

Supporting Information

Varying Layer Graphene Oxide Liquid Crystal: Fabrication, Characterization and Applications

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Experimental Section

Materials

All the chemicals were analytic grade reagents and used without further purification. Graphite powder (ACROS, cas#7782425), Potassium peroxydisulfate ($K_2S_2O_8$, $\cong 99.5\%$), Phosphorus (V) oxide (P_2O_5 , $\cong 98\%$), Sulfuric acid (H_2SO_4 , 95~98%), Potassium permanganate ($KMnO_4$, purity: $\cong 99\%$), Hydrogen peroxide (H_2O_2 , $\cong 30\%$), Hydrochloric acid (HCl, 36~38%), deionized water.

Characterization

Tapping-mode AFM (Nanoscope IIIA) were carried out by first depositing GO sheets from their dispersions on pre-cleaned wafer. TEM was performed on a JEM-2100 with an accelerating voltage of 200 kV. Raman spectra were recorded on a Renishaw Microscope System RM2000 with laser wavelength 532nm. X-ray photoelectron spectroscopy (XPS) was performed using a Thermo ESCALAB 280 system with Al/K (photon energy =1486.6 eV) anode mono X-ray source. POM observations were performed with an Olympus BX51 POM. SEM images were taken on a JEOR JSM-6700F field-emission SEM system. X-ray diffraction (XRD) patterns of samples were measured on a Y-2000 X-ray Diffractometer with copper $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) operating at 40 kV and 40 mA. The tensile properties of the GO and rGO films were measured using a tensile tester (UTM2203, Shenzhen Suns Technology Stock Co., Ltd, China) with a 100N load cell at a strain rate of 5 mm/min. A linear four-point probe system (ST-2258C) was employed to measure the room temperature conductivity of the films.

Synthesis of Graphite Oxide.

Graphite oxide is synthesized from graphite powder (ACROS, cas#7782425) by a modified Hummers method.^{1,2} For the preparation of GO, three main steps were

involved in a typical procedure.

In the preoxidation step, $K_2S_2O_8$ (8.4g) and P_2O_5 (8.4g) were added into the solution of concentrated H_2SO_4 (40 mL), which were placed in a 500 mL round-bottom flask and the temperature was kept at 80 °C. Graphite powder (10 g) was then added into H_2SO_4 solution. The mixture was stirring for 4.5 hours. After cooling to the room temperature, the mixture was diluted with deionized water (1.5 L) and then transferred to a large beaker and allowed to settle overnight. The following day the mixture was carefully vacuum-filtered via a 0.22 μm polycarbonate membrane and washed with deionized water (1.5 L). The solid was dried at 35 °C in the drying oven.

In the following oxidation step, the preoxidized graphite powder (3 g) was put into cold (0 °C) concentrated H_2SO_4 (138 mL). $KMnO_4$ (18 g) was added slowly under vigorous agitation to keep the temperature of the suspension below 10 °C. The mixture was then stirred below 10 °C for 2 h. Next, it was heated to 35 °C and kept stirring for another 2 h. Successively, deionized water (276 mL) was slowly added into the mixture in an ice bath for the purpose to keep the temperature not exceed 50 °C. The diluted suspension was stirred at 50 °C for 2 h and then transferred to a large beaker. After that, deionized water (920 mL) was added into the suspension to terminate the reaction. Then, 30% H_2O_2 (20 mL) was dropwise dipped into the suspension until its color turned bright yellow. The mixture was placed until the top layer was nearly clear and the supernatant was removed.

The remaining mixture was centrifuged and washed with 10% HCl (0.9 L) solution followed by deionized water to wash until the supernatant became neutral. The resulting solid was dried in an oven at 40 °C.

Preparation of different sheet layers of graphene oxide and corresponding graphene oxide liquid crystals.

Graphite oxide (2 g) was added into deionized water (1600 ml). The aqueous dispersion of GO was obtained by ultrasonication for 30 min at 240 W, which was

marked the original GO. Firstly, the original GO was centrifuged at the speed of 10,000 rpm (10,610 g) for 5.5 hours. During this period, the bottom gel was taken out every 30 min from centrifugal tubes and eleven samples could be obtained. To get larger quantities, the 12th sample was obtained by centrifugation at the speed of 11,000 rpm (12,840 g). Then the obtained twelve samples were concentrated by further centrifugation at the speed of 10,000 rpm (10,610 g) for 30 min, respectively. Thus, graphene oxide liquid crystals with different sheet layers of GO would get eventually.

