

Synthesis of graphene nanosheets with good control over the number of layers within the two-dimensional galleries of layered double hydroxides

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Supporting materials include:

Part I. Experimental details

Preparation

Characterization

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Part I. Experimental details

Preparation

Preparation of LDH

The mixture of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.1 mol), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (0.025 mol) was dissolved in 300 mL of deaerated water (all the water used in the following experiments was deaerated in order to remove carbon dioxide and hence avoid competitive intercalation by carbonate anions in the LDH), and an emulsion was then formed by adding MMA (in various quantities) and sodium dodecyl sulfonate (6.8 g, 0.025 mol). The LDH sample was prepared by adding 70 mL of an aqueous solution containing NaOH (10 g) into the above emulsion with stirring (1000 rpm) under N_2 at room temperature. The mixture was then heated at 80 °C for 8 h under N_2 with a stirring speed of 300 rpm. After the reaction was completed, the precipitate was filtered, washed with several hundred milliliters of hot water and dried at 50 °C for 10 h. LDH-1, LDH-2 and LDH-3 were obtained by adding different amounts of MMA, namely 3 g (0.03 mol), 8 g (0.08 mol), and 20 g (0.2 mol), respectively, in the preparation of LDH. In other words, the MMA:DSO molar ratios in these materials are 1.2, 3.2 and 8.0, respectively. Finally, the chemical formulas of the produced three LDHs calculated based upon the elemental analysis are listed in the following table.

Name	Chemical formulas
LDH-1	$\text{Mg}_{0.80}\text{Al}_{0.20}(\text{OH})_2\text{DSO}_{0.20}\text{MMA}_{0.18} \cdot x\text{H}_2\text{O}$
LDH-2	$\text{Mg}_{0.81}\text{Al}_{0.19}(\text{OH})_2\text{DSO}_{0.19}\text{MMA}_{0.50} \cdot x\text{H}_2\text{O}$
LDH-3	$\text{Mg}_{0.80}\text{Al}_{0.20}(\text{OH})_2\text{DSO}_{0.20}\text{MMA}_{1.59} \cdot x\text{H}_2\text{O}$

Preparation of graphene nanosheets

Graphene nanosheets were synthesized by heating 10 g of LDH-1, LDH-2 or LDH-3 in Ar flow of 50 sccm at atmospheric pressure from room temperature to 900 °C and then maintaining the temperature at 900 °C for 2 h in a mixture flow of H_2 (5 sccm) and Ar (50 sccm). And then the resulting calcined LDH was treated with 10

wt.% hydrochloric acid etching (3 L) under ultrasonication in order to dissolve the solid metal oxide components leaving pure graphene nanosheets. The resulting suspension was neutralized with NaOH to pH 5-7 and dialyzed with a dialysis membrane (spectrum MD31, 100-500 Molecular Weight Cutoff) for 3 days. The suspension retained in the dialysis bag was concentrated to give 4 L of a graphene nanosheets aqueous dispersion. The aqueous dispersion of monolayer (5.5 $\mu\text{g/mL}$), bilayer/trilayer (30 $\mu\text{g/mL}$) and multilayer (<6 layers) (96 $\mu\text{g/mL}$) graphene nanosheets were obtained from LDH-1, LDH-2 and LDH-3, which equated to 22 mg, 120 mg and 380 mg of dried powder, respectively.

Characterization

Scanning electron microscopy (SEM)

SEM was carried out in a field emission scanning electron microscope (Hitachi, S-4700) with voltage of 20 kV and current of 10 μA . SEM samples were prepared by drop-drying the samples from their aqueous suspensions onto silicon substrates.

High resolution transmission electron microscopy (HRTEM)

HRTEM observations were carried out on a JEOL JEM-3010 electron microscope with an accelerating voltage of 200 kV. HRTEM samples were prepared by drop-drying the samples from their diluted aqueous suspensions onto copper grids.

Atomic force microscopy (AFM).

