Electronic Supplementary Information (ESI)

for

Controllable copper deficiency in $Cu_{2-x}Se$ nanocrystals with tuning localized surface plasmon resonance and enhancing chemiluminescence †

Shao Qing Lie[a], Dong Mei Wang[a], Ming Xuan Gao[a], and Cheng Zhi Huang*[ab]*

[a] Key Laboratory of Luminescence and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, P. R. China.

[b] College of Pharmaceutical Sciences, Southwest University, Chongqing, 400715, P. R. China.

**Corresponding author:wangdm@swu.edu.cn,and chengzhi@swu.edu.cn*

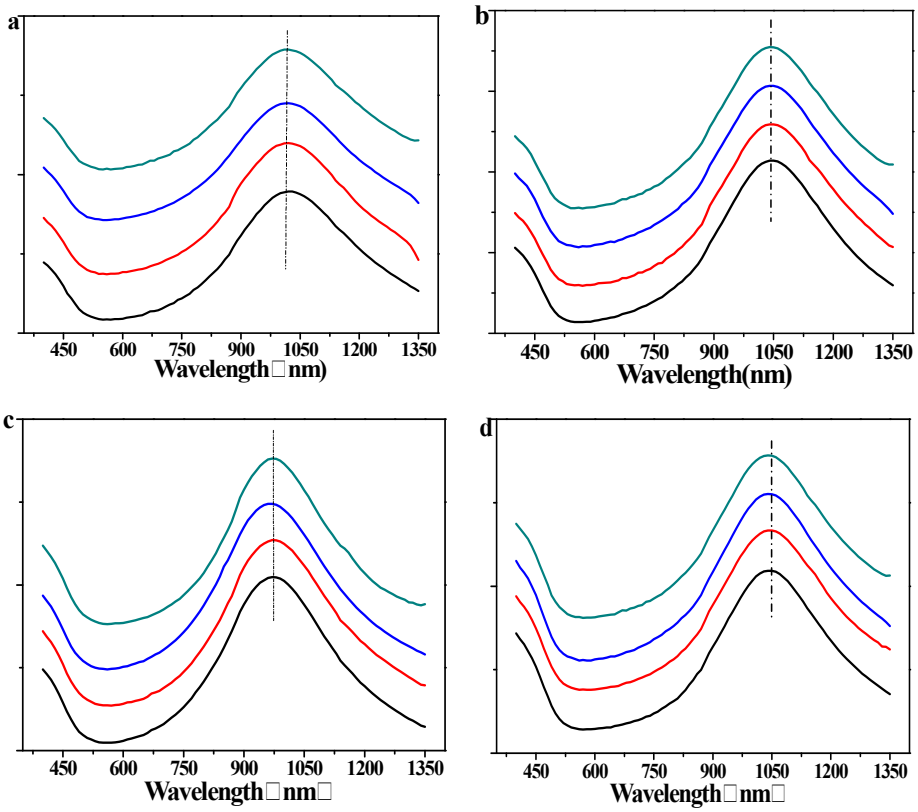

Fig. S1 The stability of $Cu_{2-x}Se$ NCs by monitoring the absorption change every 7 days within a mouth when stored in 4 ◦C refrigerator. (a) $Cu_{2-x}Se$ NCs stablized by CTAB, (b) $Cu_{2-x}Se$ NCs stablized by SDS, (c) $Cu_{2-x}Se$ NCs stablized by PSS, (d) $Cu_{2-x}Se$ NCs stablized by PVP.

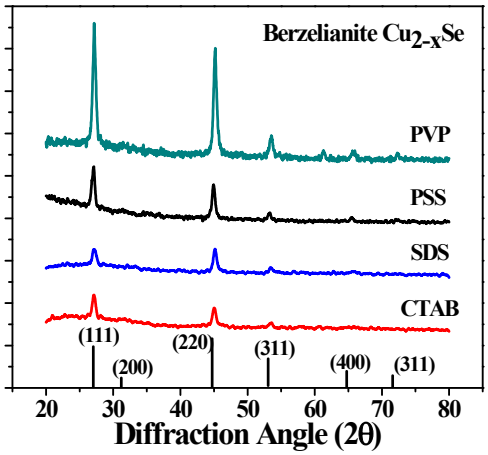

Fig. S2 X-ray diffraction patterns of crystalline $Cu_{2-x}Se$ NCs. XRD of the nanostructures prepared in the presence of surfactants confirmed that the as-prepared $Cu_{2-x}Se$ are generally cubic berzelianite phase. ($Cu_{2-x}Se$, PDF card 06-0680)

