Development of ratio-metric sensing and white light harvesting materials based on all-copper Nanoclusters

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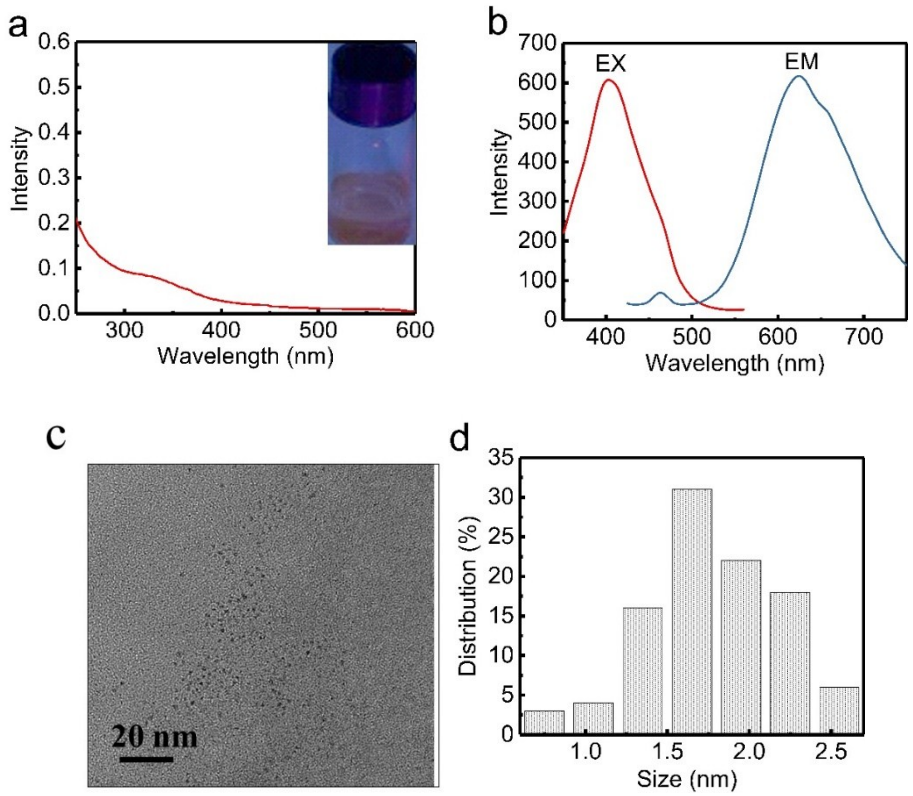

Fig. S1. (a) UV-Vis absorption spectrum of the slowly formed R-CuNCs-0 after overnight reaction; (b) The fluorescence excitation (red line) and emission (blue line) spectra of the R-CuNCs-0; (c) Typical TEM images and (d) statistic size distributions of the R-CuNCs-0.

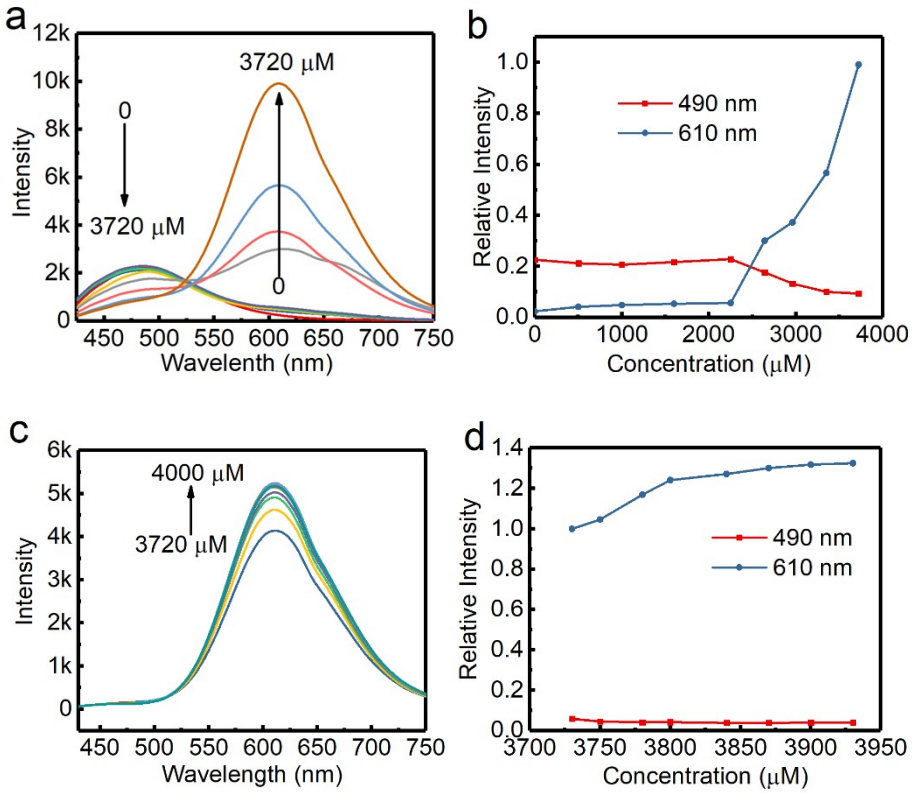

Fig. S2. Fluorescence emission spectra (a, c) and the intensity at 490 nm, 610 nm (b, d) for the generation of G-R-CuNCs as a function of Cu^{2+} (a, b, 0-3720 μM; c, d 3720 -4000 μM) in the presence of 500 μL of THPS (0.079%) and 500 μL of G-CuNCs with the slit widths of (a, b) 10 nm for both excitation and emission, (c, d)10 nm for excitation and 5 nm for emission.

