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In situ fabrication of CdMoO₄/g-C₃N₄ composites with improved charge separation and photocatalytic activity under visible light irradiation

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ABSTRACT

To further improve the charge separation and photocatalytic activities of g-C₃N₄ and CdMoO₄ under visible light irradiation, CdMoO₄/g-C₃N₄ composites were rationally synthesized by a facile precipitation-calcination procedure. The crystal phases, morphologies, chemical compositions, textural structures, and optical properties of the as-prepared composites were characterized by the corresponding analytical techniques. The photocatalytic activities toward degradation of rhodamine B solution were evaluated under visible light irradiation. The results revealed that integrating CdMoO₄ with g-C₃N₄ could remarkably improve the charge separation and photocatalytic activity, compared with those of pristine g-C₃N₄ and CdMoO₄. This would be because the CdMoO₄/g-C₃N₄ composites could facilitate the transfer and separation of the photoexcited electron-hole pairs, which was confirmed by electrochemical impedance spectroscopy, transient photocurrent responses, and photoluminescence measurements. Moreover, active species trapping experiments demonstrated that holes (h⁺) and superoxide radicals (·O₂⁻) were the main active species during the photocatalytic reaction. A possible photocatalytic mechanism was proposed on the basis of the energy band structures determined by Mott-Schottky tests. This work would provide further insights into the rational fabrication of composites for organic contaminant removal.

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1. Introduction

Photocatalytic technology has attracted extensive attention owing to its enormous potential in splitting water into hydrogen, reducing CO₂ to solar fuels, nitrogen photo-fixation, and degrading harmful contaminants [1–6]. Efficient separation and transfer of photocatalytic charge carriers is still one of the main bottlenecks to improving the photocatalytic efficiency [7–10]. To overcome this problem, various effectual strategies have

been considered, such as morphology regulation [11,12], defect engineering [13], heteroatom doping [14–16], and fabrication of composites [17–20]. Among them, integration of two different semiconductors with well-matched energy band structures to form composites is regarded as a facile and feasible avenue toward improving the separation efficiency of photogenerated electron-hole pairs.

Recently, graphitic carbon nitride (g-C₃N₄), with a layer structure, has been receiving more interest because of its low

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cost, nontoxic nature, high stability, visible-light response, and possibility of large-scale preparation. Moreover, an appropriate conduction band (CB) potential (about -1.12 eV vs. NHE) endows it with a strong capability to accept photoinduced electrons [21–27]. However, the photocatalytic activity of pristine $g\text{-C}_3\text{N}_4$ is always low owing to the fast recombination of the photogenerated charge carriers. Inspired by the abovementioned heterostructure composites, tremendous efforts have been made to fabricate $g\text{-C}_3\text{N}_4$ -based composites, e.g., $\text{SnS}_2/g\text{-C}_3\text{N}_4$ [28], $\text{TiO}_2/g\text{-C}_3\text{N}_4$ [29], $\text{CdS}/g\text{-C}_3\text{N}_4$ [30], $\text{BiOBr}/g\text{-C}_3\text{N}_4$ [31], $\text{Fe}_2\text{O}_3/g\text{-C}_3\text{N}_4$ [32], and so on [33–44]. These composites have all displayed significantly enhanced photocatalytic activities, compared with that of bare $g\text{-C}_3\text{N}_4$, which may be attributed to the effective transfer and separation of photoinduced charge carriers.

Cadmium molybdate (CdMoO_4) as a class of metal molybdates (MMoO_4 , $M = \text{Ni, Ba, Cd, Pb, etc.}$) has also received considerable attention because of its promise for application in the photocatalytic field [45–47]. However, the relatively wide band gap (about 3.4 eV) restricts its photocatalytic activity, as it is only active under ultraviolet light irradiation. In this regard, some strategies have been employed to extend the light response range, such as elemental doping and engineering composites with narrow band gap semiconductors [48–50]. Since $g\text{-C}_3\text{N}_4$ is a visible-light-driven semiconductor, it can be considered as a candidate that couples with CdMoO_4 to enhance the light harvesting capacity. Moreover, the CB and valence band (VB) potentials of CdMoO_4 are both lower than those of $g\text{-C}_3\text{N}_4$, which suggest a well matched energy band structure that is favorable for the formation of a type II heterostructure composite. To date, there are very few reports on the fabrication of $\text{CdMoO}_4/g\text{-C}_3\text{N}_4$ composites. Zhao et al. [51] prepared the $\text{CdMoO}_4/g\text{-C}_3\text{N}_4$ heterojunction *via* a simple mixing-calcination method. The resultant composite displays a remarkable improvement in the photocatalytic activity toward rhodamine B (RhB) degradation and CO_2 reduction. On the other hand, intimate interfacial contact between two different semiconductors is vitally important, as it will affect the transfer and separation efficiency of charge carriers. Hence, it is still a challenge to fabricate $\text{CdMoO}_4/g\text{-C}_3\text{N}_4$ composites with close interfacial contact by a facile approach.

