emission of the sample. Solution samples are introduced into the plasma in an atomized state through the narrow tube in the center of the torch tube.

The ICP technique was developed for optical emission spectrometry (OES) by Wendt and Fassel at Iowa State University in the United States, and by Greenfield et al. at Albright & Wilson, Ltd. in the United Kingdom in the mid1960s. ICP-OES is one of the most powerful and popular analytical tools for the determination of trace elements. The technique is based upon the spontaneous emission of photons from atoms and ions that have been excited in a radiofrequency (RF) discharge. Liquid and gas samples may be injected directly into the instrument, while solid samples require extraction or acid digestion so that the analytes will be present in a solution. The sample solution is converted to an aerosol and directed into the central channel of the plasma. A schematic diagram of a typical ICP-OES instrument with the detection system in radial mode is shown in **Figure 3**.



Chpt. VII-Figure 3. Diagram of a typical ICP-OES instrument with radial configuration of the detection system, highlighting the most important parts. [1]

The instrumentation associated with an ICP-OES system is relatively simple. A portion of the photons emitted by the ICP is collected with a lens or a concave mirror. This focusing optics forms an image of the ICP on the entrance aperture of a wavelength selection device such as a monochromator. The particular wavelength of light exiting the monochromator is converted to an electrical signal by a photodetector. The signal is amplified and processed by the detector electronics, then displayed and stored by a computer

The coversion of solid samples into representative solutions (so called "digestion") is the first step for the analytical procedure. By using microwave technology, it is possible to heat up the sample solution extremely fast and perform digestions at high pressures and temperatures, due to the applied pressure vessels even far above the boiling point of the used acids. The possibility to perform digestions at higher temperatures reduces the digestion time down to only a few minutes. This rate acceleration is based on the Arrhenius Law, which states as a rule of thumb that the digestion speed is doubled when increasing the reaction temperature by 10°C. Acid digestion is the most often used wet-chemical sample preparation techniques. By using concentrated acids or mixtures, matrices of inorganic samples can be totally destroyed or dissolved, and the whole sample can be brought into solution. Depending on samples, during thus thesis, we have tried severak acids as digestion media, such as Nitric acid (HNO₃, 65%), Hydrochloric acid (HCl, 30-37%), Hydrofluoric acid (HF, 40-48%), or Aqua regia, HCl+HNO₃ (volume ratio 3:1).

In this work, the doping element (W, Nb, Ti, Al and V) content was operated in a 720-ES Inductively Coupled Plasma-Optical Emission Spectrometers (ICP-OES, Varian Inc.).

3. CHNS

Elemental analysis is an important technique in petroleum chemistry. Using an automated analyzer, rapid and accurate weight percentage carbon, nitrogen, hydrogen, sulfur, and oxygen (CHNS/O) data can be obtained.

For CHNS determination, the analyzer operates with the dynamic flash combustion of the sample. Samples are weighed in tin containers and introduced into the combustion. After combustion, the resulted gases are conveyed by a helium flow to a layer filled with copper, then swept through a GC column that provides the separation of the combustion gases, and finally, detected by a Thermal Conductivity Detector (TCD). (Figure 4).



Chpt. VII-Figure 4. CHNS/O configuration.

In this work, carbon content of each sample was determined by CHNS elementary analyzer (Thermo Fisher Scientific).

4. Morphology

4.1.SEM

Scanning Electron Microscopy (SEM) is a powerful technique to examine the surface and morphology of the materials. High magnification images, with a good depth of field can be obtained. When used in conjunction with the closely-related technique of energy-dispersive X-ray microanalysis (EDX, EDS, EDAX), the composition of individual crystals can be determined.

A normal scanning electron microscope operates in high vacuum. The basic principle is that a beam of electrons is generated by a suitable source, typically a tungsten filament or a field emission gun. The electron beam is accelerated through a high voltage (*e.g.* 20 kV) and pass through a system of apertures and electromagnetic lenses to produce a thin beam of electrons., then the beam scans the surface of the specimen by means of scan coils. Electrons are emitted from the specimen by the action of the scanning beam and collected by a suitably positioned detector. The electron-matter interaction are shown in **Figure 5**.

There are different types of electron image. The two most common are the secondary electron image (SEI) and the backscattered electron image (BEI). The SEI is used mainly to image fracture surfaces and gives a high resolution image. The BEI is used typically to image a polished section; the brightness of the BEI is dependent on the atomic number of the specimen or, for compounds, the average atomic number.

The SEM instrument is made up of two main components, the electronic console and the electron column. The electronic console provides control knobs and switches that allow for instrument adjustments such as filament current, accelerating voltage, focus, magnification, brightness and contrast. The electron column is where the electron beam is generated under vacuum, focused to a small diameter, and scanned across the surface of a specimen by electromagnetic deflection coils. [4]

Annex



Chpt. VII-Figure. 5. Diagram illustrating the phenomena resulting from the interaction of highly energetic electrons with matter.

