Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Hierarchically $ZnIn_2S_4$ nanosheet-constructed microwire arrays: template-free synthesis and excellent photocatalytic performances

Xinglong Tu,[a] Jing Lu,[b,*] Ming Li,[c] Yanjie Su,[c] Guilin Yin[a,b] and Dannong He[a,b,*]

a. School of Material Science and Engineering, Shanghai Jiao Tong University, No. 800 Dongchuan Road, Shanghai 200240, P.R. China

b. National Engineering Research Centre for Nanotechnology, No. 28 East Jiangchuan Road, Shanghai 200241, P.R. China

c. Key Laboratory for Thin Film and Microfabrication of the Ministry of Education, Department of Micro/Nano Electronics, School of Electronics, Information and Electrical Engineering, Shanghai Jiao Tong University, Shanghai 200240, P.R. China

***Corresponding authors:**

Email: jinglu2004@163.com and hdn_nercn@163.com

Part 1: Growth process of indium nanowires shell in detail

Three different complexes, tetrahedral $[In(TAA)_4]^{3+}$, octahedral $[In(TAA)_6]^{3+}$and tetrahedral $[Zn(TAA)_4]^{2+}$, are formed through chemical reaction between TAA and Zn^{2+} (or In^{3+}) in solution. Then $In(S)_4$, $In(S)_6$ and $Zn(S)_4$ species are produced via a hydrolysis reaction due to the existence of trace water contained in ethylene glycol and the crystal water (originating from $InCl_3 \cdot 4H_2O$).[1] Then three metal sulfur species, which formed on the surface of the nanowire core, combine together in situ to generate compounds (Zn_xIn_ySz) as the shell of indium nanowires. The process can be described as the following equations:

$$In^{3+} + TAA \rightarrow [In(TAA)_4]^{3+} + [In(TAA)_6]^{3+} \quad (1)$$

$$Zn^{2+} + TAA \rightarrow [Zn(TAA)_4]^{2+} \quad (2)$$

$$[In(TAA)_4]^{3+} + [In(TAA)_6]^{3+} + H_2O \rightarrow In(S)_4 + In(S)_6 \quad (3)$$

$$[Zn(TAA)_4]_2+ + H_2O \rightarrow Zn(S)_4 \quad (4)$$

$$In(S)_4 + In(S)_6 + Zn(S)_4 \rightarrow ZnxInySz \quad (5)$$

Reference

1. M. Tang, Q. Tian, X. Hu, Y. Peng, Y. Xue, Z. Chen, J. Yang, X. Xu and J. Hu, Crystengcomm, 2012, 14, 1825-1832.

Part 2: Photostability evaluation details of the optimal $ZnIn_2S_4$ sample.

The photostability of the optimized $ZnIn_2S_4$ samples (obtained in 2 h reaction) were evaluated as the following process. The photocatalytic degradation rate of MO under visible light irradiation was measured for 5recycles. After each run, the sample would be washed by deionized water and then dried at 50℃ for 30 minutes before repeating the measurement.