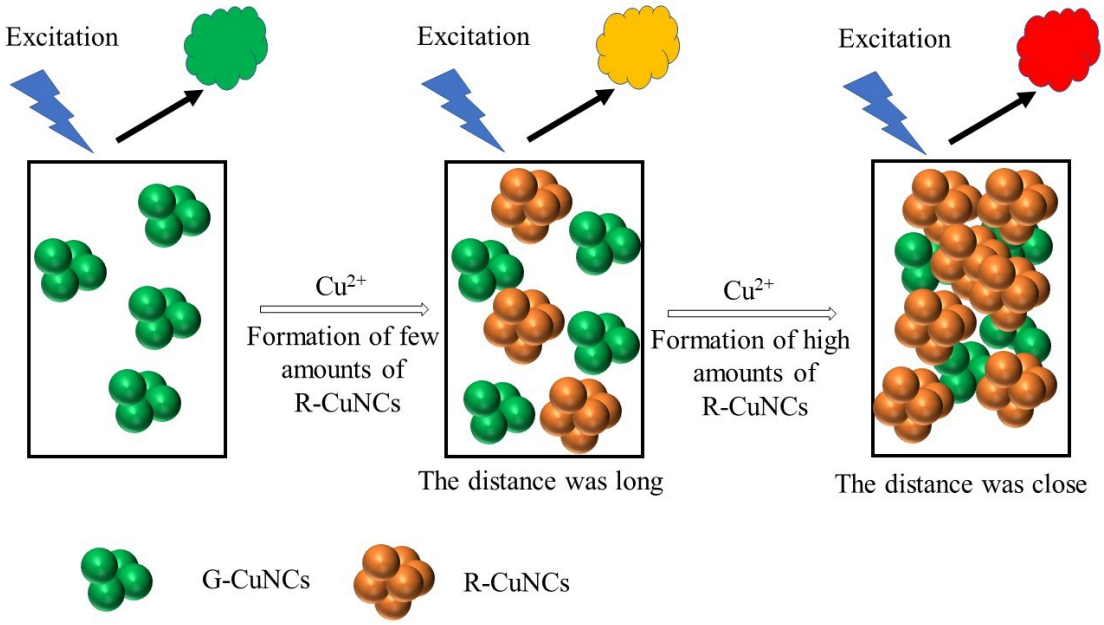

Fig. S3. Scheme for the formation of R-CuNCs with different concentrations and the approximation to G-CuNCs as the concentration becomes concentrated.

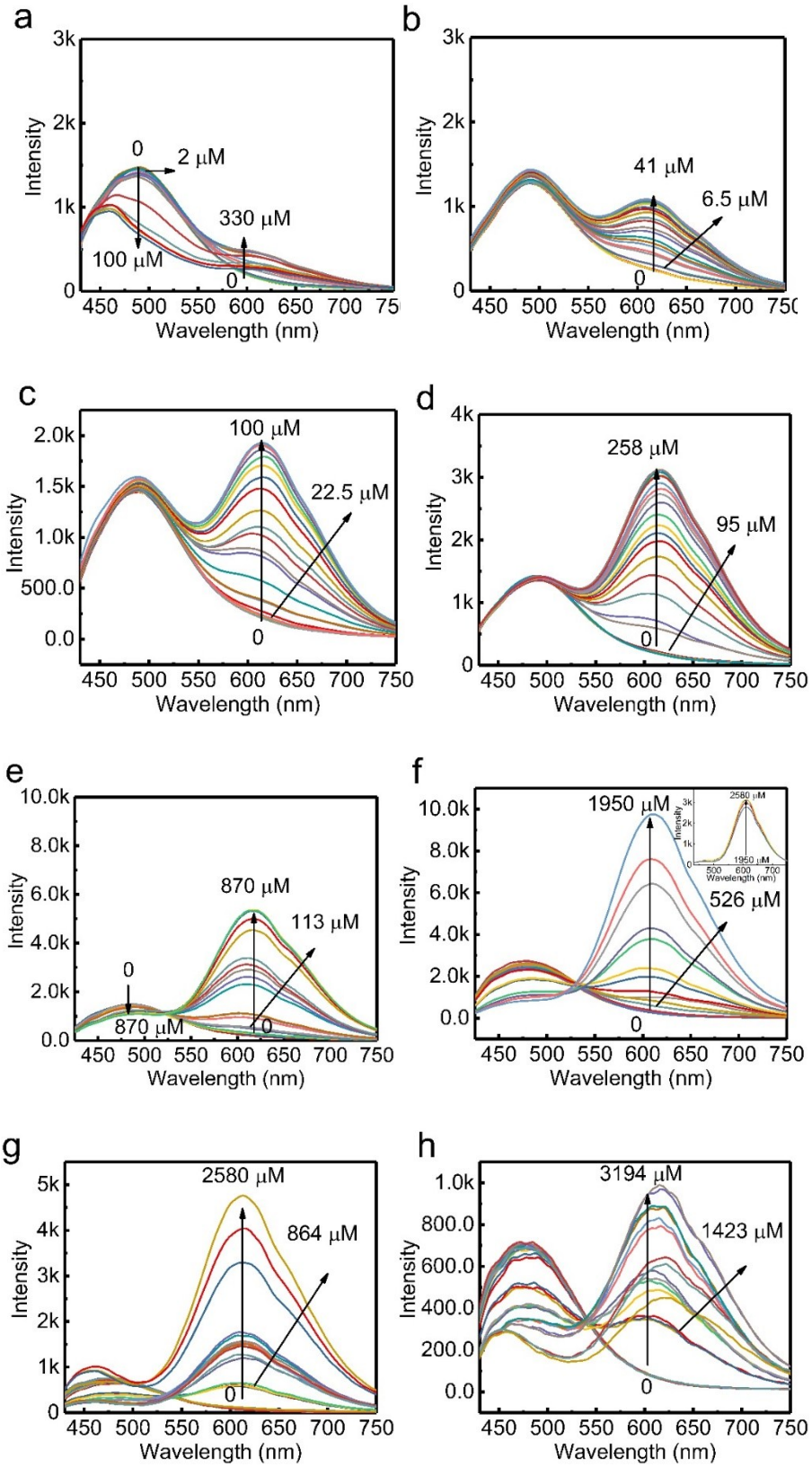

Fig. S4. Fluorescence emission spectra for the generation of G-R-CuNCs in the presence of 150 ul of G-CuNCs with the slit widths of 10 nm for both excitation and emission as a function of the amounts of THPS (0.079%): a, 0 μL, b, 3 μL, c, 30 μL, d, 50 μL, e, 100 μL, f, 250 μL, g, 750 μL, h, 1000 μL. Inset for f (with the slit widths of 10 nm for excitation and 5 nm for emission).

