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Construction of carbon nitride and MoS₂ quantum dot 2D/0D hybrid photocatalyst: Direct Z-scheme mechanism for improved photocatalytic activity

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ABSTRACT

Graphite-like carbon nitride (g-C₃N₄)-based compounds have attracted considerable attention because of their excellent photocatalytic performance. In this work, a novel direct Z-scheme system constructed from two-dimensional (2D) g-C₃N₄ nanoplates and zero-dimensional (0D) MoS₂ quantum dots (QDs) was prepared through the combination of a hydrothermal process and microemulsion preparation. The morphologies, structures, and optical properties of the as-prepared photocatalysts were characterized by X-ray diffraction, X-ray photoelectron spectroscopy, atomic force microscopy, transmission electron microscopy, and UV-vis diffuse reflectance spectroscopy. In addition, the photocatalytic performances of the prepared 2D/0D hybrid composites were evaluated based on the photodegradation of rhodamine B under visible-light irradiation. The results demonstrated that the introduction of MoS₂ QDs to g-C₃N₄ greatly enhanced the photocatalytic efficiency. For the optimum 7% MoS₂ QD/g-C₃N₄ photocatalyst, the degradation rate constant was 8.8 times greater than that of pure g-C₃N₄ under visible-light irradiation. Photocurrent and electrochemical impedance spectroscopy results further demonstrated that the MoS₂ QD/g-C₃N₄ composites exhibited higher photocurrent density and lower charge transfer resistance than those of the pure g-C₃N₄ or MoS₂ QDs. Active species trapping, terephthalic acid photoluminescence, and nitro blue tetrazolium transformation experiments were performed to investigate the evolution of reactive oxygen species, including hydroxyl radicals and superoxide radicals. The possible enhanced photocatalytic mechanism was attributed to a direct Z-scheme system, which not only can increase the separation efficiency of photogenerated electron-hole pairs but also possesses excellent oxidation and reduction ability for high photocatalytic performances. This work provides an effective synthesis approach and insight to help develop other C₃N₄-based direct Z-scheme photocatalytic systems for environmental purification and energy conversion.

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1. Introduction

In recent decades, photocatalysis technology has been proven to be a green method for resolving environmental issues and the energy crisis [1–5]. In particular, the development of novel visible-light-driven photocatalysts with low cost, excellent stability, and high activity has attracted considerable attention [6–8]. Graphitic carbon nitride (g-C₃N₄) with a two-dimensional (2D) nanosheet structure is a new type of metal-free semiconductor for visible-light photocatalysts and has attracted significant attention because of its suitable band gap ($E_g = 2.7$ eV), excellent chemical stability, and low cost [9–12]. However, the photocatalytic efficiency of g-C₃N₄ is limited by the low quantum efficiency and fast recombination of photo-generated charges [13–15]. Thus, developing novel g-C₃N₄-based photocatalysts with high quantum efficiency is highly desirable, and various strategies have been developed, including heterojunction construction [16,17], surface deposition of noble metals [18,19], and nonmetal doping [20–22]. However, these techniques cannot overcome the inherent deficiencies, such as the high recombination rate and low separation efficiency of photogenerated electron-hole pairs [23,24]. Therefore, finding a new route to improve the photocatalytic performance of g-C₃N₄ remains a great challenge.

It is well known that a Z-scheme photocatalytic system possesses enhanced separation efficiency of photoinduced electrons and holes on different semiconductors as well as strong redox ability [25,26]. Unfortunately, traditional Z-scheme systems consist of two individual semiconductors with noble metals or the electron acceptor/donor pairs as the electron mediator [27–29], and this type of structure has some drawbacks such as backward reactions and the reduction of light absorption, consequently inhibiting practical application. The construction of mediator-free direct Z-scheme systems only containing two semiconductor components has thus become promising and important. Recently, many g-C₃N₄-based photocatalytic systems with a direct Z-scheme mechanism have been constructed, such as g-C₃N₄/TiO₂ [30,31], g-C₃N₄/BiVO₄ [32], and g-C₃N₄/Ag₂CrO₄ [33], with enhanced separation efficiency of photoinduced electrons and holes. Therefore, it is a great challenge to design a novel and highly efficient direct Z-scheme g-C₃N₄-based photocatalytic system.

