Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information for:

L-cysteine-induced chiroptical activity in the assemblies of the gold nanorods and its use in ultrasensitive detection of copper ions

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Experimental

Materials. Sodium borohydride ($NaBH_4$), chlorauric acid ($HAuCl_4 \cdot 3H_2O$), cetyltrimethylammonium bromide (CTAB), sodium citrate, silver nitrate ($AgNO_3$), trisodium citrate, N-acetyl-L-cysteine (L-NAC), L-glutathione (L-GSH) L-oxidized glutathione (L-GSSG), 4-mercaptopyridine (4-MP), L-cysteine (Cys) and L-ascorbic acid (AA) were purchased from Alfa Aesar and used as received. Copper(II) chloride dihydrate ($CuCl_2 \cdot 2H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), chromium (III) nitrate nonahydrate ($Cr(NO_3)_3 \cdot 9H_2O$), calcium chloride ($CaCl_2$), nickelous nitrate ($Ni(NO_3)_2 \cdot 6H_2O$), zinc chloride ($ZnCl_2$), lead (II) chloride ($PbCl_2$), cadmium (II) chloride ($CdCl_2$), manganese (II) chloride ($MnCl_2 \cdot 4H_2O$), ammonium iron(II) sulfate hexahydrate ($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$), and mercury (II) perchlorate ($Hg(ClO_4)_2 \cdot 6H_2O$) were at least analytical reagent grade and purchased from Beijing Chemical Reagent Company (Beijing, China). Milli-Q water (18 MΩ cm) was used for all solution preparation.

Typical synthesis of GNRs. GNRs were synthesized using the well-developed seed-mediated growth method. Briefly, CTAB-capped Au seeds were synthesized by chemical reduction of $HAuCl_4$ with $NaBH_4$: CTAB (7.5 mL, 0.1 M) was mixed with $HAuCl_4$ (100 μL, 25 mM) and diluted with water to 9.4 mL. Then, ice-cold $NaBH_4$ (0.6 mL, 0.01 M) was added under magnetic stirring. The solution color turned immediately from bright yellow to brown, indicating the formation of Au seeds. The Au seeds were used within 2-5 h. For a typical preparation of the GNRs, in a growth solution consisting a mixture of CTAB (100 mL, 0.1 M), $HAuCl_4$ (2 mL, 25 mM), $AgNO_3$ (105 μL, 0.1 M), AA (552 μL, 0.1 M), and adding seed solution (120 μL) to initiate the growth of GNRs. The resultant reaction solution was gently mixed by inversion and then left undisturbed After 12 h, AA (0.1 M, 55.2 μL) was added twice with 40 min interval. The reaction mixture was reacted for 24 h. The GNRs were purified by centrifuging at 12000 rpm for 5 min twice. The precipitate was collected and redispersed in deionized water. The rod concentration is estimated from the extinction value of the GNRs suspension at 400 nm ($E_{400\ nm}$) and the mean size of the rods from TEM. The molar extinction coefficient of the GNRs at 400 nm is $2.02*10^3\ M^{-1}\ cm^{-1}$. According to Lambert-Beer law, $E_{400\ nm} = 2.02*10^3*l*C_{Au}$, l and C_{Au} are optical path and gold atom concentration, respectively. From the TEM images, the diameters and lengths of GNRs were measured. And the mean volume of single GNR (V_0) was obtained by assuming a cylindrical shape with two half sphere endcaps (see Fig. S1). The GNRs molar concentration in the suspension can be estimated as $V_m*C_{Au}/A*V_0$, V_m and A are molar volume of gold atom (10.2 cm^3/mol) and Avogadro's constant, respectively.

Cu^{2+} detection. Trisodium citrate (0.15 mM) was added into 0.1 nM GNRs suspension stabilized with 0.5 mM CTAB to initiate the SS assembly of the GNRs. After incubation in a 27°C waterbath for 30 min, the mixture of Cu^{2+} with different concentrations and 0.6 μM Cys (pre-incubated in a 27°C waterbath for 20 min) was added and continued incubation at same condition for 30 min. The total volume of the sample was 1 mL. Then, the CD spectra were recorded.

