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Original Research

Photocatalytic enhancement of Mg-doped ZnO nanocrystals hybridized with reduced graphene oxide sheets

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Abstract

Hybridization of Mg-doped ZnO and reduced graphene oxide (MZO–RGO) were synthesized through one pot reaction process. Crystallization of MZO–RGO upon thermal decomposition of the stearate precursors was investigated by X-ray diffraction technique. XRD studies point toward the particles size with 10–15 nm, which was confirmed by transmittance electronic microscopy, and also indicates that graphene oxide has been directly reduced into its reduced state graphene during the synthesis. Graphene hybridized MZO photocatalyst showed enhanced catalytic activity for the degradation of methylene blue (MB). The degree of photocatalytic activity enhancement strongly depended both on the coverage of graphene on the surface of MZO nanoparticles and the Mg doping concentration. The sample of 2 wt% graphene hybridized 5 at% Mg-doped ZnO showed the highest photocatalytic activity, which remained good photocatalytic activity after nine cycling runs.

Keywords: Mg-doped ZnO nanocrystals; Reduced graphene oxide; Nanohybrids; Photoactivity

1. Introduction

Low-cost semiconductor photocatalysts with high photocatalytic efficiency offer great potential for environmental purification and converting photon energy into chemical energy. As a wide band gap (3.37 eV at 300 K) semiconductor with large exciton binding energy (60 meV), ZnO is a promising versatile material, which has been intensively studied in the fields of blue–violet light emitting diodes (LEDs), ultraviolet detector, solar cells, field-effect transistors (FETs), sensors, photocatalysts [1,2]. Though ZnO is photocatalytically active, its band gap is not wide enough to utilize the high-engergy solar radiation. The bandgap of ZnO can be controlled via divalent substitution on the cation site. Substituting Mg on Zn site widens the bandgap of ZnO, and it is possible to obtain wide band gap Mg-doped ZnO alloys with different ratios of Mg doping, which could be in favor of photocatalytic activities of ZnO under ultraviolet (UV) light irradiation [3,4].

Graphene is a single two-dimensional carbon sheet with the same structure as the individual layers in graphite. Presently graphene-inorganic nanocomposites have been successfully synthesized and showed novel composite properties which were not found in the individual component [5–12]. Recently, it has been found out that the hybridization of ZnO with reduced graphene oxide (RGO) nanocomposites could improve photoelectric response effectively and also enhance the efficiency of charge separation and transfer, in which it was illustrated that the semiconductor surface would produce photoinduced electron–hole pairs which adsorb on the surface, resulting in the enhancement of conductivity under UV light irradiation [7,13–15].

In this paper, we discover the synthesis of Mg-doped ZnO–RGO nanohybrids through one pot reaction to achieve the composites in situ, which demonstrates a significant enhancement of the photocatalytic activity of nanocomposites under UV light irradiation. The approach we describe here will be promising for the future development of high-efficiency photocatalysts and optoelectronic devices.

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2. Experimental

2.1. Materials and measurements

All the reagents were analytical grade. The structural properties were analyzed using Cu Kα radiation (λ= 1.5406 Å) in the X-ray diffractometer (XRD, Bruker D8). The XRD data were collected for the 2θ range of 5° to 70° with step 0.01°. Transmission electron microscropy (TEM) images were obtained by Philips CM12/STEM Transmission Electron Microscope with an accelerating voltage of 120 kV. Fourier Transform Infrared (FT-IR) spectra were recorded in the 4000–400 cm^{-1} region by Bruker VERTEX-70 Fourier transform infrared spectrometer. Ultraviolet–visible (UV–vis) spectra of liquid methylene blue (MB) solution and solid MZO–RGO nanocomposites were performed on RAYLEIGH UV-1801 ultraviolet–visible spectrophotometer and SHIMADZU UV-2250 Ultraviolet–visible spectrometer, respectively. Samples were analyzed using a Thermo Scientific DXR dispersive Raman micro-spectrometer. It was equipped with a 532 nm Nd-YVO_4 laser, an automated confocal microscope (Olympus BX51) with a software-controlled x–y–z stage, and a Peltier-cooled charge-coupled device (CCD) detector. The Olympus MPlan-BD 100X objective (numerical aperture 0.9) was used. The laser beam with an output power of 24 mW irradiated the sample with a maximum power of 10 mW and an estimated spot size of 1 μm. The application of a grating with 900 grooves per mm and a pinhole with 25 μm diameter produced Raman spectra from 3500 cm^{-1} to 50 cm^{-1} with a spectral resolution of about 3 cm^{-1}. Raman spectra were collected in 10 accumulations of 5 s each, and peaks were identified by Thermo Scientific OMNICTM software. The frequencies of the Raman bands were monitored by 1001 cm^{-1} band of the standard polystyrene before and after each measurement, and the band-frequency accuracy was about 0.5 cm^{-1} (1σ level). All measurements were conducted under conditions of atmosphere pressure, room temperature (21 ± 1 °C) and humidity $< 50\%$.

