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Thiomolybdate $[Mo_3S_{13}]^{2-}$ Nanocluster: A Molecular Mimic of MoS_2 Active Sites for Highly Efficient Photocatalytic Hydrogen Evolution

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Thiomolybdate $[Mo_3S_{13}]^{2-}$ nanocluster, as a molecular mimic of MoS_2 edge sites, showed high efficiency in catalyzing photochemical H₂ evolution from a molecular system of Ru(bpy)₃Cl₂-ascorbic acid (H₂A) under visible light irradiation (\geq 420 nm), achieving a turnover number of 1570 and an initial turnover frequency of 335 h⁻¹ for H₂ evolution based on [Mo₃S₁₃]²⁻ catalyst.

Artificial photocatalytic H₂ evolution via water splitting provides an appealing solution to convert solar energy into clean fuel.¹⁻³ Various photocatalytic H_2 evolution systems have been developed yet a highly efficient and cost-effective H₂ evolution catalyst is indispensable to achieve a high efficiency for large-scale H₂ evolution reaction (HER).^{4,5} As the bestknown HER catalyst, Pt is sufficiently active but the scarcity and high cost of Pt limit its widespread application, which in turn largely spurred the studies for searching earth-abundant HER catalysts. As one of the most promising candidates to replace Pt, MoS₂ in various forms loaded on a semiconductor or in a photosensitized system has shown high catalytic activity for photocatalytic HER.⁶⁻¹³ In addition to MoS₂, a variety of molecular Mo-S complex analogues mimicking edge sites of MoS₂ have also been successfully designed and employed for electrocatalytic HER.¹⁴⁻¹⁹ Among them, the [Mo₃S₁₃]²⁻ nanoclusters containing three distinct sulfur ligands (Fig. 1a) can be viewed as the edge active sites of MoS₂ with an appropriate atomic structure for effective HER catalysis. In fact, the supported $\left[\text{Mo}_3\text{S}_{13}\right]^{2\text{-}}$ nanoclusters require a very small overpotential to achieve high current density for electrocatalytic HER.^{15,16} In addition, [Mo₃S₁₃]²⁻ nanoclusters are quite stable in acidic aqueous solution and can achieve a single cluster dispersion on proper supports that not only

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also can be regarded as a molecular HER catalyst achieving a maximum exposure of active sites. However, there are only few cases that reported the use of $\left[\text{Mo}_3\text{S}_{13}\right]^{2^-}$ as a cocatalyst supported on semiconductors for photo(electro)catalytic HER and dye degradation, $^{20\text{-}24}$ no studies report on using $\left[\text{Mo}_3\text{S}_{13}\right]_2^2$ nanoclusters as a HER catalyst to catalyze H₂ evolution from a molecular system. Herein, we report, for the first time, the use of $\left[\text{Mo}_3\text{S}_{13}\right]^2$ as an efficient HER catalyst in a molecular photocatalytic system consisting of Ru(bpy)₃Cl₂ as a photosensitizer and ascorbic acid

merge homogeneous and heterogeneous electrocatalysis but

consisting of Ru(bpy)₃Cl₂ as a photosensitizer and ascorbic acid (H₂A) as a proton source and sacrificial electron donor. Under visible light irradiation (\geq 420 nm), a high turnover number of 1570 and an initial turnover frequency of 335 h⁻¹ based on [Mo₃S₁₃]²⁻ catalyst could be achieved, which is much higher than that of in-situ photochemically generated Pt, amorphous MoS_x nanoparticles, and colloidal MoS₂ nanoparticles synthesized by solvothermal method.



Fig. 1 (a) Top and side view models of a single $[Mo_3S_{13}]^{2^{\circ}}$ nanocluster. Blue, Mo; yellow, S. (b) XRD pattern of $(NH_4)_2Mo_3S_{13^{\circ}}xH_2O$ (x=0-2) with a reference spectrum of the $(NH_4)_2Mo_3S_{13^{\circ}}2H_2O$ crystals (JCPDS No: 76-2038). (c, d) High-resolution XPS spectra of (c) Mo 3d and (d) S 2p for $[Mo_3S_{13}]_2^{2^{\circ}}$ nanoclusters.

