Electronic Supplementary Material (ESI) for Nanoscale.

Supporting information

The selective formation of graphene ranging from two-dimensional sheets to three-dimensional mesoporous spheres

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Experimental details:

Preparation of graphene sheets and mesoporous spheres

All chemicals were of analytical grade and were used as received. Sodium, urea and hexachlorobutadiene were purchased from Sigma-Aldrich. In a typical procedure, a large trunk of sodium with a shining surface (0.2g) and hexachlorobutadiene (ca. 20 ml) were added to a 50 ml stainless steel 5500 HPLC reactor (Parr Instrument Company, America). The sealed reactor was then placed in an oil-bath to react for 40 h at 240 ^{o}C. After the reactor cool down to room temperature naturally, black products formed were collected through centrifugation at 8000 rpm, rinsed with ethanol and a mixture (1:1) of ethanol and deionized water for several times. The obtained black solid product was then dried at 240 ^{o}C for 2 h and was denoted as GS-240 in the following discussion.

For the preparation of mesoporous sphere, the empty portion of the autoclave was filled with 5.0 MP argon gas, while all other conditions were kept the same as those used in the above experiment. For comparsion, in another typical procedure, a large trunk of sodium with a shining surface (0.2g) was placed in a 20 x10 mm cylindrical crucible and then hexachlorobutadiene (ca. 20 ml) was added to fill up the crucible. To prevent sodium from floating out of the crucible during the reaction, a piece of copper foil was used to loosely seal the crucible. After placing the reactant-filled crucible in a 50 ml Teflon lined stainless steel autoclave, about 20 ml hexachlorobutadiene was added to fill up the autoclave. The sealed autoclave was then placed in an oven to react for 40 h at 240 ^{o}C. We have confirmed that Cu has no catalytic role in the above reaction; however, Cu film seemed to prevent sodium from being covered by graphene particles. Such coverage would otherwise render the reaction incomplete (i.e., partial consumption of the limiting reagent sodium). The reaction temperature and time were optimized systematically in this study, which showed that when the temperature was lower than 220 ^{o}C, there was no black product after 40 hrs (see Figure S1 in the supplementary document). After the autoclave cool down to room temperature naturally, black products formed inside the crucible were collected through centrifugation at 8000 rpm, rinsed with ethanol and a mixture (1:1) of ethanol and deionized water for several times. The black solid products were then dried at 240 ^{o}C for 2 h under the protection of argon to ensure that no hexachlorobutadiene residue was left inside the porous products (the boiling temperature of hexachlorobutadiene is 230 ^{o}C). Thermogravimetric analysis (TGA) confirms that drying at 240 ^{o}C removes hexachlorobutadiene residues trapped inside the nanospheres (shown in Figure S2 in the supplementary document). The above dried product is denoted as MG-240 in the following discussion. For thermal treatment, the above dried graphene was heated to a preselected temperature such as 800，900，1000, 1100，or 1200 ^{o}C for 1 h under the protection of argon, and the thus-obtained products are denoted respectively as MG-800, MG-900, MG-1000, MG-1100 and MG-1200 in the following context.

Nitrogen-doping of Graphene

For nitrogen doping treatment, the dried MG-240 was mixed with urea in a mortar and was grinded thoroughly for 5 minutes. The mixture was then placed in a tube reactor at a preselected temperature 1000 ^{o}C (or noted otherwise) for 1 h under the protection of argon which was flew at a rate of 50 cc/min. The resulting products were subsequently washed 5 times with toluene to remove unreacted urea, where the solids were collected through centrifugation each time. In the last step, the solid was dried in a vacuum oven at 120 ^{o}C for 5 h. Based on the molar ratio of graphene nanosphere and urea in the initial mixture, such as 1:1, 1:2, 1:4, or 1:6, the obtained products are denoted respectively as NMG-1/1, NMG-1/2, NMG-1/4 and NMG-1/6. For comparasion, the dried GS-240 was mixed with urea in a mortar 1:4 and was then placed in a tube reactor at a preselected temperature 1000 ^{o}C for 1 h under the protection of argon which was flew at a rate of 50 cc/min. The obtained product is denoted as NGS-1/4.

