Photodegradation of Reactive Black BL-G by Anatase TiO_2-Graphene Nanocomposites

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Abstract. Anatase TiO_2-graphene (ATG) nanocomposites were prepared via a facile one-step solvothermal method. The samples were characterized by X-ray diffraction (XRD), Fourier transform infrared (FT-IR) spectroscopy, Raman spectra and transmission electron microscopy (TEM). During the solvothermal reaction, anatase TiO_2 nanoparticles with diameters ranging from 5 to 10 nm were deposited on the carbon sheets, and the deoxygenation of graphite oxide (GO) was achieved at the same time. Compared with the mere anatase TiO_2 nanoparticles, the combination of anatase TiO_2 nanoparticles and graphene produced a significant effect on its photocatalytic activity evaluated by the degradation test of Reactive Black BL-G (RB BL-G) under UV irradiation. Our studies also determined the relative influences of the mass ratio of TiO_2/GO and heat treatment temperature on the photocatalytic activities.

Introduction

Over the past decades, TiO_2 has been received widely interest due to its photocatalytic properties, high photostability, and relative nontoxicity.[1-5] For TiO_2, there are three naturally occurring polymorphs, anatase, rutile and brookite.[6] It is generally accepted that the anatase phase is the most active in photocatalytic application, and the high crystallinity and large surface area are beneficial to improve the photoactivity.[7, 8] Among various TiO_2-based materials, the composites of TiO_2 and carbon (TiO_2-C) are currently being considered for many applications including their potential use to address the escalating environment problems.[9] However, there are still several problems hinder the further applications of the present TiO_2-C composites, for example, the marked decrease in adsorptivity and a reduction in the amount of UV rays reaching the anatase surface.[9, 10] In order to overcome these disadvantages, it is of great significance to explore new carbon substrates and design facile routes to obtain novel TiO_2-C composites possessing high photocatalytic activity.

Graphene, a one-atom-thick sheet of hexagonally arrayed sp^2-bonded carbon atoms, has exhibited outstanding mechanical, thermal, electrical, and optical properties and extremely high specific surface area ($2600m^2/g$).[11-13] In view of the unique structure of graphene, the combination of TiO_2 and graphene is promising to enhance the charge separation and decrease the possibility of recombination of electron-hole pairs in electron-transfer processes, which increase the number of holes participated in the photooxidation process and enhanced the photocatalytic activity.[14] Some studies have focused on the application of TiO_2-graphene composites in Li-ion insertion properties,[15] UV-Assisted photoreduction of the graphite oxide (GO),[16] and hydrogen evolution from water photo-splitting under UV-vis illumination.[17] To the best of our knowledge, few studies on the photodegradation of organic pollutant of anatase TiO_2-graphene (ATG) have been reported so far. Most recently, P25-graphene photocatalyst was reported to show higher performance than bare P25, [18] while the synthesis of high performance and low-cost TiO_2-graphene composites still need further study. Herein, we describe a facile and controllable solvothermal route to synthesis of ATG nanocomposite possessing much higher photocatalytic activity than pure anatase TiO_2.

Experimental

Preparation

GO was prepared from powdered flake graphite (400 mesh) by a modified Hummers method as described previously [19, 20] Nanocomposites with different mass ratios of TiO_2/GO were synthesized. The typical route, for example, when the mass ratio of TiO_2/GO was 6:1, is as follows: A 80 mg portion of GO was dispersed in 35 mL ethanol by sonication for 30 min, forming stable graphene oxide colloid. Then 2.0 ml tetrabutyl titanate [Ti (O-Bu) $_4$] was added with magnetic stirring for 15 min. The resulting suspension was transferred into a 50 ml Teflon-lined stainless steel autoclave and sealed tightly. The autoclave was then heated to 180 °C and kept there for 24 h. After the solvothermal treatment, the nanocomposite, was labeled as ATG_{ratio} (e.g., $ATG_{6.0}$, $ATG_{2.4}$ and $ATG_{0.6}$) was then centrifuged, and washed with deionized water several times. The resulting products were dried in air at 60 °C overnight. For comparison, anatase TiO_2 was synthesized in the absence of GO via a similar procedure. Finally, heat treatment of $TG_{6.0}$ was done in air at different temperatures (200°C, 300°C and 400°C, respectively) for 3 h; the nanocomposite was labled as $ATG_{6.0}$-200, $ATG_{6.0}$-300 and $ATG_{6.0}$-400.

