



# Uniform ALD deposition of Pt nanoparticles within 1D anodic TiO<sub>2</sub> nanotubes for photocatalytic H<sub>2</sub> generation



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## ABSTRACT

In the present work we investigate the utilization of Pt nanoparticles produced by atomic layer deposition (ALD) within anodic TiO<sub>2</sub> nanotube (NT) layers for photocatalytic H<sub>2</sub> production. By varying the number of ALD cycles, Pt nanoparticles with different diameters were produced, uniformly decorating the tube walls. The Pt nanoparticle size (2–15 nm), the Pt mass loading and areal density were strongly dependent on the number of Pt ALD cycles. The deposited Pt nanoparticles turned out to be highly effective as a co-catalyst for photocatalytic H<sub>2</sub> generation. The most effective performance for solar light photocatalysis was reached after 26 ALD cycles (yielding an optimal area coverage with particles of diameter ≈ 7 nm). For UV light, the optimum photocatalytic efficiency was reached after 40 ALD cycles.

## 1. Introduction

Since the pioneering work of Fujishima and Honda in 1972, the production of H<sub>2</sub> by photocatalytic splitting of H<sub>2</sub>O on semiconductors has been extensively investigated [1]. Among the different photocatalysts studied, titanium dioxide (TiO<sub>2</sub>) received wide attention mainly due to its suitable conduction and valence band edge position for photogenerated charge carriers reacting with water as well as for its nontoxicity and stability against photocorrosion [2]. The TiO<sub>2</sub> conduction band edge lies higher than the redox potential of water (−0.45 and 0 V vs. NHE, respectively, at pH 0) [3]. Therefore, it is possible to reduce H<sub>2</sub>O to H<sub>2</sub> by photoexcited electrons that cross the TiO<sub>2</sub> band gap (E<sub>g,TiO2</sub> ≈ 3.0–3.2 eV) [4,5].

However, pristine TiO<sub>2</sub> shows low efficiencies for H<sub>2</sub> production and a kinetically slow electron transfer to reactants. Nanostructured photocatalysts can be employed in order to improve the electron transfer efficiency. In particular, one dimensional (1D) nanostructures, such as anodic TiO<sub>2</sub> nanotubes (NTs), have attracted significant attention in photocatalysis and photoelectrochemistry during the last decade as the growth conditions can be easily adjusted, leading to a large palette of nanotubular geometries [6–12]. 1D TiO<sub>2</sub> structures can promote directional charge transport and orthogonal electron-hole separation and thus enhance photocatalytic reaction rates [13]. However, except for

nanstructuring to reach reasonable H<sub>2</sub> evolution from TiO<sub>2</sub> photocatalysts, co-catalysts are usually decorated onto the substrate. These co-catalysts aid charge separation and transfer; most typical are noble metal nanoparticles (such as Au, Pd and Pt) [14,15].

Of these, Pt is the most efficient co-catalyst for the H<sub>2</sub> generation reaction. Pt nanoparticles at the TiO<sub>2</sub> surface can enable efficient electron transfer at the catalyst/environment interface by providing a favorable solid state junction to TiO<sub>2</sub>, and additionally catalyze the hydrogen recombination reaction (2H<sup>0</sup> → H<sub>2</sub>) [16].

In the case of TiO<sub>2</sub> NT layers, different Pt decoration methods have been described – the most frequently used techniques are various wet chemical routes, photodeposition methods, and conventional sputter deposition onto the NT layer [16–19]. However, these techniques often lead to a non-homogeneous particle distribution: in general, there is a higher loading at the tube mouth and a lower level of deposition deeper in the tube. This accumulation at the tube mouth becomes increasingly severe, the higher the aspect ratio of the nanotube layers [20,21].

In recent years atomic layer deposition (ALD) has become a prime method for deposition of a wide variety of materials such as oxides, sulfides and metals, among others [22–24]. In addition, it is one of the few methods enabling homogeneous and conformal deposition of secondary material into high-aspect-ratio structures [25]. The effective utilization of ALD for deposition of various materials within TiO<sub>2</sub>

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nanotube layers has been demonstrated e.g. for oxides [26–30] and sulfides [31,32], yielding interesting synergistic effects. Even though the use of ALD to deposit Pt nanoparticles on various catalytic supports has been reported in previous works [33–35], no reports show effective deposition of Pt nanoparticles within high aspect ratio 1D TiO<sub>2</sub> tubular nanostructures.

