Electronic Supplementary Information (ESI) for

Mn_{13}-clusters based coordination polymer as co-catalyst of CdS for enhanced visible-light driven H_2 evolution

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Part I: Experimental Section

1. The synthesis of CdS nanoparticles (CdS NPs)

CdS NPs were prepared by a precipitation-hydrothermal method. Firstly, 0.5 g $Cd(Ac)_2 \cdot 2H_2O$ was added into 10 ml deionized water followed by stirring for 2 hours. Secondly, 3 ml 0.49 M Na_2S aqueous solution was added into the salts solution at the same time, followed by stirring for 3 hours. Finally, the mixed suspension was transferred to a 23 ml Teflon-lined autoclave and kept at 180 °C for 10 hours. The final products were washed by deionized water and ethanol for three times, respectively, and dried at 60 °C for 24 hours.

2. The synthesis of Mn_{13}-polymer

A mixture of $MnCl_2.4H_2O$ (0.197g), $KMnO_4$ (0.033g), *tert*-butylphosphonate acid (0.140g), 4,4'-trimethylenedipyridine (4,4-TDP) (0.303 g) and CH_3OH (40 mL) was stirred at room temperature for 5 h. The filtrate was remained at room temperature after the solution was filtered. The CH_3OH naturally evaporated, and the crimson Mn_{13}-polymer crystals were formed after two weeks.

3. The synthesis of Mn_{13}-polymer/CdS

Mn_{13}-polymer/CdS was synthesized by mechanically mixing Mn_{13}-polymer with the CdS NPs in a mortar inside a glovebox filled with Argon gas. For example, 20 mg of as-synthesized CdS NPs were added into the mortar, followed by addition of 0.5 mg Mn_{13}-polymer (2.4 wt%). Then the mixture was mechanically ground inside the glovebox until the final products transformed into the fine powders. In the same way, the nominal weight ratios of Mn_{13}-polymer to CdS were 4.5, 7.0, 9.0 and 11.0 wt%, respectively.

4. Photocatalytic H_2 production test

The photocatalytic H_2-production reactions were performed in a 100 ml Pyrex flask with a white-light emitting-diode (LED) working as the light source with a UV-cutoff filter (≥ 420 nm) and using Mn_{13}-polymer/CdS as catalyst at room temperature, along with triethanolamine aqueous solution 80 ml (TEOA 16 vol.%) as an electron donor. Then Argon gas was purged into the dispersion of photocatalyst for 20 mins to eliminate the air and keep the reactor under anaerobic conditions. After photocatalytic H_2 production, 0.2 ml gas was pumped intermittently by injection syringe, and the produced H2 was tested by gas chromatograph.

5. Electrochemical and photoelectrochemical tests

The polarization curves were carried out in a standard three-electrode system in 0.5M Na_2SO_4 aqueous solution, using the as-prepared samples as the working electrode, Ag/AgCl (saturated KCl) as a reference electrode, and the Pt wire as the counterelectrode. The current frequency is 1200 Hz. The EIS measurements were tested in the same condition over a range from 1 to 2×10^5 Hz with an AC. For the TCP experiment, the light source was a 300 W Xenon light with a UV-cutoff filter (≥ 420 nm) under the conditions of 0.2 M Na_2S and 0.04 M Na_2SO_3 mixed aqueous solution.

