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Article

Promotion of activation ability of N vacancies to N₂ molecules on sulfur-doped graphitic carbon nitride with outstanding photocatalytic nitrogen fixation ability

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ABSTRACT

Nitrogen vacancies and sulfur co-doped g-C₃N₄ with outstanding N₂ photofixation ability was synthesized via dielectric barrier discharge plasma treatment. X-ray diffraction, ultraviolet-visible spectroscopy, N₂ adsorption, scanning electron microscopy, X-ray photoelectron spectroscopy, photoluminescence spectroscopy, and temperature-programmed desorption were used to characterize the as-prepared catalyst. The results showed that plasma treatment cannot change the morphology of the as-prepared catalyst but introduces nitrogen vacancies and sulfur into g-C₃N₄ lattice simultaneously. The as-prepared co-doped g-C₃N₄ displays an ammonium ion production rate as high as 6.2 mg·L⁻¹·h⁻¹·g_{cat}⁻¹, which is 2.3 and 25.8 times higher than that of individual N-vacancy-doped g-C₃N₄ and neat g-C₃N₄, respectively, as well as showing good catalytic stability. Experimental and density functional theory calculation results indicate that, compared with individual N vacancy doping, the introduction of sulfur can promote the activation ability of N vacancies to N₂ molecules, leading to promoted N₂ photofixation performance.

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1. Introduction

The nitrogen content of the earth is very abundant, and nitrogen accounts for 78% of the air composition. However, owing to the strong chemical and biological inertia of nitrogen, most living organisms cannot directly absorb it. Therefore, artificial nitrogen fixation technology has a very important impact on modern industry and agriculture. At present, the main artificial nitrogen fixation technology is the Haber–Bosch process, which has high energy consumption. This process has

not met the new requirements of modern industry, of being “energy saving, green, and environmentally friendly.” Therefore, it is urgent to develop new artificial nitrogen fixation technology. Photocatalytic redox technology is being paid more and more attention by researchers owing to its mild conditions, energy-saving potential, and environmental friendliness [1–3]. To date, this technology has been applied to multiple research fields, including degradation of organic matter, photohydrolysis of water to produce hydrogen, oxidative desulfurization, organic synthesis, and synthesis of hydrogen peroxide [4–8]. In

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particular, Schrauzer et al. [9] discovered the nitrogen photo-fixation process over an Fe-doped TiO₂ catalyst in 1977. Since then, photocatalytic nitrogen fixation technology has been considered to be one of the best alternatives to the traditional Haber–Bosch method.

Graphite carbon nitride (g-C₃N₄), a nonmetallic semiconductor material, has become a focus of active research in the fields of chemistry and the environment in recent years owing to its numerous advantages [10]. It has been applied in many fields, including gas storage [11,12], fuel cells [13,14], as well as photocatalysis [15,16]. Cao et al. [17] prepared amine-functionalized ultrathin graphitic carbon nitride for N₂ photofixation. The synthesized g-C₃N₄ nanosheets exhibited a large surface area, high reduction potential, enhanced charge-carrier separation rate, and promoted N₂ fixation ability. Hu et al. [18] synthesized flower like copper-doped g-C₃N₄ via a novel molten salt-assisted microwave process. The NH₄⁺ production rate for the as-prepared catalyst was 35-fold higher than that of neat g-C₃N₄. Li et al. [19] prepared KOH-treated g-C₃N₄ for N₂ photofixation using CH₃OH as a proton source. The etching of catalysts by KOH introduced the break of the C=N in the s-triazine of g-C₃N₄ and the graft of the K ion, leading to a promoted charge separation and N₂ fixation ability. However, owing to the lower light energy density and mild reaction conditions, the reactant N₂ molecules are difficult to activate, which makes the photocatalytic nitrogen fixation performance unsatisfactory. Recent studies have shown that surface defects of the catalyst can effectively adsorb and activate reactant molecules. Dong et al. [20] and Ma et al. [21] reported that, as surface defects, nitrogen vacancies could activate N₂ and promote interfacial electron transfer, leading to an improved N₂ photofixation ability. Hu et al. [22] and Li et al. [23] found that sulfur vacancies in ternary metal sulfide and oxygen vacancies in Bi-OBBr nanosheet have a similar effect on N₂ photofixation.

