Electronic Supplementary Information (ESI)

Non-injection synthesis of L-shaped wurtzite Cu-Ga-Zn-S alloyed nanorods and the advantageous application in photocatalytic hydrogen evolution

Zheming Liu,[a] Aiwei Tang,[a,*] Jun Liu,[b,c] Dongxu Zhu,[a] Xifeng Shi,[d] Qinghua Kong,[a] Zhijie Wang,[b,c,*] Shengchun Qu,[b,c] Feng Teng,[a] and Zhanguo Wang[b,c]

[a] Key Laboratory of Luminescence and Optical Information, Ministry of Education, School of Science, Beijing JiaoTong University, Beijing 100044, China.

[b] Key Laboratory of Semiconductor Materials Science, Beijing Key Laboratory of Low Dimensional Semiconductor Materials and Devices, Institute of Semiconductors, Chinese Academy of Sciences, Beijing, 100083, China.

[c] College of Materials Science and Opto-Electronic Technology, University of Chinese Academy of Sciences, Beijing, 100049, China

[d] Engineering Research Center of Pesticide and Medicine Intermediate Clean Production, Ministry of Education, Chemical Engineering and Materials Science, College of Chemistry, Shandong Normal University, Jinan 250014, China

*Corresponding authors:

Aiwei Tang, E-mail: awtang@bjtu.edu.cn.

Zhijie Wang, E-mail: wangzj@semi.ac.cn.

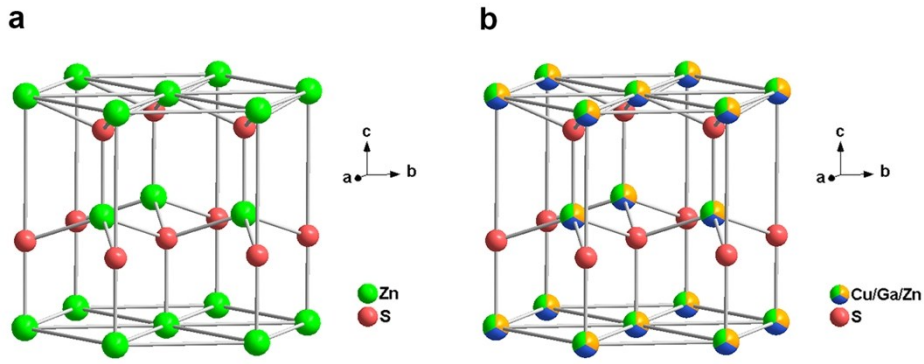

Figure S1. The modes of crystal structures of (a) wurtzite ZnS and (b) wurtzite Cu-Ga-Zn-S (CGZS), in which the yellow, blue, green and red spheres represent copper, gallium, zinc and sulfur elements, respectively.

The crystal structure of CGZS can be represented by the wurtzite structured ZnS, where Cu, Ga and Zn occupy the same Zn positions.

XRD patterns refinement results are list as follows:

Rwp= 8.31% Rp= 6.42%

Crystal data:

Compound	Cu-Ga-Zn-S
Crystal phase	Wurtzite
Space group	*P6₃mc* (No. 186)
Lattice parameter	a=b= 3.79 Å
	c= 6.23 Å

Atomic coordinates：	x/a	y/b	z/c
atomic position for S:	1/3	2/3	3/8
atomic position for Cu:	1/3	2/3	0
atomic position for Ga:	1/3	2/3	0
atomic position for Zn:	1/3	2/3	0

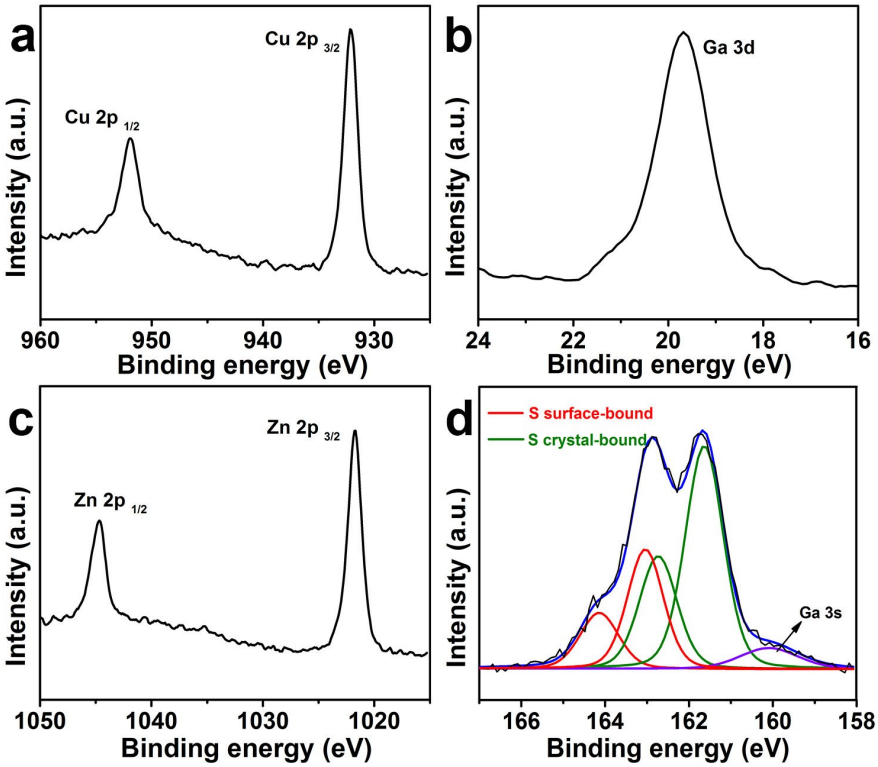

Figure S2. XPS spectra of L-shaped CGZS nanorods: (a) Cu 2p, (b) Ga 3d, (c) Zn 2p and (d) S 2p.

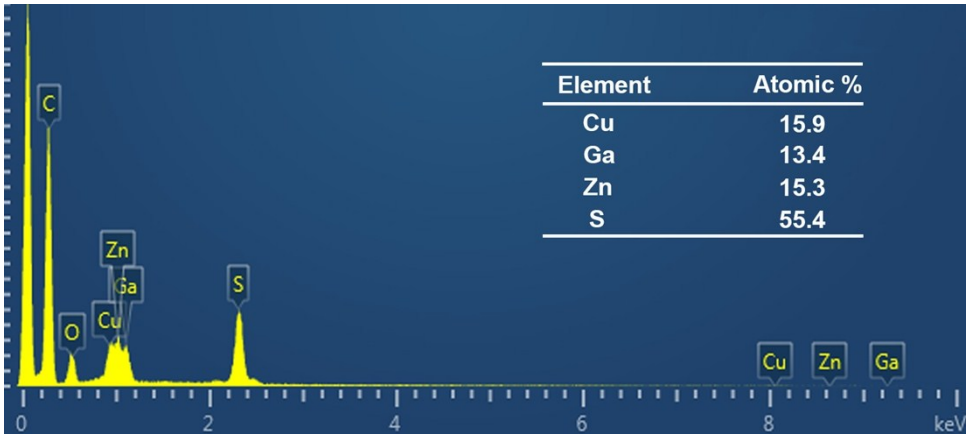

Figure S3. EDS spectrum of L-shaped CGZS nanorods, and the atomic percentages of four elements are given in the inset table.

