Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

Exploring Graphene Oxide Intrinsic Electroactivity to Elucidate the Non-covalent Interactions with DNA Oligonucleotides

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Experimental Details

Materials

Graphene oxide nano-colloids (GONCs), sodium chloride (NaCl) and sodium phosphate dibasic salt (Na_2HPO_4) were purchased from Sigma-Aldrich (Singapore). All single-stranded DNA (ssDNA) oligonucleotides were purchased from Integrated DNA Technologies with 20 nucleobases each as Polyadenylic acid – Poly(A), Polycytidylic acid – Poly(C), polyguanylic acid – Poly(G), and polythymidylic acid – Poly(T). For all experiments, ultrapure water was attained using Milli-Q ion-exchange column (Millipore) with resistivity of 18.2 ΩM cm. Phosphate-buffered saline solution (0.01 M Na_2HPO_4; 0.1 M NaCl; pH 7.4) was used throughout the experiments. GONCs were diluted using ultrapure water (1 mg mL^{-1}), and ultrasonicated for 1 hour at room temperature to obtain a GONC homogeneous dispersion before use. Disposable electrical printed (DEP) carbon chips were purchased from BioDevice Technology (Nomi, Japan). Each unit comprises of a three-electrode system, inclusive of a carbon-based working and counter electrodes, and an Ag/AgCl reference electrode.

Equipment

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) measurements were performed using μAutolab type III electrochemical analyzer (Eco Chemie, Ultrecht, The Netherlands) connected to a computer and controlled using General-Purpose Electrochemical System (GPES) software version 4.9. The parameters applied for all DPV measurements were the following: 0.05 modulation time, 0.5 s interval time, 0.01 V step potential, 0.02 V modulation amplitude, and 0.02 V s^{-1} scan rate. PBS buffer solution was used for DPV measurements with the raw data corrected with a baseline correction of peak width 0.1 by using the GPES software. All washing steps and incubations of analyte were performed in a TS-100 thermal-shaker (Biosan, Riga, Latvia).

Procedures

GONCs was immobilized on the DEP chip surface through dry physical adsorption. GONC solution (3 μL) at concentration of 1 mg mL^{-1} was casted onto the clean, bare electrode surface and dried under a lamp. Poly(A), Poly(C), Poly(G) and Poly(T) in PBS buffer at optimum concentration of 40 μM were dropcasted on GONC platform and dried in oven at 60 °C for 10 minutes. The electrodes were then washed in PBS buffer for 5 minutes at 25 °C under gentle stirring. The ssDNA oligonucleotide modified DEP chips were then incubated in Eppendorf tubes with various concentrations of the complementary target oligonucleotide in PBS buffer solution. The incubation step was performed for 30 minutes at 42 °C with gentle stirring. Two subsequent washing steps were conducted in PBS buffer solution at 42 °C for 5 minutes each. For the negative control experiments, the non-complementary target sequences were used as follows: Poly(C) for Poly(A) and Poly(T); Poly(A) for Poly(C) and Poly(G).

Material Characterization

GO material characterization was first performed by X-ray photoelectron spectroscopy and results are shown as both survey and high-resolution C 1s spectra in Figure S1A. Characteristic signals from carbon and oxygen are seen in the survey spectrum, indicating a highly oxidized material with a C/O ratio of 2.99. The deconvoluted C 1s spectrum shows four prominent peaks, with the one at 284.3 eV having binding energy characteristic of the sp^2 carbon; the peak at 286.5 eV was attributed to the C–O single bond; and the peaks observed at 288.1 and 289.5 eV were assigned to the C=O double bond in carbonyl and carboxylic moieties. FTIR profile depicted in Figure S1B shows characteristic peaks at 1060 cm^{-1}, 1535 cm^{-1}, 1650 cm^{-1}, and 3300 cm^{-1}, which indicate the stretch of alkoxy C–O and aromatic C=C bonds; the bend of –OH bond; and the stretch of C=O and –OH bonds respectively. Figure S1C shows the morphology of GO material, which appears as highly exfoliated structure. In addition, particle size distribution from normal distribution curve provided a mean size of 484±45 nm, as analysed from STEM images (see Figure S2).

