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► **To cite this version:**

Pascal Brault. Plasma deposition of catalytic thin films: Experiments, Applications, Molecular modeling. *Surface and Coatings Technology*, 2011, 205 (Supplement 2), pp.S15-S23. 10.1016/j.surfcoat.2011.01.052 . hal-00604084

HAL Id: hal-00604084

<https://hal.science/hal-00604084v1>

Submitted on 28 Jun 2011

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Plasma deposition of catalytic thin films: Experiments, Applications, Molecular modeling

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Abstract:

Plasma deposition of catalytic thin films is reviewed in view of highlighting some interesting features. Plasma sputtering, plasma enhanced chemical vapor deposition and plasma enhanced metalorganic chemical vapor deposition and their preferential use in various kind of catalytic films are described. Fuel cell electrodes, gas sensors and photocatalytic films are emphasized as significant applications. As example, magnetron sputtering deposition is successfully used for growing fuel cell electrodes with high performances. Doping doped TiO₂ photocatalysts are deposited using various kind of plasma depending on the expected film morphology. Gas sensors are well designed when using plasma deposition. Plasma treatment of catalysts offers a suitable alternative to thermal treatments. Finally, associated simulations, especially recent progress in molecular dynamics simulations of catalytic films growth are surveyed. This is a suitable way to understand basic mechanisms of catalytic film growth.

Keywords:

Plasma deposition; catalytic films; nanocluster; fuel cells; photocatalytic TiO₂; gas sensor, catalyst treatment, catalyst functionalization, molecular dynamics simulations, thin film growth.

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1. Introduction

Heterogeneous catalysis is of primary importance in many chemical and electrochemical processes. To be efficient a solid catalyst is usually a supported assembly of nano-sized particles, eventually dispersed on a support with a large surface area [1,2]. Due to environmental concerns, both the catalyst usage conditions and catalyst preparation methods will suffer from severe international rules. The development of new and environmentally friendly catalyst preparation methods is a very challenging task in the industry. This should also satisfy the fabrication cost and preparation time reductions and if possible in increasing the catalysis efficiency and selectivity. Plasma technologies have been involved in catalysis with some success [3-5] and they are ready to be popular. Most of the studies are related to ultra-fine particles production, direct catalyst deposition on a support [6,7] and also assistance of catalytic reactions [8,9]. Some applications will directly benefit from advances in plasma technologies, among them fuel cells electrodes, photocatalytic films (mainly TiO₂ and variants) and gas sensors due to the interest of the thin film geometries [10]. Catalyst location control and loading reduction, avoiding expensive noble metal catalysts (e.g. platinum), miniaturization for mobile applications or lab- on-chip, morphology of the catalytic film [11–17] are requirements that can be reached using plasma technologies. This article is thus reporting recent advances in the successful use of low or high pressure non thermal plasmas for catalytic thin film growth.

2. Plasma experiments

Catalyst chemical synthesis is currently used for producing catalyst on an industrial scale and/or being subject to research studies. The chemical routes include impregnation–reduction method, colloidal route, carbonyl route, microemulsion and electrochemical methods [18]. Due to expected environmental limitations, the use of solvents and other products which are

toxic at some level, will be prohibited or limited on an undefined timescale. So searching for alternative “clean” technologies, which can also minimize the thermal budget, is an up-to-date challenging effort.

Plasma technologies are one of the candidates for building clean technological process ready to use on an industrial scale, because they are already available in many companies. The advantages of plasma lie in the ability to generate active species which are chemically (ion or neutral radicals, excited species) and/or physically (ions, electrons) active. Moreover this allows new reaction pathways to be created as well in gas phase as at surfaces (walls, substrates). Basically plasma chemistry will lower reaction thresholds, improve catalyst activity and selectivity. Surface plasma treatments are intended to catalytic thin film deposition and catalytic surface functionalization

Plasma sputtering deposition (PSD) and plasma enhanced chemical vapor deposition (PECVD), including plasma enhanced metalorganic chemical vapor deposition (PEMOCVD) and combinations of these techniques are the most preferred techniques as being very attractive. Atmospheric non-thermal plasmas such as atmospheric dielectric barrier discharges are progressively used for catalyst treatment [19]. To a less extent pulsed laser deposition is also considered for catalytic film growth [20]

Plasma sputtering deposition is a fairly simple technique. A plasma is created by an electrical breakdown in a chamber filled by a sputtering gas, most often argon, possibly in a combination with a reactive gas. Argon ions generated in the plasma are attracted on one or more catalyst targets (with or without a specially designed magnetic field) and are sputtering catalyst atoms to produce on substrate an elemental or compound (alloy) catalytic film; the substrate is either a flat surface or a porous substrate. Plasma sources are of various kinds: RF, DC, pulsed DC magnetron sputter source, Inductive Coupled Plasma (ICP) source (including

helicon and Transformer Coupled Plasma (TCP) sources), RF, DC parallel plate source [21, 22]. Main advantage is the control of the sputtered particle flux, energy distributions at the target and at the substrate [23-26] by simply tuning experimental conditions. An interesting feature is the sputtered particle distribution that is non-maxwellian (contrary to vacuum evaporation) with mean kinetic energies in the range 10-30 eV. The transport of sputtered particles through the buffer gas to the substrate is the way to modify these distributions that can become thermalized if the transport path is long enough and/or the pressure is high enough. Moreover high deposition rates (up to $10\mu\text{m}\cdot\text{h}^{-1}$) are possible. Moreover excited species can exist, due collision between energetic sputtered atoms and the buffer gas atoms (e.g. argon), excited or metastable Ar created by electron collisions, which can interact with the growing film [27-32].

