Electronic Supporting information

Growth mechanism and photocatalytic performance of Double-walled and Bamboo-type TiO_2 nanotube arrays

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Experimental Section

Samples

The ordered double-walled and bamboo-type TiO_2 nanotube films were successfully synthesized by anodic oxidation of Ti foil in a NH_4F organic electrolyte. The applied method was basically similar to that described by our previous work.[1] First, Titanium foils (99.7 % purity, 0.25 mm thick, Sigma-Aldrich) were degreased prior to electrochemical experiments by sonication in acetone, 2-propanol, and methanol for 10 min each, subsequently rinsed with deionized water, and finally dried in a nitrogen stream. Anodization was performed in a neutral electrolyte medium of 0.25 % (wt) NH_4F/ethylene glycol solution using a platinum gauze cathode in an ice bath at room temperature and atmospheric pressure. The electrolyte used in the anodization is freshly prepared without any further treatment. For the electrochemical experiments, a Keithley 2400 sourcemeter controlled by a programmable voltage source from Keithley software that superimposed the AV signal was used. The voltages used were 120, 40 V; the holding time of the two voltages was 2 and 6 mins respectively. The total anodization time of the AV anodization at different stages was settled as 0.5, 4 and 10 hours respectively.

The geometry of the cell is schematically shown in Fig. S1. After anodic oxidation, the samples were rinsed with de-ionized water, and dried under forced air. The resulting amorphous titania nanotube arrays were annealed at 500 $^{\circ}C$ for 2 hours to get the anatase crystal. Heating and cooling rates were 2 $^{\circ}C\ min^{-1}$ during the annealing process.

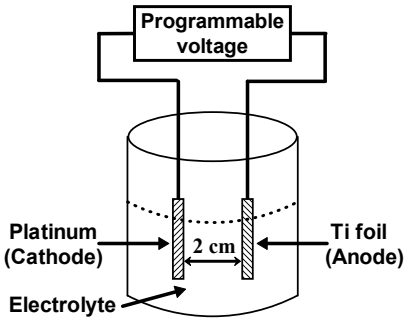

Fig. S1 Schematic diagram of the anodization setup. The distance between anode and cathode is kept at 2 cm. The exposed surface area of the anode and cathode to the electrolyte is 2 cm^2 and 4 cm^2 respectively.

Characterization

The morphology of the annealed TiO_2 nanotube arrays was characterized using a field emission scanning electron microscope (S4500 Hitachi). 5 kV were typically used to record the images. The transmission electron microscopy (TEM) images were obtained using a JEOL 1200EX transmission electron microscope operated at 80 kV. The specimens for TEM were prepared by scratching the nanotubes into ethanol and observed on a carbon-coated copper

grid. X-ray diffraction (XRD) patterns were obtained for the nanocrystal samples using a Philips PW 3710 X-ray powder diffractometer. The crystalline nature of both as-prepared and annealed TiO_2 nanotube arrays were examined using a Thermoelectron Nexus Raman spectrometer equipped with a diode laser (972 nm wavelength). All measurements were carried out at room temperature.

Photocatalytic Activity

High-molecular-weight organic molecules, namely stearic acid, were coated dropwise onto the sintered titania nanotubes with an anodization time of 10 hours from 0.02 M stearic acid in methanol. The organic coated titania were irradiated by a solar simulator (Newport 91160) at 100 mW/cm^2(1 sun) intensity. During irradiation, the ATR-FTIR was performed with a Nicolet iS10 spectrometer (Thermo Scientific). All samples were analyzed in absorption mode using an ATR element with a 2 mm diameter diamond crystal. Subsequent spectra were obtained in the same location to trace the photocatalytic decomposition. Irradiation and ATR-FTIR measurement were performed at room temperature. The photodegradation of organic molecules was quantitatively followed by monitoring the decrease of C-H signal intensity at 2800-3000 cm^{-1} via ATR-FTIR spectra.

1. Y. J. Ji, K. C. Lin, H. G. Zheng, J. J. Zhu and A. C. S. Samia, *Electrochem. Commun.*, 2011, **13**, 1013-1015.