碳化 MoS₂/掺硫 g-C₃N₄异质结的合成及其 在可见光下催化降解罗丹明 B 机理

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摘要:为了进一步提高聚合物半导体类石墨相氮化碳(g-C₃N₄)降解有机物的活性,通过简单的水热法复合得到碳化 MoS₂/掺硫g-C₃N₄异质结(MoSC/S-CN),并在可见光下研究其罗丹明 B(RhB)的降解性能。结果表明,相较于纯g-C₃N₄,最优化的 MoSC/S-CN 样品对可见光的吸收范围得到明显拓宽,并且在 100 min 内对 RhB 的降解效率为 92.5%,比纯g-C₃N₄性能提高 68.83%。一系列 的结构和光学性质表明,掺硫后再进一步与碳化 MoS₂耦合可以协同作用于g-C₃N₄,改善g-C₃N₄的能带结构,加速光生电子空穴 对的分离,有效提高光催化活性。

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Carbonized MoS₂/S-Doped g-C₃N₄ Heterojunction: Synthesis and Catalytic Degradation Mechanism of Rhodamine B under Visible Light

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Abstract: To further improve the photocatalytic activity of polymeric semiconductor, graphitic carbon nitride (g- C_3N_4), for organic degradation, carbonized MoS₂/S-doped g- C_3N_4 heterojunction (MoSC/S-CN) was prepared simply by hydrothermal method. And it was used to degrade rhodamine B (RhB) under visible-light illumination. Based on the results, it turned out that the visible-light adsorption range of optimized MoSC/S-CN became much broader, and the corresponding RhB degradation efficiency under visible-light illumination within 100 min was 92.5%, which was 68.83% higher than that of pure g- C_3N_4 . Based on a series of structural and optical characterizations, it is clear that after S doping and further coupling with carbonized MoS₂, MoSC/S-CN shows a synergistic effect. The band structure of g- C_3N_4 changes, and the photo-induced electron-hole pair separation rate is enhanced, which improves the photocatalytic activity of g- C_3N_4 effectively.

Keywords: carbonized MoS₂; S-doped g-C₃N₄; semiconductor; heterojunction; visible light

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0 Introduction

Graphitic carbon nitride (g- C_3N_4), a polymeric semiconductor with advantages of low-cost, moderate band gap (2.7 eV), and super-stability, has been investigated widely and applied to a series of photocatalytic systems^[1-2]. However, the high recombination rate of photo-induced electron-hole pairs and undesired conductivity hinder the practical application of g- C_3N_4 .

Non-metal doping is an effective way to modify the electronic structure of $g - C_3 N_4$. Based on reported results, S-doped g-C₃N₄ (S-CN) shows broadened visiblelight absorption, higher photo-induced electron-hole pair separation rate, and faster carrier mobility^[3-4]. In addition, molybdenum disulfide (MoS₂), one kind of transition metal sulfides, has been used as a super co-catalyst in photocatalyst-based heterojunctions (such as MoS₂/g-C₃N₄^[5-8] and MoS₂/TiO₂^[7,9]) for its prominent features such as super efficiency and low cost. But its metallic edges and defects still limit the further application of those heterojunctions. Fortunately, further report showed that partially carbonized MoS₂ (MoSC) exhibited excellent metallic characterization, which makes a tremendous contribution to improving the conductivity of semiconductor and electronic structure adjustment^[10-13]. Therefore, it is worth exploring a new heterojunction made up of S-CN and MoSC, which can overcome some defects of g-C₃N₄ mentioned above.

In this work, we fabricated partially carbonized $MoS_2/sulfur$ -doped $g-C_3N_4$ heterojunction (MoSC/S-CN) for the first time. Structural properties, optical properties, and rhodamine B (RhB) photo-degradation performance of MoSC/S-CN were discussed. We also investigated a series of single and binary photocatalysts as comparisons.

1 Experimental

1.1 Materials

All the chemicals used were commercially available and without any further treatment. Ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, AR) and thiourea (CH_4N_2S , AR) were used to prepare MoS₂. Dicyandiamide ($C_2H_4N_4$, AR) was used in MoS₂ carbonization. Moreover, dicyandiamide, ammonium chloride (NH₄Cl, AR) and thiourea were used in S-CN nanosheet preparation. To clarify the photocatalytic activity of the samples, RhB, *p*-benzoquinone, tertiary butanol, and triethanolamine were used in a series of experiments. Anhydrous ethanol and pure water were used as solvents. All pure water used was made in our lab.

