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Synthesis of TiO_2 mesocrystal film with enhanced photocatalytic activity

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ABSTRACT

TiO_2 mesocrystals can considerably enhance charge separation owing to their oriented superstructures, with fewer internal defects and porous properties providing more active sites. In this work, we prepared TiO_2 mesocrystal films by a direct annealing method. The morphology and crystal phase of the film were controlled by adjusting the ratio of NH_4F and the calcination temperature. Moreover, we found that Au nanoparticles loaded on a TiO_2 mesocrystal film enabled highly efficient visible light photocatalytic properties. The photocatalytic activities were studied by hydrogen generation and photoreduction of Cr(VI). This work represents a considerable advance in the development and application of the TiO_2 mesocrystals.

1. Introduction

Titanium dioxide (TiO_2) has been widely studied and applied in photocatalysis, solar energy conversion, and lithium-ion batteries owing to its ready availability, low cost, non-toxicity, and high stability [1–3]. In recent years, TiO_2 films have been widely studied, because of the difficulty of recovering powdered TiO_2 [4,5]. Hence, TiO_2 films are typically deposited on a substrate in the form of nanoparticles, to form polycrystalline and amorphous films [6,7]. Recently, films of TiO_2 nanotube arrays prepared by anodic oxidation technique have been widely used in photocatalysis, dye sensitized solar cells, and energy storage materials [8–10]. Single-crystalline anatase TiO_2 tetragonal nanosheet-array films have also been successfully prepared by hydrothermal methods [11]. The TiO_2 morphology and structure are among the most important aspects that affect their light absorption, charge separation and transfer, reactant adsorption, and photocatalytic activity [12–15].

TiO_2 mesocrystals have recently emerged and received attention as a new class of porous TiO_2 materials with oriented superstructures of arranged TiO_2 nanocrystal building blocks [16–22]. Recent articles have focused on the preparation of TiO_2 materials with tailored framework structures through the addition of different templates and additives [23–29]. However, the preparation of mesoporous single crystal TiO_2 films has not yet been reported.

Modification of TiO_2 mesocrystals with Au nanoparticles also enables visible-light-driven photocatalytic performance. Au nanoparticles have a localized surface plasmon resonance (SPR), which can absorb light in the visible region owing to a resonant oscillation of free electrons [30].

Herein, we used a facile, direct annealing approach to fabri-

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cate a TiO_2 mesocrystal film. The morphology and crystal phases of the film were controlled and the photocatalytic activity was studied for photocatalytic hydrogen generation. Moreover, we found that Au nanoparticles deposited on a TiO_2 mesocrystal film induced visible light-driven photocatalytic activity, which shows great potential for practical applications.

2. Experimental

2.1. Chemicals and materials

TiF_4, NH_4NO_3, chloroauric acid, Na_2SO_4 and $K_2Cr_2O_7$ were purchased from Aladdin (AR, Shanghai, China). P123 (amphiphilic triblock copolymer PEO-PPO-PEO ($(EO)_{20}(PO)_{70}(EO)_{20}$)) and NH_4F (AR) were purchased from Sigma-Aldrich. All the chemicals were used as received.

2.2. Preparation of TiO_2 mesocrystal films

A titanium sheet (20 × 30 mm^2) was cleaned by ultrasonic irradiation for 30 min in acetone, ethanol, and deionized water (volume ratio = 1:1:1) after being polished. The precursor solution was prepared from TiF_4, H_2O, NH_4NO_3, and P123 (molar ratio = 93:32000:444:1). The TiO_2 mesocrystal films were prepared by titanium sheet dip-coating in the precursor solution. The treated titanium sheets were calcined in air at 300, 400, 500, 600, and 800 °C for 1 h at a heating rate of 5 °C/min, respectively.

2.3. Preparation of Au/TiO_2 mesocrystal film

Chloroauric acid solution was added to the above precursor solution at contents of 0.5%, 1%, 1.5%, and 2% (mass ratio in Au/TiO_2). According to the above method, the sheets were calcined in air at 400 °C for 1 h.

