One-pot synthesis of 3D TiO₂-reduced graphene oxide aerogels with superior adsorption capacity and enhanced visible-light photocatalytic performance

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Abstract: As an alternative expanded spectrum-driven photocatalyst, TiO₂/graphene nanocomposites have been well investigated in recent years. Nowadays, reports indicated that the three-dimensional reduced graphene oxide (3DrGO) aerogels (GAs) with abundant porous structures can adsorb the organic pollutants such as dye molecules and supply multi-dimensional electron transport pathways, suggesting a significant application potential in photocatalysis. Herein, 3DrGO aerogels supported with titanium dioxide (TiO₂) were prepared by a facile one-pot hydrothermal method using ascorbic acid as a reducing agent and cross-linker. Benefited from the enhanced adsorption ability towards dye molecules owing to the high specific surface area, and the enhanced photogenerated charge separation resulting in the strong interaction between TiO₂ and GAs, the fabricated TiO₂/GAs (TGAs) products exhibited excellent photocatalytic activity in an aqueous system. Furthermore, the TGAs products also presented high stability and can be simply separated from the reaction solution for recycling, which is ultra-important for further application in photocatalysis.

Keywords: TiO₂/3DrGO aerogels, photocatalysis, dye molecules, recycle

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1. Introduction

Titanium dioxide (TiO_2) as the most attractive photocatalyst has been widely investigated in recent decades owing to its low cost, environment-friendly property, chemical stability, and high photocatalytic performance [1]. However, the broad band gaps of TiO_2 severely restrict their practical applications in the full-wavelength of solar spectrum [2-4]. Moreover, the low ionic and electrical conductivity together with the rapid recombination of photogenerated electron-hole pairs as well as the slow charge transfer rate of TiO_2 lead to practical limitations [5]. For these issues, two main approaches have been applied to overcome the drawbacks of TiO_2 on the basis of energy band engineering and conductivity improvement. One approach is expanding the optical response range from ultraviolet to visible by doping and self-doping methods [3]. Another is developing heterostructure materials constructed by jointing multiple semiconductor ingredients together [4].

Graphene, as a two-dimensional single layer of carbon atoms patterned in a hexagonal lattice, is regarded as an ideal material for forming photocatalytic nanocomposites due to its attractive properties such as excellent conductivity, large specific surface area, zero band gap, and good chemical stability [6-8]. With such fascinating performances, graphene acting as a support in the photocatalytic nanocomposites can efficiently separate electrons and holes to make the recombination of photogenerated carriers decrease. However, due to the difficulty of separating and reclaiming in the process of photocatalytic reaction, graphene nanocomposites are hard to industrialize in the near future. Fortunately, recent reports have shown that three-dimensional (3D) reduced graphene oxide aerogels (GAs) composited with semi-conductor photocatalysts may be the optimal candidates for water pollutants treatment owing to the easiness recovering of 3D composites [5]. Compared with 2D graphene, the shapes, volumes, and densities of 3D GAs can be simply controlled by changing reaction vessel features, accelerating large scale production [9]. With 3D porous structures, large practical specific surface areas and bulk volumes, the charge transfer efficiency will be enhanced dramatically, which is

beneficial for improving the photocatalytic activity. Meanwhile, the weak interaction between semi-conductor faces and graphene surface hinders the application of graphene-based photocatalysts while the GAs with 3D macroporous structure is likely to decrease the loss of semi-conductor nanoparticles from graphene surface [10]. Furthermore, the 3D GAs tends to be more easily to recycle after the degradation experiment. According to the previous reports [3-8], the outstanding photocatalytic activity of the 3D GAs-based nanocomposites can be ascribed to two primary aspects. On the one hand, this 3D structure of GAs can effectively improve the adsorption capacity by large surface areas, high pore volumes, and intense interactions between the graphene sheets and adsorbed pollutant molecules [11]. On the other hand, the GAs supported with semi-conductor nanoparticles presents enhanced photocatalytic activity owing to the efficient separation of electrons and holes as well as the effective charge transfer from semi-conductor nanoparticles to graphene network [12]. Therefore, it is highly necessary to fabricate novel and well-defined 3D graphene-based heterostructure materials for the application in wastewater treatment and energy-related areas.