PECVD is also a very interesting technique, which allows both deposition and treatments like functionalization and grafting. Ability of PECVD is to deposit films from molecular precursor in gaseous or liquid form at various rates. The basic mechanism is the polymerization in the gaseous phase or at the surface. This occurs due to radical creation by electron collision on precursors which overcome limitations occurring in Chemical Vapor Deposition (CVD). Moreover, plasma generates radiation, positive ions, neutral and metastable species, electrons that may interact with immersed surfaces [33]. So new reaction pathways are possible and thus « new » materials can be deposited as thin film with easy control of the porosity. A variant of the PECVD for which precursor are metal containing carbon bonds. Precursors are liquid or solid, so heating is often required before injection in the plasma chamber [34, 35].

3. Typical catalytic thin films

The most “simple” catalytic film is a collection of noble metal supported nanoclusters, nanocluster being the most preferred catalyst morphology [1].

Fig. 1 shows Transmission electron Microscopy (TEM) images of Pd clusters grown onto $\mu\text{c-SiC}$ obtained by ICP sputtering of a Pd wire [6, 23, 25]. The clusters have a well monodispersed size distribution. These nanoclusters were successfully tested against hydrogenation of 1,3 butadiene [6]. More generally, a parametric study of Pd sputter deposition shows a transition from nanocluster growth [36] to continuous film of very low thickness ($< 10\text{nm}$), which is of potential interest for gas separation membrane [7]. A major requirement in heterogeneous catalysis is a high surface area of the active phase. This can be achieved by decorating spherical particles (e.g. carbon) with catalyst nanoclusters, which are further randomly stacked on suitable support, providing the high area active surface. Another way is to sputter catalyst target onto porous support. As example, for building a proton exchange membrane fuel cell (PEMFC) electrode, it is proposed either to deposit Pt or Pt alloys onto uncatalyzed gas diffusion layer made with Vulcan XC72 carbon particles brushed onto a carbon cloth or paper [37]. Another way is to directly grow an active layer by Pt – carbon co-sputtering [38-40].

Another type of catalysts is oxide particles and films. They also are well suited for plasma synthesis. A very popular oxide catalyst is TiO_2 which is especially interesting for photocatalytic applications [41]. Variants are possible with many doping species: metals (Fe, Cr, W, Ni, ...), oxides (Fe_2O_3 , WO_3) of light elements (N, C, S, ..) [5]. Main interest is to increase the visible light absorption for benefiting from the solar light and/or to enhance the photocatalytic activity, for example for improving antibacterial effects, pollutant/toxic molecule decomposition, water recycling,The anatase phase is preferred in the form of nanoclusters, nanofibers, nanotubes, ..., possibly decorated with metal clusters. It can be prepared via numerous routes, especially all plasma techniques can be used and lead to various thin films morphology, those with high specific area being preferentially aimed [42-47]. When comparing on Fig. 2, the different morphologies issued from (a) PEMOCVD, (b)

Magnetron sputtering and (c) PECVD, we observe that surface disorder is greater in PEMOCVD. Growth is columnar and dense with magnetron deposition and long nanocolumns (nanofibers) are obtained using PECVD. Noble metal oxides are catalysts of hydrocarbon conversion and can also be prepared by plasma sputtering [48], which leads to performance improvement.

The field of carbon nanotubes (single wall and multiwall), nanofibers, nanowalls, and other nanostructures is subject to a huge amount of studies and are partly of interest as catalysts, eg electrochemical devices [49-53]. Deposition of catalysts on nanofibers (see Fig. 3), nanotubes arrays is a growing fields especially as fuel cell electrodes [54-59].

A kind of substrate call us to attention: anodic aluminum oxide (AAO) templates [60] (see Fig. 4a). Briefly, when oxidizing aluminum foils (thickness around 50 -100 μm) in an electrochemical bath, a hexagonal array of cylindrical nanopores (nanochannels) is created. The size and density of nanochannels is depending on bias and current of the electrochemical cell. Such 2D porous array can thus be used as template for various nanowires growth eg platinum, silicon, CdS. The use of plasma sputtering deposition allows for creating a well organized cluster assembly with gradient concentration inside the pores [61] as displayed in Fig. 4b. This could be useful when searching for localized catalytic effects near a boundary.

4. Applications

4.1 Fuel cells

A fuel cell is a power supply that converts electrochemical energy into electricity and heat by the following reactions (for a proton exchange membrane fuel cell, PEMFC): Fuel (H_2 , CH_3OH , ...) carrying hydrogen atoms that are catalytically transformed into protons at the anode side, releasing electrons and supplying an external charge ($\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$), while protons are transported through a ion conducting solid polymer electrolyte. This electrical

circuit is closed at the cathode by the catalyst (Pt) activated oxygen reduction with protons to give water and heat. The PEMFC is thus a three layer system. The electrodes (anode and cathode) have an active layer made of dispersed catalyst nanoparticle (sizes in the range 2 to 10 nm) supported on carbon VulcanXC72 particles (size in the range 20 – 100nm). This active layer of usually 20 to 50 μm is coated (painted) on gas diffusion layer, eg carbon cloth or carbon paper. The catalyst load (Pt for example) can vary from 0.3 to 2 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$ per electrode for a delivered power of $0.5 \text{W} \cdot \text{cm}^{-2}$. So a 80 kW motor requires 80g of Pt, which costs 3200 €. It is thus necessary to reduce Pt quantity and increases Pt use. Many attempts using plasma have been undergone. Recently plasma sputter deposition has reached good performances and high use of platinum and Pt quantity reduction down to $0.01 \text{mg}_{\text{Pt}} \text{cm}^{-2}$ per electrode, leading to power density of $20 \text{kWg}_{\text{Pt}}^{-1}$ [40]. In that case, Pt nanoclusters of size 0.7-2 nm (Fig. 5) where grown during Pt-Carbon magnetron co-sputtering on carbon Vulcan XC72 electrode and are present over 400 nm inside the active layer. Similar approaches involved Pt sputtering simultaneously with C_2H_4 PECVD or more generally hydrocarbon PECVD leading to carbon nanostructure decorated with some catalyst [54-59, 62]

While Pt load reduction is a challenge, the goal is also to avoid Pt and more generally noble metal catalysts. Some special molecules called metal (mainly Fe, Cu, Co, ...) porphyrins and phtalocyanins lead to promising properties [63, 64]. This comes from the metal bonding to four nitrogen atoms in a planar geometry (Fig. 6). Plasma treatments of catalytic films containing such molecules were shown to improve fuel cell performances using low pressure ICP plasma and atmospheric dielectric barrier discharge [65, 66].

