Research Article

Preparation of Nitrogen-Doped Mesoporous TiO₂/RGO Composites and Its Application to Visible Light-Assisted Photocatalytic Degradation

Xin Wen ¹, Siqin Zhao ^{1,2} and S. Asuha ^{1,2}

¹College of Chemical and Environmental Science, Inner Mongolia Normal University, Hohhot 010022, China

²Inner Mongolia Key Laboratory of Environmental Chemistry, Inner Mongolia Normal University, Hohhot 010022, China

Correspondence should be addressed to Siqin Zhao; zhaosq@imnu.edu.cn

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A series of nitrogen-doped mesoporous TiO₂ nanomaterials and nitrogen-doped mesoporous TiO₂/reduced graphene oxide (RGO) composites were successfully prepared by hydrothermal method using triammonium citrate as the nitrogen source. The effects of nitrogen and graphene oxide (GO) doping on the photocatalytic properties of the TiO₂ were investigated to optimize preparation conditions. The results showed that all prepared samples were mainly composed of the anatase phase and possessed a mesoporous structure. The use of the triammonium citrate not only significantly increased the specific surface area of the synthesized samples but also caused the partial reduction of GO to RGO, leading to further increase of the specific surface area and the improvement of quantum efficiency of the photogenerated electrons. All synthesized samples showed superior photocatalytic performance for methyl orange solution. Among them, the NMT/RGO-1.8-10 was found to be the best; the degradation rate of methyl orange solution on the sample reached 100% in 30 minutes under visible light irradiation.

1. Introduction

As extensively reported in the literature, the TiO₂ is widely used in many areas, such as environmental pollution control, new energy and biopharmaceuticals, due to its low-cost and nonpollutant properties, and strong chemical stability [1, 2]. Particularly, mesoporous TiO₂ not only has a special crystal skeleton and excellent electron transmission properties but also has a high specific surface area, and thus, it shows great application potential in the field of wastewater treatment [3, 4]. However, pure TiO₂ has the disadvantages of a wide band gap and narrow spectral band and easy recombination of photogenerated electrons and positive holes, which limits its practical application. Therefore, the modification of TiO₂ is of great significance [5–7].

Graphene is a new two-dimensional honeycomb carbon material. It is composed of a single layer of carbon atoms. It has a specific surface area up to 2630 m²·g⁻¹ and has very high electron mobility, which can rapidly transfer electrons and is beneficial for accelerating many catalytic reactions. Mean-

while, its periodically arranged two-dimensional planar structure makes it become an ideal catalyst carrier [8, 9]. Modifying TiO₂ with graphene oxide (GO) is found to be a feasible way to improve the photocatalytic performance of TiO₂, as extensively demonstrated by many studies on TiO₂/GO composites [10–12]. However, the structure of GO is largely different from that of original graphene, with the loss of the conjugated structure and superior properties of graphene during the oxidation process. Therefore, it is important to reduce GO to form reduced GO (RGO) in the process of preparing TiO₂/GO composites [13–16]. For this, two expensive organic chemicals hydrazine and hydrazine hydrate are commonly used as reducing reagents. In recent years, some cheap and environmentally friendly reagents, e.g., sodium citrate and citric acid, are used as reducing agents to prepare TiO₂/RGO composites [17, 18].

In this study, a series of nitrogen-doped mesoporous TiO₂ nanomaterials and nitrogen-doped mesoporous TiO₂/RGO composites were prepared by a hydrothermal method using triammonium citrate (TC) as the nitrogen

FIGURE 1: Schematic illustration of photocatalytic enhancement mechanism of N-doped mesoporous TiO_2/RGO composites.

source. Here, the TC not only played a good structure the directing agent role but also acted as a reducing agent, allowing the formation of partially reduced GO, which further increased the specific surface area and photogenerated electron efficiency of the resulting composite. Meanwhile, utilizing triammonium citrate also provides a nitrogen source for the composite and thus can effectively improve the photoresponse range and visible light photocatalytic performance.

