Supporting Information:

Analogous of Self-assembly and Crystallization: A Chloride-directed Orientated Self-assembly of Cu Nanoclusters and Subsequent growth of $Cu_{2-x}S$ Nanocrystals

Jiale Liu,[a] Ye Tian,[a] Zhennan Wu,[a] Lin Ai,[a] Yi Liu,[a] Jianli Cui,[b,] Weili Yu,[c] Hao Zhang,[a,]* and Bai Yang[a]*

[a] State Key Laboratory of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, P. R. China. E-mail: hao_zhang@jlu.edu.cn.

[b] Department of Hand & Foot Surgery, The First Hospital of Jilin University, Changchun 130021, P. R. China. E-mail: tsuijianli@126.com.

[c] The China-US Joint Laboratory, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, Changchun, 130033, P. R. China.

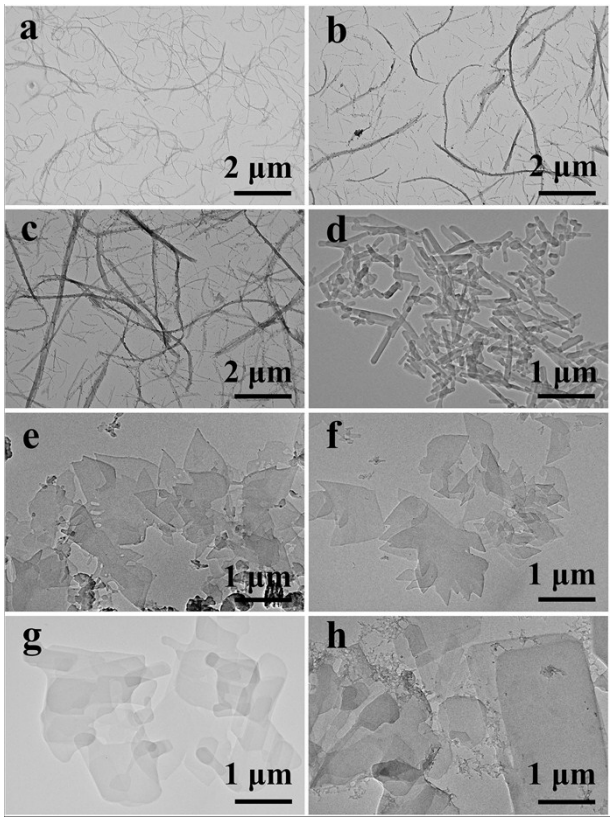

Figure S1. TEM images of the self-assembly architectures of Cu nanoclusters that are prepared with $CuCl_2$-to-$CuAc_2$ molar feed ratio of 0/10 (a), 0.5/9.5 (b), 1/9 (c), 2/8 (d), 3/7 (e), 5/5 (f), 7/3 (g) and 10/0 (h).

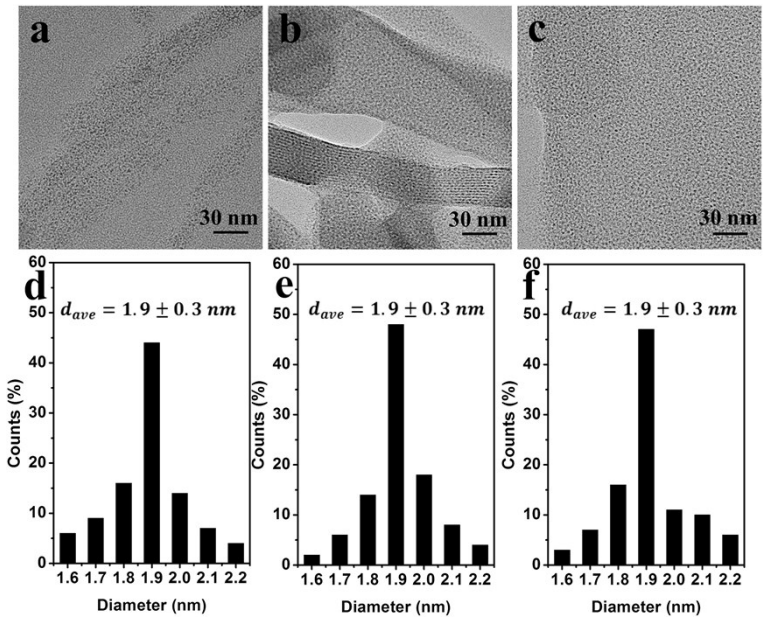

Figure S2. High magnification TEM images (a-c) and corresponding size distribution (d-f) of Cu SANWs (a, d), SANRs (b, e) and SASs (c, f) that are prepared with the $CuCl_2$-to-$CuAc_2$ molar feed ratio of 0/10 (a, d), 2/8 (b, e) and 10/0 (c, f).