4.2 Gas sensors

Beside fuel cells, an application demanding performances of plasma technologies is the development of sensors, especially gas sensors, as needed for process controls due to new

environmental management rules. As fuel cells, gas sensors are multilayered systems eventually based upon catalysis for species detection through catalytically activated reactions [11, 14, 67-71] (see Fig. 7)

Specifically, catalytic gas sensors for methane (CH_4), butane (C_4H_{10}) and hydrogen (H_2) are used mainly for preventing explosive accidents. The operation principle is catalytic oxidation of combustible gases. Thick film catalysts, which are normally noble metals such as platinum and palladium can be heated by a wire coil in an alumina bead. The catalytic combustion of the gases starts when the electrically heating catalyst material reaches the required temperature. The platinum resistance variation relative to a reference resistance called compensator is measured as the temperature due to oxidation of inflammable gases is increased [11, 14, 67-69]. Sensors for other gases such H_2S , O_2 are also studied [70,71]

4.3 Catalysts treatments

Catalyst efficiencies can be improved by suitable exposure to inert or reactive plasmas. Especially, catalyst treatments using nonthermal plasmas is becoming a growing field of interest. It is due to the obtained increase in the catalyst acidity (both Brönsted and Lewis acidities), in the dispersion and in the low-temperature activity (which is largely due to the increased dispersion of the catalysts during treatment [5]). The presence of catalyst powder is modifying the high pressure plasma indicating the effectiveness of the process (Fig. 8). Major results concern the increase in the dispersion and the stability of catalyst. Reduction of catalysts is also very active. For example, the use of microwave plasma [72], atmospheric DBD [19] have resulted in higher activity and selectivity, due to change of nanocluster sizes

5. Molecular modeling

For better understanding of the growth of metal or oxides films, as those needed for catalytic films, it is interesting to carry out molecular simulations at the atomic level. Building efficient catalytic layer needs to understand the growth of catalytic phase, in the form of metallic and oxide clusters or films. Molecular simulations as Molecular Dynamics (MD) simulations are well suited for understanding growth phenomena at the nanoscale. Molecular Dynamics simulations are based upon the resolution of Newton equations of motion. So for an ensemble of N atoms or molecules, the positions, velocities and acceleration are always known [73, 74]. If dissipation occurs, through friction terms for example, Langevin-like equations have to be solved. For simplicity, we consider the cases for which Newton's equations of motion are valid. They can be written:

$$\frac{\partial^2 \vec{r}_i(t)}{\partial t^2} = \frac{1}{m_i} \vec{f}_i, \quad \text{with the force } \vec{f}_i = -\frac{\partial}{\partial \vec{r}} V(\vec{r}_1(t), \vec{r}_2(t), \dots, \vec{r}_N(t))$$

The only information necessary to solve this set of N equations of motion is the potential energy. Resolution of these equations is carried out using stable algorithms as Verlet velocity scheme [73]. Statistical information and materials properties can be deduced by averaging over all trajectories and compared directly to experiments. Thus MD is a very powerful method for understanding molecular interactions. For illustrating this, examples of metal cluster growth and oxide films are described.

5.1 Pt deposition on model porous carbon substrate.

Pt-Pt interaction potentials (also valuable for transition elements) is given by the second moment approximation of the tight binding theory (TB-SMA) [75] and for Pt-C by an efficient Lenard-Jones potential [76]. They take the forms, respectively:

$$V_i = \sum_{i \neq j} A \exp \left[-p \left(\frac{r_{ij}}{r_0} - 1 \right) \right] - \left\{ \sum_{i \neq j} \xi^2 \exp \left[-2q \left(\frac{r_{ij}}{r_0} - 1 \right) \right] \right\}^{\frac{1}{2}} \quad \text{and} \quad V_{ij}(r_{ij}) = 4\epsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$

Calculations are performed on various model porous carbon substrates as depicted in Fig. 9. Main information that can be gathered is the radial density function which inform on the cluster/film structure, depth concentration profile, cluster size distribution if any. As a matter of fact, experiments display a Pt concentration profile [77] that can be fitted with the stretched exponential function $\rho(z,t)$, solution of a generalized diffusion equation:

$$\rho(z,t) = A(t) \exp\left[-\frac{z^{2+\theta}}{B(t)}\right].$$

As shown in Fig. 10, the calculated θ using MD simulations is in

the range -1.0 to -1.7 as for the experiments [77], indicating enhanced Pt penetration in the porous electrode.

5.2 Oxide clusters and films.

MD simulations of oxide clusters or films are a bit more difficult due to long range potential describing ionic interactions. A fairly simple potential (but not necessarily always the most efficient) is given by:

$$V_{ij}(r_{ij}) = A \exp\left(-\frac{r_{ij}}{r_B}\right) - \frac{C_6}{r_{ij}^6} + \frac{q_{ij}}{r_{ij}}.$$

Numerous strategies exists for solving Newton equations

with long range interactions as Ewald summation, ... [78]. Fig. 11 displays the evolution of a TiO₂ cluster under thermal relaxation at 300 K [79]. Atomic positions are largely modified compared to the frozen initial condition corresponding to the bulk anatase structure. This very simple potential is also able to reproduce experimental results of plasma sputtering deposition of magnesium aluminium oxide [80-82]. Evolution of the film morphology is reproduced in Fig. 12 as function of Mg content [82].