Figure 1 is a schematic illustration of photocatalytic enhancement mechanism of N-doped mesoporous TiO_2/RGO composites. It indicated that compared with pure mesoporous TiO_2 , the bandgap of nitrogen-doped mesoporous TiO_2/RGO composites was significantly reduced. It is due to the formation of an independent acceptor energy level of N 2P orbital in the valence band of the O 2p orbital, which reduced the band gap, and the absorption edge produced a certain degree of red shift [19]; it is because GO was partially reduced to RGO during the decomposition of ammonium citrate and the electrical conductivity of graphene was restored. The photogenerated e^- produced by the photocatalytic system of mesoporous TiO_2 was accepted to reduce the recombination rate of the photogenerated electron hole pairs.

2. Materials and Methods

2.1. Materials. Natural graphite scales (599 mesh) were purchased from Jinhua Biotechnology Co. Ltd., Inner Mongolia, China. Potassium permanganate (AR) was purchased from Yonghui Chemical Co. Ltd., Tianjin, China. Titanium sulfate (AR) and hydrogen peroxide (AR) were purchased from Beilian Fine Chemicals Development Co. Ltd., Tianjin, China. Polyethylene glycol (AR) was purchased from Guangfu Fine Chemical Research Institute, Tianjin, China. TC (AR) was purchased from Damao Chemical Reagent Factory, Tianjin, China. Anhydrous ethanol (AR) was purchased from Chemical Factory, Beijing, China. Concentrated hydrochloric acid (AR), methyl orange (AR), and concentrated sulfuric acid (AR) were purchased from Yongsheng Fine

Chemical Co. Ltd., Tianjin, China. They were used without further purification.

2.2. Preparation of GO. GO was prepared via a modified Hummers method reported by Hummers and Offeman [20].

2.3. Preparation of Nitrogen-Doped Mesoporous TiO_2 Nanomaterials. 0.028 g of polyethylene glycol was dissolved in 10 mL of distilled water, and then 1.2 g of titanium sulfate was added into the solution, followed by stirring for 20 min. After that, 0.24 g of TC was added and stirred for 10 min and the solution was hydrothermally reacted at 110°C for 24 h. The obtained solid was washed with absolute ethanol and distilled water and dried at 50°C for 6 h. In order to investigate the effect of TC on the properties of the nitrogen-doped TiO_2 photocatalyst, a series of samples were prepared using different dosages of TC. Thus, prepared N-doped mesoporous TiO_2 (NMT) are hereafter referred to as NMT-MR, where MR is the mass ratio of TC to TiO_2 . The following five samples were prepared in the same way mentioned above: NMT-0, NMT-0.6, NMT-1.2, NMT-1.8, and NMT-2.4.

2.4. Preparation of Nitrogen-Doped Mesoporous TiO_2/RGO Composites. A series of nitrogen-doped mesoporous TiO_2/RGO composites were prepared by adding different amounts of GO under the optimum amount ($\text{TC}/\text{TiO}_2 = 1.8$) of TC. The specific preparation method is similar to that mentioned in Section 2.3. The prepared sample was labeled as NMT/RGO-MR-m, where m is the mass (mg) of GO.

2.5. Structural and Morphological Characterization. The prepared samples were characterized by XRD (X-ray powder diffraction) (Ultima IV, Rigaku Corporation, Japan), N_2 adsorption/desorption analysis (iQ, Quantachrome Corporation, America), TEM (transmission electron microscopy) (Tecnai G2F20, FEI Electron Microscopy Corporation, America), XPS (X-ray photoelectron spectroscopy) (Axis Ultra, Shimadzu Corporation, Japan), Raman (LabRAM HR Evolution, Horichang Group Co. Ltd., Longremo city,

FIGURE 2: XRD patterns of (a) NMT-MR and (b) NMT/RGO-MR-m composites.

France), FTIR (Fourier transform infrared spectroscopy, Nicolet 6700, Nicolet Corporation, America), PL (photoluminescence) (F4500, Hitachi Limited, Japan), and UV-vis spectroscopy (UV-Vis 2550) (Shimadzu Corporation, Japan).

2.6. Measurement of Photocatalytic Performance. To prepare the solution for photocatalysis characterization, 0.25 g of the catalyst was dispersed in 250 mL (20 mg/L) of methyl orange (MO) solution. Then the resultant mixture was stirred in darkness for 30 min for adsorption-desorption equilibrium at constant temperature, followed by the irradiation with a 300W BELSRI/UV-type high-voltage xenon lamp in a XPA-type photochemical reactor. Samples were withdrawn at 10 min intervals, and the supernatant was separated by centrifugation at 10000 rpm for 20 min. The concentration of the MO in the supernatant was measured by a 722G visible spectrophotometer at 464 nm. To elucidate which active species play a key role in photodegradation of MO under visible light irradiation, control experiments were also carried out by adding different radical scavengers with the same concentration of 3 mmol/L.

