

Supporting Information

Chemoselective reduction of graphene oxide and its application in nonvolatile memory transistor

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Experimental

Materials

Graphite powder (325 mesh) was purchased from Baichuan Graphite Co., Ltd (Qingdao, China). All the other reagents were purchased from Sinpharm Chemical Reagent Co., Ltd (Shanghai, China) and used without further purification.

Preparation of GO

GO was prepared by oxidation of natural graphite powder according to the modified Hummers' method.¹ The details are described as following. Graphite (1.0 g) was added to concentrated sulfuric acid (50 mL) under stirring in an ice bath. Then potassium permanganate (6.0 g) was added slowly to the suspension to prevent a rapid rise in temperature. The mixture was transferred to 30 °C water bath, and stirred for 1 hour. Subsequently, 80 mL deionized water was added dropwise under vigorous stirring with increasing the temperature to 90 °C, and further stirred for another 30 min. Additional 200 mL deionized water and 6 mL H₂O₂ (30%) was added, turning the color of the solution from dark brown to yellow. The mixture was stirred for 5 min, then centrifugated and washed with deionized water repeatedly, and finally dried under the vacuum freeze-drying condition. The as-produced solid (100 mg) was dispersed in DMF (100 mL) to obtain the GO suspension via ultrasonication for 5min.

Preparation of CrGO, CGO

The as-obtained GO suspension was added into a round flask, then K₂CO₃ (93 mg) and AgNO₃ (67 mg) were added and refluxed at 80 °C for 16 hours. The mixture was washed with 30% HNO₃ for three times to remove the salts, then washed and centrifuged with deionized water for six times, and finally dried under the vacuum condition. Meanwhile, a contrast experiment without adding AgNO₃ was performed to study the effect of the silver catalysis on the decarboxylation. The contrast GO (CGO) was produced

by adding K_2CO_3 (93 mg) into GO suspension (100 mg GO sonicated for 5 min with 100 mL DMF solvent) and then refluxed at 80 °C for 16 hours without adding AgNO_3 . The mixture was washed with 30% HNO_3 for three times to remove the salts, then washed and centrifuged with deionized water for six times, and finally dried under the vacuum condition.

Characterization

X-ray photoelectron spectroscopy (XPS) analysis was performed on PHI5000 Versa Probe X-ray photoelectron spectrometer. A Shirley background was removed from all spectra. Thermogravimetric analysis (TGA) was recorded by a Shimadzu DTG-60H under a heating rate of 5 °C /min and a nitrogen flow rate of 20 cm^3/min . X-ray diffraction (XRD) patterns were collected in the Bruker D/MAX 2500 X-ray diffractometer with Cu K_α radiation ($\lambda = 1.540562 \text{ \AA}$). Raman spectra were collected using a WITEC CRM200 Raman system with 532 nm excitation laser. $^1\text{H-NMR}$ in CDCl_3 was recorded at 400 MHz using a Varian Mercury 400 plus spectrometer.

Device Fabrication

CrGO-based organic field effect transistor memory was fabricated on heavily-doped Si wafers with a 300 nm thick thermally-prepared silicon dioxide (SiO_2). After routine cleaning for the substrates, CrGO nanosheets solution (0.4 mg/mL dissolved in ethanol) was spin-coated on SiO_2 substrate at 3000 rpm for 40 s. Poly(methylmethacrylate) (PMMA) (Aldrich, $M_w = 120000$) was dissolved in toluene at a concentration of 10 mg/mL, spin-coated at 3000 rpm for 40 s, then annealed in oven at 80 °C for 15 min in ambient air. A 50 nm thick pentacene (Aldrich) active layer was deposited by thermal evaporation in high vacuum ($\sim 10^{-7}$ Torr), where the deposition rate was 0.6 $\text{\AA}/\text{s}$. Finally, 20 nm thick gold source and drain electrodes were thermal evaporated through a shadow mask, of which the channel length and channel width were 100 μm and 2000 μm , respectively.

