Electronic Supplementary Information

Experimental materials

All the regents used are analysis grades without further purification. $(NH_4)_6Mo_7O_{24}.4H_2O$ (Sigma-Aldrich), ammonium polysulfide solution (<25%wt) are purchased from China Sinopharm Chemical reagent Co. Ltd., Toluene (anhydrous, 99.9%), ethanol (anhydrous, 99.9%), Pluronic P123 (Sigma), tetraethylorthosilicate (TEOS, Sigma, 98%), HCl solution (anhydrous, 37%), NH_4HF_2 (anhydrous),

Experimental Section

***Synthesis of $(NH_4)_2Mo_3S_{13}.nH_2O$*:** 4.0 g of $(NH_4)_6Mo_7O_{24}.4H_2O$ (Sigma-Aldrich) was dissolved in 20 ml of water in an Erlenmeyer flask. An ammonium polysulfide solution (120 ml, <25%*wt*) as added and the flask was covered with a watch glass. The solution was then kept on an oil bath (96 ℃) for five days without stirring. Dark-red crystals of $(NH_4)_2Mo_3S_{13}.nH_2O$ precipitated and were removed by filtering, followed by washing successively with water and ethanol. To remove excess sulfur, the $(NH_4)_2Mo_3S_{13}.nH_2O$ crystals were heated in hot toluene (～80℃) for 2–4 hours. Finally, the crystals were dried in air.

***Synthesis of* SBA-15 Silica**: SBA-15 silica was obtained using Pluronic P123 and tetraethylorthosilicate (TEOS, 98%) as the starting materials. In a typical preparation, TEOS (5.58 g) was mixed with P123 (3.46 g) in 1.6 M HCl solution (38 mL) and stirred at 35℃ for 24 h. The mixture was heated at 150℃ for 24 h in static conditions in a Tefl on-lined autoclave. The resulting white precipitate was removed by filtration and dried at 80℃ overnight; it was then further calcined at 550℃ in air for 4 h with a heating rate of 1℃min^{-1}.

Synthesis of om-**CN:** First, the as-prepared SBA-15 silica was acidified using 1 M HCl solution (1.0 g silica/20.0 mL HCl) at 80℃ for 24 h, followed by drying at 80℃ for 12 h. Then, 1.0 g HCl-treated SBA-15 silica was added to 8 g liquid CA, and kept under sonication and vacuum at 55℃ for 4 h. Third, 15.0 mL water was added to the mixture, which was then centrifuged, dried, and calcined at 550℃ for 4 h. The resulting powder was treated with 4 M NH_4HF_2 solution (40 mL) for 24 h to remove the silica template, followed by filtration, washing with water and ethanol several times, and finally drying at 80℃.

***Synthesis of p*om-CN:** The typical protonation was undertaken by stirring om-CN (0.5 g) with 10mL (3, 6, 8, 12 mol/L) HCl for 4 hours in room temperature, centrifugal washing with water until neutral condition and drying at 105℃ in air overnight.

***Synthesis of MS/p*om-CN:** First, 25mg of $(NH_4)_2Mo_3S_{13}.nH_2O$ was dispersed in 100ml methanol. Then, 50mg of pom-CN or was mixed with different amounts of $(NH_4)_2Mo_3S_{13}.nH_2O$ methanol solution with stirring at room temperature for 10min. Subsequently, dried by a vacuum process to remove the methanol solution.

Characterization: The morphology of the sample was investigated by field emission scanning electron microscopy (SEM) (JSM-6700F). Transmission electron microscopy (TEM) was obtained by Zeis 912 microscope. The nitrogen adsorption–desorption isotherms were collected at 77 K using Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. Powder X-ray diffraction (XRD) measurements were performed on Bruker D8 Advance diffractometer with Cu Ka1 radiation (k = 1.5406 Å). Fourier transformed infrared (FTIR) spectra were recorded on BioRad FTS 6000 spectrometer. X-ray photoelectron spectroscopy (XPS) data were obtained on Thermo ESCALAB250 instrument with a monochromatized Al Kα line source (200 W). UV–Vis diffuse reflectance spectra (UV–Vis DRS) were performed on Varian Cary 500 Scan UV–visible system. Electrochemical measurements were conducted with a BAS Epsilon Electrochemical System in a conventional three electrode cell, using a Pt plate as the counter electrode and an Ag/AgCl electrode (3M KCl) as the reference electrode. The working electrode was prepared on indium-tin oxide (ITO) glass that was cleaned by sonication in ethanol for 30 min and dried at 353 K. The boundary of ITO glass was protected using Scotch tape. The 5 mg sample was dispersed in 1 mL of etanol by sonication to get a slurry. The slurry was spread onto pretreated ITO glass. After air-drying, the Scotch tape was unstuck, and the uncoated part of the electrode was isolated with epoxy resin. The electrolyte was a 0.5 $molL^{-1}$ Na_2SO_4 (pH = 6.8) aqueous solution without additive and was purged with nitrogen gas for 30 min prior to the measurements. The electrochemical experiments were taken on a ZAHNER Zennium workstation.

