Electronic Supporting Information for

# Macroporous 'bubble' graphene film *via* template-directed ordered-assembly for high rate supercapacitors

*Cheng-Meng Chen*[a], Qiang Zhang[b], Chun-Hsien Huang[c], Xiao-Chen Zhao[d], Bing-Sen Zhang[e], Qing-Qiang Kong[a], Mao-Zhang Wang[a], Yong-Gang Yang[a], Rong Cai[a], Dang Sheng Su*[e]*

[a] *Key Laboratory of Carbon Materials, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, P. R. China*

[b] *Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, P. R. China.*

[c] *Department of Biomedical Engineering and Environmental Sciences, National Tsing-Hua University, Hsinchu 30013, Taiwan*

[d] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian,116023, P. R. China.*

[e] *Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, P. R. China.*

*E-mail: ccm@sxicc.ac.cn; dssu@imr.ac.cn*

## Experimental:

**Synthesis of PMMA latex spheres.** Monodisperse PMMA latex spheres were prepared by the emulsifier-free emulsion polymerization. Polymerization of methyl methacrylate (MMA) monomer was carried out in a three-necked bottom flask using potassium persulfate ($K_2S_2O_8$, KPS) as the initiator. Typically, 1000 ml of deionized water was stirred at approximately 350 rpm at 75 $^{o}$C and purged with Ar. After stabilization of the temperature at an elevated level, the 400 ml of methyl methacrylate and 10.0 g of KPS was added subsequently and the reaction was allowed to proceed for 2 h, producing colloidal PMMA latex spheres. PMMA latex spheres were harvested by centrifugation and washing with deionized water once and then with ethanol twice. The as-prepared PMMA spheres were re-dispersed in deionized water to obtain an aqueous suspension (200 mg/mL) for further application.

**Hard template route for macroporous graphene film.** Graphite oxide (GO) was prepared by a modified Hummers' method, followed by ultrasonication (100 W, 45 min) in deionized water to get the graphene oxide hydrosol (3 mg/mL). The graphene oxide hydrosol (20 mL) was mixed with PMMA sphere suspension (1 mL) and sonicated for 30 min to get a homogeneous colloidal suspension, which was then vacuum filtrated on a millipore filter to realize the sandwich type assembly of PMMA sphere and graphene oxide sheets. The above composite film was peeled off from the filter and air dried at 80 $^{o}$C overnight, and the weight ratio of graphene oxide and PMMA spheres in the film was deduced to be 3:10. The composite membranes were annealed to 800 $^{o}$C (heating rate 5 $^{o}$C/min) and dwelled for 30 min in a tubular furnace. The graphene oxide within the membrane was thermally reduced into graphene, while the PMMA spheres templates were removed simultaneously, so as to get the MGFs. A control sample was prepared by a similar procedure but with no PMMA template introduced, so as to resulting in a compact graphene film (CGF).

**Textural characterization**. The morphology of the samples were characterized using a Hitachi S4800 scanning electron microscope (SEM) operated at 2.0 kV and a Philips CM200 $LaB_6$ transmission electron microscope (TEM) operated at 200.0 kV. Nitrogen adsorption–desorption measurements were performed at -196 $^{o}$C with a

Micromeritics ASAP2010 instrument. Prior to the measurements, the samples were degassed at 110 $^{o}$C for 1 h and at 250 $^{o}$C for 3 h. The specific surface areas were calculated with BET equation and the average pore diameters were estimated with desorption branches based on BJH model. The as-obtained GO, PMMA, and GO/PMMA samples were further characterized using thermal gravimetric analysis (TGA) system (STA 409PC luxx, Netzsch, Germany).

**Electrochemical measurements.** The electrochemical properties of MGF and CGF were measured in an aqueous system (electrolyte: 6.0 M KOH). A three-electrode system was employed in the measurements, whereas MGF/CGF served as the working electrode, a platinum foil electrode as counter electrode and a saturated hydrogen electrode (SHE) served reference electrode. Cyclic voltammogram (CV) curves (scan rates varying from 3 to 1000 mV/s), the Galvanostatic charge-discharge (GC) measurement, and electrochemical impedance spectroscopy (EIS) profiles were measured with a VSP BioLogic electrochemistry workstation. The electrochemical capacitances were obtained both from CV curves. The Nyquist plot was fitted by EC-Lab software.

The specific capacitance of a single electrode ($C_{elec}$) was calculated from the CV curves based on the equation,

$$\mathbf{C_{elec}= \boldsymbol{idt/dv}}$$

where *i* is the instant current in Amperes per gram of active material and *dv/dt is* the scanning rate in Volts per second.

