

铌酸锰-还原氧化石墨烯复合光催化剂的构建以及 可见光下降解亚甲基蓝

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摘要: 通过水热法和光还原方法成功地制备了铌酸锰-还原氧化石墨烯复合光催化剂。这种复合光催化剂可以明显地提高光催化降解亚甲基蓝的光催化活性, 降解效率在 60 min 内达到了 78.2%, 是单体铌酸锰降解效率的 2 倍。通过活性物质捕获实验的研究, 增强的光催化性能可以归因于还原氧化石墨烯加速了光生电子-空穴的分离效率, 进而解决了低光催化活性的问题。

关键词: 铌酸锰-还原氧化石墨烯; 光催化剂; 亚甲基蓝; 可见光

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Fabrication of RGO-MnNb₂O₆ Photocatalyst with Enhanced Visible Light Efficiency in Photocatalytic Degradation of Methylene Blue

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Abstract: RGO-MnNb₂O₆ photocatalysts were successfully prepared through the hydrothermal and photo-reduction processes. Compared with single MnNb₂O₆, the RGO-MnNb₂O₆ composites could significantly enhance photocatalytic activity for the degradation of methylene blue under visible light irradiation. Within 60 min, 78.2% of the methylene blue was removed by the optimum sample (3% RGO-MnNb₂O₆), which was about 2 times higher than that of the individual MnNb₂O₆. By further study based on the active species trapping experiments, the enhanced photocatalytic property could be ascribed to the crucial role of RGO, which widely accelerated the separation of photogenerated electron-hole pairs. In general, the RGO hybridized with MnNb₂O₆ could address the problem of low photocatalytic activity.

Keywords: RGO-MnNb₂O₆; photocatalyst; methylene blue; visible light

0 Introduction

Swage release from industries generated a fearful puzzle for environmental pollution. The discharge of waste water was often detected including organic dyes, which were usually hazardous to the human health^[1-5].

Therefore, the elimination of organic pollutes from aqueous environments has become a forcible environmental problem. However, the traditional treatments were often constrained by the low efficiency and high cost^[6-7]. Recently, the photocatalytic oxidation has been established to be a promising technique for

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environmental remediation and provided an efficiency tool for the degradation of organic dyes^[8-13]. Up to now, a lot of researchers were focused on the conventional UV-driven titanium dioxide (TiO₂) for the dyes degradation. However, the wide band gap (3.2 eV for anatase) conspicuously confined its photocatalytic applications under visible light illumination^[14-15]. Hereby, it is necessary to develop the high efficiency visible-light-driven photocatalysts^[16-22].

On the one hand, niobate semiconductors have been widely investigated in photocatalysis due to their chemical and electrochemical stability. MnNb₂O₆, as a novel transition metal niobate photocatalyst, has attracted much attention in photocatalytic applications due to its narrow band energy of 2.2 eV. Hu et al. reported that the 3D flower-like nanostructures MnNb₂O₆ exhibited the photocatalytic performance for photodegradation of methylene blue (MB) under visible light irradiation^[23]. However, surface properties of MnNb₂O₆ such as fast charge recombination at surfaces and weak surface adsorption ability have greatly limited the further improvement of its photocatalytic activity.

On the other hand, reduced graphene oxide (RGO) has been proved to be an excellent media for electron transfer because of its excellent electrical conductivity, high specific surface areas and excellent electronic mobility. A large number of RGO based photocatalysts have been successfully constructed for enhancing photocatalytic performances^[26-27]. For example, Amal and colleagues prepared BiVO₄-RGO composite using a facile single-step photocatalytic reaction. Remarkable 10-fold enhancement in photoelectron chemical water splitting reaction was observed on BiVO₄-RGO composite compared with pure BiVO₄ under visible illuminations^[28]. Shi and his group had investigated the BiPO₄-RGO samples and showed that after introducing the RGO, the photocatalytic activity have been improved by enhancing the separation of charge carrier^[29]. Hence, we envision that the RGO can be regarded as an ideal electron mediate and supporter for MnNb₂O₆ photocatalyst, which will simultaneously facilitate the charge migration and

prolong the charge lifetimes by suppressing the recombination of photogenerated electrons and holes.

