Supplementary Information

Surface-modified metal sulfides as stable H_2-evolving photocatalysts in Z-scheme water splitting with a $[Fe(CN)_6]^{3-/4-}$ redox mediator under visible-light irradiation

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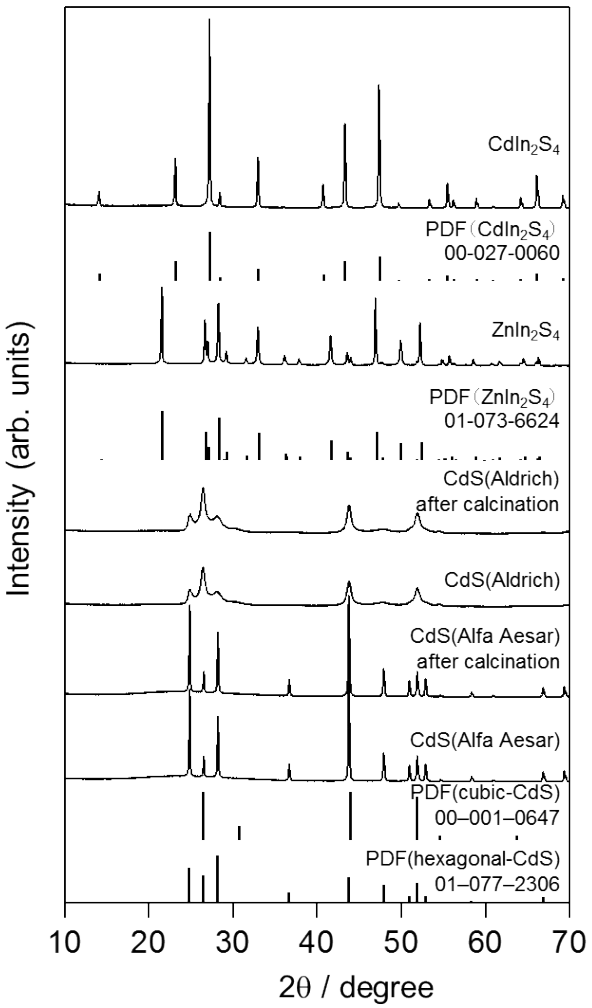

Figure S1 XRD patterns of CdS(Alfa Aesar, Aldrich) before and after calcination at 673 K, $ZnIn_2S_4$ and $CdIn_2S_4$ samples.

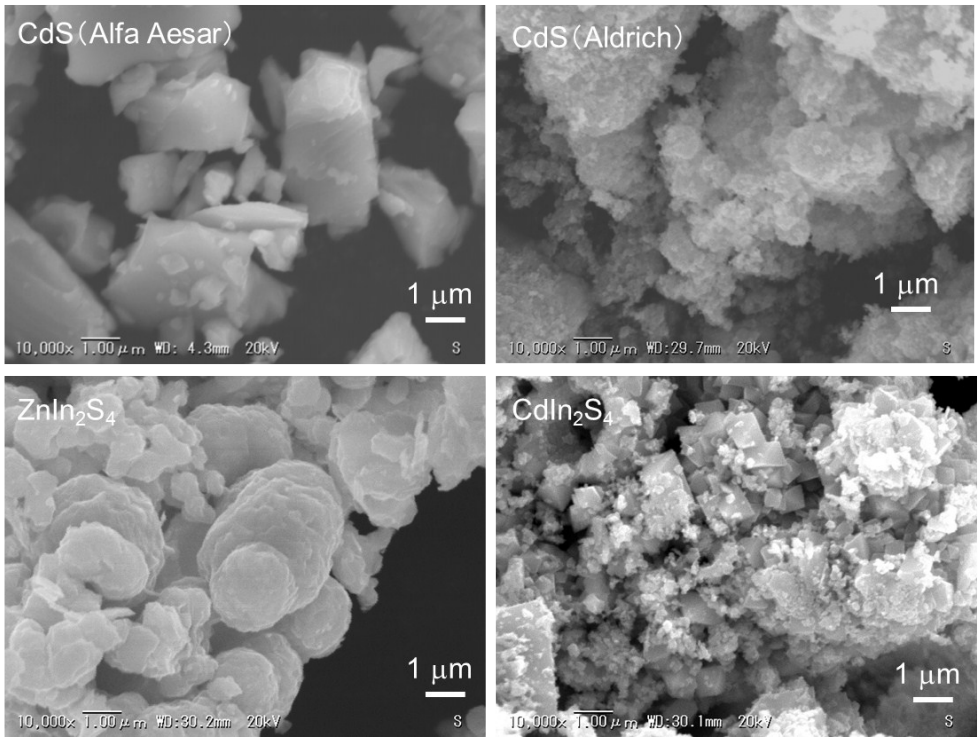

Figure S2 SEM images of CdS(Alf Aesar, Aldrich) calcined at 673 K, $ZnIn_2S_4$ and $CdIn_2S_4$.