Among the metal and nonmetal doping elements, sulfur is one of the most effective [24,25]. The sulfur doping into the g-C₃N₄ lattice can induce intrinsic electronic and band structure modulation, resulting in a shift in the absorbance edge and enhanced photocatalytic performance. In this work, N vacancies and sulfur co-doped g-C₃N₄ was prepared by dielectric barrier discharge plasma treatment. Compared with individual N vacancy doping, the introduction of sulfur can promote the activation ability of N vacancies to N₂ molecule, leading to enhanced N₂ photofixation performance. Density functional theory (DFT) calculation results confirm this point of view.

2. Experimental

2.1. Preparation and characterization

Dicyandiamide was ground for 30 min, and transferred into a crucible with a cover. The crucible was annealed at 520 °C for 2 h under an Ar atmosphere. The prepared neat g-C₃N₄ was denoted as GCN. The N vacancies and sulfur co-doped g-C₃N₄ was prepared using a DBD reactor. A mass of 0.3 g of GCN was placed into a quartz tube. Ar was allowed to pass through the quartz tube for 5 min to displace the air. With a constant H₂S

flow (50 mL/min), a high voltage of ~10 kV was supplied by a plasma generator. The discharge was maintained for 30 min, and the frequency was approximately ~10 kHz. The obtained sample was denoted as V_N-SCN. For comparison, N-vacancy-doped g-C₃N₄, V_N-CN was prepared by the same discharge procedure as V_N-SCN, but using H₂ instead of H₂S. A sulfur-doped catalyst, with the same sulfur content in the catalyst, was prepared according to previous work [24]. A mass of 0.1 g of GCN was annealed at 450 °C for 1 h at a rate of 2.5 °C/min under an H₂S atmosphere. The obtained catalyst was denoted as SCN.

The catalyst structure and optical properties were determined by X-ray diffraction (XRD, Rigaku D/max-2400) and ultraviolet-visible (UV-Vis) spectroscopy (JASCO-V-550), respectively. The catalyst morphology was observed using scanning electron microscopy (SEM, JSM 5600LV, JEOL Ltd.). The catalyst component was measured by elemental analysis (Elementar Analysensysteme GmbH). X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250 XPS system) was used to analyze the surface state of the catalyst. Al K_α radiation was used as the excitation source. Nitrogen adsorption-desorption isotherms were measured using a Micromeritics 2010 analyzer. The specific surface area (*S*_{BET}) was calculated according to the adsorption isotherm. The adsorption capacity of the reactant on the catalyst surface was measured by temperature-programmed desorption (TPD, CHEMBET-3000, Quantachrome). Photoluminescence (PL, FP-6300) spectra were acquired to investigate the charge transfer efficiency of the as-prepared catalyst.

Cambridge Serial Total Energy Package (CASTEP) plane-wave code has been executed for all the DFT calculations. The Perdew-Wang 91 function within the generalized gradient approximation (GGA) was used to calculate the exchange and correlation interactions, and the OBS method was used for the DFT-D correction. The k-points of all the slabs were separated by the scale of 0.02 per angstrom, and the cut-off energy was set to 400 eV. The C₃N₄ and the related slabs were separated from their periodic image in the z-direction by a vacuum space of 20 Å, which was adequate to eliminate any interactions between adjacent slabs.

2.2. Photocatalytic reaction

N₂ photofixation ability of the catalyst was measured by the following method. A 250-W high-pressure sodium lamp (800 > λ > 400 nm) was used as a visible light source. Sodium nitrite aqueous solution (0.5 mol/L) was used to filter the ultraviolet light portion of the light source. A mass of 0.2 g of the catalyst was dispersed into 500 mL of deionized water under stirring. Methanol (0.2 mL) was added into the suspension to trap the holes. Under the stirring, the light was turned on, and nitrogen gas at a flow rate of 80 mL/min was bubbled. Samples of volume 5 mL were obtained at given time intervals by centrifuging the suspension. The NH₄⁺ concentration was obtained by the Nessler's reagent spectrophotometry method (JB7478-87) [23,26].

Table 1

Influence of plasma treatment time on nitrogen photofixation activity of as-prepared catalysts.

