Electronic Supplementary Material (ESI) for Nanoscale
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Support information: Enhanced conductivity of reduced graphene oxide decorated with aluminium oxide nanoparticles by oxygen annealing

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Methods

Synthesis of graphene oxide

Graphite oxide were synthesized from graphite powder (325 mesh, Alfa Aesar) by a modified Hummers method[1]. H_2SO_4 (23 ml) was placed into a 250 ml round bottom flask and chilled to 0 °C using an ice bath. The mixture of graphite powder (1.0 g) and $NaNO_3$ (0.5 g) was added to the acid and stirred. $KMnO_4$ (5.0 g) was added slowly in portions to keep the temperature below 10 °C. The mixture was then allowed to react at 35 °C for 2 hours after which DI water (46 ml) was added slowly so that the temperature does not climb above 50 °C. After 2 hours stirring, 140 ml of DI water and 10 ml of 30% H_2O_2 were added to the flask to end the oxidation process. The mixture was then settled for at least one day after which the clear supernatant was decanted. The remaining mixture was repeatedly purified first with 500 ml of 10% HCl solution followed by 500 ml of DI water to remove the acid. The resulting solid was dried under vacuum. 100 mg of the resulting solid was dried in air and diluted in 200 ml of DI water to form GO dispersion that was treated with an ultrasonic probe (Cole-Parmer high-intensity ultrasonic processor, output power 100 W) for 30 min, followed by high-speed centrifugation (15500 RCF, 10 min) to remove impurities.

Graphene oxide paper

Graphene oxide paper (GO paper) was formed by filtration of the GO dispersion (150 ml) through an anodisc membrane filter (47 mm in diameter, 0.02 μm pore size; Whatman), followed by vacuum drying at room temperature and then peeling from the filter.

Samples annealing

After loading the sample into a vacuum oven at room temperature, the system was purged with argon flow overnight to remove any possible gases introduced from the ambient. The argon flow was maintained by the end of first oxygen-annealing step, in which oxygen was introduced when the temperature reached 200 °C with a ramp-up rate at 5 °C/min for 30 minutes. The second ramp-up rate was decrease to 2.5 °C/min for a slowly and gently thermal annealing (400 °C, 30 min). No any gas was allowed to introduce into the oven to maintain the high vacuum (4×10^{-5} mbar).

Characterization

The holey-carbon coated copper transmission electron microscopy (TEM) grids (Agar) were placed on the anodisc aluminium oxide membrane filters (Whatman). Aqueous graphene dispersion (~0.005mg/mL, 4 ml) was filtered through the membrane to deposit the GO sheets onto the TEM grids, and then allowed to dry in a vacuum oven at room temperature for one night before annealing. Conventional high resolution TEM (HRTEM) imaging was carried on a JEOL 2100F TEM microscope equipped with a local energy dispersive X-ray spectroscopy (EDX).

Acceleration voltage of 100 kV was used throughout the measurements with specimens at ambient temperature.

