Supplementary Information

Highly efficient reduction of graphene oxide using ammonia borane

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Descriptions of graphene oxide synthesis, characterizations, Preparation of supercapacitor electrodes and electrochemical measurement, UV-vis spectra, FT-IR spectra, XPS spectra, elemental composition, AFM images of GO and ABRGOs, electrical conductivity and specific capacitance of ABRGOs

1. Preparation of graphene oxide

A small amount of expandable graphite was charged into a 1-L beaker and heated for 10 s in a microwave oven. The graphite expanded to about 150 times its original volume. Graphene oxide was synthesized from expanded graphite according to a modified Hummers method .[S1] Typically, 1 kg of concentrated H_2SO_4 (95 wt.%) was charged into a 2L beaker equipped with a mechanical stirrer (Teflon impeller). The beaker was put into an ice bath to chill to 0°C. Seven grams of expanded graphite were gradually added under stirring to make a suspension. Then, 45 g of $KMnO_4$ was slowly added so that the temperature did not exceed 20°C. The temperature was then elevated to 35°C, and the suspension was stirred for 2 h. The beaker was then chilled again in the ice bath, and 1.5 L of deionized water was slowly added to maintain a temperature below 70°C. The mixture was stirred for 1 h and subsequently diluted with 10 L of deionized water. Fifty milliliters of H_2O_2 (30 wt%) was slowly added, and vigorous bubbles appeared as the color of the suspension changed from dark brown to yellow. The suspension was centrifuged and washed with 1M HCl solution four times, followed by centrifuging at 10,000 rpm and washings with deionized water to completely remove the acid until the pH of the GO dispersion reached 6. The as-synthesized GO dispersion was a paste. The concentration of GO was approximately 1.0 wt%, which was determined after drying the GO dispersion at 80 °C under vacuum for 24 h.

2. Characterizations

The UV-Vis absorption spectra of the ABRGOs dispersed in ethanol were measured by a microplate spectrophotometer (Spectra Max® Plus 384, Molecular Devices). Fourier transform infrared (FT-IR) spectra were measured on a Nicolet IR 200 FT-IR spectrometer (Thermo Scientific). X-ray photoelectron spectroscopy (XPS) analysis was performed on a K-alpha spectrometer (Thermal Scientific) with monochromatic Al Kα radiation (hν = 1486.6 eV). Raman spectra were measured using a confocal Raman microscope (Thermo Scientific) with 532-nm wavelength incident laser light. Atomic force microscope (AFM) images were taken using a Veeco Dimension 3100 SPM with silicon cantilever operated in the tapping mode. Thermogravimetric analysis (TGA) was performed under a nitrogen atmosphere at a heating rate of 10°C/min (Q50, TA Instruments). The electrical conductivity of ABRGOs was characterized using free-standing papers prepared by low vacuum filtration of ABRGOs dispersions in DMF onto a cotton cellulose filter paper (1.0 μm pore size, Advantec). After filtration, the free-standing papers of ABRGO were dried at 50 °C for 3 h and then at 150 °C for 3 h. Electrical resistances of the ABRGOs papers were measured by the four-point probe method (CMT-100 MP, Advanced Instrument Technology). The thicknesses of the ABRGOs papers were determined from cross-section images obtained by scanning electron microscopy (JEOL JSM-6500FE)

3. Preparation and electrochemical measurement of supercapacitor electrodes

ABRGOs electrodes were prepared following the flow-directed self-assembly method developed by Li et al.[29] Typically, 75 mL of 0.2 mg mL^{-1} a-ABRGO-3 and o-ABRGO-3 dispersions in DMF were vacuum filtrated using glass microfiber filter (Whatman, grade GF/A) to prepare self-stacked solvated ABRGOs films. Right after the filtration of ABRGO dispersions finished, 150 mL of acetonitrile was added to wash the DMF trapped in the ABRGO films. Then, solvated ABRGO films attached to the glass microfiber filters were punched into electrodes 0.9 mm in diameter. Each as-punched electrode was soaked in 1M $TEABF_4$/AN for 24 h and pressed onto a nickel foam collector of the same size, and the glass microfiber filter was carefully removed. The mass loading of active material was about 1.3 mg cm^{-2}. The electrodes were assembled in a Swagelok–type cell and were separated by a porous polymer membrane (Celgard 3501).