Compared with bulk materials, zero-dimensional (0D) quantum dots (QDs) possess unique advantages for application in photocatalysis, such as band gap tunability, strong light harvesting capability in the visible and near-infrared region, and large surface-to-volume ratios [34]. Recently, great developments of carbon, graphene, and MoS₂ QDs combined with layered materials as 0D/2D composite photocatalysts have been achieved [35–37]. Interactions between the 0D QD and 2D nanoplate moieties can make QDs more dispersive and stable, and the accelerated charge transfer from 2D nanoplates can inhibit the recombination of photoexcited charges, thereby resulting in greatly promoted photocatalytic activity [38,39]. For example, Fang et al. [40] introduced CdS QDs on the surface of graphene, leading to enhanced photocatalytic and photoelectric performance. MoS₂ QDs are potentially applicable in catalysis, fluo-

rescence sensing, and bio-imaging because of their excellent optical and electronic properties [41]. Li and coworkers [42] loaded MoS₂ QDs on graphene nanoplates, which displayed excellent hydrogen evolution reaction activity. Inspired by the aforementioned reports, an effective strategy of coupling MoS₂ QDs with other 2D layered materials was unveiled for the development of new visible-light-driven photocatalysts for environmental decontamination.

Herein, we developed a combined route using a hydrothermal process and microemulsion preparation to synthesize 2D/0D hybrid composites constructed from 2D carbon nitride nanoplates and 0D MoS₂ QDs. The as-obtained hybrid composites exhibited distinctly enhanced photocatalytic activity compared with that of pure g-C₃N₄ under visible-light irradiation. The enhanced photocatalytic activity was mainly attributed to the formation of a Z-scheme system in the 2D/0D hybrid composite. In addition, a possible Z-scheme photocatalytic mechanism for enhancing photocatalytic activity was also proposed.

2. Experimental

2.1. Catalyst preparation

Ammonium tetrathiomolybdate ((NH₄)₂MoS₄), hydrazine hydrate (N₂H₄·H₂O, 85%), and rhodamine B (RhB) were obtained from Sinopharm Chemical Reagent Co., Ltd. and used without further purification. Pure g-C₃N₄ nanosheets were prepared according to the procedures described in previous reports [43].

2.1.1. Synthesis of MoS₂ QDs

In this process, 0.1 g (NH₄)₂MoS₄ was dispersed in 20 mL of deionized water and 20 mL of ethanol, and the solution was mixed and sonicated for 30 min. Then, 1.5 mL of N₂H₄·H₂O was added dropwise to the above solution with stirring. Subsequently, the mixture was poured into a stainless-steel-lined Teflon autoclave and heated at 200 °C for 16 h. After the solution cooled naturally, it was filtered through a 0.22-μm microporous membrane and dialyzed with water. The solid samples were then obtained by evaporating the solvents.

2.1.2. Synthesis of MoS₂ QD/g-C₃N₄ composites

MoS₂ QD/g-C₃N₄ composite materials were prepared by applying a microemulsion method using hexanol (85/10 V/V versus H₂O, Aldrich), Triton X-100 (Aldrich), and *n*-heptane (105/100 V/V with surfactant Scharlau) as the cosurfactant, surfactant, and organic medium, respectively [44]. The g-C₃N₄ (0.1 g) was introduced into the microemulsion and sonicated for 10 h for further experiments. Different volumes of the MoS₂ QD aqueous solution were added dropwise into the above suspension and stirred for 24 h. The MoS₂ QD/g-C₃N₄ composites were collected by centrifugation and washed with absolute ethanol, deionized water, and acetone and then dried at 70 °C for 12 h. The MoS₂ QD/g-C₃N₄ composites were marked as x% MoS₂ QD/g-C₃N₄, where x indicates the mass fraction of the MoS₂ QDs (1%, 5%, 7%, and 10%).

2.2. Characterization

X-ray diffraction (XRD) analysis of the obtained products was performed using a D8 ADVANCE diffractometer (Cu $K\alpha$ radiation, $\lambda = 0.15406$ Å, 1 Å = 0.1 nm) in the 2θ range from 10° to 80° at room temperature. X-ray photoelectron spectroscopy (XPS) measurements were performed using a PHI ESCA-5000C electron spectrometer. Transmission electron microscopy (TEM) images were recorded using a Japan JEM-100CX II transmission electron microscope operated at an accelerating voltage of 100 kV. Atomic force microscopy (AFM) images were recorded using scanning probe microscopy (AR, MFP-3D). Diffuse reflectance ultraviolet-visible (UV-vis) absorption spectroscopy was performed using a Shimadzu UV2550 spectrophotometer with BaSO_4 as the reflectance sample. The photocurrent and electrochemical impedance spectroscopy (EIS) measurements were conducted using an electrochemical station (Chenhua Instruments, CHI660D).

