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Electronic Supplementary Information

DNA-templated formation of silver nanoclusters as a novel light-scattering sensor for label-free copper ions detection

Guoliang Liu,[a]‡ Da-Qian Feng,[a]‡ Tianfeng Chen,[a] Dan Li*[b] and Wenjie Zheng*[a]

[a] Department of Chemistry, College of Life Science and Technology, Jinan University, Guangzhou 510632, China

[b] Department of Chemistry, Shantou University, Guangdong 515063, China

**E-mail*: dli@stu.edu.cn

‡The authors equally contributed to the work.

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EXPERIMENTAL SECTION

Materials and Measurements:

Silver nitrate ($AgNO_3$), 99.9995%, and sodium borohydride ($NaBH_4$), 98%, were purchased from Alfa Aesar and used without further purification. The DNA sample (5'-$(CCCTAA)_3$CCCTA-3') was purchased from Sangon (Shanghai, China). All other reagents were all of analytical grade. All solutions were prepared with MilliQ water (18.2 MΩ cm) from a Millipore system. Unless otherwise noted, experiments were carried out in 10 mM Tris/HCl buffer solution (pH 7.0).

Fluorescence measurements were carried out by using an FLS-920 picosecond fluorescence lifetime spectrometer (Edinburgh Instruments, UK). The light-scattering spectra were measured with a model LS-55 spectrofluorometer (Perkin-Elmer, USA). UV-vis spectra were recorded by an Agilent 8453 UV-vis spectrophotometer (Agilent Technologies Co. Ltd., USA). CD spectra were determined by MOS-450 Circular Dichroism Spectrometer (Bio-Logic, France).

Preparation of silver nanoclusters (Ag NCs):

For the preparation of the DNA-Ag NCs, certain volume of $AgNO_3$ solution was introduced into aliquot volume of DNA solution (5'-$(CCCTAA)_3$CCCTA-3') in 10 mM Tris/HCl buffer solution (pH 7.0). The mixture was kept at 0 °C for 15 minutes. Then, the mixture was reduced by quickly adding $NaBH_4$ (must be freshly prepared before use) under vigorously shaking for 2 min.[1] Final concentrations were 15 μM in the DNA template, 90 μM in $AgNO_3$ and 90 μM in $NaBH_4$. The reaction mixture was kept in the dark at 4°C for another 3 hours before use.

DNA-Ag NCs based sensor for fluorescence turn-off detection of Cysteine.

Cysteine was activated by tris-(2-carboxyethyl)-phosphine (TCEP) solution (40 mM, freshly prepared) before used. As schematically demonstrated in Scheme 1, certain volume of DNA-Ag NCs was added into test tube. Then, a series of dilutions of cysteine were pipetted into the test tubes by using microsyringes before fluorescence measurement. Fluorescence spectra were made based on the data collected on the first minute after the addition of cysteine.[2] The data were repeated for three times for each experiment.

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DNA-Ag NCs/Cys based sensor for light-scattering turn-on detection of Cu^{2+} ions.

As schematically shown in Scheme 1, certain volume of DNA-Ag NCs/Cys was added into a test tube. Then, a series of dilutions of Cu^{2+} ions were pipetted into the test tubes by using microsyringes before light-scattering measurement. The light-scattering spectra were then obtained by scanning simultaneously the excitation and emission monochromators ($\Delta\lambda$ = 0 nm) from 250 to 700 nm with the excitation and emission slits 5 nm.[3] Based on the spectra, the RLS intensities were measured with the maximum peak located at 385 nm. Spectra curves were made based on the data collected on the first minute after the addition of Cu^{2+} ions. The data were repeated for three times for each experiment.

High-Resolution Transmission Electron Microscopy (HR-TEM).

HR-TEM images were taken with a TECNAI F-30 high-resolution transmission electron microscopy operating at 300 kV. The as-prepared Ag nanoclusters were dried on 300-mesh carbon-coated copper grids by slow natural evaporation.