Table S1. Generation of G-R-CuNCs in the presence of different amounts of THPS

THPS	Cu^{2+} (μM) (Response Limit)	Cu^{2+} (μM) (Brightness Limit)	Max Intensity (610 nm)	Lowest Intensity (490 nm)
0	2.0	330 μM	672	1464
3 μL	6.5	41	1616	1404
30 uL	22.5	100	2464	1540
50 uL	95	258	1086	1437
100	113	870	3087	1376
250	526	1950	>10000	<858
750	864	2580	4760	182
1000	1423	3194	439	189

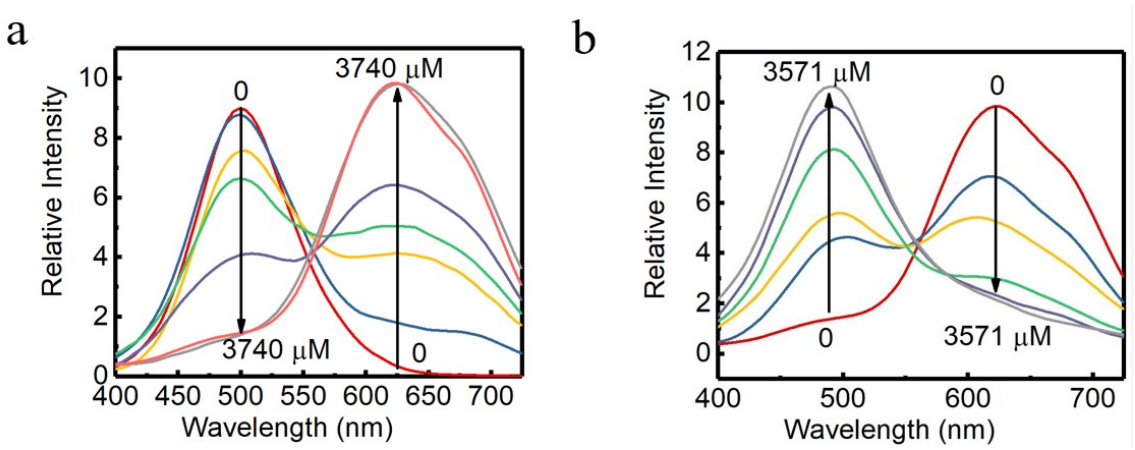

Fig. S5. (a) Fluorescence emission spectra for the evolution of R-CuNCs-2 in the presence of G-CuNCs-2 as a function of Cu^{2+}. (b) Fluorescence emission spectra of the G-R-CuNCs-2 as a function of L-Histidine.

Table S2. Comparison of the synthesis condition for fabrication water soluble R-CuNCs

CuNCs	Emission	Synthesis condition	Ligand	QY (%)	Reaction time	References
1	620 nm	37 ℃	BSA	4.1	24 h	[1]
2	627 nm	Room	DHLA	2.8	12 h	[2]
3	670 nm	25 ℃	Transferrin	6.2	3.5 h	[3]
4	600 nm	Microwave	Egg white	6.7	5 min	[4]
5	610 nm	80 ℃	GSH	5.0	10 min	[5]
6	650 nm	Dark	DNA	-	15 min	[6]
7	630 nm	Room	APBA/BSA	3.7	24 h	[7]
8	610 nm	Room	DHLA	4.8	< 2 min	This Work

For the generation of R-CuNCs by the assistance of G-CuNCs, it should be noted the volume was fixed before the introduction of Cu^{2+}. However, after that, Cu^{2+} with different volumes were combined to the system. Such type of protocol facilitated the fast finding of the optimum amounts of Cu^{2+}. On the other hand, it was worth wondering whether the volume change attributed to the combination of Cu^{2+} solution could interfere with the monitoring of the fluorescence induced by other factors. For understanding this phenomenon, the fluorescence behavior by comparing the same volume of water and Cu^{2+} solution had been investigated. By the addition of water to the system, it only indicated the influence of the volume change. On the other hand, by the combination with the same volume of Cu^{2+} solution, it would reveal the fluorescence change both for volume influence and the generation of the new product.

Herein, two system were prepared using random amounts of G-CuNCs as the assistance, which were assigned as G-CuNCs-X and G-CuNCs-Y. After that, the fluorescence behaviors were investigated by the combination of relatively high and low concentration of Cu^{2+}. It should be noticed the total volume of the pre-mixtures was fixed before the combination of water or Cu^{2+} solution. The results were demonstrated in Fig. S6. In Fig. S6a, S1 indicated the fluorescence emission spectra for the original mixture containing G-CuNCs-X; S2 demonstrated the fluorescence emission spectra for the mixture in combination with 100 μL of additional water. S3 described the fluorescence emission spectra for the mixture in combination with 100 μL of Cu^{2+} (0.1 M) solution. After the combination of water, it could be seen that it could be seen that S2 described little change for the green emission compared to S1. On the other hand, S3 significantly change the fluorescence behavior. It could be seen that the green emission was quenched while the red emission was turned on, which was attributed to the generation of high concentration of R-CuNCs due to the reduction of relatively high concentration of Cu^{2+}. By comparing S2 and S3 in Fig. S6a, it revealed the volume influence of water was insignificant compared to the generation of a new product by the addition of the solution containing Cu^{2+}. As well as this, the volume influence had also been compared to the combination with the solution containing relative low concentration of Cu^{2+} using another system, see Fig. S6b. Similarly, only little change was demonstrated for the green emission just by increasing the volume (Q2). Meanwhile, it could be seen that the red emission was turned on because of the generation of R-CuNCs, but the green emission suffered insignificant change (Q3). This was because the generation of low amounts of R-CuNCs was not significant enough to quench the green emission for G-CuNCs. For facile fabrication of G- R-CuNCs, normally no more than 200 μL of Cu^{2+} solution was added. Both results indicated there was significant difference between the volume influence and the generation of R-CuNCs. Thus, it could be concluded the volume change in the current work wouldn't interfere with the observation

of the new fluorescence phenomena. However, the combination of different amounts of Cu^{2+} solutions without fixing the total volume were only applied for synthesis and observation of the new product (R-CuNCs). For analysis application, same volume of Cu^{2+} would be employed so that to realize the accurate result.