Plasma treated time (min)	NH ₄ ⁺ production rate (mg·L ⁻¹ ·h ⁻¹ ·g _{cat} ⁻¹)
15	2.5
30	6.2
45	4.0

3. Results and discussion

The influence of the plasma treatment time on the nitrogen photofixation activity is shown in Table 1. It can be seen that the activity of the catalyst is first increased and then decreased as the treatment time is prolonged. The optimal plasma treatment time is 30 min. The photocatalytic nitrogen fixation abilities of GCN, SCN, V_N-CN, and V_N-SCN are displayed in Fig. 1a. No NH₄⁺ is formed without light, nitrogen, and photocatalyst, indicating that the photocatalytic N₂ fixation reaction occurs. GCN shows the extremely low NH₄⁺ production rate, 0.24 mg·L⁻¹·h⁻¹·g_{cat}⁻¹. For SCN and V_N-CN, the NH₄⁺ production rate obviously increases to 1.3 and 2.6 mg·L⁻¹·h⁻¹·g_{cat}⁻¹, respectively. This suggests that plasma treatment can enhance the N₂ photofixation ability of the as-prepared catalyst. V_N-SCN exhibits the highest NH₄⁺ production rate of 6.2 mg·L⁻¹·h⁻¹·g_{cat}⁻¹, which is over 25.8, 4.7, and 2.3 times higher than those of GCN, SCN, and V_N-CN, respectively.

As shown in Fig. 1b, when *N,N*-dimethylformamide (DMF, aprotic solvent) is used to replace water, no NH₄⁺ is generated over V_N-SCN. When AgNO₃ is used to trap the photogenerated electrons, the NH₄⁺ production rate also sharply decreases. These results provide a preliminary mechanism for the nitrogen fixation process. The photogenerated electrons are the

reactive species, and the water provides the protons to form NH₄⁺, as shown in Eq (1):

Figure 1c shows that the NH₄⁺ production rate for V_N-SCN remains stable after 20 h of reaction, indicating its good catalytic stability. Figure 1d displays the photocatalytic activity of reused V_N-SCN. The reaction time for each cycle is 20 h. No distinct decrease in NH₄⁺ production rate after five cycles is observed, confirming the good catalytic stability of V_N-SCN. In addition, other catalysts are also prepared and their photocatalytic N₂ fixation abilities are compared in Fig. 1e [26–28]. It can be seen that the NH₄⁺ production rate of V_N-SCN is even higher than that of noble metal Ru-loaded TiO₂, and obviously higher than other catalysts.

To confirm the nitrogen source of NH₄⁺, isotopic labeling experiments were carried out according to previous work [28]. The N₂ photofixation ability of V_N-SCN under ¹⁵N isotope-labeled N₂ was performed. The results shown in Fig. 1f indicate that a strong signal for ¹⁵N-labeled indophenol is observed in LC-MS studies, the intensity of which is distinct higher than that of the ¹⁴N:¹⁵N natural abundance ratio. This confirms that the generated NH₄⁺ comes from the N₂ photofixation process.

Figure 2a shows XRD patterns of the as-prepared GCN, SCN, V_N-CN, and V_N-SCN. Two distinct peaks located at 13.1° and 27.5° are observed for GCN, which should be attributed to the (100) and (002) crystal planes of g-C₃N₄, respectively (JCPDS87-1526). For the plasma-treated catalysts, similar characteristic peaks are shown. However, the obvious shifts to higher 2θ values are observed for the plasma-treated catalysts, which are likely due to the introduction of sulfur and nitrogen vacancies into the g-C₃N₄ lattice. It has been reported that the introduction of nitrogen vacancies can localize the electrons,

Fig. 1. N₂ photofixation ability over as-prepared catalysts (a), NH₄⁺ production ability of V_N-SCN in aprotic solvents DMF or using AgNO₃ as the electron scavenger (b), catalytic stability of V_N-SCN (c), N₂ photofixation ability of reused V_N-SCN (d), comparison of NH₄⁺ production rates of V_N-SCN and other catalysts (e), and mass spectra of indophenol prepared from different atmospheres (f).

Fig. 2. XRD patterns (a), UV-Vis spectra (b), plots of transformed Kubelka-Munk function versus the light energy (c), and N_2 adsorption-desorption isotherms (d) of as-prepared catalysts.

which change the catalyst structure [21,29]. In the case of sulfur doping, compared with replaced carbon or nitrogen, the higher electronegativity of sulfur causes a stronger interaction between the g- C_3N_4 layers. Thus, the interplanar distance is decreased after sulfur doping, leading to the change in the catalyst structure. No obvious difference in the peak intensity and width is observed among these catalysts, indicating that plasma treatment does not change the particle size of the catalyst.

