**Optimizing TiO₂ nanotube morphology for enhanced photocatalytic H₂ evolution
using single-walled and highly ordered TiO₂ nanotubes decorated with dewetted
Au nanoparticles**

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Abstract

In the present work we introduce the formation of highly ordered single-walled TiO₂ nanotubes based on anodizing nanoimprinted titanium substrates. In a first step, anodization on nanoimprinted substrates leads to the formation of highly ordered TiO₂ nanotubes. These as-formed TiO₂ nanotubes have a double-walled nature. After an optimized chemical treatment in piranha solution, the inner wall is removed and an array of single-walled TiO₂ nanotubes is obtained that has a high degree of hexagonal ordering. These single walled arrangements show an enhanced photocatalytic activity for H₂ evolution in comparison with classic self-ordered TiO₂ nanotubes.

Keywords: nanoimprinting; anodization; single walled TiO₂ nanotube; photocatalysis

1. Introduction

TiO₂ has over the past 40 years become one of the most investigated photocatalytic materials for H₂ evolution from aqueous solutions. The material inherently has suitable band-edge positions for full water splitting into H₂ and O₂ but also it is cheap, abundant and has a high photocorrosion resistance [1–3]. The photocatalytic process is initiated, if photons with a sufficient energy hit TiO₂, and thus generate electron-hole pairs. These excited carriers may then react with suitable redox couples in the surroundings at the semiconductor interface [4,5]. TiO₂ photocatalysts are typically used in the form of nanoparticle suspension or compact nanoparticle layers [6,7]. However, recently one-dimensional TiO₂ nanostructures – wires, rods, belts, and tubes – have attracted considerable attention due to beneficial geometric effects, such as directional charge transport and orthogonal electron-hole separation [8,9]. Among them, TiO₂ nanotubes (NTs) have been intensively investigated due to the ease of their fabrication and control of their morphology [2,10]. Particularly, anodic processes in an appropriate electrolyte have been found to be a simple method to grow TiO₂ NTs in a controlled array that can be to a certain extent adjusted in length, diameter and tube wall thickness [3].

In general, anodization of titanium substrates in water-based and organic-based electrolytes leads to the formation of nanotubular layers with a double wall structure and some domains of disorder [11–13]. In view of order, there are many strategies to control and improve the level of self-organization. We recently introduced a straightforward process to create highly ordered TiO₂ nanotube films by nanoimprinting [14]. Nevertheless, these tubes still show a double walled morphology. These double walled tubes contain a relatively thick inner oxide/hydroxide shell with a significant amount of contamination such as carbon and fluoride, and an outer layer that is mainly “clean” TiO₂ [15].

In the present work, we investigate the use of single walled ideally ordered TiO₂ NTs for photocatalytic H₂ evolution. Highly ordered TiO₂ NTs were fabricated on a patterned Ti foil which was imprinted by a Ni mold. The NTs were then chemically treated in piranha solution,

thus leading to the formation of single-walled TiO₂ NTs. We find the highest photocatalytic H₂ evolution efficiency for highly ordered tubes with a single wall morphology, compared to double-walled NTs and/or NTs grown on unpatterned substrates.

2. Experimental details

Ti foils (99.9%) were chemically polished by immersing in an etchant (TCP-08, Ryoko Chemical) at 50°C for 90 s. A Ni mold with ordered convex beads was set on the Ti foil and was pressed against it using a hydraulic oil press (S04-50, RIKEN) that was additionally equipped with a heating stage [14]. The pretextured Ti substrates were then anodized in ethylene glycol electrolyte containing NH₄F (0.15 M) and H₂O (3 wt%) at 35 V for 30 min. In order to apply a defined co-catalyst loading, the TiO₂ NTs were decorated with Au using a plasma sputtering deposition (Leica, EM SCD500). The amount of sputtered Au was controlled by measuring the nominal thickness with an automated quartz crystal film thickness monitor. The decorated samples were then annealed in air at 450°C for 1 h using a Rapid Thermal Annealer (30°C min⁻¹). To fabricate single-walled TiO₂ NTs, the samples after anodization were annealed in air at 150°C for 1 h, followed by a piranha treatment (1:3 vol.% of H₂O₂/H₂SO₄) at 75°C for 3 min [16,17].

A field-emission scanning electron microscope (FE-SEM Hitachi S4800) was used to characterize the morphology of the samples. To examine the chemical composition of the samples, X-ray photoelectron spectroscopy (XPS, PHI 5600, US) was employed. X-ray diffraction (XRD) performed with a X'pert Philips MPD (equipped with a Panalytical X'celerator detector) with graphite monochromized Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) was used to study the crystallographic properties of the materials. Energy-dispersive X-ray spectroscopy (EDAX Genesis, fitted to SEM chamber) was used for the chemical analysis.

Photocatalytic measurements were carried out by irradiating the TiO₂ samples with UV light (HeCd laser, Kimmon, Japan; $\lambda = 325 \text{ nm}$, nominal power of 16 mW cm^{-2}) in a quartz tube

containing a 20 vol% ethanol-water solution. An irradiation segment was 2 h. The amount of evolved H_2 was measured by a gas chromatograph (GCMS-QO2010SE, Shimadzu) equipped with a thermal conductivity detector and a Restek micropacked Shin Carbon ST column (2 m x 0.53 mm). Before the photocatalytic experiments, the reactor and the water-ethanol mixtures were purged with N_2 gas for 15 min to remove O_2 .