Herein, we develop a facile one-pot hydrothermal method to synthesize TiO_2/GAs (TGAs) nanocomposites using the raw materials of P25 (Degussa) and graphene oxide (GO). This approach chooses the green and nontoxic ascorbic acid (AA) as the reducing agent and cross-linker. The fabricated TGAs nanocomposites present high adsorption capacities and desirable photocatalytic activities towards the methylene blue (MB) molecules. Moreover, the TGAs products also exhibit recyclable stability which is valuable in the practical applications.

2. Materials and methods

2.1 Preparation of TiO_2/GAs nanocomposites

GO was prepared from natural graphite powders according to a modified Hummers method [13]. The TiO_2/GAs nanocomposites were prepared by a hydrothermal method which was presented as follows. In a typical procedure, 30 mg

of GO powders were added into a 20 mL vial with 15 mL deionized (DI) water under vigorous stirring for several hours to form a homogeneous GO dispersion (2 mg/mL). Then 10 mg, 30 mg and 90 mg of P25 (Degussa) powders were added into the GO dispersion with drastic stirring for 1 h. Subsequently, 30 mg of AA was added into the above mixture with sonication for 1 h and then transferred into vacuum oven at temperature of 95 °C for 5 h. The TiO₂/3D graphene hydrogels (TGHs) can be obtained after removing the superfluous water. Then the obtained TGHs were dialyzed by abundant DI water to remove the unreacted reducing agent. In order to acquiring the TGAs products, freeze-drying process is necessary to keep the 3D structures from destroying. In particular, the samples with different P25 adding amounts were marked as TGAs-1, TGAs-2 and TGAs-3, respectively. The 3D reduced graphene oxide (3DrGO) product as a control group was fabricated using GO (1.5 mg/mL) and AA (30 mg) in a same reaction process.

2.2 Characterization

The morphologies of the products were characterized using a JEOL 6460 field emission scanning electron microscope (FE-SEM) and a JEOL 2011 transmission electron microscope (TEM) at an accelerating voltage of 200 kV. The X-ray diffraction (XRD) analyses were carried out on a Philips 1730 powder X-ray diffractometer with Cu K α_1 radiation ($\lambda=1.5406$ Å). The UV-Vis DRS of the as-prepared samples were tested on a UV-2550 spectrophotometer in the wavelength range of 200-800 nm. Fourier transform infrared (FT-IR) spectra were obtained on Bruker VERTEX 70 FT-IR spectrophotometer (Germany). Nitrogen adsorption-desorption measurements were characterized on a Quantachrome autosorb-6 automated gas of N₂ sorption system to investigate the porous structure and the surface area of the products.

2.3 Adsorptive performance measurements

The adsorptive properties of the products were tested using MB aqueous solution. Simply, 10 mg of TGAs sample was added into the MB solution (20 mg/L, 30 mL) with stirring in dark for 1 h. 3 mL of the suspension solution was collected in every 10 min and centrifuged immediately at the speed of 10000r/min for 5 min to remove the

photocatalysts. And then the supernatant solution was analyzed by monitoring the adsorption peak at 665 nm. According to Lambert-Beer law, the absorbance of solution is in direct proportion to its concentration, therefore the MB concentration (C) can be calculated by the equation as follows [14]:

$$C = \frac{A}{A_0} \times C_0$$

Where C_0 and C are respectively the initial and residual MB concentration, A_0 and A are the absorbance of MB solution before and after adsorption experiment.

In addition, the adsorbing efficiency (η) of the products to MB solution was calculated by the following equation [15]:

$$\eta = \left(1 - \frac{C}{C_0}\right) \times 100\% = \left(1 - \frac{A}{A_0}\right) \times 100\%$$

2.4 Photocatalytic experiments

The photocatalytic performances of the products were analyzed by the degradation of MB aqueous solution. For comparison, pure P25 powders were used as a control group. The measurement was carried out at room temperature using a xenon lamp as the visible light source (model: CHF-XM-500W). The radiant flux per area unit in the vis-light range entering the reactor was tested using light intensity meter (model: oriel 70260), and the data was 58 mW/cm². The testing process and calculation method of photocatalytic efficiency (η) are the same as the adsorptive performance measurements.

