Facile One-step Production of 2D/2D ZnO/rGO Nanocomposites under Microwave Irradiation for Photocatalytic Removal of Tetracycline

Ruiqi Gang, Lei Xu,* Yi Xia,* Libo Zhang, Shixing Wang, and Rui Li

ABSTRACT: Antibiotic wastewater poses a great threat to the ecological environment and human health. Photocatalytic technology is an effective way to solve environmental pollution problems. In recent years, 2D/2D nanocomposites have received widespread attention because of their larger contact area, which can improve photocatalytic activity. However, the rapid synthesis of 2D/2D nanocomposites at low temperatures is still a challenge. Here, we demonstrated a facile one-step approach to synthesize 2D/2D ZnO nanosheet/rGO nanocomposites through microwave heating in a short time (20 min) for photodegradation of tetracycline (TC). Compared to the pure ZnO nanosheets, the ZnO/rGO-2 nanocomposites exhibited best photocatalytic activity under UV light. The enhanced photocatalytic performance could be attributed to introduction of GO nanosheets, which improves the specific surface area and pore structure and enhances the TC adsorption capacity. In addition, due to the interfacial coupling between ZnO and rGO, the charge was rapidly transferred and the recombination of photogenerated electron−hole pairs on the ZnO surface was inhibited. Our present work provided an efficient and low-temperature strategy for designing 2D/2D ZnO nanosheet/rGO photocatalysts and achieved gram-level production, which opens a new path to fabricate 2D/2D nanocomposites using microwave technology.

1. INTRODUCTION

Nowadays, pharmaceutical wastewater pollution caused by antibiotics or antiphlogistics poses threats to human health and the ecological environment of the earth. Tetracycline (TC) hydrochloride, a kind of TC broad-spectrum antibiotics, is widely used in medical, animal husbandry, agriculture, and other fields and remains in groundwater and soil. With the abuse of TC, the enrichment of TC can induce proliferation of drug-resistant bacteria. Therefore, it is necessary to develop innovative technologies for elimination of TC from aqueous environments. Photocatalytic oxidation technology has received extensive attention in academia and is regarded as a promising strategy for degradation of antibiotics. There have been a large number of reports regarding the metal oxides (TiO₂, WO₃, ZnO, Nb₂O₅, and Fe₂O₃) for photocatalytic degradation of TC. Among these metal oxides, ZnO has a strong redox ability and non-toxic and controllable morphology, which are widely adopted in the field of photocatalysis. However, the ZnO has a small specific surface area and poor carrier transport ability, leading to low photocatalytic activity.

In order to improve the photocatalytic activity, researchers are focusing on controllable synthesis of ZnO with a desired morphology and structure (nanowires, nanorods, nanotubes, nanosheets, etc.). The porous structure assembled by the 2D nanosheets endowed ZnO with a higher specific surface area, shorter charge carrier transport path, and more active sites, which is beneficial for enhanced photocatalytic performance. However, the pure 2D ZnO nanosheet photocatalysts suffered from photogenerated charge−hole rapid recombination, which limits its practical application.

Graphene (rGO), a typical 2D material, is widely used in photocatalytic systems and can be used as an ideal cocatalyst because of its ultrafast electron mobility and excellent ultraviolet light transmittance. In addition, the high specific surface area and abundant functional groups (e.g., −COOH) of graphene make it an ideal substrate for the construction of composites with semiconductor photocatalysts. Moreover, the presence of graphene not only helps to improve the adsorption capacity of target pollutants on the surface of the photocatalyst but also promotes the transport of photogenerated electrons. Until now, a series of composite photocatalysts have been...
developed based on graphene. In order to construct effective composite photocatalysts, coupling a strong interface contact between a 2D semiconductor and graphene can greatly promote photocatalytic activity. For example, Liu et al. proposed that a 2D/2D CdIn2S4/rGO multi-heterostructure prepared by a hydrothermal method could effectively photodegrade 2,4-DCP compared with CdIn2S4. Yang et al. proposed that 2D/2D g-C3N4/ZnO photocatalysts showed good photodegradation of MB. However, the above-reported synthetic strategy has problems such as low yield, excessively long preparation time, and high reaction temperature. The complex preparation process and low yield restricted practical application.

Inspired by the abovementioned research, we report a microwave-assisted one-step synthesis of 2D/2D ZnO/rGO nanocomposites for photocatalytic degradation of antibiotics. Compared with the addition of surfactants, template method, and high-temperature hydrothermal synthesis, a rapid (20 minutes) microwave-assisted one-step synthesis of 2D/2D ZnO/rGO nanocomposites for photocatalytic degradation of antibiotics. This study provides a promising strategy for the large-scale preparation of 2D/2D composite photocatalysts for degradation of TC.