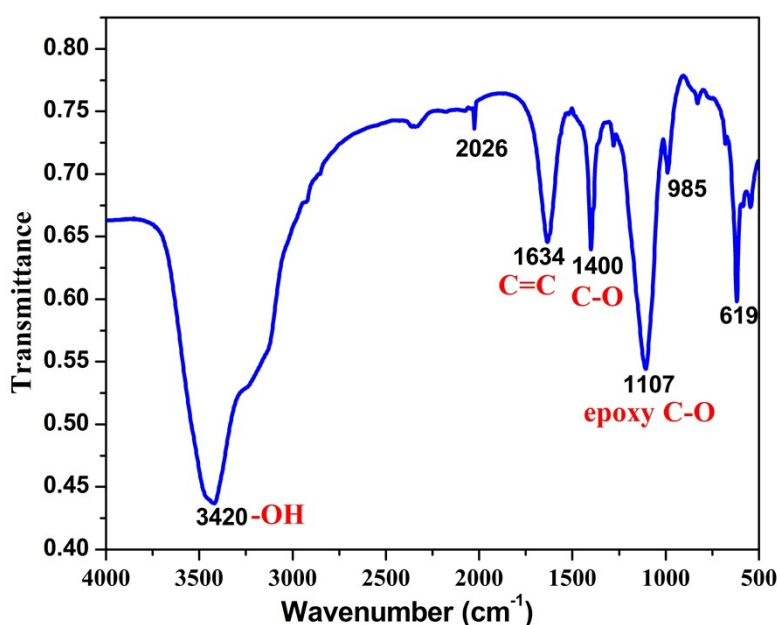


Fig. S1 FT-IR spectrum of original GO.

Fig. S1 shows the FT-IR spectrum that reveals the presence of -OH (3420 cm⁻¹), C=C (1634 cm⁻¹), C-O (1400 cm⁻¹), epoxy C-O (1107 cm⁻¹) in the original GO aqueous solution.

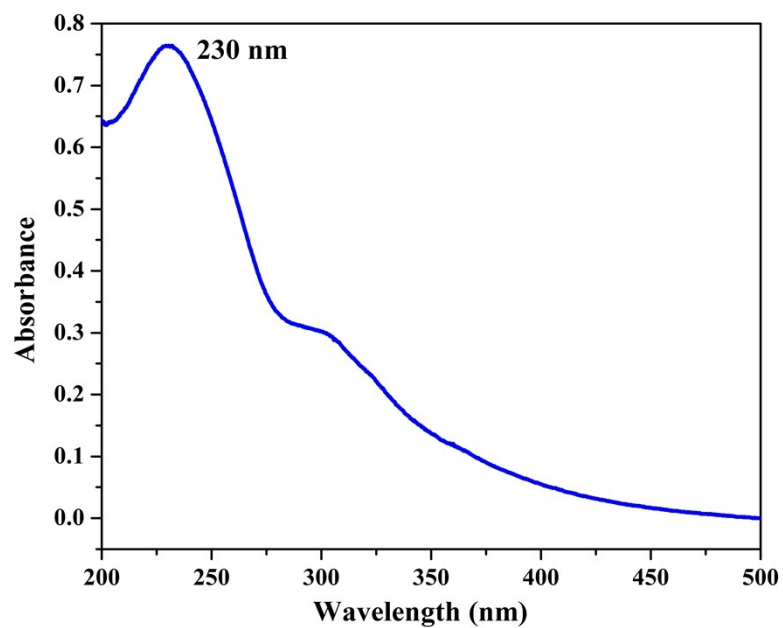


Fig. S2 UV spectrum of original GO.