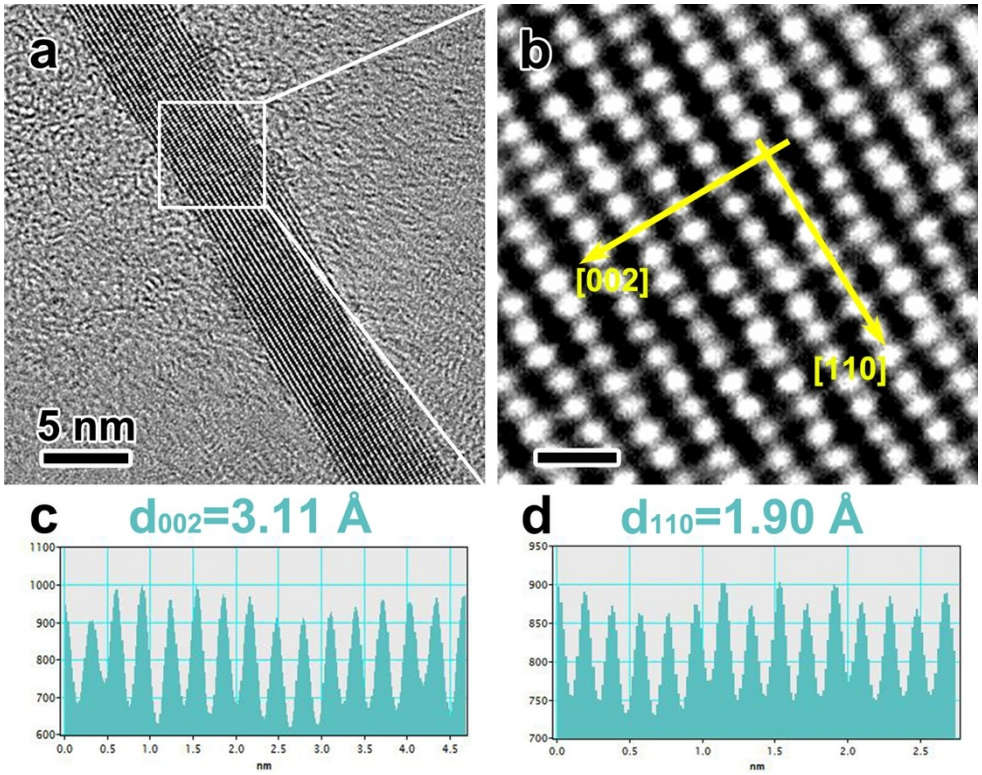

Figure S4. (a) HRTEM image of one branch of the nanorod, which corresponds to Figure 2d. (b) Selected magnified HRTEM image, which shows [002] and [110] directions of L-shaped CGZS nanorod, respectively. The scale bar is 0.5 nm. (c, d) crystalline spacing of two different directions along [002] and [110] directions, respectively.

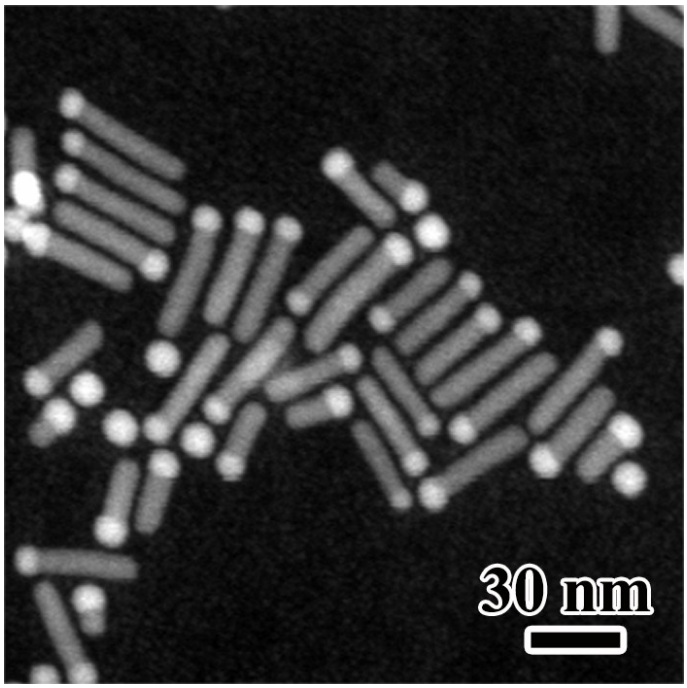

Figure S5. Dark-field TEM image of $Cu_{31}S_{16}$-ZnS HNS obtained at 23min.

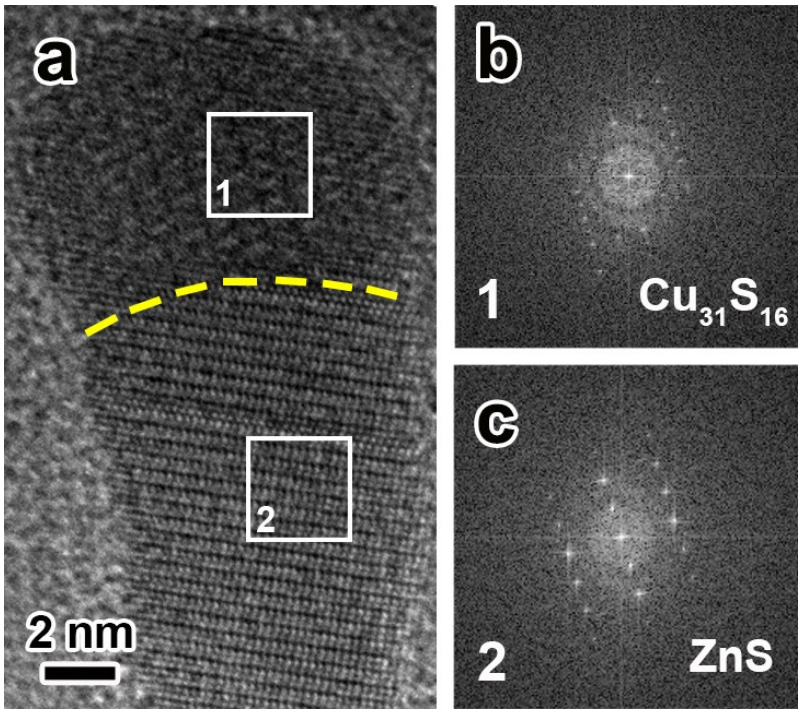

Figure S6. (a) HRTEM image of an individual $Cu_{31}S_{16}$-ZnS HNS for 23 min, whose head and stick are $Cu_{31}S_{16}$ and ZnS, respectively. (b, c) The corresponding selected area FFT patterns, which are taken from area 1 and 2 of HRTEM image, respectively.

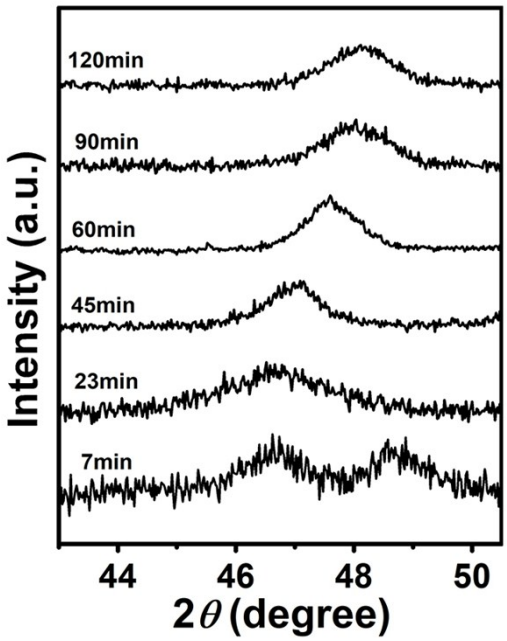

Figure S7. Magnified XRD patterns of as-obtained products obtained at different reaction time in the range of 43-51°, which corresponds to Figure 3j.

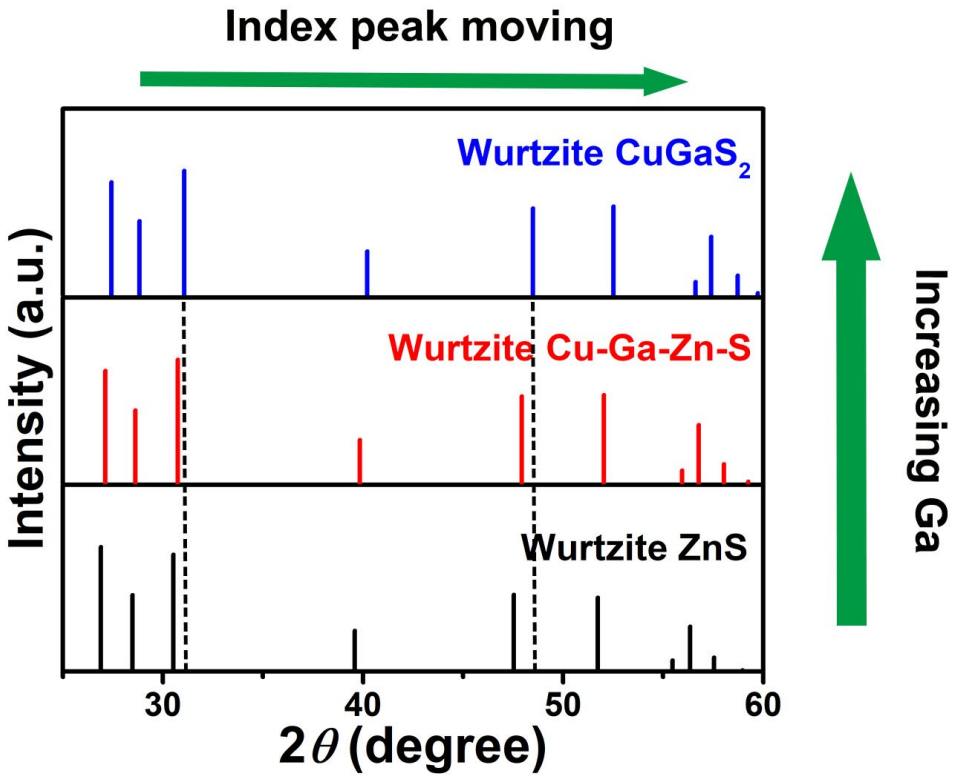

Figure S8. Comparison of diffraction lines of three different materials: standard data of wurtzite ZnS (JCPDS No. 79-2204), simulated data of wurtzite Cu-Ga-Zn-S and simulated date of wurtzite $CuGaS_2$ (from bottom to top).

