Microwave-assisted synthesis of TiO$_2$-reduced graphene oxide composites for the photocatalytic reduction of Cr(VI)

Xinjuan Liu,$^a$ Likun Pan,$^{a,*}$ Tian Lv,$^a$ Guang Zhu,$^a$ Ting Lu,$^a$ Zhuo Sun$^a$ and Changqing Sun$^b$

Received 13th June 2011, Accepted 14th August 2011
DOI: 10.1039/c1ra00298h

TiO$_2$-reduced graphene oxide (RGO) composites are successfully synthesized via the microwave-assisted reduction of graphite oxide in a TiO$_2$ suspension using a microwave synthesis system. Their morphology, structure and photocatalytic performance in the reduction of Cr(VI) are characterized by scanning electron microscopy, transmission electron microscopy, atomic force microscopy, X-ray diffraction spectroscopy and UV-vis absorption spectrophotometer. The results show that in the composite the RGO nanosheets are densely decorated by TiO$_2$ nanoparticles, which displays a good combination between RGO and TiO$_2$. TiO$_2$–RGO composites exhibit enhanced photocatalytic performance for the reduction of Cr(VI) with a maximum removal rate of 91% under UV light irradiation as compared with pure TiO$_2$ (83%) and commercial TiO$_2$ P25 (70%) due to the increased light absorption intensity and range as well as the reduction of electron-hole pair recombination in TiO$_2$ with the introduction of RGO.

1. Introduction

As a rising star in the carbon family, graphene has attracted a great deal of attention in recent years owing to its excellent conductivity, superior chemical stability and high specific surface area.$^{1–7}$ Chemical approaches, for the large-scale production of highly conducting graphene sheets, which speed up the application of graphene, have become reality. Investigations have been carried out to study the application of graphene in many fields, such as photocatalysis,$^{8–11}$ energy storage,$^{12–16}$ solar cells,$^{17,18}$ transparent electrodes,$^{19,20}$ and field emission.$^{21}$

Currently one attractive challenge is to combine these 2D carbon nanostructures with metal oxide to form hybrid materials with new functionalities.$^{22–27}$ In the meantime, such an attachment of metal oxide onto graphene may also prevent the restacking and agglomeration of graphene sheets during the reduction process due to van der Waals interactions between them. Kamat et al.$^{28,29}$ Akhavan et al.$^{30,31}$ and Bell et al.$^{32,33}$ fabricated TiO$_2$-graphene composites by carrying out UV-assisted photocatalytic reduction of graphite oxide (GO) using TiO$_2$ nanoparticles. Lambert et al.$^{34}$ studied the synthesis of TiO$_2$-graphene composites by hydrolysis of TiF$_4$ in the presence of an aqueous dispersion of GO. Zou et al.$^{35}$ synthesized TiO$_2$–graphene composites by refluxing solution mixtures of GO and peroxotitanium complexes and the composites exhibited better charge separation capability than pure TiO$_2$. Zhang et al.$^{36}$ employed a sol–gel method using tetrabutyl titanate and GO as the starting materials to synthesize TiO$_2$–graphene composites and found that both graphene content and calcination atmosphere could affect the photocatalytic H$_2$ evolution activity of the composites. Guo et al.$^{37}$ revealed that TiO$_2$–graphene composites prepared by a sono-chemical method displayed better photocatalytic performance for the degradation of methylene blue compared to commercial pure TiO$_2$. Fan et al.$^{38}$ prepared TiO$_2$ P25–graphene composites by three different methods, i.e., UV-assisted photo-reduction, chemical reduction using hydrazine and hydrothermal methods, which showed better photocatalytic performances in H$_2$ evolution from methanol aqueous solution than alone P25. Shen et al.$^{39,40}$ Zhang et al.$^{41}$ Zhang et al.$^{42}$ and Zhou et al.$^{43}$ carried out one-step hydrothermal methods to fabricate TiO$_2$–graphene composites and demonstrated that the composites exhibited much higher photocatalytic activity in H$_2$ evolution or organic degradation than pure TiO$_2$. In the photocatalysis process, graphene can act as an excellent electron-acceptor/transport material to effectively facilitate the migration of photo-induced electrons and hinder the charge recombination in electron-transfer processes due to the electronic interaction between TiO$_2$ and graphene, which enhances the photocatalytic performance of TiO$_2$.$^{37,43}$ Despite the above progress to date, as promising hybrid materials for photocatalysis, the exploration of TiO$_2$–graphene composites still has a long way to go. Especially as an inexpensive, quick, versatile technique, microwave-assisted reactions are seldom employed to synthesize TiO$_2$–reduced graphene oxide (RGO) hybrid composite materials for photocatalysis although such a method has been used successfully to fabricate RGO$^{44,45}$ and TiO$_2$.$^{36,47}$

