Electronic Supplementary Information (ESI)

High Capacity Gas Storage in Corrugated Porous Graphene with a Specific Surface Area-Lossless Tightly Stacking Manner

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1. Detailed experimental methods

1) Preparation of MgO template

First, purchased MgO powder (Sinopharm Chemical Reagent Co. Ltd.) was mixed with deionized water accompanied with ultrasonic agitation. The mixture was boiledfor 24 hr in a reflux apparatus. After filtration and drying, the material obtained was ground into a fine powder. Finally, the powder was calcined at 500°Cfor 30 min to remove water.

2) Synthesis of nanomesh graphene (NMG)

Porous graphene was synthesized by CH_4 cracking at 875 °C in a vertical quartz reactor with diameter of 50 mm and length of 1500 mm. A sintered porous plate was used as the gas distributor at the bottom of the reactor. Gas entered the bottom preheater of the reactor, then passed through the gas distributor, and finally flowed out into the atmosphere. On the top of the quartz reactor, there was a stainless steel plate with a hopper for feeding catalyst. In a typical run, the quartz reactor was mounted in an electrical tube furnace and was heated to 875 °C in an argon flow of 1000 ml/min at atmospheric pressure. Once the reaction temperature was reached, 500 ml/min CH_4 was introduced into the reactor. Then, the MgO template (about 30 g) was fed into the reactor over 5 min from the top hopper. After 10 min carbon deposition, CH_4 was turned off and the reactor was cooled to room temperature in an Ar atmosphere. The as-obtained material was collected for purification and characterization.

3) Purification

In a typical purification process, first, ~30 g unpurified material was mixed with 200 mL deionized water accompanied with violent agitation, resulting in an even suspension. Then 750 mL diluted hydrochloric acid (condensed hydrochloric acid diluted by deionized water with a volume ratio of 1:4, excessive amount) was added into the suspension, followed by reflux for 1 hour. Finally, the as-obtained black suspension was filtrated and dried at 100 °C overnight in an oven (labelled as G-W) or at -20 °C for 24 h in a freeze drying mathine (G-F). The material obtained was ground into a fine powder for characterization and application.

For contrast, the other two purification processes were also performed: ①diluted hydrochloric acid (by water, 1:1 in volume) was used; ② concentrated hydrochloric acid was directly added drop by drop.

4) Tablet pressing and volume measurement

The freeze-dried NMG sample (G-F) was used to make NMG tablets by a tablet press machine. Photos of the tablets were taken to measure their volume. The tablets can be regarded as cylinders, and the volume of the tablets was calculated by measuring the height and the diameter of the cylinders on the photos. As shown in Fig. S1, the diameter of the tablets (1.3 cm) is fixed by the mould, and the height of the pile of tablets was measured using the diameter as a ruler.

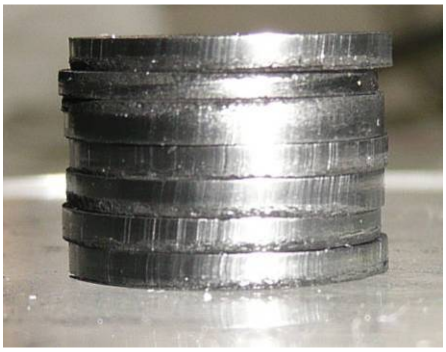


Fig. S1 A photo of piled NMG tablets.

5) Gas storage

Fig. S2 is the sketch map of the gas storage apparatus. Methane and hydrogen storage in graphene materials was performed at 274 K and up to 9 MPa. Carbon dioxide storage was tested at 274 K and up to 3 MPa since the liquefaction pressure of carbon dioxide is 3.6 MPa at 274 K. The process for methane storage and the calculation method are described as followed for an example.

Sample loading. First, the sapphire cell was dismounted from the apparatus, washed with distilled water, and dried. It was then loaded with 1-10 mL or 1-5 g graphene material, which was weighed precisely using a balance with a precision of 0.1 mg. In the case of testing methane uptake in wetted material, a certain amount of distilled water was immersed into the graphene slowly and evenly. After that, the cell was installed into the apparatus again.

