Photodegradation of Tetracycline by Bi-doped In_2O_3 Nanospheres Under Visible Light

Pingge Zhao[1,2,a], Gehong Zhang[2,b], Xian Zhang[3,c], Wenbo Wang[2,a], Xiaode Zhou[1,a]

[1]Institute of Water Resources and Hydro-Electric Engineering, Xi'an University of Technology, Xi'an, 710048, China.

[2]School of Civil Engineering, Xi'an Technological University, Xi'an 710021, China.

[3]State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing, 100085, China.

[a]email: xazhpg@sina.cn, [b]email: zghlinda@126.com,[c]email: zx2010413@163.com

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Abstract. We report on the visible-light responsive Bi-doped In_2O_3 nanospheres, which were synthesized via a simple solvothermal reaction between $Bi(NO_3)_3 \cdot 5H_2O$ and $In(NO_3)_3 \cdot 4.5H_2O$ in the presence of absolute ethanol and ethylene glycol by adding urea and annealing it at 400 ^{0}C. The effects of experimental parameters on the nanostructural and morphological behavior of Bi-doped In_2O_3 nanospheres were discussed. Photocatalysts exhibit high activity owing to both the unique structural characteristics and the Bi ion doping. The doped Bi ion inhibits recombination rate of photo-induced carriers. Furthermore, the effects of Bi ion can be clearly drawn, and the degradation ratio of Bi-doped In_2O_3 nanospheres reaches 80.81%, which is reasonable to expect the obvious Bi ion dependent activity.

Introduction

Semiconductor photocatalysis, as a kind of "green" technology, have received considerable attention in the area of environment treatment. Among the kinds of semiconductor photocatalysts, TiO_2 is the commonly used photocatalyst to decompose environmental pollutants because of its high photocatalytic activity, chemical stability, low cost, and nontoxicity. However, due to its large band-gap (3.2 eV), TiO_2 only can absorb UV light which makes up about 4% of solar energy [1] [2]. Therefore, exploring new kinds of visible-light-responsive photocatalysts is one of the most important research topics recently.

Indium oxide (In_2O_3) is an n-type semiconductor[3][4]. In_2O_3 has high conductivity and transparency, which makes it suitable for application in optoelectronics, gas sensors, photocatalysts and so on. Many methods including the organic solution synthetic routes, solvothermal methods, sol–gel, chemical vapor deposition, template routes, hot injection techniques, hydrothermal methods and microwave-assisted synthesis have been used to synthesize In_2O_3 with different morphologies. Among these methods, solvothermal method[5][6] is a promising method for large-scale fabrication of the nano-materials, owing to its simplicity, low cost and environmental friendliness. However, the investigations by this technique on In_2O_3 have been quite limited.

In our work, Bi-doped In_2O_3 (BIO) nanospheres (NSs) can be generated by adding different amounts of $Bi(NO_3)_3$. P hotocatalytic activity on BIO NSs was systemically investigated. And BIO NSs exhibited ultrahigh photocatalytic efficiency for the degradation of tetracycline under visible light irradiation.

Chemicals

Bismuth nitrate and Indium nitrate was purchased from Aladdin (China). Nitric acid , urea , $Bi(NO_3)_3$ and $In(NO_3)_3$ were purchased from Sinopharm (China). All reagents were of analytical grade without further purification and the deionized water was used in all experiments.

Catalysts synthesis

BIO NSs were prepared by a fast and moderate solvothermal method. In a typical synthesis procedure, 1 mmoL $In(NO_3)_3 \cdot 4.5\ H_2O$ and 0.02 mmoL $Bi(NO_3)_3 \cdot 5H_2O$ were firstly dissolved in 25 mL absolute ethanol and 10 mL ethylene glycol under ultrasonication and stirring for 30 min. Then 4 mmoL urea was added into the above solution and stirring for 10 min. Last, the mixture was transferred into a Teflon-lined autoclave, maintained at 180 ^{0}C for 3 h. After reaction under self-generated pressure and cooling down to room temperature, the product was collected by filtration, washed by the deionized water and absolute ethanol and dried at 60 ^{0}C for several hours. Finally, the obtained products were calcined in air at 400 ^{0}C for 2 h with a heating rate 5 ^{0}C min^{-1} and cooled under air. The products were yellow BIO NSs. For comparison, pure In_2O_3 samples were also prepared by the above method.

