

## Construction of $\text{TiO}_2$ -pillared multilayer graphene nanocomposites as efficient photocatalysts for ciprofloxacin degradation

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Cite this article as:

Xiong-feng Zeng, Jian-sheng Wang, Ying-na Zhao, Wen-li Zhang, and Meng-huan Wang, Construction of  $\text{TiO}_2$ -pillared multilayer graphene nanocomposites as efficient photocatalysts for ciprofloxacin degradation, *Int. J. Miner. Metall. Mater.*, 28(2021), No. 3, pp. 503-510. <https://doi.org/10.1007/s12613-020-2193-y>

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# Construction of TiO<sub>2</sub>-pillared multilayer graphene nanocomposites as efficient photocatalysts for ciprofloxacin degradation

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(Received: 23 July 2020; revised: 9 September 2020; accepted: 11 September 2020)

**Abstract:** We successfully constructed TiO<sub>2</sub>-pillared multilayer graphene nanocomposites (T-MLGs) via a facile method as follows: dodecylamine pre-pillaring, ion exchange (Ti<sup>4+</sup> pillaring), and interlayer *in-situ* formation of TiO<sub>2</sub> by hydrothermal method. TiO<sub>2</sub> nanoparticles were distributed uniformly on the graphene interlayer. The special structure combined the advantages of graphene and TiO<sub>2</sub> nanoparticles. As a result, T-MLGs with 64.3wt% TiO<sub>2</sub> showed the optimum photodegradation rate and adsorption capabilities toward ciprofloxacin. The photodegradation rate of T-MLGs with 64.3wt% TiO<sub>2</sub> was 78% under light-emitting diode light irradiation for 150 min. Meanwhile, the pseudo-first-order rate constant of T-MLGs with 64.3wt% TiO<sub>2</sub> was 3.89 times than that of pristine TiO<sub>2</sub>. The composites also exhibited high stability and reusability after five consecutive photocatalytic tests. This work provides a facile method to synthesize semiconductor-pillared graphene nanocomposites by replacing TiO<sub>2</sub> nanoparticles with other nanoparticles and a feasible means for sustainable utilization of photocatalysts in wastewater control.

**Keywords:** pillared structure; titanium dioxide-pillared multilayer graphene nanocomposites; photocatalysis; ciprofloxacin

## 1. Introduction

Ciprofloxacin (CIP), a synthetic third-generation fluoroquinolone antibiotic, has widely been used for the efficient treatment of a number of bacterial infections [1]. However, the bio- and photo-degradation of CIP are difficult [2]. Hence, the investigation of the photocatalytic degradation of CIP by solar energy as a potential way to solve water pollution has attracted extensive research attention [3–8].

TiO<sub>2</sub> is the most widely studied and used as a photocatalyst in commercial applications because of its advantages [9–10]. However, the wide band gap and high photoelectron–hole recombination probability hinder the improvement of the photocatalytic performance of TiO<sub>2</sub> [11]. Strategies, including doping, nanostructuring, surface modification, and heterojunction construction, have been proposed to enhance the semiconductor properties of TiO<sub>2</sub> [7,12–16]. Graphene possesses a large specific surface area, excellent conduction, and chemical stability [17], resulting in good electron transfer and electron holding capacity. When TiO<sub>2</sub> combines with graphene, the photocatalytic activity of graphene–TiO<sub>2</sub> composites is higher compared with pure TiO<sub>2</sub> [18–21] because of the effective charge transfer. Graphene–TiO<sub>2</sub> nano-

composites can be used not only in photocatalysis but also in dye-sensitized solar cells, ultraviolet photodetectors, and supercapacitors [22–26]. In addition, the good performances of these nanocomposites require a high interfacial contact [27–30] between graphene and TiO<sub>2</sub>, which is the key to improve electron transfer and reducing electron–hole recombination, especially for photocatalysts [31]. TiO<sub>2</sub> nanoparticles anchoring onto graphene sheets by chemical interaction has been verified by a significantly enhanced photocatalytic activity [32].