References

1 J. T. Petty, J. Zheng, N. V. Hud and R. M. Dickson, *J. Am. Chem. Soc.,* 2004, **126**, 5207-5212.

2 Z. G. Chen, G. L. Liu, M. H. Chen, Y. R. Peng and M. Y. Wu, *Anal. Biochem.*, 2009, **384**, 337-342.

3 D. Q. Feng, G. L. Liu, W. J. Zheng, J. Liu, T. F. Chen and D. Li, *Chem. Comm.,* 2011, **47**, 8557-8559.

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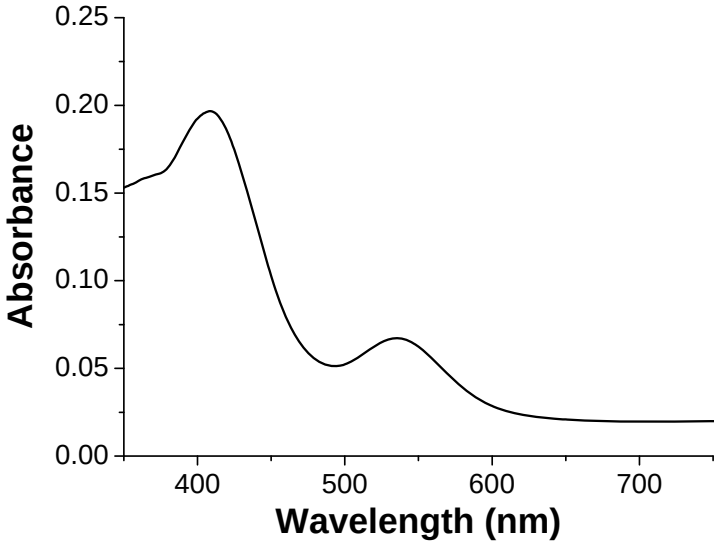

Figure S1. The absorption spectra of the synthesized DNA-Ag NCs.

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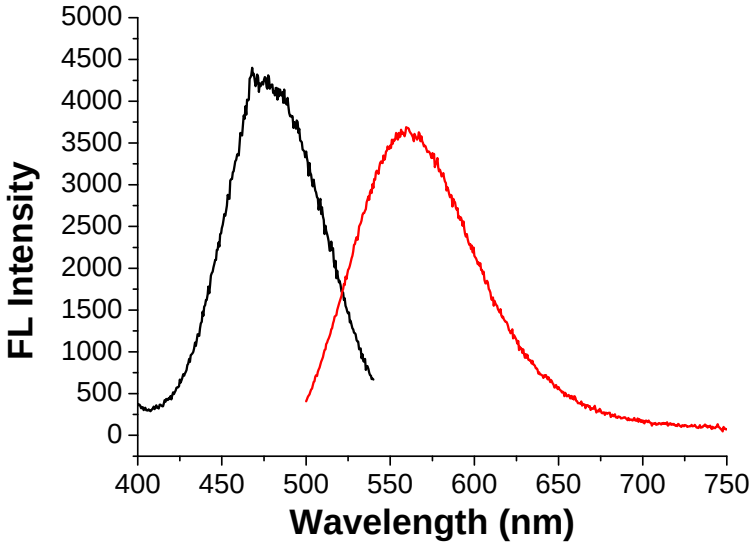

Figure S2. Fluorescence excitation (black line) and emission (red line) spectra of the synthesized DNA-Ag NCs.

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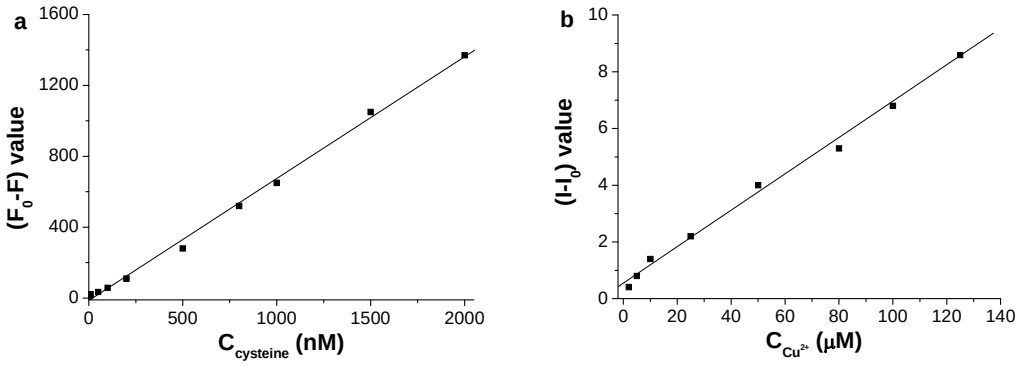

Figure S3. Linea plot results for fluorescence turn-off detecting cysteine (a) and light-scattering turn-on determining copper ions (b). The solid line represents a linear fit to the data. All experiments were performed in three times.

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

Analytes	Linear ranges	Regression equation	R value	Detection Limit
Cysteine	50-2000 (nM)	ΔI_{FL} = -13.615 + 0.688c (nM)	0.9985	20 nM
Copper ions	5-125 (μM)	ΔI_{LS} = 0. 541 + 0.063c (μM)	0.9974	0.5 μM

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Table S2. Comparison of the present approach with other reported methods for the detection of Cu^{2+} in aqueous solution.

