Supplementary material (ESI) for Journal of Materials Chemistry

Solid-State Microwave Irradiation Synthesis of High Quality Graphene Nanosheets under Hydrogen Containing Atmosphere

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List of Video included

Video_Fig 1.AVI

Description of the supplementary movie provided

The supplementary movie is real time in .avi format. The video is a supplementary description of Fig. 1 of the manuscript, which shows the entire sequence of the exfoliation process of a mixture of graphite oxide (GO) and graphene nanosheets (GNS) during solid-state microwave irradiation synthesis. The GO/GNS mixture in a quartz bottle placed inside a microwave oven (Mars 5, CEM) was exposed to microwaves at 1600 W. The video was taken in front of the microwave oven window using a Panasonic digital camera. The video consists of two parts: the exfoliation of GO in the mixture and the microwave arcing in the mixture. In the first part, the exfoliation of GO in the mixture was captured during the solid-state microwave irradiation synthesis under pulsed irradiation mode. The explosion of GO in the mixture was observed with huge volume expansion followed by the several mild exfoliations of GO/GNS powder. In the second part, the microwave arcing in the mixture was captured after the exfoliation of GO. Upon the further microwave irradiation after the exfoliation of GO, a white light appeared probably due to arc evolution from the product powder in the quartz bottle.

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Experimental detail about the electrical conductivity measurements;

We measured the electrical conductivity of graphite, graphite oxide (GO) and GNS prepared under different conditions and it is summarized in Table A. Three different methods have been reportedly used for measuring the electronic conductivity of graphene, such as 4-point probe method for graphene film, STM probe method for measuring individual graphene sheet and 2-point probe method for compressed graphene powder.[1-9] We employed the 2-point probe method combined with AC impedance method to measure the electronic conductivity of graphene-based materials using a compressed powder pellet in the form of a disc with a conductivity cell shown in Fig. S1-1. The GNS pellet was compressed under a constant pressure of 8000 psi and the AC impedance was measured with increasing pellet thickness in order to determine the electrical conductivity of GNS pellet free from contact resistance at an interface between electrode and GNS. Experimental detail about the electrical conductivity measurements is provided below.

Table A shows the electrical conductivity of pellets for 1) graphite, 2) GO prepared by Hummers method, 3) GNS prepared by solid state microwave irradiation under H_2/Ar gas atmosphere, 4) GNS prepared by solid state microwave irradiation under Ar gas atmosphere and 5) GNS prepared by microwave assisted hydrothermal synthesis. The electrical conductivity of the graphite pellet and the graphite oxide pellet was measured to be 1.53×10^{3} S/m and 4.3×10^{-2} S/m, respectively and these values are within the range of literature values reported previously.[5-7] Ruoff et al. reported the electrical conductivity of 2.5×10^{3} S/m for pristine graphite and 2×10^{-2} S/m for GO, respectively.[5] In their study, the conductivity of pristine graphite, GO and GNS was determined by fitting the conductivity of the compressed powders to the equation derived from the general effective equation.[5-6,8] GO prepared by Hummers method shows the lowest

conductivity of 4.2×10^{-2} S/m mainly due to the partially disconnected π-system caused by various oxygen-containing functional groups. Electronic conductivity was 1.25×10^{3} S/m for GNS prepared by solid state microwave irradiation under H_2/Ar gas atmosphere, 7.41×10^{2} S/m for GNS prepared by solid state microwave irradiation under Ar gas atmosphere and 2.77×10^{2} S/m for GNS prepared by microwave assisted hydrothermal synthesis. And the C/O ratio was 18.5 for GNS prepared by solid state microwave irradiation under H_2/Ar gas atmosphere, 11.45 for GNS prepared by solid state microwave irradiation under Ar gas atmosphere and 4.9 for GNS prepared by microwave assisted hydrothermal synthesis. It is clearly seen that the electronic conductivity of GNS pellets increased with increasing the C/O ratio, which could be attributed to restoring degree of π conjugated system in GO during the reduction processes.[9] This study shows that solid-state microwave irradiation of GO under H2/Ar gas atmosphere is far more effective in reducing GO compared with other treatments used in this study. It is noteworthy that the electrical conductivity, 1.25×10^{3} S/m for GNS prepared by solid state microwave irradiation synthesis under H_2/Ar gas atmosphere is of the same order of magnitude as the electrical conductivity of graphite powder (1.53×10^{3} S/m). It demonstrates that solid-state microwave irradiation treatment of the mixture powder of 90 wt.% GO and 10 wt.% GNS under H_2/Ar gas atmosphere can be developed as a procedure to prepare the high quality GNS as evidence by the C/O ratio and electrical conductivity of GNS.