Characterizations. UV/vis/NIR absorption spectra were obtained either simultaneously with the CD spectra on the CD spectrometer or from a Cary 50 UV/vis/NIR absorption spectrometer. CD measurements were conducted on a JASCO J-810 CD spectrometer. Raman spectroscopic measurements were obtained in the solution phase using a Renishaw InVia Raman microscope with a 633 nm laser (120 mW). The determination of copper element was from an inductively coupled plasma mass spectrometer (ICP-MS) (NexION300X).

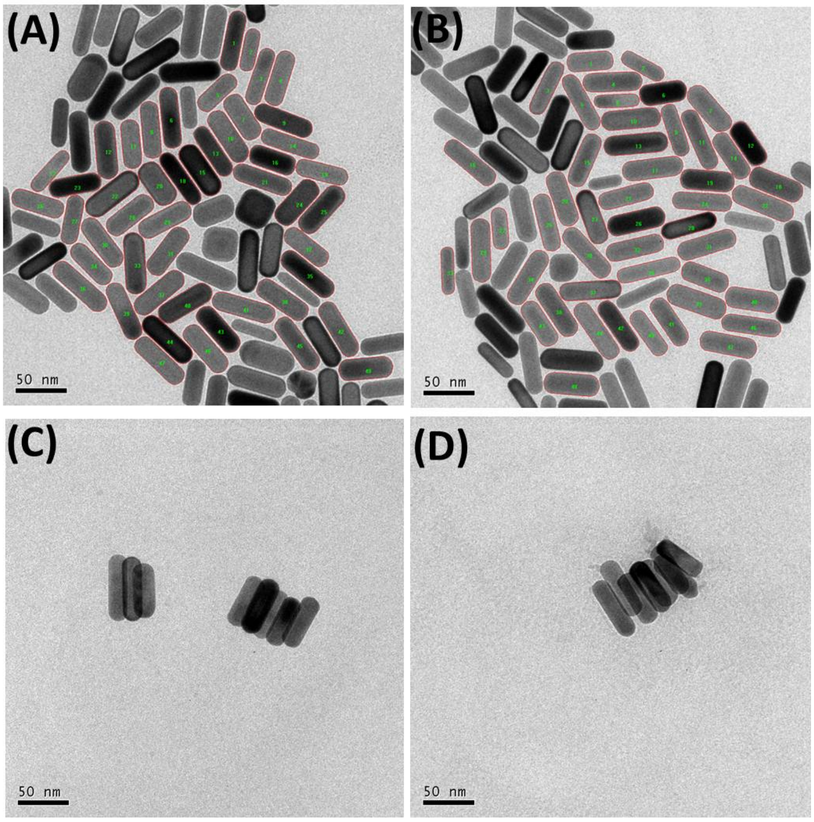

Fig. S1 TEM images of discrete GNRs (A, B) and their SS assemblies (C, D). The mean size of individual GNRs is 55.2 ± 6.2 nm long and 17.8 ± 2.6 nm wide (from 200 GNRs).