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synthesized via a simple wet-chemistry method following the reported procedures by reacting $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ with an ammonium polysulfide ((NH₄)₂S_x) solution (see detailed method in ESI[†]).²⁵ The X-ray diffraction (XRD) pattern of the obtained dark red crystals (see inset in Fig. 1b) is in good agreement with the standard XRD pattern of (NH₄)₂Mo₃S₁₃·2H₂O (JCPDS No: 76-2038). The chemical states of Mo and S elements in $[Mo_3S_{13}]^{2-}$ nanocluster was examined by X-ray photoelectron spectroscopy (XPS) (Fig. 1c and d). Mo 3d region (Fig. 1c) can be well-fitted with a single doublet of Mo 3d5/2 (229.35 eV) and Mo 3d3/2 (232.45 eV) with a peak separation of 3.1 eV, indicative of Mo with a +4 oxidation state.¹⁵ The appearance of broad S 2s peak at the higher binding energy of the Mo 3d5/2 peak indicates multiple coordinated states of S. The fitting of the S 2p region (Fig. 1d) of $[Mo_3S_{13}]^{2-}$ nanocluster reveals two distinct doublets (S 2p3/2, S 2p1/2), which could be assigned to terminal S₂² ligands (162.1 eV, 163.3 eV) and bridging S_2^{2-} ligands and the apical S²⁻ ligand (163.4 eV, 164.6 eV), respectively.¹⁵ The ratio of latter S ligands to former one is estimated to be 7.2:5.8 by assuming that the single $[Mo_3S_{13}]^{2-}$ nanocluster contains 13 S atoms. The electronic absorption spectra of (NH₄)₂Mo₃S₁₃·xH₂O dispersed in methanol and dimethyl formamide (DMF) are well consistent with the previous observations (Fig. S1, ESI[†]).^{15,20-22}

In order to verify that the $[Mo_3S_{13}]^{2-}$ nanoclusters can function as the effective mimics of MoS₂ active sites, the electrocatalytic HER activity of $[Mo_3S_{13}]^{2-}$ nanoclusters deposited onto carbon paper (10 nmol cm⁻²) were firstly measured (see experimental details in ESI[†]). As indicated in Fig. S2, ESI^{\dagger} , the $[\text{Mo}_3\text{S}_{13}]^{2-}$ nanoclusters show low overpotential of 0.3 V vs. RHE for achieving high activity (5 mA cm⁻²) for proton reduction to H₂, indicating its high potential as a cocatalyst in catalyzing H₂ evolution from a photocatalytic system. $[Mo_3S_{13}]^{2}$ Afterwards, the nanocluster catalvzed photocatalytic H₂ evolution reactions were performed in an mixed solution of organic solvent and H₂O (100 mL) containing $Ru(bpy)_{3}Cl_{2}$ and $H_{2}A$ (see experimental details in ESI⁺). As the preliminary experiments, the effect of organic solvents and the volume ratio of organic solvent to H_2O on the H_2 evolution was first optimized with the system of $Ru(bpy)_3Cl_2$ and $[Mo_3S_{13}]^{2-1}$ containing H₂A as electron donor. The activity of H₂ evolution is highest when the mixture of CH₃CN and H₂O at a volume ratio of 9 to 1 was used as solvent (Fig. S3 and S4, ESI^{\dagger}). The solvent variation for H₂ evolution from this system probably results from a number of factors including solvent polarity, stabilization of reduction intermediates, solvent coordination ability to $[Mo_3S_{13}]^{2^-}$, and the driving force for the electron transfer for inducing H₂ evolution.²⁶⁻²⁹ Additionally, the effect of the CH_3CN/H_2O ratio may be attributable to differences in the solubility of $\left[Mo_{3}S_{13}\right]^{2\text{-}}$ and $H_{2}A^{29}$ and the reduction potentials of $\left[\text{Mo}_3\text{S}_{13}\right]^{2\text{-}}$ in reaction media with different solvent dielectric constant as the CH₃CN/H₂O ratio varies. In addition, the effect of various electron donors including triethylamine (TEA), triethanolamine (TEOA), EDTA, acetic acid, lactic acid, and H₂A on the photocatalytic H₂ evolution activity from $Ru(bpy)_3Cl_2/[Mo_3S_{13}]^{2-}$ system in CH_3CN/H_2O (9/1) mixed solution was investigated, revealing that the highest H₂



