Electronic Supplementary Information

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

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1. Experimental section

1.1 Synthesis

$[Mo_3S_{13}]^{2-}$ nanoclusters

The thiomolybdate $(NH_4)_2Mo_3S_{13}\cdot xH_2O$ (x=0-2) was prepared by the method outlined by Müller et al. briefly, 4.0 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in 20 mL of water in an Erlenmeyer flask. An ammonium polysulfide solution (120 ml, 25 wt%) was added and the flask was covered with a watch glass. The solution was then kept on an oil bath (96 ^{0}C) for five days without stirring. Dark-red crystals of $(NH_4)_2Mo_3S_{13}\cdot xH_2O$ precipitated and were removed by filtering, followed by washing successively with water and ethanol. To remove excess sulfur, the $(NH_4)_2Mo_3S_{13}\cdot xH_2O$ crystals were first heated in hot toluene (80 ^{0}C) for 2-4 h followed washed by dimethylsulfoxide (DMSO) for several times. Finally, the crystals were dried in air and stored in darkness.

Colloidal MoS_2 nanoparticles

Colloidal MoS_2 nanoparticles were prepared by a simple solvothermal method according to the reported procedure in literature.[S1] In brief, $(NH_4)_2MoS_4$ (12.5 μmol) was dissolved in methanol (25 mL) containing $N_2H_4H_2O$ (50%, 0.1 mL) and an appropriate amount of poly(viny1pyrrolidone) (PVP, K30). The molar ratio of PVP (monomeric unit) to MoS_2 is 20. The solution was added to a Teflon-lined stainless steel autoclave with a capacity of 50 mL and then heated at 423 K for 3 h to obtain the colloidal MoS_2. The as-prepared colloidal MoS_2 was directly used for following photocatalytic hydrogen evolution reaction without further treatment.

[S1] X. Zong, Y. Na, F. Wen, G. Ma, J. Yang, D. Wang, Y. Ma, M. Wang, L. Sun and C. Li, *Chem Commun.,* 2009, **30**, 4536.

1.2 Characterization

X-ray diffraction (XRD) patterns were investigated with a Rigaku B/Max-RB diffractometer with a nickel filtrated Cu Kα radiation. X-ray photoelectron spectroscopy (XPS) measurements of the samples were performed on a K-Alpha surface analysis (Thermo Scientific) using X-ray monochromatization. Ultraviolet-visible (UV-vis) transmission spectroscopy was performed using a Shimadzu UV-

1800 spectrophotometer. Photoluminescence spectra were determined by a Horiba Scientific FluoroMax-4 spectrofluorometer. The fluorescence decay times were measured using the Horiba Jobin Yvon Data Station HUB operating in time-correlated single photon counting mode (TCSPC) with the time resolution of 200 ps. Nano LED diode emitting pulses at 370 nm with 1 MHz repetition rate was used as an excitation source. Light-scattering Ludox solution was used to obtain the instrument response function (prompt). The time ranges are 0.055 ns/channel in 4096 effective channels. Horiba Jobin Yvon DAS6 fluorescence decay analysis software was used to fit the model functions to the experimental data.

