New insights into the relationship between photocatalytic activity and TiO$_2$–GR composites

Yanyan Zhu,†a Yajun Wang,†a Wenqing Yao,ab Ruilong Zonga and Yongfa Zhu*a

TiO$_2$–graphene (TiO$_2$–GR) composites were synthesized via hydrothermal methods in an ethanol–water solvent. The photocatalytic oxidation, photocatalytic reduction and photoelectrochemical properties were systematically investigated to explore the real role of graphene in the TiO$_2$–GR composite photocatalysts. The pollutant degradation and adsorption results strongly indicated that the composited graphene in TiO$_2$–GR cannot enhance the photocatalytic oxidation activity in the degradation of pollutants. The migration process of photo-generated holes in the photocatalytic oxidation reaction is the rate-determining step, which cannot be promoted by the composited graphene in TiO$_2$–GR. However, composited graphene can promote the migration of photo-generated electrons in TiO$_2$–GR due to its excellent conductivity, which mainly enhances the H$_2$ evolution performance and photoelectrochemical properties.

1. Introduction

Graphene has attracted widespread attention due to its outstanding mechanical, thermal, optical, and electronic properties. Agraphene possesses excellent electron mobility, an extremely high theoretical surface area and a high adsorption capacity for organic pollutants and metal ions. Recently, graphene has been used to enhance photocatalytic performance. Many graphene-based photocatalysts have been reported, such as CdS–graphene, TiO$_2$–graphene, ZnO–graphene and so on. Graphene has been considered to enhance the photocatalytic oxidation and photocatalytic reduction activity of many semiconductor photocatalysts as a very good cocatalyst. Many reports have shown that the combination of graphene with photocatalysts can enhance their photocatalytic activity in the degradation of organic pollutants. It is a widely held belief that graphene can quickly separate and transfer photo-generated electrons from the conduction band of photocatalysts and further enhance their photocatalytic oxidation and photocatalytic reduction activity. It is well known that, as a carbon material with a high specific surface area, graphene can strongly adsorb many organic pollutants during the photocatalytic reaction process, which would affect the evaluation of graphene-based composite photocatalysts. In many reported works, dyes (methylene blue (MB), methyl orange, rhodamine B and so on) have been chosen as probes to evaluate photocatalytic activity, meanwhile, the strong adsorption effect of graphene towards the pollutants was neglected. The strong adsorption of pollutants by graphene will result in a great difference in the pollutant’s initial reaction concentration. The remaining concentration of MB over TiO$_2$ was about 4.4 times higher than that over TiO$_2$–10%GO after reaching the adsorption–desorption equilibrium. In this situation, the evaluation of the photocatalytic activity over TiO$_2$ and TiO$_2$–10%GO might not be representative of the actual activity. Moreover, the photocatalytic performance of TiO$_2$–GR gradually decreased over several reaction cycles, such that only 53% of its photocatalytic performance remained after five cycles of photocatalytic reactions. In contrast, TiO$_2$ usually maintains better stability in the photocatalytic degradation of pollutants. The above results indicate that the high photocatalytic oxidation performance of TiO$_2$–graphene may be due to the strong adsorption effect of graphene towards pollutants, rather than due to photocatalytic degradation. It is worth pointing out that different initial reaction concentrations of pollutants will lead to a great difference in the photocatalytic reaction apparent rate constant k and C/C$_0$. The lower the initial reaction concentration of the pollutant is, the higher the calculated apparent rate constant k will be. However, there is no report regarding the influence of the strong adsorption of graphene on a pollutant’s initial reaction concentration and the photocatalytic activity of graphene-based photocatalysts. Therefore, in many works, the explanations for the role of graphene may have some mistakes, because the effect of the strong...
adsorption of pollutants by graphene was not taken into account.

Moreover, in photocatalytic reduction, many reports highlight that the introduction of graphene can improve the photocatalytic evolution of \( \text{H}_2 \).\textsuperscript{22-23} Yu and co-workers prepared CdS–graphene composites and found that the CdS–graphene composites exhibited a higher \( \text{H}_2 \) evolution rate and higher quantum efficiency than pure CdS.\textsuperscript{23} Thus, key fundamental issues are naturally called into question. Can graphene really enhance photocatalytic activity?