In the present work we investigate for the first time the deposition of Pt nanoparticles by ALD within TiO<sub>2</sub> nanotube layers, and evaluate the effect of the Pt decoration on photocatalytic H<sub>2</sub> evolution under deep UV irradiation and under solar light irradiation.

## 2. Experimental

Self-ordered vertically-aligned TiO<sub>2</sub> nanotube layers were grown by anodization of Ti metal foils (0.125 mm thick, 99.5% purity). Ti foils were cleaned by sonication in acetone, ethanol and deionized water (15 min for each step), and then dried in a N<sub>2</sub> stream.

The anodization of the Ti layers was performed in a two-electrode electrochemical O-ring cell (O-ring diameter of 10 mm) with a Pt plate as cathode. The electrolyte was composed of 1.5 M lactic acid (LA, 90%, Sigma-Aldrich), 0.1 M ammonium fluoride (NH<sub>4</sub>F, 98%, Sigma-Aldrich) and 5 wt% of DI water in ethylene glycol (EG, 99.5%, Sigma-Aldrich) [36]. The anodization experiments were performed under potentiostatic conditions, using 120 V from a high-voltage potentiostat (Jaisle IMP 88 PC) for an anodization time of 10 min. After anodization, samples were sonicated to remove the nanotubular layer and a dimpled structure was left on the Ti substrate, leading to more ordered TiO<sub>2</sub> nanotubes in the subsequent second anodization. The second anodization was carried out under the same conditions (electrolyte, voltage).

Single-walled TiO<sub>2</sub> nanotubes can be obtained from as-grown TiO<sub>2</sub> nanotubes by the following procedure: the as-grown samples obtained after anodization were annealed at 150 °C for 1 h in air atmosphere, with a heating and cooling rate of 30 °C min<sup>-1</sup> using a rapid thermal annealer (Jipelec JetFirst100). Afterwards, the annealed nanotubes were etched by piranha solution (1:3 vol% of H<sub>2</sub>O<sub>2</sub>:H<sub>2</sub>SO<sub>4</sub>) at 110 °C for 70 s [37]. The as-formed single-walled TiO<sub>2</sub> nanotubes were crystallized by annealing at 450 °C, for 1 h, in air atmosphere, using a rapid thermal annealer, with a heating and cooling rate of 30 °C min<sup>-1</sup>. Reference flat TiO<sub>2</sub> layers were prepared by thermal annealing of identical Ti substrates (450 °C, 1 h, air).

Afterwards, Pt nanoparticles were deposited into TiO<sub>2</sub> nanotube layers and reference flat layers using an atomic layer deposition tool (thermal ALD, TFS 200, Beneq) and various numbers of deposition cycles: 8, 16, 24, 26, 28, 40, 48, 72. (Trimethyl)-methyl-cyclopentadienyl-platinum(IV) (Strem, elec. grade, 99%, heated up to 80 °C to obtain a proper vapor pressure) and oxygen (Messer, 99.95%) were used as Pt precursor and oxidizing agent, respectively. One ALD deposition cycle was defined by the following sequence: Pt pulse (1 s) – N<sub>2</sub> purge (5 s) – O<sub>2</sub> pulse (1.5 s) – N<sub>2</sub> purge (5 s). The deposition temperature was 300 °C using N<sub>2</sub> (99.9999%) as carrier and purging gas at a flow rate of 400 standard cubic centimeters per minute (sccm) for both purposes.

For the morphological characterization of the Pt-decorated TiO<sub>2</sub> nanotube layers, a field-emission scanning electron microscope (Hitachi, FE-SEM, S4800) and a transmission electron microscope (Philips, CM30) were used. Images from these microscopes were used to evaluate the average Pt nanoparticle diameter. In parallel, SEM images taken from the reference flat layers were used to extract a measure for the areal particle density. X-ray diffraction analysis (XRD, X'pert Philips MPD with a Panalytical X'celerator detector) using graphite monochromized CuK $\alpha$  radiation (wavelength 1.54056 Å) was performed to determine the crystalline structure of the samples. Their composition and the chemical state were characterized using X-ray photoelectron spectroscopy (XPS, PHI 5600, US) and the peak positions were calibrated with respect to the Ti2p peak at 458 eV. Energy-dispersive X-ray spectroscopy (EDAX, Genesis, fitted to SEM chamber) was also used for

the chemical analysis of the samples.

