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**Towards the understanding and control of the photo-deposition of metal nanoparticles on oxides**

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**ABSTRACT**

The photo-deposition technique under UV and UV-Vis domain for metal nanoparticles, e.g. platinum, was explored. According to the procedure employed, one can devise various complex mechanisms. This work evidences such complexities by a judicious choice of parameters, such as alcohol chain length, and media. The presence of nanoparticulated oxide anatase-phase enhances the photo-deposition process of metal nanoparticles via the so-called heterogeneous photocatalysis. A description and the effect of mixing of various chemical components in the reactor are given. The control of the nanoparticle size with water as hole-scavenger looks promising.

## 1. Introduction

The tailoring of stable highly dispersed and efficient electrocatalysts is currently a great challenge. A promising way to achieve this consists in using oxide and/or oxide-carbon composites as supports. Moreover, the technique devised to perform the metal (e.g. platinum) deposits on the support seems also to influence the nature of the interaction between the catalyst and the support. Particularly, the photo-deposition technique [1] is well adapted to induce nanoalloy formation with the metal of the support giving rise to the so-called strong metal substrate interaction (SMSI) [2, 3], thus improving the rate, e.g., the oxygen reduction reaction. The method consists in photo-irradiating an aqueous solution containing the metallic precursor, the oxide, and organic molecules serving as a hole-scavenger. The process is based on the reducing/oxidizing capability of photo-irradiated oxide nanoparticles to achieve the reduction of metallic ions into metal islands and the oxidation of adsorbed water or organic molecule. It is essential to control the synthesis of noble metal based nanoparticles, since the electrocatalytic activity depends on the chemical nature, morphology, crystallographic properties and the position of the d-band center with respect to the Fermi level. Parameters affecting the properties of photo-deposited nanoparticles are still not-well identified and understood. This study aims at understanding of the mechanism of photodeposition of Pt onto  $\text{TiO}_2$  substrate, as well as the control of the nanoparticle size.

## 2. Experimental

### 2.1 In-situ absorbance monitoring during photodeposition process

The photo-deposition procedure was carried out as follows: 52.6 mg of  $\text{TiO}_2$  (anatase), synthesized by sol-gel technique, was mixed in argon-saturated 28 mL water in a photo-reactor provided with two optical quartz windows. Additionally, 6 mL of isopropanol solution containing 34.7 mg of Pt salt ( $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ ) was added into the photo-reactor. The suspension was saturated with Ar and kept under constant stirring for 3 h. The source of ultraviolet (UV) and visible (Vis) radiation used for the experiments was a Xe-lamp (159 W, ITS PS 150-9). In order to prevent the heating of the samples, the infrared (IR) photons were avoided using a hot mirror UV (Edmund Optics, F46507), and a water filter. To follow up in-situ the reaction kinetics, a light detector (Rad Probe, LP 471) was fixed on top of the photo-reactor. The detector was connected to a photo/radiometer (Delta OHM HD 2102.2). Fig. 1 shows a scheme of the photo-reactor. A UV filter (Edmund Optics, F45311) was used to cut  $\lambda < 400$  nm. The suspension containing the  $\text{TiO}_2$  and  $\text{H}_2\text{O}$  was used to record the irradiance at the beginning of the experiment,  $A_0$ . The light detector monitored the evolution of the irradiance,  $A_1$ , with time. The ratio  $A_1/A_0$  was calculated to determine the absorbance.

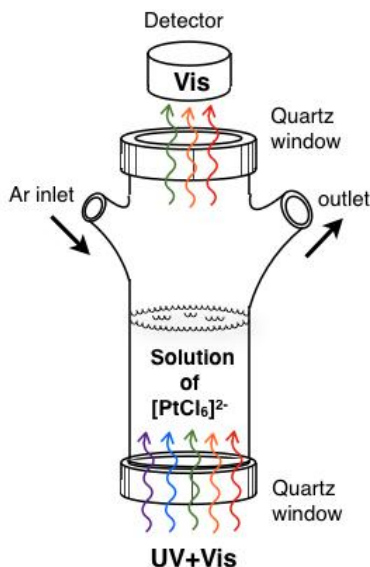


Fig. 1. Photo-reactor used to measure of absorbance changes during photo-deposition process.