2. EXPERIMENTAL SECTION

2.1. Materials. The reagents and materials for synthesis can be used directly without further purification. Commercial zinc oxide powder (ZnO, purity ≥96%), sodium hydroxide (NaOH, purity ≥98%), graphite powder (purity ≥98%), and TC (mol wt 479.01) were purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Microwave Hydrothermal Synthesis of ZnO Nanosheets and ZnO/rGO Nanocomposites. In a typical process, 0.015 mol ZnO powder is dissolved 10 mL of NaOH (10 mM) and the mixture was stirred for 2 h. Then, the solution was heated at 60 °C for 20 min under microwave irradiation. After the mixture solution cools down to room temperature, it is then filtered and washed with ethanol. The synthesis route of ZnO/rGO was similar to that of ZnO. The GO was prepared from graphite powder adopting modified Hummers’ method. In a typical process, different masses of GO (10, 50, and 100 mg) were dispersed in the mixture of ZnO and NaOH after 2 h of stirring. The solution was heated under the same conditions. After cooling to room temperature, the product was filtered, washed with ethanol, and dried at 40 °C for 12 h. Herein, the samples synthesized using different mass ratios of rGO (1, 5, and 10%) were labeled as ZnO/rGO-1, ZnO/rGO-2, and ZnO/rGO-3, respectively.

2.3. Photocatalytic Activity Measurement. The photocatalyst degradation of the as-prepared samples was evaluated using TC under a 6 W LED lamp as an ultraviolet (UV) light source. During every experiment, 25 mg of the photocatalyst was added to 50 mL of 10 mg/L TC solution. The mixture was first stirred under dark conditions for 30 min to obtain the adsorption/desorption equilibrium. Next, the mixture was subjected to irradiation with light, and a 3 mL solution suspension was obtained every 10 min, and the powder was removed. The TC concentration in the filtrate was detected using a UV−vis spectrophotometer.

2.4. Characterization. X-ray diffraction (XRD) patterns of the samples were obtained using an X-ray diffractometer (Bruker D8 ADVANCE) and Fourier transform infrared (FT-IR) spectrometer (Shimadzu, Japan). Field emission scanning electron microscopy (FESEM) images were obtained using a JSM 7401F electron microscope. The morphology of nanostructures was examined using a transmission electron microscope (Tecnai G2 F20). Chemical states of the samples were characterized using an X-ray photoelectron spectrometer (Thermo ESCALAB 250XI). The specific surface area and pore structures of the obtained samples were measured using a 

3. RESULTS AND DISCUSSION

The 2D/2D ZnO/rGO nanocomposites were one-step-synthesized by adding GO nanosheets into a Zn2+-containing solution followed by microwave heating at 60 °C for 20 min. Due to the strong interaction between the Zn2+ and functional groups (e.g., −COOH), the Zn2+ could be easily adsorbed on the surface of GO nanosheets. Therefore, Zn2+ could be in situ reformed into ZnO 2D nanosheets and the reduction reaction from GO to rGO was simultaneously carried out, resulting in the formation of 2D/2D ZnO/rGO under microwave heating. Typically, this procedure affords 1.2 g of ZnO/rGO composite photocatalysts, showing the potential of the application in practice.

The SEM images of samples are shown in Figure 1a,b. As can be seen, the sole ZnO has a typical three-dimensional flower-like structure (Figure 1a) and is self-assembled from nanosheets as we reported previously. However, due to the tight anchoring of ZnO nanosheets on the surface of rGO nanosheets, the 2D feature of rGO could be still identified, suggesting the successful in situ growth of ZnO nanosheets on the rGO platforms (Figure 1b). The effective interface coupling between the ZnO and rGO is beneficial to the separation of photogenerated carriers. As shown in Figure 1c,e, the diameter of the nanoflower is about 1.2 μm, which further proves that the nanoflower is assembled from nanosheets with a thickness of 50 nm. The lattice distances measured for the ZnO nanosheets are 0.26 nm, which correspond well with lattice distances of (001) wurtzite ZnO (JCPDS no. 46-1451). It is worth noting that when ZnO is combined with rGO, the TEM images (Figure 1d,f) show that the thickness of the ZnO nanosheets is significantly narrowed (15 nm). This result can be attributed to the space confined effects of GO or rGO, leading to the formation of ultrathin nanosheets. Both SEM and TEM results indicate that the
ZnO/rGO heterostructure was successfully synthesized by the microwave hydrothermal method. XRD was used to analyze the phase composition of ZnO and ZnO/rGO nanocomposites. As shown in Figure 2, the characteristic peaks of samples at $2\theta = 31.9, 34.3, 36.2, 47.6, 56.6, 62.8,$ and $67.8^\circ$ are attributed to (100), (002), (101), (102), (110), (103), and (112) crystal planes, respectively, indicating that the ZnO prepared by the microwave hydrothermal method has a wurtzite structure (JCPDS no. 46-1451). According to the Scherrer equation