Here, CdMoO_4 particles were directly deposited on the surface of $g\text{-C}_3\text{N}_4$ through a facile precipitation-calcination process. The $\text{CdMoO}_4/g\text{-C}_3\text{N}_4$ composites exhibited markedly enhanced photocatalytic activity, in contrast with those of pristine $g\text{-C}_3\text{N}_4$ and CdMoO_4 , as demonstrated by the degradation of RhB solution under visible light irradiation. In addition, the effects of CdMoO_4 mass ratios in the composites and the active species on the photocatalytic performance were investigated. A possible mechanism for the enhancement in the photocatalytic activity was proposed based on the experimental results.

2. Experimental

2.1. Material preparation

$g\text{-C}_3\text{N}_4$ was prepared according to our previous report [37].

Typically, 10 g of melamine was calcined at 550 °C for 3 h at the heating rate of 5 °C min^{-1} . The resulting powders were ground in agate mortar and collected for use without further treatment.

$\text{CdMoO}_4/g\text{-C}_3\text{N}_4$ composites were fabricated by *in situ* precipitation and calcination approach. As a representative example, 200 mg of as-prepared $g\text{-C}_3\text{N}_4$ was dispersed in 30 mL deionized water by ultrasonic treatment for 30 min. 18.8 mg of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and 19.7 mg of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were added to the above suspension solution with the molar ratio of $1:1$. The mixture was stirred at 40 °C for 6 h. Then, the sediments were collected by centrifugation, washed three times using deionized water, and dried at 80 °C for 12 h. After that, the products were annealed at 300 °C for 2 h in a muffle furnace. $\text{CdMoO}_4/g\text{-C}_3\text{N}_4$ composites with different mass ratios were obtained through the aforesaid procedure by adjusting the amounts of $\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ added. The actual contents of CdMoO_4 in the composites were determined by thermogravimetric (TG) measurements. Bare CdMoO_4 was synthesized by the same procedure, except for the addition of $g\text{-C}_3\text{N}_4$ at the beginning.

2.2. Material characterization

The crystal phases were identified with a Shimadzu XRD-7000 powder X-ray diffractometer (XRD) using $\text{Cu K}\alpha$ irradiation at 40 kV and 30 mA. The morphologies, elemental maps, and microstructures were recorded on a JSM-7100F field emission scanning electronic microscope (FESEM) and a JEOL JEM 2100F high-resolution transmission electronic microscope (HRTEM). TG analysis was carried out on a Hitachi STA 7300 instrument from 50 to 800 °C in air flow at a heating rate of 10 °C min^{-1} . X-ray photoelectron spectroscopy (XPS) was performed on a VG Multilab 2000 instrument with $\text{Al K}\alpha$ source that operated at 300 W, and all the spectra were calibrated with the C 1s peak at 284.6 eV. The ultraviolet-visible diffuse reflectance absorption spectra (UV-DRS) were recorded by using dry-pressed disk samples on a Purkinje General TU-1901 spectrophotometer with BaSO_4 as the reference sample. The fourier transform infrared (FTIR) spectra were recorded on a Thermo Nicolet Avatar 360 spectrometer using conventional KBr pellets. The Brunauer-Emmett-Teller (BET) specific surface areas were determined on a Micromeritics ASAP 2020 nitrogen adsorption apparatus. Prior to the BET analysis, the samples were degassed at 120 °C for 10 h to remove the adsorbed water. The photoluminescence (PL) spectra were measured at room temperature on a PerkinElmer LS55 fluorescence spectrometer with the excitation wavelength of 340 nm.

