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Synthesis and characterization of TiO₂/graphene oxide nanocomposites for photoreduction of heavy metal ions in reverse osmosis concentrate

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In this study, graphene oxide (GO), titanium dioxide (TiO₂) and TiO₂/GO nanocomposites were synthesized as the catalysts for photoreduction of endocrine disrupting heavy metal ions in reverse osmosis concentrates (ROC). The morphology, structure and chemical composition of these catalysts were characterized by scanning electron microscopy, transmission electron microscopy, powder X-ray diffraction, Brunauer–Emmett–Teller analysis, Barrett–Joyner–Halenda, Fourier transform infrared spectroscopy and Raman spectroscopy. The photocatalytic experiments showed that TiO₂/GO nanocomposites exhibit a higher photoreduction performance than pure TiO₂ and GO. Under the optimal conditions, the removal rates of Cd²⁺ and Pb²⁺ can reach 66.32 and 88.96%, respectively, confirming the effectiveness of photoreduction to reduce the endocrine disrupting heavy metal ions in ROC resulted from the combined adsorption–reduction with TiO₂/GO nanocomposites.

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1 Introduction

Reverse osmosis (RO) membrane technology is used widely in the treatment of wastewater and potable water, from which the reverse osmosis concentrate (ROC) is produced.¹ However, the treatment of ROC is still a challenge.² The ROC contains high salinity and elevated levels of ions and organics. The organics including endocrine disrupting chemicals (EDCs), emerging contaminants, persistent organic pollutants (POPs), pharmaceuticals, *etc.*, can cause significant damages to the environment. Untreated or improperly managed ROC can generate severe ecotoxicological risks and result in adverse environmental effects.^{3,4}

In particular, EDCs consist of a large group of emerging contaminants and are widely distributed in various surface and ground waters, which can disrupt the hormonal system and generate a negative health effect on reproductive, neurological and immune systems.^{5,6} Generally, EDCs can be classified into five categories: pesticides (atrazine, lindane *et al.*), persistent organic pollutants (such as DDT and its metabolites), industrial compounds (PCBs, PBBs *et al.*), chemical substances (phthalates *et al.*) and heavy metals.^{7,8} Furthermore, the endocrine systems of organisms and human as well as the reproductive system could be affected by heavy metals. Additionally,

cadmium (Cd) as the most toxic heavy metal was found in the ROC. Cd-based compounds are harmful and they can become concentrated in the ecosystem. Similarly, lead (Pb) causes neurological disorders and kidney damage, and can influence the intellectual development of humans.⁹ Heavy metals would get converted into different forms like Cd²⁺ and Pb²⁺ which are highly toxic in comparison to the metal atoms. Even if the concentration of heavy metal ions is not beyond the permissible limit, they could still cause environmental problems.¹⁰ Therefore, great attention has been paid to the removal of Cd²⁺ and Pb²⁺ from wastewater around the world in recent years. A variety of methods have been used to remove the heavy metal ions such as ion exchange, absorption, membrane filtration, precipitation, photocatalytic reduction, the electrochemical process, *etc.*¹¹ Among those processes, photocatalytic reduction has been viewed as a safe, simple, efficient, nontoxic and economical method to reduce heavy metal ions.¹² In particular, photocatalytic reduction exhibits unique advantages in treatment of low-metal ions-concentration wastewater.

It is well known that TiO₂ is a strong and common photocatalyst due to its high photocatalytic efficiency, chemical stability and antibacterial property.^{13,14} It can absorb light energy to move the electrons up to higher energy levels, generating electron–hole pairs. TiO₂ photocatalyst was irradiated by UV light to generate electron–holes which have a high redox ability to degrade pollutants. However, in the practical application, the photocatalytic efficiency of bare TiO₂ is low due to a large band gap, the rapid recombination of photogenerated electron–hole pairs, low affinity and poor selection for contaminants.^{15,16}

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In order to enhance the photocatalytic ability of TiO_2 , a variety of approaches was applied to develop TiO_2 -based composites by designing and modifying TiO_2 , such as doping with metal or nonmetallic elements, coupling with the semiconductor or incorporating nanostructured carbon materials and so on.^{14,17,18} In particular, graphene oxide (GO) has drawn much attention as a high potential and efficient material to improve the photocatalytic efficiency of TiO_2 , since its large specific surface area can facilitate the distribution of TiO_2 .^{19,20} In addition, GO can serve as an electronic transfer medium, thus reducing the rate of recombination of electron-hole pairs. The charge transfer rate of electrons will be enhanced due to narrow band gap.²¹ What's more, the organic pollutants such as EDCs could be absorbed through π - π interactions on the surface of GO.²² Moreover, GO shows a high UV light transparency benefitted from its thin-layered structure which permits UV-light absorption by TiO_2 .²³ Therefore, GO would improve the photocatalytic activity of TiO_2 greatly. Similar to GO, rGO showed advantageous enhancement of photocatalytic activity in a number of studies because it can promote charge separation and electron transfer. Due to its outstanding properties, rGO has been investigated as an efficient carbon-based hybrid nanocomposite to improve electronic or photocatalytic performance of materials.²⁴⁻²⁶ However, the key point is the oxygenous functional groups on the GO surface, such as carboxylic (-COOH), hydroxyl (-OH) and carbonyl (C=O) groups, which played an important role in the absorption. Due to the decrease of oxygenous functional groups, rGO showed a poor adsorption capacity than GO.^{27,28} Therefore, GO is an ideal substrate to adsorb heavy metal ions because its strong absorption affinity. In general, various studies have already been reported for adsorption of heavy metal ions by GO and GO-based composites. Cui *et al.* reported the EDTA functionalized magnetic GO for removal of Pb(II) , Hg(II) and Cu(II) from wastewater.²⁹ Fang *et al.* demonstrated GO- NH_2 as an adsorbent for the removal of

Co(II) ions.³⁰ In our study, TiO_2/GO nanocomposites were used to adsorb and reduce heavy metal ions.

TiO_2/GO nanocomposites have attracted much attention for degrading pollutants recently. R. Raliya and co-workers reported that TiO_2/GO suspension applied for adsorptive and photocatalytic removal of methyl orange.³¹ H. Yadav *et al.* prepared TiO_2/GO photocatalysts for the degradation of benzene gas, showing a significant degradation compared to pure TiO_2 nanoparticles.³² V. Bhatia and co-workers used $\text{TiO}_2/\text{graphene oxide}$ composites as a catalyst for the degradation of atenolol.³³

In the present work, GO and TiO_2 were synthesized by the modified Hummers method and hydro-thermal method, respectively. Then, TiO_2/GO nanocomposites photocatalyst was prepared by hydro-thermal method. Meanwhile, the morphology and structure of GO, TiO_2 and TiO_2/GO nanocomposites were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), powder X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), Barrett-Joyner-Halenda (BJH), Fourier transform infrared (FTIR) spectroscopy and Raman spectroscopy. After that, the photocatalytic effects of synthesized TiO_2/GO nanocomposites on heavy metal ions reduction were evaluated in batch modes under different conditions. Besides, an optimal experiment condition was obtained to maximize the reduction efficiency of heavy metal ions by TiO_2/GO nanocomposites in the photocatalytic reduction reaction. The synthesis route of TiO_2/GO nanocomposites and photocatalytic experiments were illustrated in Fig. 1.

