Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Supporting Information

Ni^{2+}-doped $Zn_xCd_{1-x}S$ photocatalysts from single-source precursors for efficient solar hydrogen production under visible light irradiation

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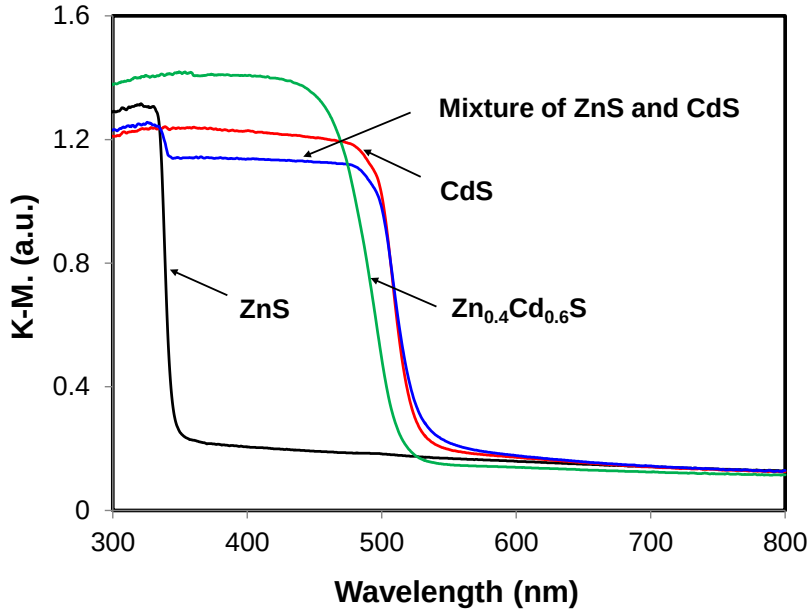

Fig. S1 UV-vis DRS of CdS, ZnS, physical mixture of CdS and ZnS, and $Zn_{0.4}Cd_{0.6}S$ solid solution.

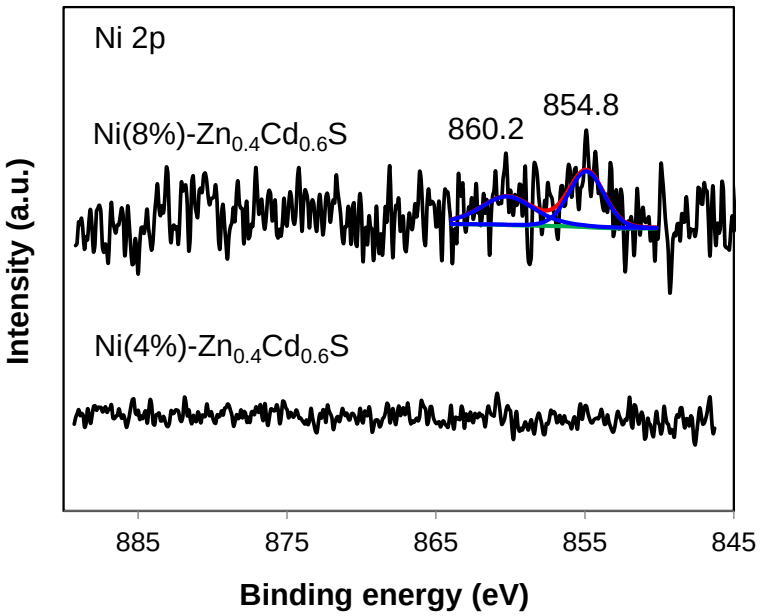

Fig. S2 XPS spectra of Ni 2p of samples Ni(4%)-$Zn_{0.4}Cd_{0.6}S$ and Ni(8%)- $Zn_{0.4}Cd_{0.6}S$.