AFM images were recorded on a digital Instruments Nanoscopy IIIa atomic force microscope. The graphene nanosheets suspension was dripped onto the mica surface. The substrate was rinsed briefly with water, blow-dried with air, and imaged by tapping mode AFM.

Raman spectroscopy

Raman spectroscopy was performed with a Renishaw RM2000 confocal Raman spectrometer with a 514 nm excitation laser (laser spot size of 0.5 μm) operated at a low power level (~ 2 mW) in order to avoid any heating effect. The graphene nanosheet sample was drop-cast onto a glass substrate for Raman measurements.

Fourier transform infrared (FT-IR) spectroscopy

FT-IR spectra were recorded with 2 cm^{-1} spectral resolution using Nicolet Model 205 spectrometer.

Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) patterns were recorded on a Shimadzu XRD-6000 diffractometer operated at 40 kV and 30 mA at the wavelength of Cu K_{α} radiation ($\lambda = 0.15406\text{ nm}$).

X-ray photoelectron spectroscopy (XPS)

XPS was performed on a PHI Quantera SXM scanning X-ray microprobe with 100 mm beam size, using an Al K_{α} ($\lambda = 0.83\text{ nm}$, $h\nu = 1486.7\text{ eV}$) X-ray source operated at 2 kV and 20 mA. XPS samples were prepared by sticking the powdered three graphene nanosheet samples to aluminium foil.

Thermogravimetric analysis–mass spectrometry (TG-MS)

Thermal analyses, including thermogravimetry (TGA), differential thermal analysis (DTG), and evolved gas analysis (EGA), were carried out using a Perkin-Elmer Pyris Diamond TG/DTG equipped with a ThermoStar mass spectrometer for analysis of gases evolved during sample heating. A heating rate of $10^{\circ}\text{C}/\text{min}$ in nitrogen with a flow rate of $20\text{ mL}/\text{min}$ and 10 mg of sample were used. Gaseous products were continually monitored for chosen mass numbers m/z (18: H_2O^+ , 41: C_3H_5^+ , 64: SO_2^+ , and 100: $\text{C}_5\text{H}_8\text{O}_2^+$).

Elemental analysis

Elemental analysis for Mg and Al was performed by inductively coupled plasma emission spectroscopy (ICP-ES) (Shimadzu ICPS-7500). Elemental analysis for C, S, O and H was carried out using an Elementar Vario EL Cube elemental analyzer.