2.3. Photocatalytic activity measurement

The photocatalytic activities were evaluated by degrading RhB solution under visible light irradiation on photoreactive equipment (BL-GHX-IV, Shanghai Bilang Instrument Co. Ltd, China). In each experiment, 30 mg of the photocatalyst was dispersed in 50 mL of RhB solution with the initial concentra-

tion of 1.0×10^{-5} mol L^{-1} . A 300 W long-arc Xe lamp was used as the light source, and was equipped with 420 nm cutoff filters. Before the irradiation, the suspensions were stirred in the dark for 30 min to achieve adsorption-desorption equilibrium between the photocatalysts and RhB molecules. At given irradiation time intervals, 4 mL of the suspension was withdrawn and centrifuged to remove the photocatalysts. The concentration of the RhB solution in the supernatant was determined on a Purkinje General TU-1810 spectrometer.

2.4. Photoelectrochemical measurement

The Mott-Schottky, EIS, and transient photocurrent response experiments were carried out on an electrochemical system (CHI 760D, Shanghai Chenhua Instruments, China) employing the standard three-electrode system. A Pt sheet and Ag/AgCl (saturated KCl) served as the counter and reference electrodes, respectively. The working electrodes were prepared as follows. 10 mg of the sample was mixed with 1 mL ethanol and 50 μ L Nafion solution by using ultrasound. Then, 0.1 mL of the mixture was dropped on indium tin oxide-doped glass with the active work area of about 1 cm^2 . A 0.1 mol L^{-1} aqueous Na_2SO_4 solution was used as the electrolyte. The Mott-Schottky tests were conducted at the frequency of 1000 Hz, with the bias potential varying from -1.0 to 1.0 V. The EIS measurements were performed in darkness at the amplitude of 5 mV under open circuit potential conditions. The frequency range was 1 Hz to 100 kHz. The transient photocurrent responses were obtained at 0.5 V bias potential. A 300 W Xe lamp acted as the light source.

2.5. Active species trapping measurement

To probe the active species in the photocatalytic reaction, triethanolamine (TEOA), isopropanol (IPA), and *p*-benzoquinone (BQ) were introduced into the system as the scavengers of holes (h^+), hydroxyl radicals ($\cdot OH$), and superoxide radicals ($\cdot O_2^-$), respectively. The measurements were similar to the aforementioned photocatalytic activity tests, except for the addition of scavengers into the RhB solution before visible light irradiation. The concentrations of TEOA, IPA, and BQ were 10, 10, and 1 mmol L^{-1} , respectively.

3. Results and discussion

3.1. Photocatalyst characterization

The actual mass ratios of $CdMoO_4$ in the composites were determined by TG measurements. As revealed in Fig. 1, single-phase $CdMoO_4$ reveals no distinct weight loss between 50 and 800 $^{\circ}C$ under air flow heating, which indicates that pristine $CdMoO_4$ is relatively stable. On the other hand, bare $g-C_3N_4$ displays a perceptible weight loss at about 500 $^{\circ}C$ and decomposes completely at around 760 $^{\circ}C$. Consequently, on the basis of the remaining weight, the mass ratios of $CdMoO_4$ in the composites can be estimated. For the $CdMoO_4/g-C_3N_4$ composites, the $CdMoO_4$ mass ratios were calculated to be 2.1, 4.8, 8.7,

Fig. 1. TG curves of pristine $g-C_3N_4$, $CdMoO_4$, and $CdMoO_4/g-C_3N_4$ composites with different mass ratios.

and 13.4 wt%. It is noteworthy that the decomposition temperatures of $g-C_3N_4$ decrease when coupling $CdMoO_4$ with $g-C_3N_4$, which may be because $CdMoO_4$ can accelerate the oxidation of $g-C_3N_4$ to gaseous products [51].

Fig. 2 exhibits the XRD patterns of $CdMoO_4/g-C_3N_4$ composites with different mass ratios, together with those of bare $g-C_3N_4$ and $CdMoO_4$. For $g-C_3N_4$, a weak peak located at about 13.0° and a strong peak situated at 27.2° are observed, which are ascribed to the (100) and (002) planes, respectively. These are the characteristic diffraction peaks of $g-C_3N_4$ that correspond to the in-planar packing motif of tri-s-triazine units and interlayer stacking of conjugated aromatic rings [32]. As for the single-phase $CdMoO_4$, the diffraction peaks are well matched with the tetragonal phase of $CdMoO_4$ (JCPDS # 85-888) [52]. Regarding the $CdMoO_4/g-C_3N_4$ composites, the feature peaks of both $CdMoO_4$ and $g-C_3N_4$ can be observed together, without other impurity phases. Moreover, the intensities of the diffraction peaks assigned to $g-C_3N_4$ gradually decrease and the peaks associated with $CdMoO_4$ become stronger with the increase of $CdMoO_4$ content in the composites. The XRD results corroborate the coexistence of $CdMoO_4$ and $g-C_3N_4$ in the composites.