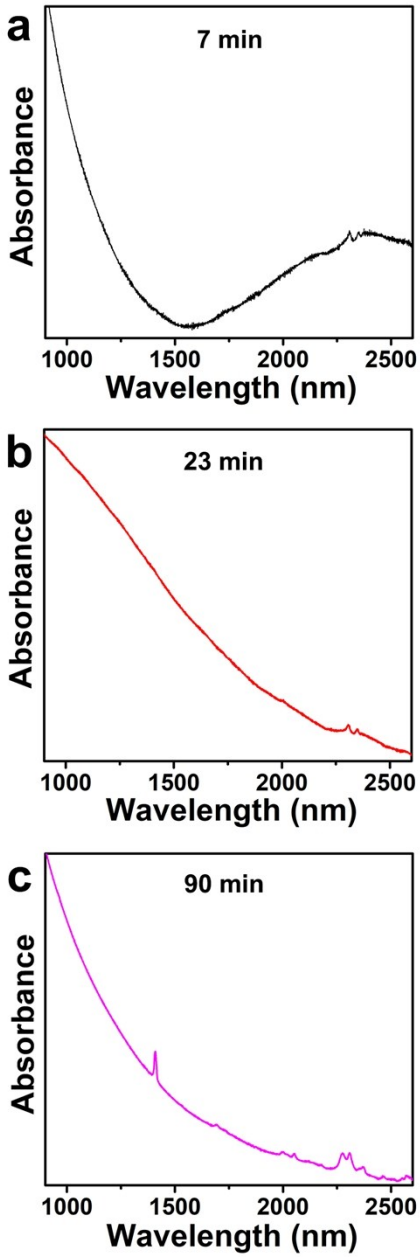

Figure S9. Near-infrared absorption spectra of the products obtained at different reaction time: (a) 7 min, (b) 23 min and (c) 90 min.

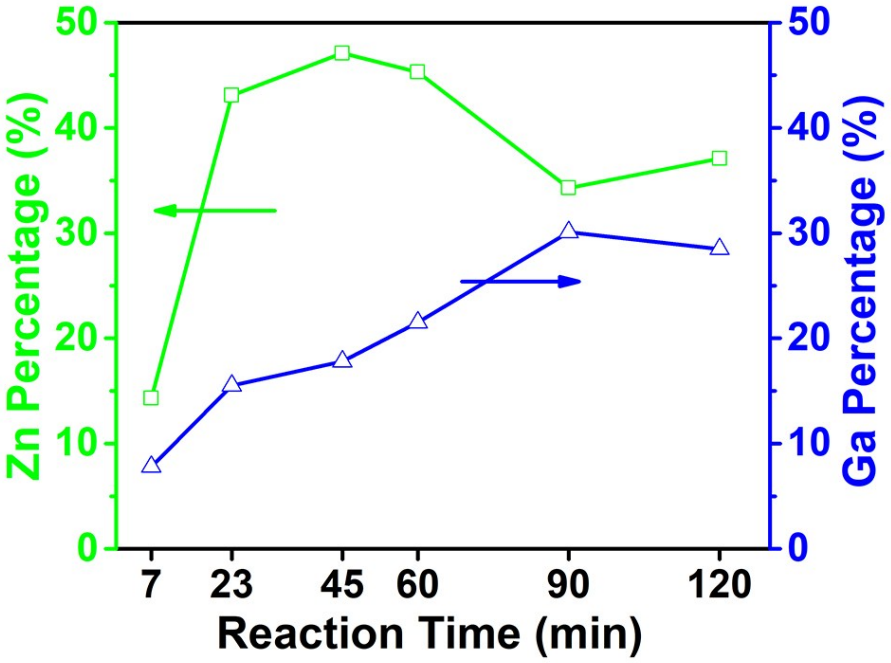

Figure S10. The relationship of actual Zn and Ga percentages in the total of all cations versus the reaction time for CGZS NCs, which are determined by EDS analysis.

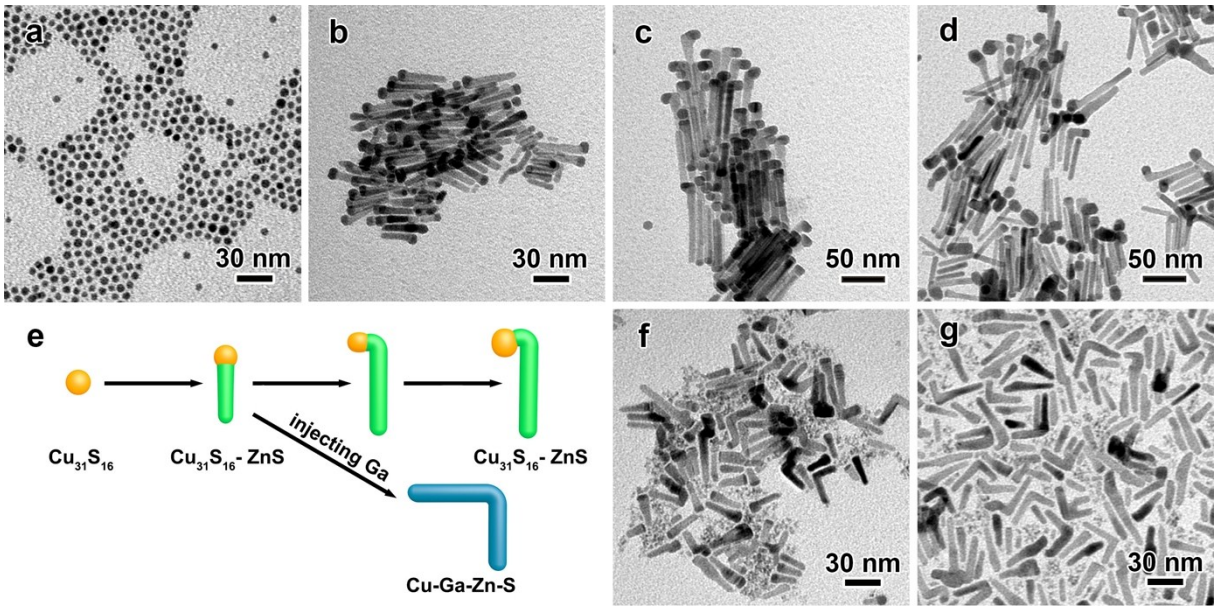

Figure S11. Temporal evolution of TEM images of the products synthesized at 240 °C without any Ga precursors: (a) 5 min, (b) 30 min, (c) 90 min, (d) 150 min. Typical TEM images of the products synthesized at 240 °C by injection of Ga precursors into $Cu_{31}S_{16}$-ZnS HNS obtained at 30 min: (f) 90 min, (g) 150 min. (e) Schematic illustration of the growth in the presence and absence of Ga precursors.