3. Results and discussion

Fig. 1 shows the schematic illustration of the TGAs products. Firstly, a homogenous mixture of GO suspension and P25 powders was hydrothermally treated at temperature of 95 °C in a Teflon-lined autoclave with adding the reducing agent and cross-linker of AA. After hydrothermally treated for 5 h, the well-defined TGHs products can be prepared. In this step, TiO₂ nanoparticles mixed with GO suspension can be fixed homogeneously on the both sides of GO by the formation of new bonds (such as -COO⁻) between TiO₂ and GO owing to the abundant -COOH and -OH groups of GO [16]. After GO was reduced, those nanoparticles were retained onto the

surface of graphene sheets by chemical attachment. Meanwhile, other free TiO₂ nanoparticles in the mixed suspension can be captured by the physical entrapment (between graphene sheets) when GO sheets shrunk and crosslinked together to form a 3D architecture. Therefore, the graphene sheets loading with TiO₂ nanoparticles can self-assemble into 3D hydrogels. Subsequently, the obtained TGHs products were dialyzed with changed DI water for two days to remove the unreacted reducing agent. Finally, in order to obtain the TGAs products with porous structure, water in TGHs products was removed by freeze-drying process for two days.

The crystalline phases of TGAs-1, TGAs-2 and TGAs-3 samples were investigated by XRD patterns (Fig. 2), for comparison, XRD pattern of pure P25 powders was also presented. As shown in Fig. 2, the peak at 22.0° in TGAs samples can be ascribed to the (002) plane of graphene sheets [17]. The characteristic diffraction peaks at $2\theta=25.3^\circ$, 37.8° , 55.1° , 62.7° , 68.7° , 70.3° and 75.0° correspond well to the (101), (004), (200), (211), (204), (116), (220) and (215) planes, respectively, of the anatase TiO₂ (JCPDS 21-1272) [18]. And the characteristic diffraction peaks at $2\theta=27.4^\circ$ and 54.3° correspond to the (110) and (211) planes, respectively, of the rutile TiO₂ (JCPDS 21-1276). Furthermore, it can be clearly seen that the crystal lattice of TiO₂ is unchanged after recombination with 3DrGO. By carefully observation, one can find that the intensity of the characteristic peaks of TiO₂ increases with the increasing of the loading percentage of the P25, implies that the composition of the TGAs can be adjusted by the initial mass ratios of GO and P25.

The morphologies and compositions of the as-mentioned products were firstly evaluated by SEM. It can be seen that the 3DrGO sample (Fig. 3a) has many porous architectures, but the graphene sheets in 3DrGO have a certain degree of stack. Compared with pure 3DrGO sample, the SEM images of TGAs products (Fig. b-d) have obviously honeycomb-like 3D structures with pore sizes ranging from mesoporous to macropore (Fig. 3f). Also, the TiO₂ nanoparticles can be seen on the graphene sheets and their loading percentage in TGAs products increase with the increasing of adding mass of P25. However, the TiO₂ nanoparticles in TGAs-3

aggregate seriously, which may influence its photocatalytic activity. The hierarchical porous structures of the TGAs products observed from SEM images were further characterized by N₂ adsorption-desorption measurements. Fig. 3e is the N₂ adsorption-desorption curves of the 3DrGO, TGAs-1, TGAs-2, and TGAs-3 products. Compared with 3DrGO (90.9 m² g⁻¹), the specific surface area of TGAs products correspond to 225.3, 174.8 and 108.1 m² g⁻¹, respectively, which increases obviously after imported TiO₂ nanoparticles. When TiO₂ nanoparticles are introduced into the reaction system, the decoration of TiO₂ nanoparticles on graphene sheets not only functionalizes the TGAs samples but also acts as the spacer to partially prevent the aggregation of the graphene sheets, which can increase the specific surface area of TGAs to a certain extent. However, the porous structures of TGAs samples may be destroyed when the additive amount of TiO₂ nanoparticles are too much, resulting in the loss of specific surface area of the products. Furthermore, the pore distribution obtained using the Barrett-Joyner-Halenda (BJH) theory indicates that all the TGAs products including the 3DrGO sample are mainly on mesoporous structures. The respective pore volume of the 3DrGO, TGAs-1, TGAs-2, and TGAs-3 products (Fig. 3f) is 0.11, 0.35, 0.30 and 0.19 cm³ g⁻¹, and the trend of which is consistent with the results of the specific surface areas.