The representative FESEM images of bare $CdMoO_4$, $g-C_3N_4$,

Fig. 2. XRD patterns of bare $g-C_3N_4$, $CdMoO_4$, and $CdMoO_4/g-C_3N_4$ composites with different mass ratios.

and 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite are exhibited in Fig. 3a–c. As can be seen, the pristine CdMoO_4 (Fig. 3a) presents an irregular granular morphology, along with severe aggregation, while $\text{g-C}_3\text{N}_4$ (Fig. 3b) displays a large blocked structure with particle sizes of about 5–10 μm . The FESEM image (Fig. 3c) of 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite reveals that there are two different morphological structures in the composites. The big blocks are assigned to $\text{g-C}_3\text{N}_4$, whereas the small particles correspond to CdMoO_4 . Energy dispersive X-ray spectrometer elemental mapping was used to further determine the distributions of different components in 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite. As illustrated in Fig. 3d–h, the composite contains C, N, Cd, Mo, and O elements. In addition, CdMoO_4 is discretely distributed on the surface of $\text{g-C}_3\text{N}_4$. Further investigations were performed by using the HRTEM to investigate the microstructure of the $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite. Fig. 3i also reveals that the composite comprises two different constituents. The dark sections correspond to CdMoO_4 , while the grey sections are associated with $\text{g-C}_3\text{N}_4$. This is because electron beams can more easily pass through $\text{g-C}_3\text{N}_4$ than through CdMoO_4 in view of their atomic weights. The red rectangular section of the TEM image is enlarged. From the HRTEM image (inset of Fig. 3i), the interplanar spacing is measured to be 0.28 nm, which corresponds to the (112) plane of CdMoO_4 . On the other hand, the lattice fringes of $\text{g-C}_3\text{N}_4$ are difficult to observe, which is in accordance with a previous report [36].

XPS was performed to further examine the surface chemical compositions and valence states of the various species. Fig. 4a depicts the XPS survey patterns of CdMoO_4 , $\text{g-C}_3\text{N}_4$, and 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite. As expected, C, N, O, Cd, and Mo elements are distinctly detected in the $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$

composite. Fig. 4b displays the high-resolution Cd 3d XPS pattern. The peaks positioned at 404.7 and 411.4 eV can be assigned to Cd 3d_{5/2} and Cd 3d_{3/2}, respectively, which are characteristic of Cd²⁺ [51]. From the Mo 3d spectra (Fig. 4c), two peaks are observed at about 231.9 and 235.1 eV, which correspond to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively. This indicates that the oxidation state of the Mo ions is +6 [51]. The high-resolution XPS C 1s patterns are shown in Fig. 4d. For CdMoO_4 , the only strong peak is found at 284.6 eV, which corresponds to the surface adventitious C. In the cases of $\text{g-C}_3\text{N}_4$ and 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite, two peaks at 284.6 and 287.6 eV are observed. The former is attributed to the surface adventitious C and the latter to the sp^2 -hybridized C of the N=C–N aromatic rings [32]. The N 1s XPS patterns (Fig. 4e) of $\text{g-C}_3\text{N}_4$ and $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite can be deconvoluted into three peaks at 398.0, 398.7, and 400.1 eV, which are related to the sp^2 -hybridized N (C=N–C) in the triazine rings, tertiary N bonded to C (N–(C)₃), and amino groups (C–N–H), respectively [32]. As demonstrated in Fig. 4f, the O 1s spectrum of CdMoO_4 can be fitted with two peaks. The peaks at 529.7 and 530.8 eV are associated with the O anions present in the lattice of CdMoO_4 and the chemisorbed O species, respectively [46]. As for $\text{g-C}_3\text{N}_4$, a peak at 532.3 eV is detected, which can be related to the C–O bonds stemming from the incomplete pyrolytic reaction of melamine [32,53]. Comparing with the spectra of CdMoO_4 and $\text{g-C}_3\text{N}_4$, the O 1s spectrum of 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite can be deconvoluted into three peaks, which correspond to O anions, chemisorbed O species, and C–O bonds, respectively.