3. Results and Discussion

3.1. Morphology and Characterization of Composites. Figure 2(a) shows the XRD patterns of nitrogen-doped mesoporous TiO_2 nanomaterials (NMT-MR). As seen in the figure, all samples exhibited similar XRD patterns. The diffraction peaks, which appeared at $2\theta = 25.6^\circ$, 37.9° , 47.8° , 54.2° , 55.3° , and 63.1° , correspond to (101), (004), (200), (105), (211), and (204) crystal faces of anatase-phase TiO_2 (JCPDS no. 21-1272) [21], indicating that the prepared nitrogen-doped mesoporous TiO_2 nanomaterials all are composed of the anatase phase. The average grain sizes of NMT-0, NMT-0.6, NMT-1.2, NMT-1.8, and NMT-2.4,

which are calculated using the Scherrer's equation, were 9.1, 8.1, 7.9, 4.4, and 5.1 nm, respectively, showing that the TC could effectively inhibit the TiO_2 crystal growth. When the amount of TC increased continuously, the grain size of nitrogen-doped mesoporous TiO_2 nanomaterials decreased first and then increased. The reason of which is that triammonium citrate is a chelating agent, and thus, it can form a network structure with Ti^{4+} during the reaction. As a result, the rapid nucleation of TiO_2 was effectively inhibited. But the addition of triammonium citrate increased the viscosity of the solution, and the colloidal particles are difficult to move. Thus, large particles were agglomerated to form [22]. In addition, the incorporation of nitrogen atoms into the crystal lattice TiO_2 also can inhibit the growth of the grain size of TiO_2 [23].

Figure 2(b) shows the XRD patterns of nitrogen-doped mesoporous TiO_2/RGO composites (NMT/RGO-MR-m). Similar to NMT-MR samples, only the characteristic diffraction peaks of anatase-phase TiO_2 appeared in all XRD patterns. No characteristic diffraction pattern of GO has been detected, maybe due to the reduction of GO to RGO by TC during hydrothermal reaction [24]. The average grain sizes of NMT-1.8, NMT/RGO-1.8-4, NMT/RGO-1.8-10, NMT/RGO-1.8-20, and NMT/RGO-1.8-40 were 4.4, 4.0, 3.7, 4.0, and 4.3 nm, respectively, indicating that the increase of the grain size of TiO_2 further is inhibited by GO doping.

Figures 3(a) and 3(b) are the N_2 adsorption-desorption isotherm curves and pore size distribution curves of different samples, respectively. The isotherm of NMT-0 was typical of a nonporous solid. In contrast, the isotherms of NMT-1.8 and NMT/RGO-1.8-10 belonged to Langmuir type IV, in which the hysteresis loops of NMT-1.8 belonged to the H1 type, while those of NMT/RGO-1.8-10 were close to the H2 type, indicating that both samples possess mesoporous structures. The use of TC for N-doping made the TiO_2 form a

FIGURE 3: N₂ adsorption-desorption isotherms (a) and pore size distribution plot (b) of NMT-0, NMT-1.8, and NMT/RGO-1.8-10.

remarkable pore structure, and the RGO-doping made the pore structure of the system more regular and orderly. In Figure 3(b), the most probable apertures of NMT-0, NMT-1.8, and NMT/RGO-1.8-10 were estimated to be 17.3, 21.6, and 19.3 nm, respectively. As shown in Table 1, the mean pore size and total pore volume of the composites tended to decrease. This is because RGO still retains many oxygen-containing functional groups and renders the layers tightly packed. When it was combined with TiO₂, the addition of RGO will hinder the formation of the mesoporous structure of TiO₂ to a certain extent. Thus, its mean pore size and total pore volume were reduced but its specific surface area obviously increased. It is mainly due to the addition of triammonium citrate, which had its own steric stabilization effect and effectively inhibited the growth and agglomeration of TiO₂ particles. The particles are uniformly dispersed. RGO as a carrier composited with TiO₂, which can increase the specific surface area of the composite material, while more surface active sites were provided and the adsorption capacity of the reactants was enhanced. Thereby, the photocatalytic performance of the composite material was positively affected.

