Supporting Information

Facile preparation of $Co_3O_4/Mn_{0.5}Cd_{0.5}S$ heterojunction with highly efficient photocatalytic H_2 production

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Materials

Cadmium acetate dihydrate ($Cd(CH_3COO)_2•2H_2O$, CP), sodium sulfate (Na_2SO_4, AR), sodium sulfite(Na_2SO_3, AR, ≥97.0%) , urea (NH_2CONH_2,AR,99%) and Thioacetamide (C_2H_5NS, 99%) and Manganese acetate tetrahydrate ($Mn(CH_3COO)_2•4H_2O$, 99%) were obtained from Beijing InnoChem Science & Technology Co., Ltd. $Na_2S.9H_2O$ (AR, ≥98.0%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Cobalt nitrate($Co(NO_3)_2·6H_2O$, AR) and Chloroplatinic acid hexahydrate($H_2PtCl_6·H_2O$,AR) were obtained from Sinopharm Chemical Reagent Co. LT. All reagents used were used without further purification.

Photocatalytic test

The photocatalytic hydrogen production tests for MCS, COMCS-20,COMCS-30 and COMCS-50 were carried out in a sealed vacuum glass apparatus. Detailed steps for the photocatalytic hydrogen production test in water were shown: 30mg of sample was dispersed in Na_2S (0.1 M) and Na_2SO_3 (0.3 M) sacrificial reagent solution (40 mL). In addition, during the control experiment to test the photocatalytic hydrogen production performance of Pt/MCS, with other conditions unchanged, an additional chloroplatinic acid solution was added and Pt was loaded on the surface of MCS by photoreduction method with a load of 1.5wt %. A 300 W Xe lamp with an optical filter larger than 420nm provides visible light and the optical power and optical power density of the lamp source are 285mW and 400mW/cm^2 respectively, the temperature is maintained at 6 ℃, and the

air in the reactant solution is removed with a vacuum pump prior to visible light irradiation. The gas was detected every 1 hour by gas chromatography and Ar was the carrier gas.

The apparent quantum yield (AQY) testing procedure remains the same as for the hydrogen production step, with the replacement of the filters with monochromatic filters (400, 420, 450, 500 and 550 nm). The equation was listed as follow:

$$AQY(\%) = \frac{2 \times amount\ of\ H_2\ molecules\ evoloed}{number\ of\ incidident\ photons}$$

Material characterizations

The microtopographies of samples were also recorded by transmission electron microscopy (TEM, JEM-2010). The lattice stripe images were recorded by high-resolution transmission electron microscopy (HRTEM). The elemental composition was tested by the STEM-EDX energy spectrometer. A Bruker D8 Advance X-ray diffraction (XRD) was used for detecting phase identification of samples. The Zate potential of catalyst was measured by Zeta potential analyzer (ZS90). Analysis of the chemical composition, chemical environment of samples and XPS VB spectrum by X-ray photoelectron spectroscopy (XPS). The UV-vis diffuse reflectance spectra (UV-vis DRS) of samples were measured using Agilent Cary 5000 UV-vis spectrometer. The photoluminescence spectra (PL) were recorded through an Agilent Cary Eclipse spectrometer with an excitation wavelength of 380 nm at room temperature. The time-resolved spectrum (TRPL) of the catalyst was obtained by transient fluorescence spectrometer FLS1000. The transient photocurrent, electrochemical impedance spectra (EIS), Linear sweep voltammetry (LSV) and Mott–Schottky (MS) measurements of the samples were performed on an electrochemical analyzer (CHI-660E, CH Instruments Ins.) in a standard three-electrode system, where 0.2 M Na_2SO_4 solution was used as the electrolyte and the as-prepared samples, a standard Ag/AgCl in saturated KCl and a platinum wire were used as the working, reference and counter electrodes, respectively. The EIS measurement was carried out under the open circuit voltage without light

irradiation and the frequency range was 0.1-10^5 Hz with an ac amplitude of 5 mV. LSV measurement was performed in 0.2 M Na_2SO_4 solution with a scan rate of 0.1V s^{-1}. In addition, CEL-NP2000 strong light power meter is used to measure the light intensity of the lamp. The work function of the sample was analyzed by ultraviolet photoelectron spectroscopy (UPS).

