

Supporting Information

A General and Rapid Approach to Crystalline Metal Sulfide Nanoparticles for Photocatalytic H₂ Generation

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Experimental

1. Synthesis of CdS

A certain amount of thiourea and cadmium acetate was mixed in 50 ml of water. After 30 min of magnetic stirring, the obtained solution was dried at 60 °C overnight. The obtained Cd-thiourea complex (200 mg) was then put into an alumina crucible (20 ml) which was covered with another crucible (40 ml). The gap between the two crucibles was stuffed with aluminum silicate. The crucibles were then transferred to a large alumina crucible (200 ml) and covered with CuO powder ($\geq 98.0\%$, Sigma-Aldrich). The crucibles were irradiated by microwave radiation for desired times in a domestic 700 W microwave oven.

2. Characterization

The crystal structure was analyzed by X-ray powder diffraction (XRD) using a DX-2700 X-ray diffractometer with Cu K- α radiation. The morphology investigated by field emission scanning electron microscopy (SEM: Hitachi S-4800) and transmission electron microscopy (TEM: JEOL JEM-2100F). UV-vis diffuse reflectance spectra (DRS) were recorded on a HITACHI U-3900 UV-Vis spectrophotometer. FT-IR measurements were carried out on a IRPrestige-21 (Shimadzu) spectrometer. Dried KBr powder was used to disperse the samples. A HITACHI F-4600 fluorometer was used to measure the photoluminescence (PL) spectra. The excitation wavelength was 320 nm. Time-resolved PL spectra were measured on a HORIB FluoroMax-4P spectrometer

at room temperature. The excitation wavelength was 325 nm. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Thermo Scientific Theta Probe XPS with a monochromatized Al K- α ($h\nu = 1486.6$ eV) source. Thermogravimetric measurements were performed in air. The Brunauer–Emmett–Teller (BET) specific surface area of the samples was collected by nitrogen adsorption–desorption at 77 K (ASAP-2020, Micromeritics).

3 Photocatalytic H₂ generation test

Photocatalytic H₂ generation reactions were performed in a 100 ml closed Pyrex reactor with a quartz window under visible light irradiation. Typically, 10 mg of well-ground catalyst powder was dispersed in an aqueous solution (20 ml) containing Na₂S (0.35 mol L⁻¹) and NaSO₃ (0.25 mol L⁻¹) as sacrificial electron donors. Pt (0.5 wt %) co-catalyst was added by injecting 106 μ l of H₂PtCl₆ solution into the reactor. The suspension was purged with argon to drive off residual air. A 300 W Xe lamp coupled with a UV cut-off filter ($\lambda > 420$ nm) was used to initiate the photocatalytic reaction. The gases produced in the reactor were analyzed periodically through a gas chromatograph (GC-1690, Kexiao, China) with a TCD detector.

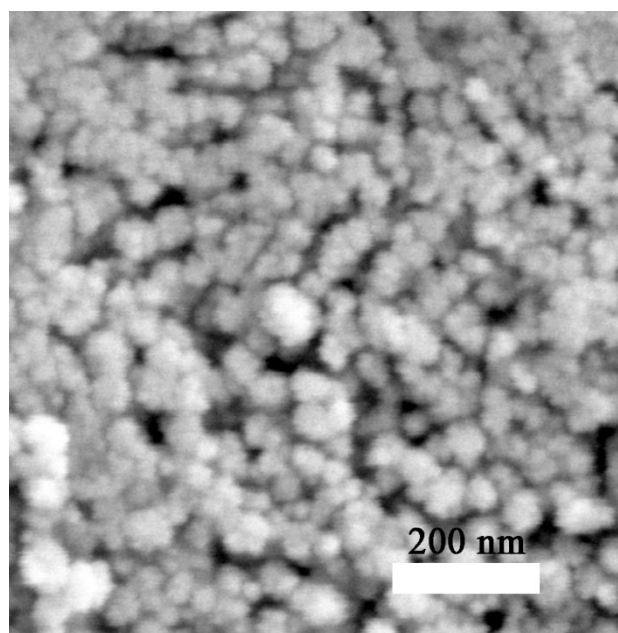


Fig. S1 SEM image of Cd-thiourea complex. The thiourea: Cd^{2+} molar ratio is 6:1.