2 Materials and methods

2.1 Synthesis of photocatalysts

2.1.1 Synthesis of GO. The modified Hummers method was used to synthesize GO.³⁴ Firstly, 2.0 g of graphite powder

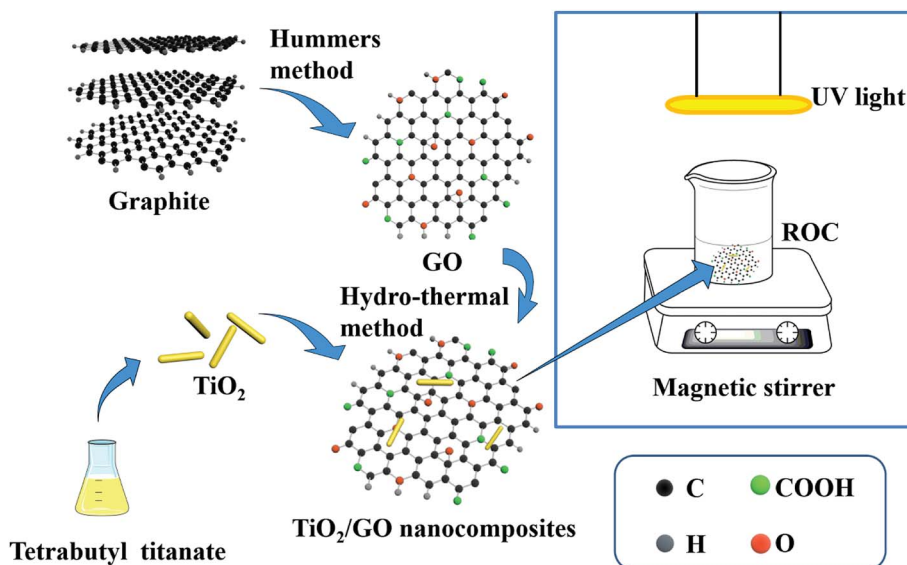


Fig. 1 The synthesis route of TiO_2/GO nanocomposites and photocatalytic experiments.



and 2.0 g of NaNO₃ with 96 mL of H₂SO₄ (98 wt%) were mixed in a beaker. Secondly, KMnO₄ (12.0 g) was added to the mixture at a slow rate under stirring. Thirdly, the beaker with reactants was placed in an ice bath for 2 h to implement the reaction at 0 °C. Fourthly, the mixture was heated to 55 °C for 1.5 h. Fifthly, 80 mL of deionized (DI) water was added drop wise into the mixture with 30 minutes. Thereafter, H₂O₂ (15 mL, 30%) was used to react with the excess KMnO₄. Remarkably, the color of the mixture was golden at this moment. The mixture solution was diluted with 200 mL of DI water, and the final resulting mixture was centrifuged and washed with DI water several times. The pH value of the mixture was adjusted nearly to 7 by dialysis and the product was dissolved with DI water at a certain proportion (1 : 5–1 : 10). After the ultrasonic treatment, the mixture was dispersed in DI water completely. The supernatant of GO aqueous colloidal suspension was decanted and the centrifuged impurities were discarded. Then, the obtained GO aqueous colloidal suspension was added drop wise into liquid nitrogen and placed in a freeze drier for about 20 h to remove water. The final product is GO. Besides, the concentration of GO aqueous colloidal suspension was about 5 mg mL⁻¹. For comparison, the reduced graphene oxide (rGO) was prepared by thermal treatment at 400 °C in nitrogen atmosphere according to the method described in the ref. 35.

2.1.2 Synthesis of TiO₂. TiO₂ was prepared by the hydrothermal method.¹⁵ 80 mL anhydrous ethanol and 2 mL C₁₆H₃₆O₄Ti was added into a 100 mL beaker. Besides, HF (0.5 mL, 40 wt%) was added drop wise into it. HF greatly controls the formation of the (101) plane of TiO₂. The mixture was stirred for about 30 min. Subsequently, the suspension was transferred into a 100 mL Teflon-lined autoclave and heated at 180 °C for 18 h. Then, the mixture was taken out when the autoclave cooled to room temperature naturally. After centrifugation, the product was washed with DI water and anhydrous ethanol several times. Then, the product was dried in a vacuum drying oven at 60 °C for 3 h. Thereafter, the white substance was obtained as TiO₂.

2.1.3 Synthesis of TiO₂/GO nanocomposites. Hydrothermal method was used to prepare TiO₂/GO nanocomposites. Firstly, 150 mg of TiO₂ was dispersed into 150 mL of DI water in a beaker. After that, a certain volume of GO aqueous colloidal suspension was added to the above solution and treated in an ultrasonic bath for 10 min. The volumes of GO aqueous colloidal suspension were 12, 16, 20, 24 and 28 mL, corresponding to 60, 80, 100, 120 and 140 mg of GO, respectively. Finally, the mixture was added dropwise into the liquid nitrogen. Then, the mixture was freeze-dried for 20 h. The product obtained was TiO₂/GO nanocomposites with various GO contents. The mass ratios of TiO₂ to GO in TiO₂/GO nanocomposites were 15 : 6, 15 : 8, 15 : 10, 15 : 12, 15 : 14, and the corresponding products were denoted as TiO₂/GO-6, TiO₂/GO-8, TiO₂/GO-10, TiO₂/GO-12, TiO₂/GO-14, respectively. Moreover, titanium dioxide/reduced graphene oxide (TiO₂/rGO) nanocomposites were prepared by thermal treatment at 400 °C in nitrogen atmosphere.

2.2 Characterization

The morphology and structure of GO and TiO₂/GO nanocomposites was characterized by SEM (Sirion 200FEI, Netherlands) and TEM (Tecnai F20, 200 kV). The crystalline pattern of samples was investigated by XRD (Cu K α radiation, Panalytical X PertPro). The BET surface area was determined by N₂ adsorption/desorption on an ASAP2020 surface area analyzer using the adsorption date branch in the relative P/P_0 pressure range going from 0.0 to 1.0. The pore size distribution of TiO₂/GO nanocomposites was obtained by BJH model. In addition, the FTIR (spectral resolution of 0.09 cm⁻¹) spectroscopy was used to determine the functional groups of GO, TiO₂/GO and TiO₂/rGO nanocomposites from 7800 to 40 cm⁻¹ on a Nicolet 5700 spectrometer (Thermo, Waltham, MA, USA). Raman spectra were obtained using a Horiba Jobin Yvon LABRAM HR Evolution at 785 nm.

2.3 Photocatalytic experiments

ROC was obtained from a petrochemical wastewater treatment plant located in Shandong, China. All the photocatalytic experiments were performed at room temperature in a 500 mL Pyrex breaker. In addition, a high-pressure 500 W Hg lamp was used as the UV light source (maximum energy at 365 nm). First of all, a predetermined amount of photocatalyst was added to wastewater (250 mL). Besides, H₂SO₄ and NaOH were used to adjust the pH value of wastewater. Before UV irradiation, the wastewater was stirred in the dark for 0.5 h to reach adsorption/desorption equilibrium. Subsequently, irradiation started and samples were collected at a specified interval. Besides, the absorbance of Cd²⁺ and Pb²⁺ was determined by a flame atomic absorption spectrophotometer of A3 series with a Beijing Purkinje General instrument (China). And the standard curve method was adopted to determine the heavy metal ions concentration of untreated and treated samples.