In this work, TiO\(_2\)–GR composites were synthesized via a hydrothermal method in an ethanol–water solvent.\textsuperscript{7,8} The photocatalytic pollutant degradation activity, photocatalytic \( \text{H}_2 \) evolution performance from water splitting and photoelectrochemical properties were systematically investigated. The real role of graphene in photocatalytic oxidation has been examined by eliminating the strong adsorption effect of graphene towards pollutants.

2. Experimental

2.1 Preparation of TiO\(_2\)–GR samples

GO was prepared from natural graphite via a modified Hummers’ method.\textsuperscript{24} The GO solution was obtained through the dispersion of the mixture into water and its concentration was calculated by drying 100 g GO solution. TiO\(_2\)–GR composites were prepared via a solvent-thermal method according to the literature.\textsuperscript{7,8} The appropriate amount of 0.523% GO solution was added into 150 mL ethanol–water (ethanol–deionized water = 1 : 2 v/v). Then 1.0 g Degussa TiO\(_2\) was added into the mixture and vigorously stirred at room temperature for 2 h. The above solution was transferred into a 200 mL autoclave and maintained at 120 °C for 24 h to achieve the reduction of GO and the deposition of TiO\(_2\) onto the graphene sheet. Finally, the resulting composite was washed with deionized water several times and dried at 60 °C. Then, TiO\(_2\)–GR composites with different weight ratios of graphene were obtained.

2.2 Photocatalytic experiment

The photocatalytic oxidation activity of the composites was evaluated in the degradation of methylene blue (MB) and phenol under 254 nm UV light. 25 mg photocatalyst was totally dispersed in a 100 mL aqueous solution of MB (11.2–37.4 ppm) or phenol (10–50 ppm). Before irradiation, the suspensions were magnetically stirred in the dark for 4 h to reach the adsorption–desorption equilibrium. 3.0 mL aliquots were sampled at certain time intervals during the experiment and centrifuged to remove the photocatalysts completely. The solution was analyzed on a Hitachi U-3010 UV-Vis spectrophotometer to get the concentration of MB. The concentration of phenol was analyzed using a High-Performance Liquid Chromatography (Lumtech HPLC) system, using a UV detector operating at 270 nm. The mobile phase was methanol and deionized water (60 : 40 v/v) and its flow rate was 1.0 mL min\(^{-1}\). The oxidative species in the photocatalytic system could be examined through trapping by tert-butyl alcohol (t-BuOH, hydroxyl radical scavenger), ethylenediaminetetraacetic acid disodium salt (EDTA–2Na, hole scavenger) and \( \text{N}_2 \) (superoxide radical scavenger).

In the photocatalytic \( \text{H}_2 \) evolution, 0.2 g photocatalyst was dispersed in a 100 mL 15% (v/v) mixed methanol–water solution under 250–380 nm UV irradiation. The amount of evolved \( \text{H}_2 \) was detected using a gas chromatograph equipped with a thermal conductivity detector (TCD).

2.3 Characterization

UV-Vis diffuse reflectance spectra (DRS) of the samples were measured using a Hitachi U-3010 UV-Vis spectrophotometer. Transmission electron microscopy (TEM) images were obtained on a Hitachi HT7700 electron microscope operating at an accelerating voltage of 100 kV. Raman spectra were measured using an HR800 confocal Raman microscope (Horiba) in the range of 200–2000 cm\(^{-1}\). The Brunauer–Emmett–Teller (BET) surface area and pore size distribution were measured using an ASAP 3020 instrument from Micromeritics.

The photocurrent and electrochemical impedance spectra were measured on an electrochemical system (CHI-660B, China) using a standard three-electrode cell under a 11 W germicidal lamp at a wavelength of 254 nm. The ITO/sample (20 mm × 45 mm) acted as the working electrode, a platinum wire acted as the counter electrode and a standard calomel electrode (SCE) acted as a reference electrode. The ITO/sample was prepared by a dip-coating method: 6 mg photocatalyst was suspended in 0.75 mL ethanol to make a slurry by ultrasonic treatment, and then dip-coated onto an ITO glass electrode. The as-prepared electrodes were dried under ambient conditions for about 12 h, and then calcined at 120 °C for 5 h in air. The electrolyte solution was 0.1 M Na\(_2\)SO\(_4\), and potentials are given with reference to the SCE. The photoelectric responses of the as-prepared photocatalysts with the light on and off were measured at 0.0 V. Electrochemical impedance spectroscopy (EIS) was carried out at the open circuit potential, and a sinusoidal ac perturbation of 5 mV was applied to the electrode over the frequency range of 0.05–10\(^5\) Hz.