Part II: Additional Figures

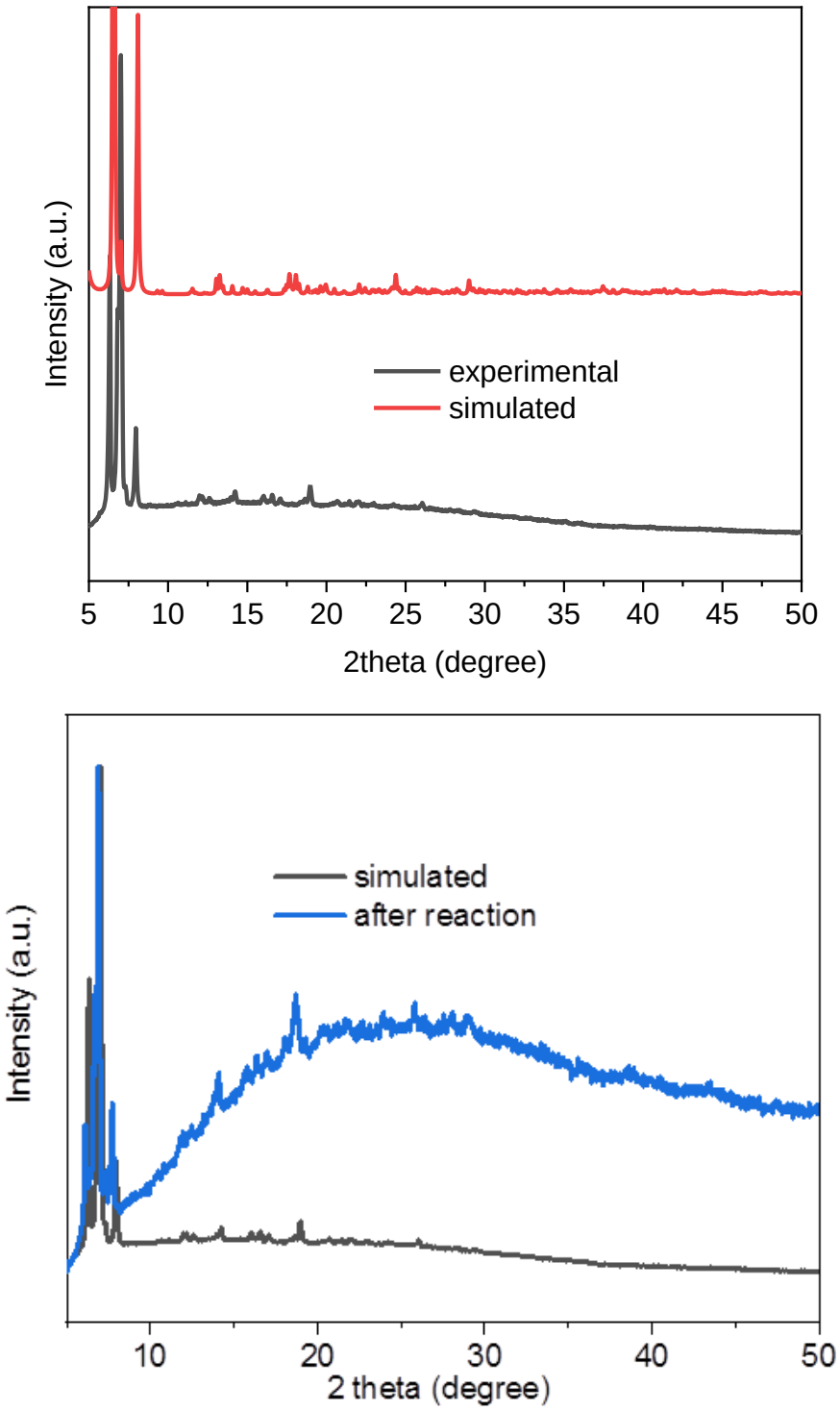

Figure S1. The PXRD patterns of obtained fresh Mn_{13}-polymer (upper); and pure Mn_{13}-polymer samples after 9h photocatalytic test under the corresponding experimental conditions (lower), suggestting the co-catalyst should be stable even under visible light illumination.

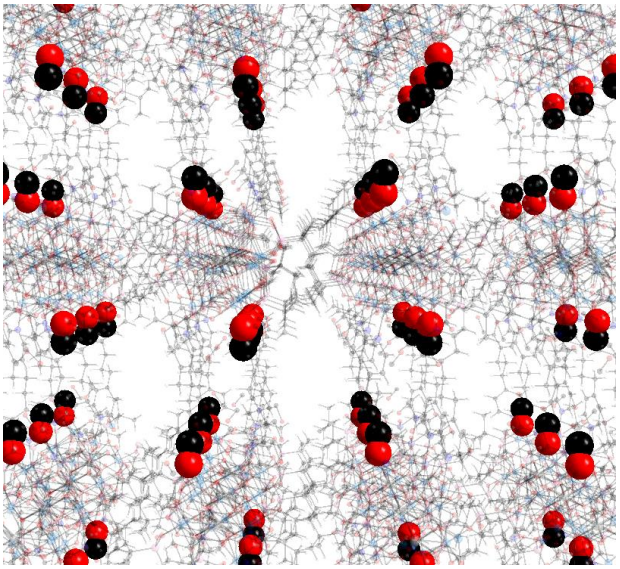

Figure S2. The packing model of Mn_{13}-polymer to highlight the CH_3OH molecules inside the channels.

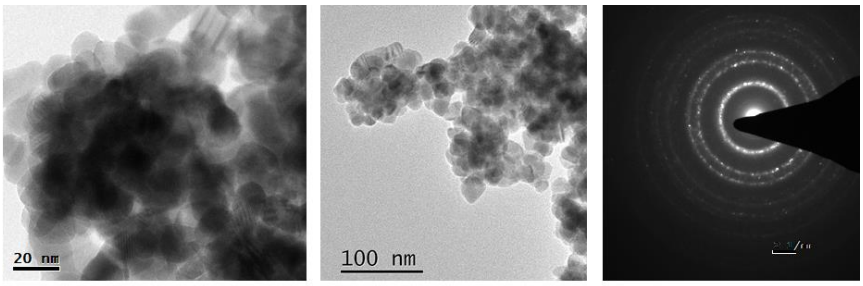

Figure S3. The typical TEM (a-b) and SAED (c) image of CdS nanoparticls.