Electrochemical measurements were carried out in 1M $TEABF_4$ in acetonitrile at room temperature using a multichannel potentiostat-galvanostat (VSP, Bio-logic, France). The potential range for CV measurements and galvanostatic charge–discharge tests was 0–2.7 V. EIS tests were carried out in the frequency range 100 kHz–0.1 Hz at open circuit potential with an ac perturbation of 5 mV.

The specific capacitances were calculated by using the equation:

$$C_s = \frac{2I\Delta t}{m\Delta V}$$

where C_s is specific capacitance, I is the constant discharge current, Δt is the discharge time, m is the mass of one electrode and ΔV is the voltage drop upon discharging (excluding the IR drop).

4. Reduction of graphene oxide by ammonia borane

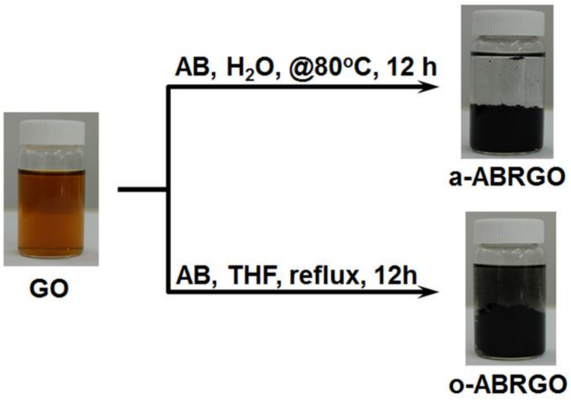

Fig. S1 Photographs of GO dispersion and ABRGO suspensions after reduction.

5. UV-vis spectra

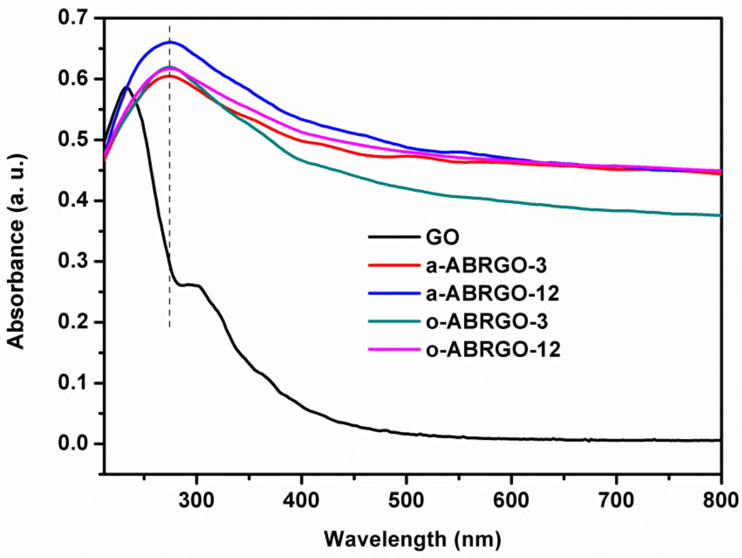

Fig. S2. UV-vis spectra of GO, a-ABRGO and o-ABRGO at different reduction time.