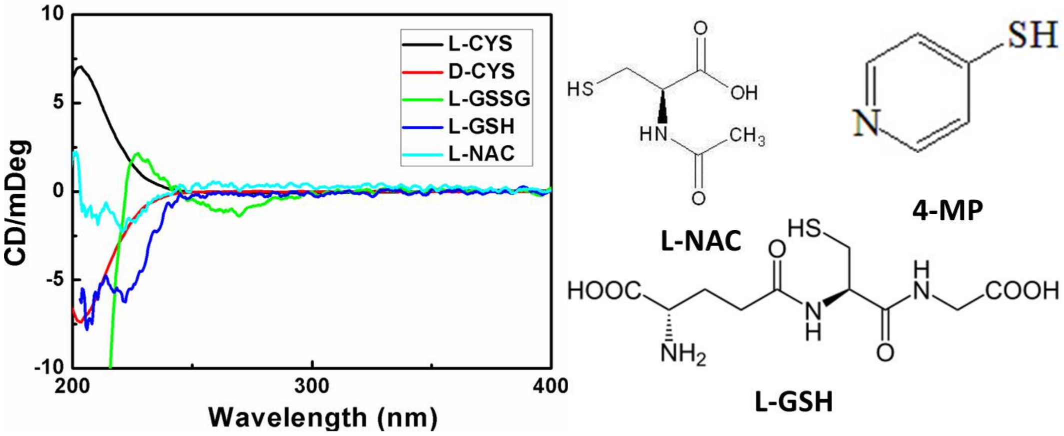

Fig. S2 CD spectra of L-Cys, D-Cys, L-GSH, L-GSSG, L-NAC at the concentration of 0.1 mM.

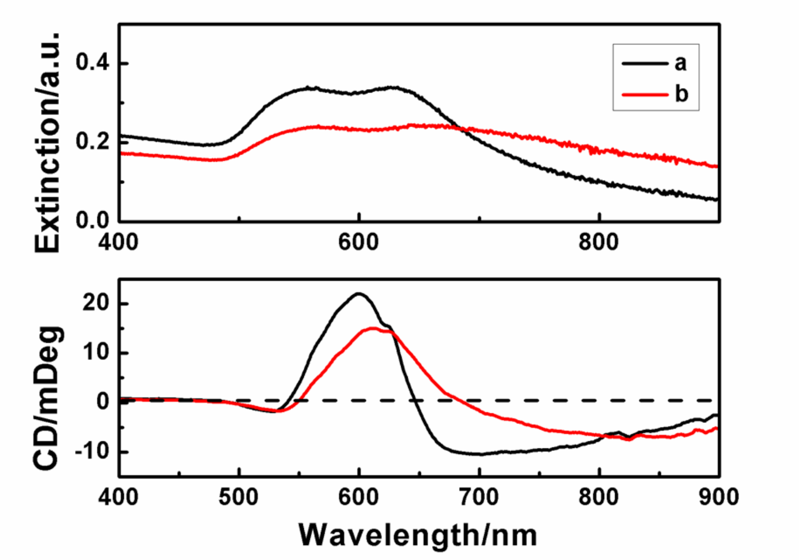

Fig. S3 Extinction (up) and CD spectra (bottom) of GNRs SS assemblies. At the same assembly conditions, assembly at 0.5 mM CTAB (a) gives good SS assemblies whereas more random assemblies are obtained at 0.3 mM CTAB (b). After adding L-Cys, the former gives better PCD response than the later, indicating a high degree of SS order is beneficial for the larger PCD responses.