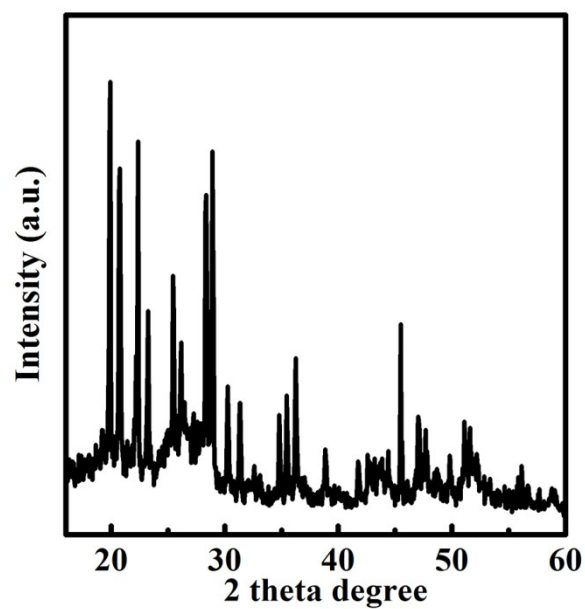


Fig.S2 XRD pattern of Cd-thiourea complex with thiourea:Cd molar ratio of 6:1.

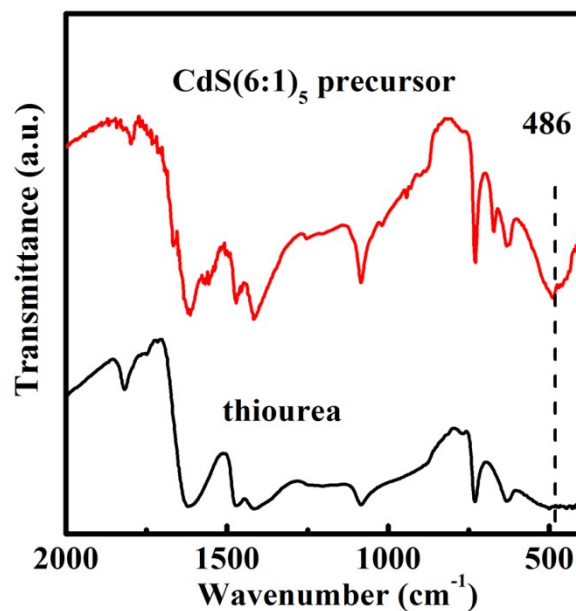


Fig. S3 FT-IR spectra of thiourea and Cd-thiourea complex with thiourea:Cd molar ratio of 6:1. The characteristic absorption peak at 486 cm⁻¹ (Cd-S coordination bond) indicates the formation of the Cd-thiourea complex.

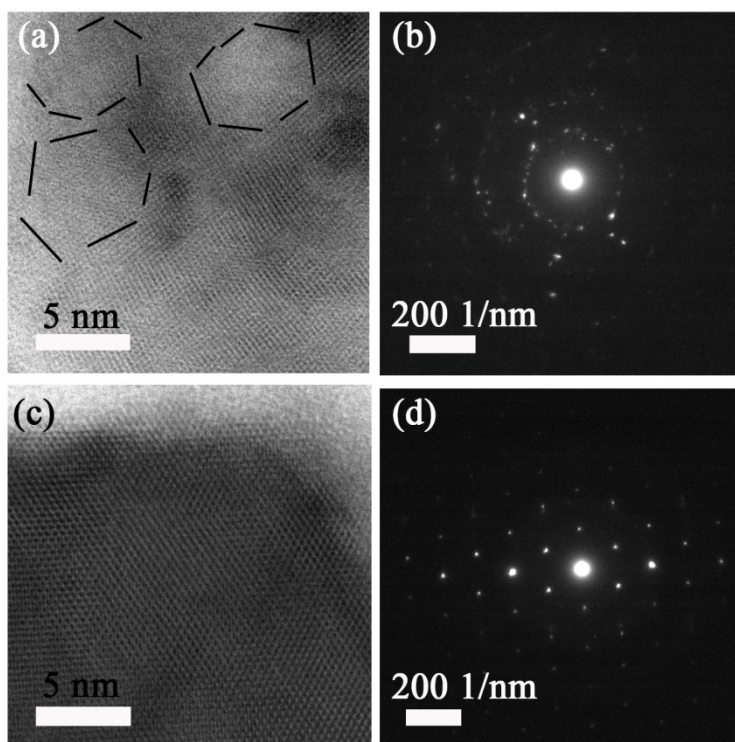


Fig. S4 HRTEM for (a) CdS(2:1)₅ and (c) CdS(6:1)₅, electron diffraction patterns for (a) CdS(2:1)₅ and (c) CdS(6:1)₅.

