Novel Carbon-Doped TiO$_2$ Nanotube Arrays with High Aspect Ratios for Efficient Solar Water Splitting

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Received September 8, 2005; Revised Manuscript Received November 1, 2005

ABSTRACT

The photocatalytic splitting of water into hydrogen and oxygen using solar light is a potentially clean and renewable source for hydrogen fuel. There has been extensive investigation into metal-oxide semiconductors such as TiO$_2$, WO$_3$, and Fe$_2$O$_3$, which can be used as photoanodes in thin-film form. Of the materials being developed for photoanodes, TiO$_2$ remains one of the most promising because of its low cost, chemical inertness, and photostability. However, the widespread technological use of TiO$_2$ is hindered by its low utilization of solar energy in the visible region. In this study, we report the preparation of vertically grown carbon-doped TiO$_2$ (TiO$_2$-$x$C$_x$) nanotube arrays with high aspect ratios for maximizing the photocleavage of water under white-light irradiation. The synthesized TiO$_2$-$x$C$_x$ nanotube arrays showed much higher photocurrent densities and more efficient water splitting under visible-light illumination (> 420 nm) than pure TiO$_2$ nanotube arrays. The total photocurrent was more than 20 times higher than that with a P-25 nanoparticle film under white-light illumination.

The photocatalytic effect in solid-state catalysis occurs when the electron–hole pair (e$^-$–h$^+$) created by photon absorption can interact with molecules close to the catalyst surface. Although TiO$_2$ has several advantages as described above, it has two critical limitations. The first is that exciton creation, the e$^-$h$^+$ precursor, is achieved only with UV light, rendering the use of solar irradiation inefficient because of the wide band gap of the most common polymorphic forms of TiO$_2$ (3.0 eV for rutile and 3.2 eV for anatase). Second, the large band-gap oxide semiconductors, such as n-type TiO$_2$ or WO$_3$ employed in photoelectrochemical devices, often have short exciton diffusion lengths, so it is mainly the carriers generated within the space charge layer that contribute to the photocurrent. To maximize the water splitting efficiency of a TiO$_2$ photoanode, one would like (1) a narrower band gap to utilize visible-light energy, (2) a high contact area with the electrolyte to increase the splitting of the e$^-$h$^+$ pairs, and (3) a thicker film to increase the total absorption of solar light (Figure 1).

Narrowing of the band gap has been reported in microcrystalline TiO$_2$ films doped with N, C, and S, with carbon-doped TiO$_2$ as one of the best in terms of band-gap width. The most common method for preparing a carbon-doped TiO$_2$ film is by direct oxidation of the Ti metal in the flame of a burner. Khan et al. reported quantitative results on a new carbon-doped rutile photoanode for the photocatalytic splitting of water, but there is still disagreement about its solar-to-hydrogen conversion efficiency.

Although these carbon-doped TiO$_2$ films exhibited enhanced photocurrents under visible-light illumination, their morphologies could not be controlled well by the flame oxidation method. Recently, our group investigated the relationship between water-splitting behavior and the TiO$_2$...
The water-splitting photocurrent was found to depend on the aspect ratio of the TiO$_2$ nanotube with 3.3-µm-length TiO$_2$ nanotube arrays producing a photoanodic response more than 10 times that of a 15-µm-thick TiO$_2$ nanoparticle (P-25) film under the same illumination conditions.

TiO$_2$ nanotube arrays with high aspect ratios were grown from a Ti substrate (0.25-mm-thick, Aldrich) by anodization in an electrolyte of 1 M (NH$_4$)$_2$H$_2$PO$_4$ + 0.5 wt % NH$_4$F. A two-electrode electrochemical setup consisting of the Ti substrate anode and a Pt wire cathode was used. The morphology depended strongly on the applied voltage. To obtain well-organized TiO$_2$ nanotubes, we applied about 15 V. As shown in Figure 2c, anodizing the Ti substrate at 20 V only produced a porous TiO$_2$ film. The anodized Ti substrate was annealed at 450 °C in oxygen for 1 h with heating and cooling rates of 2 °C/min to convert the amorphous phase to a crystalline one. To introduce the carbon dopant into the TiO$_2$ nanotube arrays, they were annealed at high temperature (500 to 800 °C) under controlled CO gas flow.