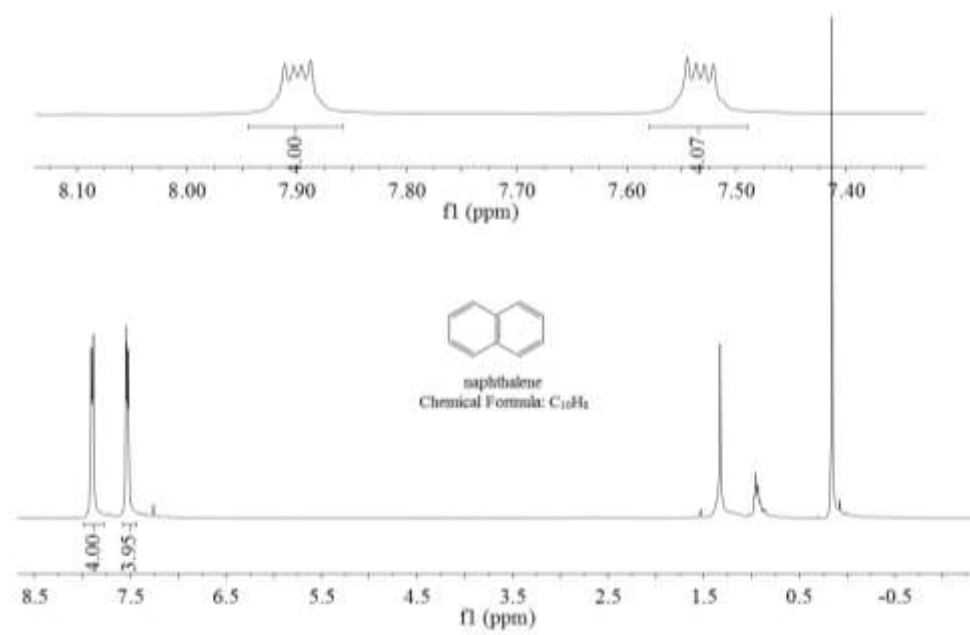


Fig. S1 ¹H-NMR of naphthalene prepared by silver(I)-catalyzed decarboxylation of 1-naphthoic acid. ¹H NMR (400 MHz, CDCl₃, ppm): 7.90 ppm (dd, J = 6.1, 3.3 Hz, 1H), 7.67-7.38 ppm (m, 1H). Other peaks are attributed to the solvent CDCl₃ (7.3 ppm), DMF and H₂O.

Table S1 Elemental composition of GO, CGO and CrGO as determined by XPS

Sample	C-O peak area (%)	C=O peak area (%)	O=C-O peak area (%)	C/O ratio
GO	46.5	7.6	3.2	2.0
CGO	46.6	7.7	3.2	1.9
CrGO	40.2	7.9	0	2.5

The C/O ratio of GO, CGO, CrGO is 2.0, 1.9 and 2.5, respectively. The increased C/O ratio of CrGO is due to the removal of carboxyl groups during the decarboxylation reaction.