3 Results and discussion

3.1 Characterization of photocatalyst

3.1.1 XRD analysis. XRD patterns related to TiO₂, GO and TiO₂/GO-8 nanocomposites are presented in Fig. 2. It can be seen that the XRD pattern of GO showed a strong peak at $2\theta = 10.54^\circ$ corresponding to the C (002) plane, indicating that the graphite was oxidized to GO successfully.²³ Meanwhile, there was no characteristic peak at around 26° , which was confirmed the successful oxidation of graphite into GO. Besides, the interlayer spacing of GO is 0.84 nm, larger than the theoretical value of graphite powder (0.34 nm), probably due to the introduction of oxygen-containing functional groups.³⁶

From the XRD pattern of TiO₂, the characteristic peaks at 2θ values of 25.28° , 37.77° , 47.99° , 54.98° and 62.63° represent the crystal planes of (101), (004), (200), (211) and (204) of anatase TiO₂, respectively,³⁷ which are in good agreement with the standard JCPDS Card no. 21-1272. Obviously, peaks of TiO₂/GO-8 nanocomposites are similar to TiO₂. However, the diffraction peak of GO at $2\theta = 10.54^\circ$ disappeared because the regular stack



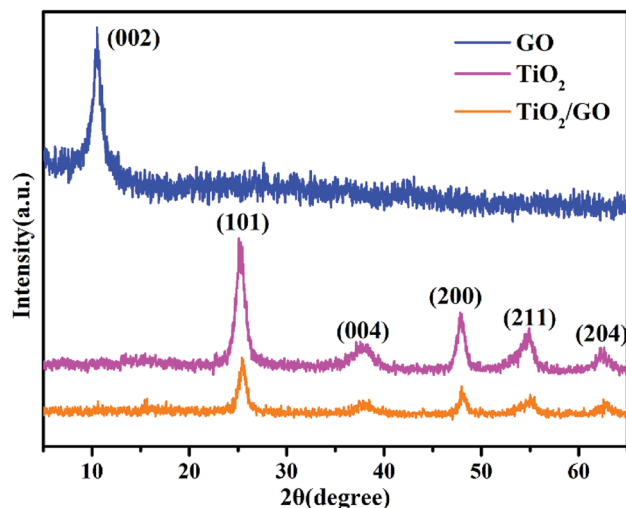


Fig. 2 XRD patterns of GO, TiO₂ and TiO₂/GO-8 nanocomposites.

of GO sheets had been destroyed due to the intercalation of TiO₂ nanoparticles.³⁸

3.1.2 SEM and TEM analysis. The morphology of GO, TiO₂ and TiO₂/GO-8 nanocomposites was characterized by SEM and TEM. As shown in Fig. 3a, the shape of GO is irregular and GO is a thin-layered structure with wrinkles. The fold structure is formed by stacking. Fig. 4a shows the multi-layer structures due to the introduction of oxidizing functional groups. From the images in Fig. 4a and b, the special layered structure of GO was observed clearly (2 layers), implying that it was helpful to the growth of TiO₂.

As shown in Fig. 4c, the morphology and size of the TiO₂ nanoparticles are similar. The TiO₂ is a rod-like nanoparticle with the average length of about 10 nm and width of about 4 nm. The selected area electron diffraction (SAED) pattern of TiO₂ (Fig. 4d) revealed that TiO₂ has a polycrystalline structure

according to a series of concentric rings with different radii. It has been calculated that the distances between the various diffraction rings and diffraction center are 0.352, 0.237, 0.190, 0.166 and 0.148 nm, respectively, corresponding to the lattice spacings of (101), (004), (200), (211) and (204) planes of anatase TiO₂ (JCPDS Card no. 21-1272). Besides, it is consistent with the results of XRD analysis.

Fig. 3c and d shows that the layers of GO curled and the well dispersed TiO₂ anchored on the GO planes. This result proved that the TiO₂ was successfully loaded onto the GO planes. Most of TiO₂ nanoparticles are situated on the edge of GO sheets as shown in Fig. 4e. Fig. 4f shows the lattice fringe is 0.35 nm, which corresponds to the lattice spacing of the (101) plane of anatase TiO₂. It is obvious that GO barely affects the morphology and crystalline pattern of TiO₂.

3.1.3 FTIR analysis. Fig. 5 presents the FTIR spectra of GO, TiO₂/GO-8 and TiO₂/rGO nanocomposites in the wavenumber range of 400–3750 cm⁻¹. The FTIR spectrum of GO indicates that there are a large number of different oxygen-containing functional groups on GO. The strong absorption bands at 576 and 1070 cm⁻¹ correspond to C–O–C stretching vibration. The peak near 1384 cm⁻¹ relates to the carboxyl (C–OH) bending vibration. The presence of an absorption band around 1630 cm⁻¹ is due to C=C stretching vibration. Other bands at 1725 and 3381 cm⁻¹ correspond to stretching vibration of oxygen containing functional groups of carboxyl (C=O) and hydroxyl (OH), respectively.³⁹ The co-existence of these two stretching vibrations shows the carboxyl (COOH) group on GO. As a result, those polar functional groups can provide anchoring sites for the adsorption of TiO₂ on the GO.

By comparison with the GO spectrum, a small amount of oxygen-containing functional groups still exist on the surface of TiO₂/GO and TiO₂/rGO nanocomposites. For the FTIR spectra of TiO₂/GO-8 and TiO₂/rGO nanocomposites, the broad band at 460.22 cm⁻¹ was originated from the stretching Ti–O–C.⁴⁰ Besides, the absorption band near 523 cm⁻¹ corresponded to

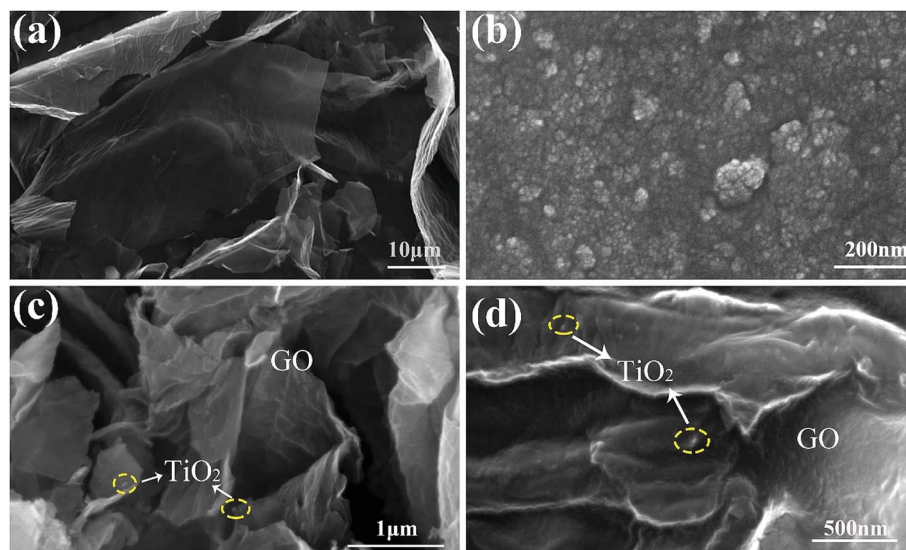


Fig. 3 SEM images of GO (a), TiO₂ (b) and TiO₂/GO-8 nanocomposites (c and d).