Figure 4 shows the TEM images of NMT-1.8 and NMT/RGO-1.8-10. The NMT-1.8 nanophase material (Figure 4(a)) was composed of spherical particles with a particle size of about 5 nm, and the pore structure formed between the particles can be clearly observed. This result indicated that the addition of triammonium citrate can effectively inhibit the growth of mesoporous TiO₂ particles and makes them evenly dispersed. It can be seen from Figures 4(b) and 4(c) that TiO₂ is uniformly attached to the layer structure of RGO. The particle size was about 4 nm,

TABLE 1: The grain size, most probable aperture, specific surface area, mean pore size, and total pore volume of NMT-0, NMT-1.8, and NMT/RGO-1.8-10.

Samples	NMT-0	NMT-1.8	NMT/RGO-1.8-10
Grain size (nm)	9.2	4.4	4.0
Most probable aperture (nm)	17.3	21.6	19.3
Specific surface area (m ² ·g ⁻¹)	154	325	412
Mean pore size (nm)	13.5	8.9	5.6
Total pore volume (cm ³ ·g ⁻¹)	8.6	11.9	8.5

which is basically the same as the results of XRD, indicating that RGO doping can effectively inhibit the agglomeration and growth of TiO₂ particles.

Figure 5 showed the X-ray photoelectron spectra of sample NMT-1.8. As seen in Figure 5(a), mainly Ti, O, C, N, and S were contained in the NMT-1.8 nanomaterial. The elemental S is mainly derived from the titanium sulfate. The peak which appeared at 284.8 eV (Figure 5(b)) was the characteristic peak of elemental C, which mainly came from the contaminated carbon source of the instrument itself during the test. The peaks at 286.41 eV and 288.70 eV were the characteristic peaks of the C-O bond and the C=O bond, respectively, which were caused by the scattering of C atoms into the lattice gap of TiO₂ to form Ti-C-O bonds during the hydrothermal process. But at 282.1 eV, it belonged to C instead of O atoms in lattice of TiO₂. But the peak at

FIGURE 4: TEM images of NMT-1.8 nanophase material (a) and NMT/RGO-1.8-10 composite with different magnification of 200 nm (b) and 20 nm (c).

FIGURE 5: (a) The survey XPS spectra of NMT-1.8. (b) High-resolution C 1s core level XPS spectra of NMT-1.8. (c) High-resolution N 1s core level XPS spectra of NMT-1.8. (d) High-resolution S 2p core level XPS spectra of NMT-1.8.

282.1 eV, assigned to C in C-Ti-O, did not appear, indicating that most of the C atoms were adsorbed on the surface of TiO₂ and only a very few number of C atoms were incorporated into the lattice of TiO₂ [25, 26]. The characteristic peak of N 1s appeared at 398–403 eV (Figure 5(c)), with a strongest peak which appeared at 399.8 eV, indicating that the element of N exists in the lattice of TiO₂ in the form of interstitial atoms. That is to say, N has been successfully incorporated into TiO₂ lattice, forming the Ti-O-N bond [27]. The peak which appeared at 170.7 eV (Figure 5(d)) corresponds to the electron-binding energy of S 2p, indicating that the S exists in the form of +6 valence on the surface of TiO₂. The presence of S generates some defects in TiO₂ and increases the surface acidity of TiO₂ [28]. The incorporation of such nonmetal elements (N, S, and C) was beneficial to improve the visible light photocatalytic performance of the system.

Figure 6(a) shows the Raman spectra of the GO, MT/GO-0-10, and NMT/RGO-1.8-10 composites. As seen in Figure 6(a), these samples showed two vibration peaks at 1340 cm⁻¹ and 1603 cm⁻¹, corresponding to the D band and the G band, respectively, and they were used to characterize the degree of sp hybrid carbon atoms and sp hybridization defects in the samples, respectively. In the MT/GO-0-10 and NMT/RGO-1.8-10 composites, two vibrational peaks appeared at 508 and 633 cm⁻¹ representing the A_{1g} and E_g modes, respectively. Both peaks are attributable to the characteristic absorption peak of anatase TiO₂, further confirming the formation of mesoporous TiO₂/GO composites [29]. In three samples, the characteristic absorption peak of TiO₂ in NMT/RGO-1.8-10 composites was relatively weak. This is because the addition of TC causes the reduction of the grain size of the NMT/RGO composite material and thus lowers the degree of crystallization. By calculation, ID/IG (intensity ratio of D band and G band) in the NMT/RGO-1.8-10 composite was 1.13. This value is larger than those of GO and MT/GO-0-10 (1.01 and 1.02, respectively). This is because the TC promoted the generation of sp carbon atoms during the hydrothermal reduction process and thus increases the ID/IG value in the TiO₂/RGO composite. The result can be attributed to the strong interaction between TiO₂ nanoparticles and RGO nanosheets, which marked more defects such as vacancies and boundaries formed in TiO₂/RGO composites.

