Structure and photocatalytic properties of TiO₂-Graphene Oxide intercalated composite

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TiO₂-Graphene Oxide intercalated composite (TiO₂-Graphene Oxide) has been successfully prepared at low temperature (80°C) with graphite oxide (GO) and titanium sulfate (Ti(SO₄)₂) as initial reactants. GO was firstly exfoliated by NaOH and formed single and multi-layered graphite oxide mixture which can be defined as graphene oxide, [TiO]²⁺ induced by the hydrolysis of Ti(SO₄)₂ diffused into graphene oxide interlayer by electrostatic attraction. The nucleation and growth of TiO₂ crystallites took place at low temperature and TiO₂-Graphene Oxide composite was successfully synthesized. Furthermore, the photocatalytic properties of TiO₂-Graphene Oxide under the irradiation of UV light were also studied. The results show that the degradation rate of methyl orange is 1.16 mg min⁻¹ g⁻¹ (refer to the efficiency of the initial 15 min). Compared with P25 powder, this kind of intercalation composite owns much better efficiency. On the other hand, the reusable properties and stable properties of TiO₂-Graphene Oxide intercalated composite are also discussed in this paper. At last, crystalline structure, interface status, thermal properties and microscopic structure of TiO₂-Graphene Oxide were characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), field emission scanning electron microscopy (FESEM) and high-resolution Transmission Electron Microscopy (HRTEM). Also, we have analyzed major influencing factors and mechanism of the composite structures which evidently improve the photocatalytic properties.

Titania, Graphene Oxide, intercalated composite, photocatalytic properties

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Nano titanium dioxide (TiO₂) has attracted great attention these years and it is widely used in photocatalytic materials [1,2], solar cells [3], gas sensors [4], opto-electronics devices [5] and other areas. The photocatalytic activity of TiO₂ depends on its crystal phase, crystallite size and crystallinity. It is known that the anatase-form of TiO₂ crystallite with small crystallite size and high crystallinity exhibits better photocatalytic property [6,7]. The overall efficiency of photon utilization by TiO₂ is however limited by electron-hole recombination, photon scattering and so on [8].

In recent years, great efforts have been made to develop carbon nanotubes (CNTs)/TiO₂ or C₆₀/TiO₂ nanocomposite

[9–13]. The coupling of TiO₂ with CNTs or C₆₀ has been shown to provide a synergistic effect which can enhance the overall efficiency of a photocatalytic process. Gao et al. [10] prepared CNTs/TiO₂ nanocomposite by a surfactant wrapping sol-gel method, and evaluated its activity towards the photocatalytic degradation of a model organic substance (methylene blue) in aqueous suspensions. The results show that CNTs/TiO₂ nanocomposite owns a twice rate enhancement with respect to TiO₂ alone. Oh et al. [11] synthesized two kinds of nanocarbon/TiO₂ composite photocatalysts, employing CNTs and C₆₀ as nanocarbon sources and titanium (IV) n-butoxide (TNB) as a titanium dioxide source. CNTs/TiO₂ nanocomposite owns much better efficiency, for the reason that it showed homogenous distribu-

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tions with only individual CNTs, covered with TiO_2 and without any aggregates between each other. Gao et al. summarized several causes for the superior photocatalytic properties of nanocarbon/ TiO_2 composite: (i) the higher surface area of the composite providing a higher adsorption capacity of reactive species; (ii) the formation of nanocarbon/ TiO_2 heterojunctions which could reduce the rate of the recombination of photoinduced electrons and holes; (iii) the possible shift of the apparent Fermi level to more positive values of the nanocarbon/ TiO_2 nanocomposite as compared to pure TiO_2 , therefore allowing the utilization of longer wavelength photons; and (iv) the absorption of photons by the bare nanocarbon surface injecting electrons into the TiO_2 conduction band and triggering the formation of reacting radicals (superoxide and hydroxyl radicals).

