

Electronic Supplementary Information for

**The Closed-Environment CVD Method for preparing three-dimensional defect controllable
Graphene Foam with conductive interconnected network for Lithium-ion Battery
application**

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This PDF file includes:

Experimental Details

Supplementary Figures S1 to S6, and Table S1

Supplementary Note

Experimental Details

Preparation of PMMA/Cu foil

100 μ l PMMA (Alfa Aesar, 550 PMMA, 8% in anisole) solution as carbon source was deposited on a 25 μ m thick Cu foil (cut to 1.5 cm \times 1.5 cm squares) by spin coating at 500 rpm for 30s and 3000 rpm for 1 min. The obtained PMMA/Cu film was solidified at 180 $^{\circ}$ C for 1 min and then repeat above process until reach the presetting amount of carbon sources. The amount of carbon sources used were 200 μ l, 300 μ l, 400 μ l, 500 μ l, 600 μ l and 700 μ l, respectively. Finally, the obtained PMMA/Cu film was dried in a vacuum oven at 70 $^{\circ}$ C for 2 h to remove the solvent.

Preparation of GF

The PMMA/Cu film and a piece of Ni foam (2.5 cm \times 0.5 cm) sealed in a quartz tube with 5kPa H₂ atmosphere; the quartz tube introduced into the furnace with 1000 $^{\circ}$ C for 20 min; the quartz within graphene on Ni foam was rapidly cooled to room temperature by removing it from the hot-zone of the furnace. To prepare freestanding 3D GF without structural failure, the Ni foam covered with graphene (G/Ni foam) was drop-coated with a PMMA solution (Alfa Aesar, 550 PMMA, 4wt% in ethyl lactate) and then heated at 180 $^{\circ}$ C for 30 min. This process solidified the PMMA to form a thin film on G/Ni foams. Freestanding 3D GF was obtained by etching of Ni foam template in a solution of 3M HCl at 80 $^{\circ}$ C for 3 h. Finally free-standing GF was obtained by dissolving the PMMA with hot acetone at 55 $^{\circ}$ C.

Synthesis of ZnO/GF

Flower-like ZnO nanoparticles anchored into 3D GF was prepared by a simply hydrothermal method. 30ml 35 mM Zn(NO₃)₂ solution was firstly stirring for 1 h. Then, a piece of G/Ni foam immersed into the Zn(NO₃)₂ solution and vacuum degassed to make good contact between G/Ni foam and the solution. Subsequently, 30ml 175mM NaOH solution was added into the resulting solution with stirring for 15min. Followed by transferring the obtained solution into a 100 ml Teflon-lined, stainless-steel autoclave and then sealed. Hydrothermal reaction was conducted at 180 $^{\circ}$ C for 12 h. Afterward, when the autoclave cooled down to room temperature, the sample ZnO/GF was washed with DI water for several times and then dried in a vacuum oven at 60 $^{\circ}$ C for 12 h. After this, the ZnO/GF composite was annealed in a tube furnace at 500 $^{\circ}$ C for 3h under Ar protection with a heating rate of 10 $^{\circ}$ C min⁻¹.

Cell Assembly and Electrochemical Measurements

To test electrochemical performance, CR 2032 coin cells were made using Celgard 2400 as the separator and 1M LiPF₆ in ethylene carbonate-diethylene carbonate (EC:DEC=1:1) as the electrolyte. Li-metal was used as the counter and reference electrode. The coin cells were assembled inside an argon-filled glovebox with oxygen and water contents below 1 and 0.1 ppm, respectively. The flower-like ZnO/GF was directly used as working electrode and assembly into a coin cell without adding any conductive or binding materials. Galvanostatic charging and discharging tests were conducted using LAND CT2001A test system within the potential range of 0.01~3.0 V vs. Li⁺/Li at various current densities. Cyclic voltammetry was performed with CHI 660E electrochemistry workstation at a scan rate of 0.1 mV s⁻¹ between 0.01 and 3.0 V vs. Li⁺/Li. Electrochemical impedance spectra (EIS) were recorded on a Zahner IM6e electrochemical workstation, in the frequency ranges from 100 kHz to 0.01 Hz.

