Electronic Supplementary Information

Uniform and Rich–Wrinkled Electrophoretic Deposited Graphene Film: A Robust Electrochemical Platform for TNT Sensing

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1. Chemicals

Graphite powder (99.99995%, 325 mesh) was purchased from Alfa Aesar and Nafion (5 wt% in lower aliphatic alcohols) was from Sigma. Analytical stock samples of TNT (1000 μg/mL solution in acetonitrile) were obtained from Sigma. **Caution**: *TNT used in the present study is highly explosive and should be handled only in small quantities.* Other chemicals, $NaH_2PO_4 \cdot H_2O$, Na_2HPO_4, HCl, NaOH, KCl and NaCl, were from Beijing Chemical Company. All stock solutions were prepared using deionized water and deoxygenated by purging with pure nitrogen.

2. Synthesis of graphene oxide

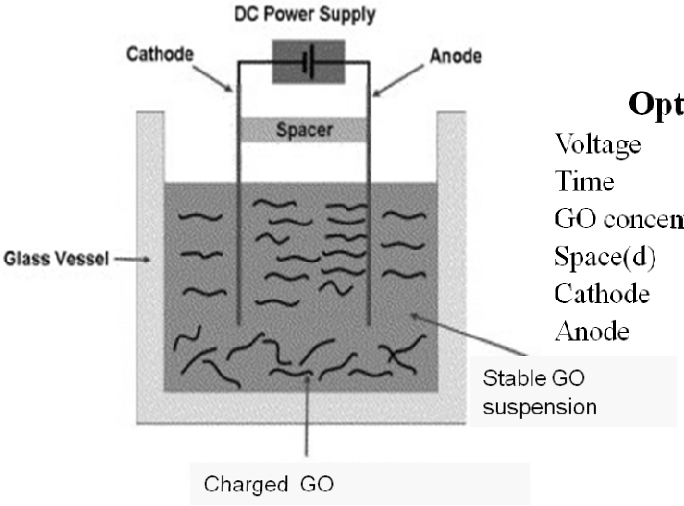
Graphite oxide was obtained through natural graphite oxidation by Hummers method (Stankovich, S.; Dikin, D. A.; Piner, R. D.; Kohlhaas, K. A.; Kleinhammes, A.; Jia, Y.; Wu, Y.; Nguyen, S. T.; Ruoff, R. S. *Carbon* **2007**, *45*, 1558). Generally, the pre-oxidized graphite powders were put into 0 ^{o}C concentrated H_2SO_4 (120 mL). Then, 15 g $KMnO_4$ was added gradually under stirring and the temperature of the mixture was kept to be below 20 °C by ice-bath. Successively, the mixture was stirred at 35 °C for 4 h, and then diluted with 250 mL dionized water by keeping the temperature under 50 ^{o}C. 700 mL water was then injected into the mixture followed by adding 20 mL 30% H_2O_2 drop by drop. The mixture was filtered and washed with 0.1 M HCl aqueous solution (1 L) to remove metal ions (like Mn) followed by dionized water to remove the acid. The resulting solid was dried in air and diluted to make graphite oxide dispersion (0.5% w/w). Finally, it was purified by dialysis for one week to remove the remaining metal species. Exfoliation was carried out by sonicating 0.1 mg/mL graphite oxide dispersion in aqueous solution under ambient condition for 1 h.

3. Characterization

The transmission electron microscope (TEM) images were obtained with Hitachi model H-800 transmission electron microscope opened at an accelerating voltage of 100 kV. The samples mixing with ethanol 5 μL were dropped on a Cu grid and left to dry in air condition for 10 h.

For AFM characterization, typically, a sample for AFM imaging was prepared by first treating a freshly cleaved mica surface with 1 M $MgCl_2$ for one minute, followed by addition of 10 μL of a sample solution onto the mica surface. The mica substrate was tilted to allow the droplet to spread on the surface. After an adsorption for one minute, the mica surface was washed twice with doubly distilled water, and dried with compressed air. The sample was then scanned in tapping mode with a Nanoscope III, Digital Instrument atomic force microscope.

