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Article

Co-MOF as an electron donor for promoting visible-light photoactivities of g-C₃N₄ nanosheets for CO₂ reduction

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ABSTRACT

A possible mechanism for boosting the visible-light photoactivities of graphitic carbon nitride (g-C₃N₄) nanosheets for CO₂ reduction via coupling with the electron donor Co-metal-organic framework (MOF) is proposed in this study. Specifically, Co-MOF as an electron donor is capable of transferring the photogenerated electrons in the lowest unoccupied molecular orbital (LUMO) to the conduction band of g-C₃N₄ to facilitate charge separation. As expected, the prepared Co-MOF/g-C₃N₄ nanocomposites display excellent visible-light-driven photocatalytic CO₂ reduction activities. The CO production rate of 6.75 μmol g⁻¹ h⁻¹ and CH₄ evolution rate of 5.47 μmol g⁻¹ h⁻¹ are obtained, which are approximately 2 times those obtained with the original g-C₃N₄ under the same conditions. Based on a series of analyses, it is shown that the introduction of Co-MOF not only broadens the range of visible-light absorption but also enhances the charge separation, which improves the photocatalytic activity of g-C₃N₄ to a higher level. In particular, the hydroxyl radical (•OH) experiment was operated under 590 nm (single-wavelength) irradiation, which further proved that the photogenerated electrons in the LUMO of Co-MOF can successfully migrate to g-C₃N₄. This work may provide an important strategy for the design of highly efficient g-C₃N₄-based photocatalysts for CO₂ reduction.

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1. Introduction

A continuous increase in the concentration of carbon dioxide (CO₂) has led to enhanced greenhouse effect, which in turn has resulted in global warming [1–3]. In order to address this issue, photocatalytic reduction of CO₂ into renewable fuels is considered as an attractive and promising solution for directly converting solar energy into chemical products [4–6]. In fact,

since the first report on the utilization of TiO₂ for the photocatalytic reduction of CO₂ into organic chemical products in 1979, tremendous efforts have been devoted to developing high-efficiency catalysts for CO₂ photoreduction [7]. In recent years, various semiconductor photocatalysts, such as Zn₂GeO₄ [8], CdS [9], Fe₃O₄ [10], g-C₃N₄ [11], SrTiO₃ [12], and TiO₂ [13,14], have been researched for diverse photocatalytic applications, including CO₂ reduction. However, these semiconduc-

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tors either display large bandgaps, which lead to quite low visible-light-driven photoactivities, or are toxic, which causes additional environmental issues. Thus, seeking environmentally benign semiconductors with moderate bandgaps is the key to addressing the issue of global warming.

Recently, g-C₃N₄ has attracted much attention as one of the most promising semiconductor materials for visible-light-driven CO₂ reduction owing to its suitable bandgap energy (2.7 eV), pollution-free property, and good chemical and thermal stabilities [15]. However, the photocatalytic CO₂ reduction performance of current g-C₃N₄ photocatalysts is still far from that required for practical applications because of the limited light absorption capability and high recombination rate of the photogenerated electron-hole pairs, which severely affect the photocatalytic CO₂ reduction activity [16]. Thus, it is necessary to increase the charge separation rate of g-C₃N₄ to some extent in order to improve the visible-light-driven CO₂ reduction activity. A variety of methods have been developed to improve the charge separation efficiency and further enhance the overall activities of g-C₃N₄-based photocatalysts [17]. Among them, coupling g-C₃N₄ with other materials with suitable conduction band (CB) positions is one of the most promising solutions to improving the performance of the photocatalytic system, as it can increase the charge separation rate [18]. Cao et al. [19] reported much higher H₂ and CH₄ production rates under visible-light illumination by employing g-C₃N₄-In₂O₃ composite as a photocatalyst, than those obtained with g-C₃N₄. Shi et al. [20] also revealed a high photocatalytic CO₂ reduction activity by combining g-C₃N₄ with NaNbO₃ nanowires.

