ChemComm

COMMUNICATION

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Cite this: Chem. Commun., 2018, 54, 13563

Received 28th September 2018, Accepted 6th November 2018

DOI: 10.1039/c8cc07784c

rsc.li/chemcomm

Encapsulating [Mo₃S₁₃]^{2–} clusters in cationic covalent organic frameworks: enhancing stability and recyclability by converting a homogeneous photocatalyst to a heterogeneous photocatalyst[†]

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We encapsulated anionic $[Mo_3S_{13}]^{2-}$ clusters in cationic COFs (EB-COF) to obtain the novel composite photocatalytic material Mo_3S_{13} @EB-COF. Comprehensive studies indicated that the Mo_3S_{13} @EB-COF was the product of a successful conversion of a homogeneous to a heterogeneous catalyst, and exhibited excellent stability and recyclability as well as a remarkable photocatalytic hydrogen evolution rate of 13 215 μ mol g⁻¹ h⁻¹ under visible-light irradiation over the course of 18 hours.

Hydrogen is considered to be the most promising source of clean energy owing to its having the highest density of energy of all chemical fuels. Water splitting is an efficient hydrogen-generating technology and has attracted great interest.¹⁻⁴ Various inorganic semiconductors,⁵ e.g., metal oxides,⁶ metal sulfides,⁷ and metal organic frameworks (MOFs),⁸⁻¹¹ have been developed as hydrogen evolution reaction (HER) photocatalysts. The nonprecious-metalbased Mo-S has been well studied due to its high catalytic efficiency and abundance in the earth.¹²⁻¹⁴ Besenbacher and co-workers pioneered the preparation of multiple active sites for anionic $[Mo_3S_{13}]^{2-}$ clusters (abbreviated as MS-c), which were shown to exhibit excellent electrocatalytic H₂ evolution activity.¹⁵ However, recent research has demonstrated that MS-c are unstable in the photocatalytic hydrogen evolution process owing to their tendency to decompose, although they display excellent photocatalytic H₂ evolution activity.¹⁶ In addition, MS-c are soluble in the majority of organic solvents and alkaline solutions as well as in pure water, which restrain their recycling and reuse applications. So designing a strategy that overcomes the drawbacks of MS-c in photocatalytic systems is highly desirable.



In the current work, we selected a two-dimensional cationic COF (EB-COF; EB: ethidium bromide) as the host material, and then utilized host-guest chemistry and ion exchange to encapsulate the anionic MS-c into the cationic EB-COF.²⁶ The obtained COF-based photocatalyst, denoted as Mo3S13@EB-COF, was found to be a stable, efficient and recyclable HER photocatalyst (Scheme 1). The strong interaction between the cationic COF and anionic MS-c ensured that $[Mo_3S_{13}]^{2-}$ did not leach out from the COF channels, and consequently enhanced the stability and recyclability of $[Mo_3S_{13}]^{2-}$. Moreover, in our strategy, the catalytic sites were uniformly distributed throughout the porous framework so that the active sites remained fully accessible without any loss of activity and quantity. Also, the HER photocatalysis of Mo₃S₁₃@EB-COF was evaluated. It showed a high hydrogen evolution rate of 13 215 μ mol g⁻¹ h⁻¹ under visible-light irradiation over the course of 18 hours. Furthermore, the HER catalytic activity level of Mo₃S₁₃@EB-COF basically remained the same after four cycles. The results demonstrated the successful conversion of the homogeneous MS-c catalyst to a heterogeneous catalyst.



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[†] Electronic supplementary information (ESI) available: Materials and instrumentation, synthetic procedures, experimental details, supplemental figures and methods. See DOI: 10.1039/c8cc07784c

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Communication



EB-COF and MS-c were prepared according to the synthetic methods reported in the literatures.^{15,26} The successful formations of EB-COF and MS-c were confirmed using powder X-ray diffraction (PXRD), whose experimental patterns were found to be in agreement with simulated PXRD patterns (Fig. S1 and S2, ESI⁺). Mo₃S₁₃(a)EB-COF was obtained by substitution of Br⁻ with $[Mo_3S_{13}]^{2-}$ in an aqueous solution of NaHCO₃. (See ESI⁺ for detailed experimental details.) The obtained Mo3S13@EB-COF was found to be insoluble in most photocatalytic solvent systems, in sharp contrast to the case of the pristine MS-c. In order to evaluate the stability of the Mo₃S₁₃@EB-COF catalyst, we conducted leaching tests after soaking the catalysts in, respectively, DMF, DMAC, MeOH, EtOH and pure water for 24 h. A UV-Vis spectroscopy investigation showed that no $[Mo_3S_{13}]^{2-}$ leached out (Fig. S3–S5, ESI†). In addition, the average diameter of the MS-c was determined to be about 1.2 nm,¹⁵ suitable for being encapsulated in the pores (1.6 nm) of EB-COF.²⁶

