Supporting Information

A sensitive graphene oxide–DNA based sensing platform for fluorescence "turn-on" detection of bleomycin

Feng Li,[a,b] Yan Feng,[b] Can Zhao[b], Peng Li [b] and Bo Tang*[a]

a College of Chemistry, Chemical Engineering and Materials Science, Key Laboratory of Molecular and Nano Probes, Ministry of Education, Shandong Normal University, Jinan 250014, China.

b College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, China.

Reagents and Instruments

Oligonucleotide was synthesized by SBS Genetech. Co., Ltd. (Shanghai, China). Bleomycin sulfate (BLM) in which the contents of A_2 and B_2 were up to 91.6% was from Melone Pharmaceutical Co., Ltd. (Dalian, China). Ammonium iron (II) sulfate hexahydrate was supplied by Aladdin Chemistry Co., Ltd. (Shanghai, China). Graphene oxide (GO) was purchased from Nanjing XFNANO Materials Tech. Co., Ltd. (Nanjing, China). The metal salts ($CuCl_2$, $ZnCl_2$, $MnCl_2$, $CoCl_2$, $CaCl_2$, $MgCl_2$, $CdCl_2$, and $Pb(NO_3)_2$) were purchased from Sinopharm Chemical Reagent Co. Ltd.(Shanghai, China). Hydrogen peroxide, urea, dopamine, ascorbate, glucose, cysteine, and human serum albumin were from Sigma–Aldrich. Phosphate buffer solution (PBS, 20 mM) with pH 7.4 was prepared by mixing the stock solution of Na_2HPO_4 and NaH_2PO_4. All other reagents were of analytical reagent grade and were used without further purification or treatment. Double distilled water (DDW) was used throughout the measurements. FL measurements were performed using an F-4500 spectrofluorimeter with a scan rate at 1200 nm/min. The excitation wavelength was at 490 nm, and the 24 photomultiplier tube voltage was

700 V. The slits for excitation and emission were set at 5 nm/5 nm.

Fluorescent measurements

For optimizing the concentration of GO, 10 μL of 2.8 μM F-ssDNA was mixed with different volumes of 100 μg mL^{-1} GO, and then buffer (20 mM PBS, 50 mM NaCl, pH 7.4) was added to give a total volume of 700 μL, with the final concentration of F-ssDNA of 40 nM. The above solutions were allowed for 30-min incubation at room temperature before FL measurement. For fluorescent assay of BLM·Fe(II)-induced DNA strand scission, 10 μL of 2.8 μM F-ssDNA, 140 μL of 100 μg mL^{-1} GO and 530 μL of buffer (20 mM PBS, 50 mM NaCl, pH 7.4) were sequentially added into a microcentrifuge tube. After 30 min reaction, the solution was transferred to a quartz cell at room temperature. The BLM samples were prepared by mixing BLM with Fe(II) ion in 1:1 molar ratio. Then, a series of a 20 μL BLM·Fe(II) solution with various concentrations were added into the quartz cell for time-dependent FL measurement at λex/λem = 490/520 nm. The final volume of the solution was also fixed at 700 μL with the final concentration of F-ssDNA and GO of 40 nM and 20 μg mL^{-1}, respectively. The control experiment was carried out under the same condition without the addition of BLM·Fe(II) solution. All experiments were performed at 25 °C and repeated three times.