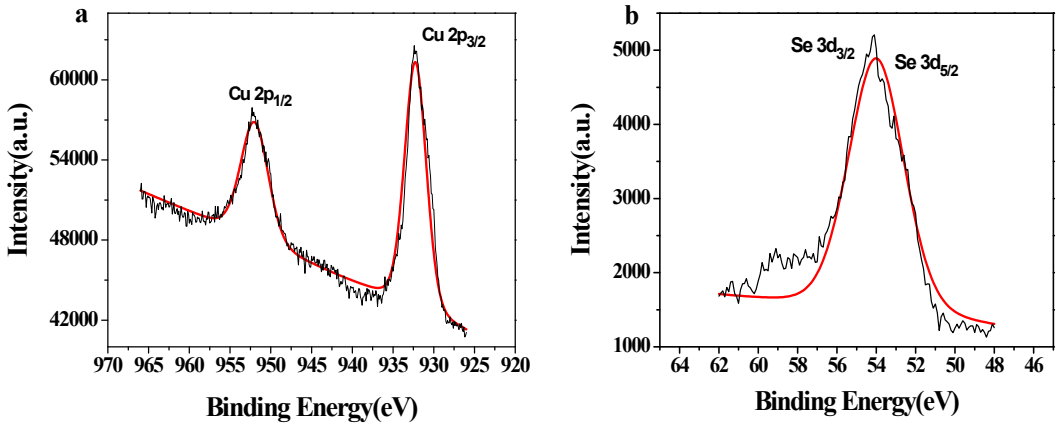

Fig. S3 X-ray photoelectron spectroscopy of $Cu_{2-x}Se$ NCs. (a) The binding energy of Cu 2p. (b) The binding energy of Se 3d.

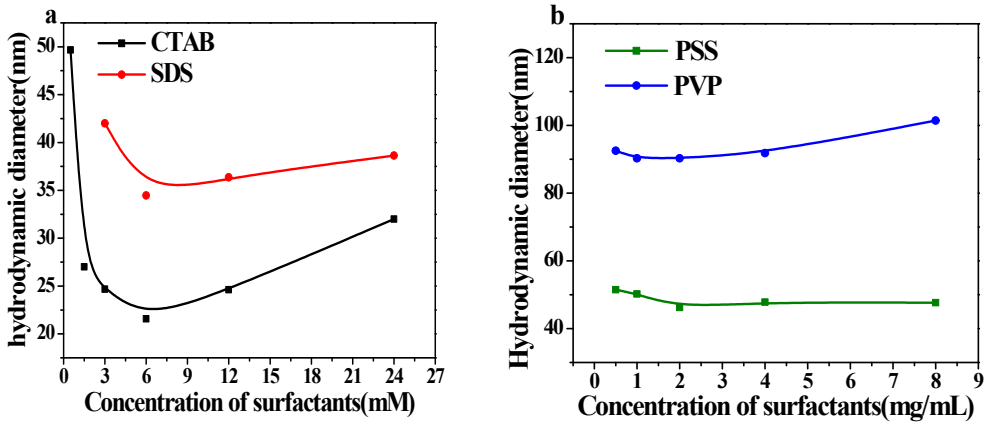

Fig. S4 The hydrodynamic diameter of nanocrystalline $Cu_{2-x}Se$ NCs. With changing the concentration of surfactants, the hydrodynamic diameter of $Cu_{2-x}Se$ NCs depended on the surfactants.

Table. S1 The comparison of the physical parameters. In presence of CTAB, SDS, PSS and PVP with different physical properties, the hydrodynamic diameter of Se NCs, Cu_2Se NCs and $Cu_{2-x}Se$ NCs were different.

surfactant	Molecular weight	electric charge	Hydrodynamic diameter of Se NCs	Hydrodynamic diameter of Cu_2Se NCs	Hydrodynamic diameter of $Cu_{2-x}Se$ NCs
CTAB (6 mM)	364.45	+57.9 mV	29.18 nm	22.56 nm	22.18 nm
SDS (6 mM)	288.38	-38.9 mV	32.8 nm	36.6 nm	35.8 nm
PSS (2 mg/ml)	70000	-55.9 mV	44.28 nm	47.73 nm	45.72 nm
PVP (2 mg/ml)	55000	+7.7 mV	88.26 nm	83.07 nm	82.33 nm