The specific capacitance of the cell ($C_{cell}$) was calculated from GC profiles based on the following equation,

$$\mathbf{C_{cell}= (I\triangle t)/\triangle U}$$

where I is the discharge current in Amperes per gram of active material, $\triangle t$ is the discharge time in second, and $\triangle U$ is the voltage window from the end of the $\mathrm{IR}_{\mathrm{drop}}$ to the end of the discharge process in Volts.

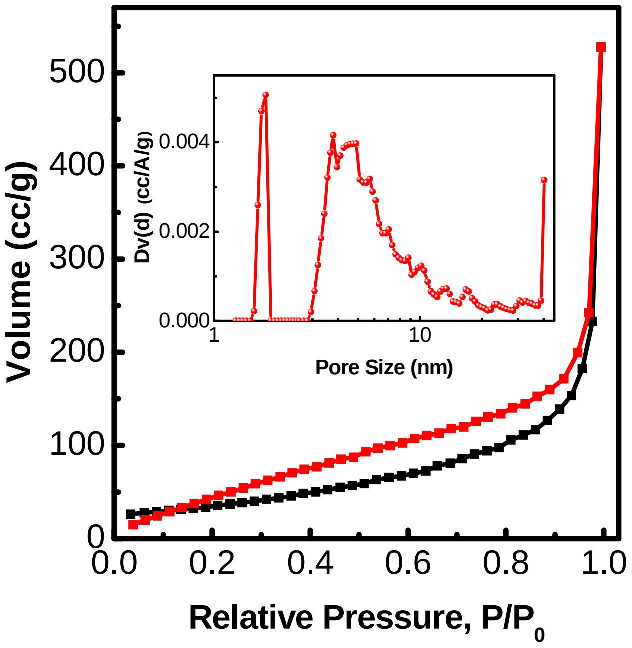

**Fig. S1** $N_2$ physic sorption isotherm (Inset shows the DFT pore size distribution) of MGF.

**Fig. S2** Digital photo of a compact graphene film (CGF) fabricated by a routine filtration method.

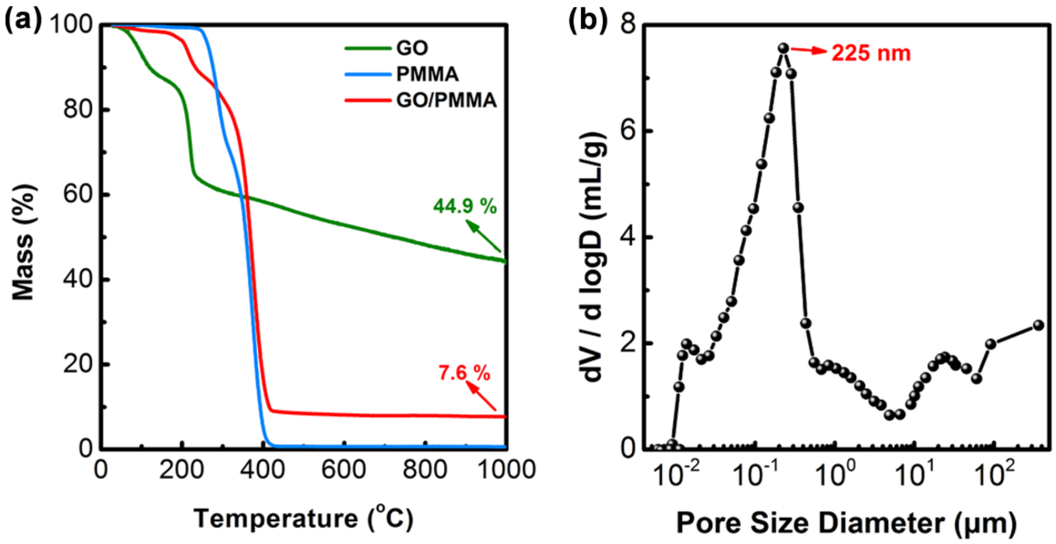

**Fig. S3** (a) TG curves of GO, GO/PMMA composite and bare PMMA template; (b) Pore size distribution of MGF by Hg penetration analysis