Photocatalytic hydrogen evolution: Photocatalytic H_2 production was carried out in a Pyrex top-irradiation reaction vessel connected to a glass-closed gas circulation system. For each reaction, 50 mg catalyst powder was dispersed in an aqueous solution (100 mL) containing lactic acid (10 vol%) as sacrificial electron donor. The reactant solution was evacuated several times to remove air completely prior to irradiation under a 300W Xe lamp and a water-cooling filter. The wavelength of the incident light was controlled by using an appropriate long pass cut-off filter. The temperature of the reactant solution was maintained at room temperature by a flow of cooling water during the reaction. The evolved gases were analyzed by gas chromatography equipped with a thermal conductive detector (TCD) with argon as the carrier gas.

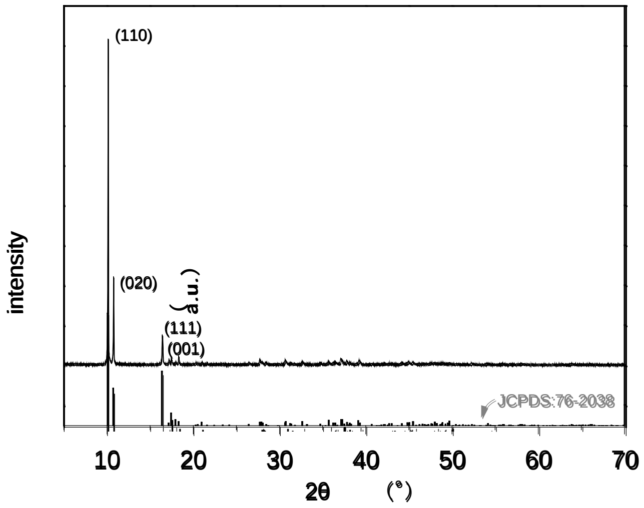

Fig.S1 Powder XRD pattern of $(NH_4)_2Mo_3S_{13}.nH_2O$ with a simulated reference spectrum of the $(NH_4)_2Mo_3S_{13}.nH_2O$ crystal structure displayed at the bottom (Joint Commission for Powder Diffraction Standards (JCPDS):#76-2038).

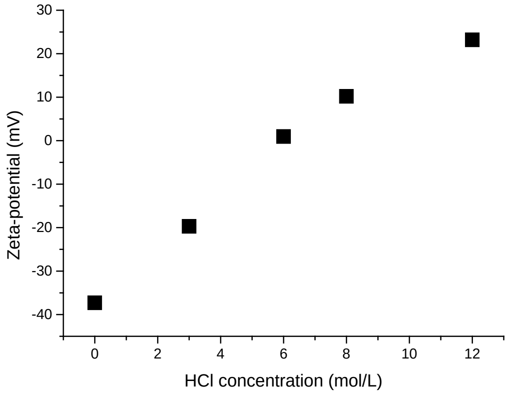

Fig.S2 Zeta potential of pom-C_3N_4 with respect to HCl contentration.

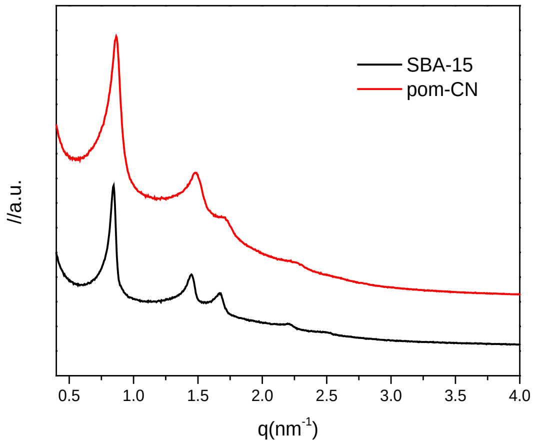

Fig.S3 SAXS patterns of pom-CN and SBA-15 silica.