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Fig. 2 The turnovers of H₂ evolution from different systems in a mixed solution of CH₃CN/H₂O (100 mL, 9/1). Conditions: $[Mo_3S_{13}]^2$, Pt, MoS_x, or colloidal MoS₂ (10 μ M); Ru(bpy)₃Cl₂ (100 uM); H₂A (100 mM); light source, Xe lamp (300 W), ≥420 nm; irradiation time is 5 h. The Pt (10 μ M) and MoS_x (10 μ M) nanoparticles were prepared by in-situ photochemical reduction of H₂PtCl₆ and (NH₄)₂MoS₄, respectively. The colloidal MoS₂ (10 μ M) was prepared according to the procedures reported in ref [11].

evolution activity could be obtained when H_2A was used because H_2A can serve as both proton source and electron donor, and can be most easily oxidized (Fig. S5, ESI[†]).²⁸ In addition, as a cheap alternative to Ru(bpy)₃Cl₂, the commonly used organic dye Eosin Y (EY) was also tested as a photosensitizer for $[Mo_3S_{13}]^2$ catalyzed photocatalytic H_2 evolution reaction from CH_3CN/H_2O (9/1) mixed solution containing H_2A or TEOA as an electron donor (Fig. S6, ESI[†]). The results show that no or only trace amount of H_2 is produced, indicating that the EY is inactive as a photosensitizer to induce



Fig. 3 (a) H₂ evolution from systems containing Ru(bpy)₃Cl₂ (100 μ M), H₂A (100 mM), and different amount of [Mo₃S₁₃]² in a mixed solution of CH₃CN/H₂O (100 mL, 9/1). (b) H₂ evolution from systems containing [Mo₃S₁₃]² (10 μ M), H₂A (100 mM), and different amount of Ru(bpy)₃Cl₂ in a mixed solution of CH₃CN/H₂O (100 mL, 9/1). Light source, Xe lamp (300 W) with a cut-off filter of 420 nm. Insets in panel (a) and (b) are the initial rate of H₂ evolution versus [Mo₃S₁₃]² and Ru(bpy)₃Cl₂ concentrations, respectively.

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Fig. 4 Quenching of PL emission of Ru(bpy)₃Cl₂ (20 μ M) excited at 450 nm by adding different amounts of (a) H₂A and (b) [Mo₃S₁₃]²⁻ catalyst.

an efficient H₂ evolution might due to the incompatibility of EY with H₂A and weak interaction between excited state EY and $[Mo_3S_{13}]^{2-}$ nanoclusters. Under optimum reaction conditions of $Ru(bpy)_3Cl_2/H_2A$ system, the H_2 evolution over time under visible light was continuous during the 5 h reaction. The turnover of H₂ evolution reaches 508 versus the $[Mo_3S_{13}]^2$ catalyst within 5 h of irradiation. Control experiments indicate that the Ru(bpy)₃Cl₂ photosensitizer, $[Mo_3S_{13}]^{2-}$, H₂A, and light are all essential for H₂ evolution; the absence of any of them yielded unobservable to trace amount of H₂ (Fig. 2). These results suggest that the $[Mo_3S_{13}]^{2-}$ could serve as an efficient HER catalyst in catalyzing the H₂ evolution from a molecular system under visible light. In addition, we compared the catalytic H₂ evolution activity of $[Mo_3S_{13}]^{2-}$ with that of Pt, amorphous MoS_x, and colloidal MoS₂ nanoparticles in $Ru(bpy)_3Cl_2/H_2A$ system. The Pt and amorphous MoS_x nanoparticles were prepared by in-situ photochemical reduction and only show 7 and 10 turnovers for H₂ evolution, respectively, which is much lower than that of $[Mo_3S_{13}]^{2-}$. Moreover, the colloidal MoS₂ nanoparticles synthesized by solvothermal method exhibits the lowest turnover (ca. \sim 2) for H_2 evolution. The high catalytic activity of the $[Mo_3S_{13}]^{2-}$ for H_2 evolution could be mainly attributed to the high activity of uncoordinated S edge sites of $[Mo_3S_{13}]^{2^-}$ along with its molecular dispersion feature in reaction media that render the maximum exposure of active sites for H^+ reduction to H_2 .