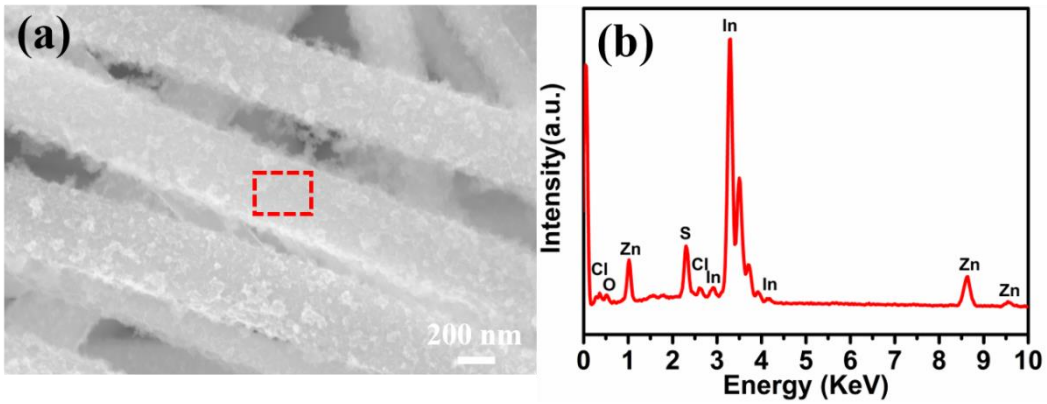

Fig. S1 (a) Top view SEM image of indium nanowires in 30min reaction. (b) The shell EDS of indium nanowires acquired from the rectangular region in (a).

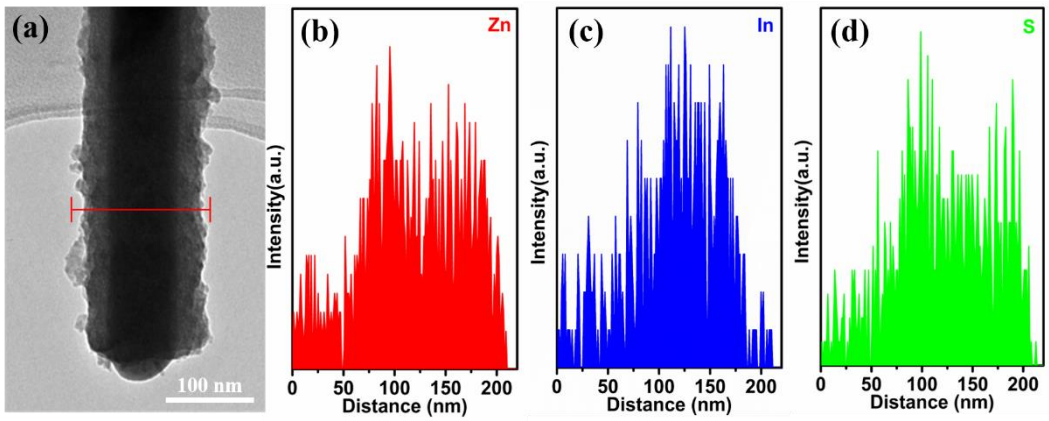

Fig. S2 (a) TEM image of the indium nanowires in 30min reaction. (b) Line scanning mappings corresponding to (a).

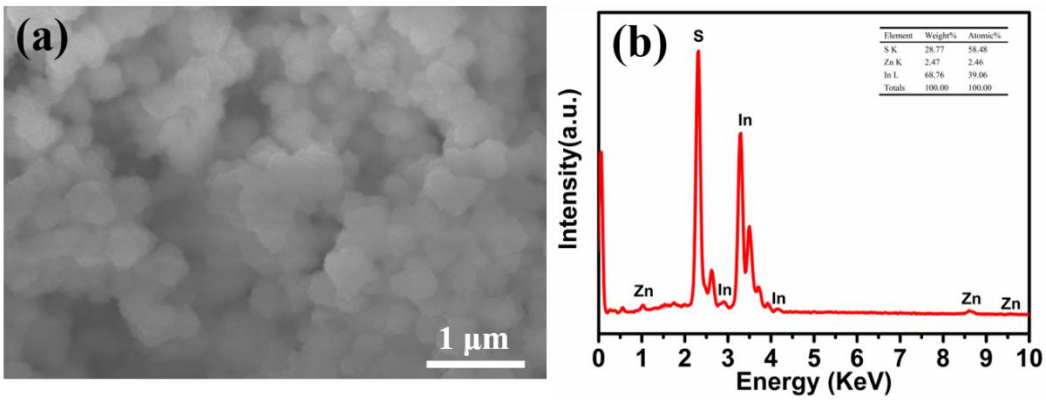

Fig. S3 (a) SEM image of powder sample from solution obtained in 30min reaction. (b) The corresponding EDS spectrum of the powder sample.

