

# Development of catalytic microreactors by plasma processes and sol-gel processes Xi Rao

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# Université Pierre et Marie Curie

Ecole doctorale 391 : Sciences Mécaniques, Acoustique, Electronique et

Robotique de Paris IRCP, UMR 8247 (CNRS-Chimie ParisTech) Equipe Procédés, Plasmas, Microsystèmes

# Développement de microréacteurs catalytiques par procédés plasma et procédés sol-gel

Par RAO Xi

Thèse de doctorat en : Chimie - Génie des Procédés

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## Abstract of the thesis

The related research on microfluidic systems is being important in the chemical synthesis area in recent years. Elaborating microfluidic systems that are based on microreactors and consequently use them for high efficiency heterogeneous catalytic reaction appears as very attracting. In the first part of this work, three related aspects are systematically investigated: (i) Amine functionalization on various substrate surfaces using plasma enhanced chemical vapor deposition (PECVD) process; (ii) Synthesis of gold nanoparticles (AuNPs) and their immobilization on substrate surfaces; (iii) Immobilization of AuNPs on zeolites and their deposition on substrate surfaces. In the second part of this work, the particle catalysts (AuNPs and AuNPs@zeolite) are prepared and silanized. The catalysts particles are then linked to the channel surface of cyclic olefin copolymer (COC) microreactors, which are pre-functionalized with amine using PECVD method. Finally, the catalytic microreactors are connected into the pre-designed microfluidic system. The catalytic performance of the system is investigated through benzyl alcohol oxidation reaction in water medium.

First of all, in order to develop a universal method of preparation of channel surfaces that could be further immobilized with catalysts, polymerized APTES coatings were deposited on different substrates using a homemade low pressure plasma reactor in which glass, silicon and COC are used as starting substrate materials. The influence of the different plasma parameters, including active gas, deposition time, working pressure and working power is investigated. The successful deposition of the APTES coating with similar structure on various substrates demonstrates that PECVD is a promising functionalization method in a wide range of application. The study of the active gas that could be used for the functionalization indicates that O<sub>2</sub> is not appropriated due to the formation of high amount of SiO<sub>2</sub>-like structures. The study of the deposition time indicates that the appropriate time range is 14~40s, in

order to diminish the functional change ascribed to exposure of coating to plasma. The investigation on the working pressure evidences the change of the thickness of the coating and chemical structure with an increasing pressure. The competition between fragmentation and/or poly-recombination of the APTES molecules and normal ionic or/and radical polymerization determines the coating chemical composition and functional groups. The study on different working powers indicates the various surfacial properties with increasing power. The coating stability increases when the power is increased between  $25\sim40$ W, indicating a high cross-linked structure due to a higher plasma power. However, the intensity of fragmentation of APTES is also enhanced with increasing power. When the power is too high, the amine functions are lost during fragmentation. The comparison of amine proportion of the total composition and coating stability in this study indicates optimization plasma conditions for APTES deposition:  $Q_{APTES}=10$  sccm,  $Q_{Ar}=20$  sccm, P=30W, p=1.0 mbar, t=40s.

Thereafter, the comparison study of wet chemistry and plasma processes to functionalize substrate with APTES precursor and the ability of such modified surfaces to immobilize gold nanoparticles are processed. The results clearly evidenced that plasma polymerized coatings from APTES precursor exhibit better hydrophilicity, higher coating thickness, as well as higher amine groups density, leading to a further higher coverage and amount of 13 nm gold(0) nanoparticles. The XPS spectra of gold immobilized surface evidenced the appearance of another new contribution at 289.2 assigned to O-C=O bond due to the citrate anions from gold nanoparticles as well as an increase of protonated amine groups during immobilization procedure, indicating AuNPs were bound to R-NH<sub>3</sub><sup>+</sup> species.

The AuNPs are also immobilized on Y type zeolite (d=450 nm) using APTES and MPTES, respectively. The APTES and MPTES are both proved good linkage reagents for gold immobilization. For a comparison study of experimental data, the APTES is evidenced the better linker as it provides higher amount of gold loading at the same condition. Subsequently the zeolite and AuNPs@zeolite are functionalized with CES and then deposited on amine pre-functionalized COC surface. The results show a good attachment of carboxylate on both particle surfaces. In high resolution  $C_{1s}$ , the O-C=O at low BE (289.6eV) of free carboxylic acid and the O-C=O at high BE (291.6eV) of O-C=O'Na<sup>+</sup> implies the pH of zeolite solution for further deposition should be adjusted to an appropriate value to obtain the maximum amount of free O-C=O'. Thus, the pH value of 8.4 is used as pKa<sub>NH2</sub> is 10.6 and pKa<sub>COOH</sub> is 2.5. The SEM image shows a complete and even coverage over the entire substrate surfaces from zeolite and Au@zeolite deposited COC substrates. The coating stability tested in hydrodynamic flows evidences a good coverage after 72h, indicating our method for depositing the zeolite and Au@zeolite particles on COC surface is fairly stable in hydrodynamic flows and could be further used for preparation of catalysts immobilized in microfluidics.

Finally, the microreactors with gold catalysts (AuNPs, zeolite, and Au@zeolite) are employed in our microfluidic system and used for benzyl alcohol oxidation in water medium. The gold-immobilized microreactor shows a stable high selectivity to benzaldehyde (about 94%) even when it is continuously used for at least 9 hours without obvious loss of activity. However, the conversion in this type of microreactor is not high (about 20%). The Y-zeolites exhibit an ability to absorb benzyl alcohol when it is used in the microchannel. Finally, gold nanoparticles supported on Y-zeolites perform the best catalytic activity in our study, as a relatively high benzyl alcohol conversion of 42.4% as well as the highest benzaldehyde selectivity (> 99%) is obtained in our study. Based on the previous results, the absorption-catalysis mode of benzyl alcohol in AuNPs-zeolite system is also built up in this thesis.

# **Chapter I: Bibliography**

### **1.1 Introduction**

Microreactors, defined as miniaturized devices with characteristic dimensions below 1 mm, have been widely used as a versatile tool in chemical engineering within the past two decades. Since the time of their birth, this kind of devices attracted great attention due to the significant advantages they offers such as higher reaction speed and yield, better reliability, finer degree of process control, safer experimental manipulation, etc. Furthermore, instead of stirring or shaking, continuous flow conditions in microchannel provide an impressive effort in terms of automation compared to conventional heterogeneous catalysis in stationary reactors. Therefore, their study has been recently recognized as a new area of science, which is generally termed as microfluidics.

### **1.2 General introduction of microfluidic systems**

#### **1.2.1** The development of microsystems

These artificial systems, called microfluidic reactors or microreactors, are fabricated using new technologies and could employ fluid flows operating under unusual and unexplored conditions. Therefore, this domain refers to devices and methods for the control and manipulation of fluid flows with length scales less than a millimeter. In fact, this field began about 35 years ago, with the development of micro-electro-mechanical systems (MEMS). Thereafter, during the 80~90's, a sort of maturation in the domain of MEMS prevailed, resulting in considerable diversifications for various applications (e.g. physics, chemistry, biology and so on). Later in the 90's, miniaturization and MEMS gave birth to a new discipline called microfluidics: the science and technology of systems that process or manipulate small

amounts of fluids ( $10^{-9}$  to  $10^{-18}$  liters), using channels with dimensions of tens to hundreds of micrometers <sup>[1]</sup>. The first applications of microfluidic technologies have been in the analysis field, and then these miniaturized devices were expended in other fields: i.e. electrophoretic separation, electro-osmotic pumping, diffusive separation systems, micromixers, DNA amplifiers, cytometers and chemical microreactors [2-4]. Thus, all sorts of microfluidic systems began to be fabricated in recent years which offer a number of useful mentioned capabilities. Nowadays, these systems continue to play a growing and tremendous interest due to their promising applications from both academic and industrial points of view. There are many journals now reporting applications at the micron scale (e.g., Lab-on-a-Chip, Sensors and Actuators, Analytical Chemistry, etc.). Since the birth of microfluidic systems, more than 70,000 papers (from Web of Science, ~2015) have been published on the field of microfluidics which demonstrates that this field is currently an extremely –hot" research area.

#### **1.2.2** Microfluidic systems for chemical engineering

Due to the a high surface-area-to-volume ratio of microfluidics, the latter allow a significantly enhanced process control and heat management for chemical reactions, giving nearly gradientless conditions, which are desirable for the determination of reaction kinetics <sup>[5, 6]</sup>. They enable the performance of endo- or exothermic reactions in quite unusual reaction regimes that can be difficult to manage in traditional chemical engineering systems <sup>[7]</sup>. In addition, the usage of microchannels in chemistry offers a couple of other advantages, such as a high energy input per volume, a high efficiency, narrow residence time distributions and reproducible results. The reactions carried out in microsystems lead to higher purity and yield of the desired products compared to conventional systems. More benefits can be drawn in minimizing the need of performing collateral reactions and the formation of undesirable by-products. In other words, the selectivity of the targeted products is improved by avoiding the formation of unwanted chemical species <sup>[8, 9]</sup>.

Another relevant advantage of using microfluidic systems is seen from the synthesis of compounds that sensitively depend on its reaction environment <sup>[10]</sup>. Compared to the conventional methods, microfluidic systems provide a completely controlled environment inside the microchannels and thus, the degradation of sensitive products can be avoided. Furthermore, the use of pumps, valves and computer-controlled elements offers the opportunity to automate the whole process, increase reproducibility and autonomy, reduce possible risks associated to hazardous reagents and provide real-time information regarding the reaction evolution <sup>[11]</sup>.

All those features mentioned previously, as well as the development of immobilized catalysts on inner microchannel surfaces <sup>[12]</sup>, envision a promising possibility to dedicate a microfluidic system to catalytic reactions. Indeed, catalytic microreactors provide a high efficient performance for heterogeneous catalytic reactions without exhibiting several drawbacks e.g. pressure drop control, clogging, that appear in traditional catalytic systems <sup>[13]</sup>. As a matter of fact, the studies of continuous-flow catalytic microreactors e.g. preparation, characterization, application, etc. have been successfully launched to the various catalytic reactions in recent years. For example, Thakur et al. reported the fabrication of different carbon nanofiber layers containing palladium particles synthesized inside the channels of silicon based microreactors, which is a potential for the reduction of aqueous nitrite solution <sup>[14]</sup>. Rahman et al. developed a novel catalytic hollow fiber membrane microreactor that generates hydrogen from ethanol for vehicular applications <sup>[15]</sup>. Wang et al. announced a gold-immobilized microchannel flow reactor for oxidation of various alcohols and the results reveal high conversion and yield rate as well as excellent stability during four days (Fig. I-1)<sup>[16]</sup>.



Fig. I-1 A scheme of gold immobilized microfluidic system<sup>[16]</sup>.

#### 1.2.3 Materials for microreactors fabrication

Technical obstacles in making simple microfluidic systems are one of the essential problems that need to be solved for achieving science objectives. Certainly the most important issue is the choice of a suitable raw material. As shown in (Fig. I-2), different materials can be used as a starting material.

Polydimethylsiloxane (PDMS) is an important and commonly used material to fabricate opticalfluidic microreactors due to its advantages e.g. excellent optical transparency, chemically inert, easily fabrication <sup>[17]</sup>. However, PDMS is naturally hydrophobic and intrinsically inactive <sup>[18, 19]</sup>, which makes difficult to spread the catalyst during its immobilization. Moreover, the bonds available for surface functionalization are usually weak and chemically unstable. Therefore, the catalyst particles are not retained on the PDMS substrate, lowering the durability of the catalytic microreactor.

Glass is another typical used material for microchips. Glass-made microreactors are particularly useful for the analysis of amino-acids, proteins and DNA, organic reaction, and synthesis of nanoparticles due to the advantages of glass e.g. excellent optical transparency, thermal conductivity, surface stability, solvent compatibility, and good biological compatibility and so on <sup>[20, 21]</sup>. Moreover, the latter can be easily functionalized with diverse chemical reagents <sup>[22, 23]</sup>. In spite of the many advantages of using glass, applications of glass-based microreactors are limited due the difficulties of building complicated nanoscale channels in chips. Therefore, a low-cost and fast prototyping method for fabrication is urgently needed for glass made microreactors.

Silicon is also used for the fabrication of microreactors <sup>[14, 24, 25]</sup>. However, it doesn't exhibit a better potential compared to PDMS and glass. Besides, the weak mechanical properties and intransparency awfully restrict its scope of application.

Metals, e.g. high-thermal-conductivity stainless steels or alloys, could be considered as one of the raw materials for microreactor fabrication due to its extraordinary heat transfer characteristics <sup>[26]</sup>. Taking account into their resistance to corrosion, thermal properties and thermal response, and ability to handle mechanical stresses induced by the local process environment, different metallic materials can be chosen. However, an important issue resides in the fact that microchannels are very difficult to fabricate on the metal surface at high precision. Therefore, the resulting manufacturing process (e.g. mechanical micromachining, laser micromachining, etc.) has a huge cost <sup>[27].</sup>

Cyclic olefin copolymer (COC) has recently emerged as a highly attractive raw material for the elaboration of microreactors <sup>[28]</sup>. In contrast to other polymers used for lab-on-a-chip applications, it is highly resistant to chemicals including polar solvents. This means that the COC's scope of application could be extended to other field like the organic electrochemistry applications <sup>[29]</sup>. Moreover, COC is highly transparent in the visible and near ultraviolet regions making this polymer very interesting for photochemistry applications <sup>[30-32]</sup>. However, the surface of COC is also hydrophobic. In order to expand its application, surface modification of COC and the subsequent immobilization of catalysts are still tough challenges <sup>[33]</sup>.



Fig. I-2 Microreactors made by different materials: (a) PDMS; (b) Glass; (c) Silicon; (d) Metal; (e) COC.

#### **1.2.4** Fabrication methods

Conventional lathe milling machining technology is the first method that is used for microreactor fabrication. After several decades of development, the participation of computer numerical control system made this technique more attractive, especially when duplication of the same part is required <sup>[34]</sup>. Micro-electro discharge machining (EDM) and laser micromachining are the advanced techniques based on machining technology, which have the capability of producing structures with minimum feature sizes by precisely controlling the dimensions of microchannels <sup>[27]</sup>. However, when the channel size is too small (e.g. nanoscale), the fabrication of microsystems becomes difficult.

Soft lithography is a printing technique for creating microstructures using a light source. A light sensitive photoresist is spun onto the wafer, forming a thin layer on the surface. The resist is then selectively exposed by shining light through a mask which contains the desired pattern. The resist is then developed and the pattern transfers from the mask to the wafer. In recent years, this method has been diversified into nanoimprint lithography <sup>[35]</sup>, LIGA (lithography, electroforming, and molding) <sup>[34]</sup>, <sup>16</sup>

microelectronics-photolithography, electron-beam lithography, etc. <sup>[36]</sup> Due to its feature, this method requires complex machining facilities and numerous processing steps.

Chemical etching is a technology that usually uses an etchant to remove the unwanted work-piece material by a controlled dissolution. This method has attracted a lot of attention due to its attendant advantages, such as low cost, fast processing, no burring on the edges of the walls and easy processing of very thin materials. However, the difficulty of precisely controlling the dimensions of the microchannels due to isotropic etching behavior, has limited its applications. Moreover, the toxic etchants used in the chemical etching process are not environmentally friendly.

Molding replication method is also used for microreactor fabrication and offers the advantages of being a low cost and easy-to-process method. Indeed, in the latter, the relatively expensive step only resides in the manufacture of a single master. Thereafter, identical structures can be reproduced in mass quantity. Several techniques like microinjection molding, casting and hot embossing have been recently developed <sup>[37-39]</sup>. However, these techniques display the same drawbacks as a high machining precision is needed.

#### 1.2.5 Other components of a microfluidic system

Besides the fact that a microreactor is the core party of a microfluidic system, other components are required in order to obtain a complete integrated system. In order to gain the connection between a microfluidic system and the exterior world or couple more than one systems, a standardized way of linkage without leaks was introduced. The idea originates from the connection of electronic circuits and has developed several solutions in laboratories. For example, the press-fit connectors that are based on compression sealing between the PDMS and the inserted tubing (or needle), were preferred because they are easy to plug/unplug and compatible with moderate pressures. This type of connections, shown in Fig.I-3, is used in single



channel and several parallel channels<sup>[40]</sup>.

*Fig. I-3 Press-fit connectors for different type of microreactors: (a) single channel; (b) parallel channels* <sup>[40]</sup>.

Pumps and valves are used to control the fluidic flow systems. It is commonly known that samples in microreactors are always diluted in a large volume so that they can be more easily handled. However, this creates a series of difficulties, including the management of fluid volumes, needing for sensitive instrumentation, etc. In other words, this means that the injection of fluids becomes very difficult when the sample is very small. Thus, in order to obtain a well-controlled fluidic flow, pumps and valves should be specifically designed at very high operate precision for the microsystem.

Moreover, some micro-tools are designed for specific requirements of various research targets. In some experiments, the rapid well-mixed reagents are vitally important to achieve fast and accurate analysis under precise control of smallest reagents consumption. As shown in Fig. I-4, the micromixer is a device based on mechanical microparts used to mix fluids, which could quickly transform complex liquids, such as heterogeneous fluids, into homogenous liquids <sup>[41]</sup>. Various micro-filters and micro-separators are also developed for the aspects of separating small target samples in a homogeneous mixture <sup>[42, 43]</sup>. For example, the first step in deoxyribonucleic acid (DNA) extraction from human blood involves separation of red blood cells (RBCs) from white blood cells (WBCs) <sup>[44]</sup>. Such microfluidic devices provide significant advantages, such as a smaller geometrical size, shorter analysis



time, lower sample/reagent consumption and disposability, and so on.

Fig. I-4 A design drawing of a micromixer chip (Micronit).

#### 1.2.6 Sealing of a microreactor

One of the important properties of PDMS is that it can be sealed to itself or other substrates both reversibly and irreversibly without an adhesive. Therefore, PDMS is easy to be used to enclose channels <sup>[45]</sup>. Furthermore, for permanent sealing a broad range of surface modification techniques such as plasma, wet chemistry, and photochemistry is developed. For instance, the use of oxygen plasma and heating process could briefly provide the ideal permanent bonding for PDMS chips <sup>[40]</sup>. However, the drawbacks of PDMS, including adsorption of hydrophobic molecules, short-term stability after surface treatment, swelling in organic solvents, water permeability, and incompatibility with very high pressure operations, strongly limits its wider application in industry.

As a consequence, thermoplastics have been preferred as low-cost and mass-producible alternatives. Among this class of polymers, cyclic olefin copolymer (COC) is taken into account <sup>[46]</sup>. The hot pressuring process is a conventional method for introducing thermal fusion bonding on COC surface with a relative high strength <sup>[47]</sup>. However, the deformation and/or collapse of the channel might occur as the

substrates are heated to temperatures near or above the glass transition temperature at a high pressure. Alternatively, the drawback of this method could be resolved by solvent-based bonding techniques which don't require a high temperature. Thus, the hot pressuring technique usually consists in the use of a compatible solvent that is applied on the COC substrates for the sealing of such microsystems.

### **1.3 Plasma surface modifications of microchannels**

#### **1.3.1** Definition of a plasma

Plasma is a partially ionized gas consisting of an equal numbers of positive and negative charges, with a different number of un-ionized neutral molecules <sup>[48]</sup>. It has to be noted that a plasma-like behavior occurs once a remarkably small fraction of the gas has undergone ionization. Thus, fractionally ionized gases exhibit most of the exotic phenomena characteristic of fully ionized gases. In fact, at temperatures near or exceeding atomic ionization energies, atoms similarly decompose into electrons and positively charged ions. When the charges move, they generate electric currents along with magnetic fields. As a result, they are affected by each other's fields. Nevertheless, because the charges are no longer bound, their assemblage becomes capable of collective motions of great vigor and complexity and such an assemblage is termed plasma. Scientists have successfully developed plasma technologies in materials science since the 1960s. As plasma demonstrates quite different properties from those of common substances in the gaseous, liquid or solid state due to its high energy level, plasma is commonly admitted as the fourth state of matter. In fact, 99% of the substances in the universe exist in a state of plasma, mostly in countless giant stellar stars <sup>[49]</sup>.

#### 1.3.2 Applications of plasma

Plasma can be divided into two categories as it can be generated at different temperatures <sup>[50]</sup>: cold plasma and thermal plasma (Table I-1). Depending on different working power, the plasma enables various applications for plasma technologies: surface coatings, waste destruction, gas treatments, and chemical synthesis and so on. Thermal plasmas can be artificially generated using a high voltage, high temperature arc, which is the basis for the corona discharge process and for the plasma torch used to vaporize and redeposit metals. Cold plasmas are always used in surface modifications and organic cleaning. This type of plasma is generated within a vacuum chamber where atmospheric gases have been evacuated (typically below 0.1 torr); the low pressure allowing a relatively long free path of accelerated electrons and ions. Since the ions and neutral particles are at/near ambient temperatures, the long free path of electrons, which are at high temperature or electron volt levels, have relatively few collisions with molecules at this pressure and the reaction remains at a low temperature.

	Cold plasma	Thermal plasma
	Te>>Th	Te=Th
Properties	Lower electron density:	High electron density:
	$< 10^{19}  \mathrm{m}^{-3}$	$10^{21} \sim 10^{26}  \mathrm{m}^{-3}$

Table I-1 Main characteristics of cold and thermal plasma

In the plasma surface modification process, glow discharge plasma is created by applying a voltage between electrodes in a reaction chamber containing with low-pressure gas. The gas is then energized by one of the following types of energy: radio frequency (13.56 MHZ), microwaves (2.45 GHz), and alternative or direct current. The energetic species in plasma include ions, electrons, radicals, metastables, neutrals species in different excited levels, and photons in the short-wave ultraviolet (UV) range. Surfaces in contact with the gas plasma are bombarded by these energetic species and their energy is transferred from the plasma to the solid. These energy

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transfers are dissipated within the solid by a variety of chemical and physical processes. In terms of the highly unusual and reactive chemical environment of plasma, many plasma-surface reactions occur and the high-density of ionized and excited species in the plasma can change the surface properties of materials <sup>[51]</sup>. The application for plasma interaction on the surface can be divided into four categories <sup>[50]</sup>: (i) to tailor interfacial properties between reinforcement and matrix materials; (ii) to increase wear or erosion resistance of surface; (iii) to enhance adhesion strength or minimize porosity of the coatings; (iv) to functionalize the surface of materials, e.g. plasma treatment including cleaning, etching, crosslinking, grafting and plasma deposition, respectively.

#### **1.3.3** Plasma enhanced chemical vapor deposition (PECVD)

As known to all, plasma enhance chemical vapor deposition (PECVD) is a kind of chemical vapor deposition (CVD) technique based on the reaction between the gaseous precursor that is introduced into the chamber (or vapor of a liquid carried by gas) and another molecule in the gas phase. The most important advantage compared with CVD is the reaction can occur at much lower temperature due to the assistance of the plasma reactive media for the dissociation of the precursor <sup>[52]</sup>.

Furthermore, controlling the plasma chemical reactions and plasma-surface interactions, could optimize the film composition and microstructure. The processes leading to the deposition of thin films in the plasma environment include reactions in the gas phase, transport toward the surface involving specific energetic considerations, and reactions at the surface, giving rise to film formation and microstructural evolution, and providing specific film functional properties.

Numerous reports show that this method can be used in various areas for different application, i.e. deposition inorganic films like oxides, nitrides and carbides of metals; deposition of organic thin films like polymers, hard carbon films, crystalline diamond; even deposition of inorganic-organic mixture thin films like metal-organic catalysts. It could be also employed for the treatment of different substrates such as stainless steel, NiTi SMA, glass, PDMS, silicon, COC and so on. Concerning the deposition on organic materials, the glow discharge is efficient at creating a high density of free radicals, both in the gas phase and in the surface of organic materials, including the most stable polymers. These surface free radicals are created by vacuum ultraviolet light generated in the primary plasma. The surface free radicals then are able to react either with each other, or with species in the plasma environment. Thus, optimization of the deposition involves identification of discharge characteristics giving rise to the formation of large densities of free radicals that diffuse toward the surface.

Of course, in the deposition processes discharge characteristics are not the only controlling parameters. If we consider the whole PECVD system and the properties of coating, plenty of parameters have to be discussed. They can be generally divided into two catalogues: external parameters including pressure, gas flow, discharge excitation frequency, power supply and the resulting internal' plasma characteristics like the electron (plasma) density, the electron energy distribution function (EEDF), electrical potentials, and fluxes of different species toward the surfaces exposed to plasma. As we mentioned before, the nature of plasma is the balance between collisional ionization and recombination. This makes EEDF as an essential parameter for plasma processing because it represents how many electrons are available for the ionization and other plasma reactions. However, EEDF is affected by all external parameters in a complex way, especially, the discharge field frequency is the important factor influencing on how the plasma interacts with the exposed surface. Therefore, plasma systems are varied due to different frequency: Low-, medium- and radio-frequency (LF, MF, and RF (standard RF frequency is 13.56 MHz)) deposition systems. Note that higher frequency leads to higher power efficiency, which could avoid surface charging and plasma instabilities. It means the ionization and dissociation rates are higher in the microwave plasma than in RF plasma. As a consequence, with the development of PECVD microwave discharge is introduced into plasma system to provide high electron (plasma) density and high ion flux. Based on this system, MW/RF dual mode plasma, remote MW/RF plasma, electron cyclotron resonance plasma is developed as well.

Actually, for a certain system, the frequency is almost fixed; the other parameters play a very important role to affect the characteristics of coating including mechanical, optical, electrical and tribological properties. The details will be discussed in the following section.

#### **1.3.4** Influence of the parameters during PECVD process

The reality in plasma process is that a steady state population of atoms is continuously fed by gas flow and continuously pumped in the vacuum system. Thus, it is important to describe the amount of gas flowing in pumping system: on one hand it is the volume of gas passing per second, which is measured by pumping speed S; on the other hand it's the number of molecules contained in that volume gas, which is defined by its pressure <sup>[53]</sup>. Kim et al. report that the characteristics of the coatings changed by increasing the total pressure in the deposition processing <sup>[54]</sup>, as shown in Fig. I-5. Increase in pressure improves the grain structure and size due to the change of favorable growth plane. Furthermore, the cause of enhancement of the diamond film quality with increasing total pressure was investigated. The results show enhancement is related to the increase in promoter intensity (in this case is CH) in the plasma.



*Fig. I-5 Raman spectra of thin films at total pressures of (a) 27.5, (b) 40, (c) 60, (d) 150 and (e) 250Torr*<sup>[54]</sup>.

Moreno et al.<sup>[55]</sup> found that the deposition pressure and the SiH<sub>4</sub>/H<sub>2</sub> flow rate ratio had an important influence on the structural, optical and electric characteristics of the films. AFM results showed that higher gas flow rate ratios resulted in an increment on silicon clusters density on the film surface. The effects of the CH<sub>4</sub> flow rate on properties of a-SiC<sub>x</sub>:H films are also investigated by Lien et al.<sup>[56]</sup>. As increasing the carbon content in the films, the band gap and deposition rate also increased, while the absorption coefficient and conductivity of the films decreased. It was found that the grain size becomes larger with an addition of the incorporation of carbon atoms into the films. By investigating the influence of Ar flow rate on deposition rate and structural properties of hydrogenated silicon germanium (SiGe:H) films, Tang et al. show that the addition of Ar in the diluted gas efficiently improve the deposition rate and crystallinity due to an enhanced dissociation of source gases and bombardment on growth surface <sup>[57]</sup>. Considering the gaseous is a mixture with complicated constitute, flow ratio has been reported as another important parameter in

### plasma deposition [58-60].



Fig. I-6 AFM height images, the cross-section profiles and the values of root mean square roughness (RMS) of thin films deposited during 45 min at different power: (A) 100 W, (B) 200 W and (C)  $300 W^{[61]}$ .

The plasma sustained by the RF power is the key parameter of the plasma deposition system. Micromorphology of coating is strongly affected by the induction power of plasma. As discussed in [62]: sheath voltage (V) and gas pressure (P) are the two main factors influence on ion energy as the relationship  $\underline{-}\underline{E}_{ion} \neq V^{\frac{4}{5}} P^{-\frac{1}{2}}$ , where the sheath voltage is directly proportional to input plasma power.



Fig. I-7 FESEM images of the SiNWs and spherical microstructures prepared using HW-PECVD at different RF-power<sup>[63]</sup>.

Thus, increase of RF power is predictable to generate higher kinetic energy ions when the pressure is fixed in plasma process; thereafter the ionic species in plasma sheath bombard the substrate <sup>[61]</sup> and force the catalyst droplets on the growth surface into large number of small droplets. Guzenda et al. had calculated the values of RMS (calculated for images of comparable quality (Fig. I-6)) were 4.6 nm, 6.4 nm and 11.6 nm for titanium oxide films deposited at power of 100 W, 200 W and of 300 W respectively <sup>[64]</sup>. In this work, the film roughness measured with AFM is clearly dependent on the deposition power, which was also observed in Ref. <sup>[65]</sup>. Furthermore, Chong et al. describe the transformation of SiNW<sub>s</sub> microstructures using different RF power (Fig. I-7), two types of SiNW<sub>s</sub> were observed on film <sup>[63]</sup>. These results imply it is controllable to fabricate coating with different microstructure and size by adjusting plasma generator power.



*Fig. I-8 EDX spectra scan on catalyst droplet and nanowire stem at different rf power. The inset in each spectrum is the high magnification FESEM view of SiNW*<sup>[63]</sup>.

Except for the ion bombardment, another significant effect of power difference is dissociation of molecules that influences on chemical composition of the ionic species. Actually, different step of reactions occurs after dissociation in the plasma deposition. Increase in RF power resulted in an increase in primary dissociation and limited the following reaction. It is reported that after SiH<sub>n</sub> (n=1, 2, 3, which depending on the energy of electron. The threshold energy for SiH<sub>3</sub> generation (8.75 eV) is the lowest compared to SiH<sub>2</sub> and SiH <sup>[66]</sup>) is generated from dissociation of SiH<sub>4</sub> molecules, second gas-phase reaction occurred between SiH<sub>4</sub> species and SiH<sub>4</sub> parent molecules to form higher silane species (Si<sub>n</sub>H<sub>m</sub>).