Materials Characterization

Field emission scanning electron microscopy (FE-SEM, Hitachi S4800) was used to characterize the morphologies of the synthesized samples. Transmission electron microscopy (TEM) images were taken using a FEI Tecnai G2 F30 microscope. Raman spectroscopy was recorded by LabRam HR800 with 1.96 eV (632.8 nm) excitation laser. The XPS measurements were performed with a Thermo VG ESCALAB250 X-ray photoelectron spectrometer. The electrical conductivity of GF was measured by four-point probe method (SB100A).

Supplementary Figures



Fig. S1 Photograph of the sealed quartz tube with PMMA/Cu film and Ni foam. (a) before

reaction, (b) after reaction

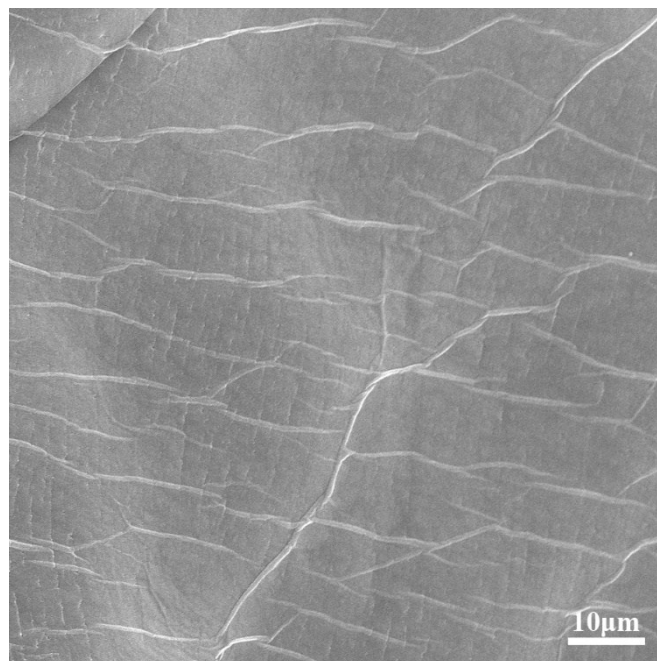


Fig. S2 SEM images of the graphene films adhering to the surface of a nickel foam. Ripples and wrinkles of the graphene films are observed.

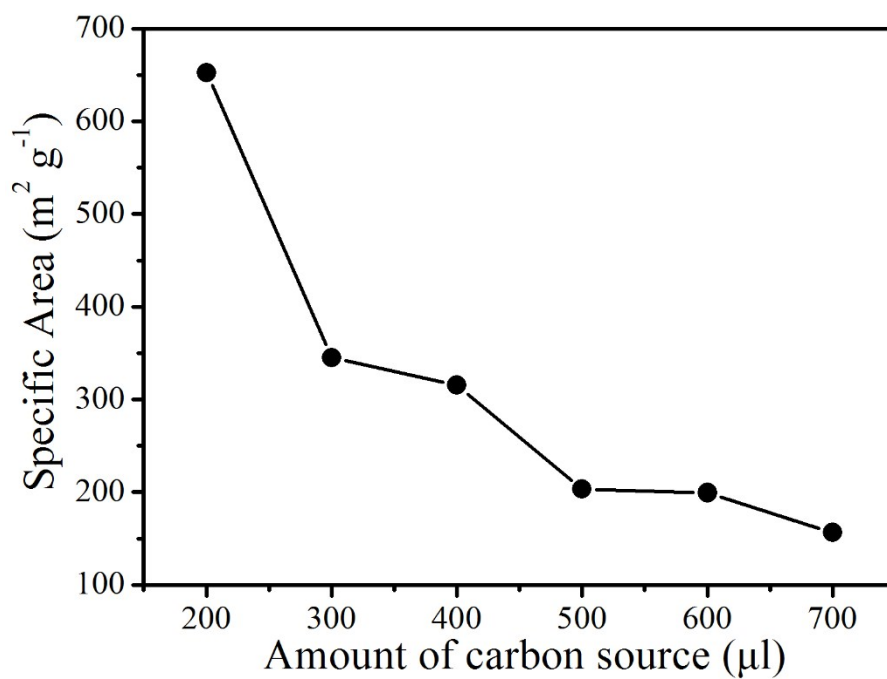


Fig. S3 The specific surface area of GFs as a function of the amount of carbon source.