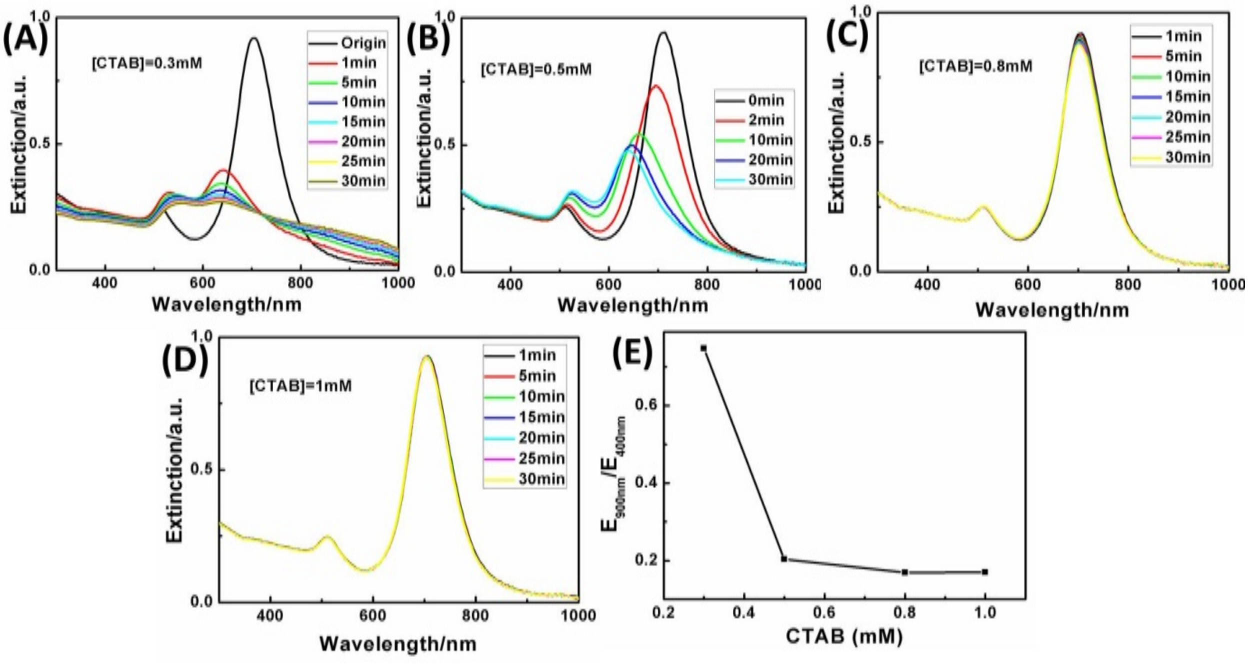

Fig. S4 Effect of CTAB concentration in the assembly solution: evolution of extinction spectra of the GNRs dispersed in different concentrations of CTAB after adding citrate (A-D). E_{900nm}/E_{400nm} nm vs CTAB concentration indicating the order of degree in SS assemblies (E). Other conditions: [GNR] = 0.1 nM, [citrate] = 0.15 mM.

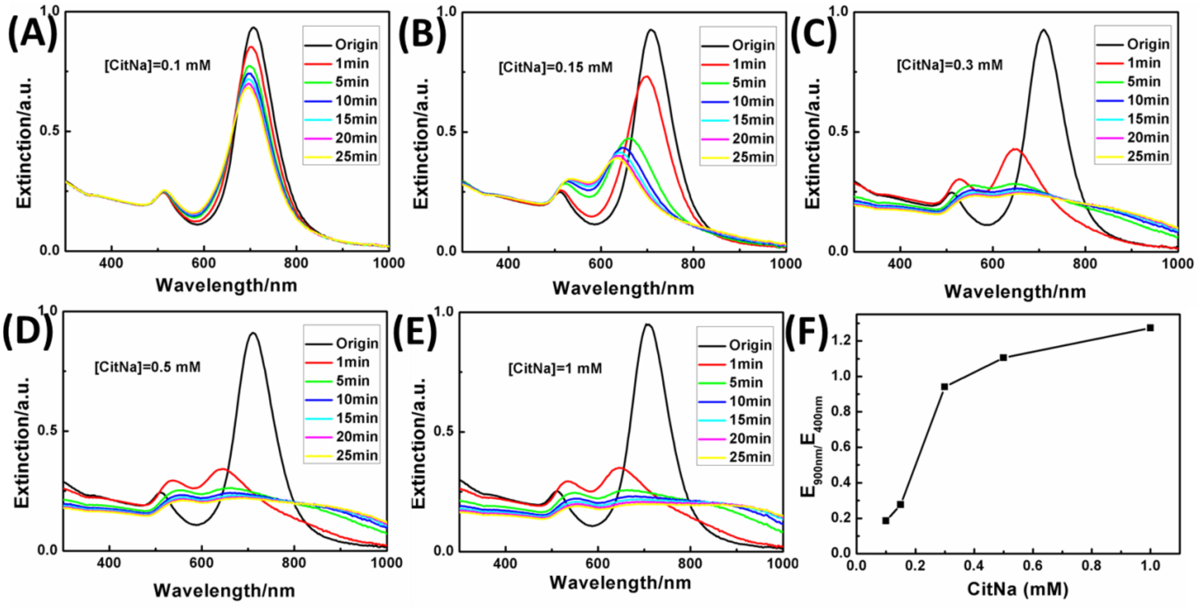

Fig. S5 Effect of trisodium citrate concentration: evolution of extinction spectra of the GNRs at different concentrations of citrate (A-E), and E_{900nm}/E_{400nm} nm vs citrate concentration (F). Other conditions: [CTAB] = 0.5 mM, [GNRs] = 0.1 nM.