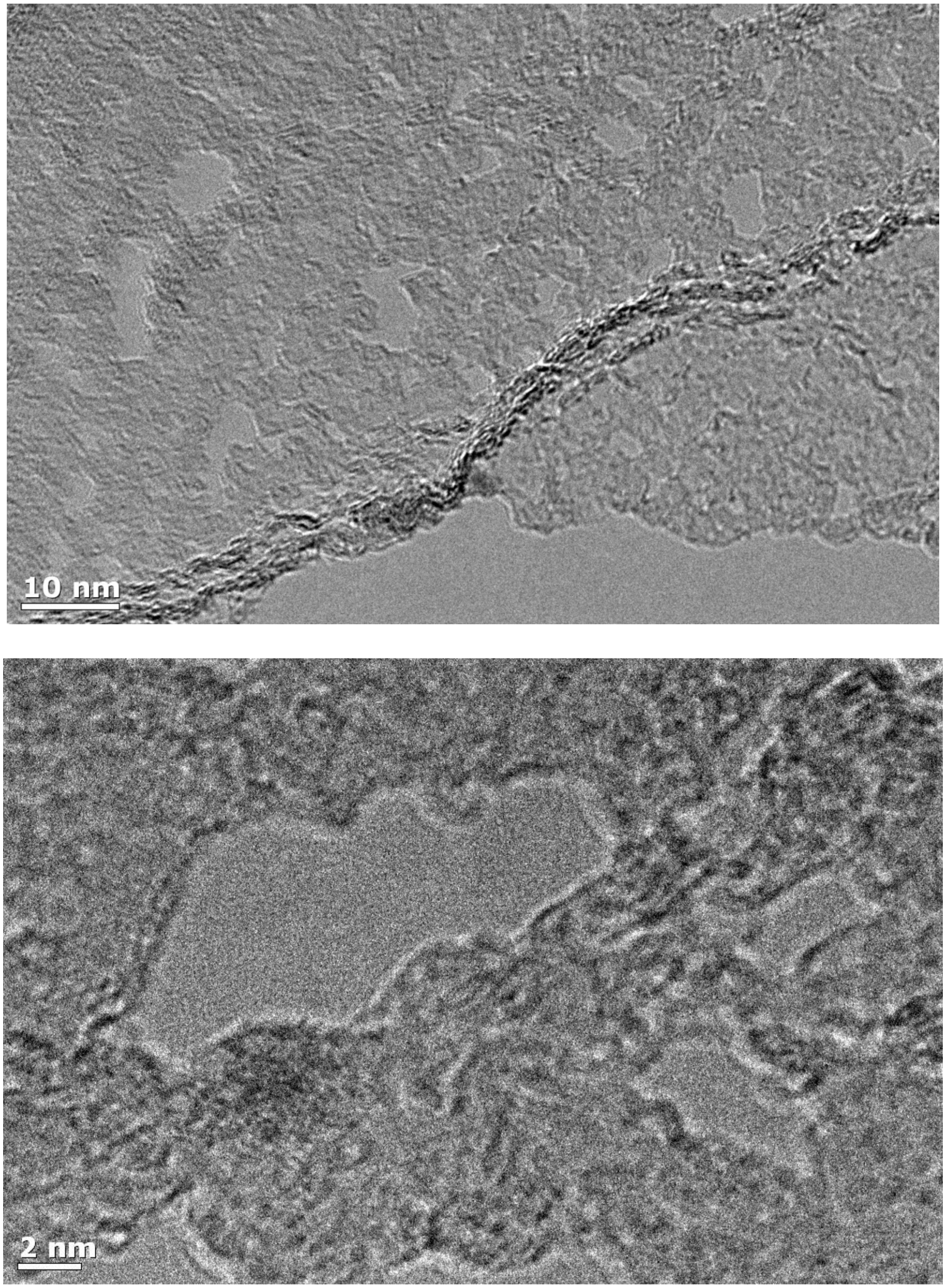

Figure S 1 HRTEM images of thermal-annealed reduced graphene oxide film. Scale bars: (top) 10 nm, and (bottom) 2 nm. No any aluminium oxide nanoparticle can be found in the graphene plane after a conventional thermal annealing without oxygen gas flow.

The GO samples for Atomic Force Microscopy (AFM) analysis were fabricated on a 300 nm SiO_2 coated silicon substrate by spin coating aqueous GO dispersion at 2000 rpm for 1 minute. In order to get a uniform film, 3 times repeated coatings were carried out prior to annealing. AFM images of GO or reduced GO on a freshly cleaved mica surface were taken with a Veeco™ DI CP-II AFM microscope in contact mode, using a diamond tip mounted at the end of a steel cantilever.

XPS measurements were performed with a VG Scientific ESCALab Mark II X-ray photoelectron spectrometer using a non-monochromated Al Kα x-ray source (hν = 1486.6 eV). Survey spectra were collected covering the full binding energy (BE) range 0-1200eV using a step size of 1eV and pass energy of 50eV, whereas the high resolution spectra of C1s, Al2p and Al KLL were collected using a step size of 0.2eV and pass energies of 20eV. To compensate for surface charging, all binding energies were corrected with reference to the C1s peak at 284.5eV. Peak fitting and deconvolution of the high resolution spectra were achieved using CasaXPS software and were fitted according to mixed Gaussian–Lorentzian components and a non-linear Shirley background.

Raman microscope were used to image individual graphene sheet which deposited on SiO_2 substrates before and after thermal annealing. The spectra were recorded using a ×100 objective lens in ambient conditions, with a laser excitation wavelength of 633 nm and 1,800 lines per mm grating. A low power level (< 1 mW) was used to avoid any heating effect

Fourier transform infrared spectroscopy (FTIR) of GO paper before and after thermal annealing were performed with a Perkin-Elmer Spectrum One spectrometer between 4000cm^{-1} and 540cm^{-1} using a single reflection horizontal attenuated total reflection (ATR) accessory.

