

Electronic Supplementary Material for

High quality, low-oxidized graphene via anodic exfoliation with table salt as an efficient oxidation-preventing co-electrolyte for water/oil remediation and capacitive energy storage applications

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S1. Electrochemical exfoliation experiments

Unless otherwise stated, all the materials and chemicals used throughout this study were obtained from Sigma-Aldrich. Milli-Q deionized water (Millipore Corporation; resistivity: 18.2 M Ω ·cm) was employed in all the experiments. The electrochemical (anodic) exfoliation experiments were carried out in a two-electrode setup consisting of a high purity graphite foil piece (Papyex I980, acquired from Mersen; dimensions: $\sim 40 \times 25 \times 0.5$ mm³) as the working electrode and a platinum foil (thickness: 0.025 mm) as the counter electrode. Both electrodes were immersed in an aqueous electrolyte solution (80 mL) incorporating 0.1 M Na₂SO₄ as the main electrolyte and a given molar concentration of another chemical species as the electrolyte additive. Although best results in terms of preventing oxidation of the exfoliated graphene nanosheets were obtained with NaCl, other electrolyte additives tested included KCl, KBr, KI, NaBH₄, Na₂SO₃, sodium citrate, vitamin C and ethanol. To trigger its delamination, a positive voltage (10 V) was applied to the graphite foil electrode for 60 min by means of an Agilent 6614C DC power supply, while keeping the platinum counter electrode parallel to the graphite foil surface at a distance of about 2 cm. During the electrolytic process the outer layers of the graphite electrode were seen to swell and expand, giving rise to many millimeter-sized fragments that detached from the electrode and tended to float on the aqueous solution. Subsequently, these fragments as well as the swollen graphitic material that had not yet detached from the electrode (retrieved by gently scraping with a spatula) were collected, rinsed off with copious amounts of water through filter paper and dried overnight at room temperature under reduced pressure. The resulting product was transferred either to a water/isopropanol mixture (65/35 v/v%), to an aqueous solution of the dispersant flavin mononucleotide (FMN, 1 mg mL⁻¹) or to the organic solvent *N,N*-dimethylformamide (DMF), sonicated in an ultrasound bath cleaner (J.P. Selecta Ultrasons system, 40 kHz) for 3 h and finally centrifuged at 200 g for 20 min (Eppendorf 5424 microcentrifuge) to obtain a colloidal suspension (supernatant) of graphene nanosheets in these solvents.

S2. Characterization techniques

The obtained materials were characterized by field emission scanning electron microscopy (FE-SEM), scanning transmission electron microscopy (STEM), atomic force microscopy (AFM), UV-vis absorption spectroscopy, Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and measurement of electrical conductivity and water contact angle. FE-SEM and STEM images were recorded in a Quanta FEG 650 microscope (FEI Company) at 25 kV. Specimens for STEM were prepared by drop-casting ~40 μL of graphene dispersed in water/isopropanol onto copper grids (200 mesh) covered with a thin continuous film of amorphous carbon. AFM imaging of the graphene nanosheets was performed in the tapping mode of operation with a Nanoscope IIIa Multimode apparatus (Veeco Instruments), using rectangular silicon cantilevers (spring constant: ~40 N m^{-1} ; resonance frequency: 250-300 kHz). To this end, the nanosheets were deposited onto pre-heated (~50-60 $^{\circ}\text{C}$) highly oriented pyrolytic graphite (HOPG) substrates by drop-casting their colloidal dispersion in water/isopropanol. UV-vis absorption spectroscopy was accomplished in a double-beam He λ ios α spectrophotometer (Thermo Spectronic). Raman spectra were acquired in a Horiba Jobin-Yvon LabRam instrument at a laser excitation wavelength and incident power of 532 nm and 2 mW, respectively. XPS was carried out on a SPECS apparatus under a pressure of 10^{-7} Pa using a non-monochromatic Al K_{α} X-ray source (11.81 kV, 100 W). Specimens for both Raman spectroscopy and XPS were prepared by drop-casting graphene dispersions in water/isopropanol onto pre-heated (~50-60 $^{\circ}\text{C}$) stainless steel disks 12 mm in diameter until a thin, continuous graphene film with a lustrous gray tone became visible to the naked eye. The electrical conductivity of paper-like graphene films was measured on the basis of the van der Pauw method using a home-made setup consisting of an Agilent 6614C DC power supply and a Fluke 45 digital multimeter. The graphene films were prepared by vacuum filtration of graphene dispersions in water/isopropanol through polycarbonate membrane filters (Whatman; diameter: 25 mm; pore size: 0.2 μm) and were cut into $12 \times 12 \text{ mm}^2$ square pieces for the measurements, with their thickness being estimated by both FE-SEM and a high precision electronic caliper (Digimatic Micrometer, model MDC-25PX, from Mitutoyo). Measurement of water contact angles was carried out on the paper-like graphene films by carefully dropping 2 μL of water on the films with a pipette and immediately taking images of the droplet using a standard digital camera attached with

a macro lens. Contact angles were determined from the recorded images through analysis with ImageJ software.

