Electronic Supplementary Information (ESI)

From one-dimensional to two-dimensional wurtzite $CuGaS_2$ nanocrystals: non-injection synthesis and photocatalytic hydrogen evolution

Zheming Liu,[a] Jun Liu,[b,c] Yanbin Huang, [b,c] Jing Li,[d] Yi Yuan,[a] Haihang Ye,[a, #] Dongxu Zhu,[a] Zhijie Wang[b,c,*] and Aiwei Tang[a, *]

[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]School of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, P. R. China

*Corresponding authors:

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

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

XRD patterns refinement results:

Rwp= 7.81% Rp= 6.08%

Crystal structure:

Compound	$CuGaS_2$
Phase name	Wurtzite
Space group	$P6_3mc$ (NO.186)
Lattice parameters	a= 3.749 Å
	c= 6.189 Å

Atomic parameters:

	x/a	y/b	z/c	Occ.
Atomic position for S：	1/3	2/3	3/8	1
Atomic position for Cu：	1/3	2/3	0	1/2
Atomic position for Ga：	1/3	2/3	0	1/2

Figure S1

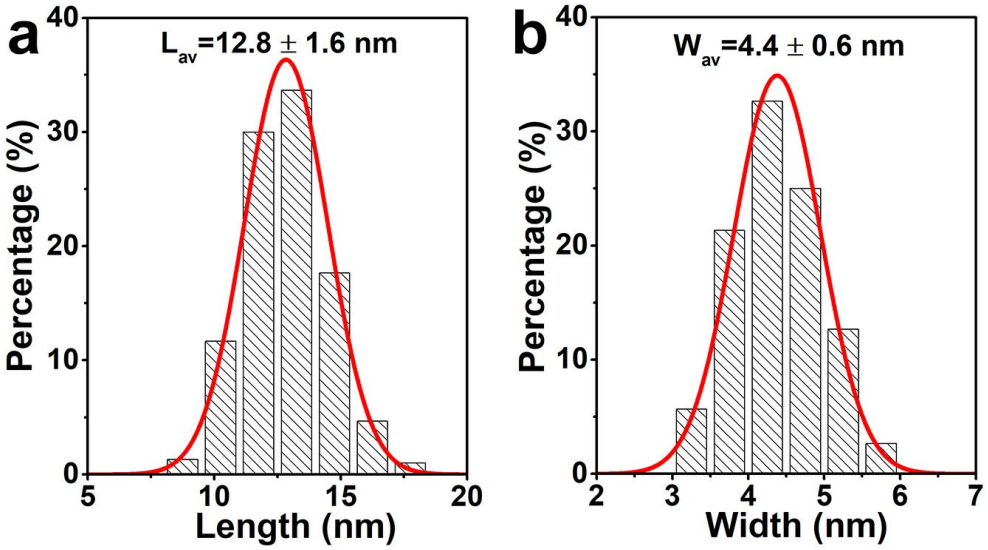


Figure S1. Size distribution histograms of (a) length and (b) width of 1D CGS nanorods.

Figure S2

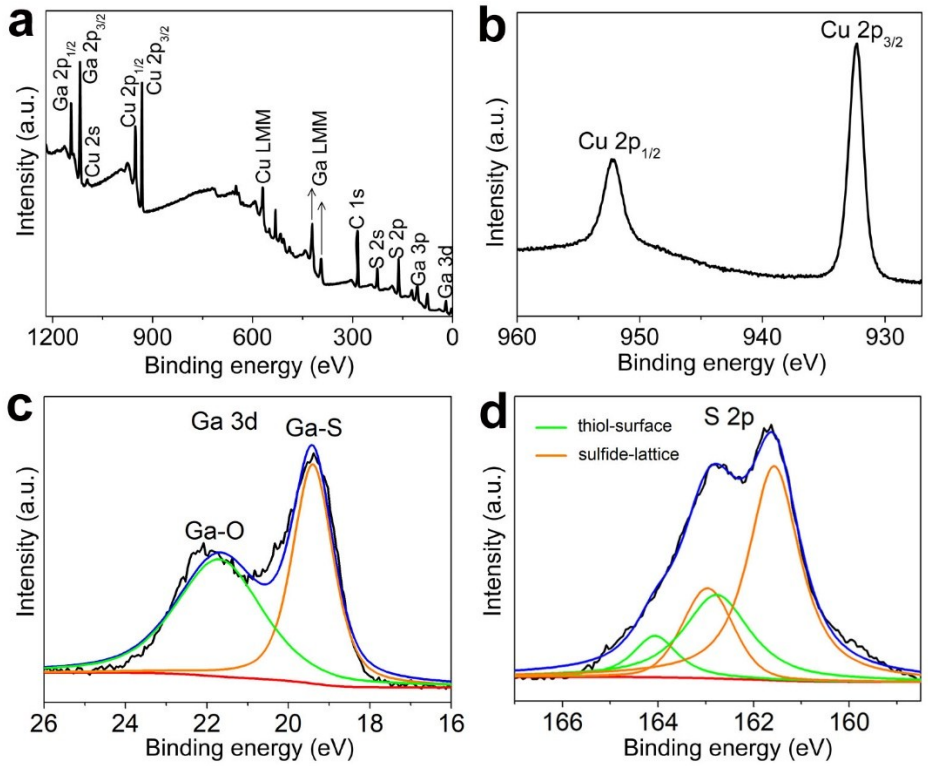


Figure S2. XPS spectra of 1D CGS nanorods synthesized at 240 °C for 60 min: (a) full-scan spectrum; (b) Cu 2p; (c) Ga 3d and (d) S 2p.

