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Hydrothermal synthesis of novel heterostructured Fe_2O_3/Bi_2S_3 nanorods with enhanced photocatalytic activity under visible light

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ABSTRACT

The development of efficient visible-light photocatalyst heterostructures remains a major concern for obtaining desirable material properties and effective carrier transformation. Here, we demonstrate, for the first time, the synthesis of novel heterostructures of Fe_2O_3/Bi_2S_3 nanorods via a one-step hydrothermal route and employed effectively as visible-light-driven photocatalysts for the degradation of organic pollutants of methylene blue dye (MB) and phenol. TEM and FE-SEM images displayed that Fe_2O_3/Bi_2S_3 heterostructure is nanorods with ~30–60 nm diameter and 0.5–1 μm length. The newly prepared Fe_2O_3/Bi_2S_3 nanorods exhibit greatly enhanced photocatalytic activity toward both MB and phenol compared to pure Bi_2S_3 and the heterostructure with low molar ratio of 0.06 Fe_2O_3/Bi_2S_3 exhibits the best photocatalytic activity under visible light irradiation. A maximum degradation efficiency of MB and phenol ~90% and 96% was accomplished using Fe_2O_3/Bi_2S_3 nanorods compared to only 60% and 69% using pure Bi_2S_3, respectively. The photodegradation rates for MB and phenol are promoted respectively as ~2.6 and 3 times using Fe_2O_3/Bi_2S_3 heterostructure higher than pure Bi_2S_3. Photoluminescence spectra measurement along with the calculation of relative band alignment indicated that Fe_2O_3/Bi_2S_3 heterostructure significantly suppress the recombination of photogenerated charge carriers, which is beneficial to improve the photocatalytic activity. The facile synthesis approach, unique photocatalytic activity and excellent reusability of the current Fe_2O_3 modified Bi_2S_3 nanostructure make it a promising photocatalyst for the environmental remediation related fields.

1. Introduction

Water pollution is a dominant component of environmental concerns and remains a major problem to be solved for a better quality of life. Contaminated wastewater is widely generated as effluents from different industries including petrochemical, textile, pharmaceutical and others [1]. Phenol is classified among the most toxic compounds and can present at considerable concentration in some industrial effluents [2]. In general, the concentration of phenol may vary from a few ppm up to 4 g/L, in a severe pollution case[3], whereas according to the Environmental Protection Agency (EPA) regulations, the maximum allowed level of phenol is 5 ppm (19 mg/m^3) [4]. Even at very low concentration, phenol can be a very harmful to living organisms. For example, ingestion of phenol-contaminated water in human body may cause protein degeneration, erosion of tissues, damages to the kidneys, liver, etc., [5]. Another type of organics includes synthetic dyes which are often found in the environment as a result of their wide industrial uses such as in cosmetics, colored paper, textiles, inks, plastics and food. More than 100,000 different commercial dyes and pigments are available with ~7–10 tons of dyestuff produced annually [6,7]. The discharge of very low level concentration of dyes (~1 ppm for some dyes) would have hazardous effects on environment as well as the biological life [2]. Wastewater is one of the main sources that releasing ~10–15% of the overall dye production into the environment [8]. The natural decomposition of some dyes could lead to the formation of carcinogenic compounds [9,10]. Therefore, there has been increasing interest to harness and develop the advanced oxidation processes (AOPs) as efficient, advantageous approach for

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the degradation of organic species in wastewater. Among the AOPs, photocatalysis under visible or ultraviolet (UV) light is a key strategy for water decontamination as it can lead to fast, complete mineralization of pollutants with no harmful residues and has been extensively studied as a technology of choice in this field [11–13].

The design of new heterostructured semiconductors using a simple, efficient technique is an existing challenge in materials science and chemical engineering fields [14]. The fabrication of appropriate heterostructure would provide better band gaps alignment which could lead to an effective separation of the photogenerated charge carriers [15]. Good overlapping between the electronic states of the heterostructure interface likely promotes intra-particle charge transfer [16,17]. Unique category of heterostructures is the plasmonic nanoparticles coupled with different semiconductors including for examples Au-supported CdS catalysts and Au/TiO_2 nanohybrids for the photocatalytic hydrogen production [18,19], AgNPs/black phosphorus nanosheets for visible-light photocatalysis [20] and AuNPs with $CH_3NH_3PbI_3$ perovskite structures [21]. Such unique material characteristics make it possible for the harvesting of solar light, and hence their potential uses in photocatalysis, optoelectronics, photovoltaics, and others [22]. Binary metal chalcogenides with a formula $A_2{}^{V}B_3{}^{VI}$ (A = As, Sb, Bi; B = S, Se, Te) are categorized as one of the leading, attractive class of materials [23]. Particularly, bismuth sulphide (Bi_2S_3) is well studied for its potential applications in photo-electrochemical solar cells [24,25], lithium ion batteries [26], gas sensors [27], Schottky diodes [28], thermoelectricity [29], and hydrogen storage [30]. Bi_2S_3 has a direct narrow band gap (1.3–1.7 eV) [31], which could absorb visible light ($\lambda \leq 800$ nm), allowing its proper use as a visible-light photocatalyst [32]. However, due to its narrow band gap, a rapid recombination of the photogenerated charge carriers is often observed, which limits greatly the photocatalytic activity under either UV or visible light irradiation [14]. On the other hand, transition metal oxides have special interest in developing cost-effective, alternative photocatalysts to the conventionally employed noble metal-based catalysts [33]. Among these, Fe_2O_3 has been explored as low-cost, environmental friendliness catalysts for a range of catalytic processes including oxidations [34], couplings [35], and alkylation-based processes [36]. Having a band gap of ca. 2.2 eV, Fe_2O_3 could act also as a visible-light-driven photocatalyst [37]. Nevertheless, the photocatalytic activity of pure Fe_2O_3 is not satisfactory owning to its low carrier mobility, short life of minority carriers (~10 ps) and diffusion length (~2–4 nm) [38]. Aiming to overcome these limitations, we present a simple hydrothermal route for synthesizing heteronanostructure of Fe_2O_3/Bi_2S_3 nanorods, which, to the best of our knowledge, has not been developed so far. The as-obtained Fe_2O_3 modified Bi_2S_3 nanorods exhibited enhanced photocatalytic activities for degrading both methylene blue (MB) dye and phenol as a two models of organic pollutants under visible light irradiation. The synthesis and characterization of Fe_2O_3/Bi_2S_3 photocatalyst, mechanism of catalytic performance along with its reusability have been addressed and thoroughly discussed.

