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1. Introduction

There are growing concerns over organic pollutants in daily life as these have a number of effects on human health. Methods to eradicate organic pollutants in water and air are being greatly investigated. Researchers have found that disintegration of organic pollutants by photocatalytic degradation using photocatalysts is an effective method.¹⁻⁴ Semiconductor nanomaterials have been regarded as the most promising photocatalysts due to their efficient degradation activity for pollutants in water and air.⁵⁻⁷ Among the different semiconductors, TiO₂ is the most famous one because of its superior properties of low cost, environment friendliness and recycling performance.8 However, the practical application of TiO₂ is limited by its wide bandgap, unsatisfying response to visible light and short lifetime of lightinduced charge-carriers.^{9,10} Hence, the development of simple, efficient and sustainable visible-light-induced photocatalysts has attracted much attention. Transition metal sulfides, such as CdS,¹¹ CuS,¹² Cu₂S¹³ and ZnS,¹⁴ with controllable electronic

One-pot synthesis of 3D Cu₂S–MoS₂ nanocomposites by an ionic liquid-assisted strategy with high photocatalytic activity[†]

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Novel 3D Cu₂S-MoS₂(x:y) nanocomposites with different proportions of Cu₂S (x) and MoS₂ (y) are synthesized successfully by a one-step hydrothermal method with the assistance of the ionic liquid [BMIM]SCN. The characterization results show that the nanocomposites are self-assembled from nanosheets of Cu₂S and MoS₂, they display nanoflower morphology and a typical mesoporous structure. The fabrication mechanism of the nanocomposites is investigated using time-dependent experiments, which indicate the key role of the ionic liquid (IL) in the synthesis process. Furthermore, TAA is used as a sulfur source instead of the IL to form a Cu₂S-MoS₂ nanocomposite, with the aim of further investigating the effects of the IL on the morphology of the composite. Photodegradation of MB under visible light irradiation experiments were used as probe reactions to evaluate the photocatalytic performance of the as-prepared samples. All the nanocomposites show better catalytic activity than Cu₂S and MoS₂ monomers. Among the different Cu₂S-MoS₂(x:y) nanocomposites, the Cu₂S-MoS₂(1:1) composite exhibits the most excellent photocatalytic performance and cycling stability.

structures due to their rich d electrons, have been used as effective photocatalytic semiconductors for pollutant degradation. Among these, cuprous sulfide (Cu_2S), a p-type semiconductor with a bulk band gap of 1.2 eV, has excellent absorption ability in the visible wavelength region, which lies in the optimum range for solar energy utilization. Up to now, Cu₂S has been reported as an ideal visible-light-absorbing and photoelectric material for solar cells,15 biosensors,16 solar energy conversion17 and efficient photocatalysis.¹⁸ However, the high rate of photo-generated electron-hole recombination limits the practical application of Cu₂S as photocatalysts. It is well known that both the adsorption ability of light and recombination rate of photo-generated electron-hole pairs have significant effects on photocatalytic reactions.¹⁹ Therefore, intensive efforts have been made to develop heterojunctions or composites, which are aiming to extend the lifetimes of the photo-induced charge carriers for higher efficiency of degradation. Heterostructures or composites usually have larger specific surface areas than those of the two components and there are interfaces between the two components. These structural advantages provide an extended light response range, separation rate of photo-generated electron-hole pairs and lower the activation energy barrier for chemical reaction, which could effectively enhance the photocatalytic performance to the singlecomponent semiconductor.²⁰⁻²² In recent years, some semiconductor heterojunctions or composites such as Cu₂S-Bi₂WO₆, Bi₂WO₆-g-C₃N₄, Cu₂S-MoO₃, V₂O₅/MoO₃, Fe₂O₃-TiO₂-graphene

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aerogel, CuS–Cu $_2$ S^{23–34} *etc.* have been reported as photocatalysts with enhanced activities.