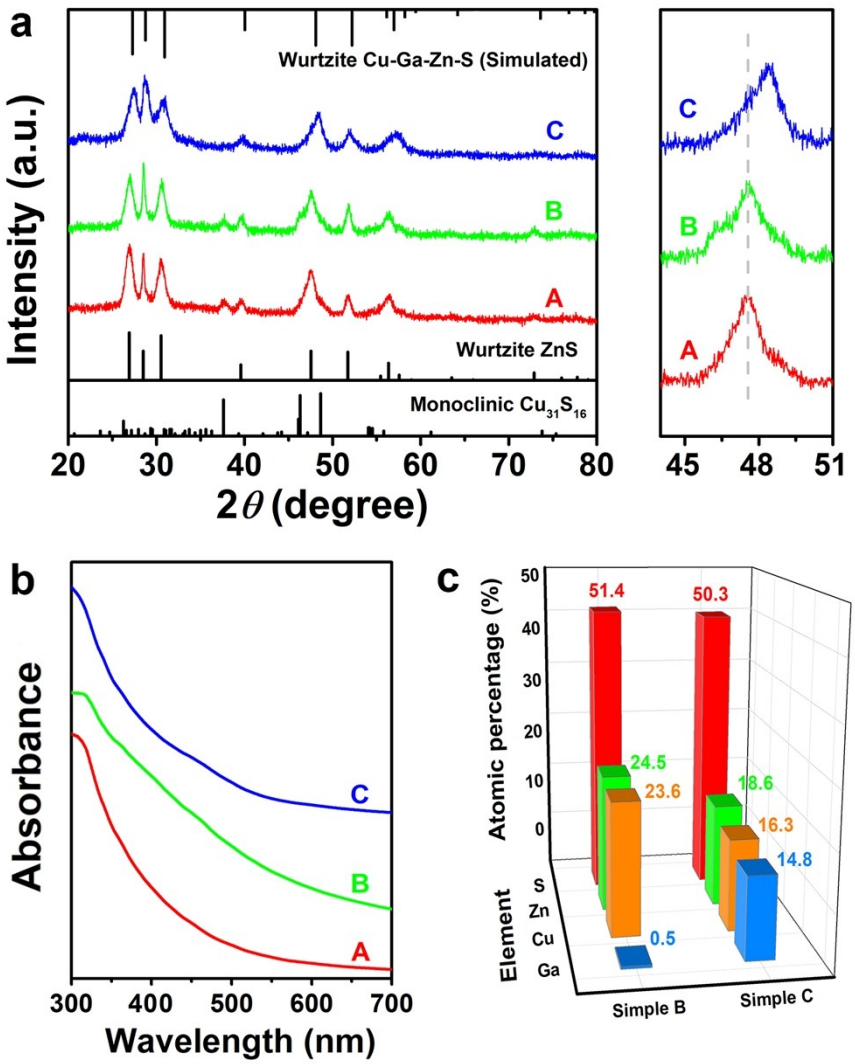

Figure S12. (a) XRD patterns (left) of the products obtained before and after injection of Ga precursors, and the bottom diffraction lines represent the standard data of wurtzite ZnS (JCPDS No. 79-2204) and standard data of monoclinic $Cu_{31}S_{16}$ (JCPDS No. 23-0959), and the top lines stand for simulated data of wurtzite Cu-Ga-Zn-S, and the right picture is the magnified XRD patterns in the region of 44-51°. Note that A, B represent the products obtained at 30 min (red line) and 150 min (green line) without injecting any Ga precursors, and C represents the product obtained at 150 min after injecting Ga precursors in to $Cu_{31}S_{16}$-ZnS HNS at 30 min (blue line). (b) Corresponding UV-Vis absorption spectra of three different samples. (c) Atomic percentages of different composition for the product B and C, which are determined by EDS results.

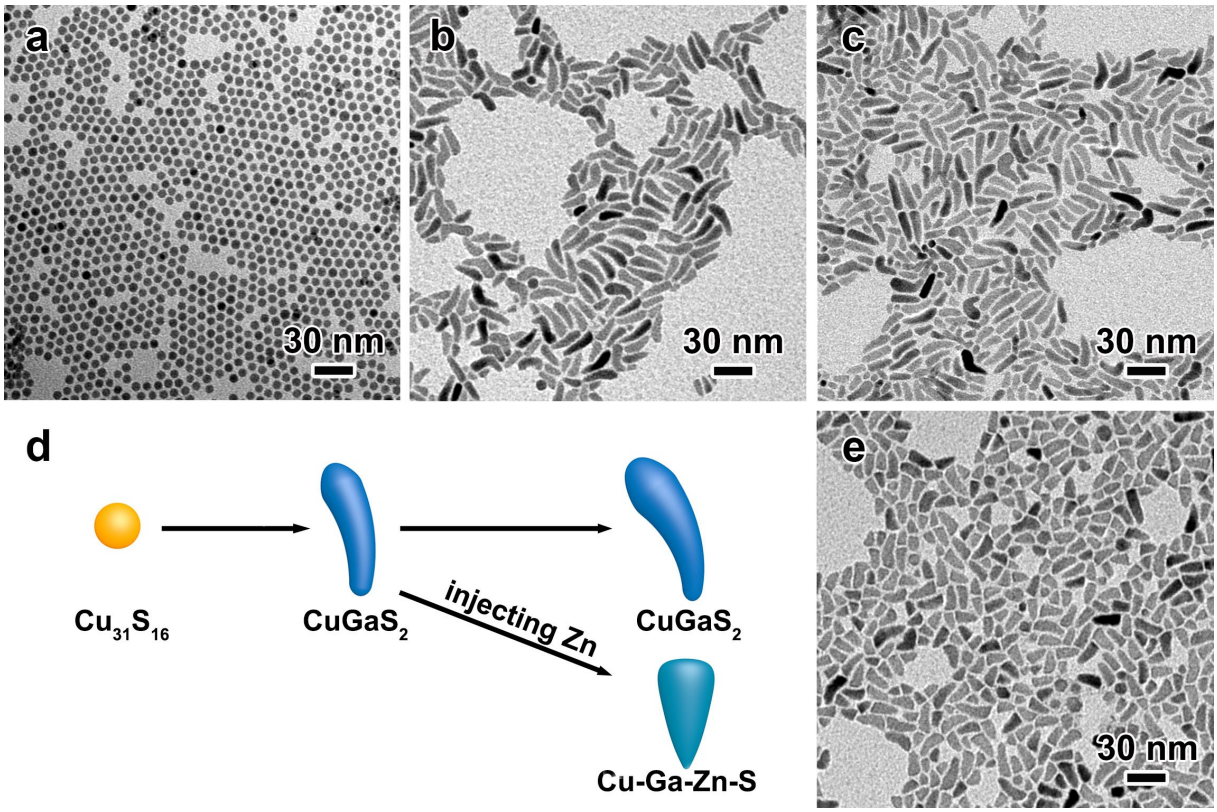

Figure S13. Temporal evolution of TEM images of $CuGaS_2$ NCs synthesized at 240 °C over reaction time: (a) 0 min, (b) 90 min, (c) 210 min. (e) Typical TEM image of the product obtained at 210 min synthesized by injection of Zn precursors into $CuGaS_2$ NCs at 90 min. (d) Schematic illustration of the growth before and after injection of Zn precursors.

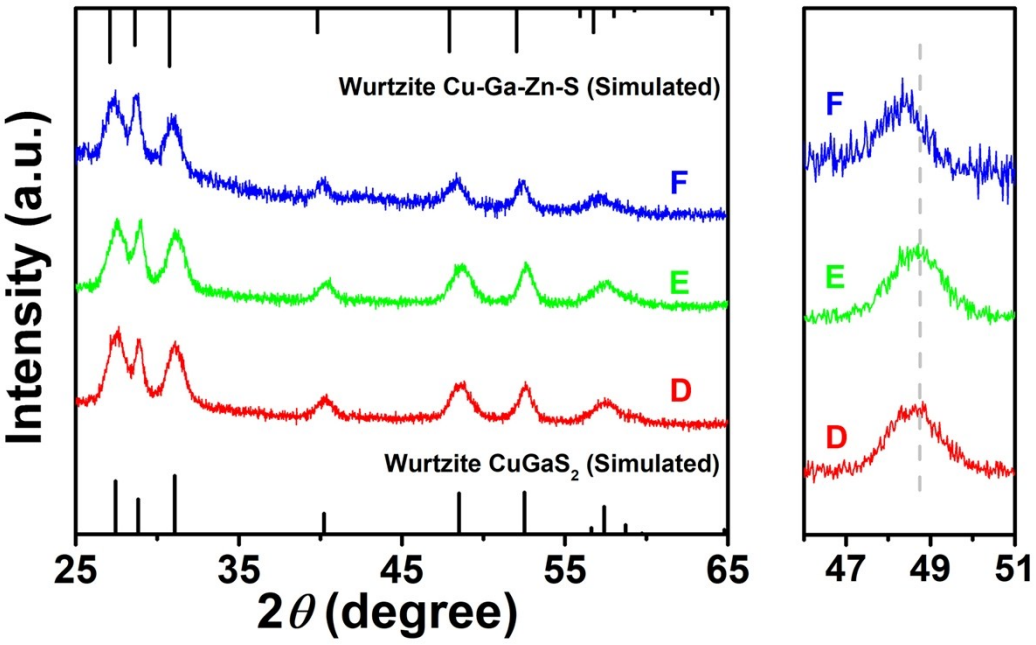

Figure S14. XRD patterns (left) and the corresponding magnified ones (right) in the region of 46-51° of the products synthesized before and after injection of Zn precursors, and the bottom lines represent the simulated data of wurtzite $CuGaS_2$ and the top lines stand for simulated data of wurtzite Cu-Ga-Zn-S. The letters D-F from bottom to top represent the products obtained at 90 min (red line) and 210 min (green line) without injecting Zn precursors, and the products obtained at 60 min after injection of Zn precursors into $CuGaS_2$ NCs obtained at 150 min (blue line).