In the system of $Ru(bpy)_3Cl_2/[Mo_3S_{13}]^{2-}$ with $Ru(bpy)_3Cl_2$ at fixed concentrations (100 μ M), the initial rate of H₂ evolution exhibits a first-order dependence on the concentration of $[Mo_3S_{13}]^{2-}$ (Fig. 3a). At 2 μ M $[Mo_3S_{13}]^{2-}$ this system exhibits exceptionally high activity, a turnover number of 1570 versus $[Mo_3S_{13}]^{2-}$ after 5 h reaction and an initial turnover frequency (TOF) of 335 h^{-1} for H₂ evolution could be achieved (Fig. S7, ESI^{\dagger}). With the increasing $[\text{Mo}_3\text{S}_{13}]^{2-}$ concentrations, the amount of H₂ evolved is gradually increased, but the TON does not follow the linear relationship with catalyst concentration, and the initial TOF reaches a plateau at higher catalyst concentrations. When the concentration of $Ru(bpy)_3Cl_2$ is increased from 25 to 800 μ M at a fixed concentration of $[Mo_3S_{13}]^{2-}$ (10 μ M), both TON and initial TOF versus catalyst reaches a maximum at 400 µM Ru(bpy)₃Cl₂ (Fig. 3b), together with a rapid decrease in TON versus $Ru(bpy)_3Cl_2$ (Fig. S8, ESI^{\dagger}), which indicates that at this concentration of $Ru(bpy)_3Cl_2$ the H_2 evolution activity of the system becomes limited by the



 $\label{eq:scheme 1} \begin{array}{l} \mbox{Proposed reaction mechanism for the $[Mo_3S_{13}]^2$ catalyzed photocatalytic H_2 evolution from a molecular system of $Ru(bpy)_3Cl_2$ and H_2A under visible light irradiation. } \end{array}$

catalyst concentration.

To gain an insight into the electron transfer process and the reaction mechanism for photocatalytic H₂ evolution from the $Ru(bpy)_{3}Cl_{2}/[Mo_{3}S_{13}]^{2}$ system, the photoluminescence (PL) properties of the Ru(bpy)₃Cl₂ in CH₃CN/H₂O (9/1) solution were studied, as shown in Fig. 4. With the addition of different amounts of H₂A (Fig. 4a), PL emission of Ru(bpy)₃Cl₂ at ~607 nm by the light excitation of 450 nm is quenched following linear Stern-Volmer behavior (Fig. S9, ESI⁺) with a rate constant k_q of 1.984×10⁷ M⁻¹·s⁻¹, which is consistent with that H₂A can act as a proton source and its ascorbate anion (HA⁻) can function as a reductive quencher for excited-state of $Ru(bpy)_3^{2^+}$ to $Ru(bpy)_3^{+}$.¹¹ Notably, $[Mo_3S_{13}]^{2^-}$ catalyst can also effectively quench the excited state of $Ru(bpy)_3^{2^+}$ via a oxidative quenching pathway (Fig. 4b). It is also noted that the fitting of the combined Stern-Volmer plot shows two linear regions with a transition point at 0.5 μ M [Mo₃S₁₃]²⁻ (Fig. S10, ESI⁺), from which two rate constants are extracted. Both rate constants (4.04×10¹² and 1.18×10¹² M^{-1} ·s⁻¹) are more than five orders of magnitude faster than that for H₂A and approach the diffusion-controlled limit, indicating the higher dispersion of $[Mo_3S_{13}]^{2-}$ catalyst at lower concentrations, while the smaller $k_{\rm q}$ of 1.18×10¹² M⁻¹·s⁻¹ obtained with higher [Mo₃S₁₃]² concentrations suggests a strong interaction probably derived from the electrostatic force between cationic $Ru(bpy)_3^{2+}$ and anionic $[Mo_3S_{13}]^{2-}$ nanoclusters.³⁰

Above results suggest that when H_2A and $[Mo_3S_{13}]^{2-}$ catalyst coexist in the system, both reductive and oxidative quenching may involve and compete in the electron transfer process for H_2 evolution from excited state of $Ru(bpy)_3^{2+}$. However, the oxidative quenching of excited $Ru(bpy)_3^{2+}$ would dominate because of the much larger k_q for oxidative quenching than k_q for reductive quenching even though higher concentration of H_2A (100 mM) is used relative to $\left[Mo_3S_{13}\right]^{2\text{-}}$ catalyst (10 $\mu M)$ under H_2 evolution conditions.^{31,32} Moreover, it should also be inferred that the H_2 evolution induced by electron transfer from the ${}^{*}Ru(bpy)_{3}^{2+}$ to $[Mo_{3}S_{13}]^{2-}$ catalyst via a oxidative quenching pathway would be more feasible since there is a strong electrostatic force between positively charged * Ru(bpy)₃²⁺ and negatively charged $[Mo_{3}S_{13}]^{2-}$ nanoclusters, which would expect to render a fast electron transfer from excited state of $Ru(bpy)_3^{2+}$ to $[Mo_3S_{13}]^{2-}$ catalyst. Above results indicate that the photocatalytic H₂ evolution reaction from the Ru(bpy)₃²⁺/[Mo₃S₁₃]²⁻/H₂A molecular system most likely proceed via a oxidative quenching mechanism, as shown in