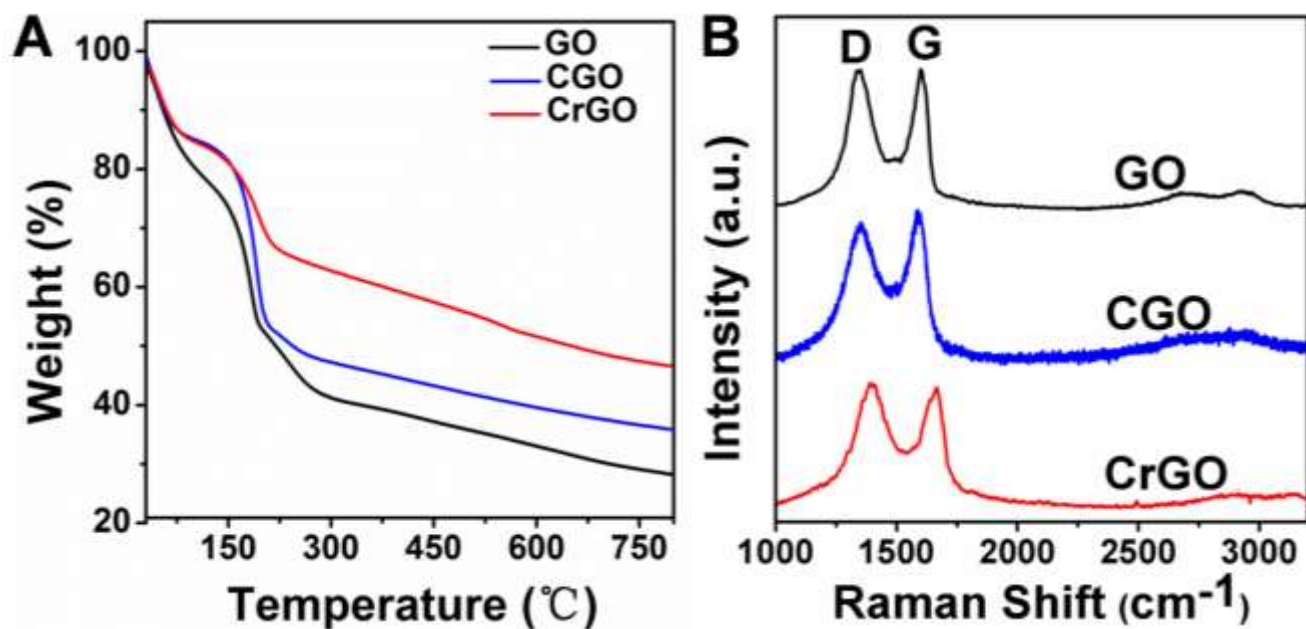


Fig. S2. (A) TGA analysis of GO, CGO and CrGO. (B) Raman spectra of GO, CGO and CrGO.

The decarboxylation of GO was further evidenced by thermogravimetric analysis (TGA). **Fig. S2 (A)** shows the thermal stability of GO, CGO and CrGO. All these samples show a rapid mass loss below 80°C due to the removal of adsorbed water molecular. However, a significant mass loss was observed during the period of 106-208 °C, which is attributed to the decomposition of the oxygen functional groups.² Compared to GO and CGO, CrGO shows a smaller mass loss in the range of 106 °C to 208 °C. On one hand, the mass loss behavior confirms that the partial oxygen functional groups in CrGO are retained after the chemoselective decarboxylation. On the other hand, the smaller mass loss is assigned to the removal of labile carboxyl groups during the decarboxylation reaction,³ suggesting CrGO is a promising stable electroactive material as compared to GO.

Raman spectroscopy was performed to study the structural characterization of GO, CGO and CrGO. As shown in **Fig. S2 (B)**, the Raman spectrum of GO shows a typical G band at 1600 cm⁻¹ and D band at 1340 cm⁻¹. Compared to GO, both D and G band of CGO show a small peak shift, suggesting the subtle difference in GO structure before and after the reduction. However, CrGO shows an obvious peak shift with the G band at 1665 cm⁻¹ and D band at 1400 cm⁻¹. The I_D/I_G value of GO, CGO and CrGO is 0.98,

0.99 and 1.05, respectively. The increased value of CrGO is attributed to the partial restoration of sp^2 domains after the decarboxylation of GO, suggesting the partial reduction of GO.⁴