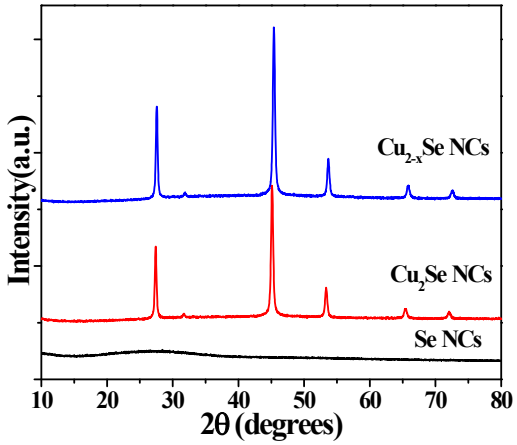

Fig. S5 X-ray diffraction patterns of Se NCs, $Cu_{2-x}Se$ NCs and $Cu_{2-x}Se$ NCs. XRD of the nanostructures prepared in the presence of PSS and the diffraction patterns illustrated a significant shift of diffraction peaks during the conversion from $Cu_{2-x}Se$ NCs to $Cu_{2-x}Se$ NCs.

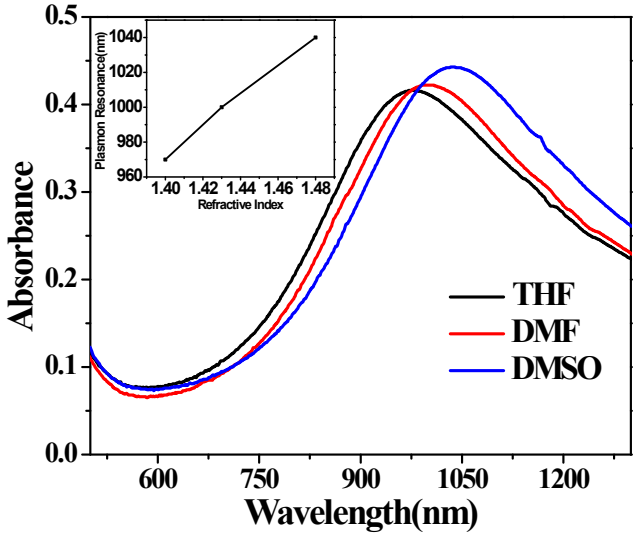

Fig. S6 Localized surface plasmon resonances in absorbance spectra of $Cu_{2-x}Se$NCs capped by PSS. $Cu_{2-x}Se$ NCs dispersed in three different solvents with different refractive index: tetrahydrofuran (THF, 1.4), dimethylformamide (DMF, 1.43) and dimethyl sulfoxide (DMSO, 1.48). The inset showed the dependence of LSPR frequency upon solvent refractive index.