Herein, we prepared the simple yet efficient visible-light-driven RGO-MnNb₂O₆ photocatalysts by the simple hydrothermal and photo-reduction methods. MB was chosen as target pollutants to explore the photocatalytic performance. Furthermore, tentative mechanism of the enhanced photocatalytic activities was also discussed based on the active species trapping experiments.

1 Experimental

1.1 Syntheses of GO and MnNb₂O₆

GO was synthesized via the oxidation of graphite using the improved Hummers' method^[30]. The synthesis process of MnNb₂O₆ was as follows: firstly, 0.5 g Nb₂O₅ and 3.37 g KOH were added into 60 mL of distilled water and then transferred into a 100 mL Teflon-lined stainless steel autoclave at 180 °C for 3 days. After cooling naturally, the clear solution of [Nb₆O₁₉]⁸⁻ was obtained. Then, the above solution (4 mL) was diluted with 10 mL distilled water. The pH of obtained aqueous solution was adjusted to 7.8 by the addition of HCL solution. After that, 0.035 g MnCl₂·4H₂O and 1 g K₂SO₄ were dissolved in above solution with continuous stirring for 30 min. Finally, the obtained precursor was transferred into a 50 mL Teflon-lined stainless autoclave at 260 °C for 24 h. The products were filtered, washed with distilled water, and dried in a vacuum at 60 °C for 12 h.

1.2 Synthesis of RGO-MnNb₂O₆

RGO-MnNb₂O₆ samples were synthesized through the method of surface assembling. Typically, a certain amount of GO (1, 3 and 5 mg) was dissolved in 100 mL water to form a transparent solution. Then 100 mg MnNb₂O₆ in certain ratio were added into the above GO solution under vigorous stirring for 30 min. The obtained suspension was exposed to the full-range irradiation of a 300 W xenon lamp for 3 h to reduce the GO into RGO. The final product collected by centrifugation, dried at 60 °C in air, which referred to as 1% RGO-MnNb₂O₆, 3% RGO-MnNb₂O₆, and 5% RGO-MnNb₂O₆.

1.3 Characterization

X-ray diffraction (XRD) patterns measurement was undertaken using a D/MAX-2500 diffract meter (Rigaku, Japan) with a nickel-filtered Cu $K\alpha$ radiation source ($\lambda=0.154\ 056\ \text{nm}$, $U=50\ \text{kV}$, $I=300\ \text{mA}$, $2\theta=5^\circ\sim 80^\circ$). The X-ray photoelectron spectroscopy (XPS) was obtained by a Thermo ESCALAB 250X (America) electron spectrometer using $150\ \text{W}$ Al $K\alpha$ X-ray sources. The scanning electron microscopy (SEM) was obtained by the Hitachi S-4800 eld emission SEM (FESEM, Hitachi, Japan) to observe the morphology of the as-prepared samples. Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were gathered on an F20 S-TWIN electron microscope (Tecnai G2, FEI Co.), equipping with a $200\ \text{kV}$ accelerating voltage. The photoluminescence (PL) spectra for solid samples were obtained on a F4500 (Hitachi, Japan) photoluminescence detector. UV-Vis absorption spectra were (DRS) were collected using a Shimadzu UV-Vis 2550 spectrophotometer. Reflectance measurements were performed on powdered samples, using a standard BaSO_4 as a reference.

1.4 Photocatalytic analysis

The photocatalytic activity of as-prepared samples was evaluated by the degradation of MB. A $250\ \text{W}$ xenon lamp with a cut-off filter was used to remove the wavelength less than $420\ \text{nm}$. In details, $50\ \text{mg}$ of the sample powers were dispersed into the $100\ \text{mL}$ solution of MB ($10\ \text{mg}\cdot\text{L}^{-1}$), in order to insured the adsorption equilibrium, the suspensions were kept stirring for $30\ \text{min}$ in darkness before irradiation. At the same irradiation intervals, $6\ \text{mL}$ aqueous solution were sampled and separated from the suspended catalyst particles for analysis. The photocatalytic degradation ratio was tested via the intensity changes of the absorption peak at $664\ \text{nm}$ to determine the concentration of MB at different times by the same UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan).

