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Synthesis of nitrogen-doped graphene–ZnO nanocomposites with improved photocatalytic activity

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ABSTRACT

A series of nitrogen-doped graphene–ZnO (NG–ZnO) nanocomposites with different weight addition ratios of nitrogen-doped graphene have been prepared via a facile sol–gel method. ZnO nanoparticles (NPs) in diameter of 8–20 nm were distributed on the surface of NG, which exhibit higher photocatalytic activity, recyclability and stability than ZnO NPs toward degradation of methyl orange in water under ultraviolet light irradiation. The ZnO NPs with 2 wt% NG content exhibited the highest photodegradation efficiency of methyl orange (96.4% in 15 min), which was about 1.23 times of pure ZnO NPs (78.2% in 15 min).

1. Introduction

As known to all, in order to overcome the drawbacks of the high recombination rate of photogenerated electron–hole pairs in broadband gap semiconductor ZnO [1,2], efforts have been done via combination ZnO with other components including semiconductor [1], noble metals [3], and graphene [4–7]. Graphene is an excellent supporting and electron-transport material for its large surface area, superior electrical conductivity and mechanical properties [8,9], and its properties can be adjusted by controlling its morphology and tailoring its electronic structure. For example, after nitrogen doping, carbon atoms spin density and electrical conductivity changes, and Fermi level will be higher than the Dirac point [10]. It has been revealed that nitrogen doping could significantly increase the electron conductivity, improve the electron-donor properties and enhance the binding ability of graphene. Thus, we expect nitrogen-doped graphene (NG)–ZnO nanocomposites will have good performance for the photocatalytic degradation of organic dyes, since NG/CdS [11,12], and NG/ZnSe [13] nanocomposites possess enhanced visible light photocatalytic activity. Herein we reported a facile route to prepare ZnO nanoparticles (NPs)–NG composites. The as-obtained nanocomposites had high photocatalytic activity, recyclability and stability toward the decomposition of methyl orange (MO) in water under ultraviolet (UV) light irradiation. It was found that the 2 wt% NG–ZnO nanocomposite had the best photocatalytic activity and good resistance of photocatalytic corrosion in the absence of sacrificial reagents.

2. Experimental

All the chemicals were of analytical grade and used as received without further purification. Graphene oxide (GO) [14,15], and ZnO NPs [16] were prepared by reported methods. NG containing 6.1 at% N was prepared via a solvothermal treatment of GO and diethylenetriamine (DETA). Typically 80 mg GO was dispersed in 80 mL of distilled water and 10 mL DETA under ultrasonication for 1 h, then the mixture was transferred to a 100 mL Teflon-sealed autoclave and maintained at 180 °C for 12 h. The resulting NG was centrifuged, washed by water thrice and ethanol for once, and redispersed in distilled water with sonication for 6 h to form 1 mg/mL suspension. NG–ZnO nanocomposites were obtained by a typical procedure as follow. 0.96 g zinc acetate dehydrate was dissolved in 50 mL anhydrous ethanol and magnetically stirring for 15 min, and then certain amount of the above NG suspension (1, 3, 7, 10.5 and 17.5 mL) was added in, respectively. The mixture was magnetically stirred for 12 h, and heated to 60 °C in oil bath, then 0.735 g lithium hydroxide in 50 mL ethanol was added dropwise within 10 min. After reaction last at 60 °C for 1 h under vigorously stirring, the resulting composites, labeled as x wt% NG–ZnO (x referred to the mass ratio value of NG and ZnO, $x=0.33, 1, 2, 3, 5$), were recovered by centrifugation, washed by water and ethanol thrice and dried at room temperature in vacuum for 12 h.

Structure, morphology and composition of the products were characterized by X-ray diffraction (XRD, Philips X'Pert PRO,

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Holand), scanning electron microscopy (SEM, Hitachi S-4800), transmission electron microscopy (TEM) (Philips CM300), and X-ray photoelectron spectroscopy (XPS, Escalab 250, USA), respectively. UV–vis diffuse reflectance spectra were recorded by a Shimadzu UV-2450 spectrometer at room temperature.

The photodegradation test was carried out by using 300 W UV lamp. MO solution (40 mL, and 10 mg/L) containing 30 mg of catalyst was put in a sealed glass beaker and stirred in the dark for 30 min to ensure adsorption–desorption equilibrium. After UV-light illumination at regular time intervals, the absorbance of MO solution was monitored by a Hitachi U-4100 UV–vis spectrophotometer.

3. Results and discussion

The GO can be transferred to NG containing 6.1 at% N through the solvothermal treatment of GO and diethylenetriamine at 180 °C for 12 h, which is confirmed by XPS (Fig. S1). The survey scan spectrum of NG showed the presence of the principal C1s, O 1s and N 1s core levels, with no evidence of impurities (Fig. S1(a)) [12]. The N 1s peak (Fig. S1(d)) could be resolved into three peaks centered at 398.8, 400.0 and 400.7 eV, which are corresponded to pyridinic N, pyrrolic N and graphitic N, respectively [12,13,17].

XRD patterns of the as-prepared pure ZnO, 2 wt% NG–ZnO and 2 wt% GO–ZnO are shown in Fig. 1(a). All the peaks can be indexed to crystal planes of hexagonal ZnO (JCPDS no. 36-1451). However, the apparent diffraction peak of NG or GO sheets was not discerned in the XRD patterns of composites, these suggest that the layer-stacking regularity of NG or GO sheets would be disrupted and a low fraction of NG or GO sheets did not influence the lattice structure of ZnO crystal [7,18]. The average crystallite sizes of ZnO in pure ZnO, 2 wt% NG–ZnO and 2 wt% GO–ZnO, were calculated to be *ca.* 6, 8 and 18 nm, respectively, by using the Scherrer formula for the (110) facet diffraction peak.

