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Enhanced activity of bismuth-compounded TiO_2 nanoparticles for photocatalytically degrading rhodamine B solution

Jia Wang, Liqiang Jing*, Lianpeng Xue, Yichun Qu, Honggang Fu

The Laboratory of Physical Chemistry, School of Chemistry and Material Sciences, Heilongjiang University, Harbin, 150080, PR China

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ABSTRACT

TiO_2 nanoparticles compounded with different amounts of bismuth were prepared by a sol–gel method, and the effects of compounding bismuth on the phase transformation, photoinduced charge separation and photocatalytic activity for degrading rhodamine B solution were mainly investigated, along with enhancement mechanism of photocatalytic activity of TiO_2 nanoparticles by compounding bismuth species. It can be confirmed that, by means of X-ray diffraction (XRD), surface photovoltage spectroscopy (SPS) and ultraviolet–visible diffuse reflectance spectroscopy (UV–vis DRS), compounding bismuth can extend the optical response, and effectively inhibit the phase transformation process from anatase to rutile, consequently greatly improving the anatase crystallinity so as to promote the photoinduced charge separation. These factors are responsible for the increase in the photocatalytic activity of TiO_2 compounded with an appropriate amount of bismuth species.

1. Introduction

Among various oxide semiconductor photocatalysts, TiO_2 has been proven to be one of the most suitable materials for widespread environmental applications because of its several attractive features, such as chemical and biological inertness, stability against photocorrosion, non-toxicity, high redox ability and less cost. In the last two decades, the fundamental and application researches on TiO_2 photocatalysis have been extensively documented [1–4]. Generally speaking, the separation and recombination of photoinduced charge carriers are in competing process, and the photocatalytic reaction is effective only when photoinduced electrons and holes are trapped on the surfaces, respectively. Although a great many of works about semiconductor photocatalysis have been published, the detailed photocatalytic mechanisms and factors affecting the photoactivity are still needed to explore further.

It has well been recognized that there are two bottleneck drawbacks associated with TiO_2 photocatalysis, namely, high charge recombination rate in itself and low efficiency for utilizing solar light, which would greatly hinder the commercialization of this technology. To overcome the above two problems, many attempts have been made to increase the utilization of visible light and enhance the separation situation of charge carriers. Among those attempts, compounding or doping transitional metal is one of the most efficient methods. There have been many papers published about TiO_2 photocatalysts compounded or doped with Zn, Sn, Cu, Si, Ca, Al, Mn, Fe, Ni, V, Ag, rare-earth metal, etc. [4–13]. However, relative few papers about TiO_2 compounded or doped with Bismuth (Bi) species have reported up to now [11–17]. Rengaraj et al. reported that doping Bi could improve the photocatalytic activity of TiO_2, attributed to the increase in the efficiency of charge separation on the basis of the photoluminescence quenching. However, to the best of our knowledge, systematic studies on effects of compounding Bi on the phase transformation and the photoinduced charge separation by means of SPS measurement, together with their relationships with the photocatalytic activity, have never been reported so far. The SPS, which is a kind of action spectroscopy based on optical absorption, is an effective tool to investigate the photophysics of excited states generated by adsorption in the aggregate state, providing some important information, surface states and charge separation and/or recombination [9,10].

In the present work, the photocatalytic activity of TiO_2 nanoparticles is improved by compounding an appropriate amount of Bi species, and the activity enhancement is mainly attributed to the increase in the photoinduced charge separation situation based on the SPS analysis, resulting from the high crystallinity and the Bi-O polyhedral acting as electron trapping centers, as well as to the visible response. Moreover, it can be suggested that the SPS measurement be used to preliminarily evaluate the photocatalytic activity of the resulting TiO_2 quickly. This work will be valuable for the practical application of TiO_2 photocatalysts, and also help

* Corresponding author. Tel.: +86 451 86608616; fax: +86 451 86673647.
E-mail address: Jinglq@hlju.edu.cn (L. Jing).

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us understand the photophysical and photochemical processes of nanosized semiconductor well.

2. Experimental

All the used reagents are of analytical grade without further purification, and the deionized water is employed to prepare the solutions in our experiments.

2.1. Preparation of materials

The TiO_2 nanoparticles were prepared by a sol-gel process [8]. In a typical process, 5 mL of $Ti(OBu)_4$ was dissolved in 5 mL of absolute C_2H_5OH to produce $Ti(OBu)_4$–C_2H_6OH solution. Meanwhile, 5 mL of water and 1 mL of HNO_3 (67%) were added to another 20 mL of absolute C_2H_5OH in turn to form an ethanol–nitric acid–water solution. After the two resulting solutions were stirred for 30 min, respectively, the $Ti(OBu)_4$–C_2H_5OH solution was slowly added dropwise to the ethanol–nitric acid–water solution under vigorously stirring to carry out a hydrolysis. Then, a semitransparent sol was gained after continuously stirring for 1 h. Subsequently, the sol was dried at 60 °C in the air for about 24 h to produce dry gel powder after grinding. Finally, TiO_2 nanoparticles were obtained by calcining the dry gel precursor at certain temperature for 2 h. To synthesize Bi-compounded TiO_2 samples, the desired amount of $Bi(NO_3)_3$ was dissolved in an appropriate amount of ethanol–nitric acid–water solution prior to the hydrolysis. The remaining procedures were the same as described above.

