Electronic Supplementary Material (ESI) for Analytical Methods.

Electronic Supplementary Information

Fluorescent G-Quadruplex-NMM DNA Probe for Detection of Sliver Nanoparticles in Aqueous Media

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Experimental Section

Materials and Reagents. The purified G-quadruplexes oligonucleotide (G-DNA: 5'-TGGGTAGGGCGGGTTGGGAAA-3') was synthesized by Sangon Biotech. Co., Ltd. (Shanghai, China). The stock solution of G-DNA (100 μM) was prepared in 10 mM Tris-Ac, 1 mM EDTA buffer (pH 8.0) and stored at -20 °C before use. NMM and different size citrate-stabilized AgNPs were obtained from Sigma-Aldrich (China). The used metal salts were purchased from Sinopharm Group Chemical Reagent (Shanghai, China). All aqueous solutions were prepared with ultrapure water.

Detection of Ag^+ Based on G-DNA-NMM Probe. 250 μL of G-DNA (0.8 μM) was prepared in 20 mM Tris-Ac, 4 mM EDTA buffer (pH 8.0) and heated to 90 °C for 5 min. 250 μL different concentrations of Ag^+ was then added to this solution and cooled slowly to room temperature for 30 min. After that, 1 mM of KAc and 0.05 % of Triton X-100 was added and the mixture was incubated for another 30 min to form G-quadruplex structures. Finally, the 1 μM of NMM was added and the fluorescent spectra of mixture were recorded with a Cary Eclipse spectrophotometer (Varian, Inc.) with the following settings: excitation wavelength = 399 nm, excitation slit = 10 nm, emission slit = 5 nm.

Detection of AgNPs Based on G-DNA-NMM Probe. Oxidation reaction of AgNPs to Ag^+ was performed under acidic condition with H_2O_2 [24] . A solution of AgNPs (10 nm, 20 nm, or 100 nm) was added to a solution of 1 mM H_2O_2 and 1 μM H_3PO_4, and incubated at room temperature for 30 min. The resulting solution was directly added to the heated G-DNA solution and incubated for another 30 min. After that, 1

mM of KAc and 0.05 % of Triton X-100 was added to allow the G-DNA to form G-quadruplex structures. Finally, 1 μM of NMM was added and the fluorescence of mixture was recorded with a Cary Eclipse spectrophotometer (Varian, Inc.).

Preparation of G-DNA-hemin complexes modulated by Ag^+, AgNPs, or H_2O_2. The G-DNA-hemin complexes were prepared following the procedures described in the literature with little modified. Briefly, G-DNA was prepared in 10 mM Tris-Ac buffer (pH = 8.0) containing 5 mM KAc and 0.01% Triton X-100. The DNA solution was heated to 90 °C for 5 min and then cooled slowly to room temperature. To this solution was added different concentrations of Ag^+, AgNPs or H_2O_2 and incubated for another 30 min at room temperature. Then, hemin (0.5 μM) was added to the mixture and held for 1 h. After that, ABTS (2 mM) and H_2O_2 (2 mM) was added and the absorbance at 420 nm of the reaction product $ABTS^+$ was recorded by UV-vis spectrophotometer.

Analysis of Environmental Water Sample. We collected water sample from Dongbu Reservoir (Hefei, China). AgNPs samples were prepared with standard solutions of AgNPs. Then, the samples were oxidized to Ag^+ with a solution of 1 mM H_2O_2 and 1 μM H_3PO_4. The resulting solution was directly added to the heated G-DNA solution and incubated for another 30 min. After that, 1 mM of KAc and 0.05 % of Triton X-100 was added to allow the G-DNA to form G-quadruplex structures. Finally, 1 μM of NMM was added and the fluorescence of mixture was recorded with a Cary Eclipse spectrophotometer.

