Supporting Information

Label-free fluorescent detection of copper (II) using DNA-templated highly luminescent silver nanoclusters

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Experimental Section

Reagents and Materials: All chemicals used were obtained from commercial sources and directly used without additional purification. All of synthetic oligonucleotides were purchased from Sangon Inc. (Shanghai, China) with the sequences listed in Table S1. Unless otherwise noted, all samples were prepared using distilled water purified by a Milli-Q water purification system (Millipore Corp., Bedford, MA). Silver nitrates ($AgNO_3$) were purchased from Sinopharm Chemical Reagent Company (Shanghai, China). Sodium borohydride ($NaBH_4$) was obtained from Tianlian Fine Chemical Co., Ltd. (Shanghai, China). $ZnCl_2$, $CoCl_2$, $NiCl_2$, $CaCl_2$, $MnCl_2$, $BaCl_2$, $PbCl_2$, $FeCl_3$, $MnCl_2$ and $CdCl_2$ were purchased from Lingfeng Fine Chemical Co., Ltd. (Shanghai, China).

Table S1. Sequences of DNA used in this work.

Name	Sequence
T1:	5'-ATCCTCCCACCGGGCCTCCCACCATAAAAACCCTTAATCCCC-3'
C1:	5'-GCTTCTTTGTTGGGTTCTTTGTTGCAAAAACCCTTAATCCCC-3'
C2:	5'-AGCGTAGAGACTGACCGTACTGTGCAAAAACCCTTAATCCCC-3'
C3:	5'-CCCTTAATCCCC-3'

Instrumentation: Fluorescence was measured in a fluorescence microplate reader (Bio-Tek Instrument, Winooski, USA) using a black 384 well microplate (Fluotrac

200, Greiner, Germany). Transmission electron microscope (TEM) measurements were performed on Jeol JEM-2100 instrument operated at an accelerating voltage of 80 kV. Samples for TEM studies were prepared by placing a drop of DNA-templated silver nanoclusters (DNA-AgNCs) solution on a copper grid. The films on the TEM grids were allowed to dry for 2 min following that the extra solution was removed using a blotting paper. Photographs were taken with Nikon D3100 digital camera (Tokyo, Japan).

Preparation of DNA-templated Luminescence Silver nanoclusters (DNA-AgNCs): The synthesis of DNA-AgNCs was according to the reported method with minor modification.[1] Briefly, 3 µM DNA template or control DNA and 20 µM $AgNO_3$ were sequentially added and mixed with sodium phosphate buffer (20 mM, pH 6.6), and the reaction mixture was incubated at room temperature, in the dark, for 20 minutes. 20 µM $NaBH_4$ was added and the reaction mixture was incubated at room temperature, in the dark, for one hour. Following reduction of Ag^+ ions, highly fluorescent DNA-AgNCs were produced with fluorescence emission at 628 nm.

Quantum Yield Measurement. UV–vis and PL spectra were obtained on a Shimadzu UV-2450 spectrometer and a Cary Eclipse (Varian) fluorometer, respectively (Fig. S2). PL quantum yields (QYs) were determined by comparing the integrated emission of the AgNCs samples in water with that of fluorescent dye rhodamine 6G (QY =95% in ethanol) with identical optical density (0.05–0.1) at the excitation wavelength according to the reported method.[2] Excitation wavelength of AgNCs was set at the absorption peak of the AgNCs samples at 564 nm. Excitation wavelength of rhodamine 6G was set at the absorption peak of the rhodamine 6G samples at 525 nm.

Data Analysis. The GraphPad Prism 5.0 software (GraphPad Software, San Diego, CA) was employed to perform the data processing. Each sample was repeated in duplicate, and data were averaged.