Graphite Oxide (GO) is a non-stoichiometric material in which the lamellar structure of graphite is conserved. It is obtained through the reaction of graphite with strong oxidants such as potassium permanganate in concentrated sulfuric acid [14–18]. The process of strong oxidation makes many oxygen-containing groups such as carboxyl ($\text{C}=\text{O}$), hydroxyl ($\text{C}-\text{OH}$), epoxide ($\text{C}-\text{O}-\text{C}$) covalently attached to its layers [19–21]. In addition, the spatial distribution of functional groups on the carbon skeleton is also different. The epoxide and hydroxyl groups are near each other, and the carboxyl is more likely to be located at the edges of graphite oxide. These oxygen-containing groups embedded in carbon sheets in GO lamellar make the interlayer distance increase from 0.335 nm of the starting graphite to 0.7–1.0 nm and the distance depends on the degree of oxidation and the interlayer water content of GO [22]. Furthermore, oxygen-containing groups also enable GO to exhibit excellent hydrophilic properties and rich intercalation chemistry [23, 24].

Much interest has been focused on nano-scale materials based on layered GO and conducting polymers [25–27] since the resulting nanocomposite could possess physical properties derived synergistically from both components, such as enhancement in electrical conductivity and mechanical strength [28]. Higashika et al. [26] firstly prepared aniline-GO composite, and polyaniline/GO composite was successfully synthesized by using an in-situ polymerization method. However, Rabin et al. [28] demonstrated that polyanilines could be directly inserted into GO without preparation of precursor intercalation compounds. The synthetic methodology for the insertion could be extended to other conductive polymers such as polypyrrole [27]. These nanomaterials can be used in rechargeable battery electrode materials.

In this study, TiO_2 -Graphene Oxide composite was successfully prepared at low temperature (80°C) with single and multi-layered graphite oxide mixture (graphene oxide) and titanium sulfate ($\text{Ti}(\text{SO}_4)_2$) was used as initial reactants. Plenty of oxygen-containing groups (such as $\text{C}=\text{O}$) located in the interlayer of graphene oxide were consumed during

the nucleation and growth of TiO_2 crystallites, which means graphene oxide has been partly reduced. In addition, the activity of TiO_2 -Graphene Oxide towards the photocatalytic degradation of methyl orange in aqueous suspensions is much more efficient than that of Degussa P25 powder. In the end, we discussed the reusable and stable properties and the main reasons responsible for the superior photocatalytic properties of TiO_2 -Graphene Oxide.

1 Experimental section

1.1 Materials

Reagents included concentrated sulfuric acid and sodium hydroxide were of analytic purity except titanium sulfate (chemical pure), purchased from Sinopharm Chemical Reagent Co, Ltd (SCRC) and without further purification before utilization. High purity deionized water made by ourselves was used as solvent. GO was prepared by modified Hummer method, the previous work carried out by our group [29]. P25 powders were purchased from Evonik Degussa.

1.2 Preparation of TiO_2 -Graphene Oxide

4.8 g $\text{Ti}(\text{SO}_4)_2$ was added into 180 mL of 1.25 M ($1 \text{ M} = 1 \text{ mol L}^{-1}$) H_2SO_4 solution to reach a $\text{Ti}(\text{SO}_4)_2$ acid solution.

GO was exfoliated by sodium hydroxide solution with different concentrations. A colloidal solution of graphene oxide was obtained by mixing 10 mL of GO with 10 mL of sodium hydroxide solution and sonicating for 30 min.

Graphene oxide solution was added immediately into $\text{Ti}(\text{SO}_4)_2$ acid solution which was preheated to 80°C in hot water bath. The resulting solution was stirred at 80°C for 2 h, and the dark precipitate of TiO_2 -Graphene Oxide was filtered out, washed with deionized water repeatedly and dried at 80°C for 12 h.