1.3 Electrocatalytic hydrogen evolution reactions

The electrochemical measurements were carried out in a standard three-electrode electrochemical set-up using a CHI660E potentiostat. The saturated Ag/AgCl and graphite rod were used as reference electrode and counter electrode, respectively. The working electrodes were prepared by drop-casting $[Mo_3S_{13}]^{2-}/CH_3CN$ solution onto the carbon paper (HESEN, HCP030P, thickness, 0.3 mm). Carbon paper were electrochemically active at 1.65 V vs. Ag/AgCl for 2 min in a phosphate buffer (pH 7) prior to the $[Mo_3S_{13}]^{2-}$ deposition.[S2] The loading amount of $[Mo_3S_{13}]^{2-}$ on carbon paper was controlled to be 10 nmol cm^{-2}. The electrocatalytic activity of $[Mo_3S_{13}]^{2-}$ towards HER was examined by obtaining polarization curves using linear sweep voltammetry (LSV) at a scan rate of 1 mV s^{-1} in a 0.5 M H_2SO_4 solution. All the applied potentials are reported as reversible hydrogen electrode potential scale using E (*vs*. RHE)=E (*vs*. Ag/AgCl)+0.2142 V after IR correction. Potentiostatic EIS was used to determine the uncompensated solution resistance (R_s). The reference electrode was calibrated with a Pt wire as the working electrode for the reversible hydrogen potential in the electrolyte solution purged with N_2 for 30 min and saturated high purity H_2 prior to the measurements.[S3]

[S2]. J. Kibsgaard, T. F. Jaramillo and F. Besenbacher, *Nat. Chem.,* 2014, **6**, 248.

[S3]. X. L. Yang, A.-Y. Lu, Y. H. Zhu, M. N. Hedhili, S. X. Min, K.-W. Huang, Y. Han and L.-J. Li *Nano Energy* 2015, **15**, 634.

1.4 Photocatalytic hydrogen evolution reactions

The photocatalytic hydrogen production experiments were performed in a sealed Pyrex reactor (250 mL) with a top flat quartz window for light irradiation and a silicone rubber septum was fixed on its side for sampling produced H_2 in the headspace of reaction cell. A 300 W Xe lamp (CEL-HXF300) equipped with an optical 420 nm cut-off filter was used as light source. In a typical experiment, $Ru(bpy)_3Cl_2$ and the $[Mo_3S_{13}]^{2-}$ catalyst were added to a mixed solution of CH_3CN/H_2O (9/1) containing 100 mM H_2A with magnetic stirring. Before irradiation, the reaction system was thoroughly degassed by evacuation. The reaction solution was continuously stirred and maintained at 304 K by a flow of cooling ethanol. The amount of evolved H_2 was determined using a gas chromatograph (Tech comp; GC-7890II) with a thermal conductivity detector, a 5 A molecular sieve column, and with N_2 as carrying gas.

2. Additional figures

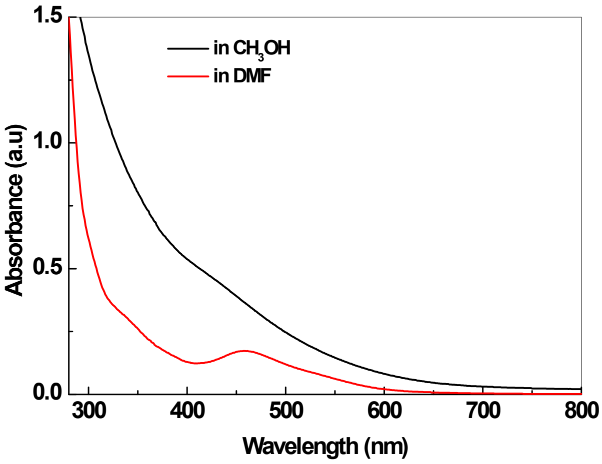


Fig. S1 UV-vis absorption spectra of $[Mo_3S_{13}]^{2-}$ (10 μM) in methanol and DMF.

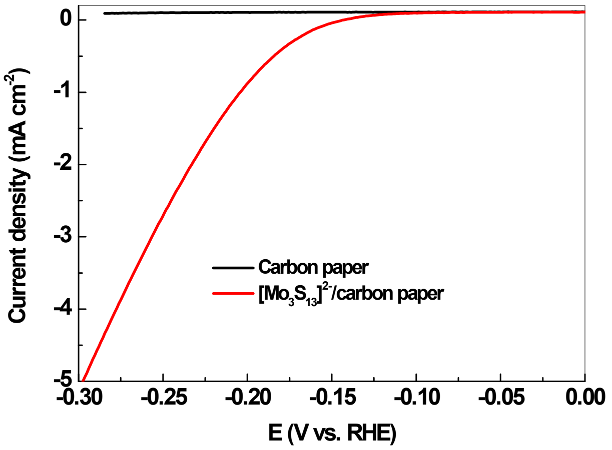


Fig. S2 The polarization curves for the $[Mo_3S_{13}]^{2-}$ deposited on carbon paper. The present current is normalized by the geometrical area of carbon paper and the potential is measured after internal resistance correction.

