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Efficient synthesis of sunlight-driven ZnO-based heterogeneous photocatalysts

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ABSTRACT

A series of ZnO-based heterogeneous photocatalysts, including Ag-ZnO, ZnO- and Ag-ZnO-reduced graphene oxide (rGO) nanocomposites, was successfully synthesized by a one-pot solvothermal route. The as-synthesized products were systematically characterized using combined techniques of X-ray diffraction, X-ray photoelectron spectrometry, electron microscopy, and energy dispersive spectrometry. The resulting ZnO-based photocatalysts exhibited selective photocatalytic behavior towards the degradation of different organic dyes under solar light irradiation. Compared with plain ZnO nanoparticles, the heterogeneous nanocomposite photocatalysts of Ag-ZnO, ZnO- and Ag-ZnO-rGO showed significantly improved photocatalytic activities. The Ag-ZnO nanocomposite exhibited the highest photocatalytic efficiency, which can be ascribed to its core-shell structure with strong interfacial coupling between the Ag shell and the ZnO core as well as the surface plasmon resonance effect of the Ag. The ZnO- and Ag-ZnO-rGO nanocomposites displayed excellent recyclability, due to the strongly coupled interactions between the ZnO or Ag nanoparticles and the rGO support. The ZnO-rGO nanocomposite is the most promising candidate for photocatalysis application with excellent comprehensive performance. This study will not only provide guidance for the selection of ZnO-based heterogeneous photocatalysts, but also open new opportunities for the synthesis of other heterogeneous photocatalysts.

1. Introduction

With the rapid development of economy, environment pollutions and resource shortages are becoming a serious problem facing our society. Semiconductor photocatalysis is regarded as an efficient, green, and environmentally friendly technology for environment remediation and energy conservation, as it utilizes only solar energy to decompose pollutants [1], inhibit bacteria [2], split water to generate H_2 and O_2 [3], convert greenhouse gas CO_2 to organic molecules [4], *etc*. After the first photocatalytic water splitting using TiO_2, semiconductor photocatalysts have received increasing research attentions [5–7]. To date, a great number of semiconductor photocatalysts, including binary compounds such as TiO_2 [8], ZnO [9], WO_3 [10], GaN [11], and C_3N_4 [12], and ternary compounds such as BiOX (X = Cl, Br and I) [13], Bi_2WO_6 [14], $BiVO_4$ [15], $ZnWO_4$ [16], and Ag_3PO_4 [17], have been reported. It is generally accepted that oxide semiconductors are promising candidates for photocatalytic applications, due to their high chemical and photoelectrochemical stability, easy to produce, low cost, and good controllability. Among various oxide semiconductors, TiO_2 is the most widely studied photocatalyst [18–20]. However, TiO_2 absorbs only UV light due to its wide band gap (3.2 eV), thus unsuitable for applications under solar light. Another similarly widely studied photocatalyst is ZnO. Although the photocatalytic efficiency of ZnO is not as high as TiO_2, it is still considered as a competitive and promising alternative for TiO_2, owing to its nontoxicity, biocompatibility, low manufacturing cost, ease of crystallization, and high electron mobility [21,22]. In addition, ZnO has been demonstrated to exhibit enormous applications in electronic devices such as piezoelectric nanogenerator [23], varistor [24], ultraviolet (UV) lasers [25], and solar cells [26]. Notably, ZnO is susceptible to photo-corrosion, which could significantly influence the recyclability of ZnO as photocatalyst. Thus, the development of novel ZnO-based photocatalysts with high light-harvesting efficiency and ideal photocatalytic stability is an important subject of research.

The construction of heterogeneous photocatalysts is an effective strategy to improve both the photocatalytic activity and stability of semiconductor photocatalysts. The multiply integrated functional components could offer the combined advantages for a photocatalytic process, *i.e.* enhanced light absorption, and efficient charge separation and transfer between the interfaces of single components [27]. In the past decades, noble metal-ZnO heterogeneous photocatalysts were intensively investigated, due to the surface plasmon resonance (SPR) effect

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of the noble metal. For example, Au-ZnO hybrid nanoarchitecture [28], Au-ZnO nanopyramids [29], Ag-ZnO nanorods array [30], Ag-ZnO composite [31], Ag-ZnO hybrid nanospindles [32], Ag-ZnO flower heterostructure [33], and Ag-ZnO nanocomposite [34], have been synthesized. These ZnO-based composites indeed exhibited improved photocatalytic activities compared with pure ZnO. Recently, coupling of ZnO with graphene and it derivatives such as graphene oxide (GO) and reduced graphene oxide (rGO) has been studied [35–40]. Similar to the metal-ZnO heterojunctions, the GO or rGO in the hybrid composites could facilitate the heterogeneous reactions at the interface between GO or rGO and the ZnO and promote the charge separation and transfer, leading to the restriction of electron-hole recombination, thus they display superior photocatalytic activities.

To date, a large number of ZnO-based heterogeneous photocatalysts have been studied and they have been found to exhibit significantly improved photocatalytic properties compared to the pure ZnO photocatalysts. However, these works have been focused mainly on the photocatalyst fabrication and photocatalytic performance assessments. Little attention has been devoted to the direct comparison of different categories of ZnO-based heterogeneous photocatalysts. Without such comparison, the design and selection criteria for ZnO-based heterogeneous photocatalyst with optimal and comprehensive performance remain unclear. In addition, an effective route to the synthesis of different categories of ZnO-based heterogeneous photocatalysts is still lacking and needs further studied.

