Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Fabrication of a ternary $CdS/ZnIn_2S_4/TiO_2$ heterojunction for enhancing photoelectrochemical performance: Effect of cascading electron-hole transfer

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Table S1

Elemental composition of the $CdS/ZnIn_2S_4/TiO_2$ architecture film obtained from TEM-EDX data.

Elements	Atomic composition (%)
O K	24.06
S K	25.16
Ti K	23.82
Zn K	0.29
Cd L	23.45
In L	3.22

Reaction mechanism of CdS formation

The aqueous ammonia solution was reacted with $Cd(NO_3)_2$ to produce the white precipitate of $Cd(OH)_2$. The excess amount of aqueous ammonia solution dissolves the $Cd(OH)_2$ and forms the tetra amine cadmium $\left[Cd((NH_3)_4\right]^{+2}$. Addition of thiourea to this solution, the CN_2H_2 and SH^- products could be formed. Then, SH^- reacts with $\left[Cd((NH_3)_4\right]^{+2}$ and form the CdS. The reaction mechanism is given below (reaction 1 to 4).

$$Cd(NO_3)_2(aq) + 2NH_4OH(aq) \rightarrow Cd(OH)_2 \downarrow +2(NH_4)(NO_3) \quad (1)$$

$$Cd(OH)_2 + 4NH_4OH \leftrightarrow \left[Cd((NH_3)_4\right]^{+2} + 2OH^- + 4H_2O \quad (2)$$

$$CS(NH_2)_2 + OH^- \leftrightarrow CN_2H_2 + SH^- + H_2O \quad (3)$$

$$\left[Cd(NH_3)_2\right]^{+2} + SH^- \leftrightarrow CdS + NH_4^+ + 3NH_3 \quad (4)$$

