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Construction of TiO_2 nanobelts-Bi_2O_4 heterojunction with enhanced visible light photocatalytic activity

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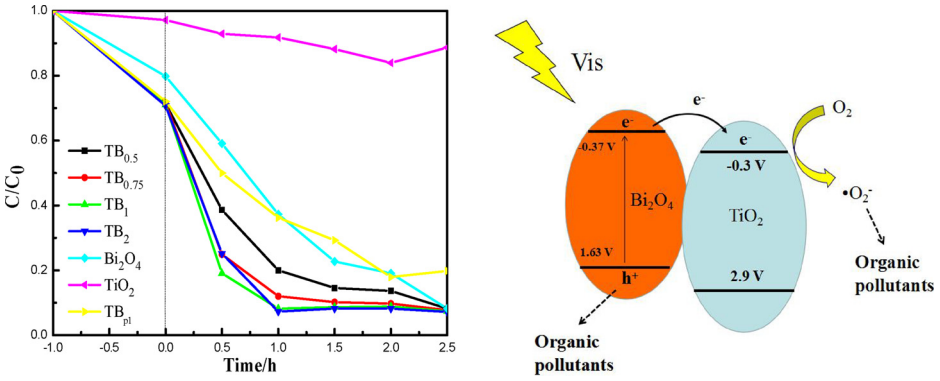
GRAPHICAL ABSTRACT



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ABSTRACT

A novel TiO_2 nanobelts-Bi_2O_4 (TB) type II heterojunction was constructed by a two step method. The photocurrent density of TB_1 (mass ratio, $Bi_2O_4/TiO_2 = 1:1$) heterostructure under visible light is up to 0.064 μA/cm^2, which is about 2 times as large as that of Bi_2O_4 (0.035 μA/cm^2). In agreement well with the photocurrent, TB_1 shows a much smaller arc radius in the electrochemical impedance spectrum than Bi_2O_4 under visible light irradiation. Therefore, in the TB hybrid, the charges migration between Bi_2O_4 and TiO_2 via the heterojunction could improve the electron/hole separation efficiency and prolong the lifetime of electron and hole. In addition, TB heterostructures with much higher specific surface area than pure Bi_2O_4 could provide more active sites for the adsorption of reactant molecules. As a result, the TB heterojunctions exhibit enhanced visible light photocatalytic activity for the degradation of methyl orange and phenol than Bi_2O_4. The hole and $\cdot O_2^-$ radicals were identified as the main reactive species in the photocatalysis process.

1. Introduction

Since Fujishima and Honda discovered the photoelectrocatalysis behavior of TiO_2 electrode, TiO_2-based materials have been extensively investigated as photocatalysts [1–7]. Owing to its wide band gap, especially for anatase TiO_2 (3.2 eV), however, TiO_2 only absorbs UV light which accounts for about 4% of the entire solar spectrum. To make full use of solar light, therefore, developing visible light responsive

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photocatalysts with narrow band gap has attracted much attention in recent years [8–14]. Bismuth-containing oxides are recognized as promising materials for their narrow band gap derived from the interaction between 6 s Bi and 2p O orbitals at the top of the valence band [15]. It has been demonstrated that Bi_2O_3 [16], $CuBi_2O_4$ [17], BiOX (X = Cl, Br, I) [18], $Bi_2Ti_2O_7$ [19], $KBiO_3$ and $NaBiO_3$, have shown excellent photocatalytic activity under visible light. Up to date, most of reported bismuth-based oxides were mainly focused on Bi^{3+} or Bi^{5+}-containing oxides, however, bismuth oxides with mixed valent states have rarely been reported.

Hameed firstly investigated the photocatalytic performance of Bi_2O_{4-x} with mixed valent states. It was found that Bi_2O_{4-x} exhibited good performance for the degradation of phenol. Furthermore, a much higher degradation rate was observed for Bi_2O_3/Bi_2O_{4-x} nanocomposite synthesized by irradiation of Bi_2O_3 with 450 W medium pressure mercury vapor lamp in the aqueous medium, compared to pure Bi_2O_3 [9]. Recently, Hameed further reported sunlight induced formation of Bi_2O_{4-x} species on the surface of Bi_2O_3 also exhibited enhanced photocatalytic activity for the degradation and mineralization of 2-chloro and 2-nitrophenol [20]. It is deemed that the formation of a trace amount of Bi_2O_{4-x} phase on the surface of Bi_2O_3 favor the visible light harvesting and photocatalytic activity improvement. $NaBiO_3$, a pentavalent bismuthate with a band gap of 2.6 eV, is an alternative promising visible light responded photocatalyst [21]. However, its photocatalytic activity is expected to be further improved to satisfy the practical application. Ding et al. developed a facile method to realize the controllable Bi^{3+} self-doping $NaBiO_3$ photocatalyst via acidic hydrolysis of $NaBiO_3{\cdot}2H_2O$ in inorganic acid aqueous solutions such as HNO_3 or HCl. In comparison with $NaBiO_3$, the Bi^{3+} self-doped $NaBiO_3$ exhibited much higher photocatalytic removal efficiency for rhodamine B and bisphenol A under visible light illumination, resulting from the extended response range of visible light and the superior separation efficiency of photogenerated h^+/e^- pairs [22]. These results indicate strongly bismuth oxides with mixed valence may be a desirable candidate for photocatalytic applications under visible light.

