

## Supplementary Information for

### Direct synthesis of highly luminescent Cu-Zn-In-S quaternary nanocrystals with tunable photoluminescence spectra and decay times

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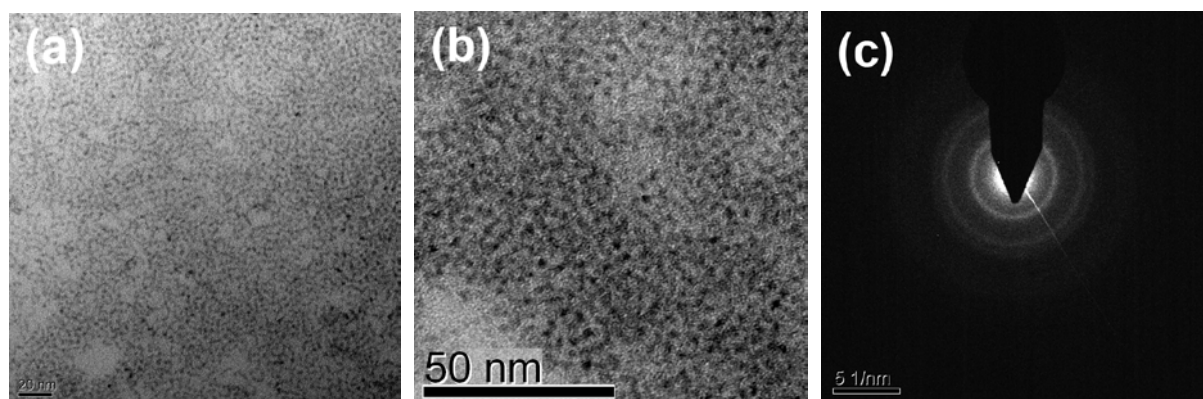
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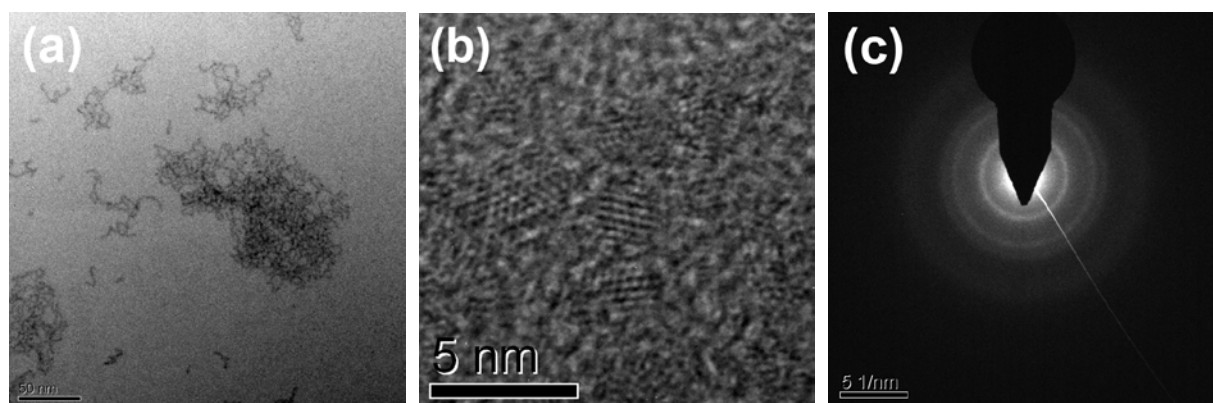
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**Table S1** Fitting results of PL decay curves of CZIS NCs with different reaction time prepared at Cu/Zn precursor ratio of 1:1, deriving from  $I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$