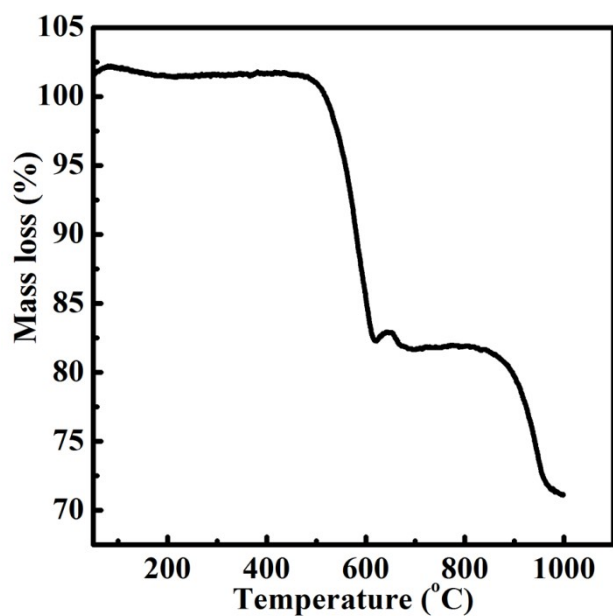


Fig. S5 TG thermogram for CdS(6:1)₅ in air. TG analysis shows a mass loss at 610 °C, revealing the existence of polymeric intermediates derived from thiourea.

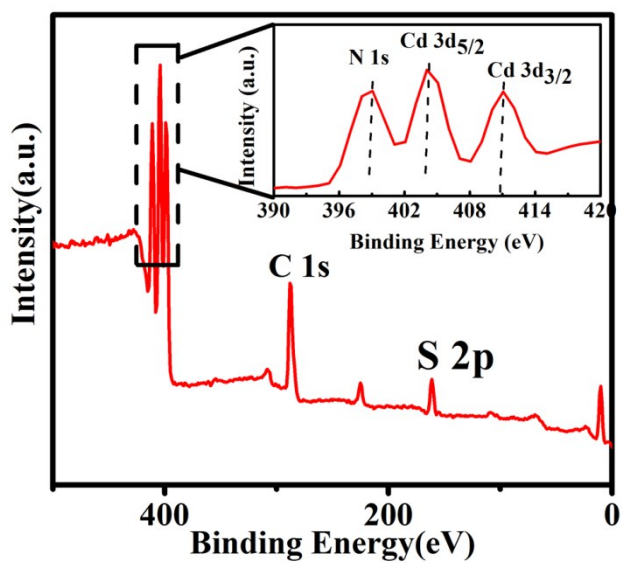


Fig. S6 XPS survey spectrum showing the existence of C, S, N, and Cd elements in CdS(6:1)₅.

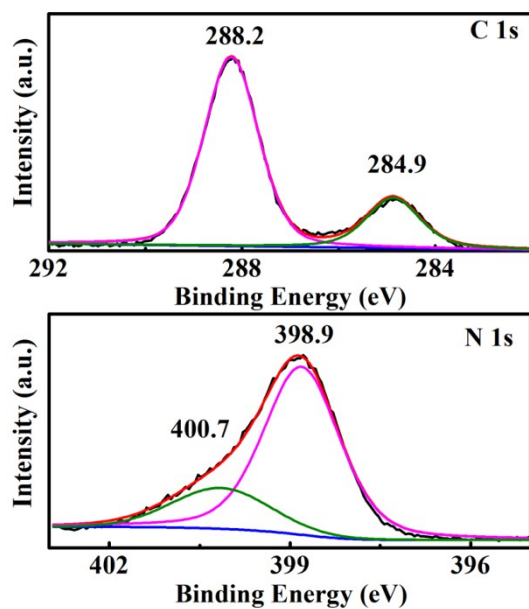


Fig. S7 XPS spectra of CdS(6:1)₅ produced by irradiating the Cd-thiourea complex for 5 min. (upper) C 1s spectrum and (lower) N 1s spectrum.

