Electronic Supplementary Information

A Facile Route to $(ZnS)_x(CuInS_2)_{1-x}$ Hierarchical Microspheres with Excellent Water-splitting Ability

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 \dagger Electronic Supplementary Information (ESI) available: Detail information of $(ZnS)_x(CuInS_2)_{1-x}$ samples; figure of TG profile, and SEM images, and EDX spectra. See DOI: 10.1039/b000000x/

| Nominated | Reaction | Zn% ^a | Cu% ^a | In% ^a | S% ^a | Bandgap | Hydrogen |
|------------------------|----------|------------------|------------------|------------------|------------------------|---------|---|
| ZnS-CuInS ₂ | time (h) | | | | | (eV) | evolving rate |
| molar ratio | | | | | | | (µmol h ⁻¹ g ⁻¹) |
| 2-1 | 6 | 23.22 | 10.79 | 11.23 | 54.66 | 2.35 | 29.78 |
| 4-1 | 6 | 33.55 | 8.68 | 7.88 | 49.90 | 2.58 | 19.46 |
| 8-1 | 12 | 35.13 | 4.87 | 4.87 | 55.14 | 2.62 | 52.14 |
| 12-1 | 12 | 38.20 | 3.47 | 3.54 | 54.79 | 2.78 | 90.72 |
| 50-1 | 14 | 49.81 | 1.27 | 1.07 | 48.15 | 3.32 | 37.16 |
| 90-1 | 16 | 47.31 | 0.74 | 0.56 | 51.40 | 3.47 | 15.02 |

Table S1 Detail information of $(ZnS)_x(CuInS_2)_{1-x}$ samples.

^a Calculated from EDX results.



Fig. S1 The calculated lattice parameters *c* of a series of $(\text{ZnS})_x(\text{CuInS}_2)_{1-x}$ samples as a function of the ZnS mole fraction. Note that the *c* was calculated by a function of $c = \sqrt{3}d_{111}$.



Fig. S2 Thermogravimetric (TG) profile of $(ZnS)_{8/9}(CuInS_2)_{1/9}$ sample. Experiment was performed on TGA/DSC of Mettler.



Fig. S3 XRD patterns (left) and SEM images (right) of $(ZnS)_{4/5}(CuInS_2)_{1/5}$ microspheres before (a) and after (b) calcination at 723 K under N₂ atmosphere.



Fig. S4 $(ZnS)_{4/5}(CuInS_2)_{1/5}$ hierarchical microspheres synthesized with ethanolamine (EA), 1-butylamine (1-BA), and diglycolamine (TGA) individually.



Fig. S5 EDX spectra of a series of $(ZnS)_x(CuInS_2)_{1-x}$ samples.