Facile decoration of TiO₂ nanoparticles on graphene for solar degradation of organic dye

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Abstract

The reduced graphene oxide is interesting material for the synthesis of TiO₂-based photocatalyst. In the present investigation, blackberry fruit, which contains high levels of anthocyanins and other phenolic compounds, was employed as a reducing agent mainly due to its high antioxidant capacity. The nano-crystalline TiO₂ was decorated on different amounts of graphene oxide with sol–gel method and then the photocatalytic activity for degradation of cationic dye was evaluated by UV spectroscopy to achieve the optimum content of graphene oxide. The decoration of anatase nanoparticles on prepared reduced graphene oxide was investigated by X-ray diffraction, scanning and transmission electron microscopy techniques. The new composite gives significantly higher activity when is compared to the compositions fabricated by graphene oxide. The compact layer provides a large TiO₂-graphene contact area and reduces the electron recombination. The decoration of TiO₂ nanoparticles, 5-10 nm, on the graphene oxide reduced by blackberry juice further improves the dye removal. The results imply that the nanoparticle decoration is the key strategy to increase the degradation capacity.

Keywords: Organic photodegradation; Green technique; Nanoparticles; Sol-gel; TiO₂-graphene.

1. Introduction

The cationic dyes are important toxic materials which have extensive application as colorants for dyeing and printing in a variety of industries. These pollutants are discharged into the natural waters by a variety of industries, including textile, plastic, tannery, paper and rubber factories. The organic dyes can generate serious problems when these harmful chemicals are accumulated even at low levels. Although, adsorption is the most common process for elimination of dyes [1], the photocatalytic degradation is currently introduced as a feasible alternative method for removing organic traces from wastewaters [2, 3].

Anatase-graphene compositions have recently attracted attention in the photocatalytic treatment of waters contaminated by dyes. The separation of photo-generated electron and hole plays a key role in the photocatalytic ability due to produce hydroxyl radicals which can oxidize dye ion [4]. Interfacial hybridization can potentially enhance activity by preventing recombination of photo-generated electron (e^-) and hole (h^+) pairs. The reduction method of graphene oxide affects the photocatalytic activity of TiO_2 -based composites [5]. The knowledge of anatase decoration represents a nontrivial challenge for many solar degradation and optimal engineering purposes [6]. A lot of experimental work has been carried out to better understand the fundamentals regarding electron and hole separation in TiO_2 based nanocomposites [7-12], but many aspects still remain to investigate the decoration of nanoparticles.

From engineering purpose, a fine control on anatase decoration is required because the performance of graphene-based system depends on the reduction state of graphene oxide and particle size distribution of TiO_2 on the sheets which strongly affect the interactions as result the electron and hole separation. The dark blackberry indicates a high concentration of antioxidants [13] as a result it can be suggested as reducing agent to help the synthesis of reduce graphene

oxide, making a good choice for green and eco-friendly preparation of TiO₂-based photocatalysts. There are no elaborate details about decoration on graphene oxide reduced in the presence of blackberry juice and to our knowledge no further investigations have been carried out until this time. Consequently, this study proposes the treatment of graphene oxide sheets with dark blackberry juice to reduce the oxygen functional groups. The produced surface may act as the conductive layer to further separate the electron and hole pairs. This study explores the effect of reduction agent on graphene oxide, TiO₂ particle size and performance of photocatalyst.

Experimental

All chemicals mentioned hereafter were of reagent grade and used as received. The water used in the experiments was previously deionized and TiO₂ nanoparticles were synthesized via a sol-gel process. 0.55 ml of tetrabutoxytitanium (Sigma Aldrich, 24412) was slowly added to 60 ml ethanol (Merck) and stirred for 3 h at 37 °C by ultra-sonication at first. The solution pH was controlled at level of 7 by addition of ammonia solution. The obtained gel was dried in a laboratory oven at 80 °C overnight to obtain a white precursor. The crystallization of TiO₂ was carried out by the calcination of precursor at 400 °C.

