Chinese Journal of Catalysis 35 (2014) 1825–1832

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journal homepage: www.elsevier.com/locate/chnjc

Article

Rhodamine B degradation and reactive oxygen species generation by a ZnSe-graphene/TiO_2 sonocatalyst

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A R T I C L E I N F O

Article history:
Received 19 April 2014
Accepted 20 May 2014
Published 20 November 2014

Keywords:
Zinc selenide
Graphene-titanium
Hydrothermal reaction
Reactive oxygen species
Sonocatalysis

A B S T R A C T

Nanostructured ZnSe-graphene/TiO_2 was synthesized by a hydrothermal-assisted approach. ZnSe-graphene/TiO_2 exhibited favorable adsorption of rhodamine B, a wide wavelength absorption range, and efficient charge separation. Reactive oxygen species were generated by the oxidation of 1,5-diphenyl carbazide to 1,5-diphenyl carbazone. The sonocatalytic reaction mechanism was proposed. These findings potentially broaden the applications of sonocatalytic technologies.

1. Introduction

Industrial dyestuffs including textile dyes are a recognized environmental hazard. Physical, chemical, and biological methods have been used to treat such waste. Advanced oxidation processes include peroxone, non-thermal plasma, photo-Fenton, ultraviolet (UV)-O_3, UV/H_2O_2, and semiconductor treatments. These organic degradation processes can achieve the complete elimination and mineralization of various pollutants.

TiO_2 is an attractive material for photoelectric conversion and photocatalysis because of its low cost, ease of production, high photochemical and biological stability, and low toxicity [1,2]. Much effort has focused on extending the absorption of TiO_2 into the visible region, and thus increasing its photocatalytic activity. Semiconductor quantum dots have attracted enormous interest because of their potential in single electron transistors [3], lasers [4], light emitting diodes [5], and infrared photodetectors [6] operated at low current and high temperature. CdS [7], Ag_2S [8], ZnSe [9], Bi_2S_3 [10], and CdSe [11,12] all have been used to sensitize TiO_2.

Graphene-based composites have attracted much attention for their potential in electronics, photocatalysis, and photovoltaic devices [13–15]. Graphene can enhance charge transport in devices. This is because its delocalized electrons within its conjugated sp^2-hybridised framework impart high conductivity. Graphene-based nanocomposites containing Pd, Ag, Au, TiO_2, and metal selenides have all been reported [16–20]. Metal selenides can impart interesting electronic and optical properties in potential applications. ZnSe has a direct band gap of ~2.7 eV, making it well suited for solar absorption. Chen et al. [21] synthesized a N-doped graphene/ZnSe nanocomposite (GN-ZnSe) by a one-pot hydrothermal process at low temperature. GN-ZnSe exhibited favorable electrochemical performance in the oxygen reduction reaction, and favorable photocatalytic activity for bleaching methyl orange under visible-light irradiation.

Sonocatalytic technologies have been proposed in recent

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DOI: 10.1016/S1872-2067(14)60158-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 35, No. 11, November 2014

years. Their high efficiency without additional oxidants can lower the cost of treatment [22]. The sonocatalytic decomposition of organic pollutants can be enhanced in the presence of a photocatalyst. Combining ultrasound with solid photocatalyst particles can provide additional nuclei for cavitation bubble formation. Ultrasound can also enhance the mass transfer of organic pollutants between the liquid phase and catalyst surface and increase the active surface area by ultrasonic de-aggregating. Photocatalysts can be excited by ultrasound-induced luminescence. Such luminescence has a wide wavelength range and increases the production of hydroxyl radicals (•OH) in the reaction mixture [23]. Reactive oxygen species (ROS) such as superoxide radical anions ($•O_2^-$), •OH, hydrogen peroxide (H_2O_2), and singlet oxygen ($^1O_2$) are also generated [24].

Understanding the sonocatalytic degradation and ROS formed during ultrasonic irradiation may enhance the degradation efficiency and yield new sonocatalysts. Herein, we hydrothermally prepared a ZnSe-graphene/TiO_2 sonocatalyst [8,19,20]. The composite was used to ultrasonically degrade aqueous rhodamine B (RhB). The generated ROS were estimating by oxidation-extraction photometry. The reasons for the high sonodegradation activity of ZnSe-graphene/TiO_2 are discussed.