Instruments

Phase structures were characterized by XRD (Bruker D8) using Cu Kα radiation (λ= 0.15406 nm). The nitrogen adsorption/desorption data were recorded at the liquid nitrogen temperature (77 K) using a Micromeritics apparatus (ASAP 2020 M), in which samples were evacuated for 10 h at 300 ^{o}C before their measurements. The specific surface area was calculated using the Brunauer-Emmett-Teller (BET) equation. Morphology of the solid products was determined by SEM (Nova Nanosem 200) operated at an acceleration voltage of 15 kV, and by TEM and high-resolution transmission electron microscopy (HRTEM) (JEOL-3010 instrument). XPS was performed on a spectrometer from Kratos Axis Ultradld, using Mono Al Kα (1486.71 eV) radiation at a power of 120 W (8 mA, 15 kV). Raman spectroscopy was collected on a Horiba Jobin Yvon LabRAM HR800 spectrophotometer, using 514 nm laser. TGA and mass spectroscopy were carried out on a PerkinElmer Pris 1 TGA /Clarus SQ 8T with a heating rate of 15 ^{o}C/min. Elemental analysis was performed with Elementar Analysensysteme GmbH vario EL.

Electrochemical measurements

All electrochemical measurements were conducted on a CHI660C electrochemical workstation using a three-electrode system, in which the reference and counter electrodes were saturated Ag/AgCl electrode and platinum foil, respectively. To prepare the working electrodes, the nitrogen-doped graphene products (i.e., NMG-1/1, NMG-1/2, etc.) were dissolved/dispersed in ethanol (1 mg/ml) and 2 μL of the slurry solution was dropped on a glassy carbon electrode (with a diameter of 3mm). After ethanol evaporates, another 2μL of the slurry was added. In total, 10 μL of nitrogen-doped graphene ethanol solution was added to a glassy carbon electrode. The above process was followed by casting with 2μL Nafion solution (5% in isopropanol) as the binder. Electroctivity of the nitrogen-doped graphene nanospheres was evaluated by CV and LSV on a rotating disk electrode (RDE) in oxygen saturated KOH solution ([KOH] = 0.1 M). Prior to each measurement, the alkaline solution was purged with high purity nitrogen or oxygen for 30 min. The solution was maintained at 25.0 ± 0.5 ^{o}C with a water bath. For comparison, commercial 40 wt% Pt-C catalyst (Vulcan XC-72R) was also investigated in this study. Typical CVs were measured between -0.8 and 0 V at a scan rate of 50 mV s^{-1}.

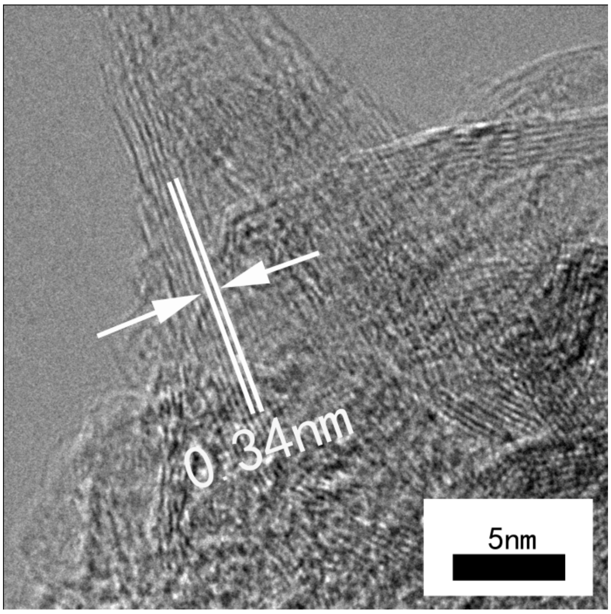

Figure S1. High resolution transmission electron microscopy (HRTEM) image of graphene nanospheres. It shows that these nanospheres are made up by few-layer graphene.

