

Supporting Information

Localized Reduction of Graphene Oxide by Electrogenerated Naphthalene Radical Anions and Subsequent Diazonium Electrografting

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EXPERIMENTAL AND TECHNICAL SECTION

S.1. Materials. Electrochemical measurements were performed in *N,N* dimethylformamide (Sigma Aldrich) and tetrabutylammonium hexafluorophosphate (Sigma Aldrich) as supporting electrolyte. Microelectrode fabrication required micrometric (10-250 μm) diameter Pt-wire (Goodfellow, purity 99.9%), glass Pasteur pipettes, silver conducting paint (Electrolube) and standard copper connection wires (diameter < 0.3 mm). Standard procedures using a puller machine (PC10 Narishige) and abrasive disks (P4000 and P1000) were adopted. The resulting electrodes had a surrounding glass thickness ranging from 20 to 200 μm , as observed with optical microscope. Nanoelectrodes were produced following a procedure described in the literature.¹

S.2. Substrate preparation. All standard chemicals and solvents of research grade were purchased from Sigma Aldrich and used as received. Si wafers covered with 150 nm-SiO₂ or pure quartz substrates were degreased in acetone and ethanol by ultrasonication and cleaned in a mixture of concentrated hydrochloric and nitric acid (3:1 ratio) at 90 °C for 1 hour. The GO preparation from graphite was performed using the standard Hummers method.² The graphene oxide film formation through the bubble deposition method used here has already been described in a previous report.³ In the present study, the substrates were exposed twice to a surfactant film containing GO flakes.

S.3. Electrochemical setup. SECM experiments were performed on the Princeton Applied Research 370 SECM Workstation. A conventional three-electrodes setup was used for the voltammetry and SECM experiments. It involved a platinum (Pt) microdisk working electrode, a zinc electrode as pseudo-reference ($E = -1$ V vs SCE, as verified by the ferrocene oxidation potential), and a 0.5 mm diameter gold wire auxiliary electrode. Zinc was used as reference electrode in order to be able to apply -2.6 V vs SCE (the apparatus limitation is -2 V / $+2$ V between the probe and the reference potentials). In order to remove the oxygen content, the whole set up was put in a plastic glovebox and degased during about 1 hour before experiment. The evaluation of the tip substrate distance for a given tip position was performed using the negative feedback response obtained when approaching to an unreduced zone. This is a standard procedure.⁴ For the 250 μ m electrode, the contact point was considered as the zero probe substrate distance. The precision achieved with such a strategy is adequate thanks to the small relative glass thickness ($R_g \approx 2$) of the probe. After reduction, we carefully washed the sample with ethanol and fresh DMF.

S.4 Electrografting and Gold nanoparticle capture

The electrochemical grafting was conducted in a single-compartment three-electrode cell with a potentiostat (Model VSP Bio-Logic SAS) in a glovebox. Ag/AgNO₃ (10 mM) electrode and a platinum wire served as reference and counter electrode, respectively. The GO/r-GO substrate with the patterned gold working electrodes was completely immersed in a solution of protonated 4-aminoethylbenzenediazonium tetrafluoroborate (10⁻³M). This compound was prepared using a procedure available in the literature,⁵ dissolved in tetrabutylammonium hexafluorophosphate (10⁻¹ M)/Acetonitrile electrolyte. The gold electrodes were connected with a passivated tungsten tip. Cyclic voltammetry technique (Scan rate: 100 mV/s; reduction between 0 V and -1 V vs Ag/AgNO₃ (10 mM); 10 cycles) was used to create the active platform for surface immobilization of gold nanoparticles (NPs). Immobilization of Gold NPs onto the ammonium-terminated Substrates was performed using a commercial Gold NP suspension (Sigma Aldrich, colloidal Gold nanoparticles 5 nm diameter, CAS: 7440-57-5). The substrate was immersed in the colloidal solution for 1 h and then thoroughly rinsed with water and ethanol.

S.5 XPS measurements

The efficiency of the electrogenerated naphthalene radical anion reduction was studied by X-ray Photoelectron Spectroscopy (XPS, KRATOS Axis Ultra DLD) with a monochromated Al K α line operating at 1486.6 eV. The vacuum in the sample chamber was maintained at 5x10⁻⁹ Torr during the measurements. The spectrometer was calibrated by assuming the binding energy of the Au 4f_{7/2} line at 84 eV with respect to the Fermi level. For the determination of O/C ratio, the C1s, O1s and Si2p area were normalized using the Scofield correction factors (respectively 0.817, 2.93 and 1 for Si2p, O1s and C1s). In all spectra, the Si2p peak associated to SiO₂ underlying

substrates was observed at the usual value of 99.5 eV. In order to extract the ratio O/C from the measurements, the contribution of the oxygen coming from the underlying SiO₂ layer was removed. For this, the Si2p peak was integrated and corrected using Scofield correction factors. Then the oxygen coming from SiO₂ was determined as the double of the corrected Si2p contribution. The remaining oxygen part (total corrected area of O1s minus oxygen from SiO₂) is attributed to the oxygen present in GO or r-GO and divided by the C1s peak area. See details in Table S1.

Substrate area \ Calculus intermediates	C1s peak area (CPS.eV)	O1s peak area (CPS.eV)	Corrected O1s peak area (CPS.eV)	Si2p peak area (CPS.eV)	Corrected Si2p peak area (CPS.eV)	Remaining oxygen part (O1s - SiO ₂) (CPS.eV)	O/C x100
GO	8263.3	10398	3548.8	285.0	348.8	2851.1	34.5
Naphthalene radical anion r-GO	9997	4098	1398.6	223.0	272.9	852.7	8.5

Table S1: Intermediate results for the evaluation of the O/C ratio from XPS measurements.

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- (4) Lhenry, S.; Leroux, Y. R.; Hapiot, P. *Anal. Chem.* **2013**, *85*, 1840.
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