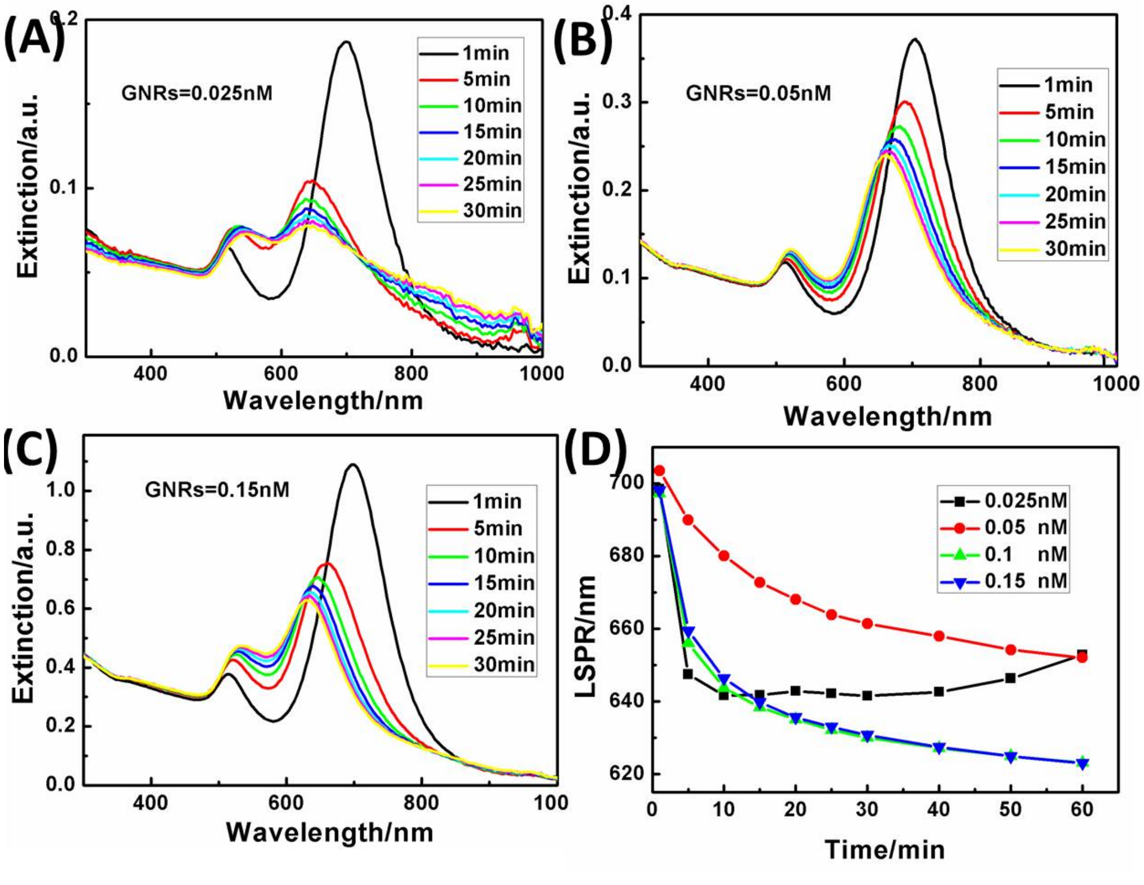

Fig. S6 Effect of GNRs concentration: evolution of UV-vis-NIR extinction spectra of the GNRs at different concentrations of GNRs after adding citrate (A,B,C), and LSPR maximum vs time (D). Other conditions: [CTAB] = 0.5 mM, [citrate] = 0.15 mM.