6. FTIR spectra

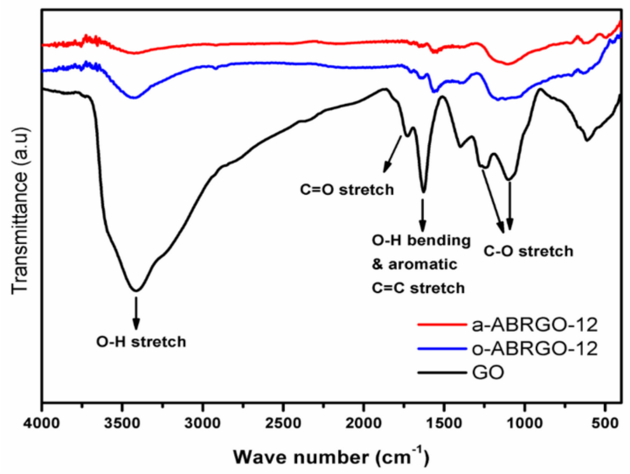

Fig. S3 FTIR spectra of GO and ABRGOs

The FT-IR spectra were used to further characterize the reduction of GO by ammonia borane. The FT-IR spectrum of graphene oxide exhibits representative peaks at 3415, 1730, 1627, 1245 and 1090 cm^{-1} corresponding to O-H stretch, C=O stretch, aromatic C=C and O-H bending, epoxy C-O stretch and alkoxy C-O stretch, respectively. [S3] After AB reduction, FT-IR spectra of ABRGOs show three broad peaks at 3430, 1560 and 1154 cm^{-1} corresponding to O-H stretch, aromatic C=C stretch and O-H bending, and C-O stretch respectively, which is consistent with previous reports.[S3,S4] The intensity of these peaks greatly decreased in comparison to those of GO, indicating that most of oxygen functional groups were removed upon reduction.

7. XPS spectra

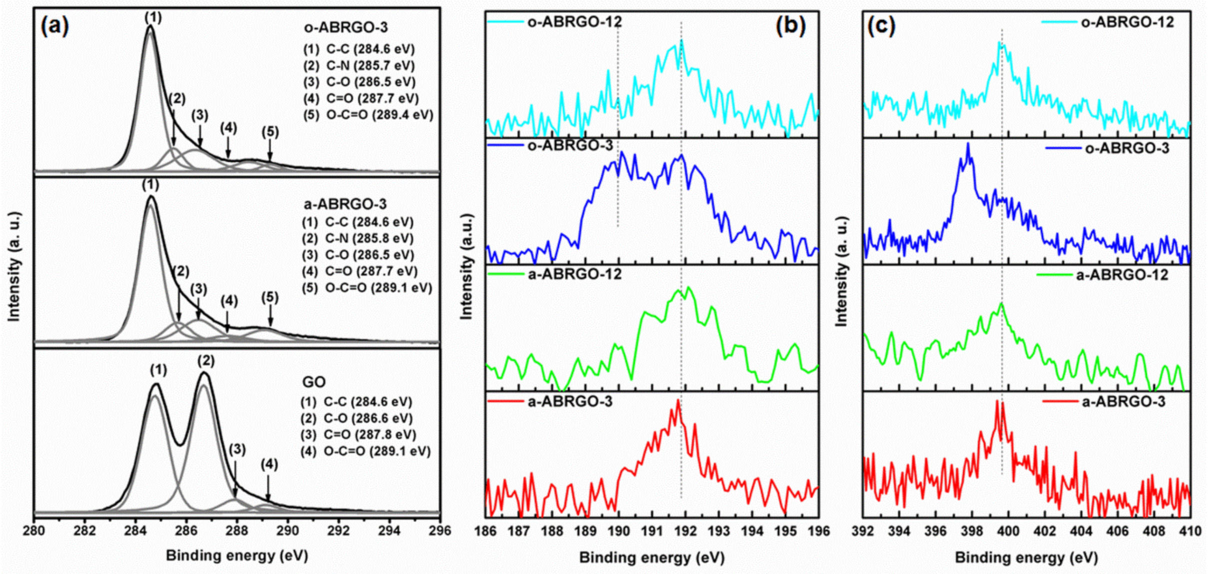

Fig. S4. (a) C1s, (b) B1s and (c) N1s XPS spectra of GO and of ABRGOs at different reduction time and solvents.