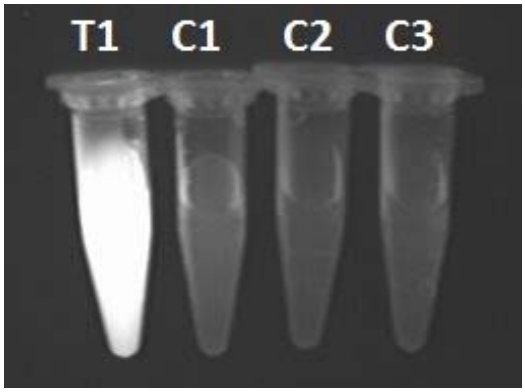

Fig. S1 An image of the highly fluorescent DNA-AgNCs (DNA template: **T1**, and other control DNA: **C1**, **C2**, and **C3**) took under the gel imaging system.

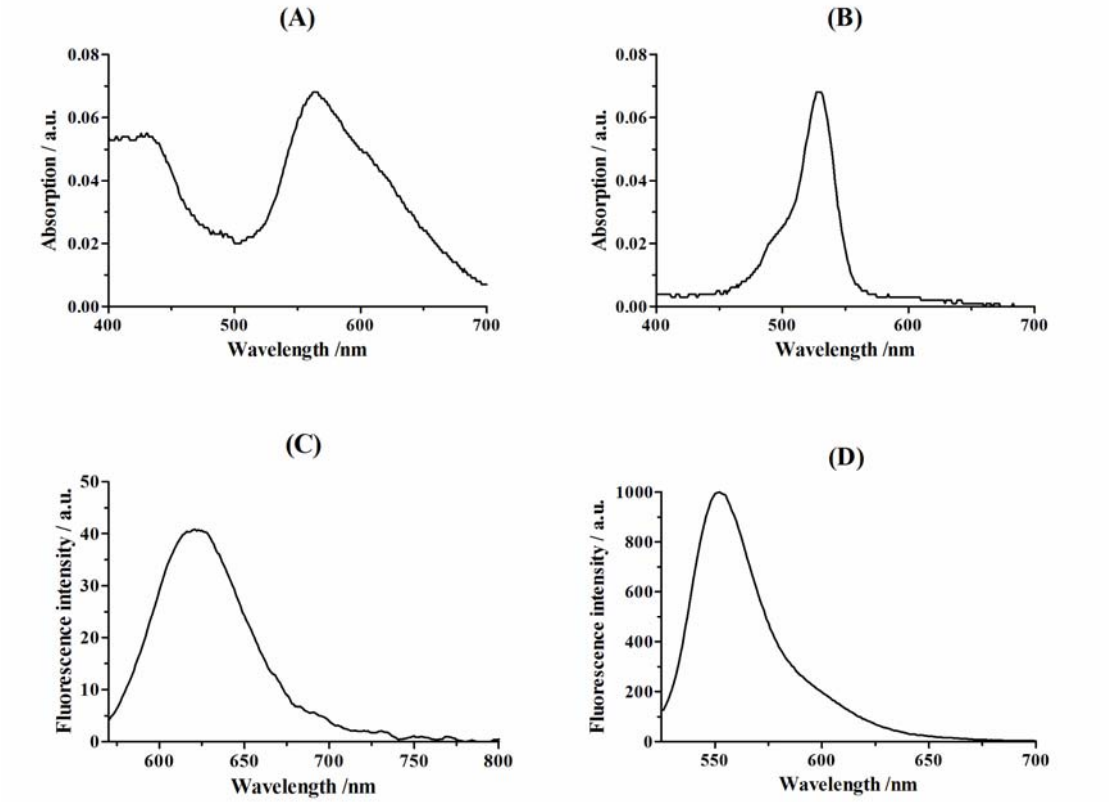

Fig. S2 Typical absorption spectra of (A) the fluorescent DNA-AgNCs and (B) fluorescent dye rhodamine 6G; The emission spectra of (C) the fluorescent DNA-AgNCs excitation at 564 nm and (D) fluorescent dye rhodamine 6G excitation at 525 nm.