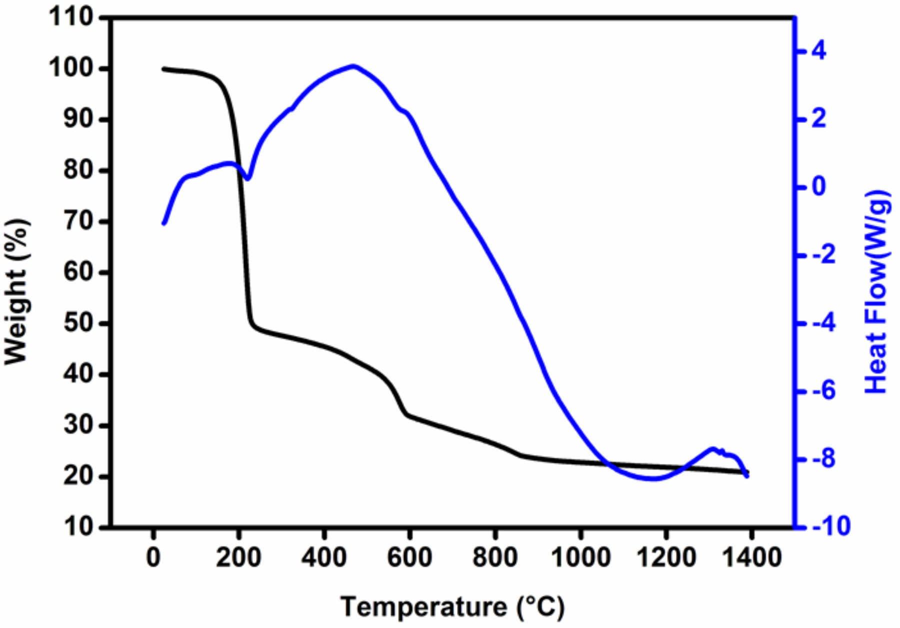

Figure S2. TGA of the graphene products shown in Figure 1c. The significant mass loss at about 210 ^{o}C, which is the boiling temperature of hexachlorobutadiene, shall be due to the elimination of hexachlorobutadiene residue in pores of the solid products. This conclusion is confirmed by mass spectra of the emission gas from the TGA measurement (see Figure S6).

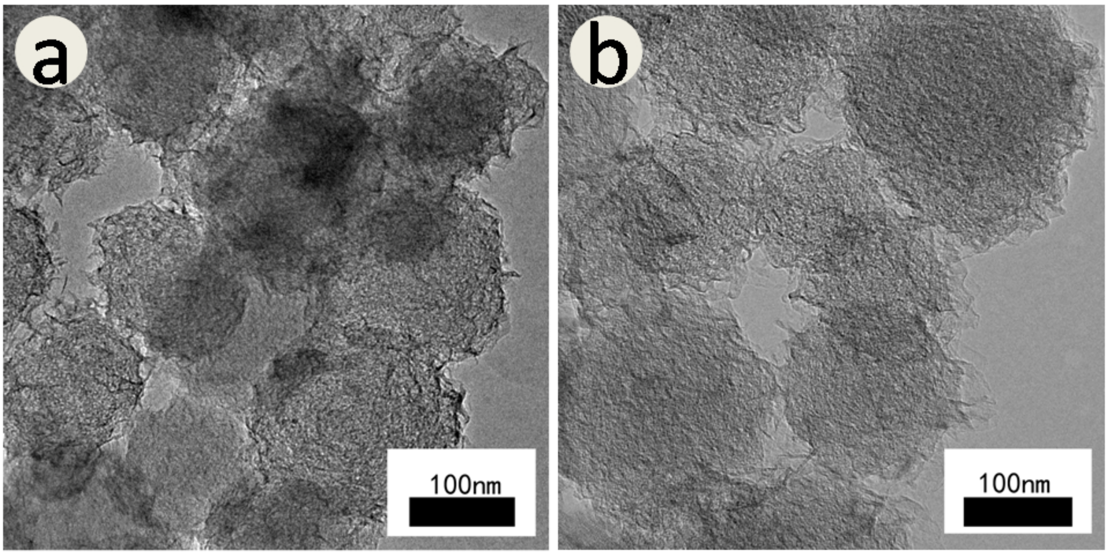

Figure S3: SEM images of graphene nanospheres after (a) heat treatment at 240 ^{o}C for one hour, and (b) nitrogen-doping at 1000 ^{o}C for one hour。