The optical property of GCN, SCN, V_N -CN, and V_N -SCN is investigated by UV-Vis spectroscopy. As shown in Fig. 2b, GCN shows an absorption edge of ~ 460 nm. For SCN and V_N -CN, obvious red-shifts of the absorption edges are observed. Because of the co-doping effect, V_N -SCN displays the further red-shift of the absorption curve. The bandgaps, calculated by Kubelka-Munk functions [30], are 2.66, 2.57, 2.54, and 2.49 eV, respectively, for GCN, SCN, V_N -CN, and V_N -SCN (Fig. 2c). In general, S_BET can determine the number of reactive centers, thereby affecting the catalytic activity. Figure 2d shows the N_2 adsorption and desorption isotherms of GCN, SCN, V_N -CN, and V_N -SCN. All the catalysts exhibit isotherms of type IV. The S_BET for GCN, SCN, V_N -CN, and V_N -SCN are 8.8, 9.0, 8.7, and 9.2 m^2/g , respectively. No significant difference was observed among them, indicating that the plasma treatment does not change the S_BET value of the as-prepared catalyst. To confirm the presence of nitrogen vacancies, the C/N ratio of the as-prepared catalyst was measured by elemental analysis. The result shows that the C/N ratio of GCN is 0.74. The value for V_N -CN increases to 0.78, indicating the presence of nitrogen vacancies. For SCN, the C/N ratio is 0.76, which is again higher than that of GCN. This result indicates that the sulfur is likely doped into the g- C_3N_4 lattice by replacing N atoms, leading to the increased C/N ratio. In the case of V_N -SCN, the C/N ratio is further promoted to 0.81, which

is presumably due to the co-doping effect. In addition, the sulfur contents in SCN and V_N -SCN are very close (0.65 wt% and 0.67 wt%, respectively).

SEM was used to observe the morphology of the prepared catalysts. As shown in Fig. 3a, GCN displays a graphite-like layered structure. For the plasma-treated catalysts (Fig. 3b–3d), the similar morphology of the layered structure is observed. No remarkable difference is observed among the four catalysts, indicating that plasma treatment does not affect the catalyst morphology.

The surface states of the as-prepared catalysts were determined by XPS. As shown in Fig. 4a (C 1s region), the XPS curve of GCN can be divided into three peaks. The peak at 284.6 eV is the adventitious carbon. The peak around 285.9 eV is assigned to the terminal $\text{C}-\text{NH}_x$ in the heptazine unit. The peak with the binding energy of 287.9 eV is attributed to the sp^2 hybridized C atom ($\text{N}-\text{C}=\text{N}$) in the ring structure [31]. For V_N -CN, the similar

Fig. 3. SEM images of GCN (a), SCN (b), V_N -CN (c), and V_N -SCN (d).

Fig. 4. XPS spectra of as-prepared catalysts in the region of C 1s (a), N 1s (b), S 2p (c), and VB XPS (d).

peak positions to GCN are observed. In the case of the two sulfur-doped catalysts SCN and V_N -SCN, the binding energies are obviously shifted to higher values. This is probably due to the sulfur being doped into the g-C₃N₄ lattice by replacing the nitrogen atom next to the terminal C-NH_x in the heptazine unit, thereby leading to the change in the chemical environment of the two adjacent carbon atoms, as shown in Fig. 5. Because of the higher electronegativity of sulfur than nitrogen, the electron density of the carbon atoms adjacent to the sulfur atom decreases, causing the higher binding energy. In Fig. 4b, the N 1s spectra for all the catalysts can be divided into two peaks. The binding energies of 398.2 and 400 eV are assigned to the C=N=C and N-(C)₃ bonds in g-C₃N₄, respectively [32]. No obvious peak position shift is observed among the four catalysts.

Fig. 5. Diagram of possible structure of V_N -SCN.

However, the peak area ratio for N-(C₃)/(C=N=C), as calculated by XPS data, is reduced from 0.20 for GCN and SCN to 0.17 for V_N -CN and V_N -SCN. This result definitely indicates that the N vacancies are located at the N-C₃ sites, as shown in Fig. 5.