2. Experimental

2.1. Materials

Ethylene glycol and anhydrous ethanol were purchased from Daejung Chemical Co. (Korea). $ZnCl_2$, selenium metal powder, and NH_4OH (28%) were purchased from DaeJung Chemicals & Metal Co., Ltd. (Korea). Anhydrous Na_2SO_3 (95%) was purchased from Duksan Pharmaceutical Co., Ltd. (Korea). Titanium(IV) *n*-butoxide (TNB, $C_{16}H_{36}O_4Ti$, Kanto Chemical Company, Tokyo, Japan) was used as the Ti source in the preparation of TiO_2 and graphene/TiO_2 composites. Anatase TiO_2 (99.7%, Sigma-Aldrich, USA) with a particle size of <25 nm was used as a comparative sample. RhB (99.99+%, Samchun Pure Chemical Co., Ltd., Korea) was used as a model pollutant. All chemicals were used without further purification, and distilled water was used throughout experiments.

2.2. Synthesis of ZnSe-graphene/TiO_2

Graphite oxide (GO) was prepared from graphite according to the Hummers-Offeman method [19]. In brief, graphite powder (10 g) was dispersed in cold concentrated sulfuric acid (230 mL, 98 wt%, dry ice bath). $KMnO_4$ (30 g) was gradually added under cooling and vigorous stirring to prevent the temperature from exceeding 293 K. The dry ice bath was replaced with a water bath, and the mixture was heated to 308 K for 30 min under continuous stirring, with gas allowed to release. Deionized water (460 mL) was slowly added, which rapidly increased the solution temperature up to 371 K. The reaction was allowed to proceed for 40 min to increase the degree of GO oxidation. Reaction of the resulting bright-yellow suspension was terminated by adding distilled water (230 mL) followed by hydrogen peroxide (30%, 250 mL). The solid product was collected by centrifugation (3000 rpm), washed with 5% HCl until SO_4^- was no longer detectable with $BaCl_2$, washed three times with acetone, and air dried overnight in a vacuum oven. GO was transformed into graphene oxide sheets by sonication for 30 min at 308 K.

In a typical procedure, about 300 mg of GO and 22 mg of $ZnCl_2$ were ultrasonically dispersed in 100 mL of ethylene glycol for 1 h using a digital sonifer. This yielded a graphene oxide nanosheet (GONS)/Zn^{2+} solution (denoted solution A) [25]. Na_2SO_3 (5 g) and Se powder in 30 mL of water were refluxed for 1 h to form a Na_2SeSO_3 solution (denoted solution B). Solution B and 6 mL of NH_4OH (28 wt%) were added to solution A, which was heated to 333 K for several minutes. A colloidal TiO_2 solution in 35:15:4 ethanol:H_2O:TNB (denoted solution C) was added to the above mixture. The resulting solution was transferred to a polytetrafluoroethylene-lined stainless steel autoclave, which was then sealed. The contents were heated to 433 K for 6 h. The reaction was allowed to cool to room temperature. The precipitate was collected by filtration, washed thoroughly with water, dried in a vacuum oven at 353 K for 12 h, and then heated to 773 K for 1 h. ZnSe/TiO_2 [26] and GR-TiO_2 [19] were similarly prepared with a little modification.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra (FTS 3000MX, Biored Co., Korea) were recorded on a Perkin-Elmer spectrometer from KBr pellets. Spectra were recorded over the range 4000–400 cm^{-1} at 4 cm^{-1} resolution, with forward and reverse mirror speeds of 10 and 6.2 kHz, respectively. Crystal structures were observed by X-ray diffraction (XRD, Shimatz XD-D1, Japan) at room temperature with Cu K_α radiation. Diffuse reflectance ultraviolet-visible (DRS UV-vis) spectra were recorded using a spectrophotometer (Neosys-2000) equipped with an integrating sphere assembly. Morphologies were analyzed by scanning electron microscopy (SEM, JOEL JSM-5200, Japan) at an operating voltage of 3.0 keV. The SEM microscope was equipped with an energy dispersive X-ray (EDX) attachment. Transmission electron microscopy (TEM, JEOL JEM-2010, Japan) images were collected at an accelerating voltage of 200 kV and were used to examine particle sizes and distributions. Specific surface areas were determined using the BET method from N_2 adsorption isotherms at 77 K using a BET analyzer (Monosorb, USA).

2.4. Ultrasonic degradation of organic dye solutions

A controllable serial-ultrasonic apparatus (Ultrasonic Processor, VCX 750, Korea) was used to irradiate the RhB solution. The apparatus was operated at an ultrasonic frequency of 20 kHz and output power of 750 W through manual adjusting (3.04×10^6 J). In a typical experiment, 0.2 g of control sample and nanocomposite were added to 100 mL of RhB solution (2×10^{-5} mol/L). The suspension was magnetically stirred for 120 min in the dark to establish adsorption equilibrium. The concentration of adsorbed RhB (C_{ads}) was then measured, and the