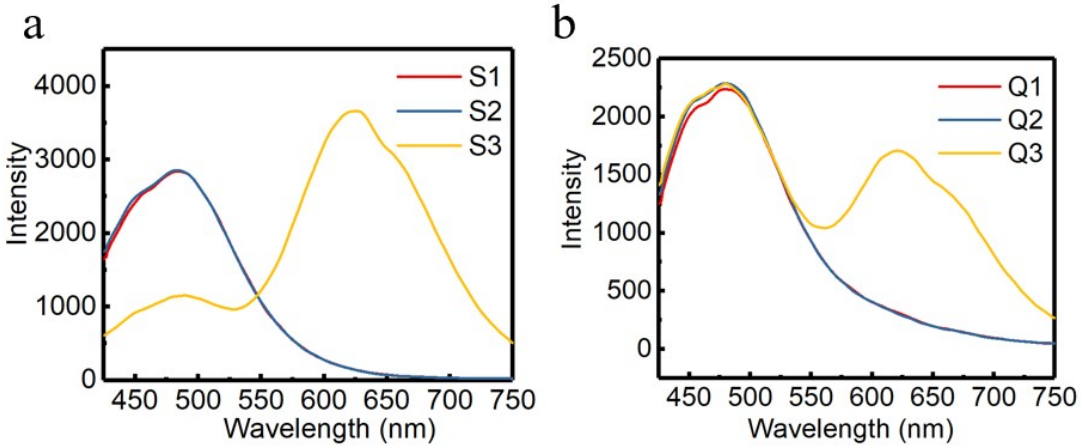

Fig. S6. Fluorescence emission spectra influenced by different factors. a: S1, (G-CuNCs-X + THPS); S2 (G-CuNCs-X + THPS + 100 μL H_2O); S3(G-CuNCs-X + THPS + 100 μL 0.01 M Cu^{2+}). B : Q1 (G-CuNCs-Y + THPS); Q2(G-CuNCs-Y + THPS + 100 μL H_2O); Q3(G-CuNCs-Y + THPS + 100 μL 0.01 M Cu^{2+}).

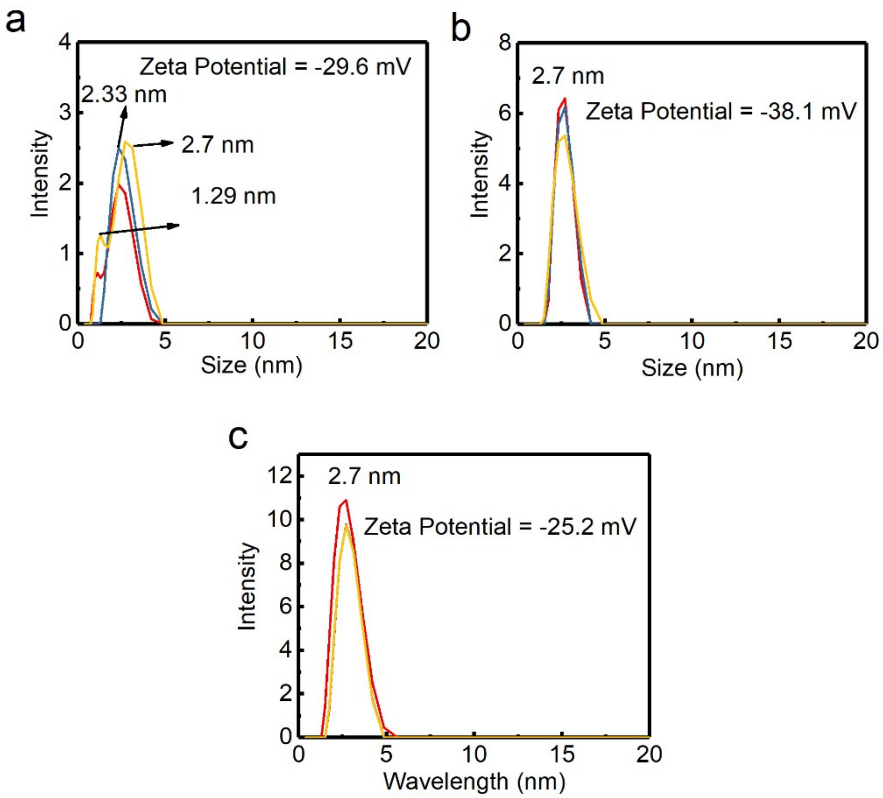

Fig. S7. DLS (repeated 3 times for three samples) and zeta potential investigation of (a) G-CuNCs-1, (b) G-R-CuNCs-1 and (c) R-CuNCs-0.

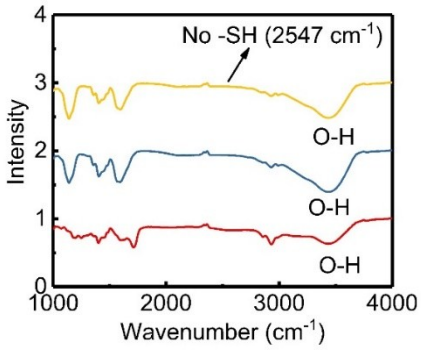

Fig. S8. FT-IR spectra of G-CuNCs-1 (red line), G-R-CuNCs-1 (blue line) and R-CuNCs-0 (yellow line).