2.2. Synthesis of graphene oxide (GO)

Graphene oxide (GO) was synthesized by a modified Hummers method [9,16]. At room temperature, 1.0 g of $NaNO_3$ and 50 mL of concentrated H_2SO_4 were weighed and placed into a conical flask. Then, 1.0 g of natural graphite was added into the conical flask with stirring, and this mixed solution was dropped to 0 °C in an ice-bath. Under the condition of ice-bath, 6.0 g of $KMnO_4$ was added into the mixture gradually under slowing stirring for 1 h. Then the solution was vigorously stirred for 3 h after the temperature rise to 25 °C. During this process, the color of the mixed solution was from green to brownish black. After adding 150 mL of twice-distilled water, the solution was heated up to 98 °C, and stirred for another 30 min. And then 30 mL H_2O_2 was added into the mixture when the temperature dropped to 60 °C. Finally, the mixed solution was washed for three times by 5 wt% HCl solution through centrifugation and ultrasonication. The remained sediment was dried at 60 °C for 24 h in the vacuum.

2.3. Synthesis of MZO–RGO nanohybrids

We use zinc stearate ($Zn(St)_2$) as zinc source and magnesium stearate ($Mg(St)_2$) as magnesium source. In the synthesis, the total molar quantity of precursors was set as 5 mmol. We obtained different Mg-doping levels by varying the molar concentrations of $Mg(St)_2$ in the precursors. According to the theoretical amount of the product of MZO, the added amount of GO for the synthesis is 2 wt% in the product of MZO–RGO.

The synthesis process of MZO–RGO nanohybrids with different Mg-doped concentration is as following. First, Zn $(St)_2$ and 40 mL of octadecene (ODE) were mixed into standard three-necked flask (250 mL) for heating, with removing the O_2 and H_2O (gas) in the system by N_2. 0.5 h later, the condensate water device was connected to the flask and then the system was heated to 270 °C. Meanwhile, the mixture of $Mg(St)_2$, GO and 10.0 g of octadecanol (ODA) were weighed and melted in a 50 mL beaker, which were stirred and heated by magnetic stirrer. Then the hot mixture solution was injected quickly into standard three-necked flask quickly, and the temperature of the system kept about 270 °C. The reaction lasted for certain time under the temperature of 270 °C. Finally, cooling the temperature down to 100 °C and then adding 80 mL ethyl acetate, the product was separated and purified by cyclohexane and methanol, respectively. The subsequent sediment was dried at 80 °C for at least 5 h in the vacuum oven.

2.4. Photocatalytic activity of MZO/RGO nanohybrids

About 12 mg of MZO–RGO nanoparticles were dispersed in 10 mg/L methylene blue (MB) solution with the volume of 21 mL [13], with lighting under the UV lamp (OSRAM ULTRA-VITALUX, 220 V, and 300 W). During the irradiation, we put the mixed suspension on the magnetic stirrer to make the nanoparticles dispersed homogeneously in the MB solution. The solution was collected every 15 min. In the cycling experiment, each time 12 mg MZO–RGO nanoparticles were dispersed in the fresh 10 mg/L MB solution with the volume of 21 mL, under the irradiation time of 30 min.

3. Results and discussion

3.1. Structural analysis

The crystalline structures of graphene oxide (GO) and Mg-doped ZnO/reduced graphene oxide (RGO) nanohybrids are demonstrated in Fig. 1. There is no characteristic peak of the (0 0 1) reflection of GO at $2\theta = 11.1°$ [17] in the XRD patterns of MZO–RGO nanocomposites. It indicates that graphene oxide has been directly reduced into its reduced state graphene through one pot reaction. As shown in Fig. 2 the concentration of Mg^{2+} and RGO and the reaction time have not changed the hexagonal wurtzite structure of ZnO (JCPDS card