Figure S3

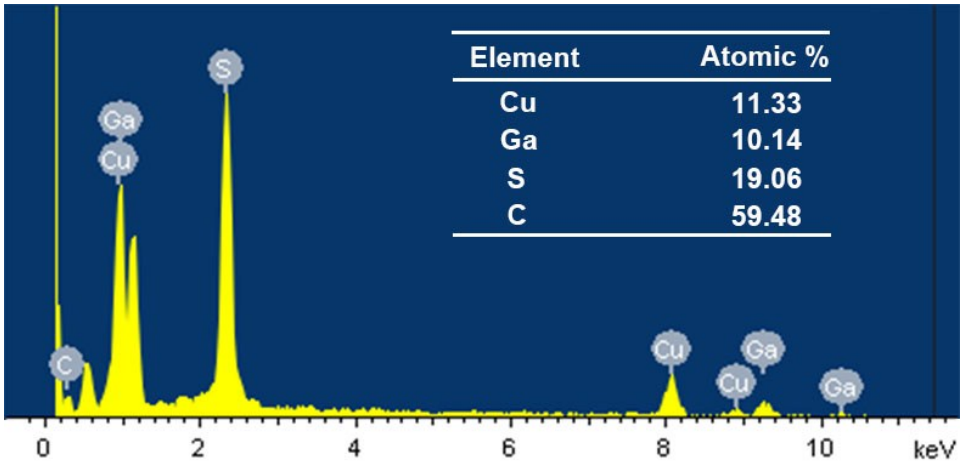


Figure S3. EDS result of 1D CGS nanorods, and the atomic percentages of different elements are given in the inset table.

Figure S4

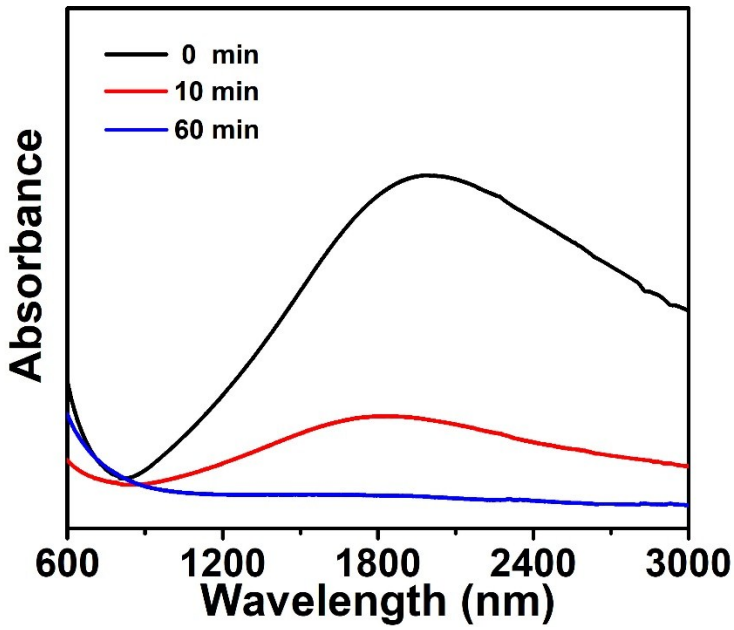


Figure S4. Near-infrared absorption spectra of 1D CGS NCs obtained at different reaction time: 0 min (black line), 10 min (red line) and 60 min (blue line).

Figure S5

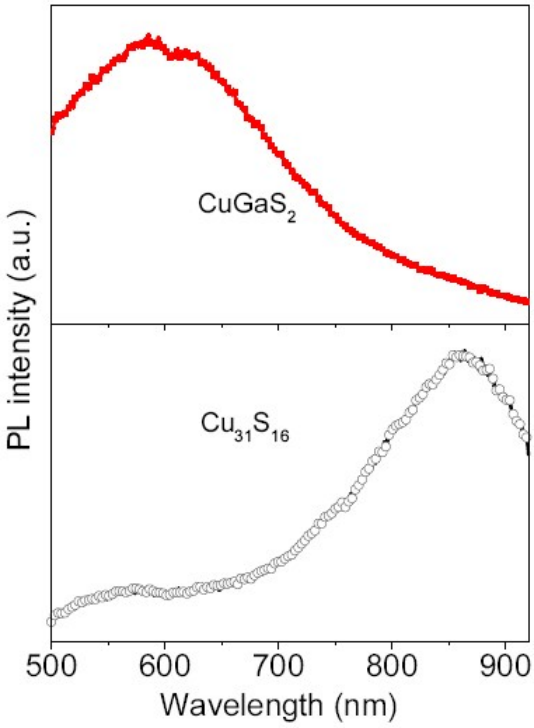


Figure S5. PL spectra of solid 1D CGS nanorods (top) and 0D $Cu_{31}S_{16}$ nanospheres (bottom) with an excitation wavelength of 440 nm laser.

