UV-assisted photocatalytic synthesis of ZnO–reduced graphene oxide composites with enhanced photocatalytic activity in reduction of Cr(VI)

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A R T I C L E  I N F O

Article history:
Received 25 July 2011
Received in revised form 15 December 2011
Accepted 15 December 2011

Keywords:
ZnO
Reduced graphene oxide
Photocatalysis

A B S T R A C T

ZnO–reduced graphene oxide (RGO) composites are successfully synthesized via UV-assisted photocatalytic reduction of graphite oxide by ZnO nanoparticles in ethanol. Their morphology, structure and photocatalytic performance in reduction of Cr(VI) are characterized by scanning electron microscopy, transmission electron microscopy, atomic force microscopy, X-ray diffraction spectroscopy, UV–vis absorption spectrophotometer, respectively. The results show that in the composites the RGO nanosheets are decorated densely by ZnO nanoparticles, which displays a good combination between RGO and ZnO. ZnO–RGO composites exhibit an enhanced photocatalytic performance in reduction of Cr(VI) with a maximum removal rate of 96% under UV light irradiation as compared with pure ZnO (67%) due to the increased light absorption intensity and range as well as the reduction of electron–hole pair recombination in ZnO with the introduction of RGO.

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1. Introduction

As an emerging carbon material with unique two-dimensional conjugated chemical structure, graphene has attracted a great deal of attention in recent years owing to its good conductivity, superior chemical stability and high specific surface area [1–3], as well as its potential applications in photocatalysis [4–6], energy storage [7–9], solar cells [10,11], transparent electrodes [12,13], and field emission [14]. Currently one attractive challenge is to combine these 2D carbon nanostructures with metal oxide to form hybrid materials with good functionalities [15–24]. Investigations have been carried out to produce graphene-based materials via reduction of exfoliated graphite oxide (GO), such as chemical reduction using hydrazine or NaBH4 [4,25,26], and high temperature annealing reduction [27]. However, in these methods, hazardous reducing agent or high temperature is normally required. Therefore, the development of facile and practical reducing methods still remains a challenging issue.

As an environmental-friendly and efficient approach, ultraviolet (UV)-assisted photocatalytic reduction of GO using semiconductor oxides, typically TiO2 or ZnO, has been applied to synthesis graphene-based composite materials [28–30]. This one-step strategy can be used to fabricate high quality graphene based composite without using any stabilizing reagent. Williams et al. [31,32] and Akhavan et al. [33–35] fabricated ZnO–graphene or TiO2–graphene composites by carrying out UV-assisted photocatalytic reduction of GO by ZnO or TiO2 in ethanol solution. Ng et al. [36,37] synthesized the composites of graphene and TiO2, WO3, or BiVO4 via a one-step UV or visible light induced-photocatalytic reduction process and they exhibited higher photoelectrocatalytic efficiencies than their patent materials. Despite the above progress to date, the exploration on the synthesis of graphene-based composite materials by UV-assisted photocatalytic reduction method is not nearly enough. Especially the application of the as-synthesized graphene-based composite materials such as ZnO–graphene in photocatalysis is seldom reported so far. In ZnO–graphene hybrid materials, ZnO acts as photocatalyst, to excite the electrons from valence band to conduction band and create electron–hole pairs, which can migrate and initiate redox reactions with water and oxygen, and then degrade organic molecules or reduce metal ion absorbed on the surface of ZnO [38–44]. Graphene acts as an excellent electron-transport material in the process of photocatalysis, so that the hybridization of ZnO with graphene can hinder the recombination of charge carriers and increase the photocatalytic performance [4,25].

In this work, we have successfully fabricated ZnO–reduced graphene oxide (RGO) composites via UV-assisted photocatalytic reduction of GO by ZnO nanoparticles in ethanol and investigated their photocatalytic performances. ZnO–RGO composites exhibit...
an enhanced photocatalytic performance in reduction of Cr(VI) under UV light irradiation as compared with pure ZnO.

2. Experimental

The ZnO nanoparticles used in this work were produced by a reaction similar to that described by Yang and Chan [45]. 25 ml of 1.0 M ZnSO₄ solution was added dropwise into 30 ml of 2.0 M NH₄HCO₃ solution under vigorous stirring at 60 °C in a water bath for 1 h. The as-synthesized white precipitate was isolated by filtration, washed for three times with distilled water and ethanol, and then dried in a vacuum oven at 60 °C for 24 h. Finally, the product was calcined at 600 °C for 1 h to obtain white powder of ZnO.