This reaction usually involved short lifetime species of  $SiH_2$  and SiH rather than  $SiH_3$ , increase in RF power reduces the formation of  $SiH_3$  species in the plasma and thus reduced the formation of nucleation sites for Si film growth as a result of abstraction of Si-H bonds and the growth of ordered Si:H film as a result of diffusion of SiH<sub>3</sub> radicals into these growth sites. It indicates RF power is also a key parameter to influence on the chemical composition of coating, as shown in Fig. I-8.

The growth rate of coating are investigated by Sun et al. <sup>[65]</sup> and Seo et al. <sup>[67]</sup>, respectively. Both of them figure out the deposition rate increase with the rise of RF

power in a certain range. Moreover, in the work of Seo et al., a stable deposition rate state was sustained when the power was continuously increased (Fig. I-9 (a)). However, contrary results are also described in ref. <sup>[60]</sup>, this decrease may be due to the back etching that occurs during the deposition process (Fig. I-9 (b)).



*Fig. I-9 Effect of RF power variation on the growth rate of the deposited film (a) reported by Seo et al.*<sup>[67]</sup>; *(b) reported by Mahajan et al.*<sup>[60]</sup>.

Other parameters like working time (Fig. I-10<sup>[68]</sup>), inter-electrode distance (Fig. I-11<sup>[69]</sup>) and so on also take efforts on the characteristics of coating. Some results are exhibited as follow:



Fig. I-10 (i) SEM images of CNWs. (a, c, e, g) Top view, (b, d, f, h) cross sectional view.
Growth time: (a, b) 30 s, (c, d) 60 s, (e, f) 90 s, (g, h) 120 s; (ii) Raman spectra of CNWs with different growth times <sup>[68]</sup>.



*Fig. I-11 Change of OES intensity with changing inter-electrode distance* <sup>[69]</sup>.

#### **1.3.5** Amino functionalization by PECVD method

The surface of heterogeneous catalyst takes a particular place among the surfaces with specific requirements. Because of economic and environmental concerns: catalytic processes require continuous improvements. One way to achieve these improvements is to find out new modes for the preparation of catalytic materials that promote the desired reactions <sup>[70]</sup>. In decades, scholars pay attention to develop a modified surface for catalysts attachment. In order to gain an immobilizable coating with good adhesion strength, organic compounds are introduced into the surface. Conventionally, silanization agents with functional end-groups, e.g. –NH<sub>2</sub>, -SH, -COOH ... are often used for functionalizing surface <sup>[23, 71-74]</sup>. For example, organic amines allylamine is usually chosen most often as a plasma medium to obtain amine functionalities, which are important for the immobilization of catalytic metal particles <sup>[75]</sup>. With the development of research, plasma polymerization of other chemicals containing amine groups such as VTES, HMDSO, APTES, TES, HBDS and so on also show the potential for plasma functionalization.

Among those candidates, 3-aminopropyltriethoxysilane (APTES) (CAS Number: 919-30-2) with a chemical structure as presented in Fig. I-12 is considered as the most popular functionalization reagent and has been widely used in current research <sup>[73, 76, 77]</sup>. As one of the silane-coupling agents, it even exhibits the enhanced adhesion to inorganics like silica, whereas there was no activity at all without the plasma treatment. On one hand APTES exhibits good adhesion to substrate such as glass, PDMS, COC, etc. through the formation of Si-O bonds, on the other hand it provides the amino groups that could bound to catalytic nanoparticles through electrostatic interaction <sup>[78]</sup>. However, few publications focus on introducing this chemical into plasma system, the most commonly used method is through a wet chemical treatment <sup>[22]</sup>. Since Barbarossa et al.<sup>[79]</sup> reported the deposition of thin film by plasma polymerization of AA/3-APTES mixture in 1992, few developments continued in recent years. Four years later, Akovali et al.<sup>[80]</sup> reported the different

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exhibitions of silicon and tin containing organic compounds including VTES, HMDS, APTES, TES and HBDS, which were used as the precursor in plasma surface modification. In 2010, two important publications both reported the successful deposition by PECVD with good adhesion, respectively <sup>[81, 82]</sup>. Various surface characterization techniques have been employed and aimed to understand and further control the fabrication of APTES nanostructures by PECVD on thermoplastic substrates in ref.<sup>[81]</sup>. Gandhiraman et al.<sup>[82]</sup> confirms the presence of siloxane functionality is essential for film adhesion to substrate and indicates the presence of amine and amide functionalities, which are both important to further immobilization. In recent years, the use of PECVD for functionalizing APTES has undergone enormous expansion, however it remains only a few reports and still needs to be intensively studied <sup>[83-87]</sup>. Especially, the parameters such as gas selection, deposition time, working pressure, working power, substrate materials and so on, which strongly affect the resulting structure, coverage of the layers, etc., haven't been systemic investigated yet.



Fig. I-12 Chemical Structure of APTES

### 1.4 Catalysts and their immobilization

#### 1.4.1 Gold nanoparticles (AuNPs) as catalysts

In the perspective of chemical engineering, heterogeneous catalysis has acquired a vital role since it is a very efficient green approach. The main concepts of 32

green catalysis are as follows: (i) usage of eco-friendly solvents; (ii) avoidance of hazardous wastes; (iii) usage of recyclable catalysts; (iv) mild reaction conditions; and (v) high efficiency and selectivity. Over the past few years, heterogeneous catalysis by nano-gold catalysts has attracted the attention of researchers because it is a highly proficient substitute for non-separable and pollutant homogeneous catalysis. Actually gold is usually viewed as the most stable metal, but surprisingly it has been found that Au nanoparticles less than 3~5 nm in diameter are catalytically active for CO oxidation below room temperature <sup>[88]</sup>. Henceforward, the usage of gold nanoparticles (AuNPs) as an important catalyst for different kinds of chemical reactions (e.g. oxidation <sup>[89, 90]</sup>, hydrogenation <sup>[91]</sup>, hydroamination <sup>[92]</sup>, ring expansion <sup>[93, 94]</sup>, coupling reactions <sup>[95, 96]</sup>, etc.) has been studied after 90s. Besides, it has long been known that gold nanoparticles can strongly adsorb visible light due to the surface plasmon resonance (SPR) effect, which features a collective oscillation of conducting electrons of AuNPs with the electromagnetic field of the incident light. The feature indicates the AuNPs could become a quite efficient visible-light photocatalyst at ambient conditions in the photooxidation.

#### 1.4.2 Zeolite as a support material

Supported gold nanoparticles (GNPs) have been widely used in many catalytic reactions. Metal-support interaction (MSI) plays an important role in affecting the catalytic performances of supported nanocatalysts <sup>[97]</sup>. The nature of the support appears to be a critical point in determining the catalytic reaction mechanism <sup>[98]</sup>. For example, in the case of low-temperature CO oxidation, a support-assisted mechanism depended on the cooperation between metal and support is proposed when the reducible oxides are used. In the ref.<sup>[98]</sup>, the active oxides favor to provide reactive oxygen in a molecular form and dissociates at the metal-support interface, subsequently the carbon monoxide that chemisorbed on metallic gold particles is oxidized by those reactive oxygen. Also for non-reducible (-inert") oxides, such as
alumina and silica, little assistance is expected from the support and the reaction is supposed to proceed only on gold metal particles, where CO and  $O_2$  are both adsorbed and activated (gold-only mechanism). The other benefit of using supports is to achieve highly dispersed gold particles. It is well known that when the size of a gold nanoparticle is small enough its catalytic activity could be enhanced due to either a higher density of reactive defective sites or to a gradual change in the electronic structure of gold while decreasing size. However, gold particles tend to aggregate during catalytic reactions. Subsequently it would cause the decrease of surface energy of nanosize gold particles. To ensure an efficient reaction in heterogeneous catalysis, the active phase on the catalyst surface must be highly dispersed over a large specific surface area. Therefore, catalytically active species are usually immobilized on supports as very fine particles on the surface of a highly porous support material with high thermo stability, high surface area, and suitable mechanical strength <sup>[99]</sup>.

Zeolite is the broad term used to describe a family of minerals called tectosilicates. These minerals contain small pores that provide a generous surface area. Zeolites are constructed of tetrahedral AlO<sub>4</sub> and SiO<sub>4</sub> molecules bound by oxygen atoms <sup>[100]</sup>. Currently, there are 40 known natural zeolites and in excess of 140 synthetic zeolites (e.g. silicalite, ZSM-5, Beta, mordenite, faujasite and so on). Zeolites can be custom made by manipulating the structure, silica-alumina ratio, pore size, and density. The faujasite (FAU) type zeolite has cavities with a diameter of 1.3 nm interconnected by pores of 0.74 nm; depending on the Si/Al ratio, it can be classified into X type (Si/Al = 1.0~1.5) and Y type (Si/Al > 1.5). Y type zeolite (See Fig. I-13) plays an important role in chemical industry due to its large surfaces, strong acid sites, excellent shape selectivity <sup>[101]</sup> and has attracted researchers' attention in recent years. Many applications have been reported such as separation of chemicals <sup>[102]</sup>, catalysis <sup>[103, 104]</sup> and so on. More important, other metals catalyst can be incorporated into zeolites to obtain specific catalytic properties. A certain number of studies were carried out on the preparation of gold-based catalysts supported on

zeolites <sup>[105, 106]</sup>. Okumura et al. report the performance of gold loaded on Y type zeolite in the CO-O<sub>2</sub> reaction <sup>[107]</sup>. Zhang and co-workers announce a catalytic activity improvement in alcohol oxidation with Au-zeolite catalysts and furthermore propose a photo oxidation mechanism that originates from zeolite absorption <sup>[108]</sup>. Compared with other supports, zeolite could atomically disperse gold catalyst with a high degree of uniformity <sup>[109]</sup>; Moreover, zeolite could be considered as a specific catalyst in some reactions <sup>[110-112]</sup>.



Fig. I-13 Structures of Y type zeolite.

## 1.4.3 Synthesis of AuNPs

Gold nanoparticles have been synthesized by various methods. Conventionally, the Turkevich method is widely used to produce water-soluble gold nanoparticles, in which  $AuCl_4^-$  is reduced by sodium citrate in water <sup>[113]</sup>. Over the last six decades, the results from different research groups on the study of Turkevich method indicate the key process parameters for AuNPs synthesis are the pH of the reaction mixture, the reactant concentrations, the ionic strength, which affect the distribution of hydroxy-chloroauric species in solution, the zeta potential and the screening strength to alter the rates of reduction, nucleation and aggregation; and thereby, influence the final particle size distribution. For example, Fig. I-14 shows the influence of adding chloroauric acid and citrate on the size of AuNPs <sup>[115]</sup>.



Fig. I-14 Effect of reversing the order of addition of reactants. Overall chloroauric acid concentration was maintained constant at 0.254 mM. (a-f) Representative Transmission electron Microscope (TEM) (a and b) and Field Emission Scanning Electron Microscope (FESEM) images (c-f) with histograms of particle size distributions as insets for colloids synthesized by the standard and reversed order of addition of reactants at three MR values of 20.8, 5.2 and 1.0<sup>[114]</sup>.



Fig. I-15 (a) Final spectra obtained for GNPs synthesis undertaken with a citrate to gold ratio of 5 at different pH. (b) Time evolution of the absorbance at the final  $k_{max}$ (pH 4.5: $k_{max} = 540$  nm, pH 7:  $k_{max} = 523$  nm, pH 9:  $k_{max} = 540$  nm) as a function of time for synthesis undertaken at different pH<sup>[115]</sup>.

## 1.4.4 Immobilization of AuNPs

Conventionally the immobilization of gold nanoparticles is done through an intermediate layer of organic molecules pre-deposited on the solid surface. Due to the terminal functional groups from organic molecules, the nanoparticle could be anchored on the surface through electrostatic or chemical interactions <sup>[12, 23, 78]</sup>. These connections should also be stable over time and the interaction of the nanoparticles with the surface should be strong enough to ensure that the nanoparticles remains attached to the surface during further functionalization and upon utilization. Among the large variety of available organosilanes, aminopropyltriethoxysilane (APTES) <sup>[12]</sup> and (3-mercaptopropyl)trimethoxysilane (MPTES) <sup>[12, 23]</sup> with functionalities (amine group and thiol group) are the most commonly used linkage reagents, which are respectively related to the electrostatic bonding and covalent bonding to gold (The immobilization process is shown in Fig. I-16 <sup>[12]</sup>). However, it is still not clear which reagent is better for gold supported on zeolite, even though it has been announced that weak interaction originates from electrostatic bonding, while strong interaction obtained from covalent bonding



Fig. I-16 Gold nanoparticle immobilization with APTES and MPTES anchoring agent <sup>[12]</sup>.

## 1.4.5 Deposition zeolite and gold@zeolite on substrate surface

Assembly of small molecules in the form of thin films or organization of small molecules into highly ordered arrays of molecules on various substrates has been the focus of intense interest since the rise of materials chemistry. During the last two decades, nanobuilding blocks (1~10 nm) have been evidenced to be easily organized, however micrometer-sized building blocks have not yet been considered as a class of building blocks despite the fact that the ability to organize them will make materials chemistry flourish <sup>[116]</sup>. The fact is that the zeolites or zeolites@gold with a usual size range of 100~1000nm encounter obstacles for well-organization on substrate surfaces.



*Fig.I-17 Procedure to attach zeolite-A crystals onto glass through surface-tethered aminopropyl and EP groups*<sup>[117]</sup>.

Depending on the conception of immobilizing gold, the assembly of zeolites or zeolites@gold on the substrate surface could be also prepared through electrostatic and/or covalent molecules <sup>[118, 119]</sup>. For example, Kulak et al. deposited the monolayer of aminopropyl-tethering zeolite-A microcrystals on 3-(2, 3-epoxypropoxy) propylsilyl (EP)-coated glass plates (Fig. I-17) <sup>[117]</sup>. In order to create a strong adhesion between surface and zeolites or zeolites@gold, the linking reagent is the key factor for functionalized assembly. For amine substrate surface, а carboxyethylsilanetriol sodium (CES) has been reported a promising linkage reagent as it would provide good connection for negative changed zeolite and positive charged substrate surface through the presence of  $-NH_3^+/-COO^-$  zwitterionic pairs <sup>[120]</sup>. However there are few articles that report the use of CES for attaching zeolite catalysts. The study of this link reagent could be a promising progress in the field of assembling zeolite on surfaces.

## 1.5 Application: oxidation in microreactors

## 1.5.1 Liquid phase oxidation of benzyl alcohol and its products

Benzaldehyde is an important organic intermediates or valuable components, which has widespread applications in perfumery, dyestuff and agro chemical industries <sup>[121, 122]</sup>. Commercially, it is obtained mainly through the hydrolysis of benzal chloride and the oxidation of toluene <sup>[123]</sup>. However, benzaldehyde produced from the former route inevitably suffered from the problem of chlorine contamination while the selectivity in the latter is very poor. Thus, it is a challenge to develop an environmentally benign reaction process with high product selectivity. Recently the study of liquid phase oxidation of alcohols to aldehydes, in particular benzyl alcohol to benzaldehyde, is evidenced as an important organic transformation and has been a hot topic in modern organic synthesis <sup>[124]</sup>. The oxidation reactants commonly used in this process are oxygen <sup>[125]</sup>, hydrogen peroxide <sup>[126, 127]</sup> or even air <sup>[128]</sup> instead of stoichiometric amounts of inorganic or organic oxidants. The advantage of using such oxidants lies in the formation of water as the sole co-product and the low cost of the oxygen/air and therefore the selective oxidation of benzyl alcohol reaction with supported gold catalysts and hydrogen peroxide are considered as a beautiful example of -green" chemistry. Moreover, as the mild reaction conditions (e.g. lower temperature or atmospheric pressure) are used for creating a simplified reaction route, the presence of base are evidenced to be essential for reaction activity (as reaction promoter)<sup>[124]</sup>.

Although the target product is benzaldehyde, other by-products are also

obtained after the reaction. In previous report <sup>[129]</sup>, Benzyl alcohol can undergo a range of reactions, namely (a) oxidation to form benzaldehyde (2), benzoic acid (3), and benzyl benzoate (4); (b) disproportionation to form benzaldehyde (2), toluene (5), and water ; (c) dehydration to form dibenzylether (6); and (d) self-condensation (benzylation) to form anthracene (7) and stilbene (8) as shown in Fig. I-18. In low temperature liquid-phase oxidation only reactions (a) and (b) are typically observed as the reactions are highly dependent on the reaction conditions. Obviously, it will be a huge challenge to improve the selectivity to benzaldehyde by avoiding the formation of benzoic acid and benzyl benzoate.



*Fig. I-18 Reactions involving benzyl alcohol 1 over gold-containing catalysts: (a) oxidation, (b) disproportionation, (c) dehydration, and (d) self-condensation (benzylation)*<sup>[129].</sup>

### **1.5.2** Influence of reaction conditions

The reaction variables such as reaction time, temperature, catalyst amount (e.g. gold loading), substrate to oxidant mole ratio, amount of solvent etc. influence the benzyl alcohol conversion and selectivity to benzaldehyde <sup>[126, 129, 130]</sup>. For example, the main oxidation product from benzyl alcohol is benzaldehyde with benzoic acidand benzyl benzoate as by-products (Fig. I-18 (a)), indicating that the oxidation occurs within the consecutive reactions. Based on the reaction route, to increase the conversion of benzyl aclohol, the reaction time needs to be prolonged <sup>[131]</sup>. However, the selectivity to benzaldehyde will be decreased due to subsequent reaction of <sup>40</sup>



benzaldehyde to benzoic acid and/or benzyl benzoate (Fig. I-19<sup>[126]</sup>).

Fig. I-19 Effect of reaction time on the conversion of benzyl alcohol and product selectivity

[126]



*Fig. I-20 Dependence of the conversion of BzOH and selectivity to BzH on amount of the catalyst* <sup>[127]</sup>.

The temperature is another essential parameter that affects the on the reaction. From the reports of Yu et al., Behera et al. <sup>[131]</sup>, Wang et al. <sup>[16]</sup> and so on, the appropriate temperature should be set between 20~100 °C. It is also noticed that benzyl alcohol conversion largely increases <sup>[127]</sup> but benzaldehyde selectivity exhibits a significantly drop when it reaches the high temperature <sup>[131]</sup>. Besides, the catalyst amount take an effort on the oxidation as Ma et al. investigate the influence of different gold loading and the results indicate variation of benzyl alcohol conversion and selectivity to benzaldehyde are observed with increasing gold amount <sup>[124]</sup>. The change of catalytic activity by using various amount of catalyst is also reported in the work of Yu et al. (Fig. I-20 <sup>[127]</sup>). Therefore, the suitable reaction conditions should be strictly selected for our study.

The size of AuNPs is also considered as the key factor to affect the catalytic activity, theoretically the decrease of size of gold particle would benefit in exposing more active sites, subsequently leads to the improvement of catalytic effect <sup>[132, 133]</sup>. In Ref. [12], the bigger particle size of the citrate-Au (15nm) exhibits obivious weaker catalytic activity compared to the 2-3 nm size of the PVA- and PVP-Au nanoparticles. Moreover, compared with pure AuNPs, the supported gold particles have been reported to perform higher catalytic efficiency for the oxidation of alcohols <sup>[124, 134]</sup>. The nature of support is important for determining the gold catalyst's performance, various supports used for gold would result in different catalytic activities, for example, Karimi et al. test using a number of selected Au-supported catalysts such as Au@SBA15, Au@SBA-15-Pr-NR<sup>3+</sup>X, Au@SBA-15-Ph and Au@TiO<sub>2</sub> under the same reaction conditions and with the same loading of Au, but only <5%, 28%, 40% and 15% yields of benzaldehyde are obtained after oxidation <sup>[125]</sup>. On the other hand, the activity of supported gold nanoparticles is not only influenced by the nature of the support but it can also be affected by other factors including size of particles, surface area and pore size distribution of the support. It's very important to take those factors into account in our study.

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## 1.5.3 Recent studies of using microsystem for benzyl alcohol oxidation

There are only two released publications focusing on the application of AuNPs immobilized microchannels for benzyl alcohol oxidation in recent years: Ftouni et al. <sup>[12]</sup> announce a series of gold-immobilized capillary column microfluidic devices used for this reaction. In their study, three different types of gold nanoparticles (Citrate-Au, PVP-Au, PVA-Au) are immobilized onto the fused silica inner wall with two different linkers (APTES and MPTES). The oxidation of benzyl alcohol in the presence of  $H_2O_2$  is carried out under the reaction conditions (80 °C, resident time = 639 s). The results shown in Fig. I-21 reveal a very high selectivity to benzoic acid whatever the size of gold particles is used in microsystem.



Fig. I-21 Benzoic acid yields as a function of the microreactor composition within time <sup>[12]</sup>.

Wang et al. <sup>[16]</sup> evidence that gold-immobilized capillary column microfluidic devices could be utilized for converting various alcohols into the desired products quantitatively. They use an amine functionalized capillary column microreactor (50 cm length, 250 mm inner diameter), which is immobilized with microencapsulated AuNPs. The benzyl alcohol oxidation is firstly carried out in an organic solvent

(1-Phenylethanol) with oxygen gas. Almost 99% conversion was retained after 4 days and no leaching of gold was observed, indicating a good stability of gold immobilized on channel surface. Moreover, the scope of the aerobic oxidation of alcohols in this reactor is studied using benzylic, aliphatic, allylic, and other alcohols. All the alcohols are successfully oxidized to the corresponding ketones in excellent yields. However, in this work the selectivity to benzaldehyde is also not high when only AuNPs is used (53%), especially taking account into the reported benzyl alcohol oxidation in batch <sup>[108, 124, 129]</sup>, implying an optimization should be processed in the future work. The previous reports confirm that the concept of developing microreactor immobilized with gold nanoparticles is a feasible solution for the oxidation of benzyl alcohol; To date, the method used for nanoparticles immobilization consists in wet chemistry silanation with organic compounds, which is a conventional method and has exhibited many disadvantages i.e. long treatment time, low functionality amount, etc. The development of other immobilization methods like plasma-deposited APTES has extended the scope of the conception for preparation fixed nanoparticle catalyst on microchannel surface. Furthermore, it could be extended with zeolites supported gold. Therefore, the benzyl oxidation carried out in microreactors by immobilizing the gold@zeolite catalyst on the microchannel wall, would benefit from not only the high efficient mass transfer due to the nature of microreactor, but also the combination effect of a gold-zeolite catalysis system. Predictably, this microreactor would exhibit better catalytic performance than that in batch.

## **1.6 Objectives of this work**

This work aims not only at designing and fabricating new microfluidic chips for benzyl alcohol oxidation, but also at developing a methodology of plasma devoted to the surface functionalization with linkage reagent in order to anchor catalyst particles in the next step. We also expect to obtain a better gold particle covered surface through preparing gold immobilized surfaces using different functionalization methods with the same link reagent. Moreover, the comparison study of using different reagent will show us the better linkage reagent for attaching gold. Based on the same conception of using linkage reagent, we hope to acquire a good assembly of zeolite or Au@zeolite deposition on surface. In order to achieve those goals, we firstly investigate the influences of plasma parameters on the formation of amine contained polymerized coatings during Plasma enhanced chemical vapor deposition (PECVD) process. The highest amount of amine is obtained through optimizing the plasma conditions. Thereafter, nanosize gold particles are immobilized on amine functionalized glass substrate surfaces using wet chemistry method and PECVD method with (3-aminopropyl)triethoxysilane (APTES), respectively. The comparison study would evidence the advantage of using PECVD. Then, AuNPs are immobilized on Y type zeolite with APTES and (3-mercaptopropyl)trimethoxysilane (MPTES) at the same conditions. The results would give advice for choosing a better linkage reagent for our future study. Also, based the same idea of using ATPES and MPTES, another linkage reagent carboxyethylsilanetriol sodium (CES) is used for functionalizing zeolite and gold@zeolite. Subsequently, zeolites and gold@zeolites are deposited on the amine functionalized COC substrates and then tested for its possibility for using in microfluidic system. For the oxidation of benzyl alcohol, a COC made microfluidic chip is designed and fabricated by molding replication method. And then the chips are functionalized and immobilized with catalysts including gold, zeolite and gold@zeolite. Finally, the chips with catalysts are integrated in our microfluidic system consisted with syringe pumps, teflon connection tubes and micromixer chip. Benzyl alcohol and hydrogen peroxide in water are injected into the microsystem and catalysed by different catalytic microreactors, the products are collected at the end of system and characterized for identification the benzyl alcohol conversion, benzaldehyde selectivity and yield.

## 1.7 Outline

Seven chapters are included in this thesis. Chapter I introduces the research background of microsystem, PECVD and catalysts. Chapter II describes the characterization techniques related to the study of surface functionalization, gold immobilization and catalytic reaction in microsystems. Chapter III is about the study of amine functionalization on surface using PECVD. The comparison study of immobilization of AuNPs on substrate using wet chemistry method and PECVD method are discussed in the chapter IV. The immobilization of AuNPs on zeolite as well as the deposition of zeolite and Au@zeolite is studied in the chapter V. Chapter VI shows the application of our microsystems for benzyl alcohol oxidation. And finally chapter VII summarizes the whole research results and draws attention to the future research.

# **Chapter II Characterization methods**

## 2.1 Contact angle measurement

As shown in Fig. II-1, contact angle  $\theta$  is defined as the angle between tangent of gas-liquid interface and that of solid-liquid interface formed at the three phases' boundary where liquid, vapor and solid intersect. According to Young's equation (Equation II-1), there is a relationship between the contact angle  $\theta$ , the surface tension of the liquid  $\sigma_l$ , the interfacial tension  $\sigma_{sl}$  between liquid and solid and the surface free energy  $\sigma_s$  of the solid.

Equation II-1



Fig. II-1 Contact angle on surface.

The instrument generally called contact angle meter is used to measure the static contact angle, advancing and receding contact angles, and surface tension. The current generation of contact angle instruments is consisted with cameras and software to capture and analyze the drop shape and is better suited for dynamic and advanced studies. Based on the principle of water contact angle meter (Fig. II-2), it always includes:

- Sample stage and its control system
- Dosing system and its control system
- Vision system and its control system
- Environment chamber
- Drop shape analysis software

In this work, static water contact angle measurements were performed with a

GBX-3S processing system.



Fig. II-2 Schematic diagram of a contact angle meter.

## 2.2 Fourier Transform infrared spectroscopy (FTIR)

Infrared spectroscopy is an important technique in organic chemistry. It is an easy way to identify the presence of certain functional groups in a molecule. Also, one can use the unique collection of absorption bands to confirm the identity of a pure compound or to detect the presence of specific impurities. Fourier Transform Infrared (FT-IR) spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. A solution for measuring all of the infrared frequencies simultaneously was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal –interferogram" which has all of the infrared frequencies –encoded" into it. The signal could be measured in very short time. However, the measured interferogram signal cannot be interpreted directly. A means of –decoding" the individual frequencies is required. This can be accomplished via a well-known mathematical technique called the Fourier transformation. This transformation is performed by the computer which then presents the user with the desired spectral information for analysis. As shown in Fig. II-3, the essential parts of a FTIR spectrometer include:

- The IR source
- The interferometer
- Beamsplitter
- Mirror
- The sample compartment
- The detector
- The computer



Fig. II-3 Schematic diagram of a FTIR spectrometer (Thermo Nicolet).

As the sample is placed in the sample compartment, infrared energy is emitted from a glowing black-body source. This beam passes through an aperture which controls the amount of energy presented to the sample and then it enters the interferometer where the -spectral encoding" takes place. Thereafter, the resulting interferogram signal exits the interferometer. Henceforward, the beam goes into the sample compartment where it is transmitted through or reflected off of the surface of the sample, depending on the type of analysis being accomplished. This is where specific frequencies of energy, which are uniquely characteristic of the sample, are absorbed. Finally, the beam passes to the detector for final measurement. The detectors used are specially designed to measure the special interferogram signal. The measured signal is digitized and sent to the computer where the Fourier transformation takes place. The final infrared spectrum is then presented to the user for interpretation and any further manipulation.

FTIR spectroscopy includes the absorption, reflection, emission, or photoacoustic spectrum obtained by Fourier transform of an optical interferogram. FTIR spectroscopy has been used as the dominant technique for measuring the infrared (IR) absorption and emission spectra of most materials. The major advantage of the FTIR technique over dispersive spectroscopy methods is that practically all compounds show characteristic absorption/emission in the IR spectral region, therefore, they can be analyzed both quantitatively and qualitatively.

In attenuated total reflectance (ATR) mode, the detection depth is generally 1-2 $\mu$ m deep, but can be much less or a bit more dependent upon the material. Black, highly absorbing materials tend to have lower sampling depths and sometimes provide too weak a signal as a result. In transmission mode, area of analysis is about 1mm × 1mm. Liquid layer thickness may be from sub-micrometer to a few millimeters. Sample material may be dispersed on KBr pellets. The sample lateral dimensions may be at least 12 in × 12 in.

In this work, infrared spectra were acquired using a Fourier Transform Infrared Spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a germanium coated potassium bromide beam splitter (Bruker Ten-sor 27 spectrometer). Attenuated Total Reflectance mode was employed and the investigation range is from 600 and 4000 cm<sup>-1</sup> in order to obtain an overview of the main functional groups present in as deposited coating. The FTIR spectra were recorded after 44 scans with a resolution of 4 cm<sup>-1</sup>. Diffused Reflectance Infrared Fourier Transform (DRIFT) spectras were recorded on Tensor 27 spectrometer (Bruker, UK) in the range of 4000~400 cm<sup>-1</sup> using the KBr disk method.

# 2.3 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS), also known as ESCA (Electron spectroscopy for chemical analysis), is a surface-sensitive quantitative spectroscopic

technique that measures the elemental composition at the parts per thousand range, empirical formula, chemical state and electronic state of the elements that exist within a material. XPS spectra are obtained by irradiating a material with a beam of X-rays while simultaneously measuring the kinetic energy and number of electrons that escape from the top 0 to 10 nm of the material being analyzed. The conception of XPS originates from photoelectron effect as shown in Fig. II-4.