To date, TiO<sub>2</sub> is usually loaded on the surface of multilayer or single-layer graphene in TiO<sub>2</sub>–graphene nanocomposites [23–24,26,33–37]. Graphene–TiO<sub>2</sub> nanocomposite photocatalytic degradation rates differ, as will be compared later. To the best of our knowledge, TiO<sub>2</sub>-pillared multilayer graphene nanocomposites (T-MLGs), which are formed through the insertion of TiO<sub>2</sub> nanoparticles into the interlayer spacing of multilayer graphene, have rarely been reported. Their special structure (pillared structure) can improve the photocatalytic efficiency by reducing photoelectron–hole recombination probability, which was verified by intercalating TiO<sub>2</sub> into the interlayer regions of layered materials, e.g., HTaWO<sub>6</sub> and K<sub>2</sub>Ti<sub>4</sub>O<sub>9</sub> [16,38]. Therefore, to enhance the

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photocatalytic activity of  $\text{TiO}_2$ , we synthesized T-MLGs via a facile method as follows: dodecanediamine pre-pillaring, ion exchange ( $\text{Ti}^{4+}$  pillaring), and interlayer *in-situ* formation of  $\text{TiO}_2$  by hydrothermal method. The preparation and photocatalytic activity for CIP degradation of T-MLGs were investigated in detail in this work.

## 2. Experimental

### 2.1. Synthesis of photocatalyst

All chemicals were of analytical reagent grade and used as received without any further purification.

#### 2.1.1. Dodecanediamine pre-pillared graphene oxide intermediate

Dodecanediamine pre-pillared graphene oxide (GO) was prepared by Margarita's method [39]. First, 100 mg GO was dispersed in 16.5 mL deionized water via ultrasonication. Then, 4.16 mmol 1,12-dodecanediamine was dissolved in 17.5 mL ethanol, and the mixture was added dropwise to GO suspension under continuous stirring at room temperature for at least 48 h. Then, GO/dodecanediamine was centrifuged, washed with deionized water and absolute ethanol for several times, and dried at 80°C for 24 h. Finally, dodecanediamine pre-pillared GO was prepared successfully. GO with thickness of 0.8–1.2 nm was purchased from Nanjing Xian-Feng Nanomaterials Technology Co. Ltd., China.

#### 2.1.2. Ion exchange ( $\text{Ti}^{4+}$ pillaring)

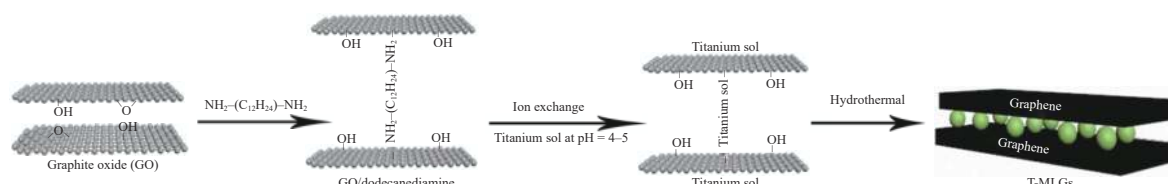


Fig. 1. Schematic diagram for synthesis process of T-MLGs.

### 2.2. Characterization

The crystal structures were analyzed by X-ray diffraction (XRD, D/MAX2500PC Rigaku,  $\text{Cu K}\alpha$ ). The surface morphologies were investigated by scanning electron microscopy (SEM, Hitachi S-4800) and high-resolution transmission electron microscopy (HRTEM, JEM-2010). Raman spectrum was detected by DXR laser Raman spectroscopy. Fourier transform infrared spectra (FTIR) were measured on a Nicolet 470 FT-IR spectrometer. The photoluminescence (PL) spectra were obtained using a fluorescence spectrometer (PE, LS-S5). The excitation wavelength was 380 nm.

### 2.3. Photocatalytic degradation of the CIP solution

A total of 20 mg  $\text{TiO}_2$  or 20 mg T-MLGs were dispersed in 40 mL CIP aqueous solution (15 mg/L). First, the mixtures were magnetically stirred for 30 min in the dark to establish the adsorption–desorption equilibrium of CIP on the

The  $\text{TiO}_2$  sol was prepared before the  $\text{Ti}^{4+}$  exchange with dodecanediamine, which was prepared in accordance with the previously procedure reported by Chen *et al.* [40].  $\text{TiO}_2$  sol was adjusted to pH of 4–5 by 0.1 M ammonia solution. Then, the dodecanediamine pre-pillared GO was scattered dropwise into mixture mentioned above under magnetic stirring for 24 h to complete the  $\text{Ti}^{4+}$  exchange with dodecanediamine. After filtering, washing, and drying at 65°C for 24 h, the precursor powder was obtained.

