Electronic Supplementary Information (ESI)

Facile synthesis of reduced graphene oxide in supercritical alcohols and its lithium storage capacity

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Reduced graphene oxide (RGO) synthesis in supercritical methanol or in supercritical ethanol

Graphene oxide (GO) was prepared using natural graphite flakes (325 mesh, Sigma Aldrich) by a modified Hummers method as originally presented by Kovtyukhova, et al.[1, 2] A certain amount of GO (0.07 g) was dispersed in methanol or in ethanol. Methanol (HPLC grade) was obtained from J. T. Baker (Phillipsburg, N.J., USA) and ethanol (HPLC grade) was obtained from Honeywell, B&J (Muskegon, MI, USA). The dispersion was sonicated using an ultrasonic bath cleaner and then introduced into a Hastelloy C-276 reactor with the inner volume of 11 ml. After being tightly sealed, the reactor was immersed into a molten salt bath (KNO_3:$NaNO_3$:$Ca(NO_3)_2$ in the weight ratio of 46:24:30) which was heated to an experimentally desired temperature of 400 °C. The reactor was constantly shaken for experimentally desired times of 15 min-2 h. After the reaction, the reactor was rapidly cooled to room temperature by immersing it in a cold water bath. After cooling, the produced RGO suspension was filtered through a nylon filter paper with a pore size of 0.2 µm in diameter (Pall Corp, USA). Wet RGO powder was dried in a vacuum oven at 70 °C for 4 h.

RGO synthesis in a continuous process

A custom-built, continuous flow reactor apparatus was used to deoxygenate GO to RGO. Details of the apparatus and experimental procedures were described in the previous paper [3]. Only a short description is given here. The apparatus consists of feed tanks, high-pressure pumps, a preheater line, a tubular reactor, heat furnaces, cooling units, metal filter units, a back pressure regulator, a liquid container, isolation and safety valves, pressure gauges, thermocouples, and associated tubing. The reactor was made of stainless steel 316 with an inner diameter of 8 mm and an inside height of 290 mm, giving a volume of 14.58 cm^3. The methanol flow rate was fixed to 6 g/min and the GO dispersion flow rate was fixed to 6 g/min. The concentration of GO in the feed tank was 0.001g/ml. The synthesis conditions were 300 bar, 400 ^{o}C, a residence time of ~ 17 s. After the reaction, the particles in metal filters were collected, washed, filtered and dried at 70 ^{o}C in a vacuum oven for 4 hour.

Characterization

The X-ray diffraction (XRD) pattern of the samples was characterized using X-ray diffraction (Rigaku RINT2000, Tokyo, Japan) analysis with Cu Kα radiation at 40 kV and 50 mA. The morphology of the samples was obtained by transmission electron microscopy (TEM) with Tecnai-F20 (FEI Co., Eindhoven, Netherland) operated at 200kV. Samples for the TEM investigations was prepared by first dispersing the particles in dimethylformamide (DMF) under the aid of ultrasonication and then dropping the suspension on a copper TEM grid coated with a holey carbon film. The functional groups on the surface of the samples were characterized using a NICOLET iS10 FT-IR spectrometer (Thermo Electron Co. NJ, USA). Thermal characteristic of the samples was analyzed using a DuPont Instrument TGA 2950 thermal analyzer. For the TGA analysis, each sample was located in a platinum crucible and was heated at a rate of 5 ^{o}C/min from 30 to 800 ^{o}C with a flow of high purity nitrogen (50 ml/min). Elemental analysis of samples was analyzed using CHNSO Analyzer (elemental analysis by combustion). C, H, N and S were analyzed using Thermo Elemental Analyzer Scientific Flash 2000 (Thermo Scientific USA). O was analyzed using FISONS-EA 1108 Elemental Analyzer (Thermo Scientific USA). X-ray Photoelectron spectroscopy (XPS) was performed using a PHI 5000 Versa Probe (ULVAC-PHI) spectrometer. Spectra were obtained by irradiating each sample with 100 µm x 100 µm spot of monochromated aluminum Kα X-rays at 1486.6eV under ultrahigh vacuum conditions. The survey scans were acquired with a pass energy of 117.40 eV, and high-resolution scans were acquired with a pass energy of 23.50 eV. UV-vis absorption spectra were recorded using a double beam Jasco V-530 UV Spectrophotometer (Tokyo, Japan). The spectra were taken from diluted sample in dimethylformamide at a concentration of 0.016 g/ml. The Brunauer-Emmett-Teller (BET) surface area was determined using a Belsorp-mini II apparatus (BEL Inc., Osaka, Japan). Bulk powder conductivity was measured using a four-point probe method. Briefly, a given quantity of powder (0.8-1.7 g) was poured into a poly(ethylene) tube with an inner diameter of 5 mm. The powder was manually compressed between four steel plungers that closely matched the tube's inner diameter. A Maccor Series 4000 Battery Test System (Oklahoma, USA) was connected to the plungers and was used to measure DC resistance by a four-point probe method at room temperature.