Figure S6

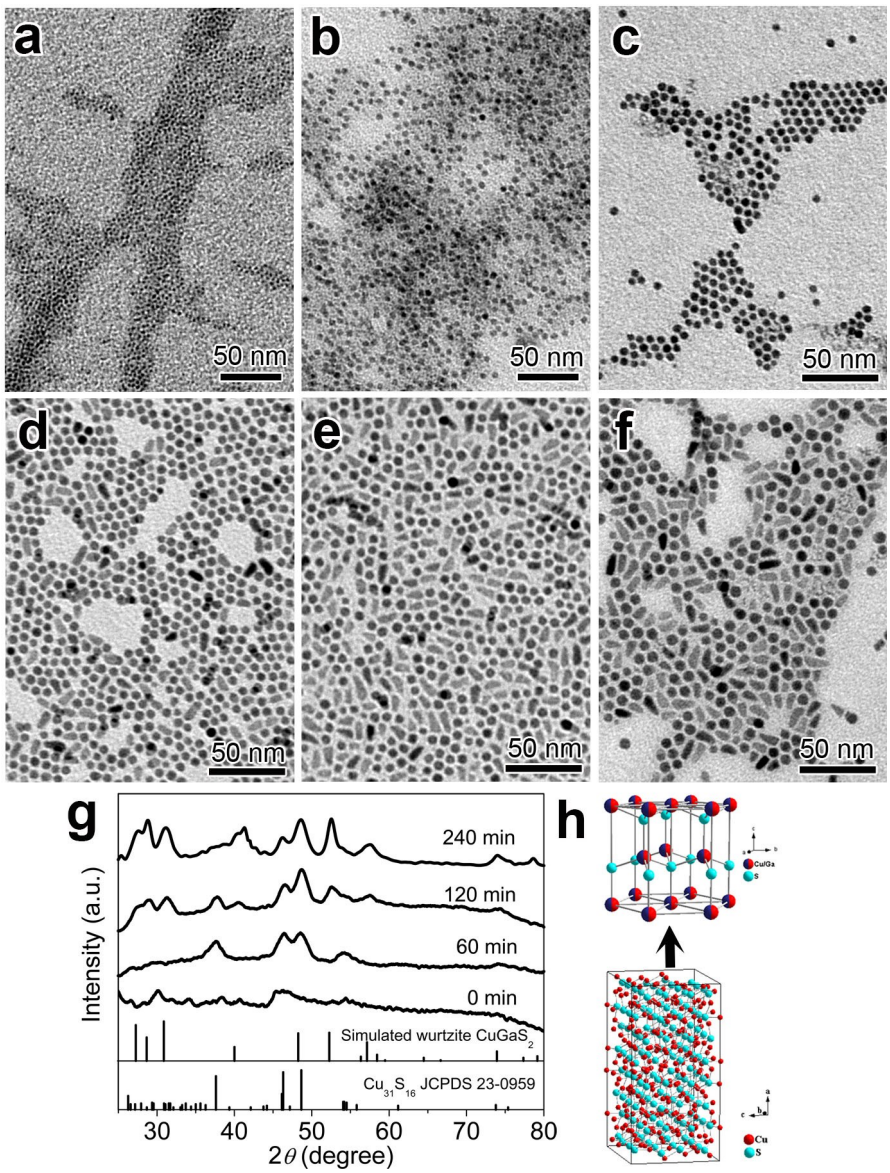


Figure S6. (a-f) TEM image of CGS NCs obtained at 200 °C for different reaction time: (a) 0 min; (b) 30 min; (c) 60 min; (d) 90 min; (e) 120 min; (f) 240 min; (g) the corresponding XRD patterns, and the bottom vertical lines represent the diffraction lines of simulated wurtzite CGS and standard monoclinic $Cu_{31}S_{16}$ (JCPDS No. 23-0959); (h) schematic model of the phase transition from monoclinic $Cu_{31}S_{16}$ to wurtzite CGS.

