Electronic Supplementary Material (ESI) for Analyst
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Supporting Information

A simple and sensitive sensor for rapid detection of sulfide anions using DNA-templated copper nanoparticles as fluorescent probes

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1. Materials and methods

1.1. Chemicals and oligonucleotides. Sodium ascorbate, 3-(N-Morpholino)-propane sulfonic Acid (MOPS), 2, 6-pyridinedicarboxylic acid (PDCA), Tween 80, sodium oleate, NaCl, $CuCl_2$, $MgCl_2$, Na_2S, NaF, NaBr and other used anionic compounds were commercially available and were at least analytical grade. All solution was prepared with Milli-Q water (18.25 MΩ cm^{-1}) from Millipore system. DNA was synthesized by Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China). DNA 1 is complementary with DNA 2, and DNA 3 is a random oligonucleotide, these oligonucleotide sequences are listed as follows:

DNA 1: 5'-TACTCATACGCTCATACGTTCATCACGACTACACA-3'

DNA 2: 3'-ATGAGTATGCGAGTATGCAAGTAGTGCTGATGTGT-5'

DNA 3: 3'-TTATTATGCATGCGAAGTGAGTGGATGGATGTCGA-5'

1.2. Sensor Preparation. At first, equimolar amounts of DNA 1 (500 nM) and DNA 2 (500 nM) were mixed in MOPS buffer (MOPS (10 mM) and NaCl (150 mM), pH 7.5); The resulting solution was heated at 95°C for 5 min and then cooled down to room temperature. Next, Tween 80 (0.005%) and sodium ascorbate (1 mM) were added into the above solution and mixed well. At last, $CuSO_4$ (100 μM) was added and mixed well. The formation of CuNPs completed within 10 min as monitored by fluorescence spectroscopy, *i. e.*, the increase of fluorescence intensity at 585 nm (λ_{ex} = 340 nm). The final solution containing dsDNA-CuNPs complex was used as the sensor for the detection of S^{2-}.

1.3. Fluorescence measurement for the sensor. Sulfide anions (5 μL) of different concentrations were mixed with the sensor (500 μL). After a 5 min incubation, the

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fluorescence spectra of the mixture were recorded by a Perkin-Elmer LS-55 Fluorescence Spectrometer (Perkin-Elmer, USA) at room temperature (λ_{ex} = 340 nm, λ_{em} = 585 nm).

1.4. Atomic force microscopy (AFM) imaging. The sample of dsDNA-CuNPs solution (0.5 μl) was deposited onto a thin silicon pellet (XinKe, China), left to adsorb for 10 min and then blow dried with nitrogen. Then the sample was scanned in a tapping mode using VEECO Dimension 3100 Atomic Force Microscope with scan rate of 1 Hz. All the images were analyzed by using Digital Instruments NanoScope (version 5.31) software.

1.5. Preparation of river water samples. River water samples collected from Pearl River (Guangzhou, China) were filtered through a 0.2 μm membrane. Aliquots of the river water were spiked with different amounts of S^{2-}.

2. Results

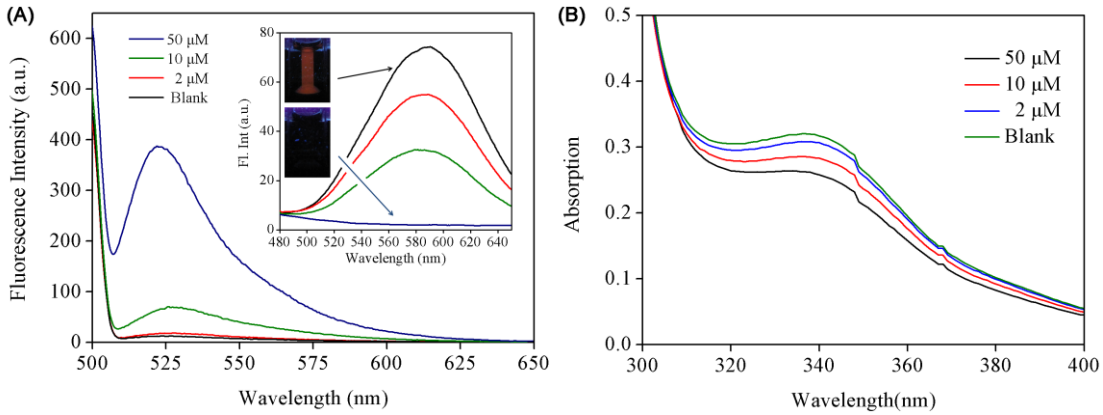

Fig. S1 (A) Fluorescence emission spectra (λ_{ex} = 498 nm) of the dsDNA-SYBR Green I complex with various concentrations of S^{2-}. Inset shows fluorescence emission spectra (λ_{ex} = 340 nm) of dsDNA-CuNPs and photograph of different dsDNA-CuNP solutions upon excitation under a hand-held UV lamp (365 nm); (B) UV-vis absorption spectra of dsDNA-CuNPs in the presence of different amounts of S^{2-}.