2 Results and discussion

2.1 Morphology and structure

The morphology of as-prepared samples was

detected by SEM. The MnNb_2O_6 exhibited a uniform hexagonal nanoflower structure with excellent dispersion in Fig.1a. From the SEM image of $\text{RGO-MnNb}_2\text{O}_6$ in Fig.1b, the RGO layer could be observed in certain positions because of the tight contact between MnNb_2O_6 and RGO. Fig.1c showed the TEM of single hexagonal nanoflower MnNb_2O_6 . The TEM of single RGO was shown in Fig.1d, the obvious wrinkles and folds exhibited clearly the 2D structure of the transparent graphene sheets. In $\text{RGO-MnNb}_2\text{O}_6$ composites (Fig.1e), RGO sheets were uniformly attached on MnNb_2O_6 surfaces. The HRTEM image of composites in Fig.1f was further to characterize the structure of $\text{RGO-MnNb}_2\text{O}_6$, the distinct lattice fringes with spacing of $0.167\ \text{nm}$ corresponded well to the (311) facet of MnNb_2O_6 .

The crystalline phases of the composites were investigated via XRD. As shown in Fig.2, the pristine MnNb_2O_6 showed a series of sharp diffraction peaks, which can be indexed into columbite phase (JCPDS

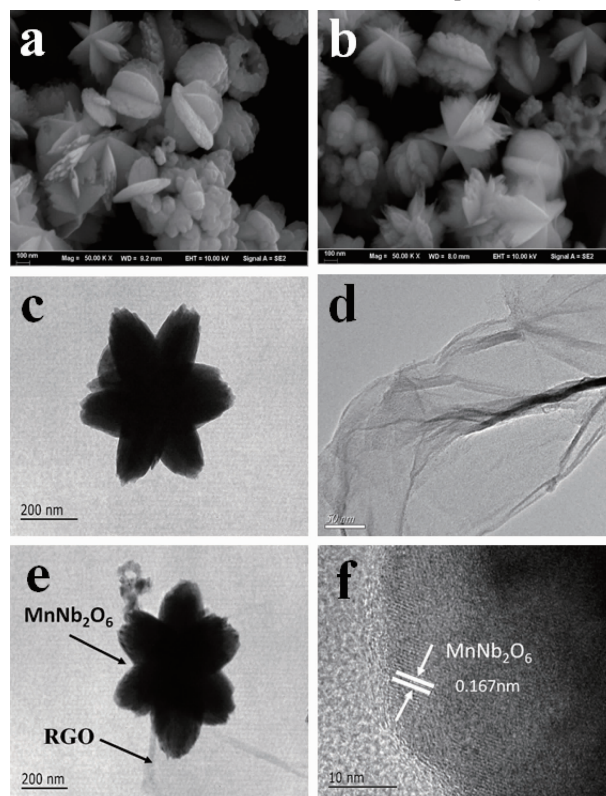


Fig.1 SEM images of MnNb_2O_6 (a) and $\text{RGO-MnNb}_2\text{O}_6$ (b); TEM images MnNb_2O_6 (c), GO (d) and 3% $\text{RGO-MnNb}_2\text{O}_6$ (e); HRTEM image of 3% $\text{RGO-MnNb}_2\text{O}_6$ (f)

72-0484) with no observable impurities. For the RGO-MnNb₂O₆ composites, with increasing the amount of RGO, no obvious changes were found in these patterns, which suggested that the introduction of RGO had no obvious influence on the MnNb₂O₆ crystalline structure. Notably, no diffraction peaks of RGO could be observed in the RGO-MnNb₂O₆ composites, which may be due to the low amount of RGO. On the other hand, the main characteristic peak of RGO at 24.5° may be overlapped with the strong peak of MnNb₂O₆ at 24.1°.

