available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Environmental and Energy Catalysis for Sustainable Development)

Unique electronic structure of Mg/O co-decorated amorphous carbon nitride enhances the photocatalytic tetracycline hydrochloride degradation

Xiaolu Wu, Min Fu *, Peng Lu, Qiuyan Ren, Cheng Wang

College of Environment and Resources, Chongqing Key Laboratory of Catalysis and New Environmental Materials, Chongqing Technology and Business University, Chongqing 400067, China

ARTICLE INFO

Article history:

Received 10 December 2018

Accepted 9 January 2019

Published 5 May 2019

Keywords:

g-C₃N₄

Electronic structure

Visible light photocatalysis

Tetracycline hydrochloride degradation

Environmental remediation

ABSTRACT

g-C₃N₄ is a hot visible light photocatalyst. However, the fast recombination of photogenerated electron-hole pairs leads to unsatisfactory photocatalytic efficiencies. In this study, Mg/O co-decorated amorphous carbon nitride (labeled as MgO-CN) with a unique electronic structure was designed and prepared via a combined experimental and theoretical approach. The results showed that the MgO-CN exhibited an increased light absorption ability and promoted charge separation efficiency. The Mg and O co-decoration created a unique structure that could generate localized electrons around O atoms and enhance the reactant activation capacities via the C→O←Mg route. This could dramatically promote the O₂ molecule activation on the catalyst surface to generate reactive species (•O₂⁻/•OH). The optimized MgO-CN exhibited a high photocatalytic activity for the degradation of tetracycline hydrochloride in water, which was five times higher than that of pristine g-C₃N₄. The present work could provide a new strategy for modifying the electronic structure of g-C₃N₄ and enhancing its performance for environmental applications.

© 2019, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

In the last decade, the potential environmental risks of antibiotics have raised worldwide attention [1,2]. Therefore, the elimination of antibiotics in wastewater has become an important issue for human health and environmental protection. Among them, tetracycline antibiotics are the second largest class of antibiotics, which are widely produced and used in human and veterinary medicine [3]. Some tetracycline antibi-

otics may be strongly carcinogenic or tumorigenic. Various methods, including biodegradation, adsorption, the Fenton reaction, and photochemical technology [4–6], aimed specifically at promoting the elimination of antibiotics. However, these methods have obvious disadvantages, including poor stabilities and high prices of the materials, which have limited their practical applications in industry [7,8]. Therefore, the development of new technology for antibiotic treatment in wastewater is urgent.

* Corresponding author. Tel/Fax: +86-23-62768474; E-mail: fumin1022@126.com

This work was supported by the Specialized Innovation of Social and People's Livelihood in Chongqing (cstc2016shmszx20012), Converting Outstanding Achievements of University-Funded Projects of Chongqing (KJZH17122), the National Natural Science Foundation of China (5160080705), the Key Laboratory Open Project from Chongqing Technology and Business University (1556036), the Scientific and Technological Research Program of Chongqing Municipal Education Commission (KJ130704), and Innovative Research Project from Chongqing Technology and Business University (yjscxx2016-060-34)

DOI: S1872-2067(19)63300-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 40, No. 5, May 2019

In recent years, visible light photocatalysts have received widespread attention and been extensively used in various fields for environment pollution treatment [9]. Photocatalysis, which involves catalysts with strong oxidation abilities, can enable complete mineralization for the degradation of tetracycline antibiotics [10,11]. Several new types of photocatalysts have been developed, such as TiO_2 [12], CdS [13], WO_3 [14,15], and BiOI [16]. However, the majority of these photocatalytic materials have low visible-light photocatalytic activities and stabilities [17], which are still far from satisfactory. The semiconductor photocatalyst $\text{g-C}_3\text{N}_4$, as a metal-free two-dimensional conjugated semiconductor, is produced from inexpensive raw materials and is harmless and non-toxic. $\text{g-C}_3\text{N}_4$ is physically and chemically stable, and the stability is tunable [18]. It has been recognized as a promising photocatalyst [19,20]. However, $\text{g-C}_3\text{N}_4$ has an sp^2 periodic interlayer melon arrangement hybrid array of characteristic units and weak van der Waals (vdW) attractions, which causes difficulties for electron transfer [21,22].

During the photocatalytic process, electron-hole recombination is easily realized on the catalyst surface, leading to limited photocatalytic activity [23–25]. To solve this problem, many strategies have been developed, such as inner architecture modification [24,27,28] and surface functionalization (surface modification and formation of heterojunctions) [29–33]. Surface modification of $\text{g-C}_3\text{N}_4$ can improve the optical and charge transfer properties. For inner architecture modification, amorphous carbon nitride has a much smaller bandgap than the partially crystalline graphitic carbon nitride. This increases the light absorption ability, which leads to an enhanced photocatalytic efficiency, such as black phosphorus and Pt [34–37]. These surface and amorphous modifications are useful strategies for reducing the recombination rate of the charge carriers and transport across the interfaces. However, studies related to alkaline metal oxide modified $\text{g-C}_3\text{N}_4$ are scant. Thus, the $\text{g-C}_3\text{N}_4$ structure was properly designed and customized in this study.