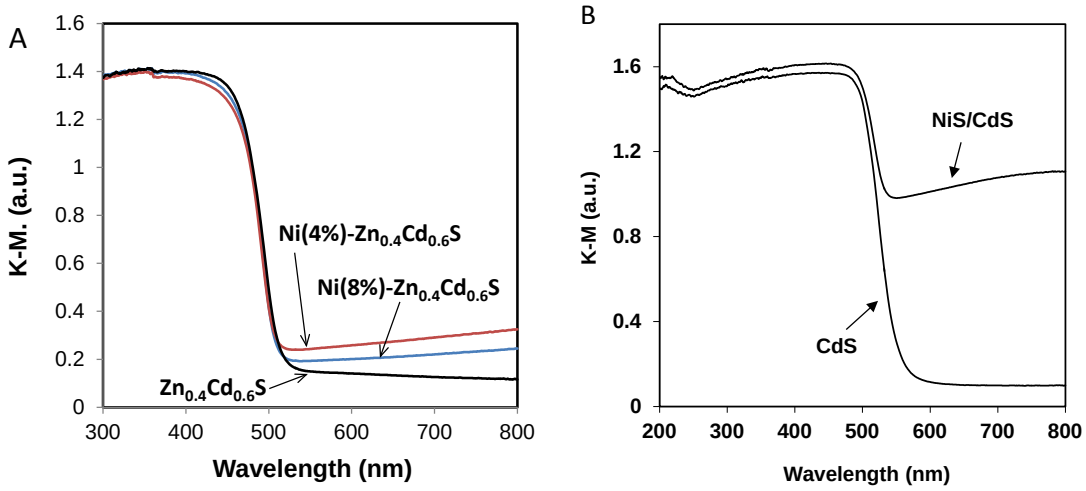

Fig. S3 UV-vis DRS spectra of (A) Ni(4%)-$Zn_{0.4}Cd_{0.6}S$ and Ni(8%)-$Zn_{0.4}Cd_{0.6}S$, and (B) NiS/CdS (from Ref. 4: Zhang et al.).

We detected the formation of $S_2O_3^{2-}$ ions during photocatalytic reaction based on the following self-redox equation.

$$Na_2S_2O_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2 + S \qquad (S1)$$

After 4 h of photocatalytic reaction, the reaction mixture was centrifuged to remove solid catalyst particles. Excess $Zn(NO_3)_2$ was added to the clear supernatant to precipitate S^{2-} and SO_3^{2-} ions. After removing the precipitates by centrifugation, concentrated aqueous HCl (37 wt%) solution was added to the clear supernatant. The formation of elemental S precipitate with a light yellow color can be observed as shown in Fig. S4E, indicating the existence of $S_2O_3^{2-}$ ions in the solution. Control experiments were also carried out and the results are shown in Fig. S4A-D. The presence of $S_2O_3^{2-}$ ions in the reaction mixture implied that the reactions described in Equations 5 and 6 (Page 15) took place.

