

Supporting Information

Hollow-tunneled Graphitic Carbon Nanofibers Through Ni-diffusion-induced Graphitization as High-performance Anode Materials

Yuming Chen,^a Xiaoyan Li,^a Xiangyang Zhou,^{b*} Haimin Yao,^a Haitao Huang,^c Yiu-Wing Mai^{ad}
and Limin Zhou^{a*}

^a Department of Mechanical Engineering, The Hong Kong Polytechnic University, Hong Kong, China. Tel: 852-2766 6663; Fax: 852-2365 4703 E-mail: mmlmzhou@polyu.edu.hk .

^b School of Metallurgy and Environment, Central South University, Changsha, Hunan, China. E-mail: hncsyjy308@163.com.

^c Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong, China.

^d Centre for Advanced Materials Technology (CAMT), School of Aerospace, Mechanical and Mechatronics Engineering J07, The University of Sydney, NSW 2006, Australia.

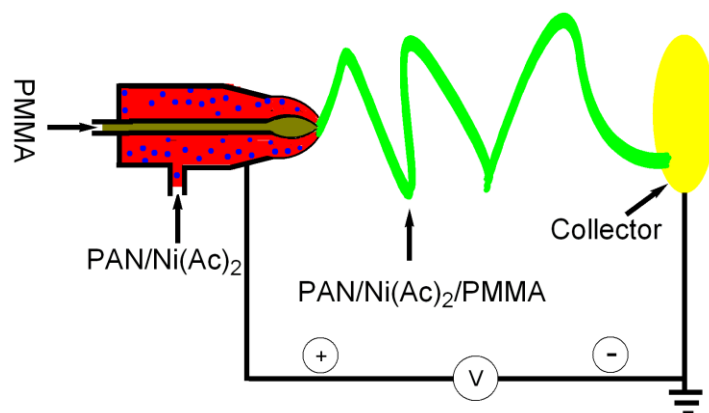


Figure S1. Schematic illustration of the coaxial electrospinning technique used to prepare the PAN/Ni(Ac)₂/PMMA composite nanofibers.

Table S1 shows various materials from different calcining treatments

	Precursor	Vacuum	Pumping Speed at T	Heating time at T
Sample 1	PAN/Ni(Ac) ₂	— (Ar)	—	6 h, 700°C
Sample 2	NCNNs	~ -750 Torr	Quick or slow, room T	0.5 h, 700°C
Sample 3	NCNNs	~ -750 Torr	Slow (0.5 h), 700°C	—
Sample 4	NCNNs	~ -375 Torr	Quick, 700°C	0.5 h, 700°C
Sample 5	PAN/Ni(Ac) ₂	~ -750 Torr	Quick, 700°C	6 h, 700°C
Sample 6	PAN/Ni(Ac) ₂ /PMMA	~ -750 Torr	Quick, 700°C	6 h, 700°C