$^a$Engineering Research Center for Nanophotonics & Advanced Instrument, Ministry of Education, Department of Physics, East China Normal University, Shanghai, China. E-mail: likpan@phy.ecnu.edu.cn; Fax: +86 21 62234321; Tel: +86 21 62234132
$^b$School of Electrical and Electronic Engineering, Nanyang Technological University, Singapore, 639798, Singapore
In this work, we successfully synthesize TiO$_2$–RGO composites via microwave-assisted reduction of GO in TiO$_2$ suspensions using a microwave system. Microwave irradiation can heat the reactants to high temperature in a short amount of time by transferring energy selectively to microwave absorbing polar solvents. Thus it can facilitate mass production in a short time frame with little energy cost$^{48-50}$ and forms an intimate contact between TiO$_2$ and RGO.$^{51,52}$ which is crucial for the formation of electronic interactions and interelectron transfer at the interface.$^{53}$ TiO$_2$–RGO composites exhibit enhanced photocatalytic performance for the reduction of Cr(VI) under UV light irradiation as compared to pure TiO$_2$ and commercial P25.

2. Experimental

2.1 Synthesis of the TiO$_2$–RGO composite

4 ml tetrabutyl titanate was first dissolved in 10 ml ethanol by stirring for 30 min at room temperature to obtain solution A. 2 ml deionized water and 5 ml acetic acid were added into 7 ml ethanol by stirring for 30 min at room temperature to obtain solution B. Solution B was then added dropwise into solution A under vigorous stirring. Subsequently, the mixture solution was continuously stirring at 40 $^\circ$C for the hydrolysis of tetrabutyl titanate until a transparent sol was formed. Finally, the sol was dried in air at 100 $^\circ$C for 24 h, grinded and heated at 500 $^\circ$C for 1 h. A white powder of anatase TiO$_2$ was obtained.

Commercial graphite powder was used as the starting reagent for the synthesis of GO via a modified Hummers method, which has been described in our previous works.$^{17,24-27}$ 1.8 mg ml$^{-1}$ of GO solution and 16 mg of the as-synthesized anatase TiO$_2$ were dispersed in 20 ml distilled water, which was placed in a 35 ml microwave tube, and then the solution was sonicated for 30 min to produce a uniform dispersion. A dilute NaOH solution was added dropwise into the solution to form a brownish-black suspension with a pH value of 9. The mixture was then put into an automated focused microwave system (Explorer-48, CEM Co.) and treated at 150 $^\circ$C with microwave irradiation power of 150 W for 10 min. It was observed that the color of suspension had changed to a grayish-black, indicating the chemical reduction of the GO sheets.$^{55}$ The as-synthesized TiO$_2$–RGO samples with 0.6, 0.8, 1.0, 1.2 wt.% RGO, named as TG-1, TG-2, TG-3 and TG-4, were isolated by filtration, washed three times with distilled water, and finally dried in a vacuum oven at 60 $^\circ$C for 24 h. Pure RGO was also synthesized by direct microwave assisted reduction of the GO suspension in an aqueous solution for comparison. The photocatalytic performance of commercial TiO$_2$ (Degussa P25) was also investigated for comparison.

2.2 Characterization

The surface morphology, structure and composition of the samples were characterized by atomic force microscopy (AFM, Veeco Dimension 3100), field-emission scanning electron microscopy (FESEM, Hitachi S-4800), high-resolution transmission electron microscopy (HRTEM, JEOL-2010), Fourier transform infrared spectroscopy (FTIR, NICOLET NEXUS 670), X-ray diffraction spectroscopy (XRD, Holland Panalytical PRO PW3040/60) with Cu K$_\alpha$ radiation (V = 30 kV, I = 25 mA), and energy dispersive X-ray spectroscopy (EDS, JEM-2100), 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 340 nm excitation line of a Xe lamp as the light source.