To reduce the recombination rate of electrons-holes and extend the charge carrier lifetimes, a series of Mg/O co-decorated amorphous carbon nitride samples were prepared by a simple one-step in-situ co-pyrolysis method. The graphitic carbon nitride with an amorphous structure achieved short-range electron transport. This created electron-hole separation and suppressed charge recombination, thereby improving the photocatalytic activity. We proposed that MgO could modify the surface of carbon nitride and new active centers could be formed. The adsorption capacity and O_2 activation were promoted to generate radicals and participate in the photocatalytic degradation of the antibiotic tetracycline hydrochloride (TC). In the present study, a simple and effective modification method to increase the photocatalytic activity was developed. The Mg/O co-decorated amorphous carbon nitride had a significant effect on the TC degradation. It is crucial to understand the mechanism of the photocatalytic reaction to promote the development of photocatalytic technology.

2. Experimental

2.1. Materials

Urea, magnesium carbonate tetrahydrate, L-ascorbic acid, and ethylenediamine tetraacetic acid disodium salt were purchased from Kelong Chemical Agents (China). Tetracycline hydrochloride was purchased from Biosharp Deionized Chemical Agents (China). Isopropanol was purchased from Chongqing Horizon Chemical Industry (China). Water was used in all the experiments.

2.2. Catalyst preparation

The MgO-CN composites were synthesized as follows. First, 10 g of magnesium carbonate tetrahydrate was dissolved in 30 mL of deionized water and ultrasonically stirred for 30 min. This solution was dried at 80 °C for 10 h, after which the precursor in an alumina crucible was heated at 580 °C for 4 h (20 °C/min), and MgO powder was obtained. A certain amount of the prepared MgO powder and 10 g of urea were added to deionized water and ultrasonically stirred for 1 h. The solid composite precursor was dried at 60 °C for 10 h and calcined at 550 °C for 2 h (10 °C/min) to yield MgO-CN powder. Composites with different mass ratios of MgO to urea were labeled MgO-CN-0.4 , MgO-CN-0.8 , MgO-CN-1.2 , and MgO-CN-1.5 , corresponding to mass ratios of 0.4, 0.8, 1.2, and 1.5 wt%, respectively.

2.3. Characterization

X-ray diffraction (XRD, D8 Advance, Bruker Co., Germany) with $\text{Cu K}\alpha$ radiation was used to characterize the crystal structures and phase compositions of the synthesized samples. Fourier-transform infrared spectroscopy (FT-IR, IR Prestige-21, Shimadzu, Japan) was employed to characterize the chemical bonds present on the composite surface. Scanning electron microscopy (SEM, JSM-7000F, JEOL, Japan) and transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan) were used to examine the morphologies and microstructures of the products. N_2 adsorption-desorption analysis (BET-BJH, ASAP 2020, Micromeritics) at –196 °C was employed to determine the surface areas and pore size distributions of the prepared samples. UV-vis diffuse reflectance spectroscopy (UV-vis DRS, UV-2550, Shimadzu, Japan), with 100% barium sulfate as a reference, was used to analyze the optical properties and band gaps. The photoluminescence (PL, F-7000, HITACHI, Japan) spectra were obtained to probe the charge-recombination rates of the electron-hole pairs of the samples. Electron spin resonance (ESR) measurements were used to identify the active species in the photodegradation process.

2.4. Photocatalysis test

The photocatalytic behavior of the prepared composite samples was assessed by the degradation removal efficiency of TC in aqueous solutions. In a typical run, 100 mg of photocatalyst and 100 mL TC solution (30 mg/L) were stirred with a magnetic bar to achieve adsorption-desorption equilibrium in

Fig. 1. XRD patterns of (a) MgO, (b) CN and MgO-CN-X samples.

the dark. After adsorption equilibrium, the sample was exposed to visible light irradiation for a certain time using a 12 W LED lamp (>400 nm) to initiate the photocatalytic reaction. At time intervals, a certain amount of solution was collected and immediately centrifuged at 5000 rpm, after which these aliquots were analyzed using a UV/Vis spectrophotometer (Shimadzu Inc., Japan). The characteristic absorption band of TC is at 357 nm [38]. The degradation rate (η) of TC is calculated as $\eta = (1 - C_t/C_0) \times 100\%$, where C_0 denotes the initial concentration of the TC solution and C_t denotes the concentration of the TC solution at time t .

2.5. Trapping experiments for visible-light-induced production of active species

Isopropyl alcohol (IPA), ascorbic acid (AA), and ethylenediamine tetraacetic acid disodium salt (EDTA-2Na) were utilized to scavenge $\bullet\text{OH}$ radicals, $\bullet\text{O}_2^-$ radicals, and holes, respectively. First, 100 mL of TC solution (30 mg/L) and 0.1 g of photocatalyst were stirred with a magnetic bar to achieve the adsorption-desorption equilibrium in the dark. The mixed solutions with different trapping agents were irradiated under visible light to initiate the photocatalytic reactions. The samples used in the ESR experiments were dissolved in a 50 mmol/L 5,5-dimethyl-1-pyrroline-*N*-oxide (DMPO) solution tank (aqueous dispersion for DMPO- $\bullet\text{OH}$ and methanol dispersion for DMPO- $\bullet\text{O}_2^-$) before irradiation by visible light.