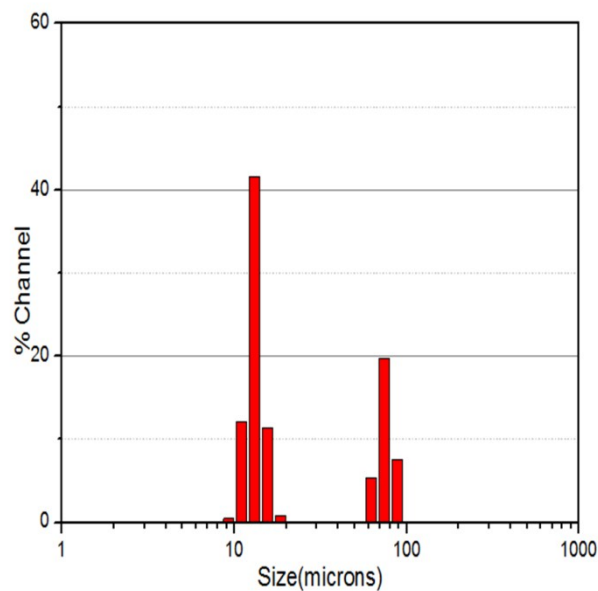


Fig. S8 Size distribution of CdS(6:1)₅. The average size is ~ 30 μm , showing the heavy aggregation as illustrated by SEM observation (Fig. 2b).

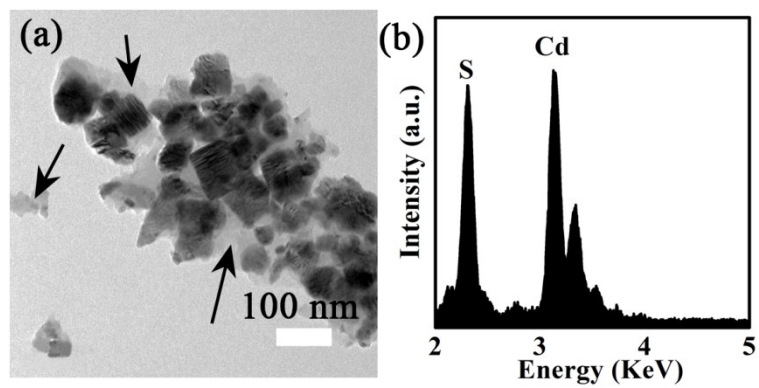


Fig. S9 (a) TEM image of CdS(6:1)₅. Arrows indicate the polymeric intermediates for g-C₃N₄, (b) EDS of a CdS(6:1)₅ particle as well as the 1:1 Cd:S molar ratio.

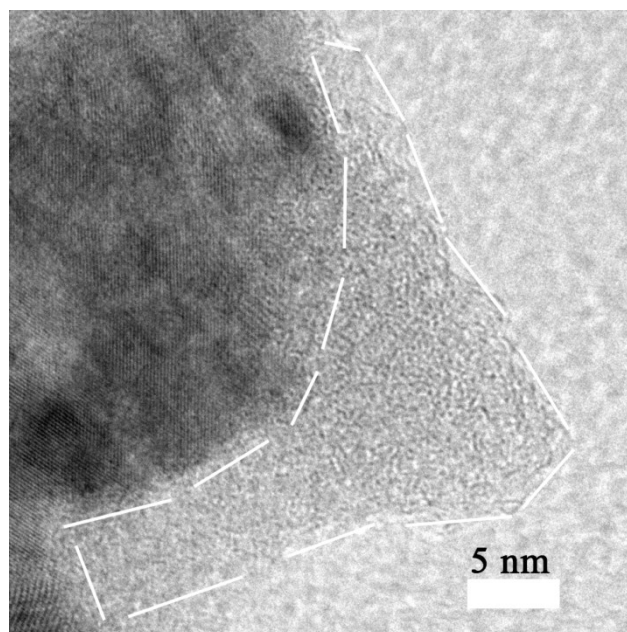


Fig. S10 TEM image showing the polymeric intermediate for g-C₃N₄ (outlined by dashed line) in CdS(6:1)₅.