Molybdenum disulfide (MoS₂) has a layered structure consisting of Mo–S–Mo sandwiched in a graphite-like manner. MoS₂ nanostructures have been found to have a superior response to visible-light illumination due to their layered structures. Hence, MoS₂ nanostructures are usually used as co-catalysts to improve photocatalysts in terms of catalytic activity and stability against photo corrosion.^{35–39} Nano-MoS₂ has a high conduction band energy level, which makes it an electronic trapper and it can easily transfer electrons to Cu₂S. The extended electronic channels allow longer separation-times of photo-generated electronholes. However, the reported Cu₂S–MoS₂ composites were usually synthesized by complex preparation procedures and have small specific surface areas.^{40,41}

In this paper, Cu_2S-MoS_2 composites are facilely synthesized by a one-pot strategy with the assistance of an IL and hydrothermal conditions. Comparing with the other synthesis methods, a one-pot strategy is relatively simple and convenient. The fabrication mechanism of the nanocomposites with the assistance of the IL is investigated using time-dependent experiments. Furthermore, the photocatalytic performance of the Cu_2S-MoS_2 nanocomposites, Cu_2S and MoS_2 are investigated using the photodegradation of MB solution under visible-light irradiation. The influence of the proportions of Cu_2S and MoS_2 on the morphology, structure and photocatalytic performance are discussed. Moreover, a Cu_2S-MoS_2 composite is synthesized using TAA as a sulfur source instead of the IL, and the key role of the ionic liquid in the synthesis of Cu_2S-MoS_2 composites is also discussed.

2. Experimental

2.1 Synthesis of $Cu_2S-MoS_2(x:y)$ materials

Different amounts of $Cu(CH_3COO)_2 \cdot H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.033 g and 0.099 g; 0.044 g and 0.088 g; 0.066 g and 0.066 g; 0.088 g and 0.044 g; 0.099 g and 0.033 g) with 0.366 g [BMIM]SCN were dissolved in 16 mL deionized water. After a white precipitate was formed, the solution was stirred for 30 min. Then, the solution was transferred into a 20 mL autoclave for hydrothermal synthesis and heated at 200 °C for 24 h. Finally, the precipitate was washed with deionized water and ethanol, and then dried at 60 °C. The samples were labelled $Cu_2S-MoS_2(x:y)$, in which x:y is the ratio of Cu_2S to MoS_2 in the samples.

 Cu_2S was synthesized under the same conditions with 0.066 g $Cu(CH_3COO)_2{\cdot}H_2O,\ 0.366$ g [BMIM]SCN and 16 mL deionized water without the molybdenum precursor.

 MoS_2 was also synthesized under the same conditions with 0.066 g $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O,$ 0.366 g [BMIM]SCN and 16 mL deionized water.

 $Cu_2S-MoS_2(1:1)$ -T was synthesized using thioacetamide (TAA) as the sulfur source instead of [BMIM]SCN: 0.066 g $Cu(CH_3COO)_2$ ·H₂O, 0.066 g $(NH_4)_6Mo_7O_{24}$ ·4H₂O and 0.134 g TAA were dispersed in 16 mL deionized water. After stirring for 30 min,

the solution was transferred into a 20 mL autoclave for hydrothermal synthesis at 200 °C for 24 h. $Cu_2S-MoS_2(1:1)$ -T was obtained after washing and drying procedures.