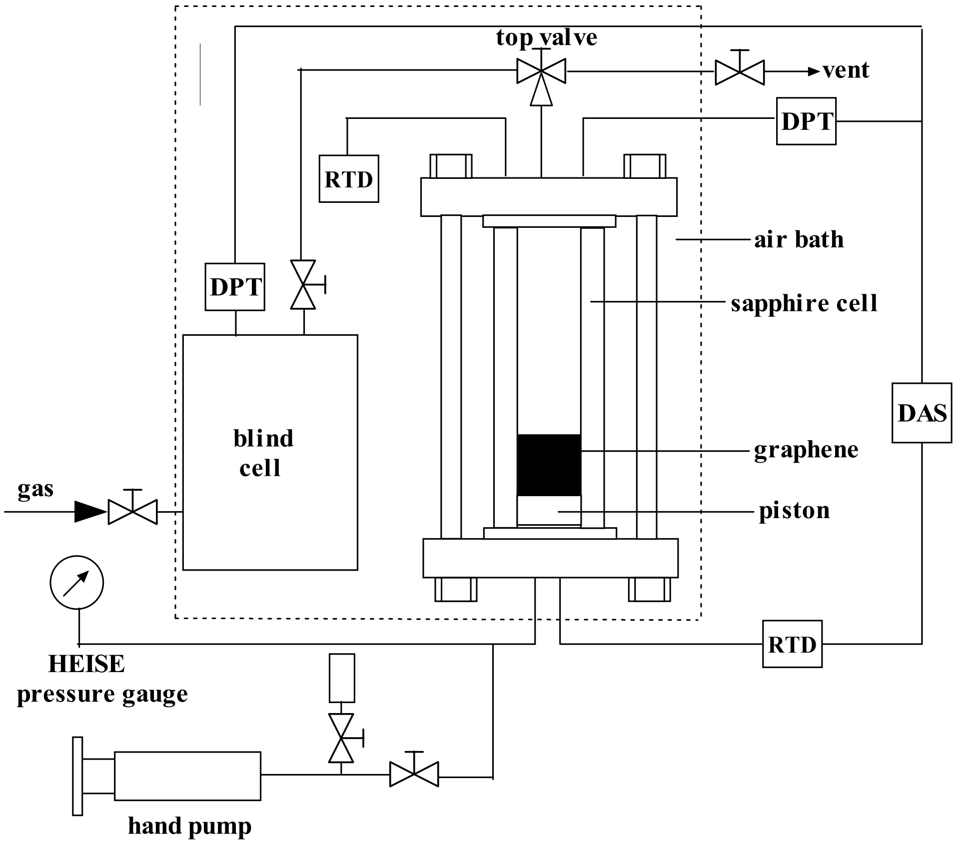


Fig. S2 Gas storage apparatus. RTD, resistance thermocouple detector; DPT, differential pressure transducer; DAS, data acquisition system.

Gas storage. First, the system including the sapphire cell, the blind cell and the high pressure gas line was vacuumed to -0.1 MPa. Then, top valve of the sapphire cell was closed and blind cell was charged with methane until desired pressure was achieved. The temperature of the air bath (T) was adjusted to 274 K and kept constant for 3 hr. Once the temperature (T) and the pressure of the blind cell (P_0) were stable, the mole number of methane in the blind cell (N_0) could be calculated by

$$N_0 = \frac{P_0 V_0}{Z_0 RT} \tag{1}$$

where the compressibility factor Z_0 is calculated with the Benedict-Webb-Rubin-Starling equation of state, V_0 is the volume of the blind cell plus tubes connecting two cells and R is the molar gas constant (8.314 $\mathrm{J{\cdot}mol^{-1}{\cdot}K^{-1}}$). After that, the valve between the blind cell and the sapphire cell was slowly opened, and then, methane entered the sapphire cell to start gas adsorption in the graphene material. Due to the gas adsorption, the system pressure would decrease and finally come to a stable pressure (P_1). The mole number of the total methane uptake (N_t) was calculated by subtracting the mole number of gas in the final state from N_0, using the following equations

$$N_{\mathrm{t}} = N_0 - \frac{P_1 V_1}{Z_1 RT} \tag{2}$$

$$V_1 = V_0 + V_{\mathrm{s}} - V_{\mathrm{C}} \tag{3}$$

where Z_1 is the compressibility factor at T and P_1, V_1 is the volume of the free space in the sapphire cell and the blind cell, V_{s} is the volume of the sapphire cell and V_{C} is the volume of the carbon material.

The gravimetric capacity of the total methane uptake (M_{t} in mmol/g or W_{t} in mg/g) was determined by

$$M_{\mathrm{t}} = \frac{N_{\mathrm{t}} \times 1000}{m} \tag{4}$$

$$W_{\mathrm{t}} = \frac{N_{\mathrm{t}} M \times 1000}{m} \tag{5}$$

where m is the mass of the carbon material, M is the molecule molar mass of methane.