Extensive efforts have been taken to find a material that can be combined with g-C₃N₄ to boost the charge separation efficiency and thereby improve the photocatalytic CO₂ reduction performance. Recently, Co-metal-organic framework (MOF), a typical MOF, has received significant attention owing to its excellent features that offer promise in important applications in the photocatalytic field [21]. The narrower bandgap of Co-MOF leads to a wider range of visible-light absorption. Furthermore, its lowest unoccupied molecular orbital (LUMO) potential is highly negative and matches with the CB level of g-C₃N₄. Therefore, Co-MOF was selected for combining with g-C₃N₄ to improve the charge separation efficiency and enhance the photocatalytic activity of g-C₃N₄.

Based on the above discussion, a possible mechanism for enhanced photocatalytic CO₂ reduction of g-C₃N₄ nanosheets via coupling with the electron donor Co-MOF was proposed. As had been expected, a series of Co-MOF/g-C₃N₄ nanocomposites were fabricated that displayed remarkable photocatalytic CO₂ reduction activities that far exceeded that of pristine g-C₃N₄ nanosheets. Based on our analysis, the improved photocatalytic activity is attributed to the widened visible-light absorption range and to efficient charge separation between Co-MOF and g-C₃N₄. This work may provide a new perspective for promoting the photocatalytic performance of g-C₃N₄.

2. Experimental

2.1. Synthesis of samples

All the reagents used in this work were of analytical grade and employed without further purification. 2-Methylimidazole (2-Melm), cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O), methanol (CH₃OH), urea, and deionized water were used in all the reaction systems.

For the synthesis of g-C₃N₄, urea was heated at 550 °C for 4 h under N₂ atmosphere to prepare g-C₃N₄ nanosheets. Finally, the acquired light yellow product was ground for further experimental work, and the sample has been named CN here.

Co-based MOF materials were synthesized via the low-cost and large-scale coprecipitation method. In a typical synthesis, 2 mmol Co(NO₃)₂·6H₂O and 12 mmol 2-Melm were first dissolved in 30 mL and 10 mL methanol, respectively. Then, the solution of 2-Melm was added slowly to the solution of Co(NO₃)₂·6H₂O with vigorous stirring. After the two solutions were mixed thoroughly, the resulting solution was aged at room temperature for 24 h. The purple products obtained were centrifuged and washed with ethanol several times and then dried at 60 °C. Herein, the material has been named Co-MOF.

The composites Co-MOF/g-C₃N₄ were synthesized through a facile method. A certain amount of g-C₃N₄ was added to methanol and placed in an ultrasonic bath for 3 h to exfoliate the g-C₃N₄ completely. Then, Co-MOF of different masses was dispersed in the above solution with ultrasonication for 1 h. Finally, the suspension was dried at 60 °C. Here, the obtained samples of Co-MOF/g-C₃N₄ composed of 1%, 2%, 3%, 5%, 10%, 20%, and 50% Co-MOF (wt%) have been named Co-CN1, Co-CN2, Co-CN3, Co-CN5, Co-CN10, Co-CN20, and Co-CN50, respectively.

2.2. Characterization

The morphologies and sizes of the samples were analyzed by transmission electron microscopy (TEM; JEM-2100 electron microscope, Japan) and scanning electron microscopy (SEM; Hitachi, S-4800). X-ray diffraction (XRD) measurements were performed with a Bruker D8 Advance instrument using Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$). The Fourier transformed infrared (FT-IR) spectra were measured on a Perkin-Elmer Spectrum One spectrometer by using KBr pellets. The diffuse reflectance spectra (DRS) of the photocatalysts were obtained using a UV-visible spectrophotometer (SHIMADZU UV-2550) in the wavelength range 200–800 nm. Thermogravimetric analysis (TGA) was carried out from 20 °C to 800 °C in air atmosphere by using a thermal analyzer (TGA-7, Perkin-Elmer, USA). The N₂ adsorption and desorption isotherms were analyzed with Tristar II 3020. The pore size distribution charts were obtained by the Barrett-Joyner-Halenda method. The elemental compositions of the catalysts were determined using X-ray photoelectron spectroscopy (XPS; Kratos-AXIS ULTRA DLD apparatus with Al (mono) X-ray source). The photoluminescence (PL) spectra were measured by a Hitachi F-4600 fluorescence spectrophotometer loaded with a 150 W Xe lamp at the excitation wavelength of 370 nm.