2.3. Photocatalytic test

The photocatalytic activity of the samples was investigated based on the degradation of RhB (10 mg/L) under visible-light irradiation. The optical system for the photocatalytic reactions consisted of a 350 -W Xe lamp and a cut-off filter (excluding light of $\lambda > 420$ nm). In a typical photocatalytic experiment, 25 mg of the catalyst was added into 50 mL of the RhB aqueous solution and magnetically stirred for 1 h in the dark to reach adsorption/desorption equilibrium before the irradiation. During irradiation, 4 mL of the suspension was removed every 3 min and centrifuged (8000 rpm, 5 min) before measurement. Then, the dye concentration was monitored by measuring the

maximum UV absorbance at 553 nm for RhB.

2.4. Quantification of $\cdot\text{O}_2^-$ and $\cdot\text{OH}$

To quantitatively compare the $\cdot\text{O}_2^-$ production amount over different photocatalysts, a nitro blue tetrazolium (NBT) transformation experiment was performed [45]. The NBT concentration was 2.5×10^{-5} mol/L, and this experiment was similar to the RhB photodegradation test except that RhB was replaced by NBT. The concentration change of NBT was examined using a Shimadzu UV-5500PC spectrophotometer. To determine the amount of $\cdot\text{OH}$ produced from the as-prepared photocatalysts, TA (5×10^{-4} mol/L in NaOH solution (2 mmol/L)) was used as a probe molecule to react with $\cdot\text{OH}$, generating a highly fluorescent product 2-hydroxyterephthalic acid (HTA) [46], whose concentration reflected the yield of $\cdot\text{OH}$ measured by a Hitachi F-4600 fluorescence spectrophotometer.

3. Results and discussion

XRD patterns of the pure $\text{g-C}_3\text{N}_4$ and MoS_2 QD/ $\text{g-C}_3\text{N}_4$ composites are presented in Fig. 1(a). The XRD pattern of $\text{g-C}_3\text{N}_4$ exhibited a pronounced diffraction peak at 27.18° and a weak diffraction peak at 13.23° , corresponding to the periodic stacking of layers and the lattice planes parallel to the c -axis, respectively. The peak at 13.23° was nearly invisible compared with that reported in the literature [47]. This result may be caused by the decreased planar size of the $\text{g-C}_3\text{N}_4$ layers. For MoS_2 QD/ $\text{g-C}_3\text{N}_4$ composites, no obvious MoS_2 peaks were observed for MoS_2 QD additions of less than 7% , which may be attributed to the low mass fraction of MoS_2 in the composites. Upon increasing the mass fraction of the MoS_2 QDs to 10% , one typical

Fig. 1. (a) XRD patterns of pure $\text{g-C}_3\text{N}_4$ and MoS_2 QD/ $\text{g-C}_3\text{N}_4$ composites and (b–f) XPS spectra of MoS_2 QD/ $\text{g-C}_3\text{N}_4$ composites.

peak of the MoS₂ (006) plane and the diffraction peak of the g-C₃N₄ (002) plane were detected, confirming the successful formation of a MoS₂ QD/g-C₃N₄ hybrid composite.

To verify the components and chemical state of the MoS₂ QD/g-C₃N₄ composites, XPS measurements were conducted. The XPS results (Fig. 1(b–f)) indicate that the sample contained elemental C, N, Mo, and S and a small amount of O. The small amount of O may originate from surface absorption and oxidation. In the high-resolution C 1s spectra (Fig. 1(c)), the peaks at 284.6 and 288.08 eV correspond to *sp*² C–C bonds of graphitic carbon and *sp*²-hybridized C atoms (N–C=N) in the triazine. The N 1s spectra (Fig. 1(d)) can be fitted by three peaks at 398.53, 399.49, and 400.85 eV, which are attributed to a N atom *sp*²-bonded to two carbon atoms (C–N=C), tertiary nitrogen (N–(C)₃), and C–NH₂ functional groups, respectively. The O 1s peak can be attributed to H₂O adsorbed on the surface of the photocatalyst [48]. In Fig. 1(e), the binding energies of 229.2 and 232.43 eV are attributed to Mo 3d_{5/2} and Mo 3d_{3/2}, respectively, indicating that Mo is in the form of Mo⁴⁺ in the MoS₂ QDs. The peak at 162.06 eV in Fig. 1(f) is attributed to S 2p_{3/2}, and the peak at 163.23 eV can be assigned to S 2p_{1/2}, which are associated with the divalent S in the MoS₂ QDs [49,50]. The XPS and XRD results reveal the formation of a composite material with chemically bound interfaces between g-C₃N₄ and MoS₂.

