

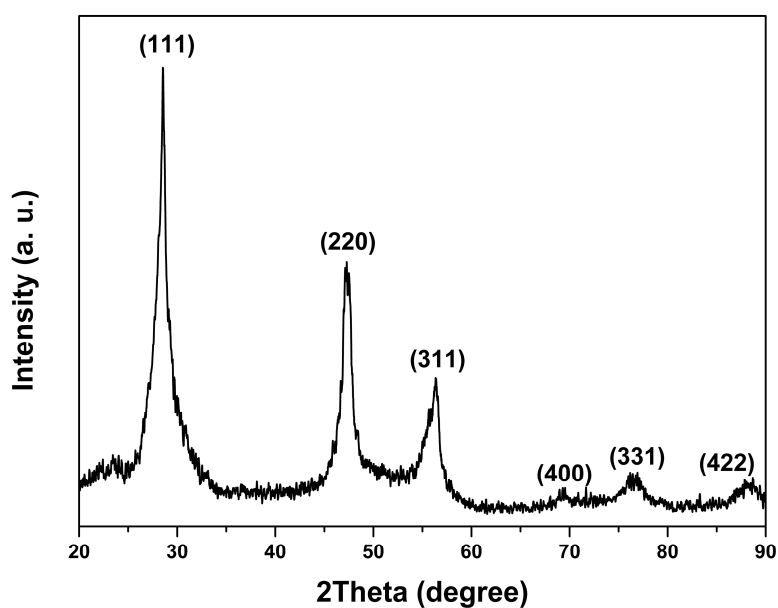
## Supporting Information

# Hierarchical architectures of porous ZnS-based microspheres by assembly of heterostructure nanoflakes: lateral oriented attachment mechanism and enhanced photocatalytic activity

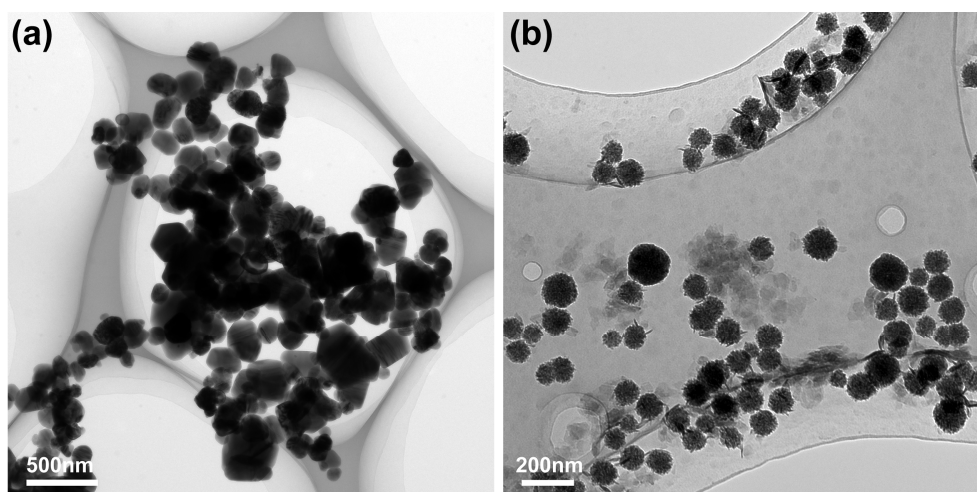
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**Figure S1.** XRD pattern of sample D synthesized at 240 °C for 24h and heat-treated again in deionized water for another 240 h at 240 °C.



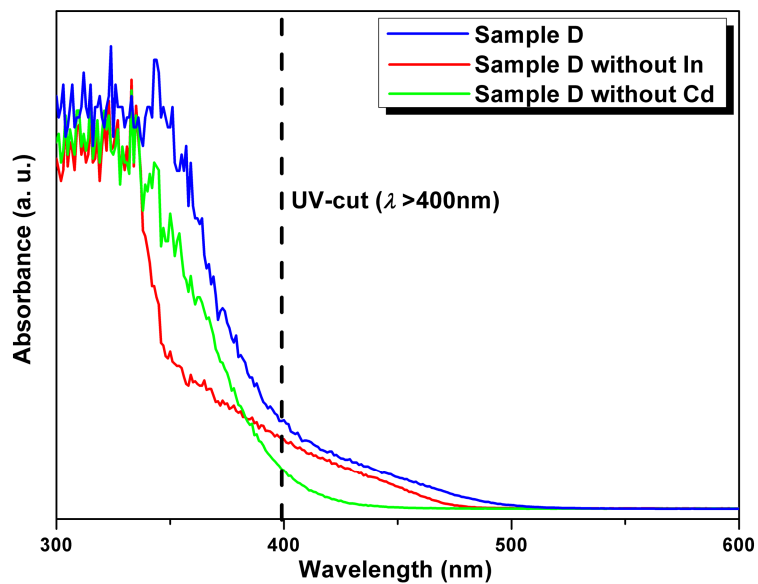
**Figure S2.** TEM images of (a) single Cd-doped ZnS and (b) single In-doped ZnS. Amounts of single-component dopant are equal to sample D.