2.3. Hydroxyl radical ($\bullet\text{OH}$) measurements

Coumarin fluorescence strategy was adopted to analyze the number of $\bullet\text{OH}$ produced during the photocatalytic reaction process. In this system, 50 mg of the product was dissolved in 40 mL aqueous coumarin solution (0.001 mol L^{-1}), and then, the solution was stirred adequately for 10 min and illuminated with a 300 W Xe lamp for 1 h. The solution was separated by centrifugation and poured into a Pyrex glass cell. The obtained solution was analyzed through fluorescence measurement of 7-hydroxycoumarin by using a spectrofluorometer at the excitation wavelength of 390 nm (Perkin-Elmer LS55).

2.4. Photoelectrochemical measurements

Photoelectrochemical measurements were carried out by using a computer-controlled CHI-660 electrochemical workstation (Chenhua Instrument, Shanghai, China) with a 300 W Xe arc lamp as the light source. The sample was transformed into a film that served as the working electrode, and a Pt foil and Ag/AgCl (with saturated KCl) were used as the counter and reference electrodes, respectively. Aqueous $0.5 \text{ mol L}^{-1} \text{ Na}_2\text{SO}_4$ solution was used as the electrolyte. Before the experiments, high-purity N_2 gas was passed through the electrolyte for 30 min. For preparing the working electrodes, conductive fluorine-doped tin oxide (FTO)-coated glasses were used as substrates after thoroughly washing them with ethanol and deionized water. The working electrodes were prepared as follows. 0.1 g of the as-prepared sample was added to 1 mL isopropyl alcohol under vigorous stirring. 0.05 g of Macrogol-2000 was added to the above solution and thoroughly mixed using ultrasonic irradiation for 10 min. After that, the suspension was subjected to vigorous stirring for 30 min, and then, 0.05 mL acetylacetone was added to it. The obtained solution was kept under adequate stirring for a week. The mixture was painted onto a $1 \text{ cm} \times 1 \text{ cm}$ FTO glass electrode, which was the efficient surface area, by doctor blade method. Finally, the electrode was dried at room temperature and annealed at 150°C for 2 h under N_2 atmosphere. The specific CO_2 electrochemical reduction step was procedurally the same as the photoelectrochemical measurements mentioned above, except that the Na_2SO_4 electrolyte was introduced into CO_2 instead of N_2 before the test.

2.5. Catalytic performance

The photocatalytic performance of the typical samples was evaluated for visible-light-driven CO_2 reduction. The entire reaction took place in a 100 mL cylindrical steel reactor at room temperature and the irradiation area was 3.5 cm^2 . 20 mg of the powder sample was dispersed in 4 mL water under constant stirring and then loaded into the reactor. High-purity CO_2 was passed through the reaction system to remove air and establish a balance between adsorption and desorption before the irradiation. The samples were irradiated using a 300 W Xe lamp with a 420 nm cutoff filter (PLSSXE300/300UV, Perfect-light, Beijing), and the light intensity was 455 mW cm^{-1} . Finally, the generated gases were analyzed and quantified using a gas

chromatograph (GC2002). All the photocatalytic reactions were measured twice and the data reported are the average values to ensure accuracy.

3. Results and discussion

The morphological properties of the typical samples were characterized by TEM and SEM (Fig. 1). The ultrathin nanosheets observed for pure CN are shown in Fig. 1(a) and Fig. 1(d). The high surface-to-volume ratio of these ultrathin nanosheets significantly increased the number of reaction-active sites, which facilitated the photocatalytic reduction [22]. In addition, Fig. 1(b) and Fig. 1(e) show that the Co-MOF structure was successfully deposited on the surface of CN while the nanosheets structure remained intact. Fig. 1(c) and Fig. 1(f) show the polyhedral structure and solid texture of pure Co-MOF, respectively. The color of pure Co-MOF is bright purple. Therefore, with the increase in Co-MOF content of the nanocomposite, the color of Co-MOF/g- C_3N_4 gradually changed to purple.