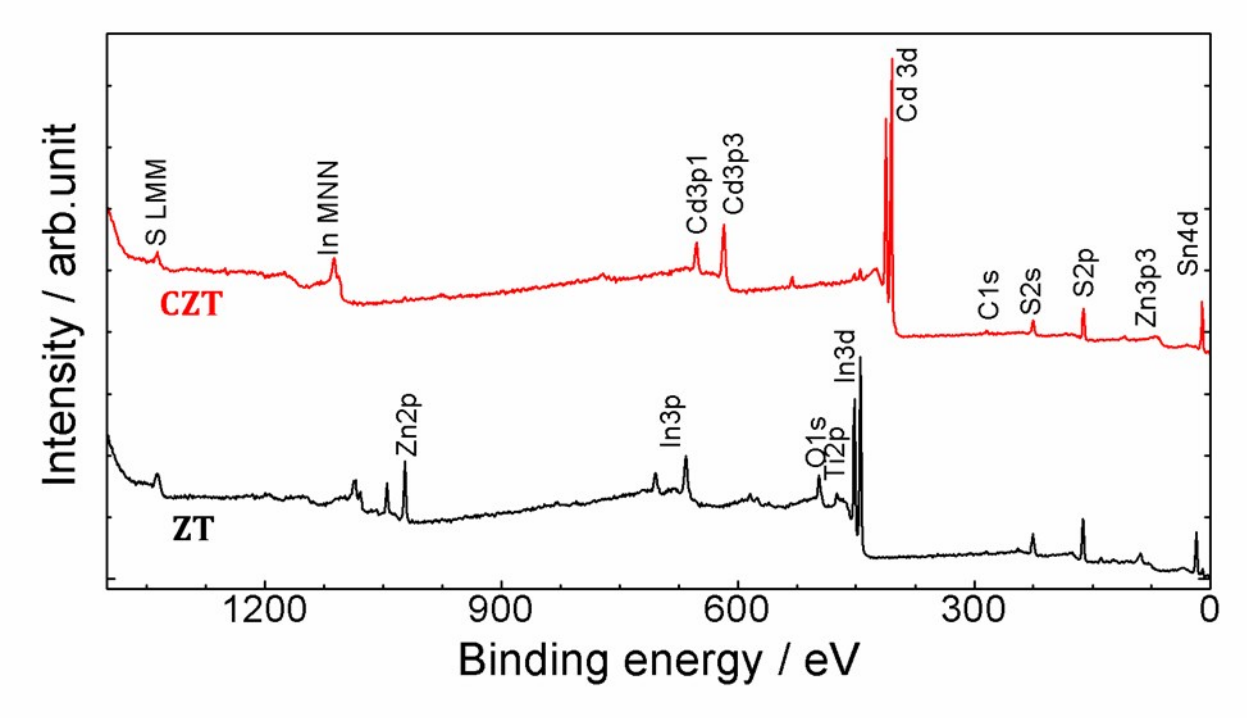

Figure S1 XPS survey spectra for $ZnIn_2S_4/TiO_2$/FTO and $CdS/ZnIn_2S_4/TiO_2$/FTO films