Characterization

Powder X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advance diffractometer with Cu Kα radiation (λ≈ 1.54 Å). Fourier transform infrared (FTIR) spectra were carried out using a Shimadzu IR Prestige-21 spectrometer. Raman spectra were run on a Renishaw Raman microscope. Transmission electron microscopy (TEM) images were taken with a JEOL JEM-2100 transmission electron microscope.

Photocatalytic Activity

The photocatalytic activities of the samples were evaluated by the decomposition of Reactive Black BL-G (RB BL-G) under UV irradiation using an XPA photochemical reactor (Nanjing Xujiang Factory of Electrical Engineering, Jiangsu, China). The irradiation was provided by a 500 W high-pressure mercury lamp with the main wave crest at 365 nm. The initial concentration of RB BL-G in a quartz reaction vessel was fixed at approximately 20mg·L^{-1} with as-prepared catalysts loading of 0.2g·L^{-1}. The solution was kept in the dark for 30 mins to reach an adsorption-desorption equilibrium with magnetic stirring. The reaction cell (450 mL) was bubbled with air at a flow rate of 40mL·min^{-1}. At periodic intervals of time, the extent of RB BL-G decomposition was analyzed by recording variations of the absorption band maximum (595 nm) of RB BL-G using a BRAIC UV-1201 spectrophotometer.

Results and Discussion

Characterization of ATG Nanocomposites

The solvothermal method has been found to be a versatile method for the synthesis of a variety of TiO_2 nanoparticles with narrow size distribution and disparity [21] Furthermore, the graphene oxide could be reduced to graphene via solvothermal reaction as described previously [22] Figure 1 shows the XRD patterns of GO and $ATG_{6.0}$, the spectral features of nanocomposites with other mass ratios are similar. The as-synthesized GO (Figure1a) shows a sharp peak at around 2θ = 10.5°, corresponding to the (001) reflection of GO and the interlayer spacing (0.86 nm) was much larger than that of pristine graphite (0.34 nm) due to the introduction of oxygen-containing functional groups on the graphite sheets.[23] From Figure 1b, all the diffraction peaks of the $ATG_{6.0}$ can be indexed to synthesized anatase TiO_2 (JCPDS 21-1272, a=b=3.785Å, c=9.514 Å), and the (001) reflection peak of layered GO has almost disappeared, suggesting that the regular stacks of GO are exfoliated.[24]

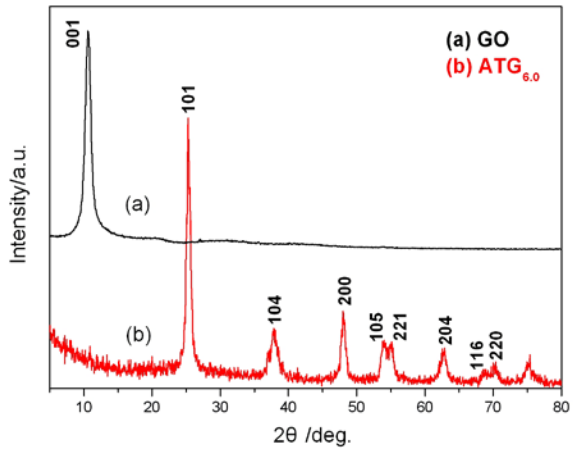

Figure1XRD patterns of samples (a) GO and (b) $ATG_{6.0}$.