Fig. II-4 Photoelectron effect for XPS analyses

The main parts of a XPS system include:

- The X-rays source
- The ultra-high vacuum (UHV) stainless steel chamber with UHV pumps
- The electron collection lens
- The electron energy analyzer
- The mu-metal magnetic field shielding
- The electron detector
- The moderate vacuum sample introduction chamber
- The sample mounts
- The sample stage

## • The set of stage manipulators

The characterization process is as follows (Fig. II-5): Firstly, the sample is introduced in an ultrahigh vacuum chamber and irradiated with an X-ray beam. Then, the kinetic energy of emitted photoelectrons of all elements (except H and He) present at the surface is precisely measured. Meanwhile, the kinetic energy of the photoelectrons is determined by an electron energy analyzer. Finally, the identity, chemical state and quantity of an element are determined through from the binding energy determined from kinetic energy and intensity of a photoelectron peak. Area of peaks used in combination with sensitivity factors allow to calculate mole fractions with a detection limit of a few tenths of percent. A detailed analysis of certain well-resolved peaks allows quantifying functionalities present at the surface. On most recent systems the minimum spatial resolution is of about 15 µm and 5 µm for XPS analysis and XPS imaging respectively.



Fig. II-5 Schematic diagram of a XPS instrument.

In this work, the XPS spectra were collected using PHI 5600-ci XPS spectrometer (Physical Electronics, Eden Prairie, MN, USA). For survey and high resolution spectra, the anode used was a monochromatic Al (1486.6 eV) and a Mg K  $\alpha$  (1253.6 eV) X-ray sources at 200W, respectively. Analyses were performed with a 45° angle from the surface. The analyzed surface area was 0.005 cm<sup>2</sup>.

# 2.4 Spectroscopic ellipsometer

Ellipsometry is an optical technique for investigating the dielectric properties (complex refractive index or dielectric function) of thin films. An amplitude ratio and the phase difference is measured by recording a change in polarization as light reflects or transmits from a material structure. The measured response depends on optical properties and thickness of individual materials. Thus, ellipsometry is primarily used to determine film thickness and optical constants. However, it is also applied to characterize composition, crystallinity, roughness, doping concentration, and other material properties associated with a change in optical response.

The main components of a commercially XPS system include (Fig. II-6):

- The light source
- The polarizer
- The compensator (optional)
- The sample holder
- The analyzer
- The detector



Fig. II-6 Schematic diagram of an ellipsometer.

Electromagnetic radiation is emitted by a light source and linearly polarized by a polarizer. It can pass through an optional compensator (retarder, quarter wave plate)

and falls onto the sample. After reflection the radiation passes a compensator (optional) and a second polarizer, which is called an analyzer, and falls into the detector. Instead of the compensators, some ellipsometers use a phase-modulator in the path of the incident light beam. Ellipsometry is a specular optical technique (the angle of incidence equals the angle of reflection). The incident and the reflected beam span the plane of incidence. Light which is polarized parallel to this plane is named p-polarized (p-polarized). A polarization direction perpendicular is called s-polarized (s-polarized), accordingly.

In this work, a spectroscopic ellipsometer (Horriba UVISEL) was used for the investigation of the coating thickness, the operation conditions are 100 wavelengths between 250 and 830 nm at an angle of incidence of 75°.

## 2.5 Field-emission scanning electron microscopy (FESEM)

A scanning electron microscope is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons, which is considered to be a "non-destructive" characterization technique and could be repeatedly used for the same materials. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition. The electron beam is generally scanned in a raster scan pattern, and the beam's position is combined with the detected signal to produce an image.

The essential parts of all SEMs include (Fig. II-7):

- ◆ Electron source ("Gun")
- Electron lenses
- Sample stage

• Detectors for all signals of interest

• Display/Data output devices

• Infrastructure requirements:

- Power supply
- Vacuum system
- Cooling system
- Vibration-free floor
- Room free of ambient magnetic and electric fields



Fig. II-7 Schematic diagram of a scanning electron microscope.

Accelerated electrons in a SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE that are reflected from the sample by elastic scattering), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathode-luminescence-CL) and etc. In most cases, the type of signals produced by SEM is secondary electrons and backscattered electrons, which are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples, respectively.

In applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 50,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (EDS), crystalline structure, and crystal orientations (EBSD). The design and function of the SEM is very similar to the EPMA and considerable overlap in capabilities exists between the two instruments.

In this work, an FEI SIRION field-emission scanning electron microscope (FE-SEM) was used to examine the morphology of different titanium structures at an accelerating voltage of 20 kV. In order to obtain good electrical conductivity, the samples are coated with Pt or C. The mean elemental composition of each sample surface was analyzed with energy dispersive X-ray spectrometer (EDS) incorporated into the scanning electron microscope using the –area scanning" mode.

# 2.6 Transmission electron microscopy (TEM)

Transmission electron microscope (TEM) is in principle similar as a scanning electron microscope and can be applied to investigate some parameters of samples: e.g. morphology, chemical interdiffusion, grain size and orientation. Moreover, high-resolution transmission electron microscopy (HRTEM) imaging is a type of phase-contrast imaging and can reveal crystalline defects, second-phase or amorphous layers and atomic-resolution structure across boundaries, as well as information on the topography of the interface, provided that it is properly aligned in the direction of the electron beam. Otherwise, the selected-area electron diffraction (SAED) can be performed inside HRTEM image to obtain the crystallinity of samples. Energy-dispersive X-ray spectroscopy (EDS) was used to identify the chemical composition.

The basic set-up of the TEM includes:

- The electron gun
- The acceleration stage
- The condenser lens system
- The specimen stage
- The objective aperture

The most common mode of operation for a TEM utilizes bright field imaging. In the bright field mode, an aperture is placed in the back focal plane of the objective lens which allows only the direct beam to pass. In this case, the image results from a weakening of the direct beam by its interaction with the sample. As the electron beam passes through the sample, it is affected by the structures and composition of samples. Thicker regions of the samples or regions with a higher atomic number or crystalline areas will appear dark, while regions with no sample will appear bright. The transmitted beam is then projected onto a phosphor viewing screen or to be detected by a CCD camera. TEM gives sub-nanometer resolution but it requires extensive sample preparation for high resolution imaging.

In this work, the nanoscale morphology of the prepared nano-particulate materials (size, shape) was characterized by a 2000FX transmission electron microscope (JEOL, JAPAN) operating at 200 kV with LaB6 filament as the electron-beam source. Energy-dispersive X-ray spectroscopy (EDS) was used to identify the gold loading amount.

## 2.7 Zeta potential

Zeta potential is a scientific term for electrokinetic potential in colloidal dispersions (Fig. II-8). From a theoretical viewpoint, the zeta potential is the electric potential in the interfacial double layer (DL) at the location of the slipping plane relative to a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. The zeta potential is caused by the net electrical charge contained within the region bounded by the slipping plane, and also depends on the location of that plane. Thus it is widely used for quantification of the magnitude of the charge, which corresponds to the degree of electrostatic repulsion between adjacent, similarly charged particles in a dispersion.



Fig. II-8 Principle of zeta potential.

Zeta potential is not measurable directly but it can be calculated using theoretical models and an experimentally-determined electrophoretic mobility or dynamic electrophoretic mobility. Electrokinetic phenomena and electroacoustic phenomena are the usual sources of data for calculation of zeta potential. The zeta potential measurement is carried out by a dynamic light scattering instrument equipped with a zeta potential measurement analyzer.



Fig. II-9 Schematic diagram of a dynamic light scattering instrument.

The essential parts of a dynamic light scattering instrument include (Fig. II-9):

- The laser source
- The attenuator
- The sample cell
- The detectors
- The digital signal processor

In practice, measurements are made by adding a small amount of suspension or emulsion to the measurement cell and inserting the cell into the instrument. The particle motion due to the applied electric field is measured by light scattering. The particles are illuminated with laser light and therefore the particles scatter light. From the known applied electric field and measured particle velocity, the particle mobility is readily determined. Zeta potential is then calculated from mobility by using a model, the most common of which is the Smoluchowski model.

In this work, zeta-potential measurements were performed using a zetasizer Nano ZS from Malvern instrument.

# 2.8 X-ray diffraction (XRD)

X-ray diffraction as a non-destructive technique is commonly used to

determine the structural properties of crystalline materials. In 1912, German physicist Von found that the intensity of ray strengthens in some directions and weakens in some other ones was observed when a beam of X-ray goes through the crystal. Thereafter, the study of crystal structure was developed via investigating diffraction patterns. With the discovery of Bragg's law, the conditions that diffraction would happen could be briefly identified. The diffraction effects are observed when electromagnetic radiation impinges on periodic structures with geometrical variations on the length scale of the wavelength of the radiation. The interatomic distances in crystals and molecules amount to 0.15~0.4 nm which correspond in the electromagnetic spectrum at of X-rays having photon energies between 3 and 8keV. Analysis of diffraction peak can provide the following information: identification of compound or phase, crystallinity, strain, crystallite size, orientation. For phase identification, each crystal has its unique structural parameter and produces a unique diffraction pattern. If different crystals are mixed, superposition of diffraction pattern appears without interfering each other. Different phases of the same compound could be identified with the diffraction data.



Fig. II-10 Schematic diagram of a diffractometer.

As shown in Fig. II-10, X-rays are generated in a cathode ray tube by heating a

filament to produce electrons, accelerating the electrons toward a target by applying a voltage, and bombarding the target material with electrons. When electrons have sufficient energy to dislodge inner shell electrons of the target material, characteristic X-ray spectra are produced. These spectra consist of several components, the most common being K $\alpha$  and K $\beta$ . K $\alpha$  consists, in part, of K $\alpha$ 1 and K $\alpha$ 2. K $\alpha$ 1 has a slightly shorter wavelength and twice the intensity as K $\alpha$ 2. The specific wavelengths are characteristic of the target material (Cu, Fe, Mo, Cr). Filtering, by foils or crystal monochrometers, is required to produce monochromatic X-rays needed for diffraction. Kaland Ka2 are sufficiently close in wavelength such that a weighted average of the two is used. Copper is the most common target material for single-crystal diffraction, with CuK $\alpha$  radiation = 1.5418Å. These X-rays are collimated and directed onto the sample. As the sample and detector are rotated, the intensity of the reflected X-rays is recorded. When the geometry of the incident X-rays impinging the sample satisfies the Bragg Equation, constructive interference occurs and a peak in intensity occurs. A detector records and processes this X-ray signal and converts the signal to a count rate which is then output to a device such as a printer or computer monitor.

The essential parts of the diffractometer include:

- X-ray tube: the source of X Rays;
- Incident-beam optic: condition the X-ray beam;
- Goniometer: the platform that holds and moves the sample, optics, detector, and/or tube;
- Receiving-side optics: condition the X-ray beam after it has encountered the sample;

• Detector: count the number of X-rays scattered by the sample.

In this work all the X-ray diffraction (XRD) patterns were collected on an X'Pert Pro diffractometer with CuKa radiation operating at 45 kV and 40 mA in the range of 5~55° (PANalytical, Netherland).

# 2.9 Ultraviolet-visible spectroscopy (UV-Vis)

Ultraviolet and visible (UV-Vis) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Ultraviolet-visible spectroscopy (UV-Vis) involves the spectroscopy of photons in the UV-visible region. The absorption of UV or visible radiation is not induced by the molecular vibrations like in the IR spectroscopy but by the electronic transitions. At nanometer scales, electron cloud can oscillate on the nanoparticles surface and absorb electromagnetic radiation at a particular energy. This is so-called surface plasmon resonance. The energy of the radiation can be calculated by the equation:

#### γ Equation II-2

Thus the energy of the radiation in the visible range is generally: 36 to 72 kcal/mole while that in the ultraviolet range goes as high as 143 kcal/mole. This energy irradiated on the molecules can result in changes in the electronic nature of the molecule i.e. changes between ground state and excited states of electrons within the system. The electrons in a molecule can be of one of three types: namely  $\sigma$  (single bond),  $\pi$  (multiple-bond), or non-bonding (n- caused by lone pairs). When imparted with energy in the form of light radiation, these electrons get excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) and the resulting species is known as the excited state or anti-bonding state. Most of the absorption in the ultraviolet-visible spectroscopy occurs due to  $\pi$ -electron transitions or n-electron transitions. Each electronic state is well defined for a particular system i.e. a double bond in 2-butene would have a particular energy level for the  $\pi$ -electons which when absorbs a specific (or quantized) amount of energy would get excited to the  $\pi^*$  energy level for the electrons. The different transitions between the bonding and anti-bonding electronic states are presented in Fig. II-11.



Fig. II-11 Different transitions between the bonding and anti-bonding electronic states when

light energy is absorbed in UV-Visible Spectroscopy.

The essential parts of a spectrometer include:

- The light source
- The entrance slit
- The dispersion device
- The exit slit
- The sample holder
- The detector



Fig. II-12 Schematic diagram of a UV-Vis spectrometer.

When a sample is exposed to light energy that matches the energy difference between a possible electronic transition within the molecule, a fraction of the light energy would be absorbed by the molecule and the electrons would be promoted to the higher energy state orbital. A spectrometer records the degree of absorption by a sample at different wavelengths and the resulting plot of absorbance (A) versus wavelength ( $\lambda$ ) is known as a spectrum. The wavelength at which the sample absorbs the maximum amount of light is known as  $\lambda$ max.

In this work, a spectrophotometer (Ocean optics, USA) was used to obtain UV-Vis absorption spectra of colloidal AuNPs.

## 2.10 High performance liquid chromatography (HPLC)

High-performance liquid chromatography (HPLC; formerly referred to as high-pressure liquid chromatography), is a technique in analytical chemistry used to separate, identify, and quantify each component in a mixture. It relies on pumps to pass a pressurized liquid solvent containing the sample mixture through a column filled with a solid adsorbent material. Each component in the sample interacts slightly differently with the adsorbent material, causing different flow rates for the different components and leading to the separation of the components as they flow out the column. Conventionally, the HPLC is classified into two different types: (1) Normal phase HPLC, the polar compounds in the mixture being passed through the column will stick longer to the polar silica than non-polar compounds will. The non-polar ones will therefore pass more quickly through the column. The column is filled with tiny silica particles and the solvent is non-polar. A typical column has an internal diameter of 4.6 mm (and may be less than that), and a length of 150 to 250 mm. However, it isn't the most commonly used form of HPLC. (2) Reversed phase HPLC, the column used has the same size but the silica is modified to make it non-polar by attaching long hydrocarbon chains to its surface typically with either 8 or 18 carbon atoms in them. There will be a strong attraction between the polar solvent and polar molecules in the mixture being passed through the column, on the contrary there won't be as much attraction between the hydrocarbon chains attached to the silica (the stationary phase) and the polar molecules in the solution. Polar molecules in the mixture will therefore spend most of their time moving with the solvent. It is noted that reversed phase HPLC is the most commonly used form of HPLC.

The typical HPLC system includes (Fig. II-13):

- The solvent reservoir
- The pump system
- The sample injection system
- The HPLC column
- The detector
- The processing unit and display system

During the characterization, solvent used as mobile phase must be degassed to eliminate bubbles before being mixed. The elimination of oxygen dissolved in solvent will improve the detection of UV detector. The mixture of solvent is driven into chromatography column under high pressure. The sample is injected automatically. The detector is used to record the components flowing through the column. There are various detectors depending on different principle of detection such as inflorescent detector, UV detector and photochemical detector and so on. Different components flowing through column will be recorded as different peaks. In the most cases, a UV detector is used as some organic components are able to absorb the UV light of various wavelengths. When a beam of UV light shine through the stream of liquid flowing through the column, a UV detector on the opposite side of the stream will show a reading, which indicates how much UV is absorbed by the liquid. Given that the solvent similarly absorb UV light, it is essential to avoid the UV spectrum of solvent. The output will be recorded as a series of peaks representing different components in the solution.



Fig. II-13 Schematic diagram of a HPLC system

# Chapter III Deposition of amine groups by means of APTES PECVD process

# 3.1 Abstract

A low-cost, high reproducible and ecofriendly plasma enhanced chemical vapor deposition (PECVD) was used to prepare polymerized thin coating of amine groups by a homemade plasma reactor. (3-aminopropyl)triethoxysilane (APTES) was chosen as precursor, providing the terminal amine functionalities for further catalyst immobilization. In this work, we studied the influence of plasma process parameters (gas composition and deposition time) on the physico-chemical properties of plasma polymerized coatings. The study has been carried out on different substrates i.e. Cyclic Olefin Copolymer (COC), glass and silicon substrates. Special attention has been paid to assess the amine content, using different complementary surface analyses such as water contact angle measurement (WCA), X-ray photoelectron spectroscopy (XPS), Fourier Transform infrared spectroscopy (FTIR) and spectroscopic ellipsometer. The results clearly evidence that under optimized conditions, PECVD is a universal method for depositing APTES on various substrates.

Keywords: PECVD, amine groups, APTES

# **3.2 Introduction**

Recently, micro- and nanofluidic channel surfaces immobilized with catalysts have been widely used in the system on a chip due to their advantages such as continuous flow mixing, high recovering frequency, low clogging risk, etc. <sup>[12, 16,</sup> <sup>135-137]</sup> The key point for developing immobilizable channel surfaces that could be further immobilized lies in the raw materials for reactor fabrication and the modified surface for catalysts immobilization (or deposition). From a manufacturing point of view, materials including glass, polymers and silicon are considered as potential candidates and have been reported for microchip fabrication in the last two decades <sup>[30,</sup> <sup>138-142]</sup>. On the other hand, silanization agents with functional end-groups, e.g. -NH2,-SH,-COOH... are often used for functionalizing surface [23, 143-147], thereby allowing further binding to catalysts. Among known reagents, the (3-aminopropyl)triethoxysilane (APTES), an aminosilane with a chemical formula NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub> is considered as one of the most popular surface modification reagents and has been widely used <sup>[12, 146, 148]</sup>. The alkoxy groups of the silane molecules react with the hydroxyl groups on the substrate surface leading to the formation of Si-O bonds and leaving the terminal functional amine groups available for catalysts immobilization<sup>[149]</sup>. Naturally, the silanization process includes two steps: the substrate surface hydroxylation and the APTES ethoxy hydrolysis. In spite of massive researches on APTES silanization, the most popular experiment conception is still to dedicate the process to wet chemistry treatment <sup>[22, 150]</sup>, which is commonly used for years however appealing many drawbacks, e.g. long reaction time, complicated process, low deposition rate, etc. <sup>[151-153]</sup>

Plasma enhanced chemical vapor deposition (PECVD) offers another alternative and the opportunity to overcome those mentioned above by providing a simplified fast deposition process, which is reported being low-cost, high reproducible and ecofriendly <sup>[154, 155]</sup>. Due to the characteristics of plasma polymerization of organosilion compounds <sup>[75, 156, 157]</sup>, the unique functionalization coating that is <sup>68</sup>

achieved by a plasma process exhibits good chemical stability, high degree of cross linking and strong bonding strength to substrate compared to the coating that is fabricated by wet chemistry treatment. Although PECVD has undergone enormous expansion in the field of surface modification during years, it remains only a few reports about applying this technique for APTES deposition <sup>[81, 83, 85-87, 158]</sup>. Moreover, the ability of organosilane molecules to polymerize on the surface, the resulting structure, coverage of the layers and so on, which are highly dependent on several process parameters such as gas selection, deposition time, working pressure, power supply, substrate materials..., have not been systemically studied in already released publications.

The main aim of this work is to functionalize different materials using PECVD with APTES and then to further the understanding of influence of different plasma parameters on coating characteristics. In order to achieve this goal, polymerized APTES coatings were deposited on different substrates using a homemade low pressure plasma reactor. The deposited thin coatings were characterized by complementary analytical techniques such as water contact angle (WCA), X-ray photoelectron spectroscopy (XPS), Fourier Transform Infrared-Attenuated Total Reflectance (FTIR-ATR) spectroscopy and ellipsometry measurements.

## **3.3 Experimental**

### 3.3.1 Materials and chemicals

Glass, Cyclic Olefin Copolymer (COC) and silicon dishes were cut into small rectangular flakes with length × width of 8mm × 8mm. Glass flakes were cleaned by using an aqueous 20% RBS detergent solution purchased from TumaChem (in water) in ultrasonic bath for 10min and then were rinsed by deionized water, while silicon and COC were ultrasonically cleaned in ethanol and acetone for 10min for each, respectively. Finally, all the samples were dried by high pressure air. APTES
$(NH_2(CH_2)_3-Si(OC_2H_5)_3, 100g, 98\%)$  was purchased from VWR, ethanol and acetone were analytic reagent grade. Pure Ar, O<sub>2</sub> and N<sub>2</sub> were used for generating plasma; purity of each was higher than 99.99%.

# 3.3.2 APTES plasma polymerization



Fig. III-1 The bell-jar reactor used for the plasma deposition of APTES.

The homemade experimental device used for the APTES plasma deposition is a bell-jar reactor, including a blade-type HV electrode-grounded cylinder, a pumping system (a turbo molecular pump and a chemical pump), a gas bubbling tube and an industrial low-frequency power generator (70kHz, STT-France), as shown in Fig. III-1. The detail device introduction has been described elsewhere <sup>[159]</sup>. The Samples is fixed by a double-face scotch tape on the central vertical band of the rotating grounded cylinder around which was previously wrapped by low-density polyethylene film (LDPE, Goodfellow). As the width of plasma discharge zone is estimated to 0.5 mm, the surface of the cylindrical grounded electrode is divided in 44 zones. For a rotation speed of 1 turn/s, the real treatment time ( $t_{real}$ ) for each zone (i.e., the plasma exposure time of a zone of the sample) is obtained from the following 70 equation:

### Equation III-1

where  $t_{exp}$  is the experience time. All the times mentioned in the following of this will be  $t_{real}$ .

The bell-jar chamber was initially evacuated by a turbo molecular pump (Pfeiffer) and a chemical pump (Pfeiffer) until pressure reaches 10<sup>-3</sup> mbar. Thereafter the working pressure was maintained at an accurate prescribed value by solely using the chemical pump during plasma was working on. Once the power generator was turned on, the plasma was produced in the gap between the stainless steel blade (hollow) and the grounded rotating cylinder. The former electrode also served for gas introduction; the gaseous APTES monomer was produced by bubbling gas (Ar) in a 20 mL round-bottom flask containing the APTES liquid heated at a constant temperature of 80°C. The whole PECVD process includes 2-step protocol:

(i) Pretreatment.

This step activates the surface before deposition since the oxygen present as traces in the reactor is excited by Ar plasma, which leads to a partial oxidation of the topmost layer <sup>[142]</sup>. It will provide a better adhesion of the deposited film. Moreover, the Ar pretreatment is also benefit in cleaning off the surface of the samples from eventual adsorbed atmospheric contaminants. The working pressure was fixed at 0.7mBar, the samples were subjected to a 20 W plasma treatment (gas: Ar; gas inlet: 1#; flow rate: 10 sccm) during 5 s.

(ii) APTES deposition

After pretreatment, the system was pumped down by fully loading chemical pump. Then, a gaseous mixture composed of active gas (gas: Ar,  $O_2$  or  $N_2$ ; gas inlet: 1#; flow rate: 20 sccm) and vector gas (gas: Ar; gas inlet: 2#; flow rate: 10 sccm) with APTES was introduced in the reactor. The parameters used in this work are presented in Table III-1.

After plasma deposition, the chemical pump was fully loaded again while the

turbo molecular pump was stopped immediately. The freshly coated flakes were kept under vacuum for 1 h before venting, in order to reduce post-oxidative reactions between radicals formed on the film surface and atmospheric oxygen <sup>[160]</sup>.

Active gas	Substrate	Working pressure (mbar)	Working power (W)	Deposition Time (s)	Precursor and Carrier gas
Ar, O <sub>2</sub> , N <sub>2</sub> ,	Glass, Si,	0515	10 40	5 80	APTES/Ar,
Flow:20sccm	COC	0.5~1.5	10~40	3~80	Flow: 10sccm

Table III-1	Plasma	parameter	in	this	work
10010 111 1	1 institu	parameter	<i>uu</i>	11110	110110

# 3.3.3 Characterization

Static water contact angle measurements were performed with a GBX-3S processing system using deionized water (liquid droplet volume: 4  $\mu$ L). The reported advancing contact angle value corresponds to the average of three measurements on different areas of each sample. In order to study the stability of the APTES coatings, the samples have been rinsed by deionized water and evaluated afterwards.

Infrared spectra were acquired using a Fourier Transform Infrared Spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a germanium coated potassium bromide beam splitter (Bruker Ten-sor 27 spectrometer). Attenuated Total Reflectance mode was employed and the investigation range is from 600 and 4000 cm<sup>-1</sup> in order to obtain an overview of the main functional groups present in as deposited coating. The FTIR spectra were recorded after 44 scans with a resolution of 4 cm<sup>-1</sup>.

XPS spectra were collected using PHI 5600-ci XPS spectrometer (Physical Electronics, Eden Prairie, MN, USA). For survey and high resolution spectra, the anode used was a monochromatic Al (1486.6 eV) and an Mg K  $\alpha$  (1253.6 eV) X-ray sources at 200 W, respectively. Analyses were performed with a 45° angle from the surface. The analyzed surface area was 0.005 cm<sup>2</sup>. Curve fitting for the high

resolution  $C_{1s}$  core level peaks was done by using the XPS PEAK Software (version4.1) by means of a least square peak fitting procedure using a Gaussian-Lorentzian function (30% Lorentzian) and a Shirley baseline fitting. For the deconvolution procedure, the full width at half maximum (fwhm) are maintained constant with reference to the fwhm of the  $CH_x$  component. Depending on the carbon bond and its more or less electron negative partner, the carbon groups were assigned to the corresponding positions. The quality of the peak syntheses were evaluated by themaximal residual standard deviation (residual STD) method. An analysis was considered significant if the residue is close to unity. On each sample, three different spots were analysed. Finally, the binding energy scale was corrected for the neutraliser shift by using the  $C_{1s}$  signal from saturated hydrocarbon at 285.0 eV as an internal standard.

The coating thickness was investigated by a spectroscopic ellipsometer (Horiba UVISEL) using 100 wavelengths between 250 and 830 nm at an angle of incidence of 75°. The thickness is average value of three measurements performed at three different spots on silicon wafers coated with APTES film. In order to study the stability of the APTES coatings, the samples have been rinsed by deionized water and evaluated afterwards.

# 3.4 Results and discussion

### 3.4.1 Active gas selection

Ar,  $O_2$  and  $N_2$  are the most frequently used active gas for PECVD process and has been introduced for APTES deposition in as reported studies <sup>[83, 84]</sup>. In order to investigate the influence of different active gas,  $Ar/O_2/N_2$  was separately used for generating plasma during APTES deposition process on glass; and the plasma parameters are presented in Table III-2.

Table III-2 Plasma parameters for the study of active gas selection

Active gas	Substrate	Working pressure (mbar)	Working power (W)	Deposition Time (s)	Precursor and Carrier gas
Ar, O <sub>2</sub> , N <sub>2</sub> ,	Glass	0.5	25	5	APTES/Ar,
Flow:20sccm	Olass	0.5	23	5	Flow: 10sccm

The initial result regarding plasma-polymerized thin coatings concerns water contact angle as a function of active gas selection as shown in Fig. III-2. Compared to the wettability of the original glass surface (WCA<sub>raw glass</sub> $\approx 0^{\circ}$ ), WCA data verifies an increase of water contact angle after plasma deposition performed on glass surfaces. The changes of WCA before and after plasma polymerization could be related with the chemical structure of APTES. The hydrophobic alkane groups in APTES may result in the increase of WCA, which is consistent with reported research <sup>[161]</sup>.



Fig. III-2 WCA measurements of glass substrates treated with APTES using different active

gases.

It also can be noticed that WCA on glass substrate varies with different active gas used for generating plasma. Almost the same wettability on surfaces treated in Ar and N<sub>2</sub> (WCA<sub>Ar</sub>=  $55.9^{\circ}\pm0.7$ , WCA<sub>N2</sub>=  $56.0^{\circ}\pm1.2$ ) is obtained while higher hydrophilicity (WCA<sub>O2</sub>=  $20^{\circ}\pm2.4$ ) is observed when O<sub>2</sub> is used as active gas. These results clearly indicate that similar coating chemical composition with high amount of alkane groups are formed on two surfaces treated in Ar and N<sub>2</sub>, whereas in contrast, a coating with less alkane groups was formed when deposited using O<sub>2</sub> due probably to the formation of volatile CO and CO<sub>2</sub> molecules by oxygen radicals present in the plasma chamber. The film stability was also investigated using washing procedure in water. The tiny difference obtained after 3 times washing on each three coatings, evidences a good stability of the different plasma polymerized coatings.

The chemical composition of glass surfaces before and after APTES plasma polymerization is presented in Fig. III-3 and Table III-3. XPS Results highlight differences on the chemical composition of coatings using different active gases: it could be seen that the characteristic N<sub>1s</sub> peak changes from the background noise level to the prominent peak at about 400 eV when Ar or N<sub>2</sub> is used (Fig. III-3). However, no change of  $N_{1s}$  peak is shown when  $O_2$  is used. It is also noticed that there is  $Na_{1s}$  peak appearing after plasma deposition due to the sodium coming from glass substrate. Furthermore, as shown in Table III-3, Ar and N2 used in APTES plasma polymerization leads to sharp increase of N and C, while the signal of O and Si decreased. Taking the chemical composition of APTES into account, it is certified that the glass surfaces have been covalently linked with APTES. When  $O_2$  is used as reactive gas during plasma deposition process, we observe a drastic increase of O as well as the decrease of N and C revealing that APTES is probably transformed into SiO<sub>2</sub>-like structure by losing -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-NH<sub>2</sub> and/or -CH<sub>2</sub>CH<sub>3</sub> <sup>[83]</sup>, which is attributed to the oxidative effect of O<sub>2</sub> plasma. The deposition process leads to more hydrophilic coatings, which is in good agreement with WCA measurements (Fig. III-2).