Part II. Supplementary Figures

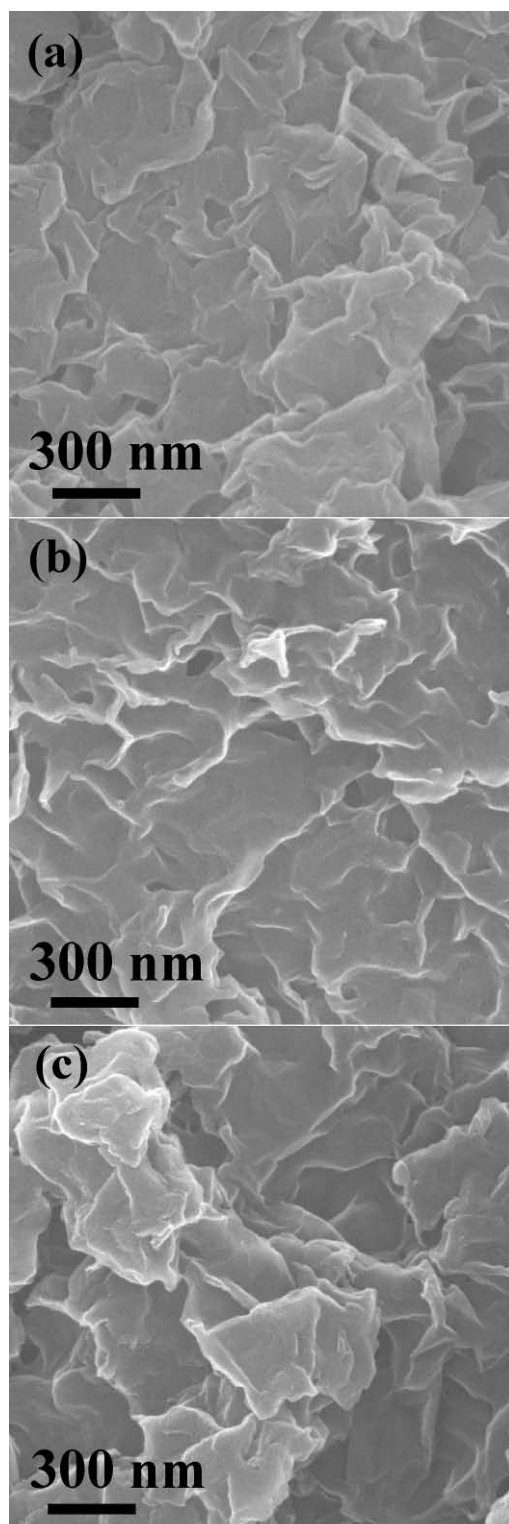


Figure S1 SEM images of (a) LDH-1, (b) LDH-2 and (c) LDH-3. The three LDHs have a similar morphology—folded lamellae.

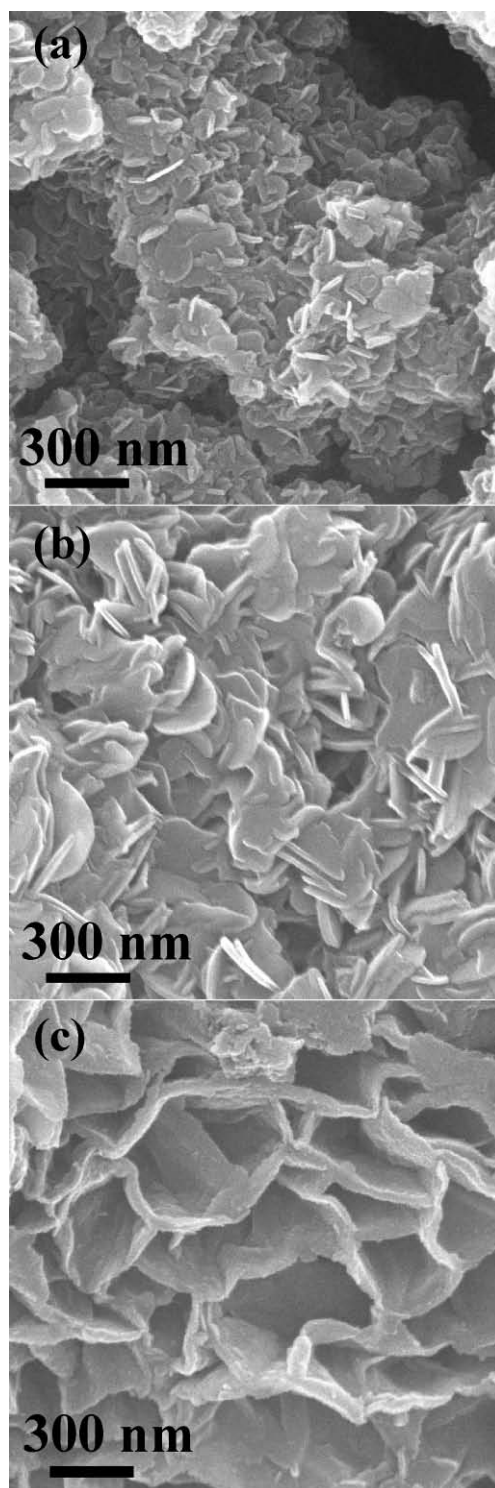


Figure S2 SEM images of calcined LDHs (a) c-LDH-1, (b) c-LDH-2 and (c) c-LDH-3. The size of the c-LDH particles increased with increasing quantity of MMA, and the average size of the platelets was from a few hundred nm to more than 1 μm .