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Table A. Electrical conductivity of pellets for graphite, GO prepared by Hummers method, GNS prepared by solid state microwave irradiation under H_2/Ar gas atmosphere, GNS prepared by solid state microwave irradiation under Ar gas atmosphere and GNS prepared by microwave assisted hydrothermal synthesis.

Sample	Conductivity (S/m)	Literature value (S/m)
Graphite	1.53×10^3	2.5×10^3 [a]
Graphite oxide	4.3×10^{-2}	2×10^{-2} [b]
GNS prepared by solid state microwave irradiation under H_2/Ar atmosphere	1.25×10^3	2.4×10^3 [c]
GNS prepared by solid state microwave irradiation under Ar atmosphere	7.41×10^2	
GNS prepared by microwave assisted hydrothermal synthesis	2.77×10^2	

[a,b,c] Conductivity of graphite, graphite oxide and reduced graphite oxide reported in reference 5.

The AC impedance of the natural graphite (45 *u*m nominal particle size, Aldrich), graphite oxide (GO) prepared by Hummers method and graphene nanosheets (GNS) prepared in this study was measured using a carbon pellet in the form of a disc with the 2-point probe method in a cell that is schematically shown in Fig. S1-1 (electrode Area = 1.33 cm2). VMP2 (Biologic) was used to measure the AC impedance of the graphene-based samples. The electrical conductivity was calculated from the impedance data measured in the frequency range from 1 Hz to 100 Hz at the AC amplitude of 5 mV for graphite and the three different types of GNS prepared in this study. For GO, impedance was measured in the frequency range from 10 mHz to 10 kHz at the AC amplitude of 1V.

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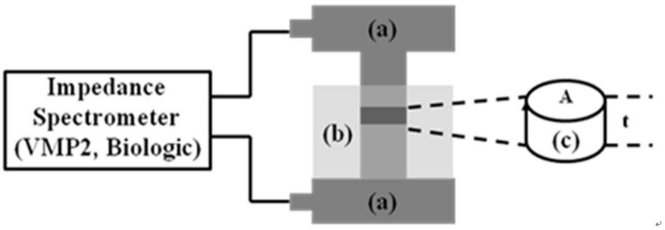

Fig. S1-1 Schematic of the AC impedance cell used for electrical conductivity measurement of carbons using 2-point probe method: (a) stainless top electrode and fixed bottom electrode, (b) poly(methyl methacrylate) (PMMA) mold, and (c) carbon pellet with an area A and thickness t.

Fig. S1-2 shows the typical Nyquist plots for graphite and GO. Since graphite is very conductive and acts as a pure resistor of high conductivity, its Nyquist plot is ideally represented as a point in the real part of impedance on X-axis. This indicates that the impedance of graphite is independent of the AC frequency. On the contrary, the Nyquist plot of the GO shows a depressed semi-circle, which indicates that its electrical equivalent circuit is a parallel combination of a capacitor and a resistor.