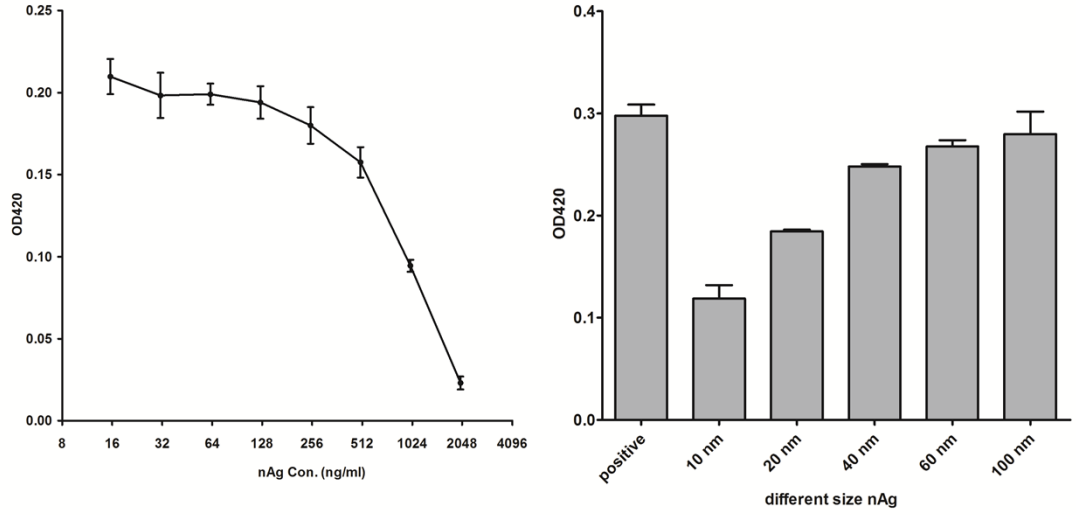

Fig. S1

Fig. S1 Inhibition of the peroxidase activity of G-DNA-hemin by different sizes of AgNPs (4 μM).

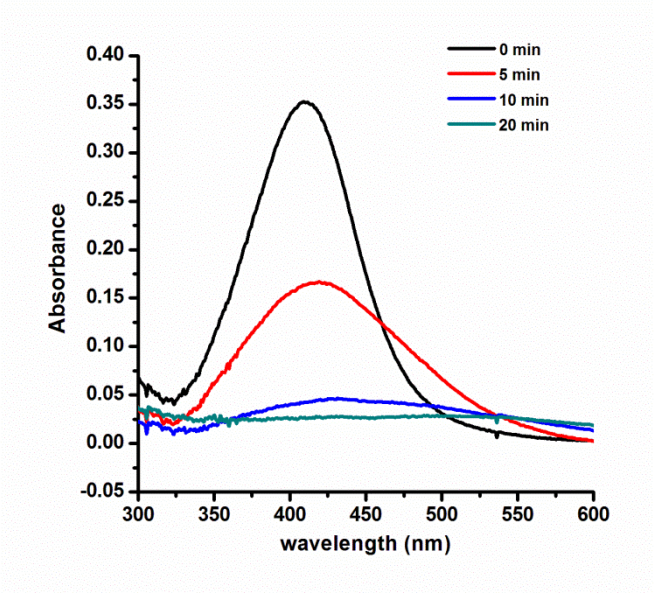

Fig. S2

Fig. S2 Time-dependence of the equilibration of AgNPs (20 nm) to Ag^+ ions by H_2O_2 under acid condition.

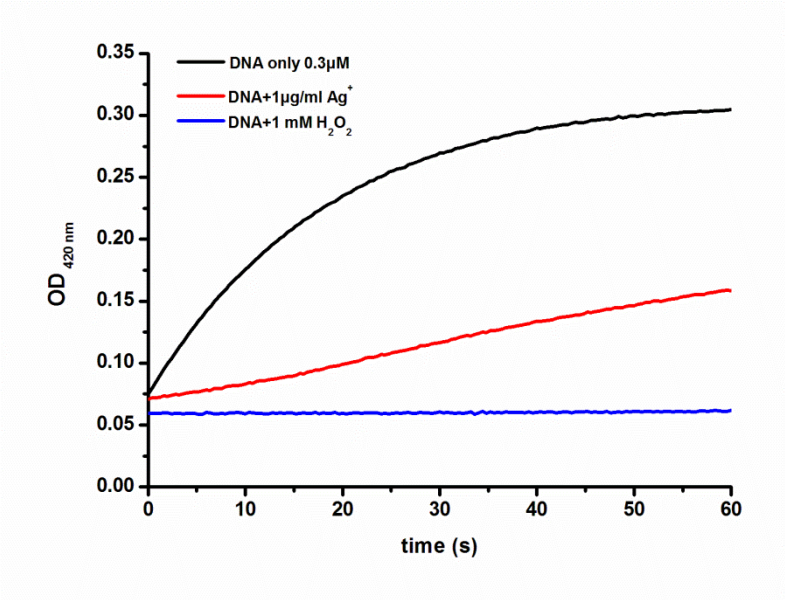

Fig. S3

Fig. S3 Kinetics curves for the ABTS-H_2O_2 reactions catalyzed by the G-DNA-hemin complex after incubated with Ag^+ (1 μg/ml) or H_2O_2 (1 mM).