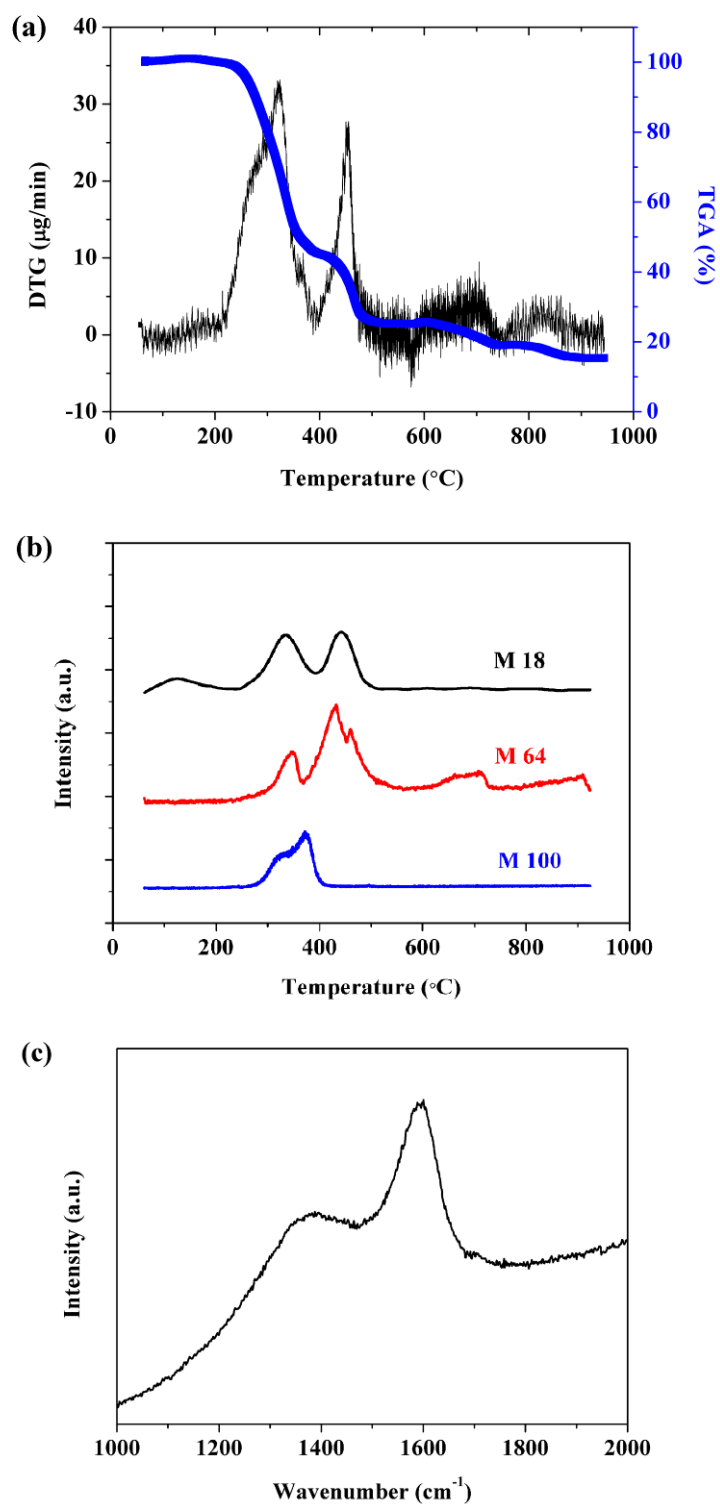


Figure S3 (a) TGA and DTG derivative curves of LDH-2; (b) TG–MS spectra obtained for sample described in (a). M 18, M 64 and M 100 correspond to H₂O (for MMA and LDH decomposition), SO₂ (for DSO decomposition) and C₅H₈O₂ (for MMA) species, respectively; (c) Raman spectrum of the final sample derived from LDH-2 after heating at 250 °C and acid etching.