For the photocatalytic H<sub>2</sub> generation experiments, the samples were immersed into 20 vol% ethanol–water solutions within a sealed quartz tube. The ethanol–water solution (volume ~7 mL) and the cell headspace (volume ~8 mL) were purged with N<sub>2</sub> gas for 20 min prior to photocatalysis.

Two different light sources were used for the photocatalytic experiments: (i) a CW-laser emitting UV light ( $I_0 = 60 \text{ mW cm}^{-2}$ ,  $\lambda = 325 \text{ nm}$ ), and (ii) an AM 1.5 solar simulator (300 W Xe,  $I_0 = 155 \text{ mW cm}^{-2}$ , light spot size ~20 cm<sup>2</sup>, Solarlight) calibrated to 100 mW cm<sup>-2</sup>. In order to determine the amount of generated H<sub>2</sub>, the gas that evolved under irradiation was accumulated within the headspace of the quartz reactor and was then analyzed by gas chromatography (using a GCMS-QO2010SE chromatograph, Shimadzu), withdrawing 200  $\mu\text{L}$  samples with a gas tight syringe.

For total reflectance measurements, a Lambda 950 UV/Vis spectrometer (Perkin Elmer) was employed in a range of 800–200 nm using an integrating sphere. The irradiated beam size was 0.785 cm<sup>2</sup>, and interval of wavelength step was 2 nm. As a background reference, a white-flat reference was used.

## 3. Results and discussion

TiO<sub>2</sub> NT layers were produced as described in the [Experimental Section](#). Fig. 1a, b shows SEM images of a typical layer grown to a thickness of 7  $\mu\text{m}$ , after a treatment to obtain a single wall structure and after annealing at 450 °C in air to crystallize the tubes [37,38]. The SEM images show these tubes to have a diameter of  $\approx 100 \text{ nm}$ , and to be uniformly single walled from top to bottom (Fig. 1a, b).

The TiO<sub>2</sub> nanotube layers were then decorated with Pt nanoparticles using ALD by applying different numbers of cycles, as described in the [Experimental Section](#). The ALD process shows a nucleation delay and following and growth mechanism of Pt in line with previous reports [33–35]. The nucleation delay that occurs during the initial ALD cycles of noble metals has been reported to be due to the lack of adsorption sites [39,40] and/or large differences in the surface energy between substrate and noble metal [41,42]. Fig. 1c–h gives representative SEM and TEM images of the Pt nanoparticles loaded within TiO<sub>2</sub> nanotube layers and they clearly show the presence of Pt nanoparticles even at their lowest (deepest) parts (Fig. 1f and h). These images confirm the capability of ALD to deposit Pt particles into high-aspect-ratio tubes in a homogeneous and conformal fashion [26–30].

A detailed inspection of the Pt nanoparticles produced by different number of ALD cycles was carried out within TiO<sub>2</sub> nanotube layers. First Pt clusters (detectable by TEM) were formed using 20 ALD cycles. Fig. 1c, d shows the corresponding TEM images, in which small Pt nanoparticles (average diameter ~2 nm) can be seen. After this initial growth, Pt nanoparticle decoration becomes visible by SEM. Fig. 1e–h shows the SEM cross-sections of TiO<sub>2</sub> NT after 40 and 72 cycles. The corresponding average particle diameters increased to 11 and 15 nm, respectively. The same growth trend was also observed on reference flat TiO<sub>2</sub> layers.

Fig. 2a shows the size distribution of Pt nanoparticles within the TiO<sub>2</sub> nanotubes, evaluated from the SEM images by statistical analysis. As can be seen, the average Pt nanoparticle size increases as the number of ALD cycles increases. The particles are, however, not entirely monodispersed in size, as revealed by the standard deviation displayed via the error bars. However, this size distribution is well in line with the mass increase obtained from EDX as shown in Fig. 2b. The additional EDX data shown in Fig. 2c represent a semiquantitative measure of the average Pt mass loading, because as the Pt loading increases the information depth of EDX decreases (for unloaded TiO<sub>2</sub> nanotube layers the EDX information depth is typically around 5–10  $\mu\text{m}$ ) [43]. Nevertheless, the trend of a dramatic increase in Pt mass loading after first 20 cycles is evident and further confirmed by the XRD data in Fig. 2d and XPS data in Fig. 2e. In accordance with this, the areal density of

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