In the S 2p region (Fig. 4c), it is clear that no binding energy is observed for GCN. The binding energies for SCN and V_N -SCN are located at 163.8 eV, which is attributable to the doping sulfur in the form of the S-C bond, as shown in Fig. 5 [33,34]. Figure 4d shows the valence band (VB) XPS results of the as-prepared GCN, SCN, V_N -CN, and V_N -SCN. The VB positions are estimated to be +1.70, +1.82, +1.84, and +1.97 V for GCN, SCN, V_N -CN, and V_N -SCN, respectively. Therefore, their conduction band (CB) positions, as calculated from the bandgap energy, should be -0.96, -0.75, -0.70, and -0.52 V. Because the redox potential of N₂/NH₃ is -0.0922 V [35], all the samples are theoretically feasible for the photocatalytic reduction of N₂ to NH₄⁺. It is noted that both sulfur doping and nitrogen vacancy introduction can shift the CB and VB to more positive positions. Because of the co-doping effect, the CB of V_N -SCN displays a shift of 0.44 V compared with GCN. It is known that a photocatalyst with a more positive CB position should show a lower reduction ability. However, the experimental result is just the opposite, indicating that the effect of doping on the band structure is not the main factor for the promoted photocatalytic activity.

In heterogeneous catalytic reactions, chemisorption is a key step to activate the reactant. Figure 6 displays the N₂-TPD curves of the as-prepared GCN, SCN, V_N -CN, and V_N -SCN. It is shown that only one desorption peak around 100–110 °C is observed for GCN, which should be assigned to the physical adsorption of N₂ molecules [36]. For SCN, almost the same desorption curve as that for GCN is shown. In the case of the nitrogen-vacancy-doped catalysts, V_N -CN and V_N -SCN, apart from

Fig. 6. N_2 -TPD of as-prepared GCN, SCN, V_N -CN, and V_N -SCN.

the physical adsorption near 100 °C, another desorption peak at ~220 °C can be clearly observed. This peak should be attributed to the chemical adsorption of N_2 molecules on the catalyst surface, indicating that the nitrogen vacancies can act as chemical adsorption sites to activate the N_2 molecules. This is consistent with previous results [20,21]. Moreover, it is shown that the desorption peak area for V_N -SCN at ~220 °C is much larger than that for V_N -CN. It is deduced that the introduction of sulfur can increase the activation ability of the nitrogen vacancies to the adsorbed N_2 molecules.

Figure 7a shows PL spectra of the as-prepared GCN, SCN, V_N -CN, and V_N -SCN. The excitation wavelength is 380 nm. GCN displays a broad fluorescence emission peak, the wavelength of which is close to its absorption edge shown in the UV-Vis spectrum. SCN, V_N -CN, and V_N -SCN show similar PL spectra to GCN, whereas their intensities are obviously lower. This indicates that both nitrogen vacancies and doped sulfur can promote the separation rate of electron-hole pairs [37,38]. The PL intensities of GCN, SCN, V_N -CN, and V_N -SCN under Ar and N_2 atmospheres are compared and shown in Fig. 7b. It is shown that, for GCN and SCN, the atmosphere does not influence their PL intensities. However, in the case of nitrogen-vacancy-doped catalysts, V_N -CN and V_N -SCN, the PL intensity under an N_2 atmosphere is much lower than that under an Ar atmosphere. This indicates that the atmosphere can influence the charge separation

efficiency of nitrogen-vacancy-doped catalysts, but not GCN and SCN. This is probably due to the fact that N vacancies could trap the photogenerated electrons, and subsequently transfer these electrons to the adsorbed nitrogen molecules. Because the two bonding orbits of the N_2 molecule are occupied, the transferred photoelectron has to occupy the empty antibonding orbits, causing the N_2 activation (Fig. 7b inset). However, this electron-transfer phenomenon cannot occur under the Ar atmosphere, leading to the different charge-separation efficiency.

DFT calculations are used to confirm the effect of sulfur doping on the activation of N_2 molecules over nitrogen vacancies. Figure 8 shows the optimal N_2 adsorption model and the charge density difference of the N_2 molecule adsorbed on V_N -CN and V_N -SCN. The optimized models show that, for both V_N -CN and V_N -SCN, N_2 is chemisorbed at the nitrogen vacancy by bonding with the three nearest C atoms. The $N\equiv N$ bond length for a free N_2 molecule is 1.157 Å [18,28]. This value increases to 1.331 Å when N_2 chemisorbs over V_N -CN. In the case of V_N -SCN, the $N\equiv N$ bond length further increases to 1.415 Å. In addition, the adsorption energies (E_{ab}) of an N_2 molecule on the nitrogen vacancies are -3.52 and -4.54 eV for V_N -CN and V_N -SCN, respectively. It is known that the larger the E_{ab} , the lower the adsorption capacity. These results indicate that the introduction of sulfur can promote the activation ability of the nitrogen vacancies to the adsorbed N_2 molecules.