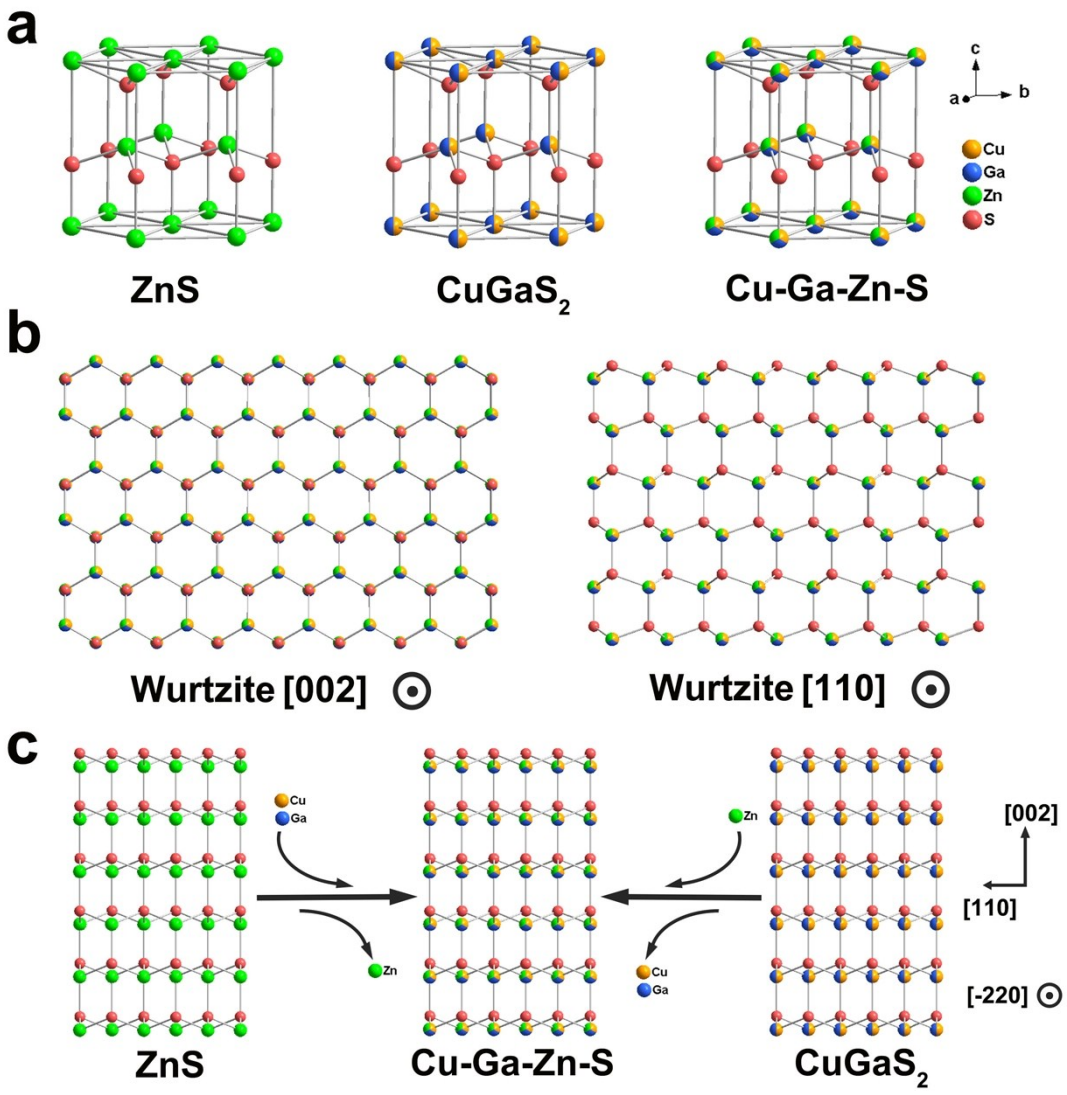

Figure S15. (a) The schematic model of wurtzite structures for three different materials: ZnS, $CuGaS_2$ and Cu-Ga-Zn-S. The yellow, blue, green and red spheres represent copper, gallium, zinc and sulfur, respectively. (b) Crystallographic model of the wurtzite structures viewed from different directions: the [002] (left) and [110] (right) directions for depicting the arrangement of the atoms of (002) and (110) facets. (c) Crystallographic model of cation exchange along two approaches: the left represents ZnS structure as starting phase and the right stands for $CuGaS_2$ structure as starting phase viewed form [-220] direction, which are exchanged to Cu-Ga-Zn-S structure.

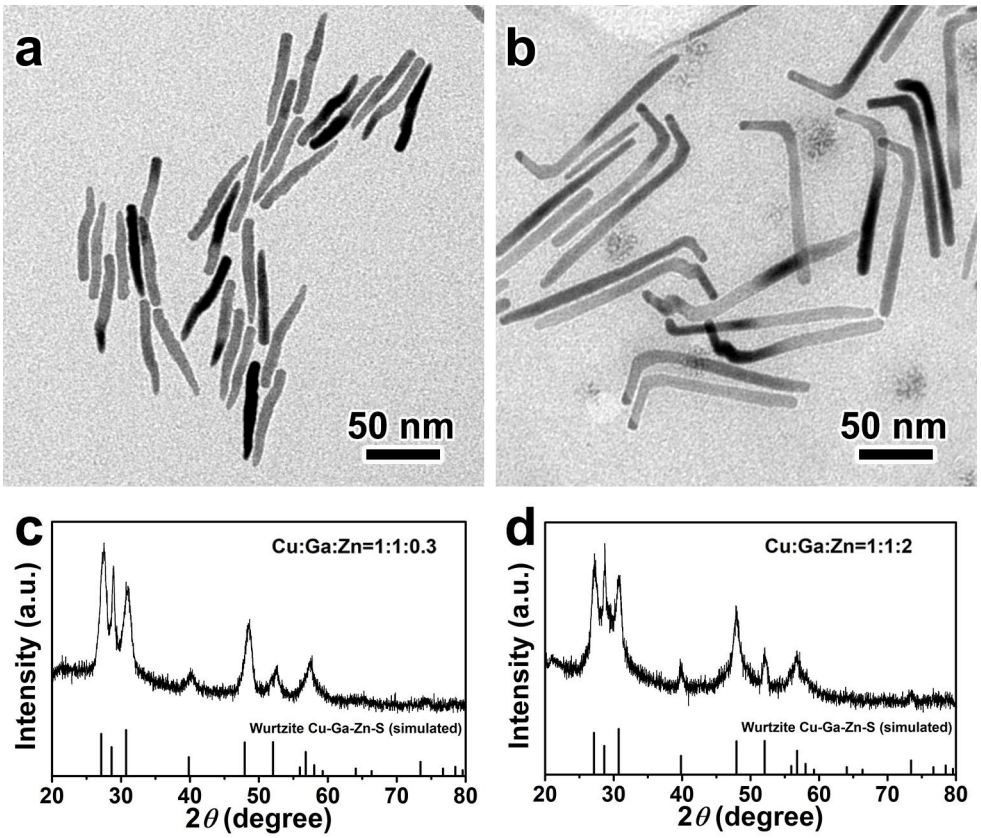

Figure S16. TEM images (top) and XRD patterns (bottom) of the products synthesized using different of Cu/Ga/Zn precursor ratios: (a, c) 1:1:0.3 and (b, d) 1:1:2.