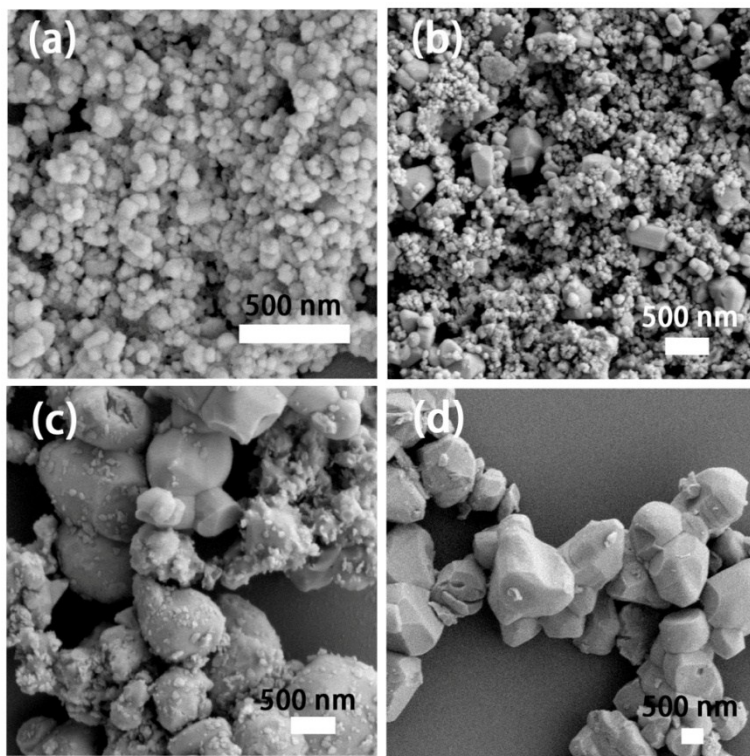


Fig. S11 SEM images of CdS(6:1)_t (t=5, 10, 20, and 35) samples, a: CdS(6:1)₅, b: CdS(6:1)₁₀, c: CdS(6:1)₂₀, and d: CdS(6:1)₃₅. The prolonged microwave-heating time causes the CdS particles to increase in size.

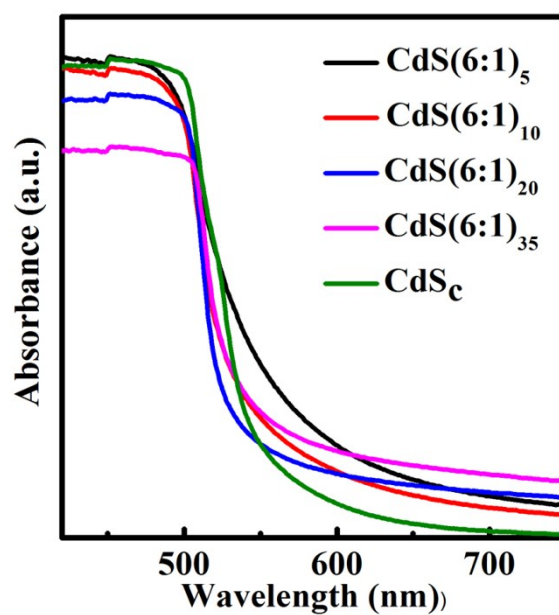


Fig. S12 UV-Vis diffuse reflectance absorption spectra of $\text{CdS}(6:1)_t$ samples obtained by irradiating the Cd-thiourea complex for different times. The results clearly show that the absorption edge of $\text{CdS}(6:1)_t$ ($t=10, 20$, and 35) samples is essentially the same as that of CdS_c .