1.3 Photocatalytic experiments

The photocatalytic activity of the as-prepared samples was characterized under UV light irradiation using methyl orange (MO) as a target. The process was as follows: 50 mg of the sample was dispersed in 50 mL of aqueous MO solution with the concentration of 20 mg L^{-1} . Fresh air was bubbled for the purpose of stirring and oxygen supply. High pressure Hg lamp (250 W, $\lambda \geq 365 \text{ nm}$) was used as a UV source. Suspensions were collected every 15 min to monitor the degradation of MO. The transmittance (T_i) of the centrifuged suspensions was measured at 483 nm. Absorbance (A_i) was obtained by Lambert-Beer law ($A_i = 2 - \lg T_i$). And then photocatalytic rate (D_i) was available according to the following equation:

$$D_i = (A_0 - A_i) / A_0, \quad (1)$$

where A_0 is the absorbance of MO solution at 483 nm before exposing under UV light.

1.4 Reusable performance and stable performance tests

The reusable performance test of the sample proceeds as follows. Wash the sample which experienced a degradation process for 60 min several times with a certain amount of deionized water. Dry and recomplete another degradation process, repeat the procedure three times. P25 powders are used as the comparison sample under the same conditions.

The stable performance test of the sample proceeds as follows. Expose the sample at room temperature for 0–8 weeks. Test photocatalytic performance of the sample respectively after stored 1, 2, 4 and 8 weeks. P25 powders are used as the comparison sample under the same conditions.

1.5 Characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/Max-rB12 kW X-ray diffractometer in the diffraction angle range $2\theta=5^\circ\text{--}60^\circ$ at a rate of $5^\circ/\text{min}$ using Cu $K\alpha$ radiation ($\lambda=0.15418\text{ nm}$). Chemical bonding between the functional groups and carbon atoms was confirmed by X-ray photoelectron spectroscopy (XPS, PHI 5000C ESCA System). The thermal performance of samples was characterized by the thermogravimetric analysis (TGA, STA 449 C Jupiter). The morphology of the as-prepared samples was observed using a field emission scanning electron microscope (FE-SEM, Quanta 200 FEG) and high resolution transmission electron microscopy (HRTEM, JEM2010).

2 Results

2.1 XRD analysis

Figure 1(a) shows the XRD data of TiO_2 -Graphene Oxide nanocomposite, in which graphene oxide was used as an intercalation matrix and it was obtained by exfoliating GO with 0.2 M NaOH. TiO_2 crystallites in the intercalated structure consisting of mixed anatase and rutile phase, in which anatase phase shows more content. (101), (004), (200) crystal surface diffraction peaks that are marked with square shapes are assigned to anatase, and the other four characteristic diffraction peaks of (110), (101), (111), (211) which are marked with round shapes are assigned to rutile phase. The average crystal size of TiO_2 in TiO_2 -Graphene Oxide under different conditions is about 9 nm. Furthermore, a very slight diffraction peak which is marked with a pentagon shape at $2\theta=11^\circ$ belongs to (002) crystal of GO. Compared to (002) diffraction peak of GO in Figure 1(b), the diffraction peak intensity of TiO_2 -Graphene Oxide at $2\theta=11^\circ$ is obviously reduced, and the X ray diffraction peak of GO(100) crystal at $2\theta=42^\circ$ totally disappears. These results explain that the layered GO pretreated with sodium hydroxide

Figure 1 XRD patterns of (a) TiO_2 -Graphene Oxide, GO exfoliated by 0.2 M NaOH (b) GO.

solution has been exfoliated to a great extent and formed graphene oxide, $[\text{TiO}]^{2+}$ groups in the solution adsorbed on the surface of graphene oxide and then the nucleation and growth of TiO_2 crystallites took place in the lamellar structure of graphene oxide, and finally formed TiO_2 -Graphene Oxide nanocomposite. The faint diffraction peak of GO which still existed in the XRD pattern which shows that a small quantity of GO was not exfoliated thoroughly, which may not play a part in the intercalating process of TiO_2 -Graphene Oxide.