Synthesis of $Mn_{0.5}Cd_{0.5}S$ catalyst

1.1029g $Mn(CH_3COO)_2•4H_2O$ and 1.1993g $Cd(CH_3COO)_2•2H_2O$ were dissolved in 20ml deionized water. 1.0142 g of TAA was dissolved in 20 ml of deionised water and a mixture containing Cd^{2+} and Mn^{2+} was subsequently added to the solution and stirred continuously for 30 minutes. After the reaction, the reaction solution was placed in a Teflon high-pressure reactor and reacted hydrothermally at 130 °C for 10 h. The catalyst was washed several times alternately with deionized water and anhydrous ethanol and dried at 60°C to obtain the $Mn_{0.5}Cd_{0.5}S$, noted as MCS.

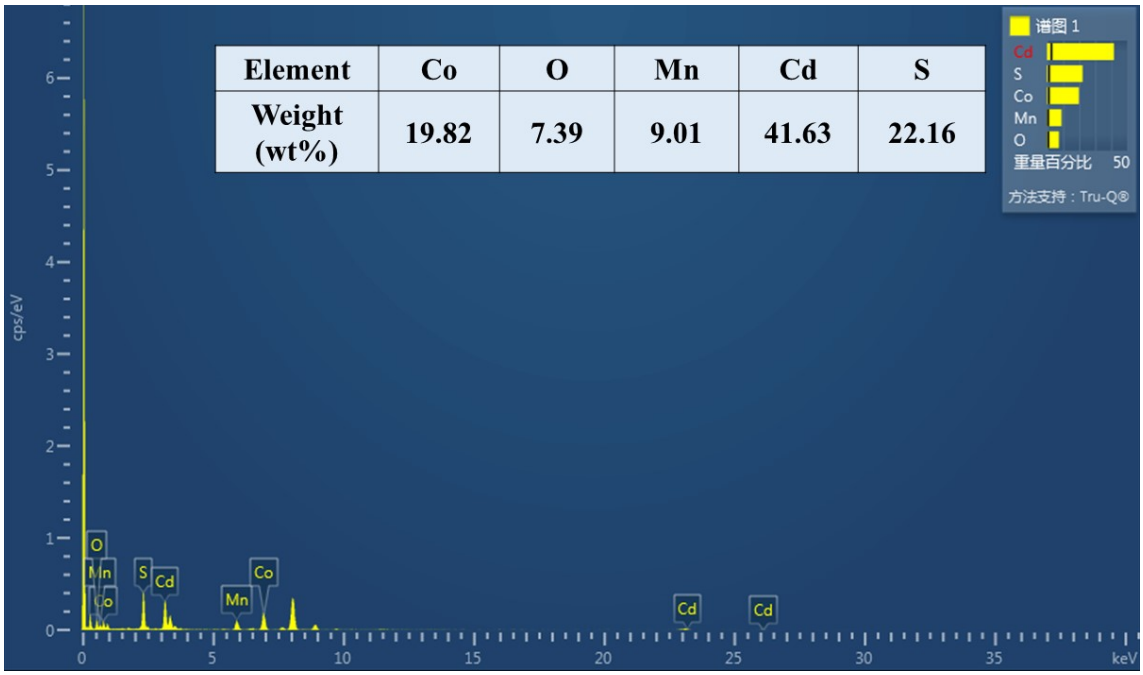

Fig. S1 TEM-EDS spectra and contents of Co, O, Mn, Cd and S elements of COMCS-30.

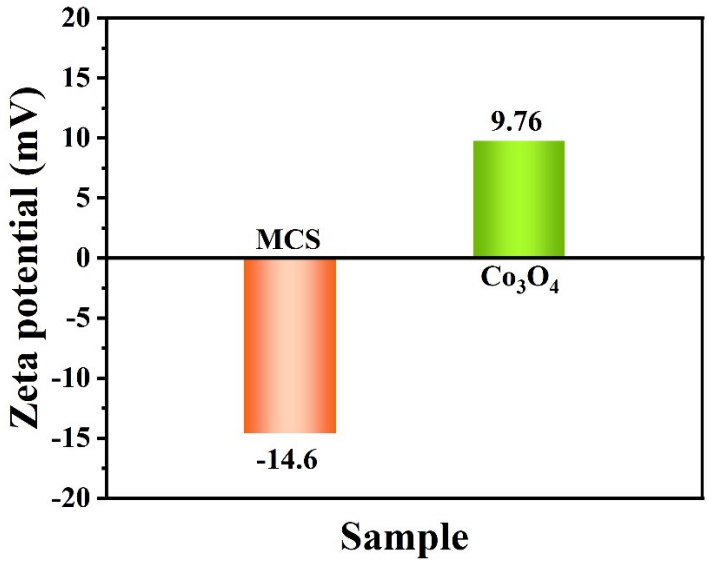

Fig. S2 Zeta potential of MCS and Co_3O_4.

