Electronic Supporting Information

Strategy and Mechanism for Controlling Direction of Defect Evolution in Graphene: Preparation of High-Quality Defect-Healed and Hierarchically Porous Graphene

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Fig. S1. Digital images of GO, EtOH intercalated GO and GE.

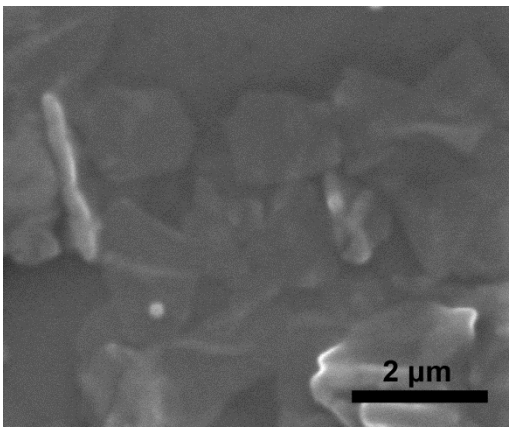


Fig. S2. SEM image of GE sheet.

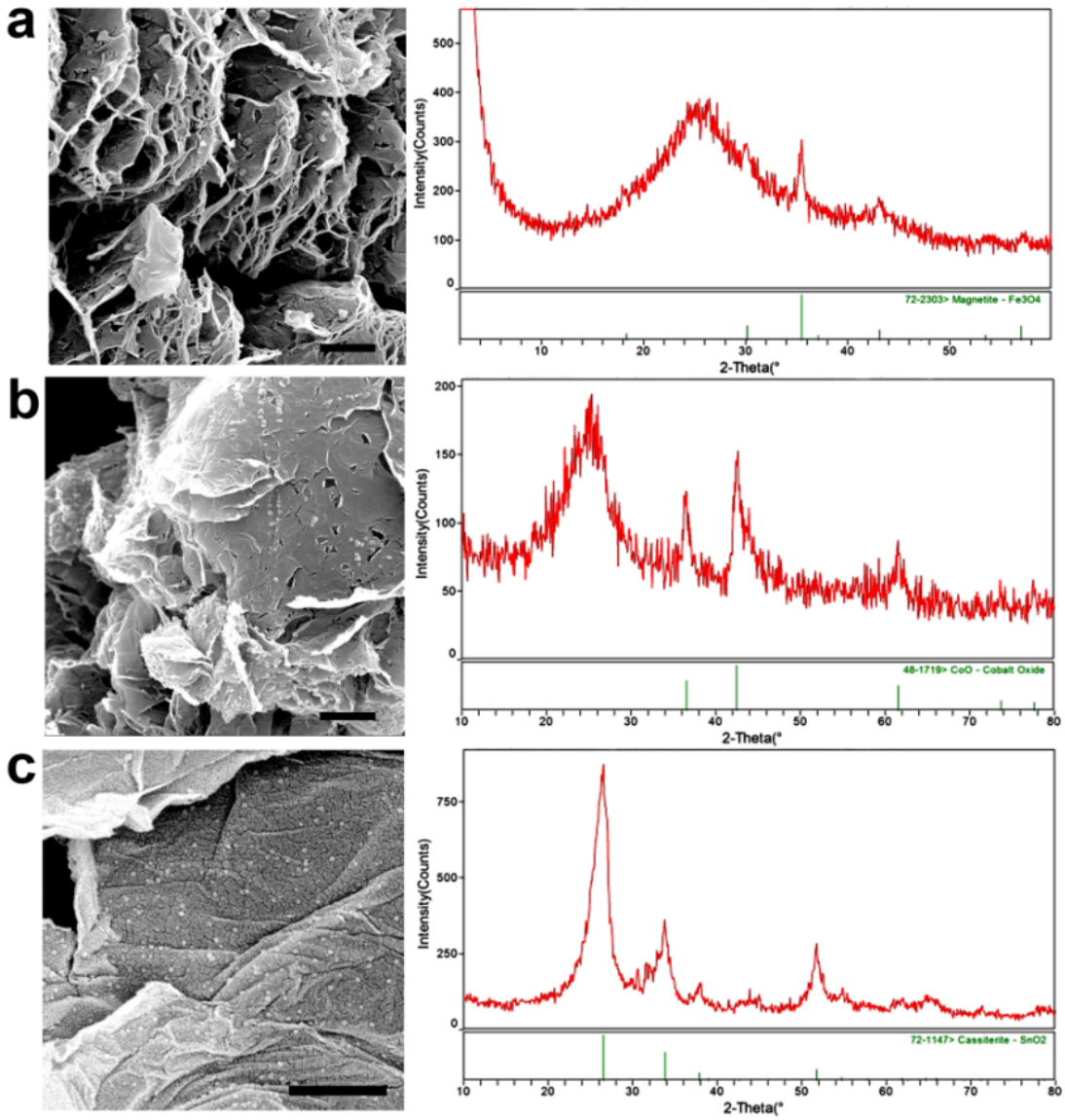


Fig. S3. SEM of graphene-based materials loaded with metal-oxide nanoparticles, (a) Fe_3O_4@GNSM, (b) CoO@GNSB and (c) SnO_2@GE, and the corresponding XRD patterns. Scale bars, 500 nm.

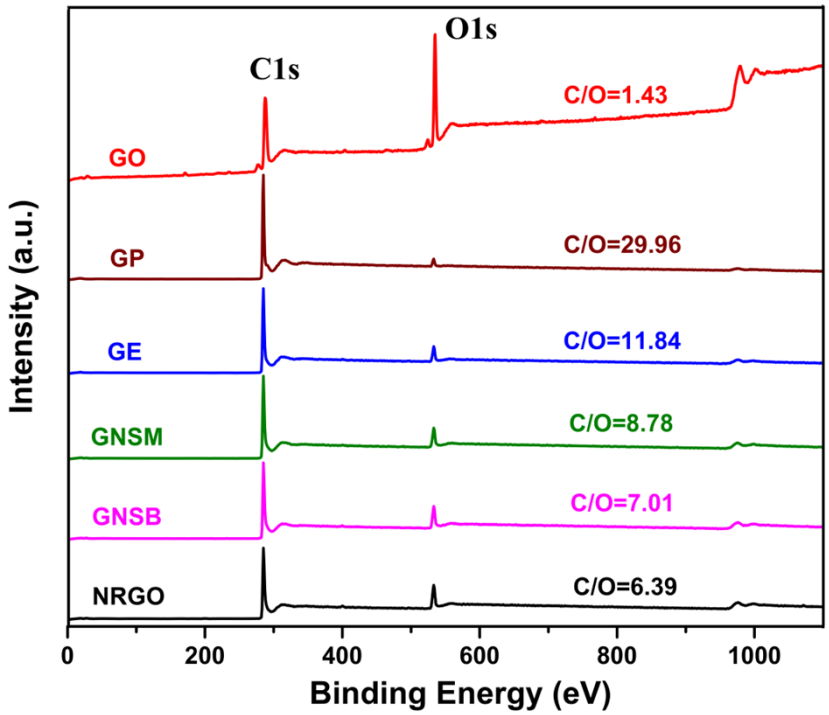


Fig. S4. XPS spectra of GO, GP, RGOs.

