Supporting Information

Triple-coaxial Electrospun Amorphous Carbon Nanotubes with Hollow Graphitic Carbon Nanospheres for High-Performance Li Ion Batteries

Yuming Chen,^a Zhouguang Lu,^a Limin Zhou,^{*a} Yiu-Wing Mai,^{a,b} and Haitao Huang^c

^aDepartment of Mechanical Engineering, The Hong Kong Polytechnic University, Hong Kong, China

^bCentre for Advanced Materials Technology (CAMT), School of Aerospace, Mechanical and Mechatronics Engineering J07, The University of Sydney, NSW 2006, Australia ^cDepartment of Applied Physics, The Hong Kong Polytechnic University, Hong Kong, China Email: mmlmzhou@inet.polyu.edu.hk

Preparation of precursor solution for electrospinning. Polyacrylonitrile (PAN, MW = 150

000, Aldrich) solution with a concentration of 6 wt.% was used as the middle fluid. The solution was then prepared by dissolving 1 g PAN in 16.67 g dimethylformamide (DMF) solvent at 80 °C with vigorous stirring. The outer fluid was a mixture of polyvinyl pyrrolidone (PVP, 0.5 g, MW ~1 300 000, Aldrich) and nickel acetate (Ni(Ac)₂·4H₂O, 2 g, Advtechind) in 13 mL DMF. Mineral oil (Aldrich) was employed as the inner fluid.

Fabrication of coaxial PVP/Ni(Ac)₂/PAN@Oil composite nanofibers. The set-up for triple-coaxial electrospinning is shown in Fig. 1a. In brief, the spinneret consists of novel triple stainless-steel tubes with diameters of 1.5 mm (outer), 0.91 mm (middle) and 0.61 mm (inner). The area of all the spinnerets was fixed at 0.0029 cm². The distance between cathode and

anode was kept at 20 cm and a high voltage of 17 kV was applied to the syringe needle tip and the metal collector by using the power supply. Typical feeding rates for the triple solutions were set at 0.02 mm/min (KATO Tech Co., Ltd). All experiments were conducted at room temperature in air.

Preparation of amorphous carbon nanotubes decorated with hollow graphitic carbon nanospheres. The as-collected electrospun fibers were stabilized in $H_2(5\%)/N_2(95\%)$ at 250 °C for 2 h, and then carbonized in a tube furnace at 600 °C in H_2/N_2 for 3 h to obtain amorphous carbon nanotubes decorated with Ni nanoparticles encapsulated in graphitic carbon nanospheres (ACNNNGCNs). The heating rate was fixed at 5 °C/min. Resultant samples were further treated by HCl at room temperature to obtain amorphous carbon nanotubes decorated with hollow graphitic carbon nanospheres (ACNHGCNs).

Characterization. The composition and crystal structure of the obtained materials were characterized by X-ray diffraction (XRD, Philips, X'Pert Pro MPD). The morphology of the nanotubes was examined using a JEOL 6300F field-emission scanning electron microscope (JEOL, Japan) operated at 5 kV. High -resolution transmission electron microscopy (HRTEM) was performed using a JEOL 2010 TEM (JEOL, Japan) operated at 220 kV with Energy-dispersive X-ray spectroscopy (EDS). Raman spectroscopy of all samples was obtained by a Jobin-Yavon T6400 micro-Raman system with an Ar⁺ laser. The pore-size distribution was calculated using the Barrentt-Joyner-Halenda (BJH) method (Micromeritics,

ASAP2020).

Electrochemical characterization. The ACNHGCNs (80 wt.%), carbon black (10 wt.%) and poly(vinyl difluoride) (10 wt.%, PVDF) binder in N-methlpyrrolidone (NMP) were mixed homogeneously. The obtained slurry was pasted on copper foil using the doctor blade technique to prepare the electrode film, followed by dehydration in a vacuum oven for 10 h. For comparison, the ACNNNGCNs and amorphous carbon obtained from PAN with treatment at 600 °C for 3 h in H_2/N_2 electrodes were prepared with the same procedure. Electrochemical test cells were assembled in an argon-filled glove-box by the coated copper disk as the working electrode, lithium metal foil as the counter/reference electrode, and 1 M solution of LiPF₆ in a 1:1 vol/vol mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) as the electrolyte. Celgard 2400 film was used as a separator film. Charge (lithium insertion) and discharge (lithium extraction) were conducted by using an Arbin automatic battery cycler at several different current densities between the cut-off potentials of 0 and 3 V. The ac impendence spectra were carried out on a CHI 660C electrochemical workstation by applying a sine wave with an amplitude of 5.0 mV over the frequency range from 100 kHz to 0.01 Hz



Fig.S1 FESEM image of ACNHGCNs.



