



# Photodeposition of precious metals onto mesoporous TiO<sub>2</sub> nanocrystals with enhanced their photocatalytic activity for methanol oxidation

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## ABSTRACT

Herein, we report a facile synthesis method for mesoporous TiO<sub>2</sub> nanocrystals using the F127 tri-block copolymer as a template. Then, precious metals (Au, Pd and Pt) have been photodeposited onto mesoporous TiO<sub>2</sub>. The prepared photocatalysts have been compared with Aeroxide TiO<sub>2</sub> P-25 by the determination of the formation rate of HCHO generated by the photooxidation of CH<sub>3</sub>OH. The TEM results indicated that the lattice fringes exhibit the typical distances, TiO<sub>2</sub> (1 0 1) (3.54 Å) and TiO<sub>2</sub> nanoparticles with an average diameter of 10 nm particles are not agglomerated and quite uniform in size and shape. TEM images of mesoporous Pd/TiO<sub>2</sub>, Pt/TiO<sub>2</sub> and Au/TiO<sub>2</sub> clearly show Pd, Pt and Au nanoparticles are well dispersed and exhibit diameters of 12, 3 and 5 nm, respectively. The dependence of HCHO formation rate on the precious metals/TiO<sub>2</sub>, behaves quite differently depending on types of precious metals as electrons sink. The photocatalytic efficiency of mesoporous TiO<sub>2</sub> has been enhanced by photodeposition of Au, Pt and Pd in the order Pd > Pt > Au. The increased photocatalytic activity of Pd/TiO<sub>2</sub> more than either Pt/TiO<sub>2</sub> or Au/TiO<sub>2</sub> can be attributed to the density of states in the vicinity of the Fermi level of Pd is high and consists mainly of contributions from d electrons. To the best of our knowledge, the measured photonic efficiency  $\xi = 17.8$  of Pd photodeposited onto mesoporous TiO<sub>2</sub> is found to be among the highest  $\xi$ -values reported up to now.

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## 1. Introduction

TiO<sub>2</sub> is an interesting material for photocatalytic applications and it is regarded as the most efficient and environmentally benign photocatalyst [1–5]. It has been widely used as a photocatalyst for the removal of hazardous organic substances and as an electrode material for dye-sensitized solar cells due to its strong oxidizing and reducing ability under UV light irradiation [6–8]. The photocatalytic activity of a semiconductor is largely controlled by (i) the light absorption properties, e.g., light absorption spectrum and coefficient, (ii) reduction and oxidation rates on the surface by the electron and hole, (iii) and the electron–hole recombination rate [9]. TiO<sub>2</sub> in a mesoporous structure is interesting in the sense that it generally has a high surface area in a continuous structure rather than in discrete particles [10]. This continuity can be expected to make the electron transfer within the material easier, resulting in higher activity [11–16]. The modification of the TiO<sub>2</sub> with precious

metals can alter the charge-transfer properties between TiO<sub>2</sub> and the surrounding environment, thus improving the performance of TiO<sub>2</sub> nanomaterials and a good candidate material for photocatalytic reactions [11–20]. Depending on the preparation conditions, photodeposition procedures typically yield small metal deposits ranging from a few to around 20 nm in diameter [21]. The size and dispersion of the metal deposits on the TiO<sub>2</sub> particles will, however, be critical for the control of their photocatalytic activity. Given the strong effect of deposit size and dispersion, the development of preparation methods providing a close control over the deposit size is essential [22–24]. Murdoch et al. [25] have demonstrated that Au particles in the size range 3–30 nm on TiO<sub>2</sub> are very active in hydrogen production from ethanol. It was found that Au particles of similar size on anatase nanoparticles delivered a rate two orders of magnitude higher than that recorded for Au on rutile nanoparticles. Surprisingly, it was also found that Au particle size does not affect the photoreaction rate over the 3–12 nm range. In addition, a high uniformity of both, precious metals and TiO<sub>2</sub>, in size and shape also appears to be essential for achieving enhanced photocatalytic activities [25–29]. On the other hand, the generation of hydroxyl ( $\bullet$ OH) radicals plays a key role in the generally accepted mechanism of the heterogeneous photocatalytic degradation of organic pollutants in aqueous suspensions of TiO<sub>2</sub>

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[9,30]. In order to quantify the rate of  $\cdot\text{OH}$  generation, it has been proposed to use a well-known  $\cdot\text{OH}$  scavenger, i.e.,  $\text{CH}_3\text{OH}$ . Photooxidation of  $\text{CH}_3\text{OH}$  is a process in which photogenerated holes oxidize hydroxide ions adsorbed at the surface of  $\text{TiO}_2$  nanoparticles to produce highly oxidizing ( $\cdot\text{OH}$ ) radicals, which subsequently attack adsorbed pollutant molecules. This primary step of HCHO formation initiates a series of degradation reactions that ultimately lead to mineralization of the pollutants. It has been reported that a considerable fraction of the HCOOH formed on the photocatalyst surface is decomposed into  $\text{CO}_2$  and  $\text{H}_2\text{O}$  on the spot without being released from the surface [31,32].