3. Results and discussion

3.1 Intrinsic role of graphene in the photocatalytic performance of TiO\(_2\)–GR

Graphene has a good selective adsorption ability for many organic pollutants, such as dyes, as a high BET surface area carbon material.\textsuperscript{25} The adsorption and degradation of MB over TiO\(_2\) and TiO\(_2\)–GR composites were investigated at various MB initial concentrations (Fig. 1 and S1–S3†). Before irradiation, the suspensions were stirred in the dark for 4 h to reach the adsorption–desorption equilibrium. As is well known, the photocatalytic oxidation process conforms to pseudo-first order kinetics.\textsuperscript{26} When the initial concentration of MB was low (3.7 ppm, Fig. 1a), the remaining MB concentrations (initial reaction concentrations of MB) in the solution over TiO\(_2\), TiO\(_2\)–1% GR, TiO\(_2\)–5% GR and TiO\(_2\)–10% GR were 3.4 ppm, 2.5 ppm, 1.5 ppm and 1.1 ppm after reaching the adsorption–desorption
equilibrium in the dark. It should be mentioned that the remaining MB concentration over TiO$_2$–10% GR is 1.1 ppm, which is only 31% of the initial MB concentration (3.7 ppm). However, the remaining MB concentration in TiO$_2$ was 3.4 ppm, which means that the initial reaction concentration of MB in the solution with the TiO$_2$ system was much higher than those in the solutions with the TiO$_2$–GR composites. These great differences in the MB initial reaction concentration can be observed in most previously reported works.$^{9,16,27}$ Apparently, a comparison of the photocatalytic activities of TiO$_2$ and TiO$_2$–GR, by calculating the apparent rate constant $k$, cannot be reasonably made under these conditions. More importantly, in a photocatalytic reaction, the different initial reaction concentration of a pollutant would result in a different calculated apparent rate constant $k$. The lower the initial reaction concentration of MB is, the higher the calculated apparent rate constant $k$ will be.$^{19,28}$ Therefore, TiO$_2$–1% GR, TiO$_2$–5% GR and TiO$_2$–10% GR were shown to have higher apparent rate constants and better photocatalytic performance than TiO$_2$.$^{13,14,16}$ In the meantime, excess black graphene would absorb a lot of light and inhibit the efficient absorption of photons by TiO$_2$ in the TiO$_2$–10% GR system. The TiO$_2$–5% GR composite showed the best photocatalytic performance, with a maximal apparent rate constant $k$ of 0.234 min$^{-1}$, which was 76% higher than that of TiO$_2$ (0.133 min$^{-1}$). Analogous results were also observed with other low initial MB concentrations (11.2 ppm and 18.7 ppm) and the results are shown in Fig. S1 and S2.$^\dagger$

When the initial concentration of MB was high (37.4 ppm, Fig. 1b), the remaining MB concentrations in solution over TiO$_2$, TiO$_2$–1% GR, TiO$_2$–5% GR and TiO$_2$–10% GR after reaching the adsorption–desorption equilibrium in the dark were 36.7 ppm, 35.5 ppm, 34.0 ppm and 31.8 ppm, respectively, which were 98, 95, 91 and 85% of the initial MB concentration, respectively. There was no obvious difference between TiO$_2$ and the TiO$_2$–GR composites in terms of the remaining MB concentrations, indicating that the pollutant’s initial reaction concentrations were almost the same. Under these conditions, the photocatalytic activities of the TiO$_2$–GR composites were not higher than that of TiO$_2$. Analogous results could be obtained in another high initial MB concentration reaction (29.9 ppm, Fig. S3†). Based on the above results, the following can be speculated: the essential photocatalytic oxidation activity of TiO$_2$–GR is not higher than that of TiO$_2$; the higher calculated apparent rate constant $k$ of TiO$_2$–GR is due to the great difference in the initial reaction concentration of MB caused by the strong adsorption by graphene. After eliminating the adsorption–desorption equilibrium by increasing the initial concentration of MB, the calculated apparent rate constant $k$ of the TiO$_2$–GR composites is not higher than that of TiO$_2$.

