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Short communication

Colored titania nanocrystals and excellent photocatalysis for water cleaning

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ABSTRACT

Colored titania has attracted enormous attentions due to its visible light absorption and wide range of applications. Here, we demonstrate an effective approach to obtain colored titania with enhancing solar absorption by introducing disorder in the surface of titania through Al reduction. As prepared black TiO_{2-x} possesses solar energy absorption up to 88%. The recombination centers of light-induced electrons and holes are reduced in acid solution, which ensures the excellent photocatalytic activity of the black TiO_{2-x} in the photo-oxidation of organic molecules in water.

1. Introduction

The important semiconductor TiO_2 has been found applications in a wide range of technological innovations [1–3]. When used as a photocatalyst, TiO_2 absorbs only ultraviolet (UV) light (anatase with a bandgap of 3.2 eV and rutile with a bandgap of 3.0 eV) [4,5]. Anion-doping has been widely used to modify the electronic structures and consequently light absorption ranges of TiO_2 [4,6–10]. Different from impurity incorporation, self-doping produces Ti^{3+} species in TiO_2 and has also been demonstrated to effectively improve the solar absorption [11,12]. Recently, some hydrogenation methods are demonstrated to enable efficient visible-light absorption, resulting in the formation of black TiO_2 and UV light photocatalytic activity [13–18]. The improved solar absorption is attributed to additional intermediate electronic states induced by the hydrogen insertion into the lattice of TiO_2 [14]. However, this absorption enhancement is really ineffective for visible-light photocatalysis [6,19–22]. Considering the danger and difficulty in controlling a typical hydrogenation process (high temperature, high pressure, pure hydrogen, *etc.*), an alternatively facile and effective method is imperative to be developed. In our previous research, non-contact aluminum-reduction method was developed to prepare black titania that showed great enhancement in photocatalytic activity [18, 23,24]. In the approach, the melted Al acted as a reductant in a two-zone vacuum furnace and lowered oxygen partial pressure to provide the kinetic driving force to reduce TiO_2. Considering that the mixture of metallic aluminum and oxides are well known as thermites, here we attempt to get the partially reduced titania more easily by a simple method through good controlling of the annealing temperature.

In this research, we have modified an old technique to partially reduce titania (Degussa P25) with aluminum under a low-temperature (<500 °C) to generate blue and black titania. This technique was developed half a century ago for the rapid aluminothermic reduction reaction of titania to make Al-Ti alloys.

2. Experimental section

2.1. Preparation of partially reduced TiO_{2-x}

TiO_2 samples (P25, 20 − 30 nm in size) and aluminum powder with weight ratio of 1:1 were well mixed, compressed into a plate under 2 MPa, and put into a quartz tube. The tubes were evacuated to 10 Pa and sealed to resist oxygen in the subsequent reduction procedure. The tubes were then heated to 400, 500 and 600 °C, respectively, and then kept for 4 h. The color of titania was adjusted by changing the temperature of heat-treatment. After cooled, the samples were treated with HCl (10%) for 2 h to remove the excess Al. The temperature is a key factor for Al-reduction. Another influence factor is the ratio of Al powder and TiO_2. Here, the appropriate ratio is 1:1 to produce the black titania that possess most efficient absorption for solar light and is effective for photocatalysis, as shown in Figs. S1 and S2 of Supporting Information. For simplicity, the titania discussed below was prepared with the equal ratio of Al powder and TiO_2.

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2.2. Solar light photocatalytic degradation

The solar-light photocatalytic activity was investigated by monitoring the decomposition of methyl orange in an aqueous solution under solar light irradiation. Titania sample (100 mg) was dispersed in methyl orange solution (100 mL, 20 mg/L) condition. After stirring for 30 min in dark, the suspension was illuminated with a 400 W iodine gallium lamp. The suspension was cooled by the water circulating jacket. About 4 mL suspension was withdrawn every 1 min for the following analysis after centrifugation. The concentration of aqueous methyl orange was determined with a UV-vis spectrophotometer by measuring peak intensity at 464 nm for the neutral solutions and 506 nm for the acidic ones. For MO degradation in acidic solution (pH = 1), the suspension with titania was stirring for 4 h before solar-light irradiation.

2.3. Sample characterizations

The samples were investigated with TEM (JEOL JEM 2100 F), XRD (Bruker D8 Avance), XPS (RBD upgraded PHI-5000C ESCA system with Mg Kα radiation ($h\nu = 1253.6$ eV)) and Raman spectra (Thermal Dispersive Spectrometer using a 10 mW laser with an excitation wavelength of 532 nm).