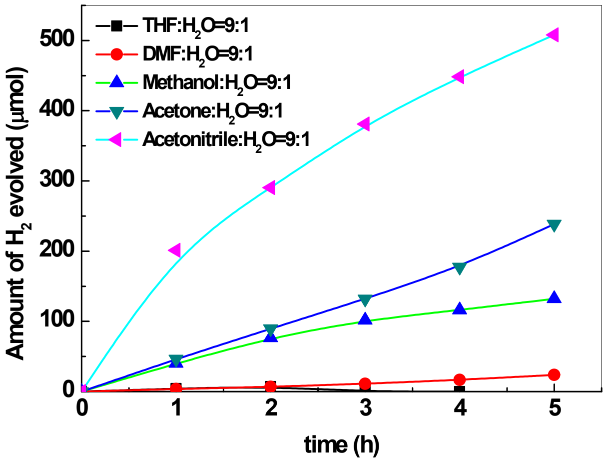


Fig. S3 Time courses of photocatalytic H_2 evolution from a mixed solution of organic solvent and H_2O (100 mL, 9:1) containing $[Mo_3S_{13}]^{2-}$ (10 μM), $Ru(bpy)_3Cl_2$ (100 uM), and H_2A (100 mM). Light source, Xe lamp (300 W) with a cut-off filter of 420 nm.

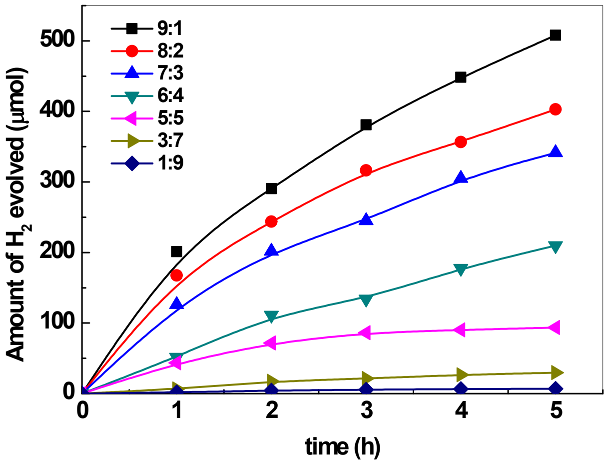


Fig. S4 Time courses of photocatalytic H_2 evolution from a mixed solution of CH_3CN and H_2O (100 mL) with different volume ratio of CH_3CN to H_2O containing $[Mo_3S_{13}]^{2-}$ (10 μM), $Ru(bpy)_3Cl_2$ (100 uM), and H_2A (100 mM). Light source, Xe lamp (300 W) with a cut-off filter of

420 nm.