Electrochemical property measurement

Charge/discharge properties of the prepared samples were measured using a 2032 coin-type cell. The active material (90 wt%) and polyvinylidene fluoride (PVDF) as a binder (10 wt%) in n-methyl-2-pyrolidone (NMP) were mixed using a homogenizer (Nihonseiki Kaisha LTD. Tokyo, Japan). The slurry was then coated onto a Cu foil. After vacuum drying at 80 ^{o}C for 24 h, the electrode discs with a diameter of 1.77 cm^2 were punched and weighed. The electrolyte was 1M $LiPF_6$ dissolved in ethylene carbonate/dimethyl carbonate/ethylmethyl carbonate solvent (volume ratio of EC:DMC:EMC= 1:1:1). The cells were assembled in a dry room. The cells were galvanostatically charged and discharged in the voltage range from 3 to 0.005 V vs. Li/Li^+. The cyclability for 40 cycles was recorded at constant rate of 50 mA/g. All the electrochemical measurements were made with a Maccor Series 4000 Battery Test System (Oklahoma, USA) at room temperature.

Fig. S1 GO dispersed in methanol (left) and RGO dispersed in methanol (right). GO dispersion was quite stable in methanol while most of RGO in methanol precipitated at the bottom of the vial.

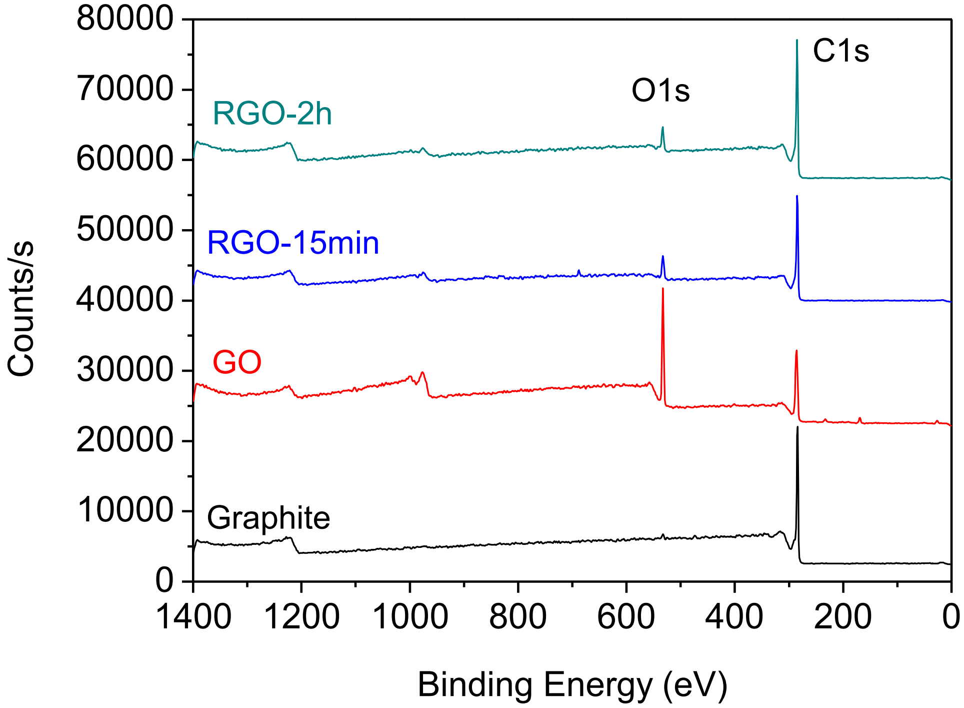

Fig. S2 XPS survey scan of graphite, GO, RGO-15min, and RGO-2h.

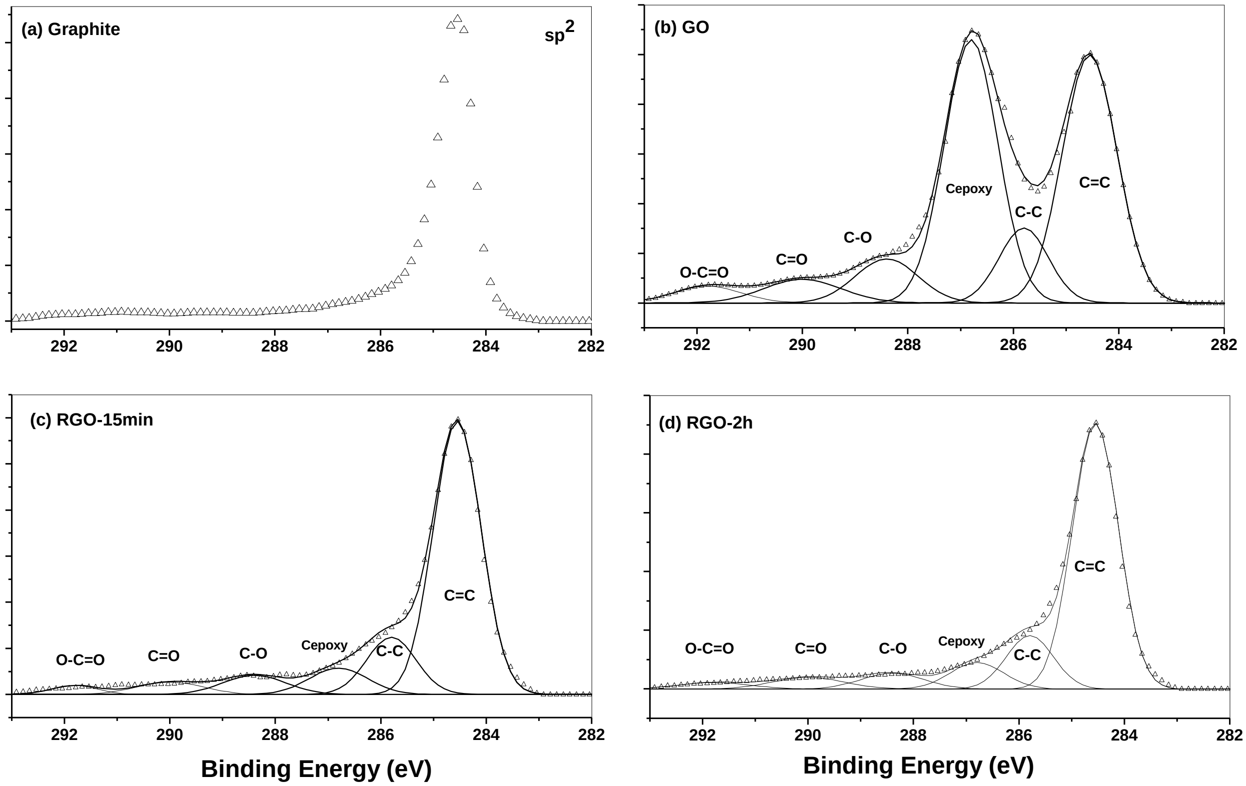

Fig. S3 XPS high-resolution scan of graphite, GO, RGO-15min, and RGO-2h.

