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Controlled anodic growth of TiO_2 nanobelts and assessment of photoelectrochemical and photocatalytic properties

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ABSTRACT

We report on the formation of TiO_2 nanobelts (NBs) by electrochemical anodization of titanium in an electrolyte comprised of water, NH_4F and ethylene glycol. The morphology of TiO_2 NBs is considerably controlled by the composition of electrolyte, applied voltage, anodization time and calcination temperature. We find that the TiO_2 NBs originate from nanotubes (NTs), and it is the combined result of field-assisted etching and chemical dissolution at the mouth of tubes. The TiO_2 NBs bend and deflect into bundles due to the action of capillary forces between adjacent NBs during the postgrowth cleaning and evaporative drying process. Furthermore, we evaluate the photoelectrochemical (PEC) and photocatalytic (PC) performance of the TiO_2 NBs, with results suggesting that the TiO_2 NBs exhibit higher PEC and PC activities than NTs owing to its specific morphology. This TiO_2 nanostructure is expected to be applied in pollutants elimination, photocatalytic decomposition of water and other novel applications.

1. Introduction

TiO_2 photocatalysts have attracted tremendous interest in recent years because of their promising applications in hydrogen generation, solar cells and removal of pollutants from water and air [1–4]. It is well known that the photoelectrochemical (PEC) and photocatalytic (PC) performances of TiO_2 photocatalysts are influenced considerably by the semiconductor morphology [5,6]. Perfect morphology could greatly enlarge effective surface area for the contact and reaction of gases or liquids, and also markedly improve the light response and separation of photogenerated electron–hole pairs [7,8]. Consequently, considerable efforts have been made to control the synthesis of TiO_2 nanocatalysts with desired morphology.

TiO_2 nanotubes (NTs) formed by electrochemical anodization, due to its simple synthesization, high surface area, good physical and chemical stability and easily functionalized architecture, have demonstrated superior performance in self-cleaning applications [9], scaffolds for excitonic solar cells [10] and photocatalysts [11]. However, despite the impressive progress in tuning the diameter, wall thickness, length and pattern order of anodically formed TiO_2 NTs, there is still an unmet need for the practical application, for example, the less effective surface area and the stronger recombination of photoexcited electron–hole pairs.

In this work, we try to improve the PEC and PC activities of TiO_2 photocatalysts by designing specific morphology. Herein, we prepared successfully the self-organized TiO_2 nanobelts (NBs) originating from NTs by a simple anodization using a fluoride-containing viscous organic electrolyte. Higher effective surface area and more active sites are expected to be obtained for TiO_2 NBs. The morphology of TiO_2 NBs was characterized by SEM and TEM. The influences of the various parameters that control TiO_2 NBs growth, including composition of electrolyte, applied voltage and anodization time, were discussed in detail. Additionally, the PEC and PC activities of the prepared TiO_2 NBs were tested. Our studies indicate that the TiO_2 NBs nanostructure is able to enhance significantly the PEC and PC efficiency compared to TiO_2 NTs. The shape dependence of their enhanced PEC and PC activities was also proposed. In order to further optimize the properties, we explored the formation mechanism of TiO_2 NBs. This novel TiO_2 nanostructure is promising in environmental application and water splitting.

2. Experimental

2.1. Synthesis of TiO_2 NBs

Prior to anodization, titanium foils (10 mm × 90 mm × 0.5 mm, 99.8% purity) were degreased by ultrasonically cleaning in

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ethanol and acetone for 30 min separately, followed by a distilled water rinse. Then pickling was carried out in a mixed acid of HF:HNO_3:H_2O = 1:4:5 (vol) for 30 s, after that, the titanium foils were rinsed with deionized water and dried in air at 105 °C.

TiO_2 NBs were prepared by potentiostatic anodization of titanium foils (with exposed area of 4 cm^2) in a standard two-electrode electrochemical cell with platinum foil as the cathode and titanium foil as the anode. All the anodization experiments were carried out in an electrolyte containing ammonium fluoride (NH_4F, from 0.25 to 0.75 wt%), water (from 1 to 10 vol%) and ethylene glycol (EG) (as the solvent) at 25 °C. The applied voltage for electrochemical treatment was in the 40–80 V range and kept for a required time. The distance between the two electrodes was 2 cm. After electrochemical anodization, the as-prepared NBs were cleaned immediately with distilled water and dried in air at 105 °C, then annealed in air at different temperatures for 2 h. The TiO_2 NTs, as the comparative samples, were prepared in electrolyte containing EG, NH_4F (0.5 wt%) and water (10 vol%) at 40 V (the SEM image was shown in Fig. 1f).

2.2. Characterization

A scanning electron microscope (SEM, America QUANTA200F) was used to characterize the top view and cross-sectional morphology of the anodized samples. The single TiO_2 nanobelt was examined by transmission electron microscopy (TEM, F-30ST, Tecnai) at an accelerating voltage of 300 kV.

2.3. Evaluation of the PEC and PC activities of TiO_2 NBs

The PEC performance was assessed by measuring the photocurrent and open-circuit voltage (V_{oc}) response using a electrochemical workstation (Model 263A Potentiostat/Galvanostat, Princeton, U.S.A.) in a standard three-electrode configuration with a Pt foil as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Na_2SO_4 solution (0.5 mol L^{-1}) was used as the supporting electrolyte. A 35 W HID Xenon light (Philips) with the central wavelength of 500 nm was used as the simulative solar light source. The distance between the working electrode and the light is 3.5 cm.