TEM, HRTEM, and AFM analyses were further used to characterize the morphology and size of the MoS₂ QDs and MoS₂ QD/g-C₃N₄ composites (Fig. 2). The TEM image of the MoS₂ QDs in Fig. 2(a) clearly shows that the as-obtained QDs exhibited good monodispersity and that their size was smaller than 5 nm. Fig. 2(b) shows the Gaussian distribution of the particle size of the MoS₂ QDs. The average particle size of the prepared QDs was approximately 1.8 ± 0.7 nm. The HRTEM image in Fig. 2(c) shows that the QDs exhibited a highly paralleled and ordered lattice fringe, confirming their high crystallinity. The lattice fringe spacing was approximately 0.20 nm, which is in good agreement with previously reported results [51–54]. The *d* spacing of the MoS₂ QDs matches well with the (006) lattice of hexagonal crystal MoS₂. Furthermore, the size of the QDs was confirmed by AFM characterization (Fig. 2(d)); the height of the QDs was ~3 nm, which was similar to the TEM results. The representative TEM image of g-C₃N₄ in Fig. 2(e) reveals that the g-C₃N₄ nanosheets were composed of thin layers with wrinkles and irregular folding structures, which can provide a wide attachment plane for MoS₂ QDs. A TEM image of the MoS₂ QD/g-C₃N₄ composite is shown in Fig. 2(f), which reveals that some MoS₂ QDs were deposited on the surface of the sheet-like g-C₃N₄. The elemental maps of the MoS₂ QD/g-C₃N₄ composite (Fig. 2(g)) clearly reveal the uniform distribution of elemental C, N, Mo, and S in the composite, confirming that the MoS₂ QD/g-C₃N₄ composites were successfully prepared.

UV-vis diffuse reflectance spectroscopy (DRS) was used to determine the optical properties of the pure g-C₃N₄, MoS₂ QDs, and MoS₂ QD/g-C₃N₄ samples. The corresponding UV-vis spectra are presented in Fig. 3. The pure g-C₃N₄ had an absorption edge at approximately 450 nm, which is consistent with previously reported results [55], whereas the MoS₂ sample exhibited a strong absorption edge at ~420 nm. However, the spectra

Fig. 2. (a) TEM image and (b) corresponding particle size distribution histogram; (c) HRTEM image; and (d) AFM image of MoS₂ QDs. TEM images of (e) pure g-C₃N₄ and (f) MoS₂ QD/g-C₃N₄ composites. (g) SEM image of MoS₂ QD/g-C₃N₄ composites and elemental maps showing the spatial distribution of C, N, Mo, and S.

show the consequence of variation in the MoS₂ QD content after loading MoS₂ QDs on g-C₃N₄. The light-absorption ability in the entire spectral range of the composites was gradually enhanced upon increasing the content of MoS₂ QDs, suggesting the contribution of absorption by the MoS₂ QDs. More remarkably, compared with the other samples, the 7% MoS₂ QD/g-C₃N₄ sample exhibited the highest absorption intensity over the entire spectral range. Similar phenomena have been reported in the literature [56], and the enhanced absorption was explained as the strong electronic coupling between two semiconductors. Therefore, in the present system, the absorption enhancement indicates strong electronic coupling between the MoS₂ QDs and g-C₃N₄ nanoplates, which is beneficial for enhanced photocatalytic activity.

The band edge positions are important because of their di-

Fig. 3. (a) UV-vis DRS spectra of pure g-C₃N₄, MoS₂ QDs, and MoS₂ QD/g-C₃N₄ composites; (b–d) Plots of $(\alpha h\nu)^{1/2}$ versus energy ($h\nu$) for determining the band gap energies of the g-C₃N₄, MoS₂ QDs, and MoS₂ QD/g-C₃N₄ composites.

rect effect on the redox reactions occurring at the particle surface. The band gaps of the prepared samples were calculated from the spectra with the help of a Tauc plot using the following equation:

$$\alpha(h\nu) = A(h\nu - E_g)^{n/2}$$

where α , h , ν , E_g , and A are the absorption coefficient, Planck constant, light frequency, band gap energy, and a constant, respectively. n is determined by the type of optical transition of the semiconductor ($n = 1$ for direct transition and $n = 4$ for indirect transition) [57]. For the pure g-C₃N₄ and MoS₂ QDs, the values of n are both 4 [57]. The band gap energies of the g-C₃N₄, MoS₂ QDs, and (1%, 5%, 7%, and 10%) MoS₂ QD/g-C₃N₄ composites were determined to be 2.76, 2.98, 2.74, 2.73, 2.72, and 2.75 eV, respectively (Fig. 3(b–d)).