The graphene oxide was synthesized from natural graphite (104206, purity > 99 wt%, Merck, Germany) powder by a modified hummer technique [14]. The wet chemical technique was applied for synthesis of TiO₂-graphene oxide (TO) and TiO₂-reduced graphene oxide (TR). In the first one, the TO synthesis involves a graphene oxide and ethanol colloid (1.0 g l⁻¹) preparation by ultra-sonication to form a stable suspension at 37 °C and dropwise adding titaniumbutoxide, 0.55-1.20 ml, into the colloid. A long time was required to achieve the stable dispersions (3 h) and the pH of suspensions was adjusted at level of 7 by adding the appropriate amounts of hydrochloric acid (37 wt%, Merck) and ammonia solutions. In the second one,

graphene oxide (0.2 g) was firstly introduced into blackberry juice (40 ml), resulting in a homogeneous dispersion. The suspension was then stirred for 6 h followed by ultra-sonication and centrifugation. The precipitated material was washed for several times with deionized water and dried in the oven for 24 h at 65 °C. The prepared reduced graphene oxide was dispersed in ethanol with the same procedure and then mixed with 0.67 ml of titaniumbutoxide under a strict pH control. In both cases a longer calcination (2 h) at 400 °C is required to stabilize the TiO₂ crystallites on graphene oxide or reduced type.

FTIR spectra of graphene oxide and reduced graphene oxide were obtained with Nexus 670 (Thermo Nicolet, Germany) and each spectrum was collected after 32 scans between 400 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹. In order to identify the crystallite phases, the powder X-ray diffraction was recorded by a Brucker XRD (Model D8-Advance, Karlsruhe, Germany) at 40 kV and 30 mA with Cu-K α radiation. The powder was scanned at a rate of 0.02 °s⁻¹ in the range of 10-80°. The crystallite size of anatase was calculated from the broadening in the XRD pattern according to the Scherrer equation [5].

The morphology of the obtained products was characterized by scanning electron microscope (SEM, Leo 1430 VP-Germany) and transmission electron microscope (TEM, Model CM30, Philips, Nederland). Brunauer–Emmett–Teller specific surface area of powders (BET, PHS 1020, China) was determined by nitrogen adsorption apparatus after degassing the samples at 100 °C.

All degradation experiments were carried out in a stirred batch glass vessel under solar irradiation. The reactor temperature was maintained at isothermal condition, i.e., 25 °C. For each experiment, 25 ml of cationic dye solutions (Methylene blue, C₁₆H₁₈ClN₃S, 115943, Merck) with concentrations of 3.0 and 5.0 mg l⁻¹ were continuously stirred with a certain amount of the photocatalysts (12 mg) for several times, 5-80 min. Before the solar irradiation, the solutions

containing photocatalysts were stirred in the dark space to reach the equilibrium adsorption. The dye concentration analysis of decant solutions were immediately made by using UV-vis spectrophotometer (PG, Ltd., UK) at a wavelength of 663 nm. The removal capacity, mg g^{-1} , and photocatalytic performance, wt%, were determined from the initial and liquid-phase concentrations of dye solutions at each irradiation time. All of the experiments were repeated three times for precisely calculating the removal capacity and performance.

2. Results

The FTIR spectra of graphene oxide and reduced graphene oxide are presented in Fig. 1. The graphs indicate the stretching of hydroxyl group around 3450 cm^{-1} , and the C–O group stretching at 1030 cm^{-1} . The peak at 1630 cm^{-1} is related to the vibrations of adsorbed water molecules. The peaks in the range of $600\text{--}800 \text{ cm}^{-1}$ are related to the =C–H bands. The peaks in the range of $400\text{--}600 \text{ cm}^{-1}$ could be assigned to the C–O and C–C bending vibrations.

Fig. 1. FTIR spectra of prepared graphene oxide and reduced graphene oxide.

The C=O carbonyl stretching at 1730 cm^{-1} is observed in graphene oxide spectrum which confirms the presence of oxygen functional groups after the oxidation process. After the reduction of graphene oxide, the oxygen functionality (C=O) disappeared. In order to effectively

eliminate oxygen functional groups on carbon planes, strongly acidic environment is required. The peak at 2950 cm^{-1} indicates the asymmetric stretching vibrations of aliphatic C–H in reduced graphene oxide.

The structure of TiO_2 , TO and TR powders analyzed by XRD show the typical peaks of polycrystalline anatase after calcination at 400°C , Fig. 2. The polycrystalline anatase structure was confirmed by (101), (004), (200), (105), and (211) diffraction peaks, referring to JCPDS card No. 21-1272. However, the evolution of rutile is not observed. The purity of prepared powders was specifically controlled by calcination at 400°C .

Fig. 2. XRD patterns of TiO_2 TO and TR powders synthesized by sol-gel method.