Inspired by the previous works, Wang et al. [23] revealed the physicochemical and photocatalytic performance of monoclinic dibismuth tetraoxide (Bi_2O_4), with the formula of $Bi^{3+}Bi^{5+}O_4$, which was firstly prepared by Kumada et al. [24], but its application as photocatalyst was not studied previously. Theoretical calculation and experimental results indicated that Bi_2O_4 has band gap energy of 2.0 eV, and the response wavelength can be up to 620 nm. Furthermore, this Bi_2O_4 exhibited favorable activity for the degradation of typical dyes such as rhodamine B, methyl orange, and methyl blue, as well as colorless aromatic compounds including phenol and 4-nitrophenol. However, the fast charges recombination in Bi_2O_4 under visible light results in the loss of photocatalytic activity [25,26]. In order to develop Bi_2O_4 as a promising photocatalyst with high activity for versatile pollutant degradation under visible light, it is highly desirable to decrease the recombination probability of photoinduced charge carriers and enhance the photocatalytic ability.

Construction of heterostructured hybrid by coupling two or more components with matched band edge potential is generally regarded as an effective strategy to promote the charges separation and enhance photocatalytic activity of photocatalysts. For the case of Bi_2O_4, up to date, heterostructured composites such as Bi_2O_4/Fe_3O_4, Bi_2O_4/BiOBr and g-C_3N_4/Bi_2O_4 exhibited enhanced visible light photocatalytic activity on account of the improved separation efficiency of electron-hole pairs [25,27–30]. The edge potential of the valence-band maximum (VBM) of Bi_2O_4 is less positive while the conduction-band minimum (CBM) is more negative than that of TiO_2 [23,31]. Thus, combination of TiO_2 with Bi_2O_4 could have a staggered gap (Type II) offset, forming type II heterojunction. Under visible light excitation, this heterojunction effect will drive the photoinduced electrons of Bi_2O_4 to move to the conduction band of TiO_2, while the photogenerated holes of Bi_2O_4 will be still reserved in the valence band of Bi_2O_4 due to its less positive potential of valence band, resulting in highly efficient separation of electron-hole pairs. However, there have been no reports on Bi_2O_4-TiO_2 heterojunction photocatalysts up to now except our work. Recently, we synthesized core-shell structured Bi_2O_4@TiO_2 heterojunction with obviously enhanced visible light photocatalytic activity [26]. Nevertheless, it is hard to control the reaction kinetics for heterogeneous nucleation and the growth of TiO_2 on Bi_2O_4 because of titanium precursors with great reactivity [26,32].

In this work, a novel TiO_2 nanobelts-Bi_2O_4 heterojunction was designed and prepared by a two-step method. Firstly, TiO_2 nanobelts were synthesized by a simple hydrothermal procedure followed by acid corrosion treatment, using TiO_2 (P25) as raw materials. Then, one-pot hydrothermal method was used to fabricate TiO_2 nanobelts-Bi_2O_4 heterojunction. Compared with Bi_2O_4, the obviously enhanced photocurrent density and notably decreased arc radius in the electrochemical impedance spectrum of TiO_2 nanobelts-Bi_2O_4 heterostructure under visible light irradiation, prove a much lower recombination probability and a much higher separation efficiency of the electron–hole pairs at the TiO_2/Bi_2O_4 interface. In addition, TiO_2 nanobelts-Bi_2O_4 heterostructure with higher specific surface area could provide more active sites for the adsorption of reactant molecules. As a result, the TiO_2 nanobelts-Bi_2O_4 heterojunctions exhibit enhanced visible light photocatalytic activity for the removal of methyl orange and phenol than Bi_2O_4. The hole and $\cdot O_2^-$ were identified as the main reactive species in the photocatalysis process.

2. Experimental

2.1. Synthesis of TiO_2 nanobelts

Typically, 0.3 g TiO_2 powder (P25) was dispersed into 60 mL 10 M NaOH aqueous solution under violent stirring, and then transferred into a 100 mL Teflon-lined stainless steel autoclave, hydrothermally treated at 180 °C for 48 h. After cooled naturally to room temperature, the precipitate was washed to neutral with plenty of deionized water. The obtained wet powder was immersed in 0.01 M HCl for 36 h and then thoroughly washed with deionized water. Then, the obtained sample was dispersed in 0.02 M H_2SO_4 aqueous solution and maintained at 100 °C for 12 h. After that, the products were filtered and washed to remove any impurities, and dried at 70 °C overnight. Finally, the acid-corroded products were calcined at 600 °C for 2 h to obtain anatase TiO_2 nanobelts [33].

2.2. Preparation of TiO_2 nanobelts-Bi_2O_4 heterojunction

TiO_2 nanobelts-Bi_2O_4 heterojunction was prepared by hydrothermal method [23]. In a typical synthesis, a certain amount of TiO_2 nanobelts and sodium bismuthate were dispersed in 60 mL deionized water and stirred for 30 min. The mixed precursor suspension was sealed into an autoclave and heated at 160 °C for 12 h. After cooling down naturally, the resultant product was filtrated and washed with deionized water for three times. At last, the as-prepared powers were dried at 60 °C overnight and named as TB_x, where x means the mass ratio of Bi_2O_4 to TiO_2. As a control, the physical mixture of TiO_2 nanobelts and Bi_2O_4 was also prepared. Bi_2O_4 was mixed with TiO_2 nanobelts in a mass ratio of 1:1 and ground in a mortar for 30 min. As-prepared physical mixture of TiO_2 nanobelts and Bi_2O_4 was named as TB_{p1}.

2.3. Characterization

The phase structure of the prepared samples was measured by the X-ray powder diffraction technique using a Rigaku X-ray diffractometer. The morphology characteristics of samples were observed by field-emission scanning electron microscopy (FE-SEM, Zeiss, Sigma) and JEM 2100 transmission electron microscope (TEM). Specific surface areas were obtained by using Quantachrome ASIQM000-200-6 automated