Fig. S2 shows the UV spectrum that reveals the presence of C=C-C=C (230 nm), C=O (the shoulder: 280-320 nm).³

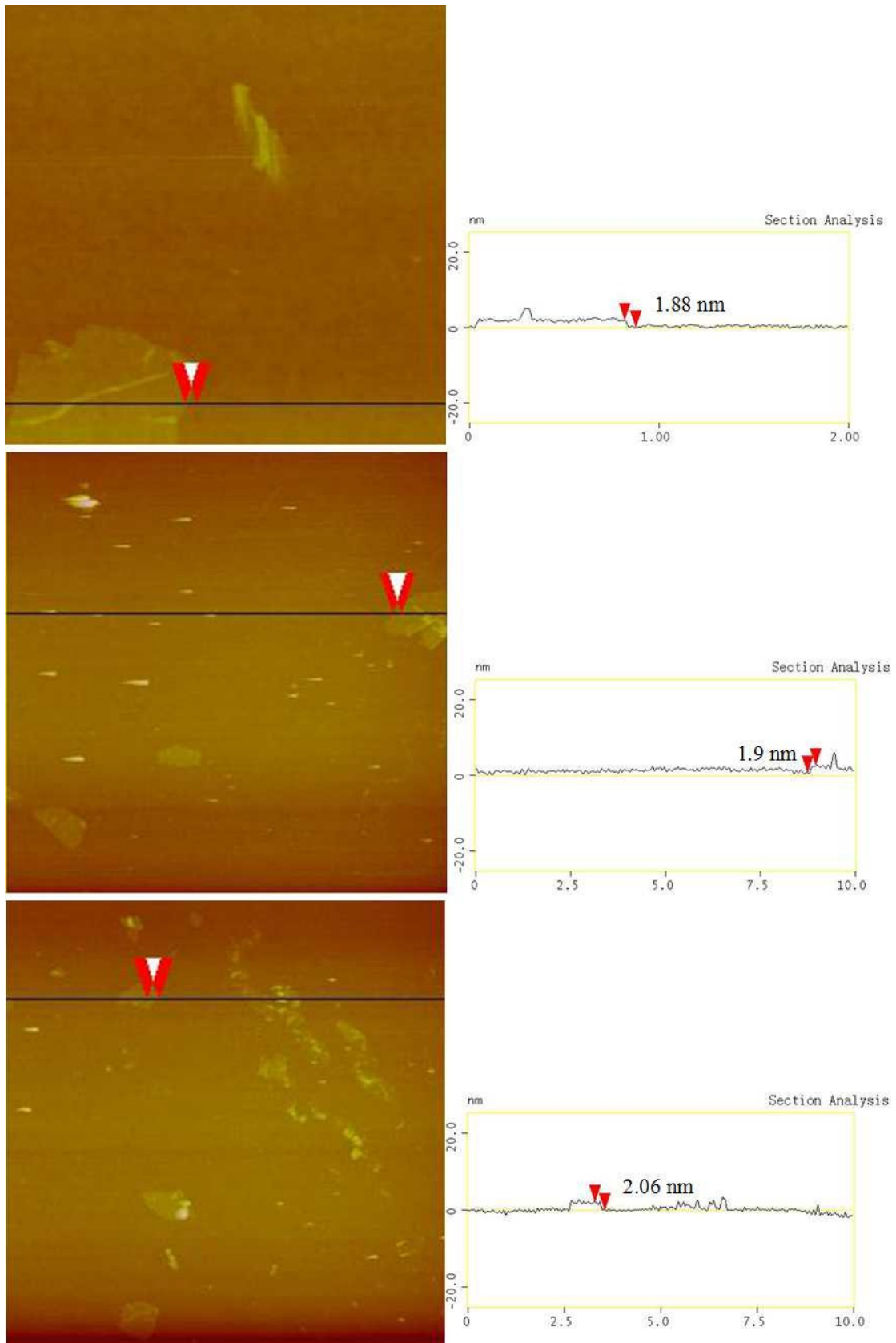


Fig. S3 AFM images of GO-1.