The Fourier transform IR (FT-IR) spectra and ¹³C MAS solid-state nuclear magnetic resonance (NMR) spectrum of Mo₃S₁₃@EB-COF were found to be consistent with those of EB-COF, indicating that the keto form connectivity and bonding mode remained intact after the ion exchange. As shown in Fig. S6 (ESI⁺), the FT-IR spectra showed the typical C=C (1590 cm^{-1}) and C-N (1280 cm^{-1}) stretching vibrations. In the ¹³C solid-state NMR spectrum, the signals at 165.1 ppm and 191.2 ppm were assigned to the C=C and C=O carbons, respectively (Fig. 1a and Fig. S7, ESI⁺). According to the PXRD analysis, no crystalline $[Mo_3S_{13}]^{2-}$ was observed. The disappearance of crystallinity in Mo₃S₁₃@EB-COF might be ascribed to the channels having become occupied with large $[Mo_3S_{13}]^{2-}$ molecules, which apparently was specifically responsible for greatly reducing the diffraction intensity of the 100 facet (Fig. S1, ESI⁺).²⁷ The N 1s peak of Mo₃S₁₃@EB-COF in the X-ray photoelectron spectroscopy (XPS) (401.75 eV) showed a significant positive shift compared to that of the initial EB-COF (401.45 eV), which may have been due to a strong interaction between $[Mo_3S_{13}]^{2-}$ and COF (Fig. S8, ESI[†]).

Nitrogen adsorption-desorption measurements at 77 K revealed a very low Brunauer-Emmett-Teller (BET) surface area value of 4 m² g⁻¹ for Mo₃S₁₃@EB-COF, but a much higher value, of 704 m² g⁻¹ for pristine EB-COF. The significantly decreased BET surface area and disappearance of micropores



Fig. 1 (a) ¹³C MAS solid-state NMR spectrum of EB-COF and Mo₃S₁₃@EB-COF. (b) Nitrogen sorption isotherms for EB-COF and Mo₃S₁₃@EB-COF; the inset shows the pore size distributions of EB-COF and Mo₃S₁₃@EB-COF. (c) EDS elemental mapping of Mo₃S₁₃@EB-COF.

were the result of anions $[Mo_3S_{13}]^{2-}$ having almost fully occupied the pores of EB-COF (Fig. 1b). An SEM-energy dispersive X-ray spectrometry (SEM-EDS) elemental analysis and mapping results of Mo_3S_{13} @EB-COF confirmed that Mo and S elements were homogeneously distributed throughout the framework, and that there was no Br element in Mo_3S_{13} @EB-COF, demonstrating that $[Mo_3S_{13}]^{2-}$ completely exchanged with Br⁻ of the initial EB-COF (Fig. 1c and Fig. S9, S10, ESI†). The loading of $[Mo_3S_{13}]^{2-}$ was measured using ICP-MS to be about 39.93 wt% in the host EB-COF, consistent with the elemental analysis results (Table S1, ESI†).

The photocatalytic hydrogen evolution ability of pure MS-c was first accessed in the fluorescein/MS-c/triethylamine (TEA) system, which displayed appreciable hydrogen production (Fig. S11–S13, ESI[†]). Encouraged by these results, we performed photocatalytic hydrogen evolution tests of Mo₃S₁₃@EB-COF by using Xe lamp irradiation ($\lambda > 420$ nm) and optimized the experimental conditions including the photosensitizer, sacrificial agent, as well as solvent, etc. (for detailed Experimental details, see ESI,[†] Fig. S14–S18). Finally, Ru(bpy)₃Cl₂ was chosen as the photosensitizer, ascorbic acid (L-Vc) was used as a sacrificial agent, and the optimized solvent was DMF/H_2O (v/v = 1:1). Notably, Mo₃S₁₃@EB-COF displayed an efficient, long-lasting, stable photocatalytic hydrogen evolution rate of 13 215 μ mol g⁻¹ h⁻¹ over the course of 18 hours of illumination under the optimized conditions (Fig. S19, ESI[†]). EDS results of the filtrate after photocatalytic hydrogen evolution confirmed the absence of any residual Mo



Fig. 2 (a) Hydrogen evolution levels of Mo₃S₁₃@EB-COF, MS-c, EB-COF and Mo₃S₁₃@MIL-100(Fe) under visible-light irradiation ($\lambda > 420$ nm), with the same conditions. (b) Cycling test for Mo₃S₁₃@EB-COF under visible-light irradiation, for specifically 4 cycles of 5 hours each.

and S elements (Fig. S20, ESI†), and less than 0.01 wt% $[{\rm Mo}_3S_{13}]^{2-}$ was measured using inductively coupled plasma mass spectrometry (ICP-MS), which all proved the negligible leaching of $[{\rm Mo}_3S_{13}]^{2-}$ during the photocatalytic reactions.

