Supplementary Information

Experimental section

Materials: Graphene oxide was synthesized by a modified Hummers method¹ from graphite powder (Alfa Aesar, $\lceil 20 + 80 \text{ mesh}$). Ethylenediamine and 18-crown-6 ether were both brought from Sigma-Aldrich. 1-Ethyl-3(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC), and N-Hydroxysuccinimide (NHS) were purchased from Alfa Aesar (Ward Hill, MA). Dialysis membrane was purchased from Pierce (3000 MWCO). All other regents were of analytical reagent grade. Ultra-pure water (>18.2 M Ω , Milli-Q, Millipore) was used for the preparation of all the solutions.

Instrumentation: Fluorescence measurements were carried out using a JASCO FP-6500 spectrofluorometer with the slit width for the excitation and emission of 5 nm. Fourier transform infrared spectroscopy (FTIR) measurements were carried out with a BRUKER Vertex 70 FTIR spectrometer. The sample was prepared as pellets using spectroscopic grade KBr. The thermogravimetric analysis (TGA) was recorded with a RIGAKU Standard type with a heating rate of 10 °C min⁻¹ from room temperature to 800 °C. Atomic-force microscopy (AFM) measurements were performed using a Nanoscope V multimode atomic force microscope (Veeco Instruments, USA) under ambient conditions. AFM samples were prepared by dropping the solution on mica. After 30 min, samples were washed once by ultra-pure water. The in-situ energy dispersive X-Ray spectroscopy (EDS) analysis were performed using a using a HITACHI S-4500 instrument. To determine the elemental composition at each point on the sample, the substrate was accurately positioned using an encoded x–y translation stage, and the locations were recorded. The EDS samples were prepared by casting 18C6E-rGO (washed with ultrapure water for three times after

equilibrated with cations) on silicon sheet.

Sensing of potassium (K^+): In a typical measurement, a 20 µg mL⁻¹ Am-CD and 14 µg mL⁻¹ 18C6E-rGO solution was prepared in 20-fold diluted (with 5 mM MES buffer, pH 6.8, 80 vol% MeOH) mimic extracellular matrix. Thereafter, different concentrations of KCl were added to the above solution and the mixtures incubated for 10 min before measurement.

Preparation of aminated carbon dots (Am-CDs): Carbon dots (CDs) were prepared from candle soot as the reported method.² Candle soot was refluxed in 5 M nitric acid for 12 h, and purified by centrifugation at 13000 rpm for 30 min to remove unreacted soot and non-fluorescent large sized particles. The obtained supernatant CDs were neutralized by Na₂CO₃ and dialyzed against pure water. The CDs were then aminated with ethylenediamine through an EDC-NHS coupling protocol. The reaction product was subsequently dialyzed for obtaining Am-CDs. The fluorescence intensity of Am-CDs remains unchanged under continuous 356 nm illumination for up to 60 min, which suggests good photostability.

Preparation of 18C6E-rGO hybrids: For the preparation of the18C6E-rGO hybrids, the homogeneous graphene oxide dispersion was mixed with 18C6E aqueous solution and sodium hydroxide, and then the mixture was reduced with hydrazine at 80 °C for 24 h.³ After reduction and non-covalent fictionalization, a black dispersion was obtained, and the excess of 18C6E was removed with five successive cycles that involved centrifugation, decantation, and resolubilization to ultimately yield 18C6E-rGO hybrid. After that, the 18C6E-rGO hybrid was dialyzed through semipermeable menbrames to remove impurities and excess 18C6E.

References

(a) W. S. Hummers and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339; (b) Y. Xu, H. Bai, G. Lu, C. Li and G. Shi, J. Am. Chem. Soc., 2008, 130, 5856.

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- (a) W. Wei, K. Qu, J. Ren, X. Qu, *Chem. Sci.*, 2011, 2, 2050-2056; (b) L. Feng, C. Chen, J. Ren and X. Qu, *Biomaterials*, 2011, **32**, 2930.



Fig. S1 AFM topographical images and height profiles of rGO and Am-CD mixture.



Fig. S2 AFM topographical images and height profiles of the 18C6E-rGO-Am-CD complex.



Fig. S3 Fluorescence emission spectra of Am-CDs (20 μ g mL⁻¹) in the presence and absence of 14 μ g mL⁻¹ bare rGO in 5 mM MES buffer (pH 6.8, 80 vol% MeOH). No obvious signal change was observed, and this implied that no nonspecific adsorption of Am-CDs on the rGO surface occurs. One thing should be mentioned that there is hardly any oxygen-related group on the surface of rGO (data not shown). This is totally different to graphene oxide.



Fig S4 Fluorescent photograph of the sensor in absence (left) and presence (right) of potassium ion (10 mM).



Fig S5 Linear relationship of fluorescence of 18C6E-rGO-Am-CDs system against sample volume by keeping the potassium concentration at 10^{-5} M. About 2.8 µg 18C6E-rGO in rGO was dispersed in 10^{-5} M KCl with sample volume ranging from 1 to 10 mL. After equilibrium, each sample was concentrated to 0.2 mL through centrifugation. Subsequently, 4 µg Am-CD was added to each sample and the fluorescence intensity at 520 nm was monitored.



Fig. S6 Fluorescence titration spectra of 18C6E-rGO-Am-CD complex in the presence of different concentrations of KCl (0.5-100 mM) in diluted mimic extracellular matrix. (b) Linear relationship between donor fluorescence intensity and potassium concentrations. The F_0 and F are fluorescence intensities at 520 nm in the absence and the presence of K⁺, respectively. Excitation: 472 nm.



Fig. S7. AFM characterization of Am-CDs. The result shows that the average particle size of the Am-CDs is 3.2±0.9 nm.



Fig. S8 FTIR spectra of (a) as prepared CDs, and (b) Am-CDs.

The FTIR spectrum of Am-CDs shows the characteristic amide I band (C=O) at 1667 cm⁻¹ and amid II band at 1640 cm⁻¹, which provides the qualitative evidence that amino groups have been covalently linked on the surface of CDs. Besides, after amination, the band at 1760 cm⁻¹ (-COOH) disappeared. This also indicated that the carboxyl groups on the surface of as prepared CDs were reacted with ethylenediamine. The results of zeta potential measurements provide further evidence for supporting this analysis. The zeta potential of the pristine CDs was -12.6 mV, suggesting the surface of CDs was negatively charged due to carboxyl groups. While the zeta potential of Am-CDs was 13.8 mV after amination, indicating the surface was positively charged, due to the conversion of carboxyl groups to amino-groups.



Fig. S9 FTIR spectra of (a) rGO, (b) 18C6E-rGO, and (c) 18C6E. The appearance of characteristic infrared bands of 18C6E indicate clearly that 18C6E cannot be removed from 18C6E-rGO hybrids by dialysis; thus, 18C6E molecules have covered the surface of rGO.



Fig. S10 AFM characterization of 18C6E-rGO hybrid. The AFM height image shows that the thickness of the 18C6E-rGO is about 2 nm



Fig. S11 TGA analysis of (a) rGO, (b) 18C6E-rGO, and (c) 18C6E. According to the result, the

amount of 18C6E molecules in 18C6E-rGO hybrids was determined to be 20 wt%.