1.2 Synthesis

1.2.1 Synthesis of carbonized MoS₂

Typically, MoS_2 was firstly prepared according to the literature^[10]. Ammonium molybdate tetrahydrate (2.48 g) and 5.32 g thiourea were added into pure water (60 mL) under stirring. After stirring for 1 h, the solution was transferred to an autoclave with a Teflon lining of 100 mL. The crystallization was carried out in a temperature - constant oven at 200 °C for 24 h. Black solids were obtained after crystallization, and washed by water and anhydrous ethanol, then centrifuged for three times. The final black solids were dried under 60 °C for 24 h. The ground solid was MoS_2 . After that, 500 mg MoS_2 and 4 g dicyandiamide were mixed and calcined under $Ar - H_2$ at 450 °C. The final solid was MoSC.

1.2.2 Synthesis of S-doped $g-C_3N_4$

Typically, 3 g dicyandiamide, 15 g ammonium chloride, and 0.05 g thiourea were added into 50 mL ultrapure water and dissolved at 80 °C. Then, the stirring was kept until the mixture became a uniform powder mixture. The uniform powder was then put into a crucible and calcined in a muffler at 550 °C for 4 h, and the heating and cooling rate were 2 °C • min⁻¹. The obtained light-yellow powder was S-CN nanosheet.

1.2.3 Synthesis of carbonized MoS_2/S - doped g - C_3N_4 composites

MoSC/S-CN composites were fabricated by hydrothermal method. 0.5 g S-CN was dispersed in ethanol solution. Then, MoSC was also dispersed in ethanol solution. Four samples were made by adding specific amounts of MoSC (7.5, 15, 30 and 50 mg, respectively). Both S-CN and MoSC dispersions were treated by ultrasound for 1 h. After that, MoSC dispersion was added dropwise into S-CN dispersion and kept stirring for 1 h. Then the mixture was heated at 90 °C for 5 h within a sealed autoclave after treated by ultrasonic for 2 h. The obtained dry solids were ground and calcined at 300 °C for 2 h, and the heating and cooling rates were 5 °C \cdot min⁻¹. The prepared samples were marked as MoSC/S-CN-1.5%, MoSC/S-CN-3.0%, MoSC/S-CN-6.0% and MoSC/S-CN-10%, respectively.

For comparison, composites of $MoS_2/CN - 3.0\%$ and $MoS_2/S-CN-3.0\%$ were also prepared. The synthesis processes were the same as that of MoSC/S-CN-3.0% as described above except that MoSC and S-CNwere changed into MoS_2 and CN for $MoS_2/CN - 3.0\%$, and MoSC was changed into MoS_2 for $MoS_2/S-CN-3.0\%$.

1.3 Characterization

X-ray diffraction (XRD) was used for detecting the crystal phase of the samples (XRD-6100, Shimadzu Corporation, Japan). The wavelength of Cu target was 0.154 1 nm, the accelerating voltage was 40 kV, the accelerating current was 30 mA, the scan range was 2θ =5° ~80°, the scanning rate was 5 (°) \cdot min⁻¹ and the scanning step was fixed at 0.02°. Scanning electron microscopy (SEM) was used for observing the surface morphology of the samples (Sigma, Zeiss, Germany). It should be noted that the samples were ultrasonicated and treated by gold sputtering for 50 s before applied for SEM. The accelerating voltage was 20 kV. Highresolution transmission electron microscopy (HRTEM) was applied for observing the structure in detail (JEM 2100F, JEOL, Japan). The accelerating voltage was 200 kV. Photocatalytic reaction was carried out in a photochemical reaction instrument (XPA, Xujiang Electrics and Mechanics Manufacturing Company, China). Optical properties were separately measured by UV-visible diffuse reflection spectra (UV-Vis DRS, Lambda 750, PerkinElmer Corporation, UK) for powder samples, photoluminescence spectroscopy (PL, OmniPL -LF325, Zolix Corporation, China), X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo Scientific Corporation, USA), and electrochemical system for measuring photocurrent density, M-S (Mott-Schottky) plot and EIS (electrochemical impedance spectroscopy) Nyquist plot (CHI660E, Chenhua Instrument Limited Corporation, China). During using DRS, BaSO₄ was chosen as a reference, and the measurement range was from 200 to

800 nm. For PL, the Xeon lamp was the visible-light source, the activation wavelength was 325 nm, and the scanning range was from 300 to 800 nm. For XPS, Al $K\alpha$ was the source gun type, and the enegy step size was 1.0 eV.

