



One-step synthetic approach for core-shelled black anatase titania with high visible light photocatalytic performance

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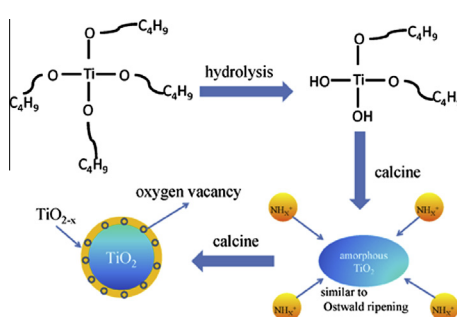
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HIGHLIGHTS

- Black core-shelled anatase was prepared using a simple one-step synthetic method.
- A possible mechanism for the formation of such core-shell structure is proposed.
- Ethanol absolute has critical effect in preventing phase transition of titania.

GRAPHICAL ABSTRACT



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ABSTRACT

Black core-shelled anatase titania were successfully prepared using a simple one-step synthetic method by calcining colloid titania precursor in N₂ flow under atmospheric pressure. The physicochemical properties of the as-prepared samples were characterized by various techniques such as X-ray diffraction, high resolution transmission electron microscopy, etc. The samples demonstrate a unique core-shelled structure and electron paramagnetic resonance spectra reveal the presence of high concentration of Ti³⁺ and oxygen vacancies at the surface, which accounts for their black appearance. A possible mechanism for the formation of such core-shell structure is proposed based on the results (X-ray photoelectron spectra, etc) of products prepared under different ration between urea and hydrochloric acid. Ethanol absolute is found to have critical effect in preventing phase transition of titania (from anatase to rutile) upon elevated temperatures. The black appearance of the sample powder (high visible light absorption) as well as slow electron/hole recombination rate after introducing oxygen vacancies/N species signify the core-shelled anatase titania as an efficient visible light active photocatalyst.

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1. Introduction

Eliminating the organic pollution in water by searching for efficient semiconductor photocatalysts has attracted considerable attentions. Titanium dioxide (TiO₂) is one of the most widely used photocatalysts owing to its exceptional properties, such as low

cost, high stability and non-toxicity, etc. [1–5]. Due to its wide band gap (~3.2 eV for anatase) and fast electron/hole recombination rate, many attempts have been made to modify TiO₂ in order to improve its light absorption and photocatalytic activity. One of the most efficient methods is to tailor its band gap by nonmetals doping, such as sulfur, carbon and nitrogen [6–8]. For example, nitrogen doping induces visible-light responsive photocatalytic activity by mixing the N 2p and O 2p states to narrow the band gap [9]. However, their visible light absorption and electron/hole separation ration are still not satisfactory.

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Recently, black titania prepared from hydrogenating TiO_2 nanocrystals attracts many attentions owing to narrow band gap (~ 1.54 eV) and high photocatalytic performance under solar light irradiation [10]. Hydrogen inserting into the lattice of TiO_2 induces additional intermediate electronic states, which extends its solar energy absorption [10,11]. However, the high H_2 -pressure process in the method limits its wide application. A number of new synthetic methods for black titania were reported, for instance (1) aluminothermic reduction reaction; (2) hydrogen gas annealing; (3) solution evaporation process [11–13]. Among these three methods, the first one prepares core-shell structured $\text{TiO}_2@ \text{TiO}_{2-x}$ for the first time and eliminates security risks of using hydrogen gas annealing. The $\text{TiO}_2@ \text{TiO}_{2-x}$ samples show excellent photocatalytic activity under UV and visible light irradiation, as the structure not only introduces oxygen vacancies in the titania surface but also increases the structural openness by inducing surface disordering [11,14]. Nevertheless, the method is time-consuming (two step) and requires rigorous reaction condition: prepare white anatase titania firstly and then turn to black color by aluminothermic reduction process (pressure lower than 0.5 Pa). Thereby, it is highly desired to explore a simple and economic synthetic approach to synthesize black core-shelled anatase titania with strong visible light absorption and high photocatalytic performance.

Herein, based on the preparation method of black TiO_{2-x} we reported before [15], we demonstrate the preparation of black core-shell structured anatase titania by calcining colloid titania precursor in N_2 flow under atmospheric pressure, which solves the above disadvantages of aluminothermic reduction method. The black core-shell structured anatase titania shows excellent visible light absorption and photocatalytic activity because of the introduction of amounts of oxygen vacancies and N doping. A possible formation mechanism of core-shell structure is proposed based on the results of products prepared under different ration between urea and hydrochloric acid. And ethanol absolute in the method has great effect on preventing phase transition of titania (from anatase to rutile) when calcined under 550°C .

