

Chromium-doped titanium dioxide thin-film photoanodes in visible-light-induced water cleavage

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Abstract

A new method for the synthesis of nanocrystalline anatase Cr-doped TiO₂ colloids from nanotubes utilizing the hydrothermal ion-intercalation (HII) method has been devised using hydrothermal treatment in an acidic environment. To investigate the photoelectrochemical reaction that occurs when water is split into H₂ and O₂ under visible light, a Cr-doped TiO₂ thin film served as a model photoelectrode. The photoelectrochemical activity of Cr-doped TiO₂ was higher than that of the undoped sample. The photoelectrochemical activity of photoelectrodes increased drastically with increased chromium doping. A red shift in the band gap was induced by Cr doping of TiO₂. It was revealed that the Cr-doped TiO₂ photoelectrode was able to utilize a wide range of light in the visible region of the spectrum. At high Cr concentrations, the lower photoelectrochemical activity is attributed to the effect of Cr³⁺ ion recombination and excess Cr³⁺ ions forming secondary phase Cr₂O₃.

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1. Introduction

Titanium dioxide and its nanotubes are important and multifunctional materials used as pigments, photocatalysts, photovoltaic materials, dye-sensitized solar cells, gas sensors, optical coatings, photoconductors, and UV filters [1–4]. However, the main disadvantage of TiO₂ as a photoanode is related to poor absorption of sunlight due to its wide band gap (ca. 3 eV). The most promising method for improving the photo-responsiveness of TiO₂ is doping with metal ions [5–10]. Doping TiO₂ with Cr has been found to promote photoelectrochemical water decomposition and photo-degradation of organic compounds using solar energy [11–17]. TiO₂ thin film doped with Cr is suitable for use as a photoanode because of its small band gap of <3 eV, enabling it to absorb most of the photons of the solar spectrum [11–15]. Photocatalytic Cr-doped TiO₂ thin films solve some of the problems surrounding Cr-doped TiO₂ powder photocatalysts. Such problems include:

post-reactive separation of the photocatalyst from the suspension, difficulty in applying materials in continuous flow systems, and the necessity of continuous stirring to ensure good powder dispersion and to induce aggregation of suspended particles when present in high concentrations.

Different methods were used to prepare metal-ion-doped TiO₂: impregnation [18], co-precipitation [14], sol-gel [19,20], and the hydrothermal treatment method [6–10]. Titanate nanotube aggregates prepared by NaOH treatment of TiO₂ (both with and without subsequent acid washing) recently have been shown to possess large surface area [21–28]. The preparation of titanate nanotubes doped with metal-ions derived from hydrothermal treatment with alkali solutions also has been reported; and the products have been extensively studied [6–10]. Metal-ion-doped TiO₂ in the form of nanotubes is expected to have larger specific surface area and pore volume compared to nanoparticles. Hydrothermal treatment with alkali solutions is of particular interest because metal-ion-doped nanotube aggregates can be easily produced at low temperatures.

Over the last few years, the structure of nanotubes produced by alkaline hydrothermal treatment considered as the layered structure titanate nanotubes. The ion exchangeability of the

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titanate nanotubes was demonstrated by hydrothermal substitution of transition-metal-ions [24,25,28–30]. The present study is devoted to the development of a “hydrothermal ion-intercalation” (HII) method, in which Cr^{3+} ions can intercalate into the interlayer of the titanate species formed during hydrothermal treatment of TiO_2 [22–26,28–30]. Knowledge of the nanotube formation mechanism is crucial to the development of this method. Through this HII process the agglomeration of the introduced metal ions is retarded and thus the degree of metal ion dispersion via titanate nanotubes is expected to be high. Cr-doped TiO_2 thin films derived from titanate nanotubes are analyzed so as to yield correlations between the structural features of the species and photoconversion efficiency in the photo-cleavage of water.

2. Experimental

2.1. Colloid synthesis and characterization

Nanotube aggregates were synthesized using commercially-available P25 TiO_2 (Degussa, Germany; surface area = $50 \text{ m}^2/\text{g}$) as the precursor. The preparation was analogous to those previously reported [21–30]. P25 (3 g) was hydrothermally treated with 10N NaOH (100 mL) in a Teflon-lined autoclave at 130°C for 24 h. The slurry was then washed with 0.1N HNO_3 solution (1 L) several times until a pH value of 1.6 was reached. After filtration, the obtained solid was dried at 100°C for 3 h to yield nanotubes.