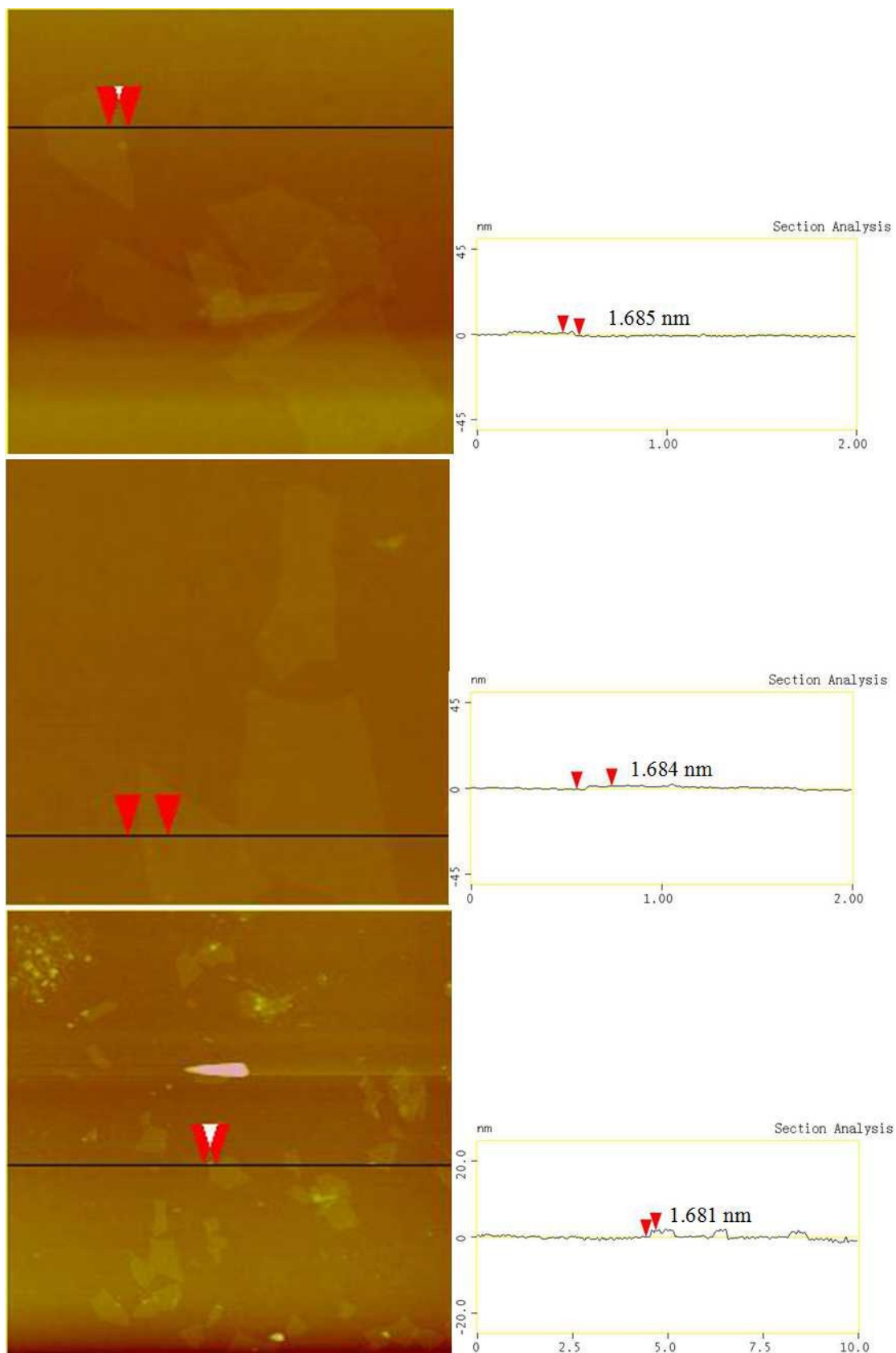


Fig. S4 AFM images of GO-6.