2.2 Characterization

The crystalline structures of the as-prepared samples were characterized using X-ray powder diffraction (XRD) (Bruker D8 FOCUS, Cu K_{α} radiation, $\lambda = 0.15056$ nm). SEM images were obtained using a ZEISS MERLIN Compact (Field Emission) scanning electron microscope. TEM images of the samples were collected using a Tecnai G2 F20 transmission electron microscope. Elemental analysis was performed using an Elementar vario EL cube. A Varian 725-ES inductively coupled plasma spectrometer was used to measure the metal content in the as-prepared samples. Ultraviolet-visible (UV-Vis) diffuse reflectance spectroscopy (DRS) of the samples was carried out using a Cary 100 UV-Vis spectrophotometer and the scanning range was 200-800 nm. X-ray photoelectron spectra (XPS) and Auger electron spectroscopy (AES) experiments were conducted using a Kratos Axis Ultra DLD multi-technique X-ray photoelectron spectrometer. The specific surface area (SSA) and pore size of the resultant samples were investigated using an Autosorb-1-MP 1530VP automatic surface area and porosity analyzer. Samples were degassed at 200 °C for 3 h and then analyzed at -196 °C.

2.3 Photocatalytic measurements

The photocatalytic performance of the as-prepared Cu₂S-MoS₂ samples was evaluated using the photocatalytic degradation of MB aqueous solution under visible-light illumination using a 500 W Xe lamp. The temperature inside the reactor was maintained at 20 °C via a continuous circulation of water surrounding the reactor. In the experiment, 50 mg of the photocatalyst was dispersed in 60 mL of MB aqueous solution $(10^{-4} \text{ mol } \text{L}^{-1})$. The suspension was stirred with a magnetic stirrer for 60 min in darkness before irradiation, which ensured the adsorptiondesorption equilibrium of the MB aqueous solution on the photocatalyst. 60 mL of MB aqueous solution $(10^{-4} \text{ mol L}^{-1})$ without photocatalyst was used as a control reaction with continuous magnetic stirring. At the 15 min interval, an aliquot of the mixture was taken out and centrifuged at 8000 rpm for 3 min. Then, the supernatant solution was analysed using a UV-Vis spectrophotometer (Shimadzu UV-2450). The characteristic absorption peak of MB was 664 nm in the UV-Vis absorption spectra.

Results and discussion

3.1 Characterization of the photocatalysts

Fig. 1a–e shows the SEM images of Cu₂S–MoS₂ samples with different proportions of Cu₂S and MoS₂ (calculated from ICP measurements). It can be seen that all the samples are assembled from nanosheets, showing the nanoflower morphology. The average diameters of nanoflowers in Fig. 1a–e vary from 0.3 μ m to 1.5 μ m along with the variation of the Cu–Mo ratio. In addition, the dispersity of the samples is different. Among the samples, Cu₂S–MoS₂(1:1) displays the most regular structure



Fig. 1 (a-e) SEM images of $Cu_2S-MoS_2(x : y)$: (a) 1:3, (b) 1:2, (c) 1:1, (d) 2:1 and (e) 3:1; (f) XRD patterns of samples.

with a diameter of 0.8-1 µm. The X-ray diffraction (XRD) diagram gives the specific composite of Cu, Mo and S elements in Fig. 1f. As shown by the red line of PDF card 53-0522 (Fig. 1f), the peaks at 15.9°, 27.7°, 36.1°, 46.2° and 54.7° could be attributed to the {100}, {111}, {210}, {220} and {311} planes of Cu₂S. The characteristic peaks at 39.5° , 60.1° and 70.1° correspond to the {103}, {008} and {108} planes of MoS₂ (blue line of PDF card 37-1492). The broad peak at 32.3° is an overlapping peak which is caused by the overlap of the $\{200\}$ plane of Cu₂S and the $\{100\}$ plane of MoS22. Moreover, the peaks at 9.0° and 17.6° are attributed to low crystallinity of the MoS₂{002} plane.⁴² After annealing treatment, the two peaks shifted to 14.3°, which is attributed to the {002} plane reflection. In Fig. 1f, diffraction peak intensity increases when the ratio of Cu₂S to MoS₂ increases from 1:3 to 1:1, and then decreases dramatically when the ratio increases from 1:1 to 3:1. This means that the $Cu_2S-MoS_2(1:1)$ composite exhibits the best long-term ordered structure, which is in agreement with the SEM results. The XRD pattern of the prepared pure Cu₂S is shown in Fig. S1 (ESI[†]), which corresponds with PDF card 53-0522. The Cu₂S exhibits nanoflower morphology assembled with some nanosheets as shown in Fig. S2 (ESI⁺). The XRD pattern and SEM image of pure MoS₂ are shown in Fig. S3 and S4 (ESI⁺), respectively. It can be seen that its XRD pattern can be assigned to PDF card 37-1492 with a rod-shaped morphology. Compared with pure Cu₂S and MoS₂, the composites show a more regular morphology, which may have an impact on the photocatalytic performance of $Cu_2S-MoS_2(x:y)$ composites.