Figure 2 (a and b) shows scanning electron microscope (SEM) images of a TiO$_2$ nanotube array with a ~3 µm length. The pore diameter was about 70 nm, and the wall thickness was 20 nm. Figure 2d shows a comparison of the photocurrent density vs applied potential curves for two undoped TiO$_2$ photoanodes with different morphologies and one commercial P-25 TiO$_2$ photoanode under Xe lamp irradiation (~100 mW/cm$^2$). At 0.4 V, the photocurrent density of a TiO$_2$ nanotube array (~2 µm length) was more than 60% greater than the value for a nanoporous TiO$_2$ film with a similar thickness. This suggests that TiO$_2$ nanotube arrays can harvest solar light more effectively than photoanodes with an irregular structure under the same illumination conditions. In addition, the TiO$_2$ nanotubular structure also shows a steeper increase in the photocurrent with applied potential. Thus with the TiO$_2$ nanotubes, e$^-$-h$^+$ pairs induced by photon absorption split more readily compared to a nanoporous structure. The nanotube arrays also produced a photoanodic response more than 10 times higher than a 15-µm-thick TiO$_2$ (P-25) nanoparticle flat film because incident photons are more effectively absorbed on a flat electrode, probably because of an increased light penetration depth and better scattering within a regular pore structure. In addition, the induced e$^-$-h$^+$ pairs in the TiO$_2$ nanotubular structure might be extracted more efficiently than the 15-µm-thick TiO$_2$ (P-
bulk recombination rate and surface recombination rate of current increases. Even though the tube length increases, the more photons are absorbed and, consequently, the photovoltaic efficiency decreases. This smaller photocurrent can also be explained by a combination of increased resistance and a decrease in the electric field within the film. An increase in bulk recombination rate at more positive potentials was a function of the tube length. A theoretical expression of photocurrent density as a function of TiO2 nanotube length was evaluated by measuring the photocurrent density at more positive potentials. Shown in Figure 5a is the observed photocurrent density of a TiO2 nanotube array under visible-light (λ > 420 nm) illumination. The photocurrent is essentially the same as the dark current, showing that there is no photocatalytic activity under visible light for undoped TiO2 nanotube arrays. Figure 4a is an SEM image of carbon-doped TiO2 nanotube arrays annealed at 600 °C under a CO gas flow. No significant morphological change was observed. This thermal treatment did not destroy the nanostructure of the as-prepared TiO2 nanotube array. X-ray photoelectron spectroscopy (XPS) confirmed enhanced carbon incorporation (Figure 4b). In addition, the color change of the nanotube array upon carbon incorporation demonstrates an effect on their optical response in the visible wavelength range. By adjusting the temperature of heat treatment, the doping concentration of carbon in the TiO2 nanotube array could be controlled between 8 and 42% (as determined from the XPS peaks). No appreciable signal related to carbide (281.5 eV) was observed, showing that the amount of Ti-bonded carbon was very low. The photooxidation activity of the TiO2-Cx nanotube array was evaluated by measuring the photocurrent in 1 M KOH electrolyte. Shown in Figure 5a is the observed photocurrent density of a TiO2-Cx nanotube array under visible light. The TiO2-Cx nanotube array showed obvious enhanced photocatalytic activity under visible light compared to undoped TiO2 nanotube arrays. The proposed model for visible-light absorption in doped TiO2 is due to substitution of oxygen by another atom, such as N or C, which results in a mix of N,C-2p and O2p states. Moreover, the total photocurrent under white-light illumination was larger than that of the undoped TiO2 nanotube array. This shows that the gain from improved visible-light absorption is larger than any loss from reduced photocatalytic activity under UV light absorption. Optical transitions for crystalline semiconductors can be deduced from the variation of the absorption coefficient near the band edge. For direct band gaps \( E_g \), the optical absorption near the band edge is given by

\[
\alpha = A (h \nu - E_g)^n / h \nu
\]  

where \( A \) is a constant and \( n \) equals 0.5 for an allowed direct transition. The allowed direct transition of an electron from the valence band to the conduction band by light energy is not phonon-assisted and does not require a simultaneous change in momentum. Equation 1 is most appropriate to use when the applied potential is far from the flatband potential. By assuming that the photocurrent \( j_{ph} \) is proportional to the absorption coefficient, \( \alpha \), the band-gap energy...
of the TiO$_2$-C$_x$ nanotube array was determined from a plot of $(j_{ph}h\nu)^{1/2}$ versus $h\nu$ (Figure 5b). The linear portion of this curve indicates a transition above an optical band-edge and an intercept of about 2.22 eV, (corresponding to the band-gap energy of the TiO$_2$-C$_x$ nanotube array). This energy is slightly larger than the earlier reported value of $\sim$2 eV.\(^{10}\)

The role of the doping concentration causing a photocurrent increase was supported by the study of the photocurrent versus annealing temperature. Measurements of the photocurrent were carried out at each annealing step (Figure 5c). Significant changes of the photocurrent occurred up to 600 °C because of the increased activity under visible-light illumination, indicating carbon diffusion and doping was taking place. However, from 700 °C, the photocurrent density decreased, suggesting that higher doping decreases photocatalytic sites. By collecting the gases at the TiO$_2$ and Pt counter electrode during the photoreaction, we observed a 2.1:1 volume ratio of hydrogen and oxygen.