To prepare Cr-loaded nanotubes using the “hydrothermal ion-intercalation” (HII) method, an appropriate amount of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added to the TiO_2/NaOH mixture for hydrothermal treatment; followed by HNO_3 washing. The crystalline Cr-doped TiO_2 anatase colloid used as the thin-film photoanode was prepared by hydrothermally treating the low-pH nanotube suspension at 240°C for 12 h. This Cr-doped TiO_2 colloid is denoted as H240. The resultant colloidal solution was concentrated to contain 13 wt.% Cr-doped TiO_2 through evaporation under reduced pressure. Mesoporous films constituted of P25 were used for the purpose of comparison. In preparing the P25 colloid, 14 mL of deionized water and 0.2 mL of acetyl acetone were added to 6 g of P25 powder in a mortar and ground to mechanically separate the aggregated TiO_2 particles. An appropriate amount of Triton X-100 surfactant was added to the mixture to disperse the P25 [31].

The crystalline structure of the Cr-doped TiO_2 particles was analyzed using powder X-ray diffraction (Rigaku, RINT2000) with $\text{Cu K}\alpha$ radiation. The surface area and pore size distribution of the Cr-doped TiO_2 powders were determined using a nitrogen adsorption apparatus (Micromeritics, ASAP 2010). The microstructures of the Cr-doped TiO_2 particles were explored with high-resolution transmission electron microscopy (HR-TEM, Hitachi FE-2000) and scanning electron microscopy (SEM, Jeol JSM-6700F). Diffusion reflection spectra were obtained using a UV-vis spectrometer (UV-vis, Cary 100 Conc.). The electron binding energy of Cr to the TiO_2 was studied by X-ray photoelectron spectroscopy (XPS). The XPS spectra were recorded on a Fisons VG ESCA210

spectrometer utilizing $\text{Al K}\alpha$ radiation. Charging effects were corrected by adjusting the C 1s peak to 284.6 eV.

2.2. Photoanode characterizations

Nanocrystalline Cr-doped TiO_2 films were prepared by spreading a viscous Cr-doped TiO_2 dispersion onto a conducting glass substrate ($3.0 \text{ cm} \times 1.5 \text{ cm}$, F-doped SnO_2 overlayer TCO glass; TEC 8, Hartford Glass Co, transmission $>80\%$, sheet resistance $15 \Omega/\text{sq}$). The viscous Cr-doped TiO_2 dispersion was obtained by mixing the preceding colloidal solutions (of H240 and P25) with polyethylene glycol (PEG, molecular weight = 20,000) at a PEG/colloids of 0.4. The apparent area of the film was $0.5 \text{ cm} \times 0.5 \text{ cm}$. The Cr-doped TiO_2 -coated substrate was subsequently calcined at 450°C in air for 30 min. This coating procedure was conducted multiple times to generate different film thicknesses. The film thickness was measured using an Alpha-Step 200 profiler (Tencor Instruments). For electrochemical experiments, a typical three-electrode cell was employed; the Cr-doped and undoped TiO_2 thin films served as working electrodes, a saturated calomel electrode (SCE) as a reference, and a Pt-sputtered conducting glass as a counter electrode. A 3 M KOH solution provided electrolytes. The surface of the working electrode exposed to the electrolyte was square, with an area of 0.25 cm^2 . All photoelectrochemical measurements were determined by recording the current–voltage (I – V) curves using a CHI 614B instrument. An Oriel 300-W Xe lamp was used in conjunction with an IR filter (Oriel 59044) and an UV filter (Oriel 59480). The A.M. 1.5 Global filter (Oriel 81094) was placed in the light beam to simulate A.M. 1.5-type solar emission. The intensity of the visible light illuminating the working electrode was fixed at $50 \text{ mW}/\text{cm}^2$; which was measured by a thermopile (Oriel 71964). An applied potential range of -0.9 V to 0.6 V was used at a scan rate of $10 \text{ mV}/\text{s}$.

3. Results and discussion

It is generally recognized mild treatment of TiO_2 (i.e., a low temperature (130°C) and short duration (24 h)) produces specimens in intermediate states that subsequently transform into tubes by means of “soft-chemical” reactions during the post-treatment steps [21,24,27]. In our previous work, the products obtained from NaOH treatment at 130°C for 24 h contained no tubular structures and were found to be sensitive to post-treatment washing. After washing with HCl at a $\text{pH} < 8$, titanate nanotubes became the dominant component of these specimens. Thus, we suggest that the titanate nanotube structure be assigned the formula $\text{A}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ ($\text{A} = \text{Na}$ or H) [28].

In this work, our attention is focused on convenient preparation of metal ion-doped TiO_2 thin-film photoanodes possessing strong photoelectrochemical activity in visible light. This work describes a newly developed “hydrothermal ion-intercalation” (HII) method in which Cr^{3+} ions intercalate into the interlayer of the titanate species. Fig. 1 shows the TEM image of the Cr-loaded specimens derived from the P25 TiO_2

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