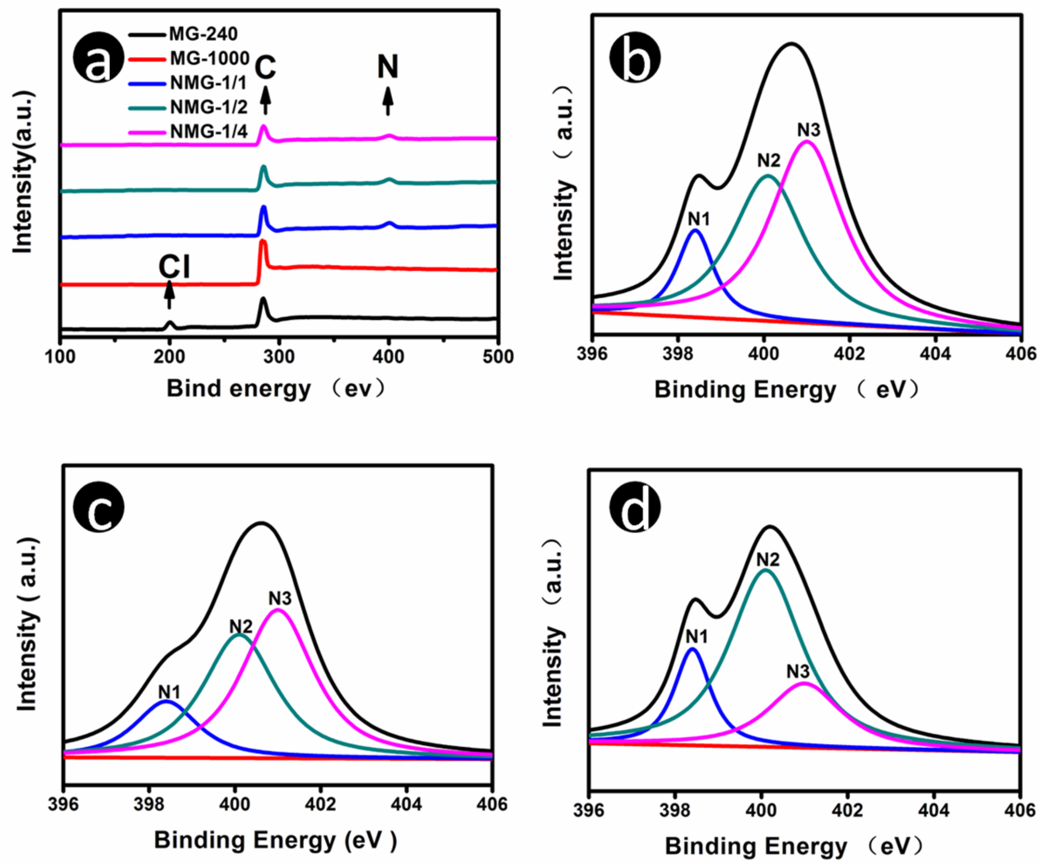

Figure S4. (a) XPS spectra of various graphene products; (b) to (d) deconvoluted N1s peaks showing different forms of nitrogen atoms (N1: pyridinic; N2: pyrrolic; N3: Graphitic) in the products of (b) NMG-1/1, (c) NMG-1/4 and (d) NMG-1/4.