The degradation capacity and photocatalytic performance of pure anatase, TO containing different amounts of graphene oxide and TR composites are compared, Table 1, in which the starting solution concentration was 3.0 mg l^{-1} . The photocatalytic activity of anatase is very low however; the degradation capacity linearly increases with rise in the graphene oxide content and remains constant in the range of 9.0-11.0 wt%, approximately. The performance slightly

decreases when the graphene content arises up to 11.0 wt.%. The performance of composite containing 9.0 wt% graphene oxide can be related to the increase in the dye adsorption. The reported data indicates that the maximum dye degradation was achieved by TR composite. Although, the capacities of pure anatase and TO are comparable, the performances of these materials are nearly 40 and 10 % lower than that for TR composite. Actually, the degradation capacities of studied materials follow the order: TR > TO > anatase. Namely, the degradation capacity of anatase is 3.2 mgg^{-1} while the capacities of TO composites are 1.35-1.62 times of that for anatase.

Table 1. Degradation capacities and performance of synthesized photocatalysts over 40 min.

Composite	Graphene content (wt%)	Degradation capacity (mgg^{-1})	Performance (%)
Anatase		3.2	51.4
TO	5.0	4.4	69.5
	7.0	4.8	77.4
	9.0	5.2	83.4
	11.0	5.0	80.1
TR	9.0	5.7	93.4

Actually, the removal rate of dye increases with reduction of graphene oxide in the presence of blackberry juice. From another point of view, strong adsorption of dye ions might occur on reduced graphene oxide sites near to the openings or inside certain pores. Thus, it could be concluded that the greater active sites on the surface of TR composite are available for dye ions. The only clear conclusion that could be drawn and applied to the studied composites is that their performances are directly proportional to adsorption and electron-hole pair separation.

According to the experimentally obtained data, TO and TR composites could be successfully applied as effective photocatalysts for dye removal from aqueous solution.

Fig. 3 shows the dye degradation capacities of TiO_2 , TO and TR composites as function of solar irradiation time when the initial solution concentration was 5.0 mg l^{-1} . The degradation capacity increases with increasing solar irradiation time for studied photocatalysts. The maximum degradation capacity of TR composite is 10.2 mg g^{-1} which is significantly higher than that for TiO_2 and TO at the same condition. The degradation rate increased rapidly in the presence of TR and then became slower until the equilibrium was reached. This increase in the rate of dye removal at the first stage can be attributed to the plenty active sites on the nanocomposite, which were occupied by the adsorbate ions. As time passes, the aggregation of dye ions around the photocatalyst may hinder the migration and consequently diffusion of adsorbate ions inside the material. As can be seen in Fig. 3, the effect of blackberry juice on adsorption as well as degradation cannot be ignored. TR composite removes 98 wt% of dye from an aqueous solution over 60 min while 47 and 82 wt% of methylene blue is degraded by TiO_2 and TO at the same irradiation time, respectively. In addition, the results indicate that the dye degradation was not reached to the equilibrium in the presence of TiO_2 and TO.

Fig. 4 displays the SEM images of anatase, TO and TR composites. The anatase nanoparticles were agglomerated to form bigger particles after calcination, Fig. 4(a). The irregularly shaped agglomerates were observed, indicating large particles with a small surface area. The porous structure was typically obtained by addition of graphene oxide (9.0 wt%) to composition, Fig 4(b). In order to facilitate the transfer of electrons, the anatase nanoparticles were decorated on graphene oxide sheets. The hybrid material shares a relatively rougher texture when anatase particles are deposited on the surface of graphene oxide, thus there are no independent TiO_2

agglomerates. When graphene oxide was presented in the tetrabutoxytitanium solution, a layer of hydrolyzed titania was loaded either on the surface or in the pores.

Fig. 3. Dye degradation capacity (solid line) and concentration (dash line) versus solar irradiation time.

TR composite shows the honeycomb morphology and it is more porous and looser than TO due to employment of reduced graphene oxide, Fig. 4(c). However, the SEM image shows the formation of small TiO_2 particles. The agglomeration of primary particles during the preparation could be significantly decreased by using reduced graphene oxide. As a consequence, TR composite calcined at 400 °C results in a uniform structure. There are no large agglomerated particles as shown in Fig. 4(c). Therefore, graphene oxide treatment by blackberry juice could be considered as a pre-stabilization step to prevent the extensive agglomeration. Obviously, TR composite shows the superior morphological feature in comparison to pure anatase and TO composite. Although the same content of second phase is employed to prepare the photocatalysts, the surface area of materials can be increased by treatment of graphene oxide in

the presence of blackberry juice, which is also confirmed by the direct relationship between the specific surface area and the photocatalytic activity. The coarsening of anatase nano-crystallites in TO composite leads to a lower surface area. However, an optimum point may be present to attain the maximum performance. Though the anatase particle size is decreased by reduction of graphene oxide, the drastic adhesion between TiO_2 and reduced graphene oxide probably improves the photocatalytic activity.