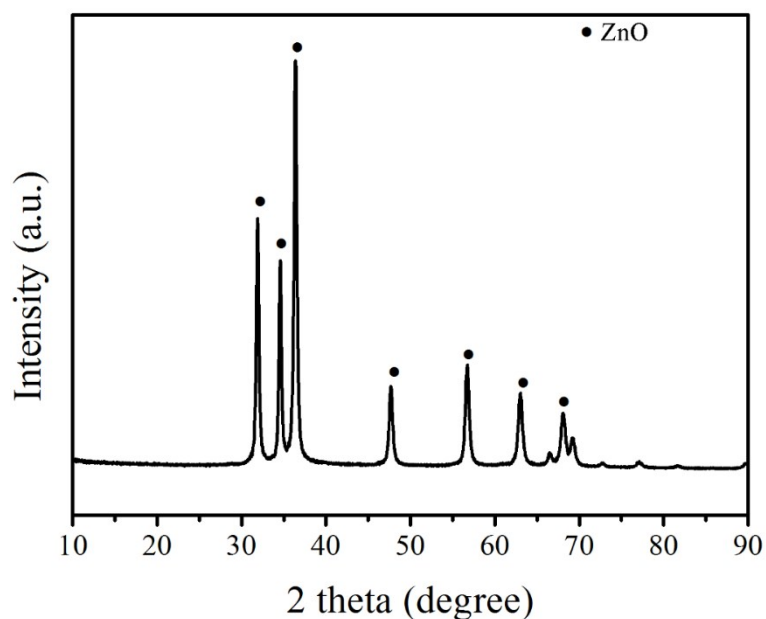


Fig. S4 XRD pattern of ZnO particles from precipitate of ZnO/GF hydrothermal reaction.

Table S1 The intensity of peak presenting different bonding and the intensity ratio between defect peak and total peak

Sample	C-C	C-O	C=O	I_D/I^*
300 μ l	26026.87	8545.20	1669.22	28.18%
500 μ l	51660.02	25635.08	4237.78	36.64%

* $I_D = I_{C-O} + I_{C=O}$; $I = I_{C-C} + I_{C-O} + I_{C=O}$

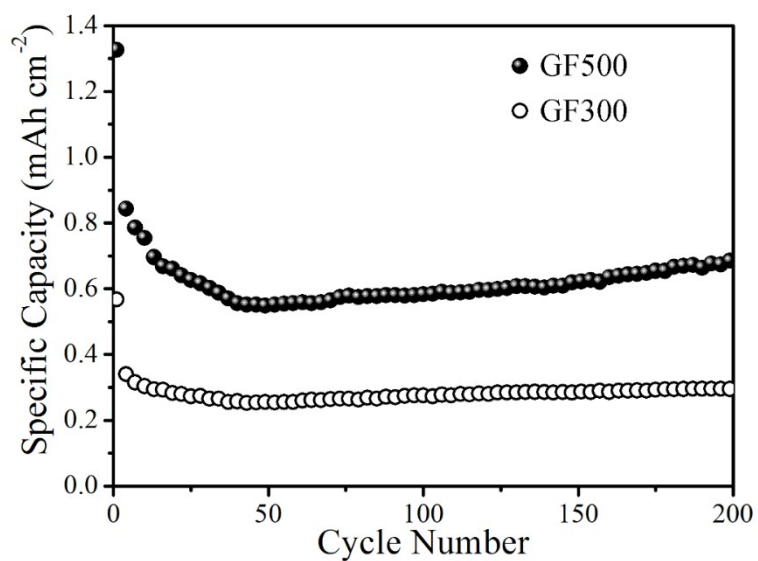


Fig. S5 Cycling performance of ZnO/GF300 and ZnO/GF500 at a current density of 50 μ A cm^{-2} and 80 μ A cm^{-2} , respectively.