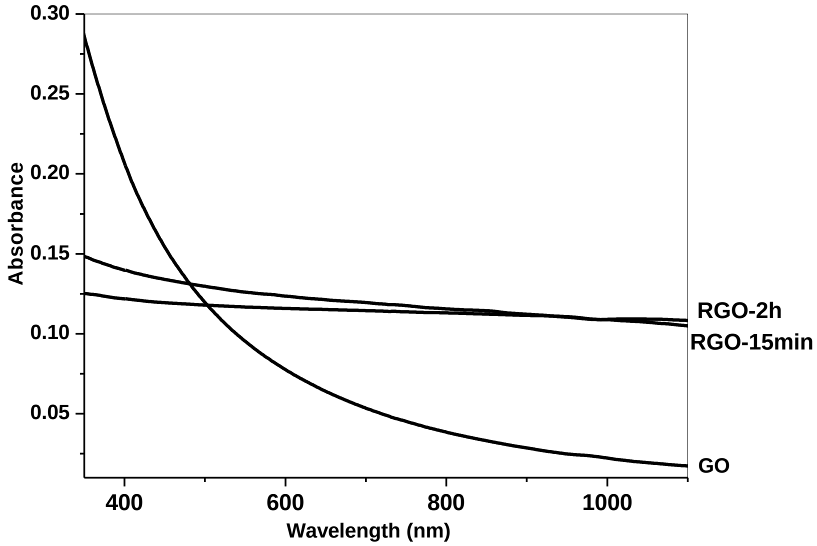

Fig. S4 UV-vis spectra of GO, RGO-15min, and RGO-2h. The GO and RGO powder were dispersed in dimethylformamide (DMF) at a concentration of 0.016 g/ml.

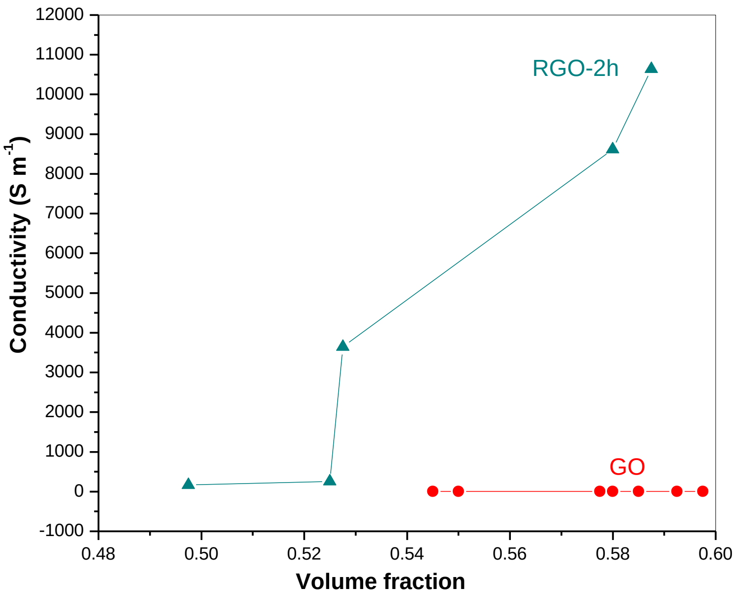

Fig. S5 Powder electronic conductivity of GO, and RGO-2h as a function of volume fraction. The conductivity was measured using a four-point method to eliminate contact resistance

Table S1. Atomic compositions and C/O ratio measured by XPS and elemental analysis, and conductivity of graphite, GO, and RGO.