The photocatalytic activities of the MoS₂ QD/g-C₃N₄ composites were investigated based on the degradation of RhB under visible-light irradiation. All the MoS₂ QD/g-C₃N₄ photocatalysts clearly exhibited higher photodegradation activities than that of pure g-C₃N₄ (Fig. 4(a)). The 7% MoS₂ QD/g-C₃N₄ photocatalyst exhibited the highest photocatalytic activity with almost complete degradation of RhB within 12 min. To investigate the kinetics of the RhB degradation by the MoS₂ QD/g-C₃N₄ photocatalysts, a pseudo-first-order reaction model was applied to describe the experimental data as follows: $-\ln(C/C_0) = k_{app}t$, where k_{app} is the pseudo-first-order reaction rate constant, C_0 is the adsorption equilibrium concentration of RhB, t is the reaction time, and C is the concentration of RhB at the reaction time [58]. The plots of $-\ln(C/C_0)$ vs. illumination time are linear (Fig. 4(b)), suggesting that the photodegradation reactions follow pseudo-first-order kinetics. The apparent reaction rate con-

stant k for the photodegradation of RhB was calculated by linear fitting of the experimental data. The k values of the MoS₂ QD/g-C₃N₄ composites were much higher than that of g-C₃N₄. In particular, the 7% MoS₂ QD/g-C₃N₄ composite exhibited the highest k value (0.30 min⁻¹), which was approximately 8.8 times higher than that of g-C₃N₄ (0.034 min⁻¹). In addition, a comparison of our findings with the photocatalytic activities of various MoS₂/g-C₃N₄ composites reported by other researchers is presented in Table 1, which also indicates that the MoS₂ QD/g-C₃N₄ composites exhibited excellent photodegradation activity. Fig. 4(c) shows the temporal evolution of the absorption spectra of RhB under visible-light irradiation in the presence of the 7% MoS₂ QD/g-C₃N₄ photocatalyst. The intensity of the absorption peak at 553 nm gradually decreased with increasing irradiation time and almost disappeared after 9 min, indicating that the MoS₂ QD/g-C₃N₄ composite exhibited excellent photocatalytic activity during the reaction. Trapping experiments were performed to explore the photocatalytic mechanism of the MoS₂ QD/g-C₃N₄ composites and the effects of different scavengers on RhB degradation in detail (Fig. 4(d)). In this experiment, *p*-benzoquinone (BZQ), disodium ethylenediamine tetraacetate (Na₂-EDTA), and butyl alcohol were used as scavengers for superoxide radicals, photo-generated holes, and hydroxyl radicals, respectively [59]. As shown in Fig. 4(d), the degradation efficiency of RhB under visible-light irradiation decreased significantly when BZQ was used as the scavenger for the superoxide. In contrast, the addition of Na₂-EDTA and butyl alcohol only slightly affected the photodegradation of RhB, implying that $\cdot\text{OH}$ and h^+ played a relatively minor role in the enhanced photocatalytic performance. Based on these re-

Fig. 4. (a) Photocatalytic degradation and (b) pseudo-first-order kinetics for degradation of RhB with pure g-C₃N₄ and MoS₂QD/g-C₃N₄ composites; (c) Absorption spectral changes of RhB; (d) Trapping experiment results during the photocatalytic degradation of RhB.

sults, it can be concluded that $\cdot\text{O}_2^-$ is the main oxygen active species for the MoS₂ QD/g-C₃N₄ Z-scheme photocatalyst for RhB degradation.