2.2 XPS analysis

Figure 2(a)–(d) show XPS C1s of graphite(PG), graphite oxide(GO) and TiO_2 -Graphene Oxide (GO exfoliated by 0M NaOH and 0.2 M NaOH). In Figure 2(a), the sp^2 -hybridized carbon peak appeared near 284.6 eV with a well-known asymmetric line shape. A few additional peaks after oxidation developed due to the functional groups. The spectra were deconvoluted into five peaks of $\text{sp}^2(\text{C}-\text{C}, 285.1\text{ eV})$, hydroxyl($\text{C}-\text{OH}, 286.1\text{ eV})$, epoxide($\text{C}-\text{O}-\text{C}, 287.3\text{ eV})$, conjugated carboxyl($\text{C}=\text{O}, 288.3\text{ eV})$ and carboxyl($\text{COOH}, 290.0\text{ eV})$ groups in the graphite oxide, as is shown in Figure 2(b). Figure 2(c) and (d) show the XPS C1s of TiO_2 -Graphene Oxide in which GO was exfoliated by 0 M NaOH and 0.2 M NaOH respectively and the shape of five peaks mentioned above suffered some degree of change.

Table 1 shows the XPS data of GO and TiO_2 -Graphene Oxide such as binding energies and relative area percentages. Compared to GO, the area percentages of $\text{C}=\text{O}$ in TiO_2 -Graphene Oxide reduced sharply. To TiO_2 -Graphene Oxide(c), with the decline of $\text{C}=\text{O}$, the content of $\text{C}-\text{C}$ evidently increased. This can be interpreted by the nucleation and growth of TiO_2 in graphene oxide layer, where $\text{C}=\text{O}$ was consumed abundantly and partly reduced to $\text{C}-\text{C}$. Additionally, to TiO_2 -Graphene Oxide(d), the content of

Figure 2 XPS spectra of C1s The spectra are deconvoluted into five peaks of sp^2 , C–OH, C–O–C, C=O and COOH (a) graphite; (b) graphite oxide; (c) TiO_2 -Graphene Oxide(GO exfoliated by 0 M NaOH); (d) TiO_2 -Graphene Oxide (GO exfoliated by 0.2 M NaOH).

Table 1 XPS data of GO and TiO_2 -Graphene Oxide deconvoluted into five peaks; Binding energies(eV) and relative area percentages

	C–C	C–OH	C–O–C	C=O	COOH
GO	285.1	286.1	287.3	288.3	290.0
	22.86%	31.30%	21.91%	21.40%	2.53%
0 M NaOHc	285.1	286.0	287.2	288.3	289.9
	34.74%	34.82%	22.46%	4.74%	3.25%
0.2 M NaOHd	285.1	286.0	287.1	288.2	289.9
	16.4%	56.63%	19.03%	1.60%	6.31%

C=O decreased much more evidently while COOH increased slightly. We speculate that as GO was exfoliated by 0.2 M NaOH, GO lamella broke into smaller flakes and the edge area of the formed graphene oxide flakes increased, which caused much more content of C=O and COOH. In addition, OH^- introduced from the alkaline solution can further react with graphene oxide. Therefore, the area percentages of C–OH enhanced obviously while the content of C–C decreased. These results show that C=O has the priority to react with $[TiO]^{2+}$ during the formation of TiO_2 which makes it decrease sharply, while COOH and C–OH react with $[TiO]^{2+}$ more difficultly, but the presence of these groups can improve the dispersion of graphene oxide.

Figure 3(a)–(b) describe XPS $Ti2p$ of TiO_2 -Graphene Oxide (GO exfoliated by 0 M NaOH(a) and 0.2 M NaOH (b)). The $Ti2p$ region can be decomposed into several contributions corresponding to the different oxidation states of titanium. Each contribution consists of a doublet between the $2p_{3/2}$ and $2p_{1/2}$ peaks. For each doublet, the ratio of the area of the two peaks $A(Ti2p_{1/2})/A(Ti2p_{3/2})$ is equal to 0.5

and the binding energy difference, $\Delta E_b = E_b(Ti2p_{1/2}) - E_b(Ti2p_{3/2})$ is always 5.7 eV, as previously reported [30,31].