The molecular structures of pristine $\text{g-C}_3\text{N}_4$, CdMoO_4 , and $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ with different mass ratios were investigated

Fig. 3. FESEM images of (a) CdMoO_4 , (b) $\text{g-C}_3\text{N}_4$, and (c) 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite; Elemental maps of 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite: (d) C, (e) N, (f) Cd, (g) Mo, and (h) O; (i) TEM and HRTEM images of 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite.

Fig. 4. XPS patterns of g-C₃N₄, CdMoO₄, and 4.8 wt% CdMoO₄/g-C₃N₄ composite. (a) Survey spectra; (b) Cd 3d; (c) Mo 3d; (d) C 1s; (e) N 1s; (f) O 1s.

based on their FTIR spectra, and the relevant results are presented in Fig. 5. As for g-C₃N₄, the absorption bands in the range 1200–1650 cm⁻¹ correspond to the stretching vibrations of the C–N aromatic ring [32]. The peak at about 812 cm⁻¹ can be assigned to the characteristic breathing mode of the tri-s-triazine units [32]. In addition, the broad absorption bands centered at 3430 and 3164 cm⁻¹ are attributed to the stretching vibrations of the O–H bonds of adsorbed water and the terminal N–H groups, respectively. For single-phase CdMoO₄, a characteristic absorption peak appears at around 783 cm⁻¹, which corresponds to the stretching vibration of the O–Mo–O bonds in the [MoO₄]²⁻ tetrahedrons [52]. In the case of CdMoO₄/g-C₃N₄ composites, the characteristic peaks of g-C₃N₄ are clearly observed, while the peak belonging to CdMoO₄ is only found in the CdMoO₄/g-C₃N₄ composites with large mass

ratios. Moreover, the feature absorption peak of CdMoO₄ in the CdMoO₄/g-C₃N₄ composites displays a slight shift from 783 to 757 cm⁻¹, which may be due to the strong interaction between CdMoO₄ and g-C₃N₄. This also implies that CdMoO₄ and g-C₃N₄ have formed an interface with intimate contact.

UV-DRS were used to study the optical properties of g-C₃N₄, CdMoO₄, and CdMoO₄/g-C₃N₄ composites. As revealed in Fig. 6, single-phase CdMoO₄ and g-C₃N₄ show steep absorption band edges at around 360 and 455 nm, respectively. The band gaps of CdMoO₄ and g-C₃N₄ are estimated to be 3.44 and 2.73 eV, respectively, from the equation $E_g = 1240/\lambda_g$, where E_g is the band gap and λ_g is the absorption band edge. For CdMoO₄/g-C₃N₄ composites, they exhibit similar absorption band edges to that of bare g-C₃N₄ in the visible light region. This indicates that integration of CdMoO₄ with g-C₃N₄ does not influence the structure of g-C₃N₄. It is noted that both the 8.7 wt% and 13.4 wt% CdMoO₄/g-C₃N₄ composites display another

Fig. 5. FTIR spectra of pure g-C₃N₄, CdMoO₄, and CdMoO₄/g-C₃N₄ composites. (a) g-C₃N₄; (b) 2.1 wt% CdMoO₄/g-C₃N₄; (c) 4.8 wt% CdMoO₄/g-C₃N₄; (d) 8.7 wt% CdMoO₄/g-C₃N₄; (e) 13.4 wt% CdMoO₄/g-C₃N₄; (f) CdMoO₄.

Fig. 6. UV-DRS of pristine g-C₃N₄, CdMoO₄, and CdMoO₄/g-C₃N₄ composites with different mass ratios.

Fig. 7. Nitrogen adsorption-desorption isotherms and the corresponding pore size distribution curves of g-C₃N₄ and 4.8 wt% CdMoO₄/g-C₃N₄ composite.

absorption edge in the ultraviolet light region, which corresponds to the intrinsic optical absorption of CdMoO₄.