The electrical conductivities of TrGO and OrGO were measured at room temperature by the four probe van der Pauw method using a homemade Hall measurement system at 0.5 Tesla. TrGO and OrGO papers were cut into specimens of 5 mm square × 1 μm in thickness.

For UV-Vis measurement, a thin film of the water-soluble GO sheets was fabricated on a quartz substrate by spin coating followed by annealing to prepare TrGO and OrGO samples. The spin coating process of GO sheets is the same as that for AFM samples. UV−Vis absorption spectra were recorded in a a single beam Biochrom UV-VIS spectro-photometer Libra S22 at room temperature.

Photoluminescence (PL) spectra were recorded on a Jobin Yvon SPEX Fluorolog-3-P spectroscope and a 450 W Xe lamp was used as the excitation source. The PL excitation (PLE) spectrum recorded with the PL emission wavelengths at 600 nm shows only one sharp peaks at 400 nm.

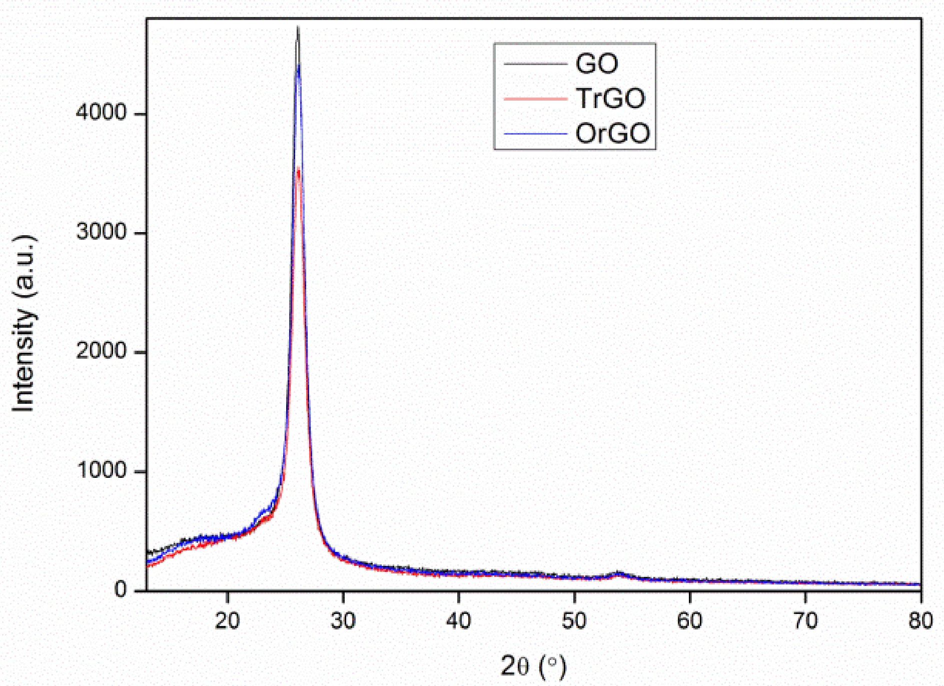

Figure S 2 X-ray diffraction (XRD) pattern of GO, TrGO and OrGO papers. The characterization was carried out in a Siemens D500 powder X-ray diffractometer at 40keV and 25mA with Cu Kα line as the excitation source radiation (λ=1.5406 Å).

The distinct peaks at 13.0° in the XRD spectra of the GO papers corresponding to the layer-to-layer distance (d-spacing) of approximately 3.4 Å that is equal to the interlayer separation in graphite. The numbers of perpendicularly stacked GO and reduced GO sheets in the paper material were calculated by using the classical Debye−Scherrer equation

$$\tau = \frac{\mathrm{K}\lambda}{\beta \cos\theta}$$

$$n = \frac{\tau}{d}$$

where K is the shape factor, λ is the x-ray wavelength, β is the full width at half maximum (FWHM), θ is the Bragg angle, τ is the thickness, and *d* is the interlayer spacing. The thickness was found to be 6.8 Å which corresponds to 2 stacked graphene oxide sheets.

Reference

(1) Hummers, W. S.; Offeman, R. E. *J. Am. Chem. Soc.* **1958,** *80*, 1339-1339.