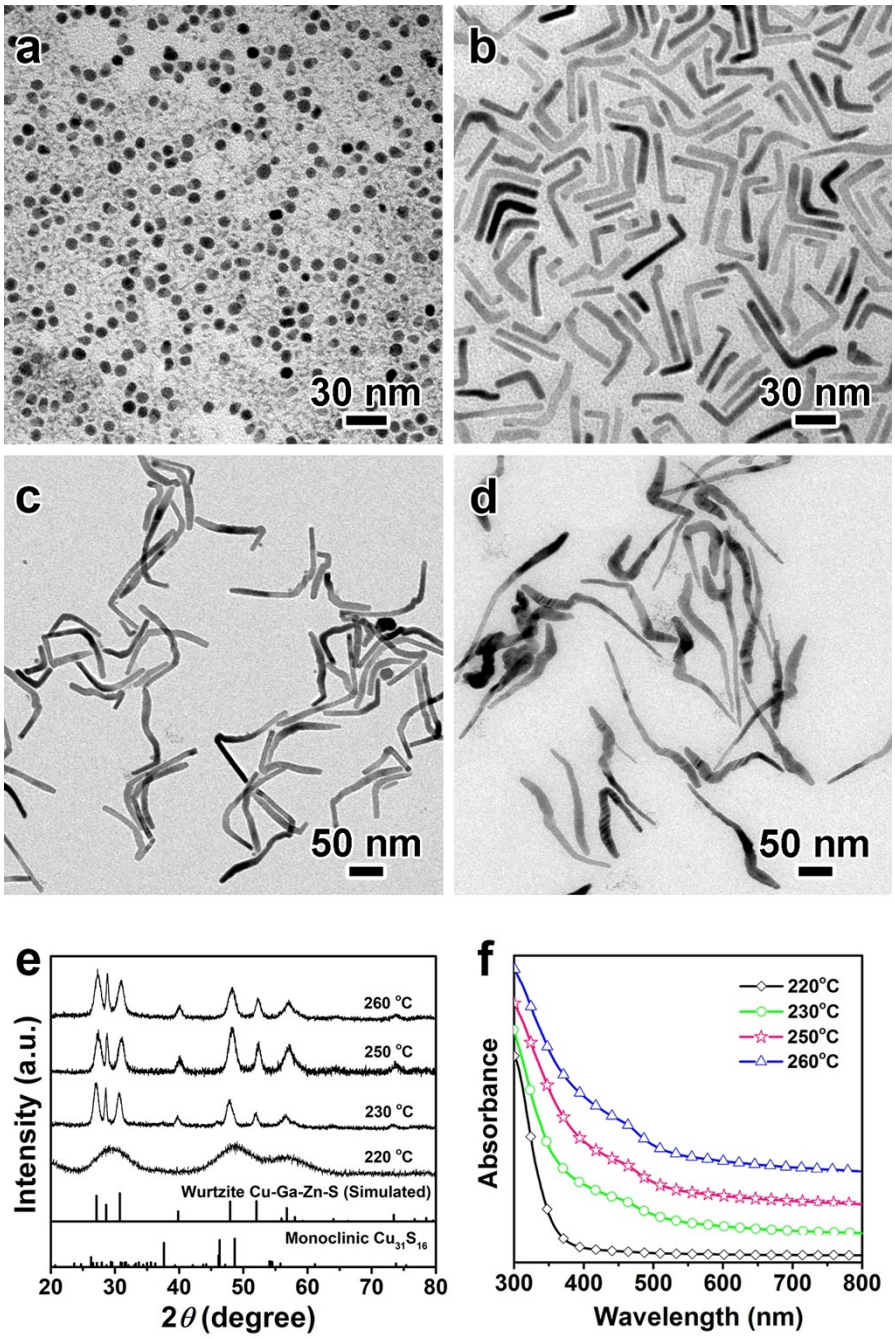

Figure S17. TEM images of CGZS NCs synthesized under different reaction temperatures: (a) 220 °C, (b) 230 °C, (c) 250 °C, (d) 260 °C; (e) the corresponding XRD patterns, and the bottom lines represent the diffraction lines of simulated wurtzite Cu-Ga-Zn-S and standard monoclinic $Cu_{31}S_{16}$ (JCPDS No. 23-0959), (f) the corresponding UV-Vis absorption spectra.

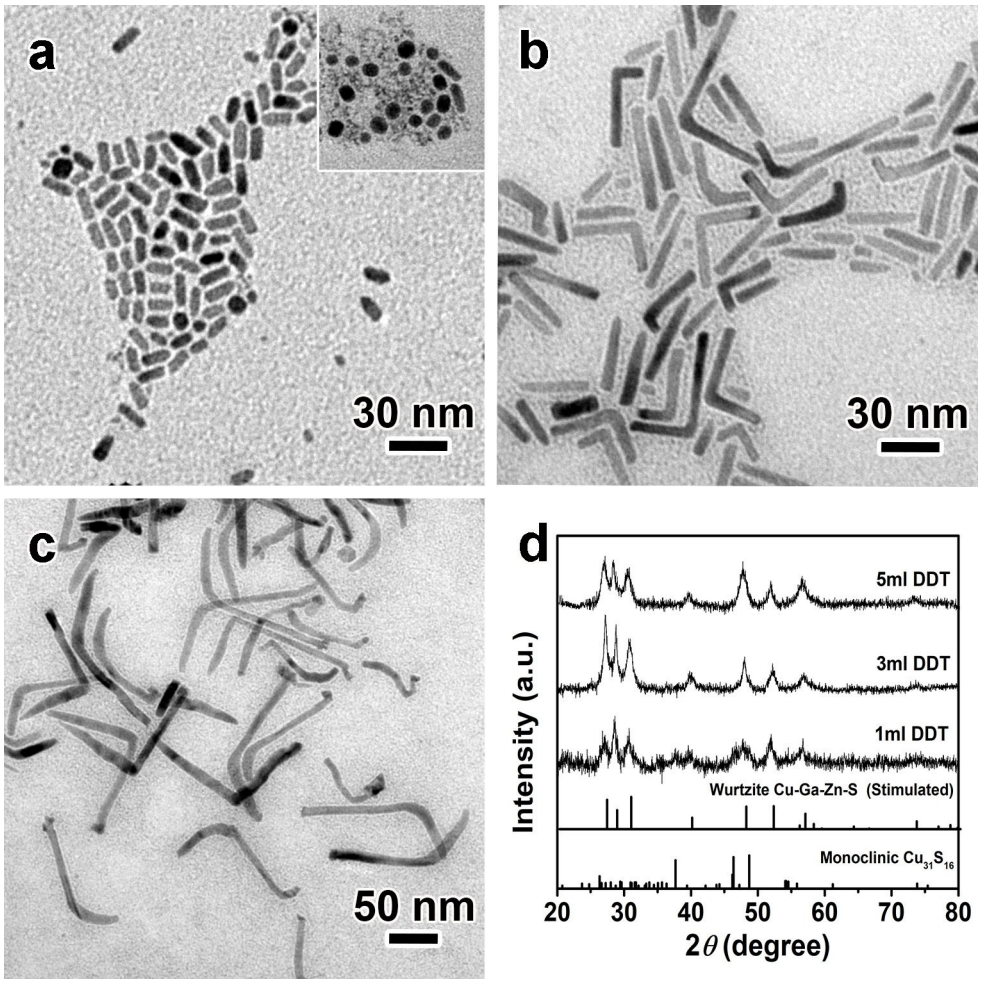

Figure S18. TEM images of CGZS NCs synthesized under 230 °C at 90 min in the presence of different DDT dosage: (a) 1 mL, (b) 3 mL, (c) 5 mL, and the inset shown in a) indicates the presence of $Cu_{31}S_{16}$ NCs and some smaller nanodots in the presence of 1mL DDT. (d) The corresponding XRD patterns, and the bottom lines represent the diffraction lines of simulated wurtzite Cu-Ga-Zn-S and standard monoclinic $Cu_{31}S_{16}$ (JCPDS No. 23-0959).

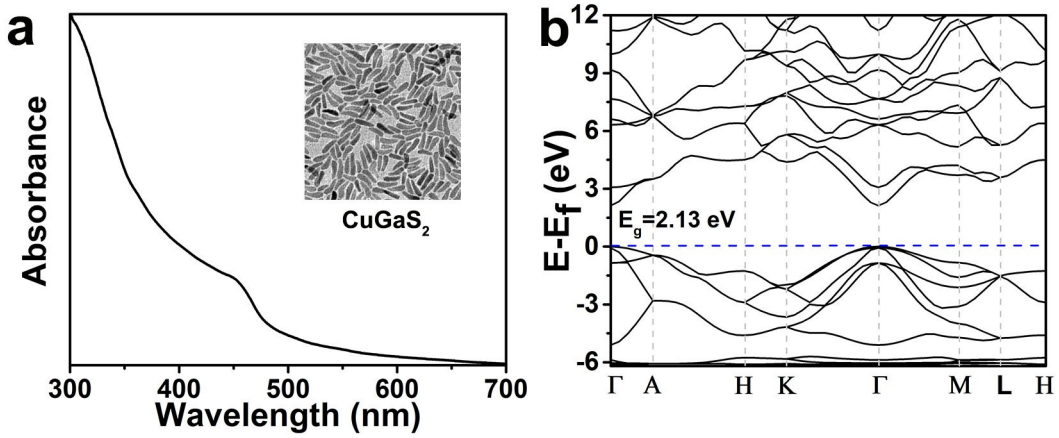

Figure S19. (a) UV-Vis absorption spectrum of tadpole-like $CuGaS_2$ NCs, and the inset shows TEM image of $CuGaS_2$ NCs. (b) Calculated electronic band structure of bulk $CuGaS_2$ and Fermi level are set to zero and marked as blue dash lines.