2.6. DFT calculations

DFT-D2 calculations were carried out with the “Vienna ab initio simulation package” (VASP5.4) [39]. A plane-wave expansion basis set with a cut-off energy of 450 eV was employed. We used $3 \times 3 \times 1$ Monkhorst-pack k-point grid for the structural optimization and to calculate the electron structure. Before the electronic properties were determined, the atoms were relaxed until the residual force was less than 0.03 eV/Å.

3. Results and discussion

3.1. Microstructure characterization of composites

3.1.1. XRD analysis

The XRD patterns of MgO are shown in Fig. 1(a). The sharp peaks at 36.9° , 42.9° , 62.3° , 74.7° , and 78.6° correspond to the (111), (200), (220), (311), and (222) planes, respectively, and were the characteristic peaks of MgO [40]. The patterns of the CN and MgO-CN samples with different mass ratios of MgO are shown in Fig. 1(b). Pure g-C₃N₄ has two typical diffraction peaks at 13.1° (in-plane tri-s-triazine units) and 27.6° (interplanar stacking of aromatic segments), which are attributed to the (100) and (002) lattice planes [41–43], respectively. The signature diffraction peaks of MgO were not observed because of the low loading mass of the MgO nanoparticles in the composites. With increased loading amounts, the intensities of the CN signals decreased. These results indicated that the aromatic systems of the in-plane periodicity were destroyed. Accordingly, the layers with periodic accumulation were re-disturbed, and amorphous carbon nitride was generated.

3.1.2. FT-IR spectra analysis

Fig. 2 shows the FT-IR spectra of the CN, MgO, and MgO-CN-1.2 samples. The typical IR peaks of g-C₃N₄ were detected at 810 and 1230–1640 cm^{-1} , which were attributed to the breathing mode of the triazine units and the characteristic stretching modes of aromatic C–N ($\text{C}(\text{sp}^2)\text{--N}$, $\text{C}(\text{sp}^2)=\text{N}$) heterocycles, respectively [44,45]. The peak in the 3000–3500 cm^{-1} region was assigned to the N–H stretching and bending vibrations. The strong and broad peaks of MgO located in the

Fig. 2. FT-IR spectra of CN, MgO, and MgO-CN-1.2 samples.

Fig. 3. SEM and TEM images of prepared (a, b) CN, (c, d) MgO, and (e, f) MgO-CN-1.2 samples.

450–600 cm^{-1} region were attributed to the stretching vibrations. The absorption peaks at 1643 and 3418 cm^{-1} were as-

signed to the bending vibrations of water [46], respectively. The band at 1488 cm^{-1} was assigned to the carbonate ions on the surface of the sample due to the absorption from carbon dioxide in the atmosphere [47]. The vibration peaks of the MgO-CN-1.2 composite were slightly weaker than those of pure g-C₃N₄. Moreover, for the modified photocatalyst, the intensities of these peaks decreased, and the N-H stretching at 3160 cm^{-1} also weakened due to the addition of Mg. Less exposure of the surface amino groups was observed [48,49]. Note that the peak at 2160 cm^{-1} represents the N=C=N stretching vibrations [50], indicating that the C–N heterocycles were deformed. This result also implies that the insertion of MgO in the urea polymerization only destroys the periodic interlayer melon arrangement but simultaneously maintains the basic strand atomic structures. As a result, these characteristics can afford unique amorphous arrangements of short-range order and long-range disorder of CN.

3.1.3. Micro-morphology analysis

The morphologies CN, MgO, and MgO-CN-1.2 were analyzed by SEM and TEM. As shown in Fig. 3(a–c), a stack of porous thin nanosheets was observed in the SEM image of CN. The MgO was composed of bulk and dense thick layers. The MgO-CN sample manifested a flake and sheet-shaped morphology. The TEM images, as shown in Fig. 3(d–e), showed the microstructures of the samples. The CN consisted of layered nanosheets. The lattice fringes of the MgO samples can be clearly observed. The HRTEM image in Fig. 3(e) shows that the lattice of MgO-CN-1.2 was not detected, which further clarified the formation process of the amorphous carbon nitride. This TEM result implies that the introduction of MgO can induce the

Fig. 4. (a) C 1s, (b) N 1s, (c) O 1s, and (d) Mg 2p XPS spectra of the samples.

Fig. 5. (a) N_2 adsorption-desorption isotherms and (b) pore size distribution curves of CN, MgO, and MgO-CN-X samples.

amorphization of pristine CN, and the difference in the photocatalytic activity was not caused by the morphology.

3.1.4. Surface species analysis

The surface chemical compositions and bonding configurations of the CN and MgO-CN-1.2 composites were investigated by XPS. In the XPS spectra, the binding energies of Mg and O were identified. The C 1s spectrum (Fig. 4(a)) deconvoluted into peaks at 284.6 and 288.1 eV, corresponding to adventitious hydrocarbons and sp^2 -bonded carbon in $N-C=N$ groups, respectively. The N 1s spectra of the CN and MgO-CN-1.2 composites were usually fitted into four peaks (Fig. 4(b)). The peaks at 398.4 and 399.9 eV indicated the formation of sp^2 hybridized aromatic nitrogen ($C=N-C$ groups) and hybridized tertiary nitrogen ($N-(C)_3$ groups), respectively. The peaks at 401.4 and 404.1 eV were not obvious. This can be also observed in the O 1s spectra (Fig. 4(c)). The peaks at 532.9 eV in the O 1s spectra were attributed from surface adsorbed water. Compared to pure CN, an additional peak at 531.8 eV in the O 1s spectrum of MgO-CN-1.2 appeared, which was ascribed to $N-C-O$ formation during calcination with air. The XPS peaks of the Mg 2p spectra (Fig. 4(d)) of the MgO-CN-1.2 composites were located at 49.8 eV.

