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Highly active and thermo-stable anatase TiO_2 photocatalysts synthesized by a microwave-assisted hydrothermal method

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ABSTRACT

Phase-pure anatase titanium dioxide (A-TiO_2) with high thermal stability is synthesized by a microwave-assisted hydrothermal (MAH) method. The samples are characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N_2 adsorption–desorption isotherms, and photoluminescence spectra (PL) analysis. The photo-electrochemical responses are examined via linear sweep voltammetry (LSV), intensity-modulated photocurrent spectroscopy (IMPS), and intensity-modulated photovoltage spectroscopy (IMVS). The photocatalytic activity of TiO_2 nanoparticles (NPs) has been confirmed through the methylene blue (MB) de-colorization under the simulated sunlight. The results show that the as-prepared TiO_2 nanocrystals possess thermal stability for the anatase-to-rutile phase transformation up to 900 °C. The phase-pure A-TiO_2 annealed at 800 °C exhibits a much higher de-colorization rate than the commercially available TiO_2 (Degussa P25) powders. The higher photocatalytic activity of this sample is due to its enhanced crystallinity, leading to a lower rate of electron/hole pair recombination and a larger photocurrent density in comparison with all other samples and P25. The sample annealed at 900 °C shows the highest specific activity on MB de-colorization, demonstrating the importance of thermal stability and crystalline phase.

1. Introduction

Titanium dioxide (TiO_2) is a photocatalyst possessing the semiconductor characteristics, which has been used in environmental remediation such as waste water treatment or air purification [1–5]. Among various oxide semiconductor photocatalysts, TiO_2 is a very important and promising material due to its biological and chemical stability, strong oxidative power, cost effectiveness, and long-term durability [5–7].

Nowadays, TiO_2 with high crystallinity and high thermal stability is of importance. The former involves the photocatalytic activity and the latter concerns about the thermal durability in the process. Many applications of TiO_2-coated materials such as bathroom tiles, sanitary wares, and self-cleaning glass require high processing temperature and therefore, high thermal stability is a necessary property as well [8–10]. However, TiO_2 in the anatase phase (A-TiO_2) undergoes an irreversible phase transformation to the rutile crystal at about 600 °C under normal conditions, which restrains its applications at high temperatures [11,12]. This phase transformation is determined by intrinsic parameters such as initial particle size, impurity content, and starting phase as well as extrinsic ones such as atmosphere and powder compaction [13,14]. According to the potential applications of TiO_2, thermal stability becomes one of the necessary demands.

Many efforts have been dedicated on the synthesis of thermally stable TiO_2 with a pure anatase phase. Kutty et al. investigated the effect of $SO_4{}^{2-}$ as an impurity on the formation of anatase [15]. The results come out that $SO_4{}^{2-}$ could retard the formation of rutile TiO_2 (*R*-TiO_2) due to its strong chemical coordinating ability which facilitates the formation of the anatase phase. Li et al. prepared A-TiO_2 with highly thermal stability and specific surface area by the solvothermal method [16]. They found that the anatase-to-rutile phase transformation could be up to 800 °C with a high specific surface area (102.9 m^2/g). Besides, some researchers have retarded the phase transformation by doping TiO_2 with metallic or nonmetallic ions [7,11]. However the introduction of dopants not only changes the intrinsic properties of TiO_2 but also generates secondary impurity phase which acts as a recombination center and therefore reduces the photocatalytic activity of TiO_2 [6,16].

Based on the above considerations, phase-pure A-TiO_2 nanocrystals adsorbed with $SO_4{}^{2-}$ are designed to effectively retard the phase transformation of A-TiO_2 into R-TiO_2 in this work. In addition, a simple, energy-and-time-saving microwave-assisted hydrothermal method is employed to obtain the above desired microstructure to create thermal stability. The result shows that the phase

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transformation of as-prepared A-TiO_2 occurs slowly at *ca.* 900 °C and the samples annealed at 700–900 °C are well-crystallized and exhibit high photocatalytic activities. These properties are promising for several applications such as photocatalytic organic degradation (*e.g.*, MB de-coloration in this work) and dye-sensitized solar cells (*e.g.*, in our preliminary test, incorporating large crystalline A-TiO_2 particles (annealed at 800 °C) into standard small-crystal-sized ones reduces sensitizer aggregation, interfacial recombination, and ionic diffusion for the porphyrin-based dye-sensitized solar cells, achieving an improved power conversion efficiency of 9.5%).

2. Experimental

2.1. Sample preparation

Phase-pure, nanocrystalline A-TiO_2 nanoparticles (NPs) were prepared by a microwave-assisted hydrothermal (MAH) method. All chemicals were analytical grade and used without further purification. For preparing A-TiO_2 NPs, 5 mL $TiCl_3$ was oxidized by stoichiometric H_2O_2 for the oxidation of Ti^{3+} to Ti^{4+}. Then, a 20 mL 0.5 M H_2SO_4 solution was added into the above solution. This mixture was exposed to the high-intensity ultrasound bath for 25 min, and then, transferred to a microwave reactor (CEM, USA) to form A-TiO_2 NPs at 200 °C for 20 min. The resultant solution was cooled down to room temperature, centrifuged and rinsed with de-ionized (DI) water for several times. The final precipitates were dried in an oven at 85 °C for 12 h to obtain the white as-prepared TiO_2 NPs (denoted as TU). In order to investigate the thermal stability and physicochemical characteristics of TiO_2, 0.5 g as-prepared TiO_2 NPs were annealed at various temperatures (from 400 to 1000 °C) for 2 h under an air atmosphere. The annealed samples were denoted as T_x where x represents the annealing temperature.