6. Conclusion.

As a summary of this short review, plasma technologies are very efficient for designing catalyst thin films, especially plasma deposition is very well suited for controlling catalyst

content and localisation in a layer, which is out of range of standard chemical means, which always provide homogeneously dispersed catalysts on a thickness not less than 5 to 10 μm . Numerous successes have been recorded for applications in fuel cells for which plasma deposited electrodes have a very low catalyst content and a very good efficiency. Photocatalysis (TiO_2 films and its derivatives) benefits from versatility of plasma deposition methods for allowing a wide range of photocatalysts geometry (films, nanotube, complex nanostructure, porous films). The catalytic films in gas sensor technology use plasma deposition in a same way as for microelectronics. Catalyst treatment and functionalization make use of new plasma technology of atmospheric DBD for avoiding thermal treatments. As a consequence, catalyst treatments are softer and more efficient in the way of catalyst efficiency and durability.

From the point of view of green chemistry, the use of plasma at least represents a reduction in the use of chemicals, especially the use of noble metals and precursors. It gives also the possibility also for giving up the use of toxic chemicals, especially by using plasma sputtering deposition. Moreover, the electrical energy consumption for nonthermal plasma catalyst treatments is not high.

Molecular simulations, as Molecular Dynamics, are able to provide relevant insight into basic mechanisms of cluster and film growth leading to the possibility of designing more efficient catalytic cluster assemblies or thin films.

Acknowledgements

I am indebted to people who contributed to the past and present catalytic thin film projects at GREMI or through collaborations or during deep discussions, which finally leads me to write such a review, especially: A.-L. Thomman, A. Caillard, A. Ennajdaoui, H. Rabat, M. Cavarroc, M. Mougnot, C. Coutanceau, S. Baranton, C. Lamy, J. Durand, S. Roualdes, G. Pourcelly, P. Buvat, C. Jossierand, F. James, J.-L. Rouet, R. Boswell, C. Charles, D.B. Graves, S. Wu.

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Figure captions

Figure 1: TEM pictures of Pd nanocluster growth on SiC by ICP sputter deposition taken different Pd loading (a) $0.1 \mu\text{g}_{\text{Pd}}\cdot\text{cm}^{-2}$, (b) $1.0 \mu\text{g}_{\text{Pd}}\cdot\text{cm}^{-2}$ and (c) $3.0 \mu\text{g}_{\text{Pd}}\cdot\text{cm}^{-2}$. Scale bars are 10 nm (from Ref. 6).

Figure 2: TiO_2 photocatalytic thin films deposited by (a) PE-MOCVD (using bis(2-N-(2-hydroxy-2-methylethylimino)-4-pentanoate)titanium(IV) (from Ref. 42), (b) reactive magnetron sputtering (from Ref. 43), (c) PECVD (using $\text{Ti}(\text{OC}_3\text{H}_7)_4$ TIPP) (from Ref. 44),

Figure 3: Images of a carbon nanofiber (CNF) array surrounded by sputtered Pt nanoparticles: (a) SEM image of Pt deposited on a CNF array, (b) TEM images of an isolated Pt decorated CNF, (c-e) details of the Pt cluster distribution along the CNF;: The three pictures corresponds to zone marked in (b), from Ref. 56.

Figure 4: Hexagonal array of cylindrical pores decorated by platinum clusters grown by plasma sputtering (a) top view (b) cross-section. Pt clusters appear as white zones, from Ref. 60.

Figure 5: High Resolution TEM micrographs of plasma sputter deposited Pt nanoclusters on carbon particles. Dark areas are Pt clusters. Courtesy: C. Coutanceau, LACCO, Poitiers, France.

Figure 6: Drawing of the metal-porphyrin: cobalt tetramethoxyphenylporphyrin (Co-TMPP) atomic structure

Figure 7: (a) and (b) Typical architectures of catalytic gas sensors from Ref. 67 and 68, (c) the structure of a catalytic Pt thick layer from Ref. 11 and (d) palladium decorating titanate nanotubes, from Ref. 69

Figure 8: Photos of high pressure glow discharge without (a) and with catalyst powder (b). I: negative glow space; II: positive column space (catalyst powder located on the bottom, from Ref. 5)

Figure 9: Three model carbon porous substrates:

- a) A column of amorphous carbon height 20 nm, diameter 9.2 nm (this is equivalent to a column periodic lattice leading to a porosity = 34 %)
- b) A non compact stacking of amorphous carbon spheres (2.26 g.cm^{-2}), with diameter between 0.3 et 1.3 nm (porosity 60%)
- c) A cylindrical pore height 20 nm, diameter 9.2 in amorphous carbon box $10 \times 10 \times 20 \text{ nm}^3$ (this is equivalent to a lattice of cylinder with porosity = 66 %)

Figure 10: Snapshot of Pt deposits on carbon substrates of Fig. 11 with the corresponding Pt depth profile. The value θ of the fitting function is given on the plot.

Figure 11: 3 nm anatase cluster. (i) initial, (f) and final structures at 300 K. Oxygen and titanium ions are dark and light colors, respectively, from Ref. 79

Figure 12: Snapshots of $\text{Mg}_x\text{Al}_y\text{O}_z$ thin films using a simple pair potential wich is successfully compared to sputtering experiments, from Ref. 82.