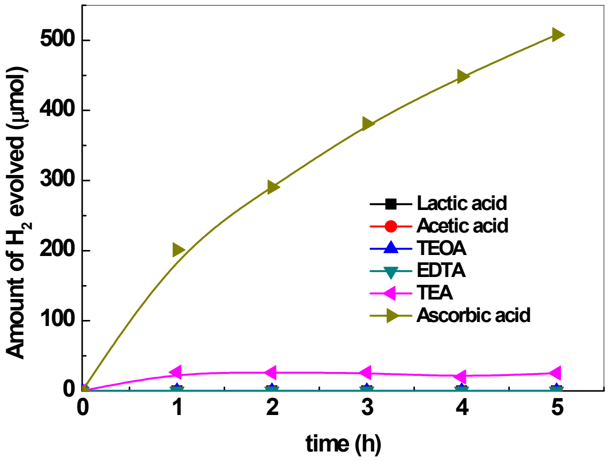


Fig. S5 Time courses of photocatalytic H_2 evolution from $Ru(bpy)_3Cl_2/[Mo_3S_{13}]^{2-}$ system in the presence of different electron donors (100 mM) in CH_3CN/H_2O (100 mL, 9/1) solution. Conditions: $[Mo_3S_{13}]^{2-}$ (10 µM); $Ru(bpy)_3Cl_2$ (100 uM); light source, Xe lamp (300 W) with a cut-off filter of 420 nm.

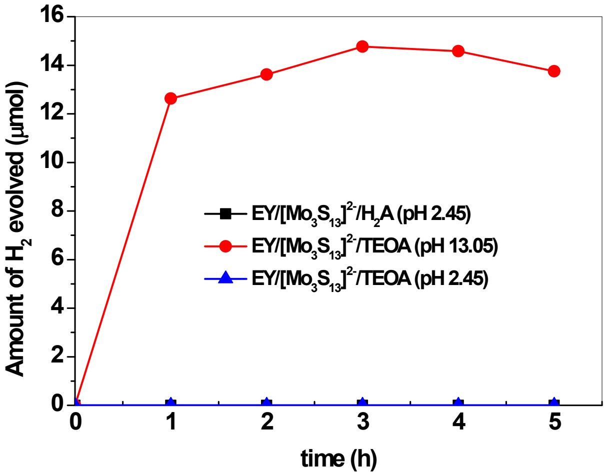


Fig. S6 Time courses of $[Mo_3S_{13}]^{2-}$ catalyzed photocatalytic H_2 evolution from CH_3CN/H_2O (100 mL, 9/1) solution containing H_2A or TEOA solution at different pH values as electron donor. Conditions: $[Mo_3S_{13}]^{2-}$ (10 µM); $Ru(bpy)_3Cl_2$ (100 uM); H_2A or TEOA solution, 100 mM, 100mL; light source, Xe lamp (300 W) with a cut-off filter of 420 nm.

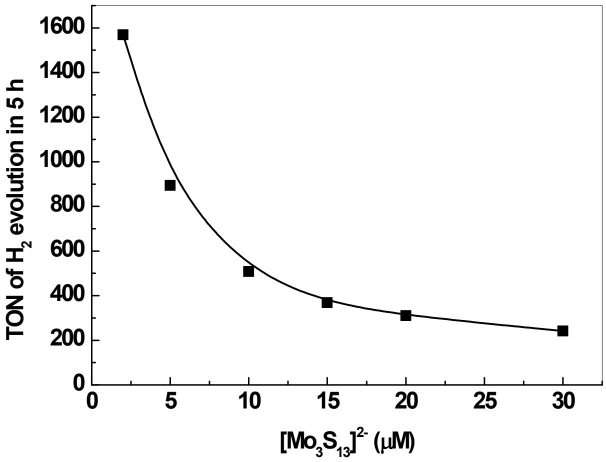


Fig. S7 TON of H_2 evolution from $Ru(bpy)_3Cl_2/[Mo_3S_{13}]^{2-}$ system in CH_3CN/H_2O (100 mL, 9/1) solution containing 100 mM H_2A. Conditions: $Ru(bpy)_3Cl_2$ (100 uM); light source, Xe lamp (300 W) with a cut-off filter of 420 nm.