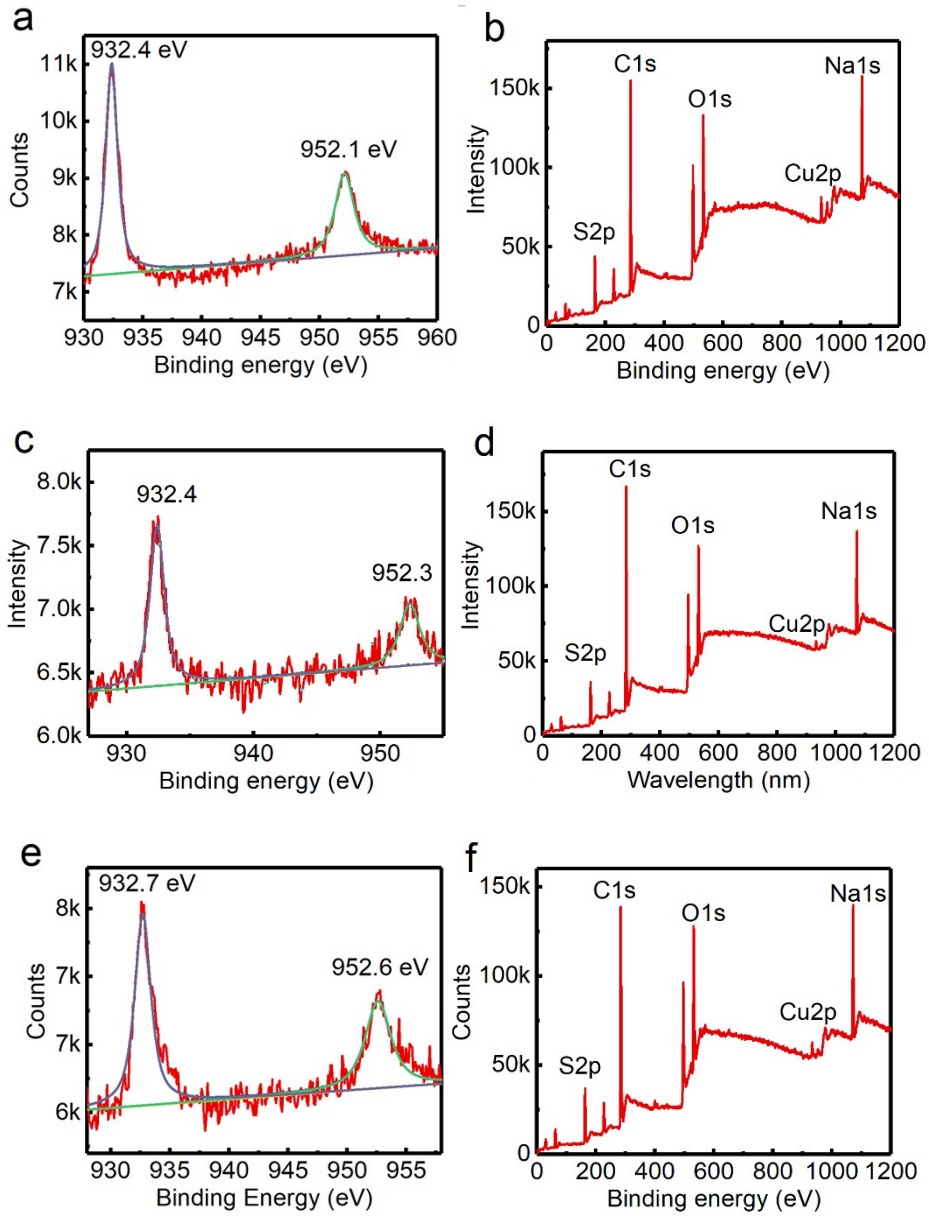

Fig. S9. XPS investigation of Cu 2p (a, c, e) and survey (b, d, f) for (a, b) G-CuNCs-1, (c, d) G-R-CuNCs-1 and (e, f) R-CuNCs-0.

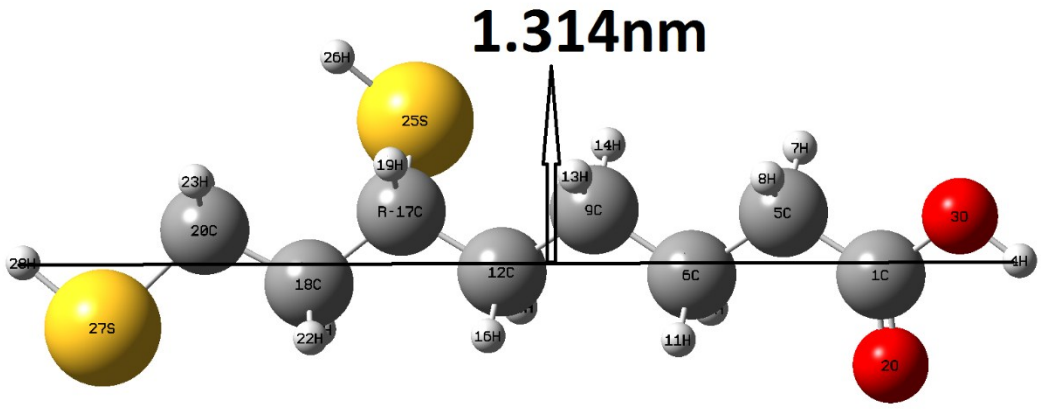

Fig. S10. Diameter of the protection ligand (DHLA).

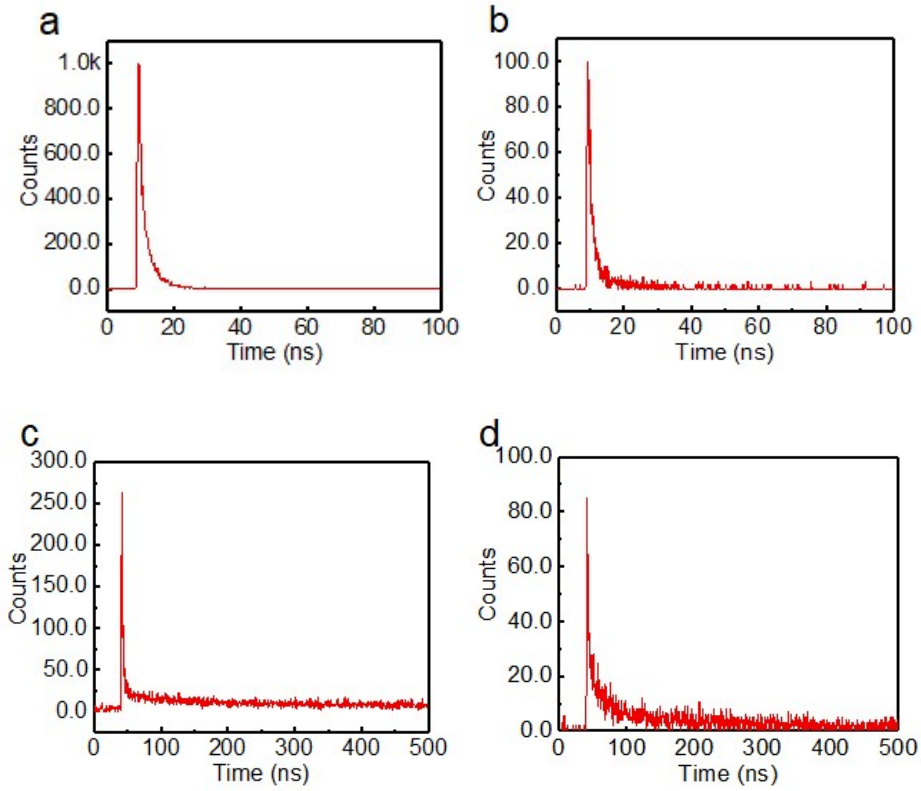

Fig. S11. Life time study excited at 400 nm for (a) the donor in the presence of the acceptor (G-CuNCs-a) (emission, 490 nm), (b) the donor alone (G-CuNCs-b) (emission, 490 nm), (c) the enhanced R-CuNCs in the presence of catalysis (R-CuNCs-a) (emission, 610 nm), and (d) the slowly formed R-CuNCs (R-CuNCs-b) (emission, 610 nm).