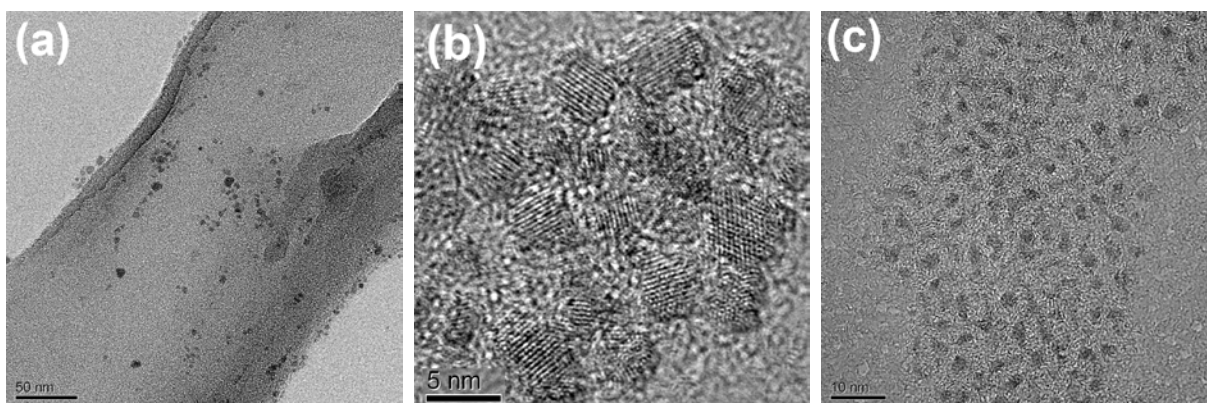
Reaction time	$\tau_1/\text{ns}$	$A_1\%$	$\tau_2/\text{ns}$	$A_2\%$	$\tau_3/\text{ns}$	$A_3\%$	$\tau_{\text{av}}/\text{ns}$
30 min	11.4	36.2	59.0	42.2	175.5	15.9	112.6
60 min	14.3	30.3	77.4	45.7	222.9	19.0	149.2
90 min	15.0	28.1	83.7	44.9	250.3	20.4	172.2



**Fig. S1** TEM image (a), (b) and corresponding SAED pattern (c) of CZIS NCs prepared at Cu/Zn precursor ratio of 1:5

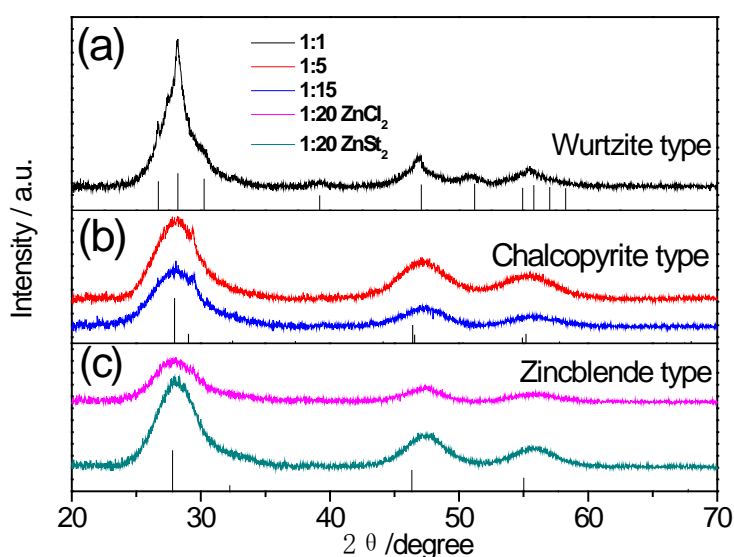


**Fig. S2** TEM image (a), HRTEM image (b), and corresponding SAED pattern (c) of CZIS NCs prepared at Cu/Zn precursor ratio of 1:20



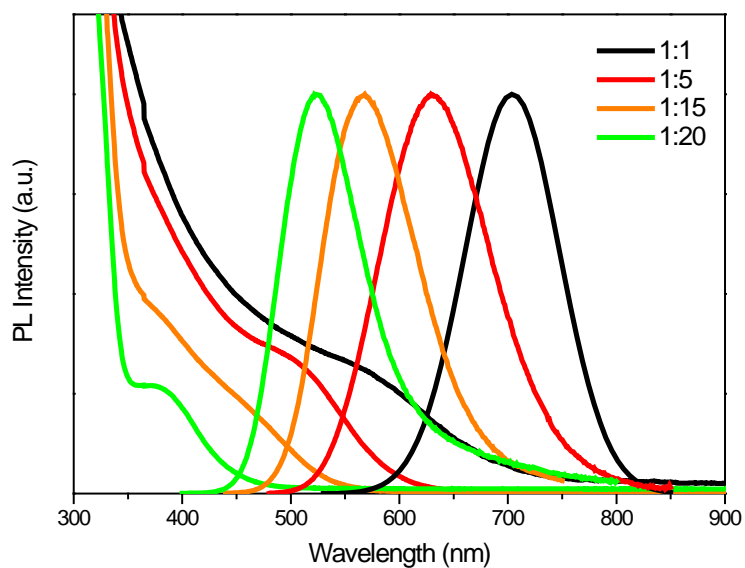
**Fig. S3** (a) TEM image and (b) HRTEM image of CZIS NCs prepared at Cu/Zn precursor ratio of 1:1, (c) TEM image of CZIS NCs prepared at Cu/Zn precursor ratio of 1:15.