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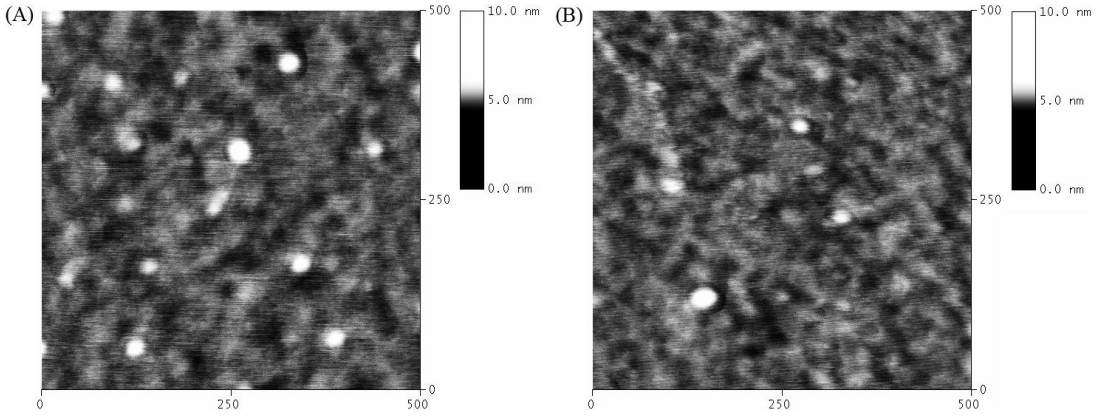

Fig. S2 AFM image of dsDNA-CuNPs before (A) and after (B) addition of sulfide anions (50 μM).

To explore how S^{2-} reduces the fluorescence of dsDNA-CuNPs, SYBR Green I (SG) was used in following experiments (SG can bind to the major groove of dsDNA, where the CuNPs accumulate, and the resulting dsDNA-SG complex emits florescence at 520 nm, λ_{ex} = 498 nm). Aliquots of double-stranded DNA-CuNPs solution were first treated with 2, 10 and 50 μM S^{2-} separately, and the emission spectra were measured at 585 nm (λ_{ex} = 340 nm). Then the treated solutions were stained with SG, and the emission spectra of SG of the solution were measured at 520 nm (λ_{ex} = 498 nm). As shown in Fig. S1A, the untreated dsDNA-CuNPs solution (black curve) has very low emission at 520 nm, while its emission at 585 nm was high (inset, black curve; orange red light under UV illumination). These results indicate that the CuNPs have formed and occupied the major groove of dsDNA, which prevents SG from binding to dsDNA. When the solution was treated with 2 μM of S^{2-}, the emission of SG increased (red curve). Contrarily, the emission of dsDNA-CuNPs decreased (inset, red curve). These changes can also be observed in the case of addition of 10 μM S^{2-} (green curve). The results reveal that CuNPs were removed form dsDNA upon the addition of S^{2-}. In the presence of excess S^{2-} (50 μM), the fluorescence of CuNPs was completely disappeared (inset, blue curve), and no reddish orange light was observed under UV illumination, implying the complete destroy of the dsDNA-CuNPs. Meanwhile, the fluorescence at 520 nm increased (blue curve) dramatically, suggesting the existence of large quantity of free dsDNA. The fluorescence increase of SG upon the increase of S^{2-} demonstrated that S^{2-} caused the dissociation and the fluorescence reduction of the dsDNA-CuNPs. The UV-vis

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absorption spectra of the solution with different amounts of S^{2-} were further measured. As shown in Fig. S1B, the dsDNA-CuNPs solutions have a peak absorbance at 340 nm, and the absorption intensities decrease with the increases of S^{2-}. In addition, by AFM, we were able to observe that dsDNA-CuNPs formed (about 10 nm) and 90% nanoparticles disappeared when 50 μM S^{2-} was added (Fig. S2). These observation further demonstrated that S^{2-} caused the dissociation of dsDNA-CuNPs, resulting in the fluorescence reduction of the dsDNA-CuNPs.

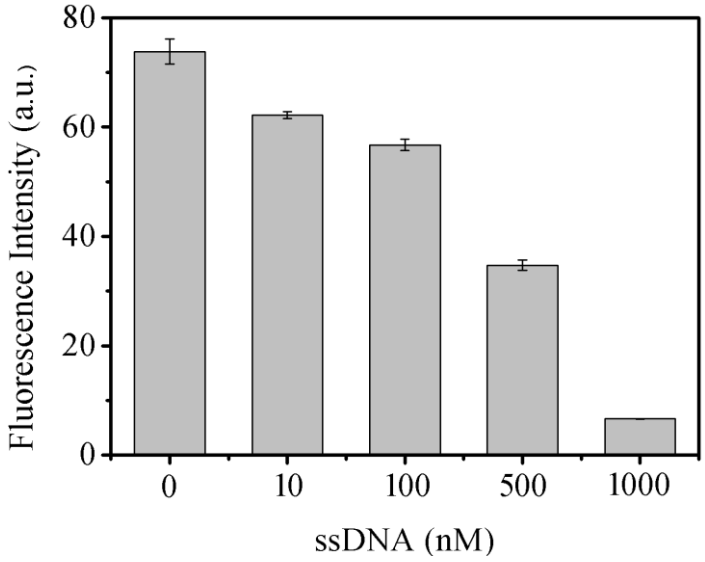

Fig. S3 Effect of ssDNA on the dsDNA-templated formation of CuNPs.