The crystal structures and the phases of the products were obtained by XRD. Fig. 2(a) shows the XRD patterns of the original CN, Co-MOF, and Co-MOF/g- C_3N_4 nanocomposites. The sharp peaks observed in the XRD pattern of Co-MOF indicate that an advanced crystalline material was obtained. This is consistent with the results in previous reports [23–25]. Thus, we successfully synthesized Co-MOF. The two diffraction peaks observed at 13.3° and 26.7° in the XRD pattern of pristine CN are attributed to the in-plane trigonal N linkages of tri-triazine units and to the stacking of conjugated aromatic systems, respectively [26]. It is obvious that, with the increase in the amount of Co-MOF, the peaks at 13.3° and 26.7° are weakened. Moreover, the composites with higher Co-MOF contents showed the diffraction peaks of CN and Co-MOF distinctly, which indicated a two-phase composition of CN and Co-MOF in these samples.

The FT-IR spectra of the photocatalysts are shown in Fig. 2(b). For the Co-MOF samples, the bands observed between 600 and 1500 cm^{-1} are attributed to the stretching and bending modes of the imidazole ring. The peak observed at 1580 cm^{-1} is assigned to the stretching mode of the $\text{C}=\text{N}$ bond in the ligand

Fig. 1. SEM images of (a) CN, (b) Co-CN2, and (c) Co-MOF, and TEM images of (d) CN, (e) Co-CN2, and (f) Co-MOF.

Fig. 2. (a) XRD patterns; (b) FT-IR spectra; (c) UV-vis DRS; (d) Bandgap patterns; (e) N₂ adsorption-desorption isotherms; (f) TGA curves.

2-Melm. The bands at 2929 and 3135 cm⁻¹ originated from the stretching of the C–H bond of the aromatic ring and the aliphatic chain of 2-Melm, respectively [27]. The bands of 1200–1700 cm⁻¹ are primarily attributed to the typical stretching vibrations of CN heterocycles. The peaks in the range 3000–3500 cm⁻¹ correspond to the stretching vibration modes of NH and NH₂ groups. The peak observed at around 811 cm⁻¹ in the spectrum of CN corresponds to the typical breathing mode of the triazine unit. The characteristic peak intensity of Co-MOF decreased gradually with the decrease in the amount of Co-MOF, and the peak disappeared eventually. Notably, the peak at 811 cm⁻¹ for CN shifted to a higher wavenumber for Co-CN50 composite, as shown in the inset of Fig. 2(b), which indicated the existence of some interactions between CN and Co-MOF; unfortunately, when the Co-MOF content was low, this phenomenon was not obvious [28].

The optical absorptions of pure CN, Co-MOF, and Co-MOF/g-C₃N₄ composite samples were analyzed using their UV-vis DRS. As observed in Fig. 2(c), CN displayed only weak visible-light absorption at ~460 nm, whereas Co-MOF exhibited an intense absorption band in the range 420–700 nm. Notably, compared with that of CN, the Co-MOF/g-C₃N₄ composites showed increased absorptions (by different degrees) in the visible-light region. Meanwhile, the absorption edges of the composites slightly red-shifted with the increase in Co-MOF content, which indicated increased absorption ability in the visible region, compared to that of CN, thereby, more electron-hole pairs were generated in the photocatalytic process [29]. It is expected that the composites will show improved photocatalytic activity compared to that of CN because of the higher number of photocarriers generated in the reaction system [30]. As shown in Fig. 2(d), the bandgap energies (E_g) of

the photocatalysts were calculated from Tauc's plots using $(\alpha h\nu)^{1/2} = A(h\nu - E_g)$, where α , h , ν , E_g , and A are the absorption coefficient, Planck's constant, light frequency, bandgap energy, and a constant, respectively [31]. Thus, the E_g of CN, Co-CN2, Co-CN10, and Co-MOF are approximately 2.70, 2.67, 1.96, and 1.94 eV, respectively.