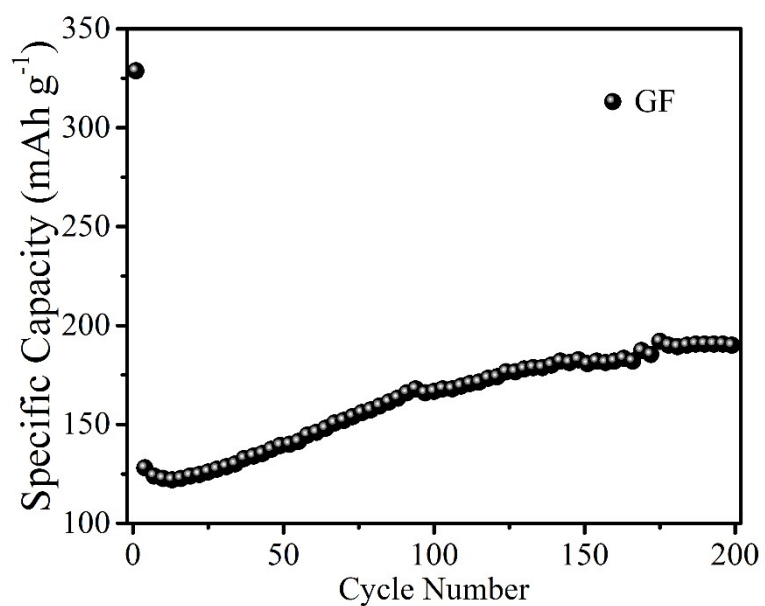


Fig. S6 Cycling performance of pure graphene foam (GF) at a current density of 200 mA g⁻¹.

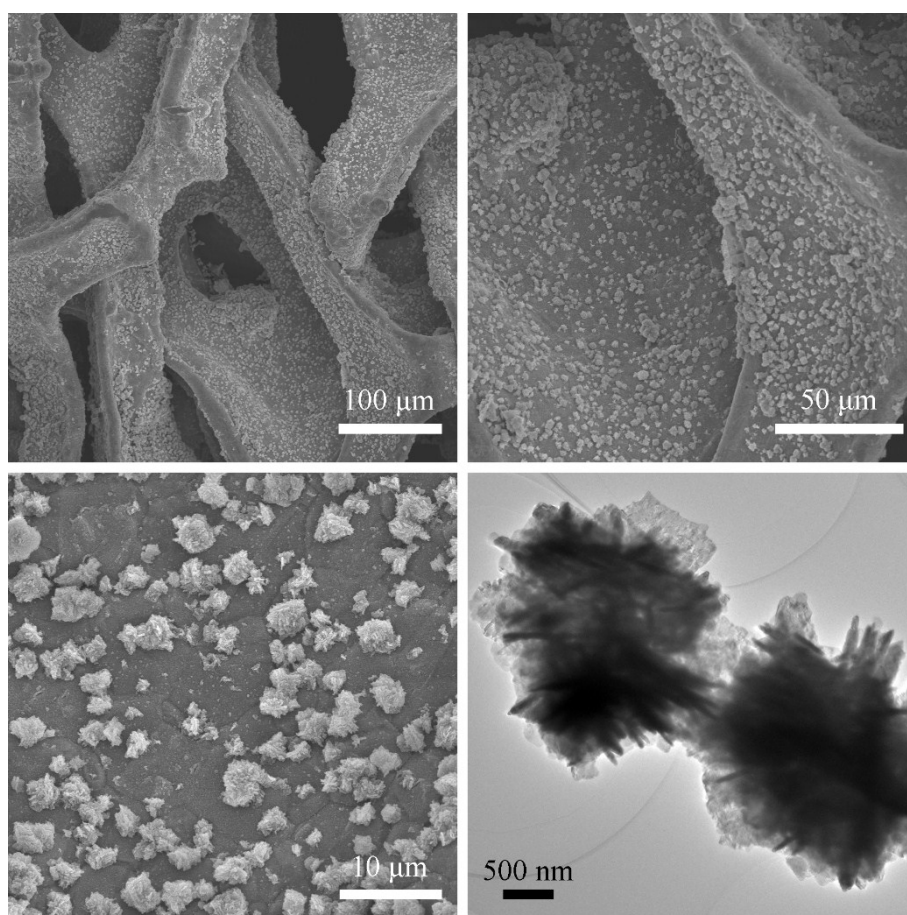


Fig. S7 Morphology and structure of ZnO@GF after 200 cycles at a current density of 200 mA g⁻¹. (a-c) Low- and high-resolution SEM micrographs of ZnO@GF after cycling. (d) TEM micrographs of an integrate ZnO particle with graphene sheet after cycling.