Commercial graphite powder was used as the starting reagent for the synthesis of GO via modified Hummers method, which has been described in our previous works [46,47]. A certain amount of 1.8 mg/ml GO solution and 1 g ZnO nanoparticles were dispersed in 60 ml ethanol and sonicated for 30 min to produce uniform dispersion. UV-assisted photocatalytic reduction of GO by ZnO nanoparticles in ethanol was carried out in a 100 ml cylindrical quartz glass vessel using a 500 W high pressure Hg lamp with the main wave crest at 365 nm for about 7 h under ambient conditions and magnetic stirring. After UV irradiation, it was obviously found that the color of suspension had changed into grayish-black, indicating the successful chemical reduction of GO sheets [48]. It should be noticed that no further reduction of GO under UV irradiation for longer time is observed by Fourier transform infrared spectroscopy (FTIR) measurement which is normally used to characterize the degree of converting GO to RGO. The as-synthesized ZnO–RGO samples with 0.6, 0.8, 1.0, 1.2 wt.% RGO, named as ZG-1, ZG-2, ZG-3, ZG-4 were isolated by filtration, washed for three times with distilled water, and finally dried in a vacuum oven at 60 °C for 24 h.

The surface morphology, structure and composition of the samples were characterized by atomic force microscopy (AFM, Veeck Dimension 3100), field-emission scanning electron microscopy (FESEM, Hitachi S-4800), high-resolution transmission electron microscopy (HRTEM, JEOL-2010), X-ray diffraction spectroscopy (XRD, Holland Panalytical PRO PW3040/60) with Cu Kα radiation (V = 30 kV, I = 25 mA). Renishaw Raman spectrometer (Via + Reflex) system with a 514.5 nm excitation source, and FTIR (NICOLET NEXUS 670), respectively. The UV–vis absorption spectra were recorded using a Hitachi U-3900 UV–vis spectrophotometer. Photoluminescence (PL) spectra were recorded on a HORIBA Jobin Yvon fluoromax–4 fluorescence spectrophotometer, using the 325 nm excitation line of a Xe lamp as light source.

The photocatalytic performance of the as-prepared samples was evaluated by photocatalytic reduction of Cr(VI) under UV light irradiation. The samples (1 g/l) were dispersed in 60 ml Cr(VI) solutions (10 mg/l) which were prepared by dissolving K₂Cr₂O₇ into
deionized water. The mixed suspensions were first magnetically stirred in the dark for 0.5 h to reach the adsorption–desorption equilibrium. Under stirring, the mixed suspensions were exposed to UV irradiation produced by a 500 W high pressure Hg lamp with the main wave crest at 365 nm. At certain time intervals, 2 ml of the mixed suspensions were extracted and centrifugated to remove the photocatalyst. The filtrates were analyzed by recording UV–vis spectra of Cr(VI) using a Hitachi U-3900 UV–vis spectrophotometer. It is known that the photocorrosion is one of major problems for ZnO photocatalyst, which significantly decreases its photocatalytic activity. Therefore, the photo-stability of as-prepared sample was evaluated for reduction of Cr(VI) under UV light irradiation during a three-cycle experiment.

3. Results and discussion

To indicate the acquirement of RGO, an aqueous solution of ZnO–RGO was dropped onto the hydrophilic-treated silicon for AFM measurement. Fig. 1 shows the AFM image of as-prepared ZG-3. It is observed that ZnO nanoparticles are attached onto the surface of RGO sheet, which is demonstrated in the height profile diagram containing the sharp peaks with the height of ∼40 nm. The profile also shows that the thickness of the RGO is 4.16 nm, corresponding to the RGO of five or six layers based on theoretical values of 0.78 nm for single layer graphene and the thickness contribution form oxygen-containing groups on the faces [46].

Fig. 2(a) and (b) show the FESEM images of ZnO and ZG-3. The morphologies of ZG-1, ZG-2, and ZG-4 (not shown here) are similar as the one of ZG-3. It is clearly observed that the surface of curled RGO nanosheets is packed densely by ZnO nanoparticles, which displays a good combination between RGO and ZnO. From low-magnification HRTEM image of ZG-3 in Fig. 2(c), it is clearly seen that the RGO sheets are decorated by ZnO nanoparticles. The RGO sheets act as bridges for the connection between different ZnO nanoparticles, which could significantly increase the separation of photo-generated carriers, and enhance the photocatalytic performance. Fig. 2(d) shows a high-magnification HRTEM image of ZG-3.

Fig. 3 shows the XRD patterns of ZnO, ZG-1, ZG-2, ZG-3 and ZG-4. All of the diffraction peaks match the standard data for a wurtzite-structure (JPCDS 36-1451) of ZnO, which demonstrates that the presence of RGO does not result in the development of new crystal orientations or changes in preferential orientations of ZnO. No typical diffraction peaks for RGO ((002) diffraction peak at 26° and (1 0 0) peak at 44.5°) can be observed in the composite, which might be due to the low amount and relatively low diffraction intensity of RGO.
The UV–vis absorption spectra of ZnO, ZG-1, ZG-2, ZG-3 and ZG-4 are shown in Fig. 6. The sharp characteristic absorption peak at 374 nm indicates the presence of good crystalline and impurity suppressed ZnO nanostructures. It is observed that the absorbance of ZnO–RGO composite increases even in visible light region with the increase of RGO content, which is similar to those reported in hybridization of TiO$_2$ with graphite-like carbon layers or RGO [5,20]. Such an increase in absorbance may be due to the absorption contribution from RGO, the increase of surface electric charge of the oxides and the modification of the fundamental process of electron–hole pair formation during irradiation [25]. In addition, the red shift in the absorption edge of ZnO–RGO composite obtained by extrapolating the linear portion of the curve to zero absorbance as compared to pure ZnO is ascribed to the chemical bonding between semiconductor photocatalyst and RGO, which is similar to the result in the case of TiO$_2$–RGO composite materials [17,18]. Therefore, the presence of RGO in ZnO can increase the light absorption intensity and range, which is beneficial to the photocatalytic performance.