The BET surface areas of the samples were obtained from the N₂ adsorption-desorption isotherms. Fig. 2(e) shows that the BET area of Co-MOF is 2149.13 m² g⁻¹, which is due to the unique structure of Co-MOF. After the Co-MOF modification, the BET area of the Co-MOF/g-C₃N₄ nanocomposite increases, which is beneficial for improving the photocatalytic activity [32,33]. The CO₂ adsorptions of CN and Co-CN2 in air and CO₂ gas were separately investigated by infrared spectroscopy (though the results are not shown in this article). In air, the CO₂ adsorption peak area of Co-CN2 sample is 1.77 times that of pure g-C₃N₄. Similarly, the CO₂ adsorption peak area of Co-CN2 sample is 2.18 times that of pure g-C₃N₄ in CO₂ gas. The photocatalysis of the samples will be discussed in detail later.

TGA was carried out to determine the CN and Co-MOF contents of the composites and estimate their thermal stabilities. As shown in Fig. 2(f), all the photocatalysts displayed good thermal stability in air. The decomposition of pure Co-MOF started at 330 °C and the weight loss was about 65.6% between 330 °C and 400 °C, which was related to the removal of guest molecules [34]. The weight of residual Co-MOF remained stable up to 800 °C. In addition, the pure CN sample showed a total weight loss in the temperature range 500–680 °C, which might be attributed to the collapse of the CN nanosheets [35]. Surprisingly, the thermal stability of Co-CN2 was worse than that of CN; the main weight loss was observed between 430 °C and 510 °C, however, this was higher than that of the Co-MOF sam-

ple. It was understandable that the amount of Co-MOF in the Co-CN2 was slightly less than the designed value, based on the TG result.

XPS measurements were carried out to explore the chemical statuses of the elements, which are displayed in Fig. 3. The patterns showed not only the existence of Co, C, N, and O elements in Co-MOF and Co-CN2, but also the C and N of CN (Fig. 3(a)). Fig. 3(b) presents the corresponding XPS VB spectra of CN and Co-MOF. The VB positions of the samples were calculated to be ~ 1.58 and ~ 0.73 eV, respectively. In the N 1s spectra (Fig. 3(c)), the four peaks observed at 398.4, 399.0, 400.6, and 404.2 eV were ascribed to the sp^2 C=N=C bonds, tertiary nitrogen N-(C)₃ groups, amino groups (C-N-H), and charging effects in the heterocycles, respectively [36,37]. However, only two peaks at 399.4 and 398.4 eV were detected for the Co-MOF sample, and they were assigned to pyrrolic-N and pyridinic-N, respectively [38]. In the C 1s spectra shown in Fig. 3(d), three peaks at 284.5, 286.2, and 288.0 eV were detected. The first peak corresponded to sp^2 C=C bonds. The second one was assigned to the sp^2 C=N bonds. The last peak pertained to N=C-N coordination [39]. It is worth noting that the binding energy of Co-CN2 photocatalyst revealed a slight red-shift compared to that of CN. At the same time, the intensities of the peaks were also different for the two samples, which proved the existence of interaction in Co-CN2 composite [40].

In Fig. 3(e), the O 1s peak observed at 531.9 eV for Co-MOF corresponds to its lattice O, which is shifted to 532.3 eV for Co-CN2 composite, and the other peaks at ~ 533.3 and 533.8 eV are assigned to the OH group. It is obvious that the two peaks of Co-CN2 red-shift compared to that of Co-MOF, which indicates interaction between the Co-MOF nanoparticles and the CN sheets [41]. In the Co 2p spectrum of Co-MOF (Fig. 3(f)), two

main peaks are observed at 781.13 and 796.63 eV, which correspond to Co 2p_{3/2} and Co 2p_{1/2}, respectively [42]. In general, the chemical states of N are similar for CN and Co-CN2, but the chemical states of C and O are different. Similar phenomena were reported for g-C₃N₄-based photocatalysts such as BiPO₄/g-C₃N₄, Ag₂CrO₄/g-C₃N₄, and Ag₃VO₄/g-C₃N₄ composites. The shift in binding energy indicated the interaction between Co-MOF nanoparticles and g-C₃N₄ sheets [43–45].