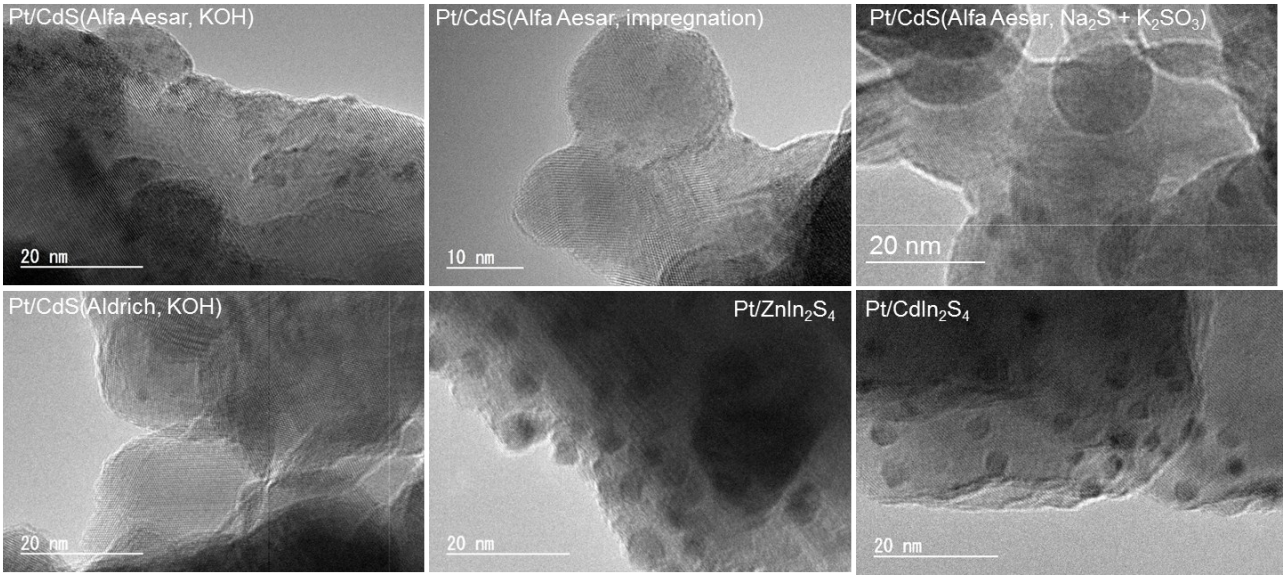

Figure S3 TEM images of various Pt-loaded metal sulfides.

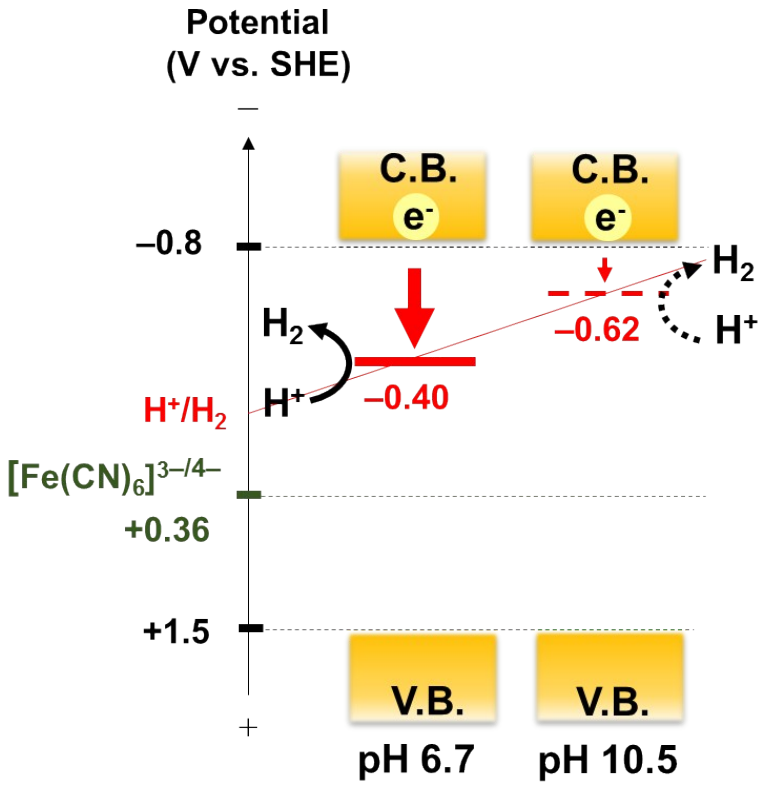

Figure S4 Illustration of influence of pH of reaction solution on initial rate of H_2 evolution over Pt/CdS