## 2.2 TEM characterization

The morphology of particles was examined with a TEM on a JEOL JEM-2001 equipped with a LaB<sub>6</sub> filament. The samples were characterized under an accelerating voltage of 200 kV and a resolution of *ca.* 0.19 nm.

## 3. Results and discussion

To investigate the direct reduction of platinum precursor in the presence of isopropanol, the following experiments were performed. In short, an aqueous solution containing both [PtCl<sub>6</sub>]<sup>2-</sup> and isopropanol were successively photo-irradiated by a Xe-lamp equipped either with or without a UV filter. The variation of absorbance of the solution was monitored in-situ. Results are displayed in Fig. 2.

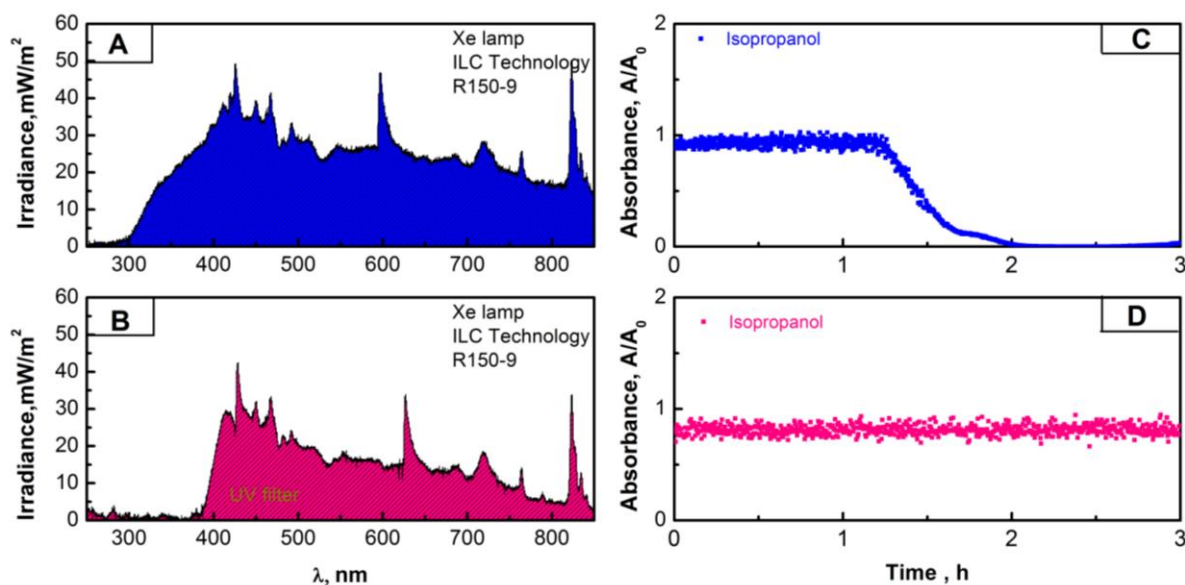
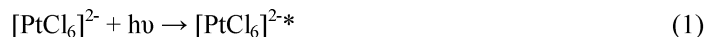
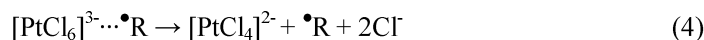
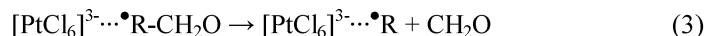


Fig. 2. (A) Output spectrum of the Xe lamp, (B) output XE lamp spectrum with an UV filter, (C) Absorbance evolution of  $[\text{PtCl}_6]^{2-}$  + isopropanol under irradiation using spectrum (A), and (D) Absorbance evolution under irradiation using spectrum (B).

By comparing the results obtained in Figs. 2C and 2D, one can infer that only the UV spectral region is responsible to modify the absorbance of the solution. Indeed, the energy,  $h\nu$ , of this spectral region affects the platinum precursor  $[\text{PtCl}_6]^{2-}$  electronic structure by the electronic  $d-d$  transition with a maximum peak at 300 nm [4, 5]. The photochemical reaction scheme follows [6-8]:



The excited complex is then able to react with the alcohol molecule to form a radical complex ( $[\text{PtCl}_6]^{3-} \cdots \bullet\text{R}$ ) as represented by equations. (2) – (4):



Thereafter, the dissociation of  $[\text{PtCl}_4]^{2-}$  to form  $\text{Pt}^{2+}$  species is done [5], equation (5). This latter is then reduced to form platinum clusters, equation (6).



