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Core-shell structured TiO_2 as highly efficient visible light photocatalyst for dye degradation

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ABSTRACT

TiO_2 is one of the most important photocatalysts, but it is inefficient for visible light photocatalysis due to its large band gap. Herein, the unique core-shell structured TiO_2 photocatalyst was synthesized by a one-step hydrogen treatment at temperature of 400–600 °C. The novel catalyst exhibited excellent performance for visible light photocatalytic dye degradation at room temperature. Even under weak visible light ($40\,mW\,cm^{-2}$) illumination, its degradation efficiency for methylene blue dye was 400% higher than that of pristine TiO_2. Such a large enhancement can be attributed to the stable Ti^{3+} centers inside the core for visible light photocatalytic activity and the disordered shell for dye adsorption.

1. Introduction

Complicated structured dyes have been used to meet the growing demand in textile industries and about 20% of the total dyes was released into the water bodies during the dyeing process [1–3], which causes serious water pollution. Several approaches have been employed to remove dyes from water, such as adsorption [4], biodegradation [5], chlorination, and ozonation [6]. However, they are suffering issues of high costs and more concentrated by-products (namely, the pollutants are not been purified radically). Alternatively, heterogeneous photocatalysis, which is an advanced oxidation process, works as a destructive technology, leading to the full mineralization of most organic pollutants to avoid the generation of toxic degradation products (such as aromatic amines that are carcinogenic to human) [2,4]. Most of photocatalysts are N-type semiconductors with a large band gap, but some of them (CdS, MoS_2, and Cu_2O) can produce toxic ions after the chemical or photochemical reaction and some are not efficient enough [7–10].

TiO_2 is a promising photocatalyst for waste water treatment due to its low-cost, large-availability, and non-toxicity [11]. However, the wide band gap of TiO_2 can only absorb ultraviolet light (about 4% of total solar spectrum), limiting its photocatalytic efficiency [12]. Several strategies have been explored to extend the TiO_2 absorption spectrum into visible light range, such as doping with metal or non-metal ions [13–16]. However, the photocatalytic efficiency of doped TiO_2 isn't much improved because the dopants would act as electron-hole recombination centers [17]. In 2011, Mao and co-workers reported a new method through turning TiO_2 into black color by hydrogen treatment, increasing the visible light absorption dramatically [18]. The enhanced density of oxygen vacancies in the black TiO_2 was believed to suppress the recombination of holes and electrons, boosting the photocatalytic efficiency [19,20]. The Ti^{3+} created in the hydrogen-treated TiO_2 could act as an electron donor, leading to visible light photocatalytic activity [21–24]. So far, however, a little attention was paid to the hydrogen-treated TiO_2 for the visible light degradation of dyes. This happened probably due to the general recognition that the Ti^{3+} sites formed from partial reduction of TiO_2 could be easily re-oxidized in air or water. Therefore, the stability of Ti^{3+} in air or aqueous dye solutions is important for practical applications [25].

Recently, Cheng and his coworkers successfully synthesized a crystalline Ti^{3+} core/amorphous Ti^{4+} shell structured rutile TiO_2 with a two-step process [26]. In the process, rutile TiO_2 was thermally reduced with H_2 to form Ti^{3+} defects in TiO_2 and then hydrothermally fluorinated in hydrofluoric acid to create an amorphous surface layer on TiO_2. The crystalline Ti^{3+} core/amorphous Ti^{4+} shell structured rutile TiO_2 exhibited the enhanced photocatalytic activity for hydrogen production from H_2O/CH_3OH under 1.5 G sunlight irradiation. This was attributed to the overturned population of surface-reaching holes and electrons enabled by this core/shell structure. In contrast, a reversed core-shell structured TiO_2 nanofibers, in which crystalline Ti^{4+} core/

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amorphous Ti^{3+}-containing shell structured TiO_2, was synthesized by the hydrothermal synthesis and subsequent heat treatment in hydrogen flow. The TiO_2 NFs showed excellent solar light absorption and photocatalytic performance [27].

In this work, the novel core-shell structured TiO_2 nanoparticles, in which Ti^{3+} centers are inside the crystal core and the disordered Ti^{4+}-based layer constitutes a shell, were successfully synthesized by a simple one-step hydrogen treatment process. Furthermore, such a core-shell structured TiO_2 exhibited excellent visible light photocatalytic performance for dye degradation.

2. Experimental

2.1. Preparation of hydrogenated TiO_2

Sigma-Aldrich P-25 titanium dioxide was treated by hydrogen in a corundum tube furnace as follows: the corundum tube was evacuated with a mechanical pump for 30 min, followed by introducing H_2 for 10 min, then pumping for 30 min, and finally introducing H_2 for the hydrogen treatment of TiO_2 at a selected temperature (400–600 °C) for 12 h. The obtained samples of TiO_2 treated by hydrogen at 400, 450, 500, 550, and 600 °C were denoted as TiO_2-H400, TiO_2-H450, TiO_2-H500, TiO_2-H550, and TiO_2-H600, respectively.