To confirm that the TiO$_2$ nanotube structure was the enabling factor in this doping process, we carried out the same experimental protocol with a TiO$_2$ film of P-25. Following the identical thermal treatment under CO gas flow to produce carbon doping, the photocurrent was still much lower than that of the TiO$_2$-C$_x$ nanotube array but was slightly higher than the P-25 film without carbon doping.

In conclusion, we have demonstrated significant progress toward the goal of enhancing photocatalytic activity of TiO$_2$, by using aspect-ratio-controlled TiO$_2$ nanotube arrays as a starting material for preparing a novel photocatalyst with a smaller band gap. The unique structure of the TiO$_2$ nanotube array produced by controlling the anodizing conditions favors the incorporation of carbon by heating with CO at temperatures up to 600 °C. This investigation shows that a chemical approach to decreasing the band gap can be combined with the control of morphology to maximize solar energy harvesting. Although in this study, water oxidation on the TiO$_2$-C$_x$ nanotube array was investigated, the valence band of the semiconductor is more positive than that required for other photocatalytic reactions of organic or inorganic species (e.g., alcohol, I$^-$, Br$^-$, and SCN$^-$), so that C-doped TiO$_2$ nanotubes could find use in other applications.

**Methods.** *Preparation of Photoanode.* Titanium foil was degreased by sonicating in 2-propanol and methanol and then rinsing with deionized water and drying in a nitrogen flow. It was positioned between two plastic substrates and then pressed against an O ring in an electrochemical cell with a
0.8 cm² exposed area. All electrolytes were prepared from reagent-grade chemicals. The anodizing process consisted of a potential ramp from 0 V to a given potential (e.g., 15 V) at a 1 V/s sweep rate followed by holding at the desired applied potential for various times in 1 M (NH₄)₂HPO₄ + 0.5 wt % NH₄F. After the preparation of the TiO₂ nanotube array, the samples were rinsed with deionized water and annealed at 450 °C for 1 h. For comparison, a ~15-μm-thick film of TiO₂ nanoparticles (P-25) was printed on another Ti foil and then sintered at 450 °C for 1 h.

Surface Characterization. Scanning electron microscopy (SEM, LEO 1530) was employed for the structural and morphological characterization of the TiO₂ nanotube array. Chemical compositions of as-prepared samples were characterized by X-ray photoelectron spectroscopy (XPS, PHI 5600 XPS). XPS were performed in an ultrahigh vacuum analysis chamber (base pressure < 1 × 10⁻⁶ Pa) equipped with an electrostatic hemispherical analyzer. Before measurement, the samples underwent a surface-cleaning procedure by argon-ion sputtering to remove chemisorbed species.

Electrochemical Characterization. Electrochemical experiments were carried out using a three-electrode configuration with a Pt wire counter electrode and a saturated Ag/AgCl reference electrode (CH instruments, CHI 660). The potential was swept linearly at a scan rate of 50 mV/s. Photoelectrochemical water splitting experiments were conducted in 1 M KOH electrolyte. The 1 cm² working electrode was swept linearly at a scan rate of 50 mV/s. Photoelectrochemical characterizations were performed in a 1 cm² working electrode with a Pt wire counter electrode and a saturated Ag/AgCl reference electrode (CH instruments, CHI 660). The potential was swept linearly at a scan rate of 50 mV/s. Photoelectrochemical characterizations were conducted in 1 M KOH electrolyte. The 1 cm² working electrode was measured light irradiance was 100 mW/cm². For visible-light illumination, the light was passed through an optical filter, which cut off wavelengths below 420 nm.

Acknowledgment. Support of this research by the National Science Foundation (CHE 0202136) and partial fellowship support for J. H. P. was provided by a Korea Research Foundation Grant (KRF-2004-214-D00266). We thank C. R. Luman for helpful discussions.

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