The volumetric capacity of the total methane uptake (S_{t}, v(STP)/v) was determined by

$$S_{\mathrm{t}} = \frac{N_{\mathrm{t}} \times 22400}{V_{\mathrm{C}}} \tag{6}$$

where 22400 mL/mol is the molar gas volume at standard temperature and pressure.

The mole number of methane adsorped in the pores of the carbon material (N_{p}) was calculated by subtracting the mole number of gas in the free space in the carbon material from N_{t}, using the following equation

$$N_{\mathrm{p}} = N_{\mathrm{t}} - \frac{P_1 V_{\mathrm{c}} \varepsilon}{Z_1 RT} \tag{7}$$

$$\varepsilon = 1 - \frac{V_{\mathrm{f}}}{V_{\mathrm{C}}} = 1 - \frac{m}{\rho_{\mathrm{f}} V_{\mathrm{C}}} \tag{8}$$

where ε is the void ratio of the carbon material, V_{f} is the framework volume of the carbon material, ρ_{f} is the framework density of the carbon material (2.2 g/mL). The net storage capacity of carbon material excluding the free gas in the void of carbon material bed is then defined as,

$$S_{\mathrm{n}} = \frac{N_{\mathrm{p}} \times 1000}{m} \tag{9}$$

6) Characterization

The NMG samples were characterized by TEM (JEM 2010 operated at 120 kV), SEM (Quanta 200F), atomic force microscope (AFM, SPM-9600), Raman spectroscopy (Renishaw RM2000, 633nm), X-ray photoelectron spectroscopy (XPS, PHI700) and thermogravimetric analysis (TGA, Q500) in air flow with a temperature scan of 10°C/min. The specific surface areas (SSA) and pore size distribution of the samples were measured by N_2 adsorption at 77 K using a Micrometritics ASAP 2010. The mesopore distribution (1.7-300 nm) was calculated by the Barrett-Joyner-Halenda (BJH) method. The micropore distribution (<2 nm) was calculated by the original Horvath-Kawazoe (HK) method. The SSA was calculated by the Brunauer-Emmett-Teller (BET) method. A degasification at 300°C for 30 min was performed before the nitrogen adsorption.

2. Supplementary images

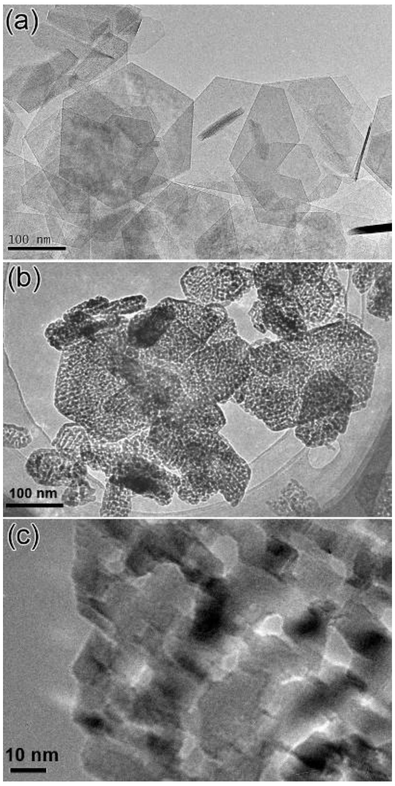


Fig. S3 TEM images of $Mg(OH)_2$ layers (a) and porous MgO layers after calcination (b, c), which is used as templates for the synthesis of NMG.