The BET specific surface areas and pore size distribution curves of pristine g-C₃N₄ and 4.8 wt% CdMoO₄/g-C₃N₄ composite were obtained by nitrogen adsorption-desorption measurements, as revealed in Fig. 7. It can be seen that these two adsorption-desorption curves belong to type IV isotherm with type H3 hysteresis loops, which imply the existence of porous structures in these samples. This also indicates that introduction of CdMoO₄ in g-C₃N₄ does not significantly block or change the pore structures of g-C₃N₄. The corresponding pore size distribution curves (inset) reveal that the pore size distributions mainly range from 25 to 100 nm, which confirm the presence of

porous structures in these samples. Additionally, the BET specific surface areas of g-C₃N₄ and 4.8 wt% CdMoO₄/g-C₃N₄ composite are calculated to be 27.2 and 25.6 m² g⁻¹, respectively, which represent a slight decrease in the specific surface area after the hybridization of CdMoO₄ and g-C₃N₄.

3.2. Photocatalytic activity and mechanism

The photocatalytic performances of the as-prepared photocatalysts were evaluated by degrading RhB solution under visible light irradiation. As shown in Fig. 8a, the blank experiment reveals that RhB is quite stable under visible light illumination, which ruled out self-degradation of RhB. The decolorization percentage is estimated as C/C_0 , where C is the concentration of RhB after adsorption and light irradiation for a certain time interval, and C_0 is the initial concentration of RhB. Single-phase CdMoO₄ reveals a very low adsorption and photocatalytic activity, with a decolorization percentage of 16.1% after 180 min visible light irradiation. Bare g-C₃N₄ displays moderate photocatalytic activity, with the decolorization percentage being 77.8% for 180 min of visible light irradiation. The CdMoO₄/g-C₃N₄ composites exhibit remarkable improvements in the photocatalytic activities. After 30 min dark adsorption and 180 min visible light illumination, the decolorization percentages are about 86.3%, 96.7%, 86.7%, and 80.1% for 2.1, 4.8, 8.7, and 13.4 wt% CdMoO₄/g-C₃N₄ composites, respectively. Obviously, the 4.8 wt% CdMoO₄/g-C₃N₄ composite exhibits the best photocatalytic activity. The degradation process could be fitted with the pseudo-first-order kinetic model, in which the value of the apparent reaction rate constant (k) is equal to the corresponding slope of the fitting curve. As depicted in Fig. 8b,

Fig. 8. (a) Comparison of the photocatalytic activities of different samples. (A) CdMoO₄; (B) g-C₃N₄; (C) 2.1 wt% CdMoO₄/g-C₃N₄; (D) 4.8 wt% CdMoO₄/g-C₃N₄; (E) 8.7 wt% CdMoO₄/g-C₃N₄; (F) 13.4 wt% CdMoO₄/g-C₃N₄; (G) No photocatalyst; (b) Pseudo-first-order kinetic curves of the corresponding samples; (c), (d), and (e) Temporal evolutions of the spectra during the photocatalytic degradation of RhB over CdMoO₄, g-C₃N₄, and 4.8 wt% CdMoO₄/g-C₃N₄; (f) Stability experiments of the photocatalytic degradation of RhB solution over 4.8 wt% CdMoO₄/g-C₃N₄ composite.

Fig. 9. XRD patterns of 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite before and after the cyclic photocatalytic experiment.

the reaction rate constant of 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite is about 2.32 times higher than that of bare $\text{g-C}_3\text{N}_4$. The temporal UV-visible spectral changes of the RhB solution during the adsorption and photocatalytic reactions over CdMoO_4 , $\text{g-C}_3\text{N}_4$, and 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite are displayed in Fig. 8c–e, respectively. As for $\text{g-C}_3\text{N}_4$ and $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite, the maximal absorbance wavelengths of RhB shift gradually from 554 to 498 nm, along with a gradual decrease in the maximal absorbance, which suggest stepwise removal of the *N*-ethyl groups of RhB molecules. The stability of

$\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite was investigated by cyclic degradation of RhB solution. After every 180 min of the photodegradation reaction, the separated photocatalysts were washed and dried. As demonstrated in Fig. 8f, the photocatalytic degradation efficiency is still 92.4% after three successive experiments.

Furthermore, XRD was also used to evaluate the stability of the photocatalysts; the results are shown in Fig. 9. The pattern of the used $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite is similar to that of the fresh one. However, the peak intensities ascribed to CdMoO_4 reduce, indicating that slight photocorrosion occurs on CdMoO_4 .

