Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

A highly selective and sensitive ON-OFF sensor for silver ions and cysteine by light scattering technique of DNA-Functionalized gold nanoparticles

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Preparation and characterization of gold nanoparticles

Gold nanoparticles were prepared by citrate reduction of $HAuCl_4$.[1] All glassware was cleaned with aqua regia washings (cleaning solution), rinsed with MilliQ water (18.2 MΩ cm), and oven-dried prior to use. Briefly, after boiling a 100 mL of the 0.01% $HAuCl_4$ solution, 3.5mL of the 1.0% trisodium citrate solution was quickly added with vigorous stirring. The color of the solution changed to deep red in a few seconds and the reduction of trisodium citrate to $HAuCl_4$ was practically complete after 7 min of boiling. The solution was cooled naturally to room temperature and then diluted to 100 mL. The average diameter of the prepared gold nanoparticles was about 16 nm as characterized by transmission electron microscope (TEM, see Figure S1a). Besides, the sharp peak in the UV-vis spectrum suggested it was the single size gold colliod (see Figure S1b).

Functionalization of the gold nanoparticles (Au NPs) with oligonucleotide probes

DNA-functionalized Gold nanoparticles (Au NPs-S-DNA) was prepared according to the literature method with a little modification.[2] To 4.0 mL of gold colloid solution (prepared above) was added 100 μL of the 5'-thiol-capped single strand DNA (10 μM, HPLC grade) which was activated by tris-(2-carboxyethyl)-phosphine (TCEP) solution (40 mM, freshly prepared) before used. The mixture solution was magnetically stirred to facilitate the hybridization at room temperature for 24 hours. Then, the solution was stored in a drawer at room temperature for at least 24 hours. After that, the nanoparticle solutions were centrifuged and redispersed in phosphate buffer (10 mM NaH_2PO_4/Na_2HPO_4, PH 7.0). The particles were washed three more times and then redispersed in the detection buffer. Finally, the probe solutions (Probes A and B) were put into the dark circumstance at room temperature for another 24 hours before used. The final concentrations of the probe solutions were estimated from their measured absorption at 520 nm and published values for extinction coefficients of the unmodified particles.[3] Melting experiments were carried out on a Cary UV-300 spectrophotometer at one-degree increments. The UV-vis spectra were obtained by monitoring the extinction at 520 nm for the dispersed 16 nm nanoparticle probes.

Light-scattering turn-on detection of Ag^+ using DNA-S-Au NPs conjugates sensor

As schematically shown in Scheme 1, AuNPs-S-DNA complex (Probe A, 200 μL and Probe B, 200 μL) and Na (I) ions (5 μL, 2M) were first mixed. Then, a series of dilutions of Ag (I) ions was

pipetted into the test tubes by using microsyringes before Light-scattering measurement. Spectra curve was made based on the data collected on the first minute after the addition of Ag (I) ion. The light-scattering spectra were then obtained by scanning simultaneously the excitation and emission monochromators ($\Delta\lambda$ = 0.0 nm) from 250 to 700 nm with the excitation and emission slits 5.0 nm. Based on the spectra, the RLS intensities were measured with the maximum peak located at 391.0 nm. Spectra curve was made based on the data collected on the first minute after the addition of Ag (I). The data were repeated for three times for each experiment.

Light-scattering turn-off detection of cysteine using DNA-S-Au NPs/Ag^+ complex sensor

AuNPs-S-DNA complex (Probe A, 200 μL and Probe B, 200 μL) and Na (I) ions (5 μL, 2M) were first mixed. Then, appropriate concentration of Ag (I) ions was added. After that, a series of volumes of cysteine were pipetted into the test tubes by using microsyringes. The light-scattering spectra were then recorded by scanning simultaneously the excitation and emission monochromators ($\Delta\lambda$ = 0.0 nm) from 250 to 700 nm with the excitation and emission slits 5.0 nm. Based on the spectra, the RLS intensities were measured with the maximum peak located at 391.0 nm. Spectra curve was made based on the data collected on the first minute after the addition of cysteine. The data were repeated for three times for each experiment.