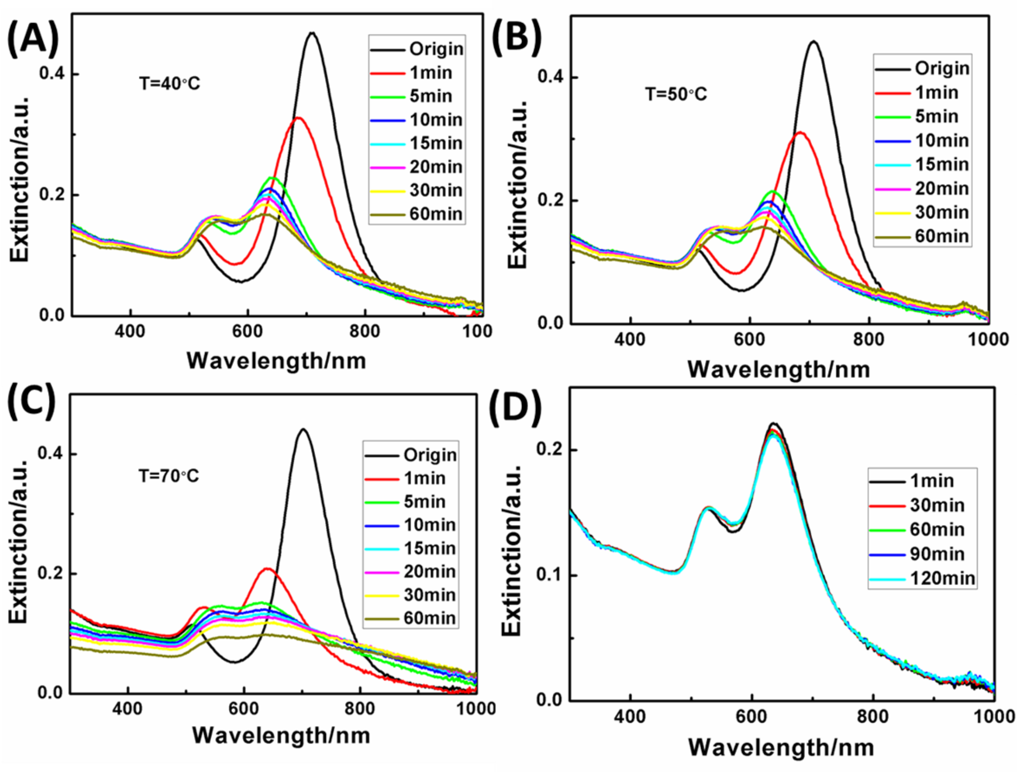

Fig. S7 Effect of temperature during the assembly course: evolution of extinction spectra of the GNRs dispersed in different temperature after adding trisodium citrate (A, B, C). Extinction spectra of GNRs first assembled at 70°C for just 1 min and then incubated at 30°C for different periods (D). Other conditions: [CTAB] = 0.5 mM, [GNR] = 0.05 nM, [citrate] = 0.15 mM.