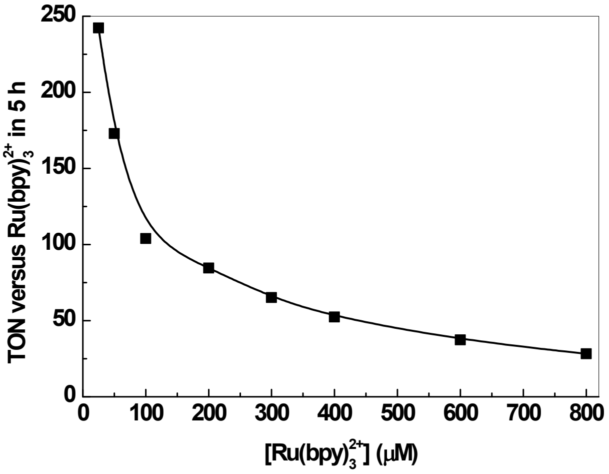


Fig. S8 TON of H_2 evolution from $Ru(bpy)_3Cl_2/[Mo_3S_{13}]^{2-}$ system in CH_3CN/H_2O (100 mL, 9/1) solution containing 100 mM H_2A. Conditions: $[Mo_3S_{13}]^{2-}$ (10 μM); light source, Xe lamp (300 W) with a cut-off filter of 420 nm.

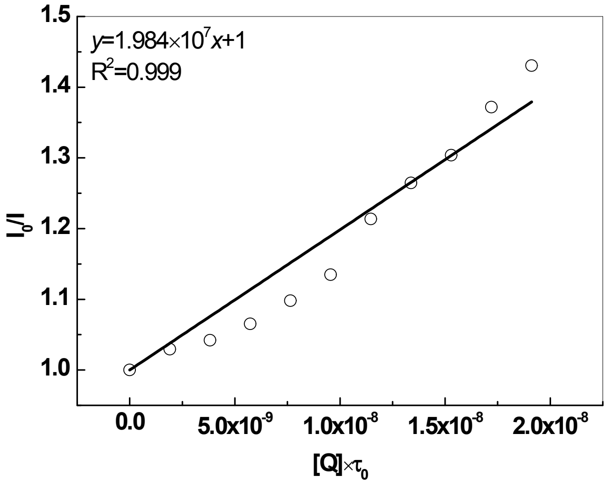


Fig. S9 Stern-Volmer plot of the emission quenching of $Ru(bpy)_3Cl_2$ solution (20 μM) by H_2A in CH_3CN/H_2O (9/1).

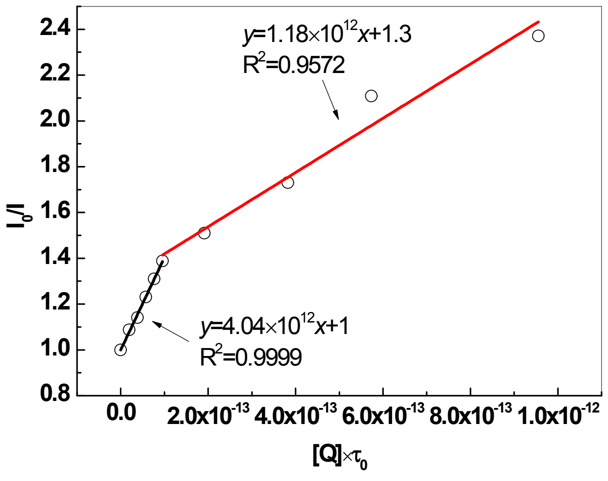


Fig. S10 Stern-Volmer plot of the emission quenching of Ru(bpy)$_3$Cl$_2$ solution (20 μM) by [Mo$_3$S$_{13}$]$^{2-}$ in CH$_3$CN/H$_2$O (9/1).

