Electronic Supplementary Information for:

A simple and sensitive method for visual detection of phosgene based on the aggregation of gold nanoparticles

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Apparatus and reagents

UV-vis spectra were recorded in 1-cm quartz cells with a TU-1900 spectrophotometer (Beijing Purkinje General Instrument Co., Ltd). Color photographs were taken with a Canon 710 IS digital camera. The sizes and aggregation patterns of Au NPs were determined by transmission electron microscopy (TEM, JEOL JEM-1011). All glasswares were cleaned with aqua regia (3:1 HCl/HNO_3) before use.

$HAuCl_4$, trisodium citrate, tetrahydrofuran (THF), and N,N-dimethylformamide (DMF) were obtained from Beijing Chemicals Ltd. Cysteine was purchased from Sinopharm Chemical Reagent Co., Ltd. Trisphosgene was obtained from Sigma-Aldrich. Other reagents employed were all of analytical grade, and were used without further purification. Deionized and distilled water was used throughout. All the experiments were carried out at room temperature.

Preparation and Characterization of Au NPs

Au NPs of 13 nm were prepared by the trisodium citrate reduction of $HAuCl_4$ following the reported method.[S1] Briefly, 50 mL of aqueous $HAuCl_4$ (0.25 mM) solution was heated to reflux with vigorously stirring and 1.3 mL of trisodium citrate (1%, w/v) was then added into the solution rapidly. The color of solution changes from light yellow to wine

red in about 3 min, indicating the formation of Au NPs. The solution was cooled to room temperature with continuous stirring and then stored in a refrigerator at 4 °C overnight prior to use. A 2-mL portion of the as-prepared Au NPs solution was diluted with 1 mL water. To the diluted Au NPs solution (about 2 nM), added was an appropriate amount of cysteine (final concentration 10 μM), followed by sonication for 30 min. After standing for 1 h without disturbance, the cysteine-modified Au NPs solution was obtained.

The size and monodispersity of Au NPs were determined by TEM. Samples for TEM analysis were prepared by placing about 20 μL of Au NPs solution on the carbon-coated copper grid and then drying at room temperature. The concentration of the as-prepared Au NPs was determined to be 3 nM by using a molar absorptivity of 2.7×10^8 M^{-1} cm^{-1} at 520 nm for 13-nm Au NPs.[S2] The average diameters of unmodified and cysteine-modified Au NPs are 14.9 nm and 16.2 nm (Fig. S1), respectively. Similar to the previous observation,[S3] the modification of Au NPs leads to an increased average diameter.

Visual and colorimetric assay of triphosgene and phosgene

Triphosgene solutions (5 mM) were prepared by dissolving in THF. To a 3-mL solution of the cysteine-modified Au NPs (2 nM), an appropriate volume of triphosgene solution was added, followed by the supplementary addition of THF to its total volume of 30 μL in the reaction system. The color change of the mixture can be monitored immediately by the naked eye, or quantitatively measured after 1 h with UV-vis spectrophotometer. In the meantime, a corresponding reagent blank containing no triphosgene was prepared and measured under the same conditions for comparison. The solutions of triphosgene and cysteine were prepared freshly before each experiment.

Liquid phosgene was prepared by dropping DMF into the solution of triphosgene (20%, w/w) in cyclohexane in a salt-ice bath (about –10 °C), and the liquid phosgene was used to produce the standard mixed gas of phosgene and air. The cysteine-modified Au NPs solution (3 mL) was exposed to the mixed gas with different concentrations (0-2.5 mg/L) of phosgene for 1 min with stirring. The color change of the reaction solution was recorded or photographed immediately.