Figure S7

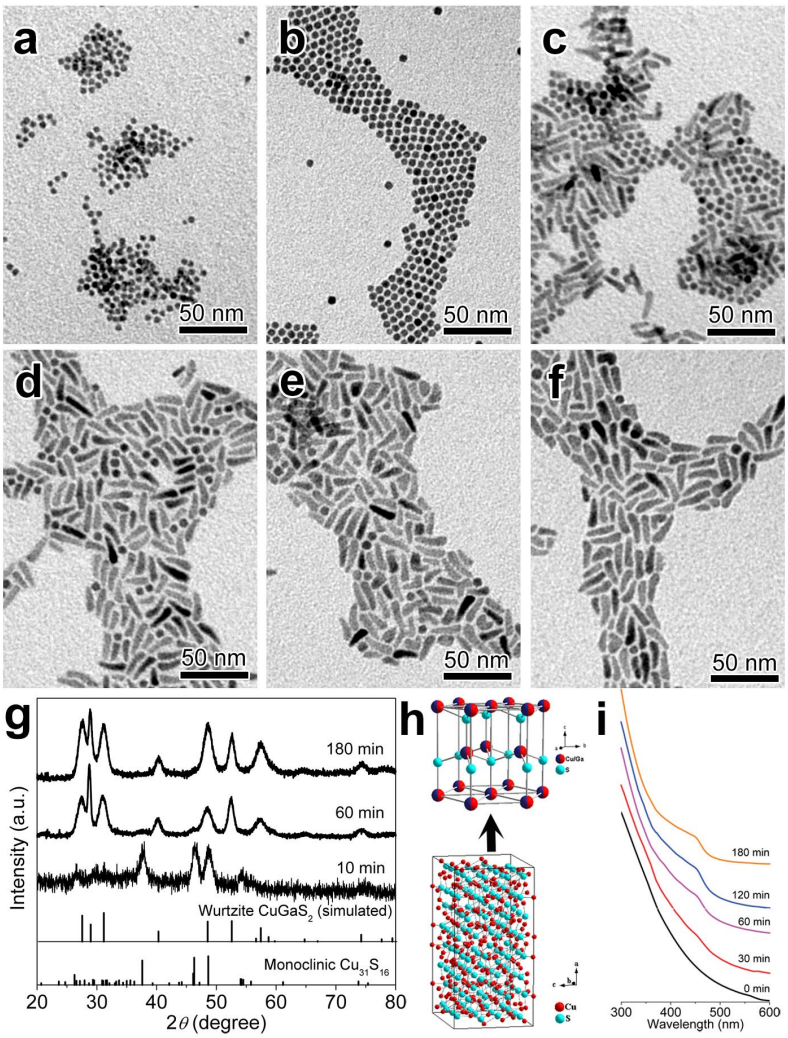


Figure S7. TEM images of CGS NCs synthesized at 220 °C for different reaction time: (a) 0 min; (b) 10 min; (c) 30 min; (d) 60 min; (e) 120 min; (f) 180 min; (g) XRD patterns of the products obtained at 10 min, 60 min and 180 min, and the bottom lines represent the diffraction lines of simulated wurtzite CGS and standard monoclinic $Cu_{31}S_{16}$ (JCPDS No. 23-0959).; (h) schematic model of the phase transition from monoclinic $Cu_{31}S_{16}$ to wurtzite CGS; (i) the corresponding evolution of the UV-Vis absorption spectra.

Figure S8

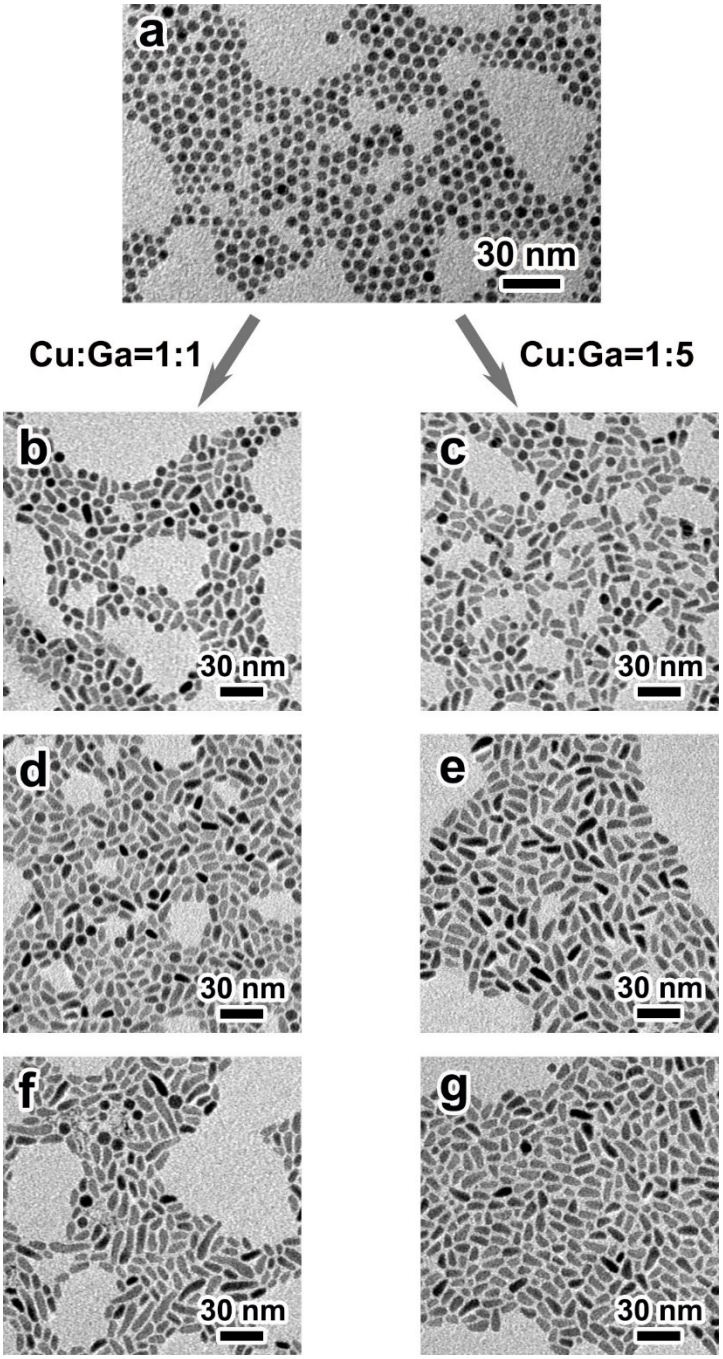


Figure S8. Temporal evolution of TEM images of products synthesized with different Cu/Ga molar ratios at 200 ° C: (a) $Cu_{31}S_{16}$ nanospheres. Typical TEM images of the products synthesized by injecting Ga precursors into $Cu_{31}S_{16}$ NC seeds with Cu/Ga molar ratio of 1:1 and 1:5 for different reaction time: (b, c) 120 min, (d, e) 240 min and (f, g) 360 min.