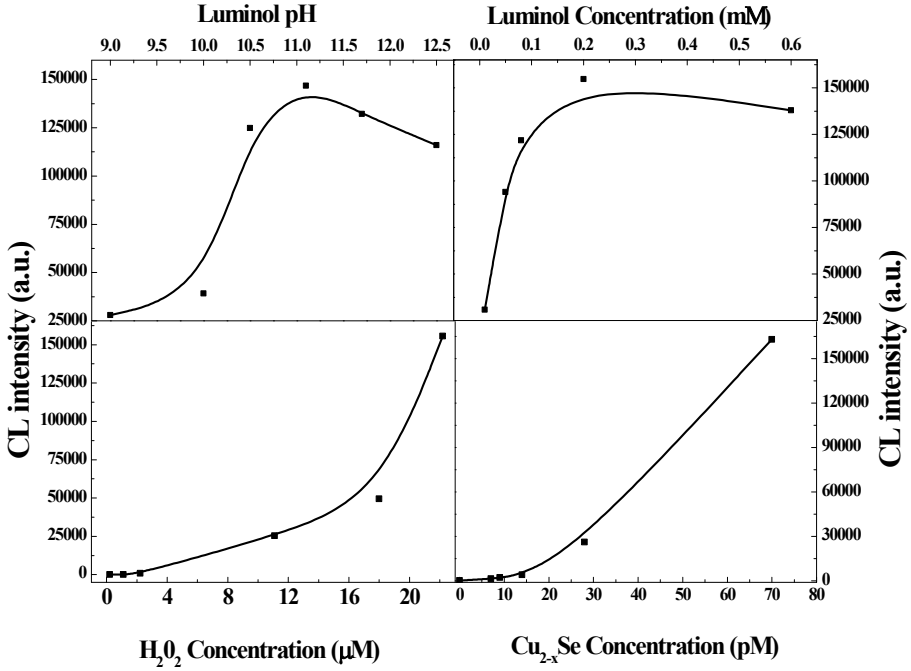

Fig. S7 Effects of the reactant conditions on luminol-H_2O_2 CL system in the presence of PSS-$Cu_{2-x}Se$. (a) Effect of luminol pH: 2.0×10^{-4} M luminol, 22.2 μM H_2O_2, 70.0 pM PSS-$Cu_{2-x}Se$. (b) Effect of luminol concentration: NaOH medium (pH 11.1), 22.2 μM H_2O_2, 70.0 pM PSS-$Cu_{2-x}Se$. (c) Effect of H_2O_2 concentration: 2.0×10^{-4} M luminol in NaOH medium (pH 11.1), 70.0 pM PSS-$Cu_{2-x}Se$. (d) Effect of PSS-$Cu_{2-x}Se$ concentration: 2.0×10^{-4} M luminol in NaOH medium (pH 11.1), 22.2 μM H_2O_2.

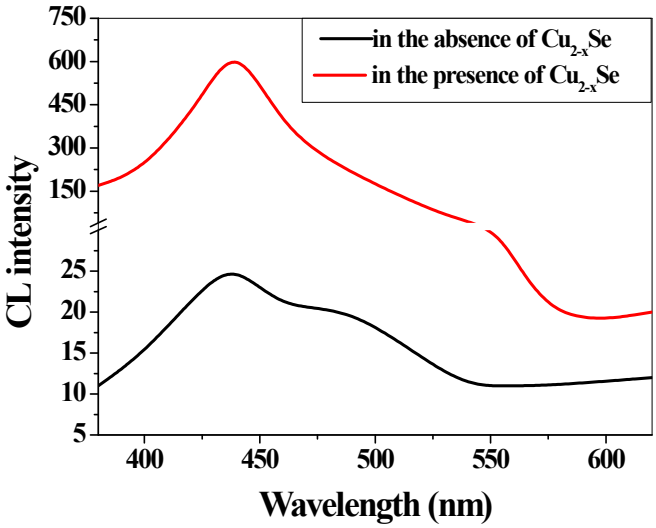

Fig. S8 Chemiluminescent spectra of (a) luminol-H_2O_2-PSS-$Cu_{2-x}Se$, and (b) luminol-H_2O_2. Final concentrations: luminol, 2.0×10^{-4} M; H_2O_2, 22.2 μM; PSS-$Cu_{2-x}Se$, 70.0 pM.