#### 2.1.3. Interlayer *in-situ* formation of $\text{TiO}_2$ by hydrothermal method

First, the precursor powder was dispersed in 30 mL deionized water via ultrasonication. Then, the mixed solution was transferred to a 50 mL Teflon-lined autoclave and reacted at 200°C for 4 h and cooled to 25°C naturally. Afterward, the precipitates were centrifuged, washed with deionized water and absolute ethanol until the filtrate was neutral, and dried at 80°C for 4 h. Finally, the T-MLGs were prepared successfully.

By controlling the amount of  $\text{TiO}_2$  sol, T-MLGs with different  $\text{TiO}_2$  weight percentages of 10.4wt%, 64.3wt%, and 94.1wt% were obtained and denoted as T-MLG-10.4, T-MLG-64.3, and T-MLG-94.1, respectively.  $\text{TiO}_2$  as a control was prepared in the same experiment condition by hydrothermal method.

Fig. 1 illustrates the preparation process of T-MLGs.

sample surface. A 5 W light-emitting diode (LED) lamp (white light, wavelength  $\lambda > 420$  nm) was employed as the light source. The CIP solution (3 mL) was extracted and centrifuged at a rate of 8000 r/min for 2 min every 30 min. The concentration change of CIP was determined using the spectrophotometric method (CE3021, Shanghai Precision & Scientific Instrument Co. Ltd., China) at 276 nm.

$$\text{Degradation rate} = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

where  $C_0$  and  $C_t$  are the concentrations of the initial CIP and CIP after  $t$  min irradiation, respectively.

## 3. Results and discussion

Fig. 2 shows the XRD patterns of GO, GO/dodecanediamine, GO/ $\text{TiO}_2$  precursor, and T-MLGs with different  $\text{TiO}_2$  contents. Compared with GO, the (001) peaks of

GO/dodecanediamine and GO/TiO<sub>2</sub> precursor shifted toward lower angles (from 11.1° to 7.3° and 11.1° to 7.67°, respectively), indicating the enlargement of interplanar distance as shown in Fig. 2(a). The large interplanar distance indicated that dodecanediamine or TiO<sub>2</sub> sol had intercalated into the lamellar GO sheets [41]. Fig. 2(b) shows the XRD patterns of T-MLG-10.4, T-MLG-64.3, T-MLG-94.1, and pure TiO<sub>2</sub>. All samples showed a similar crystal structure, suggesting the formation of T-MLG nanocomposites after 200°C hydrothermal treatment. The intensity of the diffraction peaks increased as the TiO<sub>2</sub> content increased. The diffraction patterns had five broad peaks at 25.3°, 37.8°, 48.0°, 54.0°, and 62.7°, corresponding to the (101), (004), (200), (211), and (204) planes of TiO<sub>2</sub> (JCPDS No. 21-1272), respectively.

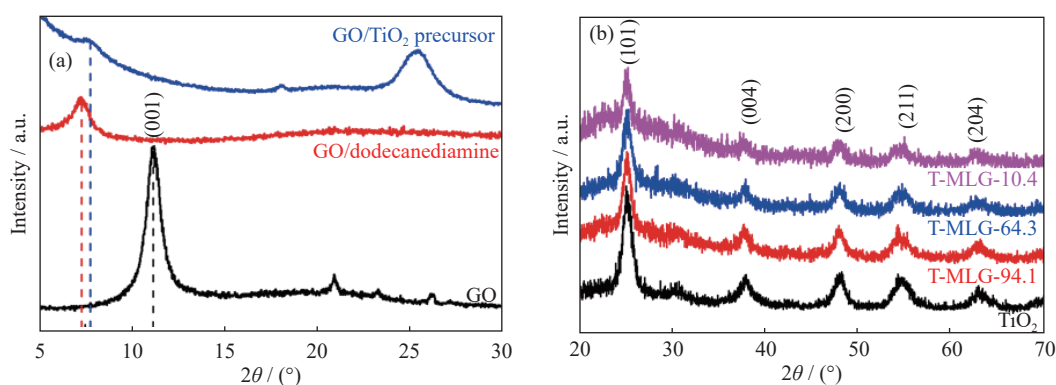


Fig. 2. XRD patterns of (a) GO, GO/dodecanediamine, and GO/TiO<sub>2</sub> precursor and (b) T-MLGs with different TiO<sub>2</sub> contents.