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Scheme 1. Under visible light irradiation (\geq 420 nm), the Ru(bpy)₃²⁺ absorbs visible light photon to form excited state ^{*}Ru(bpy)₃²⁺, which (*E*(Ru(bpy)₃³⁺/^{*}Ru(bpy)₃²⁺)=-0.79 V vs. SCE)³² was then oxidatively quenched by direct transferring electrons to the [Mo₃S₁₃]²⁻ nanoclusters and then to the undercoordinated S active sites, where the H⁺ are reduced to H₂ (*E*(H⁺/H₂)=-0.10 V vs. SCE). At the same time, the oxidative Ru(bpy)₃³⁺ (*E*(Ru(bpy)₃³⁺/Ru(bpy)₃²⁺)=+1.33 V vs. SCE)³² is reduced back to its ground state by H₂A (*E*(HA⁻/HA⁻)=+0.47 V vs. SCE)²⁸, thereby complete the catalytic cycles.

In addition, the H_2 evolution stability of the $Ru(bpy)_3^{2+}$ - $[Mo_3S_{13}]^{2}$ -H₂A system is examined. Fig. S11 in the ESI⁺ shows that the H₂ evolution reaction ceases after 6 h light irradiation. The same system is then evacuated and subject to light irradiation; however, no observable H₂ formation could be detected (not shown). Subsequently, when 100 μ M Ru(bpy)₃²⁺ was added into above system, the H₂ evolution could be revived but the efficiency is decreased by ~50%, implying that the deactivation of the system is most likely because of the degradation of the $Ru(bpy)_3^{2+}$ (Fig. S12, ESI⁺) and the $[Mo_3S_{13}]^{2-}$ catalyst is more stable. In fact, the UV-vis spectra of $\left[\text{Mo}_3\text{S}_{13}\right]^{2\text{-}}$ catalyst aged in CH₃CN/H₂O (9/1) solution in the presence or absence of H₂A shows no any obvious change after 24 h in darkness, and the aged $\left[Mo_{3}S_{13}\right]^{2\text{-}}$ catalyst shows nearly the same H_2 evolution activity as the fresh $[Mo_3S_{13}]^{2-}$ catalyst (Fig. S13 and S14, ESI⁺). In the third run, the system only produce trace amount of H_2 even although additional fresh 100 μM $Ru(bpy)_{3}^{2+}$ was added. This imply that the $[Mo_{3}S_{13}]^{2-}$ catalyst might eventually decompose and convert to certain species that is inactive in catalyzing H₂ evolution. Attempts to isolate the deactivated catalyst is failed and further studies is ongoing to unravel the deactivation mechanism of the $[Mo_3S_{13}]^2$ catalyst during the visible-light-induced H₂ evolution processes.

In summary, we have shown that $[Mo_3S_{13}]^{2-}$ nanoclusters is an effective mimic of edge sites of MoS₂ crystals in efficiently catalyzing H₂ evolution reaction from a molecular photocatalytic system of Ru(bpy)32+-H2A under visible light irradiation. The single cluster dispersion feature of $[Mo_3S_{13}]^{2^-}$ in a proper solvent render a maximum exposure of active sites at molecular level, thus $[Mo_3S_{13}]^{2-}$ nanoclusters were found to have higher activity for H₂ evolution than the most-active Pt, amorphous MoS_x, and colloidal MoS₂ nanoparticles. This work not only shows the capability of $[Mo_3S_{13}]^{2-}$ nanoclusters as a highly active H₂ evolution catalyst in the molecular systems for solar to chemical fuel conversion, but also provides a new insight to understand the relationship of Mo-S based homogeneous and heterogeneous HER catalysts. Our continuous efforts are now focused on the immobilization of $[Mo_3S_{13}]^{2-}$ on the conductive substrates or photoactive materials to construct recoverable, more stable, and efficient photocatalytic H₂ evolution systems for long-term application.

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