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta}$$

where $\lambda$ is the wavelength of the X-ray radiation equal to 0.15405981 nm, $k$ is a constant (0.89), $\theta$ is the diffracting angle, and $\beta$ is full width of the peak at half maximum. The calculated (100) grain sizes of pure ZnO were 46.5 nm. After introduction of rGO, the grain sizes of ZnO are calculated in Table 1. These results suggested that the presence of rGO affects the growth of ZnO nanosheets.

However, the characteristic peak of rGO was not found in the spectrum, which may be due to the low content of rGO in the composite. In addition, the characteristic peaks of ZnO did not shift after adding rGO, indicating that the introduction of rGO did not affect the phase structure of ZnO.

In order to further confirm the successful formation of ZnO/rGO composites, Raman and FT-IR spectroscopic measurements were performed. The Raman spectra of ZnO and ZnO/rGO nanocomposites are shown in Figure 3a. For pure ZnO, the three main peaks at 102, 328, and 437 cm$^{-1}$ can be assigned, respectively, to the $E_{2}^{low}$, $E_{2}^{high}$, and $E_{2}^{high} - E_{2}^{low}$ mode of the ZnO wurtzite structure. The Raman spectra of GO showed two typical characteristic peaks at 1354 cm$^{-1}$ (D-band) and 1588 cm$^{-1}$ (G-band). The D-band was contributed to sp$^3$ defects in graphene, while the G-band provides information about vibrations of ordered sp$^2$ carbon atoms in the hexagonal lattice of GO. It was found in the nanocomposite that the main Raman peaks of rGO and ZnO coexist, further confirming the formation of the nanocomposite. The intensity ratio between the D band and G band ($I_D/I_G$) increased from 0.99 (GO) to 1.03 and the G band slightly blue-shifts, confirming the partial reduction from GO to rGO.

In order to further confirm the elemental composition of the nanocomposite, the XPS spectra of ZnO/rGO were exhibited. In Figure 4a, the main elements of the nanocomposite are Zn, O, and C. From Figure 4b, the diffraction peaks of C–C and C–O are at 284.7 and 286.1 eV, respectively. In addition, a very weak diffraction peak of $-COOH$ was found at 288.8 eV, indicating that the graphene oxide was reduced. As shown in Figure 1.

Figure 1. SEM images of (a) ZnO nanosheets and (b) ZnO/rGO nanocomposite. TEM images of (c,e) ZnO nanosheet and (d,f) ZnO/rGO nanocomposite ZnO nanosheets, showing ultrathin ZnO nanosheets after being associated to rGO.

FIGURE 2. XRD patterns of the ZnO nanosheet and ZnO/rGO composites.

Table 1. Grain Sizes for Pure ZnO and ZnO/rGO

| rGO (mass fraction) | 0  | 1% | 5% | 10% |
|---------------------|----|----|----|-----|
| ZnO (nm)            | 46.5 | 40.3 | 33.7 | 39.7 |

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Figure 4c, the binding energies of Zn 2p3/2 and Zn 2p1/2 are 1021.9 and 1044.8 eV, respectively, corresponding to Zn2+ of ZnO.37 The O 1s XPS spectrum of ZnO/rGO (Figure 4d) can be deconvoluted into three peaks, which are Zn −O (529.3 eV), adsorbed oxygen (530.4 eV), and C −Zn (531.9 eV).37 It is worth noting that there is C −Zn in the O 1s spectrum, which means that there is a strong interaction at the interface between ZnO and rGO, which further indicates that the ZnO/rGO composite was successfully prepared. The data analysis proved the successful synthesis of ZnO/rGO and was in accordance with the result of Raman and FT-IR results.

The BET surface areas of obtained samples and their pore size distribution are investigated in Figure 5. The specific surface areas of ZnO and ZnO/rGO are 14.281 and 19.130 m²/g, respectively (Figure 5a). From the pore size distribution (Figure 5b), it can be seen that pore sizes displayed three peaks located at 3–4, 7, and 15 nm, respectively. After introduction of rGO, the ZnO/rGO nanocomposite showed pore size distributions centered at 5 and 18 nm. The morphology of pure ZnO is a sphere formed by the self-assembly of nanosheets, and the nanocomposite is similar to an array of ZnO nanosheets randomly grown on graphene, so the pore structure of the two is significantly different. Compared with...
ZnO, ZnO/rGO had a larger mesoporous volume, which can be attributed to the rich mesoporous structure and large specific surface area.\(^{38}\) The improvement of the specific surface area and average pore diameter of composites will be beneficial for an effective transport path for adsorption, which could enhance the photocatalytic performance.