Instrumentation

A Model LS-55 spectrofluorometer (Perkin-Elmer, USA) was used to measure the light-scattering spectra. The TEM images of the colloidal gold nanoparticles were acquired on a JEM-1400 transmission electron microscope (JEOL, Japan).

Notes: The limits of detection (LODs) are given by $3S_0/S$, where 3 is the factor at the 99% confidence level, S_0 is the standard deviation of the blank measurements (n=12), and S is the slope of the calibration curve.[4]

Reference

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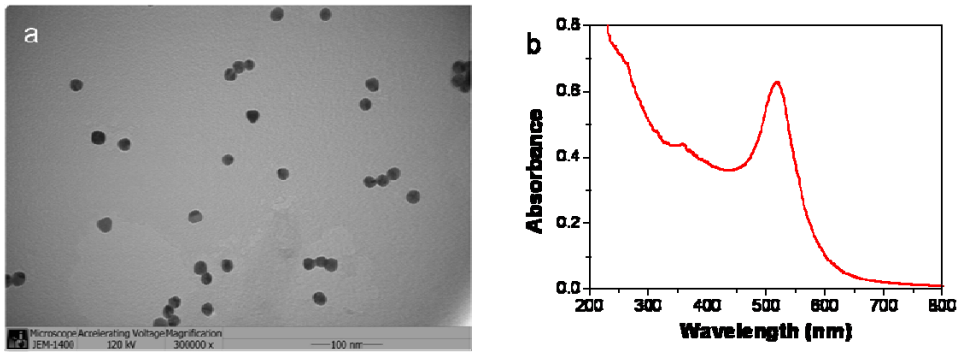
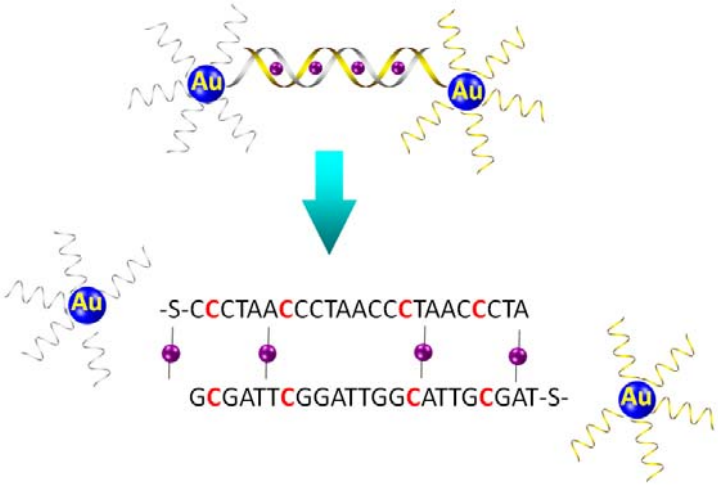


Figure S1. Typical TEM images (a) and UV-vis spectrum of prepared gold nanoparticles (b).

Probe A (PA): Au NP-5'HS-CCCTAACCCTAACCCTAACCCTA3'

Probe B (PB): Au NP-5'HS-TAGCGTTACGGTTAGGCTTAGCG3'

DNA-linked aggregates:



Scheme S1. Schematic illustration of DNA-linked aggregates by DNA-functionalized gold nanoparticles sensor in the presence of Ag^{+} ions.

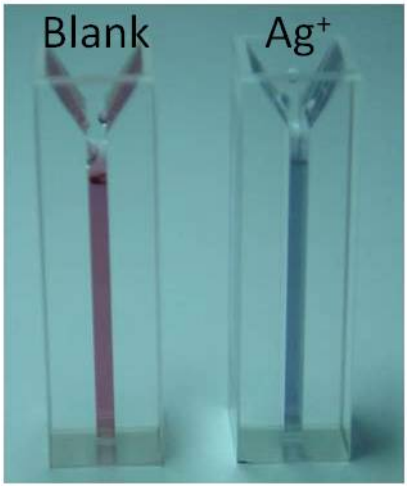


Figure S2. Color response of DNA-S-Au NPs detection system (Probe A and Probe B) in the presence of Ag^{+} ions.