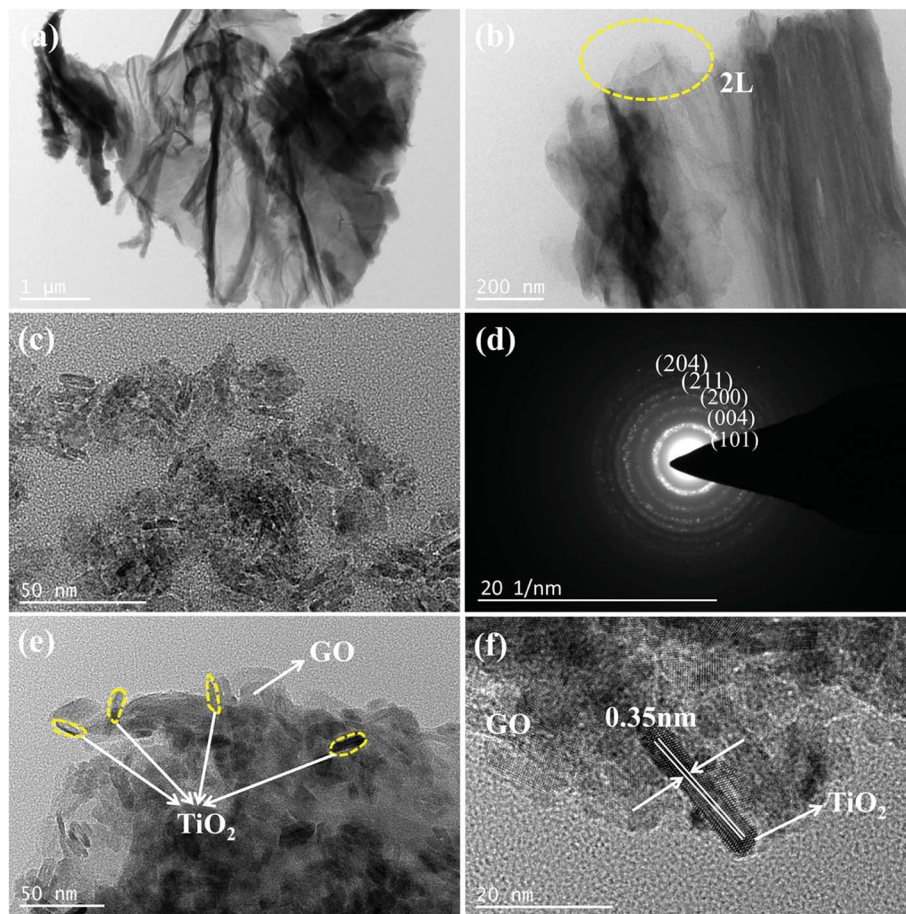


Fig. 4 TEM images of GO (a and b), TiO_2 with the SAED pattern (c and d), and $\text{TiO}_2/\text{GO-8}$ nanocomposites (e and f).

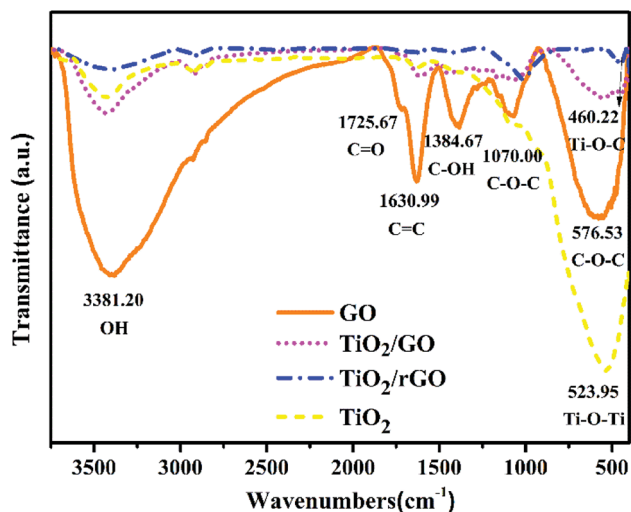


Fig. 5 FTIR spectra of GO, TiO_2 , $\text{TiO}_2/\text{GO-8}$ and TiO_2/rGO nanocomposites.

the Ti–O vibration.⁴¹ Furthermore, peak strength of TiO_2/rGO nanocomposites is lower than TiO_2/GO nanocomposites and some of the peaks even disappear. From the FTIR spectrum of TiO_2/rGO nanocomposites, few peaks indicating the oxygen-

containing functional groups can be seen after reduction. These oxygen-containing functional groups demonstrate the successful preparation of GO and provide anchoring sites for the adsorption of heavy metal ions on the $\text{TiO}_2/\text{GO-8}$ nanocomposites. It had been confirmed that the oxygen-containing functional groups played an important role in the adsorption of heavy metal ions.⁴²

3.1.4 Raman analysis. Fig. 6 shows the Raman spectra of GO, $\text{TiO}_2/\text{GO-8}$ and TiO_2/rGO nanocomposites in the range of 250–2500 cm^{-1} . Raman spectroscopy is used to characterize the structural defects and demonstrate the irregular structure of products. In all samples, there are two bands that can be observed obviously. The first band is the D band for sp^3 in plane vibrations of bonded carbon, corresponding to the degree of irregular structure and defect in the graphite layer. Another band is the G band associated with vibrations of sp^2 carbon atoms, which is bound with the symmetry and crystallization of carbon.⁴³ In Table 1, the shifting of the D band from 1363 to 1344 cm^{-1} and the G band from 1600 to 1593 cm^{-1} showed a red shift for $\text{TiO}_2/\text{GO-8}$ and TiO_2/rGO nanocomposites, due to the introduction of oxygen-containing functional groups into GO during the strong oxidation reaction.⁴⁴ These functional groups such as hydroxyl and carboxyl were bonded at the GO layer boundaries, resulting in many defects. Moreover, the D



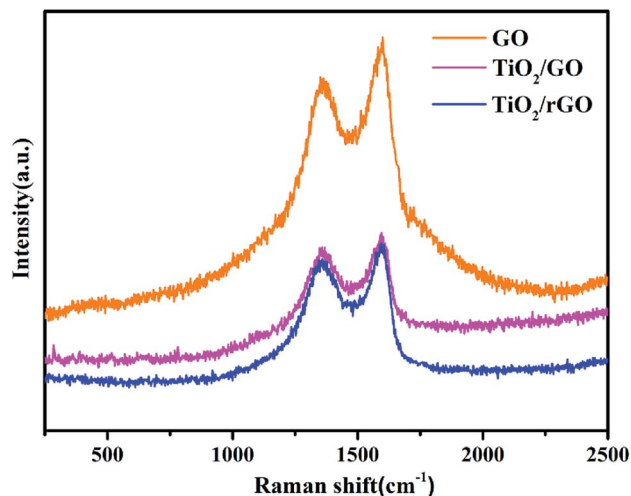


Fig. 6 Raman spectra of GO, TiO₂/GO-8 and TiO₂/rGO nanocomposites.

Table 1 Comparison of the peak position and intensity of samples

| Samples | W_D (cm ⁻¹) | W_G (cm ⁻¹) | I_D | I_G | I_D/I_G |
|-----------------------|---------------------------|---------------------------|-------|-------|-----------|
| GO | 1363 | 1600 | 925 | 1032 | 0.896 |
| TiO ₂ /GO | 1358 | 1595 | 481 | 519 | 0.927 |
| TiO ₂ /rGO | 1344 | 1593 | 446 | 491 | 0.908 |

and G band values shifted towards the lower values and the D/G intensity ratio (I_D/I_G) decreasing from 0.927 to 0.908 showed that the GO had been well reduced to rGO.⁴⁵ The D/G intensity ratio (I_D/I_G) roughly correlates to the amount of the graphene clusters and defects in the disordered carbon.¹⁵ The I_D/I_G ratios of TiO₂/GO-8 and TiO₂/rGO nanocomposites are 0.927 and 0.908, respectively, both of which are higher than GO (0.896). This result indicates that loading TiO₂ on GO increases the defects. It may be caused by the strong chemical bonding between TiO₂ and GO.^{21,46} Therefore, the I_D/I_G ratio of TiO₂/GO nanocomposites is the highest among all samples, which reveals that more defects exist in TiO₂/GO nanocomposites and the graphitization degree of nanocomposites is lower than TiO₂/rGO nanocomposites and GO.