Characterization

The crystal structure of samples was determined by X-ray diffraction (XRD) method using Cu Kα radiation (λ=1.54178 Å). The chemical composition of the samples was determined by scanning electron microscope-X-ray energy dispersion spectra (SEM-EDX) with an accelerating voltage of 25 KV. Scanning electron microscopy (SEM) images were collected on an S-4800 field emission SEM (SEM, Hitachi, Japan). Transmission electron microscopy (TEM) was collected on an F20 S-TWIN electron microscope (Tecnai G2, FEI Co.), using a 200 KV accelerating voltage. UV-vis diffused reflectance spectra of the samples were obtained from a UV-vis spectrophotometer (UV2550, Shimadzu, Japan), $BaSO_4$ was used as a reflectance standard.

Photocatalytic degradation of tetracycline

The photodegradative reaction for tetracycline (TC) was carried out at 298 K in a photochemical reactor under visible light. The photochemical reactor contains 0.1 g BIO catalyst and 20 mg/L of 100 mL TC solution. To determine the initial absorbency of samples, the reactor was kept into darkness for 30 min to reach absorption equilibrium. The photochemical reactor was irradiated with a 250 W Xenon lamp which was located with a distance of 8 cm at one side of the containing solution. UV lights with wavelengths less than 420 nm were removed by a UV-cutoff filter in the visible-light-driven TC degradation experiment. The sampling analysis was conducted in 10 min interval. The photocatalytic degradation ratio (DR) was calculated by the following formula:

$$DR = \left(1 - \frac{A_i}{A_0}\right) \times 100\% \qquad (1)$$

A_0 is the initial absorbance of TC that reached absorption equilibrium, while A_i is the absorbance after the sampling analysis.

The absorbance of TC was measured by a UV-vis spectrophotometer with the maximum absorption wavelength at 357 nm.

Morphology and structure

The morphology and crystalline structure of the as-obtained BIO NSs are visualized by SEM and TEM images. In the low-magnified SEM image (Figure 1a), the sphere-like morphology of the products can be clearly observed, and it reveals the diameter of the BIO NSs structure is about 500-800 nm which is within nano-scale level. In the high-magnified SEM image (Figure 1b), the average diameter of a single BIO NSs is about 600 nm, and the sphere character of BIO can be found obviously. For comparison, we prepared pure In_2O_3 (Figure 1c), the diameter of pure In_2O_3 NSs is about 500-800 nm, and the sphere-like character of In_2O_3 can be found. That is to say, BIO NSs and pure In_2O_3 NSs have the same morphology. The morphology of BIO has not changed compared with pure In_2O_3. In the TEM image (Figure 1d) of BIO NSs, which further reveals the

sphere character of the obtained BIO NSs.

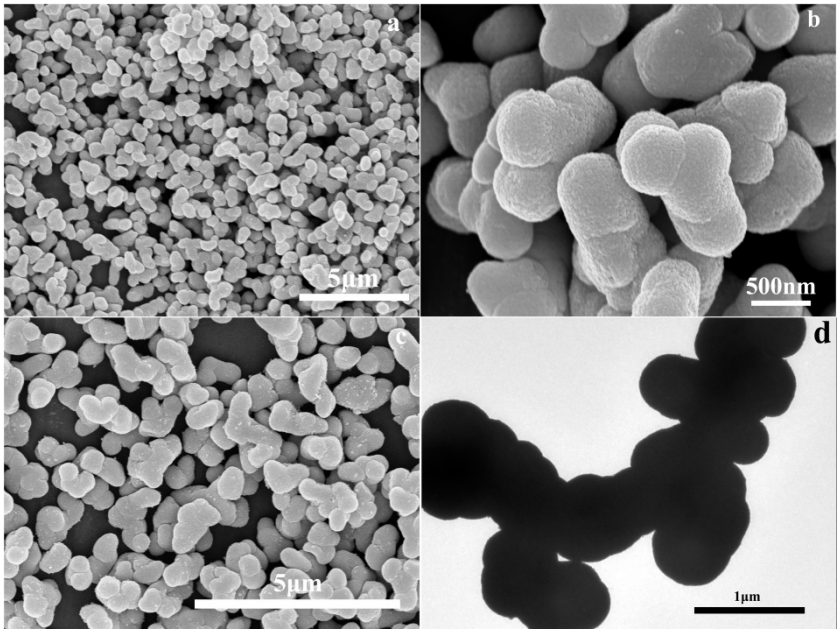

Figure 1. SEM images of BIO NSs in (a) low and (b) high magnifications with the magnified specific area , (c) SEM images of pure In_2O_3 NSs and (d) TEM image of BIO NSs.