Moreover, TiO$_2$ and the TiO$_2$–GR composites were used to adsorb and photocatalytically degrade colorless phenol. Fig. 2 shows the adsorption and photocatalytic degradation of 10.0 ppm phenol over TiO$_2$ and the TiO$_2$–GR composites. After the adsorption–desorption equilibrium was reached, the remaining phenol concentrations in the TiO$_2$ and TiO$_2$–GR systems were basically the same, suggesting that the initial reaction concentrations of phenol were almost the same. In this case, the photocatalytic activities of the TiO$_2$–GR composites were lower than that of TiO$_2$. These results strongly highlight that the essential photocatalytic activity of TiO$_2$–GR is not higher than that of TiO$_2$ after eliminating the adsorption effect of graphene. Moreover, the adsorption and photocatalytic degradation of phenol over TiO$_2$ and TiO$_2$–GR in 30.0 ppm and 50.0 ppm phenol initial concentrations were also investigated and analogous results could be obtained (Fig. S4 and S5†). These results further confirm our speculation: that the photocatalytic activity of TiO$_2$–GR cannot truly be enhanced by the composites
graphene when the adsorption effect of graphene towards the pollutants is eliminated.

The \( \text{H}_2 \) evolution performance of TiO\(_2\) and the TiO\(_2\)–GR composites was evaluated to reveal the intrinsic effect of graphene on photocatalytic reduction. As shown in Fig. 3, all of the TiO\(_2\)–GR composites show higher \( \text{H}_2 \) evolution activity than TiO\(_2\). The \( \text{H}_2 \) evolution performance of the TiO\(_2\)–GR composites first increased and then decreased with an increase in the graphene loading amount. The TiO\(_2\)–8% GR composite exhibits the optimum \( \text{H}_2 \) evolution activity (30.3 \( \mu \text{mol h}^{-1} \)), which is 51.6 times higher than that of TiO\(_2\). However, a further increase in the proportion of graphene results in a decrease in the \( \text{H}_2 \) evolution activity. It is reasonable that the introduction of a large proportion of graphene will inhibit the efficient absorption of photos by TiO\(_2\) and further lead to a decreased photocatalytic performance. Thus, a suitable amount of graphene is important for optimizing the \( \text{H}_2 \) evolution performance of TiO\(_2\)–GR composites. The excellent electron mobility and high surface area of graphene can effectively promote the migration of photo-generated electrons, increase the reaction space, and act as a \( \text{H}_2 \) evolution cocatalyst, leading to an enhanced \( \text{H}_2 \) evolution performance.\(^{23,29}\)

Fig. 4 shows the photocurrents of the TiO\(_2\) and TiO\(_2\)–GR composites. The TiO\(_2\)–GR composites exhibit a higher photocurrent than TiO\(_2\), and the photocurrent of the TiO\(_2\)–GR composites first increases and then decreases as the graphene loading amount increases. The excellent electron mobility of graphene can effectively promote the migration of photo-generated electrons, leading to an enhanced photocurrent. TiO\(_2\)–8% GR presents the highest photocurrent, which is consistent with the \( \text{H}_2 \) evolution performance findings.

