Electronic Supplementary Information

Hydrothermal Synthesis of Zinc Indium Sulfide Microspheres with Ag^+ doping for Enhanced H_2 Production by Photocatalytic Water Splitting under Visible Light

Fan Li, [a] Jianheng Luo, [a] Guoping Chen, [a] Yuzun Fan, [b] Qingli Huang, [a] Yanhong Luo, [a] Dongmei Li *[a] and Qingbo Meng *[a]

[a] *Key Laboratory for Renewable Energy, Chinese Academy of Sciences; Beijing Key Laboratory for New Energy Materials and Devices; Beijing National Laboratory for Condense Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing, China. Fax: +86-10-82649242; Tel: +86-10-82649242; E-mail: qbmeng@iphy.ac.cn, dmli@iphy.ac.cn*

[b] *Key Laboratory of Bio-Inspired Smart Interfacial Science and Technology of Ministry of Education, Beijing Key Laboratory of Bio-inspired Energy Materials and Devices, School of Chemistry and Environment, Beihang University, Beijing 100191, PR China.*

XRD patterns of $ZnIn_{1.5}S_{3.25}$ samples prepared by adjusting pH values (adding different amounts of hydrochloric acid) at 160 ℃ for 6 h

The influence of different amounts of hydrochloric acid in the preparation process on the composition of $ZnIn_{1.5}S_{3.25}$ is also investigated, as demonstrated in Fig. S1. It can be seen that when no extra hydrochloric acid was added, the diffraction patterns can be indexed to a cubic phase (JCPDS: 48-1778). When 0.25 and 0.5 mL of hydrochloric acid were added, respectively, the hexagonal phase (JCPDS: 65-2023) appears with a relatively low crystallinity, and the solid solutions are indeed the mixture of the two structures. Further increasing hydrochloric acid to 1 mL, the pure hexagonal phase is obtained (plot D in Fig. S1). However, when 1.5 mL or more were added, the unexpected crystal phase of sulfur was observed (marked diffraction peaks in Fig. S1). Obviously, the hydrochloric acid significantly influences the crystal structures of $ZnIn_xS_{1+1.5x}$ solid solution, which are in agreement with Li and Chen' work.[1]

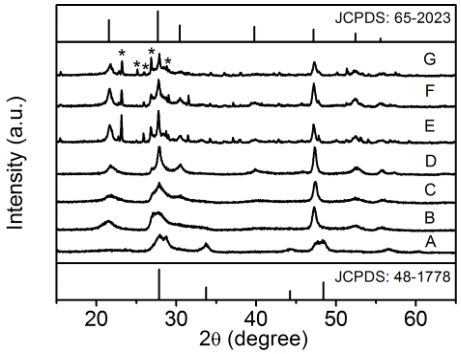

Fig. S1 XRD patterns of $ZnIn_{1.5}S_{3.25}$ solid solution samples prepared by adding different amount of hydrochloric acid at 160 ℃ for 6 h. The amounts of hydrochloric acid are (A) 0 mL; (B) 0.25 mL; (C) 0.5 mL; (D) 1.0 mL; (E) 1.5 mL; (F) 2.0 mL; (G) 2.5 mL. The plot D is the same as the plot D in Fig. 1.

Scanning electron microscope (SEM) images for the $ZnIn_{1.5}S_{3.25}$ sample prepared by different hydrothermal temperature and hydrothermal time with 1 mL hydrochloric acid

The morphologies of the $ZnIn_{1.5}S_{3.25}$ samples prepared by different hydrothermal temperature and hydrothermal time at 160 ℃ with 1 mL hydrochloric acid added are investigated by SEM images. Fig. S2 shows the change of morphologies by varying the hydrothermal temperature. It is found that, the morphologies of the samples prepared with different hydrothermal temperature are similar except the broken of the plate-like hierarchical microsphere for the sample hydrothermally at 200 ℃ (shown in Fig. S2e). A hollow structure is thus suggested from the broken microsphere. Furthermore, the morphologies of the $ZnIn_{1.5}S_{3.25}$ samples prepared for 9 h shows a more disordered structure than the other two samples, as shown in Fig. S3, which may be the reason of the lower photocatalytic H_2 evolution rate in comparison to the samples hydrothermally for 3 h and 6 h.