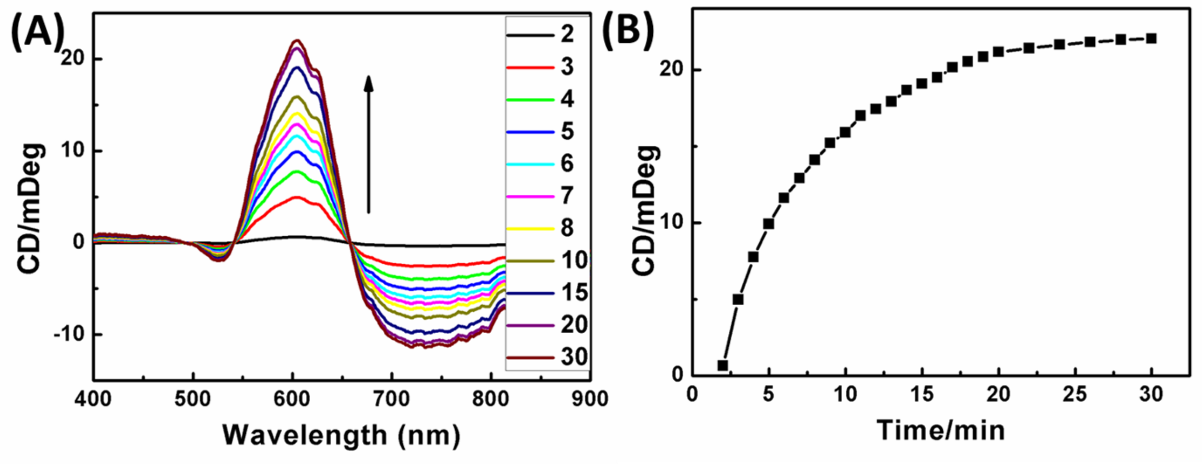

Fig. S8 Evolution of CD spectra (A) after adding L-Cys and the PCD intensity vs time (B).

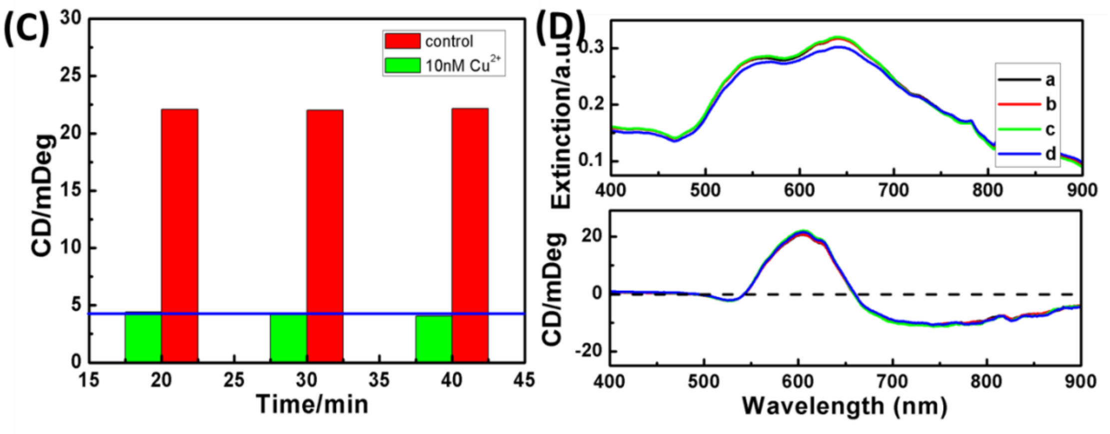

Fig. S9 Effect of incubation time of Cu^{2+} and L-Cys mixture on PCD signals (A) and tolerance of the PCD signal to pH changes: (a) 10 μM HCl, (b) 1 μM HCl, (c) H_2O, and (d) 1 μM NaOH. Other conditions were the same: [GNR] = 0.1 nM,([GNR] = 0.05 nM in (B)) [citrate] = 0.15 mM, and [CTAB] = 0.5 mM.

Table S1 Analytical performances of various strategies based on the surface plasmon resonance (SPR) absorption of gold nanoparticles/nanorods for copper detection in aqueous solution

Technique in detail	**LOD**	**Ref.**
Aggregation of gold nanoparticles based on copper catalyzed click chemistry	50 μM	1
Catalytic leaching of silver-coated gold nanoparticles	1 nM	2
Oxidation of gold nanoparticles by copper -catalyzed H_2O_2 oxidation	0.05 μM	3
Copper –induced aggregation of gold nanoparticles	0.01 μM	4
Copper -induced aggregation of cysteine–modified gold nanorods	0.34 μM	5
Copper- catalyzed etching of gold nanorods	2.7 nM	6
Copper-modulated formation of core−shell gold nanorods	**2 fM**	7
Oxidation of gold nanorods by copper -catalyzed H_2O_2 oxidation	4.96 nM	8
Copper- catalyzed leaching of silver from silver-coated gold nanorods	3 nM	9
Copper -catalyzed etching of gold nanorods by dissolve oxygen	0.22 μM	10
PCD change in L-cystein driven GNRs SS assemblies caused by copper- catalyzed oxidation of L-cysteine	2.6 pM	herein

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