Fig. III-3 XPS survey spectra of glass substrates treated with APTES PECVD process using

#### different active gases.

Table. III-3 XPS measurements of surface chemical composition of glass substrates treated

					•			
Sampla type	0	С	Si	Ν	Na	0/6:	C/S:	N/C:
Sample type	(at. %)	0/51	C/SI	IN/51				
Original glass	52.3	23.8	19.5	0.7	3.8	-	-	-
Theoretical APTES	-	-	-	-	-	3	9	1
Tripod structure	-	-	-	-	-	3	3	1
APIES								
APTES in Ar	34.5	48.4	10.2	5	1.9	3.4	4.7	0.49
APTES in O <sub>2</sub>	51.4	22.3	14.3	0.4	11.6	3.6	1.6	0.03
APTES in N <sub>2</sub>	36.2	42.3	8.9	3.9	8.7	4.1	4.8	0.44

with APTES using different active gases.

Moreover, compared with the XPS result of unreacted APTES from others report <sup>[22]</sup>, the coatings deposited using Ar and N<sub>2</sub> both present higher oxygen content:  $at\%O_{Ar}$ = 34.5 and  $at.\%O_{N2}$ = 36.2, while  $at\%O_{report}$  = 21.72, indicating that partial oxidation of APTES molecules also occurs when the Ar or N<sub>2</sub> is used. It could be also

seen from the relative atomic percentages that O/Si ratio lies in the range 3.4~4.1, which is higher than the theoretical value obtained from APTES (O/Si= 3). This result also illustrates that the organic parts of APTES are probably partly oxidized during plasma process. The oxidation occuring in Ar and N<sub>2</sub> plasma is probably due to excitation of O<sub>2</sub> present as traces in the plasma chamber. Furthermore, it is also noticed that both C/Si and N/Si ratio obtained under Ar (C/Si= 4.7, N/Si= 0.49) and  $N_2$  plasmas (C/Si= 4.8, N/Si= 0.44) are significantly lower than the one obtained with an unreacted APTES molecule (C/Si= 9, N/Si= 1), which could be explained by the fact that crosslinking occurs during plasma deposition in both active gases. However, the C/Si ratios are still higher than the theoretical value of 3, which is calculated if APTES had perfectly adsorbed in a -tripod structure" with each of the three Si-O groups forming a siloxane bond with hydroxyl-terminated glass substrate. The observation of higher C/Si means that during the deposition process, not every APTES has perfectly bonded to surface through Si-O-Si bonds by losing three ethoxy on tails. Several hypotheses can be done regarding the complexity of the chemical structures obtained during plasma process: one of the possibilities is APTES molecule could lose three ethoxys forming -tripod structure"; another possibility is it loses only one or two ethoxys from three tails; moreover it could even keep three ethoxys and bind to surface through the interaction between -NH<sub>2</sub> and actived surface. This speculation is also supported by another report <sup>[151]</sup>. The higher observed C/Si ratio, the more ethoxy groups exist in the coating.

The  $C_{1s}$  core level peak was investigated and the high resolution  $C_{1s}$  spectra of coatings deposited on glass using different active gas are presented in Fig. III-4. All the functionalities that should be obtained from APTES are present in Figs. III-4(a) and (b): the peak at 284.2 eV ( $C_1$ ) corresponds to C-Si, the peak at 285.0 eV ( $C_2$ ) corresponds to C-C, C=C and C-H groups, the peak at 286 eV ( $C_3$ ) to C-N, the peak at 286.6 eV ( $C_4$ ) to C-O, and the peak at 288.1 eV ( $C_5$ ) to N-C=O and/or C=O groups. However, it is significantly dissimilar to the sample that was deposited with APTES

using  $O_2$  as shown in Fig. III-4(c). The spectrum exhibits only  $C_2$ ,  $C_4$  and  $C_5$ , and the absence of  $C_1$  (C-Si groups) and  $C_3$  (C-N groups) components, evidence our previous speculation that the loss of -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-NH<sub>2</sub> and/or -CH<sub>2</sub>CH<sub>3</sub> occurs in  $O_2$  plasma. Moreover, the high Si content present in the coating implies the formation of another silicon bond, which is another evidence of the formation of a SiO<sub>2</sub>-like structure. Additionally there is another new peak at 289.2 eV which could correspond to O-C=O groups (C<sub>6</sub>), indicating an intensive oxidation during plasma deposition process. Quantification of high resolution spectra provided in Table III-4, reveals that the proportion of  $C_1$  in Fig. III-4(b) is much lower than that in Fig. III-4(a). If we look back to the chemical structure of APTES (NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>–Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>), it is obviously seen the silicon related chemical bonds are C-Si and O-Si, thus the proportion of O-Si in Si could be briefly calculated from the equation:

#### Equation III-2

The decrease of the proportion of C-Si in  $C_{1s}$  means a rise of O-Si in the coating and thus indicates more APTES molecule are oxidized to SiO<sub>2</sub>-like structure due to the replace of C-Si by O-Si when N<sub>2</sub> is used. Moreover, lower C-N (C<sub>3</sub>) observed in Fig. III-4(b) also supports the speculation that more  $-CH_2CH_2CH_2NH_2$  are lost in N<sub>2</sub> plasma <sup>[83]</sup>. Taking into account the elemental composition of C<sub>1s</sub>, the proportions of C-N (C<sub>3</sub>) bond in the coatings are estimated from the equation:

#### Equation III-3

The calculated values are:  $C-N_{Ar}= 5.0\%$ ,  $C-N_{N2}= 3.9\%$ . This result indicates that more amine groups are present in the coating when Ar is used as active gas, which is an important result for subsequently further immobilization of catalysts.



Fig. III-4 High-resolution XPS spectra of glass substrates treated with APTES plasma using different active gases: (a)Ar; (b) $N_2$ ; (c) $O_2$ .

Difforant			(				Amine (relative
active gas	C <sub>1</sub> (%)	C <sub>2</sub> (%)	C <sub>3</sub> (%)	C <sub>4</sub> (%)	C <sub>5</sub> (%)	C <sub>6</sub> (%)	to total composition, %)
Ar	20.1	53.0	10.4	11.5	5.0	-	5.0
N2	13.3	63.7	9.3	7	6.7	-	3.9
02	-	82.8	-	7.8	2.6	6.8	-

Table III-4 Relative contribution of the deconvoluted components of the  $C_{Is}$  peaks.

### 3.4.2 Influence of various substrates

In order to investigate the difference of coatings deposited on various substrates, glass/COC/Si flakes were used, respectively. Ar was employed as active gas and the plasma parameters are presented in Table III-5. Water contact angle results shown in Figure 5 indicate that the surface wettability changes after deposition and similar wettability of coatings is obtained using the same parameters whatever the nature of the substrate is. The study of coating stability upon several washing steps highlights that the chemical property of plasma polymerized coatings is barely affected by substrate variation, as a tiny change of WCA occurs (Fig. III-5).

Table III-5 Plasma	parameters for	the study of inf	luence of	various sul	bstrates.
	P				

Active gas	Substrate	Working pressure (mbar)	Working power (W)	Deposition Time (s)	Precursor and Carrier gas
Ar	Glass/COC/	0.5	25	40	APTES/Ar,
Flow:20sccm	Si	0.5	23	40	Flow: 10sccm



Fig. III-5 WCA measurements of APTES coatings deposited on glass, COC and Silicon

## substrates.

Infrared data of APTES coatings were collected on three substrates after plasma polymerization. All ATR-FTIR spectra presented in Fig. III-6 show similar features between 4000 and 600 cm<sup>-1</sup>, which originate from the chemical characteristics of the APTES and the absorption intensity is closely related to the coating thickness. APTES coating carried out on glass substrate shows weaker absorption compared to the ones obtained on COC or Si substrates, which indicates that different coatings thickness are obtained ; this difference may be due to the presence of  $O_2$  in glass substrates which could favor the etching phenomena during plasma processing. The spectrum is dominated by a strong absorption peak around 1050 cm<sup>-1</sup> corresponding to Si-O-C and Si-O-Si from polymerized APTES or physisorbed APTES, another absorption peak presenting a shoulder at 1150 cm<sup>-1</sup> could also contribute to short chain Si-O-Si in a more cross-linked structures <sup>[162]</sup>.



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Fig. III-6 FTIR-ATR spectra of APTES coatings deposited on various substrates: (a) on Glass, (b) on COC, (c) on Si.

It is reported that the absorption bands around 1050cm<sup>-1</sup> are more characteristic for long chain while a band around 1150 is assigned to short chain Si-O-Si, indicating the formation of cross-linked siloxane groups <sup>[83, 86, 159]</sup>. The most important structural information regarding our study is the appearance of primary amine bands in the region between 1400 and 1700 cm<sup>-1</sup>; a dominating vibrational mode at 1620 cm<sup>-1</sup> is observed due to the presence of NH<sub>2</sub> group originating from APTES <sup>[75, 154]</sup>, whereas the vibrational mode centered at 1400 cm<sup>-1</sup> could correspond to C-N from amines or amides <sup>[83]</sup>. Another absorption band presented at 1750cm<sup>-1</sup> corresponding to C=O groups also evidences the existence of amides, revealing an oxidation of amines groups due to oxygen traces present during plasma deposition process. The asymmetric and symmetric deformation modes of the CH<sub>2</sub> and CH<sub>3</sub> groups from ethoxy moieties of APTES are observed around 2950 and 2870 cm<sup>-1</sup>, respectively. The presence of these two modes indicates the existence of ethoxy groups in adsorbed APTES, presumably due to low remaining parts of unhydrolyzed

APTES. Besides the appearance of a broad absorption band between 3400 and 3250 cm<sup>-1</sup> corresponding to the symmetric and asymmetric NH stretch modes from amino group also proves the successful deposition of APTES on three different surfaces.

Furthermore, the elemental compositions of the corresponding coating on various substrates determined by XPS are presented in Table III-6. It can firstly be observed that, in comparison with the coating deposited on Si, the coatings carried out on glass and COC exhibit more similar O/Si, C/Si and N/Si ratio. The result implies similar chemical structures on glass and COC, which is also supported by WCA results and FTIR spectra. The huge ratio difference on Si is probably due to the high percentage of Si atoms etched from the substrate leading to contamination of the gas phase and as a consequence, to the incorporation of Si atoms into the polymerized coating.

various substrates. 0 С N Sample Si Na O/Si C/Si N/Si (at. %) (at. %) (at. %) (at. %) (at. %) type APTES 36.6 43.5 11.2 5.8 2.9 3.3 3.9 0.52 on glass APTES 45.9 12.9 6.9 2.7 3.6 0.53 34.3 on COC APTES 40.2 5.5 0.28 35.2 19.2 2.1 1.8 on Si

Table III-6 XPS measurements of chemical composition of APTES coatings deposited on

High resolution  $C_{1s}$  spectra of APTES deposited on different substrates lead to the conclusion that the similar contributions and proportion are obtain on the different substrate surfaces. (cf. Fig. III-7 and Table III-7). All the results clearly indicate that plasma polymerization leads to efficient APTES deposition on all the substrates that are potential materials for microreactor fabrication.



Fig. III-7 High-resolution XPS spectra of APTES coatings deposited on various substrates: (a)

on Glass; (b) on COC (c) on Si.

		Amine				
Different active gas	C <sub>1</sub> (%)	C <sub>2</sub> (%)	C <sub>3</sub> (%)	C <sub>4</sub> (%)	C <sub>5</sub> (%)	(relative to total composition, %)
Glass	23.2	44.8	12.7	8.7	10.5	5.5
COC	23.2	46.7	12.5	9.2	8.4	5.7
Si	22.5	40.8	13.8	12.9	10	5.5

Table III-7 Relative contribution of the deconvoluted components of the  $C_{ls}$  peaks.

## 3.4.3 Influence of deposition time

The growth of APTES coating using Ar plasma is also investigated in our study, the plasma parameters are shown in Table III-8. The thickness of coating presented in Fig.III-8 and Table III-9 show as the deposition time increases the coating thickness linearly increases and the growth rate is 1.9 nm/s, which can be explained by the consistent number of active species per precursor molecule that are produced at fixed gas flow, plasma power and working pressure. The WCA data shown in Table III-9 highlight values change as the deposition time increases, which illustrate the variations of the surface chemical structure. It could be reasonably speculated that at 5 s, the higher WCA is due to a partial coverage of the underlying substrate by the plasma polymerized coating; thereafter, with the increase of deposition time (14~40 s), a full coverage of the substrate is obtained with a high density of polar groups. However, it seems that longer deposition time (>40 s) may also result in the change of molecular polarity and subsequently causes higher WCA data, due probably to bombardment of the reactive polar groups with extremely energetic vaccuum-ultraviolet-light (VUV) that could lead to a sort of overtreatment. 86

Active gas	Substrate	Working pressure (mbar)	Working power (W)	Deposition Time (s)	Precursor and Carrier gas
Ar	Glass/COC/	0.5	25	5 80	APTES/Ar,
Flow:20sccm	Si	0.5	25	5~80	Flow: 10sccm

Table III-8 Plasma parameters for the study of influence of deposition time

Indeed, for a general growth mechanism (shown in Fig. III-9), as power is employed the electric field between electrodes begins to generate free electrons and ions, that are subsequently accelerated leading to collisions with APTES monomer molecules. The monomer molecules are excited to higher energy states, primarily by inelastic collisions with the energetic electrons, and decomposed into fragments (i.e. radicals, ions, atoms and more electrons). They move to the substrate and then covalently bind to the active surface at favorable sites. When deposition is processed, they continuously bind to each other and form an amorphous polymerized coating <sup>[81, 154]</sup>. As the deposition time increases, fragments of radicals are varied and subsequently the chemical structure on surface is changed <sup>[154, 163]</sup>.

Deposition	<b>Th</b> :	Water conta	Water contact angle on different substrates(°)					
time (s)	Glass	COC	Si					
5	7.7±4	55.9±0.7	50.9±1.0	54.3±0.6				
14	25.3±4	37.7±1.7	39.9±0.8	39.4±0.5				
40	82.4±8	31.3±1.9	33.2±0.7	37.2±1.0				
80	150.1±7	40.6±0.5	49.3±0.7	43.8±1.0				

Table III-9 Water contact angle and ellipsometry analysis of APTES coating deposited on

various substrates.



Fig. III-8 Analysis of the coating thickness as a function of deposition time.



Fig. III-9 Mechanism of APTES deposition on surface by PECVD: (a) Activation of substrate surface by plasma; (b) Fragmentation of APTES by plasma; (c) Deposition of APTES fragments; (d) Polymerization of APTES..

The FTIR-ATR spectra of depositing APTES on COC with varying time

presented in Fig. III-10 highlights changes with increasing deposition times. The band in the region of 3400~3250 cm<sup>-1</sup> (Fig. III-10(a)) associated with the symmetrical and asymmetrical NH stretch modes increased with increasing deposition time, which could be explained by the increase of coating thickness. In contrast, the peak intensity associated with carboxylate functions at around 1750 cm<sup>-1</sup> (Fig. III-10(b)) follows this trend: :

$$I(C=O)_{5s} < I(C=O)_{80s} < I(C=O)_{14s} < I(C=O)_{40s}$$

The N-H bending (scissoring) vibration of primary amines is observed generally in the 1650~1590 cm<sup>-1 [164]</sup> region of the spectrum (Fig. III-10(b)). The band is medium to strong in intensity and is moved to slightly higher frequencies when the compound is associated. Also, we can clearly see that the peak center of amine is slightly shifted from 1590 cm<sup>-1</sup> to 1660 cm<sup>-1</sup> with increased deposition time. The shift of peak to higher wave frequencies (~1620 cm<sup>-1</sup>) indicates an increase of the free amines, which are transformed from H-bonded amines <sup>[154, 165]</sup>. However, as the peak center is moved to 1660 cm<sup>-1</sup>, the vibrational mode is assigned to amide, imine or oxime groups, implying an amine bicarbonate salt could possibly be oxidized during plasma process <sup>[83, 162]</sup>. It can be explained as following: at the beginning of plasma deposition process, the amount of free amines and esters increases as well as the coating thickness with increasing deposition time. Meanwhile, the growing coating is being exposed to the plasma during the process and longer exposure durations enhances the risk of an overtreatment with oxidative reactions. The functional groups e.g. amines and esters on the growing film surface, might undergo functional changes induced by plasma generated species such as ions, charged radicals and energetic VUV<sup>[163]</sup>. This phenomenon suggests the optimal deposition time in our study should not be longer than 40 s.



Fig. III-10 FTIR-ATR spectra of APTES coatings deposited on COC for different time: (a) High wavenumber scanning region; (b) Low wavenumber scanning region.

To further investigate the growth of plasma polymerized coating on glass, we performed XPS analyses and gave elemental composition and atomic percentage ratio C/Si, O/Si and N/Si for different deposition times (Table III-10). It can first be observed that after 5 s, plasma polymerization leads to the synthesis of more inorganic thin films as the carbon content decreases and nitrogen content increases, which could be related to partial loss of organic monomer. The maximum value of C/Si as well as the minimum value of N/Si obtained at 5 s indicates the monomers are not sufficiently deposited on the surface due to a very short plasma deposition time. C/Si and N/Si are observed to be similar indicating a higher crosslink of aminopropyl chains when deposition time is 14 s, 40 s and 80 s, suggesting the optimal time in our study should be longer than 5s.

glass for different treatment times.									
Deposition	0	С	Si	Ν	Na	O/Si	C/Si	N/Si	
time	(at. %)								
5	34.5	48.4	10.2	5	1.9	3.4	4.7	0.49	
14	33.9	43.1	11.5	5.6	5.6	3.0	3.7	0.49	
40	36.6	43.5	11.2	5.8	2.9	3.3	3.9	0.52	
80	33.2	42.6	11.3	5.9	7.1	2.9	3.8	0.52	

Table III-10 XPS measurements of chemical composition of APTES coatings deposited on

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The percentage contribution of each functional group of the total  $C_{1s}$  spectrum with increasing deposition time is presented in Table III-11. It reveals that the maximum  $C_3$  proportion (C-N) is obtained at deposition time of 14 s and 40 s. A sharply decrease of C-O proportion (C<sub>4</sub>) after 5 s could be related to the formation of a siloxane bond by losing ethyl groups from Si-O-CH<sub>2</sub>CH<sub>3</sub>. However, C<sub>4</sub> proportion increases when the deposition time increases from 14 s to 80 s.

Different			C <sub>1s</sub>			Amine (relative to total
time	<b>C</b> <sub>1</sub> (%)	C <sub>2</sub> (%)	C <sub>3</sub> (%)	C <sub>4</sub> (%)	C <sub>5</sub> (%)	composition, %)
5s	20.1	53.0	10.4	11.5	5.0	5.0
14s	21.9	49.1	12.4	7.9	8.7	5.3
40s	23.2	44.8	12.7	8.7	10.5	5.5
80s	23.4	47.1	11.3	10.2	8.0	4.8

Table III-11 Relative contribution of the deconvoluted components of the  $C_{1s}$  peaks.

It is to be noticed that in FTIR-ATR data, the peak center of amine shifted to longer wave number, indicating the formation of imine or oxime. In other words, the increase of deposition time would probably cause the increase of C=N amount in coating. In C<sub>1s</sub> the binding energy of C=N is between that of C-N and C=O <sup>[83]</sup>, it makes difficulty for separating this contribution due to its similar binding energy to C-O. Consequently, the C<sub>4</sub> peak, centered at 286.7 eV is attributed not only to C-O but also to C=N bond. Thus, the increase of imine or oxime in coating leads to increase of C<sub>4</sub> after 14 s. C<sub>5</sub> proportion increases with increasing deposition time; however, a dramatic decrease occurs after 40 s and agrees with the same trend presented in FITR spectra. Compared with the composition of coating deposited at 40 s, a decrease of the proportion of C<sub>3</sub> component is observed when the deposition time reaches 80 s. The results suggests deposition time in our system should not be longer than 40 s, as the excessive exposure to the plasma that causes by longer deposition time, would result in structural changes of amine groups on the as deposited coating surface. Finally, the

maximum amine proportion is obtained when deposition time is 40 s and this should be confirmed in the future by derivatisation reactions in order to assess the amine density.

### 3.4.4 Influence of working pressure

In order to investigate the influence of working pressure, APTES were deposited using plasma conditions shown in Table III-12. The first results regarding plasma-polymerized APTES coating concern the water contact angle obtained as a function of various pressures and are shown in Table III-13. A extremely drastic WCA decrease is observed as the working pressure increases from 0.5 to 0.7 mbar, but no obvious change could be seen when the pressure is increased during 0.7~1.5 mbar. The results imply an increase of hydrophilic groups in coating since the pressure is higher than 0.5 mbar.

Active gas	Substrate	Working pressure (mbar)	Working power (W)	Deposition Time (s)	Precursor and Carrier gas
Ar Flow:	Glass/COC/	0515	25	40	APTES/Ar,
20sccm	Si	0.3~1.3	23	40	Flow: 10sccm

Table III-12 Plasma parameters for the study of working pressure

On the other hand, the table indicates stronger WCA differences between substrates before and after wash as the working pressure is higher than 0.7 mbar, which in other word, could be related to the decrease of coating stability in water with increasing pressure. This trend is also proved by the results from ellipsometer shown in Fig. III-11. At the lowest pressure of 0.5 mbar, the deposition rate is quite low (around 2.1 nm/s). Increasing working pressure at 0.7 mbar results in a sharp increase of the deposition rate (Fig. III-11(a)). Firstly, the deposition rate is directly proportional to pressure, it increases upon increasing the pressure during lower values range ( $0.5\sim1.0$  mbar), Secondly followed by a decrease during higher values range (1.0~1.5 mbar). Besides, it should also be highlighted that the deposition rates obtained in this study are considerably higher than the ones acquired by other researchers using vacuum plasma technology. For example, Gubala et al reported a low deposition rate of 0.08 nm/s when APTES was plasma polymerized on COP slides <sup>[84, 154]</sup>; Lecoq et al announced a deposition rate 0.7~1.0 nm/s <sup>[83]</sup> by using O<sub>2</sub> and N<sub>2</sub> for PECVD. Besides, it is also interesting that the increase of pressure leads to a stronger loss of coating thickness indicating weaker coating stability was produced at higher working pressure, as shown in Figs. III-10(b).

As it is well known that during plasma polymerization processes the formation of polymers starts from the activation of monomers into radicals. This process essentially depends on fragmentation of the monomer by the plasma, which is dominantly controlled by collision rate. When the working pressure is increased, the mean free path of the plasma particles decreases leading to an increase in the collision rate <sup>[166]</sup>. Subsequently the fragmentation and/or poly-recombination of the monomer molecules increases and finally causes increase of functional groups and deposition rate. However it is noticed that increase of pressure also causes increase of monomer density, in other word, for a sufficient polymerization more energy is needed for leading more activated species and a higher deposition rate. Nevertheless for a fixed plasma power, the supplied energy becomes insufficient to cause fragmentation of monomer when the pressure is continuously increased and thus deposition rates could not keep on increasing or in contrast drop back at higher working pressure. It has been evidenced by the results presented in Fig. III-11(a).

Table III-13 Water contact angle of APTES coating deposited on various substrates at

Working pressure		Water contact angle on different substrates(°)								
	Gl	ass	C	DC	Si					
(mbar)	Before	After	Before	After	Before	After				
	wash	wash	wash	wash	wash	wash				
0.5	31.3±1.9	34.3±1.3	33.2±0.7	38.2±1.1	37.2±1.0	37.7±0.9				
0.7	6.7±2.0	21.1±1.3	8.1±1.3	17.9±1.2	5.8±0.4	25.5±1.0				
1.0	4.3±2	24.4 ±2.2	6.6±1.3	24.9±2.3	5.5±0.5	26.8±1.4				
1.5	4.1±0.5	23.3±0.6	5.2±1.1	25.2±0.7	5.3±0.8	26.7±1.7				

different pressures.



Fig. III-11 Ellipsometer results of APTES coating deposited on Si at different pressure: (a)

Working pressure

Coating growth rate; (b) Coating wash stability.

The analysis of FTIR and XPS spectra could help us for the determination of the coatings composition by varying working pressure. FTIR spectra of coatings on COC are presented in Fig. III-12. Firstly, it can be underlined that all of the spectra obtained for APTES coatings show all expected peaks as described in literatures <sup>[83, 154, 167]</sup>. Due to the feature of infrared spectroscopy, the peak intensity of coating is essentially affected by coating thickness, especially in the case of thickness at nanoscale. Taking into account that different deposition rates were obtained when different pressures were used, apparently the change of peak intensity during coating fabricated at different working pressure could not be related to quantitative bonds composition. However, it is possible to qualitatively realize the relative bonds content from each spectrum.



Fig. III-12 FTIR spectra of APTES coating deposited on COC at different pressure.

The absorption band, presented at 1750 cm<sup>-1</sup> corresponding to C=O that originates from amide or carboxyl, are probably formed due to the oxidation of ATPES, meanwhile the absorption peak centered at 1620 cm<sup>-1</sup> could be assigned to C-N that originates from APTES molecule. For spectrum the ratio of relative peak intensity of C=O/C-N could be measured from Fig. III-12 and the results reveal the ratio decreases first with an increase of working pressure from 0.5 to 1.0 mbar,

however it finally increases varying pressure during  $1.0\sim1.5$  mbar. Although all the treatment conditions are identical, the radicals created in the plasma fluctuate according to different working pressure as a result of collision rate changing. Consequently they would react differently with the surface and a variable C=O and C-N absorption peak intensity is thus expected.

The elemental compositions and atomic percentage ratio C/Si, O/Si and N/Si of the corresponding coatings fabricated at various working pressure on glass substrates determined by XPS are presented in Table III-14. It could be observed that, in comparison with the coating fabricated at pressure of 0.5, 0.7 and 1.5 mbar, the working pressure at 1.0 mbar leads to the synthesis of the most organic coating as the highest carbon content is observed. During the plasma polymerization process, the fragmentation of APTES monomer becomes drastic with increasing working pressure and consequently it leads to higher deposition rate and more functional groups. Thus, the highest nitrogen content as well as carbon is obtained from the coating prepared at 1.0 mbar. A maximum value of C/Si and N/Si ratios obtained at this condition indicates that the highest amount of polymerized APTES is obtained on the surface <sup>[83]</sup>. On the contrary, the O/Si ratio reaches the minimum value at this condition means it can be assumed that lowest oxidation of organic parts present in coating. Actually, besides increase of the fragmentation and/or poly-recombination of the APTES molecules that benefits in depositing APETS molecules on surface, the higher working pressure also causes decrease of mean free path of electrons, and therefore, the electrons gain less energy from the electric field leading to the increase of their collision rate with neutral molecules and consequently resulting in normal ionic or/and radical polymerization <sup>[166]</sup>, finally it results in the formation of other chemical bonds in the coating (e.g. -OH). It is evidenced from that the increase of oxygen content and O/Si ratio is obtained when the pressure is changed from 1.0 mbar to 1.5 mbar. Thus, the working pressure dependence of coating composition and functional groups results from a counterbalance of these two processes. Based on the presented

results, it could be reasonably assumed that the former process is preferable at low pressures (<1.0 mbar), the C/Si and N/Si ratio increase with increasing pressure. However, the latter process becomes dominant when pressure is higher than 1.0 mbar and consequently causes the fall of C/Si and N/Si ratio in the coating fabricated at 1.5 mbar.

Table III-14 XPS measurements of chemical composition of APTES coating deposited on glass

				-					
Working	0	С	Si	Ν	Na				
pressure	(at. %)	O/Si	C/Si	N/Si					
(mbar)	(	(	(	(	(				
0.5	36.6	43.5	11.2	5.8	2.9	3.3	3.9	0.52	
0.7	35.0	46.0	10.2	7.6	1.1	3.4	4.5	0.74	
1.0	31.9	49.7	10.2	7.8	0.4	3.1	4.9	0.76	
1.5	36.0	45.1	11.1	6.7	1.1	3.2	4.1	0.60	

at different pressure.

High resolution XPS spectra of  $C_{1s}$  and their relative contribution of the deconvoluted components are shown in Fig. III-13 and Table III-15. For C<sub>1s</sub> deconvolution, the contribution of peak C1 centered at 284.2 eV corresponding to C-Si show a decrease when increasing working pressure. It has been discussed in previous part that the parts of the monomer are partially lost and/or oxidation during plasma polymerization process, and therefore one of the possibilities is that the C-Si bond could be replaced by O-Si bond resulting in formation of squasi-SiO<sub>2</sub>-like structure in polymerized APTES coating. At a low pressure, oxygen radicals are preferred to react with organic parts of APTES (i.e. ethoxy functional groups on Si-O tails), with increasing pressure, as well as the activation of more APTES monomers the fragmentation of oxygen also becomes stronger, and oxygen radicals begin to oxidize Si-C bonds and therefore leading to formation of hydrophilic quasi-SiO<sub>2</sub>-like structures, in accordance with the WCA results as shown in Table III-13. The enhancement of oxidation is also evidenced by the increase of C<sub>4</sub> of C-O and C<sub>5</sub> of C=O when the pressure is increased from 0.5 to 1.5 mbar. C<sub>2</sub> at 285 eV corresponding to C-C and C<sub>3</sub> at 286.0 eV corresponding to C-N increase first but followed by a 98

decrease at higher value (>1.0 mbar) evidence our assumption that the functional groups are changed due to the competition between fragmentation and/or poly-recombination of the monomer molecules and normal ionic or/and radical polymerization. Besides, a new peak C<sub>6</sub> centered at 289.1 eV corresponding to O-C=O appears when pressure is higher than 1.0 mbar, agreeing with this trend. Here for APTES polymerization, the best working pressure is 1.0 mbar as highest amine contribution of 7.9% is obtained.



Fig. III-13 High-resolution XPS spectra of APTES coating deposited on COC at different pressure: (a)0.5 mbar; (b)0.7 mbar; (c)1.0 mbar; (d)1.5 mbar.

