Electronic Supplementary Material (ESI) for Catalysis Science & Technology

Electronic Supplementary Information

Band Engineering of Cu^{2+} Doped $In_{2x}Zn_{3(1-x)}S_3$ Solid Solution with High Photocatalytic Activity for H_2 Production under Visible Light

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Scanning electron microscope (SEM) images and Brunauer-Emmett-Teller (BET) measurements

The morphologies of $In_{2x}Zn_{3(1-x)}S_3$ and Cu(y)-$In_{1.4}Zn_{0.9}S_3$ solid solution samples are investigated by SEM images and Brunauer-Emmett-Teller (BET) measurement. Their morphologies of all the samples except ZnS show plate-like hierarchical structures with over 1μm in size (Fig. S1d-h, Fig. S2). BET measurements further prove the plate-like hierarchical structures of the samples. The samples exhibit a typical type IV isotherm with a distinguishable H3-type hysteresis loop (Fig. S3), indicating that the samples are comprised of loose aggregates of plate-like particles. [1, 2]

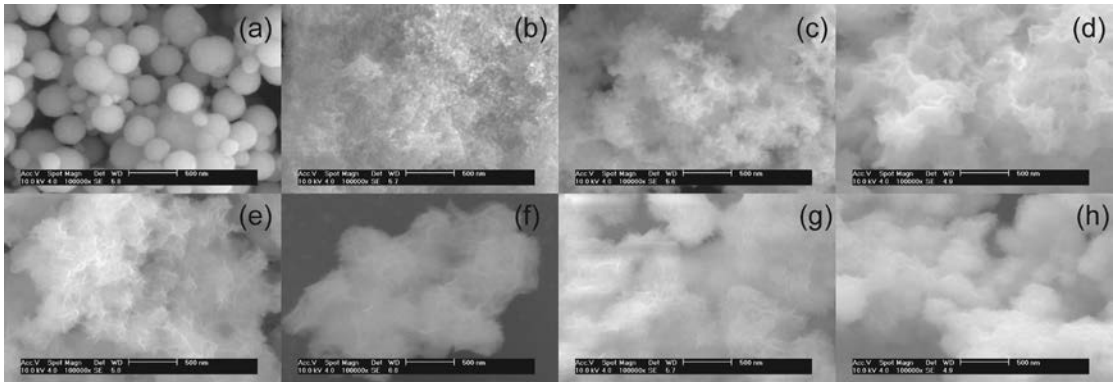

Fig. S1 SEM images of as-prepared $In_{2x}Zn_{3(1-x)}S_3$ solid solution samples. The x values of samples are (a) 0; (b) 0.25; (c) 0.55; (d) 0.65; (e) 0.7; (f) 0.75; (g) 0.85; (h) 1.The scale bar is 500nm.

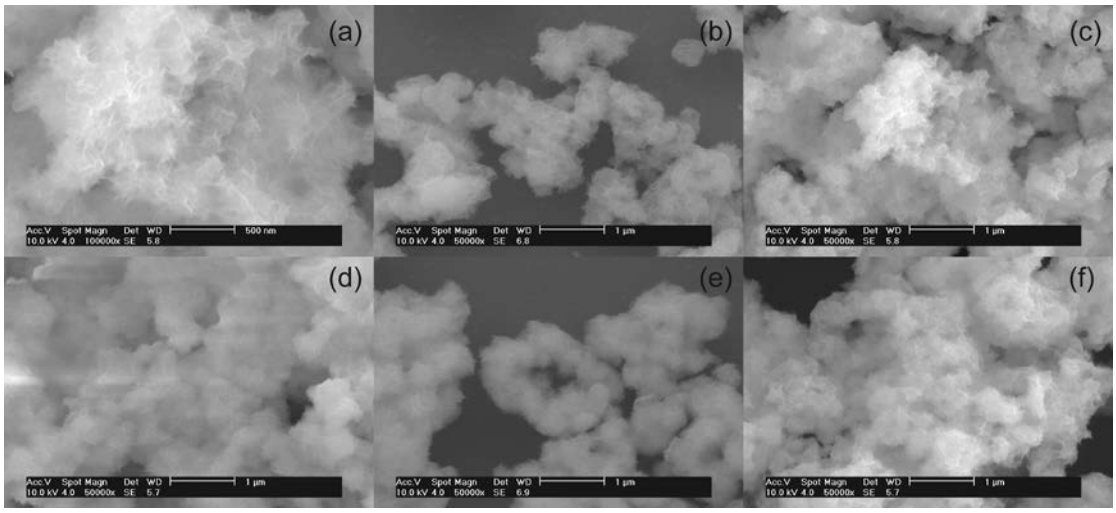

Fig. S2 SEM images of as-prepared Cu(y)-$In_{1.4}Zn_{0.9}S_3$ samples. The y values of samples are (a) 0; (b) 0.67%; (c) 1%; (d) 2%; (e) 2.5%; (f) 4%. The scal bar is 500nm for (a) and 1μm for rest of the images.