In order to confirm that the electrons transfer between N_2 molecules and catalyst, the charge density difference of the N_2 adsorbed on V_N -CN and V_N -SCN is compared. The light pink and green isosurfaces stand for the charge accumulation and depletion, respectively. The results shown in Fig. 8 indicate that, for both V_N -CN and V_N -SCN, the electron accumulation and depletion occur on the $N\equiv N$ bond and the nearest three C atoms of $g\text{-C}_3\text{N}_4$, respectively. This confirms that the electron-transfer process from the nitrogen vacancies to the adsorbed N_2 molecule occurs. Moreover, the electron density of the N_2 molecule adsorbed on V_N -SCN is much higher than that of on V_N -CN (-0.08 and -0.05 e for V_N -SCN and V_N -CN, respectively), confirming that the introduction of sulfur can endow the nitrogen vacancies with a higher electron-donating ability to activate N_2 molecules, leading to an increased N_2 photofixation ability.

Fig. 7. PL spectra of GCN, SCN, V_N -CN, and V_N -SCN under N_2 atmosphere (a) and a comparison of their PL intensities under Ar and N_2 atmospheres (b).

Fig. 8. Optimal N₂ adsorption model and the charge density difference of the N₂ molecule adsorbed on VN-CN (a) and VN-SCN (b).

4. Conclusions

In this work, N vacancies and sulfur co-doped g-C₃N₄ with outstanding N₂ photofixation ability was synthesized via dielectric barrier discharge plasma treatment. The plasma treatment cannot change the morphology of the as-prepared catalyst but introduces nitrogen vacancies and sulfur into the g-C₃N₄ lattice simultaneously, leading to enhanced visible light absorption and shifted band positions. The as-prepared co-doped g-C₃N₄ displays an ammonium ion production rate as high as 6.2 mg·L⁻¹·h⁻¹·g_{cat}⁻¹, which is 2.3 and 25.8 times higher than those of individual N-vacancy-doped g-C₃N₄ and neat g-C₃N₄, respectively, as well as showing good catalytic stability. Experimental and DFT calculation results indicate that, compared with individual N vacancy doping, the introduction of sulfur can increase the N≡N bond length and reduce the adsorption energy of the N₂ molecule, leading to a higher activation ability to the N₂ molecule. In addition, the electron density of the N₂ molecule adsorbed on VN-SCN is much higher than that on VN-CN, confirming that the introduction of sulfur can endow nitrogen vacancies with a higher electron-donating ability to activate N₂ molecules, leading to an increased N₂ photofixation ability.