Recently, we have shown that Pt nanoparticles can be selectively deposited onto oxide sites of oxide-carbon composites [3, 9, 10]. However the photo-deposition process is not yet well controlled and optimized. By designing

different experiments in which the components of the reaction medium are systematically varied, we seek to understand the photo-deposition process to control the particle size and distribution on  $\text{TiO}_2$ . As a result, the changes in the absorbance of different solutions were monitored in-situ. The results are contrasted in Fig. 3. In each panel, a scheme illustrates a possible mechanism.

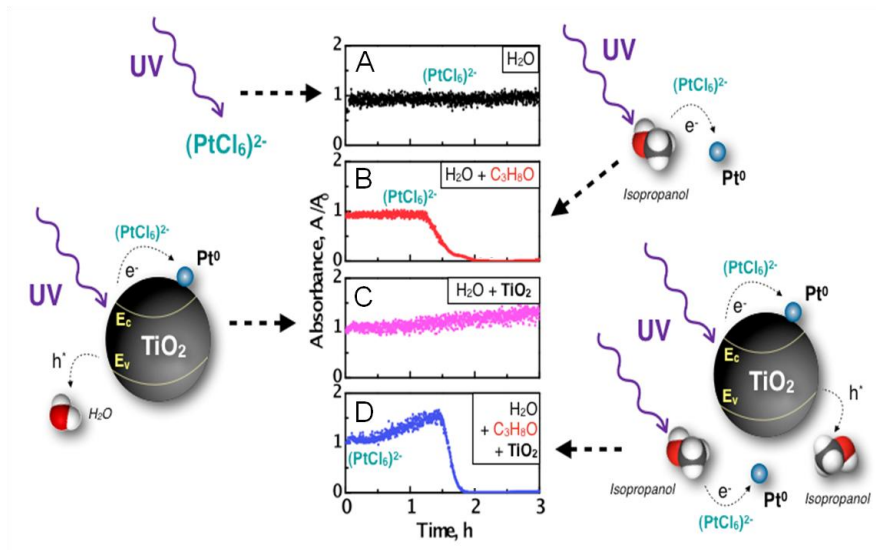
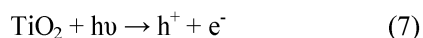
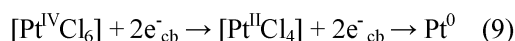
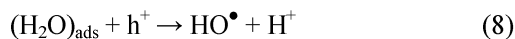


Fig. 3. Absorbance evolution of an aqueous mixture containing  $[\text{PtCl}_6]^{2-}$ ,  $\text{TiO}_2$ , and isopropanol.

From Fig. 3A it looks clear that no variation in the absorbance occurs under UV irradiation when the mixture contained water and  $[\text{PtCl}_6]^{2-}$ . We can assume that no formation of a radical complex, equation (2) takes place in water, and platinum nanoparticles are not generated. However, the presence of isopropanol enhances the deposition of metal clusters. This is confirmed by the change of the absorbance at  $t \geq 1\text{h}$ , and confirmed by the TEM analysis, Fig. 4A. Figs. 3C and 3D depict the phenomenon of heterogeneous photocatalysis induced by  $\text{TiO}_2$  (anatase). In both cases the formation of platinum clusters takes place cf. Figs. 4B and 4C. In the absence of a powerful hole-scavenger, e.g., alcohol (Fig. 3C) the formation of platinum clusters occurs as follows: Firstly, one consists in the hole ( $h^+$ ) – electron ( $e^-$ ) pair generation at the oxide semiconductor under UV illumination:



The absence of any applied electrical field at the particle favors the hole-electron recombination. Under this condition, the formation of  $\text{OH}^\bullet$  radicals from adsorbed water via holes is therefore limited, as a result the reaction process channel via the conduction band (cb) is also limited, but stochastic events are possible that leads to the photogenerated electrons to reduce the platinum complex. The process can be summarized in equations (8) and (9):