3.1.5. Surface area and pore structure

Fig. 5(a) shows the BET surface area measurement of the samples. All samples were classified into a type-IV curve with H3 hysteresis loops at relative pressures ranging from 0.5 and 1.0, corresponding to mesoporous structures. Fig. 5(b) shows the relative pore-size distributions [51]. For comparison, the

specific surface areas and total pore volumes of the CN, MgO, and MgO-CN-X samples are listed in Table 1. The specific surface area of CN was $129.13 \text{ m}^2/\text{g}$ after the coupling with MgO. The surface areas of the MgO-CN-X samples gradually decreased, as the MgO could plug the pore structures, leading to low surface areas and slight decreases of the pore sizes. Based on the photocatalytic activities for TC degradation, the specific surface area and porous structure were not the critical factors for improving the photocatalytic activity.

3.2. Optical and electronic properties

3.2.1. Optical properties and band structures

The optical properties of CN and MgO-CN-1.2 were investigated by UV-vis diffuse reflectance spectroscopy. As shown in Fig. 6(a), an adsorption band up to 225 nm appeared for MgO. The MgO-CN-1.2 exhibited intensified absorption over the entire range of wavelengths due to Mg and O co-decoration. The E_g values of the MgO-CN-1.2 and pristine CN were obtained from the $(ah\nu)^{1/2}$ vs. $h\nu$ plots shown in Fig. 6(b), which indicate that the band gaps of pristine CN, MgO, and MgO-CN-1.2 were 2.75, 5.39, and 2.48 eV, respectively. The conduction band (CB) and valence band (VB) positions of CN were -1.15 and 1.60 eV, respectively, whereas those of MgO-CN-1.2 were -1.01 and 1.47 eV. The VB and CB edges of MgO-CN exhibited down-shifts compared to those of pristine CN. The calculated densities of states (DOSs) are shown in Fig. 6(c), which were used to estimate the band energy. Compared with pristine CN, the band gap of MgO-CN-1.2 narrowed significantly and shifted to a lower energy level, which agreed with the UV-vis results. The reduced band gap of MgO-CN-1.2 can be ascribed to the MgO doping. The narrowed band gap reduced the energy required to excite electrons. Fig. 6(d) shows the PL spectra of CN and MgO-CN-1.2. MgO-CN-1.2 had lower fluorescence intensity, which is beneficial for separation efficiency. Mg/O co-decorated amorphous carbon nitride can achieve an optimized band structure and enhance the efficiency of electron-hole separation.

3.2.2. Structures and electron localization

DFT was further employed to determine the electronic structures to analyze the effect of Mg/O co-decorated amor-

Table 1

BET specific surface areas, total pore volumes, and peak pore sizes of CN, MgO, and MgO-CN-X samples.

Sample	A_{BET} (m^2/g)	Total pore volume (cm^3/g)	Peak pore size (nm)
CN	129.13	0.71	3.8/32.6
MgO-CN-0.4	71.48	0.44	3.7/24.7
MgO-CN-0.8	58.48	0.32	3.7/24.6
MgO-CN-1.2	34.55	0.16	3.6/24.5
MgO-CN-1.5	21.11	0.11	3.5/24.4
MgO	62.60	0.40	3.2/16.2

Fig. 6. (a) UV-vis DRS, (b) the band gap determination, (c) calculated total density of states (TDOS), and (d) PL spectra of different photocatalysts.

phous carbon nitride on the electron delivery. Fig. 7(a) and 7(b) show the electronic structure of the Mg/O co-decorated g-C₃N₄. The charge difference distribution of the MgO-CN calculated using DFT is shown in Fig. 7(c). We found that the O atom received electrons from adjacent C, N, and Mg atoms, which was attributed to the differences in electronegativities

Fig. 7. (a) Optimized local structures g-C₃N₄. (b) Optimized local structures of MgO decorated g-C₃N₄ samples. (c) Charge density difference of MgO-CN. Grey, brown, red, and orange spheres depict N, C, O, and Mg atoms, respectively. Charge accumulation and depletion are represented by blue and yellow colors, and the isosurfaces were both set to 0.005 eV Å⁻³ in (c). (d) Optimized local structure and electronic localization function (ELF) of O atom dissociation in CN.

between the C, N, Mg, and O elements. Inducing an O atom into the CN could aggregate electrons and provide active sites to promote the activation of O₂ and H₂O molecules on the catalyst surface to generate reactive species. The electron localization function (ELF, Fig. 7(d)) implies that Mg/O co-decoration can provide electronic localization, which could have specific transport orbitals (C→O←Mg) for intralayer electron transfer.