The crystallographic phase purity and elementary composition of the as-synthesized BIO NSs were characterized by x-ray diffraction (XRD) and energy dispersive X-ray (SEM-EDX) analysis. As shown in Figure 2a, all characteristic peaks of BIO NSs can be readily indexed to the phase of In_2O_3, which is in good agreement with the standard card (JCPDS No. 06-0416). As compared different patterns with each other, we can clearly see that the they possess the same sharp peaks, suggesting the high crystallinity of them. In our experiments, prolonging the time of solvothermal reaction to 24 h makes no difference to the intensity and shape of peaks in XRD pattern of BIO NSs. It means the reaction time of 3 h is enough for the crystallization of BIO NSs. Figure 2b shows the SEM-EDX image of the as-prepared BIO NSs, in which the signals of Bi, In and O can be clearly observed. It also suggests that Bi element is mixed into the lattice of In_2O_3. The only impurity signal of Pt is ascribed to the substrate of the SEM-EDX analysis itself. No other impurity signals can be observed in the spectrum, indicating the elementary composition of our BIO NSs are pure.

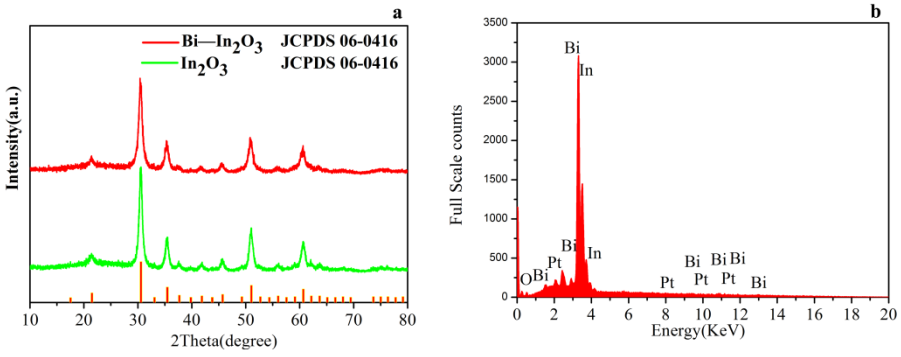

Figure 2. (a) XRD patterns and (b) SEM-EDX spectrum of BIO NSs.

Photocatalytic degradation of TC

To probe the potential application of BIO NSs in photocatalytic degradation of TC, we evaluated the photocatalytic degradation of TC by BIO NSs in relation to pure In_2O_3 NSs under visible-light. As shown in Figure. 3, the DRs of blank, pure In_2O_3, and BIO NSs for 60 min are 6.16 %, 59.92% and 80.81%, respectively. Compared with pure In_2O_3 NSs, the photodegradation with blank is

merely lower. Compared with In_2O_3 NSs, the photodegradation significantly increased by further doped Bi. Therefore, the effects of Bi as doped ion can be clearly drawn, for the DR of BIO NSs is over 1.3 times than that of In_2O_3 NSs, which is reasonable to expect the obvious doping ion activity. So the BIO NSs as a visible light photocatalyst for antibiotic water treatment are efficient and promising.

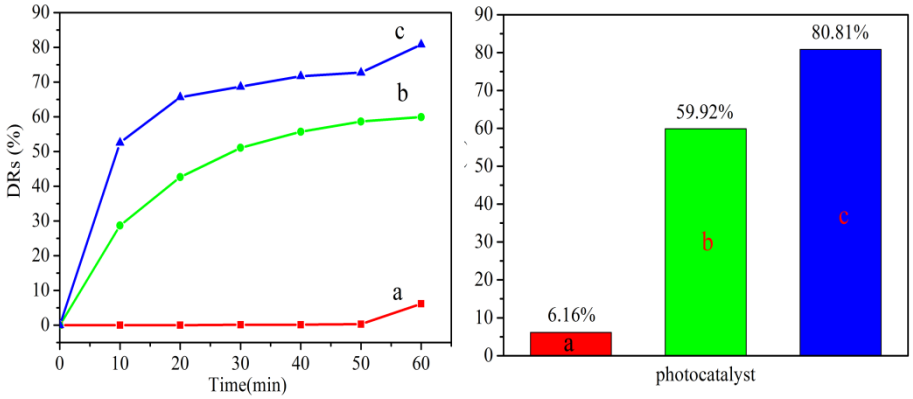

Figure 3.Photocatalytic degradation ratios of TC with (a) Blank, (b) pure In_2O_3 and (c) BIO NSs.

Conclusion

In this report, a fast and convenient solvothermal synthetic method for the preparation of BIO NSs has been proposed. Significant enhancement of doped activity has been clearly found on BIO NSs compared with pure In_2O_3 NSs. Our work highlights the facile and fast solvothermal synthesis of BIO NSs photocatalyst which exhibits higher visible-light-driven activity than pure In_2O_3 NSs for photocatalytic degradation of TC.

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