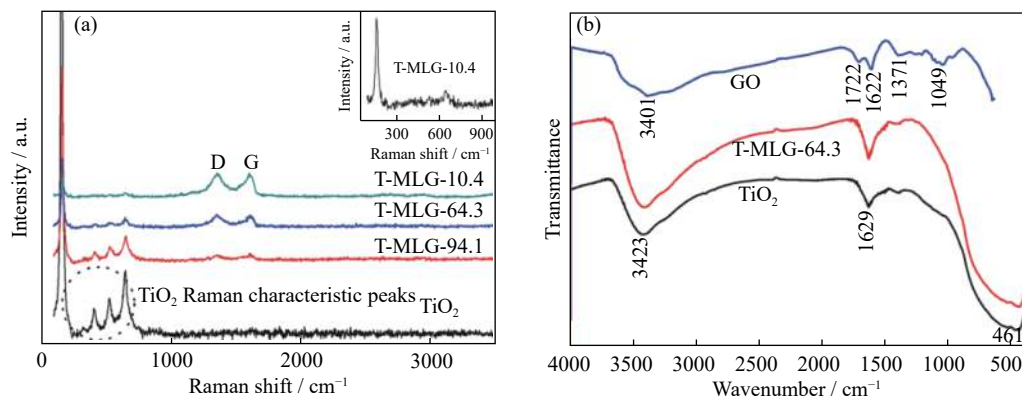


Fig. 3. Raman spectra of (a) pure TiO<sub>2</sub> and T-MLGs; (b) FTIR spectra of GO, T-MLG-64.3 and pure TiO<sub>2</sub>. Inset in (a) shows partial enlarged drawing of T-MLG-10.4.

Although the existence of graphene and TiO<sub>2</sub> has been confirmed by Raman spectra, the connection between TiO<sub>2</sub> and graphene should be studied further by FTIR spectra. Fig. 3(b) displays the FTIR spectra of GO, T-MLG-64.3, and TiO<sub>2</sub>. The absorption bands at 3401, 1622, and 1371 cm<sup>-1</sup> in GO and T-MLG-64.3 indicated the presence of O–H stretching vibrations, skeletal ring vibrations of C=C, and tertiary C–OH groups [43], respectively. The absorption bands at 1722 and 1049 cm<sup>-1</sup> showed the C=O and C–O stretching vibrations of COOH groups, respectively. However, both ad-

However, no typical peak of graphene was observed in T-MLGs by XRD. Raman scattering was performed to confirm the existence of graphene in the nanocomposites.

As shown in Fig. 3(a), the Raman characteristic peaks at 160, 409, 531, and 654 cm<sup>-1</sup>, which belong to TiO<sub>2</sub>, were observed in all T-MLGs, thus confirming the existence of TiO<sub>2</sub> and consistent with the observation from the XRD in Fig. 2(b) [20]. Furthermore, two main peaks were observed at 1363 (peak D) and 1612 (peak G) cm<sup>-1</sup> for all T-MLG samples, signifying the existence of graphene in T-MLGs. The intensity of graphene significantly decreased as the TiO<sub>2</sub> content increased (Fig. 3(a)). The reason may be the replacement of the graphene surface by TiO<sub>2</sub> nanoparticles [42].

sorption bands disappeared on T-MLG-64.3, indicating the reduction of GO after hydrothermal treatment [44–46]. Meanwhile, the peaks at 3423, 1629, and 461 cm<sup>-1</sup> in TiO<sub>2</sub> nanoparticles and T-MLGs corresponded to the stretching and bending vibrations of –OH and Ti–O stretching mode, respectively. TiO<sub>2</sub> nanoparticles evidently existed in the T-MLGs. The broad absorption at 461 cm<sup>-1</sup> in T-MLG-64.3 was considerably plumper than that in TiO<sub>2</sub>, and this result was ascribed to the formation of Ti–O–C vibration in T-MLG-64.3 [44]. The presence of Ti–O–C bonds indicated the



chemical interaction between  $\text{TiO}_2$  and graphene [47].

