# $GeO_2$ Encapsulated in Carbon/Graphene Nanocable for Superior Lithium Storage Performance

Xu Zhang[a,b], Wei Wei[b]*, Kefeng Wang, Guoqing Xiao[a], Maotian Xu[b]*,

[a.] *College of Materials Science and Engineering , Xi'an University of Architecture and Technology, Xi'an 710055, P. R. China*

[b.] *School of Chemistry and Chemical Engineering, Henan Engineering Center of New Energy Battery Materials, Henan Key Laboratory of Bimolecular Reorganization and Sensing, Shangqiu Normal University, Shangqiu 476000, P. R. China. E-mail: weiweizzuli@163.com, xumaotian@163.com.*

## Experimental

### Materials synthesis

In a typical synthesis procedure, polyacrylonitrile (0.5 g, PAN, MW150000, Aldrich) were added in N, N-dimethylformamide (6.0 g, DMF, 99.8%, Aladdin) with vigorous stirring until the solution turn clear. Next, 0.015 g graphene oxide (GO) powder was poured into the above solution and kept stirring for another 2 h. At last, commercial $GeO_2$ powder (0.4 g, Alfa Aesar) were added and keep vigorous stirring overnight in order to ensure the completely dissolve of $GeO_2$. The precursor solution was transferred into a plastic syringe connected to a stainless steel needle (internal diameter: 0.9 mm). By using a precision propeller, the flow rate was set at 0.15 mL $min^{-1}$. A square aluminium foil at a distance of 15 cm to the needle was employed to collect the products. The electrospinning voltage was set at 15 KV by a high voltage power supplier. The as-prepared membrane products with an area of ~ 100 $cm^2$ was first dried in an electric vacuum oven (80 ˚C, 10 h) and then annealed in a tube furnace (700 ˚C, 6 h) with a heating rate of 10 ˚C $min^{-1}$ (Ar, 99.999%). The final $GeO_2$/nanocable product exhibits black membrane appearance. $GeO_2$/nanofiber were prepared in the same procedure with the absence of GO powder.

### Characterizations

The morphologies and microstructures of the samples were characterized by using scanning electron microscopy (SEM, Zeiss Gemini-500), transitions electron microscopy (TEM, JEOL JEM-2100F) accompany with selected area electron diffraction (SAED). The elemental maps of $GeO_2$/nanocable were obtained by using TEM energy dispersive spectrum (EDS). The surface elements of samples were analyzed using an X-ray photoelectron spectroscopy (XPS, Kratos Axis Ultra DLD); the samples' X-ray diffraction patterns (XRD, Bruker, D 8) was recorded between 10˚ and 90˚ at a scan rate of 6˚ $min^{-1}$. The Brunauer-Emmett-Teller (BET) specific surface area and pore size distribution were determined by Nitrogen adsorption-desorption method (Nova 2200e). Raman spectra were collected by LabRAM HR800 system at the excitation wavelength of 532 nm in the range of 50 ~ 3500 $cm^{-1}$. TGA was performed on a Pyris Diamond TG/DTA (PerkinElemer Inc., USA) instrument. Samples were heated from room temperature to 1000 ˚C with a heating rate of 10 ˚C $min^{-1}$ in oxygen atmosphere.

### Electrochemical measurements

$GeO_2$/nanocable and $GeO_2$/nanofiber membranes were cut into 14 mm disks with a mass load of 5 mg and directly used as anode electrodes for LIBs. The CR2032 coin-type cells were assembled with lithium as the reference electrode and polypropylene (PP) micro-porous film as separator in an Ar-filled glove box. 1 M $LiPF_6$ in ethylene carbonate (EC)–diethyl carbonate (DEC) (1: 1 by volume) was used as the electrolyte. Cyclic voltammetric (CV) tests were performed on an electrochemical workstation (Shanghai Chenhua, 660E) at a scan rate of 0.2 mV $s^{-1}$ between 0.0 and 3.0 V. The galvanostatic charge/discharge cycling tests were carried out between 0 and 3.0 V at different current densities on a LAND CT2001A battery tester. Electrochemical impedance spectroscopy (EIS) technique was performed on the same type electrochemical workstation as above at an open circuit voltage with an amplitude of 10 mV, in the frequency range from 100 kHz to 0.01 Hz. In the EIS study, $GeO_2$/nanocable and $GeO_2$/CNF were used as working electrodes with Li foils as the anode and reference electrode. The cells were charged or discharged to a given potential at 200 mAh·$g^{-1}$ and then balanced at the potential for 2 h prior to testing.