Fig. S4 Top view SEM image of the broken $ZnIn_2S_4$ sample in 2 h reaction.

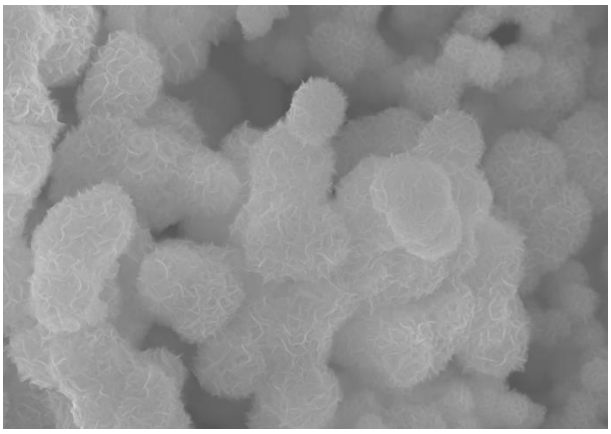

Fig. S5 SEM image of powder sample from solution obtained in 1.5 h reaction

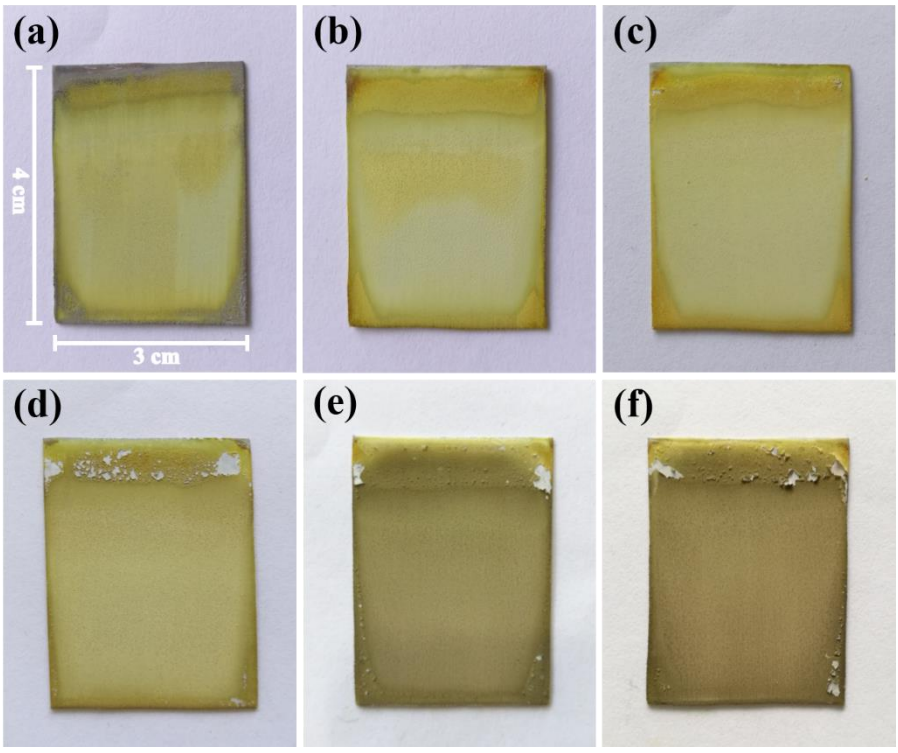

Fig. S6 Optical images of samples obtained in different reaction time.