In Figure 3, it is characterized by a main doublet composed of two symmetric peaks situated at $E_b(Ti2p_{1/2}) = 464.7$ eV and $E_b(Ti2p_{3/2}) = 459.1$ eV, this main doublet is assigned to Ti^{IV} . From the data of Table 2, we can find that titanium in these two kinds of composite are almost four valence state, the molar contents are accounted for 96.37% and 96.99% respectively. In addition, the symmetric peaks of the corresponding doublet situated at $E_b(Ti2p_{1/2}) = 463.1$ eV and $E_b(Ti2p_{3/2}) = 457.4$ eV are assigned to Ti^{3+} and the molar contents are much lower (3.63% and 3.01% respectively). The binding energy position of Ti^{2+} situated at $E_b(Ti2p_{1/2}) = 461.7$ eV and $E_b(Ti2p_{3/2}) = 456$ eV, but we have not found the XPS peaks of Ti^{2+} in both composites.

2.3 TG analysis

Figure 4 depicts the TGA curve of TiO_2 -Graphene Oxide composite (GO exfoliated by 0.2 M NaOH). There are three

Figure 3 XPS spectra of Ti2p (a) TiO₂-Graphene Oxide(GO exfoliated by 0 M NaOH); (b) TiO₂-Graphene Oxide (GO exfoliated by 0.2 M NaOH).

Table 2 XPS data of TiO₂-Graphene Oxide and binding energies(eV) and relative area percentages

	Ti ^{IV} 2p _{3/2}	Ti ^{IV} 2p _{1/2}	Ti ^{III} 2p _{3/2}	Ti ^{III} 2p _{1/2}	Ti ^{II} 2p _{3/2}	Ti ^{II} 2p _{1/2}
0 M NaOH(a)	459.1 96.37%	464.7 96.37%	457.4 3.63%	463.1 3.63%	456.0 0%	461.7 0%
0.2 M NaOH(b)	459.0 96.99%	464.7 96.99%	457.4 3.01%	463.1 3.01%	456.0 0%	461.7 0%

obvious weight loss stages. The first stage is from room temperature 25°C to 135°C which can be attributed to the dehydration process of water molecules in the interlayer of graphene oxide. The second is from 135°C to 280°C, it is due to the burning decomposition of oxygen-containing groups attached to graphene oxide layers. And the third stage is from 280°C to 740°C which can be assigned to the burning decomposition of carbon skeleton. The mass ratio of TiO₂ particles in the TiO₂-Graphene Oxide composite is about 57.0% which is consistent with the high temperature heat-treatment results listed in Table 3. According to the TGA curve and heat-treatment results of TiO₂-Graphene Oxide, we can speculate the mass ratio of H₂O, graphene oxide and TiO₂ in composite is 1:3.5:6.4.

2.4 FE-SEM analysis

Figure 5 reveals the SEM images of TiO₂-Graphene Oxide in which GO was separately exfoliated by 0 M NaOH (Figure 5(a), parallel to graphene oxide layer) and by 0.2 M NaOH (Figure 5(b), parallel to graphene oxide layer, Figure

Figure 4 TGA curve of TiO₂-Graphene Oxide.

Table 3 Heat-treatment results of TiO₂-Graphene Oxide (GO exfoliated by 0.2 M NaOH) at 1200°C for 2 h in air atmosphere

	Sample mass before heat treatment (mg)	Sample mass after heat treatment (mg)	Residual mass percentage
TiO ₂ -Graphene Oxide (0.2 M NaOH)	200	117.6	58.8%

5(c), perpendicular to graphene oxide layer).

