Electronic Supplementary Information

Graphene oxide–Ru complex for label-free assay of DNA sequence and potassium ions via fluorescence resonance energy transfer

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EXPERIMENTAL SECTION

Chemicals

$[Ru(bpy)_2(pip)]^{2+}$ was prepared and characterized according to the literature[1]. All DNA synthesis reagents were ordered from Shanghai Sangon Biotechnology Co. Ltd. (Shanghai, China) and used without further purification. DNA stock solution was obtained by dissolving oligonucleotides in 10 mM Tris-HCl buffer (pH 7.4) and was stored at 4 ℃ before use. The concentration of oligonucleotide was determined using the absorbance at 260 nm. Graphite powder of spectrographic grade was purchased from Sinopharm Chemical Reagent Co. Ltd. (China). All other reagents were of analytical grade.

Apparatus

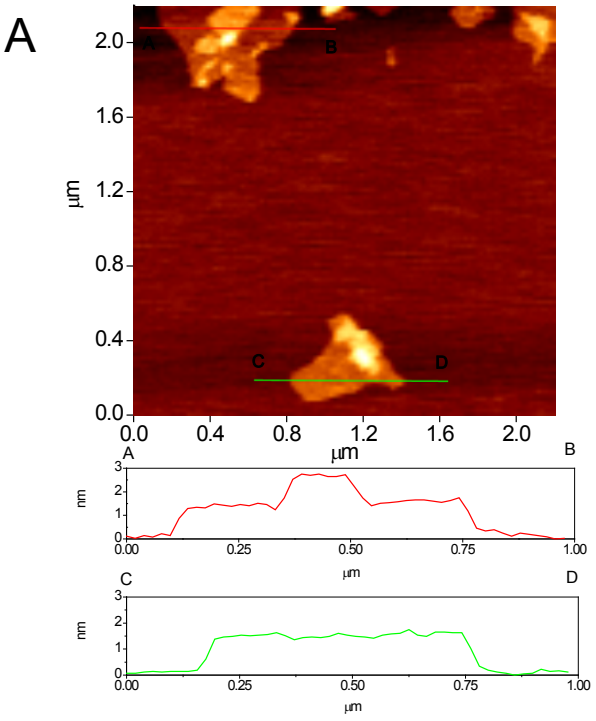
Atomic force microscopy (AFM) was conducted with a Park AFM XE-100 microscope (Park Systems Corp.**).** Lambda Bio 40 UV/Vis Spectrophotometer (Perkin-Elmer, USA) was used to quantify the oligonucleotides. The PL spectra were recorded at room temperature on an F-7000 fluorescence spectrophotometer (Hitachi) with a quartz cell (2 mm). The excitation and emission slit width were both 10 nm. The FT-IR spectrum was recorded on a Nicolet 400 Fourier transform infrared spectrometer (Madison, WI).

Synthesis of graphene oxide

The graphene oxide (GO) was synthesized from natural graphite powder based on modified Hummers method[2, 3]. Then, the as-prepared graphite oxide was subjected to ultrasonication for 30 min (1000 W, 20% amplitude). Finally, a homogeneous GO

aqueous dispersion (1 mgmL^{-1}) was obtained and used for further use. The graphene oxide was then characterized with tapping-mode AFM (Fig. S1), Raman and FT-IR (Fig. S2).

A droplet of graphene oxide dispersion (about 0.01 mgmL^{-1}) was cast onto a freshly cleaved mica surface, followed by drying at room temperature. From the view of the typical AFM image, the average thickness of GO sheet was about 1.5 nm. The FT-IR spectra of GO and graphite provide the information of successful synthesis of GO. The broad and intense peak of O-H groups is centered at 3386 cm^{-1}, the peak at 1736 cm^{-1} is attributed to the C=O group, the peak at 1624 cm^{-1} peak is due to the stretching vibrations of C=C or unoxidized graphitic domains in GO, the C-OH stretching peak is at 1225 cm^{-1}, the C-O stretching peak is at 1054 cm^{-1}, and the peak at 1384 cm^{-1} is due to the vabritions of K-Br. Raman spectrum of graphite showed a strong peak assigned to the vibration of sp^2-bonded carbon atoms at 1580 cm^{-1} (G band) and a very weak peak assigned to the vibration of bonds in plane terminations of disordered graphite at 1150 cm^{-1} (D band). The Raman spectrum of GO showed the well-documented D and G bands. This phenomenon indicated the formation of some sp^3 carbon in GO.