Cyclic voltammetry and Differential Pulse Voltammograms (DPVs) were carried with the CHI 440 (CH Instruments, Inc., Austin, TX). Glassy carbon electrode (CHI 104, CH Instruments, Inc.) acted as the working electrode, and an Ag/AgCl as the reference electrode, platinum wire as the counter electrode respectively. Impedance measurements were conducted in 5 mM $[Fe(CN)_6]^{3-/4-}$ aqueous solution containing 100 mM KCl using a PARSTAT 2273 electrochemical system (Princeton Applied Research) with frequency from 0.1 Hz to 100 kHz and amplitude of 250 mV.



Optimum conditions

Voltage	120 V
Time	3 min
GO concentration	0.01 g/mL (DMF)
Space(d)	1 cm
Cathode	platinum plate
Anode	glassy carbon electrode

Figure S1. Schematic representation of homemade electrophoretic deposition set and the detail electrophoresis deposition conditions of the GO.

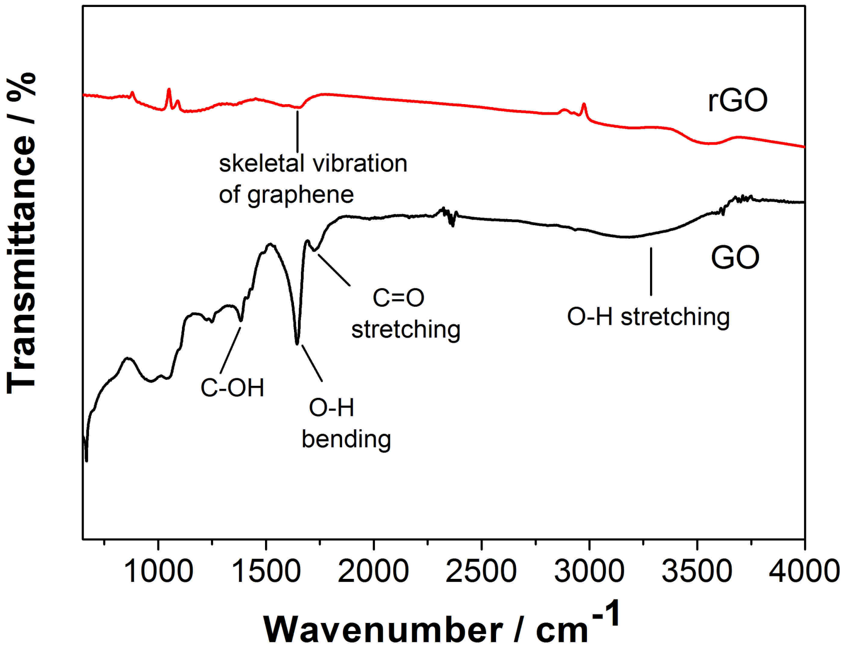


Figure S2. FT-IR analysis of GO and rGO film.