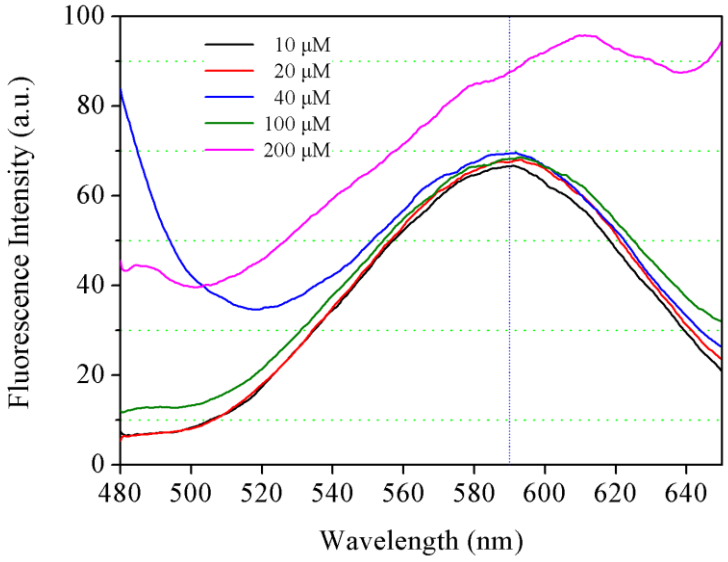

Fig. S4 Effect of sodium oleate on the formation of CuNPs.

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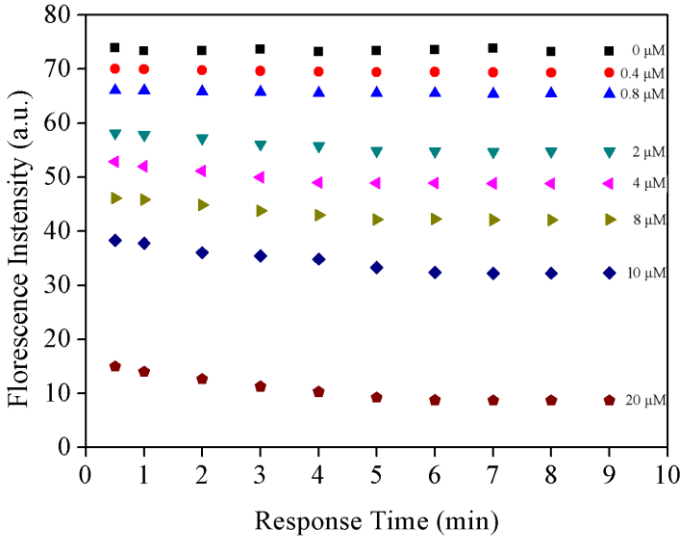

Fig. S5 Kinetics study for fluorescence intensity changes of dsDNA-CuNPs probes in the presence of various amounts of S^{2-}.

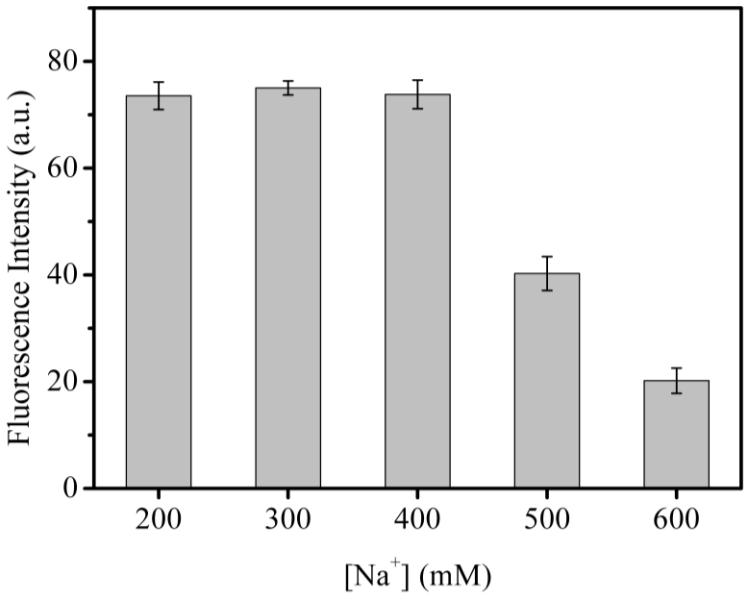

Fig. S6 Effect of the concentration of Na^+ on the fluorescence intensity of dsDNA CuNPs.

Table S1 Measurements of S^{2-} spiked in river water

River water	S^{2-} spiked (μM)	S^{2-} measured (μM)[a]	Recovery (%)
1	0.5	0.57±0.02	114.0
2	5	4.93±0.19	98.6
3	13	13.28±0.12	102.2

[a]Average of five measurements±standard deviation.