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References

- [1] A. Fujishima, T. N. Rao, D. A. Tryk, *J. Photochem. Photobiol. C*, **2000**, 1, 1–21.
- [2] P. V. Kamat, *Chem. Rev.*, **1993**, 93, 267–300.
- [3] M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann, *Chem. Rev.*, **1995**, 95, 69–96.
- [4] S. Z. Hu, X. Y. Qu, P. Li, F. Wang, Q. Li, L. J. Song, Y. F. Zhao, X. X. Kang, *Chem. Eng. J.*, **2018**, 334, 410–418.
- [5] S. E. Guo, Z. P. Deng, M. X. Li, B. J. Jiang, C. G. Tian, Q. J. Pan, H. G. Fu, *Angew. Chem. Int. Ed.*, **2016**, 55, 1830–1834.
- [6] G. L. Li, C. S. Guo, M. Yan, S. Q. Liu, *Appl. Catal. B*, **2016**, 183, 142–148.
- [7] M. B. Ansari, H. L. Jin, M. N. Parvin, S. E. Park, *Catal. Today*, **2012**, 185, 211–216.
- [8] K. Chen, X. M. Zhang, X. F. Yang, M. G. Jiao, Z. Zhou, M. H. Zhang, D. H. Wang, X. H. Bu, *Appl. Catal. B*, **2018**, 238, 263–273.
- [9] G. N. Schrauzer, T. D. Guth, *J. Am. Chem. Soc.*, **1977**, 99, 7189–7193.
- [10] X. C. Wang, K. Maeda, X. F. Chen, K. Takanebe, K. Domen, Y. D. Hou, X. Z. Fu, M. Antonietti, *J. Am. Chem. Soc.*, **2009**, 131, 1680–1681.
- [11] Q. Li, J. Yang, D. Feng, Z. Wu, Q. Wu, S. S. Park, C. S. Ha, D. Zhao, *Nano Res.*, **2010**, 3, 632–642.
- [12] S. S. Park, S. W. Chu, C. Xue, D. Zhao, C. S. Ha, *J. Mater. Chem.*, **2011**, 21, 10801–10807.
- [13] Y. Zheng, J. Liu, J. Liang, M. Jaroniec, S. Qiao, *Energy Environ. Sci.*, **2012**, 5, 6717–6731.
- [14] Y. Zheng, Y. Jiao, J. Chen, J. Liu, J. Liang, A. Du, W. Zhang, Z. Zhu, S. C. Smith, M. Jaroniec, G. Lu, S. Qiao, *J. Am. Chem. Soc.*, **2011**, 133, 20116–20119.
- [15] T. Xiong, W. L. Cen, Y. X. Zhang, F. Dong, *ACS Catal.*, **2016**, 6, 2462–2472.
- [16] F. Dong, Z. W. Zhao, Y. J. Sun, Y. X. Zhang, S. Yan, Z. B. Wu, *Environ. Sci. Technol.*, **2015**, 49, 12432–12440.
- [17] S. H. Cao, H. Chen, F. Jiang, X. Wang, *Appl. Catal. B*, **2018**, 224, 222–229.
- [18] S. Z. Hu, X. Y. Qu, J. Bai, P. Li, Q. Li, F. Wang, L. J. Song, *ACS Sustain. Chem. Eng.*, **2017**, 5, 6863–6872.
- [19] X. M. Li, X. Sun, L. Zhang, S. M. Sun, W. Z. Wang, *J. Mater. Chem. A*, **2018**, 6, 3003–3011.
- [20] G. H. Dong, W. K. Ho, C. Y. Wang, *J. Mater. Chem. A*, **2015**, 3, 23435–23441.
- [21] H. Q. Ma, Z. Y. Shi, S. Li, N. Liu, *Appl. Surf. Sci.*, **2016**, 379, 309–315.
- [22] S. Z. Hu, X. Chen, Q. Li, Y. F. Zhao, W. Mao, *Catal. Sci. Technol.*, **2016**, 6, 5884–5890.
- [23] H. Li, J. Shang, Z. H. Ai, L. Z. Zhang, *J. Am. Chem. Soc.*, **2015**, 137, 6393–6399.
- [24] J. D. Hong, X. Y. Xia, Y. S. Wang, R. Xu, *J. Mater. Chem.*, **2012**, 22, 15006–15012.
- [25] K. Wang, Q. Li, B. S. Liu, B. Cheng, W. Ho, J. G. Yu, *Appl. Catal. B*, **2015**, 176–177, 44–52.
- [26] W. R. Zhao, J. Zhang, X. Zhu, M. Zhang, J. Tang, M. Tan, Y. Wang,

Graphical Abstract

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Promotion of activation ability of N vacancies to N_2 molecules on sulfur-doped graphitic carbon nitride with outstanding photocatalytic nitrogen fixation ability

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The introduction of sulfur can promote the activation ability of N vacancies to N_2 molecules, leading to the promoted N_2 photofixation performance of graphitic carbon nitride.

Appl. Catal. B, **2014**, 144, 468–477.

