

Supplementary Information for

High-yield production of highly conductive graphene via reversible covalent chemistry

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1. Experimental section

Preparation of GA dispersion. Natural graphite powder (12000 mesh, Qingdao Huatai Co., Qingdao, China) was treated by oleum (20% SO₃, Sinopharm Chemical Reagents, Beijing) at room temperature for 24 h to form OIG. After vacuum filtration through a polytetrafluoroethylene (PTFE) membrane with pores of 200 nm, the obtained bluish OIG (100 mg) slurry was put into 5 mL NMP solution containing 50 mg TCNE (98% Alfa Aesar) and ultrasonicated for 5 min. The resultant sample was incubated at 45 °C in dark for 72 h to further perform the Dienes-Alder reaction. Successively, the mixture was filtrated through a PTFE membrane (pore size: 200 nm) followed by repeated washing with acetone to remove excessive TCNE and finally dried in air. 5 mg of the dried TCNE intercalated graphite was put into 5 mL NMP and sonicated (Ningbo Xinzhi SBL-15DT at 50% amplitude) for 1 h. The obtained GA dispersion was centrifuged at 2000 rpm for 60 min (Beijing Jingli LG16-W centrifuge) to remove the indispersible residual, and a black dispersion of GA was collected.

Retro-Dienes-Alder reaction. GA dispersion was stirred at 100 °C for 3 h to remove TCNE addends to form eGA. This dispersion was then instantly vacuum filtrated through a PTFE membrane before cooling to remove cleaved TCNE. A mild sonication of the membrane in NMP gave a stable dispersion of eGA. Likewise, in the case of deposited GA on a silica chip, retro-Dienes-Alder reaction was carried out by soaking the chip in NMP at 100 °C for 3 h followed by repeated washing with ethanol.

Preparation of graphene dispersion by conventional liquid-phase exfoliation. The procedure for conventionally liquid-phase exfoliation was well-documented.^{S1} In this case, 5 mg natural graphite powder (12000 mesh, Qingdao Huatai Co., Qingdao, China) was sonicated in NMP (5 mL) followed by centrifugation and decantation under the same conditions used for preparing GA dispersion.

Characterization. XRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu K α radiation. Samples for XRD studies were graphite powder, OIG after washing by water, GA and eGA thin films. The graphene-based films were fabricated by filtrating the corresponding dispersions and followed by vacuum drying at room temperature overnight. UV-vis absorption spectra were taken out by using a Hitachi U-3010 UV-visible spectrometer. Raman spectra are acquired by the use of a HORIBA LabRAM HR Evolution Raman spectrometer with a 514-nm He-Ne laser beam. The step for Raman mapping was controlled to be 0.2 μm . Raman samples were prepared by pipetting 10 μL of GA dispersion onto a silicon chip (0.5 cm \times 0.5 cm) with a 300 nm-thick SiO₂ coating followed by vacuum drying at room temperature for 24 h. XPS was carried out using an ESCALAB 250 photoelectron spectrometer (ThermoFisher Scientific). TEM images were acquired by using a HITACHI H-800 TEM. HRTEM images were taken out on a Tecnai G2 F20 S-Twin HRTEM. TEM and HRTEM samples were prepared by drop casting dispersions onto holy carbon grids followed by vacuum drying at room temperature. SEM (Sirion 200, JEOL) and AFM (SPM-9600, Shimadzu) were employed to study the sizes and thicknesses of GA sheets. The electrical conductivities were measured by a conventional four-probe technique using a Guangzhou Kunde KDY-1 test unit.

2. The absorption coefficients of GA, eGA, and graphene dispersions

In order to measure the concentrations of GA and graphene dispersions, we measured their absorption coefficients (α). According to Lambert-Beer law ($A/d=\alpha C$, where A is absorbance, C is concentration and d is cell thickness), the absorbance of a graphene dispersion is proportional to its concentration. The concentration of dispersion was measured by weighing its solid content. Then, the absorbance at 660 nm divided by cell thickness is plotted versus concentration to give the $\alpha_{660} = 1941$ and $1498 \text{ L g}^{-1} \text{ m}^{-1}$ for graphene and GA respectively (**Fig. S1**). The α_{660} value of our graphene dispersion is comparable to those reported in the literature.^{S1,S2} Compared with graphene, GA showed a reduced optical absorbance due to its disrupted π -system. After retro-Diels-Alder reaction, eGA exhibits a partially restored absorbance with $\alpha_{660} = 1639 \text{ L g}^{-1} \text{ m}^{-1}$.