This photo-reduction process becomes more complex in presence of isopropanol, cf. Fig. 3D. Indeed, one can imagine several parallel pathways to explain the formation of platinum nanoparticles. The usual mechanism to explain the phenomenon consists in considering that electron-hole pair generation at the  $\text{TiO}_2$  under UV illumination, equation (7), the recombination process is somehow inhibited to a certain extent due to the interaction of alcohol and metal complex species at the semiconducting oxide surface which favors the photo-oxidation of the alcohol via holes and photo-reduction of metal ions of the complex via electrons. Other competing mechanisms previously described may also be involved. The first one results from the excitation of  $[\text{PtCl}_6]^{2-}$  under UV irradiation, equations (1) to (6). The second consists in using water as hole scavenger, equation (8). In the first stage of the reduction process a continuous increase of the solution absorbance of the solution can be clearly seen in Figs. 3C and 3D. The rate of increase is probably related to electron-hole pair recombination and/or to the (cb) electron yield to be transferred to  $[\text{PtCl}_6]^{2-}$  complex species.

After 3 h of irradiation, the samples tested in process in Figs. 3B, 3C and 3D were analyzed by TEM, Fig. 4. These figures clearly show that the morphology and the size of the nanoclusters greatly depend on the experimental conditions.

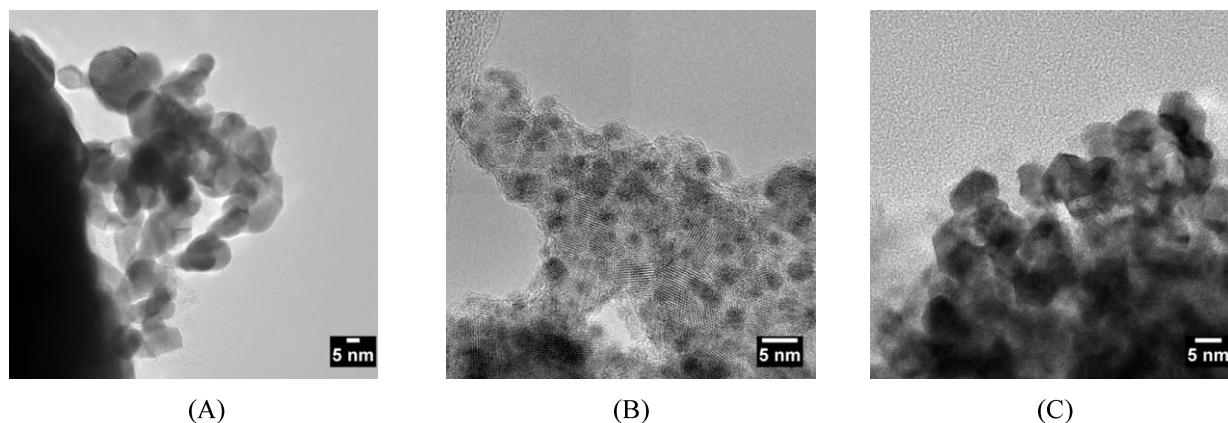


Fig. 4. Low magnification TEM images showing the size and morphology of Pt photosynthesized in (A) water/isopropanol, (B) water solution and  $\text{TiO}_2$ , (C) water/isopropanol and  $\text{TiO}_2$ , after 3 hours of irradiation.

The mean size of platinum nanoparticles has been determined for samples obtained by processes shown in Figs. 3B, 3C, and 3D. They were 10.0, 1.9 and 7.5 nm, respectively. Summing up, small and highly dispersed nanoparticles can be obtained by using only water,  $\text{TiO}_2$  and  $\text{H}_2\text{PtCl}_6$  as reactants, whereas bigger and agglomerated particles are obtained in the other cases. The photolysis process and the absence of a support lead to the agglomeration of Pt nanoparticles (Fig. 4A). Additionally the morphology of particles is highly affected by the procedure used. It seems that particles photo-deposited in presence of water and isopropanol are highly faceted.



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#### **4. Conclusions**

In this work, the concomitant occurrence of different mechanisms during the photo-deposition process of Pt nanoparticles onto TiO<sub>2</sub> in the presence of water and alcohol, are evidenced. By measuring the irradiance light transmitted through the photo-reactor, it was possible to monitor, in real time, the photo-deposition process. Additionally, encouraging perspectives concerning the control of the nanoparticle size by just using water as hole-scavenger to realize the photo-deposition are given. Interesting information is obtained to optimize the process in order to decrease the amount of precious metals used as cathode materials for fuel cells.

#### **5. Acknowledgements**

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