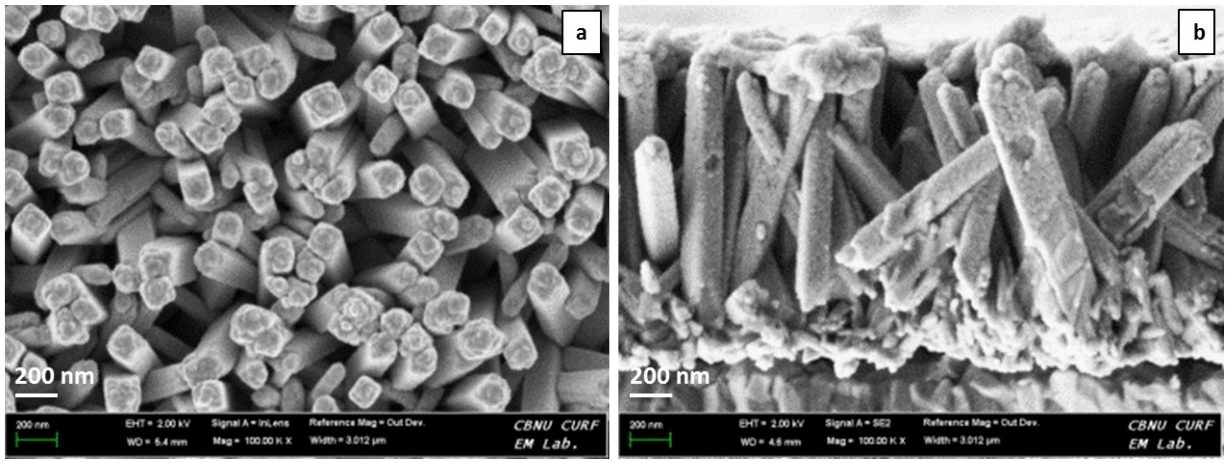

Figure S2 (a) SEM top view and (b) cross section view of CdS/TiO_2

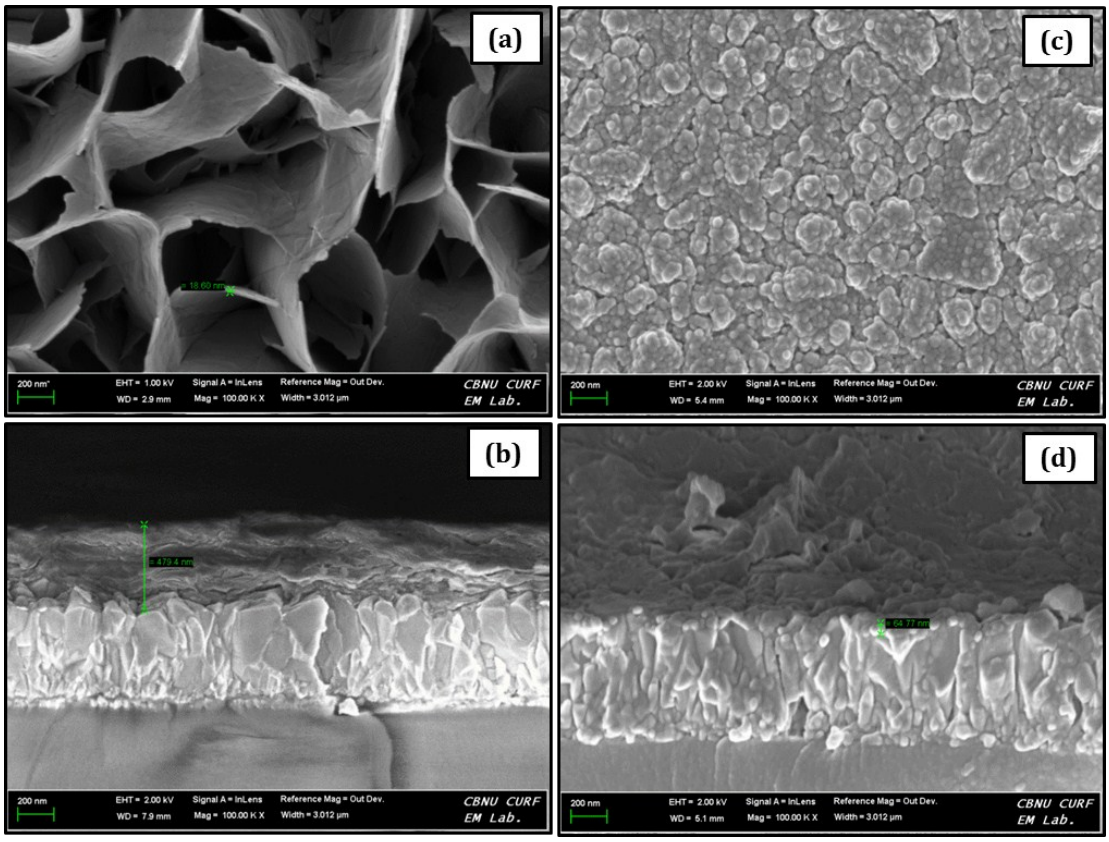

Figure S3 Surface and cross-sectional morphologies of (a-b) $ZnIn_2S_4$ and (c-d) CdS deposited on FTO substrate

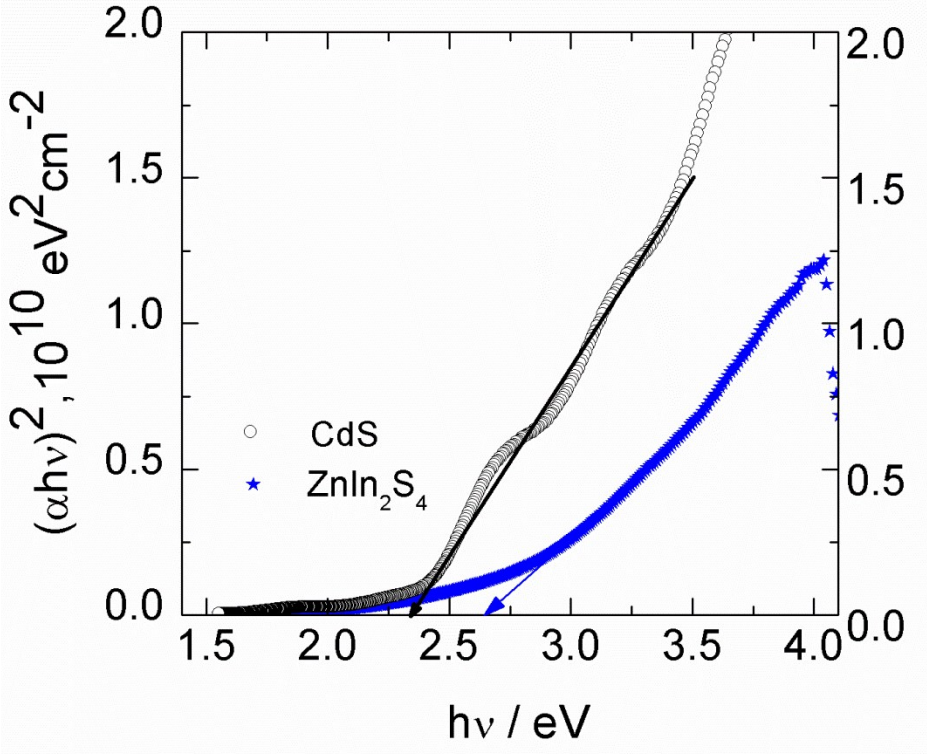

Figure S4 Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for CdS and $ZnIn_2S_4$ samples