Method	LOD	Linearity	Ref.
ICP-AES	4 nM	-	17
ICP-MS	Several nM	-	18
Fluorescent fiber optical probe	1.2 μM	0.78-6.3 μM	19
Fluorescent DNA-Ag NCs probe	8 nM	10-200 nM	7
PMAA-Ag NCs fluorescent probe	8 nM	10-6000 nM	4b
CN-DPA fluorescent probe	Several μM	2-5 μM	6b
Fluorescence turn-on probe	0.261 μM	-	20
DNA-Ag NCs LS probe	0.5 μM	5-125μM	This work

-: The value was not provided in the literature.

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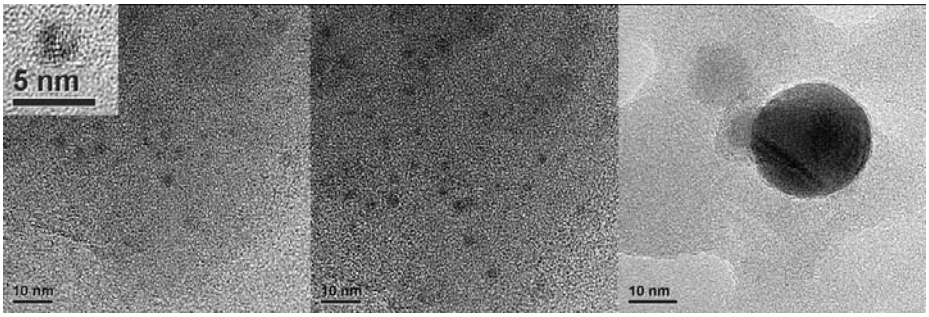

Figure S4. HR-TEM image of DNA-Ag NCs (left), DNA-Ag NCs/cysteine (middle), DNA-Ag NCs/cysteine + Cu^{2+} (right). Conditions: The concentration of DNA was kept at 15 μM. 2.5 μM cysteine, 10 mM; Cu^{2+}, 1 mM.

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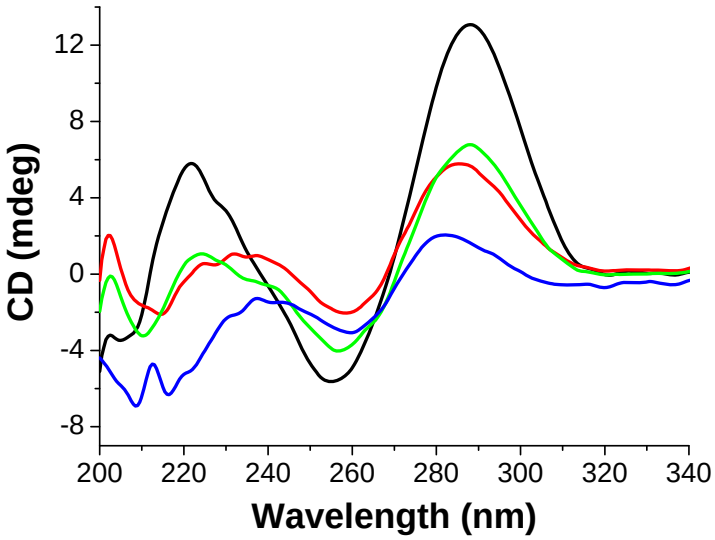

Figure S5. CD spectra of the solutions of cytosine-rich (C-rich) ssDNA alone (black line), DNA-Ag NCs (red line), DNA-Ag NCs in the presence of cysteine (2.5 μM, green line), DNA-Ag NCs + cysteine (2.5 μM) + Cu^{2+} (0.25 mM, blue line).

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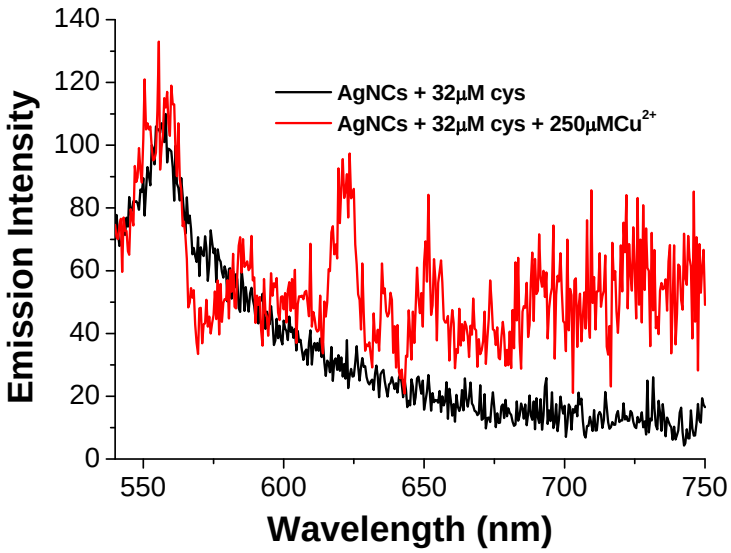