Figs. 4(a)–4(c) show the SEM micrographs of T-MLG-10.4, T-MLG-64.3, and T-MLG-94.1, respectively. T-MLGs with low  $\text{TiO}_2$  content exhibited a plate-like morphology (Fig. 4(a)). With the increase in  $\text{TiO}_2$  content,  $\text{TiO}_2$  uniformly decorated and existed on the interlayer of graphene with high density (Figs. 4(b) and 4(c)). Moreover, the alveolate morphology of T-MLGs may be mainly attributed to the dehydroxylation and dehydration of  $\text{TiO}_2$  gel precursor to oxide pillars after hydrothermal treatment [48]. The morphology of T-MLG-64.3 was further investigated by transmission electron microscopy (TEM). As shown in Figs. 4(d) and 4(e),  $\text{TiO}_2$  nanoparticles were embedded in the graphene sheets. The HRTEM image of T-MLGs in Fig. 4(f) demonstrated that the  $\text{TiO}_2$ -pillared structure was obtained successfully. The evidence was the enlarged interplanar distance of

graphene sheets from 0.34 to 0.516 nm (inset in Fig. 4(f)).

T-MLGs were prepared successfully via a facile method as follows: dodecanediamine pre-pillaring, ion exchange ( $\text{Ti}^{4+}$  pillaring), and interlayer *in-situ* formation of  $\text{TiO}_2$  by hydrothermal method based on the above analysis.

The photocatalytic degradation of CIP (natural pH of 5.8) with 0.5 g/L photocatalysts was carried out in accordance with the preliminary experiment [49]. The adsorption property is an important factor affecting the photocatalytic performance. As shown in Fig. 5(a), the adsorption capacity of photocatalysts toward CIP after dark stirring for 30 min followed the order: T-MLG-64.3 > T-MLG-10.4 > T-MLG-94.1 >  $\text{TiO}_2$ . T-MLG-64.3 exhibited the best adsorption property. A blank without photocatalyst was also prepared under the same conditions to eliminate the effect of photolysis. Self-degradation rate was 3% after 150 min due to negli-