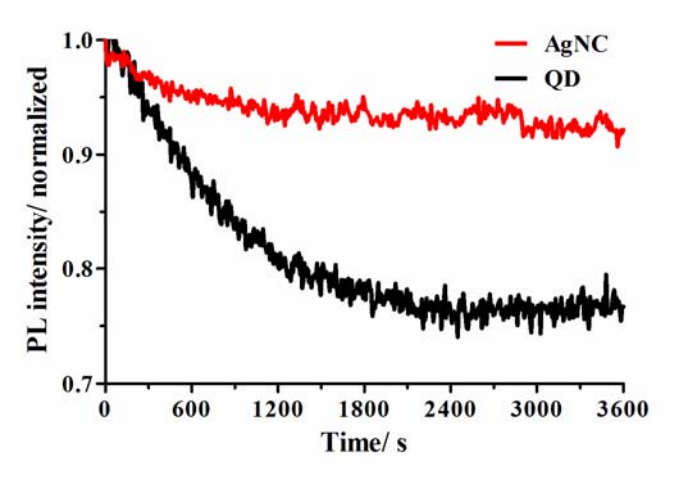

Fig. S3 Comparison of photostability between DNA-AgNCs and quantum dots (CdTe@CdS) with continuous excitation at 564 nm.

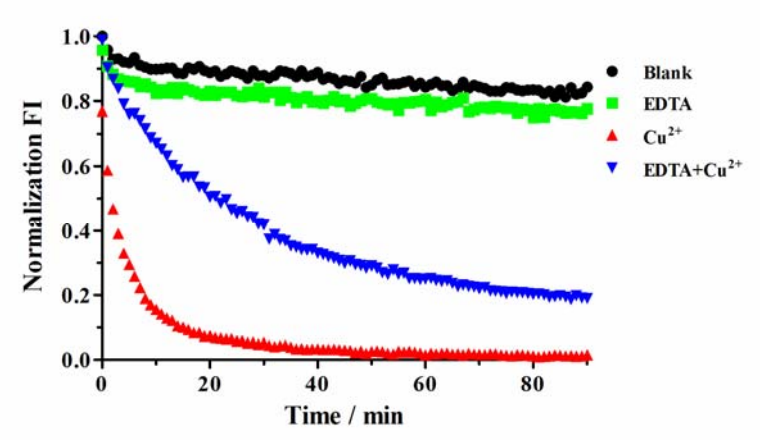

Fig. S4 Time-course behavior of fluorescent DNA-AgNCs challenged to the sample of EDTA, Cu^{2+}, and EDTA+Cu^{2+}, respectively (Ex: 564 nm, Em: 624 nm).

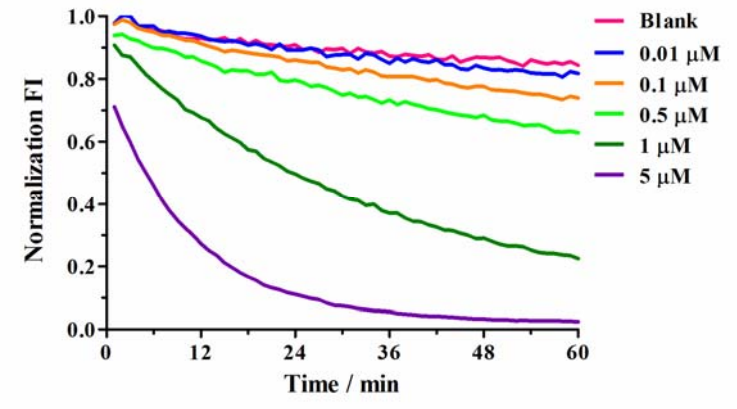

Fig. S5 Time-course of the fluorescent change of DNA-AgNCs in the prescence of various concentrations of Cu^{2+} (Ex: 564 nm; Em: 624 nm).

References:

1. J. Sharma, H. C. Yeh, H. Yoo, J. H. Werner, J. S. Martinez, *Chem. Commun.* 2011, **47**, 2294.
2. (a) X. Zhong, M. Han, Z. Dong, T. J. White, W. Knoll, *J. Am. Chem. Soc.* 2003, **125**, 8589. (b) X. Zhong, Y. Feng, W. Knoll, M. Han, *J. Am. Chem. Soc.* 2003, **125**, 13559. (c) M. Grabolle, M. Spieles, V. Lesnyak, N. Gaponik, A. Eychmuller, U. Resch-Genger, *Anal. Chem.* 2009, **81**, 6285.