Table S3. Fluorescence life time analysis for the CuNCs

NCs	t1	t2	t3	t
G-CuNCs-a	0.157	0.575	2.944	2.402
G-CuNCs-b	0.084	0.326	1.335	1.268
R-CuNCs-a	0.436	3.065	117.849	92.072
R-CuNCs-b	1.4348	13.073	120.173	88.269

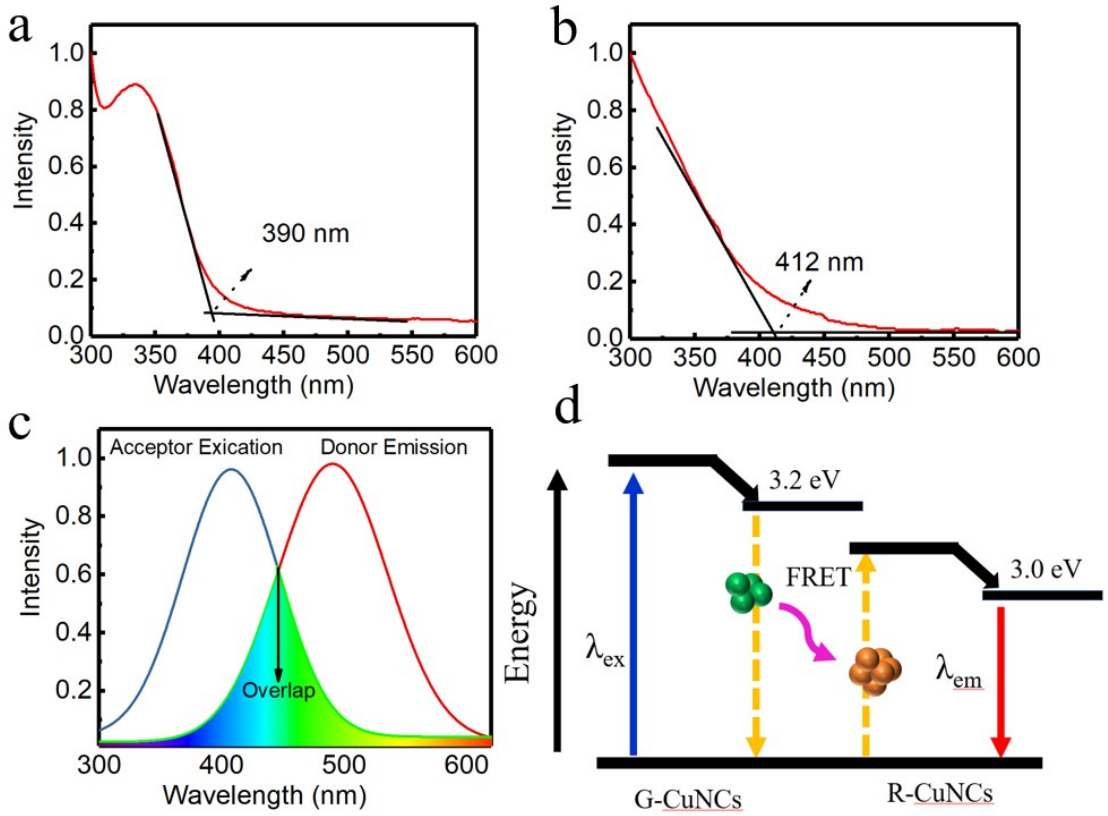

Fig. S12. (A) UV-Vis absorption spectrum of G-CuNCs and R-CuNCs, (B) the spectral overlap of the donor emission and the acceptor excitation; Scheme for then energy transfer from the donor to acceptor.