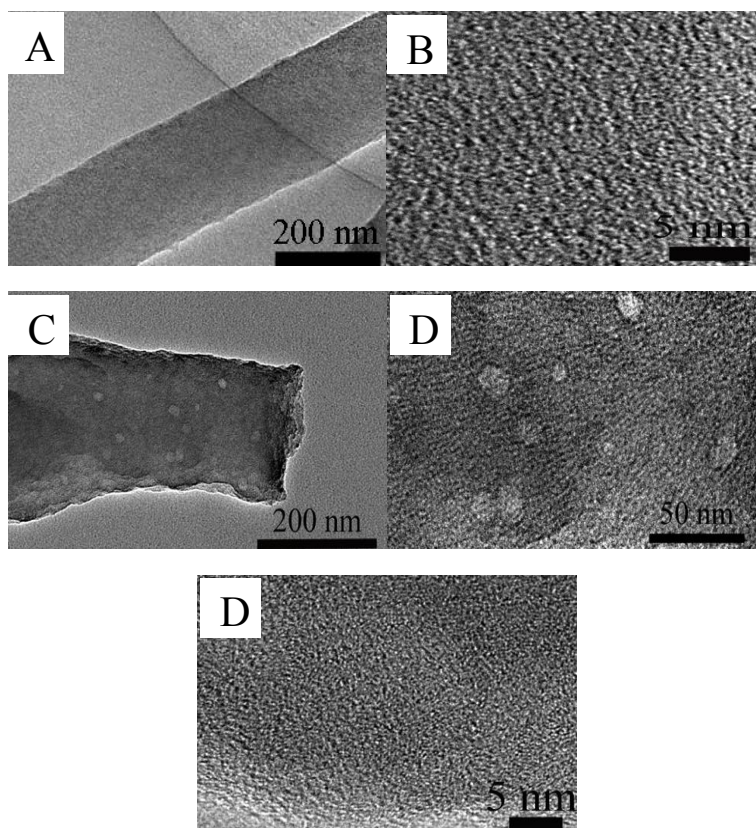


Figure S2. (A, B) TEM and HRTEM images of amorphous carbon nanofibers (ACNFs) by calcining PAN nanofibers in Ar at 700 °C for 6 h. (C, D) TEM images of porous amorphous carbon nanofibers (PACNs) by calcining PAN/PMMA composite nanofibers in Ar at 700 °C for 6 h at low- and high- magnification, respectively. (E) HRTEM image of PACNs.

In Figure S2A, TEM image of a single carbon nanofibre shows a smooth surface. The HRTEM image of the sample reveals that the carbon is amorphous (Figure S2B). It is clear that some pores exist in carbonaceous materials by calcining PAN/PMMA composite nanofibers (Figure S2C, D). The prepared porous carbonaceous materials are amorphous carbon (Figure S2E).

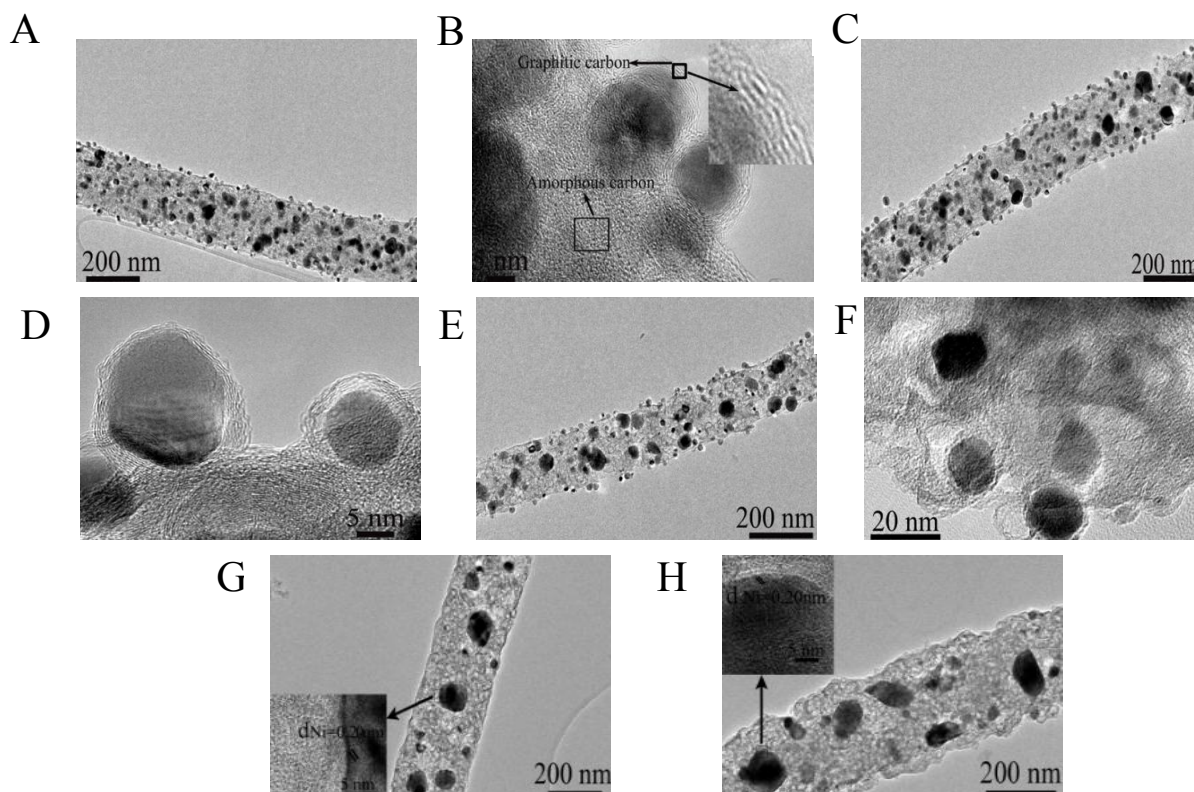


Figure S3. TEM and HRTEM images of various typical nanofibers: (A, B) by adjusting the vacuum of tube furnace to ~ -750 Torr by pumping at room temperature and then calcining the N-doped carbon/Ni nanofibers (NCNNs) at 700°C for 0.5 h; (C, D) by calcining NCNNs at 700°C with subsequent slow (0.5 h) pumping to a final vacuum of ~ -750 Torr; (E, F) by calcining NCNNs at 700°C with subsequent rapid pumping to a final of ~ -375 Torr, which was then maintained for 0.5 h; by directly calcining (G) PAN/Ni(Ac)₂ composite nanofibers or (H) PAN/Ni(Ac)₂/PMMA composite nanofibers at 700°C with sudden pumping to a final vacuum of ~ -750 Torr, maintained for 6 h and controlled by rapidly switching pumping valve on and off.