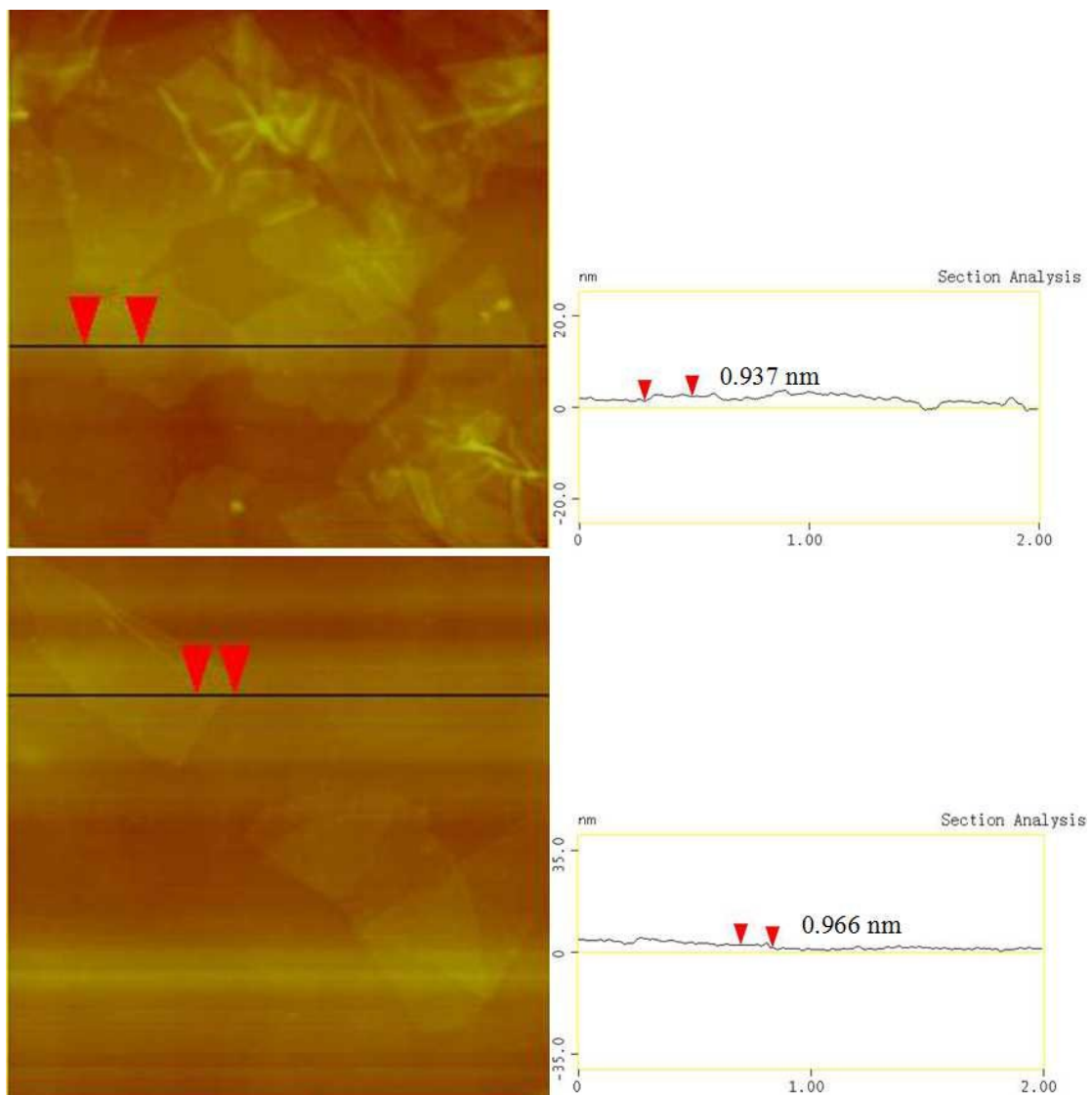


Fig. S5 AFM images of GO-12.

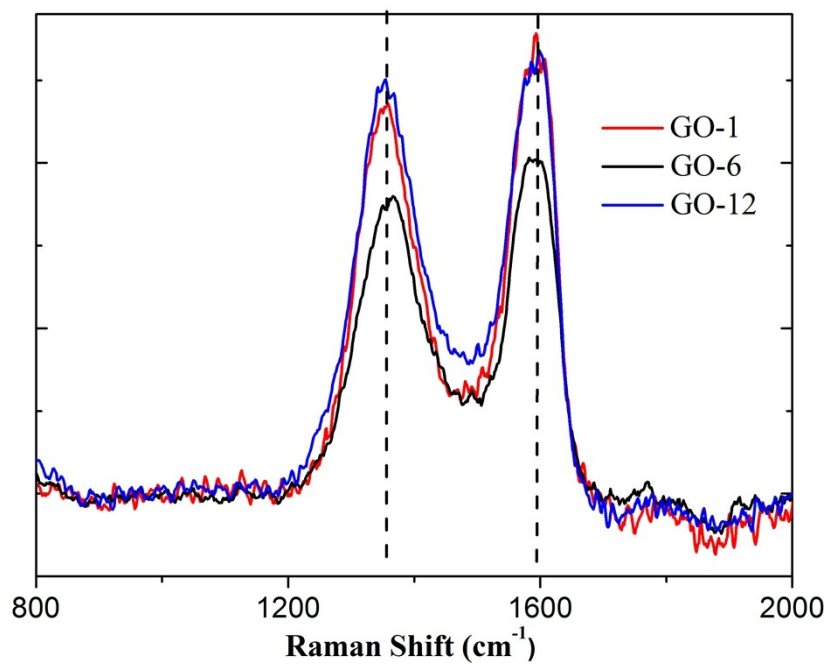


Fig. S6 Raman spectra of GO-1, GO-6 and GO-12 films.