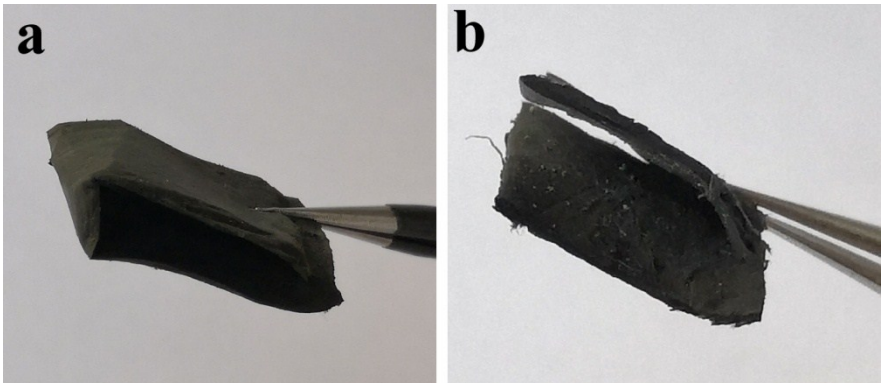


Figure S1. Flexibility comparison between $GeO_2$/nanocable and $GeO_2$/CNF.

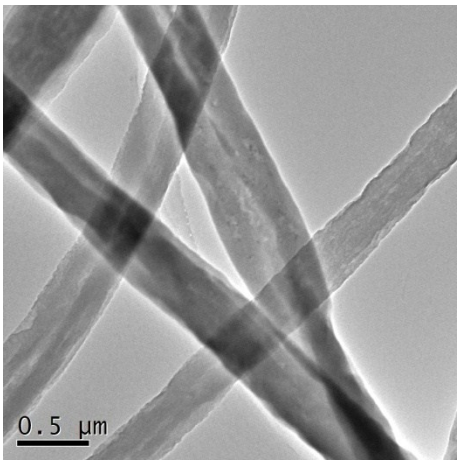


Figure S2. TEM image of the prepared $GeO_2$/CNF sample.

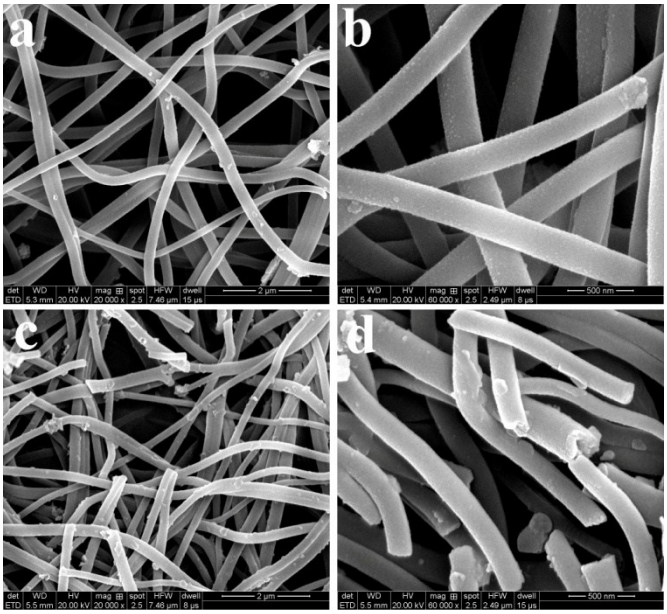


Figure S3. SEM images of (a, b) $GeO_2$/nanocable and (c, d) $GeO_2$/CNF electrodes after 10 cycles. From the SEM images it can be seen that all of the $GeO_2$/nanocable's basic structure maintained intact, while fracture occurred in most of the $GeO_2$/CNF.

Table S1 Parameters of Equivalent Electrical Circuits corresponding to Nyquist plots of $GeO_2$/nanocable and $GeO_2$/CNF electrodes in Figure 4e.

| Sample | Rs (Ω) | Rct (Ω) | CPE-T (F) | CPE-P | W-R (Ω) | W-T(s) | W-P |
|---|---|---|---|---|---|---|---|
| $GeO_2$/nanocable | 1.46 | 135 | $2.28*10^{-4}$ | 0.73 | 33.8 | 0.30 | 0.42 |
| $GeO_2$/CNF | 1.61 | 331 | $7.96*10^{-6}$ | 0.78 | 81.0 | 0.22 | 0.44 |