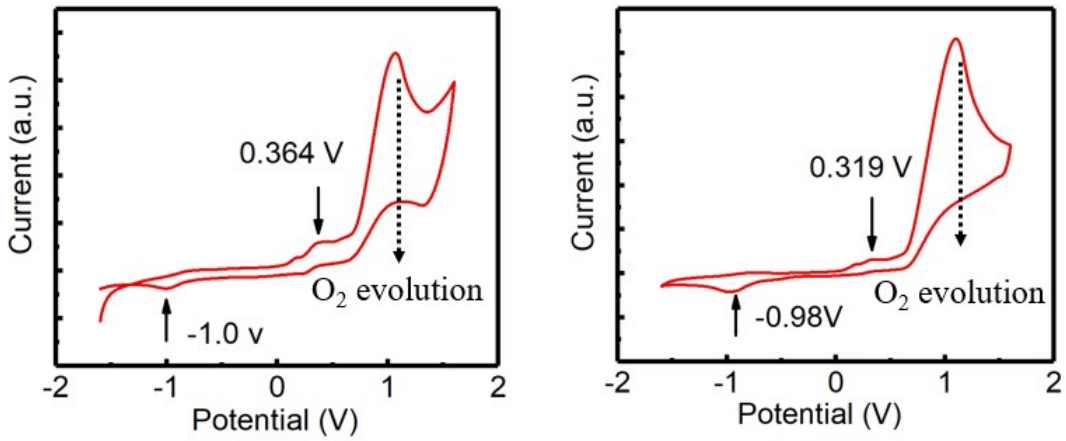

Fig. S13. Cyclic Voltammogram of CuNCs

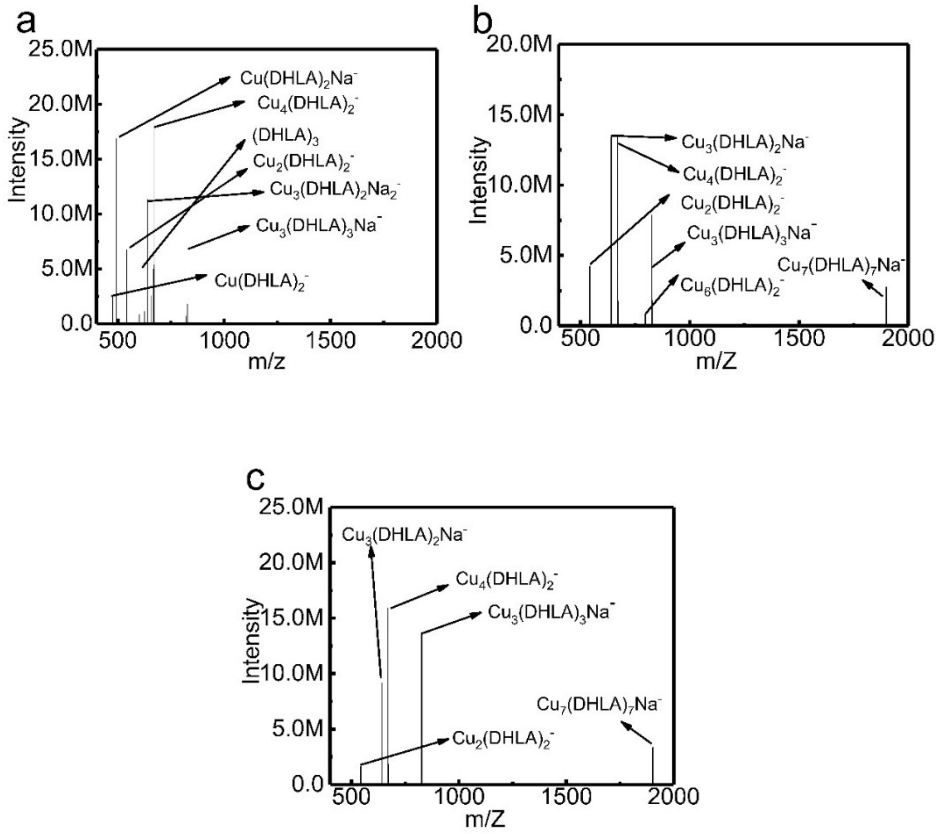

Fig. S14. Negative mode for the ESI-MS of (a) G-CuNCs-1, (b) G-R-CuNCs-1 and (c) R-CuNCs-0.

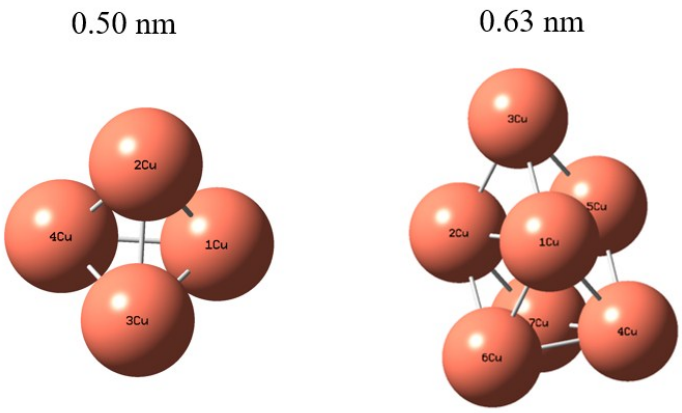

Fig. S15. The size of the CuNCs for Cu_4 and Cu_7.

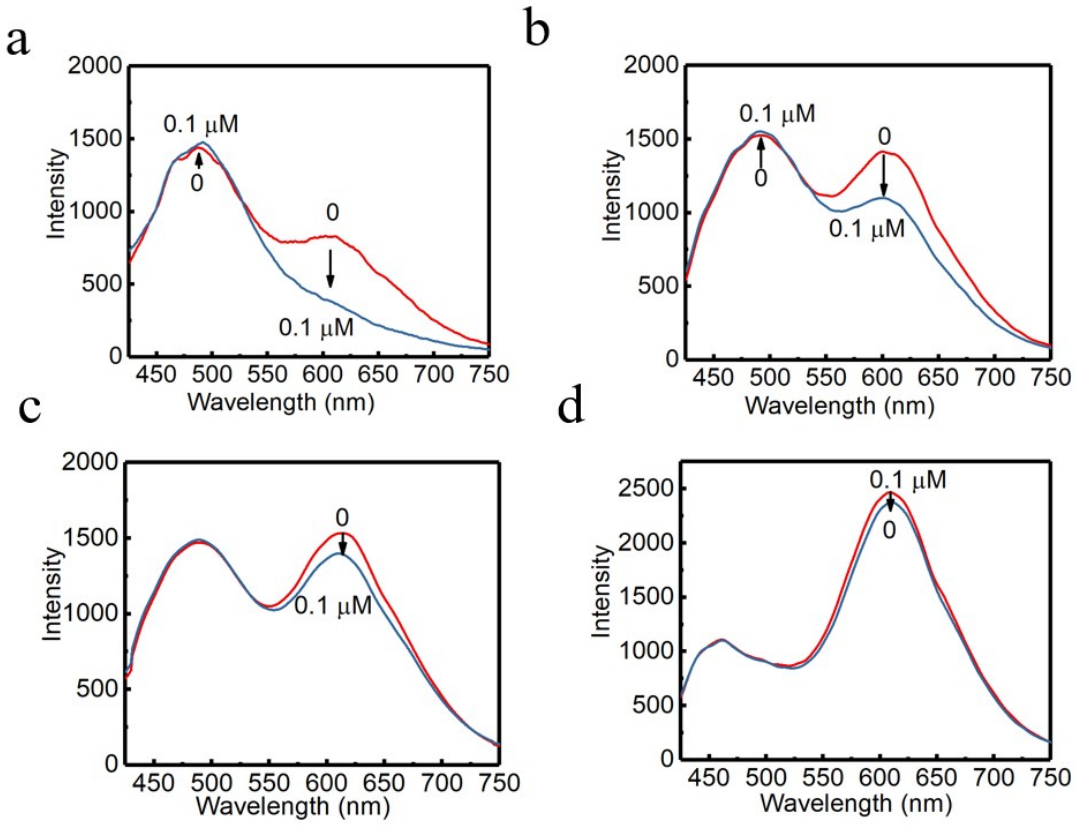

Fig. S16. Fluorescence emission response of G-R-CuNCs in the presence of 0.1 μM S^{2-} where G-R-CuNCs were prepared using different amounts of THPS (0.079%) (a, 2 μL; b, 10 μL; c, 20 μL; 40 μL).

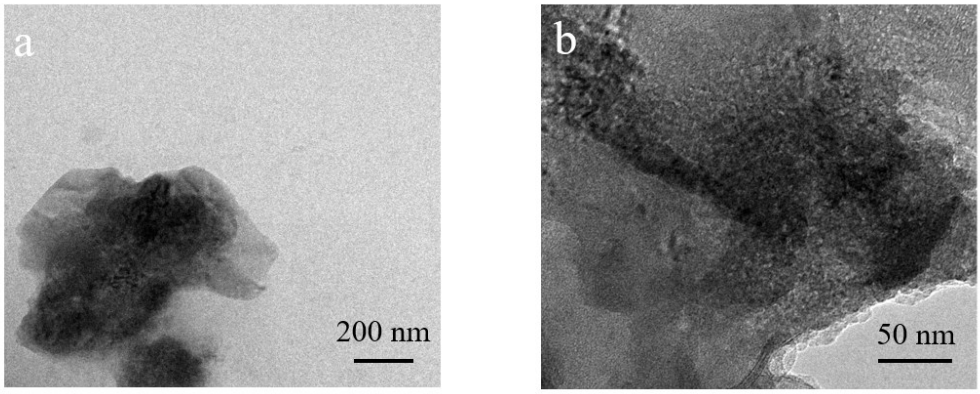

Fig. S17. TEM for G-R-CuNCs-3 in the presence of S^{2-} (10 μM) with relatively lower (a) and larger enlargement (b).