Figure 6(b) shows the FT-IR spectra of MT/GO-0-10 and NMT/RGO-1.8-10 composites. After the CT reduction treatment, the stretching vibration peak of C=O at 1730 cm⁻¹ was significantly weakened, indicating that TC can completely reduce GO. And the deformation vibration peak of C-O at 1040 cm⁻¹ was also relatively weakened, indicating the decrease of oxygen content in RGO [30].

The PL spectra of NMT-0, MT/GO-0-10 and NMT/RGO-1.8-10 are shown in Figure 6(c). All samples exhibited a molecular fluorescence spectrum curve in the range of 360–700 nm, with a similar shape and different intensity. The fluorescence intensity of NMT/RGO-1.8-10 was the weakest. It is generally believed that the recombination of charge carriers has an effect on the emission of photoluminescence. The intensity of the molecular fluores-

cence spectrum was stronger and the photogenerated e⁻ and h⁺ were easily combined [31]. Therefore, among the three samples, the recombination rate of light-emitting e⁻ and h⁺ for NMT/RGO-1.8-10 was the lowest, probably due to the reduction of GO by TC.

Figures 6(d) and 6(e) show the UV-Vis spectra of NMT-MR and NMT/RGO-MR-m composites. As seen in Figure 6(d), the NMT-0 nanomaterial only absorbs the light in the ultraviolet region. On the other hand, the absorption edge of nitrogen-doped mesoporous TiO₂ nanomaterials underwent a certain degree of red shift; particularly, the red-shifting degree of the NMT-1.8 nanomaterial was the most obvious. Meanwhile, the absorption intensity in the ultraviolet region was obviously increased. Compared to NMT-0, the absorption edge of nitrogen-doped mesoporous TiO₂/RGO composites also showed a certain degree of red shift (Figure 6(e)) and their absorption intensity obviously increased in the ultraviolet and visible regions. According to the formula of $E_g = 1240/\lambda_g$, the band gaps of NMT-0, NMT-1.8, and NMT/RGO-1.8-10 were calculated to be 3.14, 3.04, and 2.57 eV, respectively. Among these, the band gap of NMT/RGO-1.8-10 was the narrowest and it also had a certain absorption in the visible region, which is probably due to the incorporation of N into the TiO₂ lattice [32]. The photoelectron effect of RGO was very large, so the composite of RGO further broadened the photoresponse range of mesoporous TiO₂. However, with the increase of the amount of RGO, the absorption intensity of the composites showed a tendency of being strengthened first and then weakened in the visible light region. The broadening of the photoresponse range of the composites was beneficial to the improvement of the visible light photocatalytic performance of the composites.

3.2. Photocatalytic Study. In the process of photocatalytic testing, samples were stirred in a dark room for 30 min to achieve adsorption equilibrium and then irradiated by visible light. Figure 7(a) shows the photocatalytic degradation curves of MO on nitrogen-doped mesoporous TiO₂ nanomaterials under visible light irradiation. As shown in the figure, the nitrogen-doped mesoporous TiO₂ nanomaterials exhibited better photocatalytic degradation efficiency than pure mesoporous TiO₂. For sample NMT-1.8, in the former 20 min, the degradation rate of methyl orange was about 80% and it reached 100% within 1 hour. The photocatalytic degradation curves of methyl orange on nitrogen-doped mesoporous TiO₂/RGO composites are shown in Figure 7(b). After combination with RGO, the adsorption performance of nitrogen-doped mesoporous TiO₂ was significantly improved and the adsorption rate of MO solution reached about 40% under the condition of stirring 30 min in a dark room. For sample NMT/RGO-1.8-10, the degradation efficiency of MO by adsorption-photocatalytic double effect reached about 95% within 20 min. The high adsorption performance of this sample may be due to its large specific surface area (412 m²/g). According to the previously reported photocatalytic mechanism of TiO₂, the organic pollutants are firstly physically adsorbed on the TiO₂ surface and then they are photocatalytically

FIGURE 6: The spectra of different samples: (a) Raman spectra, (b) FT-IR spectra, (c) PL spectra, and (d, e) UV-vis patterns.