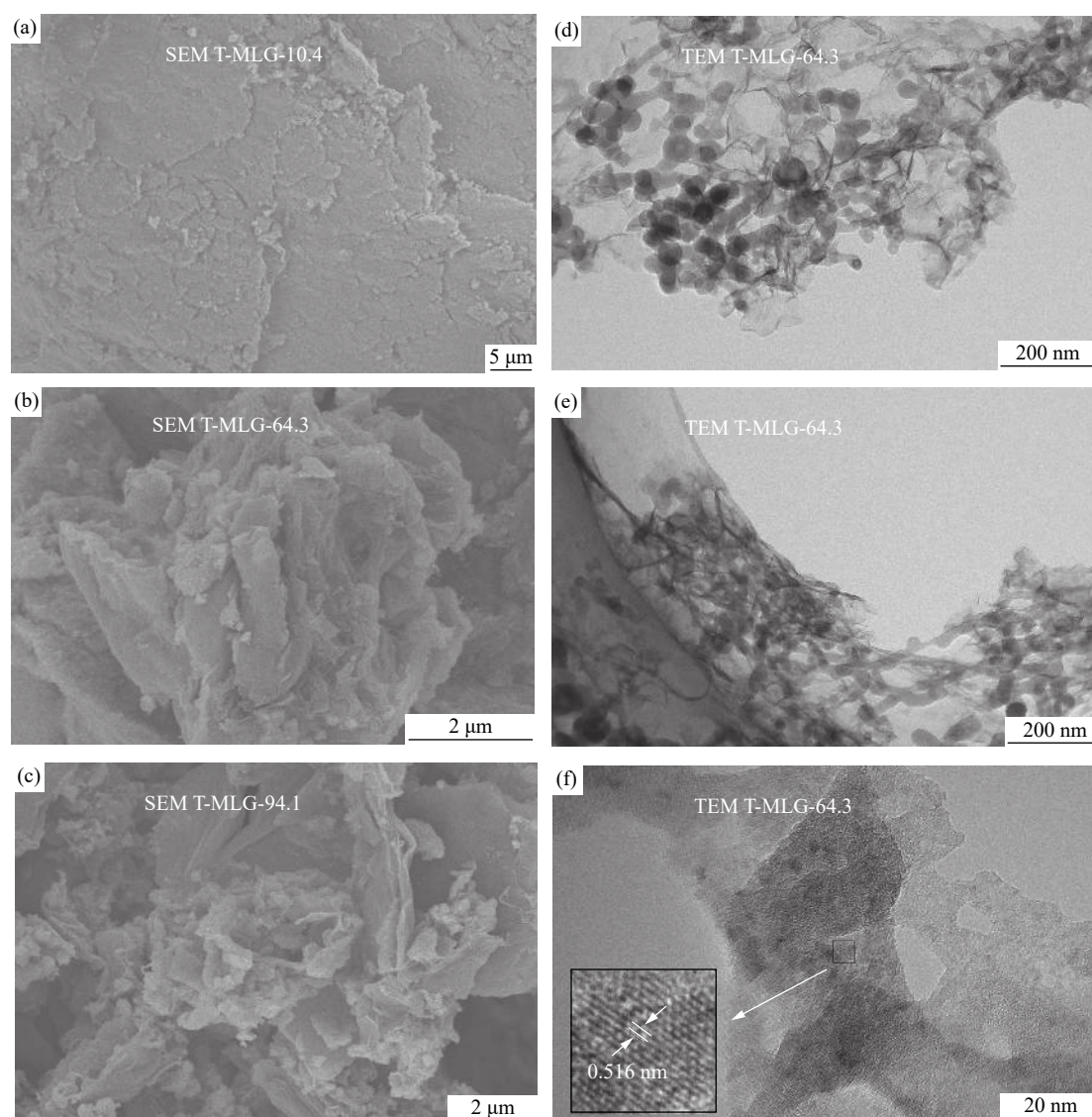


Fig. 4. SEM micrographs of (a) T-MLG-10.4, (b) T-MLG-64.3, and (c) T-MLG-94.1; (d)–(f) TEM images of T-MLG-64.3. Inset in (f) shows partial enlarged drawing.

gible photooxygenation reactions in the presence of molecular oxygen (Fig. 5(b)) [50]. To verify the enhanced photocatalytic performance of T-MLG-64.3, we performed comparative experiment for the degradation of CIP by using pure TiO<sub>2</sub> under the same conditions. The degradation efficiency of T-MLG-64.3 reached 78%, which was notably better than that of pure TiO<sub>2</sub> (42%) (Fig. 5(b)). Fig. 5(c) shows the photocatalytic degradation of CIP kinetics and the fitting results, which followed pseudo-first-order kinetics. The apparent reaction rate constant of T-MLG-64.3 was as much as 3.89 times than that of pure TiO<sub>2</sub>. Five cycles of the photocatalyt-

ic experiments were conducted to examine the photostability and structure stability of T-MLGs, and one cycle lasted for 150 min. Fig. 5(d) offered the evidence that pillared structure nanocomposites are reusable and stable in recycling photocatalytic degradation experiments. After each cycle, the photocatalyst was washed and centrifuged for several times and finally irradiated under simulated sunlight for 60 min to ensure that the CIP molecules were removed completely. For comparison, the degradation rates of different organic pollutants over different kinds of graphene/TiO<sub>2</sub> composites and TiO<sub>2</sub> are listed in Table 1.