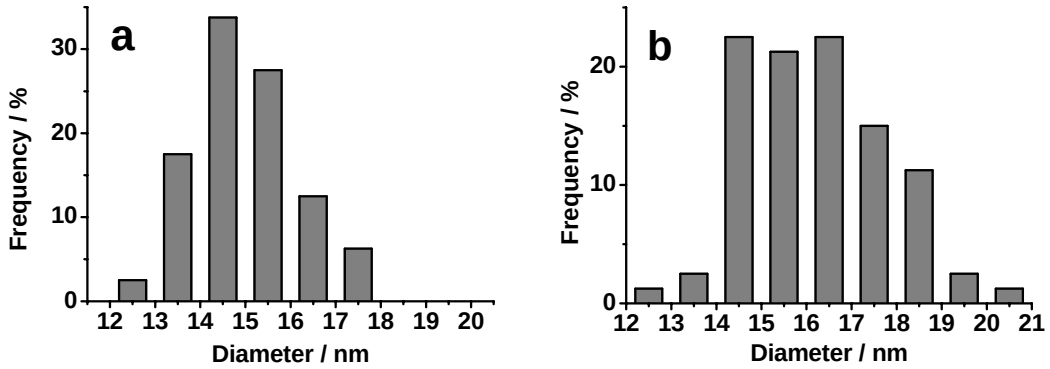

Fig. S1. The size distribution histograms of unmodified Au NPs (a) and cysteine-modified Au NPs (b). Each of the histograms was made from the TEM images by counting 80 particles.

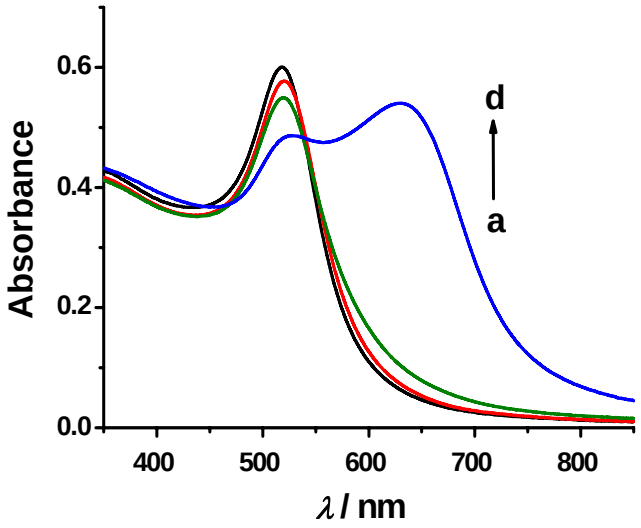

Fig. S2. Absorption spectra of different detection systems. (a) Unmodified Au NPs (2 nM) alone; (b) unmodified Au NPs (2 nM) in the presence of 40 μM triphosgene; (c) cysteine-modified Au NPs (2 nM) alone; (d) cysteine-modified Au NPs (2 nM) in the presence of 40 μM triphosgene. As can be seen, both unmodified and cysteine-modified Au NPs display a nearly identical absorption spectrum, indicating that the modification of Au NPs by cysteine hardly affects spectroscopic properties of the Au NPs. The introduction of triphosgene leads to an aggregation of only the cysteine-modified Au NPs instead of the unmodified Au NPs, concomitant with a remarkable color change. This clearly shows that only the cysteine-modified Au NPs can be used for visual detection of triphosgene.