3.1.5 N₂ adsorption–desorption isotherms and BJH analysis. Fig. 7 shows N₂ adsorption–desorption isotherms and BJH pore size distribution of TiO₂/GO-8 nanocomposites. The N₂ adsorption–desorption isotherms of the as-prepared TiO₂/GO-8 nanocomposites exhibit type IV characteristics, which is one of the main characteristics of mesoporous materials. It is further demonstrating the existence of a large number of mesopores. Major pore size distribution of TiO₂/GO-8 nanocomposites is ranged from 2 to 7 nm with a peak around 5.24 nm, which is well-defined mesoporous structure, as shown in the inset of Fig. 7. The surface area of TiO₂/GO-8 nanocomposites is calculated to be 128.41 m² g⁻¹ based on the BET model, which is greatly larger than that of pure TiO₂ (59.51 m² g⁻¹). The large BET surface area and mesoporous structure enhance the

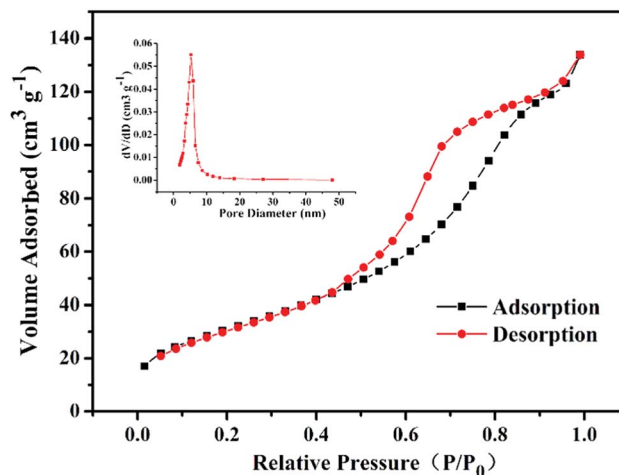
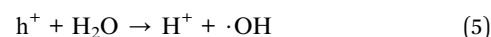
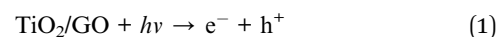


Fig. 7 N₂ adsorption–desorption isotherms and BJH pore distribution curves (inset) of TiO₂/GO-8 nanocomposites.

photogenerated electrons and holes to participate in photocatalytic activity and provide more channels for water molecule to go through, which is essential to achieve high water flux and photoreduction efficiency.

3.2 Photocatalytic performance of TiO₂/GO nanocomposites

3.2.1. Photocatalytic reduction mechanism of TiO₂/GO nanocomposites. The photocatalytic reduction mechanism of TiO₂/GO nanocomposites is shown in Fig. 8. First of all, the hydroxyl ion (OH⁻), oxygen (O₂), Cd²⁺ and Pb²⁺ in ROC are adsorbed onto the TiO₂/GO surface. Under UV irradiation, TiO₂ absorbs UV light energy and the electrons move up to a higher energy level. Meanwhile, the electron–hole pairs will be generated (eqn (1)). Electrons (e⁻) are transferred from the conduction band of TiO₂ to GO, which could enhance the photocatalytic activity of TiO₂. As a result, O₂ will be reduced to superoxide radical anion ($\cdot\text{O}_2^-$) due to the strong reduction ability of photogenerated electrons (eqn (2)). Meanwhile, Cd²⁺ and Pb²⁺ adsorbed on the surface of GO will be reduced to Pb and Cd, respectively (eqn (4) and (5)). Moreover, there might be another way to remove Pb²⁺ by the oxidation method. Residual holes within the valence band of TiO₂ would react with OH⁻ and H₂O to form hydroxyl radicals ($\cdot\text{OH}$) for oxidation reactions (eqn (5) and (6)). Hydroxyl radicals can oxidize Pb²⁺ to Pb⁴⁺, which will precipitate in the form of PbO₂ (eqn (7)). Finally, reduced and oxidized products will fall off the surface of TiO₂/GO nanocomposites.



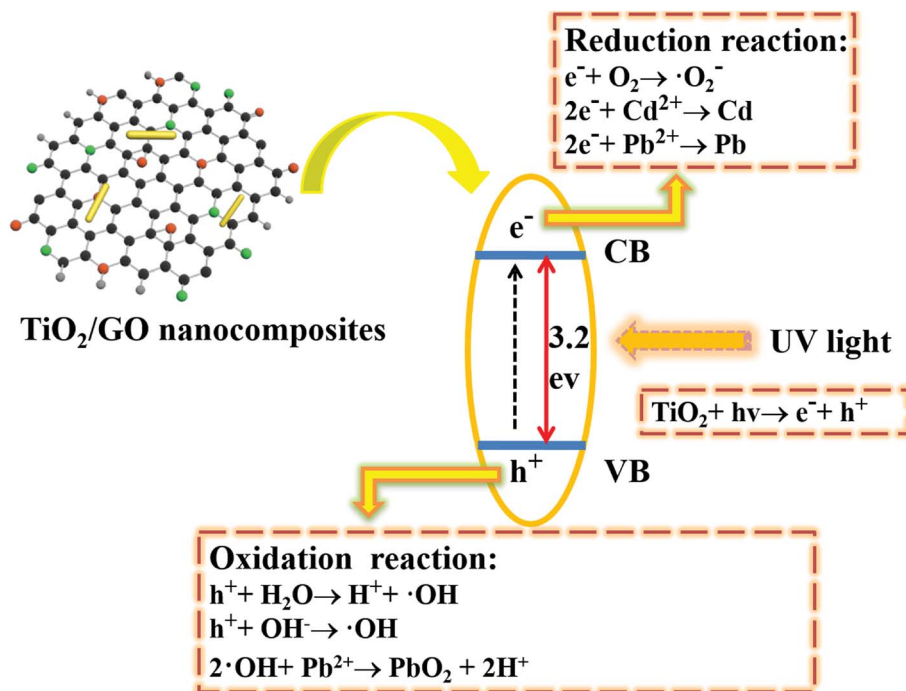
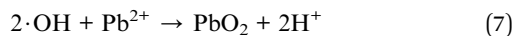


Fig. 8 Schematic diagram of the charge transfer and separation in the TiO_2/GO nanocomposites under UV light irradiation and the main steps to reduce heavy metal ions.



3.2.2 Photoreduction activity of materials. Fig. 9 depicts the corresponding kinetic curves for both Cd^{2+} and Pb^{2+} photocatalytic reduction followed a pseudo-first-order kinetic equation with a simplified Langmuir-Hinshelwood mode. According to the calculated rate constants of Cd^{2+} (Fig. 9a), the corresponding reaction rate of $\text{TiO}_2/\text{GO}-8$ ($k = 0.0090 \text{ min}^{-1}$) was 3.75 times higher than that of pure TiO_2 ($k = 0.0024 \text{ min}^{-1}$). Besides, the calculated rate constants of Pb^{2+} was shown in Fig. 9b, similarly, the reaction rate of $\text{TiO}_2/\text{GO}-8$ ($k = 0.0184 \text{ min}^{-1}$) was about 3.75 times higher than that of pure TiO_2 ($k = 0.0049 \text{ min}^{-1}$). It can be seen that TiO_2/GO nanocomposites exhibited relative larger adsorption capacity than pure TiO_2 .