Working			Amine				
pressure	C <sub>1</sub>	<b>C</b> <sub>2</sub>	<b>C</b> <sub>3</sub>	<b>C</b> <sub>4</sub>	<b>C</b> <sub>5</sub>	<b>C</b> <sub>6</sub>	(relative to total
(mbar)	(%)	(%)	(%)	(%)	(%)	(%)	composition, %)
0.5	23.2	44.9	12.7	8.7	10.5	-	5.5
0.7	19.6	47.7	14.5	9.2	9.0	-	6.7
1.0	16.2	49.7	15.5	9.6	9.0	-	7.9
1.5	15.8	40.4	12.8	13.8	10.7	6.5	5.8

Table III-15 Relative contribution of the deconvoluted components of APTES coating deposited on glass at different pressure.

## 3.4.5 Influence of working power

In this section, the influence of working power on the surface wettability, deposition rate, coating adhesion ability and chemical composition will be examined. The power is varied while maintaining other conditions as shown in Table III-16.

Active gas	Substrate	Working	Working Working		Procursor and	
		pressure	power	Time	Common gos	
		(mbar)	(W)	<b>(s)</b>	Carrier gas	
Ar Flow:	Glass/COC/	1	10 40	40	APTES/Ar,	
20sccm	Si	1	10~40	40	Flow: 10sccm	

Table III-16 Plasma parameters for the study of influence of working power

For substrates treated using 10, 20, 25, 30 and 40 W plasma power, the WCA on surface are presented in Table III-17. The hydrophilicity of coatings are improved with increasing power, especially a steep WCA decrease is highlighted when power is changed during 20~25 W, and then the value remains almost constant and indicates superhydrophilicity until 40 W. Although the deposition of species for forming a coating using plasma is a complicated process and controlled by many parameters i.e.

deposition time, working pressure, etc., working power is considered as an essential factor. Volcke et al. has shown that an increase of plasma power leads to increase of electron density <sup>[154]</sup>, which could be related to increase of collision rate for a certain mean free path of the plasma particles. In other word, an increase of working power would benefit in decomposition of the reactants into fragments during deposition process <sup>[168]</sup> and it finally causes the increase of hydrophilic functional groups like amine, amide and so on.

It is also supported by the ellipsometer results depicted in Fig. III-14(a) that presents a gradual increase of the coating deposition rate with increasing working power. Moreover, the coating stability resisting water shown in Fig. III-14(b) highlights changes with varying power. The coating loss after wash firstly increases with increasing power and reaches maximum value of about 60.4% at 25 W; thereafter, it decreases with increasing power and remain small variation during 30~40 W. Although the species present in the plasma are not known in detail, the coating growth can reasonably be explained as follows: the fragments decomposed from monomers are deposited and covalently bind to the activated surface by plasma, forming a non-organized coating.

Woulder							
working	Gl	ass	C	DC	Si		
power (w)	Before	After	Before	After	Before	After	
_	wash	wash	wash	wash	wash	wash	
10	42.1±1.6	51.2±1.0	38.2±1.2	43.0±1.7	34.4±1.2	41.7±1.8	
20	22.4±1.0	34.6±1.5	24.6±1.7	36.1±0.5	23.8±0.9	32.5±1.2	
25	4.3±2.0	24.4 ±2.2	6.6±1.3	24.9±2.3	5.5±0.5	26.8±1.4	
30	3.0±0.6	25.3±0.8	5.2±1.3	23.4±1.5	4.5±0.4	24.0±1.5	
40	0	24.8±1.2	4.7±1.2	22.2±2.3	0	20.0±0.5	

Table III-17 WCA results of APTES coating deposited on various substrates using different power.

## WCA(°)

At a low growth rate induced by low plasma density, the fragmentation is relatively slow and species could completely bind to each other, leading to a well-binded compact structure for coating. According to increasing power that benefits in deposition rate, the coating grows too fast to forming loose structure with weaker stability. On the other hand, higher power benefits in better crosslink during plasma polymerization, which is obviously improve coating stability in report <sup>[169]</sup>. The competition of the two processes results in variations of coating stability with increasing power. Obviously, the former process is dominant at low power region while the latter one is preferable at high power region. A good coating stability is acquired during 30~40 W.



Fig. III-14 Ellipsometer results of APTES coating deposited on Si using different power: (a) Coating growth rate; (b) Coating wash stability.

Fig. III-15 presents the evolution of the FTIR spectra for APTES deposited on COC using different power. The most important changes as a function of plasma power are observed in the spectral region:  $2000 \sim 1500$  cm<sup>-1</sup>. It can be seen how the band located at 1750 cm<sup>-1</sup>, which was due to C=O originating from ATPES that reacted with oxygen radicals, increases with increasing plasma power, is probably ascribed to two reasons: the increase of coating thickness or the increase of C=O bonds amount in coating. Moreover, it can be seen a new band located around 1655 cm<sup>-1</sup> due to the presence of H<sub>2</sub>O as well as another absorption peak presents as 103

shoulder at 1620 cm<sup>-1</sup> contribute to NH<sub>2</sub> related to primary amine, appears when the power is at low value of 10 W <sup>[83, 167]</sup>. Thereafter, the relative intensity of NH<sub>2</sub> increases with increasing power and become dominated peak lying around 1600~1700 cm<sup>-1</sup> when H<sub>2</sub>O absorption is observed as shoulder, indicating an obvious improvement of fragmentation of APTES for deposition by increasing power during plasma process. Another difference with increasing power is observed during the region between 1300 and 1000 cm<sup>-1</sup>. A broad peak corresponds to asymmetric stretching of the Si-O-Si due to polymerization of the siloxane structure is seen, including a band around 1150 cm<sup>-1</sup> at shoulder is assigned to short chain Si-O-Si and a band around 1050 cm<sup>-1</sup> that is more characteristic for long chain or cyclic Si-O-Si. According to literature <sup>[83, 86, 170]</sup>, the higher intensity of the band around 1150 cm<sup>-1</sup> the more cross-linked structures obtained, indicating better coating stability when the power is higher than 30 W, which is also supported by ellipsometer results.



Fig. III-15 FTIR spectra of APTES coating deposited on COC using different power.

glass using different power.											
O C Si N Na O/Si C/Si N/S											
Power (W)	(at. %)										
10	36.2	45.6	10.6	6.5	1.1	3.4	4.3	0.61			
20	34.2	48.5	9.7	6.9	0.8	3.5	5.0	0.71			
25	31.9	49.7	10.2	7.8	0.4	3.1	4.9	0.76			
30	33.9	47.5	10.1	8.3	0.2	3.4	4.7	0.82			
40	35.8	46.6	10.2	6.9	0.3	3.5	4.6	0.68			

Table III-18 XPS measurements of chemical composition of APTES coatings deposited on

The elemental composition and atomic percentage ratio C/Si, O/Si and N/Si of the coatings prepared using different working power from XPS is presented in Table III-18. The C/Si and N/Si ratio increase when power is increased during 10~25 W, indicating an increase of APTES molecules in coating. However, it is also observed that C/Si ratio decreases with increasing power during 25~40 W, corresponding to an increase of crosslinked structures. Especially, the highest N/Si ratio with relative low C/Si ratio are obtained when the working power is 30 W, indicating a coating with higher crosslink of aminopropyl chains. It has been previously discussed that the PECVD process essentially depends on fragmentation of the monomer by the plasma. In order to improve the fragmentation, the higher plasma energy is necessary for inducing more collision and consequently benefits in decomposition of monomers into fragments for deposition. It would lead to an increase of C/Si and N/Si during increasing working power from low region. Nevertheless, the higher energy also provide help for crosslinking as-deposited polymers on surface and it cause the loss of ethyl or ethoxyl groups due to the formation of Si-O-Si bond between every two -Si-O-CH<sub>2</sub>-CH<sub>3</sub> of APTES molecules, thus an decrease of C/Si ratio is observed when the power is higher than 25 W. The higher crosslink structure leads to a better coating stability as it has been observed in Fig. III-14(b). However, if the power is increased
to high region the decomposition of APTES monomers is strongly improved. As a result of this, not only the ethyl or ethoxyl groups but also the aminopropyl groups are fragmented from APTES molecules. And therefore, the N/Si ratio decreases after 30 W.



Fig. III-16 High-resolution XPS spectra of APTES coating deposited on glass using different power: (a)10W; (b)20W; (c)25W; (d)30W; (e)40W.

For the high resolution XPS analysis, the deconvoluted  $C_{1s}$  spectra are presented in Fig. III-16 and the proportions of different components in  $C_{1s}$  with

increasing deposition time are shown in Table III-19. Qualitatively all the C<sub>1s</sub> spectra look reasonably similar with a saturated hydrocarbon peak (C2, 285.0 eV), four additional peaks at 284.2 eV (C1), 286 eV (C3), 286.6 eV (C4) and 288.1 eV (C5), which are best associated to C-Si, C-N, C-O bondings and -CONH<sub>2</sub> groups, respectively. A new peak at 289.1 eV corresponding to O-C=O appears when the working power is at 40 W. Taking the constant value of Si content from Table III-18 into account, the decrease of C1 with increasing power could be related to increase of Si-O bonds in coating. On one hand, as the fragmentation of APTES monomers differ according to plasma power conditions, a variation of surface composition is expected. The enhancement of decomposition and oxidation of APTES results in forming more and more hydrophilic squasi-SiO<sub>2</sub>-like structures, which is evidenced by decrease of WCA when increasing power from 10 to 40 W; on the other hand, higher plasma power leads to intensive crosslinking among as deposited silane and consequently benefits in improving coating stability as seen in Fig. III-14(b). C<sub>3</sub> corresponding amine firstly increases with increasing power but decreases after 30 W, indicating that at the lower power the APTES monomers are activated and could react with the surface, but was not significantly dissociated <sup>[154]</sup>. With increasing power, the intensity of fragmentation of APTES is enhanced. However, if the power is too high the amine functions are lost during fragmentation and consequently the coating is formed with less C-N bonds. Also, carboxyl functions could be formed at high plasma power through rearrangement and fragmentation of radicals from APTES. Furthermore, the highest relative amine contribution to total composition of 8.7% obtained at 30 W reveals the best working power in our work.

C <sub>1s</sub>						Amine	
Power (W)	C <sub>1</sub>	<b>C</b> <sub>2</sub>	C <sub>3</sub>	<b>C</b> <sub>4</sub>	C <sub>5</sub>	<b>C</b> <sub>6</sub>	(relative to total
	(%)	(%)	(%)	(%)	(%)	(%)	composition, %)
10	21.4	41.4	9.2	16.2	11.8	-	4.2
20	19.8	42.2	13.8	13.3	10.9	-	6.7
25	16.2	49.7	15.5	9.6	9.0	-	7.9
30	13.9	41.7	18.3	12.1	14.0	-	8.7
40	13.9	35.2	16.4	16.0	10.2	8.3	7.6

 Table III-19 Relative contribution of the deconvoluted components of APTES coating

deposited on glass using different power.

# 3.5 Conclusion

In this chapter, a useful linking reagent from catalysts immobilization, APTES, was successfully polymerized on substrates through the PECVD process using a homemade bell-jar plasma reactor. The successfully deposition of APTES coating with similar structure on various substrate demonstrates that PECVD is a promising functionalization method in a wide range of application. The XPS results indicate the formation of SiO<sub>2</sub>-like structure during plasma process, which could be attributed to the oxidation of APTES by O<sub>2</sub> gas. In other words, O<sub>2</sub> is not an appropriate active gas for APTES plasma polymerization in this study. The study on thickness, WCA, FTIR-ATR and XPS of coating deposited for different times confirm the surfacial property transformation as well as chemical composition. A functional change due to coating being exposed to plasma suggests the deposition time should be in the range of 14~40 s. Furthermore, the investigation of APTES deposited using different working pressure indicates the increase of pressure benefits APTES deposition at during 0.5~1.0 mbar due to the enhancement for fragmenting APTES monomer; however a decrease of deposition rate is observed after 1.0 mbar due to the

insufficient plasma power for increased monomer density. Ellipsometer results from samples before and after wash show a weak coating stability after 0.5 mbar. The FTIR and XPS results evidence the change of chemical structure of coating with increasing pressure. The competition between fragmentation and/or poly-recombination of the APTES molecules and normal ionic or/and radical polymerization determines the final coating composition. Subsequently the results indicate the former process is preferable at low pressures (<1.0 mbar), while the latter process becomes dominant when pressure is higher than 1.0 mbar. Moreover, the study of APTES deposited using different power indicates the surfacial properties are also affected by power variation. WCA of surface increases and coating deposition rate decreases with increasing power. A decrease of coating stability is also observed as deposition increases during increasing power between  $10 \sim 25$  W; on the contrary, the coating stability increases when the power is increased after 25 W, indicating a high cross-linked structure due to higher plasma power, which is also supported by FTIR and XPS results. And the results also indicate at the lower power the APTES monomers is not significantly dissociated; the intensity of fragmentation of APTES is enhanced with increasing power, however if the power is too high the amine functions are lost during fragmentation. The comparison of amine proportion of total composition and coating stability in this study indicates optimization plasma conditions for APTES deposition:  $Q_{APTES}$ = 10 sccm,  $Q_{Ar}$ = 20 sccm, P= 30 W, p= 1.0 mbar, t= 40 s. The proposed conditions are only summarized from parts of plasma parameters. In order to confirm and obtain maximum amine groups in the process.

# Chapter IV A comparison study of two methods for glass surface functionalization and their application in gold nanoparticles (AuNPs) immobilization

# 4.1 Abstract

Immobilization of colloidal objects such as gold nanoparticles (AuNPs) on the inner surface of micro-/nano- channels has received a great interest due to the wide applications of such devices in different technologies such as sensing, catalysis, etc. It is well known that the surface functionalization step with a functional molecule that allows linking to such colloidal objects to the surface is the most crucial step for controlling their dispersion and coverage on the surface. In this chapter, we studied grafting of functional amine groups from (3-aminopropyl)triethoxysilane (APTES) on glass surfaces using two methods, i.e. (i) the conventional wet chemistry method and (ii) the plasma enhanced chemical vapor deposition (PECVD) process. The functionalized glass surfaces were characterized with water contact angle measurements (WCA), spectroscopic ellipsometry, Fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATR), scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS). The results clearly evidenced that PECVD processing exhibits better ability for grafting high-density amine groups at the topmost surface of glass and as a consequence, the further efficient immobilization of AuNPs.

**Keywords:** Surface functionnalization, wet chemistry, PECVD, amine groups, gold nanoparticles immobilization, AuNPs

# 4.2 Introduction

Gold was considered as one of the most stable –inert" metallic elements until Haruta et al. discovered that gold nanoparticles (AuNps) exhibit extremely high activity in CO oxidation below room temperature <sup>[88]</sup>. Henceforward, the unique properties of gold nanoparticles to catalyze different reactions at low temperatures have begun to gain attention from researchers <sup>[171]</sup>. Various publications that have been applying gold nanoparticles in reactions including oxidation <sup>[89, 90]</sup>, hydrogenation <sup>[91]</sup>, hydroamination <sup>[92]</sup>, ring expansion <sup>[93, 94]</sup>, and coupling reactions <sup>[95, 96]</sup> have witnessed an explosive development of using AuNps as a catalyst during the past decades.

Recently, a novel conception of building a lab on a chip that originated from miniaturizing device into micro-/nano- scale to gain a continuous homogenous mixing process with advantages such as low pollution, high safety, good reliability, precise controllability, is growing interest in chemistry, physics, biology and bioengineering areas <sup>[172]</sup>. From a chemistry point of view, the immobilization of AuNps on the inner surface of micro-/nano- channels is considered as a promising application to develop catalytic miniaturization devices <sup>[12]</sup>. With the coverage of AuNps on surfaces, the physico-chemical properties of these devices are governed by the features of AuNps. Further to say, despite variation of channel design, the catalytic characteristics of such devices will depend not only on the size and shape of the AuNps but also on their distribution and on the nature of their interaction with the surfaces. Achieving well spatial arranged AuNps is crucial to ensure high catalytic activity inside microchannels.

Traditionally, the immobilization of AuNps on the surface is ensured by the presence of organic molecules with terminal functional groups likely to give rise to electrostatic or chemical bonding. One of the commonly used molecule is (3-aminopropyl)triethoxysilane (APTES) that possesses three alkoxy groups that would react with the hydroxyl groups leading to the formation of Si–O bonds and a terminal functional amine group that is responsible for the electrostatic interaction

with the AuNps. The numerous studies dealing with the modification of surfaces with APTES have shown that the silanization step is very often done through a wet chemistry treatment <sup>[22, 23, 173]</sup>, which varies from an experimenter to another one and is time consuming. Moreover, the final surface state of the modified substrate is sensitive and may vary with experimental conditions, e.g. temperature, presence of water, concentration of APTES, etc. Alternatively, a low-cost, high reproducible and ecofriendly dry process like plasma enhanced chemical vapor deposition (PECVD) is also reported to successfully functionalize surface with APTES <sup>[83, 154]</sup>. However, it remains only a few reports about applying this technique for APTES deposited using PECVD process can be useful for further immobilization steps.

In this work, surface functionalization of glass surfaces with APTES using wet chemistry and PECVD process are studied and the efficiency of the two methods is evaluated by a further immobilization step of AuNPs on the functionalized substrates. Water contact angle measurements (WCA), spectroscopic ellipsometer, fourier transform infrared-attenuated total reflectance spectroscopy (FTIR-ATR) and X-ray photoelectron spectroscopy (XPS) were firstly used to characterize the deposited APTES layers. Finally, in order to find the best method to immobilize AuNPs in terms of coverage and dispersion of nanoparticles, we used using different methods such as scanning electron microscopy (SEM) and XPS.

# 4.3 Experimental

#### 4.3.1 Materials and chemicals

Glass dishes were cut into small rectangular flakes with length  $\times$  width of 8 mm  $\times$  8 mm. Glass flakes were cleaned by using an aqueous 20% RBS detergent solution (in water) in ultrasonic bath for 10 min and then were rinsed by deionized water before the samples were dried by compressed pressure air. APTES

 $(NH_2(CH_2)_3-Si(OC_2H_5)_3, 98\%)$  was purchased from VWR, gold(III) chloride hydrate (HAuCl<sub>4</sub>·xH<sub>2</sub>O, 99.999%) and silver nitrate (AgNO<sub>3</sub>, 99%) were purchased from Sigma-Aldrich, trisodium citrate (HOC(COONa)(CH<sub>2</sub>COONa)<sub>2</sub>·2H<sub>2</sub>O, 99%) was purchased from Alfa(Aesar). Ethanol and acetone were analytic reagent grade. Pure Ar was used for generating plasma; its purity was higher than 99.99%.

# 4.3.2 Deposition of APTES using the wet chemistry method

We used the method described by Sardar et al. <sup>[173]</sup>; the flakes were immersed in a 1:1(v/v) solution of methanol and concentrated HCl for 30 minutes, and then they were rinsed thoroughly with distilled water and left to dry overnight in an oven at 60°C. Thereafter, the clean glass flakes were placed in a 10% (v/v) solution of APTES in anhydrous ethanol for 30 minutes. The samples were sonicated and then rinsed with anhydrous ethanol and dried at 120°C for 3 h.

### 4.3.3 Deposition of APTES using PECVD method

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A homemade experimental device called bell-jar reactor was used for the APTES plasma deposition. Firstly, pre-treatment is performed for activation of surface: the working pressure was fixed at 0.7 mBar, the samples were subjected to a 20 W plasma treatment (Ar; flow rate: 10 sccm) during 5 s. The working pressure was fixed at 0.7 mbar, the samples were subjected to a 20 W plasma treatment (Ar; flow rate: 10 sccm) during 5 s. The working pressure was fixed at 0.7 mbar, the samples were subjected to a 20 W plasma treatment (Ar; flow rate: 10 sccm) during 5 s. Then the samples were functionalized and the parameters used in this work are presented in Table IV-1.

Active gas	Working pressure (mbar)	Working power (W)	Deposition Time (s)	Precursor and Carrier gas
Ar	1.0	30	40	APTES/Ar
Flow:20sccm		2.0		Flow: 10sccm

Table IV-1 Plasma parameters in this work

After plasma deposition, the chemical pump was fully loaded again while the

turbo molecular pump was stopped immediately. The freshly coated flakes were kept under vacuum for 1h before venting, in order to reduce post-oxidative reactions between radicals formed on the film surface and atmospheric oxygen<sup>[160]</sup>.

# 4.3.4 Synthesis and immobilization of AuNPs

Monodisperse gold nanoparticles were synthesized according to the work of Xia et al. <sup>[174]</sup>. In a test tube of 0.5 mL of an aqueous solution of gold(III) chloride hydrate (1 wt%), 42  $\mu$ L of aqueous silver nitrate solution (0.1 wt%) and 1.5 mL of aqueous sodium citrate (1 wt%) were mixed. The mixture was injected into 47.5 mL of boiling water under reflux which resulted in the formation of a red sol of gold NPs. Heating was stopped after 30 min and the suspension was cooled to room temperature. The pH of the suspension was adjusted to 6.2 using with NaOH (0.1 M). Glass substrates with freshly deposited APTES were then placed at the bottom of beaker for 24 h; magnetic rotation bar was used during immobilization.

# 4.3.5 Characterization of modified surfaces

Static water contact angle measurements were performed with a GBX-3S processing system using deionized water (liquid droplet volume: 4  $\mu$ L). The reported advancing contact angle value corresponds to the average of three measurements on different areas of each sample.

The coating thickness was investigated by a UVISEL spectroscopic ellipsometer (Horriba) between 250 and 830 nm at an angle of incidence of 75° on silicon wafers coated with APTES film. The thickness obtained corresponds to an average value of three measurements performed at three different spots.

Infrared spectra were acquired using a Fourier Transform Infrared Spectrometer equipped with a deuterated triglycine sulphate (DTGS) detector and a germanium coated potassium bromide beam splitter (Bruker Ten-sor 27 spectrometer). Attenuated Total Reflectance mode was employed and the investigation range is from 600 and 4000  $\text{cm}^{-1}$  in order to obtain an overview of the main functional groups present in as deposited coating. The FTIR spectra were recorded after 44 scans with a resolution of 4  $\text{cm}^{-1}$ .

XPS spectra were collected using PHI 5600-ci XPS spectrometer (Physical Electronics, Eden Prairie, MN, USA). For survey and high resolution spectra, the anode used was a monochromatic Al (1486.6 eV) and an Mg K a (1253.6 eV) X-ray sources at 200W, respectively. Analyses were performed with a 45° angle from the surface. The analyzed surface area was 0.005 cm<sup>2</sup>. Curve fitting for the high resolution C<sub>1s</sub> core level peaks was done by using the XPS PEAK Software (version 4.1) by means of a least square peak fitting procedure using a Gaussian-Lorentzian function (30% Lorentzian) and a Shirley baseline fitting. For the deconvolution procedure, the full width at half maximum (fwhm) are maintained constant with reference to the fwhm of the CH<sub>x</sub> component. Depending on the carbon bond and its more or less electron negative partner, the carbon groups were assigned to the corresponding positions. The quality of the peak syntheses were evaluated by the maximal residual standard deviation (residual STD) method. An analysis was considered significant if the residue is close to unity. Finally, the binding energy scale was corrected for the neutralizer shift by using the C<sub>1s</sub> signal from saturated hydrocarbon at 285.0 eV as an internal standard.

An FEI SIRION field-emission scanning electron microscope (FE-SEM) was used to examine the morphology of two surfaces with AuNPs using different method for APTES deposition at an accelerating voltage of 20 kV. All the samples were coated with Carbon to enhance their surface conductivity. The distribution of gold nanoparticles on the surfaces was established considering 1,000~1,500 particles. The transmission electron microscopy (TEM) images were performed on a JEOL JEM2100 transmission electron microscopy operating at an accelerating voltage of 200 kV. Samples for the TEM analysis were dropped onto a carbon coated copper grid and dried in air before TEM analysis.

# 4.4 Results and discussion

# 4.4.1 APTES deposition and surface Characterization

Contact angle measurements were performed to investigate the wettability of the two surfaces using different deposition methods (Table IV-2). The initial clean raw glass surface is superhydrophilic and the WCA ( $\approx 0^{\circ}$ ) could not be measured due to drop spreading. However, after APTES deposition by wet chemistry and PECVD the WCAs changed to  $32.9\pm0.8^{\circ}$  and  $3.0\pm0.6^{\circ}$ , respectively, indicating successful chemical modification of the surface. The changes of WCA before and after deposition are related with the hydrophobic alkane group in APTES, which results in WCAs increase according to previous results <sup>[22]</sup>.

Furthermore, the difference of WCAs between two as deposited surfaces could be due to a higher number of H-bonded amines resulting in higher contact angle are produced during APTES deposition. Although based this level of analysis, determining the relation between differences in molecular structure and surface density to contact angle is difficult, it could be reasonably speculated the presence of H-bonded amines imply the existence of physisorbed APTES in coating. However, it is well known that APTES molecule binds to the glass surface through the formation of Si-O-Si bond, which originates from the interaction between hydroxyl groups of active surface and ethoxy groups of APTES. Thus, the deposition of APTES is accompanied with loss of hydrophobic alkane groups. The increase of physisorbed APTES means the increase of alkane groups in coating and finally leads to a higher WCA value.

<b>1</b>	e		1
Deposition	WCA (°)	Thickness (nm)	Growth rate
method	WCA()	1 mckness (mm)	(nm/s)
Raw glass	0	-	-
Wet chemistry	32.9±0.8	8.7±4	0.0048
PECVD	3.0±0.6	128.8±8	3.2

Table IV-2 Table presenting (1) the water contact angle; (2) the thickness and (3) the calculated deposition rate using wet chemistry and PECVD process.

At the beginning of the wet chemistry process, acid solution treatment leads to forming massive -OH groups on glass surface, which would subsequently bond more free amines during deposition than that prepared using plasma process. Thicknesses of the two resulting coatings are presented in Table IV-2 and highlight a large difference; the calculated coating growth rate from ellipsometry using wet chemistry method is thoroughly lower than that using PECVD method.

The same conclusion could be obtained from FTIR-ATR spectra shown in Fig. IV-1(a). The peak intensity, which is closely related to the coating thickness <sup>[162]</sup>, is very weak on the glass surface treated by wet chemistry method with APTES, compared to that using PECVD process. FTIR spectra show similar features between 3000 and 2800 cm<sup>-1</sup> which originate from several CH stretch modes of the APTES backbone and ethoxy, evidencing our speculation of WCA changes. Moreover, appearances of a broad mode around 3400 and 3250 cm<sup>-1</sup> corresponding to NH, a vibrational mode at 1620 cm<sup>-1</sup> corresponding to NH<sub>2</sub> as well as modes at 1150 and 1050 cm<sup>-1</sup> corresponding to Si-O-Si indicate all the characteristic bonds of APTES have been obtained by PECVD method (black line) <sup>[154]</sup>.



Fig. IV-1 FTIR spectra of glass surface before and after functionalization with APTES using wet and dry process: (a) Survey scanning, (b) Amplification of range between  $2250 \sim 1250 \text{ cm}^{-1}$ .

The magnification of the scanning region during 2250~1250 cm<sup>-1</sup> shown in Fig. IV-1(b), reveals a mode at 1750 cm<sup>-1</sup> corresponding to C=O stretching of amide group indicating a partial oxidation of amines during functionalization: The active atomic oxygen originating from fragmentation of O<sub>2</sub> traces in chamber is probably too aggressive and the active species could break the C-H bonds and replace them with the C=O bonds by forming amide group (cf. Fig. IV-2). Moreover, the weak absorption mode around 1600 cm<sup>-1</sup> also proves the formation of APTES coating using wet chemistry method (red line). It is more interesting to note that a tiny amine peak center difference between 1620 and 1600 cm<sup>-1</sup> is observed in the two spectra; the slight shift towards lower wavenumbers indicates the transformation of free amines into H-bonded amines <sup>[154]</sup>, which is in good agreement with our previous speculation that more H-bonded amines are formed by wet chemistry method due to the higher amount of -OH generated in pretreatment with acid.



Fig. IV-2 Formation of amide during plasma process

Since the thickness of coating deposited using wet chemistry method is too small to be characterized by FTIR studies, XPS was used for investigation of the topmost surface composition thereafter. As shown in Fig. IV-3 the full XPS spectra on the same scale of the raw glass and after modification using the two methods, the N<sub>1s</sub> characteristic peak changed from the background noise level to the prominent peak around 400 eV after deposition. Moreover, the elemental composition reported in Table IV-2 after APTES deposition highlights an intensity decrease of O and Si, while N and C increase. The Na from the glass substrate is attenuated due to coverage of coating. All the results could be related to a successfully functionalization with APTES using both methods. The O/Si ratio of glass substrates functionalized using wet chemistry method ( $O/Si_{W-APTES} = 2.2$ ) is lower than the theoretical ratio of unreacted APTES (O/Siunreacted= 3), showing that the condensation reaction has occurred and a cross-linking reaction is obtained. C/Si<sub>W-APTES</sub> ratio of 2.9 is approximate to that of a -tripod structure" APTES (C/Si<sub>tripod ATPES</sub>= 3), which has a structure with each of the three Si-O-CH<sub>2</sub>-CH<sub>3</sub> groups forming a Si-O- group on glass substrate by losing ethoxy groups <sup>[151]</sup>. This is also evidenced from FTIR spectra the absorption peak presents as shoulder at 1150 cm<sup>-1</sup> is observed besides the absorption peak at 1150 cm<sup>-1</sup>. According to literature <sup>[86, 162]</sup>, the absorption band around 1050 cm<sup>-1</sup> is more characteristic for long chain or cyclic Si-O-Si, which probably originates 120

from physisorbed APTES; the band around 1150 cm<sup>-1</sup> is assigned to short chain Si-O-Si, which is possibly attributed to siloxane groups from (i) the glass substrate, (ii) condensed APTES with the glass surface, (iii) polymerized APTES <sup>[162]</sup>. The higher O/Si ratio (O/Si<sub>P-APTES</sub>= 3.4) exhibited in coating formed with PECVD process, indicates incorporation of oxygen, which could be attributed to that APTES molecules are partly oxidized by excitation of residual O<sub>2</sub> trace in chamber during plasma process <sup>[83]</sup>. It is in good agreement with FTIR spectra revealing that oxidation of APTES results in formation of C=O bonds at 1750 cm<sup>-1</sup> (cf. Fig. IV-1). C/Si<sub>P-APTES</sub> ratio of 4.7 is also higher than C/Sitripod ATPES of 3 but lower than C/Siunreacted of 9. Considering the chemical structure of APTES ( $NH_2(CH_2)_3$ -Si( $OC_2H_5$ )<sub>3</sub>), the result reveals that during the plasma deposition not every APTES molecule could lose three of its ethoxyl groups from Si-O-CH<sub>2</sub>CH<sub>3</sub> tails. Perhaps it loses only one or two ethoxys from three tails or it keeps three ethoxy groups and is physisorbed in the coating, thus the result indicates the coating deposited using plasma is consisted with complicated chemical structures and still remains ethoxy groups on part of APTES molecules' Si-O tails. The existence of strong absorption peak at 1050 cm<sup>-1</sup> perfectly supports this conclusion as it is assigned to the long chain Si-O-Si. However, the N/Si ratio obtained from plasma polymerized coating is much higher than that one obtained from wet chemistry, indicating better amine coverage on substrates.