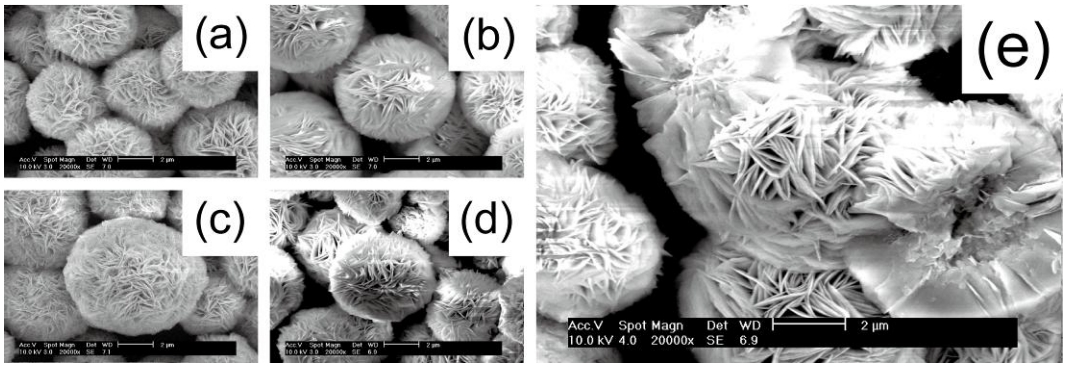

Fig. S2 SEM images of $ZnIn_{1.5}S_{3.25}$ samples prepared at different hydrothermal temperature for 6 h by adding 1 mL hydrochloric acid. The temperatures are (a) 120 ℃; (b) 140 ℃; (c) 160 ℃; (d) 180 ℃; (e) 200 ℃. The scale bar is 2 μm, and the Fig. S2c is the same figure as the Fig. 3d.

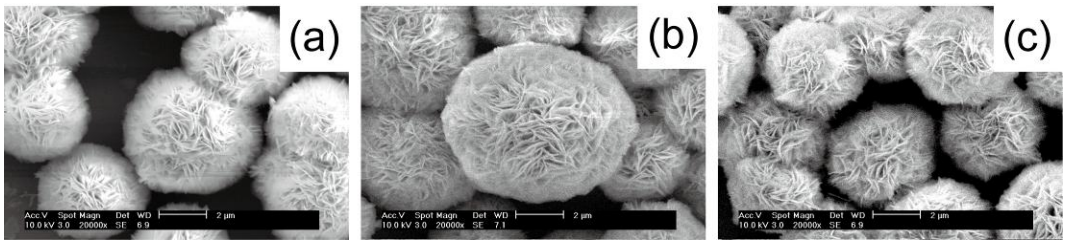

Fig. S3 SEM images of as-prepared $Zn_1In_{1.5}S_{3.25}$ sample prepared by different hydrothermal time at 160 ℃ with 1 mL hydrochloric acid added. The hydrothermal times are (a) 3 h; (b) 6 h; (c) 9 h. The scale bar is 2 μm, and the Fig. S3b is the same figure as the Fig. 3d.

Besides, the X-ray energy dispersive spectroscopy (XEDS) maps of silver, indium and zinc for Ag(1.5%)-$ZnIn_{1.5}S_{3.2575}$ sample were also investigated, as shown in Fig. S4. The maps reveal that the distribution of all the cations are homogeneous, which further proves the formation of the doped solid solution.

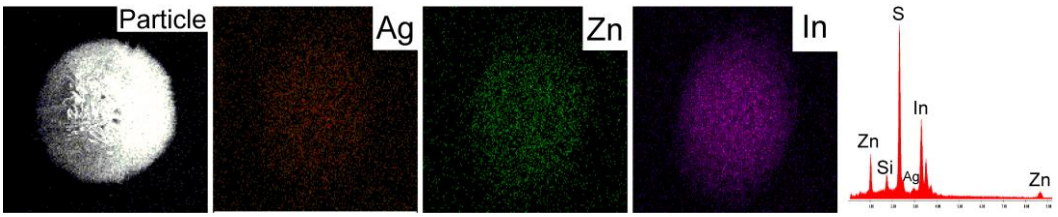

Fig. S4 XEDS maps for Ag(1.5%)-$ZnIn_{1.5}S_{3.2575}$ sample (red for silver, green for zinc and magenta for indium).

X-ray photoelectron spectroscopy (XPS) measurement

The XPS data of In3d and Zn2p of Ag(1.5%)-$ZnIn_{1.5}S_{3.2575}$ sample before and after the photocatalytic H_2 evolution reaction for 15 hours are shown in Fig. S5. The binding energies of $In3d_{5/2}$, $In3d_{3/2}$, $Zn2p_{3/2}$ and $Zn2p_{1/2}$ are 445.3 eV, 452.8 eV, 1021.8 eV and 1044.8 eV, respectively. All the results are consistent with that reported in the literatures, which illustrate that their valence states are In^{3+} and Zn^{2+}, respectively.[2-5] Besides, the binding energies of Zn and In elements after photocatalytic reaction are almost unchanged, indicating that they are quite stable in the presence of the sacrificial reagents and under visible light irradiation.