In Figure 5(a), we can find that large amounts of fine TiO₂ nano-particles are located at graphene oxide flakes which own an area of about 200 nm. The average crystal size of TiO₂ is about 9 nm. To the samples treated by 0.2 M NaOH in Figure 5(b) and (c), the size of graphene oxide flakes reduced to about 100 nm. At the same time, large-scale pieces of graphene oxide can also be observed at which TiO₂ particles are located. These broader graphene oxide layers might be due to the connection of the graphene oxide flakes during the reaction between C=O located at the edge of graphene oxide and [TiO]²⁺ induced by the hydrolysis of Ti(SO₄)₂. Compared to the stack structure of graphene oxide flakes in Figure 5(a), the generation of broader graphene oxide layers provides more positions for the nucleation and growth of TiO₂ grains.

According to the above results, the formation mechanism of TiO₂-Graphene Oxide can be elaborated as follows. When GO was exfoliated by NaOH, large amounts of hydrated sodium ions and water molecules diffused into the GO interlayer, GO lamella was exfoliated and broke into flakes which have better dispersion performances. These formed graphene oxide flakes make [TiO]²⁺ induced by the hydrolysis of Ti(SO₄)₂ diffuse from the edge of graphene oxide and the substitute the alkali metal ions existed in the interlayer. During the nucleation and growth of TiO₂ grains, a proportion of [TiO]²⁺ groups may be consumed due to the

Figure 5 FE-SEM images of TiO₂-Graphene Oxide. (a) GO exfoliated by 0 M NaOH, (b) and (c) GO exfoliated by 0.2 M NaOH.

reaction with conjugated carboxyl (C=O) located at the edges of GO layers and connect the exfoliated broken graphene oxide flakes together into broader graphene oxide layers. In addition, the XPS results show that COOH and C–O groups cannot easily react with [TiO]²⁺, while these oxygen-containing groups evidently improve the inertia state of graphite surface. And many TiO₂ grains nucleate

and grow in COOH and C–OH sites by the way of heterogeneous nucleation. However, most of the TiO₂ grains formed through a heterogeneous nucleation way in which [TiO]²⁺ groups defined TiO₂ crystals firstly generated on the surface of graphene oxide as interface. Finally these kinds of TiO₂-Graphene Oxide composites with layered structure were successfully synthesized.

2.5 HR-TEM analysis

Figure 6 gives the high-resolution TEM images of TiO₂-Graphene Oxide(GO exfoliated by 0.2 M NaOH). In Figure 6(a), the diffraction spots in TiO₂-Graphene Oxide composite correspond to different crystal plane of tetragonal-structure TiO₂ crystal cell such as (101), (004) crystal surface assigned to anatase and (301) crystal surface assigned to rutile. However, in Figure 6(b), the diffraction spots correspond to (100) crystal plane of hexagonal-structure GO crystal cell and the scattered diffraction spots below the hexagonal lattice correspond to (101) crystal surface of tetragonal-structure TiO₂ crystal cell. These results indicate the existence of TiO₂ particles beneath the graphene oxide layers though the number of TiO₂ grains is relatively small.

HRTEM tests confirmed that the TiO₂ grains can nucleate and grow in the interlayer and outer layer of graphene oxide, which agrees with the SEM analysis that TiO₂ particles uniformly distributed in both sides of graphene oxide layers.

2.6 Photocatalytic properties

Figure 7 shows the photocatalytic properties of TiO₂-Graphene Oxide under different conditions contrasted with Degussa P25 powders, in which methyl orange(MO) played a role of a target degradation product. The results show that the photocatalytic properties of TiO₂-Graphene Oxide composite (GO exfoliated by NaOH) are magnificent. Especially to the case of GO exfoliated by 0.2 M NaOH, the photodegradation efficiency to MO in 15 min is up to 87.2%, which can also be expressed as $\eta=1.16 \text{ mg min}^{-1} \text{ g}^{-1}$. As to GO exfoliated by 0 M NaOH or 0.5 M NaOH, the photocatalytic properties of TiO₂-Graphene Oxide composite are slightly worse, as the data shown in Figure 7, 66.7% in 15 min, $\eta=0.89 \text{ mg min}^{-1} \text{ g}^{-1}$ and 83.4%, $\eta=1.11 \text{ mg min}^{-1} \text{ g}^{-1}$ respectively.