 N_2 adsorption-desorption experiments were carried out to investigate the textural and structural characteristics of the resultant samples, and the results are shown in Fig. 2 and Table 1. All the samples exhibit the typical type IV adsorptiondesorption isotherm with a H3 hysteresis. This means that the samples are characterized by a mesoporous structure and slit-like pores. In addition, all of the nanocomposites show a similar pore size distribution with the maximum values located at 3.8 nm. As the proportion of Cu₂S increases, the S_{BET} of the samples increases continuously (Table 1) and all of the composites with different proportions exhibit a much higher specific surface area than that of pure Cu₂S and MoS₂. The differences in specific surface area may affect the catalytic performance of the composites.



Fig. 2 $\,N_2$ adsorption–desorption isotherms and pore size distributions of samples.

Table 1	Specific	surface	areas	of Cu ₂ s	$S - MoS_2(x)$: y)	samples
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x:y	1:3	1:2	1:1	2:1
$S_{\rm BET} ({\rm m}^2 {\rm g}^{-1})$	21.94	35.87	49.31	67.52
x:y	3:1	Cu_2S	MoS_2	(1:1)-T
$S_{\rm BET} \left({ m m}^2 { m g}^{-1} ight)$	81.93	5.55	16.67	28.94

TEM images of the $Cu_2S-MoS_2(1:1)$ nanocomposite are shown in Fig. 3a and b, and two different lattice stripes can be found in the HRTEM image of the sample. In Fig. 3b, two orthogonal lattice fringes in the top inset show crystal spacing of 0.39 and 0.56 nm, which can be assigned to the {110} and {100} planes of Cu₂S (53-0522), respectively. According to the literature,⁴³ the layered spacing of 0.89 nm in the bottom inset should be the classical {002} plane of MoS₂ (37-1492), which maybe resulted from hydrothermal synthesis of MoS₂ without annealing treatment. The existence of Cu, Mo and S is confirmed by the EDS spectrum and elemental mapping shown in Fig. 3c. As the X-ray can penetrate 1 µm thickness, we could deduce that Mo, Cu and S are all distributed in the sample with high abundance. Meanwhile, the interlayer distance of the peak at 9.0° in the XRD pattern is about 0.9 nm according to the Bragg equation, which agrees with the result of the TEM. From the electron microscopy images, EDS-mapping and XRD analysis, it is demonstrated that nanoflower like composite materials have been successfully prepared in one-pot, and these are made up of Cu₂S and MoS₂.



Fig. 3 (a and b) HRTEM images and (c) EDS spectrum and elemental mapping of S, Cu and Mo of the $Cu_2S-MoS_2(1:1)$ nanocomposite.