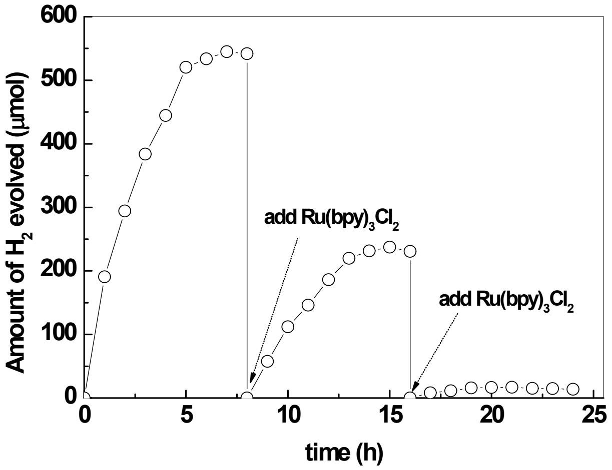


Fig. S11 H$_2$ evolution stability from Ru(bpy)$_3$Cl$_2$/[Mo$_3$S$_{13}$]$^{2-}$ system in CH$_3$CN/H$_2$O (100 mL, 9/1) solution containing 100 mM H$_2$A. Conditions: Ru(bpy)$_3$Cl$_2$ (100 uM); [Mo$_3$S$_{13}$]$^{2-}$ (10 μM); light source, Xe lamp (300 W) with a cut-off filter of 420 nm.

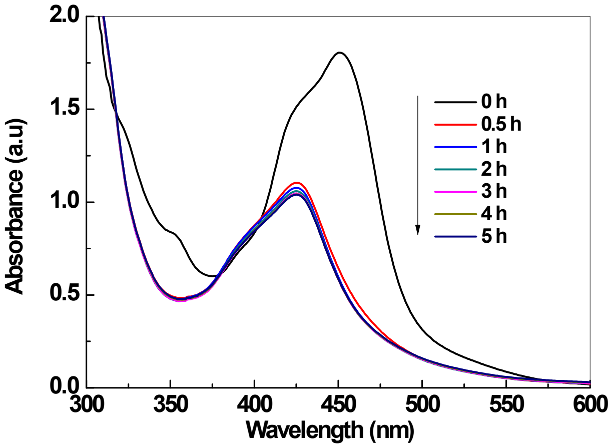
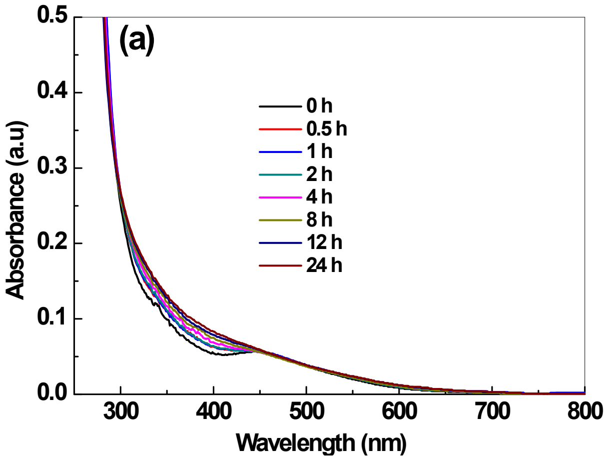


Fig. S12 Time-dependent UV-vis absorption spectra of Ru(bpy)$_3$Cl$_2$-[Mo$_3$S$_{13}$]$^{2-}$-H$_2$A photocatalytic systems under light irradiation. Conditions: Ru(bpy)$_3$Cl$_2$ (100 uM); [Mo$_3$S$_{13}$]$^{2-}$ (10 μM); light source, Xe lamp (300 W) with a cut-off filter of 420 nm.



