Electronic Supplementary Information

Developing an Efficient NiCo$_2$S$_4$ Cocatalyst for Improving Visible Light H$_2$ Evolution Performance of CdS Nanoparticles

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**Fig. S1** EDX mappings of the NiCo$_2$S$_4$/CdS sample

**Fig. S2** Evolution of H$_2$ over the 8%NiCo$_2$S$_4$/CdS composite materials and Pt/CdS composite materials with different Pt content.
**Fig. S3** Wavelength dependence of H$_2$ evolution over NiCo$_2$S$_4$/CdS sample.

**Fig. S4** Long term stability test of H$_2$ production over NiCo$_2$S$_4$/CdS and CdS samples under visible light irradiation.

**Fig. S5** Nyquist plots of CdS and NiCo$_2$S$_4$/CdS material electrodes.
Determinations of conduction and valence band potentials of NiCo$_2$S$_4$ and CdS.

In the NiCo$_2$S$_4$/CdS hybrid system, NiCo$_2$S$_4$ holds an appropriate band structure with a suitable potential relative to CdS according to the theoretical calculation. The valence band potentials of a semiconductor from the absolute electronegativity follow the empirical formulas:[1]

$$E_{CB} = X - Ec + 0.5E_g$$

$$E_{VB} = E_{CB} + E_g$$

$E_g$ is the band gap energy of the semiconductor, the values for NiCo$_2$S$_4$ and CdS are 2.5 eV and 2.4 eV, respectively.[2,3] $E_{VB}$ is the valence band (VB) edge potentials, $E_{CB}$ is the conduction band (CB) edge potentials, $X$ is the electronegativity of the semiconductor that is the geometric mean of the electronegativity of the constituent atoms (the electronegativity of an atom is the arithmetic mean of the atomic electron affinity and the first ionization energy), and $Ec$ is the energy of free electrons on the hydrogen scale (about 4.5 eV). The $X$ values for NiCo$_2$S$_4$ and CdS are estimated to be 5.33 and 5.19 eV, respectively. Thus, the $E_{CB}$ values of NiCo$_2$S$_4$ and CdS are calculated to be -0.42 and -0.51 eV, respectively. The $E_{VB}$ values of NiCo$_2$S$_4$ and CdS is estimated to be 2.08 and 1.89 eV, respectively.

References