$$2S^{2-} + 2h^{+} \rightarrow S_2^{2-} \qquad (5)$$

$$S_2^{2-} + SO_3^{2-} \rightarrow S_2O_3^{2-} + S^{2-} \qquad (6)$$

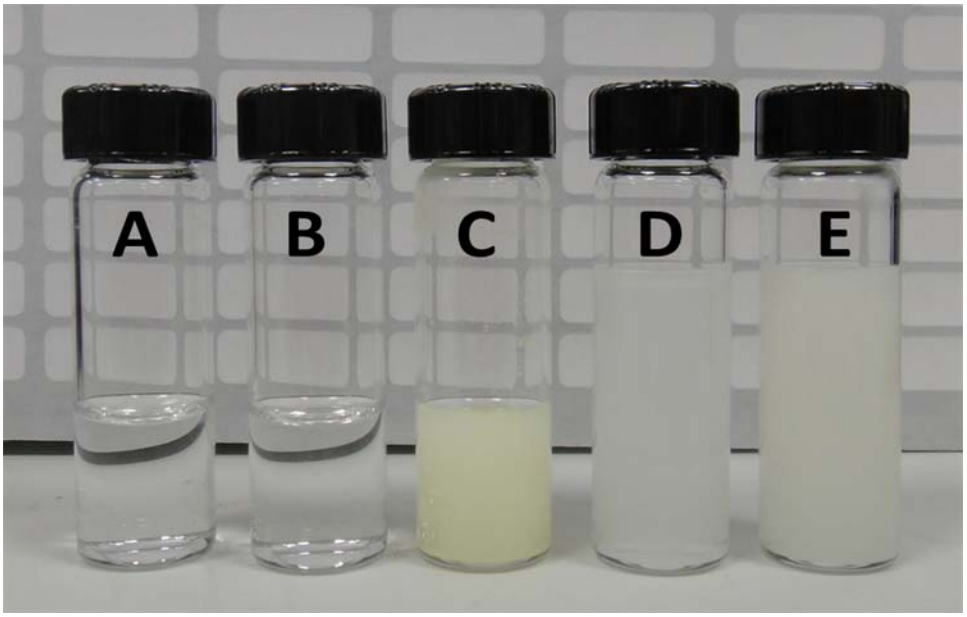

Fig. S4 Photo images of different mixtures to verify the formation of $S_2O_3^{2-}$ in the photoreaction. (A) 2 mL of 0.1 M Na_2SO_3 mixed with 1 mL of 37 wt% HCl, (B) 2 mL of 0.1 M Na_2SO_4 mixed with 1 mL of 37 wt% HCl, (C) 2 mL of 0.1 M $Na_2S_2O_3$ mixed with 1 mL of 37 wt% HCl, (D) 1 mL of 0.1 M Na_2SO_3 and 1 mL of 0.1 M Na_2SO_4 mixed with 2 mL 37 wt% HCl and (E) 2 mL of the reaction solution (after removal of S^{2-} and SO_3^{2-}) mixed with 2 mL 37 wt% HCl.

To confirm the formation of SO_4^{2-} ions by Equation (4),

$$SO_3^{2-} + 2OH^- + 2h^+ \rightarrow SO_4^{2-} + 2H^+ \qquad (4)$$

the above procedure was repeated to remove S^{2-} and SO_3^{2-} ions (by $Zn(NO_3)_2$), and $S_2O_3^{2-}$ (by HCl to form S). High speed centrifugation was applied after precipitation to remove solids formed. $BaCl_2$ aqueous solution was then added to the clear supernatant and the observation of white precipitate indicated the existence of SO_4^{2-} ions (Fig. S5B) and thus Equation (4) was proven to take place. A control experiment was also carried out using an aqueous solution of $Na_2S_2O_3$ after reacted with HCl followed by centrifugation. Upon adding $BaCl_2$ solution to the control sample, no precipitate can be observed (Fig. S5A), indicating that SO_2 formed according to the above Equation S1 did not form precipitate with $BaCl_2$.

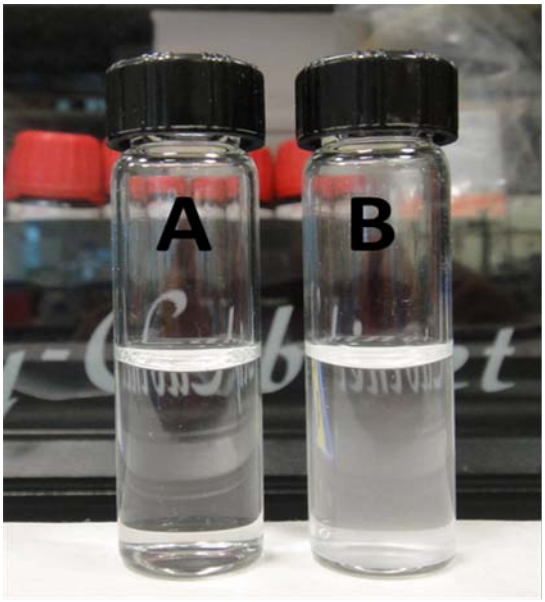

Fig. S5 Photo images of mixtures after adding $BaCl_2$ solution to verify the formation of SO_4^{2-} in photoreaction. (A) Control sample: aqueous solution of $Na_2S_2O_3$ after reacted with HCl followed by centrifugation; (B) photoreaction solution after removal of S^{2-}, SO_3^{2-}, and $S_2O_3^{2-}$.

The above results verified the proposed reaction mechanism based on Equations 2-6 in the main text.