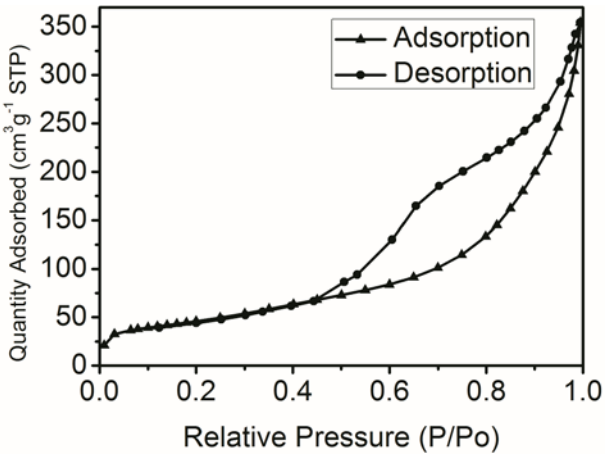

Fig. S3 Nitrogen adsorption/desorption isotherm of $In_{1.3}Zn_{1.05}S_3$ solid solution.

Besides, the X-ray energy dispersive spectroscopy (XEDS) maps of indium, zinc and copper for Cu (4%)/$In_{1.4}Zn_{0.9}S_3$ sample were also investigated, as shown in Fig. S4. The maps reveal that the distribution of all the cations is homogeneous, which further proves the formation of the solid solution.

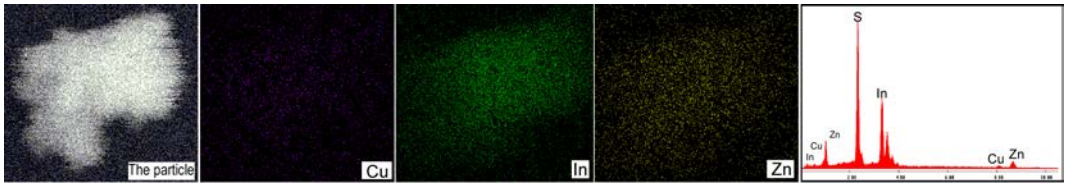

Fig. S4 XEDS maps for Cu (4%)/$In_{1.4}Zn_{0.9}S_3$ sample (Magenta for copper, green for indium and yellow for zinc).

X-ray photoelectron spectroscopy (XPS) measurement

The XPS data of In3d, Zn2p and S2p of Cu(4%)/$In_{1.4}Zn_{0.9}S_3$ sample before and after the photocatalytic H_2 evolution reaction for 15 hours are shown in Fig. S5. The binding energies of $In3d_{5/2}$, $In3d_{3/2}$, $Zn2p_{3/2}$, $Zn2p_{1/2}$, and S2p are 445.3 eV, 452.8 eV, 1021.8 eV, 1044.8 eV and 162.2 eV, respectively. All the results are consistent with that reported in the literatures. [3-6] Besides, the binding energies of all the elements after photocatalytic reaction are almost unchanged with that before the photocatalytic reaction, indicating that the doped solid solutions are quite stable in the presence of the sacrificial reagents and under visible light irradiation.

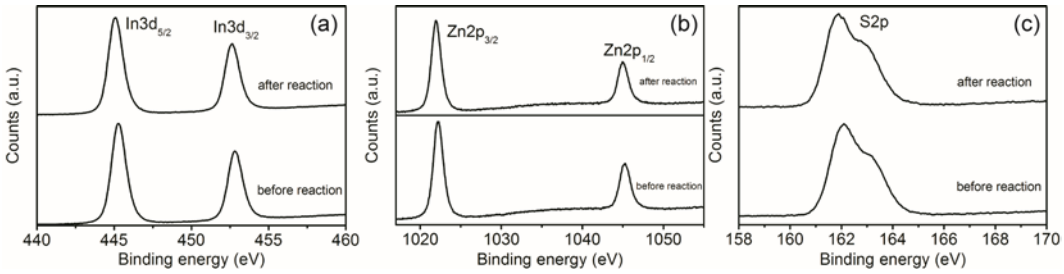

Fig. S5 XPS data collected from the surface of Cu(4%)/$In_{1.4}Zn_{0.9}S_3$ sample before and after the photocatalytic H_2 evolution reaction for 15 hours: (a) partial spectrum of In2p core-level; (b) partial spectrum of Zn2p core-level; (c) partial spectrum of S2p core-level.

References

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