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In order to further confirm the composition of the composite materials, XPS and AES were performed to investigate the valence state of the elements in $Cu_2S-MoS_2(1:1)$, the results are displayed in Fig. 4. In Fig. 4a, the high-resolution spectrum of Cu 2p shows two peaks with binding energy (BE) of 932.2 eV and 952.2 eV, which correspond to Cu $2p_{1/2}$ and Cu $2p_{3/2}$, respectively, indicating the existence of Cu¹⁺. Because no satellite peaks are detected, the existence of Cu²⁺ is excluded.⁴⁴ The AES (Fig. 4b) further confirms that the valence state of Cu is +1, since the characteristic peak associated with LMM at 569.6 eV is in accordance with the literature.45 The two peaks of Mo with BE of 229.3 eV and 232.5 eV in Fig. 4c are assigned to Mo $3d_{3/2}$ and Mo $3d_{5/2}$, respectively, which indicate that the Mo in the composite is tetravalent.⁴⁶ According to a previous report,⁴⁷ the peaks of the S 2p spectra at 162.3 eV $(2p_{1/2})$ and 161.1 eV $(2p_{3/2})$ in Fig. 4d are characteristic of S²⁻. The results demonstrate that the nanoflower like composite materials consist of Cu₂S and MoS₂. The BE values of the Cu and Mo spectra shift slightly compared with the literature as mentioned. This can be attributed to the interaction of electrons between the Cu₂S and MoS₂ components.

In order to explore the formation mechanism of Cu_2S-MoS_2 nanocomposites, a series of time dependent experiments during the preparation of $Cu_2S-MoS_2(1:1)$ were performed by intercepting the intermediates during continuous reaction time. Fig. 5a is the SEM image of the white precipitate collected after 2 h hydrothermal reaction. The image shows the morphology and the micro-bulks are about 10 µm and micro-rods about 40 µm in size. When the reaction time is prolonged to 4 h, the micro-rods become shorter around 20 µm and form hollow structures, while the micro-bulks decompose to nanoparticles (Fig. 5b). When the reaction time reached 8–12 h, the nanoparticles gather to form nanoflowers with size about 200 nm, which are assembled with nanosheets (Fig. 5c and d), while the micro-rods dissolve to less than 10 µm. After 16 h, bulges begin to form on the surfaces of nanoflowers (Fig. 5e) and the micro-rods dissolve to less than 5 µm.



Fig. 4 (a, c and d) High resolution X-ray photoelectron spectra of Cu 2p, Mo 3d and S 2p in the $Cu_2S-MoS_2(1:1)$ nanocomposite, respectively; (b) LMM spectrum of Cu in the $Cu_2S-MoS_2(1:1)$ nanocomposite.



Fig. 5 SEM images of the Cu₂S-MoS₂(1:1) nanocomposite at different reaction times (a) 2 h, (b) 4 h, (c) 8 h, (d) 12 h, (e) 16 h and (f) 20 h; (g) XRD patterns and (h) UV-Vis DRS spectra of the Cu₂S-MoS₂(1:1) nanocomposite at different reaction times at 200 °C.

After 20 h, the micro-rods are fully dissolved to form nanosheets and grow together with the nanosheets in the nanoflowers. When the time is extended to 24 h, the two kinds of nanosheet keep growing together, showing the flower like appearance of the final products (Fig. 1c). As confirmed by the XRD results (Fig. 5g), the XRD curves at 2 h should be mixed peaks of micro-bulks and micro-rods, which mainly show the signal of [BMIM]₂Mo₄O₁₃ according to the literature.⁴³ With the reaction time prolonged from 4 h to 8 h, the $[BMIM]_2Mo_4O_{13}$ peaks $(8.6^{\circ}-10.5^{\circ})$ and $21^{\circ}-49^{\circ}$) become weaker. After 12 h, the peaks of Cu₂S and MoS₂ appear. After 16 h, only Cu₂S and MoS₂ peaks remain, which is in agreement with the final XRD curves. UV-Vis DRS was carried out to investigate the optical properties of the as-prepared samples and the results are shown in Fig. 5h. When the synthetic reaction time was extended from 2 h to 24 h, the light absorption in the visible region becomes more and more broad and the absorbance capability of the composite becomes higher and higher. Meanwhile, the light absorption of the composite in the UV region is maintained. This result could be due to the more regular morphology and increased crystallinity obtained from the prolonged reaction time. So the well-developed $Cu_2S-MoS_2(1:1)$ composite at 24 h should have the best response capability and light trapping properties in the whole visible region. In addition, the UV-Vis DRS results are in accordance with the SEM analysis (Fig. 5a-f).