Figure S9

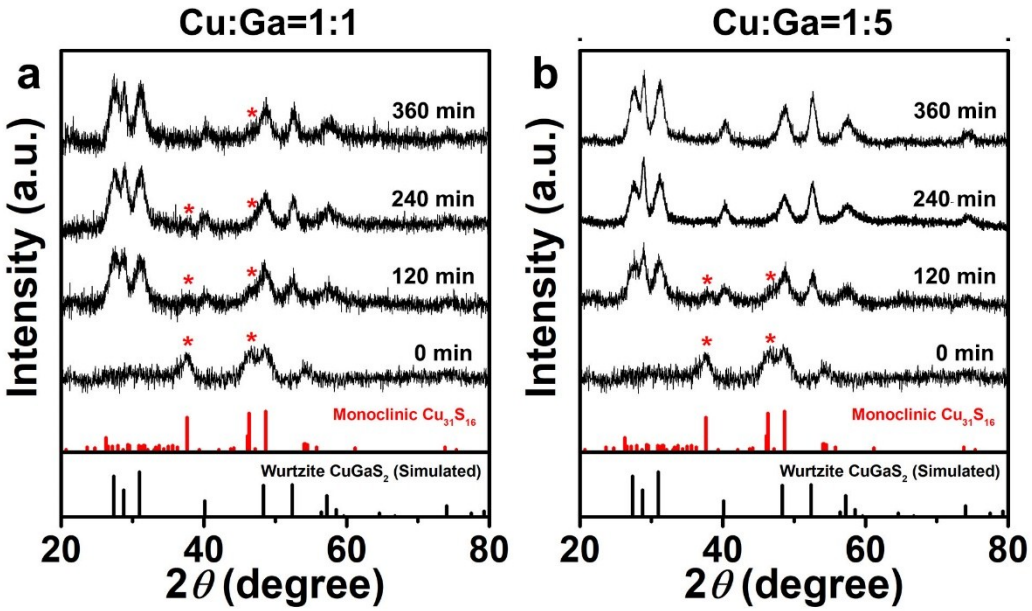


Figure S9. The XRD patterns of products synthesized by injecting Ga precursors into $Cu_{31}S_{16}$ NCs for different reaction time with Cu/Ga molar ratios of (a)1:1 (left) and (b) 1:5 (right). The bottom lines represent the diffraction lines of simulated wurtzite CGS and standard monoclinic Cu31S16 (JCPDS No. 23-0959), and star marks stand for the featured diffraction peaks of monoclinic $Cu_{31}S_{16}$ phase.

Figure S10

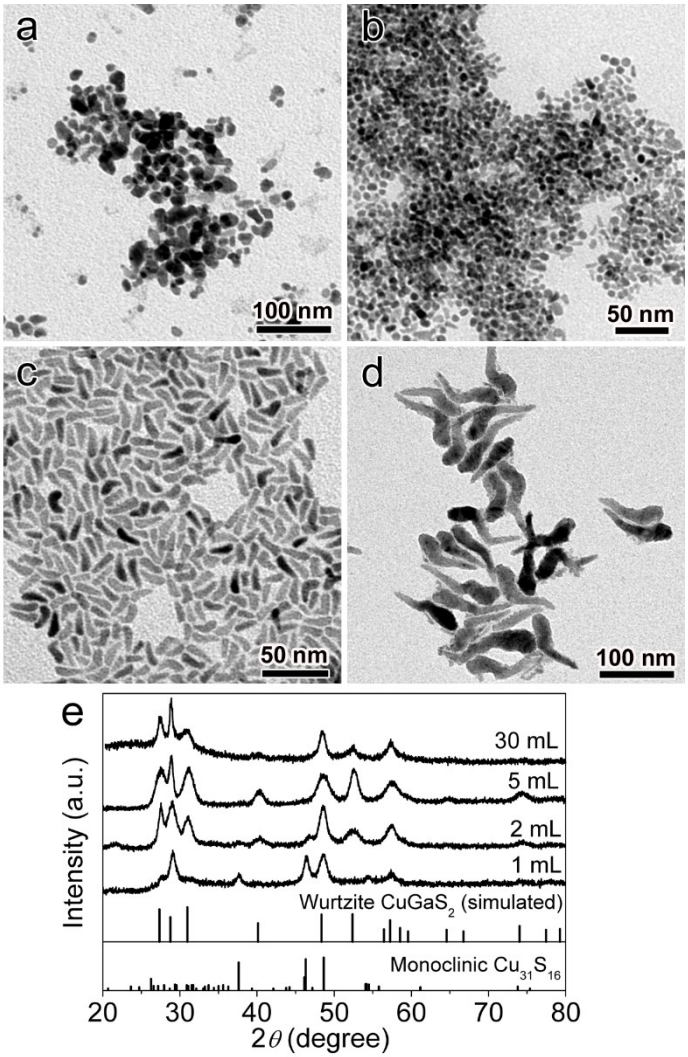


Figure S10. TEM images of CGS NCs synthesized at 250 °C for 60 min in the presence of different DDT dosage: (a) 1 mL; (b) 2 mL; (c) 5 mL and (d) 30 mL; (e) the corresponding XRD patterns, and the bottom lines represent the diffraction lines of simulated wurtzite CGS and standard monoclinic $Cu_{31}S_{16}$ (JCPDS No. 23-0959).

Figure S11

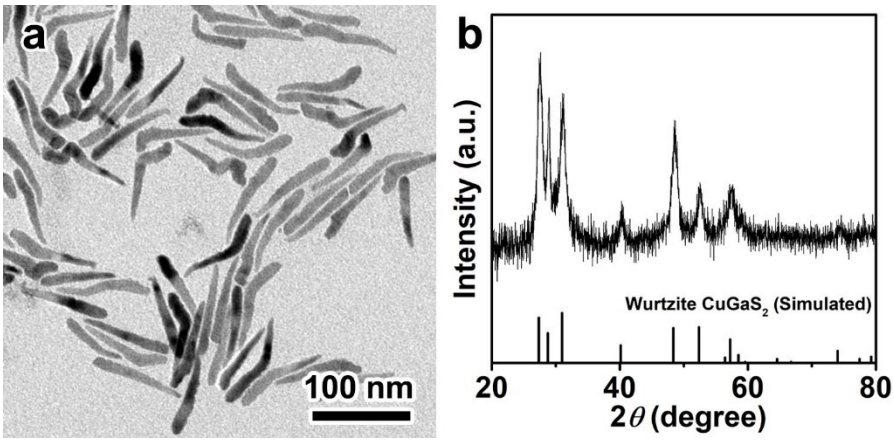


Figure S11. (a) TEM image CGS NCs synthesized at 200 ^{o}C for 240 min in the presence of 30 mL of DDT; (b) the corresponding XRD pattern, and the bottom lines represent the diffraction lines of simulated wurtzite CGS.