3.3. Photocatalytic activity of MgO-CN composites

Fig. 8(a) shows the photo-degradation efficiency of TC with the CN and MgO-CN composites. The CN exhibited a lower activity than the composites after 2.5 h of irradiation with visible light. The degradation of TC treated with MgO-CN-1.2 reached about 82%, which was higher than that of the pure g-C₃N₄ (23.5%). The fits to the kinetics of the TC degradation by g-C₃N₄ and MgO-CN-X (where X stands for the MgO percentage) are shown in Fig. 8(b). MgO-CN-1.2 exhibited the highest photo-degradation efficiency (0.01018 min⁻¹), which was five times higher than that of the CN (0.00205 min⁻¹). The photocatalytic activity results showed that after the introduction of MgO, the photocatalysis efficiency of the composites was greatly enhanced. Fig. 8(c) shows the UV-vis spectra of TC using the MgO-CN-1.2 composite photocatalyst for the specific time intervals. The decrease in the absorbance characteristic peak at 357 nm with the treatment time indicated that the TC was degraded under visible light irradiation for 2.5 h. Based on the UV-vis analysis of the TC aqueous solutions, it can be concluded that the MgO-CN-1.2 can effectively degrade TC via photocatalysis. Meanwhile, the stability of the photocatalyst is one of the

Fig. 8. (a) Photodegradation of TC by different photocatalysts. (b) The $\ln C_0/C_t$ versus time curves of the photodegradation of TC. (c) UV-vis spectra for the degradation of TC using the MgO-CN-1.2 composite. (d) The repeatability tests on the different photocatalysts for five cycles.

essential aspects for advanced photocatalytic performance. We examined the stability of the CN and MgO-CN-1.2 composite photocatalyst with five cycles. The result shows that the MgO-CN-1.2 exhibited a slight decrease of the photocatalytic activity (Fig. 8(d)). The slight decrease in the degradation rate was possibly due to the partial loss of the photocatalyst that occurred during recovery.

3.4. Mechanisms of enhanced photodegradation

The reactive species ($\bullet\text{OH}$, $\bullet\text{O}_2^-$) and holes (h^+) are responsible for the photocatalytic oxidation. To investigate the effect

Fig. 9. Radical trapping experiments for the degradation of TC by MgO-CN-1.2.

of these reactive species on the photodegrading of TC, radical trapping experiments were conducted. As shown in Fig. 9, the photocatalytic activity of MgO-CN-1.2 indicated that the addition of IPA, AA, or EDTA-2Na inhibited the photocatalysis to different degrees. Moreover, the addition of AA ($\bullet\text{O}_2$ scavengers) has the most significant influence on decreasing the photocatalytic degradation efficiency of TC. These results suggest that $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and h^+ play important roles in the photodegradation process of TC.

According to the degradation studies, the MgO-CN composites exhibited greater photoactivities than $\text{g-C}_3\text{N}_4$. The radical trapping experiment results suggested that $\bullet\text{OH}$, $\bullet\text{O}_2^-$, and h^+ enhanced the photocatalytic process of TC degradation. To further determine the amounts of reactive species present for photocatalytic TC degradation, the reactive species were identified by the ESR spin-trap. As shown in Fig. 10(a), MgO-CN-1.2 exhibited much stronger $\bullet\text{O}_2^-$ and $\bullet\text{OH}$ signals than pure $\text{g-C}_3\text{N}_4$ while reacting under visible light. The results were associated with the unique electronic structure of the Mg/O co-decorated amorphous carbon nitride. Furthermore, the improvement was beneficial for electron excitation, which prolongs the time of electron-hole recombination. Moreover, the red shift of the adsorption edge broadened the field of light adsorption, which enhanced the utilization of light. Thus, an improvement of the TC degradation was obtained. The separation of the electron-hole pairs had a significant impact on the photocatalytic reaction. The photogenerated electrons and holes were trapped by oxygen and surface hydroxyl groups on the surface of the photocatalyst to form $\bullet\text{O}_2^-$ and $\bullet\text{OH}$.

Fig. 10. DMPO ESR spin-trapping for the (a) superoxide and (b) hydroxyl radicals.

The mechanism of the photocatalytic TC degradation by the MgO-CN catalysts under visible light is illustrated in Fig. 11. In agreement with the related reports [51–53], we found that the VB holes (1.47 eV) from MgO-CN were unable to oxidize the $\text{OH}^-/\text{H}_2\text{O}$ to $\bullet\text{OH}$ radicals. However, $\bullet\text{OH}$ was detected, as shown in Fig. 10(b). Thus, $\bullet\text{OH}$ can form through O_2 reduction at the CB (−1.01 eV) via the path $\bullet\text{O}_2^- \rightarrow \text{H}_2\text{O}_2 \rightarrow \bullet\text{OH}$ [54,55]. The photocatalytic degradation mechanism is as follows:

4. Conclusions

We reported that the Mg/O co-decorated amorphous carbon nitride exhibited a high photocatalytic activity for TC degradation. Based on detailed experimental data and theoretical calculations, the mechanism of the photocatalytic activity enhancement was proposed. The Mg and O co-decoration turned the periodic interlayer melon arrangement of g-C₃N₄ into an amorphous phase, increasing the light absorption ability. The electron transport distance decreased, which was favorable for

the separation of electron-hole pairs. The Mg and O co-decoration created a unique structure that could generate localized electrons (O atoms caused electron aggregation). Moreover, the reactant activation capacity was enhanced via the $\text{C} \rightarrow \text{O} \leftarrow \text{Mg}$ route to create favorable conditions for the O_2 molecule activation on the catalyst surface. The reactive species were produced via the path $\text{O}_2 \rightarrow \bullet\text{O}_2^- \rightarrow \text{H}_2\text{O}_2 \rightarrow \bullet\text{OH}$. The ESR spectra and DFT calculations revealed the mechanism of the photocatalytic degradation of TC by the Mg/O co-decorated amorphous carbon nitride. The present work can provide new ideas and understanding of catalyst modification for large-scale environmental and remediation applications.