We take LDH-2 as an example to demonstrate the thermal decomposition process. The TGA traces for LDH-2 indicate two general regions of mass loss (Fig. S3a). The first results from the loss of interlayer water, MMA and part of DSO in the temperature range 220–400 °C. The second loss, above 400 °C, corresponds to the dehydroxylation of the lattice, which is also accompanied by loss of DSO anions. This analysis of the TGA and DTG data was confirmed by mass spectral analysis of the evolved gases during heating (Fig. S3b). The loss of water (detected as H_2O^+ at $m/z = 18$) and the loss of DSO (detected as SO_2^+ at $m/z = 64$) occurs over a wide temperature range. Some loss of MMA (detected as $\text{C}_5\text{H}_8\text{O}_2^+$ at $m/z = 100$) occurs on heating between 300 and 400 °C. However, the Raman spectrum (Fig. S3c) of the material derived by heating LDH-2 at 250 °C followed by acid etching shows that a carbonized material was obtained at this temperature (250 °C), well below the onset of decomposition of the LDH layers or volatilization of MMA. Therefore, the mechanism of formation of the graphene nanosheets can be described in three steps: first, MMA was carbonized to form amorphous carbon in the two-dimensional galleries of the LDH at ~250 °C; second, LDH decomposed to periclase at ~440 °C, which cannot aggregate into a three-dimensional material because of the intervening carbon layers; third, graphene nanosheets were generated from amorphous carbon layers via graphitization at higher temperature (~900 °C)

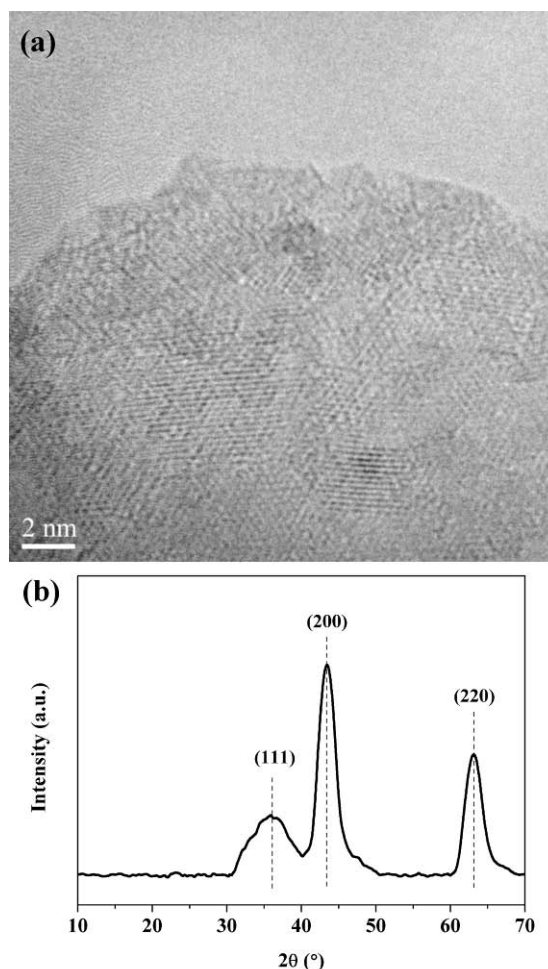


Figure S4 (a) HRTEM image and (b) XRD spectrum of LDH-0 calcined at 900 °C. No lamellar morphology can be seen in the HRTEM image (a). In the XRD pattern (b), only the peaks marked (111), (200) and (220) characteristic of periclase can be seen. There is no diffraction peak in the range between 10° to 30° characteristic of graphene or graphite intercalation compounds. This is because the decomposition of LDH layers and DSO anions occurred almost at the same temperature (440 °C). Thus the original lamellar morphology cannot be preserved by formation of amorphous carbon layers formed as is the case when MMA is present.