Based on the above results, the growth mechanism of the Cu_2S-MoS_2 composite materials can be described as a four-step process (Fig. 6). In the first step (within 2 h), two kinds of metal soluble salt react with the ionic liquid. The $Mo_4O_{13}^{2-}$ transformed from $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ could react with [BMIM]⁺, forming [BMIM]_2Mo_4O_{13} micro-rods, while Cu^{2+} reacts with SCN⁻, forming Cu_2S micro-bulks. The morphologies of the

sample in this step are micro-rods and micro-bulks (Fig. 5a) and the XRD curves show the strong characteristic peaks of [BMIM]₂Mo₄O₁₃ (Fig. 5g). The second step is the reaction within 8 h. In this step, the $[BMIM]_2Mo_4O_{13}$ micro-rods begin to react with H₂S on their surfaces and form MoS₂ crystal nuclei, while the inner part of the micro-rods would diffuse to the surface forming hollow structures by the Kirkendall effect (Fig. 5b). At the same time, the Cu₂S micro-bulks dissolve into nanoparticles and gather to form nanoflowers by Ostwald ripening (Fig. 5c). The XRD curves of this step show that the characteristic peaks of the Mo precursor become weaker (Fig. 5g). When the reaction time was prolonged to 12-16 h, the sample is in the third reaction step. In this step, [BMIM]₂Mo₄O₁₃ decomposes rapidly. The micro-hollow-rods are hard to see, while the Mo precursor just remains as nanoplates (Fig. 5d and e). The main morphology of the sample is nanoflowers with ridges on their surfaces. These should be the MoS₂ crystal nuclei adsorbed on the Cu₂S nanosheets. The XRD peaks of [BMIM]₂Mo₄O₁₃ disappeared and Cu₂S-MoS₂ peaks appeared, which can support the above view (Fig. 5g). The last step is the reaction from 16 h to 24 h. The MoS₂ nanosheets grow together with the Cu₂S nanosheets (Fig. 1c), forming the final composite material. As a result, the composite material is made up of Cu₂S and MoS₂, and should exhibit good photocatalytic activity.

To further explore the effects of the IL on the morphology of Cu_2S-MoS_2 composites, TAA was used as a substitute for the IL to synthesize Cu_2S-MoS_2 , this was labeled $Cu_2S-MoS_2(1:1)$ -T. Its XRD pattern and SEM image are shown in Fig. 7a and b, respectively. As seen in Fig. 7a, $Cu_2S-MoS_2(1:1)$ -T exhibits similar diffraction peaks to $Cu_2S-MoS_2(1:1)$, but the intensity of the diffraction peaks is obviously weaker than those of $Cu_2S-MoS_2(1:1)$. This phenomenon demonstrates that the addition of the ionic liquid could improve the long-term order of the compound structure. In addition, compared with the irregular morphology and smaller specific surface area of $Cu_2S-MoS_2(1:1)$ -T (Fig. 7b and Table 1), $Cu_2S-MoS_2(1:1)$ shows a regular 3D nanoflower morphology and much larger specific surface area (Fig. 1c and Table 1). This indicates that the ionic liquid plays



Fig. 6 Schematic representation of the synthesis of Cu_2S-MoS_2 nanocomposites.



Fig. 7 XRD patterns of Cu_2S-MoS_2 (1:1) and Cu_2S-MoS_2 (1:1)-T (a); SEM image of Cu_2S-MoS_2 (1:1)-T (b).

an important role in controlling the morphology of the composites during the preparation process, which is consistent with the literature.⁴⁸ The different morphologies and specific surface areas may have impacts on the photocatalytic performance.