The dark absorption and photoreduction activity of Cd^{2+} and Pb^{2+} using TiO_2 , GO and TiO_2/GO nanocomposites was studied. Fig. 10 and 11 illustrate the concentration of Cd^{2+} and Pb^{2+} under various operating conditions, respectively. The initial concentrations of Cd^{2+} and Pb^{2+} in the ROC were 0.155 and 0.334 mg L^{-1} , respectively. Fig. 10a and 11a shows that both pure GO and TiO_2 could reduce Cd^{2+} and Pb^{2+} to some extent. Moreover, compared with pure GO and TiO_2 , the photoreduction capability was increased significantly with the catalysis of TiO_2/GO nanocomposites. There was a large specific surface area on TiO_2/GO nanocomposites and the combination of GO with TiO_2 led to a stronger redox ability. Besides, the functional groups of TiO_2/GO nanocomposites outnumbered the unmodified TiO_2 , which helps the TiO_2/GO nanocomposites contact fully with the heavy metal ions. Furthermore, GO had a stronger adsorption of Pb^{2+} than Cd^{2+} , resulting in the higher

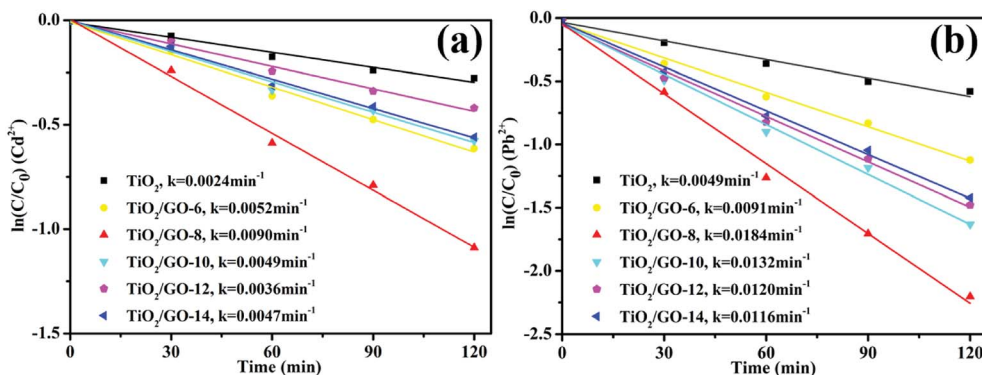


Fig. 9 The corresponding fitted reaction kinetic curves of TiO_2/GO nanocomposites with different amount of GO (pH = 6.0; $-\ln(C/C_0) = kt$, where C/C_0 is the concentration of heavy metal ions, k is the apparent first-order rate constant, t is the irradiation time).



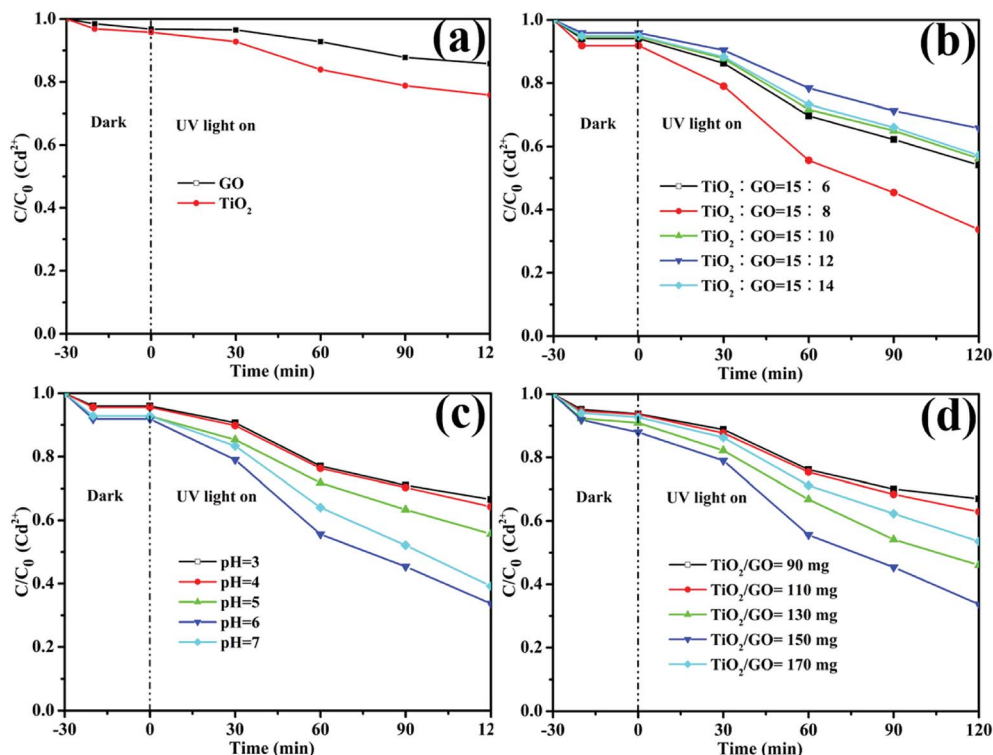


Fig. 10 The relative concentration of Cd^{2+} under different conditions. (a) Pure TiO_2 and GO, (b) the mass ratio of TiO_2 to GO in TiO_2/GO nanocomposites, (c) pH value and (d) the amount of TiO_2/GO .

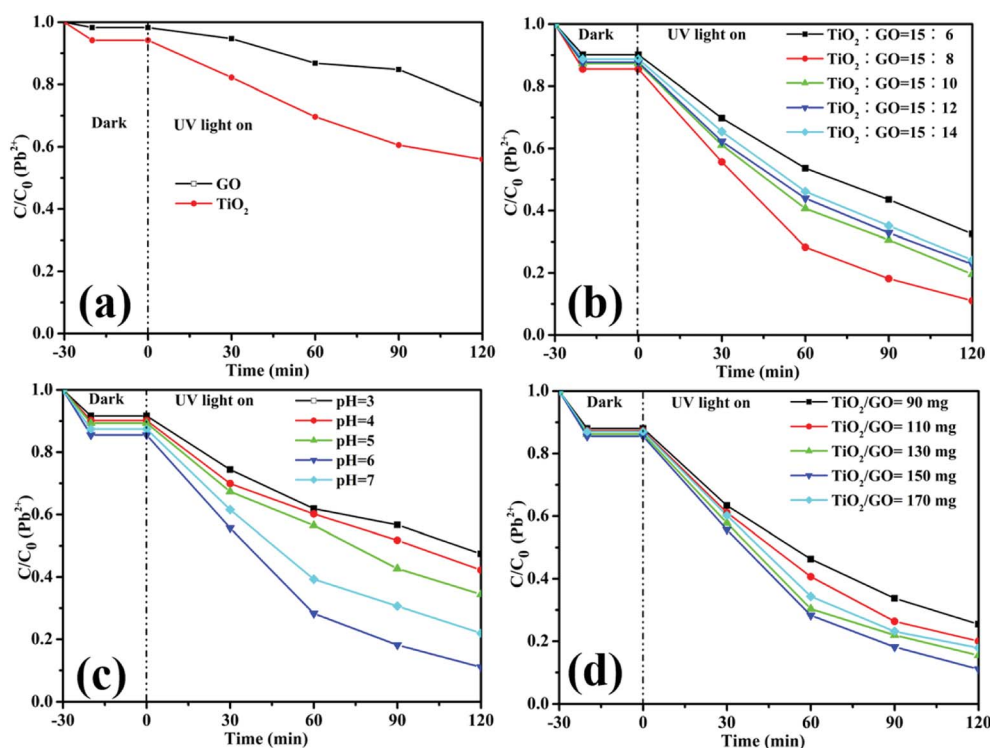


Fig. 11 The relative concentration of Pb^{2+} under different conditions. (a) Pure TiO_2 and GO, (b) the mass ratio of TiO_2 to GO in TiO_2/GO nanocomposites, (c) pH value and (d) the amount of TiO_2/GO .