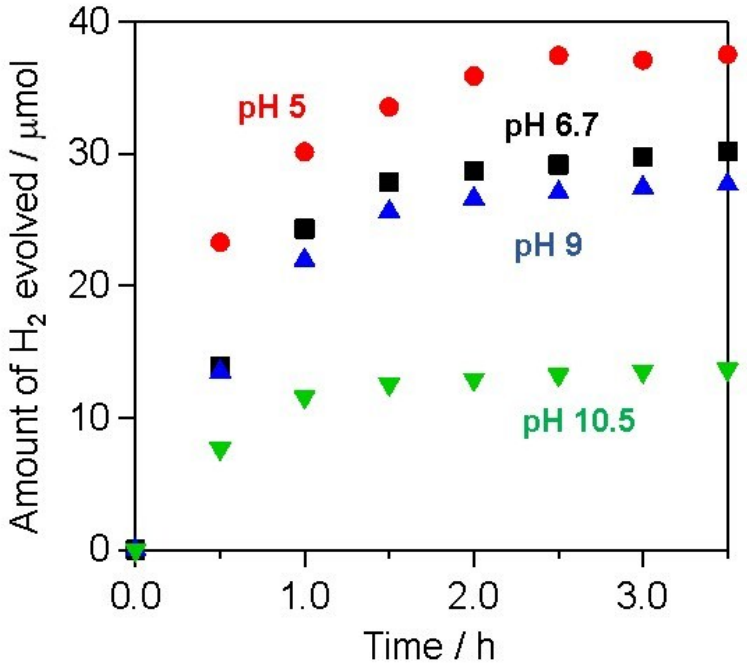

Figure S5 Time courses of H_2 evolution over Pt/CdS from aqueous $K_4[Fe(CN)_6]$ solution at different pH.

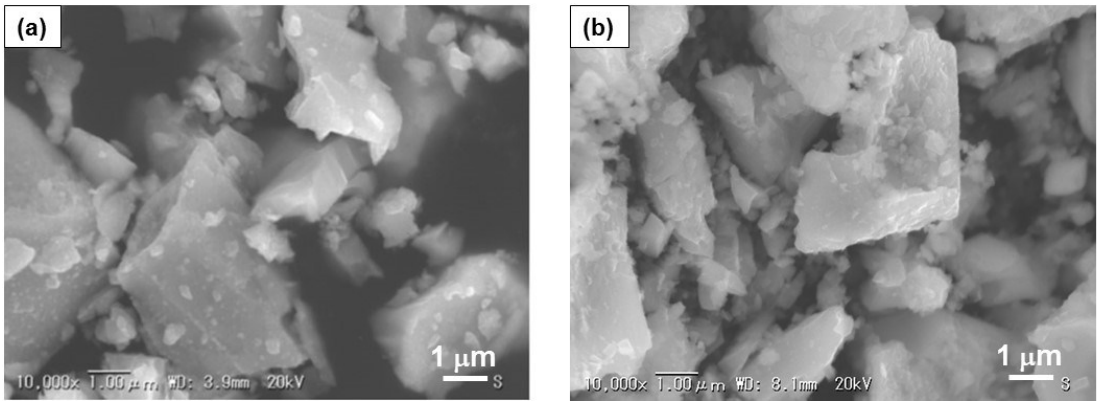

Figure S6 SEM images of Pt/CdS (a) before and (b) after reaction in BB solution (0.1 M, pH 8) containing $K_4[Fe(CN)_6]$ (5 mM).