The PC activity of TiO_2 NBs and NTs was assessed by monitoring the production of hydroxyl radicals ($^{\bullet}OH$) on the surface of simulated sunlight illuminated TiO_2 NBs and NTs, using the means of terephthalic acid (TA) fluorescence (FL) probe method [12,13]. TA combines with $^{\bullet}OH$ to become highly fluorescent product, 2-hydroxyterephthalic acid (HTA). The concentration of TA solution was 5×10^{-3} M containing 0.025 M NaOH. After irradiation for 30 min, the FL signal of HTA was measured on a JASCO (FP 6500) fluorescence spectrophotometer using an excitation wavelength of 315 nm. The PC activity of the prepared samples was also detected by photocatalytic degradation of rhodamine B (RhB) aqueous solution (5 mg L^{-1}). Prior to irradiation, the degradation cell was kept in dark for 30 min under stirring to obtain adsorption–desorption equilibrium between the organic molecules and the catalyst surface. Then, photocatalytic degradation of RhB was carried out with continuous stirring by a magnetic teflon bar. At different time intervals of irradiation, the RhB solution was collected and measured immediately. The percentage disappearance of the RhB was used to evaluate the photocatalytic activity as based on the decrease of the characteristic absorption peak of RhB at 552 nm recorded by T6 spectrophotometer. The sample solution volume for above both experiments was 35 ml. The light source is identical with that used in measurement of PEC performance, and with a distance of 2.5 cm from the photoelectrode. All the experiments were carried out at ambient temperature.

3. Results and discussion

3.1. The impact of the preparation parameters on the formation of TiO_2 NBs

The synthesis of TiO_2 NBs is not easily achievable because many factors influence its growth during the anodization process. In order to elucidate the influences of some key parameters on the TiO_2 NBs morphology, anodization was carried out by separately controlling the composition of electrolyte, applied voltage and anodization time. In addition, we also studied the influence of calcination temperature on the morphology of TiO_2 NBs.

The EG with specific amounts of deionized water was used as the solvent in controlled ambient to precisely elucidate the influence of water content on the formation of TiO_2 NBs. The SEM top-view images in Fig. 1 show the surface morphology of samples formed in a set of anodization experiments using the EG electrolyte containing water in the range of 1–10 vol% and 0.5 wt% NH_4F at 60 and 40 V. The anodization time was 3 h. From the SEM top-view images a–c, it is apparent that nanowires were obtained with water content of 1 vol% (Fig. 1a), however, typical NBs were produced with water content of 5 vol% (Fig. 1b). Furthermore, only NTs structure emerged when the water content increased to 10 vol%. These results strongly indicate that the water content in the electrolyte plays a very important role in making TiO_2 NBs structure.

The concentration of fluoride species in the electrolyte is a key factor that influences the electrochemistry synthesis of TiO_2 nanostructure, for example, TiO_2 NTs [14–17]. We have varied the content of NH_4F in electrolyte from 0.25 to 0.75 wt% to study the effect of the content of NH_4F on the formation of TiO_2 NBs. It is noted from Fig. 2(a–c) that when the NH_4F content was 0.25 wt% the NBs could not be produced under the applied voltage range from 40 to 80 V. However, increasing the content of NH_4F up to 0.5 wt% the NBs structure started to appear at applied voltage of 40 V (Fig. 1e), and perfect NBs structure was formed when the applied voltage increased up to 60 V (Fig. 1b) under same anodization time. Fig. 2(d–f) present the SEM images of the surface morphology of oxide layer formed with NH_4F content range from 0.25 to 0.75 wt% for anodization duration of 0.5 h. From the SEM images it is evident that when the NH_4F content increased up to 0.75 wt% the typical NBs structure was generated even under shorter anodization duration. Hence, we can conclude that the NH_4F content in electrolyte plays a significant role in forming TiO_2 NBs, and only when the NH_4F content reaches a sufficient amount the typical TiO_2 NBs could be formed. In addition, increasing the NH_4F content not only improves the formation of TiO_2 NBs, but also shortens the preparation time.

It is well-known that the anodization voltage usually governs the growth of the TiO_2 NTs and determines the geometrical parameters, such as length and diameter [15,17–20]. Consequently, the influence of the electric field on the formation of TiO_2 NBs was explored by varying the applied voltage. Fig. 1b and e shows the SEM images of the TiO_2 NBs anodized at 60 and 40 V in electrolyte containing 0.5 wt% of NH_4F and 5 vol% of water. It can be clearly seen that when the applied voltage was 40 V defective TiO_2 NBs were formed and partially covered by a porous layer produced at the commencement of anodization. However, normal TiO_2 NBs were produced and the initiation layer disappeared when the applied voltage increased up to 60 V, manifesting that the growth of TiO_2 NBs is a function of anodization potential, i.e., increasing anodization potential is conduced to produce NBs. But, we found that the oxide layer is easy to fall off with anodization at 80 V.

Fig. 3 shows a set of SEM images taken from the samples anodized at an applied voltage of 60 V for different anodization time. It is evident that the surface morphology of oxide layer was distinctly changed as a function of anodizing duration. We can observe that only TiO_2 NTs were formed after 0.5 h of anodization,