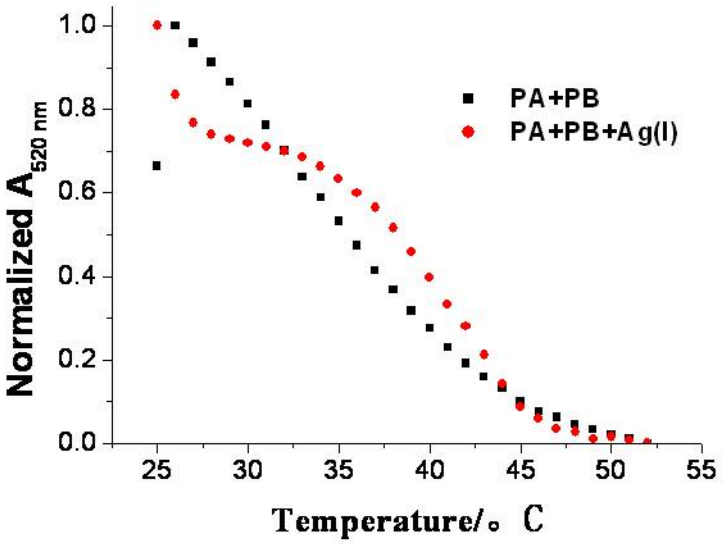


Figure S3. Normalized melting curves of the DNA-S-AuNPs/Ag^+ aggregates (Probes A and B) in the absence or present of Ag^+ solutions (10 μM).

The melting temperature (T_m) assay begins by adding an aliquot of an aqueous solution of Ag^+ at a designated concentration to a solution of the DNA-Au NP aggregates formed from probes A and B at room temperature (see above). The solution is then heated at a rate of 1 °C min^{-1} while its extinction is monitored at 520nm, where the probe DNA-S-AuNPs exhibit the maximum intensity in the visible region of the absorbance spectrum. As seen from the Fig. S3, the aggregate melt at higher temperatures after the addition of Ag^+ (increase approximately 3 °C). Thus, it can be concluded that Ag^+ stabilized the duplex DNA strands containing the C-C base mismatches because of the strong coordination of Ag^+ to the two cytosines that makes up the C-C mismatches.

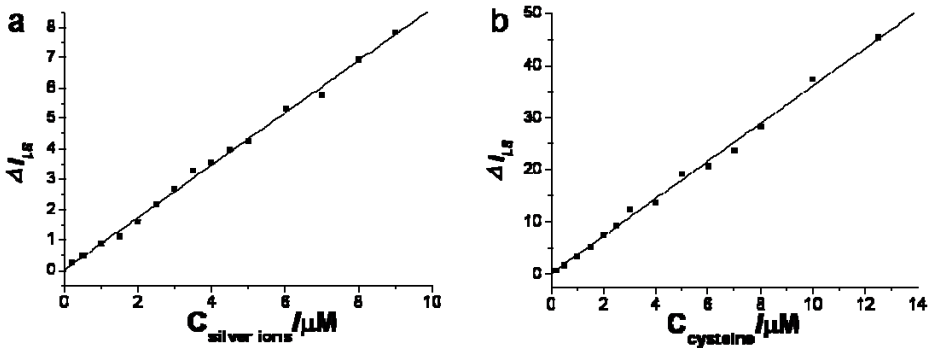


Figure S4. The change of LS intensity at 391.0 nm plotted against the concentrations of Ag^+ (a) and cysteine (b). The solid line represents a linear fit to the data. All experiments were performed in three times.

Table S1. Relationship between analyte concentration (c) and the change of LS intensity ($\triangle I_{LS}$).