Although Degussa P25 powders can degrade 91.3% MO in 60 min, such value in 15 min is only 38.4%, $\lambda=0.51 \text{ mg min}^{-1} \text{ g}^{-1}$, considerably lower than that of TiO₂-Graphene Oxide composite. This may be caused by two factors. First, TiO₂-Graphene Oxide has a better adsorption capacity than P25 powder, which makes TiO₂ particles have higher probabilities to contact with MO. Second, the average crystal size of TiO₂ in TiO₂-Graphene Oxide under different conditions is about 9 nm while the grain size of Degussa P25 powders comes up to 21 nm. Contrasted with P25, larger

Figure 6 (a), (b) HRTEM images of TiO_2 -Graphene Oxide (GO exfoliated by 0.2 M NaOH).

Figure 7 Photocatalytic properties of P25 powders and TiO_2 -Graphene Oxide under different conditions.

specific surface area of TiO_2 in intercalation composite certainly improves the photodegradation efficiency.

In addition, the properties of TiO_2 -Graphene Oxide composite (GO exfoliated by 0.2 M NaOH) are superior compared to that of the composite in which GO was exfoliated by 0 M NaOH. These results can be explained as follows, when GO was exfoliated by NaOH, hydrated sodium ions and water molecules diffused into the GO interlayer, GO lamella broke into flakes and the formed graphene oxide flakes owned better dispersion performances which provided more positions for the nucleation and growth of TiO_2 grains. In this case, when the composite is used to degrade methyl orange, more MO molecules can contact with the homogeneously distributed TiO_2 nanoparticles. Under UV light irradiation, more methyl orange molecules will be degraded and the photodegradation efficiency of the sample will be raised effectively.

2.7 Reusable performance

Figure 8 depicts the reusable performance test of TiO_2 -Graphene Oxide (a) and P25 powders (b). In Figure 8(a), TiO_2 -Graphene Oxide composite has been experienced successive degradation process (3 times) to MO and the photodegradation efficiency in 15 min is $1.16 \text{ mg min}^{-1} \text{ g}^{-1}$, $1.02 \text{ mg min}^{-1} \text{ g}^{-1}$ and $0.83 \text{ mg min}^{-1} \text{ g}^{-1}$ respectively. Compared to Figure 8(b), when P25 powders were used 3 times successively to degrade MO, the degradation rates maintained at about $\eta=0.51 \text{ mg min}^{-1} \text{ g}^{-1}$ which indicated that TiO_2 -Graphene Oxide has better photodegradation efficiency. However, with the increase of repetitions, the efficiency of TiO_2 -Graphene Oxide declined gradually. This phenomenon can be attributed to the agglomeration of TiO_2 grains formed on both sides of the graphene oxide layers which made the contact area between MO molecules and TiO_2 particles decrease and resulted in the reduction of photodegradation efficiency.

2.8 Stable performance

Figure 9 describes the stable performance test of TiO_2 -Graphene Oxide (a) and P25 powders (b). In order to test the impact of powder agglomeration on photocatalytic properties, we exposed these two kinds of photocatalysts at room temperature for 0–8 weeks. In Figure 9(a), when the composite stored at room temperature for 4 weeks, TiO_2 -Graphene Oxide powders still own great stability properties and the agglomeration is not very evident which leads to almost no decline of photocatalytic efficiency (from $\eta=1.16 \text{ mg min}^{-1} \text{ g}^{-1}$ to $\eta=1.13 \text{ mg min}^{-1} \text{ g}^{-1}$). However, when the composite was exposed at room temperature for 8 weeks, the degradation rates of TiO_2 -Graphene Oxide decreased to $\eta=0.91 \text{ mg min}^{-1} \text{ g}^{-1}$ which means that the agglomeration exacerbated and the stability became poor in this stage. In Figure

Figure 8 Reusable performance of (a) TiO_2 -Graphene Oxide (GO exfoliated by 0.2 M NaOH) and (b) P25 powders.