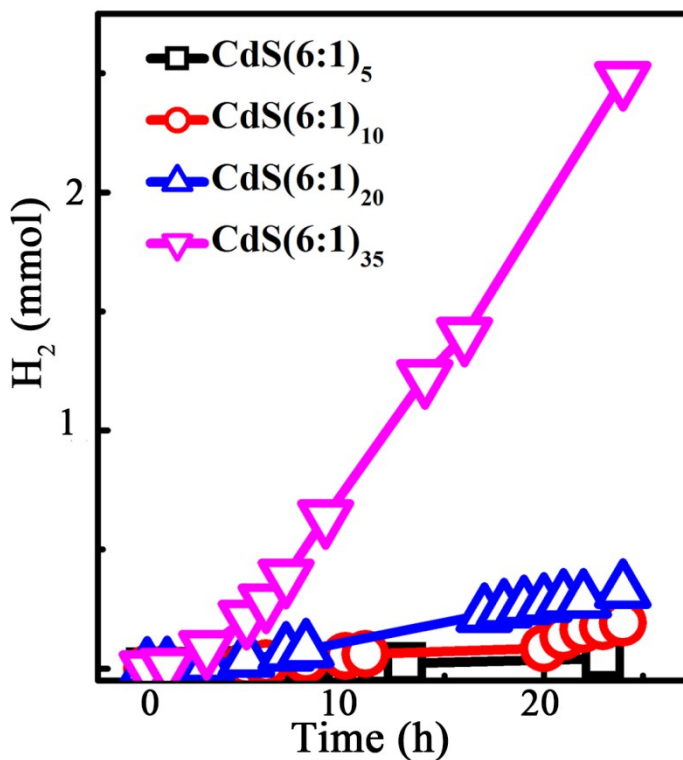
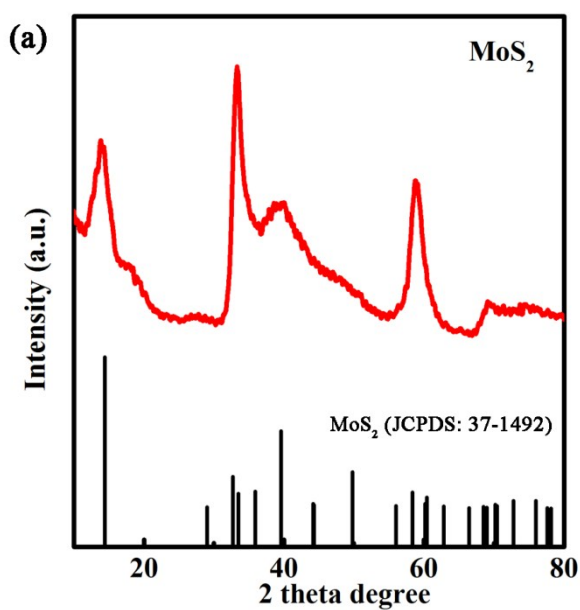


Fig. S13 long-term H_2 generation stability of $\text{CdS}(6:1)_t$ ($t=5, 10, 20$, and 35) samples.



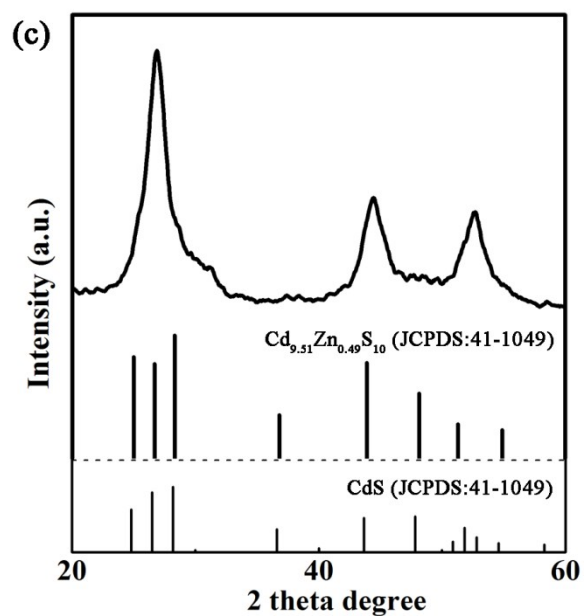
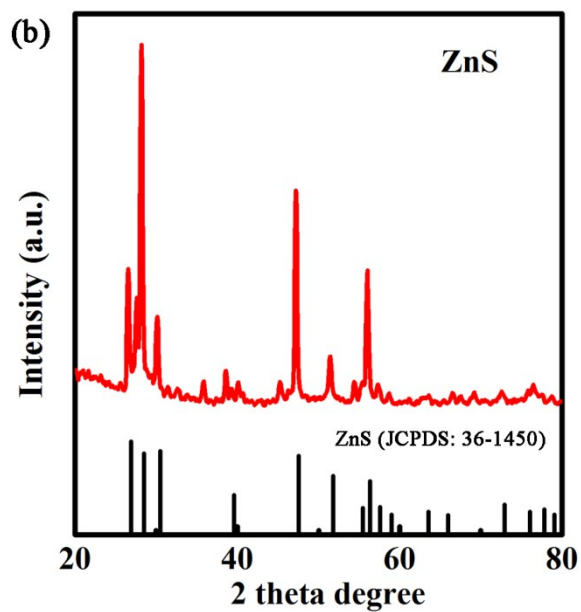


Fig. S14 XRD patterns of (a) MoS_2 , (b) ZnS , and (c) $Cd_{0.95}Zn_{0.05}S$ solid solution. The metal sulfides were prepared by microwave-irradiated M-thiourea complexes (M=Mo, Zn, and (Cd, Zn)) for 20 min. The molar ratio of thiourea:M is fixed at 4:1.