Figure S6. The emission spectrum of the DNA-Ag NCs/cys sensor in the absence (black line) or present of Cu^{2+} ions (250 μM) (red line).

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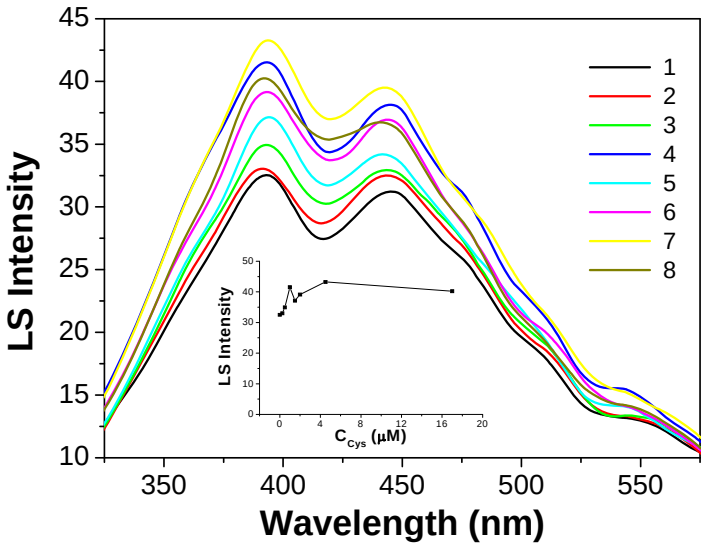

Figure S7. The effect of the concentration of cysteine (cys) on the light-scattering intensity light-scattering. The inserted figure displays the curve between light-scattering (LS) intensity and various concentrations of cysteine. Conditions: 1 (black line), DNA-Ag NCs; 2-8, 1 + cysteine (μM): 0.25 (red line), 0.5 (green line), 1 (blue line), 1.5 (cyan line), 2 (magenta line), 4.5 (yellow line), and 17 (dark yellow line).

As suggested in Fig. S7, compared with the light-scattering intensity of DNA-Ag NCs sensor in the absence of cysteine, the light-scattering signal of the DNA-Ag NCs sensor displays a weak change even introducing quite high concentration of cysteine (17 μM). Thus, it has little effect on the light-scattering intensity of DNA-Ag NCs sensor for the concentration of cysteine.

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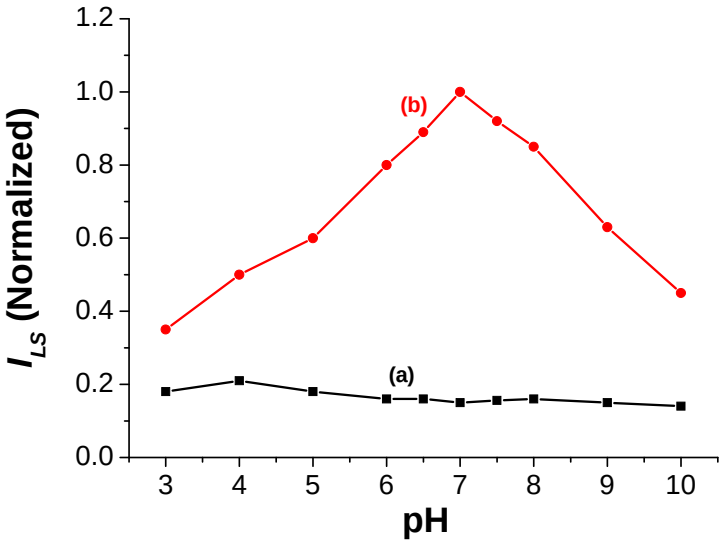

Figure S8. The effect of pH on the light-scattering intensity of DNA-Ag NCs/cys in the (a) absence and (b) presence of Cu^{2+} ions (0.5mM). Conditions: The concentration of cysteine (cys) is 1μM.