S3. Applications of the high quality, anodically exfoliated graphene

To explore their possible applications, the high quality graphene materials developed in this work were tested as adsorbents for water-soluble dyes and as sorbents for non-polar organic solvents and dyes, as well as electrodes for capacitive energy storage. In this case, the as-exfoliated graphene materials, i.e., the products directly obtained from the anodic delamination process without a subsequent sonication step (only washed with water to remove remnants of the electrolyte) were used, as they exhibited a powdery, three-dimensional morphology that was convenient for their manipulation. The dye adsorption tests were carried out by adding ~1.5 mg of graphene material to 1.5 mL of an aqueous solution of a given dye at room temperature and pH ~6, followed by gently stirring with a magnetic bar for 24 h to ensure the attainment of adsorption equilibrium and centrifuging the solution (20000 g, 20 min) to sediment the graphene component. The concentration of the dye in the resulting supernatant was then determined by means of UV-vis absorption spectroscopy and contrasted with that of the starting dye solution, which in turn allowed the amount of dye adsorbed on the graphene sample to be estimated. The adsorption experiments were performed with the following dyes (wavelengths given in parenthesis correspond to the position of the absorption peak used to measure the dye concentration): methyl orange (460 nm), methylene blue (660 nm), basic fuchsin (540 nm), methylene green (660 nm) and rose bengal (560 nm). To determine the maximum adsorption capacities of the graphene materials, different starting concentrations of the dye (typically up to 2-3 mg mL⁻¹) were probed in the tests. For the sorption of oils and non-polar solvents, a certain mass of graphene material (typically ~5 mg) was first put into a 1.5 mL centrifuge tube. Then, small known volumes of a given oil/solvent (usually around 100 µL) were successively added to the tube. Such volumes were readily taken up by the graphene sample until a point was reached where the latter became saturated, which in turn allowed to estimate the total volume of oil/solvent retained by the sorbent. Sorption tests were conducted with the following substances: toluene, hexane, dodecane, tetrahydrofuran, acetone, chloroform, ethylene glycol, ethanol, olive oil, as well as unused and used pump oil.

Testing of the high quality anodic graphene as an electrode for capacitive energy storage was accomplished in a three-electrode configuration with a Swagelok-type cell, using a paste based on a commercial activated carbon (ACF A20) as the counter electrode and Ag/AgCl (3M KCl) as the reference electrode in an acidic aqueous electrolyte (1 M H₂SO₄). The counter electrode paste consisted of a mixture of the activated carbon, polytetrafluoroethylene (PTFE) as a binder and carbon black as a conductive additive in a weight ratio of 90:5:5. The graphene working electrode was prepared by pressing the as-prepared anodic graphene under a moderate force (1 ton for 15 s) onto a graphite foil support by means of a hydraulic press. Two pieces of glass microfiber filter (grade 934-AH, from Whatman) were used as the separator. Prior to assembling the cell, the working electrode, counter electrode and separator were soaked in the electrolyte and vacuum-degassed. The assembled cell with the electrolyte was also vacuum-degassed before the measurements, which were conducted in a Biologic VSP potentiostat. Both cyclic voltammograms at different potential scan rates and galvanostatic charge/discharge curves at different current densities were recorded.

S4. Additional figures

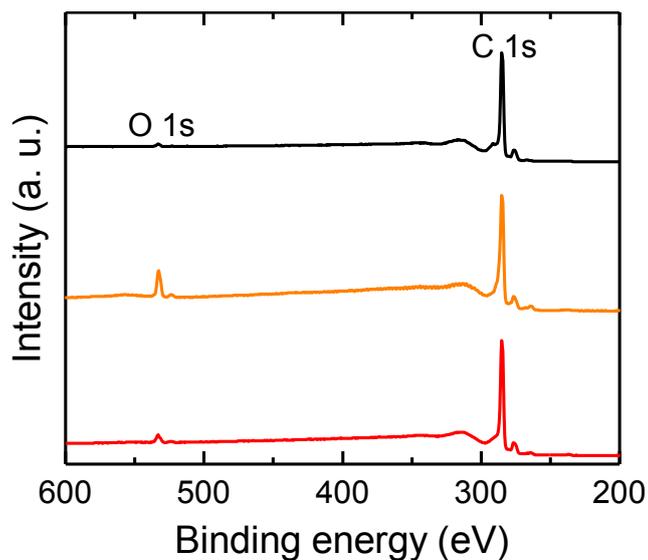


Figure S1. XPS survey spectra of the starting graphite foil (black trace), graphene anodically exfoliated in 0.1 M Na₂SO₄ electrolyte (orange trace) and graphene anodically exfoliated in 0.1 M Na₂SO₄ with 0.1 M NaCl as a co-electrolyte (red trace).