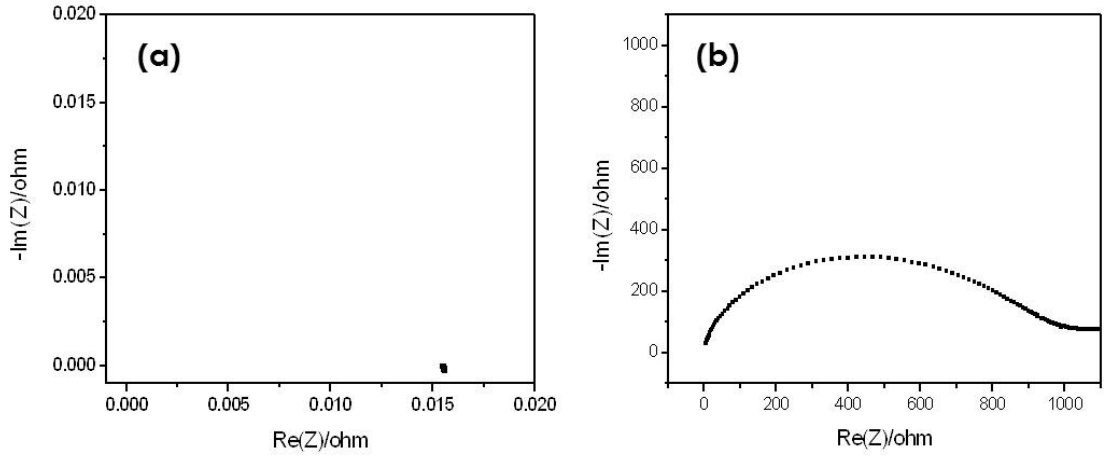

Fig. S1-2 Nyquist plots for (a) graphite and (b) GO prepared by Hummers method.

The frequency dependency of impedance can be seen more clearly in a Bode plot, as shown in Fig. S1-3 In the case of highly conductive graphite and GNS, the absolute impedance was almost independent of the AC frequency, as shown for graphite in Fig. S1-3. (a). On the contrary, the absolute impedance of GO increased gradually to a saturated level as the AC frequency was decreased to 10 mHz, as shown in Fig. S1-3. (b). Therefore, the absolute impedance taken at the lower limit of the AC frequency was used to calculate the electrical conductivity of GO.

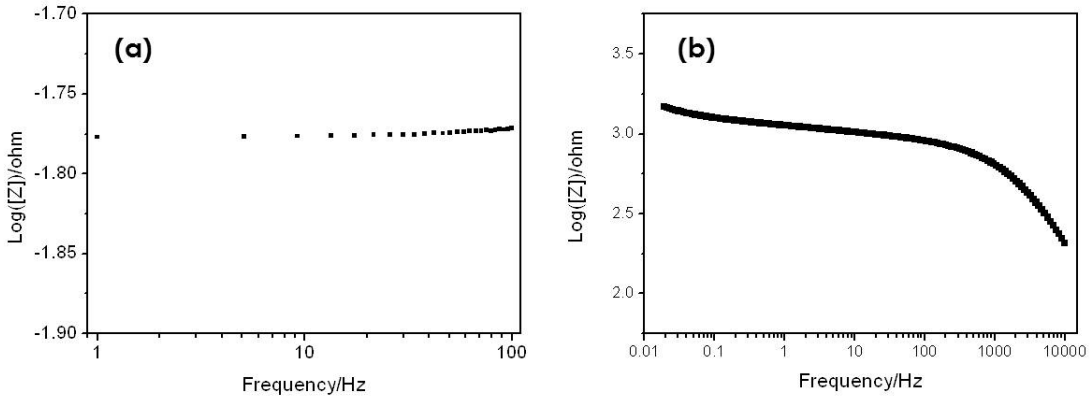

Fig. S1-3 Bode plots for (a) graphite and (b) GO prepared by Hummers method.

When the disc pellet of carbon was subjected to a constant pressure of 8000 psi using a Carver Press (Hydraulic unit model: 3912), the impedance of the pellet was observed to decrease gradually and finally reached a steady state value over 1 hour as shown in Fig. S1-4 GNS took longer than graphite to reach the steady state probably due to its morphological features. Therefore, the impedance taken at the steady state under the pressure was used to calculate the electrical conductivity of the carbon pellets.