The recombination of photogenerated electron-hole pairs is an important factor that restricts the photocatalytic performance of photocatalysts [61,62]. The transient photocurrent responses and electrochemical impedance spectra were used to examine the separation efficiency of photogenerated electron-hole pairs for the prepared samples. Transient photocurrent responses of MoS₂ QD/g-C₃N₄ and pure g-C₃N₄ were recorded for 5 on-off cycles under visible-light irradiation, as shown in Fig. 5(a). All of the samples exhibited an apparent photocurrent response under visible-light illumination, indicating that the photoelectrons shifted to the cathode and produced a photocurrent [63]. The MoS₂ QD/g-C₃N₄ composites clearly exhibited much higher photocurrent density than the pure g-C₃N₄ or MoS₂ QDs. The formation of the Z-scheme system between the MoS₂ QDs and g-C₃N₄ can effectively separate

the photoelectrons and holes, thus leading to an increase in the photocurrent and improved photocatalytic activity [64]. EIS spectra of different electrodes were obtained under visible-light irradiation to obtain further insight into the charge-transfer phenomenon and photogenerated electron-hole recombination properties over the surface of the MoS₂ QD/g-C₃N₄ composites, as shown in Fig. 5(b). The results clearly demonstrated that the MoS₂ QD/g-C₃N₄ electrode exhibited a lower charge transfer resistance than the g-C₃N₄ or MoS₂ QD electrodes, which indicates more efficient photo-generated electron-hole pair separation and faster interfacial charge transfer at the MoS₂ QD/g-C₃N₄ surface compared with those of the bare material. These results clearly demonstrate that the charge transfer/interfacial resistance over the surface of the bare electrode can be significantly reduced by the introduction of MoS₂ QDs.

It is important to understand the energy levels of MoS₂ and g-C₃N₄, which play an important role in determining the

Table 1

Comparison of photocatalytic performance of photocatalysts prepared in this work with that of other MoS₂/g-C₃N₄ photocatalysts under visible-light irradiation.

Catalyst	Decomposition rate (%)	Irradiation time (min)	Initial concentration of dye (mg/L)	Light source	Reference
MoS ₂ /g-C ₃ N ₄	RhB, 73.8%	150	10	Xe lamp	[9]
MoS ₂ /g-C ₃ N ₄	MO, 63%	300	20	simulated solar light	[15]
MoS ₂ /g-C ₃ N ₄	RhB, 80%	150	20	500-W Xe lamp	[58]
MoS ₂ /g-C ₃ N ₄	MO, 68%	180	10	simulated solar light	[59]
MoS ₂ /g-C ₃ N ₄	RhB, 100%	20	5	300-W Xe lamp	[48]
MoS ₂ /g-C ₃ N ₄	RhB, 96%	20	10	300-W Xe lamp	[60]
MoS ₂ /g-C ₃ N ₄	RhB, 100%	9	10	350-W Xe lamp	This work

Fig. 5. Transient photocurrent response (a) and electrochemical impedance spectra (b) of pure g-C₃N₄ and MoS₂ QD/g-C₃N₄ composites.

flowchart of photogenerated charge carrier transfer in the MoS₂ QD/g-C₃N₄ hybrid composites. The valence band (VB) edge positions of the MoS₂ QDs and g-C₃N₄ were estimated using the concept of electronegativity. The electronegativity of an atom is the arithmetic mean of the atomic electron affinity and the first ionization energy. The VB edge potential of a semiconductor at the point of zero charge can be calculated using the following empirical equation:

$$E_{VB} = X - E^e + 0.5E_g$$

where E_{VB} is the VB edge potential, X is the electronegativity of the semiconductor, E^e is the energy of free electrons on the normal hydrogen electrode (NHE) potential scale (approximately 4.5 eV), and E_g is the band gap energy of the semiconductor. Moreover, the conduction band (CB) edge potential (E_{CB}) can be determined using $E_{CB} = E_{VB} - E_g$. The CB and VB edge potentials of g-C₃N₄ are approximately -1.16 and 1.6 eV, respectively, whereas the CB and VB edge potentials of the MoS₂ QDs are approximately -0.29 and 2.69 eV [65], respectively. Because the CB potential of g-C₃N₄ is more negative than that of MoS₂, the photogenerated electrons in the CB of g-C₃N₄ may migrate to the CB of MoS₂ according to the traditional separation process of electron-hole pairs [66]. Thus, the accumulated electrons in the CB of MoS₂ cannot produce the main reactive species $\cdot\text{O}_2^-$ because the CB potential is more positive than that of the $E^0(\text{O}_2/\cdot\text{O}_2^-)$ (-0.33 eV vs. NHE) if transfer of photogenerated charge occurs via the traditional electron-hole transfer process [67,68]. However, the results of the trapping experiments reveal that the $\cdot\text{O}_2^-$ radical plays a major role in RhB degradation.