2.2. Characterization of materials

The crystalline phases of the samples are analyzed by X-ray powder diffraction (XRD) using a Model D/MAX-IIIB diffractometer made by Japanese Science Co., equipped with CuKα radiation (λ = 0.15406 nm). An accelerating voltage of 30 kV and an emission current of 20 mA were employed.

The samples are observed with a JEOM-1200EX transmission electron microscope (TEM).

The surface composition and elemental chemical state of the samples are examined by X-ray photoelectron spectroscopy (XPS) using a Model VG ESCALAB apparatus with MgKα X-ray source. The pressure is maintained at 6.3×10^{-7} Pa. The binding energies are calibrated with respect to the signal for adventitious carbon (binding energy = 284.6 eV). Relative quantitative analysis is carried out with the sensitivity factors supplied by this instrument.

The Ultraviolet–visible diffuse reflectance spectra (UV–vis DRS) of the samples are recorded with a Model Shimadzu UV2550 spectrophotometer.

The Surface photovoltage spectroscopy (SPS) measurement of the samples is carried out with a home-built apparatus that had been described in detail elsewhere [10,18]. The powder samples are sandwiched between two ITO glass electrodes, and the change of surface potential barrier between in the presence of light and in the dark is SPS signal. The raw SPS data are normalized with a Model Zolix UOM-1S illuminometer made in China.

2.3. Evaluation of photocatalytic activity of materials

Rhodamine B (RhB) has commonly been used as a dye, especially for paper, and as a reagent for antimony, bismuth, cobalt, niobium, gold, manganese, mercury, molybdenum, tantalum, thallium and tungsten. However, it has been found to be potentially toxic and carcinogenic. Thus, the RhB solution is chosen as a model pollutant to evaluate photoactivity of the as-prepared TiO_2. The degradation intermediates were not determined. The experiment was carried out in a 200 mL quartz photochemical reactor, open to air, having the shape of a vertical cylinder. The light was provided from a side of the reactor by a 150 W GYZ220 fluorescence high-pressure Hg lamp made in china without filter, which was placed at about 20 cm from the reactor. The RhB solution initial concentration was equal to 10 mg/L, and the treated total volume was 100 mL under continuously stirring. The solution was first stirred for 20 min after 0.1 g of TiO_2 samples was added into the reaction system, it has been shown that this period was sufficient to reach the adsorption equilibrium, then began to illuminate. The RhB concentrations at different reactive times were measured with a Model Shimadzu UV2550 spectrophotometer according to the optical characteristic absorption at the wavelength of 553 nm of RhB solution after centrifugation.

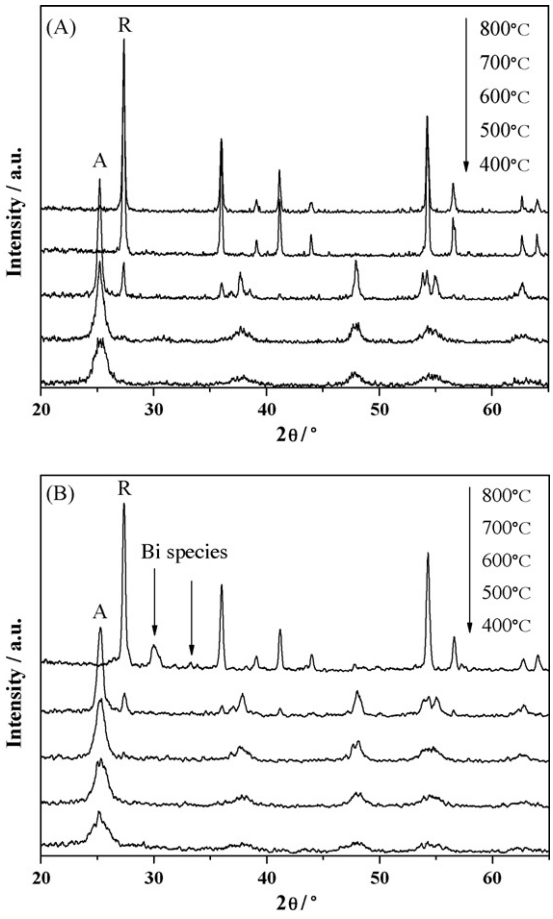

Fig. 1. XRD patterns of un-compounded (A) and Bi-compounded (B) TiO_2 calcined at different temperature.

3. Results and discussion

3.1. Measurements of XRD, TEM and XPS

The XRD peaks at $2\theta = 25.28$ and $2\theta = 27.48$ are often taken as the characteristic peaks of anatase (1 0 1) and rutile (1 1 0) crystal phase, respectively [8]. The percentage of anatase in the samples can be estimated from the respective integrated XRD peak intensities using the quality factor ratio of anatase to rutile (1.265), and the crystallite size can also be determined from the broadening of corresponding X-ray spectral peak by Scherrer formula [19]. Fig. 1 shows the XRD patterns of un-compounded (A) and 3 mol% Bi-compounded (B) TiO_2 nanoparticles calcined at different temperature.