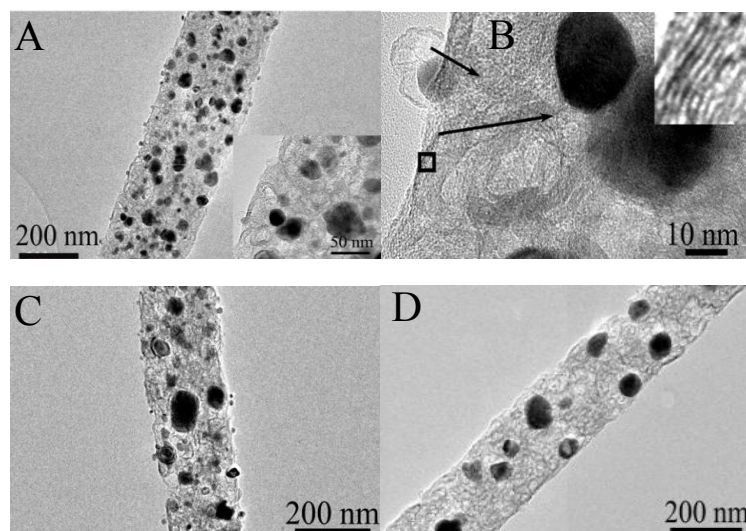


Figure S4. TEM and HRTEM images of NHTGCNN by calcining NCNN at 700 °C with subsequent sudden pumping to a final vacuum of ~ -750 Torr and maintained for 0.5 (A,B), 4 (C), and 6 h (D), respectively.

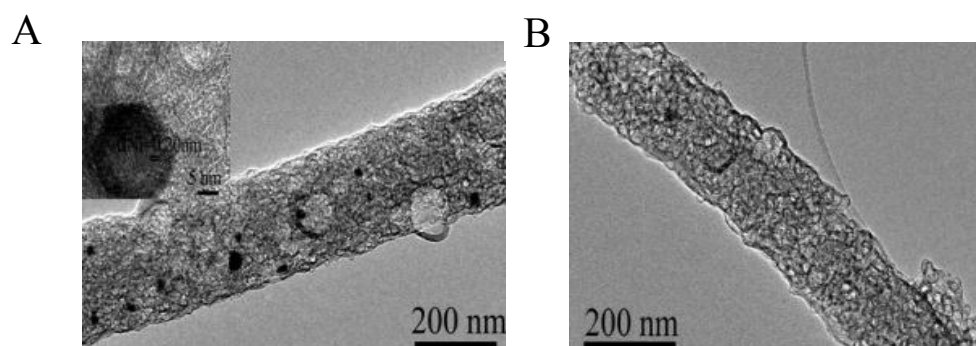


Figure S5. TEM and HRTEM images of NHTGCNs from NHTGCNNs treated with HNO_3 . NHTGCNNs were from PAN/Ni(Ac) $_2$ composite nanofibers (A) or PAN/Ni(Ac) $_2$ /PMMA composite nanofibers (B), respectively.

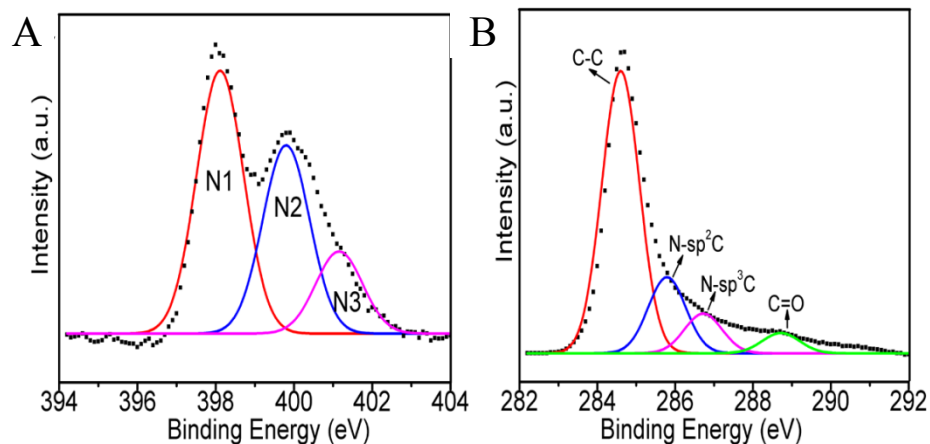


Figure S6 (A) N1s XPS spectra of ACNFs. (B) C1s XPS spectra of ANHTGCNs.