Acknowledgments

This work was financially supported by the Specialized Innovation of Social and People's Livelihood in Chongqing (cstc2016shmszx20012), the Converting Outstanding Achievements of University-Funded Projects of Chongqing (KJZH17122), the National Natural Science Foundation of China (5160080705), the Key Laboratory Open Project from Chongqing Technology and Business University (1556036), the Scientific and Technological Research Program of Chongqing Municipal Education Commission (KJ130704), and the Innovative Research Project from Chongqing Technology and Business University (yjscxx2016-060-34).

References

- [1] I. Chopra, M. Roberts, *Microbiol. Mol. Biol. Rev.*, **2001**, 65, 232–260.
- [2] S. Leong, D. Li, K. Hapgood, X. Zhang, H. Wang, *Appl. Catal. B*, **2016**, 198, 224–233.
- [3] H. Chen, S. Liu, X. R. Xu, Z. H. Diao, K. F. Sun, Q. W. Hao, S. S. Liu, G. G. Ying, *J. Hazard. Mater.*, **2018**, 343, 140–148.
- [4] Q. Z. Yi, Y. Zhang, Y. X. Gao, Z. Tian, M. Yang, *Water Res.*, **2017**, 110, 211–217.
- [5] J. Li, W. Zhang, M. Ran, Y. Sun, H. Huang, F. Dong, *Appl. Catal. B*, **2019**, 243, 313–321.
- [6] S. H. Kim, H. K. Shon, H. H. Ngo, *J. Ind. Eng. Chem.*, **2010**, 16, 344–349.
- [7] I. de Godos, R. Muñoz, B. Guieysse, *J. Hazard. Mater.*, **2012**, 229–230, 446–449.

Fig. 11. Mechanism of TC degradation with the MgO-CN composites under visible light irradiation.

Graphical Abstract

Chin. J. Catal., 2019, 40: 776–785 doi: S1872-2067(19)63300-0

Unique electronic structure of Mg/O co-decorated amorphous carbon nitride enhances the photocatalytic tetracycline hydrochloride degradation

Xiaolu Wu, Min Fu*, Peng Lu, Qiuyan Ren, Cheng Wang
Chongqing Technology and Business University

The unique electronic structure of Mg/O co-decorated amorphous carbon nitride enhanced the production of $\bullet\text{OH}$ and $\bullet\text{O}_2$ radicals as the main reactive species, which enhanced the photocatalytic tetracycline hydrochloride degradation efficiency five times compared to that of pristine g-C₃N₄.

