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Bi quantum dots on rutile TiO_2 as hole trapping centers for efficient photocatalytic bromate reduction under visible light illumination

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ABSTRACT

Bi quantum dots were deposited onto rutile TiO_2 nanoparticles by a one-pot, solvent-thermal process to create the Bi/TiO_2 (rutile) heterojunction photocatalyst. Due to the specific semimetal property of Bi, a metal to semiconductor transition occurred for Bi quantum dots, which endowed them with the hole trapping capability to enhance the charge carrier separation in rutile TiO_2 and eliminate the need of sacrificial agents for the consumption of photogenerated holes in photocatalytic reduction process. The Bi/TiO_2 (rutile) heterojunction photocatalyst demonstrated an efficient photocatalytic bromate reduction under visible light illumination without the addition of sacrificial agents in the reaction solution, and it could be easily regenerated for reuse. Different with previously reported noble/transition metal modifications as the electron trapping center, this study demonstrated a novel material design strategy of the introduction of hole trapping centers to create photocatalysts with strong photocatalytic reduction capabilities, which could be readily adopted for a broad range of technical applications.

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1. Introduction

As identified by the International Agency for Research on Cancer (IARC) as a 2 B substance (a possible carcinogen to humans) [1], the presence of bromate in drinking water from the ozonation disinfection is strictly regulated. The World Health Organization (WHO) suggested that the maximum contaminant level (MCL) of bromate in drinking water should not be over 10 $\mu g/L^{-1}$, and this standard has been adopted by many countries [2]. Various treatment technologies had been developed for the removal of bromate from drinking water, including physical adsorption [3], chemical reductions [4], and biological technologies [5]. However, their high cost, long treatment time, strict reaction conditions, and production of secondary pollutants limited their application in water treatment practice [6]. Thus, novel approaches should be developed for the removal of bromate from drinking water with high efficiency, economic feasibility, and environmental friendliness.

Since the pioneer work of Fujishima and Honda in 1972 [7], TiO_2 phtotocatalyst has been attracting great research attentions due to its potential in solar energy conversion/storage for various applications [8]. When TiO_2 is excited, both reduction and oxidation reactions could happen when photogenerated electrons and holes migrate to its surface and react with substances absorbed on/near its surface [9]. Photocatalytic reduction could provide promising solutions to hydrogen production from water splitting, CO_2 reduction for fuel production, and the removal of various environmental pollutants [10,11]. It had demonstrated that photocatalysis could be a promising technology for the removal of aqueous oxoanions from drinking water [12]. However, previous studies on the photocatalytic bromate reduction were usually conducted under UV light illumination [2,12,13], or had limited photocatalytic reduction efficiency [1,14]. To enhance the photocatalytic reduction efficiency, sacrificial agents are usually needed to deplete the photogenerated holes [12,15,16]. However, it could increase the complexity and cost of the operation, and may not be appropriate for drinking water treatment due to the addition of substances with potential hazard.

For the enhancement of the photocatalytic efficiency, noble/transition metal modification is widely used as the electron trapping center to enhance the photogenerated electron-hole pair separation due to their relatively high work functions [17–19]. However, this material design strategy could not deplete photogenerated holes with strong oxidation capability, and the addition of sacrificial agents is still needed for the efficient photocatalytic reduction. It would be most desirable to design a photocatalyst

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system for photocatalytic reduction in which the charge carrier recombination could be minimized by modifications with hole trapping and consumption capability. Thus, the addition of sacrificial agents could be removed to solve problems associated with it. As a semimetal element (a weak overlap exists between its valence and conduction bands), bismuth may provide the hole trapping and consumption capability. Unlike most metals, bulk Bi has a relatively low work function of ~ 4.22 eV [20], close to that of TiO_2 at ~4.20 eV [21]. With its size decrease into the nano range, the quantum confinement could induce a transition from metal to semiconductor on Bi with the moving up of its conduction subbands and moving down of its valence subbands [22]. So photogenerated electrons could not transfer from TiO_2 to Bi quantum dots anymore, while photogenerated holes could transfer from TiO_2 to Bi quantum dots and be consumed by oxidizing Bi^0 to Bi^{3+}. Thus, it could enhance the lifetime of photogenerated electrons for an efficient reduction process, while no sacrificial agents are needed to deplete holes. Although several Bi-modified semiconductor photocatalysts had recently been reported in literature, including Bi/TiO_2 [23], Bi/BiOCl [24], $Bi/(BiO)_2CO_3$ [25], and Bi/Bi_2O_3 [26], they relied on the traditional electron trapping or plasmonic function of Bi as a transition metal, which could not trap/consume holes for an enhanced photocatalytic reduction.

Compared with commonly used anatase TiO_2, rutile TiO_2 has a relatively smaller bandgap of ~3.0 eV, beneficial for the visible light absorption and subsequent photocatalytic activity under visible light illumination if its intrinsic fast recombination rate of photogenerated electron and hole pairs could be suppressed [27]. In this study, we developed a one-pot, solvent-thermal process to synthesize the Bi/TiO_2 (rutile) heterojunction photocatalyst. It demonstrated a superior photocatalytic reduction of bromate without the addition of sacrificial agents under visible light illumination, which could be attributed to the dual modification effects of Bi quantum dots on both the enhanced charge carrier separation and the trapping/consumption of holes.

