Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Colorimetric sensing of copper ions based on anti-aggregation of unmodified silver nanoparticles in the presence of 1,4-dithiothreitol

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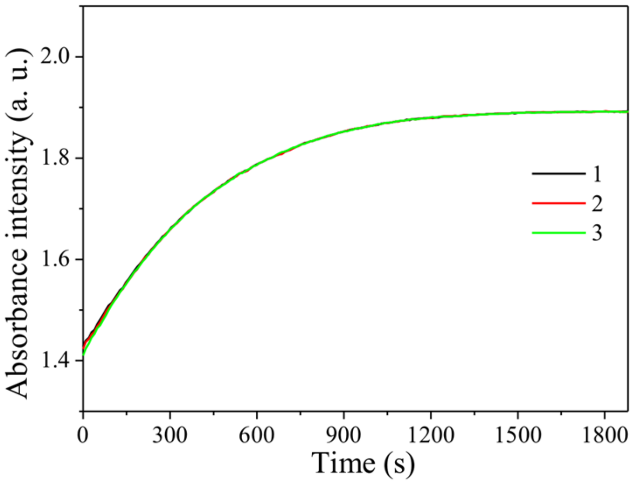

Fig. S1. UV-Vis absorbance at 270 nm for the coordination of reduced DTT (1 mM) with Cu^{2+} (10 μM) as a function of time. The different color curves represent the results of three replicated experiments.

We investigated the effects of the concentration of Hg^{2+} on the absorption spectra of Ag NPs in the absence and presence of PDCA. The interactions between Hg^{2+} and thiol species, such as DTT, glutathione, and cysteine, have been extensively studied.[1-3] When Hg^{2+} interacts with one or two thiol groups of DTT, the aggregation of Ag NPs would be alleviated. As shown in Fig. S2a, an obviously increasing A_{408} could be observed on increasing the concentration of Hg^{2+}. So, Hg^{2+} can inhibit Ag NPs from aggregation. The selectivity of the assay toward Cu^{2+} ions could be improved by the addition of chelating ligand, PDCA. The stability constants of heavy-metal ions with PDCA are logK= 20.3 (Hg^{2+}), 12.5 (Zn^{2+}), 10.9 (Mn^{2+}), 13.0 (Ni^{2+}), 22.3 (Fe^{3+}), 24.1 (Co^{2+}).[4-7] Therefore PDCA will be able to form stable complexes with Hg^{2+} or some other metal ions. Since PDCA will not be able to link with Ag NPs through the Ag-S bond in the same fashion as DTT, PDCA mostly forms complexes with Hg^{2+} in the bulk solutions, thus suppressing interference of Hg^{2+}. For a series of concentrations of Hg^{2+} investigated in the presence of PDCA, comparable results of absorbance were obtained (Fig. S2c). When the concentration of Hg^{2+} was reduced to 50 μM, the absorbance value at 408 nm of the Ag NPs was almost the same as that for the blank. As expected, the presence of PDCA masked Ag NPs toward Hg^{2+}.

