Electronic supplementary information (ESI)

Tuning the Plasmonic Resonance of Cu_{2-x}S

Nanocrystals: Effects of Crystal Phase, Morphology

and Surface Ligands

Dongxu Zhu, ^a Aiwei Tang, * ^{ab} Lan Peng, ^a Zhenyang Liu, ^a Chunhe Yang, ^a and Feng Teng*^b

^aDepartment of Chemistry, School of Science, Beijing JiaoTong University, Beijing 100044, China. E-mail: awtang@bjtu.edu.cn

^bKey Laboratory of Luminescence and Optical Information, Ministry of Education, Beijing JiaoTong University, Beijing 100044, China.



Fig.S1 XRD patterns of the product synthesized by using the Cu/S feeding ratio of 2:1, which were measured on the day of synthesis and after 50 days upon exposure to air.



Fig.S2 TEM images of the as-obtained CuS nanodisks obtained at different reaction time: (a)60 min; (b) 90 min and (c) 180 min.(d) XRD patterns of the product obtained at 180 min, and the bottom lines represent the standard diffraction peaks of the hexagonal CuS (JCPDS No.06-0464); (e) LSPR absorption spectra on the wavelength scale of the products obtained for different reaction time, and the inset shows the corresponding LSPR spectra on the energy scale; (f) LSPR wavelength as a function of the average size, and the inset shows the average size versus the reaction time.



Fig.S3 XPS spectra of Cu 2p in the as-obtained products with different phases, and all the spectra were normalized.



Fig.S4 EDS patterns of Cu_{2-x}S NCs synthesized by using different Cu/S feeding molar ratios: (a)1:1;(b)1.2:1;(c)1.4:1;(d)1.75:1;(e)2:1.



Fig.S5 The comparison of the Cu/S molar ratio between the feeding ratios and the EDS results for the different $Cu_{2-x}S$ NCs synthesized by using the different Cu/S feeding ratios.



Fig.S6 The HRTEM images $Cu_{2-x}S$ NCs synthesized by injection of S-OM precursors into Cu-OA:OM(1:1) precursors.



Fig.S7 XRD pattern of the products synthesized by injection S-OM into Cu-OM precursors, and the bottom vertical lines represent the standard diffraction peaks of monoclinic Cu_7S_4 (Roxbyite, JCPDS No.23-0958) and monoclinic $Cu_{31}S_{16}$ (Djureleite, JCPDS No.23-0959).



Fig.S8 High-resolution XPS spectra of (a) Cu 2p and (b) S 2p for the product synthesized by injection of S-OM into Cu-OM precursors.

Figure. S9



Fig.S9 FTIR spectra of the products synthesized by injection of S-OM and S-OA:OM(1:1) into the Cu-OM precursors.



Fig.S10 TEM images of the products synthesized by injection of S-OA:OM (1:1) into the Cu-OA:OM(1:1) precursors for different reaction time: (a) 5 min; (b) 10 min; (c) 30 min; (d) 60 min; (e) 120 min; (f) XRD patterns of the products obtained at different reaction time, and the bottom lines are the standard diffraction peaks of monoclinic Cu_7S_4 (JCPDS 23-0958).



Fig.S11 (a) NIR LSPR absorption spectra of the products synthesized by injection of S-OA:OM(1:1) into the Cu-OA:OM(1:1) precursors for different reaction time; (b) The calculated carrier density and the LSPR wavelength as a function of reaction time.



Fig.S12 TEM images of the products after post-treatment by DDT at 120 °C for different reaction time: (a) 30 min; (b) 60 min; (c) 90 min. (d) The average diameter of the products versus reaction time after post-treatment by DDT at room temperature and at 120 °C; (e) XRD patterns and (f) LSPR spectrum of the products after post-treatment at 120 °C for 30 min, and the inset of Figure (f) is the LSPR spectrum on the energy scale.



Fig.S13 FTIR spectra of the products (a) before and (b, c) after post-treatment by DDT: (b) at 120 $^{\circ}$ C and (c) room temperature for 2 h.