2.4. Characterization

The morphology was characterized with a scanning electron microscope (SEM, Hitachi S4800) and a transmission electron microscope (TEM, JEOL JEM-2010). The crystal structure was characterized by X-ray diffraction (XRD, D/MAX-2000 with Cu K_α radiation). The pH value was measured with a pH meter (Mettler Toledo Delta 320). Photoelectrochemical measurements were performed in a conventional three-electrode configuration with an electrochemical station (CHI660). The TiO_2 mesocrystal film was used as the working electrode, and a platinum sheet and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The transient photocurrent was measured with the use of a 10 s on-off cycle at a bias voltage of 0.5 V or zero in 50 mL Na_2SO_4 solution (0.5 mol/L). UV-Vis diffuse reflectance spectra were recorded with a spectrophotometer (Shimadzu, UV2600) with an integrating sphere attachment in the range 200 to 800 nm and with $BaSO_4$ as reflectance standard.

2.5. Photocatalytic activity tests

Photocatalytic hydrogen evolution: A double-cell reactor was used for photocatalytic hydrogen generation. The chambers were separated by ion membranes. Two pools were injected with 30 mL ethylene glycol solution (2 mol/L) and 30 mL sodium sulfate solution (0.5 mol/L), respectively. Three electrodes system were used for the hydrogen production tests. The TiO_2 mesocrystal film was used as the working electrode, and a platinum sheet and SCE were used as the counter and reference electrodes, respectively. The photocatalytic hydrogen production was initiated by a xenon lamp with a filter (λ < 400 nm). The amount of H_2 evolved within 1 h of irradiation was determined with a gas chromatograph (Ceaulight, GC-7900).

Photocatalytic reduction of Cr(VI): A Au/TiO_2 mesocrystal film was immersed in an aqueous solution containing Cr(VI) ions (10 ppm, pH ≈ 3 controlled by HCl), in a home-made reactor stirred for approximately 30 min to reach adsorption-desorption equilibrium in the dark [19,31]. The photocatalytic reduction of Cr(VI) under UV or visible light irradiation was initiated by a xenon lamp with a filter (λ < 400 nm or > 420 nm). The concentration of Cr(VI) was analyzed by a UV spectrophotometer (UV 7502/PC) at the characteristic wavelength [32], from which the reduction rate could be calculated as: ($1 - C/C_0$) (C is the test concentration, C_0 is the initial concentration).

3. Results and discussion

The structure of TiO_2 mesocrystal film annealed at 400 °C was characterized by SEM imaging. The TiO_2 mesocrystal film showed a stacked sheet structure with a size of several micrometers (Fig. 1(a)). A porous structure was clearly observed on the surface (Fig. 1(b)). As we have previously reported, the addition of NH_4F can control the thickness of the resulting TiO_2 plates [19]. Different thickness of the TiO_2 plates can be achieved through the use of different TiF_4/NH_4F contents at the same calcination temperature (400 °C). As the NH_4F content is gradually increased (Fig. 2(a), (b)), the (001) facets of the TiO_2 plates are increased and the resulting crystals become thinner. Many gaps appear between neighboring sheets, which can increase the specific surface area of the films, and are beneficial for the photocatalytic performance. As the amount of NH_4F is increased further (Fig. 2(c)), the TiO_2 plates become very thin resulting in structural collapse. Therefore, the optimum conditions for synthesis of the TiO_2 mesocrystal film were a ratio of TiF_4/NH_4F volume ratio = 1:0.8 and calcination temperature of 400 °C. A cross sectional SEM image (Fig. 2(d)) shows that the

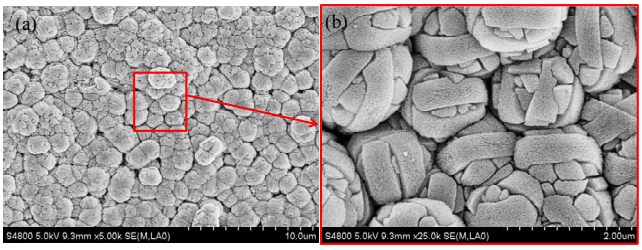

Fig. 1. (a) SEM image of the surface of TiO_2 mesocrystals film; (b) Magnified SEM image of the surface revealing porous structures.