FIGURE 7: The photocatalytic degradation curves of MO by N-doped mesoporous TiO₂ (a) and N-doped mesoporous TiO₂/RGO composites (b) under visible light irradiation.

decomposed. Therefore, the improvement of the adsorption property of the composite system was beneficial to the enhancement of the photocatalytic performance of the system. On the other hand, the use of TC as the source of N and the further doping of RGO can broaden the photoresponse range of the TiO₂ and increase its photogenerated electrons. However, when the dosage of RGO was larger than 10 mg, the degradation efficiency of MO decreased with the increase of RGO, maybe due to the formation of new recombination centers of e^- and h^+ . Therefore, the composite of RGO had an optimum recombination ratio. Thus, the visible photocatalytic activity of NMT/RGO-1.8-10 was the strongest.

The quasi-second-order dynamic model equation can be expressed as follows:

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2. \quad (1)$$

After the integral, the linear form is expressed as follows:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2}, \quad (2)$$

where k_2 is the rate constant of the quasi-secondary model; q_t is the degradation amount of MO at time t ; q_e is the equilibrium degradation amount of MO. The MO degradation data on sample NMT/RGO-1.8-10 was analyzed using the above equation, and the result is shown in Figure 8 and Table 2, which reveals that the photocatalytic degradation of MO on NMT/RGO-1.8-10 follows the quasi-secondary kinetic model.

In order to further study the photocatalytic stability and reusability of the composites, the following study was carried

FIGURE 8: Quasi-second-order dynamic plot for MO degradation on NMT/RGO-1.8-10.

out on sample NMT/RGO-1.8-10. The photocatalytic activity of the sample against MO solution under visible light irradiation for a long time (3 h) was tested, and the experiment was repeated three times at the same condition. It can be seen in Figure 9(a) that the degradation of the MO solution by sample NMT/RGO-1.8-10 was still effective under visible light irradiation within 3 hours. The degradation efficiency of MO by NMT/RGO-1.8-10 reached about 95% within 20 min. In addition, no obvious changes were found for the XRD patterns of the samples before and after photocatalytic reactions (Figure 9(b)), indicating that NMT/RGO-1.8-10 maintains its structural integrity and good stability. The changes in UV-visible absorption spectra of MO solution during the visible light irradiation was shown in Figure 9(c). As shown in the figure, the maximum absorption band of the MO solution had changed from 465 to 485 nm

TABLE 2: Result of data fitting for the quasi-second-order dynamic model.

Sample	Quasi-second-order kinetic equation	Linearly dependent coefficient	Rate constant k_2 ($\text{g} \cdot (\text{mg} \cdot \text{min})^{-1}$)
NMT/RGO-1.8-10	$y = 0.0521x + 0.056$	0.9997	0.914

FIGURE 9: The photocatalytic degradation curve of MO on NMT/RGO-1.8-10 under long time irradiation (a), the XRD patterns of the NMT/RGO-1.8-10 before and after the photocatalytic reactions (b), and UV-visible absorption spectra of the MO solution during the visible light irradiation in the presence of NMT/RGO-1.8-10 (c).

when NMT/RGO-1.8-10 was added to the solution, which is due to the weak interaction between the acidic groups on the surface of the sample and the MO molecule [33]. It is also noted that the intensity of the absorption peak of MO decreased slightly when the visible light irradiation time is equal to zero, which is mainly due to partial adsorption of MO on the NMT/RGO-1.8-10 nanocomposite. After visible light irradiation, the intensity of absorption peak of MO decreased obviously as a function of irradiation time. The color fading can be easily observed by the naked eyes

in the photocatalytic process, and after 30 min irradiation, the MO aqueous solution became a colorless solution as well as the degradation efficiency reached 100%, indicating that NMT/RGO-1.8-10 can degrade MO effectively under visible light.