photoreduction of Pb^{2+} than Cd^{2+} . This is probably attributed to the selective adsorption of the specified heavy metal ion by GO.⁴⁷

Fig. 10b and 11b illustrate that the photoreduction activities of Cd^{2+} and Pb^{2+} obtained at the mass ratio of TiO_2 to GO of 15 : 8 are higher than those obtained at other mass ratios of TiO_2 to GO. With the amount of GO increasing, the reaction rates and photoreduction activities of TiO_2/GO nanocomposites increase firstly and then decrease. The $\text{TiO}_2/\text{GO}-8$ nanocomposites displayed the highest photoreduction capability with maximal apparent rate constant k values of 0.0090 (Cd^{2+}) and 0.0184 (Pb^{2+}) min^{-1} . GO created a large surface area to improve the photocatalytic activity of TiO_2 . When GO was introduced into TiO_2 , the absorbance edge of TiO_2 shifted to the higher wavelength region due to the formation of Ti–O–C bond in TiO_2/GO nanocomposites, which helps to enhance the absorption ability of the photocatalysts.²¹ This indicates that the introduction of appropriate amount of GO has a positive influence on improving photoreduction performance of nanocomposites. However, further increasing the amount of GO lead to a significant decrease of photoreduction activity, probably owing to the reduced catalytic active sites and increased charge carriers recombination rate caused by excessive GO loading. The higher GO content introduced into TiO_2 could increase the probability of collision between photogenerated electron–hole pairs, which would increase the charge carrier recombination rate increased from the conduction band to valence band and ultimately lower the photocatalytic performance of the catalyst.³² Besides, in the $\text{TiO}_2/\text{GO}-10$, $\text{TiO}_2/\text{GO}-12$ and $\text{TiO}_2/\text{GO}-14$ nanocomposites, excess black GO would absorb a lot of light, which inhibited the efficient absorption of UV irradiation light by TiO_2 .⁴⁸ Therefore, the optimal dosage of GO is 80 mg in the hydro-thermal reaction to prepare TiO_2/GO nanocomposites, and the corresponding product ($\text{TiO}_2/\text{GO}-8$ nanocomposites) presented the best photoreduction activity. It showed a significant synergetic effect of GO with TiO_2 in the photoreduction process.

Besides, the effect of pH on the reduction of Cd^{2+} and Pb^{2+} was shown in Fig. 10c and 11c, respectively. It is obvious that the pH value had a great influence on the removal rate of heavy metal ions. One reason is that the acidity can influence the surface active sites of TiO_2/GO nanocomposites. Another reason is that the pH value was related to the state of heavy metal ions in the solution. Clearly, the photoreduction activity of Cd^{2+} and Pb^{2+} were both improved by increasing the pH value to 6. However, further increasing the value of pH will bring about a decrease of photoreduction activity, probably owing to that both ions would be hydrolyzed to produce hydroxide precipitation.⁴⁹ Therefore, the optimum pH is 6 for photoreduce Cd^{2+} and Pb^{2+} .

As shown in Fig. 10d and 11d, the photoreduction activity of Pb^{2+} and Cd^{2+} obtained at the TiO_2/GO nanocomposites dosage of 150 mg are higher than those obtained at other photocatalyst dosages. The results may be explained by the surface active sites of TiO_2/GO nanocomposites and the phenomenon of light scattering. Higher dosage might cause the aggregation of the photocatalyst, which could reduce the surface active sites of the

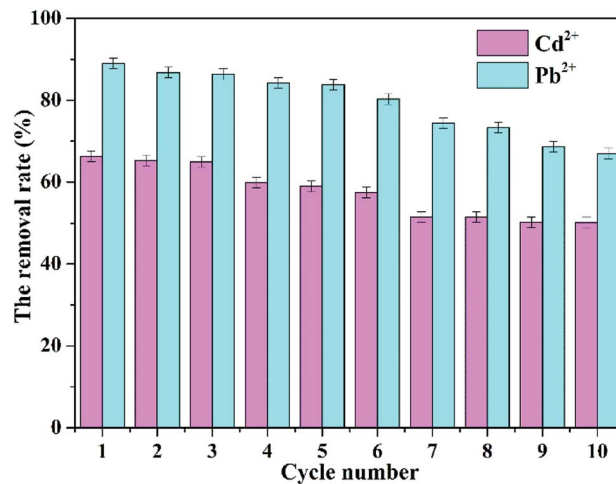


Fig. 12 Recycling tests of Cd^{2+} and Pb^{2+} for $\text{TiO}_2/\text{GO}-8$ nanocomposites.

TiO_2/GO nanocomposites. Additionally, the increase of the photocatalyst dosage resulted in the light scattering phenomenon, which could reduce the efficiency of light radiation. Therefore, 150 mg of TiO_2/GO nanocomposites exhibited the highest activity in photocatalytic reduction.

3.2.3 Photocatalytic stability of TiO_2/GO nanocomposites.

The performance stability of photocatalyst is an important indicator for its practical application. Therefore, the photocatalytic stability of TiO_2/GO nanocomposites was investigated. $\text{TiO}_2/\text{GO}-8$ nanocomposite was chosen to reduce heavy metal ions in the cycle reaction process, since $\text{TiO}_2/\text{GO}-8$ nanocomposites presented the best photoreduction activity. A pre-determined amount of photocatalyst was added to the original ROC wastewater. The proportion of photocatalyst to ROC wastewater was same with the first photocatalytic experiments. H_2SO_4 and NaOH were used to adjust the pH value of wastewater to 7. Other experimental procedures were the same as before. The photocatalyst was separated from the reaction mixture by centrifugation at 5000 rpm for 6 min after each photocatalytic experiment and then dried in vacuum at 60 °C for 6 h to recover it. After 10 cycles, TiO_2/GO nanocomposites retained 50.13% yield photocatalytic reduction of Cd^{2+} . Simultaneously, TiO_2/GO nanocomposites also maintained a satisfactory removal rate of Pb^{2+} , which was still over 66.98%. The corresponding results were shown in Fig. 12. The results showed that TiO_2/GO nanocomposites possessed excellent photocatalytic stability.

4 Conclusion

In this study, GO, TiO_2 and TiO_2/GO nanocomposites photocatalysts were synthesized by means of Hummers, hydro-thermal and freeze-drying method, respectively. Moreover, the characterization showed that the TiO_2/GO nanocomposites had stable structures and good photocatalytic activity. Especially, GO could limit the recombination of photo-generated electron–hole pairs effectively and enhance the photocatalytic activity of TiO_2 remarkably. In the photocatalytic reduction experiments,



the TiO₂/GO nanocomposites showed a higher photocatalytic activity than pure GO and TiO₂. TiO₂/GO-8 exhibit the highest reaction rate and more than 66.32% Cd²⁺ and 88.96% Pb²⁺ were reduced using a 0.6 g L⁻¹ concentration of TiO₂/GO nanocomposites at the pH 6 after 120 min irradiation. The combination of GO and TiO₂ promoted the reduction of heavy metal ions. In a word, TiO₂/GO nanocomposites were a favorable photocatalyst for the reduction of heavy metal ions to reduce their toxicity in ROC. This study provides a feasible method to solve the problem that low concentration heavy metal ions are difficult to reduce in sewage, thereby benefitting the human health, social development, and the reuse of wastewater.

Conflicts of interest

There are no conflicts to declare.