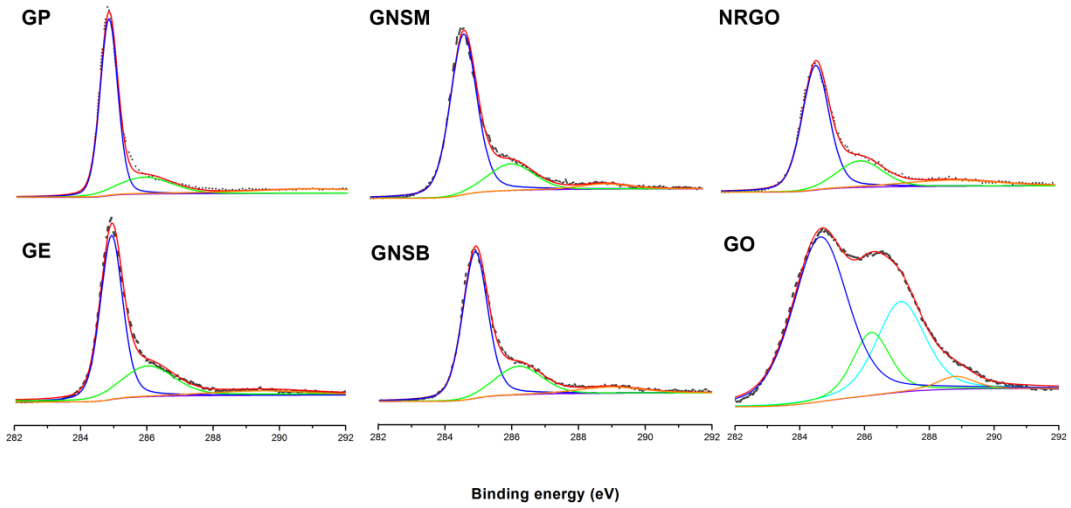


Fig. S5. C_{1s} XPS spectra of GP, RGOs and GO. Original spectra (dark grey dots), sum (red line), C=C peak (248.8 eV, blue line), C-O peak (286.5 eV, green line), O-C=O peak (289.0 eV, orange line), C=O peak (287.8 eV, cyan line) and base line (violet line).

Sample	C/wt%	O/wt%	C/O	H/wt%
GP	98.7	1.2	109.7	<0.5
NRGO	86.5	12.3	9.4	1.1
GNSB	87.3	11.9	9.8	0.7
GNSM	91.2	8.6	14.1	<0.5
GE	94.6	5.3	23.8	<0.5
GO	50.7	47.1	1.5	2.2

Table S1. EA of GO ,GP and RGOs. What XPS spectra provide are surface information of the materials, more accurate data of element contents were given by elemental analysis (EA). The C/O atomic ratio of GE is 23.8, which is much higher than any other reported reduced GOs, [2] and that of GO, GNSM, GNSB and NRGO are 1.5, 14.1, 9.8 and 9.4, respectively. It is conspicuous that the oxygen contents of GE and GNSM are signally less than others, which indicates that ethanol and methanol are not only expanding agents but also reductive agents in the course of reactions combining with the XRD and FTIR studies. The excellent reduction of GE benefits from the sufficient contact between ethanol and GO layers during the high temperature reaction.

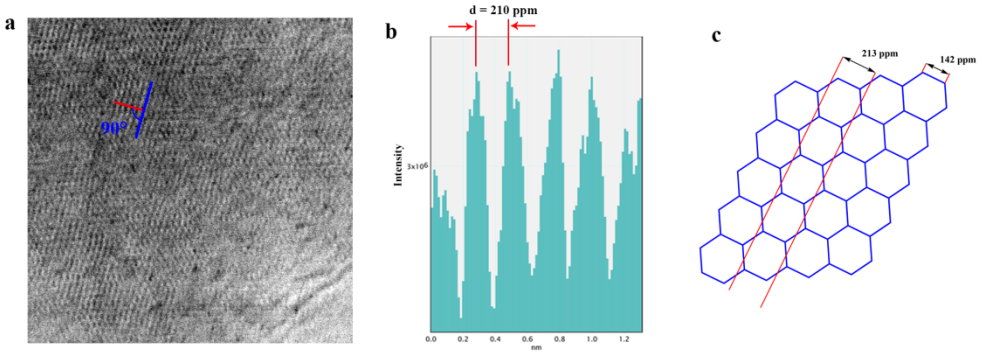
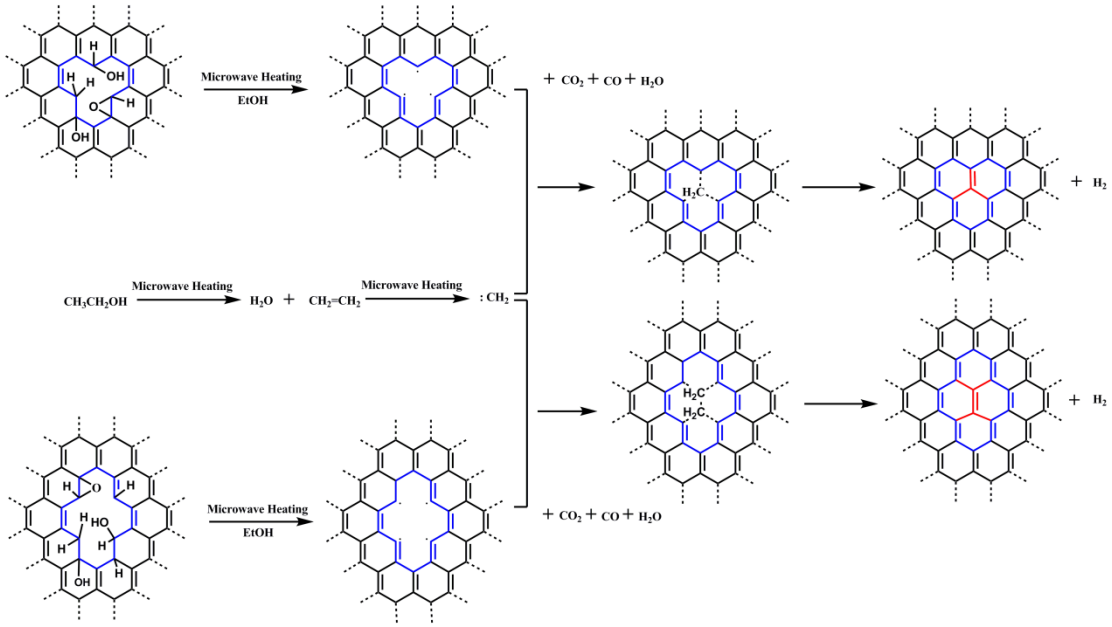