To corroborate the effective transfer and separation of the photogenerated charge carriers on the $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite, EIS and transient photocurrent response measurements were employed to evaluate the interfacial charge separation efficiency. The EIS Nyquist plots of pure $\text{g-C}_3\text{N}_4$, CdMoO_4 , and 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite are displayed in Fig. 10a. It can be observed that the diameter of the arc of $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite is smaller than those of $\text{g-C}_3\text{N}_4$ and CdMoO_4 , which suggests a lower charge transfer resistance at the electrode surface of $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite. In addition, the transient photocurrent responses (Fig. 10b) of $\text{g-C}_3\text{N}_4$, CdMoO_4 , and $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite under visible light irradiation were compared. Generally, photocurrent is mainly due to the transfer of photogenerated electrons to the counter electrode, and a higher photocurrent implies more efficient transfer of the photoexcited electrons. Evidently, the photocurrent response of

Fig. 10. (a) EIS results and (b) transient photocurrent responses of CdMoO_4 , $\text{g-C}_3\text{N}_4$, and 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite; (c) PL spectra of $\text{g-C}_3\text{N}_4$ and 4.8 wt% $\text{CdMoO}_4/\text{g-C}_3\text{N}_4$ composite; (d) Results of active species trapping experiments.

Fig. 11. Mott-Schottky curves of (a) g-C₃N₄ and (b) CdMoO₄.

CdMoO₄/g-C₃N₄ composite is larger than those of g-C₃N₄ and CdMoO₄. These results powerfully support the idea of improved separation and transfer efficiency of the photogenerated charge carriers in CdMoO₄/g-C₃N₄ composite. The steady-state PL spectra were also utilized to examine the separation and recombination processes of the photoinduced electron-hole pairs. As revealed in Fig. 10c, conspicuous PL quenching occurs in the 4.8 wt% CdMoO₄/g-C₃N₄ composite, compared with the case of pure g-C₃N₄, which suggests suppression of charge carrier recombination and enhancement of charge separation efficiency. To obtain deep insights into the photocatalytic mechanism, active species trapping experiments were performed under visible light irradiation. From Fig. 10d, the addition of IPA only slightly reduces the degradation of RhB, which indicates that $\cdot\text{OH}$ is a minor active species in the photocatalytic process. However, the addition of TEOA and BQ greatly inhibit the degradation of RhB, which indicates that $\cdot\text{O}_2^-$ and h^+ are the main reactive species in the photocatalytic system.

To determine the band energy positions and elucidate the possible transfer pathway of the photogenerated charge carriers between g-C₃N₄ and CdMoO₄, Mott-Schottky measurements were performed to determine the conductivity types and flat-band potentials of the photocatalysts. As exhibited in Fig. 11a and 11b, the flat-band potentials of g-C₃N₄ and CdMoO₄ are estimated to be -1.34 and -0.43 V (vs. Ag/AgCl, pH = 7), which are equivalent to -1.13 and -0.22 V (vs. NHE, pH = 7), respectively. Moreover, the positive slopes reveal that g-C₃N₄ and CdMoO₄ are both *n*-type semiconductors. For an *n*-type semiconductor, the CB potential is close to the flat-band potential, and therefore, the CB potentials of g-C₃N₄ and CdMoO₄ are about -1.13 and -0.22 eV (vs. NHE, pH = 7). By considering the band gap values, the VB potentials of g-C₃N₄ and CdMoO₄ are determined to be 1.60 and 3.22 eV (vs. NHE, pH = 7), respectively.

Based on the above results, a possible mechanism for the enhanced photocatalytic activity of CdMoO₄/g-C₃N₄ composites toward the degradation of RhB under visible light illumination is proposed that is based on the improvement in the separation and transfer of the photogenerated charge carriers at the in-

terface. As illustrated in Fig. 12, CdMoO₄ cannot be excited with visible light owing to its wider band gap, therefore, it exhibits a lower photocatalytic activity. On coupling CdMoO₄ with g-C₃N₄, the photoexcited electrons in the CB of g-C₃N₄ can easily transfer to the CB of CdMoO₄ through the contacted interface, since the CB potential of g-C₃N₄ (-1.13 eV vs. NHE) is more negative than that of CdMoO₄ (-0.22 eV vs. NHE). Meanwhile, the photogenerated holes tend to remain in the VB of g-C₃N₄. As a result, the photogenerated electrons and holes in g-C₃N₄ are effectively separated and recombination of the photoexcited charge carriers is greatly suppressed. The electrons in the CB of CdMoO₄ can reduce O₂ to generate $\cdot\text{O}_2^-$ radicals, while the holes in the VB of g-C₃N₄ will directly participate in the photocatalytic reaction, because the VB potential of g-C₃N₄ is less positive than the potential of $\cdot\text{OH}/\text{H}_2\text{O}$ (2.38 eV vs. NHE), and therefore g-C₃N₄ cannot oxidize H₂O to produce $\cdot\text{OH}$ radicals. The EIS results, transient photocurrent response, PL spectra, and active species trapping experiments well support this mechanism.