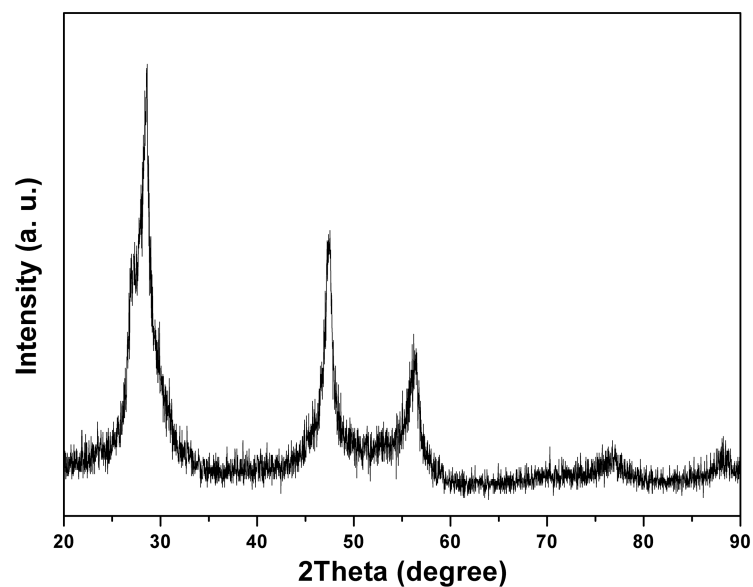
Differences between sphalerite structure and wurtzite structure in ZnS are mainly due to the form (cubic or hexagonal) and the direction ( $\langle 111 \rangle$  directions or  $[0001]$  direction) of close packing. There are tetrahedral and octahedral sites in cubic and hexagonal close packing. We calculated the radiuses of the inscribed spheres ( $R_{\text{tetrahedron}}=0.78\text{\AA}$ ;  $R_{\text{octahedral}}=1.56\text{\AA}$ ) in tetrahedral and octahedral sites of cubic sphalerite structure. For single Cd-doped ZnS, if  $\text{Cd}^{2+}$  ions occupy octahedral sites, octahedral sites could accommodate  $\text{Cd}^{2+}$  ions ( $\text{Radius}(\text{Cd}^{2+})=0.97\text{\AA}$ ) without lattice distortion, which means the position of (111) diffraction peak would not change. While  $\text{Cd}^{2+}$  ions occupy tetrahedral sites, tetrahedral sites could not accommodate  $\text{Cd}^{2+}$  ions, spacing of S atoms layers would be enlarged. According to the equation  $\lambda=2d\sin\theta$ , with the increment of Cd-doped, the position of (111) diffraction peak would move towards the low angle direction, which has been proved by Guo and coworkers<sup>1</sup>. As a result, the solution coordination model is still feasible for Cd-doped ZnS.

$$R_{\text{tetrahedron}}=\frac{\sqrt{6}}{12}a; R_{\text{octahedral}}=\frac{\sqrt{6}}{6}a; a=\text{Bond}_{\text{S-S}}=0.382\text{nm (cubic)}$$

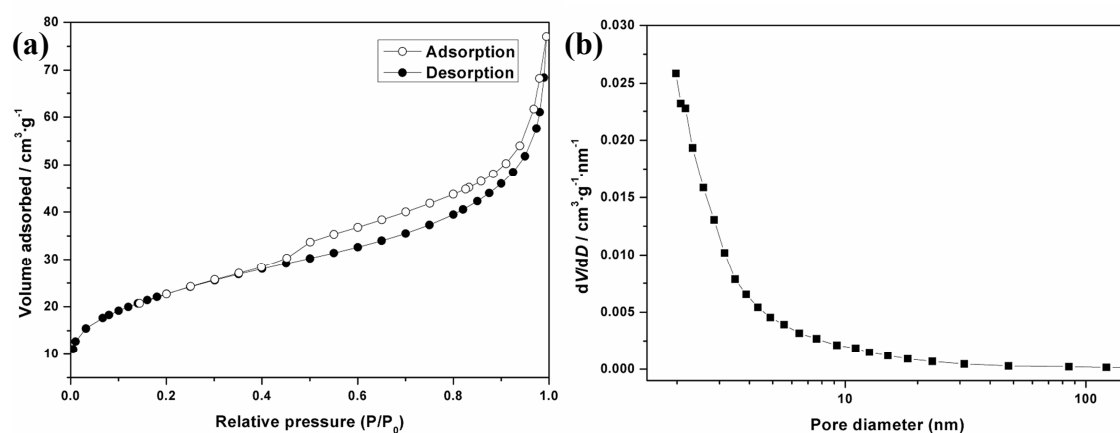
**Figure S3.** UV-vis absorption spectra for sample D and two single doped products. Amounts of single-component dopant are equal to sample D.