Fig.S6. (a) Aberration corrected TEM images of single suspended sheet of GE. (b) Intensity profiles corresponding to marked profiles in red line in (a). (c) Lattice information of graphene. The intensity profiles of GE shows the peak distance match the lattice property of graphene, confirming that the single suspended sheet of GE is a sheet of graphene.



Scheme S1. The possible radical-radical reaction mechanism of defect-healing process. We are more inclined to believe that the defect-healing process under high temperature is a complex process related to radical-radical reaction. Here we simulated the possible healing process of representative single vacancy and divacancy defect (outlined by blue). The defects are caused by the absence of some carbon atoms of graphite structure being robbed during the oxidation reaction. Therefore, there inevitably exist many oxygen moieties at the edge of defect. As proved by the mentioned characterization, GO could be reduced by ethanol during microwave heating reaction and generate CO_2, CO and H_2O, and active radicals emerge consequently at the edge of defect sites. Meanwhile, ethanol moleculars evolve into carbenes through an intramolecular dehydration and a thermal cracking process under the microwave heating. Then carbenes interact with the active radical sites and being dehydrogenated following a transient state and resulting in intact graphite structure with defects being healed (outlined by red). The generated hydrogen will participate in other reduction reactions of GO. If the defects contain more bereft carbon atoms, the healing process of these defects should be a similar course with incremental radical-radical reactions.

Table S2. Comparison of electrical conductivity of GO-derived graphene and related materials**.**

Samples	**Form**	**Conductivity (S m^{-1})**	**Process**	**ref**
GE	**Pellet**	**61,500**	**EtOH intercalated GO reduced by microwave irradiation in "graphite bath" reactor**	**Our result**
GS	pellet	56,500	Low temperature thermal exfoliation+ vacuum anneal and 1900°C	*Adv. Funct. Mater.* **21,** 3496-3501 (2011)
Reduced graphene oxide	10nm thick film	55,000	Deposited on substrate and Ar/H_2 anneal at 1100 °C	*Nano Lett.* **8,** 323-327 (2008)
Reparatively reduced film	Film	35,000-41,000	Ar/H_2 anneal and CVD process using methane at 1000 °C for one hour	*Nano Res.* **4,** 434-439 (2011)
Graphene paper	Paper	35,000	Ar anneal at 500 °C	*Adv. Mater.* **20,** 3557–3561 (2008)
CVDGO	Monolayer graphene	1,000-35,000	Ar/H_2 anneal at 500 °C+CVD process using ethylene at 800°C on SiO2 substrates	*Adv. Mater.* **21,** 4683-4686 (2009)
RG-O	pellet	30,400	Direct reduction in HI-AcOH	*Nat. Commum.* **1,** 73 (2010)
r-GO	Film	29,800	Direct reduction by hydrohalic acids	*Carbon.* **48,** 4466-4474 (2010)
CCG3	Pellet	20,200	$NaBH_4$ and H_2SO_4+ Ar/H_2 anneal at 1100 °C	*Nat. Chem.* **1,** 403–408 (2009)
Reduced GO	Compressed-powder	2,420	Direct reduction by hydrazine hydrate	*Carbon.* **45,** 1558-1565 (2007)
GNS	Pellet	1,250	Prepared by solid state microwave irradiation, H_2/Ar gas atmosphere	*J. Mater. Chem.* **48,** 2106-2122 (2010)
Reduced GO	Film	1,000	Direct reduction by flash	*J. Am. Chem. Soc.* **131,** 11027-11032 (2009)