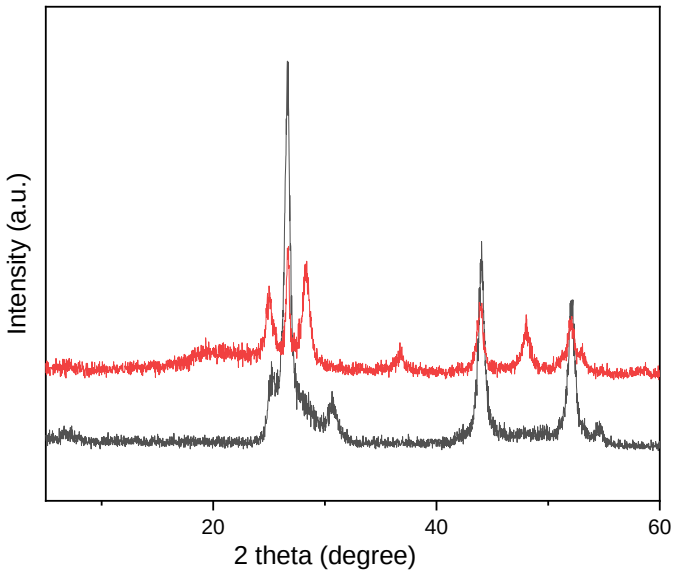

Figure S4. The XRD patterns of Mn_{13}-polymer/CdS(red line) and CdS (black line).

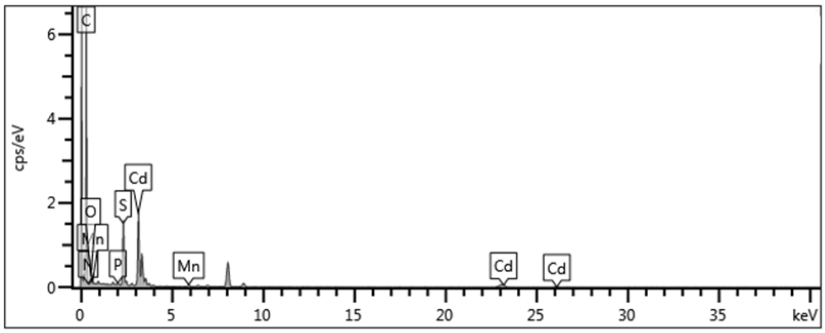

Figure S5. EDX of Mn_{13}-polymer/CdS.

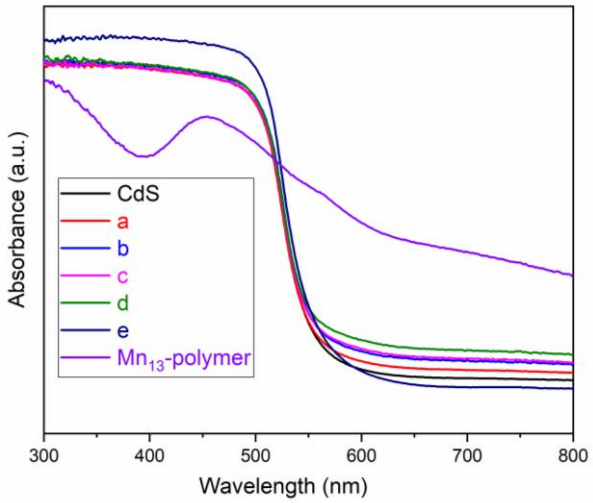

Figure S6. The UV-Vis diffuse reflectance spectra of Mn_{13}-polymer, CdS and Mn_{13}-polymer/CdS. The a, b, c, d, and e on behalf of the different amount Mn_{13}-polymer loading of 2.4, 4.5, 7.0, 9.0 and 11.0 wt%, respectively.