2. Experimental

2.1. Materials

Tetrabutyl titanate (TIANJIN GUANFU CHEMICAL RESEARCH INSTITUTE) was chemical grade. Urea (TIANJIN YONGSHENG FINE CHEMICAL Co., LTD) and Hydrochloric acid (BEIJING BEIHUA FINE CHEMICALS Co., LTD) were analytical reagent. Titanium oxide (anatase) was purchased from Aladdin Industrial Corporation.

2.2. Preparation of core-shell structured $\text{TiO}_2@ \text{TiO}_{2-x}$

Core-shell structured black titania samples were prepared based on the method for black titania reported before [15]. Tetrabutyl titanate (14 mL), urea (0 g; 0.4 g; 0.6 g; 0.8 g; 1 g; 1.2 g; 1.4 g) and ethanol absolute (20 mL) were mixed. Hydrochloric acid A.R. (1 mL), distilled water (5 mL) and ethanol absolute (10 mL) were also mixed. The second solution was gradually added dropwise to the first, and then a glass rod was used to stir the mixture until a white colloid is formed. The mixture was placed in a water bath at 35°C for 30 min. The resulting material was stirred magnetically for about 2 h and then calcined at 550°C for 3 h. The samples are named according to the calcination atmosphere and the amount of urea; that calcined in air is designated as 1.4 g(air) and that calcined in N_2 is designated as 0 g, 0.4 g, 0.6 g, 0.8 g, 1.0 g, 1.2 g and 1.4 g, respectively. In addition, titanium oxide (anatase) purchased from Aladdin Industrial Corporation is designated as white.

2.3. Visible-light photocatalytic degradation

The photocatalytic activities of the samples were evaluated by measuring the decomposition of methyl orange (MO) dye solution under visible-light irradiation. Photocatalyst (40 mg) was added to aqueous MO solution (25 mg/L, 40 mL). Prior to irradiation, the suspension was kept in the dark with magnetic stirring for 200 min to establish an adsorption-desorption equilibrium between the MO and photocatalyst. The solution was illuminated by a 350-W Xe lamp with a cutoff filter ($k \geq 420$ nm) to remove UV light. Circulating water was used to cool the solution and to prevent solvent evaporation. During the measurement process, about 4 mL of the suspensions were collected at certain time intervals (15 min) for the following analysis after centrifugation. The concentration of MO was monitored by measuring the absorbance at 464 nm using a UV/Vis spectrometer (Lambda 650 S).

2.4. Characterization

The phase composition of the samples was analyzed by X-ray diffraction (XRD, Bruker D8 Advance, Germany). The optical absorption spectra of samples were collected using a PerkinElmer UV/Vis spectrometer (Lambda 650 S) at room temperature. X-ray photoelectron spectroscopy (XPS) was analyzed on a Thermo ESCALAB 250XI equipped with monochromatized Al $K\alpha$ radiation using C 1s (284.8 eV) as the reference. Photoluminescence spectra (PL) were measured using a Fluorescence Spectrometer LS 55 (PerkinElmer) with the excitation wavelength of 320 nm, scanning rate of 700 nm/min. Electron paramagnetic resonance (EPR) spectra were recorded on a JES FA200 spectrometer at room temperature.

3. Results and discussion

The X-ray diffraction (XRD) patterns of prepared titania (Fig. 1) indicate that no phase transition is observed at different amount of urea, as characteristic diffraction peaks of all samples match the (101), (004), (200), (105), (211), (204), (116), (220) and (215) planes of anatase titania. The microstructure of titania samples is uncovered by high resolution transmission electron microscopy (HRTEM) as shown in Fig. 2. The 1.4 g(air) samples are highly crystallized, as the well-resolved lattice features are shown in Fig. 2a. In contrast, all the samples calcined in N_2 have a unique core-shell structure with a disordered surface layer coating a crystalline core. Interestingly, compared with the five samples, the thickness of the disordered layer is different at different amount of urea.

Black color indicates the enhanced light absorption of as-prepared titania. The UV-vis absorption spectra of samples are shown in Fig. 3a. In comparison to purchased white anatase titania, their absorption in visible light region is greatly enhanced. As the amount of urea increases from 0.6 g to 1.4 g, the visible light absorption remains the same, which is well consistent with the similar color of samples. In addition, taking 0.8 g sample as an example, the band gap energy is narrowed to about 1.38 eV (see insert of Fig. 3a). The strong light absorption of samples can be attributed to the induced disordered surface layer. The formation of disordered surface layer may be attributed to the occurrence of amounts of Ti^{3+} and oxygen vacancies. Given that electron paramagnetic resonance (EPR) is highly sensitive to detect paramagnetic species containing unpaired electrons, it is used to verify our assumption. As shown in Fig. 3b, the samples calcined in N_2 exhibit strong response at a g-value of ~ 2.003 which attributed to surface Ti^{3+} [14,16,17]. It can be concluded that the largest amount of Ti^{3+} and oxygen vacancies is generated in 0.6 g sample, as the signal area is proportional to the amount of Ti^{3+} [14]. In

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