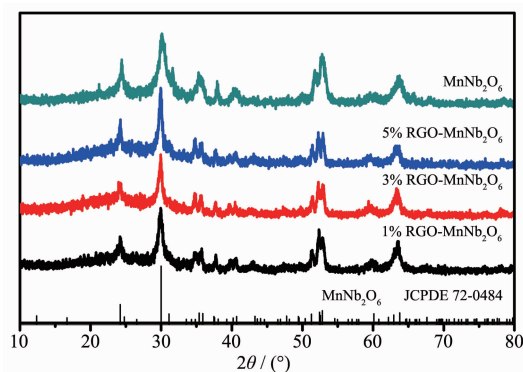


Fig.2 XRD patterns of as-prepared samples

2.2 UV-Vis absorption spectra

The light absorption spectra of MnNb₂O₆ and 3% RGO-MnNb₂O₆ samples were investigated by the UV-Vis absorption. As shown in Fig.3, bare MnNb₂O₆ showed strong absorption in the visible light range with the obvious absorption edge around 560 nm, it could be found that MnNb₂O₆ was a narrow band gap semiconductor with the band gap was about 2.2 eV. When the 3% RGO were decorated with the MnNb₂O₆, the light absorption spectrum had a strong absorption

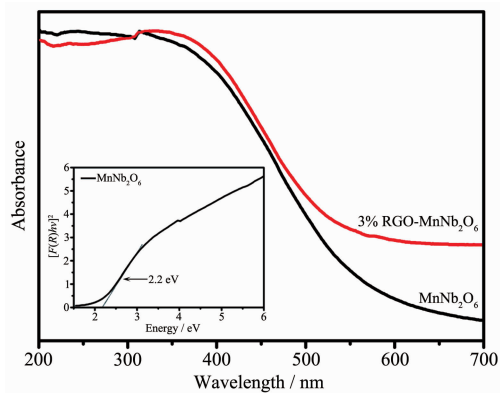


Fig.3 UV-Vis adsorption spectra with as-prepared samples and calculated band gap

over 560 nm, which illustrated that the RGO can strengthen the visible-light spectral responsive range. Similar phenomena were also observed by other researchers, which can be ascribed to the absorption of RGO^[31].

The Raman absorption spectra of pure MnNb₂O₆, GO and RGO-MnNb₂O₆ were exhibited in Fig.4. The recorded spectrum of GO exhibited two characteristic peaks located at 1 352 and 1 585 cm⁻¹, corresponding to the D and G band, respectively^[27]. In general, it was accepted that the ratio of the D to G band intensity (I_D/I_G) was related to the density of defects in graphene-based materials and the graphitization degree of carbonaceous materials. The peak intensity I_D/I_G were 0.99 of GO to 1.12 of RGO-MnNb₂O₆, the enhanced peak intensity ratios could be contributed to more defects introduced into the RGO-MnNb₂O₆, demonstrating the GO was reduced to RGO.

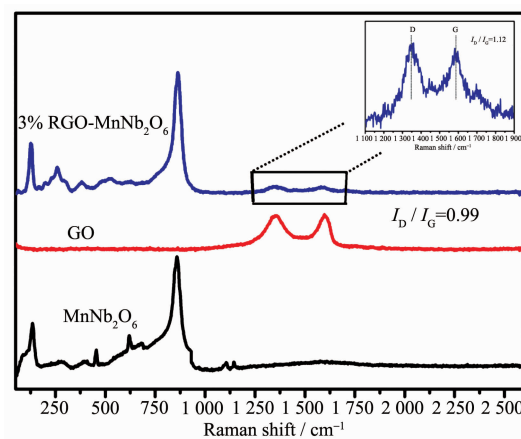
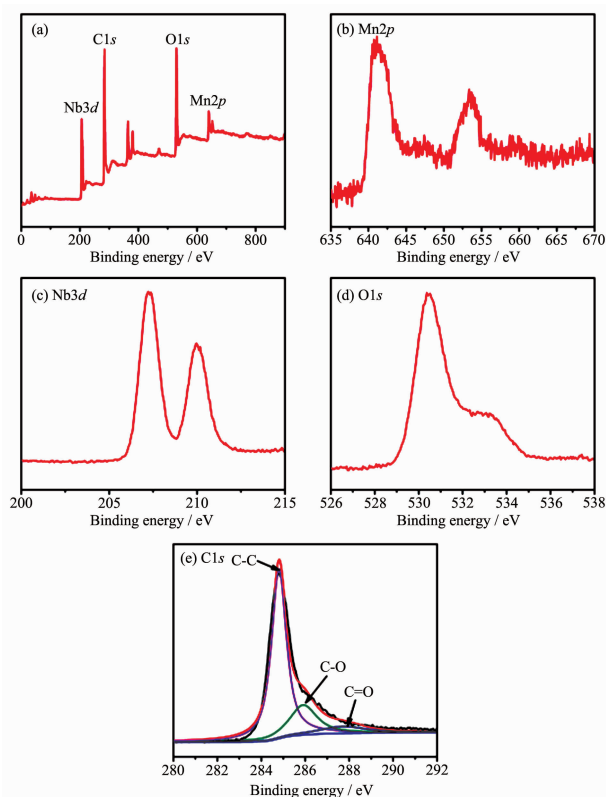