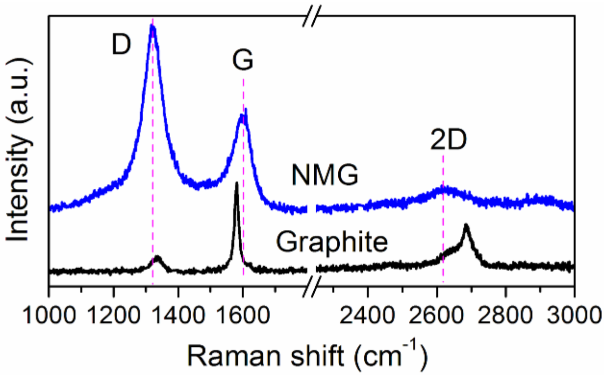
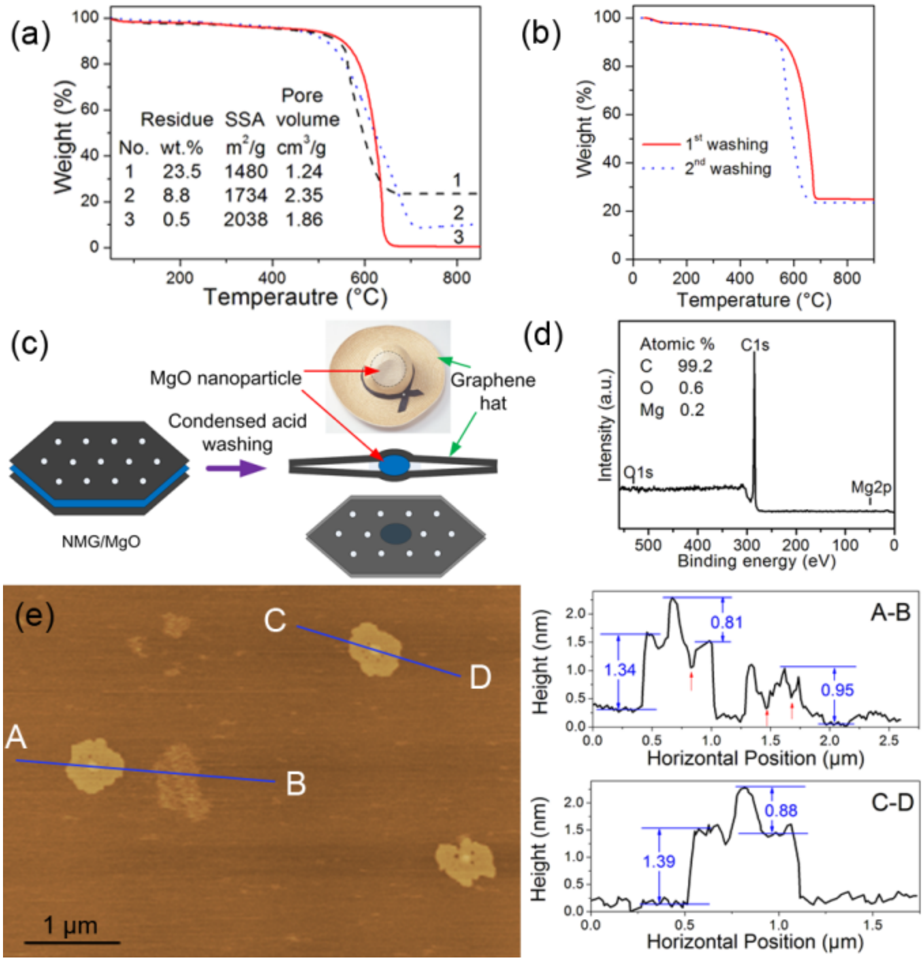


Fig. S4 Typical Raman spectrum of the NMG in comparison with graphite. The 2D peak of the NMG (2620 cm^{-1}) is obviously downshifted as compared to that of graphite (2685 cm^{-1}), indicating that the NMG is mainly composed of one to two graphene layers.[1] The upshift of G-band and the downshift of D band for the NMG can be attributed to the existence of more pores and edges.[1-2]



No.	Residue wt.%	SSA m^2/g	Pore volume cm^3/g
1	23.5	1480	1.24
2	8.8	1734	2.35
3	0.5	2038	1.86

Fig. S5 (a) TGA curves of the NMG samples purified by different processes: No.1, adding concentrated hydrochloric acid drop by drop; No.2, using 1:1 diluted hydrochloric acid; No.3, using 1:4 (V_{HCl}:V_{H2O}) diluted hydrochloric acid. (b) TGA curves of the NMG sample No.1 before and after acid washing for the second time. (d) XPS survey spectrum of the sample No.2, showing the MgO residues (8.8 wt.%) detected by TGA are covered by graphene layers. (c) A model and (e) the corresponding AFM image showing MgO particles encapsulated in combined graphene sheets.