### 3.2 Mechanism of the photocatalytic reaction

On the basis of the results for the degradation of MB and phenol, we argue that compositied graphene cannot really enhance the photocatalytic oxidation activity of TiO\(_2\). The higher apparent rate constant \( k \) of the TiO\(_2\)–GR composites is due to the lower initial reaction concentrations, caused by the strong pollutant adsorptivity of graphene. EIS and detection of the main oxidative species were performed to investigate the intrinsic role of graphene in the TiO\(_2\)–GR composites. Fig. 5 shows the EIS Nyquist plots of TiO\(_2\) and the TiO\(_2\)–GR composite photocatalysts in the dark and under UV light irradiation. The
radius of the arc on the EIS spectra reflects the solid state interface layer resistance and the surface charges transfer resistance. In the study of TiO$_2$–GR composites, EIS spectra are currently used to demonstrate the improved charge separation efficiency induced by graphene. In Fig. 5a, the arc radii of the TiO$_2$–GR composites are smaller than those of TiO$_2$ in the dark, indicating that the introduction of graphene can effectively increase the conductivity of the TiO$_2$–GR composites and reduce the surface resistance. In Fig. 5b, the EIS Nyquist plot arc radii of the TiO$_2$–GR composites are all smaller than that of TiO$_2$ under UV light irradiation, which may be attributed to two reasons: (1) improved charge separation efficiency caused by graphene or (2) the introduction of high conductivity graphene can reduce the surface resistance. As can be seen, the arc radii in the plot of the TiO$_2$–GR composites decrease with an increase in the graphene loading amount with and without light irradiation, suggesting that the surface resistance of the TiO$_2$–GR composites decreases gradually with an increase in the graphene amount. This is because the excellent conductivity of graphene can effectively reduce the surface resistance of the composite photocatalyst and promote the migration of electrons. Moreover, TiO$_2$–8% GR presents the smallest surface resistance, which is in agreement with its optimal H$_2$ evolution performance. These results indicate that graphene can promote the migration of photo-generated electrons and decrease the surface resistance of TiO$_2$–GR composites. Because graphene can only promote the migration of electrons, it can be inferred that, if the migration speed of holes is the rate-determining step in the photocatalytic reaction, forming a composite with graphene is not a valid means of enhancing the photocatalytic oxidation activity.

The detection of the main oxidative species in the photocatalytic process is important for revealing the photocatalytic mechanism. In the photocatalytic process, there are three main active species: holes, hydroxyl radicals and superoxide radicals. The main oxidative species in the photocatalytic process could be examined through the trapping by $t$-BuOH (hydroxyl radical scavenger), EDTA–2Na (hole scavenger) and N$_2$ (superoxide radical scavenger). In the degradation of MB, the photocatalytic activity of TiO$_2$ and the TiO$_2$–GR composites was greatly suppressed by the addition of a scavenger for holes (EDTA–2Na) (Fig. 6). On the contrary, the addition of a scavenger for hydroxyl radicals ($t$-BuOH) and a scavenger for superoxide radicals (N$_2$) only caused a small change in the MB degradation. These results suggest that the photo-generated holes are the main oxidative species in the TiO$_2$ and TiO$_2$–GR systems. Moreover, in phenol degradation, the photo-generated holes are also the main oxidative species of the TiO$_2$ and TiO$_2$–
GR systems. These results are shown in Fig. S6.† Therefore, the holes are the key factors in the photocatalytic oxidation reaction in TiO2 and TiO2–GR systems, and the concentration and migration speed of holes are regarded as the rate-determining factors in the photo-oxidation reaction.

It is well known that the migration rate of holes is much lower than that of electrons.33 The main oxidative species of the TiO2 and TiO2–GR systems are photo-generated holes, meaning that the improvement of the migration rate of holes is crucial for increasing the photocatalytic oxidation activity. However, the introduction of graphene can only promote the migration of electrons; thus, introducing graphene cannot effectively enhance the photocatalytic oxidation activity (Scheme 1a). The apparent enhancement of the photocatalytic oxidation activity in many reports is due to the low initial reaction concentration caused by the strong pollutant adsorptivity of graphene. In the photocatalytic reduction reaction for H2 evolution, the photo-generated electrons in the CB of TiO2 will transfer into the graphene sheet and subsequently react with the adsorbed H+ ions to form H2 (Scheme 1b).10,20,29,34 The electrons play a major role in photocatalytic H2 evolution, and graphene acts as a H2 evolution cocatalyst. Furthermore, the excellent electron mobility and high surface area of graphene can promote the migration of photo-generated electrons and increase the reaction space,21 leading to an enhanced H2 evolution activity.

3.3 Structure and morphology of the TiO2–GR composites

Table 1 shows the BET surface area and pore structure of TiO2 and TiO2–GR composites. The BET surface area of the TiO2–GR composites gradually increases with an increase in the amount of graphene. The BET surface area of TiO2–10% GR (80.6 m2 g−1) is almost double that of TiO2 (46.8 m2 g−1), meaning that the adsorption of pollutants over TiO2–10% GR is greatly enhanced.