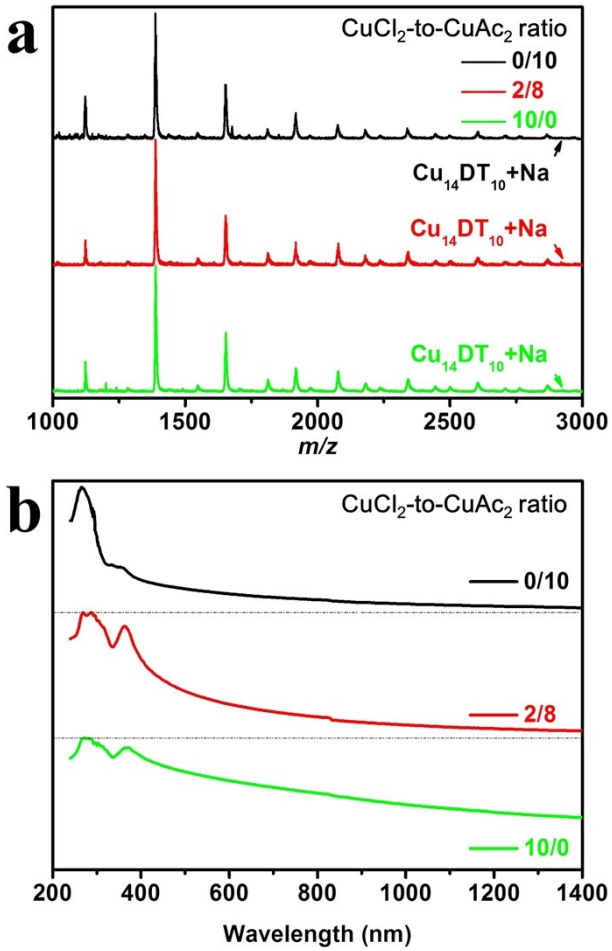

Figure S3. MALDI-TOF MS (a) and UV-vis absorption spectra (b) of the self-assembly architectures of Cu nanoclusters that are prepared with $CuCl_2$-to-$CuAc_2$ molar feed ratio of 0/10, 2/8 and 10/0, which correspond to Cu SANWs, SANRs and SASs, respectively.

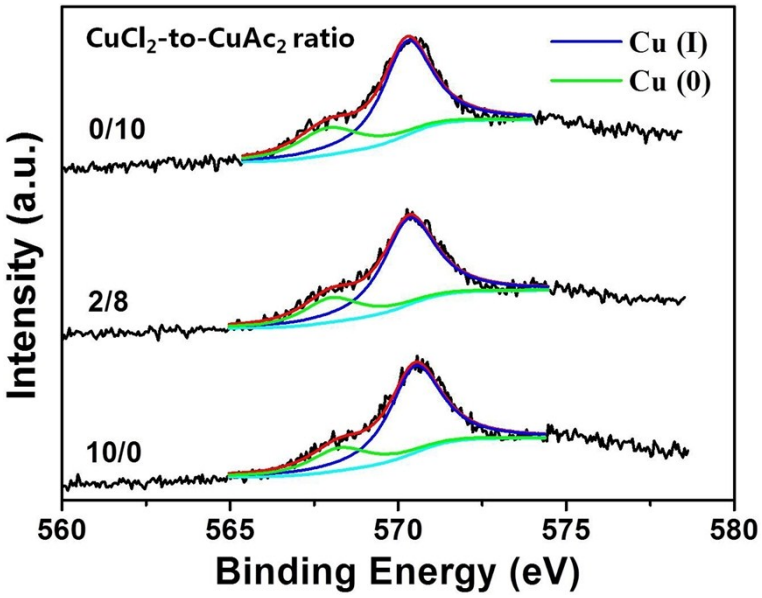

Figure S4. Cu LMM XAES spectra of Cu SANWs, SANRs and SASs that are prepared with the $CuCl_2$-to-$CuAc_2$ molar feed ratio of 0/10, 2/8 and 10/0. As to different self-assembly architectures, the Cu(I)/Cu(0) molar ratio are fixed at 1/0.41, showing the unchanged composition of $Cu(0)_4Cu(I)_{10}DT_{10}$.

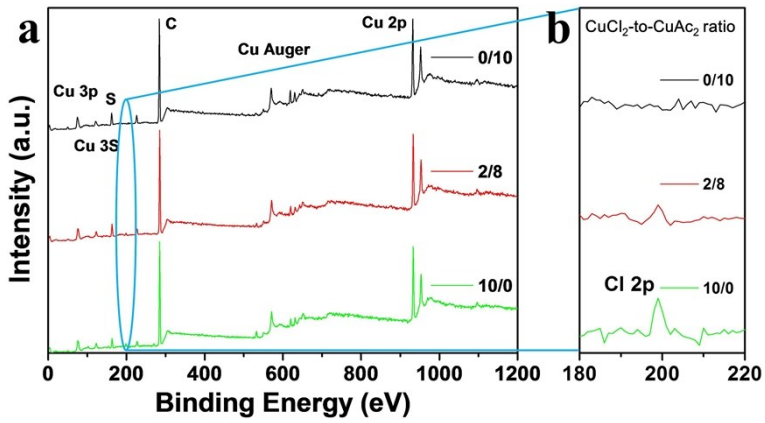

Figure S5. XPS survey spectrum (a) and Cl 2p spectrum (b) of Cu SANWs, SANRs and SASs. The Cl 2p spectrum indicates the different content of Cl^-.