TEM observations were further carried out to observe the morphologies of the TiO₂ nanoparticles. As shown in Fig. 4a, the TiO₂ nanoparticles are wrapped around by graphene sheets and the mean particle size of TiO₂ nanoparticles is about 20 nm, which is consistent with the previously report [18]. Fig. 4b shows the high-resolution TEM (HRTEM) image of TiO₂ from nanocomposites. The fringe spacing shown in the image is about 0.35 nm, which agrees well with the (101) lattice plane of TiO₂ reported in the JCPDS 21-1272 [19].

Fig. 5 depicts the UV-vis adsorption spectra of the pure 25 powders and TGAs products. The incorporation of graphene with P25 nanoparticles leads to broaden ultraviolet-visible (UV-vis) light absorption as shown in Fig. 5a. Additionally, the composites of TiO₂ loaded with 3D graphene exhibit not only a strong red shift of absorption band, but also an obvious absorption in the visible light range. The optical

band gap of the samples can be estimated by the following equation for a semiconductor [20]:

$$\alpha h\nu = A(h\nu - E_g)^2$$

Where α , ν , A , and E_g are the adsorption coefficient, light frequency, proportionality constant and band gap, respectively.

As shown in Fig. 5b, the relationship of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) has been presented. The E_g values of the TGAs samples are determined by measuring the x-axis intercept of an extrapolated tangential line from the linear regime of the curve. Compared with P25 sample (2.98 eV), the E_g values of all the TGAs products have decreases apparently (2.08 for TGAs-1, 1.59 for TGAs-2 and 1.68 for TGAs-3), which is greatly helpful for enhancing the light absorption and photocatalytic efficiency. The extended light absorption range makes the TGAs products be a good candidate for visible light photocatalysis.

Before visible-light irradiation, the mixed MB and photocatalysts were stirred for 1 h to reach adsorption equilibrium. As shown in Fig. 6a, all the TGAs products present an outstanding adsorption capacity of MB in dark due to the π - π conjugation accumulation effect between 3D graphene aerogel and dyes. The TGAs-1 sample with the highest specific surface area has the most excellent adsorption capacity, compared with that of TGAs-2 and TGAs-3 samples. The results indicate that high specific surface area of the TGAs products gives the aerogels a superior adsorption capacity of MB which increases with the increasing of specific surface area. In order to evaluate the photocatalytic performances of the as-mentioned samples, the photodegradation rate of MB over TGAs products was further investigated (Fig. 6b). For comparison, the photodegradation rate of MB over pure P25 sample was also tested. It can be seen that only 7.6% MB is degraded in 30 min when bulk TiO_2 nanoparticles are employed as the catalyst, while more than 90.0% MB is removed by the visible-light-driven TGAs catalysts during the same time. Compared with the pure P25 photocatalyst, the photodegradation efficiency of all the TGA products is enhanced dramatically. However, with the increase of P25 addition, the photodegradation rate of MB over TGAs products in the visible light irradiation increases first and then decreases (Fig.

6b). The result is consistent with some previous reports that analogous activity trend for photodegradation of MB is also observed over the P25-graphene nanocomposites [17]. Specifically, the low-dispersed TiO_2 nanocomposites in TGAs-1 sample lead to the lower photocatalytic activity than that of the TGAs-2 sample. However, the photocatalytic activity of the TGAs-3 product is lower than that of the TGAs-2 product due to the aggregation of TiO_2 nanocomposites in the composites which could bring about high recombination probability of electron-hole pairs. When the P25 addition amount is 30 mg, the corresponding TGAs-2 catalyst has the optimal photocatalytic activity which can be ascribed to the optimal TiO_2 content in the composite and a relatively lowest band gap compared with the TGAs-1 and TGAs-3 samples. The results demonstrate that the interaction between TiO_2 nanoparticles and 3D porous graphene plays a significant role in enhancing of visible light photocatalytic activity. The reason why the photocatalytic activity of TGAs nanocomposites is far better than that of pure TiO_2 nanoparticles is that the composite aerogels have enhanced light absorption and improved separation efficiency of electron and hole as well as the effective charge transfer from TiO_2 nanoparticles to graphene network [21]. In detail, for the first key, the graphene sheets with 3D porous structure can absorb more light afforded by the enlarged surface to volume ratio. Secondly, electrons in the valence band of the TGAs products can be excited to jump to the conduction band under visible light irradiation, resulting in the formation of electron-hole pairs due to the small band gap. Additionally, the recombination of electron-hole pairs is suppressed by effective charge transfer from TiO_2 nanoparticles to conjugative p structures of graphene.