- [27] O. Rusina, O. Linnik, A. Eremenko, H. Kisch, *Chem. Eur. J.*, **2003**, 9, 561–565.
- [28] S. Z. Hu, X. Chen, Q. Li, F. Y. Li, Z. P. Fan, H. Wang, Y. J. Wang, B. H. Zheng, G. Wu, *Appl. Catal. B*, **2017**, 201, 58–69.
- [29] J. Ding, W. Xu, H. Wan, D. Yuan, C. Chen, L. Wang, G. Guan, W. L. Dai, *Appl. Catal. B*, **2018**, 221, 626–634.
- [30] Y. I. Kim, S. J. Atherton, E. S. Brigham, T. E. Mallouk, *J. Phys. Chem.*, **1993**, 97, 11802–11810.
- [31] C. Li, S. Yu, H. Dong, Y. Wang, H. Wu, X. Zhang, G. Chen, C. Liu, *J. Colloid Interface Sci.*, **2018**, 531, 331–342.
- [32] Y. W. Zhang, J. H. Liu, G. Wu, W. Chen, *Nanoscale*, **2012**, 4, 5300–5303.
- [33] G. Liu, P. Niu, C. H. Sun, S. C. Smith, Z. G. Chen, G. Q. Lu, H. M. Cheng, *J. Am. Chem. Soc.*, **2010**, 132, 11642–11644.
- [34] S. Z. Hu, L. Ma, F. Y. Li, Z. P. Fan, Q. Wang, J. Bai, X. X. Kang, G. Wu, *RSC Adv.*, **2015**, 5, 90750–90756.
- [35] K. Hoshino, *Chem. Eur. J.*, **2001**, 7, 2727–2731.
- [36] W. Lei, D. Portehault, R. Dimova, M. Antonietti, *J. Am. Chem. Soc.*, **2011**, 133, 7121–7127.
- [37] X. Y. Qu, S. Z. Hu, J. Bai, P. Li, G. Lu, X. X. Kang, *New J. Chem.*, **2018**, 42, 4998–5004.
- [38] S. J. Li, X. Chen, S. Z. Hu, Q. Li, J. Bai, F. Wang, *RSC Adv.*, **2016**, 6, 45931–45937.

硫掺杂石墨相氮化碳的光催化固氮性能中氮空穴对氮气分子活化的提升作用李 政^a, 顾贵洲^a, 胡绍争^a, 邹 熊^c, 武 光^{b,*}^a辽宁石油化工大学化学化工与环境学部, 辽宁抚顺113001^b黑龙江大学化学化工与材料学院, 农作物研究院, 黑龙江哈尔滨150080^c大连理工大学化工学院, 辽宁大连116012

摘要: 地球上的氮元素十分丰富并主要以氮气形式存在。然而, 由于氮的化学及生物惰性, 大多数生物体不能直接吸收氮。因此, 人工固氮过程被称为继光合作用之后的第二大化学反应。目前工业上常用的固氮技术为Haber-Bosch法, 该方法能耗高且使用的原料氢气十分危险。因此, 寻找更加节能、绿色、安全的固氮技术迫在眉睫。石墨相氮化碳作为一种非金属半导体光催化剂近年来受到研究者青睐。氮化碳化学性质稳定, 能带宽度适中, 且耐酸碱腐蚀。然而, 氮化碳的反应活性位较少, 量子效率较低, 而且由于光能的能量密度较低, 反应物 N_2 分子难以活化, 因此光催化固氮性能并不理想。

有研究报道称晶格缺陷能作为反应活性位活化氮气分子, 提高光催化固氮性能。本文采用介质阻挡放电等离子体法制备了硫和氮空穴共掺杂的石墨相氮化碳催化剂, 考察了硫的引入对催化剂光催化固氮性能的影响。XRD, UV-Vis和氮气

吸附结果表明, 掺杂未改变催化剂的比表面积, 但使得氮化碳催化剂晶格发生了细微扭曲, 且改变了催化剂的电子结构, 降低了能带宽度. 通过XPS结果推测了硫元素与氮空穴的相对位置, 并确定硫元素取代了氮元素, 以S–C键的形式掺入到催化剂晶格中. 采用N₂-TPD法分析了催化剂对氮气分子的吸附能力, 发现氮空穴是氮气分子的化学吸附位. 硫的引入能促进氮空穴对氮气分子的吸附与活化能力. PL光谱结果证实硫和氮空穴掺杂均对电子空穴对的分离有促进作用. 不同气氛下的PL光谱结果表明, 光电子能通过氮空穴从催化剂转移至吸附的氮气分子上. DFT计算结果显示, 氮气分子吸附在氮空穴上, 吸附后的N≡N键长为1.331 Å, 小于非吸附状态的N≡N键长(1.157 Å). 而引入硫以后, 氮气分子同样吸附在氮空穴上, N≡N键长进一步增大到1.415 Å, 且氮气分子的吸附能也显著降低. 这些结果都说明硫的引入提高了氮空穴对氮气分子的吸附和活化作用. 此外, 态密度图结果显示, 光电子通过氮空穴从催化剂向吸附的氮气分子转移, 且引入硫之后吸附的氮气分子上的电子密度明显提高, 进一步证实硫的引入对氮气分子的活化作用.

关键词: 石墨相氮化碳; 氮气光固定; 共掺杂; 光催化作用; 等离子体处理

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