3. Results and discussion

The P25 TiO_2 changed to blue and black respectively after Al-reduction at 400 and 500 °C (T400 and T500), as shown in Fig. 1a. The samples were very stable and no noticeable color change happened in several months at room temperature in open air.

The morphologies of reduced titania were verified by transmission electron microscopy (TEM), as shown in Fig. 1b–d. The particle sizes of Al-reduced TiO_2 nanocrystals ranged from 20 nm to 30 nm, which were similar to the pristine TiO_2. The pristine TiO_2 nanocrystals were highly crystalline as illustrated from the well-resolved lattice features, shown in the high-resolution TEM (HRTEM) image (Fig. 1b). It was worthwhile to notice that a highly disordered surface layer surrounding the crystalline TiO_2 core was introduced into the titania nanocrystal (TiO_{2-x}) after Al reduction (Fig. 1c&d). The disordered surface layer of

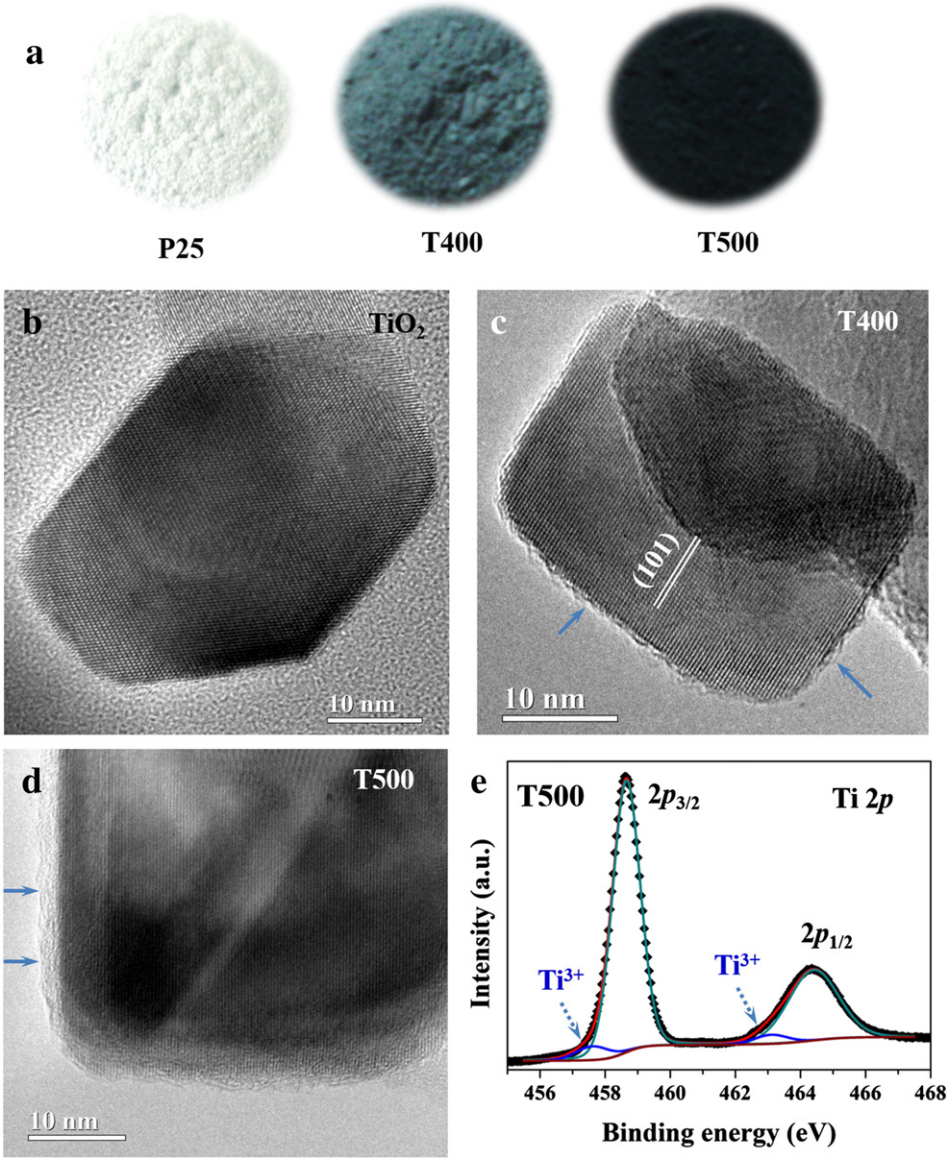

Fig. 1. (a) Photographs of pristine P25 and colored titania obtained by Al — reduction route at 400 °C (T400) and 500 °C (T500) for 4 h. (b — d) HRTEM images of pristine P25 (b) and (c, d) T400, T500. (e) Ti 2*p* XPS spectrum of T500.