In this work, the morphology of the as-prepared particles was observed by SEM using a TESCAN Vega II SBH microscope and JEOL JSM-6700F,

4.2.TEM

Transmission electron microscopy (TEM) is used to reveal sub-micrometer, internal fine structure in solids. In TEM a beam of electrons is passed through an ultra-thin specimen interacting with the specimen as it passes through. When electrons are accelerated up to high energy levels (few hundreds keV) and focused on a material, they can scatter or backscatter elastically or inelastically, or produce many interactions, source of different signals such as X-rays, Auger electrons or light. Some of them are used in TEM. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified and focused onto an imaging device, such as a fluorescent screen, on a layer of photographic film, or to be detected by a sensor such as a CCD camera.

The two available types of TEM-CTEM and STEM-differ principally in the way they address the specimen (**Figure 6**). The conventional TEM (CTEM) is a wide-beam technique, in which a close-to-parallel electron beam floods the whole area of interest and the image, formed by an imaging (objective) lens after the thin specimen from perhaps 106 pixels, is collected in parallel. The scanning TEM (STEM) deploys a fine focused beam, formed by a probe forming lens before the thin specimen, to address each pixel in series as the probe is scanned across the specimen. [5]



Chpt. VII-Figure 6. The electron beam in CTEM and STEM instruments.

In this work, High Resolution Transmission Electron Microscopy (HRTEM, JEOL 2200FS, operating at 200 kV) is used.

5. TGA

Thermogravimetric analysis (TGA) was carried out on a Setaram TGA instrument. TGA is a technique in which the mass of a substance is monitored as a function of temperature or time as the sample specimen is subjected to a controlled temperature program in a controlled atmosphere. Upon heating a material, the sample weight increases or decreases. In short, TGA measures a sample's weight as it is heated or cooled in a furnace.

A thermogravimetric consists of a sample pan that is supported by a precision balance. That pan resides in a furnace and is heated or cooled during the experiment. The mass of the sample is monitored during the experiment. To be specific, the balance operates on a null-balance principle. At the zero, or "null" position equal amounts of light shine on the 2 photodiodes. If the balance moves out of the null position an unequal amount of light shines on the 2 photodiodes. Current is then applied to the meter movement to return the balance to the null position. The amount of current applied is proportional to the weight loss or gain.

When conducting TGA test, two important experimental conditions should be controlled: (i) heating rate and (ii) purge gas. Samples are heated at a rate of 10 or 20° C/min in most cases, and lowering the heating rates is known to improve the resolution of overlapping weight loss. For the purge gas, nitrogen (N₂) is the most common gas used to purge samples in TGA due to its inert nature, whereas, helium (He) provides the best baseline. Air is known to improve resolution because of differences in the oxidative stability of components in the samples. Thus it can also be used to test the thermal stability of samples. Vacuum may be used for sample containing volatile components, which helps improve separation from the onset of decomposition since the volatiles come off at lower temperatures in vacuum.

Materials analyzed by TGA include polymers, plastics, composites, laminates, adhesives, food, coatings, pharmaceuticals, organic materials, rubber, petroleum, chemicals, explosives and biological samples. There is a wide range of applications of TGA, such as composition of multi-component system, thermal stability of materials, oxidative stability of materials, estimated lifetime of a product, decomposition kinetics of materials, the effect of reactive or corrosive atmosphere on materials, and moisture and volatiles contents on materials.



Chpt. VII-Figure 7. Seven classifications of TG curve and their corresponding interpretations. [6]

TGA records change in mass from dehydration, decomposition, and oxidation of a sample with time and temperatures. It provides quantitative measurement of mass change in materials associated with transition and thermal degradation. [6]

Morever, fingerprinting unknown polymers, moistures content, volatiles content, analysis of evolved gases can be performed using TGA coupled with FTIR (Fourier Transform InfraRed spectroscopy) or coupled with MS (Mass spectrometry), *i.e.* coupling TGA analyses with a spectroscopy giving qualitative assessment of the exhaust gas taking place during the compound'mass variation during heating or cooling.

6. DSC

Differential scanning calorimetry (DSC) is a thermal analysis technique which has been used for more than two decades to measure the temperatures and heat flows associated with transitions in materials as a function of time and temperature, illustrated in **Figure 8**. With heating or cooling any transformation taking place in a material is accompanied by an exchange of heat. DSC enables the temperature of this transformation to be determined and the heat from it to be quantified.

This technique provides quantitative information about physical and chemical changes that involves endothermic or exothermic processes, or changes in heat capacity. DSC is a widely used thermal analysis technique with applicability to polymers and organic materials, as well as inorganic materials.