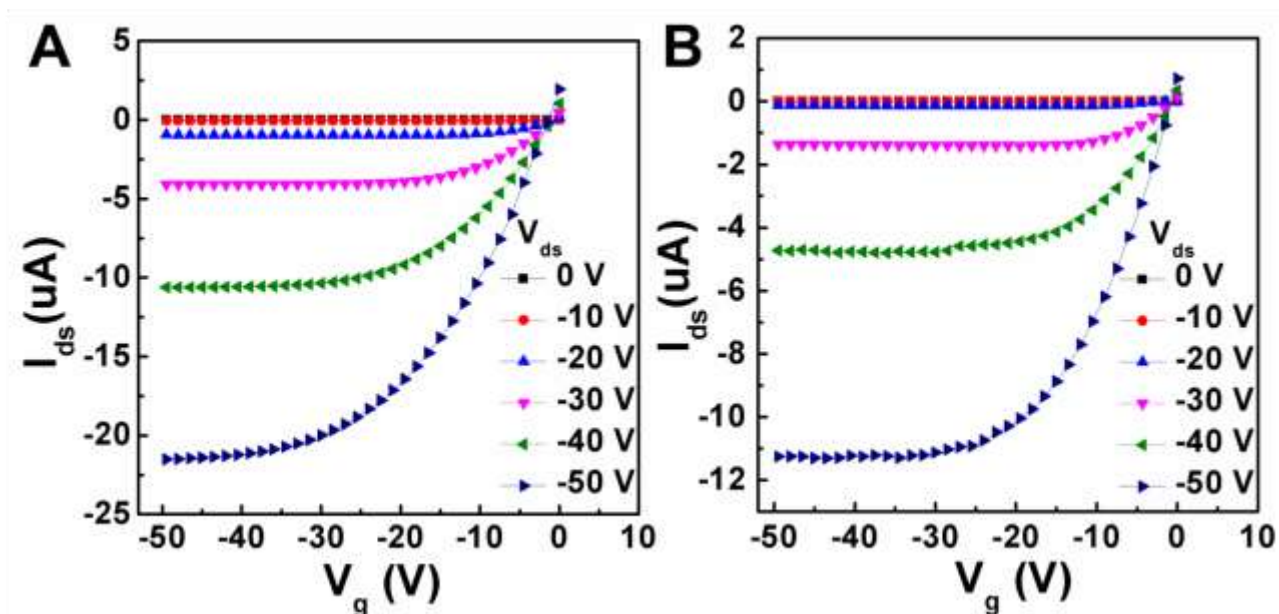


Fig. S3 Transfer curve (I_{ds} vs V_g) of (A) GO and (B) CrGO based organic field-effect transistor memory.

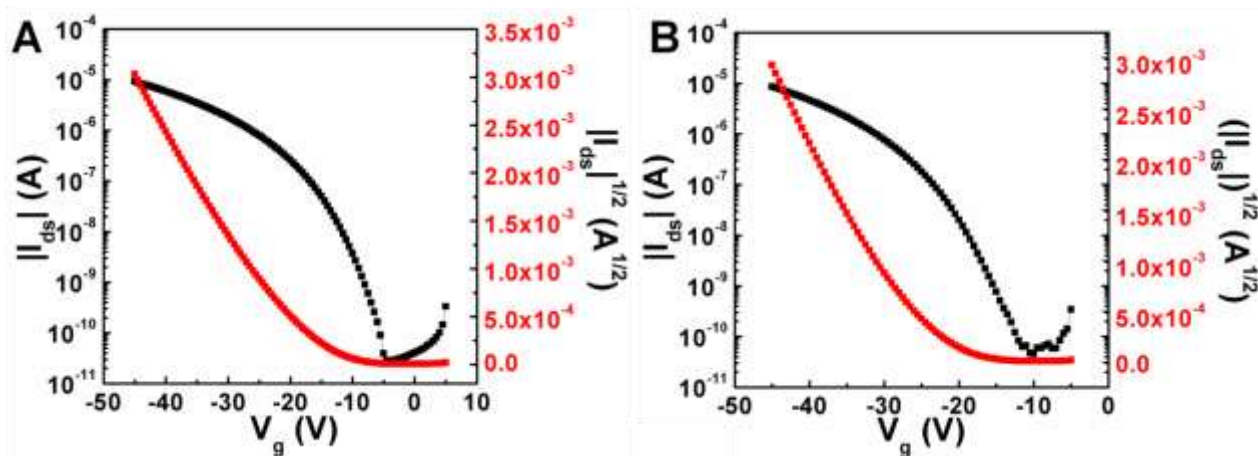


Fig. S4 Output curve (I_{ds} vs V_g) of (A) GO and (B) CrGO based organic field-effect transistor memory.

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