To further confirm the charge migration route, TA-assisted PL spectroscopy (detection of $\cdot\text{OH}$) and NBT transformation (detection agent of $\cdot\text{O}_2^-$) were performed during the photocatalytic reaction. The non-fluorescent TA molecules can react with the $\cdot\text{OH}$ radical to produce highly fluorescent HTA, which is detectable by the PL spectrometer. The PL peak intensity of the HTA is proportional to the number of produced $\cdot\text{OH}$ radicals. The PL spectra of the MoS₂ QD/g-C₃N₄ photocatalysts under different illumination times are presented in Fig. 6(a). The PL intensity of the HTA in the sample clearly increased with prolonged illumination time, indicating that the photogenerated

holes on the MoS₂ QD/g-C₃N₄ composite had sufficient oxidation potential to generate $\cdot\text{OH}$ radicals, which can react with TA to produce HTA. However, the photogenerated holes on g-C₃N₄ did not have sufficient oxidation potential to react with $\text{OH}^-/\text{H}_2\text{O}$ and generate $\cdot\text{OH}$ radicals (Fig. 6(b)). It can thus be concluded that the photogenerated holes accumulated on the surface of the MoS₂ QDs. Fig. 6(c) presents the spectra of the transformation percentage of NBT in the presence of g-C₃N₄ and the MoS₂ QD/g-C₃N₄ composite, which show a clear transformation of the percentage of NBT. In contrast, for pure MoS₂ QDs (Fig. 6(d)), almost no $\cdot\text{O}_2^-$ radicals were produced from the electrons of MoS₂ because its CB potential (-0.29 eV vs. NHE) is more positive than $E^0(\text{O}_2/\cdot\text{O}_2^-)$ (-0.33 eV vs. NHE). The results indicate that the photogenerated electrons mainly accumulated in the g-C₃N₄, which had a sufficiently high reduction potential to produce $\cdot\text{O}_2^-$. Therefore, the migration of photogenerated charge carriers in the MoS₂ QD/g-C₃N₄ hybrid composites follows the direct Z-scheme route.

Based on the above analyses, a possible Z-scheme mechanism for organic contaminant degradation using the MoS₂ QD/g-C₃N₄ hybrid photocatalyst was proposed, as illustrated in Fig. 7. Unlike the traditional model, the Z-scheme mechanism photocatalysts retained stronger oxidation and reduction abilities, which deeply contributed to the improvement of the photocatalytic performance [69–71]. Under visible-light irradiation, both MoS₂ QDs and g-C₃N₄ can absorb visible-light photons to produce photogenerated electrons and holes. In the MoS₂ QD/g-C₃N₄ hybrid photocatalyst system, the photoexcited electrons in the CB of the MoS₂ QDs rapidly transferred to the VB of g-C₃N₄, leading to the combination of photogenerated electrons in the CB of the MoS₂ QDs and photogenerated holes in the VB of g-C₃N₄. These accumulating electrons in the CB of g-C₃N₄ and holes in the VB of MoS₂ QDs then participate in the dye degradation. Consequently, the more negative potentiated electrons in the CB of g-C₃N₄ reduce the molecular oxygen to yield $\cdot\text{O}_2^-$, which induces the RhB degradation. Meanwhile, the more positive potentiated holes in the VB of the MoS₂ QDs produce rich active $\cdot\text{OH}$ radicals with powerful oxidation. In addition, holes in the VB of MoS₂ QDs can directly oxidize the organic dye. Therefore, the charge transfer of the MoS₂ QD/g-C₃N₄ compo-

Fig. 6. (a) PL spectral changes observed during illumination for the 7% MoS₂ QD/g-C₃N₄ sample; (b) PL spectral changes, and spectra of NBT transformation for (c) g-C₃N₄ and MoS₂ QDs and (d) 7% MoS₂ QD/g-C₃N₄ composite.

sites may follow a direct Z-scheme route, which could improve the photogenerated electron-hole pair separation efficiency and result in enhanced photoactivity for the degradation of organic pollutants.

Fig. 7. Schematic illustration of charge separation and transfer in the MoS₂ QD/g-C₃N₄ composites.