Figure 10(a) is the differential thermal analysis curve of NMT/RGO-1.8-10. There are three obvious exothermic peaks and two endothermic peaks in the differential thermal analysis curve. The exothermic peak appearing at 64°C is due to the removal of adsorbed water on the surface of the

FIGURE 10: The differential thermal analysis curve (a) and thermogravimetric curve (b) of NMT/RGO-1.8-10.

composite. Exothermic peak at 200°C may be attributed to the decomposition of triammonium citrate partially present on the surface of the composite. The strong endothermic peak at 300°C is mainly due to heat absorption caused by the fracture of the C skeleton structure of graphene itself. The exothermic peak which appeared at 400–650°C is mainly due to the reaction of some carbon in the reduced graphene oxide with the oxygen in the air [34]. The endothermic peak appearing at 750°C is attributable to the phase transformation of TiO₂ from anatase to the rutile phase [35].

Figure 10(b) shows the thermogravimetric curve of NMT/RGO-1.8-10. As shown in the figure, the total mass loss rate of the sample is about 40.0%. The mass loss process of NMT/RGO-1.8-10 can be roughly divided into three stages. The first stage occurs in the temperature range from 10 to 200°C, with a mass loss of 10% due to evaporation of adsorbed water on the surface of the sample. The second stage is observed in the range from 200 to 500°C, accompanied by 22% mass loss, which is caused by the thermal decomposition of the reduced graphene oxide in the sample. At this stage, the structure of the composite system begins to be damaged. The third mass loss stage occurs in the range of 510 to 750°C with a 7.1% mass loss, which was caused by the thermal decomposition of TiO₂ in the sample. The result reveals that sample NMT/RGO-1.8-10 has a good thermal stability in the temperature range from room temperature to 300°C.

In order to clarify the photodegradation mechanism of NMT/RGO-1.8-10 for MO under visible light, the effect of several scavengers was investigated. In general, the photodegradation reaction of dyes on the TiO₂-based catalyst not only produces the e^-/h^+ pair but also generates different reactive species such as $\bullet OH$ and $\bullet O_2^-$. In the present study, we used p-benzoquinone for the $\bullet O_2^-$ scavenger [36], silver nitrate [37] for the electron scavenger, EDTA for the hole scavenger [36], and DMSO for the $\bullet OH$ scavenger [38]. If the photodegradation of MO is caused by any of the above-mentioned reactive species, the reaction will be slowed or inhibited when their corresponding scavenger is added to

FIGURE 11: Effect of different radical scavengers (3 mmol/L) on the photodegradation of MO by NMT/RGO-1.8-10.

the MO solution [39]. Figure 11 shows the degradation efficiency of MO as a function of irradiation time. As shown in the figure, the addition of DMSO and EDTA had no significant effect on the photodegradation of MO. Therefore, OH radicals and holes were not the main active substances for photodegradation of MO. However, the degradation efficiency of MO over sample NMT/RGO-1.8-10 dramatically decreased with the addition of p-benzoquinone, indicating that $\bullet O_2^-$ is the main active species for photocatalytic degradation of MO. At the same time, the addition of silver nitrate also significantly reduced the degradation rate of MO, indicating that the electrons play a complementary role. As a result, the photocatalytically generated $\bullet O_2^-$ and electrons are found to be the main active substance and complementary active substances, respectively, in the photocatalytic degradation of MO.

4. Conclusion

A series of nitrogen-doped mesoporous TiO₂ nanomaterials and nitrogen-doped mesoporous TiO₂/RGO composites were prepared by hydrothermal method. For this, TC was used as a nitrogen source and reducing agent, which enabled the prepared samples to have good dispersibility, increased specific surface area, and mesoporous structure. The RGO-doping can further increase the specific surface area of nitrogen-doped mesoporous TiO₂ and effectively reduce the recombination rate of the photogenerated electron hole pairs, leading to the marked enhancement of visible photocatalytic performance. Among all the prepared samples, NMT/RGO-1.8-10 exhibited the best performance, with a grain size of 3.7 nm, most probable aperture of 19.3 nm, and a surface area of 412 m²·g⁻¹. It exhibited a strong adsorption-photocatalytic double effect. And the degradation rate of MO on the sample can reach 100% within 30 min under visible light irradiation.

Data Availability

The data (XRD, BJH, TEM, XPS (C 1s, N 1s, and S 2p), Raman, FT-IR, PL, UV-vis, and photocatalytic degradation curve relative to composites) used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

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