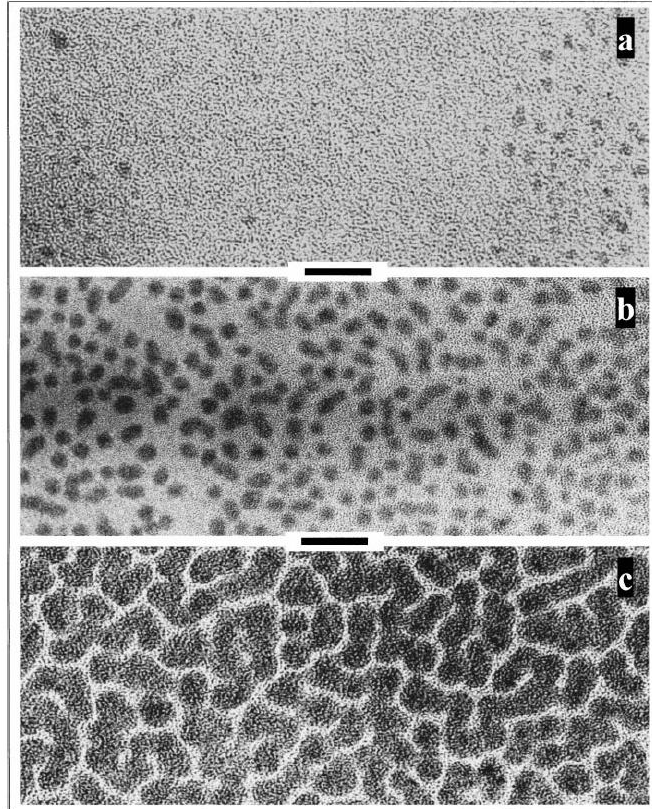


Fig. 1

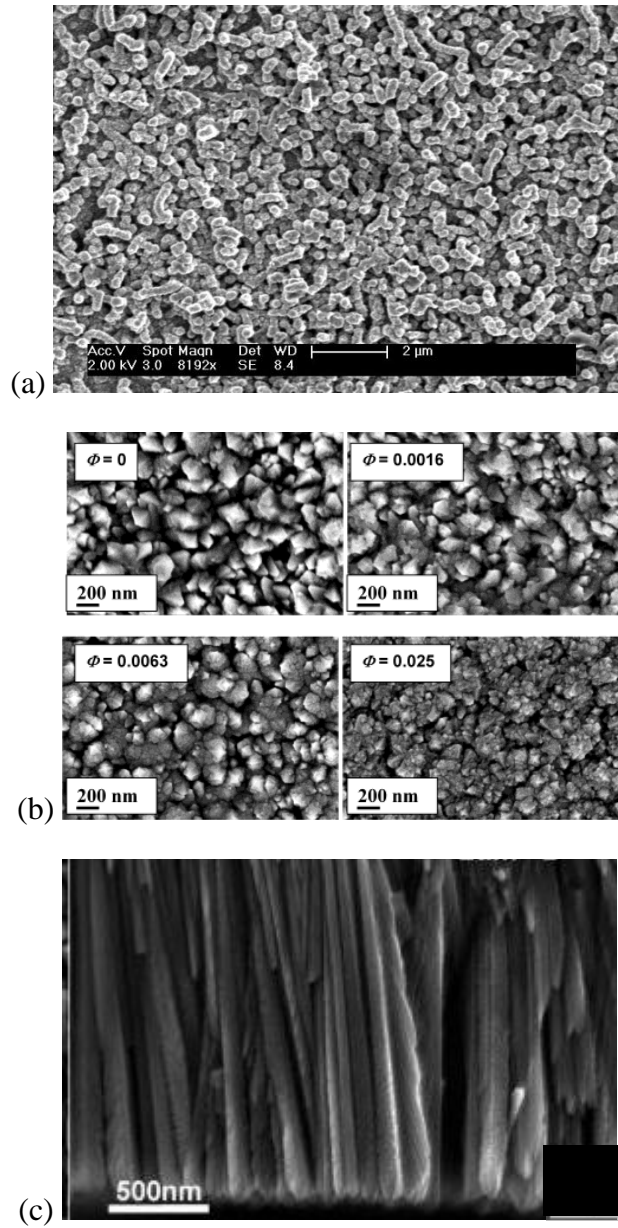


Fig. 2