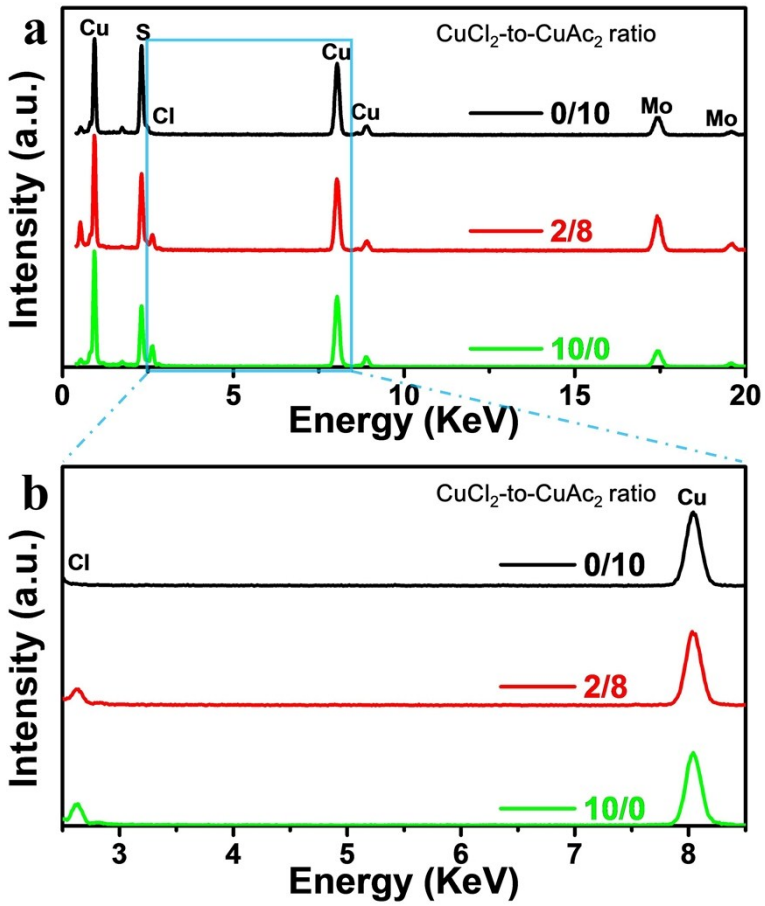

Figure S6. EDX (a) and the magnified spectra (b) of Cu SANWs, SANRs and SASs, which indicate that the real Cu-to-Cl atomic ratio is 6.89 and 3.55 in Cu SANRs and SASs. However, there is no Cl^- in Cu SANWs.

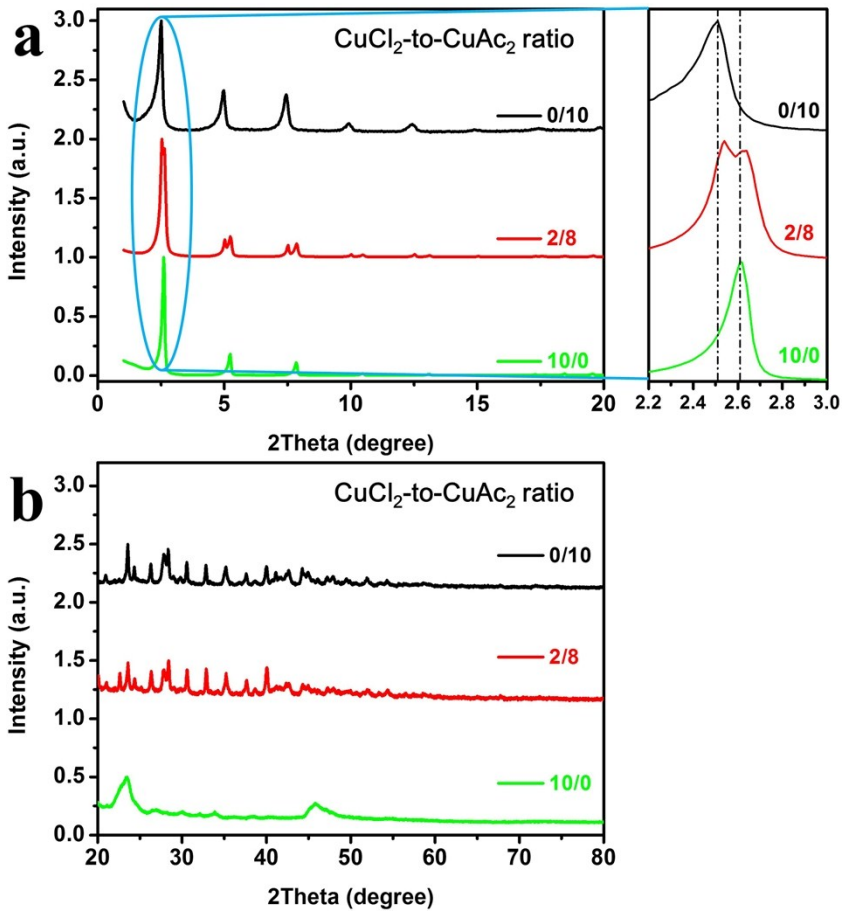

Figure S7. Small-angle (a) and wide-angle (b) XRD patterns of Cu SANWs, SANRs and SASs.

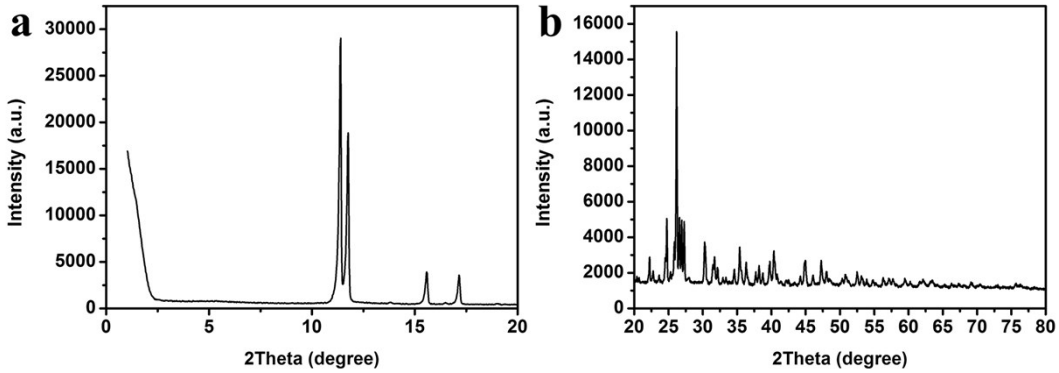

Figure S8. Small-angle (a) and wide-angle (b) XRD patterns of $CuAc_2$.