Fig. 2a shows the photocatalytic hydrogen evolution levels of the EB-COF, MS-c and Mo₃S₁₃@EB-COF. The pristine EB-COF exhibited clearly inferior hydrogen evolution (1570 μ mol g⁻¹ h⁻¹, over the course of an 8 hour illumination). As for Mo₃S₁₃@EB-COF, the catalytic rate reached 21 465 μ mol g⁻¹ h⁻¹, which is comparable to the 22 364 μ mol g⁻¹ h⁻¹ value for MS-c, implying that catalytic sites were almost fully available. This full availability was verified by inspection of the few-layer Mo₃S₁₃(@EB-COF nanosheet morphology in the photocatalytic system (Fig. S21, ESI⁺). Based on same mass of the $[Mo_3S_{13}]^{2-}$, the total hydrogen production levels of Mo_3S_{13} EB-COF and $[Mo_3S_{13}]^{2-}$ eventually reached nearly identical values, of 551 and 549 mmol g⁻¹, respectively (Fig. S22, ESI[†]), suggesting that the catalytic activity of MS-c was well retained after having been converted from the homogeneous catalyst to the heterogeneous catalyst. In addition, the apparent quantum efficiency (AQE) of Mo₃S₁₃@EB-COF in the optimized system was measured at various wavelengths (Fig. S23, ESI⁺). At 475 nm, the AQE was estimated to be as high as 4.49%. Based on the obtained hydrogen evolution rates and AQE, Mo₃S₁₃@EB-COF outperformed most reported COF-based and CTF-based photocatalytic HER systems where COF either served as the photosensitizer or support matrix and Pt as the co-catalyst (Table S2, ESI⁺). These results demonstrated the outstanding HER catalytic behavior of the Mo3S13@EB-COF composite catalyst.

To evaluate the reusability of the Mo_3S_{13} @EB-COF, we recycled the catalyst by subjecting it to centrifugation and washing several times, and then adding fresh L-Vc and Ru(bpy)₃Cl₂ as supplement (for detailed experimental details, see ESI[†]). As shown in Fig. 2b, there was no obvious performance decay after consecutive cycle tests. The FT-IR spectra of Mo₃S₁₃@EB-COF after four cycles still showed the typical C=C (1590 cm⁻¹) and C-N (1280 cm⁻¹) stretching vibrations, demonstrating its superior stability (Fig. S6, ESI[†]). In addition, the SEM-EDS results indicated that Mo and S elements were still homogeneously distributed throughout the framework (Fig. S24, ESI[†]). The Mo₃S₁₃@EB-COF after four cycles was determined using ICP-MS to have still maintained 35.23 wt% $[Mo_3S_{13}]^{2-}$, that is it lost just a little bit of [Mo₃S₁₃]²⁻compared to the pristine Mo₃S₁₃@EB-COF (39.93 wt% $[Mo_3S_{13}]^{2-}$). As expected, we successfully transformed the MS-c from a homogeneous catalyst to a heterogeneous Mo₃S₁₃@EB-COF catalyst, one displaying attractive cycling stability and excellent catalytic activity. However, when fluorescein was employed as the photosensitizer and TEA as the sacrificial electron donor, the hydrogen production level decreased sharply in the 3rd cycle, suggesting that some Mo₃S₁₃(a)EB-COF may have decomposed under the alkaline photocatalytic system (Fig. S25, ESI[†]). Although Mo₃S₁₃@EB-COF maintained remarkable catalytic activity under alkaline conditions, achieving recycling under such conditions remains a challenge.

In addition, the cationic metal organic framework (MOF) MIL-100(Fe) was prepared and used as a host material to load the MS-c.²⁸ The PXRD pattern of Mo₃S₁₃(a)MIL-100(Fe) was observed to be the same as that of MIL-100(Fe), indicating the structural integrity was unchanged after the ion-exchange process. The nitrogen sorption and SEM-EDS investigations of MIL-100(Fe) and Mo₃S₁₃@MIL-100(Fe) confirmed that MS-c was uniformly loaded throughout the framework. (Fig. S26-S28, ESI[†]). However, the hydrogen evolution rate of Mo₃S₁₃@MIL-100(Fe) subjected to an illumination of 8 hours was measured to be 2265 μ mol g⁻¹ h⁻¹, a value at least 10 times lower than those of MS-c and Mo₃S₁₃@EB-COF (Fig. 2a), implying that the MIL-100 matrix suppressed the catalytic activity of MS-c. Relative to the three-dimensional MOF framework, the EB-COF with 2D π -conjugation architecture apparently facilitated the charge carrier mobility, thus effectively improving the catalytic efficiency.²¹ The above results indicated that the 2D ionic covalent organic porous framework (EB-COF) provided an ideal platform for anchoring homogeneous MS-c photocatalyst to obtain a heterogeneous hybrid