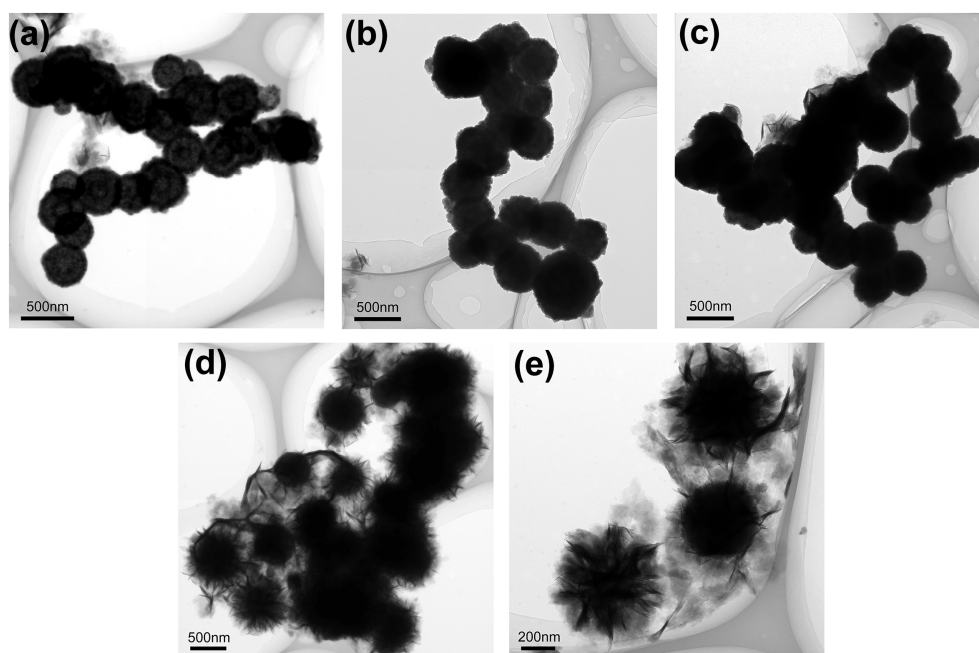
**Figure S5.** XRD pattern of sample D collected after a 12h reaction for hydrogen evolution.



**Figure S5.** Nitrogen adsorption/desorption isotherms, and (b) pore size distribution of sample D collected after a 12 h H<sub>2</sub> evolution reaction.



**Figure S6.** TEM images of (a) sample A to (e) sample E.



According to the TEM images, the morphology of as-prepared samples evolved regularly from spherical-like to flower-like with increments of the doped In and Cd amount. Sample A-C were spherical-like and they were all aggregations of nanoparticles. According to the previous literatures<sup>2</sup>, growth of nanoparticles in this system usually follows an Ostwald ripening, which means small particles grows through atom-by-atom addition to form a larger one and then aggregate to minimize

the surface energy. In our case, although the nanoparticles in initial stage were supposed to be hexagonal wurtzite ZnS nanoparticles, they would finally form a larger cubic sphalerite ZnS nanoparticles once the particle size beyond the critical size ( $\sim 20\text{nm}$ )<sup>3</sup>, with the continuous growth of nanoparticles via Ostwald ripening. As a result, almost no hexagonal wurtzite structures were found in XRD patterns of sample A-C. Simultaneously, with the continuous increments of doped In, Cd amounts, sample D was found to be the critical condition in which the flower-like morphology came out for the first time. While the amounts of doped In, Cd came to sample D, the dopants (especially the In component) were more enough to induce strong dipole field.

### References

- 1 C. Xing, Y. Zhang, W. Y, L. Guo, *Int. J. Hydrogen Energy*, 2006, **31**, 2018.
- 2 X. Yu, J. Yu, B. Cheng, B. Huang, *Chem. Eur. J.*, 2009, **15**, 6731.
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