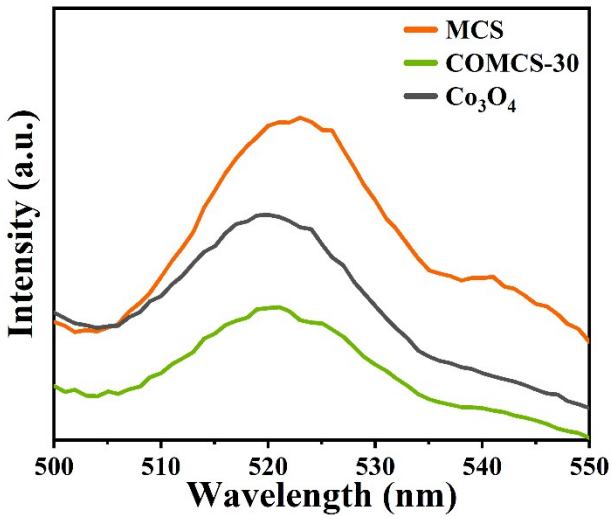

Fig. S3 Photoluminescence spectra of MCS, Co_3O_4 and COMCS-30.

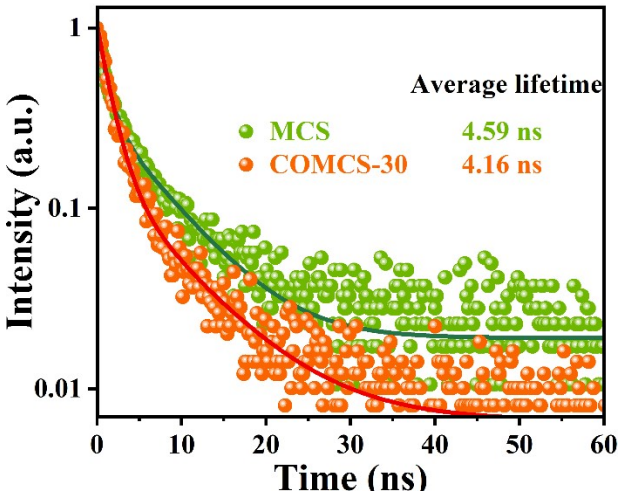

Fig. S4 TRPL spectrum and fluorescence lifetime of MCS and COMCS-30.

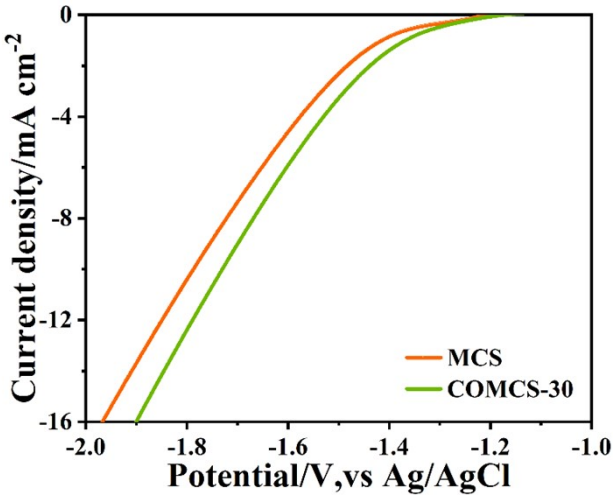

Fig. S5 Linear sweep voltammetry of MCS and COMCS-30

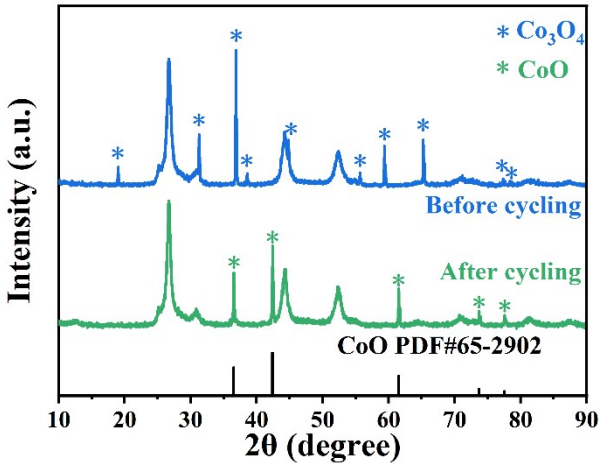

Fig. S6 XRD of COMCS-30 before and after the photocatalytic hydrogen production cycle experiment.