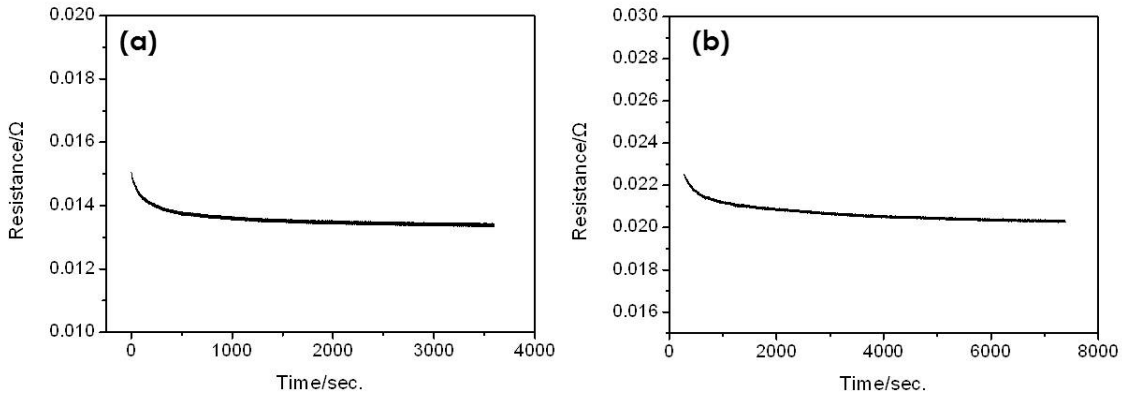

Fig. S1-4 Change in resistance of the disc pellets of (a) graphite, (b) GNS with time under a constant pressure of 8000 psi.

We prepared the carbon pellets with different thicknesses for each type of carbon and measured the resistance as a function of the thickness. Electrical conductivity of carbon was calculated from the slope of a linear line in the plot of the resistance against the pellet thickness using Equation-1. In this way, the contribution of the contact resistance at the upper electrode/carbon and carbon/lower electrode interfaces to the measured resistance would be eliminated.

$$R = \rho\ (t/A) = 1/\kappa\ (t/A) = t/(\kappa A) \qquad \text{Equation -1}$$

where R, ρ, κ and A are the resistance, resistivity, conductivity, thickness of the pellet and area of the electrode, respectively. Since the slope of the linear line in Fig. S1-5 (a), (b), (c) and (d) is $1/(\kappa A)$ and the electrode area A is known, we can calculate κ which is free from the contact resistance involved in the 2-point probe method.