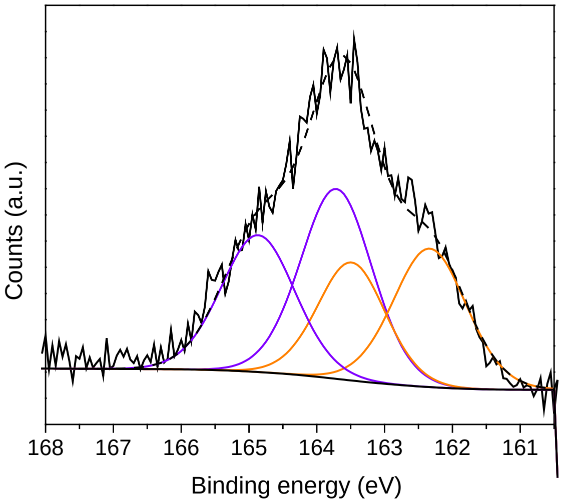

Fig.S4 XPS spectra (S 2p region) and fitted peaks of 1 *wt*% MS/pom-CN after photocatalytic hydrogen production test.

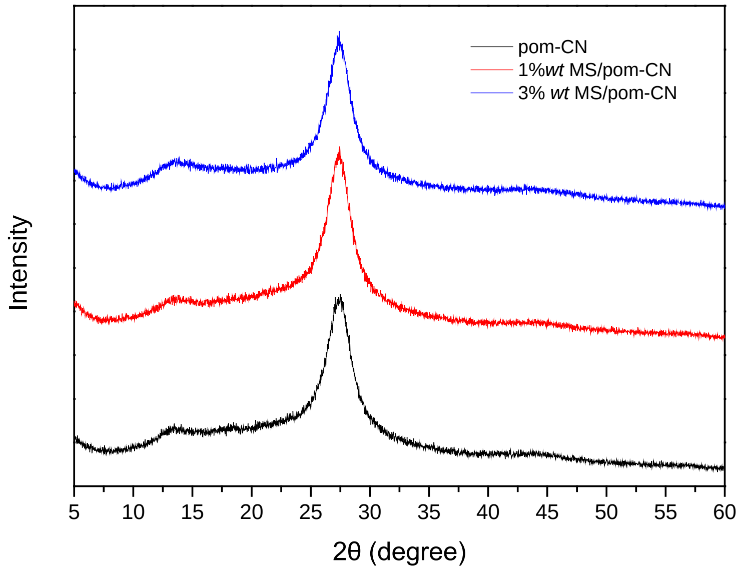

Fig.S5 XRD patterns of pom-CN and MS/pom-CN.

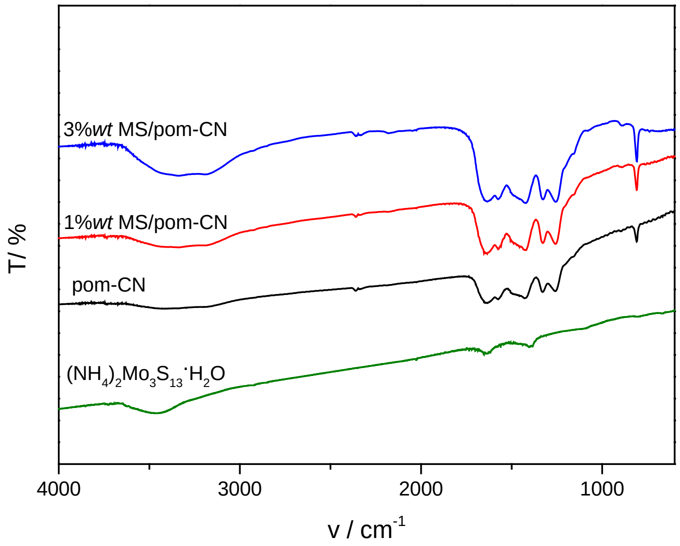

Fig.S6 FT-IR spectra of pom-CN, MS and MS/pom-CN.