3.2 Photocatalytic activity evaluation

Before light irradiation, adsorption experiments were carried out in darkness to obtain the adsorption equilibrium of MB on the Cu₂S-MoS₂(x:y) materials. To eliminate the effect of the substrate on the photocatalytic reaction, an experiment with MB solution (60 mL, 10^{-4} mol L⁻¹) without any photocatalyst was performed as a blank experiment, which indicated that the effect of MB on the photocatalytic reaction can be neglected. P-25, Cu₂S and MoS₂ were used along with the resultant Cu₂S-MoS₂ composites.

The photocatalytic results for all the catalysts are shown in Fig. 8 as are their corresponding curves of $\ln(C_0/C)$ vs. irradiation time. The rate constant values (k) of the different samples are listed in Tables 2 and 3. As seen in Fig. 8a, all of the $Cu_2S-MoS_2(x:y)$ samples show excellent adsorption capacity to methylene blue in darkness while there is great difference in photocatalytic performance. All the $Cu_2S-MoS_2(x : y)$ composites present better photocatalytic performance than Cu₂S or MoS₂. This result indicates that the existence of MoS₂ could obviously enhance the photoactive performance of the composites under visible irradiation. The more regular 3D nanoflower structure and larger specific surface area could be the reason for the enhanced photocatalytic performance compared to that of pure Cu2S and MoS_2 . In addition, the efficient electron transport between the Cu₂S and MoS₂ interface of the composites may have a positive influence on photocatalysis. Among the $Cu_2S-MoS_2(x:y)$ samples, the $Cu_2S-MoS_2(1:1)$ nanocomposite exhibits the most outstanding performance with $k = 0.0471 \text{ min}^{-1}$. As the ratio of Cu₂S to MoS₂ increases from 1:3 to 1:1, the photocatalytic efficiency increased obviously. This result may be due to the increased proportion of Cu₂S to MoS₂ which results in larger specific surface area and more regular morphology. The regular 3D structure and larger specific surface area could supply more active sites on the surface for transfer of charge-carriers and a larger contact area for substrates, thus promoting the photocatalytic performance. In addition, the number of transferred electrons on the interface of Cu₂S-MoS₂ composites could increase with the increased proportion of Cu₂S. In this case, the interface between Cu₂S and MoS₂ could improve the electron transfer efficiency and effectively inhibit

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Fig. 8 Photocatalytic degradation of MB under visible light irradiation in the presence of (a) $Cu_2S-MoS_2(x:y)$ composites; (b) $Cu_2S-MoS_2(1:1)$ composite with different reaction times; (c) $Cu_2S-MoS_2(1:1)$ composite in cycling runs and (inset) the corresponding $ln(C_0/C)$ vs. irradiation times.

charge recombination. However, as the ratio of Cu_2S to MoS_2 increases further from 1:1 to 3:1, the degradation rate of MB decreased dramatically despite of the ever-increasing specific surface area. This phenomenon should be caused by excessive MoS_2 covering the Cu_2S component, and the decreased exposed amount of Cu_2S could hinder electron transfer on the interface between Cu_2S and MoS_2 , thus in turn leading to the decrease in photoactivity. Furthermore, as the ratio of Cu_2S to MoS_2 increases from 1:1 to 3:1, the morphology of the composites becomes irregular, which can also negatively affect the photoactivity.

Table 2 The rate constant value (*k*) of $Cu_2S-MoS_2(x:y)$ samples and $Cu_2S-MoS_2(1:1)$ samples with different reaction times at 200 °C for the degradation of MB solution

Sample	$k (\mathrm{min}^{-1})$	Sample	$k ({ m min}^{-1})$
1:3	0.0135	2 h	0.0027
1:2	0.0247	4 h	0.0049
1:1	0.0471	8 h	0.0085
2:1	0.0077	12 h	0.0162
3:1	0.0058	16 h	0.0223
P-25	0.0006	20 h	0.0360
Blank	0.0002	24 h	0.0471
Cu ₂ S	0.0037	MoS_2	0.0032
$Cu_{2}^{J}S-MoS_{2}(1:1)-T$	0.0049	- 2	