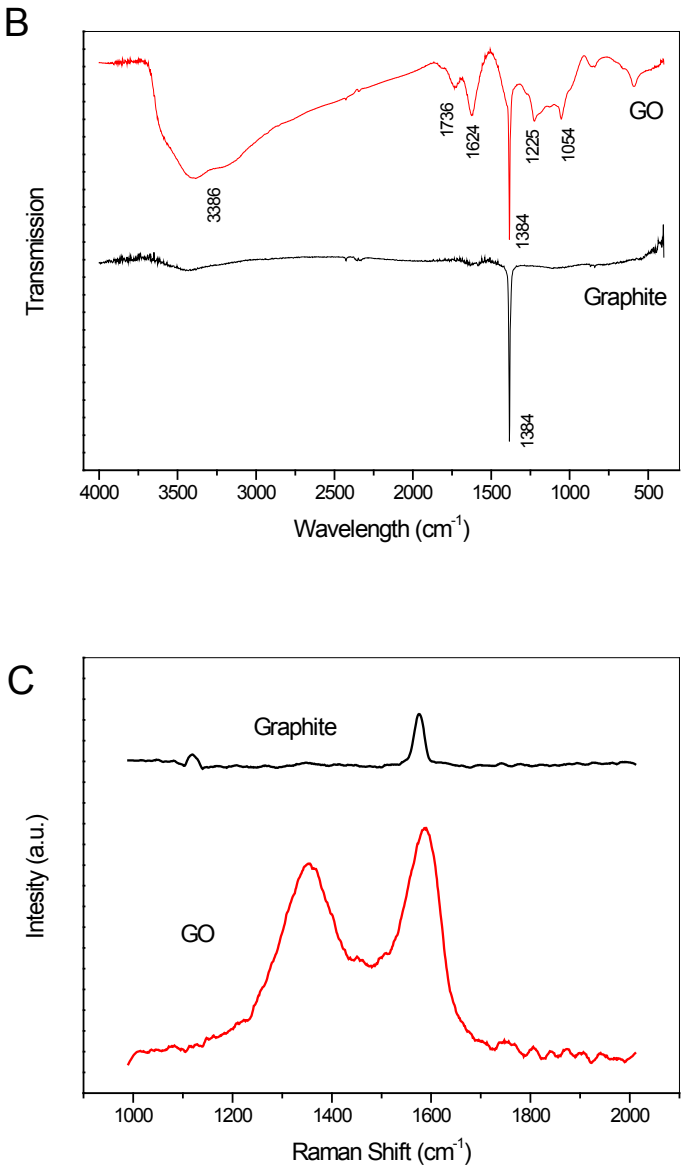


Fig. S1 (A) Tapping-mode AFM image of as-prepared GO, and height along the line in the panel. (B) FT-IR spectra of as-prepared GO and graphite. (C) Raman spectra of graphite and GO

Fluorescence detection of dsDNA and potassium ion

$Ru^{+}GO^{-}$ complex was prepared as $[Ru(bpy)_2(pip)]^{2+}$ mixed with GO in 10 mM Tris-HCl buffer (pH 7.4). Resulting mixture was sonicated at 15-20 ℃ for 20 min to get $Ru^{+}GO^{-}$ complex (the final concentrations of $[Ru(bpy)_2(pip)]^{2+}$ and GO were 5 μM and 10 μgmL^{-1}, respectively).

To recognize dsDNA, $Ru^{+}GO^{-}$ was added to reach equilibrium within 5 min after 22AG mixed to T_1 or T_2 to hybridize for about 30 min, and then the fluorescence of the mixture was detected.

Fluorescence response of aptamer-$Ru^{+}GO^{-}$ towards potassium ions: K^{+} aptamer 22AG (2.5 μM) was prepared in Tris-HCl buffer (10 mM, pH 7.4) and mixed with KCl for about 30 min at room temperature prior to the addition of $Ru^{+}GO^{-}$. The final K^{+} concentration in samples ranged from 50 μM to 500 μM. After allowing this mixture to bind, $Ru^{+}GO^{-}$ was added to reach equilibrium within 5 min, and then the fluorescence of the mixture was detected. The assay procedures for sodium, ammonium, lithium, copper, zinc, and magnesium ions (500 μM) were same as that for the potassium assay, except for using NaCl, NH_4Cl, LiCl, $CuCl_2$, $ZnCl_2$, and $MgCl_2$ instead of KCl.