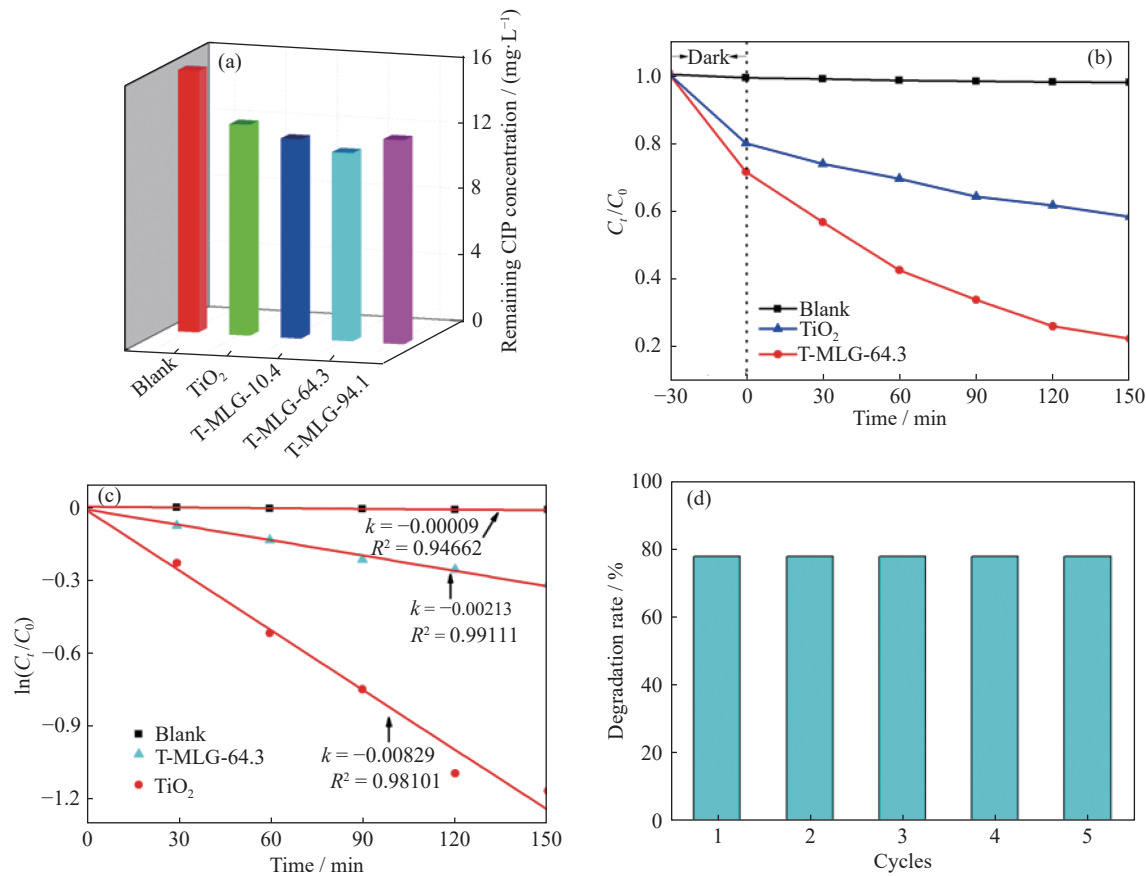


Fig. 5. (a) Adsorption of CIP in presence of different photocatalysts; (b) photocatalytic degradation of CIP; (c) pseudo-first order kinetics curves of the photocatalytic degradation of CIP ( $k$ —Apparent reaction rate constant;  $R^2$ —Coefficient of determination); (d) photo-degradation rates of CIP after repeated cycles (irradiation time of 150 min).

Table 1. Photocatalytic properties of graphene/TiO<sub>2</sub> composites in comparison with pure TiO<sub>2</sub>

Organic pollutant	Irradiation system	Graphene content in graphene/TiO <sub>2</sub> composite	Degradation rate of pollutant / %		Ref.
			Graphene/TiO <sub>2</sub> composite	Pure TiO <sub>2</sub>	
Methylene blue	Sunlight	8wt%	98.67 (45 min)	52 (2 h)	[51]
Ciprofloxacin	Sunlight	8wt%	96.73 (60 min)	65.52 (60 min)	[51]
Rhodamine-B	Solar light	0.09 g	98 (60 min)	42 (60 min)	[18]
Methylene blue	UV lamp ( $\lambda = 365$ nm)	0.01 g	~97 (150 min)	~58 (150 min)	[32]
Methylene blue	LED lamp ( $\lambda > 420$ nm)	0.01 g	~67 (150 min)	~58 (150 min)	[32]
Methylene blue	UV lamp	75wt%	~61 (70 min)	~35 (70 min)	[52]
Ciprofloxacin	LED lamp ( $\lambda > 420$ nm)	35.7wt%	78 (150 min)	42 (150 min)	This work

The PL spectroscopy intensity of T-MLG-64.3 was lower than that of pure TiO<sub>2</sub> (Fig. 6). A high PL intensity indicates the easy recombination of electrons and holes [49,53]. Thus, when TiO<sub>2</sub> intercalated into the interlayer of graphene to form a TiO<sub>2</sub>-pillared structure, graphene instantly accepted the photoinduced electron to reduce the recombination of electrons and holes and boost the electron-hole separation in TiO<sub>2</sub>.