In this work, we demonstrate the successful synthesis of a series of ZnO-based heterogeneous composite photocatalysts, including ZnO-rGO, Ag-ZnO, and Ag-ZnO-rGO, using a simple one-pot solvothermal process with $ZnCl_2$, $AgNO_3$, or both as precursors, GO as supports, and ethanol as solvent. The present solvothermal route is facile, efficient, flexible, and versatile, which could open new opportunities for the synthesis of other heterogeneous photocatalysts. The photocatalytic properties of the ZnO-based heterogeneous photocatalysts for the degradation of methyl orange (MO) and methyl blue (MB) dyes under solar light irradiation have been also compared. To the best of our knowledge, this is the first report on the direct comparison of different types of ZnO-based heterogeneous photocatalysts, which could provide selection criteria for their future environmental applications.

2. Experimental details

2.1. Materials

Zinc chloride ($ZnCl_2$, >98%), silver nitrate ($AgNO_3$, >99.8%), ethanol (EtOH), and deionized (DI) water were purchased from Sinophaem Chemical Reagent Co., Ltd. Graphene oxide (GO, >98.5%) sheets were provided by Sinocarbon™ Graphene Marketing Center. All chemicals were used as-received without further purification.

2.2. Synthesis

2.2.1. ZnO nanoparticles

100 mg of $ZnCl_2$ was firstly dissolved in 30 ml of EtOH in a centrifuge tube under ultrasonic vibration for 20 min. The solution was subsequently transferred into a Teflon-lined high-pressure reaction vessel of 50 ml capacity. The reaction vessel was sealed and then put into a Muffle furnace and heated at 200 °C for 6 h. After the vessel was naturally cooled to room temperature, we took out the product, which was washed for three times with water, and then collected by centrifugation with EtOH.

2.2.2. ZnO-rGO nanocomposite

In a typical synthesis, 5 mg of GO sheets was firstly dissolved in 25 ml of EtOH in a centrifuge tube under ultrasonic vibration for 1 h. 50 mg of $ZnCl_2$ was dissolved in 5 ml of EtOH in another centrifuge tube under ultrasonic vibration for 20 min. Then they were mixed in the Teflon-lined reaction vessel, which was heated under the same conditions as above. Finally, we collected the product by centrifugation with EtOH.

2.2.3. Ag-ZnO nanocomposite

For the preparation of Ag-ZnO nanocomposite, the procedure was as the same to the synthesis of ZnO-rGO, except that the GO sheets were replaced by $AgNO_3$. After the same heating process, we also collected the final product by centrifugation with EtOH.

2.2.4. Ag-ZnO-rGO nanocomposite

For this synthesis, we mixed the three sonicated tubes that containing 5 mg of GO sheets, 50 mg of $ZnCl_2$, and 50 mg of $AgNO_3$ in 15 ml, 5 ml and 10 ml of EtOH, respectively, into the reaction vessel, and used the same heating procedure as above. The resulting product was also washed with water for three times and then collected by centrifugation with EtOH.

2.3. Characterization

The crystal structure of the as-prepared samples was determined by X-ray diffraction using a D/MAX-2500 X-ray diffractometer with Cu K_α irradiation ($\lambda = 1.5406$ Å) at a scanning rate of 0.02°/s. The morphologies of the resultant products were studied using a FEI Tecnai G20 transmission electron microscope (TEM), operated at 200 kV. Scanning electron microscopy (SEM) imaging and energy dispersive spectrometry (EDS) analysis were performed on a SU8020 filed emission SEM machine equipped with an IXRF energy spectrometer, operated at 15 kV. The surface chemistry was characterized using a Thermo ESCALAB 250XI X-ray photoelectron spectrometer (XPS), with a monochromatic Al kR X-ray source (1486.6 eV). Peak fitting of XPS spectra was performed with the help of the XPSpeak software using Shirley background. UV–vis diffuse reflectance spectra were recorded on a Lambda 35 UV–vis spectroscope, in the wavelength range of 200–1100 nm.

2.4. Photocatalytic activity tests

For the photocatalytic evaluation, the aqueous solutions of MO and MB were used as the target pollutants. The degradation tests of MO and MB aqueous solutions were carried out outdoors at noon on sunny days under solar light irradiation at room temperature (~35 °C) in September, Shanghai. The solar irradiation intensity was in the range of 930–960 W/m^2, according to the Building Meteorological Parameter Standard (JGJ35–87) provided by Ministry of Environmental Protection of the People's Republic of China. For each test, 5 mg of the as-prepared photocatalysts were dispersed in 10 ml of MO or MB solutions with a concentration of 10 mg/l in a glass tube. Prior to the tests, the MO or MB aqueous solutions containing the photocatalysts were kept in the dark for 12 h, to reach an adsorption-desorption equilibrium, they were then exposed to the sunlight directly. After given time intervals, the suspensions were centrifuged to remove the photocatalysts completely at 5000 rpm for 5 min. Aliquots of the residual transparent MO or MB solutions were transferred to a cuvette for UV–vis diffuse reflectance measurement of the absorption spectra. The photocatalysts recovered by centrifugation were used for subsequent recyclability tests, by using the same procedures as the first cycle.

The photocatalytic efficiencies of different photocatalysts over MO or MB are defined by the relative ratios of C/C_0, where C is the concentration of MO or MB aqueous solution after sunlight irradiation at predefined time (t), and C_0 is their concentration at the equilibrium adsorption state. C and C_0 were determined by the relative absorbance (A/A_0) at 465 nm and 665 nm, respectively, where A is the absorbance of MO or MB after sunlight irradiation at predefined time (t), and A_0 is the absorbance at equilibrium.