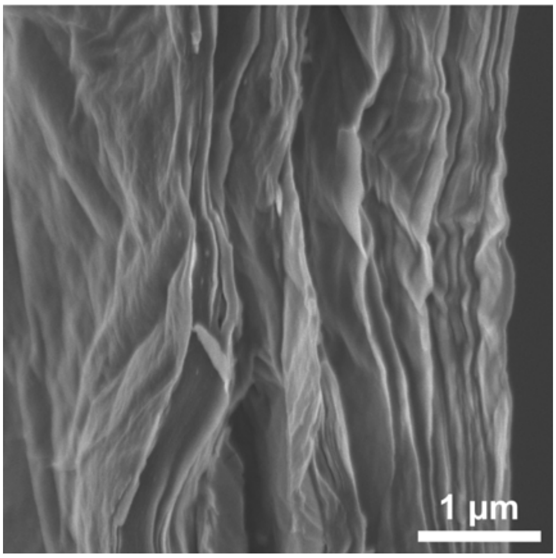

**Fig. S4** SEM image of the cross-section of a CGF

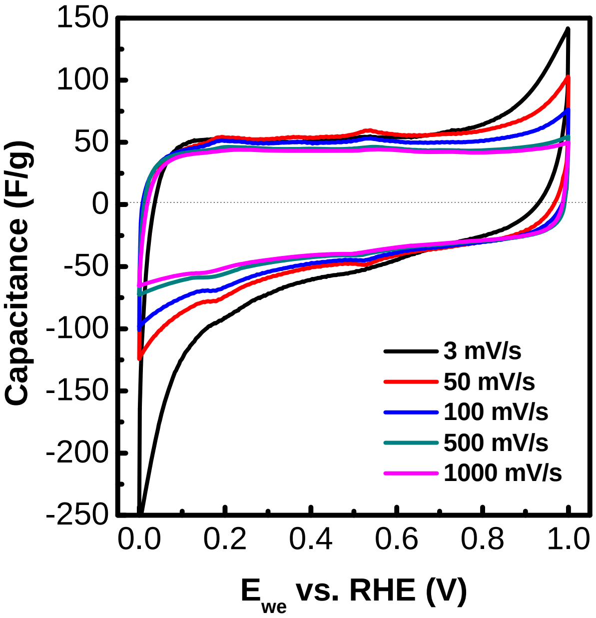

**Fig. S5** CV evolution of MGF at different scan rates from 3 to 1000 mV/s

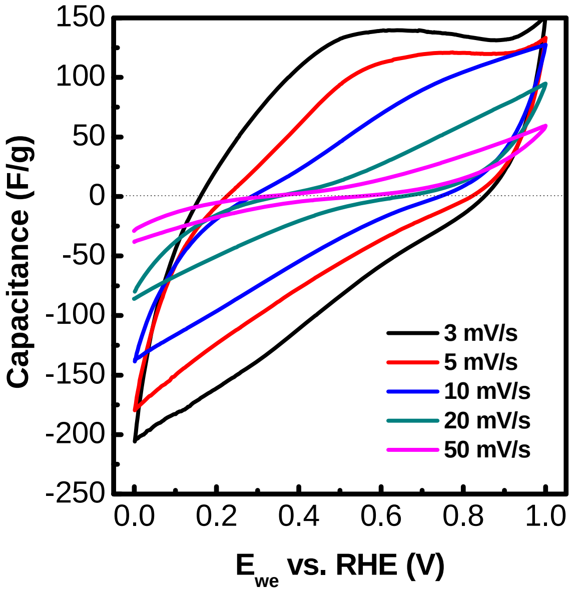

**Fig. S6** CV evolution of CGF at different scan rates from 3 to 50 mV/s

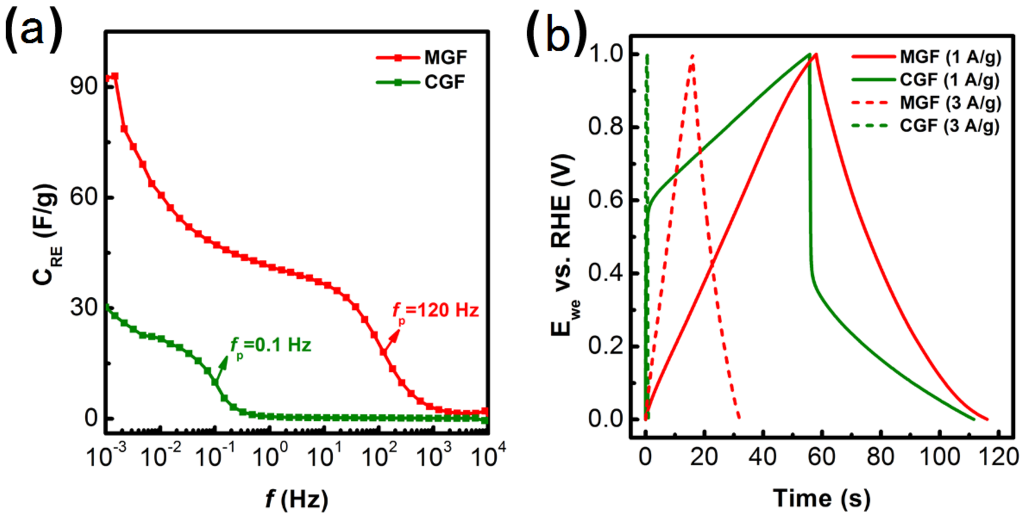

**Fig. S7** (a) Real part of complex capacitance as a function of AC frequency by EIS. (b) GC curves at current density of 1 and 3 A/g of MGF and CGF.