2. Experimental

2.1. Materials and chemicals

All chemicals were of analytical grade and were used without further purification. Degussa P25 TiO_2 nanoparticles and rutile TiO_2 nanoparticles were purchased from Aladdin Industrial Corporation (Shanghai, P. R. China). SiO_2 was purchased from Qingdao Haiyang Chemical Corporation (Qingdao, P. R. China). Ethylene glycol, polyvinylpyrrolidone (PVP, K-30), bismuth nitrate pentahydrate, sodium bromate and $HAuCl_4·3H_2O$ were purchased from Sinopharm Chemical Reagent Corporation (Shanghai, P. R. China). Deionized (DI) water (18.2 MΩ) was produced by an ultrapure water system.

2.2. Synthesis of photocatalysts

In a typical synthesis process, 1 mL 10 M HNO_3 and 9 mL DI water were added into 50 mL ethylene glycol under continuous stirring. Then, 0.061 g $Bi(NO_3)·5H_2O$ and 1 g PVP (K-30) were added into this solution successively, and the solution was stirred continuously to ensure that all reagents were dissolved. After the solution became transparent, 1 g rutile TiO_2 nanoparticles were dispersed into the solution with the molar ratio of Bi/Ti at 1%, and the mixture was stirred for another 30 min to ensure the good dispersity of these rutile TiO_2 nanoparticles before it was transferred into a 50 mL Teflon-lined stainless steel autoclave. The solvent-thermal process was conducted at 160 °C for 24 h. After the reaction, the precipitate was centrifuged, washed several times with ethanol and DI water, respectively, and then dried at 60 °C in vacuum for 12 h to obtain the final product of the Bi(1.0)/rutile TiO_2 photocatalyst. For comparison purpose, the Bi(1.0)/SiO_2 sample, the Bi(1.0)/P25 TiO_2 photocatalyst and the Au(1.0)/rutile TiO_2 photocatalyst were also prepared by the similar solvent-thermal process. For the Bi(1.0)/SiO_2 sample, Bi(1.0)/P25 TiO_2 photocatalyst, SiO_2 nanoparticles and P25 TiO_2 nanoparticles were used to replace rutile TiO_2 nanoparticles, respectively, while $HAuCl_4·3H_2O$ was used to replace $Bi(NO_3)·5H_2O$ to obtain the Au(1.0)/rutile TiO_2 photocatalyst. Pure Bi nanoparticles were prepared by a hydrothermal synthesis method as previously reported [28]. The Bi_2O_3(1.0)/rutile TiO_2 photocatalyst was prepared by the calcination of the Bi(1.0)/rutile TiO_2 photocatalyst at 400 °C for 2 h in air.

2.3. Characterization of photocatalysts

The crystal structures of samples were obtained by X-ray diffraction (XRD) on a D/MAX-2004 X-ray powder diffractometer (Rigaku Corporation, Tokyo, Japan) with Ni-filtered Cu Kα ($\lambda = 1.54178$ Å) radiation at 56 kV and 182 mA. The sample morphology and selected area electron diffraction pattern were obtained on a JEOL 2100 transmission electron microscope (JEOL Ltd, Tokyo, Japan) operating at 200 kV. EDX spectrum measurement was conducted by a Model SUPRA55 SEM system (Zeiss, Germany) equipped with energy dispersive spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were conducted on an ESCALAB 250 X-ray photoelectron spectrometer (Thermo Fisher Scientific Inc., Waltham, MA, U.S.A.) with an Al K anode (1486.6 eV photon energy, 300 W). The UV–vis spectra of samples were measured on a UV-2550 spectrophotometer (Shimadzu Corporation, Kyoto, Japan). The surface photovoltage spectra (SPS) of samples were measured with a home-built apparatus [29]. The Bi content in the Bi(1.0)/TiO_2 (rutile) catalyst was determined with an inductively coupled plasma mass- spectrometer (Perkin Elmer –SCIEX ELAN DRCe ICP-MS, Norwalk, CT, USA).

2.4. Photocatalytic reduction of bromate under visible light illumination

In this study, bromate was chosen as a model pollutant to evaluate the photocatalytic reduction performances of different photocatalysts under visible light illumination. In a typical experiment, 40 mg photocatalyst was loaded into a glass beaker, which contained 80 mL aqueous bromate solution (10 mg/L). A 300-W xenon lamp (PLSSXE300, Beijing Perfect Light Technology Co., Ltd., Beijing, P. R. China) was used as the light source, which had a glass filter to provide zero light intensity below 400 nm. Before the photocatalytic treatment, the suspension was magnetically stirred in dark for 0.5 h to reach the adsorption/desorption equilibrium. At each time interval, 5 mL suspension was withdrawn and the photocatalyst was separated by centrifugation at 10,000 rpm for 5 min. The concentrations of bromate and bromide in the supernatant solution were analyzed by ion chromatography (Dionex ICS 1100 Ion Chromatograph with a conductivity cell).

3. Results and discussion

3.1. Material design for efficient photocatalytic reduction without the addition of sacrificial agents

The deposition of Bi quantum dots on rutile TiO_2 nanoparticles is the key in our material design for highly efficient photocatalytic reduction under visible light illumination. Fig. 1a and b shows the energy band alignment diagrams for rutile TiO_2/bulk Bi and rutile TiO_2/Bi quantum dots, respectively. The conduction band (CB) bottom and valence band (VB) maximum of rutile TiO_2 are ~−0.59

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