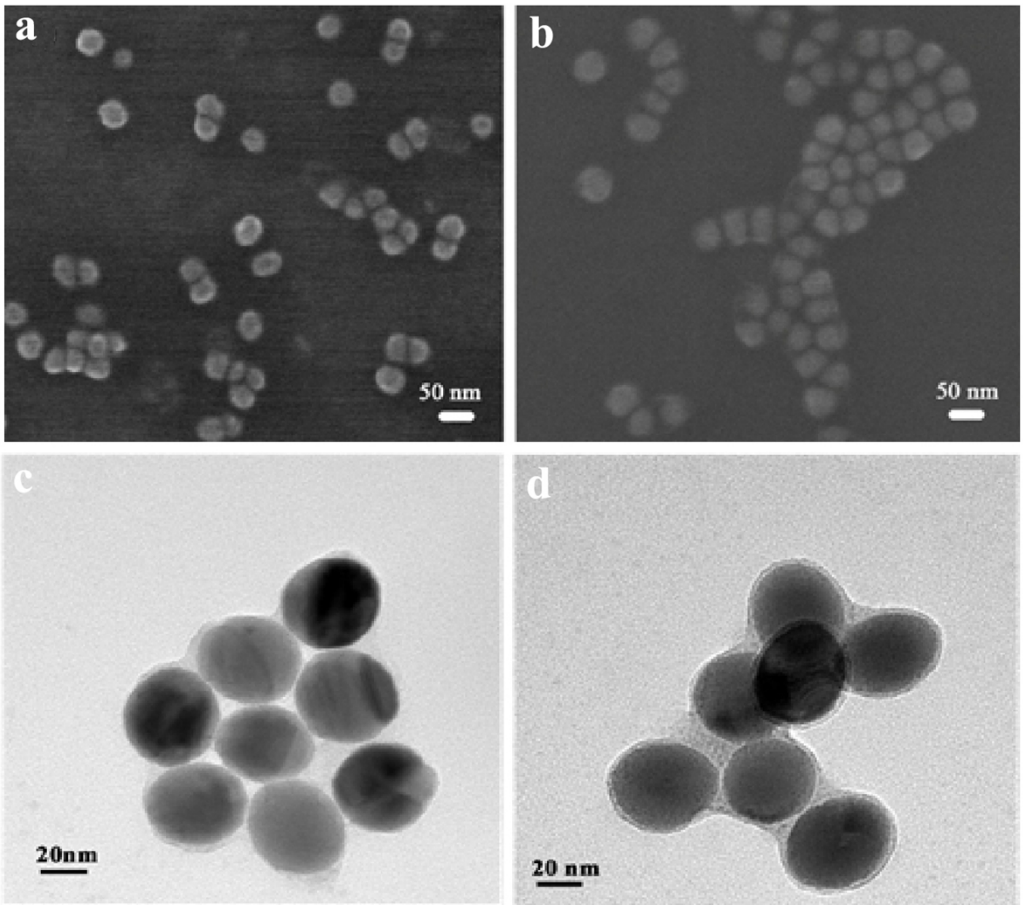

Fig. S9 SEM and TEM images of PSS-$Cu_{2-x}Se$ before (a), (c) and after (b), (d) the CL reaction.

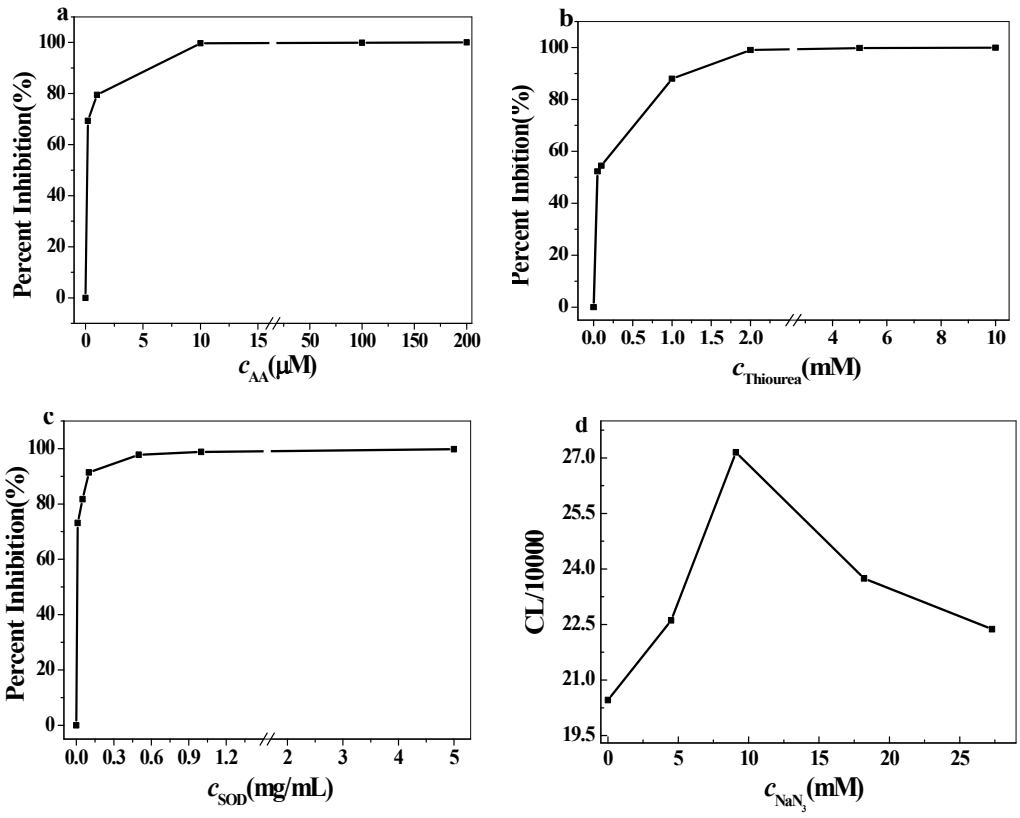

Fig. S10 Effects of the different radical scavengers of (a) AA, (b) thiourea, (c) SOD, and (d) NaN_3 on the CL intensity of luminol-H_2O_2-PSS-$Cu_{2-x}Se$ system. Final concentrations: luminol, 2.0×10^{-4} M; H_2O_2, 22.2 μM; PSS-$Cu_{2-x}Se$, 70.0 pM.