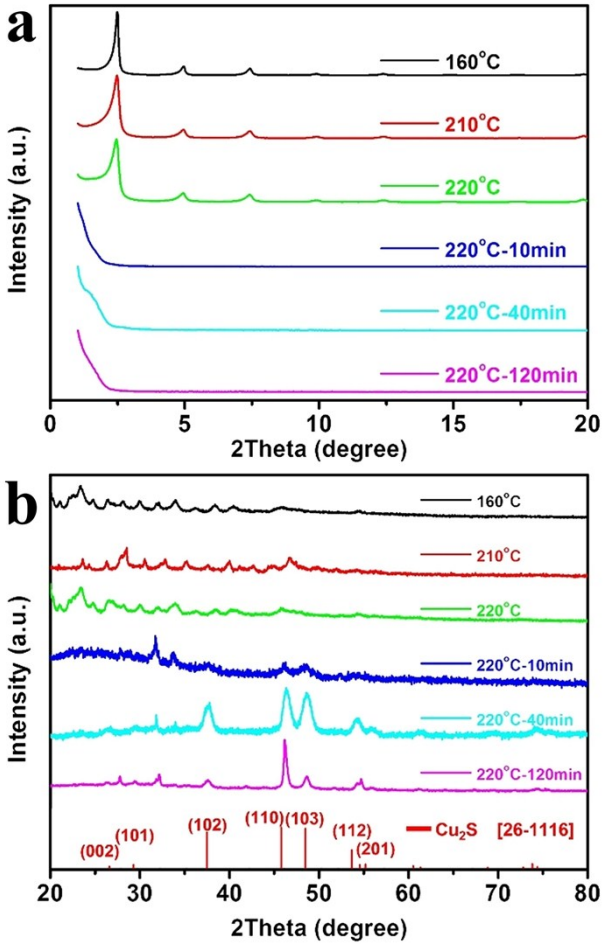

Figure S9. The process tracking small-angle (a) and wide-angle (b) XRD patterns of Cu_2S nanorods that are prepared at 160 ºC, 210 ºC, 220 ºC, 220 ºC for 10 min, 220 ºC for 40 min, and 220 ºC for 120 min.

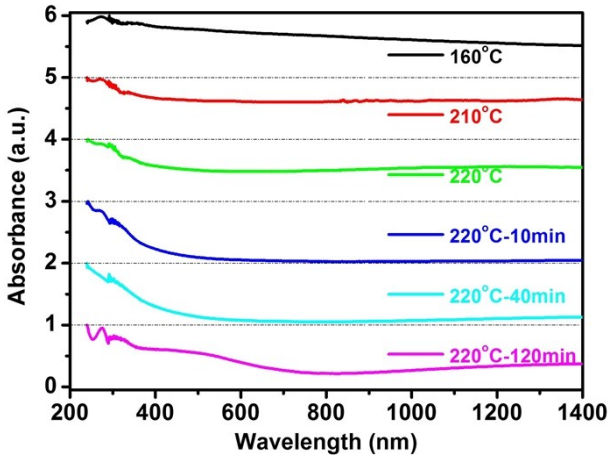

Figure S10. The process tracking steady-state absorption spectra of Cu_2S nanorods that are prepared at 160 ºC, 210 ºC, 220 ºC, 220 ºC for 10 min, 220 ºC for 40 min, and 220 ºC for 120 min.

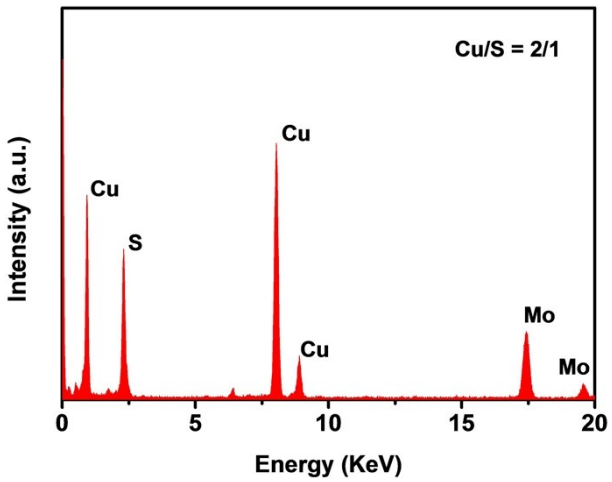

Figure S11. EDX spectrum of $Cu_{2-x}S$ nanorods, which reveals the Cu-to-S molar ratio of 2:1.

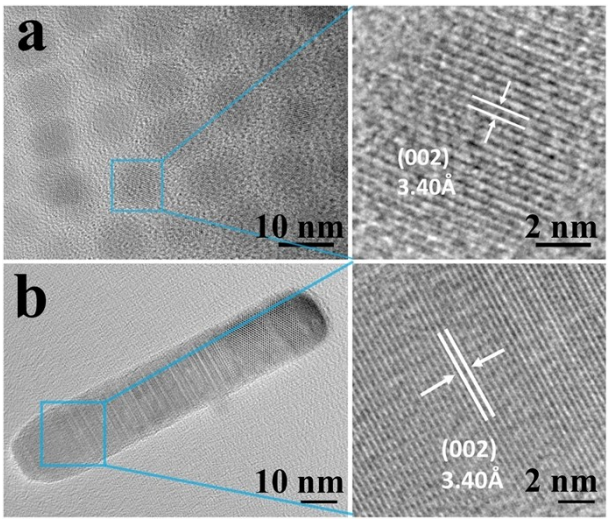

Figure S12. HRTEM images of Cu_2S nanoparticles (a) and nanorods (b) which are prepared at 220 ºC for 40 min and 120 min using $CuAc_2$ as the Cu source.