Fig. 7 shows the TEM images of TiO2 and the TiO2–GR composites. When the loading amount of graphene was low (TiO2–1% GR), the graphene sheet could not be observed (Fig. 7b). As can be seen, with an increase in the graphene loading amount (TiO2–5% GR and TiO2–10% GR), the TiO2 particles were well dispersed on the graphene sheet (Fig. 7c and d). Parts of the graphene sheets were blank and didn’t interact with TiO2, and these would become the adsorption centres for pollutants during the process of photocatalytic oxidation.9,14 However, an appropriate amount of graphene in the TiO2–GR composites is able to promote the migration of electrons and then improve the H2 evolution performance.

The range of light absorption plays a very important role in photocatalysis.4,15,16 The optical properties of TiO2 and the TiO2–GR composites were measured using UV-Vis DRS (Fig. 8). TiO2 exhibits a fundamental absorption edge at 400 nm. In the TiO2–GR composites, the addition of graphene induces a continuous background absorption band in the range of 400–800 nm. The background absorption intensity in the range of 400–800 nm gradually increases for TiO2–GR with an increase in the amount of graphene, which is in agreement with the black color of the samples. It can be observed that, at the absorption edge, the TiO2–GR spectra red shift to a higher wavelength than that of TiO2. However, it is very difficult to determine the value for this red shift, because the background absorption ranging from 400–800 nm is increased upon the addition of graphene to TiO2.7

The Raman spectra of graphene and the TiO2–GR composites are shown in Fig. S7.† As can be seen, all of the samples present two peaks at around 1350 cm−1 and 1590 cm−1, which can be attributed to the defects in the hexagonal graphitic layers.

Table 1  BET surface area and pore structure of TiO2 and TiO2–GR

<table>
<thead>
<tr>
<th>Samples</th>
<th>( S_{\text{BET}} ) (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>46.8</td>
<td>0.003</td>
<td>8.2</td>
</tr>
<tr>
<td>TiO2–1% GR</td>
<td>56.8</td>
<td>0.002</td>
<td>16.5</td>
</tr>
<tr>
<td>TiO2–5% GR</td>
<td>67.9</td>
<td>0.002</td>
<td>14.9</td>
</tr>
<tr>
<td>TiO2–10% GR</td>
<td>80.6</td>
<td>0.001</td>
<td>12.1</td>
</tr>
</tbody>
</table>

Fig. 7  TEM images of TiO2 and the TiO2–GR composites: (a) TiO2, (b) TiO2–1% GR, (c) TiO2–5% GR, and (d) TiO2–10% GR.
and that the increased apparent rate constant of photocatalytic reduction, graphene can effectively act as a cocatalyst to promote the migration of photo-generated electrons, resulting in an improved H₂ evolution activity. Our results strongly suggest that the composited graphene cannot act as a cocatalyst to promote the migration of photo-generated electrons, resulting in an improved H₂ evolution activity. Our findings is expected to counter the existing misleading message on the effect of graphene and provide new insights into the relationship between photocatalytic activity and graphene-based photocatalysts.

4. Conclusions

In this work, TiO₂–GR composites were synthesized via hydrothermal methods in an ethanol–water solvent. The role of graphene in the photocatalytic oxidation and photocatalytic reduction of TiO₂–GR composites has been systematically investigated. The pollutant adsorption and degradation results strongly suggest that the composited graphene cannot enhance the photocatalytic oxidation performance of TiO₂, and that the increased apparent rate constant k of the TiO₂–GR composite is due to the lower initial reaction concentration caused by the strong pollutant adsorptivity of graphene. In photocatalytic reduction, graphene can effectively act as a cocatalyst to promote the migration of photo-generated electrons, resulting in an improved H₂ evolution activity. Our findings is expected to counter the existing misleading message on the effect of graphene and provide new insights into the relationship between photocatalytic activity and graphene-based photocatalysts.

Acknowledgements

This work was partly supported by National Basic Research Program of China (2013CB632403), National High Technology Research and Development Program of China (2012AA062701) and Chinese National Science Foundation (21437003 and 21373121).

References