The size distribution of the resulting NCs prepared at Cu/Zn precursor ratio of 1:1, 1:5, 1:15 and 1:20 was  $5.4 \pm 1.6$  nm,  $2.5 \pm 0.5$  nm,  $2.5 \pm 0.6$  nm and  $2.3 \pm 0.7$  nm respectively.

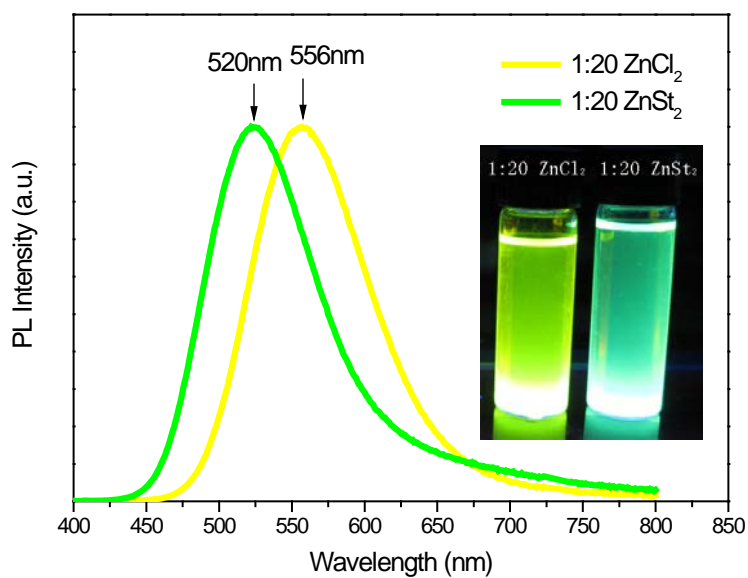


**Fig. S4** XRD patterns of CZIS NCs prepared at Cu/Zn precursor ratio of 1:1, 1:5, 1:15, 1:20 ZnCl<sub>2</sub> and 1:20 ZnSt<sub>2</sub> (a) wurtzite structure (b) chalcopyrite structure (c) zinc blend structure.

As shown in **Fig. S4**, when Cu/Zn precursor ratio was 1:1, the resulting CZIS NCs had a wurtzite structure (JCPDS 32-0340). While decreasing Cu/Zn precursor ratio to 1:5 and 1:15, the resulting CZIS NCs had a chalcopyrite structure (JCPDS 47-1371) and further decreased Cu/Zn precursor ratio to 1:20, a zinc blend structure (JCPDS 47-1370) was obtained. This interesting phenomenon is probably due to the increase of ZnS constituent in CZIS structure when Cu/Zn precursor ratio changed from 1:1 to 1:20 or the different growth temperature. The shift of the other two characteristic peaks in Fig. S4 (b) and (c) was due to the deviation of product stoichiometry from standard of chalcopyrite and zinc blend structure CZIS NCs.



**Fig. S5** Absorption and emission spectra of CZIS NCs prepared at Cu/Zn precursor ratio of 1:1, 1:5, 1:15 with  $\text{ZnCl}_2$  and 1:20 with  $\text{ZnSt}_2$ .



**Fig. S6** Emission spectra of CZIS NCs prepared at Cu/Zn precursor ratio of 1:20 with  $\text{ZnCl}_2$  and  $\text{ZnSt}_2$  as Zn precursors respectively, inset is the photograph of corresponding CZIS samples dispersed in hexane under a 365 nm UV lamp.