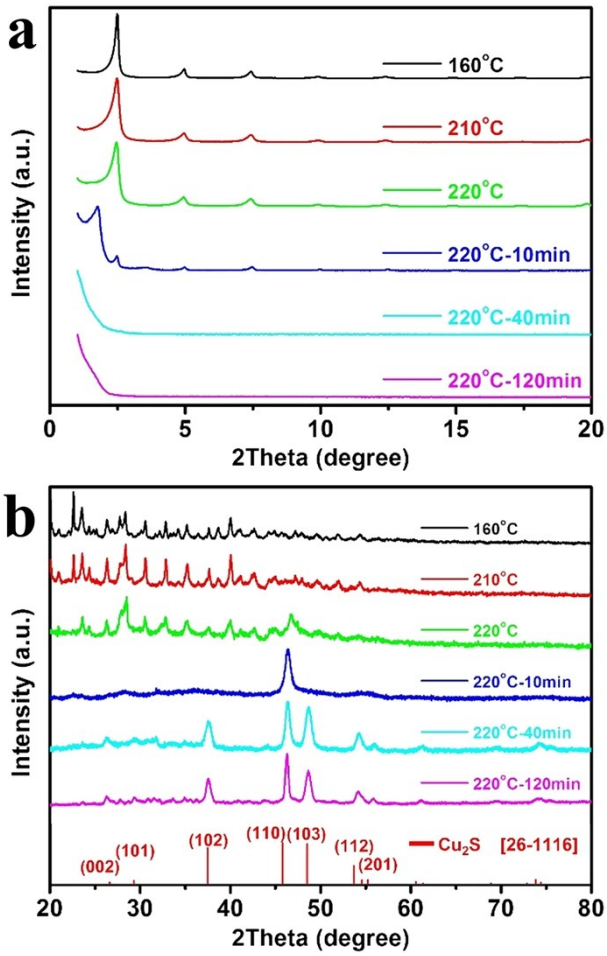

Figure S13. The process tracking small-angle (a) and wide-angle (b) XRD patterns of Cu_2S nanodisks that are prepared at 160 ºC, 210 ºC, 220 ºC, 220 ºC for 10 min, 220 ºC for 40 min and 220 ºC for 120 min.

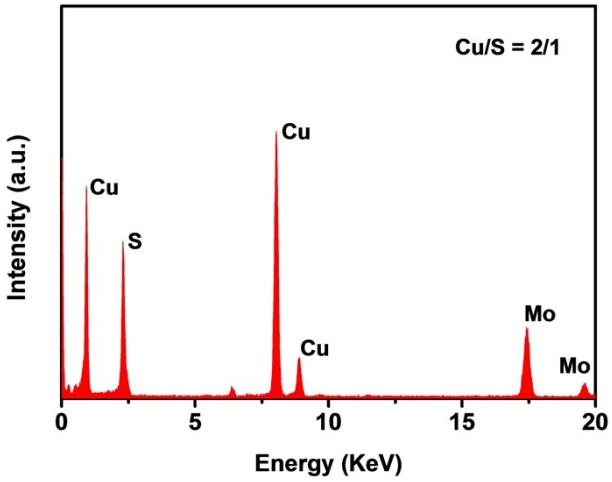

Figure S14. EDX spectrum of $Cu_{2-x}S$ nanodisks, which reveals the Cu-to-S molar ratio of 2:1.

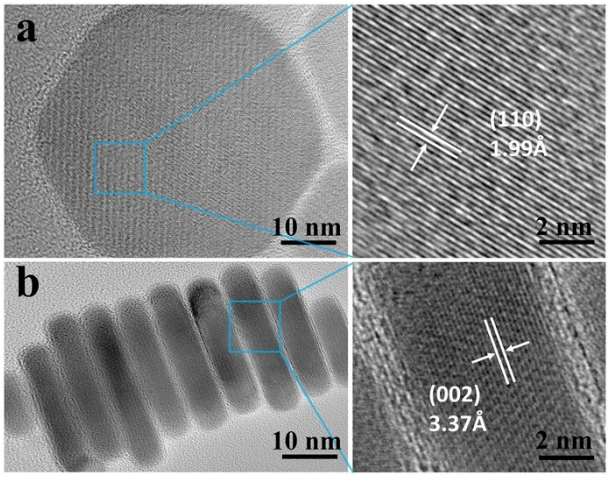

Figure S15. Up (a) and side (b) HRTEM images of Cu_2S nanodisks that are prepared at 220 ºC for 120 min with $CuCl_2$-to-$CuAc_2$ molar feed ratio of 2/8.