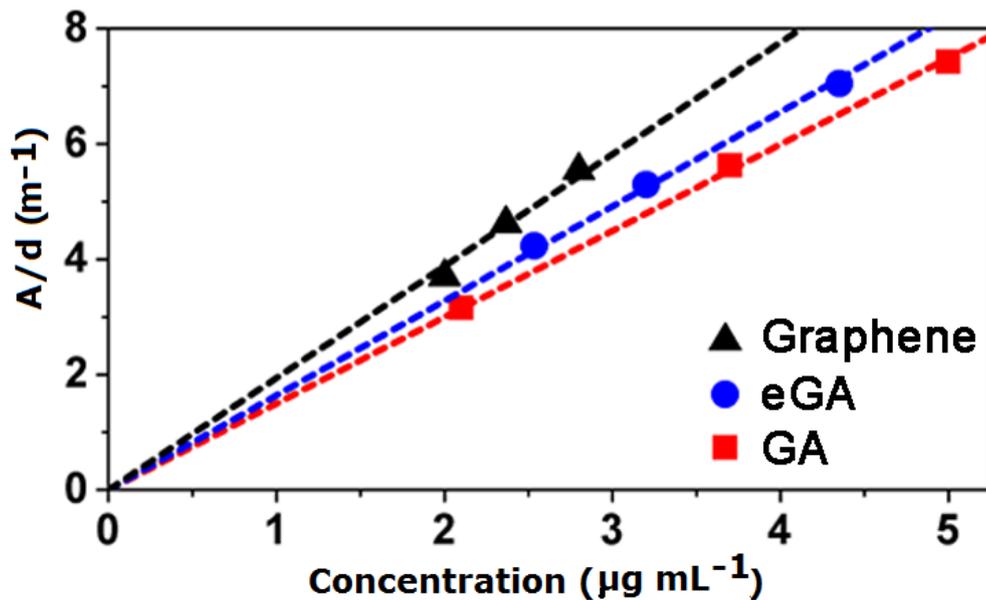


Fig. S1. Plot of A/d versus the concentration of graphene, GA or eGA.

