

Electronic Supporting Information for the Article:

A Graphene-based Fluorescent Nanoprobe for Silver(I) Ions Detection by using Graphene Oxide and a Silver-Specific Oligonucleotide

Yanqin Wen,^a Feifei Xing,^b Shijiang He,^a Shiping Song,^a Lihua Wang,^a Yitao Long,^c
Di Li,^{a*} Chunhai Fan^{a*}

^a*Laboratory of Physical Biology, Shanghai Institute of Applied Physics, Chinese Academy of Sciences, Shanghai 201800, China,*

^b*School of Science, Department of chemistry, Shanghai University, Shanghai 200444, China*

^c*School of Chemistry and Chemical Engineering, East China University of Science and Technology, Shanghai, 200237, China*

Experimental Section

Materials

The DNA oligonucleotide (SSO, 5'-FAM-CTCTCTTCTCTTCATTTTTCAACA CAACACAC-3') was synthesized by Takara Biotechnology Co. (Dalian, China) and purified by HPLC. The colored bases in this sequence are the binding site for Ag⁺. 3-morpholinopropanesulfonic acid (MOPs) was purchased from sigma. AgNO₃, LiNO₃, Ca(NO₃)₂, Mg(CH₃COO)₂, Cu(NO₃)₂, Zn(NO₃)₂, Cd(NO₃)₂, Co(NO₃)₂, Mn(CH₃COO)₂, Ni(NO₃)₂, Pb(NO₃)₂, Hg(NO₃)₂ and FeCl₃ were of analytical grade and used as received. All solutions were prepared with Milli-Q water (18 MΩ cm⁻¹) from a Millipore system. Environmental water sample was taken from a nearby river and centrifuged to remove the insoluble impurities.

Preparation of GO

GO was synthesized from graphite powder based on the Hummer's method. Briefly, graphite powder (4 g) was oxidized in a hot solution (80°C) of concentrated H₂SO₄ (24 mL) containing K₂S₂O₈ (8 g), and P₂O₅ (8 g). The resulting dark blue mixture was thermally isolated and slowly cooled to room temperature over a period of 6 h. The

mixture was diluted to 300 mL, and then filtrated with a filter membrane of 0.22 μm (Generay Biotech Co., Ltd., Shanghai, China) and dried overnight at 60°C. These preoxidized graphite powder (2 g) was added to 92 mL of cold H_2SO_4 (0°C), to which KMnO_4 (12 g) was gradually added under continuous stirring in ice-bath. After 15 min, NaNO_3 (2 g) was added to the mixture. The solution was further stirred for 2 h at 35 °C and distilled water (200 mL) was added. The reaction was stopped with the addition of a mixture of 560 mL of distilled water and 10 mL of H_2O_2 (30 %). The product was washed with HCl (1:10) and then with water, and then suspended in distilled water. The brown dispersion was extensively dialyzed to remove residual metal ions and acids, and then exfoliated via sonication for 1.5 h (300 W). Unexfoliated graphite oxide was removed by centrifugation (3000 rpm, 5 min) using Centrifuge himac-CF 16RX (Hitachi, Japan).

Fluorescence assay for Ag(I) Ions

Ag(I) ions of different concentrations were incubated in MOPS buffer (1 mL, pH 7.0) containing 50 mM of NaNO_3 and 10 nM of SSO for 5 min at 23°C. Then 20 μL of GO (0.5 $\mu\text{g}/\mu\text{L}$) was added to this mixture and the fluorescence measurement was carried out 2 min after the GO addition at 23°C.

Instruments

The fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer equipped with a Xenon lamp excitation source. The excitation wavelength was $\lambda=494$ nm, and the fluorescence measurements were carried out at 23°C.

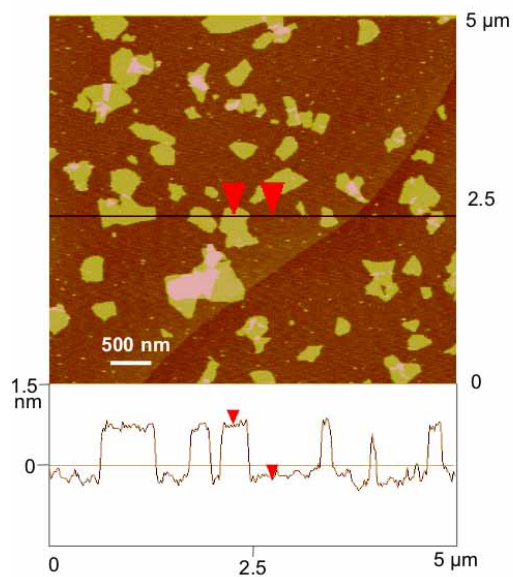


Figure S1 AFM tapping-mode image of the as-prepared GO sheets and the height profile along the dashed line in panel.

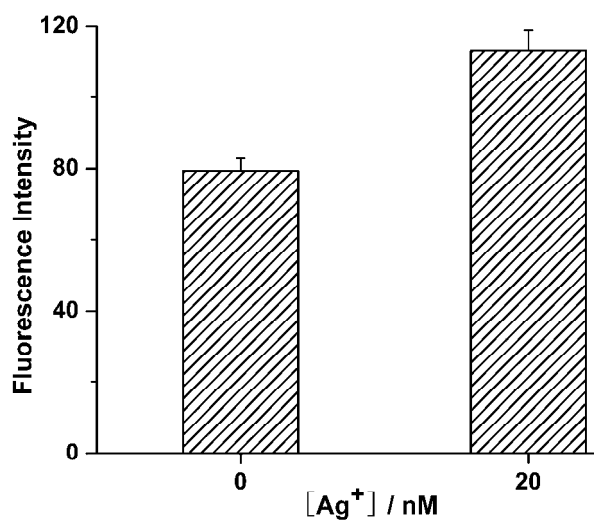


Figure S2 Comparison of the response of LOQ (20 nM of Ag⁺) with the background signal (0 nM of Ag⁺).

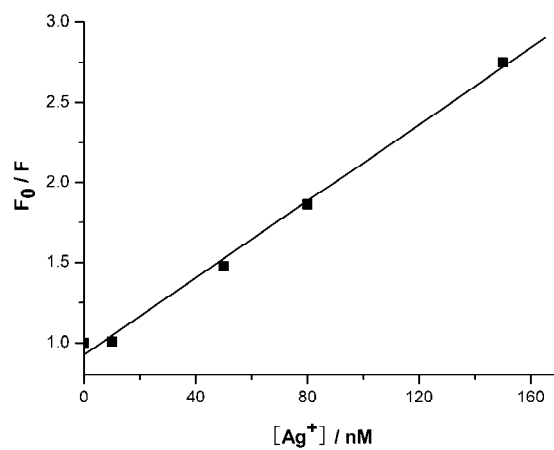


Figure S3 Stern-Volmer plot of the FAM-labeled SSO probe quenched by Ag⁺.