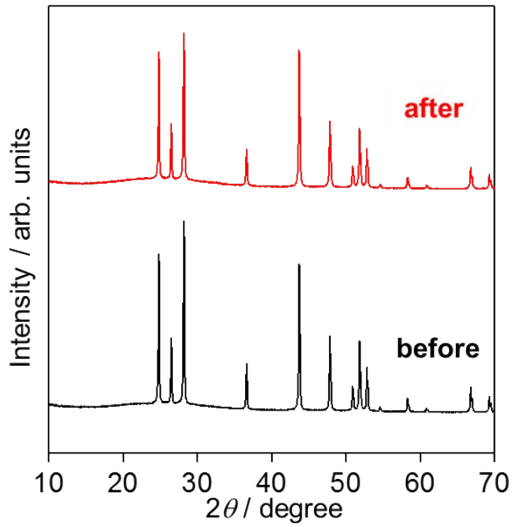

Figure S7 XRD patterns of Pt/CdS before and after reaction in BB solution (0.1 M, pH 8) containing $K_4[Fe(CN)_6]$ (5 mM).

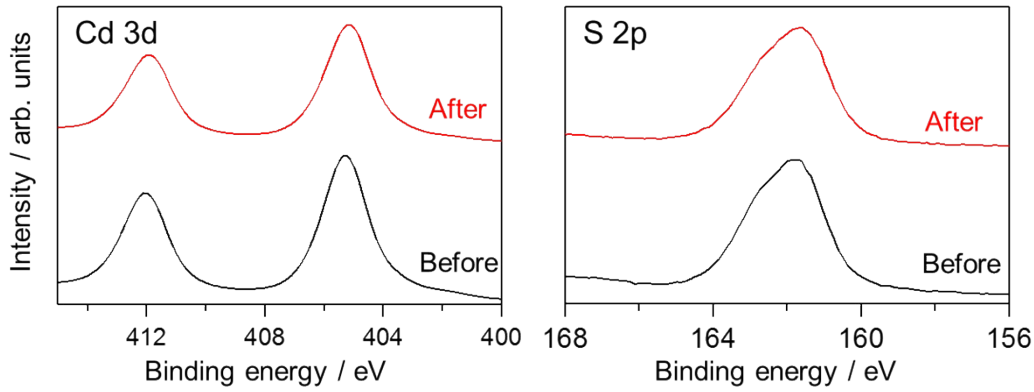

Figure S8 XPS spectra of Pt/CdS before and after reaction in BB solution (0.1 M, pH 8) containing $K_4[Fe(CN)_6]$ (5 mM).

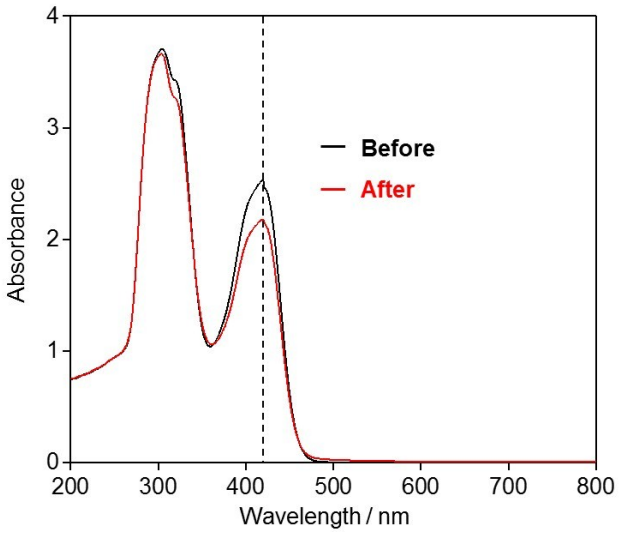

Figure S9 Photoabsorption spectra of an aqueous BB solution containing SiO_2 (50 mg), $K_4[Fe(CN)_6]$ (2.5 mM), and $K_4[Fe(CN)_6]$ (2.5 mM) before and after photoirradiation ($\lambda > 400$ nm) for 15 h.

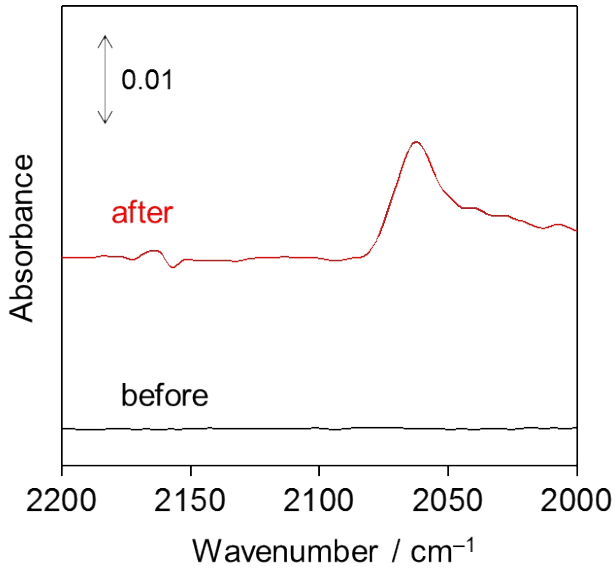

Figure S10 ATR-FTIR spectra of Pt/CdS before and after H_2 evolution in the presence of $[Fe(CN)_0]^{4-}$ without borate buffer.