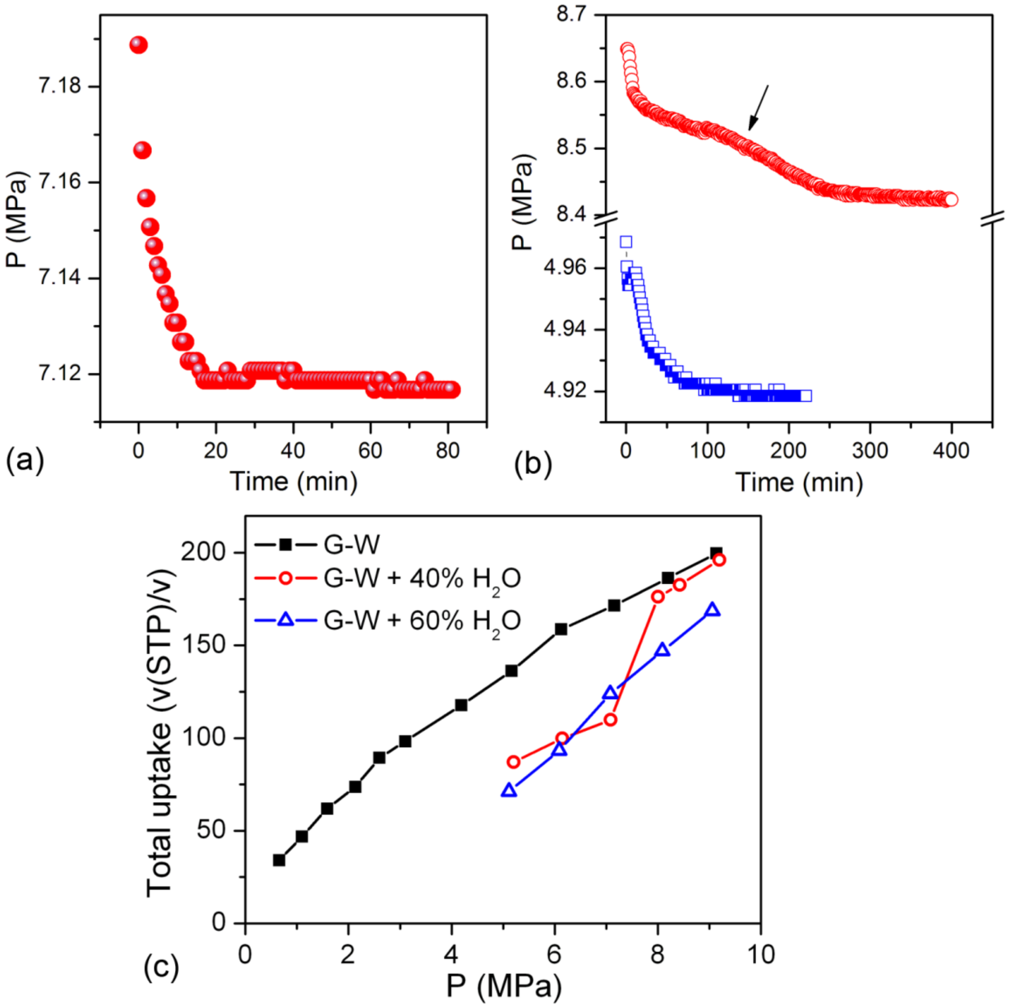


Fig. S6 (a) Typical kinetic curve of methane adsorption in dry NMG. (b) Kinetic curves of methane adsorption in wetted graphene (G-W with 40 wt. % H_2O) at different pressure. The peak contributed from the formation of methane hydrate (indicated by the arrow) can be found at ~8.5 MPa, and no hydrate was formed at ~ 5 MPa. (c) Total volumetric methane uptake of G-W and the wetted ones.

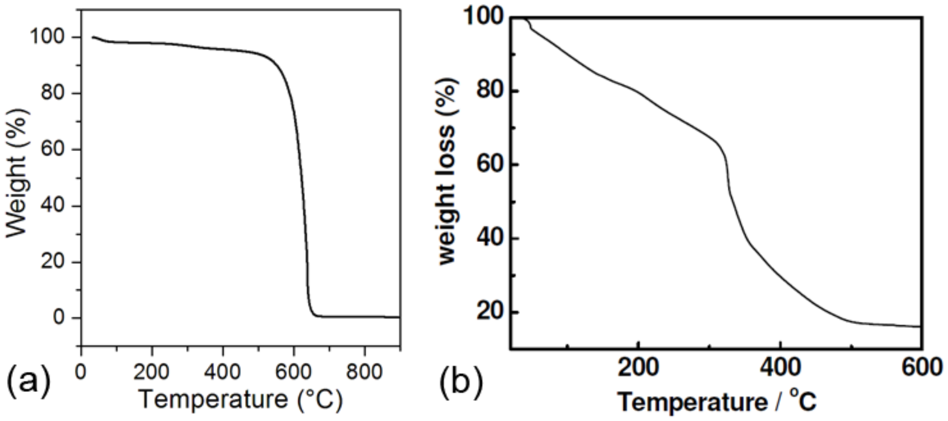


Fig. S7 TGA curves of the NMG (a) and the MOF material PCN-14 (b).[3]

Reference

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