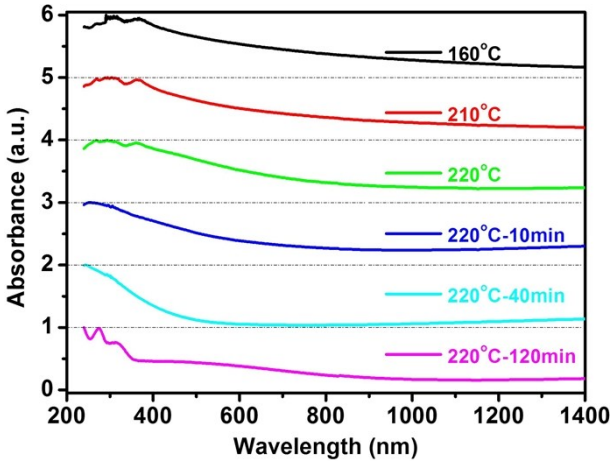

Figure S16. The process tracking steady-state absorption spectra of Cu_2S nanodisks that are prepared at 160 ºC, 210 ºC, 220 ºC, 220 ºC for 10 min, 220 ºC for 40 min, and 220 ºC for 120 min.

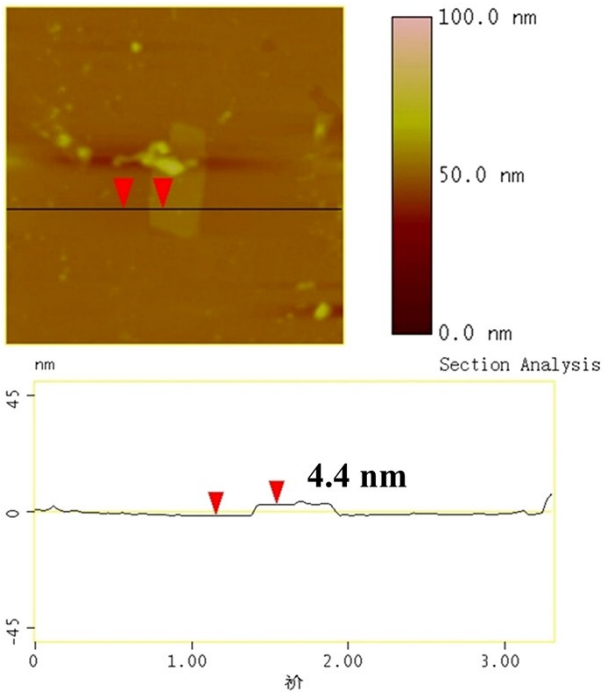

Figure S17. AFM image of $Cu_{1.8}S$ nanosheets that are prepared at 220 ºC for 120 min using $CuCl_2 \cdot 2H_2O$ as the Cu source.

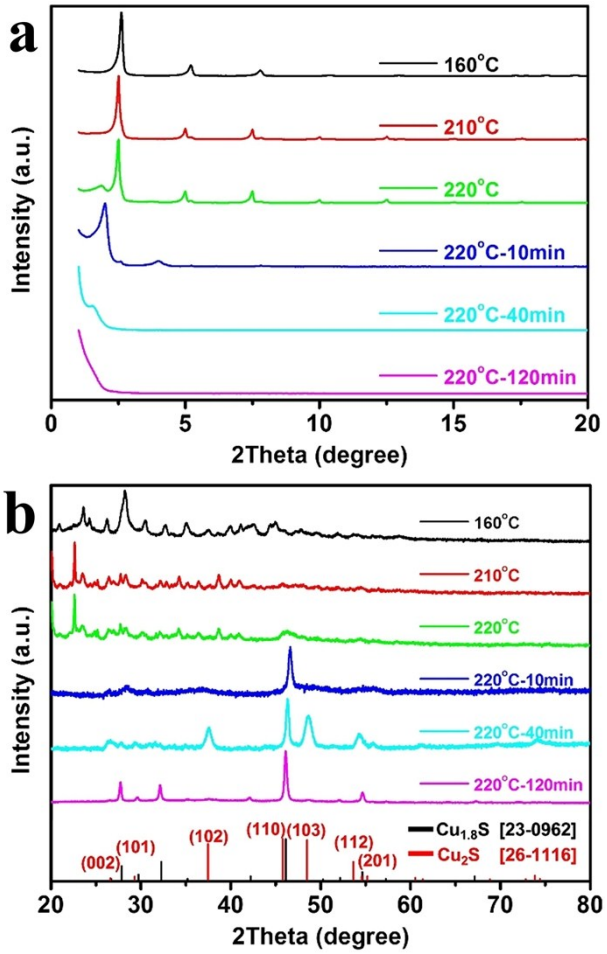

Figure S18. The process tracking small-angle (a) and wide-angle (b) XRD patterns of $Cu_{1.8}S$ nanosheets that are prepared at 160 ºC, 210 ºC, 220 ºC, 220 ºC for 10 min, 220 ºC for 40 min, and 220 ºC for 120 min.

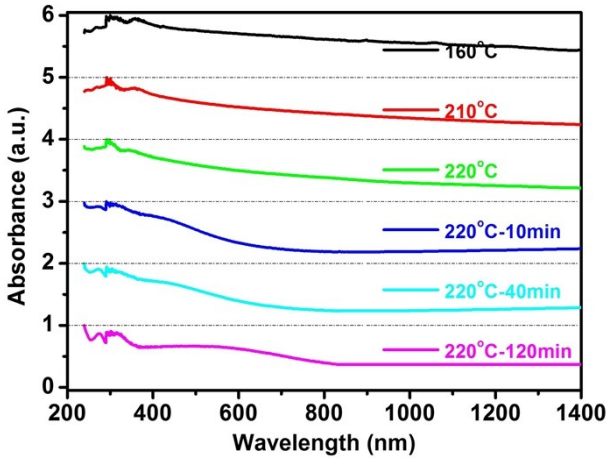

Figure S19. The process tracking steady-state absorption spectra of $Cu_{1.8}S$ nanosheets that are prepared at 160 ºC, 210 ºC, 220 ºC, 220 ºC for 10 min, 220 ºC for 40 min, and 220 ºC for 120 min.