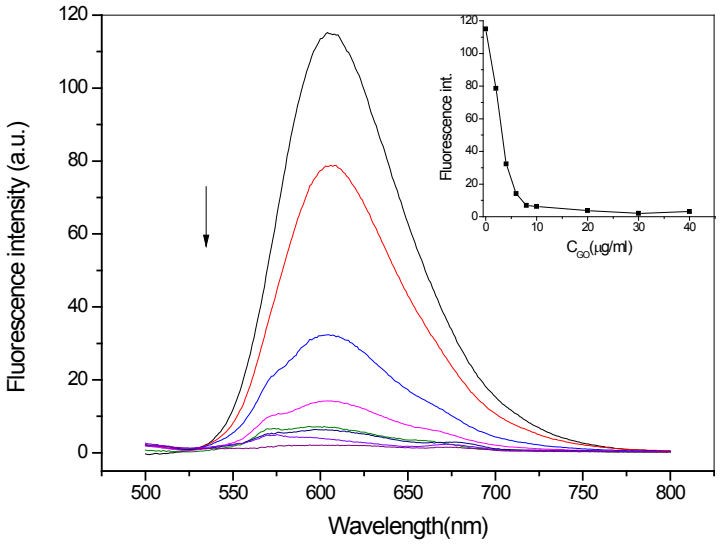


Fig. S2 Fluorescence spectra of Ru complex (5 μM) with different amounts of GO ranging from 0 to 40 μgmL^{-1}. Inset: fluorescence intensity of Ru complex and GO plotted against the concentration of GO. Excitation: 455 nm, emission: 605 nm.

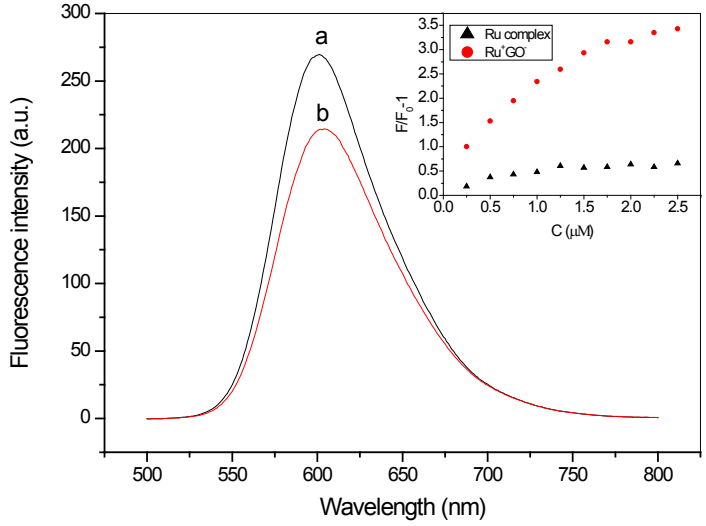


Fig. S3 Fluorescence emission spectra (excitation at 455 nm) of Ru complex (5 μM) and 22AG (2.5 μM) incubated with a) complementary DNA T_1; b) non-complementary DNA T_2. Inset: fluorescence intensity ratio of Ru complex (●)and Ru^+GO^- complex (▲) with (F/F_0-1) plotted against the concentration (C) of complementary DNA T_1. Excitation: 455 nm, emission: 605 nm.

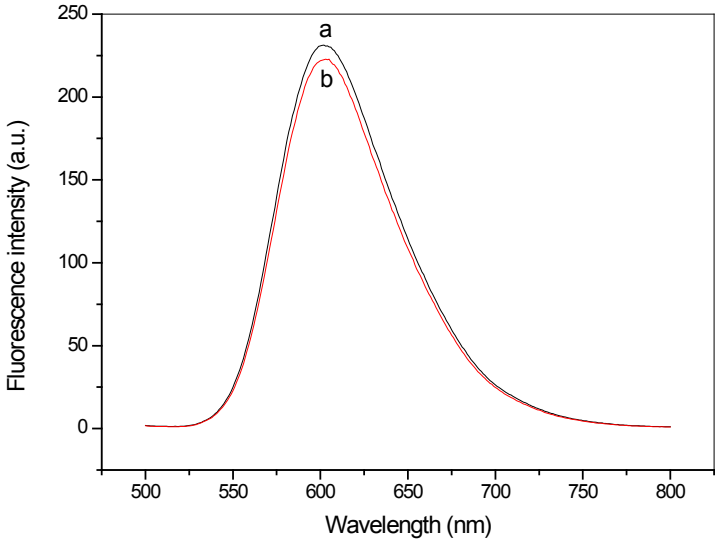


Fig. S4 Fluorescence emission spectra (excitation at 455 nm) of Ru complex (5 μM) with 2.5 μM 22AG incubated in a) 10 mM pH 7.4 Tris-HCl buffer (without K^+); b) 10 mM pH 7.4 Tris-HCl buffer (containing 500 μM KCl).Excitation: 455 nm, emission: 605 nm.

References:

1. J.-Z. Wu, B.-H. Ye, L. Wang, L.-N. Ji, J.-Y. Zhou, R.-H. Li and Z.-Y. Zhou, *J. Chem. Soc. Dalton. Trans.*, 1997, 1395-1402.

2. W. S. Hummers and R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339-1339.

3. Y. Xu, H. Bai, G. Lu, C. Li and G. Shi, *J. Am. Chem. Soc.*, 2008, **130**, 5856-5857.