Samples	XPS				Elemental Analysis					Conductivity (S/m)	Refs
	C (atomic %)	O (atomic %)	N (atomic %)	C_{1s}/O_{1s} ratio	C (wt%)	H (wt%)	O (wt%)	N (wt%)	C/O ratio		
Graphite	98.75	1.25	0	79.00	97.47	<0.3	<0.3	0	-		This study
GO	66.14	33.86	0	1.95	42.7	2.7	18.5	0	2.31	1.97 (powder)	This study
RGO-15min	89.77	10.23	0	8.78	86.5	1.4	8.5	0	10.18	NA[a]	This study
RGO-2h	92.24	7.76	0	11.89	86.6	1.5	7.8	0	11.10	10,600 (powder)	This study
Hydrazine hydrate[b]	NA[a]	NA	NA	NA	NA	NA	NA	NA	10.3	200 (powder)	Stankoviche et al.[4]
Hydrazine[c]	NA	NA	NA	NA	85.32	0.11	11.42	3.15	9.97	7,200 (paper film)	Li et al.[5]
Hydrazine monohydrate gas[d]	NA	NA	NA	8.8	NA	NA	NA	NA	NA	NA	Yang et al.[6]
Heat treatment in Ar at 1000 °C[e]	NA	NA	NA	11.36	NA	NA	NA	NA	NA	NA	Yang et al.[6]
UHV heat treatment at 900 °C[f]	NA	NA	NA	14.1	NA	NA	NA	NA	NA	NA	Yang et al.[6]
Anhydrous hydrazine, before annealing[g]	NA	NA	NA	NA	64.53	NA	11.13	NA	7.7	NA	Tung et al.[7]
Anhydrous hydrazine, after annealing[h]	NA	NA	NA	NA	80.53	NA	8.92	NA	12	NA	Tung et al.[7]
Hydrazine, air dried	NA	NA	NA	NA	NA	NA	NA	NA	11.0	1,650 (paper film)	Park et al.[8]
Hydrazine monohydrate	NA	NA	NA	12.5	NA	NA	NA	NA	NA	4160-9960 (paper film)	Fernandez-Merino et al.[9]

Sodium borohydride and sulfuric acid, air dried	NA	NA	NA	NA	81.54	0.94	12.68	<0.5	8.57	46.4	Gao et al.[10]
Sodium borohydride and sulfuric acid, annealing at 1100 °C	NA	NA	NA	NA	92.42	< 0.5	< 0.5	< 0.5	> 246	20,200 (powder)	Gao et al.[10]
Solvothermal in NMP, air dried[i]	80.4	15.6	4.0	5.15	NA	NA	NA	NA	NA	374 (paper film)	Dubin et al.[11]
Solvothermal in NMP, annealed at 1000 °C[j]	83.2	13.8	3.0	6.03	NA	NA	NA	NA	NA	57,300 (paper film)	Dubin et al.[11]
Hydriodic acid with acetic acid	NA	NA	NA	6.6	82.6	0.64	7.21	0	15.27	30,400 (powder) 7,850 (paper film)	Moon et al.[12]
Hydrothermal reduction of GO[k]	NA	NA	NA	5.6	NA	NA	NA	NA	NA	40 Ω (paper film)	Zhou et al.[13]
Methyl alcohol at 100 °C for 5 days (reflux)	NA	NA	NA	NA	73.0	1.62	24.4	Not found	4.00	3.2X10^{-5} (powder)	Dreyer et al.[14]
Butyl alcohol at 100 °C for 5 days	NA	NA	NA	NA	91.2	4.91	4.01	Not found	29.8	4,600 (powder)	Dreyer et al.[14]
L-Ascorbic acid[l]	NA	NA	NA	NA	NA	NA	NA	NA	NA	14.1 (paper film)	Gao et al.[15]
L-Ascorbic acid[m]		NA	NA	NA	NA	NA	NA	NA	NA	800 (paper film)	Zhang et al.[16]
L-Ascorbic acid[n]	NA	NA	NA	12.5	NA	NA	NA	NA	NA	2690-7700 (paper film)	Fernandez-Merino et al.[9]
Tannic acid	NA	NA	NA	2.44	NA	NA	NA	NA	NA	657 (paper film)	Lei et al.[17]
Solvothermal in propylene carbonate, at temperatures 150 °C	NA	NA	NA	8.3 (150 °C)	NA	NA	NA	NA	NA	2,100[p] 5,230[q]	Zhu et al.[18]