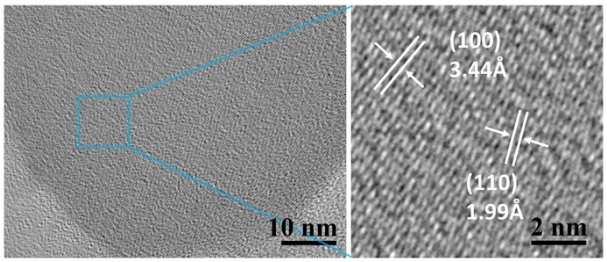

Figure S20. HRTEM images of Cu_2S nanosheets that are prepared at 220 ºC for 40 min using $CuCl_2 \cdot 2H_2O$ as the Cu source.

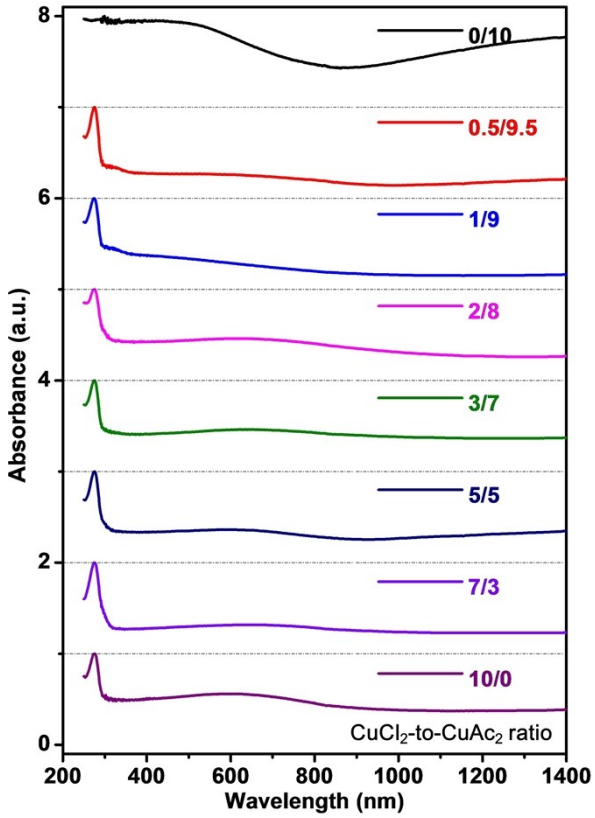

Figure S21. Steady-state absorption spectra of $Cu_{2-x}S$ nanocrystals that are prepared with $CuCl_2$-to-$CuAc_2$ molar feed ratio of 0/10, 0.5/9.5, 1/9, 2/8, 3/7, 5/5, 7/3 and 10/0.

The ratio of $CuCl_2 \cdot 2H_2O$	Diameter along (001) (nm)	Stdev	Thickness along [001] (nm)	Stdev	Diameter-thickness ratio	Stdev
0	9.94	1.10	72.52	29.12	0.16	0.06
5	15.65	2.50	8.64	0.73	1.81	0.23
10	25.52	2.80	12.95	0.94	1.97	0.11
20	35.52	4.85	11.63	0.71	3.05	0.39
30	36.77	2.43	10.88	1.06	3.41	0.37
50	41.25	5.28	9.74	1.11	4.29	0.80
70	56.85	16.11	8.04	1.24	7.24	3.33
100	93.44	24.84	4.36	--	21.43	--

Table 1. Summary of the size and diameter-to-thickness ratio of $Cu_{2-x}S$ nanocrystals that are prepared with different $CuCl_2$-to-$CuAc_2$ molar feed ratio.

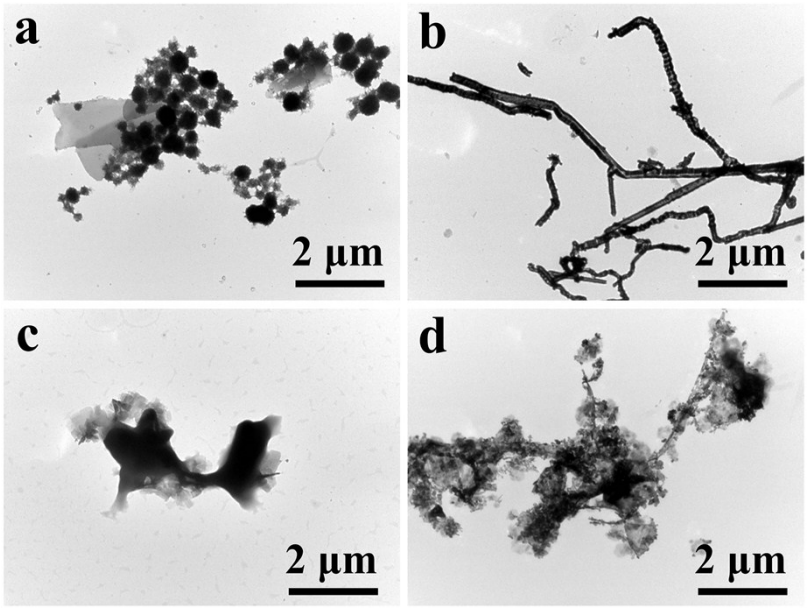

Figure S22. TEM images of the self-assembly architectures of Cu nanoclusters at 160 ºC (a, c) and the $Cu_{2-x}S$ nanocrystals fromed at 220 ºC for 120 min (b, d) using $CuBr_2$ (a, b) and CuI (c, d) as the source.