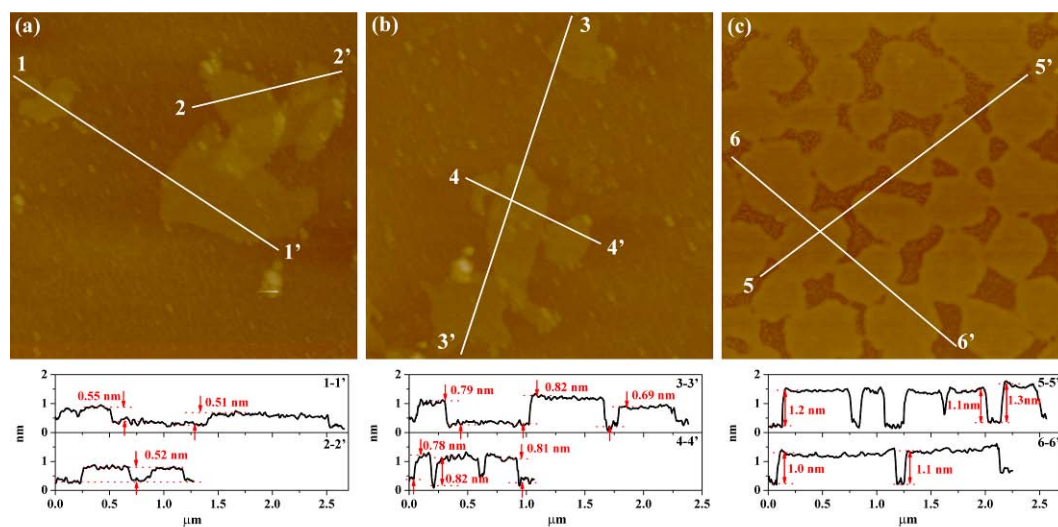


Figure S5 AFM photos of MMA-derived graphene nanosheets obtained using (a) LDH-1, (b) LDH-2 and (c) LDH-3 precursors.

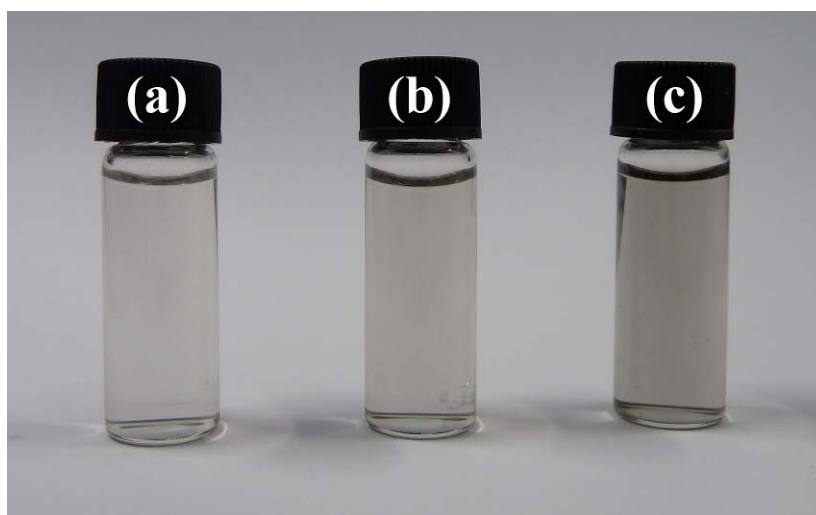


Figure S6 Photographs of the final aqueous dispersions of (a) monolayer (5.5 $\mu\text{g/mL}$), (b) bilayer/trilayer (30 $\mu\text{g/mL}$) and (c) multilayer (96 $\mu\text{g/mL}$) graphene nanosheets obtained using LDH-1, LDH-2 and LDH-3 precursors, respectively.