Fig. IV-3 XPS survey spectra of glass substrates before and after functionalization with APTES using the two described methods.

С 0 Si N Deposition Na O/Si C/Si N/Si method (at. %) (at. %) (at. %) (at. %) (at. %) 0.7 **Raw** glass 52.3 23.8 19.5 3.8 \_ Wet 33.9 44.2 15.2 3.8 2.9 2.2 2.9 0.25 chemistry 33.9 47.5 8.3 PECVD 10.1 0.2 3.4 4.7 0.82

Table IV-2 Surface chemical composition of glass substrates before and after functionalization with APTES using wet chemistry and plasma processing.

Fig. IV-4 shows the high-resolution  $C_{1s}$  spectra of all surfaces. The deconvoluted  $C_{1s}$  spectrum of the raw glass substrate (Fig. IV-4 (a)) shows only one additional peak at 286.6 eV (C<sub>4</sub>) with the major C-C, C-H peak (C<sub>2</sub>, 285 eV). This former peak could be due to presence of C-O from glass surface. The appearance of C-C/C-H region is probably due to absorbed hydrocarbon at the topmost surface of glass <sup>[175]</sup>. As shown in Figs. IV-4(b) and (c), qualitatively the C<sub>1s</sub> spectra for both coatings using different deposition methods look reasonably similar with a saturated

C-C, C-H peak (C<sub>2</sub>, 285.0 eV), a peak to lower binding energy at 284.2 eV (C<sub>1</sub>, ~-0.8 eV) corresponding to C-Si bond and three additional peaks at higher binding energy at 286 eV (C<sub>3</sub>, ~+1.0 eV) 286.6eV (C<sub>4</sub>, ~+1.6 eV) and 288.1 eV (C<sub>5</sub>, ~+3.1 eV), which are best associated to C-N, C-O/C=N and C=O/N-C=O bond, respectively. In the case of C<sub>1s</sub> spectra, the relative amount of C-N bond (C<sub>3</sub>) is higher in the coating carried out with plasma polymerization (18.3%) than that in the coating deposited using wet chemistry method (8.0%), indicating a better amine functionalization is achieved by PECVD (Table IV-3). In parallel higher amount of C-N(C<sub>3</sub>), C-O/C=N (C<sub>4</sub>) and C=O/N-C=O (C<sub>5</sub>) are obtained in plasma deposited coating with lower amount of C-C (C<sub>2</sub>) of C-Si (C<sub>1</sub>). It probably indicates that more ethoxy groups are removed from Si-O tails of APTES molecules, and subsequently they are oxidized as well as parts of amines by excited oxygen during plasma process <sup>[83]</sup>.





Fig. IV-4 High-resolution  $C_{1s}$  spectra of glass substrates before and after functionalization with APTES using different methods: (a) Raw glass, (b) using wet chemistry technique, (c) using PECVD processing.

Deposition method	C <sub>1s</sub>					Amine (relative to total composition, %)
	C <sub>1</sub> (%)	C <sub>2</sub> (%)	C <sub>3</sub> (%)	C <sub>4</sub> (%)	C <sub>5</sub> (%)	
Raw glass	-	84.1	-	15.9	-	-
Wet chemistry	19.5	56.0	8.0	9.3	7.3	3.5
PECVD	13.9	41.7	18.3	12.1	14	8.7

Table IV-3 Relative contribution of the deconvoluted components of the  $C_{ls}$  peaks.

# 4.4.2 Study of the immobilization of AuNPs

Fig. IV-5(a) shows the UV-vis spectrum of the synthesized gold nanoparticles. A narrow plasmon band is present at 520 nm, indicating a monodisperse particle size of ~15 nm  $^{[176]}$  in accordance with the results obtained from TEM and size distribution histogram (Fig. IV-5(b)).





Fig. IV-5 (a) UV-Vis spectrum of the aqueous colloidal solution of AuNPs; (b)

TEM image of the synthesized AuNPs, inset: size distribution histogram

Herein we have chosen to study the immobilization of AuNPs on amine functionalized glass surfaces using electrostatic interactions. Indeed the pH of the Au nanoparticle solution is about 6.2 which guarantees a total deprotonation of the citrate groups on AuNPs (zeta potential,  $\zeta$ = -30 mV) and a positive charge on APTES amine groups (NH<sub>3</sub><sup>+</sup>, pKa= 10.6 <sup>[177]</sup>).

Fig. IV-6 shows SEM images recorded before and after immobilization of AuNPs on the functionalized glass surfaces with APTES using the two methods. Although immobilization of gold NPs is evident using wet chemistry (Fig. IV-6(a)) and PECVD (Fig. IV-6(b)) techniques, the higher coverage in AuNPs is clearly observed when the surface was modified using plasma processing, highlighting the importance to obtain a high density of amine. However for both methods aggregates of gold nanoparticles are clearly observable, which may be attributed to destabilization of the gold colloidal suspension in contact with the APTES surface.

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Fig. IV-6 SEM images and XPS spectra of different glass surfaces before and after immobilization of AuNPs: (a) SEM of Raw glass, (b) SEM of glass functionalized with APTES using wet chemistry method, (c) SEM of glass functionalized with APTES using PECVD method, (d) XPS survey scanning, (e) Amplification of range between 100~75 eV.

Fig. IV-6 also depicts XPS survey scan obtained after immobilization of AuNPs on the APTES deposited onto glass substrates using the two methods. By comparison to the spectra obtained for raw glass and functionalized glass (Fig. IV-3), herein the spectra revealed new energy peaks due to the immobilization of gold nanoparticles onto functionalized substrates. The difference in relative peak intensity of Au<sub>4f</sub> peaks reveals that the sample prepared by PECVD has higher Au loading, which is consistent with the observed AuNPs coverage by SEM. It is also noticed that a fairly high Na content is detected compared with the surfaces before gold immobilization: When gold is immobilized on the wet chemistry functionalized surface the atomic percentage of sodium increases from 2.9% to 4.4%; When gold is immobilized on the PECVD functionalized surface it increases from 0.2% to 7.2%.. Actually, gold nanoparticles are negatively charged due to citrate anions on their surfaces, therefore the existence of sodium cations bring the charge balance for colloidal AuNps<sup>[178]</sup>. During the immobilization step, parts of negatively charged gold surface link to protonate amine by forming an electrostatic bonding, however free citrate anions still exist on parts of the particle surface, thus the sodium cations on free surface of the attached nanoparticles keep the charge balance.

For deeper investigation, we performed the high resolution XPS spectra of AuNPs on PECVD functionalized glasses (Fig. IV-7). The diffused peaks with binding energy of about 83.7 and 87.4eV can be assigned to  $Au_{4f7/2}$  and  $Au_{4f5/2}$  in the metallic state, indicating Au(0) is attached on the surface. But a shift of 0.3~0.6 eV is observed from the binding energy of bulk metallic gold (84.0 eV and 88.0 eV). This shift toward lower value is probably ascribed to negative charged gold due to the electron transfer from substrate to AuNPs <sup>[179].</sup>



Fig. IV-7 Au<sub>4f</sub> spectrum of AuNPs immobilized on plasma treated glass substrate.

In order to understand the transformation of amine during AuNPs deposition, high resolution spectra of  $C_{1s}$  and  $N_{1s}$  before and after immobilization were investigated (Fig. IV-8). The  $C_{1s}$  region of both AuNPs immobilized surfaces is fitted with five components previously mentioned for APTES functionalized glass surface: peaks at 284.2, 285, 286, 286.6, and 288.1 eV, assigned to the C-Si, C-C, C-N, C-O/C=N and C=O/N-C=O, respectively. Additionally, another new peak at 289.2 eV corresponding to O-C=O moieties is added, originating from citrate anions of AuNPs, which is an evidence of successful immobilization of AuNPs.





Fig. IV-8 High-resolution  $C_{1s}$  spectra of different treated glass substrates after AuNPs immobilization: (a) using wet chemistry method, (b) using PECVD process.

For  $N_{1s}$ , the signals of the surface before gold immobilization can be deconvoluted into two peaks at 399.7 and 400.9 eV <sup>[180]</sup>, assigned to free amines -NH<sub>2</sub> (N<sub>1</sub>) and protonated amines -NH<sub>3</sub><sup>+</sup> (N<sub>2</sub>, ~+1.2 eV), as shown in Figs. IV-9(a) and (b). The surface after gold immobilization also presents two peaks; the first is the same as N<sub>1</sub> at 399.7 eV, and the other one is observed with a slight shit, at 400.5 eV (Figs. IV-9(c) and (d)). This shift of the second peak center to lower energy could be ascribed to bounding of NH<sub>3</sub><sup>+</sup> species with gold ions <sup>[181]</sup>. However it is difficult to discriminate the contribution of amide group (N-C=O) from the amine one <sup>[23]</sup>. It is also possible to quantify the species by integrating the peak areas.

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Fig. IV-9 High-resolution  $N_{1s}$  spectra of different glass surfaces before and after immobilization of AuNPs: (a) using wet chemistry method, before immobilization; (b) using PECVD process, before immobilization; (c) using wet chemistry method, after immobilization; (d) using PECVD process, after immobilization.

Deposition method	N <sub>1</sub> (%)	N <sub>2</sub> (%)
Wet chemistry before Au immobilization	71.2	28.8
Wet chemistry after Au immobilization	59.0	41.0
PECVD before Au immobilization	74.8	25.2
PECVD after Au immobilization	54.3	45.7

Table IV-4 Relative contribution of the deconvoluted components of the  $N_{1s}$  peaks

The results presented in Table IV-4 confirm that both AuNPs-APTES-glasses have a higher percentage of protonated amines in  $N_{1s}$  than APTES-glasses, indicating

the transformation from free amine to protonated amine during immobilization. The result also proves that massive protonated amines are formed on glass surface by the acidic aqueous colloidal solution of AuNPs of pH 6.2, which would benefit in binding negative charged gold nanoparticles to substrate.

# **4.5**Conclusion

In this work, we studied the potentiality of wet chemistry and plasma processes to functionalize glass with amine groups from APTES precursor, and the ability of such modified surfaces to immobilize gold nanoparticles. Characterizations of WCA, FTIR as well as XPS confirmed the successful deposition of cross-linking APTES on glass surfaces by wet chemistry and PECVD techniques. In comparison, our results clearly evidenced that plasma polymerized coatings from APTES precursor exhibit better hydrophilicity, higher coating thickness, as well as higher amine groups density, leading to a further higher coverage and amount of gold(0) nanoparticles. However, SEM images depicted the presence of gold aggregates, indicating an optimal sonication is required to obtain better dispersion in the future. Finally, XPS studies carried out after gold immobilization highlighted the appearance of another new contribution at 289.2 eV assigned to O-C=O bond due to the citrate anions from gold nanoparticles as well as an increase of protonated amine groups during immobilization procedure, evidencing AuNPs were bound to R-NH<sub>3</sub><sup>+</sup> species.

# Chapter V Deposition of Y-zeolite and Au@Y-zeolite on amine functionalized surface

# 5.1 Abstract

Immobilization of gold nanoparticles on the zeolite is an efficiency way to improve their catalytic activity. The organic molecules grafted on surface with terminal functional groups that link to AuNPs by electrostatic or chemical bonding is the essential factor for good immobilization. In this work, linkage reagents APTES and MPTES respectively ascribed to electrostatic bound and chemical bound were used for zeolite surface functionalization, and then AuNPs were immobilized on their surfaces. The results evidenced APTES was the better linker for gold immobilization on zeolite surface as higher gold loading was observed. Furthermore, zeolite and Au@zeolite were functionalized using CES, which is a potential candidate that provides COO<sup>-</sup> groups. Consequently they were deposited on COC surface through the  $-NH_3^+/-COO^-$  zwitterionic pairs. The experimental results proved our method could deposit zeolite or Au@zeolite on COC and form a completely zeolite covered surface. The coating was also evidenced to have good stability in hydrodynamic flows and could be further used in microfluidics.

Keywords: Y zeolite, gold immobilization, functionalization, Au@zeolite deposition

# **5.2 Introduction**

The usage of gold nanoparticles (AuNPs) as catalysts for different kinds of chemical reactions is studied since decades <sup>[88-91, 171]</sup>. Although gold particles with nano size are very attractive for catalysis, a decrease of their catalytic activity in terms of aggregation occurs, which is ascribed to the decrease of the surface energy of nanoparticles in the low nanometer diameter range <sup>[182, 183]</sup>. In some cases, the serious aggregation even leads gold to show much lower activity than group VIII metals <sup>[184]</sup>.

In previous studies, supported gold has gained attractive interest since its huge benefits in improving gold catalytic efficiency was reported <sup>[185-188]</sup>. Initially, reducible metal oxides such as TiO<sub>2</sub>, ZnO and Fe<sub>2</sub>O<sub>3</sub> were preferably employed as supports for gold <sup>[189-191]</sup>. Thereafter, the attractiveness of silica materials as supports for gold catalysts increased following reports on high catalytic activity of Au/SiO<sub>2</sub> in reactions <sup>[192, 193]</sup>. Non-oxides like activated carbon (AC) are also slightly used as supports due to its unique advantages compared to oxides <sup>[194]</sup>. Furthermore, another interesting candidate for immobilizing gold is zeolite, a relative uncommon support that has a rigid structure with a three-dimensional framework forming channels and/or cages with molecular dimension<sup>[195]</sup>. In spite of being considered as an uncommon support in conventional conception, zeolite has been studied by several research groups in the last 10 years. Okumura et al. reported the performance of gold loaded on Y type zeolite in the CO-O<sub>2</sub> reaction <sup>[107]</sup>. Zhang and co-workers revealed a catalytic activity improvement in alcohol oxidation with Au-zeolite catalysts and furthermore proposed a photo-oxidation mechanism that originates from zeolite absorption <sup>[108]</sup>. Compared with other supports, zeolite could atomically disperse gold catalyst with a high degree of uniformity<sup>[109]</sup>; on the other hand, zeolite was considered as a specific catalyst in some reactions <sup>[110-112]</sup>.

To immobilize gold on zeolite, linkage reagents are usually used. The organic molecules are grafted on the surface with terminal functional groups, which would link to AuNPs by electrostatic or chemical bonding <sup>[23, 78]</sup>. One of important properties <sup>134</sup>

of grafted reagents is that they should be stable over time and the interaction of the nanoparticles with the surface should be strong enough to ensure that the nanoparticles remains attached to the surface for further utilization. Among the reported available linkage reagents, aminopropyltriethoxysilane (APTES) is the most commonly used modifier and has been proved good stability for upon catalytic reaction by Ftouni et al.<sup>[12]</sup> It is also noted that another organosilane the (3-mercaptopropyl)trimethoxysilane (MPTES) with functionalities (thiol groups) was studied in recent researches <sup>[12, 23]</sup> due to its stronger covalent bonding to gold. However, it is still not clear that which reagent is better for attaching gold to zeolite even though few papers focused on immobilizing gold on zeolite with MPTES.

Catalysis inside microsystems has been investigated intensively these last two decades <sup>[12, 196-198]</sup>. Indeed due to their very large surface-to-volume ratio miniaturized fluidic components allow significantly enhancing process control and heat management of chemical reactions <sup>[5, 6]</sup>. Instead of stirring or shaking, continuous flow conditions in microchannel provide an impressive effort in terms of automation compared to conventional heterogeneous catalysis in stationary reactors and thus the catalysis carried out in microsystem leads to higher purity and yield of the desired products compared to that in conventional systems <sup>[12]</sup>. In order to employ zeolite and zeolite supported gold to microsystems a reliable method for deposition is necessary. Although the technology of organizing nano/sub nanometer building blocks into complex structures has become common for scientists in recent years. The ability of well-controlling micrometer-sized building blocks has not yet been acquired <sup>[116]</sup>. Thus, the zeolite microcrystals with a usual size range of 100~1000nm is facing many obstacles for their further application. Despite the slow progress on this aspect, the assembly of zeolite crystals was usually directed by grafting molecules on their surface that can enable their attachment to substrates by electrostatic and/or covalent bonds <sup>[118, 119]</sup>. Since the adhesion between the surface and zeolite is sensitively affected by the nature of interconnecting molecular, it is important to choose a good

linkage for assembly. As described in Chapter III, the surface was pre-deposited with amine groups. Apparently the candidates for our study should be considered to have a good connecting ability to protonated amine. Carboxyethylsilanetriol sodium (CES) has been reported a promising linkage reagent as the uniform carboxylate group distributions on surface endow high change density on the zeolite surface <sup>[199]</sup> and consequently it would provide good connection for negative changed zeolite and surface positive charged substrate through the presence of  $-NH_3^+/-COO^-$  zwitterionic pairs <sup>[120]</sup>. Because there are no reported releases that focus on the usage of CES, this issue represents another big challenge in our study.

In the present work, in order to extend the scope of our previous strategy, we firstly immobilized citrate-Au on the surface of Y type zeolite and then deposited zeolite and Au@zeolite on the amine functionalized cyclic olefin copolymer (COC) flake surface, which will be the essential technology for preparing COC microreactors in our following work. The main goal here is to demonstrate the better linkage reagent for anchoring AuNPs on Y type zeolite surface and to show the possibility to easily construct a highly oriented assembly of zeolite and Au@zeolite crystals on COC surface by a protonated amine- carboxylate electrostatic linkage.

# 5.3 Experimental

#### 5.3.1 Materials and chemicals

COC sheet was cut into small rectangular flakes with length  $\times$  width of 8 mm  $\times$  8 mm. The flakes were ultrasonically cleaned in ethanol and acetones for 10min, respectively then the samples were dried by compressed pressure air. (3-aminopropyl)triethoxysilane (APTES) (98%) and (3-mercaptopropyl)trimethoxysilane (MPTES) (95%) were purchased from VWR, Carboxyethylsilanetriol sodium (CES) (25% in water) was purchased from Fluoro Chem, gold(III) chloride hydrate (99.999%) and silver nitrate (AgNO<sub>3</sub>, 99%) were

purchased from Sigma-Aldrich, trisodium citrate (99%) was purchased from Alfa(Aesar). Y type zeolite (CBV400) was purchased from Zeolyst International. Ethanol and acetone were analytic reagent grade. Pure Ar was used for generating plasma; its purity was higher than 99.99%.

#### 5.3.2 Synthesis and immobilization of AuNPs

5 mL of an aqueous solution of gold(III) chloride hydrate (1wt%) and 420  $\mu$ L of aqeous silver nitrate solution (0.1 wt%) were mixed with 45 mL of Millipore water and heated in flask under reflux until ebullition.1.5 mL of aqueous sodium citrate (10 wt%) was injected into the mixture. Heating was stopped after 30 min and the suspension was cooled to room temperature. Finally it resulted in the formation of a dark purple sol of gold NPs.

#### 5.3.3 Immobilization of gold on zeolite surface using APTES and MPTES

The area on zeolite particle covered by each organosilane molecule was assumed to be nominally 0.6  $\text{nm}^{2}$  <sup>[200]</sup>, the BET result of Y zeolite is 834 m<sup>2</sup>/g, the minimum quantity of APTES for functionalizing per 1mg of Y zeolite was calculated as following:

#### Equation V-1:

Where  $V_{linker}$  is volume of linkage reagent,  $n_{linker}$  is mole number of linkage reagent,  $M_{linker}$  is relative molecular mass,  $\rho_{linker}$  is density of likage reagent,  $S_{lmg}$  is total surface area of lmg zeolite, NA is Avogadro's constant.

To 100 mg of the calcined Y-zeolite powder suspended in 30 mL of anhydrous dichloromethane (DCM), 100  $\mu$ L of APTES or MPTES were added, and the slurry was stirred for 24 h at room temperature. The functionalized zeolite powder was then repeatedly washed by centrifugation to remove unreacted reagent. Next the solid was dried in a gas exchanged oven at 100 °C. The samples thus obtained were used for

gold immobilization.

The functionalized zeolite (50 mg) was dispersed in 20 mL of Millipore water and mixed with 10 mL of the colloidal gold solution under continuous stirring. After 12 h of stirring, the zeolite particles attached with gold nanoparticles were separated by centrifugation and washed with super pure water for several times, and dried in a gas exchange oven at 100 °C. The colloidal solution from first centrifugation was collected for UV-Vis test.

#### 5.3.4 Deposition of APTES using PECVD method

A homemade experimental device called bell-jar reactor was used for the APTES plasma deposition. Firstly, pre-treatment is performed for activation of surface: the working pressure was fixed at 0.7 mbar, the samples were subjected to a 20 W plasma treatment (Ar; flow rate: 10 sccm) during 5 s. Then the samples were functionalized and the parameters used in this work are presented in Table V-1.

Active gas	Working	Working	Deposition Time	Precursor and
	(mbar)	(W)	(s)	
Ar Flow:20	1.0	30	40	APTES/Ar
sccm	1.0			Flow: 10sccm

Table V-1 Plasma parameters in this work

After plasma deposition, the chemical pump was fully loaded again while the turbo molecular pump was stopped immediately. The freshly coated flakes were kept under vacuum for 1 h before venting, in order to reduce post-oxidative reactions between radicals formed on the film surface and atmospheric oxygen<sup>[160]</sup>.

#### 5.3.5 Deposition of zeolite and Au@zeolite

For functionalization of the surface, carboxyethylsilanetriol sodium (CES) was used as linkage reagent. The estimation of minimum CES quantity is the same method 138 from Ref. [200]. To 100 mg of the calcined zeolite powder or Au@zeolite powder suspended in 30 mL of anhydrous toluene, 200  $\mu$ L of CES were added, and the slurry was stirred and heated at 120 °C for 4 h. The functionalized zeolite powder was then repeatedly washed by centrifugation to remove unreacted CES. Next the precipitate was dried in an gas exchanged oven at 100 °C. Thereafter, 50 mg dried zeolite power with 20 mL of Millipore water were transferred into a beaker with stirring bar. Amine-functionalized COC flake surfaces were then dripped with as prepared colloidal zeolite and placed at the bottom of a masked beaker for 24 h. After zeolite or Au@zeolite deoposition, the samples were kept in an oven and heated at 80 °C.

#### 5.3.6 Coating stability test in flowing water

In order to test the stability and the resistance of the zeolite and Au@zeolite coating in water, the Au@zeolite deposited samples were immersed into a beaker that contains water with magnetic sitrring bar. After 12 h, 24 h, 48 h and 72 h, the samples were removed from water and characterized by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS).

#### 5.3.7 Characterizations

An FEI SIRION field-emission scanning electron microscope (FE-SEM) equipped with EDS was used to examine the size and shape of Y type zeolite and the morphology of as deposited zeolite and Au@zeolite coating on COC as well to identify the composition of the coating. Transmission electron microscopy (TEM) images captured on a 2000FX microscope (JEOL, Japan) operating at 200 kV was used for imaging the gold immobilized on zeolite surface using ATPES and MPTES. Energy-dispersive X-ray spectroscopy (EDS) was used to identify the gold content. Powder X-ray diffraction (XRD) patterns were collected on an X'Pert Pro diffractometer with CuKα radiation operating at 45 kV and 40 mA in the range of

5~55° (PANalytical, Netherland). Diffused Reflectance Infrared Fourier Transform (DRIFT) spectrum were recorded on Tensor 27 spectrometer (Bruker, UK) in the range of 4000~400 cm<sup>-1</sup> using the KBr disk method. Zeta-potential measurements were performed using a zetasizer Nano ZS from Malvern instrument. UV-Vis absorption spectra were obtained from spectrophotometer (Ocean optics, USA). XPS spectra were collected using PHI 5600-ci XPS spectrometer (Physical Electronics, USA). BET surface area values were determined at liquid nitrogen temperature using a Micromeretics ASAP 2000 equipment after outgassing the sample at 250 °C.

# 5.4 Results and discussion

#### 5.4.1 Characterization of Y zeolite

Fig. V-1(a) shows the SEM image of the Y type zeolite (CBV400) used in our study. The close inspection of the SEM images indicates that the crystals are isolated with size distributions between 300~900 nm and an average diameter of 450 nm as deduced from the histogram in Fig. V-1(b). The XRD pattern (Fig. V-1 (c)) agrees with a faujasite zeolite structure NaY as characteristic peaks at  $2\theta = 6.19^{\circ}$ , 11.86° and 15.61° are observed in accordance with literature <sup>[120, 201, 202]</sup>. The BET result obtained from the nitrogen adsorption isotherms shows an extremely high total surface area of 834 m<sup>2</sup>/g.



Fig. V-1 Characterizations of Y type zeolite used in this work: (a) SEM image; (b) size distribution histogram and (c) XRD spectrum.

# 5.4.2 Immobilization of AuNPs on Y type zeolite using APTES and MPTES

Herein, the citrate AuNPs (as described in Chapter IV) were immobilized on the Y type zeolite surface using APTES and MPTES as linkers (Scheme V-1). The APTES linker chosen due electrostatic affinity was to the of the ammonium-terminating function to the negatively charged gold nanoparticles as it has been clearly described in literature <sup>[78]</sup>. MPTES was chosen for its thiol functionality known to bind strongly with gold nanoparticles <sup>[23]</sup>. Under experimental conditions (pH= 4.2), the amino-terminated functions (pKa= 10.6) are fully protonated (acid form:  $NH_3^+$ ) and bond to the negatively charged gold nanoparticles.



Scheme V-1 Preparation method of Au@zeolite using APTES and MPTES.

In order to confirm the assembly process, zeta-potential measurements were performed at pH= 4.2 during the whole gold immobilization process. It shows that the average potential of initial Y zeolite colloids is -39.7 mV, thus the attachment AuNPs with negative zeta potential (-35 mV at same pH) would not be effective. After being functionalized with APTES and MPTES molecules, the zeta potential value respectively increased to -36.4 and -12.2 mV, indicating the efficient attachment of silanes to Y zeolite. It is important to note that APTES functionalized Y zeolite with positive charge are perfect building blocks for further decorating negatively charged
AuNPs through electrostatic interactions. After adding AuNPs to APTES and MPTES functionalized zeolites colloids, the zeta-potential was decreased to -40.2 and -44.2 mV, indicating that AuNPs indeed attached onto the surface of zeolites through electrostatic assembly process. The results of the different zeta potential measurements are summarized in Table V-2.

APTES and MPTES.							
Zeta	Original zeolite	Functionalized zeolite	Gold immobilized zeolite				
potential (mV) -	-39.7	-36.4	-40.2				
	-39.7	-12.2	-44.2				

Table V-2 Zeta potential results of zeolite before and after functionalization with

Besides, the observed DRIFT spectra of Y zeolite before and after functionalization (Fig. V-2) confirmed the successful attachment of APTES and MPTES. The absorption features of Y zeolite are a result of stretching and bending modes of the T-O units (T = Si or Al) in zeolite framework: the bands at 1150 and 725 cm<sup>-1</sup> are assigned to the asymmetric and symmetric stretching modes of internal tetrahedral, while the bands at 1030 and 792 cm<sup>-1</sup> are associated with the asymmetric and symmetric stretching modes of external linkages <sup>[201]</sup>. The broaden peak at the range 3750~3200 cm<sup>-1</sup> as well as the peak at 1650 cm<sup>-1</sup> could correspond to -OH groups existing on zeolite surface <sup>[203]</sup>.



Fig. V-2 Different DRFIT spectra of Y zeolite before and after functionalization with APTES and MPTES.

APTES functionalized zeolite is dissimilar with original zeolite: an obvious NH<sub>2</sub> absorption feature is obtained at 1580 cm<sup>-1</sup> companied with decrease of zeolite original absorption peaks at 3750, 1650, 1150, 1030, 792 and 725 cm<sup>-1</sup>, which indicates a good coverage of silane on surface with many amine functionalities. The spectrum of MPTES functionalized zeolite shows one absorption peak representing the C-S stretch at 671 cm<sup>-1</sup> with the same trend of decreasing original zeolite characteristic peaks, also revealing the successful functionalization with thiol.

Furthermore, Fig. V-3(a) shows UV-Vis spectra recorded from the as-prepared colloidal gold solution before and after immobilization on Y zeolite colloids. The absorption band at 520 nm is associated with the surface plasmon resonance (SPR) of AuNPs <sup>[204]</sup> with an average diameter of 13 nm (shown in chapter IV). The presence of this band in APTES and MPTES functionalized zeolite suspensions demonstrates the successful immobilization of gold using the two molecules. However the SPR band shifted to around 528 nm for Au@zeolite-amine, while 523 nm for

Au@zeolite-thiol. The higher shift observed in the Au@zeolite-amine suspensions can be related to a higher density of attached AuNPs to their surface compared to Au@zeolite-thiol and a smaller distance between AuNPs.



Fig. V-3 UV-Vis spectra of gold on zeolite: (a) immobilized gold on zeolite with APTES and MPTES; (b) the colloidal gold solution collected after immobilization using APTES and MPTES.

Indeed, when the gold solutions were left in contact with both zeolites (after stirring for 12 h) and after centrifugation (4000 rpm), the spectra of the supernatants as shown in Fig. V-3(b) showed that there is a drastic loss in intensity of surface plasmon resonance after gold was immobilized on APTES functionalized zeolite, indicating a higher decrease in the concentration of gold nanoparticles in aqueous solution. This clearly indicates that the amine-functionalized zeolites are better supports for gold immobilization.