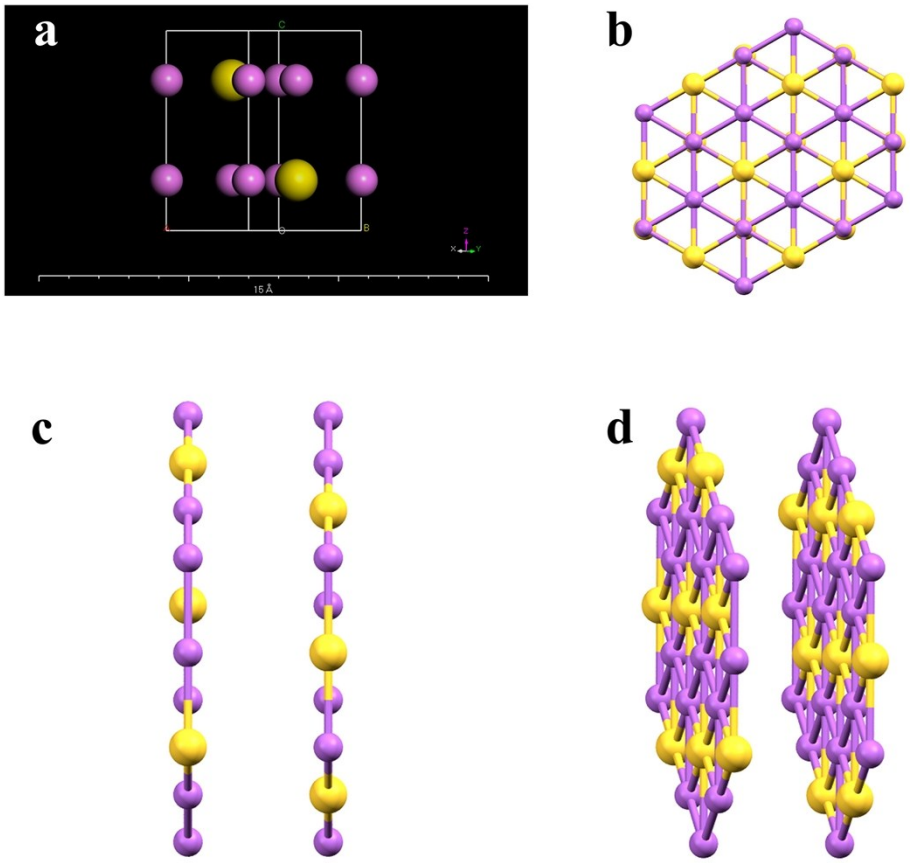

Figure S23. (a) The unit cell of hexagonal Cu_2S (chalcocite, JCPDS No. 26-1116). Crystal atom configuration ball-and-stick model diagrams of hexagonal Cu_2S along c axis (b), along b axis (c) and along b slightly inclines to c axis (d).

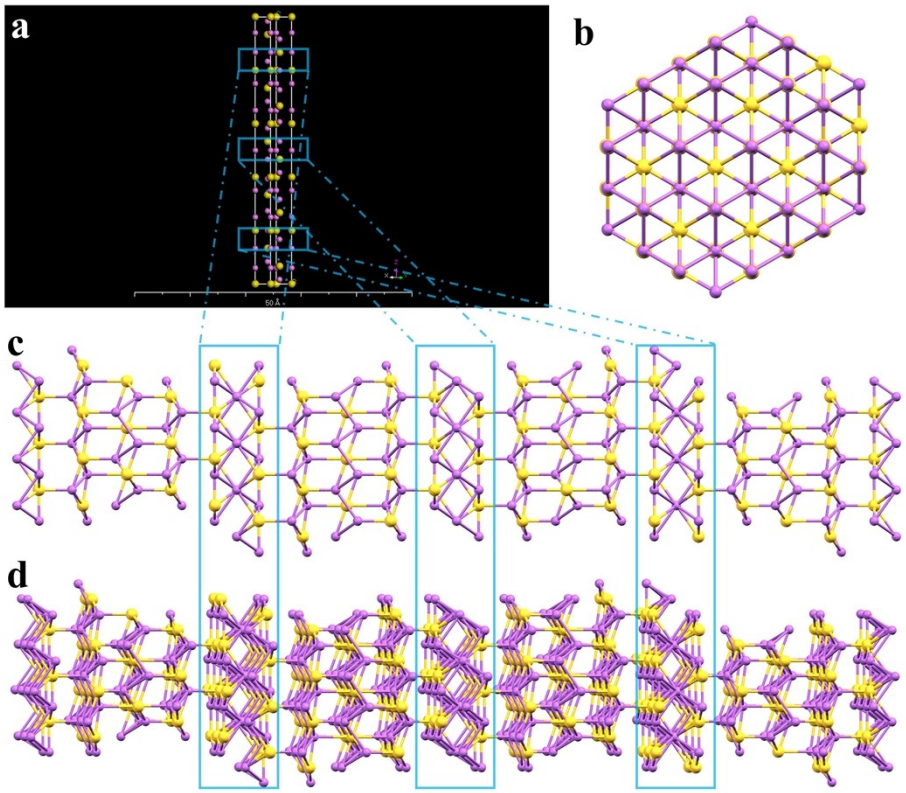

Figure S24. (a) The unit cell of hexagonal $Cu_{1.8}S$ (Digenite, JCPDS No. 23-0962). Crystal atom configuration ball-and-stick model diagrams of hexagonal Cu_2S along c axis (b), along b axis (c) and along b slightly inclined to c axis (d).