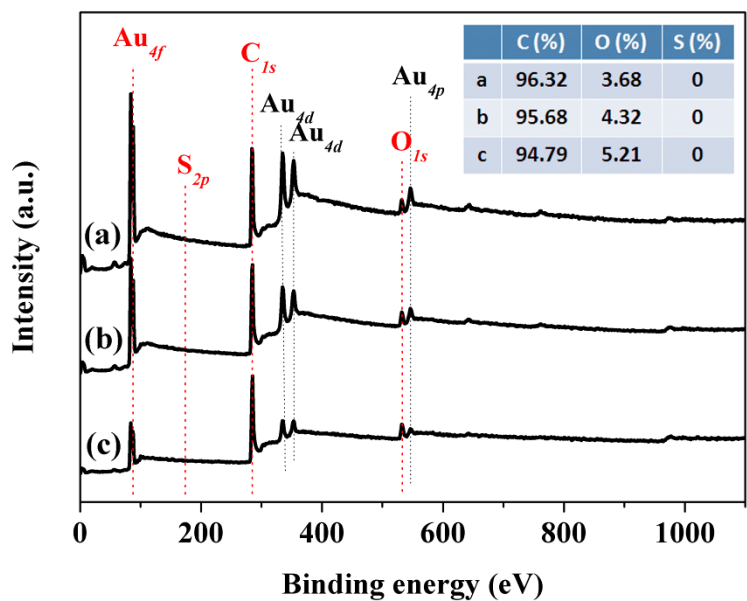
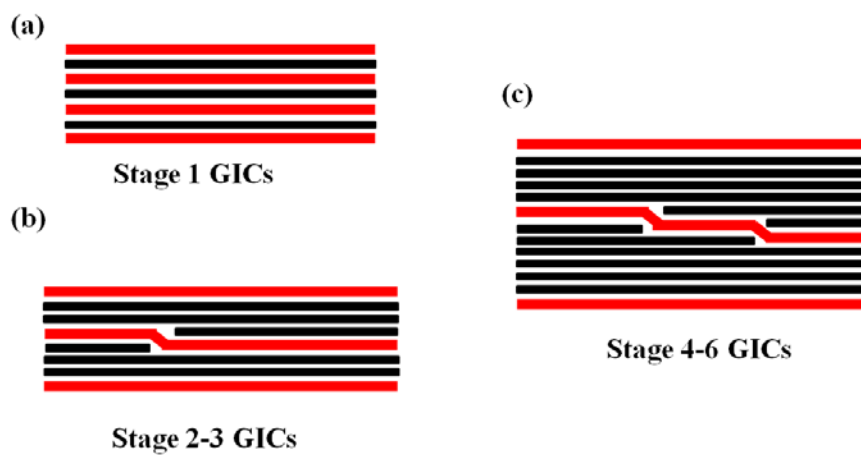


Figure S7 XPS spectra of graphene nanosheets with different numbers of layers (a) monolayer, (b) bilayer/trilayer and (c) multilayer. The insert shows the content of C, O, and S in (a), (b) and (c), obtained by integration of C_{1s} , O_{1s} and S_{2p} peaks (Au was added as a reference standard).

Table S1 Composition of monolayer, bilayer/trilayer and multilayer graphene nanosheets, which were obtained by organic elemental analysis (the instrument error is ~0.2%)

	C	S	O	H
	(%)	(%)	(%)	(%)
Monolayer graphene nanosheets	99.30	0.076	0.832	0.211
Bilayer/trilayer graphene nanosheets	98.88	0.083	0.796	0.237
Multilayer graphene nanosheets	98.86	0.089	0.817	0.229



Scheme S1 Schematic illustration of graphite intercalation compounds with various stages, which correspond to (a) c-LDH-1, (b) c-LDH-2 and (c) c-LDH-3. (The black line represents a graphene layer; red line represents a periclas layer.)