2.2. Characterization

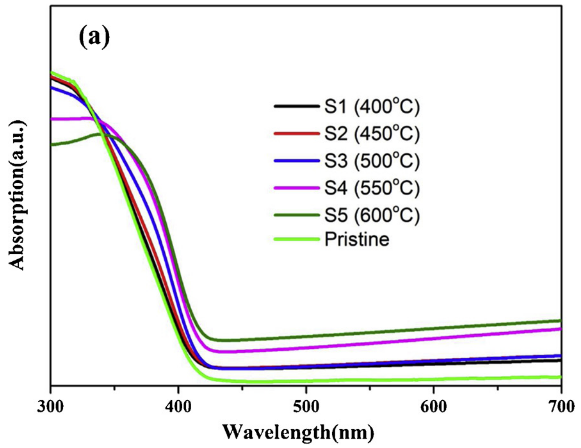
The crystal structures of the hydrogen-treated TiO_2 samples were characterized by X-ray diffraction (XRD, D8 DaVinci). Their surface morphologies were examined by transmission electron microscopy (TEM, JEOL2100 F). The UV–vis absorption spectra were obtained using a UV-2600 (Shimadzu spectroscopy and Lambda 750). The chemical states of the samples were measured with X-ray photoelectron spectroscopy (XPS, EscaLab 250Xi) and electron paramagnetic resonance (EPR, EMX-8). Their surface areas were calculated with BET model from the N_2 adsorption using ASAP 2020 PLUS HD88 instrument. The reduction of TiO_2 by hydrogen was evaluated by temperature-program reduction instrument (TP-5076). The degradation of MB was confirmed by the TOC analysis (Multi N/C 3100), Gas Chromatography (KECHUANG GC9800), and ion chromatography (ICS-5000 + /900).

2.3. Photocatalytic degradation of methylene blue

The photocatalytic performance of hydrogen-treated TiO_2 was measured by degradation of methylene blue solution (100 mL, 5 mg•L $^{-1}$) under illumination of a 500 W Xe lamp, PL-XQ500 W. The UV-cut filter was exploited to ensure the degradation under visible light. The irradiation area for the reactor is about 28 cm^2, and the light intensity reaching the reactor is about 40 mW• cm^{-2}. Before illumination, the solution was stirred for 30 min in dark to attain absorption-desorption equilibrium. Absorption capacity was measured every 30 min of irradiation.

3. Results and discussion

It is well-known that TiO_2 possesses a wide band gap of 3.0–3.2 eV, leading to its absorption ability only for UV light [21,23,24]. To obtain a band gap being small enough for visible light absorption, TiO_2 was subjected to hydrogen treatment at various temperatures. As shown in Fig. 1a, one can see that the hydrogen treatment remarkably increased the visible light absorption of TiO_2. However, its original band gap of 3 eV remained unchanged, indicating that the enhanced absorption of visible light would be due to the generation of new inter-band states. Such inter-band states were previously observed [21,23,24,28–30]. Diffuse reflectance UV–vis-NIR spectra were exploited to evaluate the inter-band states (Fig. 1b). An abrupt change at the UV–vis-NIR curve was observed at approximately 1425 nm, which is associated with a small energy gap (0.87 eV) of hydrogen-treated TiO_2. It was reported that the energy levels of oxygen vacancies are 0.75–1.3 eV below the conduction band of hydrogen-treated TiO_2 [20,31] (Fig. 2). Therefore, the observed small energy gap (0.87 eV) can be attributed to oxygen vacancies.



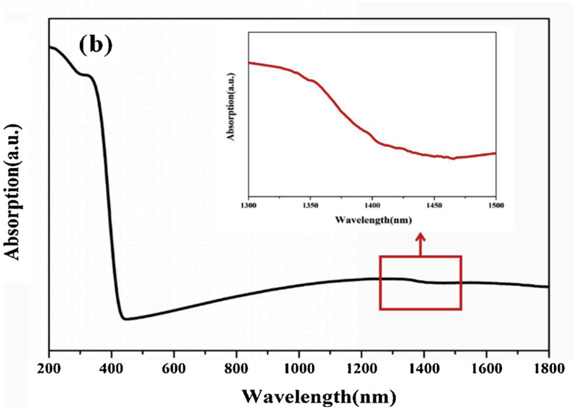


Fig. 1. (a)UV–vis absorption spectra of pristine TiO_2 and hydrogen-treated TiO_2 (TiO_2-H400: hydrogen-treated at 400 °C; TiO_2-H450: hydrogen-treated at 450 °C; TiO_2-H500: hydrogen-treated at 500 °C, TiO_2-H550: hydrogen-treated at 550 °C; TiO_2-H600: hydrogen-treated at 600 °C), (b) Diffuse reflectance UV – vis – NIR spectra of TiO_2-H600 (The inset enlarges the absorption spectrum in the range from approximately 1300 to 1500 nm).

The effect of hydrogen treatment on the crystal structure of TiO_2 was examined by X-ray diffraction (XRD). Fig. 3 shows that, when temperature for the hydrogen treatment was 450 °C or below, the diffraction pattern of TiO_2 remained almost unchanged. Only a slight decrease in peak intensity was observed, which indicates the increase in defects [1]. When the treatment temperature is above 450 °C, the ratio of anatase phase to rutile phase decreased with increasing temperature (Fig. 3). It was reported that the complete conversion of the anatase to the rutile needs a high temperature of 700 °C or above in air [31]. Interestingly, during the hydrogen treatment, all anatase phase converted into the rutile just at 600 °C (Fig. 3). This can be explained by oxygen vacancies, namely, the hydrogen treatment created the oxygen vacancies that can decrease the activation energy of TiO_2 lattice rearrangement, causing the phase transformation at lower temperature [31]. In other words, this reduced temperature of phase transformation provides an additional evidence to confirm the oxygen vacancies generated during the hydrogen treatment. The generation of oxygen vacancies by hydrogen treatment was further confirmed by temperature-programmed reduction (TPR). As shown in Fig. 4, one can see a large and broad reduction peak starting at about 300 °C, indicating the