The B1s XPS spectra in Fig. S2b exhibited small peaks at ~192 eV, which could be assigned to a BC_2 component, suggesting that boron was covalently bonded to the carbon skeleton of ABRGO. However, the B1s XPS spectrum of o-ABRGO shows another peak at 190 eV, which can be attributed to boron in B-N bond of AB.[2] Moreover, the amount of boron and nitrogen doping on ABRGO decreased with increase of reduction time, suggesting that the boron and nitrogen-doping are intermediates of reduction process.

8. Elemental composition of GO and ABRGOs

Table S1: Elemental composition of GO and other RGOs

	Solvent	Reduction time (h)	Elemental composition (atomic %)				C/O	C/N	C/B
			C	O	N	B			
GO		-	66.92	30.37	-	-	2.2	-	-
a-ABRGO	water	3	86.55	11.91	0.83	0.71	7.3	104.3	121.9
		12	92.56	6.51	0.59	0.34	14.2	156.9	272.2
o-ABRGO	THF	3	86.19	10.43	1.57	1.81	8.3	54.9	47.6
		12	89.37	9.16	0.98	0.50	9.8	91.2	178.4
RGO[4]	water	24	-	-	-	-	10.3	16.1	-
HRG[6]	DMF	12	-	-	-	-	11.0	25.7	-

9. ABRGOs dispersion in dimethylformamide

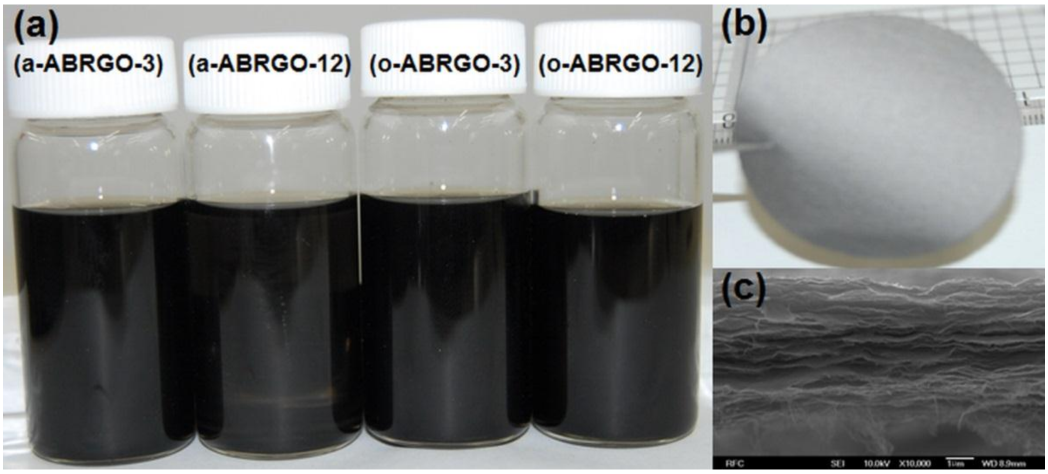

Fig. S5 (a) Dispersions of ABRGOs in DMF at a concentration of 0.2 mg mL^{-1}, except a-ABRGO-12 at a concentration of 0.025 mg mL^{-1}, (b) free-standing paper prepared by filtration of o-ABRGO-12 dispersion, and (c) SEM cross-sectional image of this paper.