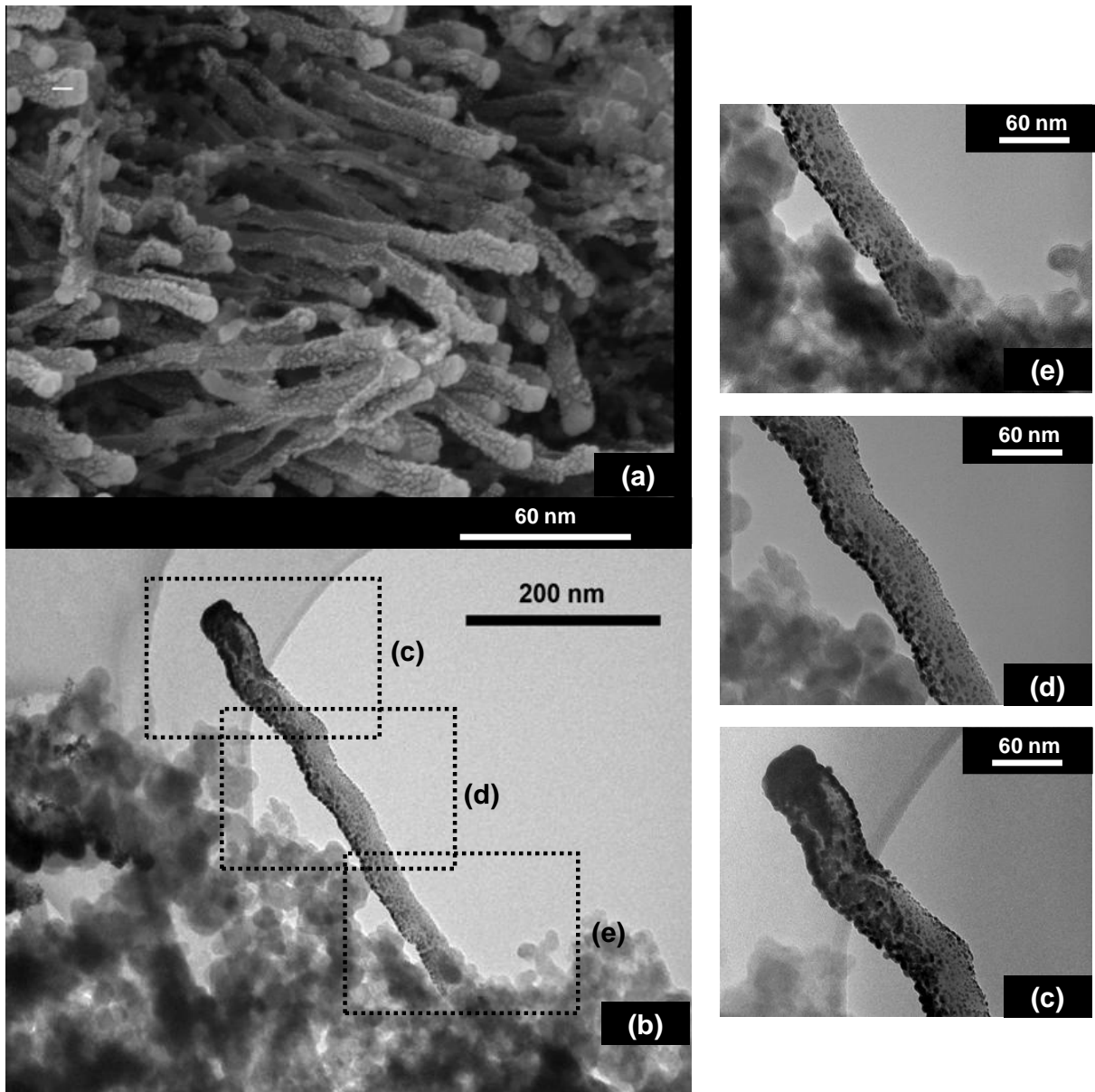


Fig. 3

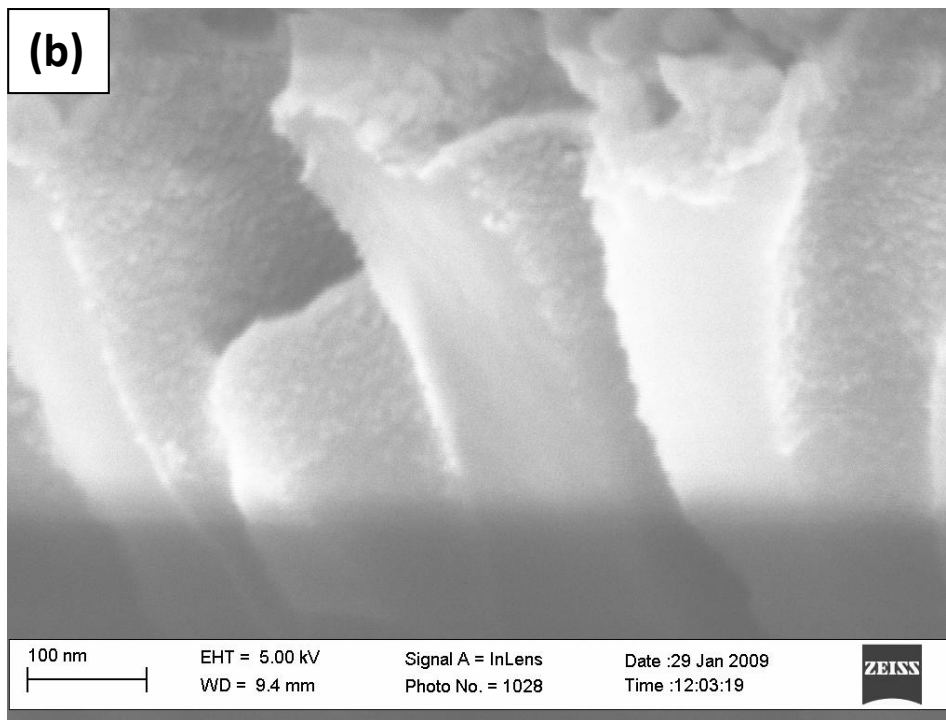
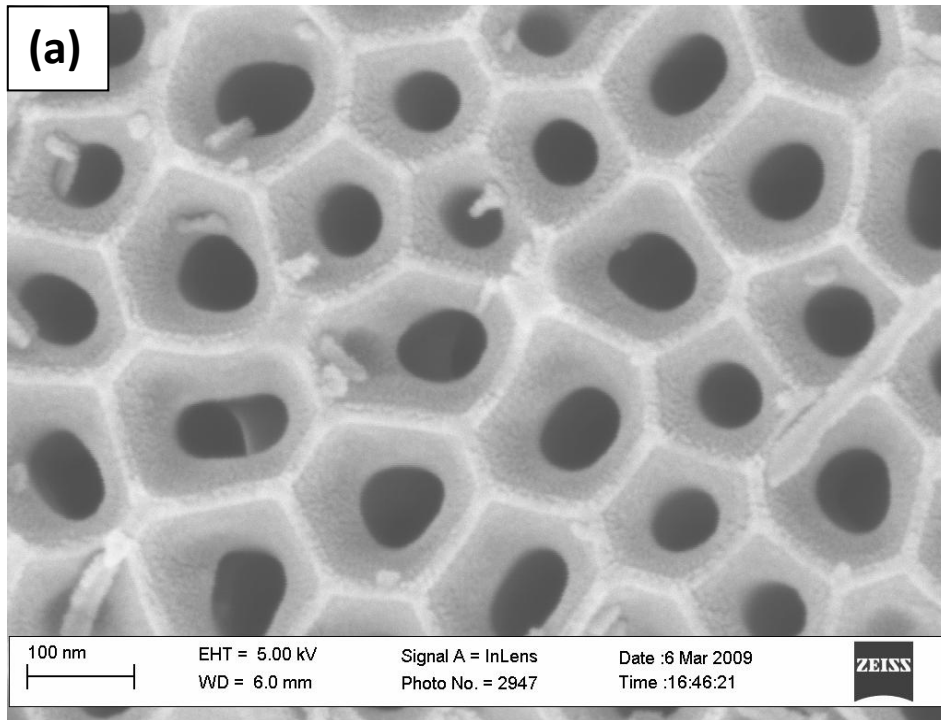