and 200 °C[o]				6.8 (200 °C)						1,800[p] 2,640[q] (paper film)	
Aerosol pyrolysis using ferrocene, thiophene, and ethanol[r]	85	15	NA	5.67	NA	NA	NA	NA	NA	NA	Campos -Delgado et al.[19]
Thermal exfoliation of GO until temperature 1050 °C[s]	NA	NA	NA	9.8	NA	NA	NA	NA	10	2,300 (paper film)	Schniepp et al.[20]
Aerosol plasma method[t]	97	3	NA	32.3	93.1	NA	4.3	NA	21.6	NA	Lambert et al.[21]

[a] NA: not available

[b] Hydrazine hydride was added to an aqueous GO dispersion, then the solution was kept at 100 °C for 24h; the elemental analysis was measured by combustion method

[c] Aqueous solutions of hydrazine (35 wt%) and NH_3 (28 wt%) was added to an aqueous GO dispersion, then the solution was kept at 95 °C for 1 h; the dispersion was filtered to form graphene film; the resulting film was dried in vacuum at 150 °C for 24 h

[d] GO film on a Si_3N_4/Si substrate was exposed to hydrazine monohydrate (98%) at 70 °C for 24 h

[e] GO film on a Si_3N_4/Si substrate annealed at 1000 °C in Ar for 30 min

[f] GO film on a Si_3N_4/Si substrate annealed at 900 °C in ultrahigh vacuum for 15 min

[g,h] GO film was dispersed and stirred in 98% anhydrous hydrazine solution for 1 week; the resulting hydrazinium graphene suspension was spin-coated on a silicon/SiO_2 substrate and then the film was annealed at 150 °C; the elemental analysis was measured by ICP-Mass

[i,j] Aqueous dispersion of GO was mixed with NMP; the resulting mixture was refluxed at ~ 205 °C for 24 h under flowing Ar; graphene film was annealed at 1000 °C

[k] GO aqueous solution was transferred to a Teflon lined autoclave and heated at 180 °C for 6 h

[l] Aqueous solution of L- ascorbic acid, L-tryptophan, NaOH, and GO was ultrasonicated for 0.5 h, then the solution was maintained at 80 °C for 24 h

[m] Aqueous solution of L- ascorbic acid and GO vigorous mixed at 23 °C for 48 h

[n] Aqueous GO suspension was reacted with L-ascrobic acid at 90 °C

[o] Sonication in propylene carbonate at 1 h, then the solution was heat-treated for 12 h in an oil bath at the temperatures 150 °C or 200 °C

[p] Air dried

[q] Annealed at 250 °C for 12 h under vacuum (~60 mtorr) in a tube furnace

[r] An aerosol was generated ultrasonically and then carried by an argon flow (0.8L/min) into a quartz tube located inside a two-furnace system heated to 950 °C (both furnaces were operated at the same temperature)

[s] Dried graphite oxide is charged into a quartz tube and purged with argon. Rapid heating (>2000 ^{o}C/min) to 1050 ^{o}C splits the graphite oxide into individual sheets through evolution of CO_2

[t] Plasma reduced graphite oxide (PRGO) was prepared by aerosoling coarsely ground GO (no solvent) through a low power (700 or 900W) microwave generated plasma with argon as the carrier and plasma gas

Table S2. XPS results of RGO prepared in supercritical ethanol (RGO-e) and RGO prepared using a continuous process in supercritical methanol (RGO-c)

Sample code	C (atomic %)	O (atomic %)	C_{1s}/O_{1s} ratio
RGO-e	92.04	7.96	11.56
RGO-c	84.28	15.72	5.36

