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Enhanced photocatalytic activity of TiO_2/carbon@TiO_2 core–shell nanocomposite prepared by two-step hydrothermal method

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ABSTRACT

A unique TiO_2/carbon@TiO_2 core–shell nanocomposite was fabricated by a two-step hydrothermal method. High-resolution transmission electron microscopy images show the size of the nanocomposites is about 50–100 nm, which are composed of well-defined crystallized titania on the shell with the TiO_2/carbon composite as the core. The existence of the amorphous carbon in the core can be proved by Raman spectra and thermogravimetric analysis. X-ray diffraction pattern and Raman spectra show that the crystalline of TiO_2 is improved after the second hydrothermal treatment and the TiO_2 are the pure anatase phase. Measurements of the photocatalytic degradation of rhodamine B show that the photocatalytic activity of TiO_2/carbon@TiO_2 core–shell nanocomposite is higher than that of the initial TiO_2/C core and pure TiO_2 because TiO_2 on the shell has high crystallinity and high content of surface oxygen vacancies (SOVs) after the second hydrothermal treatment. Moreover, the synergistic catalytic effect of the carbon in the core can also enhance the photocatalytic activity of the nanocomposite, such as retarding the recombination of photo-generated electron–hole pairs and absorbing more light.

1. Introduction

Semiconductor oxide photocatalysts is one strong technique to solve the increasingly serious environmental pollution problems. And titanium dioxide (TiO_2) has been intensively investigated as photocatalyst due to its low cost, non-toxicity, high redox ability and stability [1–3]. The photocatalytic efficiency of TiO_2 is affected not only by surface atomic structure, but also by the size, phase, shape, crystallinity, and the degree of exposure of reactive crystal facets [4,5]. For example, anatase phase shows a better photocatalytic activity than rutile because of the low recombination rate of photo-generated electrons and holes [6–9]. The photocatalytic activity of TiO_2 is also heavily dependent on the surface area especially when the geometry size is reduced to the nanometer scale, leading to a large specific surface area [10–13]. However, the actual applications of TiO_2 are greatly restricted by its low quantum efficiency and ineffective utilization of visible light, which results from its high recombination of photo-generated electron–hole pairs and wide band gap, respectively [14,15]. Therefore, how to increase the absorption of the visible light and reduce the recombination of electrons and holes is still a hot issue in the field of photocatalysis.

In the past decades, amounts of effective approaches have been developed to narrow the band gap and increase the lifetime of photo-generated electron–hole pairs. Bandgap engineering is just an effective method to optimize TiO_2 solar light harvesting capability. Doping metal or nonmetal impurities [16–19] is an interesting attempt. However, the introduction of dopants, acting as recombination centers of carriers, is a major issue affecting the photocatalytic efficiency. Surface sensitization [20–22] and coupling with other narrow band gap semiconductor materials [23–26] provide new ways to extend light absorption range of TiO_2. Moreover, these special structures can also suppress the recombination of the photo-generated carries. In view of this, combining TiO_2 with carbonaceous materials is an interesting way to increase photocatalytic activity [27,28] by virtue of a synergistic effect between carbon and TiO_2. Various kinds of carbon modification have been investigated, such as carbon-doped TiO_2 [29–33], carbon-coated TiO_2 [34–37], and mounting of TiO_2 on activated carbon, graphene or carbon nanotubes (CNT) [38–42]. From the view of solar energy utilization, a carbon@TiO_2 core–shell structure is the best choice to efficiently enhance the photocatalytic activity. However, it is difficult for TiO_2 to grow on the carbon nanosphere due to lack of

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nucleation sites. Synthesizing this structure is a meaningful topic to enhance the photocatalytic activity of TiO_2-based photocatalysts.

In the present study, a TiO_2/C@TiO_2 core–shell nanocomposite was prepared by a two-step hydrothermal method. The morphologies, structures and crystallinity of the composite were characterized by HR-TEM, XRD, Raman spectrum, UV–vis spectroscopy, and PL spectroscopy. The photocatalytic activity of the prepared composite was examined by photocatalytic degradation of rhodamine B (RhB) in water under UV light irradiation as model reactions.

2. Experimental details

All reagents were of analytical grade and used without further purification.

2.1. Preparation of the TiO_2/C nanocomposites core

The TiO_2/C nanocomposite core was prepared by a simple hydrothermal treatment mentioned in our previous work [43]. In brief, 1.64 g glucose ($C_6H_{12}O_6 \cdot H_2O$) was added into a 0.1 M 40 mL NaOH aqueous solution and then magnetically stirred for 10 min. After that, 2.12 g titanium (III) trichloride solution was slowly dropped into the mixed solution and the solution was magnetically stirred for another 1 min. The mixed solution was added into a Teflon-lined stainless steel autoclave with an inner volume of 40 mL, and the autoclave was sealed and placed in the oven. Then the oven was heated at 180 °C for 30 min. After the hydrothermal processing, the brown product was washed with deionized water and anhydrous ethanol until the washing solution pH value was close to 7. In order to expose the TiO_2 particles to the surface as the nucleation sites for the next step, the obtained product (marked as TC 01) was calcinated at 500 °C for 120 min in air at a ramp rate of 2 °C/min, which then was marked as TC 01-500.