Figure S12

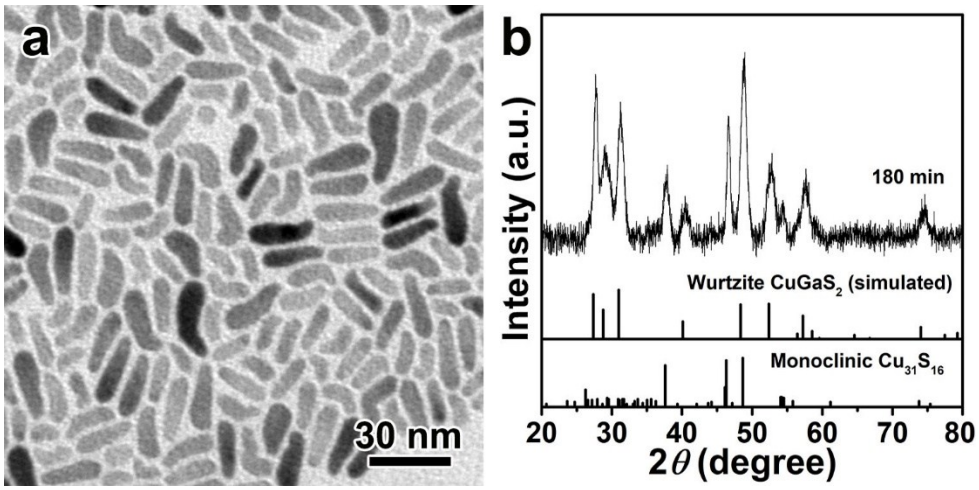


Figure S12. (a) TEM image of qusai-2D CGS nanodisks synthesized at 220 ^{o}C for 180 min in the presence of 5 mL of OM; (b) the corresponding XRD pattern, and the bottom lines represent the diffraction lines of simulated wurtzite CGS and standard monoclinic $Cu_{31}S_{16}$ (JCPDS No. 23-0959).

Figure S13

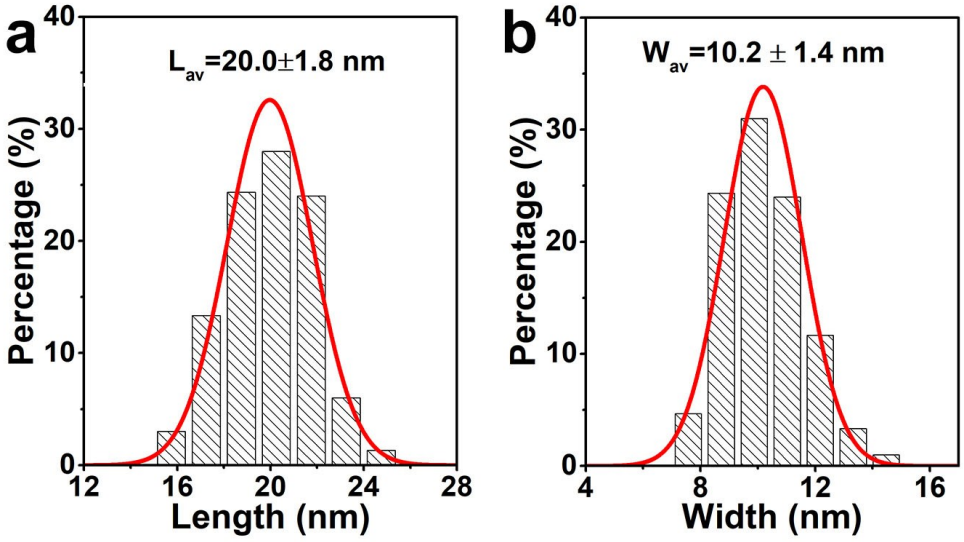


Figure S13. Size distribution histograms of (a) length and (b) width of quasi-2D CGS nanodisks.

Figure S14

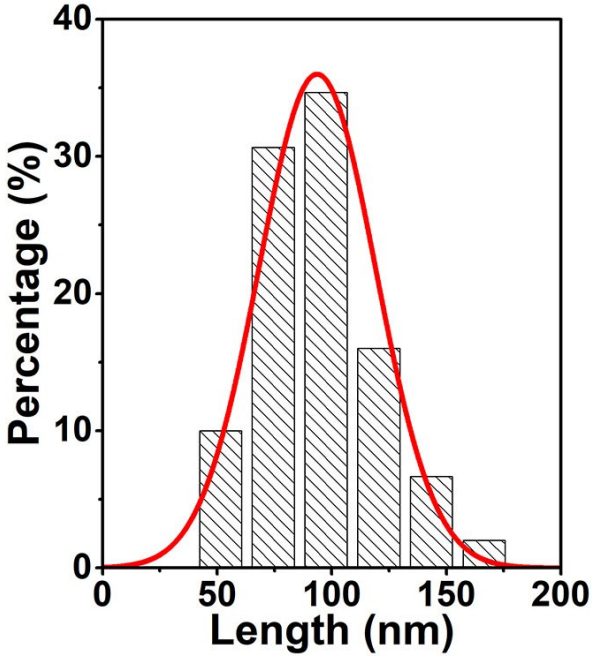


Figure S14. Size distribution histogram of 2D CGS nanoplates.