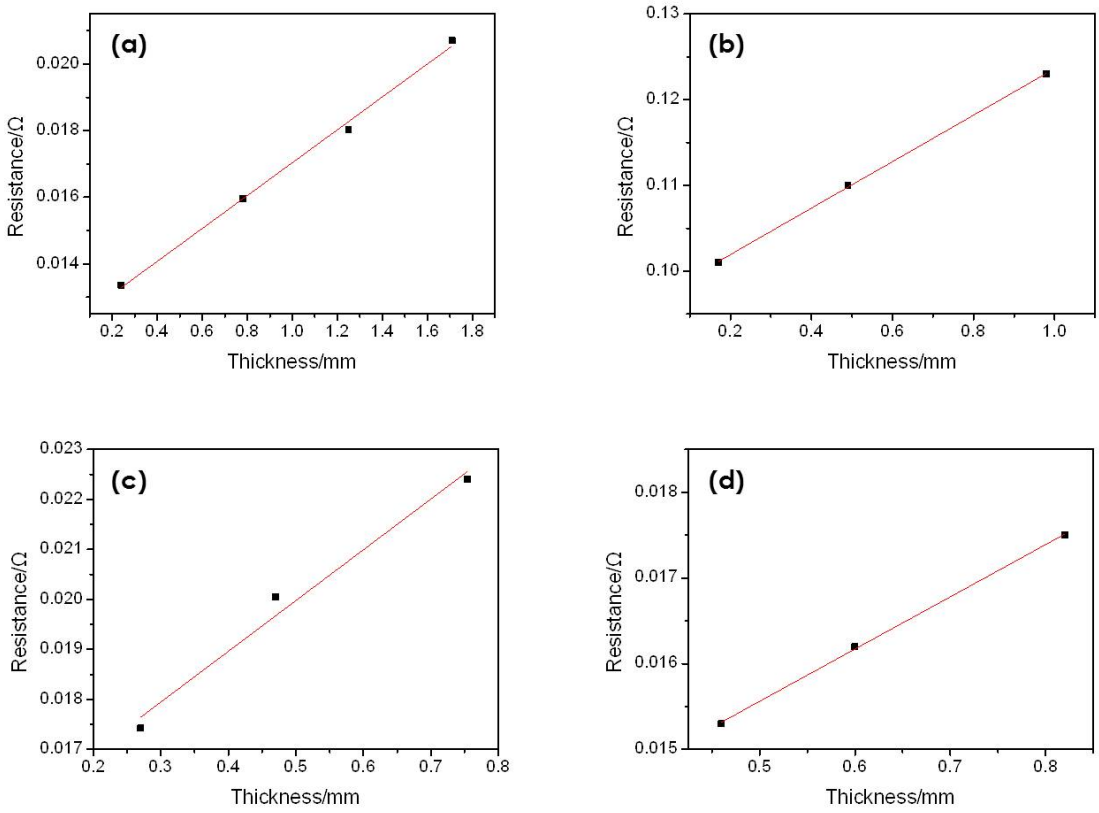

Fig. S1-5 Plots of the resistance of the carbon disc pellets against the pellet thickness for (a) graphite, (b) GNS prepared by microwave hydrothermal process (c) GNS prepared by solid state microwave synthesis under Ar gas atmosphere and (d) GNS prepared by solid state microwave synthesis under H_2/Ar gas atmosphere

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High-resolution transmission electron microscopy and electron diffraction

Fig. S2 shows high-resolution transmission electron microscopy (HR-TEM) and electron diffraction of GNS prepared by solid state microwave irradiation. Fig. S2 (a) is the typical TEM image of the edge of GNS. Fig. S2 (b) shows the electron diffraction taken at the flat edge for graphene marked in Fig. S2 (a). The hexagonal diffraction pattern of our GNS, which is similar to that of the peeled off graphene, demonstrates that GNS prepared by solid state microwave irradiation treatment of GO has a well crystallized graphene structure.[1-4] Furthermore, the inner circle spots are more intense than the outer ones, indicating that the region marked in Fig S is a single layer graphene.[1-5]

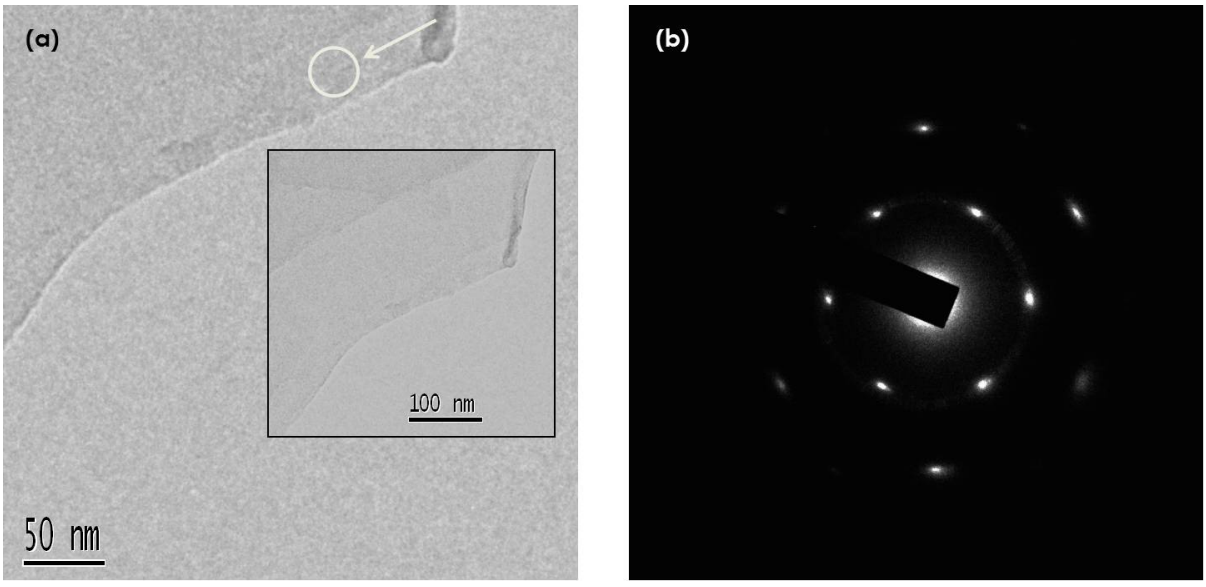

Fig. S2 (a) HR-TEM images of GNS prepared by solid state microwave irradiation synthesis and (b) electron diffraction pattern in (a)

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1 X. Li, G. Zhang, X. Bai, X. Sun, X. Wang, E. Wang and H. Dai, Nature Nanotechnology, 2008, 3, 538

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