Fig. 7 shows PL spectra of ZnO, ZG-1, ZG-2, ZG-3 and ZG-4. As compared with the spectrum of pure ZnO, the PL peak of ZnO–RGO composite displays a red shift, which is consistent to the result of UV–vis absorption spectra. Furthermore, the introduction of RGO decreases excitonic PL intensity, which indicates that the recombination of photo-induced electrons and holes in ZnO can be effectively inhibited in the composite. The inhibition effect can be explained from a view of stepwise structure of energy levels constructed in ZnO–RGO composite, as shown in Fig. 8. The conduction band of ZnO is $-4.05$ eV and valence band $-7.25$ eV (vs. the vacuum level).
respectively.\cite{4} The work function of RGO is $-4.42 \text{ eV}$\cite{52}. Such energy levels are beneficial for photo-induced electrons to transfer from ZnO conduction band to RGO, which could efficiently separate the photo-induced electrons and hinder the charge recombination in electron-transfer processes, thus enhance the photocatalytic performance \cite{10}. Therefore, the incorporation of RGO into ZnO plays an important role in the photocatalytic performance of ZnO–RGO composite.

Photocatalytic reduction of Cr(VI) by ZnO, ZG-1, ZG-2, ZG-3 and ZG-4 was performed under UV irradiation, as shown in Fig. 9. The normalized temporal concentration changes \((C/C_0)\) of Cr(VI) during the photocatalytic process are proportional to the normalized maximum absorbance \((A/A_0)\), which can be derived from the change in the Cr(VI) absorption profile at a given time interval. It is observed that Cr(VI) cannot be reduced under the dark condition even in the presence of photocatalyst (ZG-3) and ZnO–RGO composites exhibit better photocatalytic performance than pure ZnO. The photocatalytic performance of ZnO–RGO composite is dependent on the proportion of RGO in the composite. The removal rate of Cr(VI) for pure ZnO is 67%. When RGO is introduced into ZnO, the removal rate is increased to 80% and 88% for ZG-1 and ZG-2 and reaches maximum value of 96% for ZG-3. It is known that during photocatalysis, the light absorption and the charge transportation and separation are crucial factors \cite{18}. The enhancement of the photocatalytic performance should be ascribed to the increase of the light absorption intensity and range, and the reduction of electron–hole pair recombination in ZnO with the introduction of RGO in the composite, which can be confirmed from absorption and PL measurement. However, when the RGO content is further increased above its optimum value, the photocatalytic performance deteriorates. This is ascribed to the following reasons: (i) RGO may absorb some UV light and thus there exists a light harvesting competition between ZnO and RGO with the increase of RGO content, which lead to the decrease of the photocatalytic performance \cite{25}; (ii) the excessive RGO can act as a kind of recombination center instead of providing an electron pathway and promote the recombination of electron–hole pair in RGO \cite{10,52}.

The photo-stability of ZG-3 by investigating its photocatalytic performance under UV light irradiation with three times of cycling uses was studied, as shown in Fig. 10. It can be seen that the recycled use of ZG-3 for three times does not conspicuously affect its photocatalytic activity. Apparently, the composite is stable under the studied conditions and the photocorrosion effect of ZnO was effectively inhibited by RGO after hybridization \cite{53,54}.

**4. Conclusions**

ZnO–RGO composites are successfully synthesized via UV-assisted photocatalytic reduction of GO by ZnO nanoparticles in ethanol to improve the photocatalytic performance of ZnO. The experimental results indicate that (i) ZnO–RGO composites exhibit a better photocatalytic performance than pure ZnO; (ii) the photocatalytic performance of ZnO–RGO is dependent on the proportion of RGO in the composite and ZnO–RGO composite with 1.0 wt.% RGO achieves a highest Cr(VI) removal rate of 96%; (iii) the enhanced photocatalytic performance is ascribed to the increased light absorption intensity and range as well as the reduction of photoelectron–hole pair recombination in ZnO with the introduction of RGO.

**Acknowledgements**

Financial support from Special Project for Nanotechnology of Shanghai (No. 1052nm02700), the Key laboratory of new ceramics and fine processes at Tsinghua University, Project of Shanghai Normal University (DKL917), and Funds for the PhD academic newcomer award of East China Normal University (No. XRZZ011017) are gratefully acknowledged.

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