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References

- X. Wei, P. Gu and G. Zhang, *Desalination*, 2014, **352**, 18–26.
- J. Lu, L. Fan and F. A. Roddick, *Chemosphere*, 2013, **93**, 683–688.
- G. Naidu, S. Jeong, Y. Choi and S. Vigneswaran, *J. Membr. Sci.*, 2016, **524**, 565–575.
- H. Luo, H. Li, Y. Lu, G. Liu and R. Zhang, *Desalination*, 2017, **408**, 52–59.
- J. O. Tijani, O. O. Fatoba, O. O. Babajide and L. F. Petrik, *Environ. Chem. Lett.*, 2016, **14**, 27–49.
- C. Jung, A. Son, N. Her, K. D. Zoh, J. Cho and Y. Yoon, *J. Ind. Eng. Chem.*, 2015, **27**, 1–11.
- M. Gmurek, M. Olak-Kucharczyk and S. Ledakowicz, *Chem. Eng. J.*, 2017, **310**, 437–456.
- M. Llorca, M. Badia-Fabregat, S. Rodríguez-Mozaz, G. Caminal, T. Vicent and D. Barceló, *Chemosphere*, 2017, **184**, 1054–1070.
- M. A. P. Cechinel, S. M. A. G. U. D. A. Souza and A. U. D. Souza, *J. Cleaner Prod.*, 2014, **65**, 342–349.
- C. F. Carolin, P. S. Kumar, A. Saravanan, G. J. Joshiba and M. Naushad, *J. Environ. Chem. Eng.*, 2017, **5**, 2782–2799.
- C. Xiong, W. Wang, F. Tan, F. Luo, J. Chen and X. Qiao, *J. Hazard. Mater.*, 2015, **299**, 664–674.
- R. Daghrir, P. Drogui and D. Robert, *Ind. Eng. Chem. Res.*, 2013, **52**, 3581–3599.
- W. K. Jo, S. Kumar, M. A. Isaacs, A. F. Lee and S. Karthikeyan, *Appl. Catal., B*, 2016, **201**, 159–168.
- G. Peng, A. Li, D. D. Sun and W. J. Ng, *J. Hazard. Mater.*, 2014, **279**, 96–104.
- C. Lai, M. M. Wang, G. M. Zeng, Y. G. Liu, D. L. Huang, C. Zhang, R. Z. Wang, P. Xu, M. Cheng, C. Huang, H. P. Wu and L. Qin, *Appl. Surf. Sci.*, 2016, **390**, 368–376.
- L. Lin, H. Wang, W. Jiang, A. R. Mkaouar and P. Xu, *J. Hazard. Mater.*, 2017, **333**, 162–168.
- Z. Zhao, J. Sun, S. Xing, D. Liu, G. Zhang, L. Bai and B. Jiang, *J. Alloys Compd.*, 2016, **679**, 88–93.
- M. C. Rosu, M. Coros, F. Pogacean, L. Magerusan, C. Socaci, A. Turza and S. Pruneanu, *Solid State Sci.*, 2017, **70**, 13–20.
- Q. Deng, C. Chen, Q. Lei, Ji. Liang, T. Zhang and J. Jiang, *RSC Adv.*, 2018, **8**, 23382–23389.
- J. Wang, R. Liu and X. Yin, *J. Chem. Eng.*, 2018, **63**, 409–416.
- R. Atchudan, T. Edison, S. Perumal, D. Karthikeyan and Y. Lee, *J. Photochem. Photobiol., A*, 2017, **333**, 92–104.
- J. S. Lee, K. H. You and C. B. Park, *Adv. Mater.*, 2012, **24**, 1084–1088.
- Y. Sang, Z. Zhao, J. Tian, P. Hao, H. Jiang, H. Liu and J. P. Claverie, *Small*, 2014, **10**, 3775–3782.
- L. Fan, X. Li, X. Song, N. Hu, D. Xiong, A. Koo and X. Sun, *ACS Appl. Mater. Interfaces*, 2018, **10**, 2637–2648.
- X. Song, X. Li, Z. Bai, B. Yan, D. Xiong, L. Lin, H. Zhao, D. Li and Y. Shao, *Carbon*, 2018, **133**, 14–22.
- D. Xiong, X. Li, Z. Bai and S. Lu, *Small*, 2018, **14**, 1703419.
- W. Peng, H. Li, Y. Liu and S. Song, *J. Mol. Liq.*, 2017, **230**, 496–504.
- Z. Li, F. Chen, L. Yuan, Y. Liu, Y. Zhao, Z. Chai and W. Shi, *Chem. Eng. J.*, 2012, **210**, 539–546.
- L. Cui, Y. Wang, L. Gao, L. Hu, L. Yan, Q. Wei and B. Du, *Chem. Eng. J.*, 2015, **281**, 1–10.
- F. Fang, L. Kong, J. Huang, S. Wu, K. Zhang, X. Wang, B. Sun, Z. Jin, J. Wang, X. Huang and J. Liu, *J. Hazard. Mater.*, 2014, **270**, 1–10.
- R. Raliya, C. Avery, S. Chakrabarti and P. Biswas, *Appl. Nanosci.*, 2017, **7**, 253–259.
- H. Yadav and J. Kim, *J. Alloys Compd.*, 2016, **688**, 123–129.
- V. Bhatia, G. Malekshoar, A. Dhir and A. Ray, *J. Photochem. Photobiol., A*, 2017, **332**, 182–187.
- M. Nawaz, W. Miran, J. Jang and D. S. Lee, *Appl. Catal., B*, 2017, **203**, 85–95.
- Z. Zhang, J. Zhao, J. Zhou, Y. Zhao, X. Tang and S. Zhuo, *Energy Storage Mater.*, 2017, **8**, 35–41.
- W. Liu, J. Cai, Z. Ding and Z. Li, *Appl. Catal., B*, 2015, **174–175**, 421–426.
- J. Ge, Y. Ping, G. Liu, G. Qiao, E. J. Kim and M. Wang, *Mater. Lett.*, 2016, **181**, 216–219.
- P. Gao, Z. Liu, M. Tai, D. D. Sun and W. Ng, *Appl. Catal., B*, 2013, **138**, 17–25.
- B. Qiu, Y. Zhou, Y. Ma, X. Yang, W. Sheng, M. Xing and J. Zhang, *Sci. Rep.*, 2015, **5**, 8591–8596.
- J. Hu, H. Li, Q. Wu, Y. Zhao and Q. Jiao, *Chem. Eng. J.*, 2015, **263**, 144–150.
- J. Fu, G. Kyzas, Z. Cai, E. Deliyanni, W. Liu and D. Zhao, *Chem. Eng. J.*, 2018, **335**, 290–300.
- W. Tang, G. Zeng, J. Gong, J. Liang, P. Xu, C. Zhang and B. Huang, *Sci. Total Environ.*, 2014, **468–469**, 1014–1027.
- R. Atchudan and A. Pandurangan, *Microporous Mesoporous Mater.*, 2013, **167**, 162–175.
- W. Yang, Y. Li and Y. Lee, *Appl. Surf. Sci.*, 2016, **380**, 249–256.
- Y. Yang, L. Luo, M. Xiao, H. Li, X. Pan and J. Fang, *Mater. Sci. Semicond. Process.*, 2015, **40**, 183–193.



- 46 J. Henych, V. Štengl, A. Mattsson, J. Tolasz and L. Österlund, *J. Hazard. Mater.*, 2018, **359**, 482–490.
- 47 W. Peng, H. Li, Y. Liu and S. Song, *J. Mol. Liq.*, 2017, **230**, 496–504.
- 48 Y. Zhu, Y. Wang, W. Yao, R. Zong and Y. Zhu, *RSC Adv.*, 2015, **5**, 29201–29208.
- 49 J. Zhao, Y. Niu, R. Ben, H. Chen, S. Zhang, J. Jin and Y. Zhang, *Chem. Eng. J.*, 2018, **347**, 574–584.