Fig.4 Raman spectra of MnNb₂O₆, GO and 3% RGO-MnNb₂O₆

2.3 XPS analysis

XPS was carried out to analyze the surface chemical compositions of 3% RGO-MnNb₂O₆ photocatalysts in Fig.5. According to the entire XPS spectrum observations in Fig.5a, the peaks of Bi, Nb, O and C were all existed in the 3% RGO-MnNb₂O₆ sample. Fig.5b displayed two strong peaks at 641.1 and 653.6 eV, which assigned to Mn2p. The two peaks for Nb3d centered at 207.3 and 210.1 eV in Fig.5c. Additionally, the XPS signal of O1s was locating at 530.5 eV in Fig.5d. The C1s spectrum (Fig.5e) of the 3% RGO-

MnNb₂O₆ sample could be fitted into three peaks located at 284.8, 285.9 and 287.7 eV, which corresponded to C-C, C-O, and C=O, respectively. The peak intensity of C-C was much higher than that of the C-O and C=O, which suggested that most of the oxygen-containing groups were removed and the GO was reduced to RGO.



(a) survey spectrum, (b) Mn2p, (c) Nb3d, (d) O1s and (e) C1s

Fig.5 XPS spectra of 3% RGO-MnNb₂O₆ samples

2.4 Photocatalytic behaviors

In this work, MB was chosen as the target pollution to assessed the photocatalytic performance in

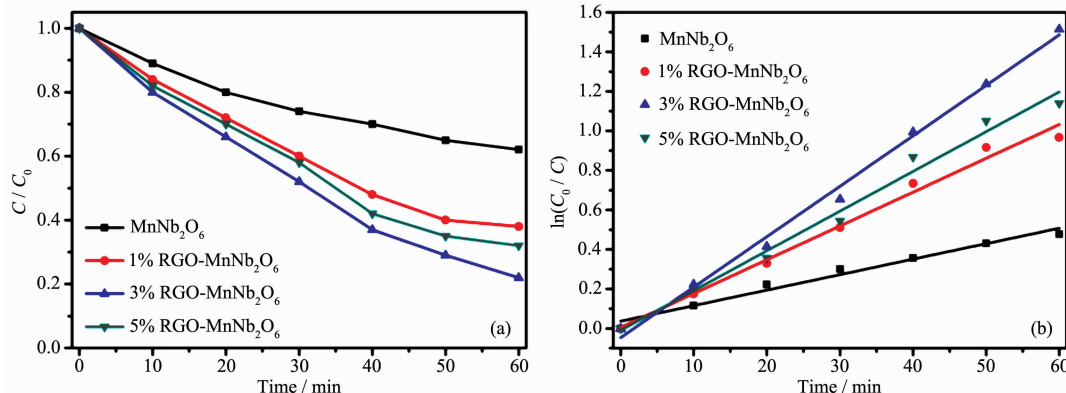


Fig.6 Photocatalytic degradation of MB with as-prepared samples (a); Pseudo-first-order reaction kinetics for MB degradation (b)

Fig.6a. Under 60 min irradiation, 38.5% of MB was degraded by pure MnNb₂O₆. With respected to the composites of RGO-MnNb₂O₆, when the two semiconductors were coupled together, the photocatalytic activities could be significantly enhanced in comparison to the pure MnNb₂O₆ catalysts, the MB degradation ratio of the 3% RGO-MnNb₂O₆ sample arrived 78.2%. However, when the RGO amount was further increased from 3% to 5%, the MB degradation ratio would be decreased, which should be because of large RGO amount (over 3%) may result from the limited light absorption.