Fig. 4

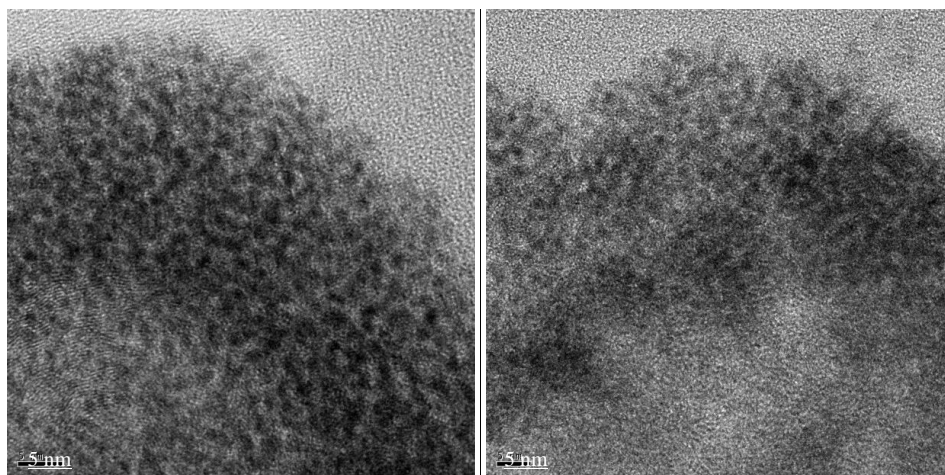


Fig. 5

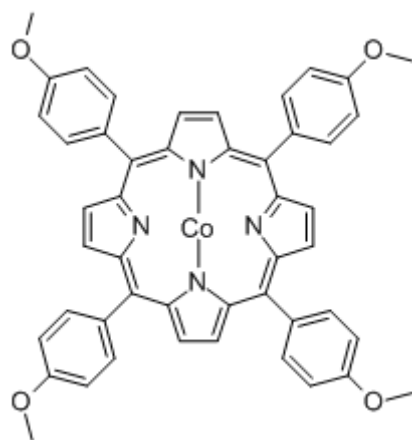
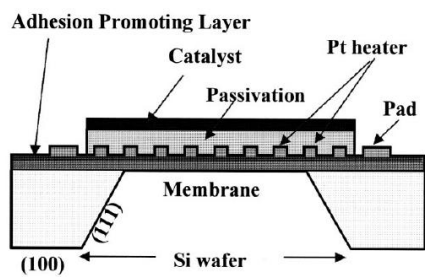
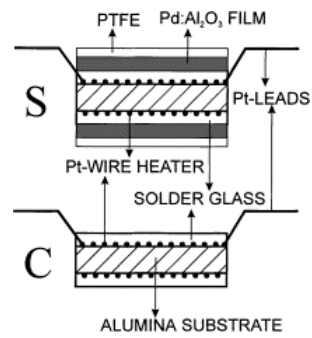


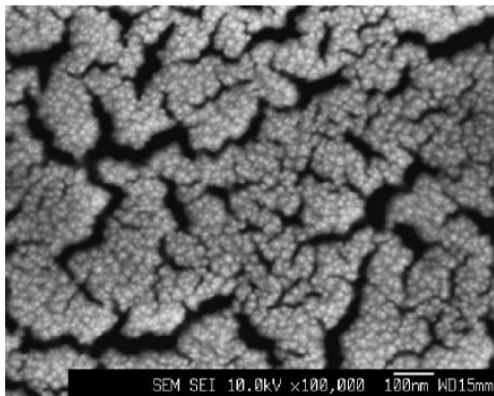
Fig. 6



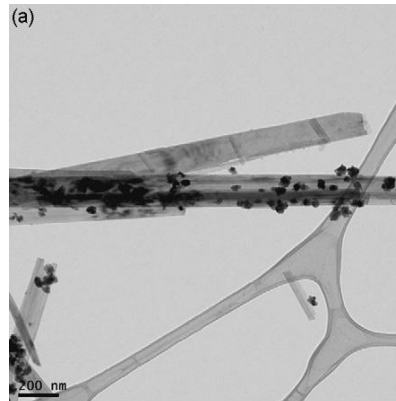
(a)



(b)

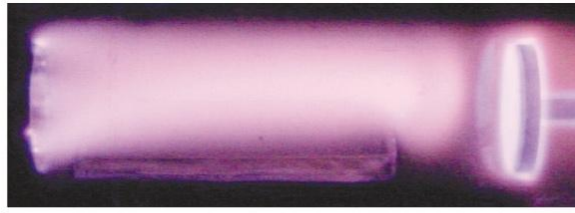


(c)

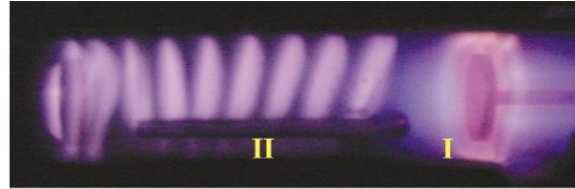


(d)

Figure 7



(a)



(b)