3. Morphology of GA flakes

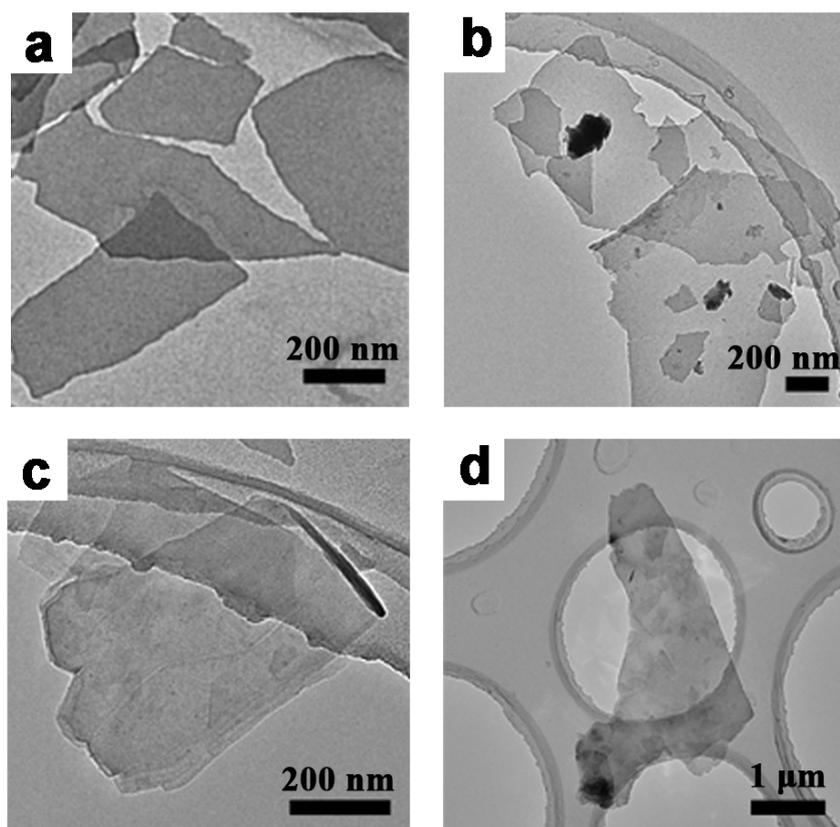


Fig. S2. TEM images of GA sheets from several hundred nanometers to several micrometers in size.

4. Thicknesses and size distributions of eGA flakes

To accurately determine the number of layers (N_G) of exfoliated GA, we measured the heights of eGA flakes, because the heights of eGA flakes can be faithfully transformed into N_G . This characterization was acquired by using AFM to measure the heights of eGA flakes deposited on a silica chip (**Fig. S3a**). The height profiles of eGA flakes usually display as terraces with a height step of ~ 1.0 nm (**Fig. S3b-d**). On the basis of this fact, we proposed that the 1.0 nm height step is the thickness of a monolayer eGA sheet. We further used this value to calculate the N_G of about 400 eGA flakes. The results reflect that most of the flakes have $N_G < 10$. More than half of the flakes have N_G less than 5. About 3% flakes are monolayer graphene (**Fig. S3e**).

SEM was employed to investigate the sizes of eGA flakes deposited on a silica chip. A typical SEM image is shown in **Fig. S4a**. By measuring the lengths of about 400 flakes, we got the histogram of size distribution of eGA (**Fig. S4b**). The average length of eGA flakes was calculated to be about $0.4 \mu\text{m}$.

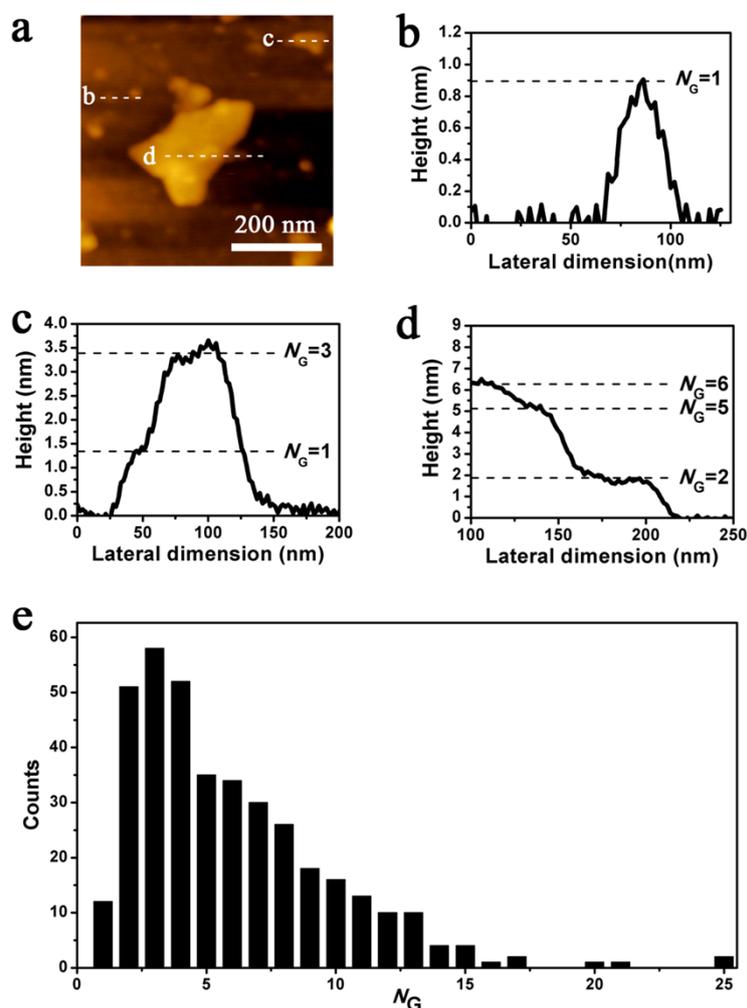


Fig. S3. Thickness statistics of eGA flakes. (a) An AFM image of typical eGA flakes. (b–d) Topographic height profiles of eGA flakes labeled in (a). (e) Histogram of N_G distribution of 400 eGA flakes.