Fig. V-4 shows XRD patterns recorded from the original zeolite powder and the functionalized zeolite powder after immobilization. It is interesting that no obvious change in peak position and peak intensity is observed after gold immobilized zeolite. This result should be attributed to the unchanged crystallinity of the zeolite after the different surface coatings with silanes and binding of gold nanoparticles <sup>[78]</sup>. Moreover these results evidence that the gold nanoparticles are only bound to the surface of the zeolite particles without entering in the pores of the zeolite which is probably due to the bigger gold size (size range 8~23 nm and average size 13 nm from TEM) compared to zeolite pore size (24.5 Å). Due to the low amount of gold (see XPS results) compared to zeolites, gold peaks could not be detected using XRD.



Fig. V-4 XRD spectra of zeolite before and after functionalization with APTES and MPTES

To compare the amounts of immobilized gold nanoparticles on zeolite surface using APTES and MPTES, the samples were characterized using TEM and EDS as shown in Fig. V-5. In all images, gold nanoparticles (dark spots) decorating the surface of the zeolite particles can clearly be seen. The gold nanoparticles on the surface are uniform in size with a diameter range of 10~20 nm, presenting a spherical shape. Moreover, as it is observed quite obviously in Figs. V-5(a) and (c), the surface of amine functionalized zeolite has a denser number of gold nanoparticles compared to thiol functionalized zeolite surface (Figs. V-5(b) and (d)), which is in accordance with the previous UV-Vis results. Moreover, the EDS results (Figs. V-5(e) and (f)) also confirm a higher gold content of 6.8% from Au-amine-zeolite compared to that of thiol functionalized zeolite (4.8%). The different gold loading ability is possibly due to two reasons: the gold is preferred to bind to amine functionality than thiol in this study. However, it has to be announced that thiol provides covalent link to AuNPs has better ability to attach gold <sup>[12, 205]</sup>. It is noticed that the pH value 4.2 of gold colloid is

much lower than pKa<sub>thiol</sub> of 10 <sup>[206]</sup>, thus only a small fraction of the thiolates are dissociated at this pH. SH groups are protonated and do not bound AuNPs through covalent bonds; on the other hand, although theoretically the amount of gold immobilized on surface is equivalent to the amount of linked silane molecules, the study of Haddada et al. <sup>[23]</sup> evidenced that MPTES had led to lower gold loading when its amount was similar to APTES at the same conditions.



Fig. V-5 TEM images and EDS results of gold on amine-zeolite and thiol-zeolite: (a) Au@amine-zeolite low magnification; (b) Au@thiol-zeolite low magnification; (c) Au@amine-zeolite high magnification; (d)Au@thiol-zeolite high magnification; (e) EDS spectrum of Au@amine-zeolite; (f) EDS spectrum of Au@thiol-zeolite.

The zeolite, APTES-zeolite, MPTES-zeolite, Au-APTES-zeolite and Au-MPTES-zeolite surfaces were further characterized by XPS analysis. The main XPS spectra are shown in Fig. V-6. For silane functionalized samples, in addition to the silicon, oxygen, alumina, sodium and carbon peaks arising from zeolite, the presence of N<sub>1s</sub> peak at 400 eV and the sulfur peak at 162 eV corresponding to the S<sub>2p</sub> indicates a good modification by both linkers <sup>[22, 207]</sup>. Furthermore, the survey scan spectra of gold immobilized samples indicate the successful immobilization on both surfaces due to the presence of characteristic Au<sub>4f</sub> peaks at 84 eV <sup>[178]</sup>. The difference in relative peak intensity of Au<sub>4f</sub> peaks reveals that the sample functionalized with APTES has higher Au loading, which is consistent with the previous results from UV-Vis, TEM and EDS.



Fig. V-6 XPS survey scan spectra of zeolite, amine or thiol functionalized zeolite and gold immobilized zeolite.

Fig. V-7 displays  $C_{1s}$  XPS spectra of original zeolite, amine functionalized zeolite, thiol functionalized zeolite and the gold immobilized zeolites. For a relative low intensity of  $C_{1s}$  spectrum from original zeolite sample (% $C_{1s}$ =5.4), three major

peaks are identified (Fig. V-7 (a)). The peak centered at 285 eV corresponds to C-C and C-H, the peak at 286.6 eV corresponds to C-O, while the peak at 284.2 eV is assigned to C-Si. All the characteristic peaks could be related from the chemical structure of Y type zeolite. An increase of  $C_{1s}$  content (% $C_{1s}$ = 25) is observed (Fig. V-7(b)), which could be attributed to a coverage of new molecule consisted with high amount of carbon in chemical structure, evidencing functionalization of ATPES on the surface. Five peaks are also identified in the  $C_{1s}$  spectrum of the amine functionalized zeolite. The peak centered at 285 eV corresponds to methylene carbons and the peak at 284.2 eV is assigned to C-Si from silane, while carbon atoms bonded to nitrogen and oxygen appear at 286 eV, 286.6 eV and 288.1 eV, which originate from amine, ethoxy and amide groups, in accordance with the previous results from literature <sup>[83]</sup>.

The increase of  $C_{1s}$  intensity (% $C_{1s}$ = 33.4) is also observed from the thiol functionalized zeolite (Fig. V-7(d)). Moreover, the  $C_{1s}$  spectrum is fitted with three peaks. The peak centered at 285 eV corresponds to methylene carbons and carbon bonded to sulfur <sup>[208-210]</sup>, the peak at 284.2 eV is assigned to C-Si from silane, while carbon atoms bonded to oxygen appear at 286.6 eV <sup>[211]</sup>. The  $C_{1s}$  region of gold immobilized zeolites are also investigated and fitted with the peaks that previously mentioned for amine and thiol functionalized surfaces, respectively (Figs. V-7(c) and (e)). Additionally, another new peak at 289.2 eV corresponding to O-C=O is added for amine-zeolite and thiol-zeolite samples, originating from citrate anions of AuNPs, which is an evidence of successful immobilization of AuNPs.



Fig.V-7 High resolution  $C_{1s}$  spectra of zeolite, functionalized zeolite and gold immobilized zeolite: (a) untreated zeolite; (b) amine functionalized zeolite; (c) Au@amine-zeolite; (d) thiol functionalized zeolite; (e) Au@thiol-zeolite.

The N<sub>1s</sub> XPS spectra of amine-zeolite and Au-amine-zeolite samples are presented in Figs. V-8(a) and (b). The signals of the surface before gold immobilization can be deconvoluted into two peaks at 399.7 and 401.6 eV, assigned to free amines -NH<sub>2</sub> (N<sub>1</sub>) and protonated amines -NH<sub>3</sub><sup>+</sup> (N<sub>2</sub>, ~+1.9 eV). When the gold is immobilized on zeolite surface, a slight change is observed: the lower BE peak is the same as N<sub>1</sub> of amine-zeolite at 399.7 eV, corresponding to free amine; however the other peak at higher BE is with a shift towards to lower BE (~0.7 eV) at 400.9 eV, which could also be assigned to protonated amine. This shift is ascribed to bounding of  $NH_3^+$  species are to gold ions <sup>[181]</sup>. Moreover, an obvious decrease of free amines indicates the transformation from free amine to protonated amine during immobilization, the result proves that under our immobilization condition that the pH value of acidic aqueous colloidal AuNPs is 4.2, the amino-terminated functions (pKa= 10.6) are massively protonated ( $NH_3^+$ ) and bond to the negatively charged gold nanoparticles.

The S<sub>2p</sub> XPS spectra of thiol-zeolite and Au-thiol-zeolite samples are shown in Figs. V-8(c) and (d). Before gold immobilization the S<sub>2p</sub> spectrum shows a single peak at 163.6 eV for S<sub>2p3/2</sub>, which is ascribed to reduced sulfur (i.e. sulfur in the SH groups) <sup>[23]</sup>. After gold immobilization, a new peak appears at 162.6 eV, which is consistent with the reported gold-thiolate binding energy for thiols adsorbed on gold surfaces <sup>[211]</sup>, indicating thiol-gold bond formation and successful gold immobilization with thiol groups in our study.



Fig. V-8 High resolution  $N_{1s}$  spectra and  $S_{2p}$  spectra of functionalized zeolite and gold immobilized zeolite: (a)  $N_{1s}$  of amine functionalized zeolite; (b)  $N_{1s}$  of Au@amine-zeolite; (c)  $S_{2p}$  of thiol functionalized zeolite; (d)  $S_{2p}$  of Au@thiol-zeolite.

The high resolution Au<sub>4f</sub>XPS spectra of Au-amine-zeolite and Au-thiol-zeolite are presented in Fig. V-9. The curve fitting of the spectrum revealed Au<sub>4f7/2</sub> and Au<sub>4f5/2</sub> components at BE values of 83.7 and 87.4 eV, which may be attributed to Au (0) specie, according to Lin et al.'s work<sup>[106]</sup>. A slight shift of 0.3~0.6 eV is observed from the binding energy of bulk metallic gold (84.0 and 88.0 eV) <sup>[212]</sup>, which could be ascribed to negative charged gold due to the electron transfer from substrate to AuNPs <sup>[179]</sup>. All studied samples reveal the presence of metallic gold species, in agreement with TEM images.



*Fig. V-9 High resolution Au*<sub>4f</sub> spectra gold immobilized zeolite: (a) Au@amine-zeolite; (b) Au@thiol-zeolite.



## 5.4.3 Deposition of zeolite and Au@zeolite on COC surface

Scheme V-2 Schematic illustration of the process for depositing zeolite and Au@zeolite on plasma functionalized COC surface.

After a comparison study of using two linkage reagents for gold immobilization on zeolite surfaces, APTES has been proved a better ability for Au loading at the same conditions. Thus, we will use Au-amine-zeolite for deposition study for further work in this thesis. The whole process for depositing zeolite and Au@zeolite on the COC surface is depicted in Scheme V-2: firstly zeolite and Au@zeolite are functionalized using carboxyethylsilanetriol sodium (CES); meanwhile, COC substrate is plasma polymerized with APTES for endowing amine groups on its surface; thereafter, as prepared colloidal zeolite and Au@zeolite solutions with adjusted pH value of 8.4 is dripped on amine functionalized COC surfaces. The samples are kept in a masked beaker for 24 h for complete deposition.

Zeta-potential measurements at pH = 8.4 were firstly used for initial investigation of the s functionalization and the results are presented in Fig. V-10. It shows that after functionalization the zeta potential value is respectively decreased from -40.7 and -41.4 mV to -43.0 and -44.2 mV, indicating the effective attachment of CES on zeolite and Au@zeolite surfaces.



Fig. V-10 Zeta potential of zeolite and Au@zeolite before and after functionalization with CES.

The zeolite and Au@zeolite samples were further characterized by X-ray photoelectron spectroscopy in order to confirm the successful attachment of carboxylate molecules. Fig. V-11 shows the obtained XPS spectra of carbon (1s), oxygen (1s), silicon (2p), sodium (1s) and alumina (2p), which originates from untreated zeolite and Au@zeolite with additional nitrogen (1s) and aurum (4f). After reaction with CES for 4h, a drastic increase of sodium peak intensity is observed in

both sampels' spectra, which is due to the high amount of sodium at the tail of CES. It clearly confirms good coverage of COONa groups on zeolite surface in this study.



*Fig. V-11 XPS survey scan spectra of zeolite and Au@zeolite before and after functionalization with CES: (a) zeolite; (b) Au@zeolite.* 

The functionalized zeolite  $C_{1s}$  curves (see Fig. V-12(a)) are reconstructed with five distinct chemically shifted  $C_{1s}$  core-level emissions. The components at 284.2, 285, and 288.1 eV are assigned to C-Si, C-C and C=O bonds of CES molecular <sup>[213]</sup>. No carbonyl carbon of esters (288.8 eV) is observed. Crucially, the O-C=O at low BE (289.6 eV) of free carboxylic acid <sup>[214]</sup> and the O-C=O at high BE (291.6 eV) that is probably ascribed to bounding of O-C=O<sup>-</sup> functionalities are to protonated sodium resulting in the shift forward to higher BE. This result implies the pH of zeolite solution for further deposition should be adjusted to an appropriate value to obtain the maximum amount of free O-C=O<sup>-</sup> (pKa<sub>COOH</sub>= 2.5). The similar contributions are deconvoluted from the functionalized Au@zeolite C<sub>1s</sub> curve as shown in Fig. V-12(b). Additionally, two new components of C-N (286 eV) and C-O (286.6 eV) that originate from APTES for anchoring gold are also observed. The results confirm CES is an efficiency linker for secondly functionalizing zeolite or Au@zeolite in this study and it could be further used for next deposition step.



Fig. V-12 High resolution C<sub>1s</sub> spectra of functionalized zeolite and Au@zeolite: (a) CES-zeolite; (b) CES-Au@zeolite.

For providing linkers on COC surface, PECVD is used and APTES is chosen as the precursor for our study. Element composition of XPS survey scans before and after functionalization is presented in Fig. V-13. The results show the intensity decrease of carbon, while oxygen, silicon and nitrogen increase. The Ca and F from the COC substrate vanish due to coverage of coating. All the results could be related to a successfully functionalization with APTES on COC. Fig. V-14 shows the

high-resolution C<sub>1s</sub> spectra of all surfaces. The deconvoluted C<sub>1s</sub> spectrum of the raw COC substrate (Fig. V-14 (a)) shows only one additional peak at 286.6 eV with the major C-C, C-H peak at 285 eV. This peak could be contributed to C-O from contamination of COC surface due to a surface absorbed oxide (e.g. H<sub>2</sub>O, CO<sub>2</sub>, etc.), which is also supported by the appearance of O<sub>1s</sub> peak in COC survey scan spectrum (Fig. V-13). As shown in Fig. V-14(b), the  $C_{1s}$  spectrum of PECVD treated COC is decovoluted with 6 contributions: a saturated C-C, C-H peak (285.0 eV), a peak to lower binding energy at 284.2 eV corresponding to C-Si bond and three additional peaks to higher binding energy at 286 eV corresponding to C-N, 286.6 eV corresponding to C-O/C=N and 288.1 eV corresponding to C=O/N-C=O, which are similar to the APTES deposition on glass under the same condition as described in Chapter III. Additionally, another new peak at 289.1 eV corresponding to O-C=O is observed for the best curve fitting, which should be related to formation of carboxyl groups during plasma polymerization process. The amine proportion of total composition in coating is around 6.7%, indicating good amine coverage on COC surface. Also, the similar  $N_{1s}$  results are shown in Fig. V-14(c): it could be deconvoluted into two peaks at 399.7 and 400.9 eV, assigned to free amines  $-NH_2$  (N<sub>1</sub>) and protonated amines  $-NH_3^+$  (N<sub>2</sub>,  $\sim+1.2$  eV). The lower protonated amines content implies the pH value should be adjusted during zeolite deposition process.



Fig. V-13 XPS survey spectra of COC substrate before and after functionalization with APTES using PECVD.



Fig. V-14 High resolution spectra of COC before and after plasma polymerization with APTES: (a)  $C_{1s}$  of Raw COC substrate; (b)  $C_{1s}$  of Amine functionalized COC surface; (c)  $N_{1s}$  of Amine functionalized COC surface.

The deposition of zeolite and Au@zeolite particles was characterized by SEM and the results are shown in Fig. V-15 and Fig. V-16, respectively. The SEM images indicate that zeolite and Au@zeolite coatings have a complete and full coverage over the entire surface of the substrates, and the morphology is similar between zeolite and Au@zeolite. Moreover, the comparison of higher magnification images of zeolite and Au@zeolite shown in Fig. V-15(c) and Fig. V-16(c) evidences the immobilization of gold particles.



Fig. V-15 SEM images of zeolite deposition on COC substrate at different magnification.



Fig. V-16 SEM images of Au@zeolite deposition on COC substrate at different magnification.

The stability under hydrodynamic flow of the Au@zeolite attached on COC substrates was also tested and characterized by SEM. After immersion in stirring water for different times ranging between 12 to 72 h and as can be seen from Fig. V-17, no obvious changes occurs on the coating even after 72 h. Only a few regions of coating are peeled off, which confirms that our coating deposition method allows a good stability of the coating in flowing water and could be further applied in microfluidic applications. The high magnification images show an increase of hollows in the coating with increasing immersion time, indicating a loss of Au@zeolite particles; however a good coverage can still be observed due to the high thickness of the coating. The EDS results shown in Fig. V-18, reveal a slight dissolution of Au@zeolite into water during the immersion as the percentage of alumina and silicon

atoms, respectively, gradually decrease. The coating exhibits extremely high stability for immersion times below 48 h as Al and Si loss can be hardly observed. After 72 h of immersion, particle dissolution occurs however at least 50% of Al and Si of initial coating remained. These results clearly demonstrate that our method for immobilization of zeolite or Au@zeolite is very strong and can be used for applications with hydrodynamic flows such as catalysis in microfluidics.



Fig. V-17 SEM images of Au@zeolite coating immersed in stirring water during 12~72 h: (a) 12 h, low magnification; (b) 12 h, high magnification; (c) 24 h, low magnification; (c) 24 h, high magnification; (e) 48 h, low magnification; (f) 48 h, high magnification; (g) 72 h, low magnification; (h) 72 h, high magnification.



Fig. V-18 EDS results of Au@zeolite coating immersed in stirring water during 12~72
h: (a) 0 h; (b) 12 h; (c) 24 h; (c) 48 h; (e) 72 h; (f) the change of at%Al and at%Si during immersion.

# 5.5 Conclusion

In the present chapter we firstly reported a comparison study of using APTES and MPTES for immobilizing gold nanoparticles (d= 13 nm) on Y type zeolite (d= 450 nm), in view of further applications in catalysis. Thereafter, the zeolite and gold anchoring zeolite are deposited on amine PECVD functionalized COC surface using CES as a linker on zeolite surface. The APTES and MPTES are both proved good linkage reagents for gold immobilization. Zeta potential, DRIFT spectra, XPS spectra reveal a successful attachment of amine and thiol groups on zeolite surface, respectively. And then UV-Vis spectra, TEM images, EDS spectra and XPS spectra prove the achievement of immobilization of gold on both as functionalized surfaces through our method. The gold nanoparticles on the surface were uniform in size with a diameter range of 10~20 nm, presenting a spherical shape. XRD spectra reveal gold particles are only attached on the surface of zeolite due to a fairly bigger size than pores in zeolite. For a comparison study of experimental data, the APTES is evidenced a better linker as it provides higher amount of gold loading at the same condition.

For zeolite and Au@zeolite deposition, the particles are functionalized with carboxyl group using CES as a linker for bounding the protonated amines on COC surface that is pre-modified using PECVD method. Zeta potential and XPS spectra exhibit a good attachment of carboxylate on both particle surfaces. In high resolution  $C_{1s}$ , the O-C=O at low BE (289.6 eV) of free carboxylic acid and the O-C=O at high BE (291.6 eV) of O-C=O'Na<sup>+</sup> implies the pH of zeolite solution for further deposition should be adjusted to an appropriate value to obtain the maximum amount of free O-C=O<sup>-</sup>. Concerning pKa<sub>NH2</sub> of 10.6 and pKa<sub>COOH</sub> of 2.5, the pH value of 8.4 was used for zeolite and Au@zeolite deposition. The SEM image shows a complete and even coverage over the entire substrate surfaces from zeolite and Au@zeolite deposited COC substrates. Moreover, the coating stability in flowing water is tested

through immersing Au@zeolite coated samples into stirring water during 12~72 h. The results evidence a good coverage after 72 h, indicating our method for depositing the zeolite and Au@zeolite particles on COC surface is fairly stable in hydrodynamic flows and could be further used for preparation of catalysts used in microfluidics.

# Chapter VI Oxidation of benzyl alcohol in catalytic microreactors

# 6.1 Abstract

The oxidation of benzyl alcohol is an important reaction in the industry. In last decade, its related research in micro fluidic system has become attractive and shown promising application potential due to the extraordinary catalysis environment provided in microchannel. Thus, it is interesting to build the micro fluidic systems based on microreactors and consequently use them for high efficiency heterogeneous catalytic reaction. In this chapter, a series of novel cyclic olefin copolymer (COC) microreactors with different catalysts immobilized on inner channel walls were successfully fabricated via combination of plasma and wet chemistry methods. The microchannels were embossing replicated from COC particles hot pressed in a sophisticated mold. Subsequently the formed microchannel inner surface was amino-functionalized using PECVD with APTES; Thereafter, AuNPs and AuNPs@zeolite were respectively synthesized, functionalized and then deposited in the microchannel to make microreactors, respectively. Finally, the microreactors were connected into the pre-designed micro fluidic system. In order to efficiently obtain benzaldehyde with low toxic products, oxidation of benzyl alcohol was carried out using various microreactors in water medium. All the reacted samples were analyzed with High Performance Liquid Chromatography (HPLC).

Keywords: COC microreactor, water medium, catalyst, benzaldehyde.

# 6.2 Introduction

The selective oxidation of alcohols to carbonyl compounds is an important reaction among the most fundamental transformations for synthetic organic chemistry, in particular for the synthesis of benzaldehyde from benzyl alcohol, which is valuable as precursor and intermediate for various industrial applications such as agrochemicals, perfumery, pharmaceuticals and so on <sup>[131, 215]</sup>. However, typical oxidation methods to perform such reactions usually require stoichiometric amounts of metal oxidants and thus generate a large amount of wastes <sup>[128]</sup>. Due to this drawback, heterogeneous catalytic systems using ecofriendly oxidants (e.g. air, oxygen, hydrogen peroxide, etc.) and preventing the formation of harmful products exhibit promising potential from a point of green chemistry <sup>[216]</sup>.

The nanosized gold particles have been considered as one of the crucial candidates for heterogeneous reactions and were widely used during the past decades <sup>[5,6]</sup>. In spite of the benefit of heterogeneous catalytic reaction, solid powder type gold nanoparticles bring a problem: when they are dedicated to the liquid phase oxidation process, the powder catalysts are difficult to be separated from reacted solution and then are hardly reclaimed after reaction, especially when the nano-size particles are used.

Anchoring catalytic active phases on surface is the solution to avoid this drawback <sup>[12]</sup>. Moreover, the rapid development of microfluidic technologies offers a solution to improve the control of catalytic reaction parameters as a result of the increased surface area-to-volume ratio <sup>[172]</sup>. Especially, some of those microfluidic devices could perform consecutive heterogeneous catalytic reactions when their channel surface are immobilized with different powder catalysts. The most important advantage is that the separation of catalysts from reactant medium is not required for fixed catalysts. Thus, the immobilization of the catalysts inside the channel of the microreactor is a concrete alternative to batch reactions for which their recycling often appears difficult.

There are various immobilization methods that could be utilized for microreactors. The most widely used method consists in modifying the surface by chemical treatment in liquid phase. Its obvious advantage is that this method is available for the closed microreactors without limitation of channel length <sup>[12]</sup>. However, wet chemistry method is limited by its disadvantages, like long reaction time, complicated process, low deposition rate and so on <sup>[20-22]</sup>. In the Chapter III, PECVD has been evidenced as a reliable surface functionalization method with relatively high efficiency. However, this method could only treat open microchannel and the available modification size is determined by the plasma device. Compared to wet chemistry method, PECVD is a simplified fast deposition method <sup>[154]</sup> and has exhibited higher deposition rate, better functionality density for functionalization process.

Ftouni et al. <sup>[12]</sup> and Wang et al. <sup>[16]</sup> have evidenced that gold-immobilized capillary column microfluidic devices could be stably utilized for benzyl alcohol oxidation, and the substrates were converted into the desired products quantitatively, which envisions that the concept of developing microreactor immobilized with gold nanoparticles (AuNPs) is a feasible solution for the aerobic oxidation of benzyl alcohol. They used APTES deposited by a wet chemistry method to immobilize the gold nanoparticles. However it has been evidenced in Chapter IV that wet chemistry treatment is not the best method for immobilizing AuNPs compared to PECVD method because this method is rather low efficient for APTES deposition, and only provides less gold loading than plasma. Therefore, it is interesting to investigate the performance of gold immobilized microreactor which is functionalized using plasma.

In heterogeneous catalysis, it is commonly known that the active phase on the catalyst surface must be highly dispersed over a large specific surface area to ensure good catalytic efficiency. The supported AuNPs have been found to be effective for the oxidation of alcohols and furthermore they perform better catalytic ability compared with pure gold <sup>[124, 134]</sup>. So far, mesoporous inorganic zeolites are of interest

as one of the support materials because they exhibit numerous edges and corners for adsorption of reactants and dispersion of AuNPs. More interesting, the Y-zeolites supported AuNPs is reported to exhibit extremely high selectivity and better conversion rate when they are dedicated to UV and/or visible light, e.g, Zhang et al. confirm highly selective production of benzaldehyde from benzyl alcohol by using gold immobilized zeolite in toluene as the solvent under UV light <sup>[108]</sup>. On one hand, the participation of faujasite zeolite provides high external surface area for heterogeneous catalytic reactions taking place; on the other hand, it exhibits the ability to adsorb reactant, which could benefit in benzyl alcohol oxidation. Nowadays, the utilization of assembled zeolites and catalysts immobilized zeolites in microfluidic system consisted with the advantages of membrane and microreactor has expanded the applications in heterogeneous catalysis in this decade <sup>[135-137, 217-220]</sup>, inspiring the conception of developing novel microreactors with gold@Y type zeolite in spite no publication has been reported until today.

Thus, it is interesting to develop new AuNPs immobilized microreactors that perform high conversion and high selectivity for benzyl alcohol oxidation. Furthermore, the zeolite is quite attractive to be considered as a support for improving catalytic activity of gold and Au@zeolites would be assembled in microchannel for the first time. In this study, we report a series of novel microreactors with various catalysts for the efficient catalytic oxidation of benzyl alcohol with hydrogen peroxide.

## 6.3 Experimental

#### 6.3.1 Fabrication of the microreactor

A chip type reactor (L×W×H: 25 mm×15 mm×5 mm) within a dumbbell like microchannel (L×W×H: 15000  $\mu$ m×500  $\mu$ m×100  $\mu$ m) was fabricated, as shown in Fig. VI-1. The microreactor was prepared by a hot pressing method. 18 g Cyclic 170 Olefin Copolymer (COC) particles (grade 6013s) were pressed into metal mold at a pressure of 9 bar using a hydraulic press. Meanwhile the mold is heated at 200 °C for 20 min. Thereafter, it was removed and cooled at room temperature. As fabricated COC chips with microchannel was cutting into small pieces of 25 mm×15 mm×5 mm. The process is shown in Fig. VI-1.



Fig. VI-1 Fabrication of COC microreactor.

# 6.3.2 Amine functionalization of microchannel by plasma enhanced chemical vapor deposition

The microreactors were ultrasonically cleaned in ethanol and acetone for 10min for each. Then all the samples were dried by compression air. The COC surfaces were masked by scotch tape except the microchannel area. APTES (NH<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>-Si(OC<sub>2</sub>H<sub>5</sub>)<sub>3</sub>, 100 g, 98%) was purchased from VWR.Co was used as precursor. Pure Ar was used for generating plasma; the purity of Ar was higher than 99.99%.

A homemade experimental device called bell-jar reactor was used for the APTES plasma deposition. The detail device introduction has been described elsewhere <sup>[221]</sup>. The microreactor was fixed by a double-face scotch tape on the central vertical band of the rotating grounded cylinder around which was previously wrapped by low-density polyethylene film (LDPE, Goodfellow). Firstly, pre-treatment is performed for activation of surface: the working pressure was fixed at 0.7 mbar, the samples were subjected to a 20 W plasma treatment (Ar; flow rate: 10 sccm) during 5

s. The working pressure was fixed at 0.7 mbar, the samples were subjected to a 20 W plasma treatment (Ar; flow rate: 10 sccm) during 5s. Then the samples were functionalized and the parameters used in this work are presented in Table VI-1.

Active gas	Working pressure	Working power	Deposition Time	Precursor and Carrier
	(mbar)	<b>(W)</b>	<b>(s)</b>	gas
A E1 00				APTES/Ar,
Ar Flow:20	1.0	30	40	Flow: 10
sccm				sccm

Table VI-1 Plasma parameters in this work

After plasma functionalization, the freshly coated microreactors were kept under vacuum for 1 h before venting, in order to reduce post-oxidative reactions between radicals formed on the film surface and atmospheric oxygen <sup>[160]</sup>. Thereafter, microreactors were taken out of chamber, and then the scotch taps were removed from the surface.

#### 6.3.3 Synthesis and immobilization of AuNPs

Monodisperse gold nanopaticles were synthesized according to the work of Xia et al.(see the reference <sup>[174]</sup>). 5 mL of an aqeous solution of gold(III) chloride hydrate (1 wt%) and 420  $\mu$ L of aqeous silver nitrate solution (0.1 wt%) were mixed with 45 mL of super pure water and heated in flask under reflux until ebullition, then 1.5 mL of aqueous sodium citrate (10 wt%) was injected into the mixture. Heating was stopped after 30 min and the suspension was cooled to room temperature. Finally it resulted in the formation of a dark purple sol of gold NPs. One volume of high concentration colloidal AuNPs were diluted with nine volume of water and the pH of the suspension was adjusted to 6.2 using with NaOH (0.1 M). Glass substrates with freshly deposited APTES were then placed at the bottom of beaker for 24 h; magnetic rotation bar was used during immobilization.

#### 6.3.4 Synthesis of Au@zeolite

To 100 mg of the calcined Y-zeolite powder, 100  $\mu$ L of APTES in 30 mL of dichloromethane (DCM) was added, and the slurry was stirred for 24 h at room temperature. The amine-functionalized zeolite powder was then repeatedly washed by centrifugation to remove unreacted APTES. And then it was dried in a gas exchanged oven at 100 °C. The samples thus obtained were used for gold immobilization.

The amine-functionalized zeolite (50 mg) was dispersed in 20 mL of super pure water and then mixed with 10 mL of the colloidal gold solution under continuous stirring. After 12 h of stirring, the zeolite particles attached with gold nanoparticles were separated by centrifugation and washed with super pure water for several times, and dried in a gas exchange oven at 100 °C.