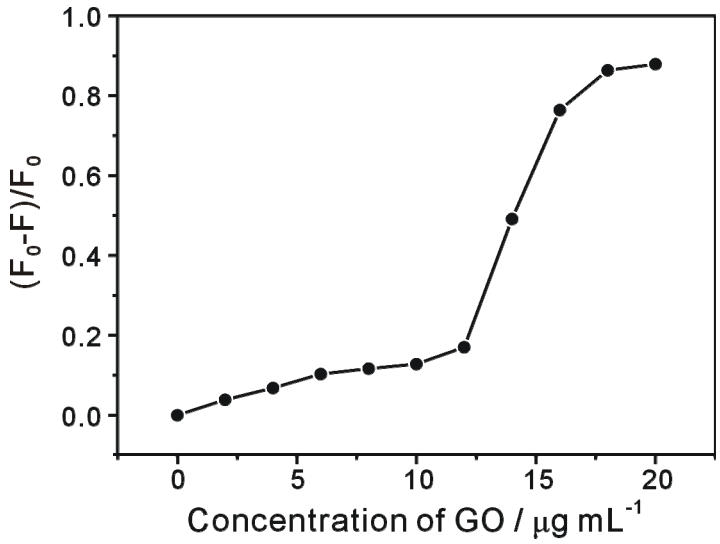

Fig. S1. FL quenching of the F-ssDNA by different concentrations of GO. The concentration of F-ssDNA was 40 nM.

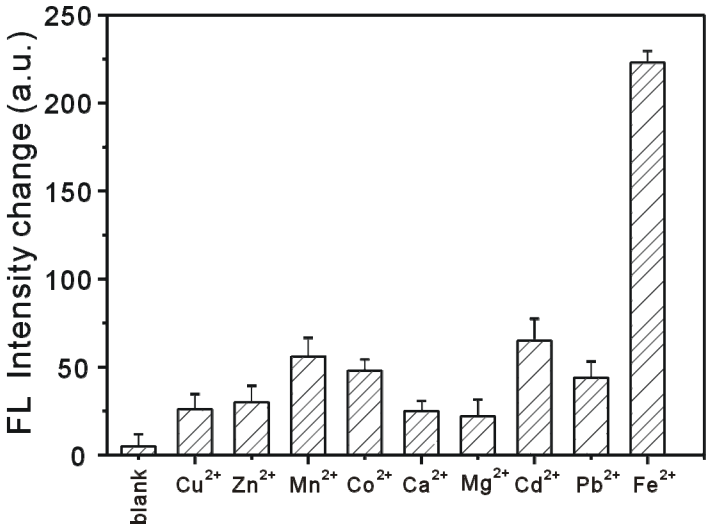

Fig. S2. FL intensity enhancement of GO–DNA complex upon incubation with the mixture of BLM and different metal ions. The concentrations of BLM and metal ions were all kept at 500 nM.

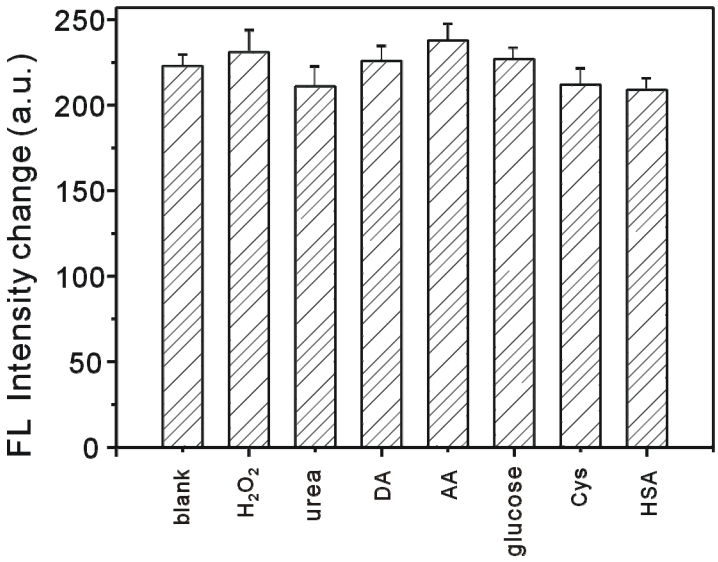

Fig. S3. FL intensity enhancement of GO–DNA complex upon incubation with the mixture of BLM·Fe(II) and the coexisting substances. The blank sample was responsible to GO–DNA complex with only addition of BLM·Fe(II). The concentrations of BLM·Fe(II) and the coexisting substances were all kept at 500 nM.

Table 1 Results for the determination of BLM in serum samples

Sample	Found (nM)	Added (nM)	Total found (nM)	Recovery (%)
1	98	50	146	96.0
2	96	100	199	103
3	98	150	252	102

All the experimental values are averages of three determinations.