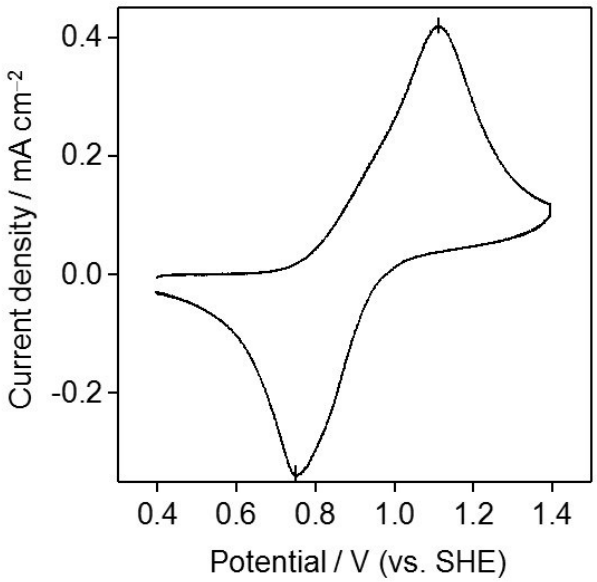

Figure S11 Cyclic voltammogram of a $K_2[CdFe(CN)_6]$ electrode in 1 M aqueous KNO_3 solution.

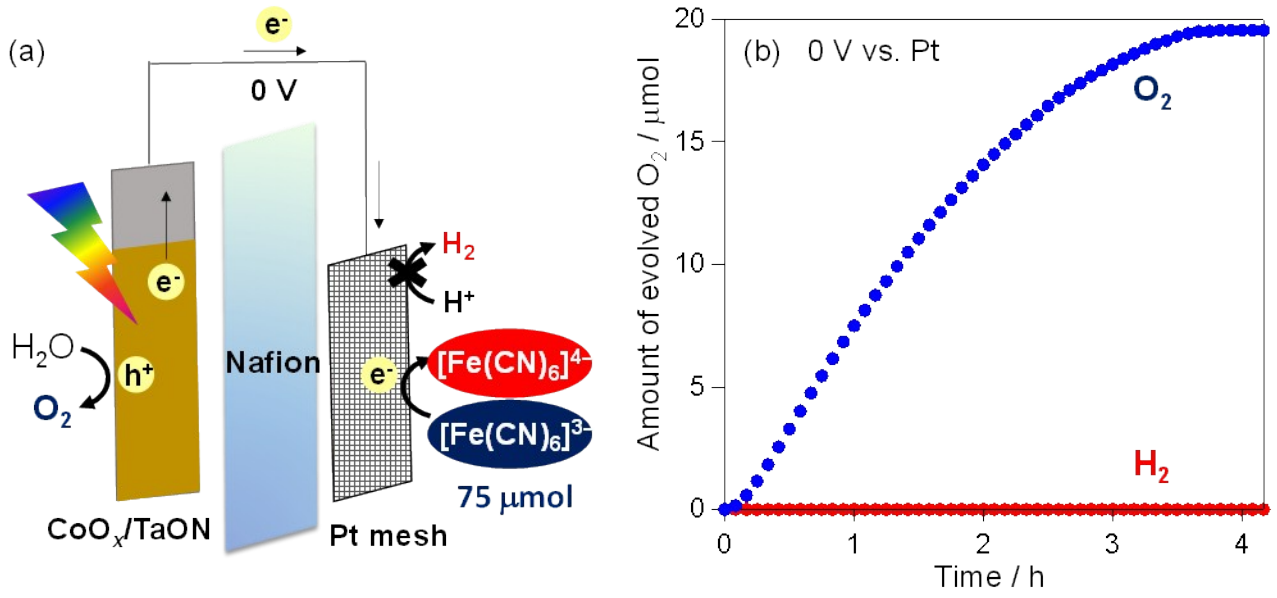

Figure S12 (a) Illustration of the reaction and (b) time course of O_2 evolution over a CoO_x/TaON photoanode using two-compartment cells divided by a Nafion membrane under visible-light irradiation (75 μmol $K_3[Fe(CN)_6]$, 0.8 M BB solution (pH 8), 0 V vs. Pt).