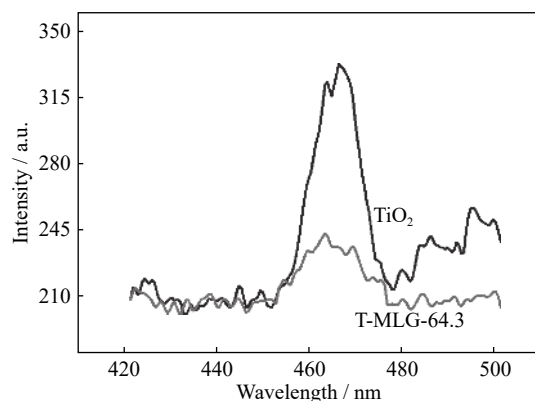


Fig. 6. PL spectra of pure TiO<sub>2</sub> and T-MLG-64.3 (excitation: 380 nm).

The active species capture experiment was conducted in this study to determine the active species that play the main role in the photocatalytic process of CIP degradation. 1 mmol·L<sup>-1</sup> isopropyl alcohol (IPA), 1 mmol·L<sup>-1</sup> triethanolamine (TEOA), and 0.1 mmol·L<sup>-1</sup> benzoquinone (BQ) were added as scavengers for hydroxyl radical (·OH), hole (h<sup>+</sup>), and superoxide radical (·O<sub>2</sub><sup>-</sup>) to CIP solution in the presence of T-MLG-64.3 photocatalyst, respectively. Other experimental conditions were the same as given for the photocatalytic degradation of CIP. Fig. 7 shows the different degradation rates after adding scavengers and the significant role of active species during photocatalysis. The degradation rates of CIP decreased from 78% of the blank to 63.8%, 16.9%, and 33.8% with IPA, TEOA, and BQ, respectively. Therefore, the hole provided the greatest contribution to CIP decomposition, followed by superoxide radical and then hydroxyl radical. The major photocatalytic process for CIP degradation using T-MLG-64.3 was proposed with the following reactions (2)–(9).

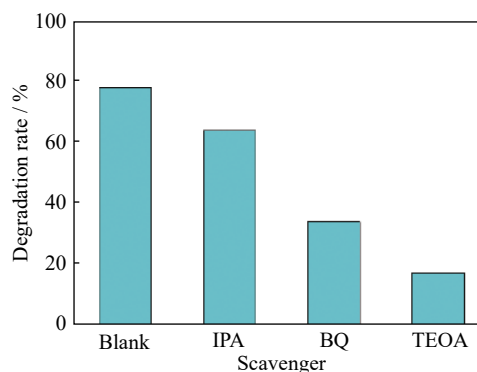
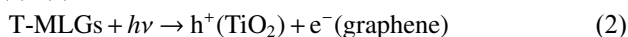


Fig. 7. Photocatalytic degradation rates of CIP for T-MLG-64.3 at presence of different scavengers after 150 min irradiation.

## 4. Conclusion

In summary, we constructed a new pillared structure of T-MLGs via a facile method as follows: dodecanediamine pre-pillaring, ion exchange (Ti<sup>4+</sup> pillaring), and interlayer *in-situ* formation of TiO<sub>2</sub> by hydrothermal method. We proved through various testing means that TiO<sub>2</sub> nanoparticles had intercalated into the interlayer of graphene to form a TiO<sub>2</sub>-pillared structure. T-MLG with 64.3wt% TiO<sub>2</sub> showed the optimum photodegradation rate and adsorption capabilities toward CIP. The photodegradation rate of T-MLG with 64.3wt% TiO<sub>2</sub> was 78% under LED light irradiation for 150 min. Meanwhile, the pseudo-first-order rate constant of T-MLG with 64.3wt% TiO<sub>2</sub> was 3.89 times that of pristine TiO<sub>2</sub>. Such result was mainly attributed to the special structure with enhanced photoinduced electron-hole separation in TiO<sub>2</sub>. Furthermore, the material exhibited high stability and reusability after five consecutive photocatalytic tests. The hole and superoxide radical were determined as the main contributors of CIP degradation. This work provides a facile method to synthesize semiconductor-pillared graphene nanocomposites by replacing TiO<sub>2</sub> nanoparticles with other nanoparticles and a feasible technical for the sustainable utilization of photocatalysts in wastewater control.

## Acknowledgements

This work was financially supported by the Youth Fund of Hebei Province Education Department, China (No. QN2017117) and the Hebei Natural Science Funds for the Joint Research of Iron and Steel, China (Nos. E2019209374 and E2015209278).

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