2.3 Photocatalytic experiments

The photocatalytic performance of the as-prepared samples was evaluated by the photocatalytic reduction of Cr(VI) under UV light irradiation. The samples (1 g l$^{-1}$) were dispersed in 60 ml Cr(VI) solutions (10 mg l$^{-1}$), which were prepared by dissolving K$_2$Cr$_2$O$_7$ in deionized water. The mixed suspensions were first magnetically stirred in the dark for 30 min 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 centrifuged to remove the photocatalyst. The filtrates were analyzed by recording UV-vis spectra of Cr(VI) using a Hitachi U-3900 UV-vis spectrophotometer.

3. Results and discussion

Fig. 1(a) and (b) show the FESEM images of RGO and TiO$_2$. The RGO nanosheets are curled and corrugated and TiO$_2$ displays uniform spherical particles. Fig. 1(c) displays the FESEM image of TG-4. The morphologies of TG-1, TG-2, and TG-3 (not shown here) are similar as that of TG-4. It is clearly observed that the surface of curled RGO nanosheets is packed densely by TiO$_2$ nanoparticles, which displays a good

![Fig. 1](https://example.com/fig1.png)

Fig. 1 Surface morphologies of (a) RGO nanosheets, (b) TiO$_2$ nanoparticles and (c) TG-4 by FESEM measurement; (d) EDS spectrum of TG-4; (e) low-magnification and (f) high-magnification HRTEM images of TG-4.
combination between RGO and TiO$_2$. The existence of TiO$_2$ in the composite has been proved by the peaks of Ti and O in EDS data (Fig. 1(d)).

Fig. 1(e) and (f) show the low-magnification and high-magnification HRTEM images of TG-4. It is clearly seen that some TiO$_2$ nanoparticles are attached onto the surface of RGO sheets. The RGO sheets act as bridges for the connection between different TiO$_2$ nanoparticles, which could significantly increase the separation of photo-generated carriers, and enhance the photocatalytic performance. The large crystallite is identified as TiO$_2$ nanoparticles. The lattice spacing measured for this crystalline plane is 0.352 nm, corresponding to the (101) plane of anatase TiO$_2$ (JCPDS#21–1272).

Fig. 2 shows the AFM image of TG-4. It is observed that the RGO has a lateral dimension of micrometres and a thickness of ~3.6 nm, corresponding to four or five carbon atom layers based on theoretical values of 0.78 nm for single layer graphene and the thickness contribution from oxygen-containing groups on the faces. TiO$_2$ nanoparticles are attached onto the surface of the RGO sheet, which is demonstrated in the height profile diagram containing the sharp peaks with the height of ~33 nm. Thus, the size of TiO$_2$ nanoparticles is about ~30 nm.

Fig. 3 shows the FTIR spectra of GO, RGO, TiO$_2$, and TG-4. The broad absorption band at 3425 cm$^{-1}$ is assigned to the hydroxyl groups of absorbed H$_2$O molecules. The absorption band at 650 cm$^{-1}$ of TG-4 is similar to that of pure TiO$_2$, which is owing to the stretching modes of Ti–O. There is a obvious decrease in the intensities of C=O (1627 cm$^{-1}$), C–OH (1183 cm$^{-1}$) and C–O (1068 cm$^{-1}$) stretching vibration peaks in RGO compared to those in GO, which suggests that microwave-assisted reduction is an effective method to remove oxygen-containing groups of GO.

Fig. 4 shows the XRD patterns of RGO, TiO$_2$, and TG-4. RGO nanosheets exhibit a (002) diffraction peak at 26$^\circ$ and a (100) peak at 44.5$^\circ$. The peaks at 25.3$^\circ$, 37.8$^\circ$, 48.0$^\circ$, 53.9$^\circ$, 55.1$^\circ$, 62.7$^\circ$, 68.8$^\circ$, 70.3$^\circ$, and 75.0$^\circ$ are indexed to (101), (004), (200), (105), (211), (204), (116), (220), and (215) crystal planes of anatase TiO$_2$ (JCPDS#21-1272), respectively. The XRD analysis further shows that the main diffraction peaks of TiO$_2$–RGO composites are similar to those of pure TiO$_2$, which demonstrates that the presence of RGO does not result in the development of new crystal orientations or changes in preferential orientations of TiO$_2$. No typical diffraction peaks of carbon species are observed in the composite, which may be due to the low amount and relatively low diffraction intensity of RGO.