The photocatalytic CO₂ reduction performance of the different samples was evaluated by measuring the CO and CH₄ production rates under visible-light irradiation. All the measurements were carried out at room temperature for 6 h, and the results are shown in Fig. 4(a). When the original CN was used as a photocatalyst, the production rates of CO and CH₄ were 3.41 and 2.11 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. It is worth noting that the highest production rates were obtained by employing Co-CN2 as the photocatalyst; one-fold increases in the CO and CH₄ yields were observed, in comparison with those of pure CN. Our findings indicate that the coupling of Co-MOF nanoparticles with CN can greatly improve the photocatalytic activity, as expected. Interestingly, the production rates first increased and then declined with an increase in Co-MOF content. This might be attributed to the reduction in active sites on the CN surface that resulted from excess Co-MOF coverage, which in turn resulted in reduced efficiency of charge separation [46,47]. Moreover, the mechanical mixture was also prepared and tested; it contained the same weight ratio of CN to Co-MOF as the Co-CN2 nanocomposite. The result showed no obvious enhancement in the photoactivity, compared to that of pure CN. Thus, the performance improvement of the composite sample can be attributed to the interaction between CN and Co-MOF. At the same time, it is crucial that Co-MOF content is appropriate.

Fig. 3. (a) XPS survey patterns; (b) Valence band (VB) XPS spectra; High-resolution (c) N 1s, (d) C 1s, (e) O 1s, and (f) Co 2p XPS spectra of the tested samples.

Fig. 4. (a) Comparison of the production rates for the typical samples; (b) Evaluation of the stability of Co-CN2 photocatalyst.

The amounts of the products CO and CH₄ increased linearly with irradiation time, as shown in the inset of Fig. 4(a). The stability of Co-CN2 sample was also evaluated, as revealed in Fig. 4(b). No obvious decrease in the production rate was observed after recycling 5 times, which indicated good stability of Co-CN2 composite.

To illustrate the role of the composites in improving the electron transfer in the reaction systems, photoelectrochemical measurements were conducted. Fig. 5(a) shows the photocur-

rent generation behavior of pure CN nanosheets and Co-CN2 nanocomposite under visible-light illumination. The photocurrent density of Co-CN2 was higher than that of CN, which suggested that much more photogenerated carriers were transferred and separated in the case of Co-CN2, which in turn increased the photocatalytic activity [48–50]. EIS was employed to further investigate the improvement in the charge transmission efficiency, and the results are shown in Fig. 5(b). The equivalent circuit of the Nyquist plots is shown in the inset of

Fig. 5. (a) Photocurrent-time profiles; (b) Results of electrochemical impedance spectroscopy (EIS) obtained in the dark and under illumination; (c) Results of electrochemical CO₂ reduction; (d) Mott-Schottky plots.

Fig. 5(b). The smaller the radius of the arc, the faster is the interfacial charge transfer [51,52]. Fig. 5(b) reveals a smaller radius for Co-CN2 than that for CN, which indicated faster charge transfer in the case of the Co-CN2 sample, which in turn improved the separation efficiency of the photogenerated electron-hole pairs. Moreover, electrochemical CO₂ reduction experiments were performed using the samples. The cathodic current of Co-CN2 was obviously higher than that of CN, as shown in Fig. 5(c). This provides strong evidence that Co-CN2 exhibits improved photocatalytic ability to reduce CO₂. Fig. 5(d) displays the Mott-Schottky plots for CN and Co-CN2. The positive slopes revealed that the materials prepared were n-type semiconductors. A smaller slope of the Mott-Schottky curve corresponds to a higher carrier density [53]. Compared with that of CN, Co-CN2 revealed a smaller slope, which suggested a higher carrier density and a smaller interface resistance for Co-CN2, which resulted in improved electron-hole separation and, thereby, enhanced photocatalytic reaction. All the electrochemical characterizations further proved our conclusions and the results were in line with our expectations.