1.4 Photocatalytic experiments

Typically, 50 mg photocatalyst was added in RhB solution (20 mg·L⁻¹, 50 mL) in a specific quartz tube under stirring. After stirring for 1 h under dark, the first sample (4 mL) was taken when the system showed the physical adsorption equilibrium, and the supernatant liquid was measured by UV-Vis spectrophotometer. Then the light (λ >420 nm) was turned on, and photocatalytic process began. The samples with the same volume were taken every 20 min. The initial concentration and concentration during photocatalytic process of the liquid was marked as c_0 and c, respectively. During the measurement for the photo - stability of optimized MoSC/S-CN heterojunction, the sample was washed and dried after every trial by centrifugation.

2 Results and discussion

2.1 Crystal structure and texture analysis

Fig. 1a shows the XRD patterns of MoS₂, MoSC, CN, S-CN, and MoSC/S-CN-3.0%, respectively. The peaks located at 2θ =13.1° and 27.4° are in accordance with the typical lattice interfaces of (100) and (002) of g-C₃N₄, respectively^[14]. Moreover, the XRD pattern of MoSC showed typical peaks of MoS₂ and MoSC at the same time. The peak of 14° indicates the (002) crystal plane of MoS₂, and the peak of 39.4° can be considered as the overlap between the lattice plane of Mo_2C (101) and MoS_2 (103), which are pretty in corresponding to the reported result^[10]. Because of the small amount of MoSC in MoSC/S-CN-3.0%, only some typical peaks of MoSC can be found. And an overlap between the peaks of $g - C_3 N_4$ (100) and MoSC (002) appeared and there was no impurity, which indicates that the target composite has been prepared successfully. The N₂ adsorption-desorption results are shown in Fig.1b. The specific surface areas for MoSC, S-CN and MoSC/S-CN-3.0% were calculated to be 41, 61 and 71 m²·g⁻¹, respectively. Obviously, more active sites should be

exposed on the surface of MoSC/S - CN - 3.0%, which faciliates higher photocatalytic activity.

From SEM images, we can find that after coupling of nanosheet-like MoSC (Fig. 2a) and silk-like S-CN nanosheet with significant wrinkle (Fig. 2b), the obtained MoSC/S-CN-3.0% showed a wide range of accumulations (Fig. 2c), which should be ascribed to the combination of MoSC and S-CN. Furthermore, the TEM and HRTEM images of MoSC/S-CN-3.0% (Fig.2d and 2e) show the apparent lattice spacings of 0.27 and 0.24 nm corresponding to MoS_2 (100) and Mo_2C (002), respectively. Obviously, MoSC/S-CN heterojunction with intimate contact surface has been prepared successfully.



Fig.1 (a) XRD patterns for MoSC, S-CN and MoSC/S-CN-3.0%, respectively; (b) Nitrogen adsorption-desorption isotherms (inset: pore-size distribution)



Fig.2 SEM images of (a) MoSC, (b) S-CN and (c) MoSC/S-CN-3.0%, and (d) TEM and (e) HRTEM images of MoSC/S-CN-3.0%, respectively

2.2 XPS analysis

The XPS survey spectrum (Fig. 3a) indicates that the main elements in MoSC/S-CN-3.0% are S, Mo, C, N and O, where O should be from the partial oxidation of the sample surface. The high-resolution XPS spectrum of C1s (Fig. 3b) displayed the peaks of standard C—C and sp^2 hybrid carbon within N—C=N at the binding energy of 284.8 and 288.2 eV, respective-



Fig.3 XPS spectra for (a) survey detection, (b) C1s, (c) N1s, (d) S2p and (e) Mo3d of MoSC-S-CN-3.0%; (f) DRS spectra, (g) PL spectra and (h) EIS Nyquist plots of CN, S-CN, MoS₂/S-CN-3.0% and MoSC/S-CN-3.0%, respectively

ly^[15-16]. Fig. 3c shows the high-resolution spectrum for N1s, and the peaks at 398.6, 399.5 and 401.1 eV correspond to sp^2 hybrid N within C—N=C, N—(C)₃ and C-N-H, respectively. The two peaks of the S2p spectrum at a binding energy of 161.8 and 163.0 eV (Fig. 3d) demonstrate the existence of thiophene-S (-C-S-C-) within S-CN^[17]. Besides, the high-resolution spectrum for Mo3d showed six fitted peaks (Fig. 3e). The peak at 226.1 eV should be attributed to the existence of S2s. The double peaks at 232.1 and 229.0 eV should be ascribed to the appearance of $Mo3d_{3/2}$, $Mo3d_{5/2}$ of $MoS_2^{[10]}$. The other two peaks at 230.8 and 228.0 eV derived from Mo^{2+} belong to Mo3dof Mo_2C . It should be noted that the peak at 235.1 eV illustrates the existence of Mo6+, which maybe from MoO_3 or $MoO_4^{2-[16,18]}$, which verify that Mo on the surface has been oxidized to some extent. Thus, MoSC has

conjoined well with S-CN in MoSC/S-CN-3.0%.