In our previous work, we have prepared the precious metals doped  $\text{TiO}_2$  networks assembled through a novel in situ preparation method starting from suitable precursors in the presence of a triblock copolymer employed as the structure directing agent [11–16]. In this contribution, we are focusing on photodeposition of precious metals onto mesoporous  $\text{TiO}_2$  networks. The newly developed photocatalysts have been compared with  $\text{TiO}_2$  P-25 (Evonik AG) by the determination of the rate of HCHO formation during the photocatalytic degradation of  $\text{CH}_3\text{OH}$  in aqueous suspensions to determine the corresponding photonic efficiencies.

## 2. Experimental

**Materials:** The block copolymer surfactant  $\text{EO}_{106}\text{-PO}_{70}\text{EO}_{106}$  (F-127,  $\text{EO} = -\text{CH}_2\text{CH}_2\text{O}-$ ,  $\text{PO} = -\text{CH}_2(\text{CH}_3)\text{CHO}-$ ), MW 12,600 g/mol,  $\text{Ti}(\text{OC}(\text{CH}_3)_3)_4$  (TBOT), HCl,  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{CH}_3\text{COOH}$  and  $\text{HAuCl}_4$ ,  $\text{H}_2\text{PtCl}_6$  and  $\text{K}_2\text{PdCl}_4$  were purchased from Sigma–Aldrich.

**Preparation of mesoporous  $\text{TiO}_2$ :** Mesoporous  $\text{TiO}_2$  nanocrystals were synthesized through a simple sol–gel process in the presence of the F127 triblock copolymer as structure directing agent. To minimize possible variables, the molar ratio of each reagent in the starting solution was fixed at  $\text{TiO}_2/\text{F127}/\text{C}_2\text{H}_5\text{OH}/\text{HCl}/\text{CH}_3\text{COOH} = 1:0.02:50:2.25:3.75$  molar ratios [33]. In particular, 1.6 g of F127, 2.3 mL of  $\text{CH}_3\text{COOH}$  and 0.74 mL of HCl were dissolved in 30 mL of ethanol and then added to 3.5 mL of TBOT. The mixture was stirred vigorously for 60 min and transferred into a Petri dish. Ethanol was subsequently evaporated at  $40^\circ\text{C}$  and a relative humidity of 40% for 12 h followed by the transfer of the sample into a  $65^\circ\text{C}$  oven and ageing for an additional 24 h. The as-made mesostructured hybrids were calcined at  $450^\circ\text{C}$  in air for 4 h at a heating rate of  $1^\circ\text{C}/\text{min}$  and a cooling rate of  $2^\circ\text{C}/\text{min}$  to remove the surfactant and to obtain ordered mesostructured  $\text{TiO}_2$ .

## 3. Photodeposition Au, Pt and Pd onto mesoporous $\text{TiO}_2$

Au, Pt and Pd/ $\text{TiO}_2$  photocatalysts were prepared by the photo-reduction method. 0.5 g mesoporous  $\text{TiO}_2$  was mixed with  $\text{HAuCl}_4$ ,  $\text{H}_2\text{PtCl}_6$  or  $\text{K}_2\text{PdCl}_4$  solution containing the equivalent amount of  $\text{Au}^{3+}$ ,  $\text{Pd}^{2+}$  or  $\text{Pt}^{4+}$  followed by the addition of methanol (1% (v/v) methanol/ $\text{H}_2\text{O}$ ) to obtain 0.5 wt% precious metals/ $\text{TiO}_2$ . The suspension was magnetically stirred for 12 h under UV illumination. After irradiation, the samples have been centrifuged, washed then dried at  $110^\circ\text{C}$  overnight to obtain Au, Pd, and Pt/ $\text{TiO}_2$ .