The morphology of the samples was investigated by SEM and TEM. It can be observed from Fig. S2 that the diameter of ZnO NPs are in 10–20 nm, and the addition of NG hardly affects the morphology of ZnO. Fig. 1(b) and (c) shows that the ZnO NPs are evidently dispersed on the surface of NG (marked by arrow) for 2 wt% NG–ZnO composite, and the size is about 10–20 nm, which is in consistence with the result of XRD.

Fig. 2(a) shows the full-scale XPS spectrum of 2 wt% NG–ZnO composite, which shows O1s at 532.05 eV, and Zn 2p3 at 1021.2 eV. Fig. 2(b) shows the high-resolution XPS spectrum of the C1s region, three main peaks located at 284.6 eV, 285.9 eV and 288.1 eV were observed, corresponding to C–C, C=N and C–N, respectively. The N1s peak (Fig. 2(c)) was fitted into three peaks, the peaks at 389.9, 399.7 and 400.5 eV correspond to “pyridinic”, “pyrrolic” and “graphitic” N, respectively [17]. These results confirmed the formation of NG–ZnO composite.

The optical properties of the samples were measured by UV–vis diffuse reflectance spectroscopy (Fig. S3(a)). It can been that an enhanced absorption in the visible light region appeared with increase in the NG content. Fig. S3(b) shows the plots of the transformed Kubelka–Munk function of light energy $(\alpha h v)^2$ versus energy (hv) for the as-prepared samples. The band gap values of the as-obtained composites were calculated and presented in Table S1, which are smaller than that of pure ZnO 3.12 eV). This indicates a band gap narrowing of the semiconductor ZnO NPs due to the introduction of NG, which can be attributed to the synergistic interaction between ZnO NPs and NG [7,12]. The narrower band gap is beneficial to harvest more light for 2 wt% NG–ZnO, leading to its higher photocatalytic activity.

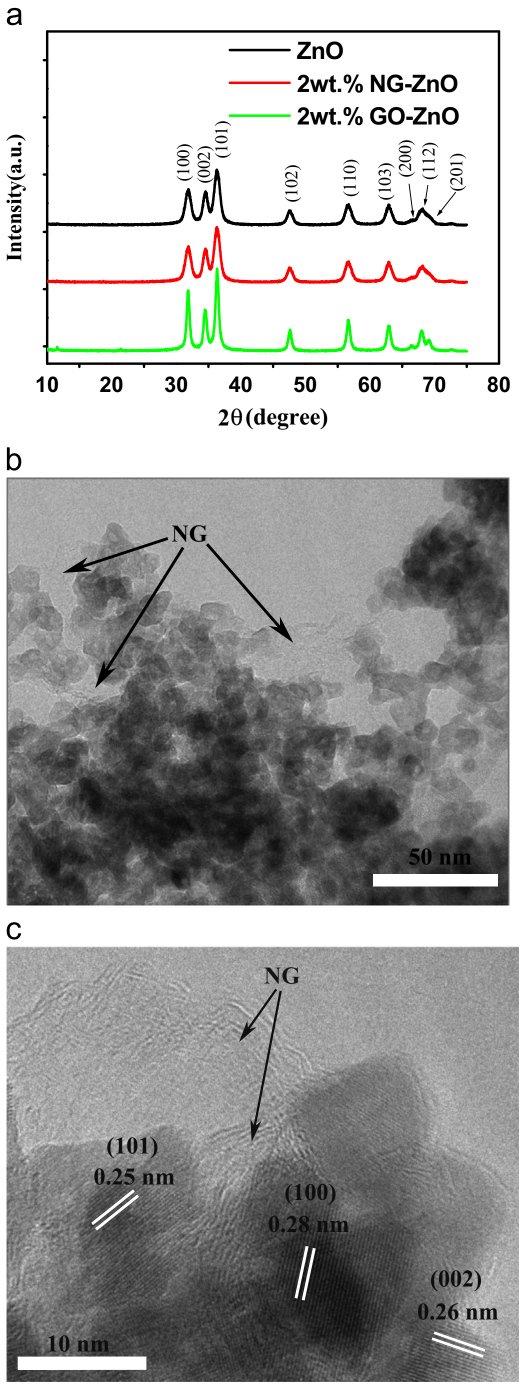

Fig. 1. (a) XRD patterns of the as-prepared ZnO, 2 wt% NG–ZnO and 2 wt% GO–ZnO. (b) TEM image and (c) HRTEM image of 2 wt% NG–ZnO.

The photocatalytic activities of the NG–ZnO nanocomposites were evaluated for the photodegradation of MO under UV light irradiation, and the results are shown in Fig. 3(a). The photocatalytic degradation efficiency of MO follows the order 2 wt% NG–ZnO > 1 wt% NG–ZnO > 3 wt% NG–ZnO > ZnO > 0.33 wt% NG–ZnO > 5 wt% NG–ZnO. The degradation rate constant also follows this order (Fig. S4 and Table S1). Obviously, the addition of an appropriate amount of NG could enhance the photoactivity effectively, while with the addition of excess amount of the NG content, the photocatalytic performance was decreased. It can be concluded that the superfluous NG should block light absorption and shield the active sites on the catalyst surface [11]. Compared to pure ZnO and 2 wt% GO–ZnO, the 2 wt% NG–ZnO shows better photocatalytic efficiency (Fig. 3(b)), since NG–ZnO has a narrower band gap and more active regions [10]. In addition, 2 wt% NG–ZnO