2.3 Light absorption properties

As shown by UV-Vis DRS spectra (Fig. 3f), compared with CN, S-CN shows much higher visible-light adsorption and the adsorption edge is broadened to some extent. After coupling with MoS₂, MoS₂/S-CN-3.0% behaved stronger visible-light adsorption and even had obvious adsorption for (near) IR light within a wavelength range of 600~700 nm. This result should be attributed to the excellent metallic characteristics of MoSC. The band gaps of CN, S-CN, MoSC, MoS₂/S-CN-3.0% and MoSC/S-CN-3.0% were calculated to be 2.65, 2.64, 1.12, 2.55 and 2.50 eV, respectively (Fig.S1).

The intensity of the emission peak in PL spectra decreased after a series of modifications for CN, and MoSC/S-CN-3.0% showed the lowest intensity, which demonstrates the highest photo-induced electron-hole

carriers separation efficiency of MoSC/S-CN-3.0% (Fig. 3g). In addition, the higher transfer efficiency of photo-induced carriers can also be indicated by the lower carrier transfer resistance of MoSC/S-CN-3.0% showed by EIS Nyquist plots (Fig.3h). The highest photocurrent density of MoSC/S-CN-3.0% further demonstrates the highest photo - induced carries separation efficiency (Fig.S2).

2.4 Photocatalytic performances

All the samples have been applied to RhB degradation under visible-light illumination (λ >420 nm) for



100 min (Fig. 4a). Among a series of single and binary samples, MoSC/S-CN-3.0% showed significantly enhanced photodegradation efficiency (92.50%), which was 68.83% higher than that of CN. The promising photocatalytic activity should be ascribed to the synergistic effect of MoSC and S-CN. It should be noted that excess incorporation of MoSC in the composite may retard the exposure of active sites and adsorption of light. Furthermore, MoSC/S-CN-3.0% was found to show excellent stability after four recycles for RhB degradation under the same conditions (Fig.4b).



Fig.4 (a) Comparison of photocatalytic activities of CN, S-CN, MoS₂/CN-3.0%, MoS₂/S-CN-3.0% and MoSC/S-CN with different MoSC mass fractions, respectively; (b) Stability of photocatalytic performance of MoSC/S-CN-3.0%

2.5 Mechanism

The role of active species on the photocatalytic activity of MoSC/S-CN-3.0% was investigated (Fig.5a). When tertiary butanol (•OH scavenger) was added, the RhB degradation efficiency hardly changed compared to the result without additives. When TEOA (h⁺ scavenger) was added, the RhB degradation efficiency showed an appropriate reduction of 50%. Moreover, after adding 1,4-benzoquinone for capturing $\cdot O_2^-$, the photocatalytic process had been retarded to a great extent, and the RhB degradation efficiency became slightly higher than that of RhB blank solution. Obviously, $\cdot O_2^-$ is the most crucial active species, and h⁺ behaves with moderate effects during the photocatalytic reaction.

Finally, the photocatalytic mechanism is proposed (Fig. 5b). Due to the narrow band gaps (E_g) of S - CN (2.64 eV) and MoSC (1.12 eV), both of S-CN and MoSC were activated under visible-light illumination, and

photo-induced electrons and holes were produced. Based on M-S plots (Fig.S3), the conductor band (CB) potentials of S-CN (-0.74 eV) and MoSC (-0.32 eV) were obtained. And because of $E_{g} = E_{CB} + E_{VB}$, the valence band (VB) potentials of S-CN and MoSC were calculated to be 1.90 and -0.80 eV, respectively. Obviously, S-CN showed a more negative CB potential than that of MoSC, and a more positive VB potential than that of MoSC, which makes both photo-induced electrons and holes transfer from S-CN to MoSC. Meanwhile, after coupling n-type S-CN and p-type MoSC, the p-n joint forms on the contact surface, and inner electric field forms^[19-20]. Therefore, it is difficult for the photoinduced electrons on CB of S-CN to transfer to CB of MoSC. The transfer is partially restricted. But the photo -induced holes accumulate continuously on the VB of MoSC. Thus, the photo-induced electrons and holes are separated effectively. Moreover, the photo-induced