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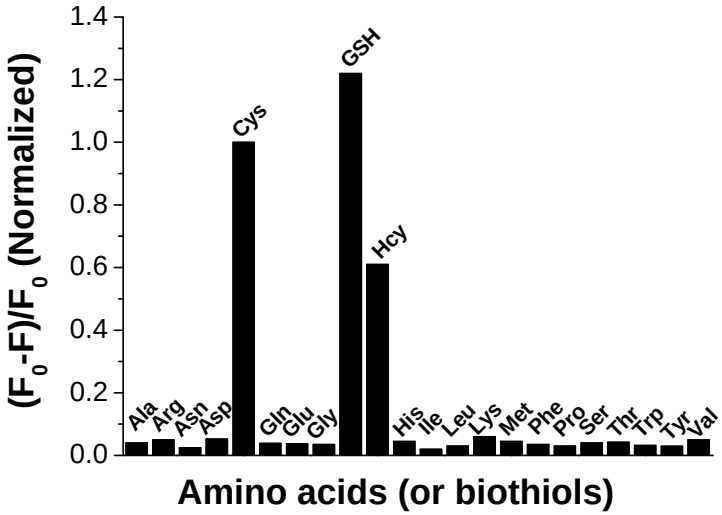

Figure S9. Fluorescence response of Ag nanoclusters in the presence of essential amino acids (10 μM).

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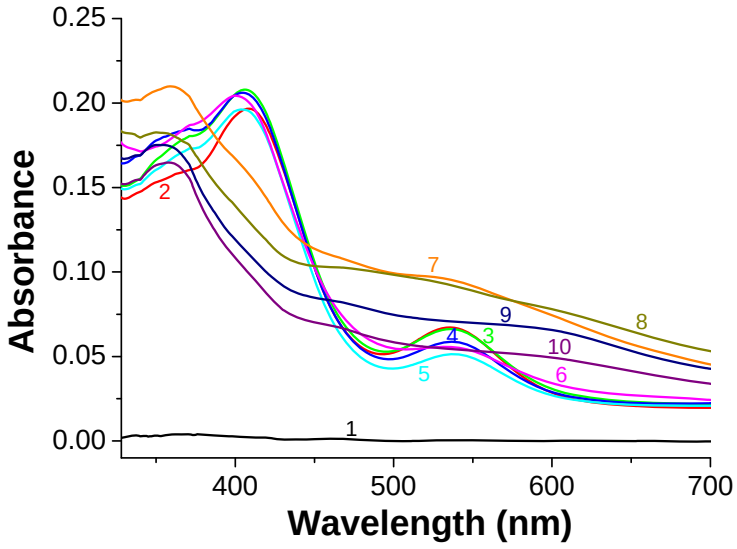

Figure S10. UV-vis spectra of the DNA-Ag NCs in the absence and presence of cysteine solution at room temperature. Conditions: 1, Blank; 2, DNA-Ag NCs; 3-10, 2 + cysteine (μM): 1, 5, 10, 20, 50, 80, 110 and 140.

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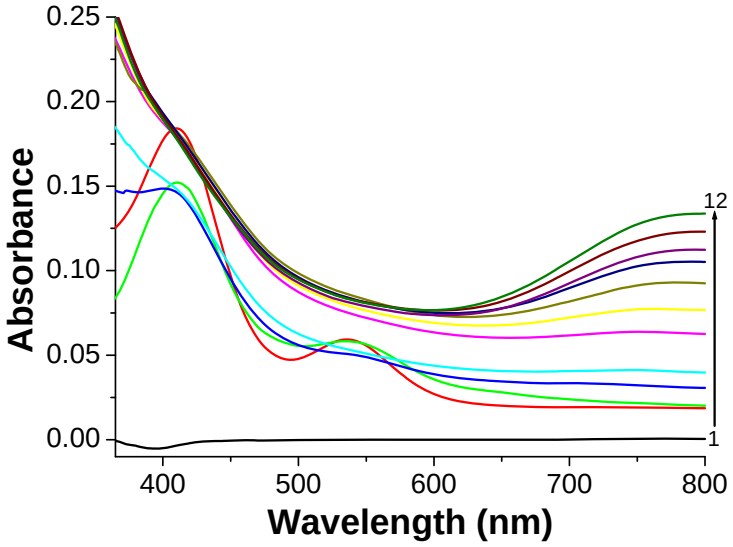

Figure S11. UV-vis spectra of the DNA-Ag NCs/cysteine in the absence and presence of copper ions at room temperature. Conditions: 1, Blank; 2, DNA-Ag NCs; 3, DNA-Ag NCs + 10μM cysteine; 4-12, 3 + Cu^{2+} (mM): 0.5, 1, 2, 3, 4, 5, 6, 7 and 8.