Figure 2a shows the FT-IR spectra of GO (curve 1) and $ATG_{6.0}$ (curve 2). The oxygen-containing functional groups of GO were revealed by the bands at 1051, 1223, 1402 and 1740 cm^{-1} (curve1), which correspond to C-O stretching vibrations, C-OH stretching peak, C-O-H deformation peak and C=O stretching of COOH groups, respectively. For $ATG_{6.0}$, the absorption band appearing at around 1620 cm^{-1} was attributed to the skeletal vibration of graphene sheets, and the bands related with the oxygen-containing functional groups almost disappeared (curve 2), indicating the graphene oxide had already been reduced to graphene during the solvothermal reaction. The broad absorption below 1000 cm^{-1} showed the stretching vibration of Ti-O-Ti bonds. Furthermore, the increment of relative intesity of D/G in the Raman spectra of $ATG_{6.0}$ correlates well with the previous studies (Fig. 2b), indicating a decrease in the average size of the sp^2 domains but an increase in number upon deoxygenation. [25] The I_D/I_G ratio of $ATG_{6.0}$ is about 1.02, which is much higher than that of GO (0.68), indicative of the transformation of GO into rGO after solvothermal treatment. The Raman spectra of $ATG_{6.0}$ with small Raman shift (below 1000 cm^{-1}) is displayed in the inset of Figure 2b, all of the picks were assigned to the modes of anatase TiO_2. A dominant peak centered at 146 cm^{-1} was associated with $E_g(v6)$ mode. Peaks centered at 395 and 510 cm^{-1} were associated with B_{1g} and A_{1g} modes, and the 633 cm^{-1} peak was assigned to $E_g(v1)$. The FT-IR and Raman results indicate that graphene sheets and anatase TiO_2 coexist in the synthesized hybrids.

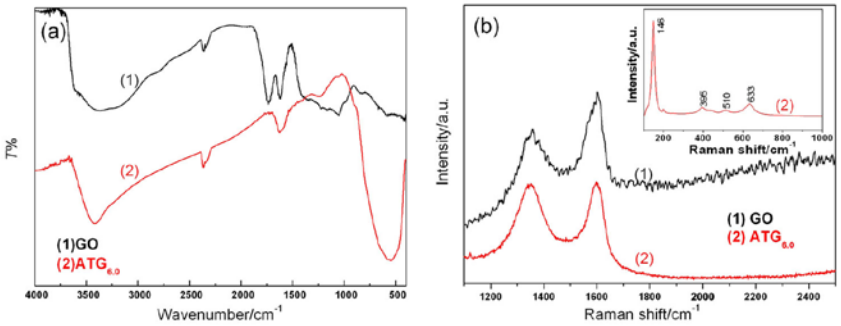

Figure2 (a) FT-IR spectra of GO (1) and ATG6.0 (2); (b) Raman spectra of GO (1) and ATG6.0 (2)

The heterostructure of as-synthesized nanocomposites with different mass ratios of TiO_2/GO were further examined using TEM. As showed in Figure 3, it is clearly seen from the panels a and b of Figure 3 that the almost transparent carbon sheets were decorated randomly by anatase TiO_2 nanoparticles with diameters ranging from 5 to 10 nm, and few particles broke away the carbon supports. Besides, anatase TiO_2 nanoparticles were inclined to accumulate along the wrinkles and edge, mainly due to the distribution of carboxylic acid groups at the edge of GO. With the increase of the mass ratio of TiO_2/GO, the graphene sheets were coated by increased number of nanoparticles (Figure 3c-f). Fig. 3e and f display the highest density of anatase TiO_2 nanoparticles

on graphene sheets, which is essential to the photocatalytic activity of the composite.