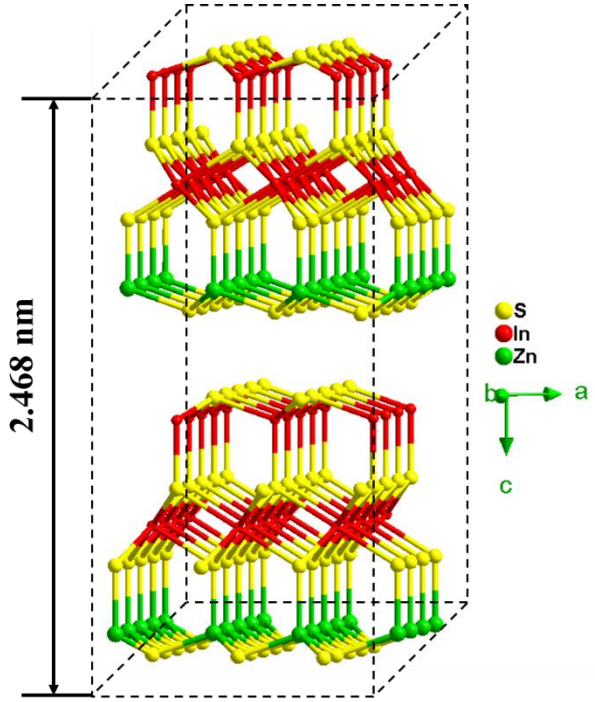

Fig. S7 The structural model of layered hexagonal $ZnIn_2S_4$.

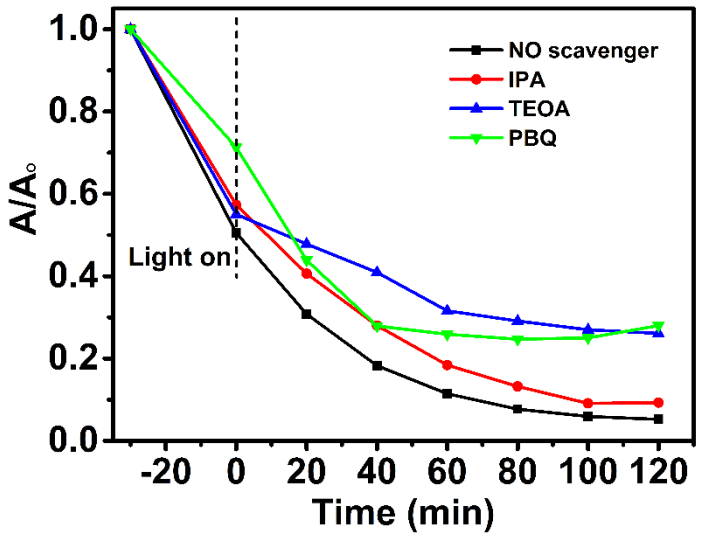

Fig. S8 Trapping experiment of active species during the photocatalytic degradation of MB over the optimal $ZnIn_2S_4$.

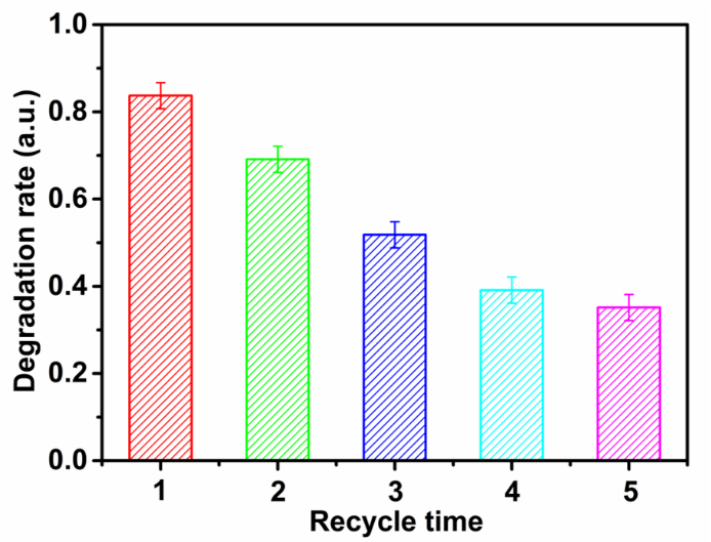

Fig. S9 The photostability evaluation of the optimal $ZnIn_2S_4$ sample.