Fig. S2 An EDS spectrum of ACNNNGCNs. The sample was dispersed on Cu film to quantify the Ni and C concentration. Detailed composition results are shown in Table S1.

| Elements | Weight % | Atomic % |
|----------|----------|----------|
| С | 82.9 | 95.95 |
| Ni | 17.1 | 4.05 |

Table S1 EDS composite profile of ACNNNGCNs.



Fig. S3 X-ray diffraction patterns of (a) ACNNNGCNs, (b) ACNHGCNs and (c) amorphous carbon. The diffraction peaks from Ni (JCPES; NO. 45-1027) are indexed in the X-ray patterns.

As shown in Fig.S3, the diffraction peaks at *circa* 44.2°, 51.5° and 76° can be assigned to the

(111), (200) and (220) diffractions of cubic Ni (JCPES; NO. 45-1027), respectively. After acid treatment, the diffraction peaks of Ni disappear, while the peaks at 24.95° and 44.75° corresponding to the (002) and (101) diffractions of carbon, still exist.



Fig. S4 HRTEM image of the wall of ACNHGCNs.



Fig. S5 Raman spectra of (a) amorphous carbon, (b) ACNNNGCNs and (c) ACNHGCNs.

Fig. S5 shows the Raman spectra of all the samples. Here, two bands are seen at ~1340 cm⁻¹ and 1580 cm⁻¹, which are assigned to the D and G bands of carbon, respectively. The D-band is assigned to structural defects and disorders, and the G-band to the vibration of sp²-bonded carbon in a 2D hexagonal lattice, i.e., C=C bond stretching.^{1,2} The intensity ratio (*R*) of D to G ($R = I_D/I_G$) indicates the degree of disorder of the carbon surface. In amorphous carbon, we obtained a large intensity of the D-band when compared to the G-band, thus indicating that the obtained carbon materials consist mainly of amorphous carbon. However, a

high intensity of the G-band and a low R value (~1) reveal that ACNNNGCNs have a higher order than the amorphous carbon, showing a large increase of the degree of graphitic crystalline structure.³ This phenomenon is similar for ACNHGCNs.



Fig. S6 An EDS spectrum of ACNHGCNs. The sample was dispersed on Cu film to quantify the Ni and C concentration. Detailed composition results are shown in Table S2.

| Elements | Weight % | Atomic % |
|----------|----------|----------|
| С | 98.4 | 99.66 |
| Ni | 1.6 | 0.34 |

Table S2 EDS composite profile of ACNHGCNs.



Fig. S7 Cycling performance of ACNNNGCNs and amorphous carbon electrodes at a current density of 50 mA/g between 3 and 0 V *versus* Li⁺/Li.



Fig. S8 (a) TEM and (b) HRTEM images of amorphous carbon.

Fig. S8a shows the smooth surface of carbon nanofibers with fiber diameter ~180 nm. Fig.S8b shows the HRTEM image of the carbon nanofibers. Clearly, the carbon is amorphous, which is similar to the results of XRD and Raman scattering.



Fig. S9 Cyclic voltammograms of ACNHGCNs in LiPF_6 with Li as counter and reference electrode at a scan rate of 0.1 mV/s.



Fig. S10 The volumetric capacity of ACNHGCNs electrodes cycled at a current density of 50 mA/g between 3 and 0 V *versus* Li^+/Li .



Fig. S11 Raman spectra of ACNHGCNs (a) before and after (b) 5, and (c) 100 charge/ discharge cycles.

As shown in Fig.S11, the R value ($R = I_D/I_G$) increases from ~1 to 1.28, indicating the

decrease of crystallinity of ACNHGCNs after charge/discharge cycles.³



Fig. S12 Pore size distribution of ACNNNGCNs calculated using the BJH method.

Fig. S12 reveals that ACNNNGCNs also exhibit two types of pore sizes between 1 and 5 nm, similar to those of ACNHGCNs, showing that the peaks between 1 and 5 nm are attributed to the calcination of the polymer precursors.

References

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