The degradation kinetics of MB by using as-prepared samples were investigated and the results were shown in Fig.6b. It can be observed that the changes of the MB concentration vs the irradiation time over the as-prepared samples conformed to the pseudo-first-order kinetics plot. The reaction rate constant (k) values enhanced through the introduction of RGO. The 3% RGO-MnNb₂O₆ sample (0.025 4 min⁻¹) exhibited the highest k value among all the samples, which was about 3.26-fold higher than that of pure MnNb₂O₆ (0.007 84 min⁻¹).

2.5 Optical and electronic properties

Photoluminescence (PL) was employed to study the recombination abilities of photoexcited electron-hole pairs. A lower PL intensity revealed the lower photoinduced charge carriers' recombination. Fig.7 exhibited the PL emission spectra of pure MnNb₂O₆ and 3% RGO-MnNb₂O₆ samples, in which both the samples showed a strong emission peak centered at around 470 nm with an excitation wavelength of 360 nm. Remarkably, the 3% RGO-MnNb₂O₆ displayed a

lower PL intensity than the sample of MnNb_2O_6 , which indicated that the recombination of photogenerated charge carriers was inhibited in the 3% RGO- MnNb_2O_6 composite.

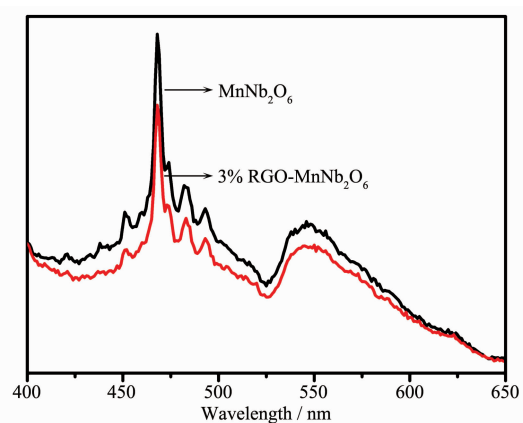


Fig.7 PL spectra and fluorescence decay curves of the MnNb_2O_6 and 3% RGO- MnNb_2O_6 sample

2.6 Photocatalytic mechanism

A series of active species trapping experiments were carried out to examine the photocatalytic oxidation mechanism with RGO- MnNb_2O_6 sample. In Fig.8, when $1 \text{ mmol} \cdot \text{L}^{-1}$ triethanolamine (TEA)^[32-36] was added to trap the holes (h^+), the photodegradation ratio was significantly declined in comparison to the reaction without TEA, revealing that the photogenerated holes (h^+) played major role in the selective oxidation of pollutant. As $1 \text{ mmol} \cdot \text{L}^{-1}$ BQ^[31] was added to trap $\cdot\text{O}_2^-$, the photodegradation ratio decreased to 50.4%, therefore, it can be concluded that $\cdot\text{O}_2^-$ took part in the oxidation reaction. On the contrary, the addition of $1 \text{ mmol} \cdot \text{L}^{-1}$ IPA (71.8%) to trapped the $\cdot\text{OH}$, the photocatalyst degradation ratio had little influence.

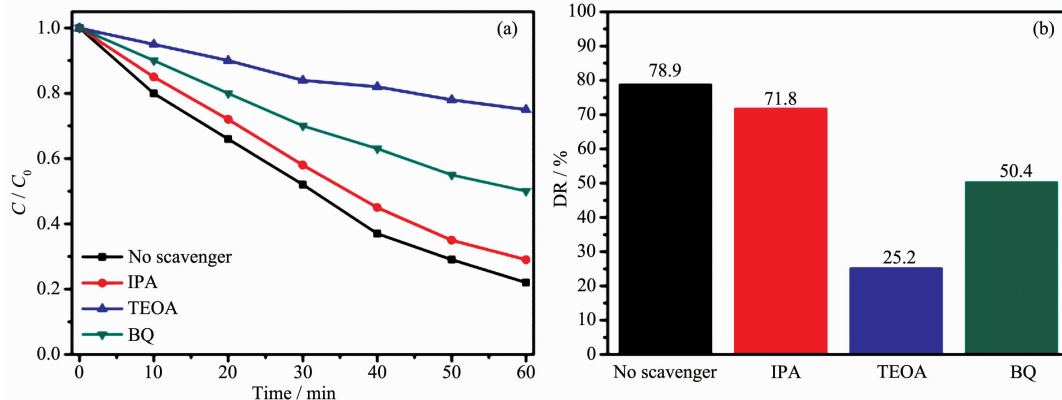


Fig.8 Photocatalytic degradation ratios of MB using different radical scavengers over 3% RGO- MnNb_2O_6 sample