Table S3. Reversible Capacity of Graphite, GO, RGO/Graphene and Turbostratic Carbon

Samples	Current Density (mA/g)	Voltage ranges (V)	Reversible capacity (mAh g^{-1})	Number of Cycles	Refs
Graphite	50	0.005 - 3	224	40	This study
GO	50	0.005 - 3	289	40	This study
RGO-2h-SSH	50	0.005 - 3	652	40	This study
Graphene nanosheet (GNS)[a]	50	0.5- 2.5	290	20	Yoo et al.[22]
Graphene nanosheet (GNS)[b]	50	0.05- 2.5	300	30	Paek et al[23]
Graphene nanosheet (GNS)[c]	50	0.005 - 3	~200	15	Pan et al.[24]
Graphene nanosheet (GNS)[d]	50	0.005 - 3	834	15	Pan et al.[24]
Graphene nanosheet (GNS)[e]	50	0.005 - 3	~700	15	Pan et al.[24]
Graphene nanosheet (GNS)[f]	50	0.005 - 3	784	15	Pan et al.[24]
Graphene nanosheet (GNS)[g]	1 C (c-rate)	0.02 - 3	~520	30	Wang et al.[25]
Graphene nanosheet (GNS)[h]	200	0.01 - 3	478	100	Wan et al.[26]
Polyacrylonitrile (PAN)- based carbon fibers[i]	50	NA[j]	~190	12	Lee et al. [27]
Poly(p-phenylene) (PPP)-based carbon[k]	NA[j]	NA[j]	680	NA[j]	Sato et al. [28]
Heat treated meso-phase carbon micro bead (MCMB)[l]	NA[j]	0 – 2	~270	NA[j]	Fujimoto et al.[29]
Heat treated meso-phase carbon micro bead (MCMB)[m]	NA[j]	0-2.5	~250	NA[j]	Tatsumi et al.[30]
Irradiated meso-phase carbon micro bead (MCMB)[n]	500	0-2	~ 320	>100	Ishiyama et al.[31]

[a] Graphene nanosheets were prepared via the chemical reduction (using hydrazine hydrate at room temperature for 24 h) of exfoliated graphite oxide sheet material

[b] Graphene nanosheets were prepared via the chemical reduction (using hydrazine hydrate at 100 °C for 24 h) of exfoliated graphite oxide sheet material

[c] Graphene nanosheets were prepared via the chemical reduction (using hydrazine hydrate at 80 °C for 24 h) of exfoliated graphite oxide sheet material

[d] Graphite oxide sheets was thermally reduced in a tube furnace in a nitrogen atmosphere with heating rate of 5°C /min at 300 °C for 2 h.

[e] Graphite oxide sheets was thermally reduced in a tube furnace in a nitrogen atmosphere with heating rate of 5°C /min at 600 °C for 2 h.

[f] Graphite oxide aqueous dispersion was added in isopropyl alcohol as scavenger of oxidative radicals (OH). The mixed solution was then put into a sealed plastic bag and irradiated for 10 min under 2 MeV/10mA conditions (140 kGy doses).

[g] Graphene nanosheets were prepared via the chemical reduction (using hydrazine hydrate at 100 °C for 2 h) of exfoliated graphite oxide sheet material.

[h] Graphite oxide sheets was thermally reduced in a tube furnace in a argon atmosphere with heating rate of 10 °C /min at 300 °C.

[i] PAN-based carbon fibers were first stabilized under tension in air at ~200 °C (10.97 MPa) and then carbonized in a N_2 environment at 1100 °C.

[j] NA: Not Available

[k] Poly(p-phenylene) (PPP) based carbon was synthesized by the Kovacic method.[32]

[l] MCMB was prepared by heat treated at 3000 °C

[m] MCMB was prepared by heat treated at 2800 °C

[n] MCMB was prepared by heat treated at 2800 °C and irradiated with an electron beam current density ~1.34 μA/cm^2 of 0.5MeV for 600 s.

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