4. Conclusions

g-C₃N₄ and MoS₂ QD 2D/0D hybrid photocatalysts were constructed using a combination of a hydrothermal process and microemulsion preparation. The addition amount of the MoS₂ QDs had a significant effect on the photocatalytic activity of the MoS₂/g-C₃N₄ composites. The optimized 7% MoS₂ QD/g-C₃N₄ hybrid photocatalyst exhibited approximately nine times higher photocatalytic activity than that of the pure g-C₃N₄. In addition, radical trapping experiments verified that $\cdot\text{O}_2^-$ played a key role in the degradation of organic pollutants. The improved photocatalytic performance was attributed to the intimate interfacial contact between the MoS₂ QDs and g-C₃N₄ and effective separation of photogenerated charge carriers resulting from the direct Z-scheme structure. Our work provides new insight for the development of other g-C₃N₄-based direct Z-scheme photocatalytic systems for environmental purification and energy conversion.

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Graphical Abstract

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Construction of carbon nitride and MoS₂ quantum dot 2D/0D hybrid photocatalyst: Direct Z-scheme mechanism for improved photocatalytic activity

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This manuscript develops a novel direct Z-scheme system constructed from g-C₃N₄ nanoplates (2D) and MoS₂ quantum dots (QDs) (0D) with high photocatalytic performances.

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2D/0D氮化碳与MoS₂量子点直接Z型光催化剂的构筑及光催化性能

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摘要: 近年来, 光催化技术作为一种“绿色”技术, 在解决环境问题和能源危机等方面有着广泛的应用. 新型可见光响应的半导体光催化材料g-C₃N₄具有二维(2D)纳米片结构, 合适的禁带宽度($E_g = 2.7 \text{ eV}$), 优异的化学稳定性和低廉成本得到广泛的研究. 但是, g-C₃N₄光催化剂本身的光生电子-空穴对复合几率高以及可见光响应范围窄等缺点, 使其在光催化领域应用中具有一定的局限性. 因此, 提高g-C₃N₄半导体材料的光催化活性成为近年的研究热点. 众所周知, Z型光催化体系的构筑不仅使材料具有较强的氧化还原能力而且有利于其光生电子-空穴的有效分离. 但传统Z型光催化体系由于贵金属的引入、复杂的反应体系限制了其在实际领域中的应用. 因此, 构筑无电子介体的直接Z型光催化体系成为光催化领域的研究热点之一. 与块状材料相比, 零维(0D)量子点材料具有带隙可调性, 可见光和近红外区域的强光收集能力等性能, 在光催化领域具有广阔的应用前景. MoS₂量子点具有优异的光学和电子性能, 因此, 在催化、荧光检测、生物成像领域有重要的应用价值.

我们结合水热和微乳溶液法合成了直接Z型g-C₃N₄/MoS₂ QDs (2D/0D)复合光催化材料, 并采用X射线衍射(XRD)、X射线光电子能谱(XPS)、原子力显微镜(AFM)、透射电子显微镜(TEM)以及紫外可见漫反射光谱(UV-vis)等表征方法对该催化剂的结构特征、微观形貌和光学性能进行分析. 并研究了g-C₃N₄/MoS₂ QDs复合材料在可见光下的光催化性能.

XRD, XPS结果表明, 复合材料由g-C₃N₄, MoS₂组成. TEM和高斯分布结果表明, MoS₂ QDs具有良好的分散性, 其尺寸小于5 nm, g-C₃N₄纳米片由具有皱纹和不规则折叠结构的薄层组成, 在g-C₃N₄/MoS₂ QDs复合材料中可以看到少量的MoS₂量子点沉积在片状g-C₃N₄的表面上. 光催化性能测试结果进一步表明, 7% MoS₂ QDs/g-C₃N₄在可见光下具有优异的光催化

性能: 可见光照射12 min内, RhB的降解效率可达100%, 降解速率常数是纯g-C₃N₄的8.8倍.

为了进一步研究g-C₃N₄/MoS₂异质结光催化剂的光催化机理, 用对苯醌、乙二胺四乙酸二钠和丁醇进行了自由基捕捉剂实验. 结果表明, 超氧自由基在降解有机染料过程中起主要作用, 羟基自由基和空穴在增强的光催化性能中发挥相对较小的作用. 通过光电流测试、材料价带导带位置计算以及[•]O₂⁻和[•]OH定量实验结果并结合文献分析认为, MoS₂量子点和g-C₃N₄之间优良的界面接触以及由直接Z型结构产生的光生电荷载体的有效分离使其光催化性能得到显著提升.

关键词: 光催化; 直接Z构型; 二维; 零维; g-C₃N₄; MoS₂量子点

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