The principle of DSC is a thermos-analytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference is measured as a function of temperature. The difference in heat flow occurs with the occurrence of two major events: (i). the heat capacity of the sample which increases with temperature (baseline); (ii), transitions that occur in the sample (events superimposed on the heat capacity baseline).



Chpt. VII-Figure 8. Differential scanning calorimetry (DSC).

The most common instrument design for making those DSC measurements is the heat flux design shown in **Figure 9**. In this design, a metallic disk is the primary means of heat transfer to and from the sample and reference. The sample, contained in a metal pan, and the reference (an empty pan) sit on raised platforms in the constantan disc. As heat is transferred from the disc, the differential heat flow to the sample and reference is measured by area thermocouples formed by the junction of the constantan disc and chromel wafers which cover the underside of the platforms.



Chpt. VII-Figure 9. Heat flux DSC schematic.

In a DSC experiment, heat capacity is measured as the absolute value of the heat flow, divided by the heating rate, and multiplied by a calibration constant, as shown below.



In this work, differential scanning calorimetry (DSC) experiment of as-obtained VO₂ powders was performed using Perkin-Elmer DSC 8000.

7. UV-Vis-NIR

A spectrophotometer measures a material's reflection or transmission by measuring light intensity at a specific wavelength which is reflected or transmit by the sample. UV-VIS and NIR spectrophotometers measure in those particular spectrums, with wavelength ranges that can span 135-3300 nm. When comparing UV-VIS/NIR spectrophotometers, take note of analysis speed, detection wavelength range, range of absorption, and stray light performance, especially with UV-VIS models. Although both single-beam and double-beam instruments are available, the double-beam type measures the sample beam and reference beam simultaneously, upping ease of use, reproducibility, and light source and detector stability. Sensitivity in UV-VIS/NIR spectrophotometers can be enhanced through the use of multiple detectors. Accordingly, the predetermined electromagnetic radiation wavelengths are for ultra-violet (UV, 300-400nm), visible (Vis, 400-765mm) and near infra-red (NIR, 765-3200nm) radiation. **Figure 10** depicts the light path for a simplified spectrophotometer with polarizing analyzer.



Chpt. VII-Figure 10. Simplified spectrophotometer with analyzer.

In this work, the reflectance spectra were measured using a Varian Cary UV-Vis-NIR spectrophotometer in a wavelength region of 200 to 2500 nm with a step of 1 nm and a band length of 2 nm. This spectrophotometer, is a single-beam spectrometer, well-adapted for the measurement of diffuse reflectance of a powder sample because is equipped with an integration sphere, as detector (*i.e.* the detector records the reflection in all the directions, thus the reduced diffuse reflectance is the complementary of the absorbance: R = 1-A). Halon polymer was used as white reference for the blank.

8. Magnetic susceptibility

A Vibrating-Sample Magnetometer (VSM) is a scientific instrument that measures magnetic properties, illustrated in **Figure 11a**. If a material is first magnetized in a uniform magnetic field (H), a magnetic moment (M) will be induced in the sample. The sample undergoes sinusoidal motion, *i. e.* mechanically vibrated. The resulting magnetic flux changes induce a voltage in the sensing coils that is proportional to the magnetic moment of the sample. The magnetic field may be generated by an electromagnet, or the superconducting magnet. VSM systems are used to measure the magnetic properties of materials as a function of magnetic field, temperature and time. They are ideally suited for research and development, production testing, quality and process control. Powder, solids, liquids, single crystals, and thin films are all readily accommodated in a VSM.

A SQUID (superconducting quantum interference device) is a very sensitive magnetomer used to measure extremely subtle magnetic fields, based on superconducting loops containing Josephson junctions. One distinguishes two different types of SQUIDs, which consist of a superconducting ring interrupted at a point (radio frequency, RF-SQUID) or two points (direct current, DC-SQUID) by a normally conducting or electrically insulating material.

The function of a SQUID is based on effect of flux quantization in superconducting rings and the Josephson effect, as illustrateed in **Figure 11b**. Through a superconducting ring only flows a magnetic flux whose size is an integral multiple of the elementary magnetic flux quantum $\Phi_0=2.07.10-15$ Vs. If the external magnetic field changes, an electric circuit current is excited in the ring which is exactly large enough to increase or reduce the magnetic flux in the superconducting ring to the nearest multiple of the flux quantum.



Chpt. VII-Figure 11. The construction and principle of (a) VSM and (b) DC-SQUID.

In this work, magnetic susceptibility was measured using both Vibrant MicroSense EZ7 and Quantum Design Magnetic Property Measurement System magnetometers. The choice of the apparatus was made in function of the temperature range of the analysis. Data were collected in both ZFC and FC mode process under an applied magnetic field of 1.5 T for both VSM and SQUID measurement.

9. References

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