Figure S15

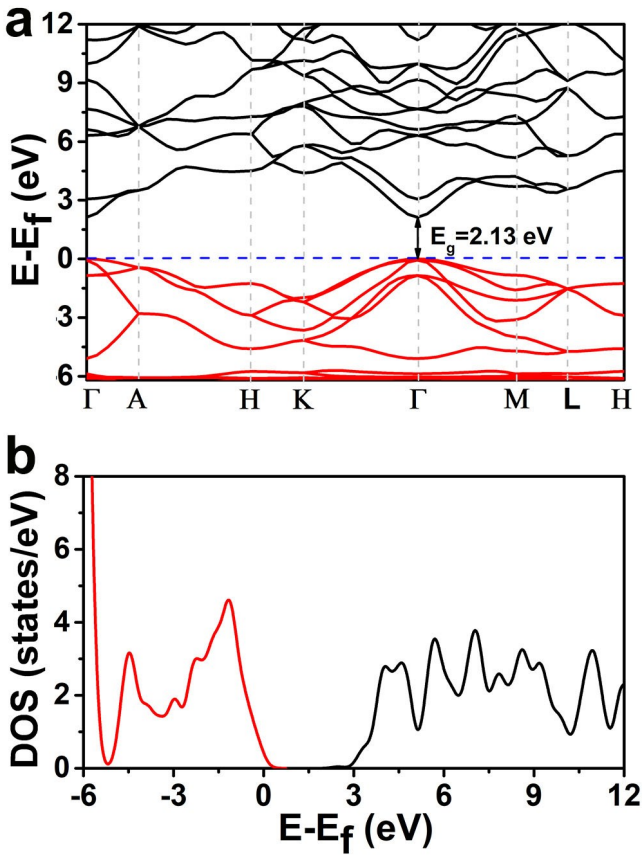


Figure S15. (a) The calculated electronic band structure, in which blue dash line represents Fermi level of bulk CGS. (b) density of state (DOS) of the bulk wurtzite CGS.

Figure S16

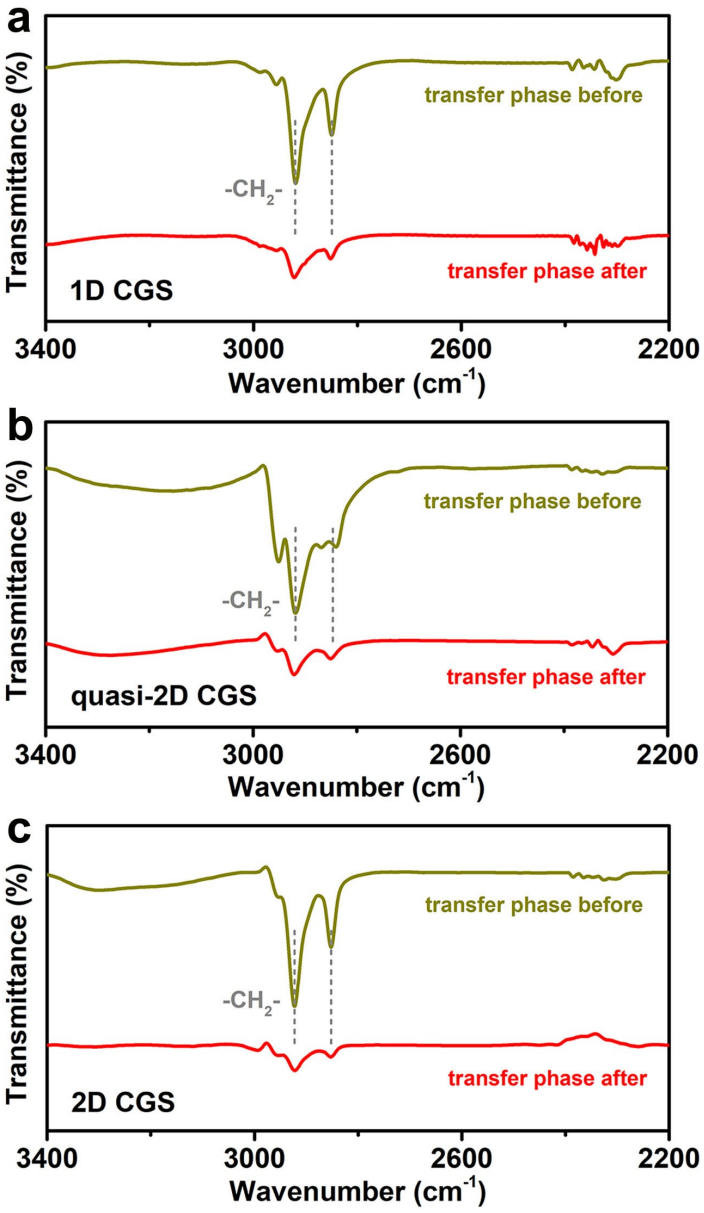


Figure S16. FTIR spectra of different dimensional CGS NCs before and after phase transfer: (a) 1D CGS nanorods, (b) quasi-2D CGS nanodisks and (c) 2D CGS nanoplates.