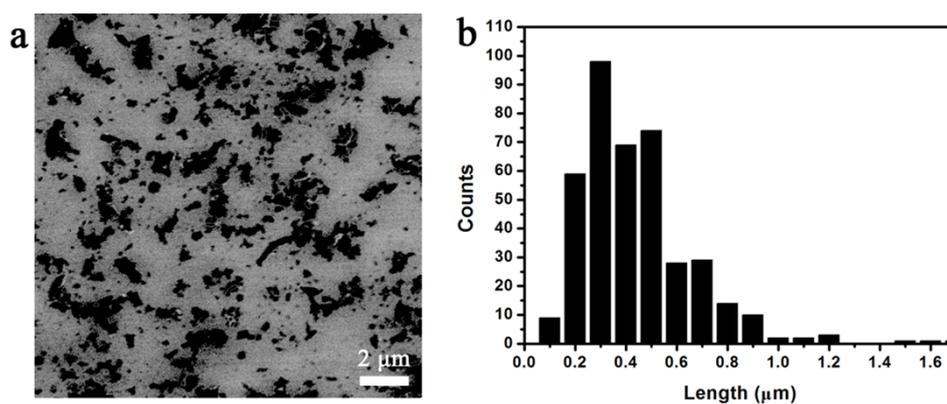


Fig. S4. Size statistics of eGA flakes. (a) A SEM image of eGA flakes. (b) Histogram of size distribution of 400 eGA flakes.

5. Conductivity measurements of Graphene, GA, and eGA films

The resistance (R) of a thin film is related to its thickness (d) by

$$R = \kappa^{-1}d^{-1}$$

where κ is conductivity. From the linear fitting plots of R versus d^{-1} in Figure S5, we calculated the κ of GA, eGA, and conventionally exfoliated graphene as 135, 1035, 1672 S m⁻¹, respectively.

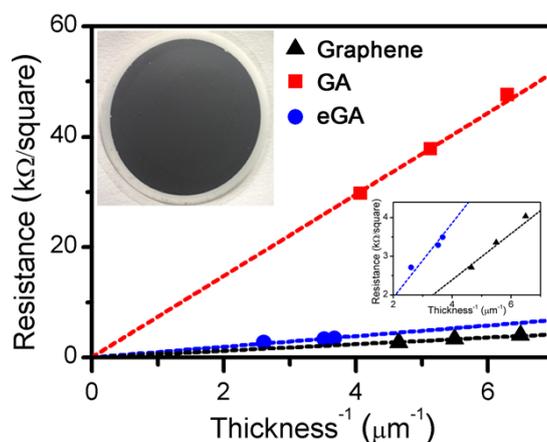


Fig. S5. Plot of resistance versus the reciprocal thickness of thin film of graphene, GA or eGA. Top left inset: photograph of a GA thin film supported by an alumina membrane. Bottom right inset: magnified regional plots of eGA and graphene films.

Supplementary Reference

- S1 Y. Hernandez, V. Nicolosi, M. Lotya, F. M. Blighe, Z. Sun, S. De, I. McGovern, B. Holland, M. Byrne, Y. K. Gun'Ko, J. J. Boland, P. Niraj, G. Duesberg, S. Krishnamurthy, R. Goodhue, J. Hutchison, V. Scardaci, A. C. Ferrari, J. N. Coleman, *Nat. Nanotechnol.*, 2008, **3**, 563.
- S2 M. Lotya, Y. Hernandez, P. J. King, R. J. Smith, V. Nicolosi, L. S. Karlsson, F. M. Blighe, S. De, Z. Wang, I. McGovern, *J. Am. Chem. Soc.*, 2009, **131**, 3611.