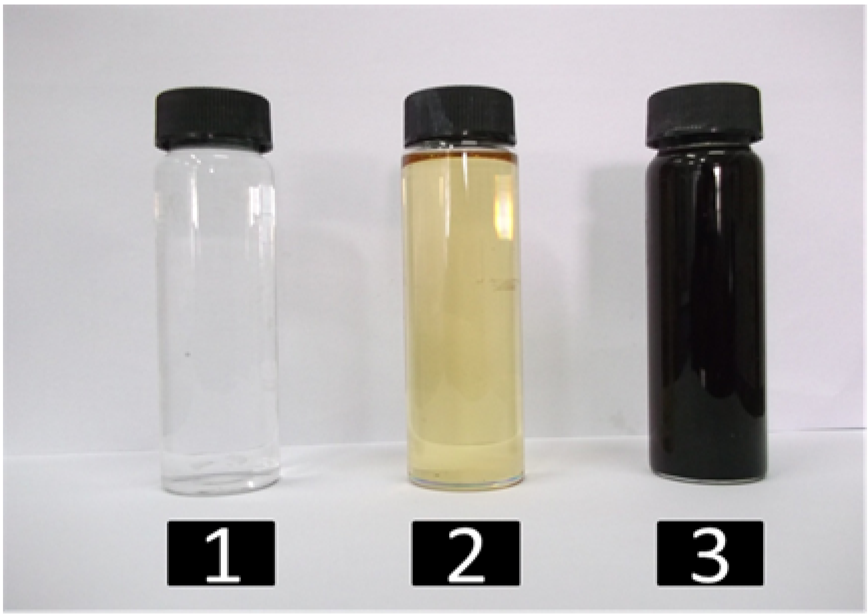

Figure S5. Snapshot of the reaction solution taken after the autoclave has been left in an oven for 40 hrs. The oven temperature was (1) 170, (2) 210, and (3) 240 ^{0}C. The above results indicate that temperature plays an important role in the synthesis.

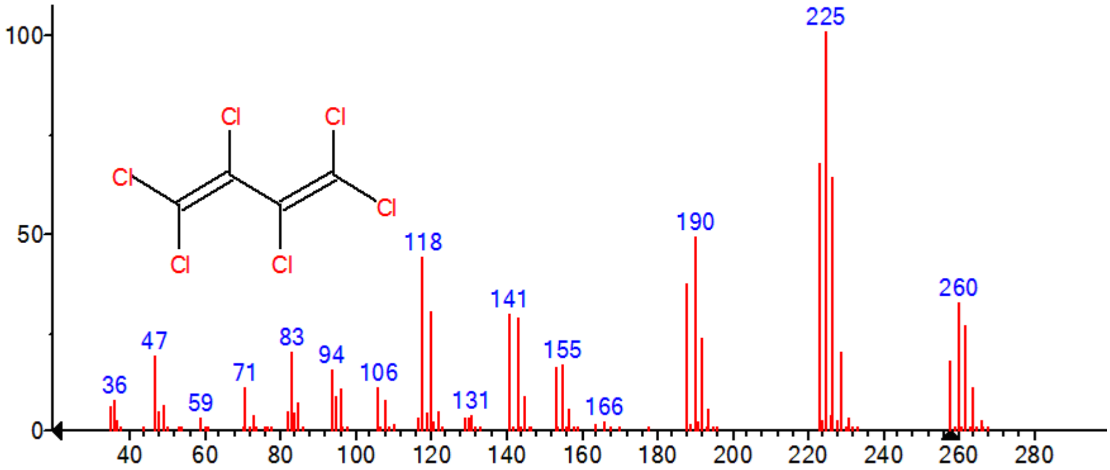

Figure S6. Mass spectrum of the emission gas from TGA experiment conducted at constant temperature 220 ^{o}C.

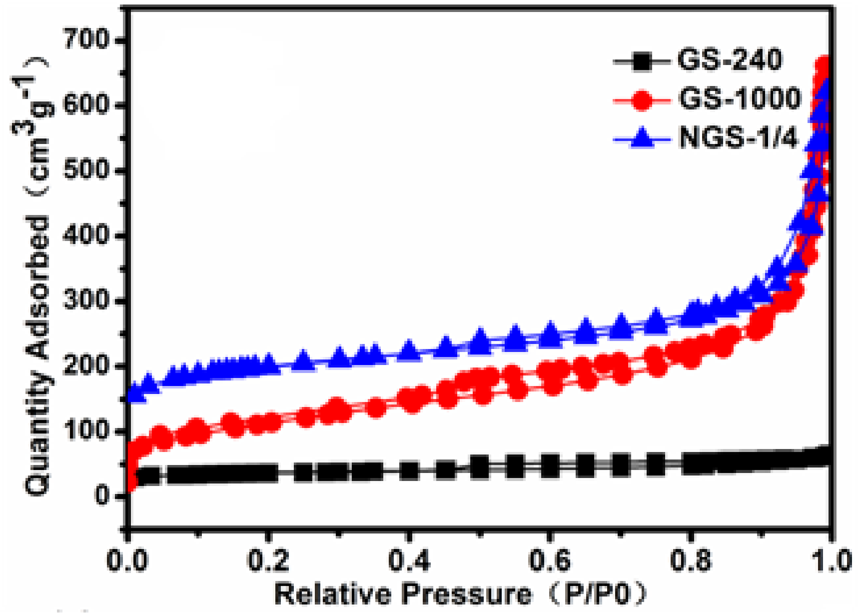

Figure S7. Nitrogen adsorption/desorption isotherm of graphene sheets.