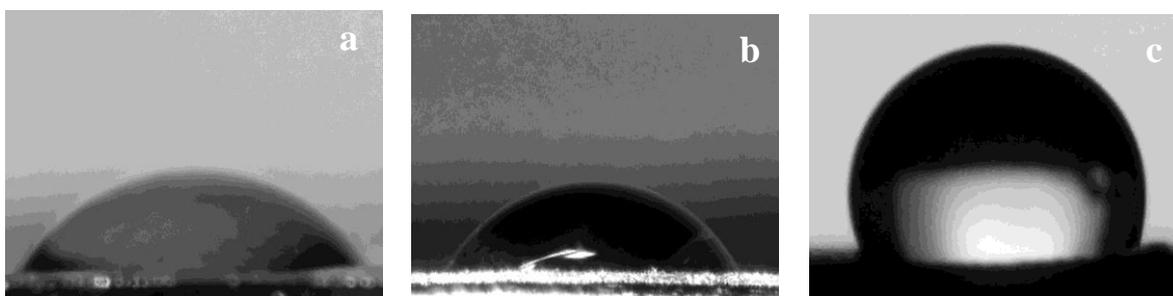


Figure S2. Digital photographs of water droplets (1–2 μ L) deposited onto the starting graphite foil (a), and vacuum-filtered films of graphene prepared by anodic exfoliation in the absence (b) and presence (c) of 0.1 M NaCl as a co-electrolyte.

S5. Additional tables

Table S1. Adsorption capacities of different dyes (methyl orange, methylene blue, methylene green, basic fuchsin and rose bengal) with a range of graphene-based materials.

Material	Adsorbate	Adsorption capacity (mg g ⁻¹)	Ref.
Graphene oxide	Methyl Orange	17	S1
CoFe ₂ O ₄ functionalized graphene	Methyl orange	72	S2
Graphene oxide/Ni-Al LDH	Methyl orange	84	S3
Graphene oxide/Ni-Cr LDH	Methyl orange	160	S4
Graphene oxide/chitosan	Methyl orange	567	S5
As-prepared anodic graphene	Methyl orange	457	This work
Reduced graphene oxide	Methylene blue	154	S6
Graphene oxide	Methylene blue	244	S7
Citric acid functionalized magnetic graphene oxide	Methylene blue	316	S8
Agar/graphene oxide composite aerogel	Methylene blue	578	S9
Porous graphene oxide/hydrogel nanocomposite	Methylene blue	714	S10
As-prepared anodic graphene	Methylene blue	415	This work
As-prepared anodic graphene	Methylene green	343	This work
Reduced graphene oxide	Basic fuchsin	34	S11
β-cyclodextrin–carboxymethyl cellulose–graphene oxide composite	Basic fuchsin	59	S12
Reduced graphene oxide/ PSSMA	Basic fuchsin	388	S13
Graphene/β-cyclodextrin composite	Basic fuchsin	426	S14
Graphene oxide/polyacrylamide	Basic fuchsin	1034	S15
As-prepared anodic graphene	Basic fuchsin	361	This work
Graphene oxide/sodium alginate/polyacrylamide hydrogel	Rose Bengal	6	S16
Graphene Oxide@PLA@HA Composite	Rose Bengal	53	S17

Microcapsule			
Graphene sheets/graphene quantum dots	Rose Bengal	587	S18
As-prepared anodic graphene	Rose Bengal	130	This work

Table S2. Range of sorption capacities of different graphene-based materials towards oils and non-polar organic solvents.

Material	Retention capacity (g/g)	Ref.
Magnetic graphene foam	7-27	S19
Hydrothermal graphene sponge	20-35	S20
Graphene-carbon nanotube aerogel	20-35	S21
GO foam	5-40	S22
N-doped graphene aerogel	40-110	S23
Graphene sponge	80-160	S24
As-prepared anodic graphene	15-30	This work

Table S3. Gravimetric capacitance values of a range of graphene-based materials determined at different current densities.

Material	Current density (A/g)	Capacity (F/g)	Ref
rGO	0.3	57	S25
rGO/carbon black	1	79	S26
rGO	0.5	82	S27
rGO	1	116	S28
rGO foam	5	125	S29
rGO	1	130	S30
graphene hydrogel	1	186	S31
graphene/PANI nanofibers	0.3	210	S25
Highly crumpled N-doped graphene nanosheets	1	246	S32
Anodic graphene	0.3	105	This work
Anodic graphene	0.5	100	This work
Anodic graphene	1	94	This work
Anodic graphene	5	63	This work

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