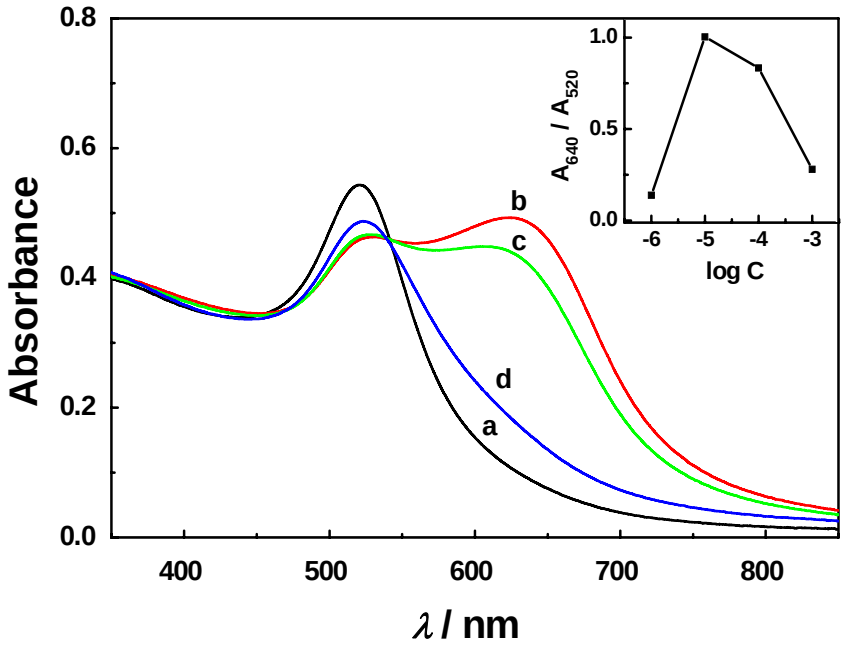

Fig. S3. The changes of absorption spectra in the reaction of triphosgene (40 μM) with Au NPs modified at varied concentrations of cysteine: (a) 1 μM; (b) 10 μM; (c) 100 μM; and (d) 1 mM. The inset shows the variation of the ratio (A_{640}/A_{520}) of the absorbances at 640 nm and 520 nm with the logarithm of molar concentration of cysteine (C).

Fig. S4. Color change of cysteine-modified Au NPs reacting with different concentrations of triphosgene: (A) 0, (B) 10, (C) 20, (D) 25, (E) 30, and (F) 40 μM.

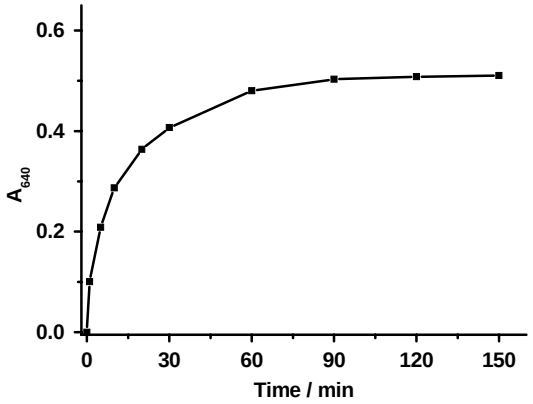

Fig. S5. The plot of the change in absorbance at 640 nm in the reaction of cysteine-modified Au NPs (2 nM) with triphosgene (40 μM) versus time. The color reaction was conducted at room temperature, and the absorbance at 640 nm was measured against the corresponding reagent blank.

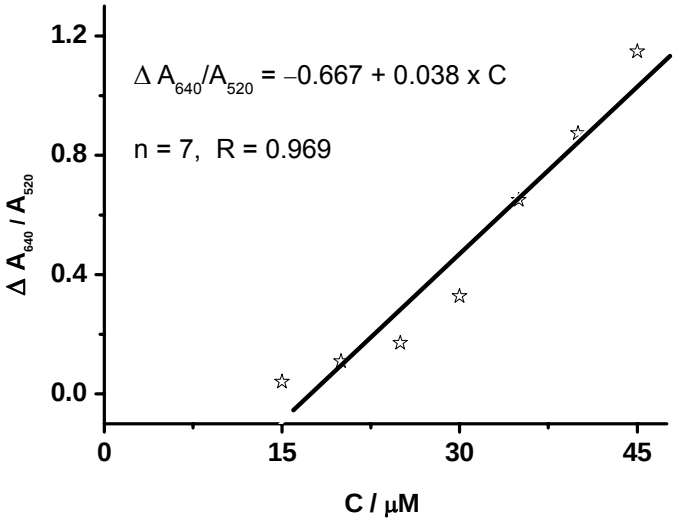

Fig. S6. The plot of the change in absorbance ratio (A_{640}/A_{520}) corrected by subtracting the corresponding absorbance ratio from the reagent blank versus the varied concentrations (C) of triphosgene from 15 to 45 μM.

References

[S1] S. K. Ghosh, A. Pal, S. Kundu, S. Nath and T. Pal, *Chem. Phys. Lett.*, 2004, **395**, 366-372.

[S2] H. Wang, Y. X. Wang, J. Y. Jin and R. H. Yang, *Anal. Chem*., 2008, **80,** 9021-9028.

[S3] J. Nam, N. Won, H. Jin, H. Chung and S. Kim, *J. Am. Chem. Soc*., 2009, **131**, 13639-13645.