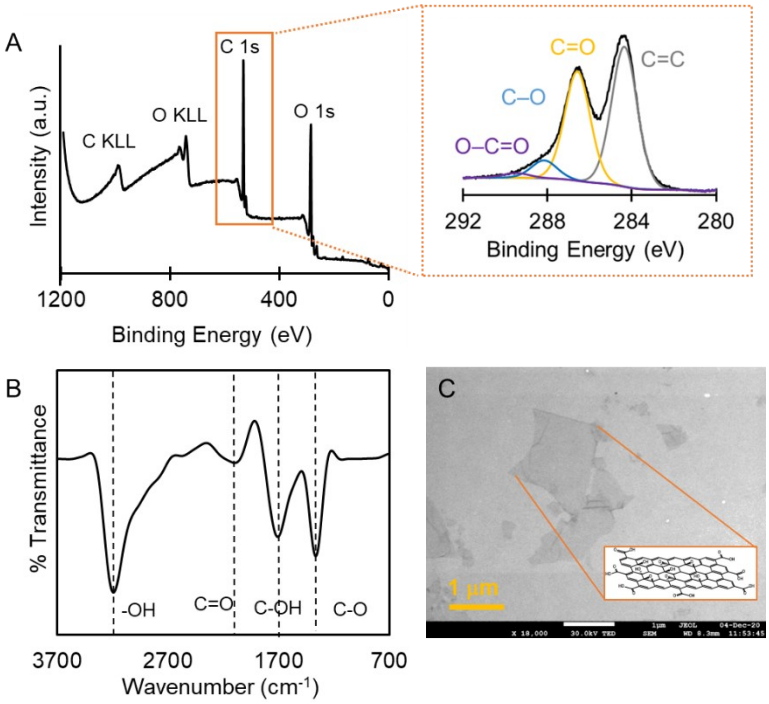

Figure S1. GONC characterization. A) X-ray photoelectron spectroscopy survey; Inset: C 1s X-ray photoelectron spectroscopy high-resolution spectrum; B) FT-IR spectrum; C) Scanning tunnel electron microscopy (STEM) micrograph.

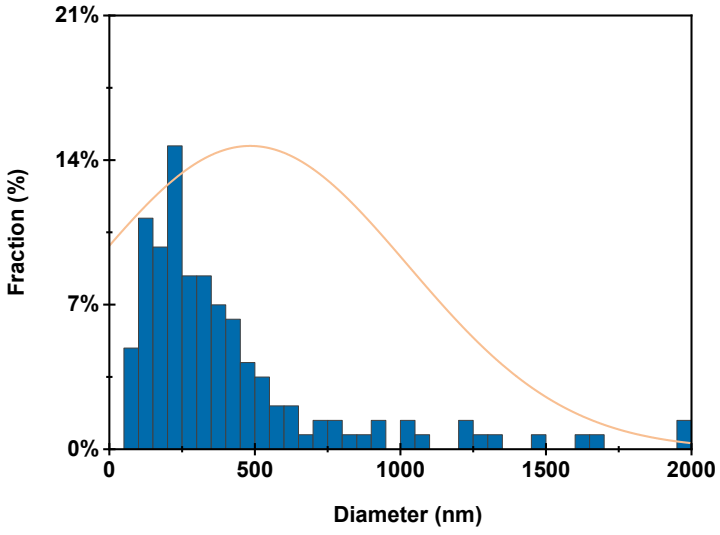

Figure S2. GO particle size distribution fitted by a Gaussian curve.

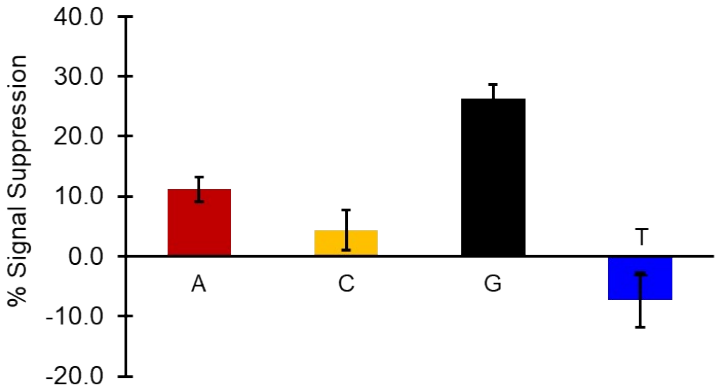

Figure S3. % Signal suppression: (GO-nucleobase)/GO × 100 after modification of GO with increasing concentrations of adenine (A), cytosine (C), thymine (T), and guanine (G). Concentration of each nucleobase: 30 μM. Error bars represent replicate experiments.

In this study the order of affinity was found to be the same as that previously reported in the literature, with guanine (G) > adenine (A) > cytosine (C) > thymine (T). This further confirms the different behaviour of the DNA nucleobases when embedded in a single nucleotide or in an oligo/polynucleotide.