- [8] H. Kim, Y. Hong, J. E. Park, V. K. Sharma, S. I. Cho, *Chemosphere*, **2013**, 91, 888–894.
- [9] J. Y. Li, X. A. Dong, Y. J. Sun, W. L. Cen, F. Dong, *Appl. Catal. B*, **2018**, 226, 269–277.
- [10] X. J. Wen, C. G. Niu, L. Zhang, C. Liang, G. M. Zeng, *Appl. Catal. B*, **2018**, 221, 701–714.
- [11] C. Xie, S. H. Yang, J. W. Shi, B. B. Li, C. Gao, C. M. Niu, *J. Colloid Interf. Sci.*, **2016**, 476, 1–8.
- [12] Y. H. Li, K. L. Lv, W. K. Ho, F. Dong, X. F. Wu, Y. Xia, *Appl. Catal. B*, **2017**, 202, 611–619.
- [13] J. Y. Hu, C. K. Yu, C. Y. Zhu, S. J. Hu, Y. Wang, N. Q. Fu, L. X. Zeng, M. S. Zhu, *Catal. Today*, **2018**, 315, 36–45.
- [14] G. Zhang, W. Guan, H. Shen, X. Zhang, W. Fan, C. Lu, H. Bai, L. Xiao, W. Gu, W. Shi, *Ind. Eng. Chem. Res.*, **2014**, 53, 5443–5450.
- [15] T. Wang, W. Quan, D. Jiang, L. Chen, D. Li, *Chem. Eng. J.*, **2016**, 300, 280–290.
- [16] A. Dehghan, M. H. Dehghani, R. Nabizadeh, N. Ramezani, M. Alimohammadi, A. A. Najafpoor, *Chem. Eng. Res. Des.*, **2018**, 129, 217–230.
- [17] Q. Zhang, I. Lee, J. B. Joo, F. Zaera, Y. Yin, *Acc. Chem. Res.*, **2013**, 46, 1816–1824.
- [18] J. Y. Li, Z. Y. Zhang, W. Cui, H. Wang, W. L. Cen, G. Johnson, G. M. Jiang, S. Zhang, F. Dong, *ACS Catal.*, **2018**, 8, 8376–8385.
- [19] X. C. Wang, K. Maeda, A. Thomas, K. Takanabe, G. Xin, J. M. Carlsson, K. Domen, M. Antonietti, *Nat. Mater.*, **2009**, 8, 76–80.
- [20] W. H. Niu, K. Marcus, L. Zhou, Z. Li, L. Shi, K. Liang, Y. Yang, *ACS Catal.*, **2018**, 8, 1926–1931.
- [21] F. Geng, R. Ma, A. Nakamura, K. Akatsuka, Y. Ebina, Y. Yamauchi, N. Miyamoto, Y. Tateyama, T. Sasaki, *Nat. Commun.*, **2013**, 4, 1632/1–1632/7.
- [22] J. Y. Li, W. Cui, Y. J. Sun, Y. H. Chu, W. L. Cen, F. Dong, *J. Mater. Chem. A*, **2017**, 5, 9358–9364.
- [23] P. Suyana, P. Ganguly, B. N. Nair, A. P. Mohamed, K. G. K. Warriar, U. S. Hareesh, *Environ. Sci.: Nano*, **2017**, 4, 212–221.
- [24] Y. Kang, Y. Yang, L. C. Yin, X. Kang, L. Wang, G. Liu, H. M. Cheng, *Adv. Mater.*, **2016**, 28, 6471–6477.
- [25] P. Chen, H. Wang, H. Liu, Z. Ni, J. Li, Y. Zhou, F. Dong, *Appl. Catal. B*, **2019**, 242, 19–30.
- [26] X. Dong, W. Zhang, Y. Sun, J. Li, W. Cen, Z. Cui, H. Huang, F. Dong, *J. Catal.*, **2018**, 357, 41–50.
- [27] W. Cui, J. Y. Li, F. Dong, Y. J. Sun, G. M. Jiang, W. L. Cen, S. C. Lee, Z. B. Wu, *Environ. Sci. Technol.*, **2017**, 51, 10682–10690.
- [28] J. Jiang, S. W. Cao, C. L. Hu, C. H. Chen, *Chin. J. Catal.*, **2017**, 38, 1981–1989.
- [29] F. Chen, H. Yang, X. F. Wang, H. G. Yu, *Chin. J. Catal.*, **2017**, 38, 296–304.
- [30] H. J. Han, M. Fu, Y. L. Li, W. Guan, P. Lu, X. L. Hu, *Chin. J. Catal.*, **2018**, 39, 831–840.
- [31] Y. H. Li, K. L. Lv, W. K. Ho, Z. W. Zhao, Y. Huang, *Chin. J. Catal.*, **2017**, 38, 321–329.
- [32] H.W. Jung, T. T. Pham, E. W. Shin, *Appl. Sur. Sci.*, **2018**, 458, 369–381.
- [33] Q. Q. Hao, Y. H. Song, H. Y. Ji, Z. Mo, X. J. She, J. J. Deng, T. Muhmood, X. W. Wu, S. Q. Yuan, H. Xu, H. M. Li, *Appl. Surf. Sci.*, **2018**, 459, 845–852.
- [34] T. Xiong, W. Cen, Y. Zhang, F. Dong, *ACS Catal.*, **2016**, 6, 2462–2472.
- [35] M. S. Zhu, S. Kim, L. Mao, M. Fujitsuka, J. Y. Zhang, X. C. Wang, T. Majima, *J. Am. Chem. Soc.*, **2017**, 139, 13234–13242.
- [36] M. S. Zhu, C. Y. Zhai, M. J. Sun, Y. F. Hu, B. Yan, Y. K. Du, *Appl. Catal. B*, **2017**, 203, 108–115.
- [37] C. Y. Zhai, M. J. Sun, L. X. Zeng, M. Q. Xue, J. G. Pan, Y. K. Du, M. S. Zhu, *Appl. Catal. B*, **2019**, 243, 283–293.
- [38] Y. Z. Hong, C. S. Li, B. X. Yin, D. Li, Z. Y. Zhang, B. D. Mao, W. Q. Fan, W. Gu, W. D. Shi, *Chem. Eng. J.*, **2018**, 338, 137–146.
- [39] G. Kresse, J. Furthmüller, *Phys. Rev. B*, **1996**, 54, 11169–11186.
- [40] N. Huo, H. Ma, X. H. Wang, T. L. Wang, G. Wang, T. Wang, L. L. Hou, J. Gao, J. Xu, *Chin. J. Catal.*, **2017**, 38, 1148–1154.
- [41] X. Wang, S. Blechert, M. Antonietti, *ACS Catal.*, **2012**, 2, 1596–1606.
- [42] J. S. Chen, Z. Hu, K. L. Lv, X. F. Wu, Q. Li, Y. H. Li, X. F. Li, J. Sun, *Appl. Catal. B*, **2018**, 232, 330–339.
- [43] Y. Zheng, L. H. Lin, B. Wang, X. C. Wang, *Angew. Chem. Int. Ed.*, **2015**, 54, 12868–12884.
- [44] Y. Li, Y. Sun, W. Ho, Y. Zhang, H. Huang, Q. Cai, F. Dong, *Sci. Bull.*, **2018**, 63, 609–620.
- [45] Z. Zhao, H. Dai, Y. Du, J. Deng, L. Zhang, F. Shi, *Mater. Chem. Phys.*, **2011**, 128, 348–356.
- [46] H. Niu, Q. Yang, K. Tang, Y. Xie, *J. Nanopart. Res.*, **2006**, 8, 881–888.
- [47] J. Fu, B. Zhu, C. Jiang, B. Cheng, W. You, J. G. Yu, *Small*, **2017**, 13,