 $\label{eq:scheme 2} \begin{array}{l} \text{Reaction scheme for the generation of } H_2 \text{ under visible-light irradiation.} \end{array}$

catalyst (Mo_3S_{13}) EB-COF) with excellent catalytic performance and enhanced cycling stability.

Furthermore, we investigated the reaction mechanism of the Ru(bpy)₃Cl₂/Mo₃S₁₃@EB-COF/L-Vc photocatalytic system. Visible light is first absorbed by Ru(bpy)₃Cl₂ to generate photoelectrons, and the ground state of Ru(bpy)₃²⁺ transitions to excited state $[Ru(bpy)_3^{2^+}]^*$.²⁹⁻³¹ To evaluate the excited state, $[Ru(bpy)_3^{2^+}]^*$ was quenched by L-Vc reductively or MO₃S₁₃(a)EB-COF oxidatively, and we acquired the fluorescence emission spectra of Ru(bpy)₃Cl₂ in the presence of L-Vc and Mo₃S₁₃@EB-COF, respectively (Fig. S29a and S30a, ESI⁺). A linear fitting of the Stern-Volmer curve yielded a rate constant (k_{sv}) of 2.58 \times 10⁴ M⁻¹ for the oxidative quenching resulting from Mo₃S₁₃(a)EB-COF (Fig. S29b, ESI⁺), whereas the k_{sv} obtained by the reduction quenching of L-Vc was 2.18 M^{-1} (Fig. S30b, ESI⁺), *i.e.*, more than 4 orders of magnitude lower than the oxidation quenching constant. Thus, we concluded that the photocatalytic HER in Mo₃S₁₃@EB-COF occurred via photoelectron transfer from the $[Ru(bpy)_3^{2+}]^*$ to Mo₃S₁₃(a) EB-COF. L-Vc apparently consumed the photogenerated holes of the photosensitizer, and the protons were reduced to H₂ by accepting the photoelectrons from the Mo₃S₁₃@EB-COF (Scheme 2).^{32,33}

We also measured the oxidative quenching rate $(k_{\rm sv})$ values of MS-c and Mo₃S₁₃@MIL-100(Fe), and they were determined to be 2.97 × 10⁴ and 6.48 × 10³ M⁻¹, respectively (Fig. S31b and S32b, ESI†). The $k_{\rm sv}$ of Mo₃S₁₃@EB-COF was found to be nearly the same as that of MS-c, but the $k_{\rm sv}$ of Mo₃S₁₃@MIL-100(Fe) was significantly lower than that of MS-c. This result can also be attributed to EB-COF having been better than MIL-100(Fe) at anchoring MS-c in the framework, since the cationic EB-COF framework had almost no limiting effect on the catalytic activity of the [Mo₃S₁₃]^{2–} anion, allowing it to play a catalytic role.

In summary, we prepared an excellent HER photocatalyst (Mo₃S₁₃@EB-COF) by anchoring MS-c in the cationic EB-COF. Taking advantage of the well-defined COF structure and strong interaction between COF and MS-c, the homogeneous molecular MS-c completely converted to the heterogeneous Mo₃S₁₃(a) EB-COF catalyst, with an accompanying significantly enhanced stability and recyclability. Investigation of the visible-lightdriven hydrogen evolution of Mo₃S₁₃@EB-COF indicated a high HER rate of 13 215 μ mol g⁻¹ h⁻¹, superior to those of most reported COF-based photocatalytic HER systems, even many systems containing noble-metal co-catalysts. Furthermore, the photocatalytic activity of Mo3S13@EB-COF remained unchanged after four HER cycles. More importantly, the atomically precisely controllable COF structure and versatile guest molecules may pave the way for developing additional novel photocatalysts.

This work was supported by the National Science Fund for Distinguished Young Scholars (No. 21825106), the National Natural Science Foundation of China (No. 21671175), the Program for Science & Technology Innovation Talents in Universities of Henan Province (164100510005), the Program for Innovative Research Team (in Science and Technology) in Universities of Henan Province (19IRTSTHN022) and Zhengzhou University.

Conflicts of interest

There are no conflicts to declare.

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