#### 6.3.5 Deposition of zeolite and Au@zeolite

For functionalization of the surface, carboxyethylsilanetriol sodium (CES) was used as linkage reagent. The estimation of minimum CES quantity is the same method from Ref. [200]. To 100 mg of the calcined zeolite powder or Au@zeolite powder, 200 µL of CES in 30 mL of Toluene was added, and the slurry was stirred and heated at 120 °C for 4 h. The functionalized zeolite powder was then repeatedly washed by centrifugation to remove unreacted CES. And then it was dried in an gas exchanged oven at 100 °C. Thereafter, 50 mg dried zeolite power with 20 mL of super pure water were transferred into a beaker with stirring bar. Amine-functionalized microreactor was then placed at the bottom of beaker for 24 h. After zeolite or Au@zeolite deposition, microreactor was moved in an oven and heated at 80 °C.

#### 6.3.6 Sealing of the catalytic microreactor

The whole microreactor surface except the catalyst deposited microchannel

was cleaned by tissue and acetone, and then the surface was daubed by sealing reagent (mixed Cyclohexane and Hexadecane,  $V_{Cyclohexane}/V_{Hexadecane}$ : 1/3). Immediately, the microreactor was moved on a 35 mm×25 mm COC flake that was prepared, pre-placed and heated at 110 °C in a hot pressing device. The COC flake was closely contacted with microchannel face. The sample was pressed at 1 ton with heating for 2 min. Finally, sealed microreactor was moved and cooled down at room temperature.

#### 6.3.7 Experimental set up of microsystem for oxidizing benzyl alcohol

The oxidation reaction system was assembled as shown in Fig. VI-2. The catalysts-immobilized microchip was connected to a glass micromixer (Micronit, TD26), which was attached to two syringes by teflon tubes. Solutions of the substrates including well mixed benzyl alcohol (2 mM) and potassium carbonate (6 mM) in water were kept in one of the syringes, while hydrogen peroxide (10 mM) in water was prepared in the other syringe. Under the control of syringe pump, chemicals were injected into micromixer at a fixed flow rate of 1  $\mu$ L/min. In these experimental conditions the calculated Re number is lower than 100, what is the condition to have the two flows perfectly mixed in TD26 micromixer. The flow exiting the micromixer was then introduced into microreactor, which was placed on a hot plate at the constant temperature of 40±5 °C. As soon as the flow exited the microchannel, the products were introduced into a collection tube containing 30 microliters of formic acid (100 mM) for terminating reaction immediately ( $H_2O_2$ +HCOOH $\rightarrow$ H\_2O+HCO\_2OH). Finally, the sample was injected into High performance liquid chromatography (HPLC) for characterization. All the experiments are performed in visible light conditions during 3 h.



Fig. VI-2 Experimental setup of the benzyl alcohol oxidation reaction in microreactors.

#### 6.3.8 Working conditions in microsystem

The residence time in the system is calculated using:

#### Equation VI-3

where V is the total volume of microchannel and v is the volumetric flow rate of the pump. When  $V = L*W*H = 1.5 \text{ cm} \times 500 \mu\text{m} \times 100 \mu\text{m} = 7.50\text{E}-10$ , v=2 uL/min. The residence time is 22.5 s.

In the catalytic microreactor, the diffusion time is the duration for all the fluid molecules diffuse to the catalytic surface. In the catalytic device, the catalyst is deposited on the bottom of the channel. The diffusion time is therefore the duration for fluid diffuses for a length of *H* where *H* is the height of the microreactor (Fig VI-3). Depends on the definition of *D* that means diffusion area in space per second from Fick's law, it could be simplified to (*the diffusion radius*)<sup>2</sup>\* $\pi$  divided by diffusion time along Y axis. When taking account into *H* as the diffusion distance, *H* equals to diffusion radius, the calculation is as follows: the height of microchannel is 100 µm, thus *r* = 100 µm

#### Equation VI-2

To calculate the diffusion coefficient at 40 °C the Wilke-Chang equation <sup>[222]</sup> was used:

where  $T_1$  and  $T_2$  denote absolute temperatures 1 and 2(K), respectively, D is the diffusion coefficient (cm<sup>2</sup>/s) and  $\mu$  is the dynamic viscosity of the solvent (Pa·s). When  $\mu_{20^\circ C} = 1.002$  Pa·s ,  $\mu_{40^\circ C} = 0.653$  Pa·s,  $T_1 = 293$  K,  $T_2 = 313$  K and  $D_{20^\circ C} = 8E-6$  cm<sup>2</sup>/s<sup>[223]</sup>, it could be calculated that  $D_{40^\circ C} = 13.1132E-6$  cm<sup>2</sup>/s.



Fig. VI-3 Diffusion of fluid in microchannel

Considering a calculated diffusion coefficient of  $1.3 \times 10^{-9}$  m<sup>2</sup>.s<sup>-1</sup> for benzyl alcohol in water at 40 °C, the corresponding diffusion time in the microreactor is about 23.94 s, which approximately equals the residence time (22.5 s) and so 1 diffusion cycles occurs along the microchannel.

# 6.4 Results and discussion

#### 6.4.1 Identification of standard retention time and peak area

At the initial part of this study, pure benzyl alcohol (1 mM), benzoic acid (1 mM) and benzaldehyde (1 mM) in water were injected into HPLC as standards. The results are presented in Fig. VI-4. The related retention time and peak area are summarized in Table VI-2.



Fig. VI-4 HPLC result of single chemical: (a) Benzyl alcohol; (b) Benzoic acid; (c) Benzaldehyde.

Peak number	Peak 1	Peak 2	Peak 3
Chemicals	Benzyl alcohol	Benzoic acid	Benzaldehyde
Concentration	1 mM	1 mM	1 mM
Retention (min)	14	21	24
Peak area (mV*Sec)	1643	782	9665

Table VI-2 Peak time and peak area of chemicals in this study

In the following parts, the concentrations of benzyl alcohol, benzoic acid and benzaldehyde were calculated knowing the peak area of standard 1 mM chemicals summarized in Table VI-2.
#### 6.4.2 Catalytic activity of gold immobilized microreactor

In order to figure out the oxidation ability of H<sub>2</sub>O<sub>2</sub> with benzyl alcohol without catalysts, a batch experiment was carried out in a classical glass reactor (volume: 5 mL) under stirring using the same conditions (Chemical: Vbenzyl alcohol (2mM)/Vpotassium carbonate (6mM)/V<sub>hydrogen peroxide (10mM)</sub> = 1:1:2; T: 40±5 °C) for 10 minutes. As shown in Fig. VI-5, a slight decrease of peak 1 from batch sample is observed compared with the reference sample, indicating a small loss of benzyl alcohol; On the other hand there is scarcely any change occurring at the position of peak 2 and peak 3, implying no products are formed in batch. Thus, it is reasonably believed that the reactant loss is due to evaporation. Therefore, no significant reaction can take place in the absence of catalyst. The sample obtained from blank micro-reactor shows almost the same level of peak 1 decrease; however the intensity of peak 3 is not zero indicating the formation of a small quantity of benzaldehyde. All the results evidence the poor conversion of benzyl alcohol without catalysts. Taking the sample from catalytic microreactor with gold into account, two changes are observed in Fig. VI-5: (1) the intensity of peak 1 is the lowest meaning that the best decomposition of benzyl alcohol is obtained in these conditions; 2) the high intensity of peak 3 indicates a high production of benzaldehyde. It is interesting to note that for all the samples the peak 2 at 21 minutes is not observed, what reveals that benzoic acid is not formed during these experiments.



Fig. VI-5 HPLC spectra of samples prepared in gold immobilized microreactor: (a)
Survey spectra; (b) Magnification of peak 2 (Benzyl alcohol). Reference sample is the mixture of one volume benzyl alcohol (2 mM), one volume potassium carbonate (6 mM) and two volumes hydrogen Peroxide (10 mM) with formic acid.

	Run 1			Run 2			Run 3			Run 4		
Type of	(0~180min)			(180~360min)			(360~540min)			(540~720min)		
sample	Con <sup>a</sup>	Sel <sup>b</sup>	Yie <sup>c</sup>	Con <sup>a</sup>	Sel <sup>b</sup>	Yie <sup>c</sup>	Con <sup>a</sup>	Sel <sup>b</sup>	Yie <sup>c</sup>	Con <sup>a</sup>	Sel <sup>b</sup>	Yie <sup>c</sup>
	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)	(%)
Batch	2.8	10.0	0.3	-	-	-	-	-	-	-	-	-
µR-blank	4.6	29.1	1.3	-	-	-	-	-	-	-	-	-
µR-Au	20.6	93.7	19.2	22.5	95.3	21.4	23.2	94.4	21.9	16.4	91.0	14.9

Table VI-3 Oxidation of benzyl alcohol using the gold-immobilized microreactor.

<sup>a</sup>Determined by HPLC with reference as a standard (result of the conversion of benzyl alcohol) <sup>b</sup>Determined by HPLC with reference as a standard (% of selectivity of benzaldehyde) <sup>c</sup>Determined by HPLC with reference as a standard (% of yield of benzaldehyde)

Actually, during the oxidation of benzyl alcohol, the acetal intermediate is generated due to the addition of water molecule on as produced benzaldehyde; thereafter it is oxidized by H<sub>2</sub>O<sub>2</sub> and consequently forms benzoic acid (Figs. VI-6(a) and (b)). Nevertheless, the benzoic acid is not stable in the mixture; the formed benzoic acid instantly reacts with the unreacted benzyl alcohol, thereby forming benzyl benzoate (Fig. VI-6(c))<sup>[131]</sup>, which could not be detected in our HPLC analysis. Moreover, the calculation results of benzyl alcohol conversion and benzaldehyde selectivity and yielding rate of different samples are shown in Table VI-3. These results confirm that the no significant catalytic conversions are shown in batch and blank microreactor samples. When gold-immobilized microreactors are used, higher benzyl alcohol conversion and better benzaldehyde yield are observed, which confirmed that the anchored gold particles are the catalytic active phase in our system. However, they are still very low than the values reported in previous work <sup>[12, 16]</sup>. This weaker catalytic activity can be attributed to two reasons: 1) the residence time of 22.5 s in our system (supporting information) is very short and thus the fluid diffusion cycle is only once along the microchannel (i.e. The residence time is higher than 600 s and the fluid diffusion cycle is 29 in the ref. [12]); 2) The citrate gold particle size of 13 nm is rather bigger, it exposes less active sites and results in a lower catalytic reactivity<sup>[183]</sup>. Thus conversion rate is predictably improved by increasing the channel length or decreasing gold particle size.

Finally, as reported in Table VI-3, benzaldehyde selectivity is around 95% when the benzyl alcohol conversion is 22.5%. Such results are similar to those reported in the literature in conventional batch reactors. For example, Ma et al. <sup>[124]</sup> obtained 98% of benzaldehyde selectivity at 25% of conversion starting with an aqueous solution containing 0.2 mol/L of benzaldehyde after 2 h of reaction using gold nanoparticles immobilized on HMS silicas. Zhan at al. <sup>[126]</sup> obtained similar results (>99% benzaldehyde selectivity at 20% conversion after 2 h of reaction) starting from an aqueous solution of benzaldehyde (30 mmol/L) and using uncalcined

bioreduction Au catalysts.

Our results are then very different than those reported by Ftouni et al. in their gold functionalized microreactors. Ftouni et al. <sup>[12]</sup> obtained indeed benzoic acid with a selectivity higher of 96% at 26% conversion , indicating that the formation of benzoic acid is more favorable.

Thus it evidences an advantage for producing benzaldehyde in microreactor compared to the system of Ftouni et al. It is also noticed that high selectivity of benzaldehyde (>90%) is obtained, evidencing that the over oxidation of benzaldehyde is not preferred to occur along our gold immobilized microchannel and subsequently forms low percentage of benzyl benzoate. Concerning this result, we could reasonably assume that the short reaction time and lower temperature lead to better selectivity to benzaldehyde. It is explained as follows: based on the benzyl alcohol oxidation route (Fig. VI-6), it could be speculated that the very short reaction time makes the oxidation of most benzyl alcohol only occurs at the step of forming benzaldehyde as it is insufficient for formation of benzoic acid; on the other hand the lower temperature also decreases the activity of decomposing hydrogen peroxide to hydroxyl radicals that favors to further oxidize benzaldehyde to benzoic acid when its amount is excessive <sup>[126]</sup>. Thus, it is important to choose reaction time and temperature to obtain high selectivity while the conversion is improved.

Furthermore, the difference of surface energy between Ftouni et al.'s work and ours could also explain the observed differences. The benzaldehyde, which is well-known as a kind of poorly water soluble chemical <sup>[224]</sup>, would adsorb better on a hydrophobic surface than on a hydrophilic surface in water solvent. Thus, when the oxygenated product (benzaldehyde) is produced on the catalysts, the adsorption of the poorly soluble benzaldehyde on the hydrophilic APTES functionalized surface is inhibited by well adsorbed water, as a consequence, the oxidation product is desorbed from catalyst surface. As the produced benzaldehyde molecules have no chance to be oxidized into benzoic acid, they thereafter move out of the microreactor with injecting

flow, resulting in the enhancement of selectivity to benzaldehyde. In Chapter III, the WCAs results have proved the PECVD method is better to form a hydrophilic surface compared with wet chemistry method for functionalizing APTES (WCA<sub>wet chemistry</sub>=  $32.9\pm0.8^{\circ}$  and WCA<sub>PECVD</sub>=  $3.0\pm0.6^{\circ}$ ), implying the microreactor prepared using our method should exhibit higher selectivity to benzaldehyde than wet chemistry functionalized microreactor (i.e. the performance in Ftouni et al.'s work).

Finally, three other experiments were carried out in the same microreactor to investigate the stability of the catalytic activity. The results evidence that benzyl alcohol is converted into the corresponding benzaldehyde with a constant conversion rate without loss of activity for at least 540 min (Table VI-3). It is also found that the system was stabilized after several hours because the lowest conversion is obtained at the first run, which agrees with previous results <sup>[16]</sup>. However, the results show a tiny decrease of catalytic activity at the last run (540 min). It can be assumed that during the reaction the existence of basic  $K_2CO_3$  could neutralize the ammonium group, which is the linker bounding AuNPs, and subsequently result in a decrease of the anchoring strength between microchannel surface and gold particles. With the extending reaction time, some of the AuNPs may be peeled off from the surface, explaining the decrease of the catalytic activity.



Fig. VI-6 The process of oxidation of benzyl alcohol in our system.

#### 6.4.3 The influence of Y-zeolite on gold in microsystem

The role of Y-zeolite for benzyl alcohol oxidation was then investigated in this study as microreactor-Y-zeolite and microreactor-Au@Y-zeolite were applied at the same condition, and their catalytic performances are shown in Fig. VI-7. When the Y-zeolite solely anchored microreactor is used, the lowest benzyl alcohol conversion, benzaldehyde selectivity and yield are observed, which confirms that the immobilized zeolite particles is not the catalytic active phase in our system. However, its conversion rate of 8.9% is higher than the value of using blank microreactor, indicating the possibility of low level adsorption of benzyl alcohol, which is essentially attributed to the interaction between hydroxyl groups of benzyl alcohol and AlO<sup>-</sup>, SiO<sup>-</sup>, Na<sup>+</sup> of zeolite through hydrogen bonds and acid-base reactions <sup>[225]</sup>. Moreover, it is found that the Au@Y-zeolite catalyst immobilized in microchannel leads to a benzyl alcohol conversion of 42.4% and the selectivity to benzyldehyde is higher than 99%. This result confirms the improvement of catalytic activity by using zeolite as a support for gold nanoparticles.



# Fig. VI-7 Oxidation of benzyl alcohol using the zeolite/Au-zeolite immobilized microreactors

<sup>a</sup>Determined by HPLC with reference as a standard (result of the conversion of benzyl alcohol) <sup>b</sup>Determined by HPLC with reference as a standard (% of selectivity of benzaldehyde)

#### <sup>c</sup>Determined by HPLC with reference as a standard (% of yield of benzaldehyde)

Theoretically, the more active sites the catalyst provides, the higher catalytic activity it performs. As the same type of AuNPs is used, the catalytic activity of the single catalyst particle is the same for each microreactor. Thus, the amount of AuNPs immobilized on the surface probably dominates their catalytic performance. Especially, in this study zeolite that has been considered as a high surface area/mass support (834 m<sup>2</sup>/g in this study) is used and as a result the number of nanoparticles per surface of channel ( $\mu$ m<sup>-2</sup>) could be higher compared to the surface concentration obtained with APTES.

In order to calculate the amount of AuNPs deposited on microchannel surface with or without zeolite, the followed hypotheses are considered: (1) the zeolite is considered as a spheric particle; (2) only the topmost layer of the deposition of AuNPs or zeolite on microchannel surface would work for catalysis process. Then, based on the Fig. IV-8(a), the amount of AuNPs deposited on per surface of microchannel could be estimated:  $N_{AuNPs-\mu R} \approx 1600/\mu m^2$ . Also, the result of Fig. VI-8(b) indicates that the microchannel surface could be completely covered by zeolites using our method. Thus, the distribution of zeolite on microchannel surface is simplified as shown in Fig. VI-8 (c) and the amount of zeolites deposited is calculated by

## — Equation VI-4

where *L* is the length of microchannel, *W* is the width of microchannel,  $R_{zeolite}$  is the radius of zeolite. Consequently, the amount of AuNPs deposited on microchannel surface using zeolite is calculated by

#### Equation VI-5

where  $N_{AuNPs-zeolite}$  is the amount of AuNPs immobilized on 1 µm<sup>2</sup> of zeolite surface,  $S_{zeolite}$  is the ball surface area of zeolite particle. When L=1500 µm, W=500 µm,  $R_{zeolite}=0.45$  µm,  $S_{zeolite}=2.54$  µm<sup>2</sup> and  $N_{AuNPs-zeolite}\approx 240/\mu$ m<sup>2</sup> (Obtained from Fig. VI-8 (d)), thus  $N_{AuNPs-zeolite-\mu R}=1505/\mu$ m<sup>2</sup>. The theoretical calculation indicates little 184 difference of AuNPs amount between the two microchannels. However, it's surprising that in Table VI-7 the much better catalytic performance is observed in microreactor-Au@Y-zeolite system when zeolite is used.



Fig. VI-8 SEM image of (a) AuNPs and (b) Au@zeolite deposited on COC in this work; (c) simplified model of zeolite particles on microchannel surface; (d) TEM image of AuNPs immobilized zeolite.

The other parameter that could also affect the performance of the catalyst is the support: indeed not only the amount of active sites provided by catalyst but also the nature of support are essential factors for the catalytic performance.

Based on the literature, the mechanism of catalysis using gold could be explained as follows <sup>[132, 133]</sup>: when the experiments are performed under natural visible light irradiation, it is preferred to active gold to produce high electronegativity due to the SPR effect. Therefore, the polarized AuNPs benefits in binding  $\alpha$ -H atoms from the cleavage of C-H bond on the methylene groups of benzyl alcohol to form Au-H bonds; On the other hand, the oscillated electrons on polarized Au-NPs can be scavenged by peroxide molecules to form reactive hydroxyl radicals <sup>[226]</sup>.

Consequently these radicals react with hydrogen from Au-H bonds to form water, while the electron-deficient Au-NPs are replenished with released electrons from adsorbed benzyl alcoholic compounds to form benzyl alcoholic radicals. These benzyl alcoholic radicals then may automatically release protonic hydrogen from the hydroxyl group (-OH) to form the C=O bond. The zeolite support alone exhibits little catalytic activity as a result of difficulty of abstracting  $\alpha$  hydrogen atoms directly from benzyl alcohol [108]. However, compared to APTES, zeolite is likely to adsorb more benzyl alcohol molecules due to positive and negative charges on its surface and subsequently provides longer contact time for gold and benzyl alcohol. With the help of zeolite, adsorbed benzyl alcohol molecules are massively converted into alcoholic radicals, which explains the improvement of conversion as zeolite is used. Moreover, it is also noted AlO<sup>-</sup>, SiO<sup>-</sup> from zeolite could benefit in abstracting protonic hydrogen from these alcoholic radical, which is considered as an essential reason for forming benzaldehyde. Once the protonic hydrogen is released from the hydroxyl group of alcoholic radical, the connection of AlO<sup>-</sup>/SiO-H<sup>+</sup> and Na<sup>+</sup>-O<sup>-</sup> pairs vanish as a results of formation of C=O, then the zeolite adsorb another benzyl alcohol molecular by free AlO<sup>-</sup>/SiO<sup>-</sup> and Na<sup>+</sup> for oxidation. Meanwhile the new formed benzaldehyde desorbs from the zeolite support immediately due to its poor affinity on zeolite. And then it moves forward with the continuously injected fluid. Its velocity is relatively high compared with the diffusion value, and therefore benzaldehyde has low possibility to react with H<sub>2</sub>O<sub>2</sub> again to form benzoic acid. It's probably the reason for the highest selectivity by using zeolite as shown in Fig. VI-7. The role of zeolite in the catalytic system and the detailed mechanism of catalysis are reasonably explained and depicted in Fig. VI-9.



Fig. VI-9 The mechanism of benzyl alcohol oxidation in gold-zeolite system.

## **6.5**Conclusion

Series of novel microreactors with gold catalysts for the oxidation of benzyl alcohol to benzaldehyde at high selectivity have been developed in this chapter. The gold-immobilized microreactor could be continuously used for at least 9 hours without any loss of activity. It also exhibits a huge potential to improve the conversion rate by increasing channel length and/or decrease gold size. Additionally, the use of several microreactors with parallel connection could be applied to produce massive benzaldehyde without other byproducts. The Y-zeolites exhibit benzyl alcohol absorption ability as it was used in the microchannel; moreover, the gold nanoparticles supported on Y-zeolites perform the best catalytic activity in our study, a relatively high benzyl alcohol conversion of 42.4% and high benzaldehyde selectivity (> 99%) are obtained. To the best of our knowledge, this is the first example of using gold or gold-supported catalysts in microreactors that performs such a high selectivity to benzaldehyde in microsystems.

# **Chapter VII General conclusions and perspectives**

## 7.1 General conclusions

In this thesis, a series of novel cyclic olefin copolymer (COC) microreactors immobilized with different catalysts on inner channel surface were successfully fabricated *via* a plasma-wet chemistry method. The COC surface was amino-functionalized using plasma-enhanced chemical vapor deposition (PECVD) with (3-Aminopropyl)triethoxysilane (APTES); Thereafter, three different types of colloid (Gold nanoparticle(AuNPs), nano Y zeolite and AuNPs@nano Y zeolite) were synthesized, functionalized and then deposited on the COC surface, respectively. The as-deposited surfaces were studied by various characterization techniques. The catalytic efficiency of different microreactors was also investigated as they were employed in the microfluidic system for oxidizing benzyl alcohol to benzaldehyde with high selectivity.

The results show that PECVD method is a common method that could deposit high amine content of (3-aminopropyl)triethoxysilane (APTES) polymerized film on various substrate surfaces. Ar and N<sub>2</sub> are good active gas for APTES plasma polymerization; however, O<sub>2</sub> is not appropriate as it leads to over oxidation of APTES and formation of SiO<sub>2</sub> like structures during deposition process. In order to obtain good deposition and reduce the functional change due to coating being exposed to plasma, the deposition time should be in the range of 14~40 s. Furthermore, the investigation of APTES deposited using different working pressure indicates the competition between fragmentation and/or poly-recombination of the APTES molecules and normal ionic or/and radical polymerization determines the coating chemical composition and functional groups. Moreover, the coating stability increases when the power is increased between 25~40 W, indicating a high cross-linked structure due to higher plasma power; however, the intensity of fragmentation of APTES is also enhanced with increasing power, if the power is too high the amine 189 functions are lost during fragmentation. The comparison of amine proportion of total composition and coating stability in this study indicates optimization plasma conditions for APTES deposition:  $Q_{APTES}$ = 10 sccm,  $Q_{Ar}$ = 20 sccm, P= 30 W, p= 1.0 mbar, t= 40 s.

Compared with conventional wet chemistry method, PECVD polymerized APTES coating exhibits better hydrophilicity, higher coating thickness, as well as higher amine group density, leading to a further higher coverage and amount of AuNPs. During immobilization process, the pH value 6.2 of colloidal solution leads to transformation of high amount protonated amines on substrate surface. After gold immobilization, the content of protonated amine groups increase as well as its XPS peak center shifts towards to lower binding energy, evidencing AuNPs are successfully immobilized through binding to R-NH<sub>3</sub><sup>+</sup> species.

The comparison study of using APTES and MPTES for surface modification and then immobilizing AuNPs on Y type zeolite, indicates the APTES is the better linker as it provides higher amount of gold loading at the same condition. The zeolite/AuNPs@zeolite particles are functionalized with carboxyl group using CES as a linker for bounding the protonated amines on COC surface that is pre-modified using PECVD method. Concerning pKa<sub>NH2</sub> of 10.6 and pKa<sub>COOH</sub> of 2.5, the pH value of 8.4 is used for obtaining more free carboxylic acid. A complete and even coverage of zeolite and AuNPs@zeolite deposition over the entire COC substrate surfaces are observed. The coating is fairly stable in hydrodynamic flows and could be further used in microfluidics.

The gold type\Y zeolite type\AuNPs@zeolite type microreactors are respectively connected into pre-designed micro fluidic system. Their catalytic performances on transforming benzyl alcohol to benzaldehyde are investigated in water medium. The gold type microreactor exhibits stable high selectivity to benzaldehyde (about 94%), however it also shows relative low benzyl alcohol conversion (about 20%). The Y-zeolites are evidenced to be not a catalytic active phase in our system; they only exhibit benzyl alcohol absorption ability as they are used in the microchannel. Moreover, the AuNPs@zeolites type microreactor performs the best catalytic activity in our study, the higher benzaldehyde selectivity (>99%) are obtained with the highest benzyl alcohol conversion (about 40%). Finally, the absorption-catalysis mode of benzyl alcohol in AuNPs-zeolite system is successfully built up.

## 7.2 Perspectives

Based on the present results and literature data, we could proposed a plasma-wet chemistry process for depositing particle catalysts on the inner channel surface of microreactors and the results of catalytic performance show that it is the first example of using gold or gold supported catalysts in microreactor that performs such a high selectivity to benzaldehyde in microsystem. Further experiments are needed to improve the catalytic activity of microreactor: on one hand, different reaction parameters such as residence time, reaction temperature, pH value, etc. should be investigated to gain a better catalytic performance in gold immobilized and Au@zeolite immobilized microreactors; on the other hand, the improvement could correspond to the optimization of catalysts: the size of AuNPs and their distribution on surface, the size and morphology of zeolite, and so on are considered to be the factors that improve on catalytic performance. Moreover, different chemical reactions could be tested in our microreactors in order to expand the scope of application in the future.

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# <u>Abstract</u>

This work aims not only at designing and fabricating new microfluidic chips for benzyl alcohol oxidation, but also at developing a methodology of plasma devoted to the surface functionalization with linkage reagent in order to anchor catalyst particles in the next step. Results show that the PECVD method is a universal method that can deposit high amine content of (3-aminopropyl)triethoxysilane (APTES) polymerized film on various substrate surfaces. Optimized plasma conditions for APTES deposition were found and lead to a better hydrophilicity of the substrates, a higher coating thickness, as well as a higher amine group density than the conventional wet chemistry method. In addition, the APTES depositions lead to a further higher coverage and amount of AuNPs when the pH value is 6.2. Moreover, the results of immobilizing AuNPs on zeolite indicate that APTES is a better linker than MPTES as it provides a higher amount of gold loading. For zeolite and AuNPs@zeolite deposition, the particles were functionalized with carboxyl group using CES as a linker for bounding the protonated amines on COC surface that is pre-modified using PECVD method. The latter coating is stable in hydrodynamic flows and could be further used in microfluidics. Finally, the gold type\Y zeolite type\AuNPs@zeolite type microreactors are respectively connected into pre-designed microfluidic system. The gold type microreactor exhibits stable high selectivity to benzaldehyde (about 94%). However, it also shows relative low benzyl alcohol conversion (about 20%). The AuNPs@zeolites type microreactor performs the best catalytic activity in our study as a high benzaldehyde selectivity (>99%) is obtained with the highest benzyl alcohol conversion (about 40%).

## <u>Résumé</u>

Ce travail vise non seulement à la conception et la fabrication de nouvelles puces microfluidiques pour l'oxydation de l'alcool benzylique, mais aussi au développement d'une méthode utilisant le plasma. Cette dernière est consacrée à la fonctionnalisation de surface avec un liant afin d'ancrer des particules de catalyseur. Les résultats montrent que le procédé PECVD est une méthode universelle permettant de déposer un nombre élevé de fonctions amines à partir de l'APTES (3-aminopropyl)triéthoxysilane sur différentes surfaces. Suite à l'étude des différents paramètres plasmas, des conditions optimales ont été trouvées. En effet, par rapport à la fonctionnalisation conventionnelle par voie humide, une meilleure hydrophilicité, une épaisseur de dépôt plus élevée ainsi qu'une densité de groupements amines plus élevée ont été obtenus sur les échantillons traités. En outre, les dépôts APTES conduisent à un recouvrement plus élevé de la surface avec une quantité d'AuNPs plus élevée lorsque la valeur du pH est de 6,2. De plus, les résultats avec les AuNPs immobilisés sur la zéolite indiquent que l'APTES est un meilleur précurseur que le MPTES car il offre une plus grande teneur en or. Pour la zéolite et AuNPs@zéolite, les particules sont fonctionnalisées par un groupement carboxyle à l'aide du CES en tant qu'agent de liaison pour les amines protonées présentes sur la surface du COC ; ce dernier étant prétraité en utilisant le procédé PECVD. Enfin, le type or zéolite de type Y  $\langle a \rangle$  AuNPs microréacteurs de type zéolite sont respectivement connectés au système microfluidique préconçu. Le microréacteur à base d'or présente une sélectivité élevée stable au benzaldéhyde (~94%). Cependant, il montre également une conversion faible d'alcool benzylique (~20%). Le microréacteur type AuNPs@zéolites réalise la meilleure activité catalytique dans notre étude, car une sélectivité élevée par rapport au benzaldéhyde (> 99%) est obtenue avec la conversion la plus élevée de l'alcool benzylique (~40%).