It is well known that •OH is produced as an intermediate product during the photocatalytic reduction of CO₂ [54]. Here, the coumarin fluorescence method was employed to explore the photocatalytic mechanism of the samples. First, the catalytic reaction was carried out in the presence of coumarin under visible-light irradiation, and then, the •OH produced under irradiation reacted with coumarin to form the luminescent

7-hydroxy-coumarin. Finally, the fluorescence spectra of 7-hydroxy-coumarin were measured under 390 nm light excitation. The fluorescence intensity of 7-hydroxy-coumarin is directly related to the amount of •OH, and thereby, to the photoactivity of the photocatalyst. As shown in Fig. 6(a), the fluorescence intensity of Co-CN2 is much higher than that of CN, which indicates that the photoactivity of Co-CN2 is higher. In order to further prove that electrons migrate from the LUMO of Co-MOF to the CB of CN, the catalytic reaction in the presence of coumarin under 590 nm light irradiation was carried out. The corresponding fluorescence spectra of 7-hydroxy-coumarin are shown in Fig. 6(b). It is noted that the 590 nm light mainly excites Co-MOF, and thus, the electrons in the LUMO of Co-MOF can migrate to the CB of CN, thereby enhancing the photocatalytic CO₂ reduction activity.

Fig. 6(c) presents the PL spectra of the Co-CN2 and pure CN photocatalysts obtained at the excitation wavelength of 370 nm. It is well known that PL is commonly used in the field of photocatalysis to analyze charge separation. Here, the PL intensity of g-C₃N₄ decreases dramatically after the Co-MOF modification. Therefore, a weaker PL peak intensity implies that Co-MOF modification decreases the recombination rate of the photogenerated electron-hole pairs, which in turn results in the photoinduced charge separation efficiency being enhanced [55–57]. The luminescence decay curves of CN and Co-CN2 were also measured to evaluate the photogenerated carrier lifetimes. As shown in Fig. 6(d), both the attenuation curves

Fig. 6. Fluorescence spectra related to the hydroxyl radicals produced under 390 nm light excitation: (a) Catalytic reaction with visible-light irradiation using Xe lamp as the light source; (b) Catalytic reaction with 590 nm light irradiation; (c) PL emission spectra obtained under 370 nm light excitation; (d) Luminescence decay curves obtained under 370 nm light excitation.

were well-fitted with double exponential functions. The average lifetime (τ) was determined using the formula $\tau = \sum_{i=1}^2 A_i \tau_i^2 / \sum_{i=1}^2 A_i \tau_i$ [58]. Clearly, the carrier lifetime of Co-CN2, which was 1759.7 ns, was much higher than that of CN (1348.0 ns), which suggested more effective electron-hole pair generation in the case of the former. The above analysis showed that Co-CN2 photocatalyst is beneficial for charge transfer and separation.

The mechanism for enhanced photocatalytic CO₂ reduction of g-C₃N₄ nanosheets via coupling with Co-MOF (an electron donor) is shown in Scheme 1. In detail, Co-MOF and g-C₃N₄ are excited to produce electron-hole pairs under visible-light illumination, and the LUMO potential of Co-MOF is more negative than the CB potential of g-C₃N₄, which results in the photoelectrons in the LUMO of Co-MOF easily transferring to the CB of g-C₃N₄. In the photocatalytic CO₂ reduction process, the electrons in the CB reduce CO₂ to CH₄ and CO, while water is oxidized by the holes in the VBs of g-C₃N₄ to produce •OH, which eventually releases O₂ and H⁺, which can increase the lifetime of the photoinduced charge carriers. This may be the main reason for the improvement in the photocatalytic activity.

4. Conclusions

Co-MOF/g-C₃N₄ nanocomposites were successfully fabricated to enhance charge separation and transfer as well as to increase the photocatalytic activity of g-C₃N₄ for CO₂ reduction via coupling with the electron donor Co-MOF. The Co-CN2 nanocomposite reveals the highest photocatalytic CO₂ reduction activity under visible-light irradiation. CH₄ and CO were detected as the main products in the reaction systems. The DRS indicated that the visible-light absorption range of the composite was broadened, which was beneficial to the occurrence of the photocatalytic reaction. In particular, the hydroxyl radical experiment under 590 nm (single-wavelength) irradiation proved that the photogenerated electrons in the LUMO of Co-MOF can migrate to g-C₃N₄ easily. Based on the experimental results, the Co-CN2 catalyst exhibited enhanced separation of photoinduced electron-hole pairs and widened range of visible-light absorption, which rendered it an excellent photo-

catalytic CO₂ reduction catalyst based on a one-fold improvement in the photoactivity. This work reveals that g-C₃N₄-based composites offer promise for important applications in the field of energy conversion and environmental purification.