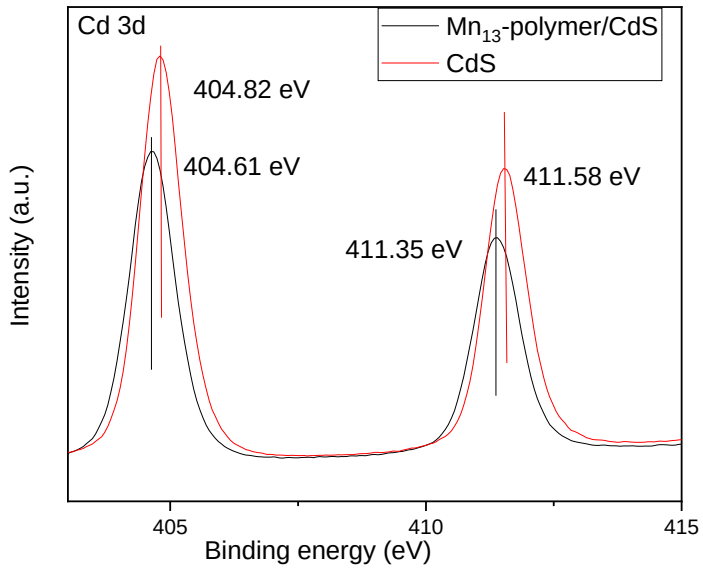

Figure S7. The XPS spectra of Cd 3d of CdS and Mn_{13}-polymer/CdS.

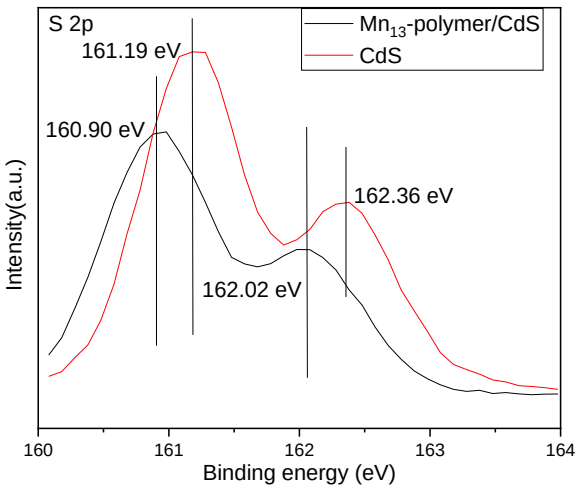

Figure S8. The XPS spectra of S_{2p} of CdS and Mn_{13}-polymer/CdS.

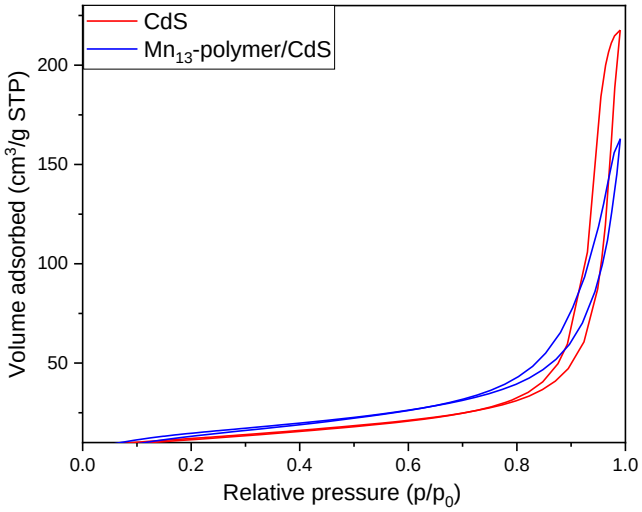

Figure S9. The N_2 sorption isotherms of CdS and Mn_{13}-polymer/CdS.

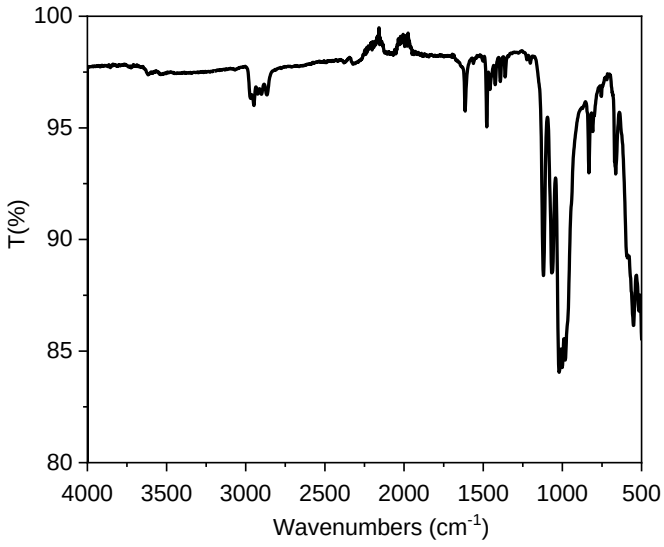

Figure S10. The FT-IR spectrum of the obtained crystals of Mn_{13}-polymer.