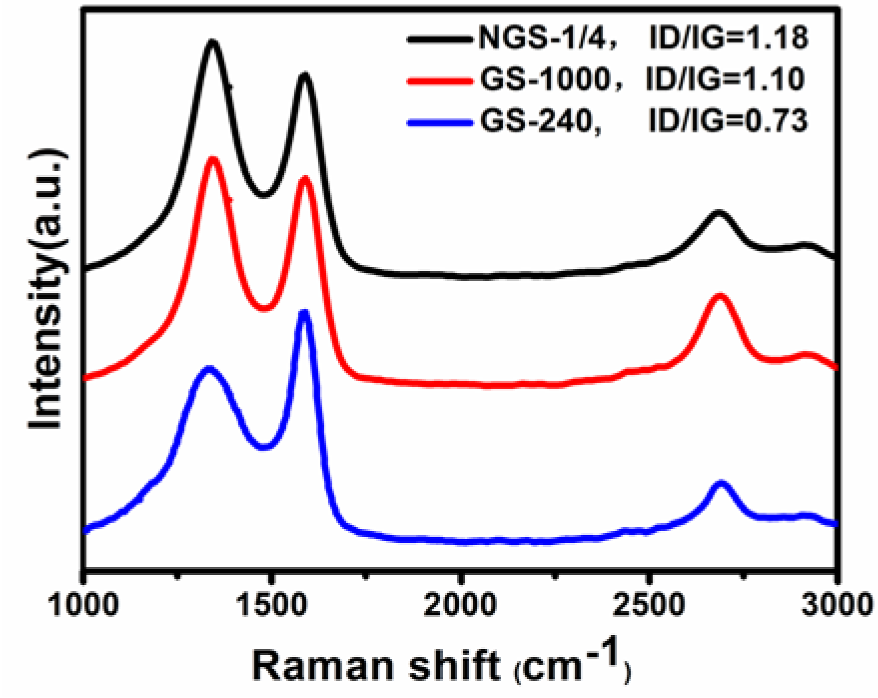

Figure S8. Raman spectra of graphene sheets (GS-240), thermal-treated graphene sheets (GS-1000), and nitrogen-doped graphene sheets (NGS-1/4).