Fig.5 (a) Free radical trapping experiments of MoSC/S-CN-3.0%; (b) Proposed mechanism of RhB photodegradation using MoSC/S-CN

electrons on CB of MoSC transfer to metallic Mo_2C . Then the photo-induced electrons and holes are further separated. As described above that $\cdot O_2^-$ and h⁺ are the main active species during the photo- degradation process, we can estimate that the photo-induced electrons on Mo_2C and CB of S-CN are trapped by O_2 to form $\cdot O_2^-$ radicals, and RhB is decomposed directly by $\cdot O_2^-$. At the same time, RhB is decomposed by photoinduced holes (h⁺) on the VB of MoSC as shown in Fig.5b. The construction of S-CN/MoSC heterojunction realizes the effective separation of photo-induced electron-hole pairs and makes significant contribution to degrading RhB under visible-light excitation.

3 Conclusions

In conclusion, S-doped $g-C_3N_4$ has been coupled with partially carbonized MoS_2 by simple hydrothermal method. The hybrid mass ratio of MoS_2/MoC_2 was optimized, and all the samples were analyzed by a series of physical and optical characterizations. Optimized carbonized MoS_2/S -doped $g-C_3N_4$ heterojunction showed a smaller band gap and appropriate VB and CB position for RhB degradation, which led to an ideal photocatalytic activity. The achievements provide a new way for discovering new materials for photocatalysis.

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References:

- [1] Ong W J, Tan L L, Ng Y H, Yong S T, Chai S P. Chem. Rev., 2016, 116:7159-7329
- [2] Prasad C, Tang H, Liu Q Q, Bahadur I, Jiang Y J. Int. J. Hydrogen Energy, 2020.45:337-379
- [3] Jiang L B, Yuan X Z, Pan Y, Liang J, Zeng G M, Wu Z B, Wang H. Appl. Catal. B, 2017,217:388-406
- [4] Zeng W X, Bian Y, Cao S, Zhu A Q, Qiao L L, Ma Y J, Tan P F, Ma Q Y, Dong R, Pan J. Appl. Surf. Sci., 2019,478:334-340
- [5] Li J, Liu E Z, Ma Y N, Hu X Y, Wan J, Sun L, Fan J. Appl. Surf. Sci., 2016,364:694-702
- [6] Li Y F, Zhou M, Cheng B, Shao Y. J. Mater. Sci. Technol., 2020,56:1-17
- [7] Liang Z Z, Shen R, Ng Y H, Zhang P, Xiang Q J, Li X. J. Mater. Sci. Technol., 2020,56:89-121
- [8] Bie C B, Cheng B, Fan J J, Ho W K, Yu J G. EnergyChem, 2021,3: 100051
- [9] Hu K H, Xian G H, Yu F X, Jia D S. J. Mater. Sci., 2010,45:2640-2648
- [10]Shao M M, Shao Y F, Ding S J, Tong R, Zhong X W, Yao L M, Ip W F, Xu B M, Shi X Q, Sun Y Y. ACS Sustainable Chem. Eng., 2019,7: 4220-4229
- [11]Zhao Z H, Qin F, Kasiraju S, Xie L X, Alam M K, Chen S, Wang D Z, Ren Z F, Wang Z M, Grabow L, Bao J M. ACS Catal., 2017,7:7312 -7318
- [12]Zhang K, Zhao Y, Zhang S, Yu H, Chen Y J, Gao P, Zhu C L. J. Mater. Chem. A, 2014,2:18715-18719
- [13]Jeon J, Lee J, Choi S, Lee B H, Song Y J, Cho J H, Yun H J, Lee S. ACS Nano, 2018,12:338-346
- [14]Qiu L F, Qiu X B, Li P, Ma M F, Chen X S, Duo S W. Mater. Lett.,

2020,268:127566

- [15]Qiu L F, Zhou Z W, Ma M F, Li P, Duo S W. Materials, 2019, 12: 3948-3964
- [16]Ye L J, Wang D, Chen S J. ACS Appl. Mater. Interfaces, 2016,8:5280-5289
- [17]Vinoth S, Mary Rajaitha P, Venkadesh A, Shalini Devi K S, Radhakrishnan S, Pandikumar A. Nanoscale Adv., 2020, 2: 4242 -
- 4250
- [18]Zeleke T S, Tsai M C, Weret M A, Huang C J, Hwang B J. ACS Nano, 2019,13:6720-6729
- [19]Ren H, Jia S, Wu Y, Wu S, Zhang T. Ind. Eng. Chem. Res., 2014,53: 17645-17653
- [20]Fan G D, Du B H, Zhou J J, Yu W W, Chen Z Y, Yang S W. Appl. Catal. B, 2020,265:118610