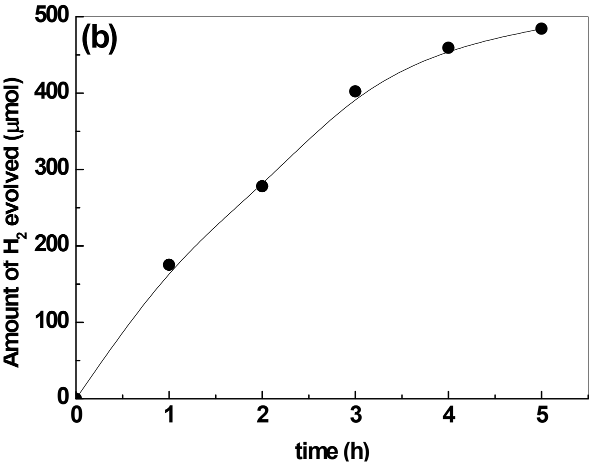


Fig. S13 (a) UV-vis absorption spectra of $[Mo_3S_{13}]^{2-}$ catalyst (10 μM) aged in CH_3CN/H_2O (100 mL, 9/1) solution with different times. (b) Photocatalytic H_2 evolution from $Ru(bpy)_3Cl_2/[Mo_3S_{13}]^{2-}$ system in CH_3CN/H_2O (100 mL, 9/1) solution containing 100 mM H_2A after the $[Mo_3S_{13}]^{2-}$ catalyst was aged in CH_3CN/H_2O solution for 24 h in darkness. Conditions: $Ru(bpy)_3Cl_2$ (100 uM); $[Mo_3S_{13}]^{2-}$ (10 μM); light source, Xe lamp (300 W) with a cut-off filter of 420 nm.

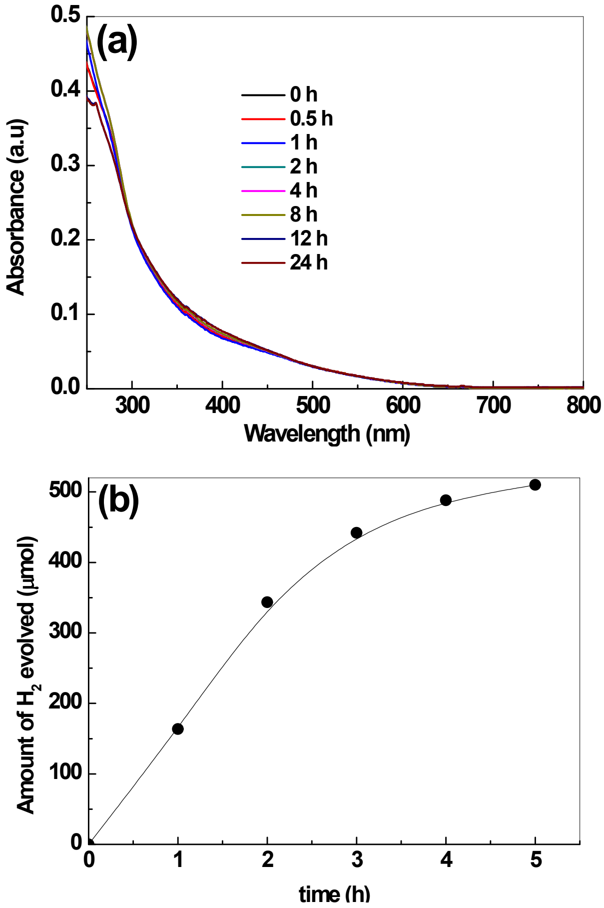


Fig. S14 (a) UV-vis absorption spectra of $[Mo_3S_{13}]^{2-}$ catalyst (10 μM) aged in CH_3CN/H_2O (100 mL, 9/1) solution containing 100 mM H_2A with different times. (b) Photocatalytic H_2 evolution from $Ru(bpy)_3Cl_2/[Mo_3S_{13}]^{2-}$ system in CH_3CN/H_2O (100 mL, 9/1) solution containing 100 mM H_2A after the $[Mo_3S_{13}]^{2-}$ catalyst was aged in CH_3CN/H_2O solution containing H_2A for 24 h in darkness. Conditions: $Ru(bpy)_3Cl_2$ (100 uM); $[Mo_3S_{13}]^{2-}$ (10 μM); light source, Xe lamp (300 W) with a cut-off filter of 420 nm.