The optical properties of ZnO and ZnO/rGO were investigated by UV−vis DRS (Figure 6a). For ZnO nanosheets, obvious absorbance edges can be observed at 380 nm, which is mainly due to the inherent band structure of ZnO.\(^{31}\) After incorporating rGO, it has the same absorbance edges, suggesting that the band gap of ZnO was not changed at all after the introduction of rGO. In the visible light region (380−800 nm), absorbance of ZnO/rGO is significantly enhanced, which can be attributed to that the color of the composite material changes from white to gray as the rGO content increases.\(^{24}\)

The photocatalytic activity of the sample was evaluated by TC degradation. As shown in Figure 7a, ZnO has the lowest degradation rate at about 40% within 60 min, which be attributed to the fast recombination rate of photoinduced electron and hole pairs. Compared with ZnO, the ZnO/rGO nanocomposite exhibits a much better photocatalytic degradation capacity under the same conditions. Among them, ZnO/rGO-2 exhibits the highest photocatalytic activity, and the degradation rate of TC can reach 95.4%. Figure 7b shows that the photocatalytic degradation data correspond to those of the pseudo-first-order kinetic model. It is worth noting that the highest \(k\) value of ZnO/rGO-2 (0.0875 min\(^{-1}\)) is about 7.9 times that of ZnO (0.011 min\(^{-1}\)). The results show that the introduction of an appropriate amount of graphene can enhance the adsorption of TC and improve the photocatalytic degradation rate and photocatalytic activity. The ZnO/rGO nanocomposite was beneficial for enhanced photodegradation of dyes or antibiotics compared to other reports, as shown Table 2.

The separation efficiency of photogenerated carriers is an important factor to evaluate photocatalytic activity. PL spectroscopy was used to explore the recombination rates of photogenerated carriers and the result are shown in Figure 7c; pure ZnO has a strong PL emission peak near 385 nm, which is mainly due to the near-band edge emission of the wide band gap of ZnO.\(^{22}\) In contrast, the PL signal intensity of ZnO/rGO is significantly weakened, indicating that the introduction of rGO is beneficial to improve the separation efficiency of photogenerated electron−hole pairs. In order to further prove that graphene can promote charge transfer, we explored the photoelectric transmission ability of ZnO/rGO through photocurrent test (Figure 7d). The photocurrent density of the ZnO/rGO-2 composite material is about 0.015 μA, which is much higher than that of ZnO, which indicates that ZnO/rGO has a stronger ability to excite carriers and can separate more electrons, which is the result of photocatalytic degradation. The photoresponse of pure ZnO is very low, which may be due to the low conductivity of ZnO which limits the electron transport.\(^{44}\) The significant increase in photocurrent density in ZnO/rGO composites is attributed to the introduction of an appropriate amount of rGO, which accelerates the electron transport efficiency and inhibits the recombination of photogenerated electron−hole pairs. How-
ever, excessive rGO acts as a recombination center of photogenerated carriers, leading to increased PL intensity. More importantly, the photogenerated carriers are recombined at the interface of ZnO and rGO. As a result, fewer electrons on the photocatalyst surface are excited to generate loop current.

The stability of photocatalysis was crucial for practical applications and the results are shown in Figure 8. After five cycles, the degradation ratio of TC was still up to 97%, suggesting stable photocatalytic performance. The photocatalytic efficiencies were slightly reduced, attributing to slight quality loss of the ZnO/rGO photocatalyst and TC molecules absorbed on the surface of samples, resulting in the active site to be occupied. This result showed that ZnO/rGO has good stability and has potential for practical application.