The UV-vis absorption spectra of TiO$_2$, TG-1, TG-2, TG-3 and TG-4 are shown in Fig. 5. It is observed that TiO$_2$ presents its characteristic absorption peak at 320 nm and the absorbance of the TiO$_2$–RGO composite increases even in the visible light region with the increase of RGO content, which is similar to those reported in the literature. 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.\(^{53}\) In addition, the red shift in the absorption edge of the TiO\(_2\)-RGO composite obtained by extrapolating the linear portion of the curve to zero absorbance, as compared to pure TiO\(_2\), is ascribed to the chemical bonding between the semiconductor photocatalyst and RGO.\(^{41}\) Therefore, the presence of RGO in TiO\(_2\) can increase the light absorption intensity and range, which is beneficial for the photocatalytic performance.

Fig. 6 shows PL spectra of TiO\(_2\), TG-1, TG-2, TG-3 and TG-4. It is observed that the introduction of RGO decreases excitonic PL intensity, which indicates that the recombination of photo-induced electrons and holes in TiO\(_2\) can be effectively inhibited in the composite. The inhibition effect can be explained from the view of stepwise structure of energy levels constructed in TiO\(_2\)-RGO composite, as shown in Fig. 7. The conduction band of TiO\(_2\) is \(-4.2\) eV and valence band \(-7.4\) eV (vs. vacuum).\(^{62}\) The work function of RGO is \(-4.42\) eV.\(^{63}\) Such energy levels are beneficial for photo-induced electrons to transfer from the TiO\(_2\) conduction band to the RGO, which could efficiently separate the photo-induced electrons and hinder the charge recombination in the electron-transfer processes, thus enhance the photocatalytic performance.\(^{17}\) Therefore, the incorporation of RGO into TiO\(_2\) plays an important role in the photocatalytic performance of TiO\(_2\)-RGO composite.

Photocatalytic reduction of Cr(VI) by TiO\(_2\), P25, TG-1, TG-2, TG-3 and TG-4 was performed under UV irradiation, as shown in Fig. 8. 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 TiO\(_2\)-RGO composites with an appropriate proportion of RGO exhibit better photocatalytic performance than pure TiO\(_2\) and P25. The photocatalytic performance of the TiO\(_2\)-RGO composite is dependent on the proportion of RGO in the composite. The removal rates of Cr(VI) for pure TiO\(_2\) and P25 are 83\% and 70\%. When RGO is introduced into TiO\(_2\), the removal rate is increased to 86\% for TG-1 and reaches maximum value of 91\% for TG-2. It is known that during photocatalysis, the light absorption and the charge transportation and separation are crucial factors.\(^{41}\) 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 TiO\(_2\) in the presence of RGO in the composite, which have been confirmed from absorption and PL measurements. 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 TiO\(_2\) and RGO with the increase of RGO content, which lead to the decrease of the photocatalytic performance;\(^{53}\) (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 pairs in RGO.\(^{17,63}\)

4. Conclusions

TiO\(_2\)-RGO composites are successfully synthesized via microwave-assisted reduction of GO in the TiO\(_2\) suspension using a microwave system and their photocatalytic performances are investigated. The experimental results indicate that (i) TiO\(_2\)-RGO composites exhibit a better photocatalytic performance than pure TiO\(_2\) and P25. (ii) The photocatalytic performance of TiO\(_2\)-RGO is dependent on the proportion of RGO in the composite and the TiO\(_2\)-RGO composite with 0.8 wt.\% RGO achieves the highest Cr(VI) removal rate of 91\%. (iii) The enhanced photocatalytic performance is ascribed to the increased light absorption intensity and range as well as the reduction of the photoelectron-hole pair recombination in TiO\(_2\) upon the introduction of RGO.

Acknowledgements

Financial support from Special Project for Nanotechnology of Shanghai (No. 1052 nm02700) is gratefully acknowledged.