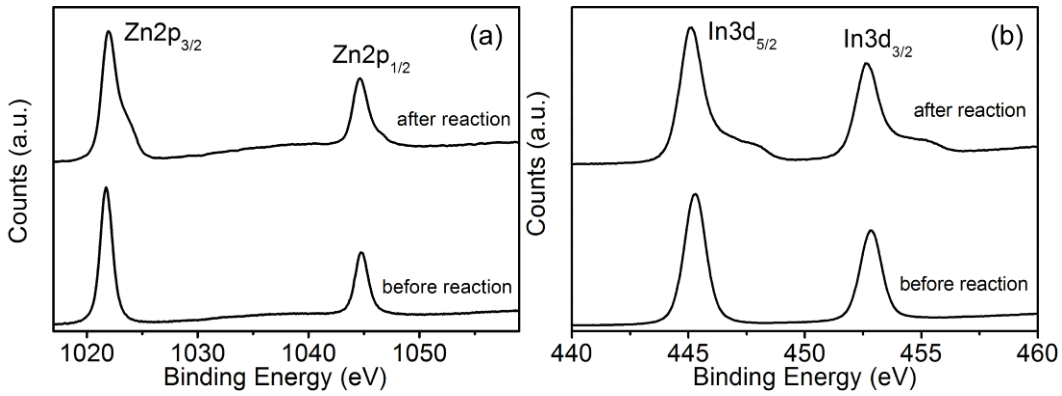

Fig. S5 XPS data collected before and after the photocatalytic H_2 evolution reaction for 15 hours from the surface of Ag(1.5%)-$ZnIn_{1.5}S_{3.2575}$ sample: (a) partial spectrum of Zn2p core-level; (b) partial spectrum of In3d core-level.

The different effects of Ru, Ag and Ru co-catalyst on photocatalytic activity

As we all know, Ag and Pt can be also used as co-catalyst. Here, we compared the photocatalytic activities of the $ZnIn_{1.5}S_{3.25}$ samples with co-catalysts of Ru, Ag and Pt. The loading procedures of Ag and Pt are the same as that of Ru. The precusor of Ag and Pt used are $AgNO_3$ and H_2PtCl_6 $6H_2O$, respectively, and the loading amount of Ag and Pt are 1.5 wt% (identical with optimal doping amount) and 2 wt% (optimal loading amount). As shown in Table S1, best performed co-catalyst for $ZnIn_{1.5}S_{3.25}$ is Ru, not Pt. However, Ag loading on the surface of the solid solution is disadvantaged to the photocatalyitc activity. Besides, H_2 evolution rate of non-loaded Ag(1.5%)-$ZnIn_{1.5}S_{3.2575}$ is 0.95 mmol h^{-1} g^{-1}, which is higher than that of $ZnIn_{1.5}S_{3.25}$ loaded with Ag. It is thus revealed that Ag performed better as a dopant in our work.

Table S1 The different effect of Ru, Ag and Ru co-catalyst on photocatalytic activities

Sample	Co-catalyst	H_2 evolution rate[c]/mmol h^{-1} g^{-1}
$ZnIn_{1.5}S_{3.25}$	Non-loaded	0.65
$ZnIn_{1.5}S_{3.25}$	Ag	0.48
$ZnIn_{1.5}S_{3.25}$	Pt	1.51
$ZnIn_{1.5}S_{3.25}$	Ru	1.85
Ag(1.5%)-$ZnIn_{1.5}S_{3.2575}$	Non-loaded	0.95

References

1. Y. Chen, S. Hu, W. Liu, X. Chen, L. Wu, X. Wang, P. Liu and Z. Li, *Dalton Trans.*, 2011, **40**, 2607.
2. G. E. McGuire, G. K. Schweitzer and T. A. Carlson, *Inorg. Chem.*, 1973, **12**, 2450.
3. C. Malitesta, D. Centonze, L. Sabbatini, P. G. Zambonin, L. P. Bicelli and S. Maffi, *J. Mater. Chem.*, 1991, **1**, 259.
4. L. S. Dake, D. R. Baer and J. M. Zachara, *Surf. Interface. Anal.*, 1989, **14**, 71.
5. E. Agostinelli, C. Battistoni, D. Fiorani, G. Mattogno and M. Nogues, *J. Phys. Chem. Solids*, 1989, **50**, 269.