To illustrate the photocatalytic process for decomposing organic dyes by RGO- MnNb_2O_6 composite, we carried out band position calculations by a plain method according to the previous paper. We can evaluate the conduction band of semiconductor by the formula^[37]:

$$E_{\text{CB}} = X - E_e - 0.5E_g$$

where E_{CB} was the CB edge potential; X was the electronegativity of the semiconductor, which was the geometric mean of the electronegativity of the constituent atoms (MnNb_2O_6 was 6.05); E_e was the energy of free electrons on the hydrogen scale (4.5 eV); and E_g was the band gap energy of the semiconductor. The E_{VB} value can be obtained by $E_{\text{VB}} = E_{\text{CB}} + E_g$. As the band gap of MnNb_2O_6 was 2.2 eV by the UV-Vis diffuse reflectance absorption spectra, the conduction band (CB) of MnNb_2O_6 was calculated to be 0.45 eV, and the valence band (VB) of MnNb_2O_6 was calculated to be 2.65 eV. On the basis of active species trapping experiments and calculated energy bands, a possible photocatalytic mechanism of RGO- MnNb_2O_6 can be drawn as shown in Fig.9. When the RGO- MnNb_2O_6 sample subjected to the irradiation of visible light, the electrons could be excited from the VB to the CB with simultaneous generation of holes in the VB. MB molecules adsorbed on the surface of MnNb_2O_6 were directly oxidized by h^+ , besides, h^+ also have few opportunities to react with $\text{OH}^-/\text{H}_2\text{O}$ to form $\cdot\text{OH}$ radicals. The photo-generated e^- in the CB can be injected into RGO, therefore hindering the recombination process of the e^-h^+ pairs and leading to an effective charge separation and stabilization. On the

other hand, e^- could transport along the RGO sheets from inner region to the surface and react with O_2 to form $\cdot O_2^-$ radicals, although $\cdot O_2^-$ radical was not efficient in the degradation of aromatic compounds such as MB molecules.

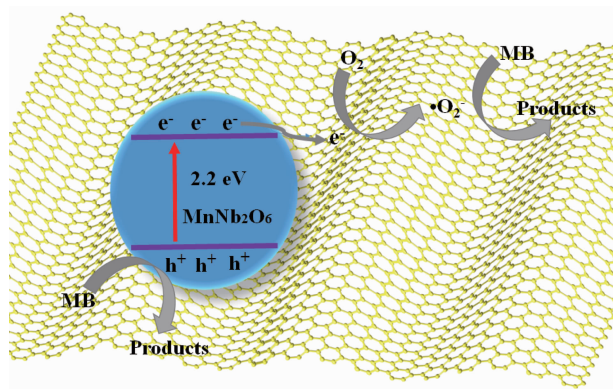


Fig.9 Schematic of the separation and transfer of photogenerated charges in the RGO-MnNb₂O₆ sample combined with the possible reaction mechanism of photocatalytic procedure

3 Conclusions

In summary, we have successfully constructed the RGO-MnNb₂O₆ composites with the hydrothermal and photo-reduction processes. The 3% RGO-MnNb₂O₆ sample exhibited best photocatalytic performance for the degradation of MB, which was about 2 times higher than that of bare MnNb₂O₆. The enhanced photocatalytic activity toward photodegrading MB under visible light irradiation could be ascribed to high charge carrier mobility of RGO, which greatly promoted efficient separation of the photoexcited electron-hole pairs as well as depressed recombination of the charge carriers. The as-designed principles outlined in this paper can be extended to other semiconductors to enhance the nanoscale heterostructures undergoing development for solar energy conversion.

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