Table 3 The rate constant value (k) of Cu₂S-MoS₂(1:1) in a cycling experiment for the degradation of MB solution

Cycle	1st	2nd	3rd	4th
$k ({ m min}^{-1})$	0.0471	0.0381	0.0288	0.0245

 MoS_2 has excellent absorption ability for visible light and transfer ability for electrons, which could result in shortened lifetimes of photo-induced charge-carriers. Therefore, a low MoS_2 proportion could depress the composite's photocatalytic performance. On the other hand, the gradual irregular morphology (shown in Fig. 1) may have a negative impact on the photocatalytic activity of the nanocomposites.

In Fig. 8a, the $Cu_2S-MoS_2(1:1)$ nanocomposite shows much higher catalytic activity than $Cu_2S-MoS_2(1:1)$ -T, which corresponds with the XRD, SEM and BET results. This indicates that ionic liquid-assisted Cu_2S-MoS_2 nanocomposites have excellent photocatalytic performance for the degradation of MB under visible light.

Fig. 8b shows the photocatalytic results of the Cu₂S–MoS₂(1:1) nanocomposite with different reaction times at 200 °C. With prolonged reaction time, the photocatalytic performance of the samples is significantly enhanced and the sample within 24 h exhibits the best catalytic performance. With the extension of the reaction, the samples exhibit more regular morphology and their response ability to visible light enhance obviously. The catalytic results are also in accordance with the SEM and UV-Vis DRS analysis.

Cycling experiments were carried out to investigate the lifetime and cycle stability of the $Cu_2S-MoS_2(1:1)$ nanocomposite and the results are shown in Fig. 8c. It can be seen that the sample still exhibits good degradation of MB after four cycles. The decreased photocatalytic performance may result from the adsorption of the substrate and products on the catalyst in reaction, which may decrease the number of active sites. In addition, this result is also attributed to the loss of catalyst in the recovery process.

After the cycling experiment, the Cu_2S -MoS₂(1:1) nanocomposite was characterized by XRD and XPS, and the results are shown in Fig. S5 and S6 (ESI[†]), respectively. As can be seen from the XRD pattern of the composite in Fig. S5 (ESI[†]), the composite still retains its structural characteristics after the experiment although peak intensity was slightly different from that before the reaction. From Fig. S6 (ESI[†]), it can be seen that the valence states of the elements in the $Cu_2S-MoS_2(1:1)$ composite did not change during the experiment. This means that the nanocomposite still retains its internal structure after cycling and that it is an excellent and stable catalyst for the degradation of MB under visible irradiation.

4. Conclusion

Novel Cu_2S -MoS₂(x:y) nanocomposites with different ratios of $Cu_2S(x)$ and $MoS_2(y)$ are synthesized successfully by a one-step hydrothermal method with the assistance of the ionic liquid [BMIM]SCN. The results show that the ratio of x:y has an obvious influence on the specific surface area as well as the photocatalytic performance of the Cu₂S-MoS₂ nanocomposites. The formation mechanism of Cu₂S-MoS₂ nanocomposites is investigated by time-dependent experiments during the synthesis of $Cu_2S-MoS_2(1:1)$. It could be deduced that the ionic liquid (IL) plays an important role in the formation of [BMIM]₂Mo₄O₁₃ intermediates, which could interact with H2S on their surfaces to form MoS_2 crystal nuclei. Among the composites, $Cu_2S-MoS_2(1:1)$ exhibits the most outstanding photocatalytic activity and reusability performance.

Due to the structural advantages and excellent absorption ability for light in the whole region, these Cu₂S-MoS₂ nanocomposites may be expected to be promising catalysts in other fields of photocatalysis.

Conflicts of interest

There are no conflicts to declare.

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