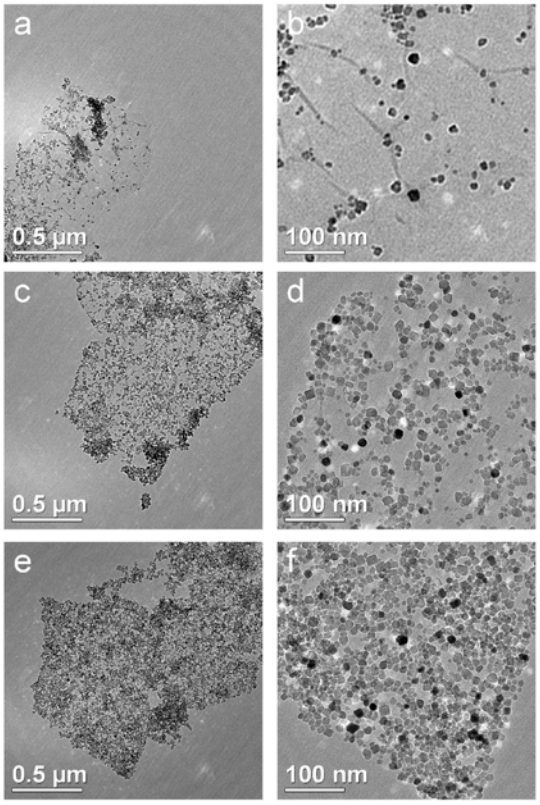

Figure3 TEM images of (a, b) ATG6.0, (c, d) ATG2.4 and (e, f) ATG0.6

Photocatalytic Properties of ATG Nanocomposites

The photocatalytic activities of a series of photocatalysts were measured by the degradation test of RB BL-G under UV irradiation, and the experimental results are shown in Figure 4 and Table 1. The normalized concentration of the solution (C/C_0) is proportional to the normalized maximum absorbance (A/A_0), therefore we can use C/C_0 instead of A/A_0. It was clear that ATG composites had higher photocatalytic activity than the bare anatase TiO_2, mainly due to its two-dimensional planar structure, which is favorable for dye adsorption, charge transportation and UV rays reaching the anatase surface. With the increase of the mass ratios of TiO_2/GO, ATG nanocomposits showed significance progress in the photodegradation of RB BL-G. Figure 4b shows the photocatalytic activities of $ATG_{6.0}$ after heat treatment at different temperature (200°C, 300°C and 400°C, respectively) for 3h. Although the absorption property of $ATG_{6.0}$ was reduced with the increase of heat treatment temperature, the photocatalytic activity was enhanced gradually (see Table 1). Heat treatment of as-prepared photocatalysts at high temperature is beneficial to the crystallization of anatase TiO_2, which plays an important role in the photocatalytic reaction. Especially, $ATG_{6.0}$-400 exhibited the highest photocatalytic activity that could degrade RB BL-G by 95.4% within 50 min (Table 1).

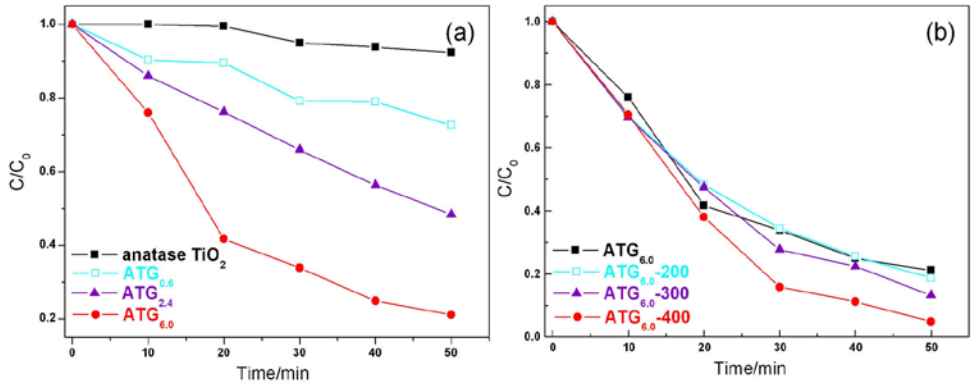

Figure 4 Photocatalytic degradation of RB BL-G by different different catalysts: (a) pure anatase TiO2 and ATG nanocomposites with different mass ratios of TiO2/GO; (b) ATG6.0 before and after heat treatment at different temperatures.

Table1 Absorption and photodecomposition rate of RB BL-G by different catalysts within 50 min.

Samples	anatase TiO_2	$ATG_{0.6}$	$ATG_{2.4}$	$ATG_{6.0}$	$ATG_{6.0}$-200	$ATG_{6.0}$-300	$ATG_{6.0}$-400
Absorption (%)	0	8.7	13.1	22.7	21.6	7.1	0.3
Removal rate of RB BL-G (%)	7.7	27.4	51.6	78.9	81.3	91.0	95.2

Conclusions

In summary, ATG nanocomposites were successfully synthesized using a simple one-step solvothermal method. The characterization data for the nanocomposites indicated that the reduction of graphene oxide and loading of anatase TiO_2 nanoparticles were achieved simultaneously. ATG photocatalyst exhibited much higher efficiency for the photodegradation of RB BL-G than mere anatase TiO_2 due to its two-dimensional planar structure. Additionally, it was found that the photocatalytic activities of the nanocomposites were highly dependent upon the mass ratio of TiO_2/GO, and influenced markedly by heat treatment temperature.

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