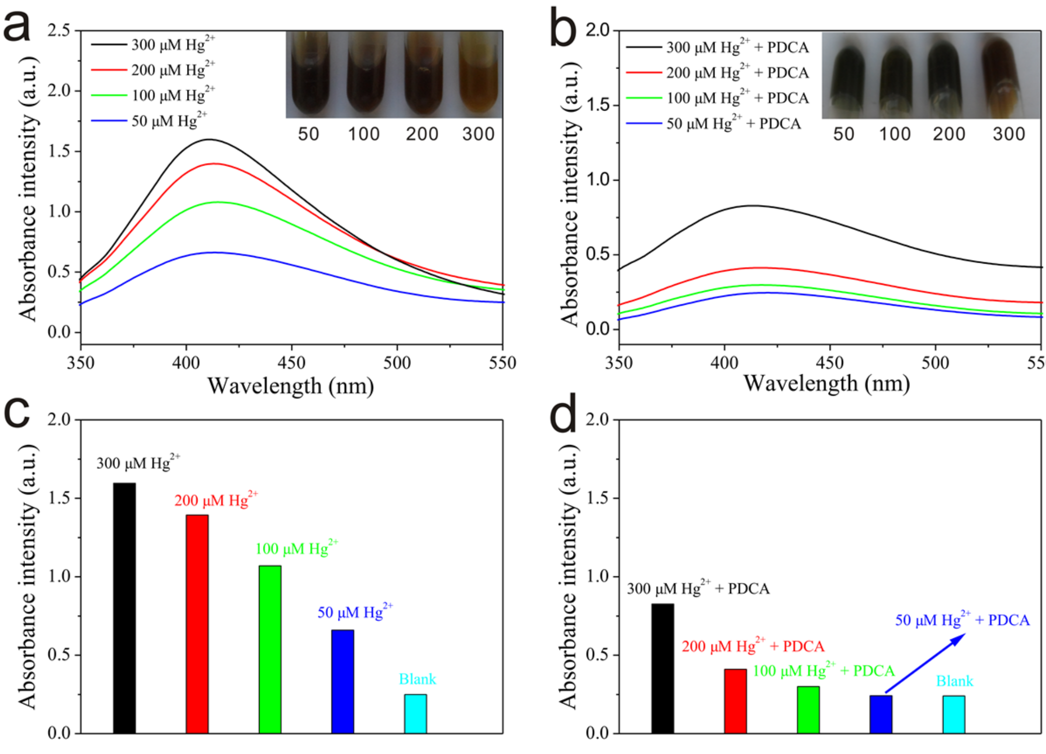

Fig. S2. The absorbance spectra of Ag NPs after the addition of mixture solutions of (a) Hg^{2+} + DTT, and (b) PDCA + Hg^{2+} + DTT. Conditions: 1 mM DTT; 5 mM PDCA. From the top to the bottom, the Hg^{2+} concentrations were 300, 200, 100 and 50 μM, respectively. The insets show the photographs of Ag NPs after incubation with various concentrations of Hg^{2+} under the corresponding measure conditions in (a) and (b), respectively. The Hg^{2+} concentrations, in μM, are listed at the bottom of the respective solutions. (c-d) The value of A_{408} corresponding to the UV-Vis spectra at the peak position in (a-b), respectively. The value of A_{408} of Ag NPs added with DTT (blank solution) was also plotted for comparison.

The UV-Vis spectra of Ag NPs were monitored to analyze the specificity of the assay in the presence of oxidizing agents. Two reagents ($KMnO_4$ and $K_2Cr_2O_7$) have been investigated, respectively. The reaction conditions were the same as the typical experiment except the added oxidizing agents that we should explore. Briefly, Cu^{2+} (2 μM) and different concentrations of $KMnO_4$ (or $K_2Cr_2O_7$) were firstly mixed well with DTT solution (1 mM) containing PDCA (5 mM) for 20 min, and then the mixture was added into the Ag NPs solution (10 mL). UV–vis spectra were recorded 10 min later.

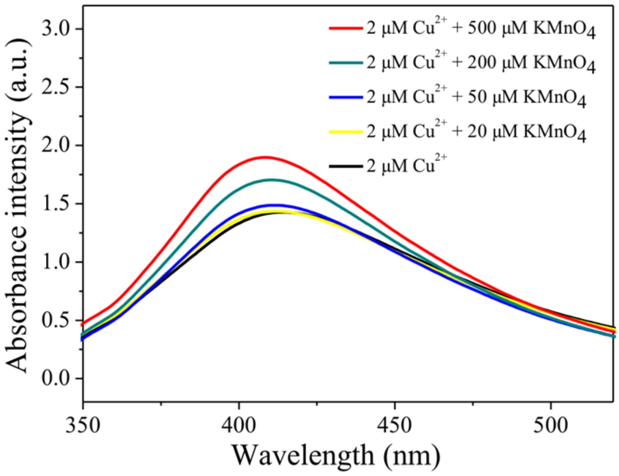

Fig. S3. UV–vis spectra of Ag NPs containing 2 μM of Cu^{2+} with the addition of various concentrations of $KMnO_4$. From the top to the bottom, the $KMnO_4$ concentrations were 500, 200, 50, 20, and 0 μM, respectively.

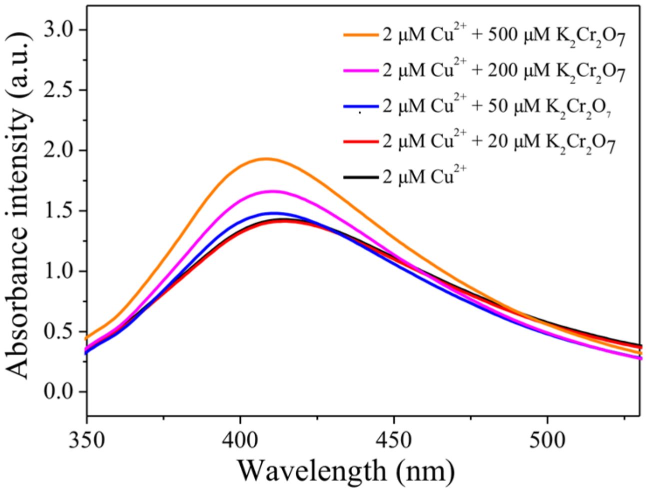

Fig. S4. UV–vis spectra of Ag NPs containing 2 μM of Cu^{2+} with the addition of various concentrations of $K_2Cr_2O_7$. From the top to the bottom, the $K_2Cr_2O_7$ concentrations were 500, 200, 50, 20, and 0μM, respectively.

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