Supporting Information

Enhanced photocatalytic hydrogen evolution efficiency using hollow microspheres $(CuIn)_xZn_{2(1-x)}S_2$ solid solutions

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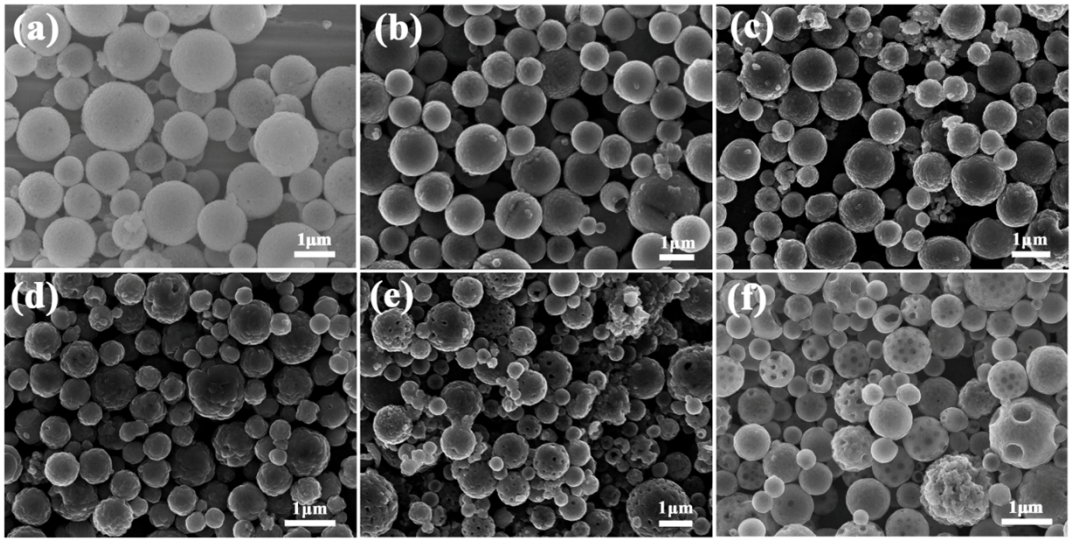

Figure S1. SEM images of $(CuIn)_xZn_{2(1-x)}S_2$ solid solutions; The values of *x* were (a) 0, (b) 0.09, (c) 0.2, (d) 0.4, (e) 0.6, and (f) 1. The samples were synthesized at 700 °C.

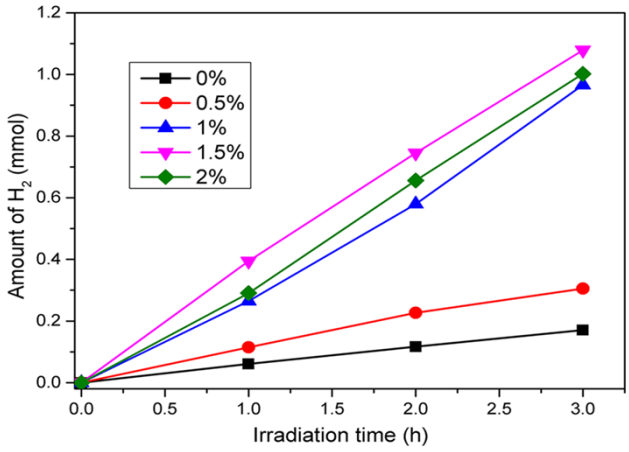

Figure S2. The rate of H_2 evolution upon the amount of Ru cocatalyst loaded on the $(CuIn)_{0.2}Zn_{1.6}S_2$ hollow spheres. Reaction condition: 50 mg $(CuIn)_{0.2}Zn_{1.6}S_2$ catalyst; 100 ml aqueous solution containing 0.35 M Na_2S and 0.25 M K_2SO_3; light source: 300 W Xe lamp ($\lambda \geq 420$ nm).

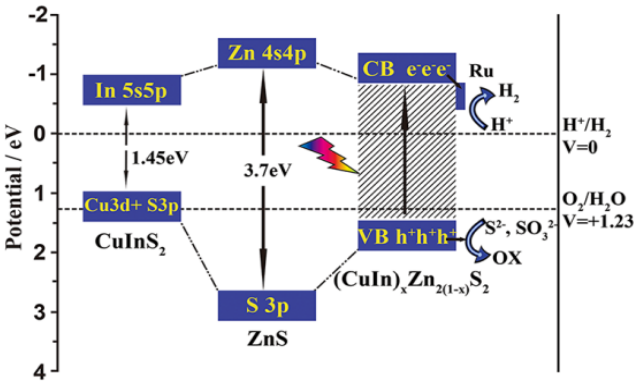

Figure S3. Band structure and charge transfer and separation process of $(CuIn)_xZn_{2(1-x)}S_2$ solid solutions.

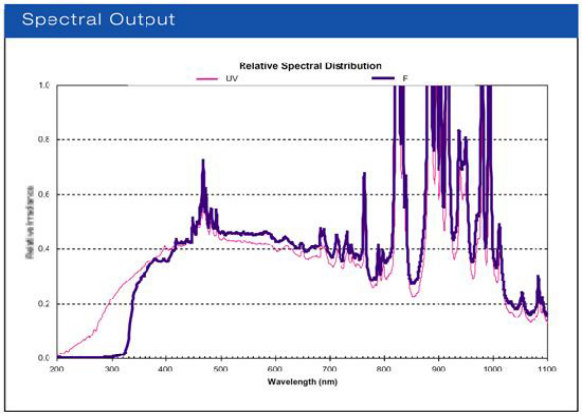

Figure S4. The emission spectrum (dark blue one) of the Xe lamp employed in the hydrogen evolution measurement.

Photocatalyst	Co-catalyst	Light source	Reactant Solution	QY	H_2 evolution	
					μmol h^{-1}	μmol h^{-1} g^{-1}
$(AgIn)_{0.22}Zn_{1.56}S_2$ (0.3 g) [4c]	Pt(3 wt%)	300 W Xe lamp(λ ≥ 420 nm)	K_2SO_3 (0.25 M)-Na_2S (0.35 M) aqueous solution.	20 %	944	3147
$AgInZn_7S_9$ (0.3 g) [4d]	Pt(3 wt%)	300 W Xe lamp(λ ≥ 420 nm)	K_2SO_3 (0.25 M)-Na_2S (0.35M) aqueous solution.	15 %	940	3133
$GuGa_2In_3S_8$ (0.3 g) [4e]	Rh(1.5 wt%)	300 W Xe lamp(λ ≥ 420 nm)	K_2SO_3 (0.5 M)-Na_2S (0.2M) aqueous solution.	15 %	3200	10667
$(CuIn)_{0.09}Zn_{1.82}S_2$ (0.3 g) [4b]	Ru(0.5 wt%)	300 W Xe lamp(λ ≥ 420 nm)	K_2SO_3 (0.25 M)-Na_2S (0.35 M) aqueous solution.	12.5 %	1227	4090
$(CuIn)_{0.2}Zn_{1.6}S_2$ (0.05 g) (This work)	Ru(1.5 wt%)	300 W Xe lamp(λ ≥ 420 nm)	K_2SO_3 (0.25 M)-Na_2S (0.35M) aqueous solution.	13.6 %	360	7200

Table S1. The comparison of the performance of the present photocatalyst $(CuIn)_{0.2}Zn_{1.6}S_2$ hollow structures with other materials.