Figure S17

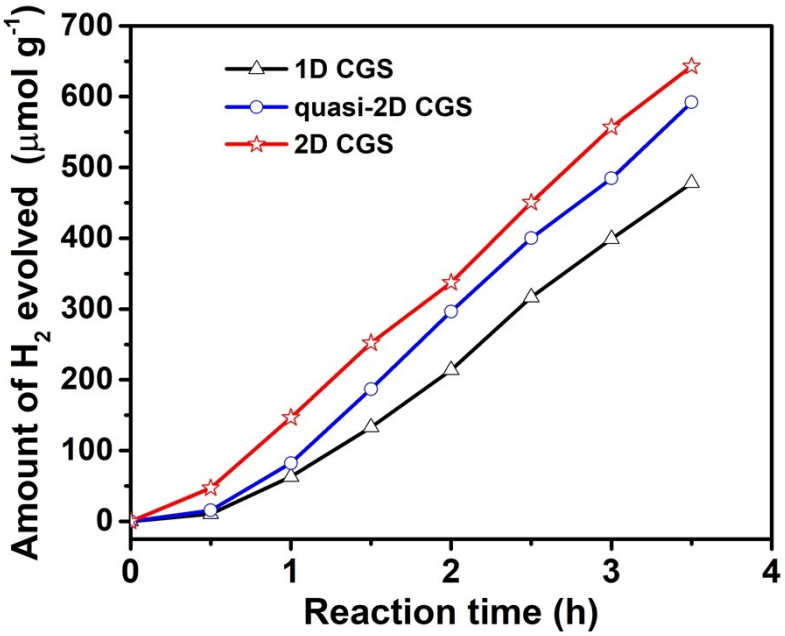


Figure S17. Photocatalytic hydrogen evolution of 1D CGS nanorods, quasi-2D CGS nanodisks and 2D CGS nanoplates under simulated solar light.

Figure S18

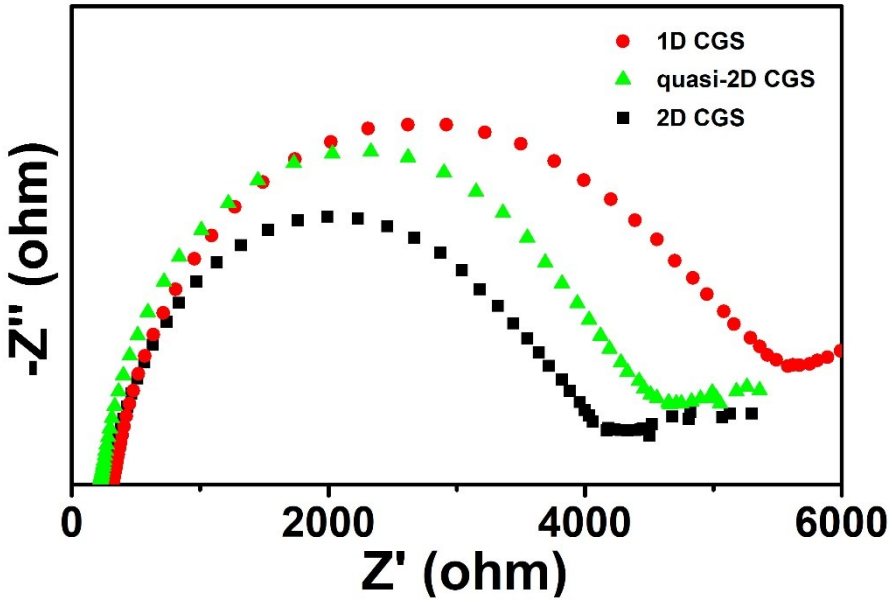
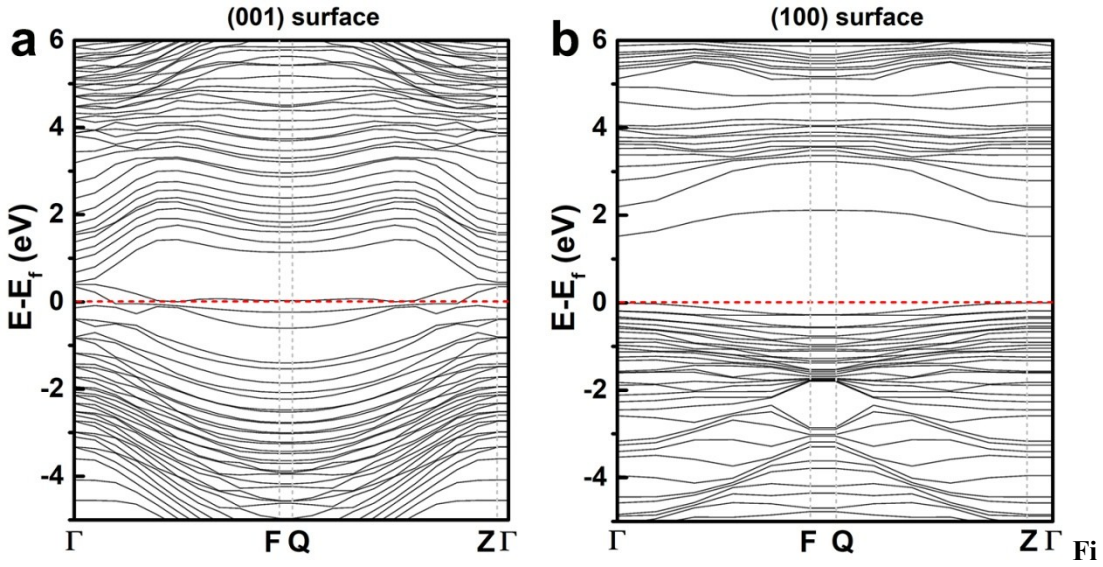


Figure S18. Nyquist plots of 1D CGS nanorods, quasi-2D CGS nanodisks and 2D CGS nanolates.

Figure S19



gure S19. Electronic band structure of different CGS surfaces: (a) (001) surface and (b) (100) surface. The red dash line represents Fermi levels of the corresponding CGS surface.