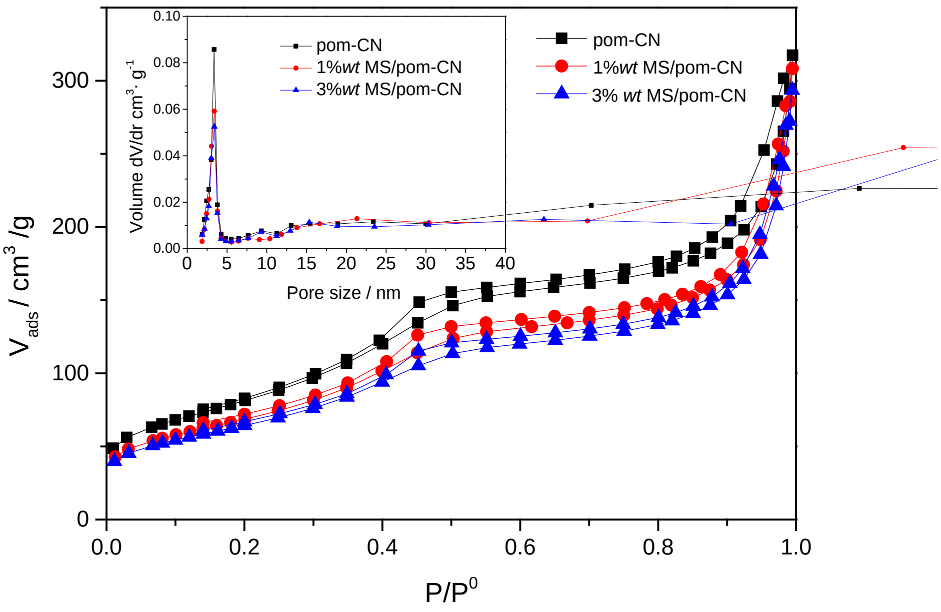

Fig.S7 Nitrogen-sorption isotherms of pom-CN and MS/pom-CN; inset: corresponding BJH pore-size distribution of pom-CN and MS/pom-CN.

Table S1 Physicochemical properties of pom-CN, 1%*wt* MS/pom-CN and 3%*wt* MS/pom-CN samples from nitrogen adsorption-desorption analysis.

catalysts	SA[a] (m^2g^{-1})	PV[b] [cm^3g^{-1}]
pom-CN	298	0.49
1*wt*% MS/pom-CN	249	0.47
3*wt*% MS/ pom-CN	234	0.45

[a] the surface area; [b] pore volume.

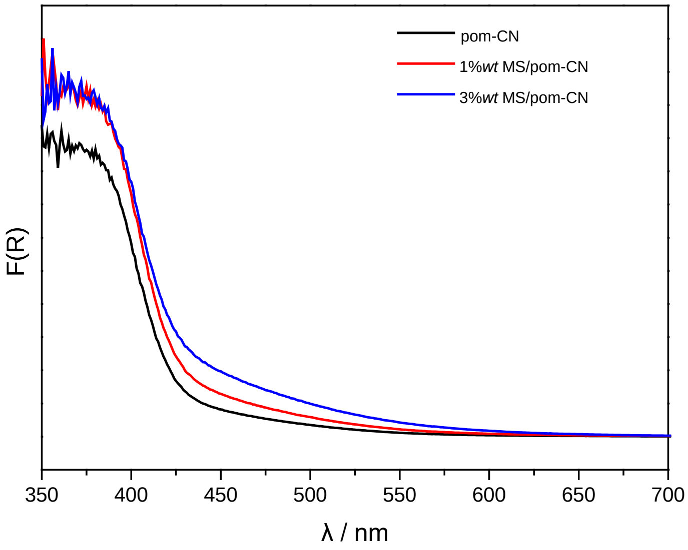

Fig.S8 UV-Vis absorption spectrum of pom-CN and MS/pom-CN.

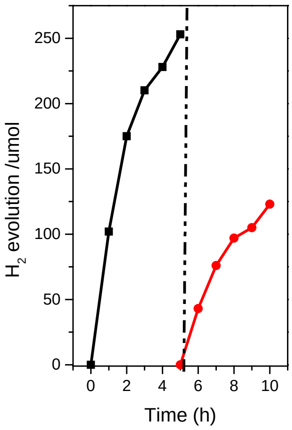

Fig.S9 The photocatalytic hydrogen-evolution stability of the 1%*wt* MS/pom-CN using triethanolamine as a sacrificial agent.