Analytes	Linear ranges, nmol/L	Regression equation	R value	Detection Limit, nmol/L
Silver ions	200-9000	$\triangle I_{LS}$ = 0.029 + 0.859c	0.9983	50
Cysteine	50-12500	$\triangle I_{LS}$ = 0.062 + 3.605c	0.9981	5

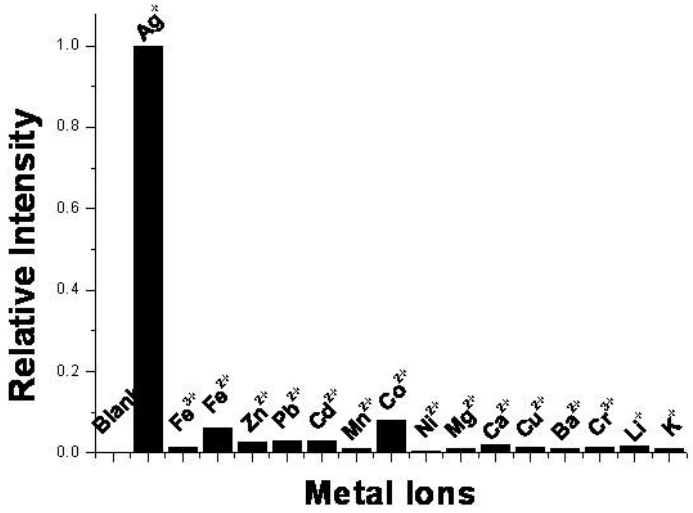


Figure S5. Selectivity of the Ag^{+} ion sensor by light-scattering turn-on strategy. All competing metal ions were tested at 25.0 μM.

Relative Intensity of Light-Scattering signal can be expressed as shown in Eq. (1):

$$\text{Relative Intensity} = (I - I_{blank}) / (I_{max} - I_{blank}) \quad (1)$$

Where I_{blank} is the light scattering intensity of the DNA-S-Au NPs aggregates without silver ions;

I_{max} is the maximum value of the light scattering intensity of the DNA-S-Au NPs aggregates in presence of metal ions;

I is the light scattering intensity of the DNA-S-Au NPs in presence of any metal ion.

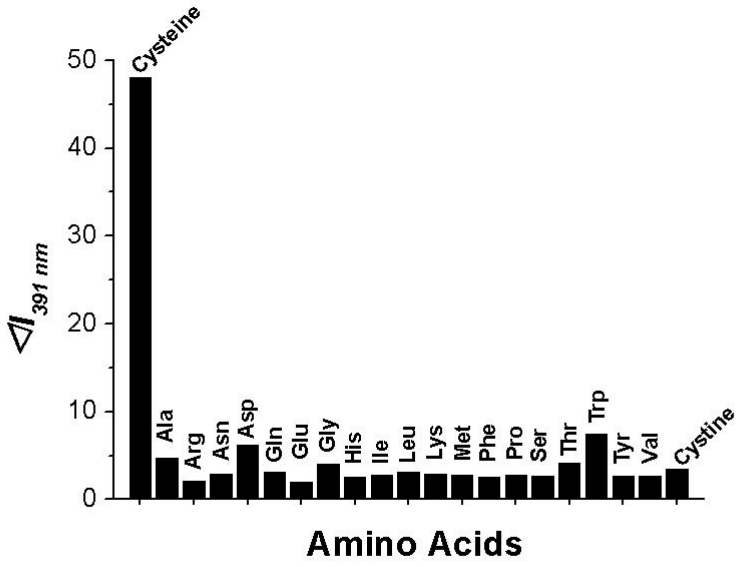


Figure S6. Selectivity of the Cysteine sensor by light-scattering turn-off strategy. All competing amino acids were tested at 250.0 μM.

Based on the spectra, the RLS intensities were measured at 391.0 nm. The increment of LS intenisty of the system was represented as $\Delta I_{LS}=I_{LS}-I^0_{LS}$, where I^0_{LS} and I_{LS} were the LS intensities of the AuNPs-S-DNA/Ag^+ system in the absence or presence of cysteine or other amino acids.