In order to further clarify the mechanism of photocatalytic degradation, ESR was used to detect the active species in the process of photocatalytic degradation. The ESR spectra of

### Table 2. Recently Reported Dye or Antibiotic Degradation Efficiency of ZnO-Based Nanocomposites

| no. | materials       | light source | dye or antibiotic     | degradation (%) | duration (min) | references |
|-----|-----------------|--------------|-----------------------|-----------------|----------------|------------|
| 1   | ZnO/rGO         | UV-light     | MB                    | 95              | 120            | 39         |
| 2   | graphene/ZnO    | UV-light     | MO                    | 92              | 120            | 40         |
| 3   | ZnO/SnO₂        | UV-light     | MB                    | 97.3            | 35             | 41         |
| 4   | GO@Fe₃O₄/ZnO/SnO₂ | UV-light  | azithromycin          | 90.06           | 120            | 42         |
| 5   | Ni/ZnO–SnO₂     | UV-light     | RhB                   | 95              | 30             | 43         |
| 6   | rGO/ZnO         | UV-light     | TC                    | 95.4            | 60             | this work  |

![Figure 7.](image_url)  
(a) Photocatalytic degradation curves of ZnO/rGO nanocomposites for the photodegradation of the TC solution under ultraviolet light; (b) pseudo-first-order kinetic plots; (c) room temperature PL spectra of ZnO and ZnO/rGO composites with excitation at 325 nm; and (d) transient photocurrent density of ZnO and ZnO/rGO nanocomposites.

![Figure 8.](image_url)  
Photodegradation performance within five cycles for ZnO/rGO-1.
ZnO/rGO and ZnO photocatalysts are shown in Figure 9. In the absence of UV light, hydroxyl radicals (·OH) and superoxide radicals (·O$_2^-$) have no obvious peaks. Under ultraviolet light irradiation, compared with pure ZnO, the ESR signal intensity of the ZnO/rGO composite ·OH and ·O$_2^-$ showed a significant increase, which indicates that the introduction of graphene can improve the oxidation ability.

To further clarify the photocatalytic mechanism of ZnO/rGO for photodegradation of TC, the free radical-trapping experiments for TC degradation over the ZnO/rGO sample were carried out, as shown in Figure 9c. Isopropanol (IPA), benzoquinone (BQ), and EDTA-2Na are used as the scavengers to remove ·OH, ·O$_2^-$, and h$^+$ during the photocatalytic process. The addition of BQ obviously changed the photocatalytic photodegradation of TC, while the degradation efficiency reduces a little in the presence of IPA and EDTA-2Na. These results reveal that the ·O$_2^-$ is the primary active species, whereas the ·OH and the h$^+$ contribute less to the TC degradation in photocatalytic reaction.

Based on the abovementioned results, the possible photocatalytic degradation mechanism can be described as follows (Figure 10). Under the irradiation of ultraviolet light, the ZnO nanosheets self-assembled to form a porous structure, which increases the contact area and interaction time, thus increasing the light utilization rate and generating more photogenerated charges and holes and electrons. However, because the recombination of carriers, electrons, and holes cannot generate enough active species, the photocatalytic degradation efficiency of ZnO is still low. After the introduction of rGO nanosheets to construct ZnO/rGO composites, due to the high charge transfer rate of graphene, the charge in ZnO CB is quickly transferred to the surface of graphene. Therefore, the recombination of photogenerated charge−hole−electron pairs on the surface of ZnO is greatly reduced, thereby effectively separating photogenerated carriers. Subsequently, the photogenerated electrons transferred from the ZnO CB to the rGO nanosheets have high reducing power, and then, the diffused water molecules are reduced in the photocatalytic reaction to generate superoxide radicals. In addition, the large specific surface area and rich pore structure of ZnO/rGO enhance the interaction between ZnO/rGO and TC molecules. Furthermore, the abundant active species (·O$_2^-$ and ·OH) of composites could efficiently react with TC to generate CO$_2$ and H$_2$O to realize the improved photocatalytic degradation activity of TC. The photocatalytic reaction process can be described in the following eqs 1−5

$$\text{ZnO/rGO} + \text{h}^+ \rightarrow \text{ZnO/rGO} + \text{h}^+ \text{e}^-$$

$$\text{H}_2\text{O} \leftrightarrow \text{H}^+ + \cdot\text{OH}^-$$

$$\text{OH}^- + \text{h}^+ \rightarrow \cdot\text{OH}^-$$

$$\text{O}_2 + \text{e}^- \rightarrow \cdot\text{O}_2^-$$

$$\cdot\text{OH}, \cdot\text{O}_2^- + \text{TC} \rightarrow \text{H}_2\text{O} + \text{CO}_2$$

4. CONCLUSIONS

In this study, we developed a facile one-step microwave-assisted gram-scale synthesis strategy to construct 2D/2D ZnO/rGO hybrid photocatalysts. Compared with ZnO nanosheets, ZnO/rGO exhibited enhanced photocatalytic activity when photodegrading TC under ultraviolet light. The
improved performance of the photocatalyst can be attributed to the rapid transmission of electrons and the efficient separation of photogenerated carriers. In addition, the porous structure of the composites enhanced the light absorption and specific surface area, which also helps to improve photocatalytic performance.

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**Notes**

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