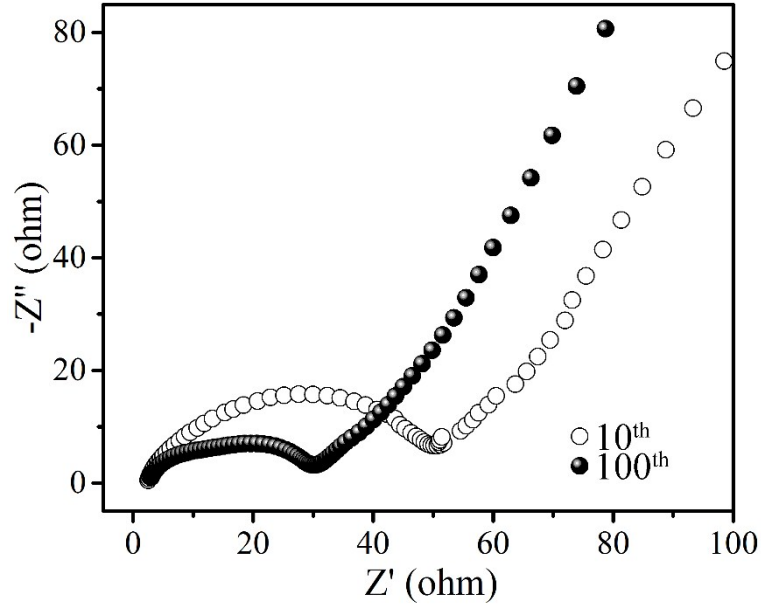


Fig. S8 Nyquist plots of the ZnO@GF electrode after the 10th and the 100th cycling at a current density of 0.2 A g⁻¹.

To further understand the excellent electrochemical performance, the SEM and TEM of ZnO@GF composite were obtained after cycling for 200 cycles at a current density of 0.2 A g⁻¹ (Fig. S7). As shown in SEM images (Fig. S7 a-c), although the morphology of ZnO particles changes, the ZnO particles still uniformly distribute on graphene surface after long cycles, which demonstrates excellent structural stability of ZnO@GF composite. The low resolution TEM image in Fig. S7d further verified that the ZnO particles are firmly attached to graphene films. Moreover, to verify the cycling stability of ZnO@GF electrode, EIS test of the ZnO@GF electrode were carried out after the 10th and the 100th cycling at a current density of 0.2 A g⁻¹ (Fig. S8). It is clearly that two Nyquist plots have similar curve, and semicircle gradually decreases with the cycle number. This fact indicates that the ZnO@GF possesses excellent structural stability and efficient charge transport.

Supplementary Note

Evaluation of specific surface area of 3D GFs and their average number of graphene layers¹

Considering that a nickel foam is fully covered by graphene after CVD growth, the surface area of the GF (SGF) is twice that of the nickel foam template used, which can be measured by nitrogen gas cryosorption (Micromeritics, ASAP2010M). Therefore, the specific surface area of GF and its average number of layers (N) of graphene sheets can be calculated as follows:

$$S_{GF} = 2 \times (S_{Ni} \times W_{Ni}) \quad (1)$$

$$S'_{GF} = \frac{S_{GF}}{W_{GF}} \quad (2)$$

$$N = \frac{S_G}{S_{GF}} \quad (3)$$

where S_{Ni} and W_{Ni} are the specific surface area and weight of the nickel foam template, respectively; S'_{GF} and W_{GF} are the specific surface area and weight of the GF, respectively; $S_G \approx 2600 \text{ m}^2 \text{ g}^{-1}$, corresponds to the theoretical value of the specific surface area of a monolayer graphene.

Reference

- S1. Z. Chen, W. Ren, L. Gao, B. Liu, S. Pei and H. M. Cheng, *Nature materials*, 2011, **10**, 424-428.