Figure S3

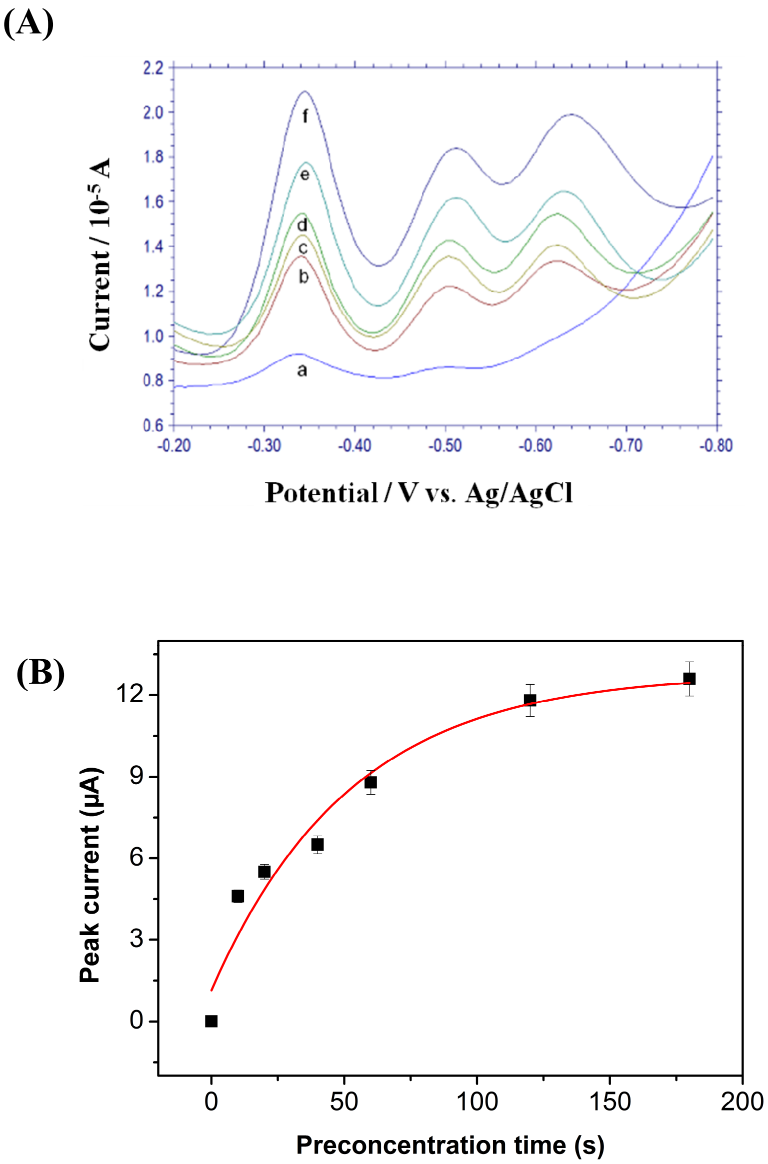


Figure S3. (A) Effect of the preconcentration time at 0.0 V vs. Ag/AgCl on electrochemical response for 100 ppb TNT for rGO film 0.1 M PBS solution (pH 6.5): (a) 0, (b) 10, (c) 20, (d) 40, (e) 60, (f) 120 seconds. Electrochemical conditions: 0.1 M PBS solution (pH 6.5), E_i: -100 mV, E_f: -800 mV; scan rate: 50 mV/s. (B) The profile of response vs preconcentration time for the TNT sensing on the graphene electrode. We found that the preconcentration potential at 0.0 V vs. Ag/AgCl could result in the good adsorptive characteristics, low and stable background current for the sensitive detection of such nitroaromatics in the stripping/detection step. It should be also noted that when the preconcentration time is up to 3 min, the current response will level off. In order to compromise the sensitivity and response time, we chose 60 s as the preconcentration time.

The electrochemical activity of this graphene-based electrode has also been studied in 0.1 M PBS containing either 4-nitrotoluene (4-NT) or 2,4-dinitrotoluene (2,4-DNT). It is found that 4-NT has only one reduction peak at -750 mV, while 2,4-DNT has two peaks at -480 and -630 mV, respectively. It is indicated that the number of reduction peaks is dependent on the number of nitro groups on the aromatic ring. Therefore, the graphene may have potential in the electrochemical detection of natroaromatic compounds with distinguishable voltamogram features.