Figure 8

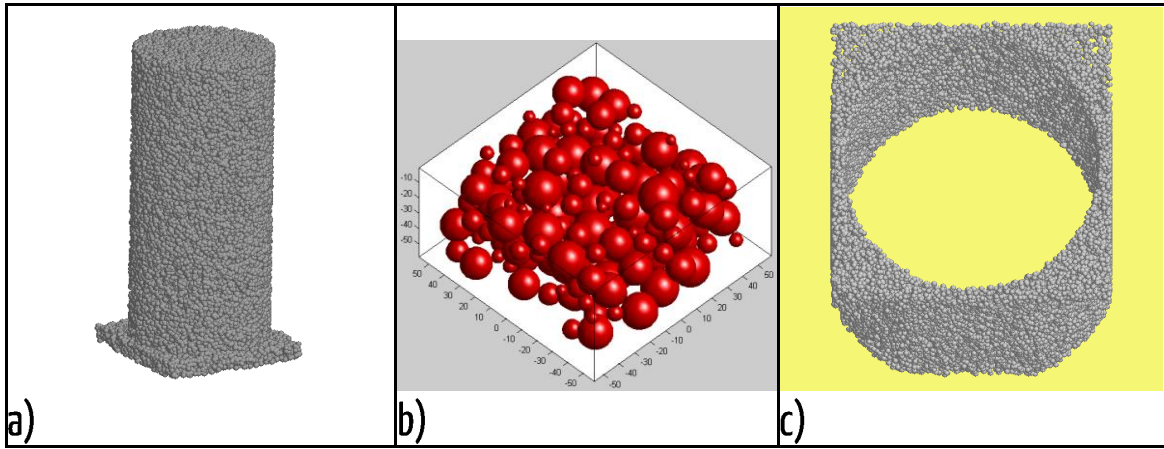


Fig. 9

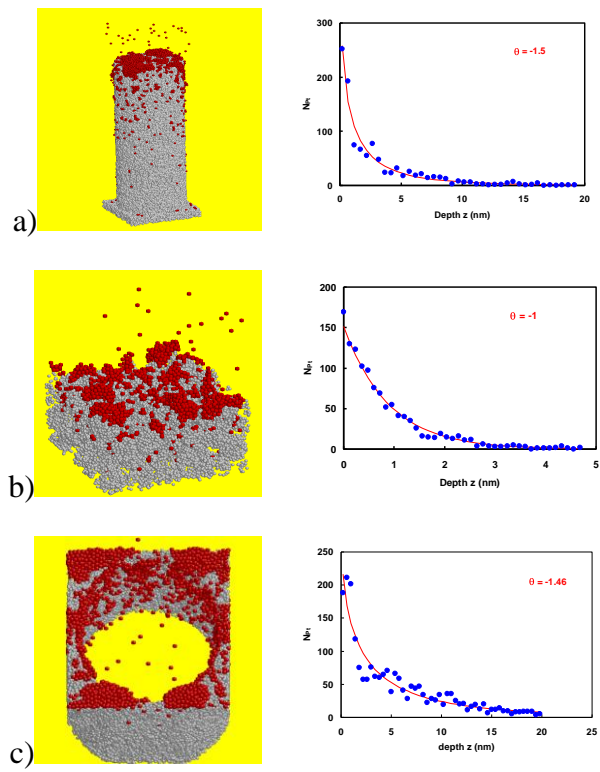


Fig. 10

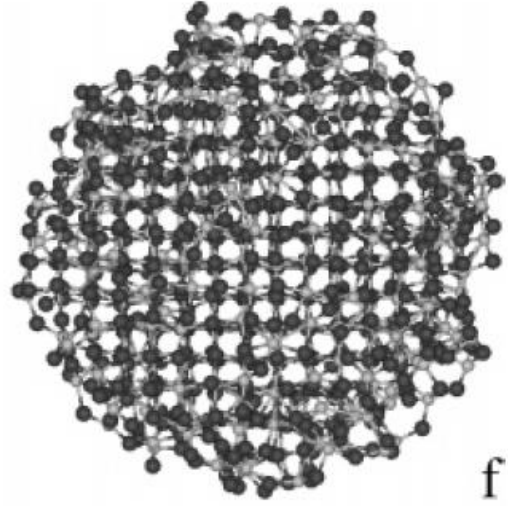
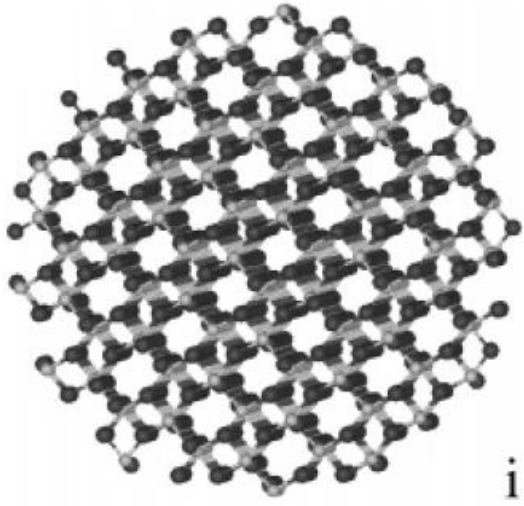


Fig 11

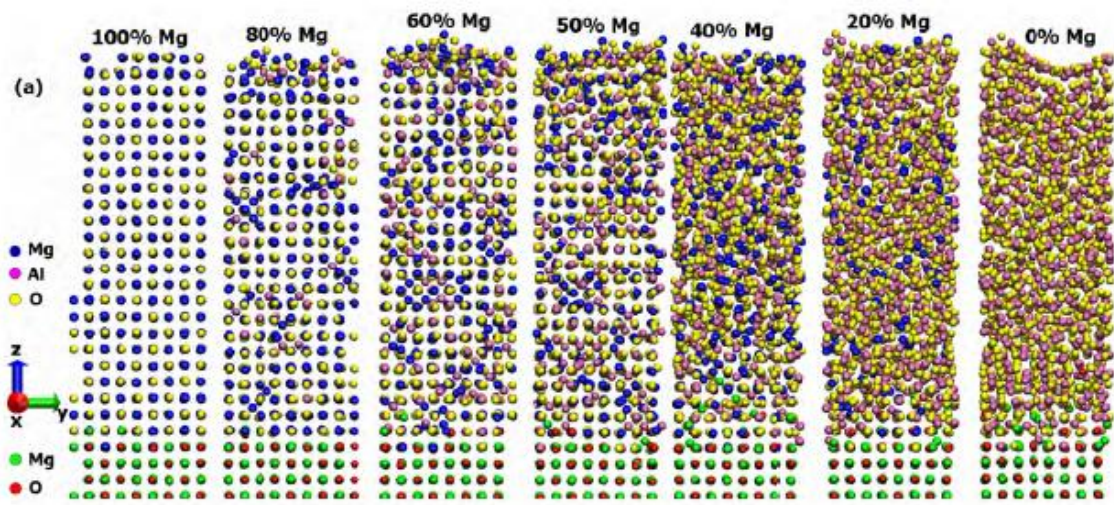


Fig. 12