10. AFM images of GO and ABRGOs

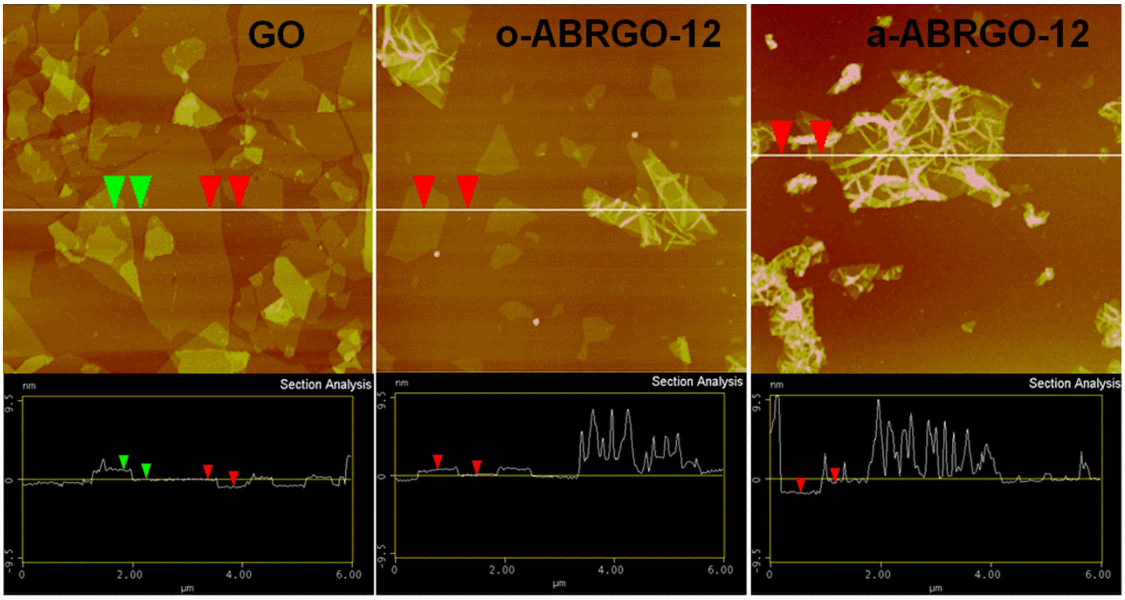

Fig. S6 AFM images of GO and ABRGOs and its height profile respectively.

The AFM image of GO clearly shows graphene oxide was fully exfolited to single sheets with lateral sizes of few microns. All of graphene oxide sheets are flat with the thickness about 1.0 nm. In contrast, a-ABRGO sheets were highly folded and wrinked. In AFM image of o-ABRGO-12, folds and wrinkles were appeared in the large sheets whereas small sheets were still flat. It is clear that the folds and wrinkles of ABRGO strongly depended on the extent of reduction.

11. Electrical conductivity of free-standing papers of ABRGOs

Table S2. Electrical conductivity of free-standing papers of ABRGOs compared with other RGOs

	Reducing agent	C/O	Conductivity (S m^{-1})	Ref.
a-ABRGO-3	AB	7.3	10800	This work
a-ABRGO-12	AB	14.2	19300	This work
o-ABRGO-3	AB	8.3	13400	This work
o-ABRGO-12	AB	9.8	20300	This work
CCG	hydrazine	8.1	7200	5
HRG	hydrazine	11.0	17000	6
CCG-P	phenylhydrazine	9.6	20900	8
r-GO	HBr	10.8	15600	14
r-GO	HI	12.0	29800	14

12. Specific capacitance of ABRGOs

Table S3. Specific capacitance of ABRGOs in comparison to other RGOs using $TEABF_4$ as electrolyte

RGOs	Electrolyte	Current density (A g^{-1})	Specific capacitance (S m^{-1})	Ref.
CMG	$TEABF_4$/AN	1.0	99	28
CMG	$TEABF_4$/PC	1.0	94	28
RG-O	$TEABF_4$/PC	1.0	122	29
SGH	$TEABF_4$/PC	1.0	115	30
SGO	$TEABF_4$/PC	1.0	140	30
aG-O	$TEABF_4$/AN	10.0	120	31
a-ABRGO-3	$TEABF_4$/AN	1.0	109	This work
o-ABRGO-3	$TEABF_4$/AN	1.0	130	This work

AN: acetonitrile; PC: propylene carbonate

References

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[S3] C. Nethravathi, M. Rajamathi, *Carbon*, 2008, **46**, 1994.

[S4] S. Park, J. An, I. Jung, R. D. Piner, S. J. An, X. Li, A. Velamakanni, R. S. Ruoff, *Nano Lett.*, 2009, **9**, 1593.