Figure 9 Stable performance of (a) TiO_2 -Graphene Oxide (GO exfoliated by 0.2 M NaOH) and (b) P25 powders.

9(b), the agglomeration of P25 powders is also obvious when the powders were exposed at room temperature for 8 weeks. The efficiency of P25 decreased from $\eta=0.51 \text{ mg min}^{-1} \text{ g}^{-1}$ to $\eta=0.40 \text{ mg min}^{-1} \text{ g}^{-1}$. Compared with the two photocatalysts, both the degradation rates of TiO_2 -Graphene Oxide and P25 powders are about 78% of the initial efficiency when exposed at room temperature for 8 weeks, which indicates that although the average grain size of TiO_2 in TiO_2 -Graphene Oxide is only nearly half of the P25, the agglomeration does not multiply. The photocatalytic properties of TiO_2 -Graphene Oxide are always superior to that of P25 powder.

3 Conclusions

(1) The TiO_2 -Graphene Oxide composite was successfully prepared at low temperature (80°C) with graphite oxide (GO) and titanium sulfate ($\text{Ti}(\text{SO}_4)_2$) as initial reactants. GO was firstly exfoliated by NaOH and formed single and multi-layered graphite oxide mixture which can be defined as graphene oxide, $[\text{TiO}]^{2+}$ induced by the hydrolysis of $\text{Ti}(\text{SO}_4)_2$ diffused into graphene oxide interlayer by electrostatic attraction, the nucleation and growth of TiO_2 crystallites took place at low temperature and TiO_2 -Graphene Oxide composite was successfully synthesized.

(2) Under the irradiation of UV light, the photodegradation efficiency of TiO_2 -Graphene Oxide to methyl orange in 15 min is up to 87.2%, $\eta=1.16 \text{ mg min}^{-1} \text{ g}^{-1}$. Compared with Degussa P25 powders, 38.4% in 15 min, $\eta=0.51 \text{ mg min}^{-1} \text{ g}^{-1}$, these intercalation composites own much better efficiency. This is due to two main reasons. The first is the better adsorption capacity of TiO_2 -Graphene Oxide composite, and the second is the smaller average grain size of TiO_2 crystallites (about 9 nm) which may be due to the limit of the unique layered structure of TiO_2 -Graphene Oxide.

(3) The photodegradation efficiency of TiO_2 -Graphene Oxide composite (GO exfoliated by 0.2 M NaOH) is superior compared to that of the sample treated by 0 M NaOH. These results can explain that when GO was exfoliated by NaOH, hydrated sodium ions and water molecules diffused into the GO interlayer, GO lamella broke into flakes and formed graphene oxide flakes owned better dispersion performances which provided more positions for the nucleation and growth of TiO_2 grains.

(4) The reusable performance test of TiO_2 -Graphene Oxide shows that the photocatalytic efficiency of the composite slightly declined but still maintained a high level when the photocatalysts had been experienced successive degradation process (3 times) to MO. Moreover, the stable performance test confirmed that when the composite was

stored at room temperature for 4 weeks, the TiO₂-Graphene Oxide powders still owned great stability properties and the agglomeration was not very evident which resulted in almost no decline of photocatalytic efficiency. However, when the composite was exposed at room temperature for 8 weeks, both the degradation rates of TiO₂-Graphene Oxide and P25 powders were about 78% of the initial efficiency which indicated that although the average grain size of TiO₂ is only nearly half of the P25, the agglomeration did not multiply. The photocatalytic properties of TiO₂-Graphene Oxide are always superior to that of P25 powder.

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