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A facile route to reduced graphene oxide–zinc oxide nanorod composites with enhanced photocatalytic activity

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ABSTRACT

In this study, highly efficient photocatalysts were synthesized by the successful hybridization of ZnO nanorods (ZnO NRs) with reduced graphene oxide (RGO) by a facile and green hydrothermal process. The photocatalytic experimental results indicated that all the RGO–ZnO NR composite photocatalysts exhibited enhanced photocatalytic activity for the degradation of Rhodamine B (RhB) under UV-light irradiation. It is found that the degree of photocatalytic activity enhancement strongly depends on the mass ratio of RGO in the composites; the highest photocatalytic activity which equals to 6.8 times as that of pristine ZnO NRs can be obtained when the loading amount of RGO is 4.0 wt.% of RGO. The enhancement of photocatalytic activity can be attributed to the synergistic effect of the effective inhibition of the recombination of photo-generated electron–hole pairs and the elevated absorption ability for dyes, due to the strong electronic interaction between ZnO NRs and RGO nanosheets. Considering the facile and green method for the reduction of GO, the present investigation can be further employed to fabricate more graphene-based composites for various environmental and energy-related applications.

1. Introduction

Heterogeneous photocatalysts such as TiO_2, ZnO, and CdS have recently been extensively studied due to their great potentials for converting photon energy into chemical energy and degradation of organic pollutants in water or air [1–3]. In particular, ZnO is one of the most promising photocatalysts to remove the pollutants in water or air, due to its non-toxicity nature, chemical stability, high photosensitivity, large exciton binding energy (ca. 60 meV) and large direct band gap (3.37 eV) [4,5], and it has been proved that ZnO can exhibit a better efficiency than TiO_2 in photocatalytic degradation for some dyes [6,7]. However, the rapid recombination of photo-generated electrons and holes is still a major limitation to achieving higher photocatalytic activity of ZnO. Therefore, to enhance the photocatalytic efficiency, it is very essential to retard the recombination of the charge carriers.

Currently, composite or hybrid photocatalysts offer great potential to exhibit higher photocatalytic activity, owing to the enhanced charge separation by the internal electric field driving force as a result of different electronic energy levels between various components [8,9]. Thus, many works have been developed to suppress the recombination of charge carriers by coupling ZnO with noble metals [10,11], transition metal ions [12,13], other semiconductors [14,15], carbon nanotubes [16,17], polyaniline [18,19] and graphite-like carbon [20]. Moreover, ZnO–graphene composites also exhibit greatly improved photocatalytic activity due to the remarkable properties of graphene such as high conductivity, superior electron mobility, and extremely high specific surface area [21–25]. So far, various routes such as hydrothermal deposition [26], chemical vapor deposition (CVD) [27], microwave-assisted synthesis [28], ultrasonic spray pyrolysis [29] and electrochemical deposition [30] have been employed to prepare ZnO–graphene composites. Considering the requirements of high temperatures, expensive substrates, special devices and rigorous experimental conditions, hydrothermal approach can be used as an easy route to synthesize ZnO–RGO among these methods. However, many additives such as hydrazine, NH_3, $NaBH_4$, and ethylene glycol [26,31–33] have been widely employed in the current hydrothermal or solvothermal process to reduce GO, which not only involves hazardous or toxicity reagent but also results in severe aggregation of RGO. Therefore, the development of facile and green hydrothermal method for ZnO–graphene composites still remains a challenging issue to be resolved.

Herein, we first elucidated a facile and green hydrothermal route to obtain RGO–ZnO NR composites, during which the preliminary attachment of ZnO NRs to the surface of GO and the succedent in situ reduction of GO to RGO were achieved successfully. The harvested RGO–ZnO NR composites were employed to decompose Rhodamine B (RhB) under UV-light irradiation which exhibited higher photocatalytic performance than pristine ZnO NRs due to the improved adsorption

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ability for dyes and the efficient separation of photo-generated electron/hole pairs by RGO. Moreover, the effect of different contents of RGO in the RGO–ZnO NR composites on the photocatalytic degradation performance was also investigated.

2. Experimental

2.1. Synthesis of graphene oxide (GO)

The graphene oxide was synthesized from natural graphite powder (99.9%) using modified Hummers method [34]. Typically, 6 g of graphite, 5 g of $K_2S_2O_8$ and 5 g of P_2O_5 were added into 24 mL of concentrated H_2SO_4 under strong stirring at 90 °C for 5 h. After the mixture was naturally cooled down to ambient temperature, 1 L of deionized (DI) water was added into the mixture and aged overnight. Then, the mixture was filtered, washed and dried to obtain the black solid, which was sequentially mixed with 250 mL of concentrated H_2SO_4 and 30 g of $KMnO_4$ in an ice bath below 10 °C and then was transferred to a water bath and magnetically stirred at 35 °C for 3 h. The resulted dark-brown paste was further diluted with a slow addition of 0.5 L of DI water and followed by a slow addition of 40 mL (30 wt.%) of H_2O_2 to quench the solution and turn the color of the solution to golden-brown. After the resultant product was centrifuged, the sample was washed with HCl (1/10) to remove metal ions, followed by washing with DI water in turn until the pH became ca.6. Finally, the product was dried at 40 °C in a vacuum to obtain the GO sample.

2.2. Synthesis of ZnO nanorods (ZnO NRs)

To prepare ZnO nanorods, a solvothermal method was adopted. In brief, 5 mL $ZnCl_2$ ethanol solution (0.2 M) was added into 35 mL NaOH ethanol solution (0.5 M) drop by drop under vigorous stirring followed by ultrasonic dispersion for 30 min to obtain a homogeneous solution. Then, the mixture was transferred into a 50 mL of Teflon-sealed autoclave and maintained at 180 °C overnight. The white precipitates were collected by centrifugation, washed by DI water and ethyl alcohol several times, and dried at 60 °C using blower under atmosphere environment for 6 h.