2. Experimental

2.1. Material

All chemicals used in this study were analytical grade reagents and were purchased from Sigma-Aldrich. Bismuth (III) nitrate penta-hydrate $Bi(NO_3)_3{\cdot}5H_2O$ and thiourea $(NH_2)_2S$ were employed as precursors of Bi and S, respectively. Iron nitrate $Fe(NO_3)_3{\cdot}9H_2O$ was chosen as a precursor for Fe_2O_3. Methylene blue (MB) dye and phenol were used as target organic molecules.

2.2. Hydrothermal synthesis of Fe_2O_3/Bi_2S_3 nanostructures

Fe_2O_3 modified Bi_2S_3 nanorods were synthesized by a one-step hydrothermal process, adapted from our recently reported method for obtaining pure Bi_2S_3 [39]. In a typical synthesis protocol, 4.0 g $Bi(NO_3)_3{\cdot}5H_2O$ and 1.25 g $(NH_2)_2S$ were first dissolved in 100 mL deionized water. Then, different amounts of $Fe(NO_3)_3{\cdot}9H_2O$ ~0.04, 0.08, 0.12, 0.16, 0.20, 0.24 and 0.28 g were added to the above solution under vigorous stirring for 10 min at 60 °C to obtain 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.07 Fe_2O_3:Bi_2S_3 molar ratios, respectively. The solution was transferred into a Teflon-lined stainless steel autoclave and heated at 180 °C for 20 h. After the autoclave was cooled to room temperature, the resulting product was separated by centrifugation and washed several times with water and absolute ethanol and finally dried at 60 °C for 8 h.

2.3. Characterization of photocatalysts

The phase and crystal structure of the as-synthesized photocatalysts were examined by X-ray diffraction (XRD) using a BRUKER D8 advance with Cu target (λ 1.54 Å). Measurements were collected at 40 kV and 40 mA, for 2θ from 10 to 80°, with a 0.05° step size and 3 s count time. For morphological investigation, a JEOL JSM-2010 transmission electron microscope (TEM) operating at 200 kV was used with recording selected-area electron diffraction (SAED) pattern. A trace amount of powder was dispersed in ethanol followed by 20 min ultrasonication. A carbon film coated copper grid was immersed into the dispersion and left for drying. FESEM (QUANTA FEG 250) equipped with energy dispersive X-ray spectroscopy (EDS) was also used for further structural and chemical analysis. X-ray photoelectron spectra (XPS) were collected using a VG Escalab 200R electron spectrometer equipped with a MgKα ($h\nu = 1253.6$ eV, $1\ eV = 1.6302 \times 10^{-19}$ J) X-ray source powered at 100 W. The binding energies (BE) were calibrated reference to the C1 s peak at 284.8 eV. The photoluminescence (PL) spectra were collected at room temperature using F-7000 FL spectrophotometer, HITACHI with a 150 W xenon lamp as an excitation source at 450 nm excitation wavelength. The band gap energy (E_g) of Fe_2O_3/Bi_2S_3 was estimated using diffuse reflectance spectroscopy (DRS). The reflectance spectra in a wavelength range 200–800 nm were measured by a JASCO V-570 UV–vis spectrophotometer equipped with a Labsphere integrating sphere diffuse reflectance accessory using $BaSO_4$ as a reference [40]. The UV–vis spectra were collected in the diffuse reflectance mode (R) and transformed to the Kubelka-Munk function F(R) to separate the extent of light absorption from scattering. The E_g values were accordingly obtained from the plot of the modified Kubelka-Munk function $(F(R)E)^2$) versus the energy of the absorbed light E, according to the following formula [41].

$$F(R)E^2 = \left(\frac{(1-R)^2}{2R} \times h\upsilon\right)^2$$

2.4. Photocatalytic properties

The photocatalytic activity of heterostructure Fe_2O_3/Bi_2S_3 nanorods was evaluated by the degradation of MB and phenol under visible light irradiation using 1000 W halogen lamp. In a typical process, 0.5 g/L photocatalyst was added to MB [10 mg/L] solution in a quartz photoreactor with water circulation for cooling. Before illumination, the solution was magnetically stirred in the dark for 30 min to reach adsorption equilibrium between the organic pollutants and photocatalysts. Subsequently, the stirred solution was photo-irradiated by visible light. The MB concentration after equilibration was denoted as the initial concentration (C_o). At given time intervals, 3 mL solution was taken and the sus-