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Scheme 1. A possible mechanism of CO₂ photoreduction.

Graphical Abstract

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Co-MOF as an electron donor for promoting visible-light photoactivities of g-C₃N₄ nanosheets for CO₂ reduction

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The Co-MOF introduced tightly contacts g-C₃N₄, which facilitates effective transfer of the photogenerated electrons from Co-MOF to g-C₃N₄, which in turn improves the separation of photogenerated charges and leads to enhanced photocatalytic activities of Co-MOF/g-C₃N₄ nanocomposites.

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Co-MOF作为电子供体用于提高g-C₃N₄纳米片的可见光催化还原CO₂性能

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摘要: 作为温室效应的主要气体CO₂浓度持续上升, 已经成为全球环境问题. 将CO₂光催化还原成可再生能源不仅可以解决CO₂带来的温室效应, 而且可以将太阳能转化为燃料物质而取代传统意义上的化石能源. 实际上光催化的研究可以追溯到1979年, 自从Inoue首次报道了光催化CO₂和水制取甲酸、甲烷等有机物, 人们一直在努力开发高效的CO₂转化光催化剂. 近年来, 随着光催化技术的快速稳定发展, 各种半导体光催化剂, 如Zn₂GeO₄, CdS, Fe₃O₄, g-C₃N₄和SrTiO₃等, 已被开发用于光催化还原二氧化碳. 在这些半导体中, 有的材料具有较大的带隙导致较低的可见光活性, 有的材料具有毒性引起额外的环境问题. 因此, 寻求具有适度带隙且环境友好的半导体材料是解决全球变暖问题的关键.

近年来, g-C₃N₄因其带隙(约2.7 eV)较窄, 具有一定的可见光吸收性能, 无污染, 以及化学和热稳定性良好等特点, 被视为理想的可见光响应光催化材料之一. 但是, g-C₃N₄光吸收有限、光生电子空穴复合率较高等缺点严重限制了其光催化活性. 为了进一步提高g-C₃N₄的CO₂可见光催化还原活性, 国内外研究者开发了许多方法来提高电荷分离效率, 进而提高g-C₃N₄光催化剂的总体活性. 在这些策略中, 将g-C₃N₄与具有合适带位置的其他材料偶联以促进电子空穴分离是提高光催化性能的有效方法之一. 由于Co-MOF具有较窄的带隙且导带位置与g-C₃N₄匹配, 我们选择Co-MOF与g-C₃N₄复合来克服g-C₃N₄的缺点, 进而达到提高其光催化活性的目的.

作为电子供体的Co-MOF能够将最低未占分子轨道(LUMO)上的光生电子转移到g-C₃N₄的导带以促进电荷分离, 同时水被g-C₃N₄价带上的空穴氧化, 最终生成氧气, 从而提高光催化还原CO₂的性能. 制备的Co-MOF/g-C₃N₄纳米复合材料在可见光照射下具有优异的光催化还原CO₂性能, 约为纯g-C₃N₄的光催化活性的2倍. 一系列分析表明, Co-MOF的引入不仅拓宽了可见光的吸收范围, 而且促进了电荷分离, 有利于提高g-C₃N₄的光催化活性. 特别是在590 nm单波长照射下进行的羟基自由基实验进一步证明了Co-MOF的LUMO上的光生电子可以转移到g-C₃N₄. 该研究结果为基于g-C₃N₄的光催化体系的合理构建提供了新思路.

关键词: Co-MOF; g-C₃N₄纳米片; 电荷分离; 可见光活性; 光催化还原二氧化碳

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