2.3. Synthesis of RGO–ZnO NR composite photocatalysts

The RGO–ZnO NR composite was obtained through a green hydrothermal method using supercritical water as both solvent and green reductant. Briefly, 0.2 g of ZnO NRs were first added to a certain amount of GO solution followed by ultrasonic dispersion for 30 min and punchy stirring for 1 h to disperse ZnO NRs adequately. Then, the mixing solution was transferred into a 50 mL of Teflon-sealed autoclave and maintained at 150 °C for 5 h, then cooled down to room temperature naturally. The resulting composites were recovered by centrifugation, rinsed with DI water for several times and fully dried in a vacuum at 60 °C for 12 h. In addition, the amount of graphene in the RGO–ZnO NR composite was controlled to be 0, 0.5, 1.0, 2.0, 4.0 and 8.0 wt.% by changing the initial volume of GO solution, and the corresponding samples were labeled as ZnO NRs, 0.5 wt.% RGO–ZnO NRs, 1.0 wt.% RGO–ZnO NRs, 2.0 wt.% RGO–ZnO NRs, 4.0 wt.% RGO–ZnO NRs, and 8.0 wt.% RGO–ZnO NRs, respectively.

2.4. Characterization

X-ray diffraction (XRD) patterns were obtained using an X'pert PRO X-ray diffractometer (Panalytical, Netherlands) from 5° to 80° with Cu $K\alpha$ as radiation source ($\lambda = 0.15406$ nm). X-ray photoelectron spectroscopy (XPS) measurements were done on a Thermo Scientific ESCALAB 250Xi XPS system with an Argon ion source. Morphological analysis was performed with an S-4800 field emission scanning electron microscope (FESEM, Hitachi, Japan) with an acceleration voltage of 10 kV. Raman spectra were obtained from a LabRAM aramis spectrophotometer (Horiba Jobin Yvon, France). Fourier Transform Infrared (FTIR) spectra were collected using a Nexus-670 FT-IR spectrophotometer (Thermo Nicolet, America). UV–Vis absorption spectra were acquired using a UV–Vis spectrophotometer (SPECORD 200, Germany).

2.5. Photocatalytic activity measurements

The adsorptivity and photocatalytic activity of the prepared samples were evaluated through the decomposition of Rhodamine B (RhB) dyes, which was performed at ambient temperature and observed based on the absorption spectroscopic technique. In a typical process, aqueous solution of RhB dyes (1×10^{-5} M, i.e., 4.79 g/L, 100 mL) and the photocatalysts (ZnO NRs/RGO–ZnO NRs, 30 mg) were dispersed in a 200 mL cylindrical quartz vessel with a diameter of ca. 8 cm. Then, the mixture was kept in the dark under stirring for 1 h to reach the adsorption–desorption equilibrium between the photocatalyst and RhB dyes and compare the adsorptivity of ZnO NRs and different mass fraction RGO–ZnO NRs before irradiation. The photocatalytic reaction was started by exposing the vessel beneath the UV irradiation (all other lights were insulated) produced by a 500 W long arc mercury lamp with the main wave crest at 365 nm (intensity at the mixture surface was 22.5 mW/cm^2, estimated with a radiometer, Model: UV-A, made in Photoelectric Instrument Factory of Beijing Normal University). Under both the dark environment and the UV irradiation, a certain amount of solution was taken out at a given time interval and centrifuged to measure the concentration of RhB dyes in the solution with a UV–Vis spectrophotometer.

3. Results and discussion

3.1. Synthesis mechanism

As shown in Fig. 1, the formation process of the RGO–ZnO NR composites comprises two major steps of the preliminary attachment of ZnO NRs to the surface of GO and the succedent in situ reduction of GO to RGO under hydrothermal treatment. On the one hand, with the

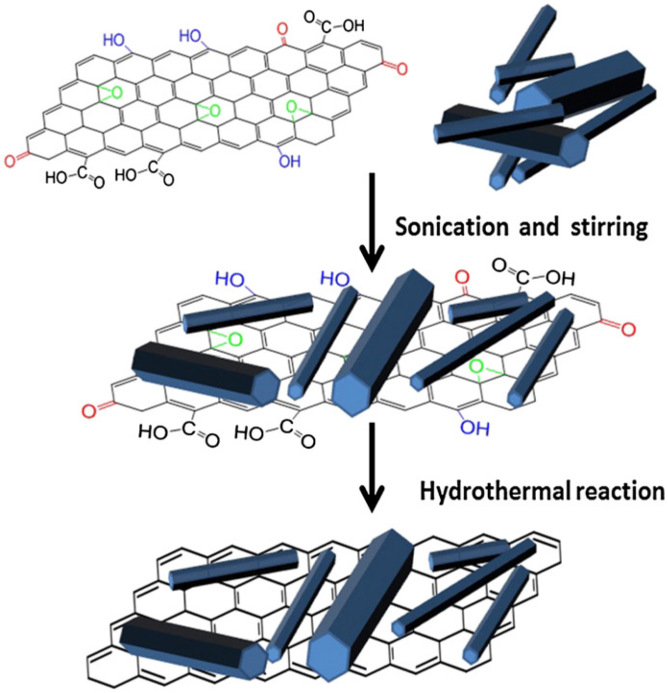

Fig. 1. Schematic illustration of the formation of RGO–ZnO NR composites.