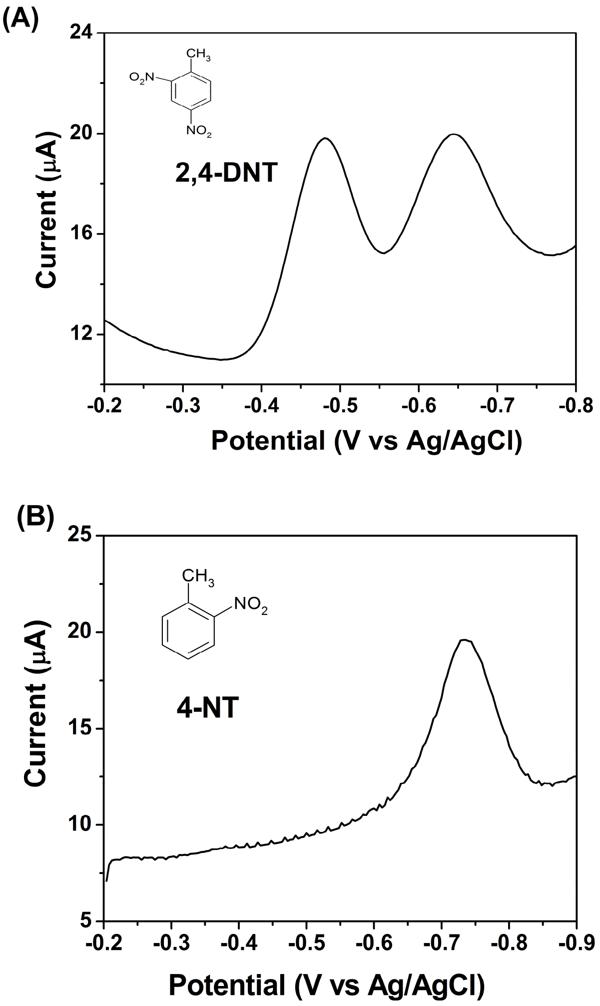


Figure S4. Differential pulse voltammetries of the rGO film modified GC electrode for 100 ppb 2,4-DNT (A) or 4-NT (B) determination after 60 s preconcentration at 0.0 V vs. Ag/AgCl. Electrochemical conditions: 0.1 M PBS solution (pH 6.5), Ei: -100 mV, Ef: -800 mV; scan rate: 50 mV/s.

In order to estimate the possibility of this graphene-based sensor for real samples, TNT was analyzed in aqueous samples of river-water and sea-water. These samples were first artificially contaminated with TNT (ref: M. Riskin, R. Tel-Vered, T. Bourenko, E. Granot, and I. Willner, *J. Am. Chem. Soc.*, **2008**, 130, 9726-9733). Figure S5 depicts the respective calibration curves obtained for the different samples.

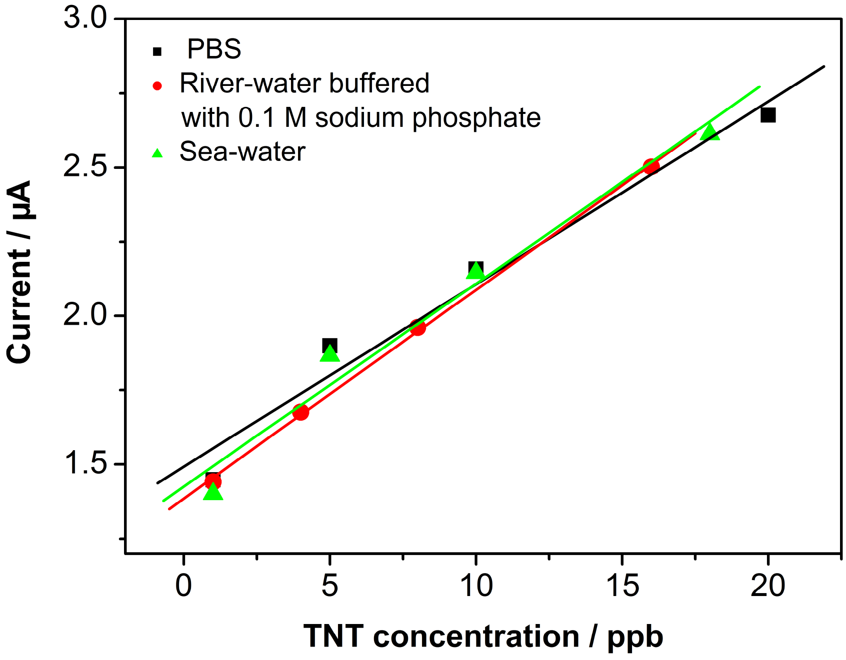


Figure S5. Calibration curves corresponding to the analysis of variable concentrations of TNT in: (a) 0.1 M PBS (pH 6.5); (b) River-water buffered with 0.1 M sodium phosphate; (c) Sea-water.