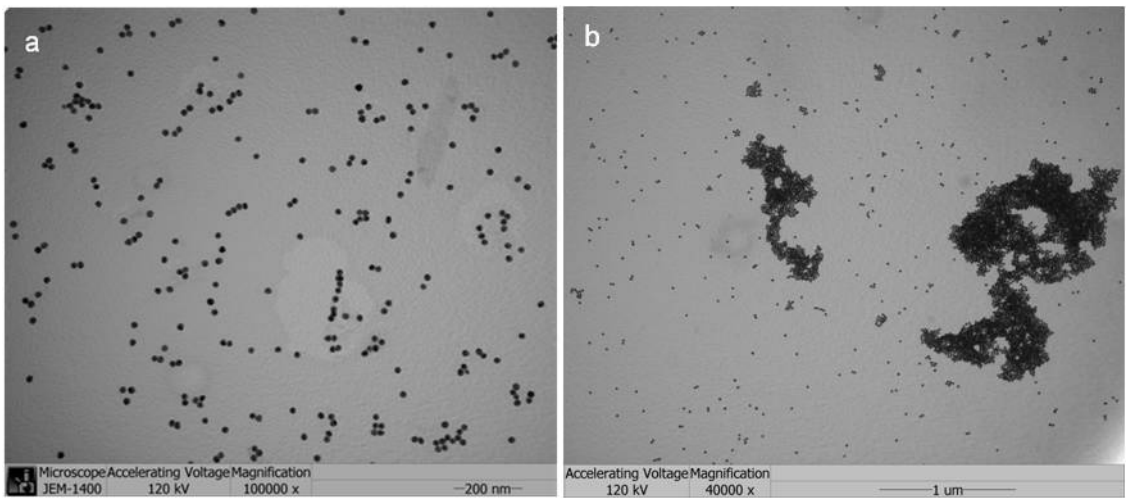


Figure S7. Typical TEM images of samples taken from the mixture solution of Probes A and B before (a) and after (b) adding Ag^+ (10 μM).

As displayed in Figure S7a, the gold nanoparticles modified by oligonucleotide probes are well monodispersed. When the Ag^+ ions was added to the incubation solution with Probes A and B, the gold nanoparticles can aggregate to form the polymeric network structure directed by DNA hybridization. Figure S7b shows the TEM image of the aggregates of the DNA-S-Au NPs/ Ag^+.

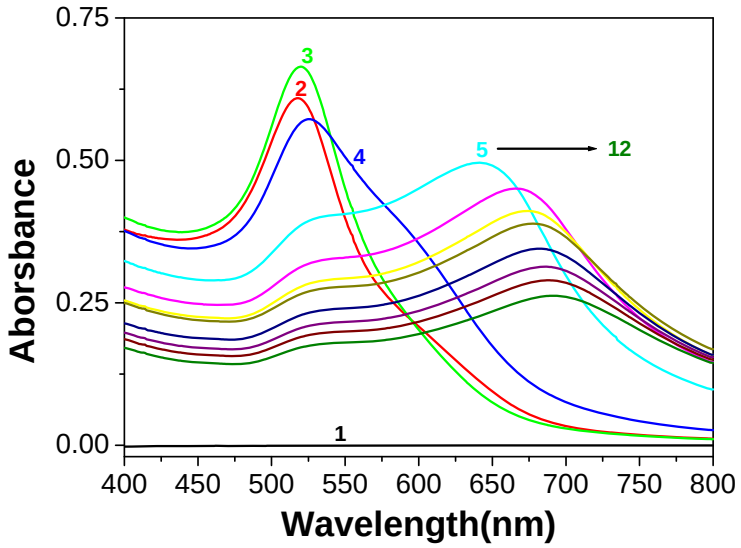


Figure S8. UV-vis spectra of the DNA-S-AuNPs/Ag^+ aggregates (Probes A and B) in the absence and presence of Cysteine solution at room temperature. Conditions: 1, Blank; 2, PA + PB; 3, PA + PB + 10 μM Ag^+; 4, PA + PB + 0.1M Na^+; 5-12, PA + PB + 10 μM Ag^+ + 0.1M Na^++ Cysteine (μM): 25, 50, 75, 100, 150, 200, 250, 375.