2.2. Characterization

X-ray diffraction (XRD) patterns were measured by an X-ray diffractometer (Ultima IV Rigaku, Japan) using a Cu target (Cu $K\alpha = 1.5418$ Å) at an angle speed of 1° (2θ)/min at 40 kV and 20 mA from 20 to 80°. The average crystallite size was estimated using the Scherrer equation (*i.e.*, $d = k\lambda/(\beta\cos\theta)$), where d is the crystallite size, λ is 0.15418 nm, k is 0.89, β is the peak width at half-maximum height, and θ is the diffraction peak of anatase (101) or rutile (110) facets. The morphology and microstructure of TiO_2 were examined by means of a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700I, Japan) and a high-resolution transmission electron microscope (HRTEM, Hitachi HF-2000, Japan). The BET surface area was derived from the adsorption data in the relative pressure (P/P_0) range between 0.05 and 0.3 from the N_2 adsorption/desorption isotherms (measured by Quantachrome NOVA 1200e, USA). The pore volume and average pore size were obtained from the nitrogen adsorption volume at the relative pressure of 0.994. All samples were degassed at 150 °C for 4 h prior to the measurements. Photoluminescence (PL) spectra were measured at room temperature on an F-4500 fluorescence spectrophotometer (Hitachi F4500, Japan). The excitation wavelength is 300 nm, the scanning speed is 600 nm/min, and the PMT voltage is 700 V. The widths of excitation slit and emission slit are both 5.0 nm. The concentration of MB was calculated from the absorbance at 664 nm by the Beer–Lambert law ($A = \varepsilon CL$), where A, ε, C, and L represent the absorbance, extinction coefficient, concentration, and the light path, respectively.

Photocurrent densities obtained from the linear sweep voltammograms were measured in 0.5 M Na_2SO_4 under a 150-W simulated sunlight (Newport 92250A-1000, USA) by an electrochemical analyzer system CHI 730D (CH Instruments, USA). An Ag/AgCl electrode (3 M KCl, Argenthal, 207 mV *versus* SHE at 24 °C) was used as the reference and a platinum wire was employed as the counter electrode. Intensity-modulated photocurrent spectroscopy (IMPS) and intensity-modulated photo-voltage spectroscopy (IMVS) were conducted by a photo-electrochemical workstation (Zahner IM6ex, German). A perturbation of 50 mV was applied and data were collected from 100 kHz to 5 mHz. Data of IMVS and IMPS were measured under the open-circuit and short-circuit states, respectively. The light source was a UV-light-emitting diode (369 nm) driven by a frequency response analyzer (UVZ01, Zahner UVZ01, German). The LED provided both DC and AC components of illumination. The AC component of the current to the LED generated a modulation (8%) superimposed on the DC component. The electrolyte was 1 M $HClO_4$ and the counter electrode was a platinum electrode.

2.3. Electrode fabrication

The 10 × 10 × 3 mm graphite (Nippon Carbon EG-NPL, N.C.K., Japan) electrode was employed as the substrate for the photocurrent densities of various TiO_2 samples. The substrate pre-treatment procedure completely followed our previous work [17]. For the photoanode, 0.5 mg TiO_2 powders were well mixed with 5 wt. % binder powders (polyvinylidene fluoride, PVDF). This mixture was supplemented with 40 μL C_5H_9NO under an ultrasonic bath. The suspension was dropped onto the substrate and dried at 85 °C overnight. The exposed surface area of all TiO_2-coated electrodes is 1 cm^2 for the photo-electrochemical characterization.

The substrate in the IMPS/IMVS analysis was 10 × 12 × 2.2 mm fluorine-doped tin oxide (FTO ECHO, Taiwan) which was rinsed with 2-propanol, acetone, methanol, and distilled water several times to remove impurities and then dried before use. A uniform TiO_2 film was loaded onto the substrate using the electrophoresis deposition method. The thickness of all TiO_2 films was controlled to be 2 μm with an exposed surface area equal to 1 cm^2. The TiO_2-loaded FTO electrodes were dried at room temperature overnight and then annealed at 450 °C for 30 min.

2.4. Photocatalytic activity

The photocatalytic activity of all samples was evaluated through the MB de-colorization under 150-W simulated sunlight irradiation (Newport 92250A-1000, USA) at room temperature. In the first step, 10 mg TiO_2 powders were suspended into a 20 mL 10 ppm MB solution under stirring in darkness for 1 h to achieve the adsorption equilibrium. Then, the photocatalytic de-colorization was conducted under the simulated sunlight irradiation. The MB concentration was determined from the absorbance at 664 nm by a UV–vis spectrophotometer (Shimadzu UV2450, Japan). Since MB can be slightly decomposed under the stimulated light irradiation, the MB de-colorization rate constant was derived from the concentration difference for the MB solutions without and with suspended TiO_2 powders under the same irradiation time.

3. Results and discussion

3.1. Material characterization

The X-ray diffraction was used to investigate the phase structure, crystallite size, and crystallinity of TiO_2 NPs annealed at various temperatures. Fig. 1a shows the effect of annealing temperature on the crystalline structure of TiO_2 prepared in this work. Clearly, the as-prepared TiO_2 (TU) powders show a pure anatase phase whose diffraction pattern is in a good agreement with JCPDS No. 21–1272. The intensity and the full width at half maximum of the anatase (101) facet become stronger and narrower with the temperature, which can be ascribed to crystal growth and improved crystallinity of A-TiO_2 NPs. On the other hand, a small diffraction peak at $2\theta = 27.4^{\circ}$