- 1603938/1–1603938/9.
- [48] M. J. Bojdys, J. O. Muller, M. Antonietti, A. Thomas, *Chem. Eur. J.*, **2008**, 14, 8177–8182.
- [49] C. L. Schmidt, M. Jansen, *J. Mater. Chem.*, **2010**, 20, 4183–4192.
- [50] S. Z. Hu, L. Ma, H. Y. Wang, L. Zhang, Y. F. Zhao, G. Wu, *RSC Adv.*, **2015**, 5, 31947–31953.
- [51] J. Y. Li, X. A. Dong, Y. J. Sun, G. M. Jiang, Y. H. Chu, S. C. Lee, F. Dong, *Appl. Catal. B*, **2018**, 239, 187–195.
- [52] J. Y. Li, P. Yan, K. L. Li, W. L. Cen, X. W. Yu, S. D. Yuan, Y. H. Chu, Z. M. Wang, *Chin. J. Catal.*, **2018**, 39, 1695–1703.
- [53] Y. H. Li, W. K. Ho, K. L. Lv, B. C. Zhu, S. C. Lee, *Appl. Surf. Sci.*, **2018**, 430, 380–389.
- [54] W. Cui, J. Li, Y. Sun, H. Wang, G. Jiang, S. C. Lee, F. Dong, *Appl. Catal. B*, **2018**, 237, 938–946.
- [55] X. Dong, J. Li, Q. Xing, Y. Zhou, H. Huang, F. Dong, *Appl. Catal. B*, **2018**, 232, 69–76.

Mg/O共同修饰无定形氮化碳的独特电子结构增强光催化对四环素盐酸盐的降解

吴晓璐, 傅敏*, 卢鹏, 任秋燕, 汪成

重庆工商大学环境与资源学院, 重庆市催化与环境新材料重点实验室, 重庆400067

摘要: 近年来, 光催化技术被广泛应用于环境和能源领域. 其中, g-C₃N₄因化学稳定性和热稳定性好、能带结构易调控而成为一种有前景的可见光光催化剂. 然而, g-C₃N₄的电子-空穴对易复合, 导致其不能充分利用太阳光, 光催化效率并不理想. 本文通过实验与理论结合的方法设计并制备了具有独特电子结构的Mg/O共同修饰的无定形氮化碳(记为MgO-CN), 以30 mg/L的四环素盐酸溶液(TC)作为目标污染物评价了其光催化性能. 经X射线衍射、扫描电镜、透射电镜、N₂物理吸附、紫外-可见光谱等表征手段分析表明, MgO-CN样品(002)晶面的衍射峰强度随着MgO含量增加而减弱, CN趋向于无定形化. 同时, MgO-CN样品的可见光吸收边带发生红移, 呈现出更强的可见光吸收能力. 此外, Mg原子和O原子共同修饰的独特电子结构可以通过C→O←Mg的电子传递路线在O原子周围产生局域电子, 从而抑制电子-空穴的复合.

光催化降解TC的实验结果表明, 在可见光照射后, 含有1.2 wt% MgO的复合样品MgO-CN-1.2具有最佳光催化活性, TC降解效率为82.0%, 比g-C₃N₄的光催化效率(23.5%)高出58.5%, 且光催化降解过程符合准一级动力学, MgO-CN-1.2的反应速率常数(0.01018 min⁻¹)是g-C₃N₄(0.00205 min⁻¹)的5倍. 自由基捕获测试实验表明, g-C₃N₄和MgO-CN-1.2样品均可以产生•O₂⁻自由基和•OH自由基, 但是MgO-CN-1.2样品的•O₂⁻和•OH信号更强. 这是由于MgO-CN-1.2样品可以吸收更大范围的可见光用于激发电子, 同时结合理论计算证明, MgO-CN内部电子在O原子周围汇集, 形成的电子定向传输通道对催化剂表面的电子-空穴复合有抑制作用, 更加有利于电子的迁移而诱导O₂生成•O₂⁻. 由于MgO-CN-1.2和g-C₃N₄的价带位置分别位于1.47和1.60 eV, 此价带上的h⁺不能与H₂O和OH⁻直接反应生成•OH, 而是由生成的•O₂⁻再与H⁺和e⁻按照O₂ → •O₂⁻ → H₂O₂ → •OH的反应途径生成•OH. 本文最后分析, MgO-CN复合物参与反应的主要活性物种为•O₂⁻, •OH和h⁺光催化降解污染物的反应机理. 其中, •O₂⁻对光催化降解TC的贡献最大, 为最主要的活性物质. 本文工作提供了一种新的策略来改变氮化碳的电子结构, 对提高其催化性能具有积极意义.

关键词: 氮化硅; 电子结构; 可见光光催化; 四环素盐酸盐降解; 环境修复

收稿日期: 2018-12-10. 接受日期: 2019-01-09. 出版日期: 2019-05-05.

*通讯联系人. 电话/传真: (023)62768474; 电子信箱: fumin1022@126.com

基金来源: 重庆市社会民生科技创新专项(cstc2016shmszx20012); 重庆市高校优秀成果转化资助项目(KJZH17122); 国家自然科学基金(5160080705); 重庆工商大学重点实验室开放项目(1556036); 重庆市教委科学技术研究项目(KJ130704); 重庆工商大学创新型科研项目(yjscxx2016-060-34).

本文的电子版全文由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).