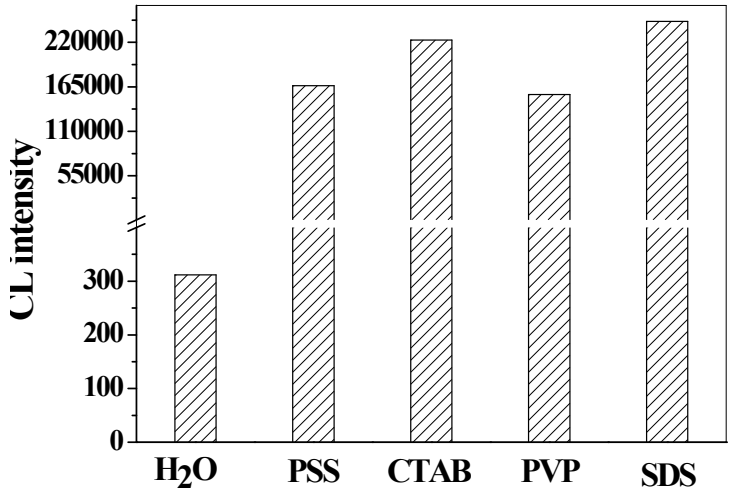

Fig. S11 Comparison of catalytic activity of different surfactant coated $Cu_{2-x}Se$ NCs. Final concentrations: luminol, 2.0×10^{-4} M; H_2O_2, 22.2 μM; $Cu_{2-x}Se$, 70.0 pM.

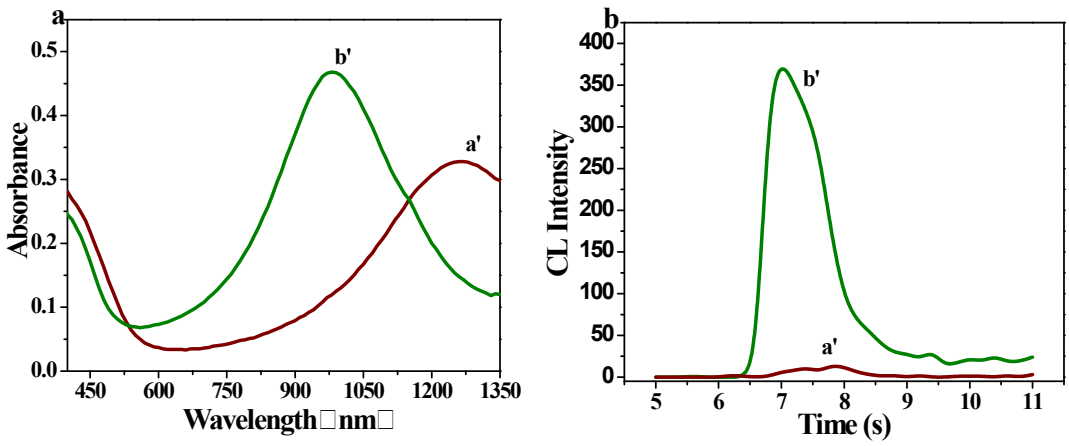

Fig. S12 Comparison of catalytic activity of PSS-$Cu_{2-x}Se$ NCs with different copper dificiency. (a) The absorption spectra of $Cu_{2-x}Se$ NCs with x~0 (a') and $Cu_{2-x}Se$ NCs with x>0 (b'). (b) Kinetic monitoring on luminol-H_2O_2 CL in the presence of a'and b', respectively. Conditions: luminol, 2.0×10^{-4} M; H_2O_2, 1×10^{-4} M. The as-prepared PSS-$Cu_{2-x}Se$ NCs had been subjected to centrifugation to remove the residual Cu^{2+} or PSS species but without dialysis.