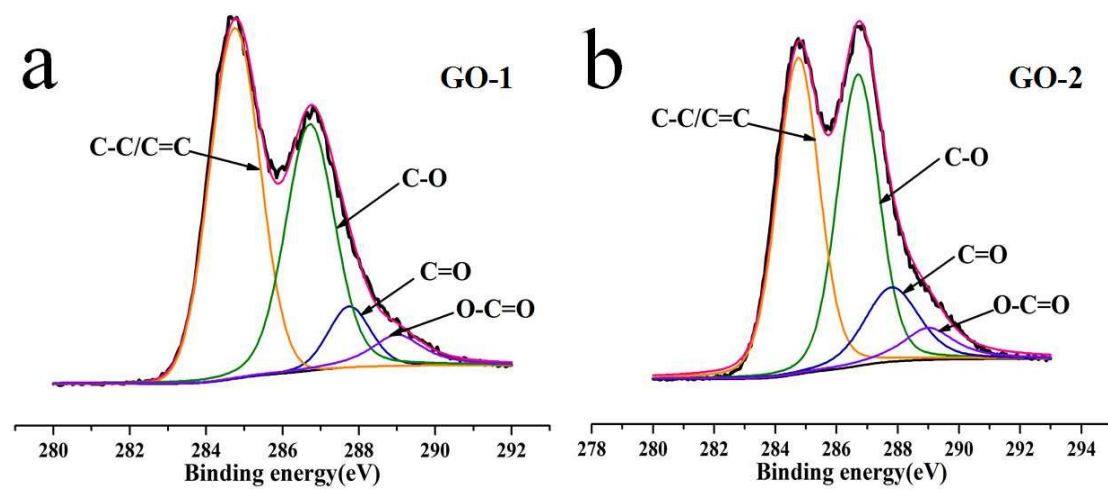


Fig. S7 Typical C1s XPS spectra of GO-1 (a) and GO-2 films (b).



Fig. S8 POM images of GO aqueous dispersions at the same concentration for GO-1, GO-6 and GO-12 in capillaries observed between crossed polarizers.

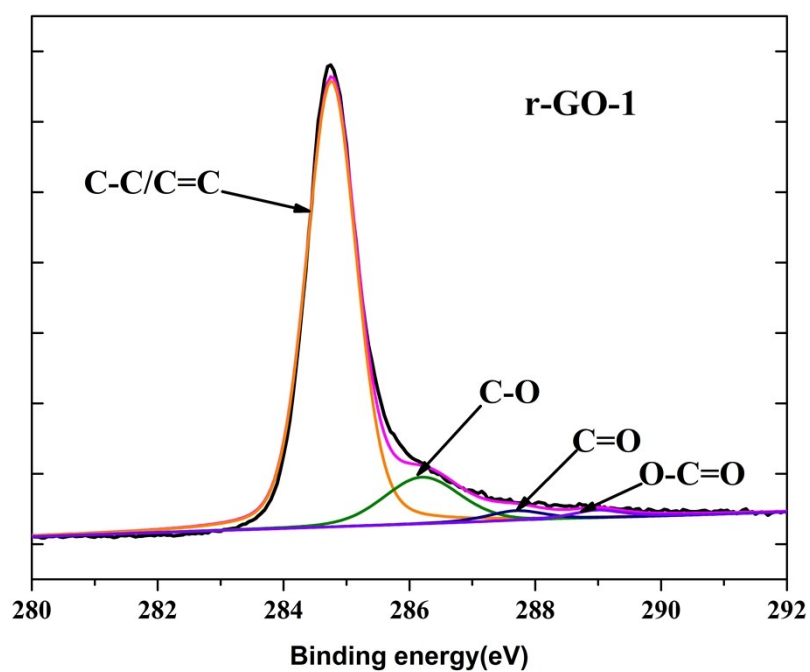


Fig. S9 C1s XPS spectrum of rGO-1 films.