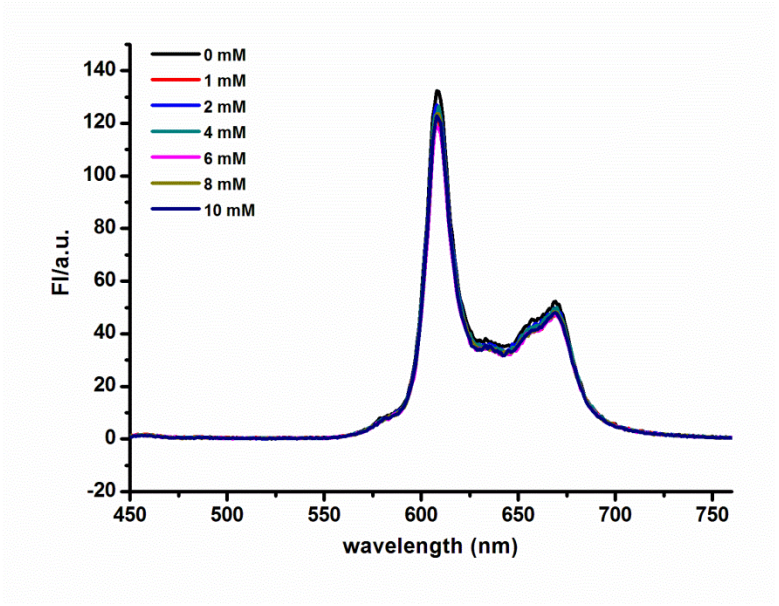

Fig. S4

Fig. S4 Fluorescence spectra of G-DNA-NMM (1 μM) on the addition of different concentrations of H_2O_2 (0-10 mM).

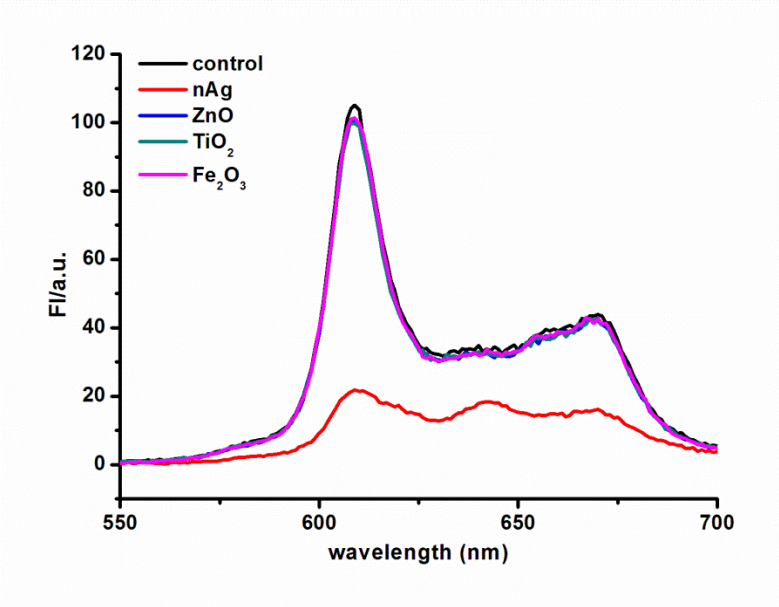

Fig. S5

Fig.S5 Fluorescence spectral changes of G-DNA-NMM (0.4 μM) on the addition of other nanoparticles (1 μg/ml), which has been treated with 1.0 mM H_2O_2 and 1.0 μM H_3PO_4. ZnO, 20 nm; TiO_2, 20 nm; Fe_2O_3, 20 nm.