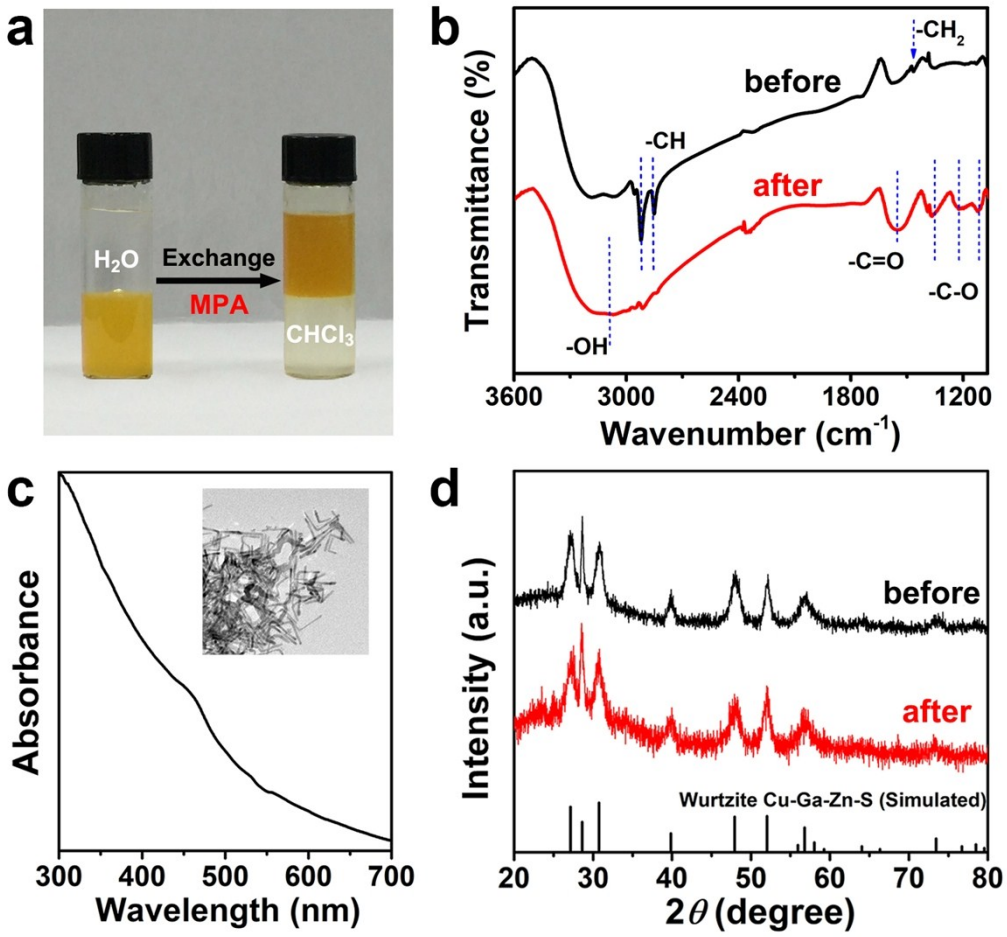

Figure S20. (a) The digital picture of the L-shaped CGZS nanorods before and after phase transfer from chloroform (left) to water (right) using 3-mercaptopropionic acid (MPA). (b) FTIR spectra of L-shaped CGZS NCs before and after phase transfer. (c) UV-Vis absorption spectrum of L-shaped CGZS NCs dispersing in water, and inset shows the TEM image of the sample transferred to water. d) XRD patterns of the products before and after phase transfer, and the bottom lines represent the diffraction lines of simulated wurtzite Cu-Ga-Zn-S.

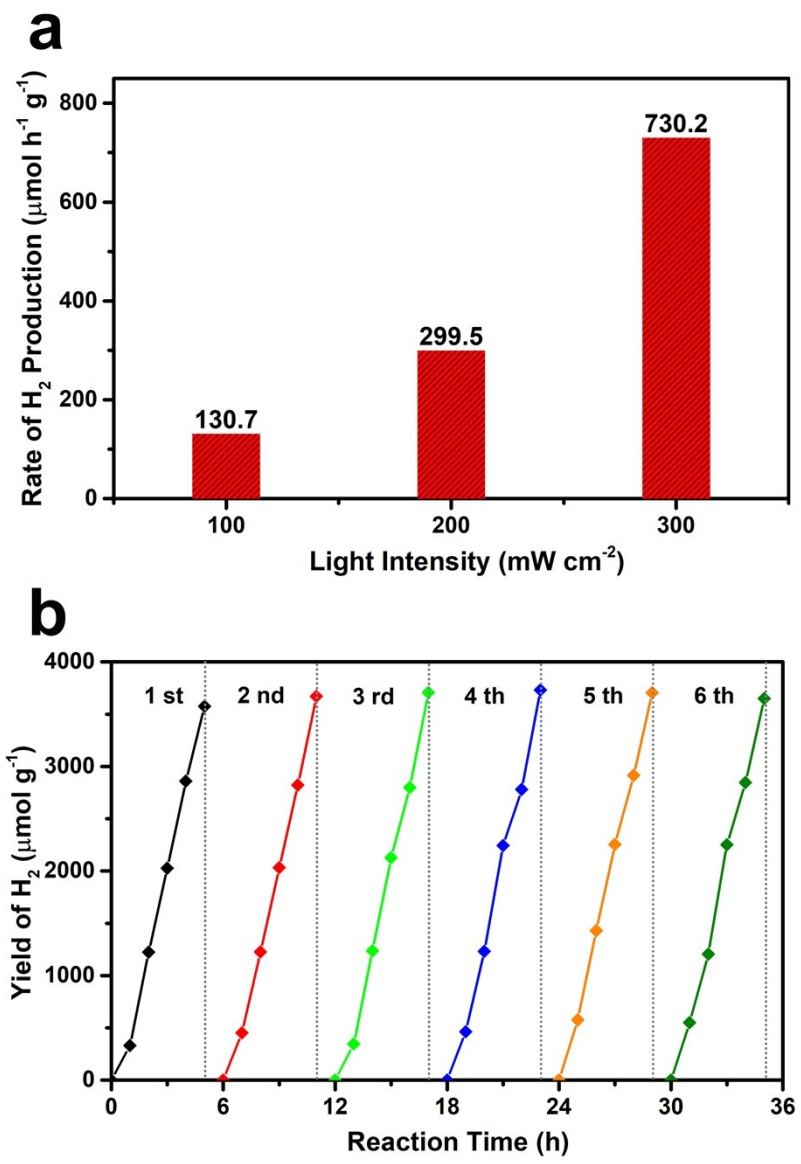

Figure S21. (a) The photocatalytic hydrogen production of L-shaped CGZS nanorods for different incident light intensity under simulated solar illumination. (b) Cycling tests of hydrogen production for L-shaped CGZS nanorods under simulated solar illumination with the intensity of 300 mW cm^{-2}.

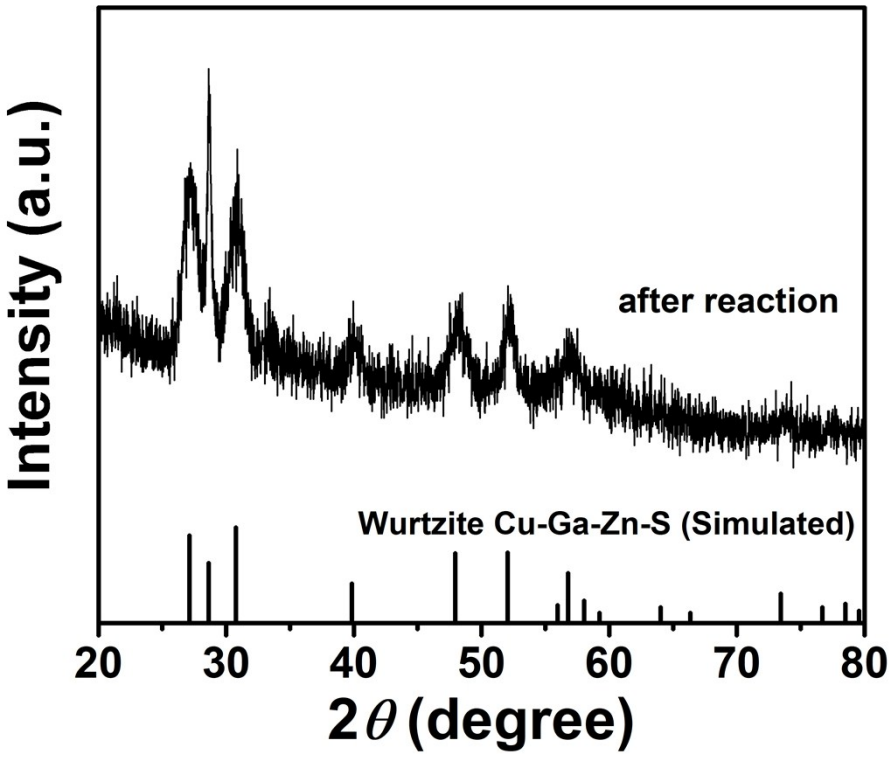

Figure S22. XRD pattern of products after photocatalytic hydrogen evolution, and the bottom lines represent the diffraction lines of simulated wurtzite Cu-Ga-Zn-S.