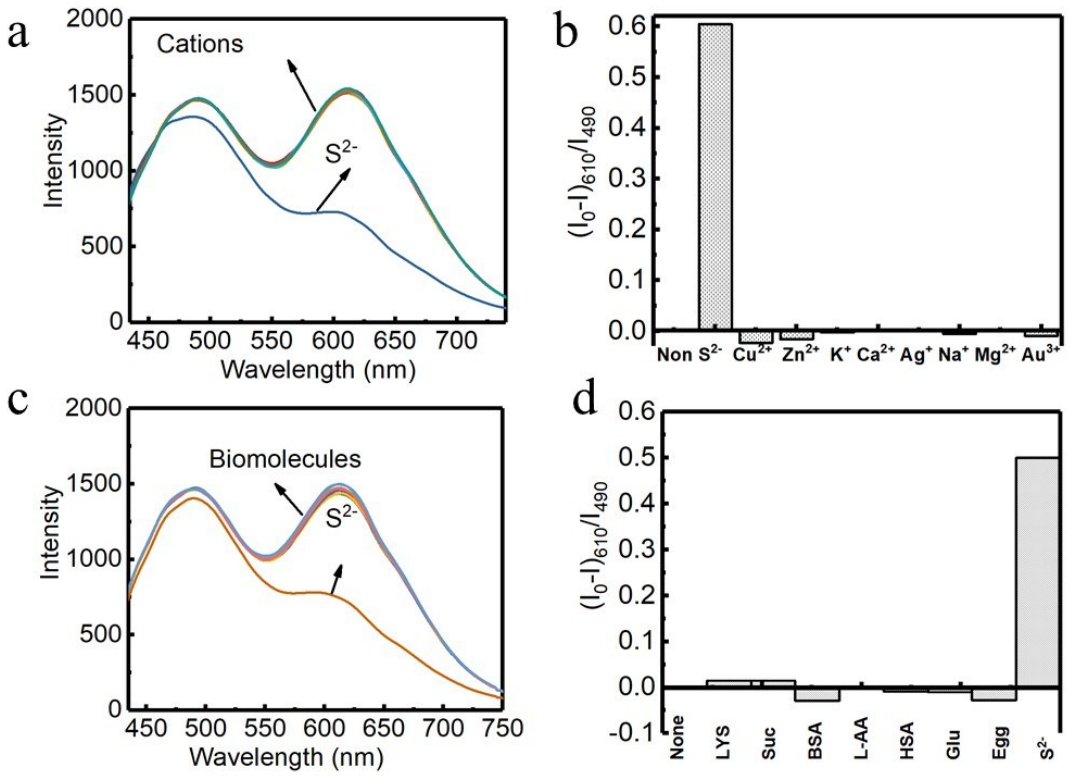

Fig. S18. Fluorescence emission spectra as a function of the cations (a) and the biomolecules (c). The fluorescence spectra with the slit widths of 10 nm for excitation and emission respectively; The corresponding intensity change ratio at 610 nm and 490 nm of the sensing system in the presence of different of cations with equivalent concentration (10 μM) (b) and biomolecules (320 ppb) (d).

Table S4. S^{2-} analysis for spiked chicken blood serum system

Serum sample	S^{2-} added/ μM	S^{2-} found/ μM	Recovery (%)	RSD(%, n=3)
	0	-	-	-
1	1.00	0.953	95.3	0.94
2	10.0	9.87	98.7	1.06
3	100	113	113	1.18

Table S5. Detection of S^{2-}/HS^{-}/H_2S by ratio-metric fluorescence sensors

Sensor	Preparation	Analyte	Linear Range (μM)	Response Time	Detection Limit	Ref.
BSA-Eu-AuAgNCs	70 ℃, 20 min	S^{2-}	0.02 - 180	8 min	6.0 nM	[8]
CNPs and BSA-AuNCs	180 °C, 12 h; 70 °C, 24 h	S^{2-}	0-53	2 min	18 nM	[8]
Chi-AuNCs	Room, 26 hour	HS^{-}	0-80	90 s	1.83 μM	[9]
HSip-1@BSA-AuNC	37 ° C, 12 h; Room, 2 h	H_2S	7-100	1 h	0.73 μ M	[10]
DHLA-CuNCs	Room, several minutes	S^{2-}	0.1-25	< 1min	< 0.1 μM	This work

Fig. S19. Pictures for fluorescence change of G-R-CuNCs-4 (Fabricated with low amounts of Cu^{2+} and THPS) by the titration of different amounts of Zn^{2+} (0.1 M) (the first three rows); The fourth row demonstrated pure G-CuNCs (G) and G-R-CuNCs-5 (R) (fabricated with high amounts of Cu^{2+} and THPS) respectively.

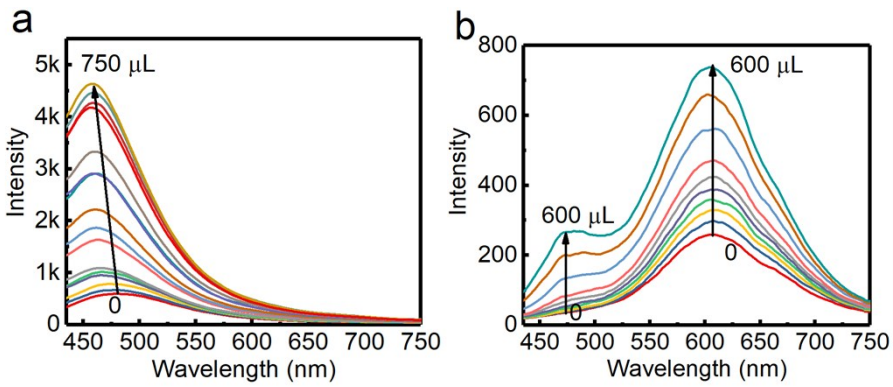

Fig. S20. Fluorescence emission spectra of G-CuNCs (a) in the presence of 50 μL of 7.9% THPS by the titration of different amounts of Zn^{2+} (0.1 M) from 50 μL to 750 μL and G-R-CuNCs-5 (b) (Synthesis condition: 500 μL G-CuNCs, 50 μL 7.9% THPS, 1200 μL Cu^{2+} (0.01 M)) with the slit widths of 10 nm for excitation and 5 nm for emission.

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