### 3.1. Characterization

Transmission electron microscopy (TEM) was conducted at 200 kV with a JEOL JEM-2100F-UHR field-emission instrument equipped with a Gatan GIF 2001 energy filter and a 1k-CCD camera in order to obtain EEL spectra. Bright and Dark field-STEM (BF and DF-STEM) were used for detecting and determining diameters of precious metals nanoparticles. Wide angle X-ray diffraction (WXR) data were acquired on a Bruker AXS D4 Endeavour X diffractometer using  $\text{Cu K}\alpha_{1,2}$ ,  $\lambda\alpha_1 = 154.060$  pm,  $\lambda\alpha_2 = 154.439$  pm

radiation and small angle X-ray diffraction (SAXRD) patterns were recorded on a Bruker D8 advance. The nitrogen adsorption and desorption isotherms at 77 K were measured using a Quanta chrome Autosorb 3B after the samples were vacuum-dried at  $200^\circ\text{C}$  overnight. The sorption data were analyzed using the Barrett–Joyner–Halenda (BJH) model with Halsey equation [34].

### 3.2. Photocatalytic activity tests

The quartz photoreactor was filled with 75 mL aqueous solution of methanol at a concentration 30 mM. UV irradiation was performed by a 450 W medium pressure xenon lamp (Osram) placed inside a quartz jacket and equipped with a cooling tube. The lamp was switched on 30 min prior to the start of the reaction to stabilize the power of its emission at  $\lambda > 320$  nm and the reactor was cooled by circulation of  $\text{H}_2\text{O}$ . Photooxidation reactions were carried out suspending 0.5 g/L of prepared samples with oxygen being purged through the reaction vessel continuously. HCHO samples were withdrawn at regular intervals from the upper part of the reactor with the catalyst being removed from the liquid phase by filtration through nylon syringe filters (pore size:  $0.45\ \mu\text{m}$ ). The photooxidation rate was determined by measuring the HCHO generated as a result of methanol oxidation during the first 60 min of illumination employing the Nash method [35]. This method is based on the reaction of formaldehyde with acetylacetone and ammonium acetate to form a yellow coloured product with a maximum of absorbance at 412 nm. The photonic efficiency was calculated for each experiment as the ratio of the HCHO formation rate and the incident light intensity as given in the following equation [36].

$$\xi = \frac{r \times 100}{I}$$

where  $\xi$  is the photonic efficiency (%),  $r$  is the photooxidation rate of methanol ( $\text{mol L}^{-1} \text{s}^{-1}$ ), and  $I$  is the incident photon flux ( $4.94 \times 10^{-6}$  Einstein  $\text{L}^{-1} \text{s}^{-1}$ ). The UV-A incident photon flow was determined by ferrioxalate actinometry [37]. The actinometry was performed in the same photochemical reactor with the same volume of actinometric solution as the photocatalytic test, eliminating the errors associated with the influence of light reflections and reactor geometry. A 10 cm water bath and a black cut-off filter (3 mm, UG1 SCHOTT glass) were used during photon flux and photonic efficiency measurements.

## 4. Results and discussions

### 4.1. Structural investigations

Mesostructured  $\text{TiO}_2$  nanocrystals were prepared using Pluronic F127 as the structure-directing agent. These nanoparticles are quite stable and grow slowly due to the slow introduction of water from the ambient environment and the esterification of acetic acid [38]. The use of surfactants enables the controlled synthesis of uniform  $\text{TiO}_2$  nanocrystals with very small particle size  $\sim 10$  nm. The synthesis pathway has been selected in order to have a  $\text{TiO}_2$  platform with uniform size and shape. The thermodynamic stability is particle-size dependent of  $\text{TiO}_2$  nanocrystals, at particle diameters  $< 16$  nm anatase has been shown to be more stable than the rutile phase [39]. Au, Pt and Pd were photochemically deposited onto the mesoporous  $\text{TiO}_2$ -yielding Au/ $\text{TiO}_2$ , Pt/ $\text{TiO}_2$  and Pd/ $\text{TiO}_2$ , respectively. The small angle X-ray scattering (SAXS) patterns of highly ordered mesoporous  $\text{TiO}_2$  as-made and of precious metal photodeposited/ $\text{TiO}_2$  are shown in Fig. 1. The as-made sample shows two well-resolved peaks, which can be indexed to the (10) and (20) Bragg reflections confirming an ordered 2D-hexagonal mesostructure of the  $P6m$  space group [33]. After  $\text{TiO}_2$  calcinations at  $450^\circ\text{C}$ , the observed intensities

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