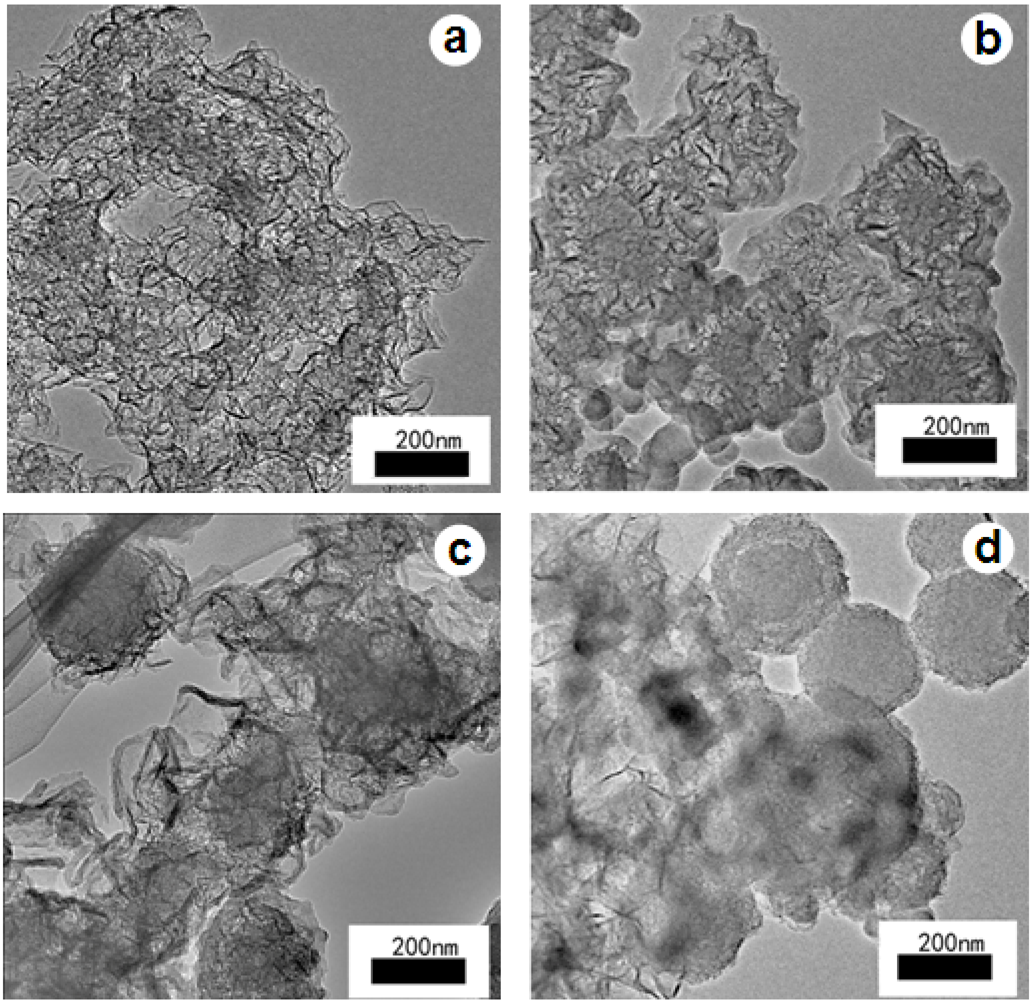

Figure S9. TEM image of the graphene products prepared under (a) atmosphere, (b) 2.0 MPa, (c) 3.0 MPa, and (4) 4.0 MPa argon gas. It illustrates that spherical products become the dominant constituent at higher gas phase pressure.

Table 1. Summary of specific surface area, pore size distribution and element distribution of the graphene nanospheres.

Samples	$S_{BET}{}^{a}$ ($m^2.g^{-1}$)	$V_{meso}{}^{b}$ ($cm^3.g^{-1}$)	BJH[c] pore Size (nm)	XPS-wt%					
				C	N1	N2	N3	N	Cl
MG-240	**122.70**	**0.265**	**3.74**	**91.20**	**-**	**-**	**-**	**-**	**8.80**
MG-800	**432.71**	**0.58**	**3.75**	**100**	**-**	**-**	**-**	**-**	**0**
MG-1000	**1030.98**	**1.27**	**3.75**	**100**	**-**	**-**	**-**	**-**	**0**
MG-1200	**107.14**	**0.18**	**3.75**	**100**	**-**	**-**	**-**	**-**	**0**
NMG-1/1	**687.14**	**0.97**	**3.75**	**99.45**	**0.042**	**0.22**	**0.29**	**0.55**	**0**
NMG-1/2	**665.43**	**0.93**	**3.75**	**99.15**	**0.071**	**0.35**	**0.43**	**0.85**	**0**
NMG-1/4	**710.44**	**1.07**	**3.75**	**98.50**	**0.15**	**0.90**	**0.45**	**1.50**	**0**
NMG-1/6	**-**	**-**	**-**	**98.38**	**0.12**	**0.81**	**0.69**	**1.62**	**0**
NGS-1/4	**410.60**	**1.153**	**-**	**98.47**	**0.16**	**0.87**	**0.50**	**1.53**	**0**

Note: N1：pyridinic N; N2: pyrrolic N; N3: Graphitic N. [a] BET surface area. [b] Mesoporous pore volume. [c] Barrett-Joyner-Halenda.

Table 2. Summary of specific surface area, pore size distribution and element distribution of the graphene sheets.

Samples	$S_{BET}{}^{a}$ ($m^2.g^{-1}$)	$S_{ext}{}^{b}$ ($m^2.g^{-1}$)	$V_{meso}{}^{c}$ ($cm^3.g^{-1}$)	$V_{micro}{}^{d}$ ($cm^3.g^{-1}$)
GS-240	**127.5**	**74.64**	**0.073**	**0.034**
GS-1000	**396.2**	**382.64**	**0.944**	**0.101**
NGS-1000	**410.6**	**321.32**	**0.981**	**0.172**

Note: [a] BET surface area. [b] External surface area (mesoporous surface area is included). [c] Mesoporous pore volume. [d] Microporous pore volume.