4. Conclusions

CdMoO₄/g-C₃N₄ composites were synthesized by a facile precipitation-calcination process. Compared with those of pristine g-C₃N₄ and CdMoO₄, the photocatalytic activities of CdMoO₄/g-C₃N₄ composites toward the degradation of RhB

Fig. 12. Proposed mechanism for enhanced photocatalytic activity over CdMoO₄/g-C₃N₄ composite.

solution were greatly enhanced, which could be ascribed to the efficient separation and transfer of the photogenerated charge carriers. EIS results, transient photocurrent response, and PL spectra confirmed the effective separation of the photoexcited electron-hole pairs. Active species trapping experiments demonstrated that h^+ and $\cdot O_2^-$ were the main active species during the photocatalytic reaction. $CdMoO_4/g-C_3N_4$ composites may be a promising photocatalyst for the degradation of organic pollutants.

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Graphical Abstract

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In situ fabrication of $CdMoO_4/g-C_3N_4$ composites with improved charge separation and photocatalytic activity under visible light irradiation

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$CdMoO_4/g-C_3N_4$ composites were rationally synthesized by a facile precipitation-calcination procedure. The enhanced photocatalytic activity of $CdMoO_4/g-C_3N_4$ composite could be attributed to the formation of type II heterojunctions that are based on their well-matched band energy structures.

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新颖CdMoO₄/g-C₃N₄复合材料的制备及其可见光增强的电荷分离和光催化活性

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摘要: 半导体光催化技术因其能够完全矿化和降解废水以及废气中的各种有机和无机污染物而受到越来越多研究者关注。尽管TiO₂作为光催化剂显示了良好的应用前景, 但其只对紫外光响应, 该部分能量大约仅占太阳光谱的5%, 从而限制了其实际应用。因此, 开发新型可见光响应光催化剂成为光催化领域的研究焦点之一。石墨相氮化碳(g-C₃N₄)作为一种光催化材料, 由于具有良好的热和化学稳定性以及可见光响应而备受关注。然而, 单纯的g-C₃N₄由于光生电荷载流子易复合, 光催化效果并不理想。为进一步提高g-C₃N₄的光催化活性, 构建g-C₃N₄基异质结复合光催化材料被认为是增强g-C₃N₄光生电子-空穴分离效率的有效方法。CdMoO₄作为一种光催化材料, 与g-C₃N₄匹配的能带有利于光生电子-空穴的分离, 从而提高g-C₃N₄的光催化活性。

本文通过便利的原位沉淀-煅烧过程, 制备了新颖的CdMoO₄/g-C₃N₄异质复合光催化材料。复合材料的晶相构成、形貌、表面化学组分和光学特性等通过相应的分析测试手段进行表征。光催化活性通过可见光下催化降解罗丹明B水溶液来评价。结果显示, 将CdMoO₄沉积在g-C₃N₄表面形成复合材料可明显提高光催化活性, 且当CdMoO₄含量为4.8 wt%时达到最佳的光催化活性。这种显著增强的光催化活性可能是由于CdMoO₄/g-C₃N₄复合物能够有效地传输和分离光生电荷载流子, 从而抑制了光生电子-空穴的复合。电化学阻抗、瞬态光电流和稳定荧光光谱测试结果证实, 通过CdMoO₄与g-C₃N₄复合可有效增强电荷分离效率。此外, 活性物种捕获实验表明, 在光催化过程中空穴(h⁺)和超氧自由基(·O₂⁻)是主要活性物种。根据莫托-肖特基实验并结合紫外-可见漫反射吸收光谱, 得到了单纯g-C₃N₄和CdMoO₄的能带结构, 提出了形成的II型异质结有助于增强光催化活性的机理。

关键词: CdMoO₄/g-C₃N₄复合物; 异质结; 电荷分离; 可见光; 光催化活性

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