Fig. 4. SEM images of (a) anatase, (b) TO and (c) TR.

Fig. 5 shows the TEM image of anatase particles formed on reduced graphene oxide sheet. The formation of nanoparticles is evident. Also it can be seen that the nanoparticles are not agglomerated which have diameter of 10-15 nm. The TEM image indicates relatively uniform particles with a hexagon shape. With calcination at 400 °C, the deviation from spherical shape is enhanced and the hexagon shape particles with high crystallinity are formed. The large particles, 20-25 nm, are observed occasionally. The boundary is clear and sharp as shown by lattice fringes in the TEM image, suggesting that the crystallinity of particles is improved with calcination at 400 °C. The TiO_2 nanoparticles are primary particles with excellent dispersivity and stability on reduced graphene oxide. The improved interconnection between the particles is observed and the diameter of major main particles is still lower than 10 nm. The reduction in the presence of

blackberry juice plays a key role for keeping the size of TiO₂ particles after calcination. In the present case, the reduced graphene oxide promotes the homogeneity, avoids the large agglomeration and prevents the recombination of TiO₂ crystalline nucleuses in the formation and calcination steps.

Fig. 5. TEM image of anatase nanoparticles formed on graphene oxide reduced in the presence of blackberry juice.

Along with the use of 9.0 wt% graphene oxide in composition, an increase in specific surface area occurs from 19.0 to 60.0 m²g⁻¹. Because the average crystallite size of anatase remains constant, 17 nm, this phenomenon can be due to the extended surface area of graphene oxide. The significant effect on specific surface area is observed due to presence of reduced graphene oxide. Reduction in the presence of blackberry juice decreases the crystallite size from 17 to 10 nm. The nano-sized particles and the wide distribution of mesopores, corresponding to the empty space on reduced graphene oxide, contribute to the large specific surface area that has been measured for the TR powder, 83.0 m²g⁻¹.

The synergistic effect of the blackberry juice on the photocatalytic activity is illustrated in Fig. 6. The prepared material is composed of nano-sized TiO₂ particles. There are both nano-

sized pores between nano-sized particles and submicron pores in the powder as shown in Fig. 4(c). It should be noted that the pores are well connected to each other. Therefore, the dye ions can diffuse through both nano and submicron pores. There are two types of diffusion routes for the ions in the bimodal-sized pores. Firstly, the large hollow spaces indicate schematically the ion diffusion through submicron pores. Secondly, the thin solid marked in Fig. 6 shows schematically the ion diffusion through the nano-sized pores. The ion diffusion is significantly enhanced due to the synergistic effect of both nano-sized pores and submicron pores. For a given pore structure, the decrease in the size of anatase nanoparticles leads to the increase in internal surface area. As a result, the composite prepared in the presence of blackberry juice can absorb more photons and contribute to an increased electron and hole densities. Since the most of irradiation is efficiently absorbed by the anatase and the recombination of electrons and holes becomes less due to presence reduced graphene oxide. Therefore, the degradation rate reaches a maximum level with improvement in anatase and graphene sheets.

Fig. 6. The mechanism of dye degradation by TR nanocomposite.

3. Conclusions

The TiO₂-graphene nanocomposite was synthesized by a facile and novel method using blackberry juice as a reducer. The decoration of anatase on graphene oxide reduced in the presence of anthocyanins and other phenolic compounds has positive effect on particle size with improving the nano-particle connection compared to that individually decorated on graphene oxide. A certain nano-particle connection leads to the increase of electron transport property. This fact means forming appropriate nanoparticle connection and destroying particle connection coexist in the agglomerates of anatase and TO. The particle connection generated on graphene oxide cannot be further improved with rising second phase content which is attributed to the significant mismatch between TiO₂ and graphene sheets. This would be responsible for the limited photocatalytic performance. The synthesis strategy described here might open a new route for fabrication of TiO₂ based nanocomposites in the development of future photocatalysts. The results showed that the coupling of the anatase and graphene oxide reduced in the presence of blackberry juice enhances the organic dye photo-degradation under solar condition. Meanwhile the appropriate decoration of TiO₂ nanoparticles, 5-10 nm, on graphene leads to the high photocatalytic activity.

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