3. Results and discussion

An example of as-formed TiO_2 NTs using the imprinting technique is shown in Fig. 1a with a double walled (DW) structure that consists of an inner shell and an outer shell. This is commonly obtained when anodization processes are conducted in an ethylene glycol based electrolyte; the formation mechanism has several times been described in literature [15,18]. These DW NTs have an inner diameter of 40 nm at the top and it narrows down to 30 nm at the bottom while the outer diameter remains unchanged at 95 nm along the length of the tube. Clearly, after anodization the NTs exhibit a very high degree of hexagonal ordering as shown in Fig. 1a-c. The intertube distance is approximately 100 nm which is exactly the same as the interval between the pitches of the Ni mold [14].

In order to remove the inner shell, a selective chemical process was conducted in piranha solution. Fig. 1b shows SEM images of the resulting single walled (SW) TiO_2 NTs. The inner diameter of the tubes is widened by two times, from 30 nm to over 60 nm. One can see that the inner shell is completely removed over the entire nanotubular layer and length ($\approx 3 \mu m$), this is particularly visible at the bottom of the tubes (cross-section image).

EDS analysis was conducted to investigate the elemental contents of the DW and SW TiO_2 NTs (Fig. 2a and b). The results show that the tube layer consists mainly of titanium and oxygen with a small amount of carbon and fluoride. The concentration of carbon and fluoride are approximately 7% and 5%, respectively, for the DW NTs. After the removal of the inner wall, these contents are relatively reduced to 3% of carbon and 4% of fluoride for SW NTs. This is

in line with previous results which show a drop of contaminants after a suitable etching treatment [16,17]. The removal of the inner shell generally improves the electron transport properties at the tubes [16,17].

Fig. 2c shows X-ray diffraction (XRD) patterns of all TiO₂ samples produced on the imprinted and non-imprinted substrates. Clearly, regarding the different titanium substrates, the as-formed TiO₂ layers are amorphous; only the peaks of the metallic Ti substrate can be observed. The NTs were then crystallized into anatase phase by a thermal annealing in air at 450°C in order to form an active photocatalyst. An intense peak at $2\theta=25.3^\circ$ for both DW and SW NTs formed on the substrates confirms the successful formation of anatase, indicating a similar crystallinity of the two structures [19]. Furthermore, the chemical composition of the TiO₂ samples was additionally confirmed by XPS characterization (Fig. 2d). The results are in line with the above EDS data that showing the NTs contains titanium, oxygen, carbon and fluorine.

In order to evaluate the photocatalytic H₂ evolution production, these DW and SW TiO₂ samples were coated with a thin layer of Au (1 nm nominal thick) that acts as co-catalyst [20–22]. The presence of Au is confirmed by XPS measurements with the appearance of the Au4f and Au4d peaks. The thermal treatment at 450°C in air not only induces crystallization of TiO₂ but also leads to the dewetting of the Au layer into Au nanoparticles that are located on the top of TiO₂ NTs (Fig. 1d and e). The diameter of Au nanoparticles is in the range of 5-10 nm.

As shown in Fig. 3, while TiO₂ alone (*i.e.*, Au free) only leads to a very small amount of H₂ generation ($0.1 \mu\text{L h}^{-1} \text{cm}^{-2}$), the Au-decorated structures show a significantly higher photocatalytic H₂ production (up to three orders of magnitude). This enhancement is ascribed to the formation of a Schottky junction between TiO₂ and Au nanoparticles, thus leading to an improved electron-hole separation [20,23]. The DW structures show an average H₂ generation rate of $125 \mu\text{L h}^{-1} \text{cm}^{-2}$. However, after a selective removal of the inner shell, an improvement of nearly 1.6 times of H₂ generation efficiency is obtained for the SW TiO₂ NTs. The enhancement here can be explained by the improved electron transport characteristics in SW

NTs owing to the removal of high contaminant inner shell [17]. Besides, it should be noted that the TiO₂ NTs grown on the imprinted substrates show a better photocatalytic H₂ performance. Such an enhancement may be attributed to the fact that anodization on imprinted substrates establishes a more uniformed top morphology than that on flat substrates, thus leading to a more homogeneous distribution of Au nanoparticles (inset in Fig. 3) and at the same time reducing the density of structural flaws in the tube layer [16,24–26]. It is also worth mentioning that the Au decoration is very stable. Repeated experiments showed a constant H₂ evolution efficiency and no change in the morphology of the Au decoration could be observed.

4. Conclusions

Overall, the present work demonstrates that highly ordered TiO₂ NTs formed by anodization on a nanoimprinted substrate can be used as an efficient photocatalyst. The photocatalytic H₂ generation efficiency is the highest if the NTs are de-cored, *i.e.* made single walled TiO₂ NTs via a selective chemical dissolution of the inner shell at the tube wall.

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Figure 1. SEM images of: a) double walled TiO₂ NTs grown on imprinted substrate; b) and c) single walled TiO₂ NTs grown on imprinted substrate; 1 nm-thick Au layer dewetted on single walled TiO₂ NTs grown on d) imprinted and e) non-imprinted substrates. The inset of c) shows the bottom layer of single walled TiO₂ NTs.

Figure 2 a) EDS results and b) atomic concentration of: double walled and single walled TiO₂ NTs (for imprinted (IP) and non-imprinted (non-IP) samples). c) XRD patterns of TiO₂ samples. d) XPS spectrum of Au-decorated TiO₂ NTs.

Figure 3 Photocatalytic H_2 evolutions measured for double-walled (DW) and single-walled (SW) TiO_2 NTs grown on imprinted and non-imprinted substrates. 1 nm-thick Au layers were sputtered on the surface of NTs followed by a thermal treatment in air at 450°C for 1 h. The inset shows the evaluation of the Au particle size distribution from SEM microscopy (such as in Fig. 1d and e).