FT-IR spectra were tested to judge whether the adsorbed MB molecules in the composite aerogels were degraded during the photocatalytic process. And the TGAs-2 product was chosen as an example. As shown in Fig. 6c, the peak around 472 and 612 cm^{-1} is corresponded to the vibration of Ti-O-Ti and Ti-O-C bands in TiO_2 , respectively. The peak at 1106 cm^{-1} is assigned to the stretching vibration band of C-O and the peak at 1328 cm^{-1} is assigned to the band of C=C in graphene sheets. The peak around 1577 and 1639 cm^{-1} are assigned to the bending vibration of C-OH band,

which indicates that GO has not been reduced absolutely and there is still some oxygen groups kept on the graphene sheets. Besides, the peak at 3428 cm^{-1} is corresponding to the stretching vibration of O-H band. Specially, the peak around 1619 cm^{-1} is assigned to the aromatic ring stretching vibration which is the strongest characteristic peak in MB molecules [11]. Compared with the pure MB molecules, the characteristic peak of MB also appears in TGAs-2 sample before photocatalytic reaction (the inserted picture of Fig. 6c) which indicates that there has formed a good interaction between the composite aerogels and the MB molecules. However, after photocatalytic reaction, the aromatic ring stretching vibration peak has disappeared which indicates that the MB molecules have been degraded and the decrease of absorbance is attributed to both the adsorption process and the photocatalytic process. Furthermore, as a result of above discussion, the fabricated TGAs products in this experiment have an excellent adsorption capacity and photocatalytic performance which play key roles in the degradation of MB molecules.

As a photocatalyst, the recycling stability is ultra-important for the practical applications. Fig. 6d is the cyclic experiments of TGAs-2 sample with and without UV irradiation. After five cycles, both of the absorption ability and the photocatalytic activity are still kept high. Definitely, 93.9% of the original adsorption ability and 96.0% of the original photocatalytic activity can be maintained (Fig. 6d). The slightly deactivation is because of the inevitable loss of catalyst during the recovery process. These results indicate that the 3D TiO_2 -reduced graphene oxide aerogels have good recycling absorption ability and excellent recycling photocatalytic performance which are essential in the practical environment protection.

4. Conclusions

In summary, the 3D TiO_2 -reduced graphene oxide aerogels were obtained via a facile one-pot hydrothermal method using AA as the reducing agent and cross-linker. With 3D porous structure, the composite aerogels have large specific surface area and high pore volume and present good adsorption capacity as well as excellent

photocatalytic activity for the degradation of MB molecules. The photocatalytic activity of composite aerogels is far better than that of pure TiO₂ nanoparticles which is due to the enhanced light absorption and improved separation efficiency of electron and hole as well as the effective charge transfer from TiO₂ nanoparticles to graphene network. Furthermore, the fabricated composite aerogels have good recycling absorption ability together with excellent recycling photocatalytic performance which is essential in the practical environment protection.

Acknowledgements

This work was supported by National Science Foundation of China (51572114) and the Senior Talent Foundation of Jiangsu University (15JDG078) as well as Students Research Project in Jiangsu University (Y14A062).

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Figure captions:

Fig. 1 Schematic illustration of the TGAs products

Fig. 2 XRD patterns of pure P25, TGAs-1, TGAs-2 and TGAs-3 products

Fig. 3 SEM images of 3DrGO, TGAs-1, TGAs-2 and TGAs-3 products (a-d), respectively; (e) nitrogen adsorption/deposition isotherms and (f) pore size distribution of the samples correspondingly

Fig. 4 TEM images of TGAs-2 sample. (a) Typical image; (b) HRTEM image

Fig. 5 (a) UV-vis spectra for the pure P25 and TGAs products; (b) the curves of the Kubelka-Munk function plotted against the photon energy

Fig. 6 Photocatalytic activities of different samples, (a) adsorption capacities of MB on different TGAs products in dark; (b) the adsorption capacities (in dark) and photocatalytic activities (in visible light) of MB on different TGAs products, for comparison, pure P25 sample was also presented; FTIR spectra of (i) MB and TGAs-2 sample before (ii) and after (iii) photocatalytic reaction, the inserted picture is the detail view of (b); (d) cycle runs of TGAs-2 products

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6