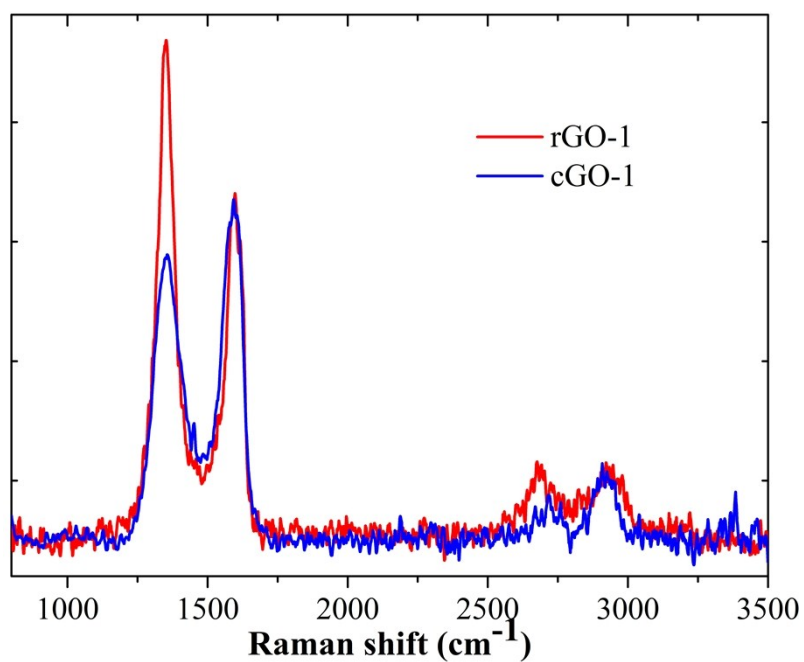


Fig. S10 Raman spectra of cGO-1 and rGO-1 films.

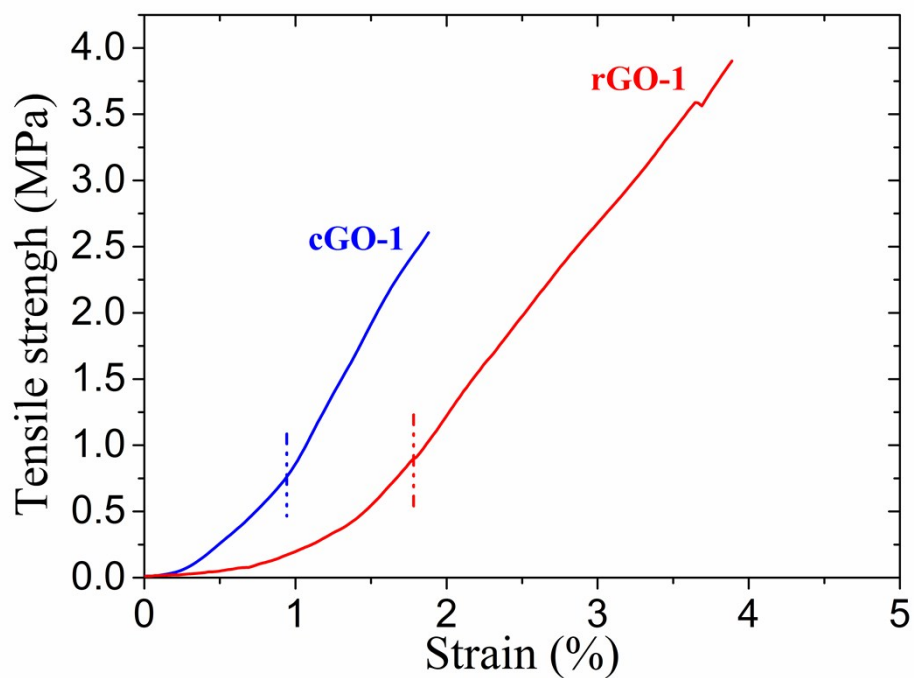


Fig. S11 Stress-strain curves of cGO-1 and rGO-1 films (b).

- 1 W. S. Hummers, R. E. Offeman, *J. Am. Chem. Soc.*, 1958, **80**, 1339.
- 2 V. C. Tung, M. J. Allen, Y. Yang, R. B. Kaner, *Nat. Nanotechnol.*, 2009, **4**, 25.
- 3 S. Attal, R. Thiruvengadathan, O. Regev, *Anal. Chem.*, 2006, **78**, 8098.