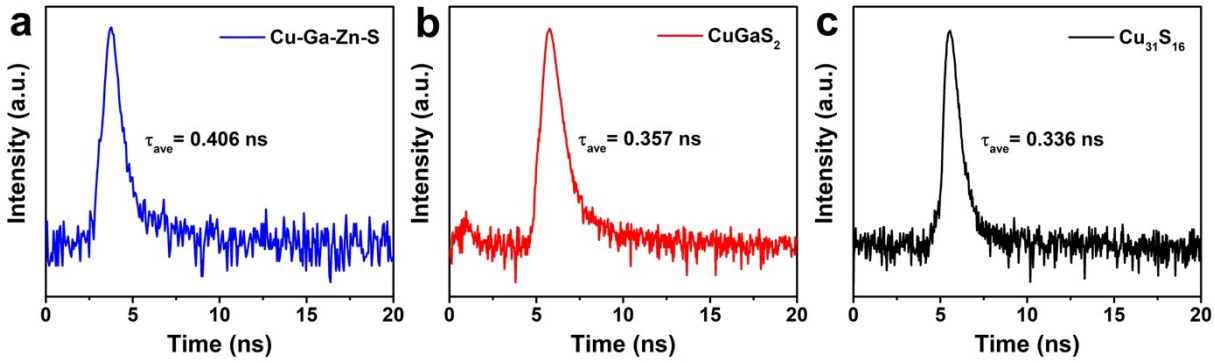

Figure S23. Transient photoluminescence spectra for different photocatalysts: (a) L-shaped CGZS NCs, (b) tadpole-like $CuGaS_2$ NCs and (c) $Cu_{31}S_{16}$ nanospheres with an excitation wavelength of 440 nm laser.

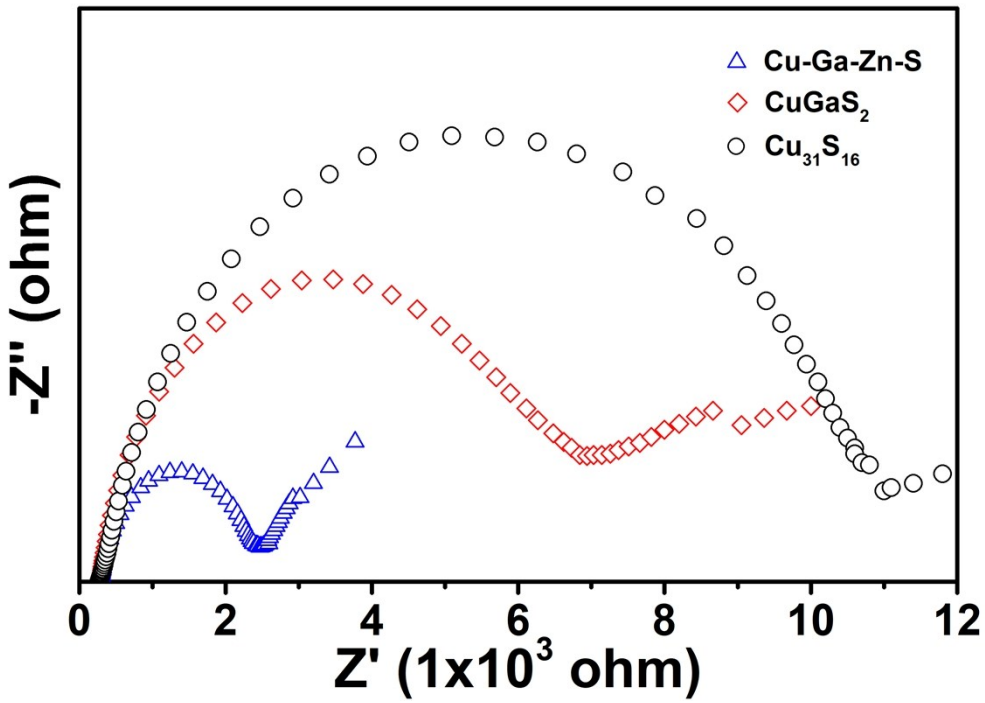

Figure S24. Nyquist plots of L-shaped CGZS NCs, tadpole-like $CuGaS_2$ NCs and $Cu_{31}S_{16}$ nanospheres.

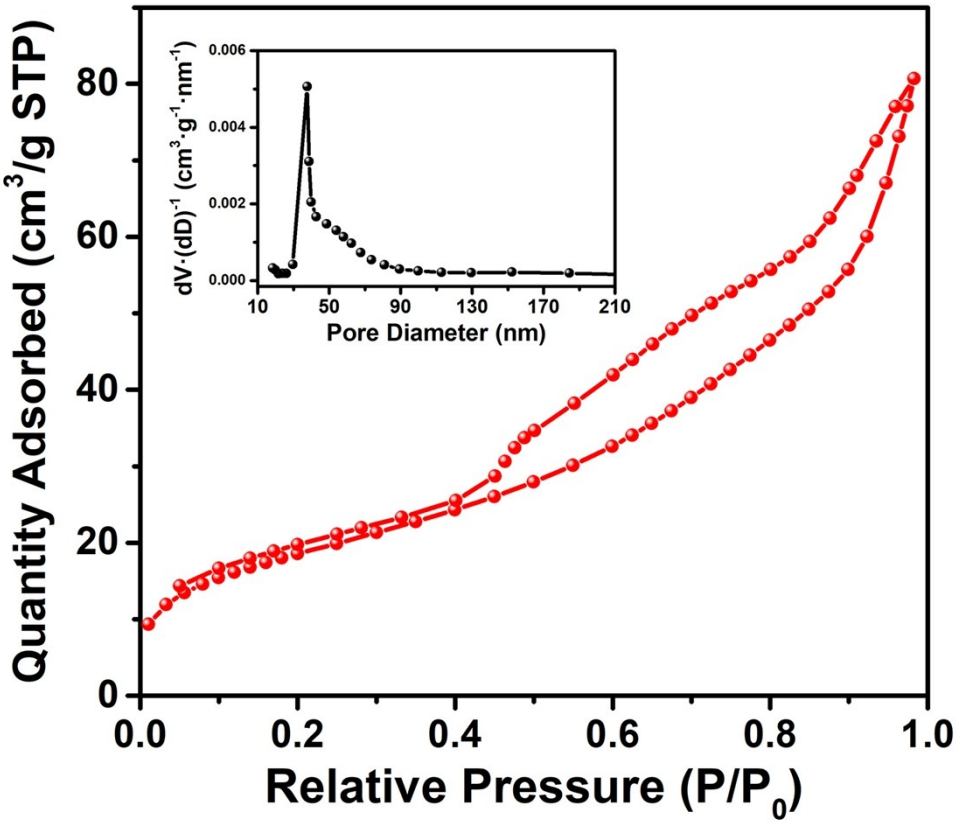

Figure S25. Nitrogen adsorption–desorption isotherms and corresponding pore size distribution curves (inset) of L-shaped CGZS NCs.

Supporting Tables:

Table S1. Summary of the lattice parameters based on the crystal structures of wurtzite $CuGaS_2$, wurtzite Cu-Ga-Zn-S and wurtzite ZnS.

Compound	a (Å)	c (Å)
$CuGaS_2$	3.75	6.18
Cu-Ga-Zn-S	3.79	6.23
ZnS	3.82	6.26

Unit cell parameter: a

Unit cell parameter: c

Table S2. Summary of actual cationic contents for different metal elements of wurtzite CGZS NCs synthesized at different reaction time

Reaction time	[Cu]	[Ga]	[Zn]
7min	77.9%	7.8%	14.3%
23min	41.4%	15.5%	43.1%
45min	35.1%	17.8%	47.1%
60min	33.2%	21.5%	45.3%
90min	35.6%	30.1%	34.3%
120min	34.4%	28.5%	37.1%

[Cu]: the copper atomic percentage in total cations ([Cu]/[Cu]+[Ga]+[Zn])

[Ga]: the gallium atomic percentage in total cations ([Cu]/[Cu]+[Ga]+[Zn])

[Zn]: the zinc atomic percentage in total cations ([Cu]/[Cu]+[Ga]+[Zn])

[Cu], [Ga], [Zn]: determined by EDS results