2.2. Preparation of the TiO_2/C@TiO_2 core–shell nanoparticles

The TiO_2/C@TiO_2 core–shell nanoparticles were also synthesized by hydrothermal method with the TiO_2/C nanocomposite as the core. In a typical synthesis process, 0.12 g as-prepared TiO_2/C nanocomposite was added into 7.0 M 40 mL HCl aqueous solution. After stirred for 20 min, 0.6 mL hydrofluoric acid (47%) was introduced. And then 0.26 g tetrabutyl titanate ($Ti(OBu)_4$) was slowly dropped into the mixed solution and magnetically stirred for another 10 min. At last, the mixed solution was added into a Teflon-lined stainless steel autoclave, and the autoclave was sealed and subsequently heated at 100 °C for 4 h. After the hydrothermal processing, the product was washed with deionized water and anhydrous ethanol until the washing solution pH value reached 7, marked as TCT 01. For comparison, pure TiO_2 nanoparticles were prepared by the same procedure through two-step hydrothermal method without the addition of the glucose, which was marked as T 01.

2.3. Characterizations and tests

The structural properties were determined by X-ray diffraction analyzer (XRD, PANalytical X'Pert) and Raman spectra (JY-HR800 Raman spectrometer). The surface morphologies and particle sizes were observed by high-resolution transmission electron microscopy (HR-TEM, Tecnai-G2-F30). To analyze the light absorption of the photocatalysts, UV–vis diffuse reflectance spectra (DRS) were obtained using a scan UV–vis spectrophotometer (TU 1901) equipped with an integrating sphere assembly, while $BaSO_4$ was used as a reference. Thermogravimetric analysis (TGA, Diamond, USA) curve was recorded at a heating rate of 10 °C/min in air. The surface area and porosity of the products were measured by the nitrogen adsorption–desorption isotherm and Barrett–Joyner–Halenda (BJH) methods on a Micrometitics ASAP 2020M accelerated surface area and porosimetry system. Photoluminescence (PL) emission spectra were measured on a luminescence spectrometer (JY-HR800 Raman spectrometer) at room temperature under the excitation light of 325 nm. The photocatalytic activity of each sample was evaluated in terms of the degradation of RhB solution (10 mg/L). The photocatalyst (50 mg) was added into a 100 mL crystallizing dish containing 50 mL RhB solution. The mixture was stirred for 30 min in the dark to ensure the adsorption/desorption equilibrium. After the dark treatment, the mixture was subsequently irradiated under a 175 W tungsten halogen lamp (UV) with magnetically stirring at ambient temperature. During the irradiation, at given time intervals (10 min), 4 mL of the solution was sampled and high-speed centrifuged to remove the residual catalysts. The filtrate was analyzed by recording the intensity variations of the absorption band maximum (554 nm) of RhB in the UV–visible spectrum using a TU-1901 spectrophotometer.

3. Results and discussion

Fig. 1 shows the schematic illustrations of the formation of TiO_2/C@TiO_2 nanoparticles. Because the growth of the titanium oxide is based on the hydrolysis of the precursor, nucleation events could continuously occur in the entire solution during the hydrothermal growth process. And a seed layer is necessary for the designate growth of the titania. Here we used a TiO_2/C composite as the seed, which was prepared by a simple hydrothermal method. The ratio of exposed TiO_2 on the surface was adjusted by calcinations treatment. Fig. 2 depicts the TEM micrographs of all the

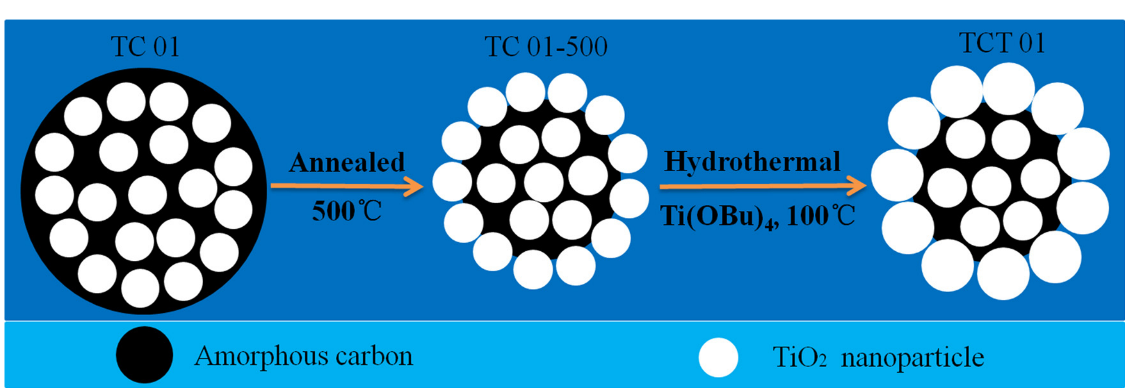

Fig. 1. Schematic illustration of the formation of TiO_2/C@TiO_2 nanoparticles.