As shown in Figure S6A, the N1s peak of ACNFs can be split into three Lorentzian peaks at ~ 398.6 , 400.1 and 401.4 eV, representing pyridinic (N1), pyrrolic (N2), and graphitic (N3) type of N atoms.¹ The N binding configuration includes 49.9 % pyridinic N (N1), 42.4 % pyrrolic N (N2) and 7.7 % graphitic N (N3). Figure S6B shows the C1s XPS spectra of ANHTGCNs. The C1s core can be resolved into four peaks at ~ 284.6 , 285.8 , 286.7 , and 288.7 eV, which are attributed to $\text{sp}^2\text{C-sp}^2\text{C}$, $\text{N-sp}^2\text{C}$, $\text{N-sp}^3\text{C}$, and C=O bonds, respectively.² The small C=O peak is due to the oxidation by HNO_3 .

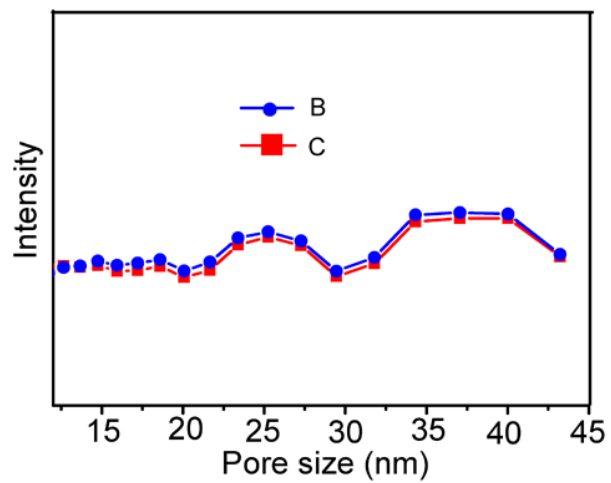


Figure S7. Pore size distribution of sample B by calcining PAN/PMMA/Ni(Ac)₂ composite nanofibers and sample C from sample B after Ni diffusion.

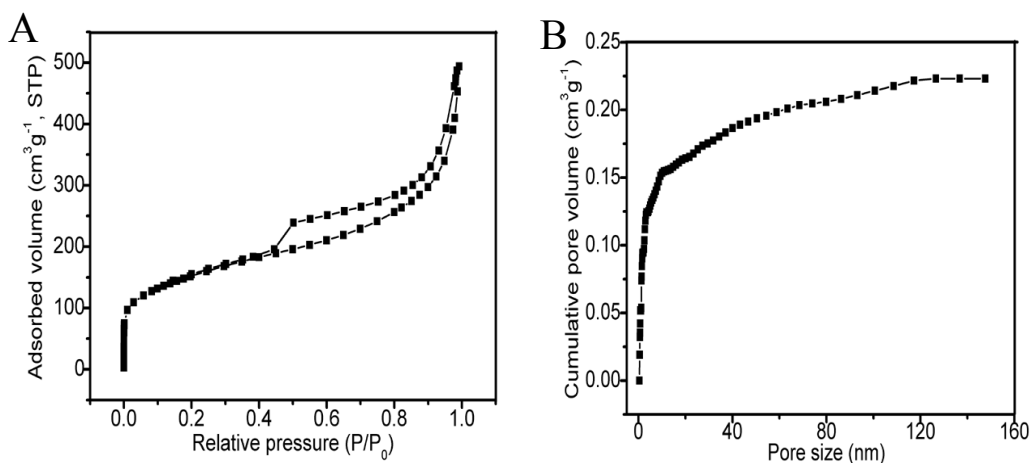


Figure S8 (A) Nitrogen adsorption-desorption isotherms and (B) cumulative pore volume of ANHTGCNs.

Figure S8A shows that the adsorption-desorption isotherm curves of ANHTGCNs possess type IV isotherms with distinct hysteresis loops, which are characteristics of the porous adsorption-desorption processes.³ The cumulative pore volume of ANHTGCNs from pores smaller than 2 nm reaches ~42.4 % of the total pore volume. Pores larger than 2 nm account for 57.6 % of the total volume of ANHTGCNs (see Figure S8B).

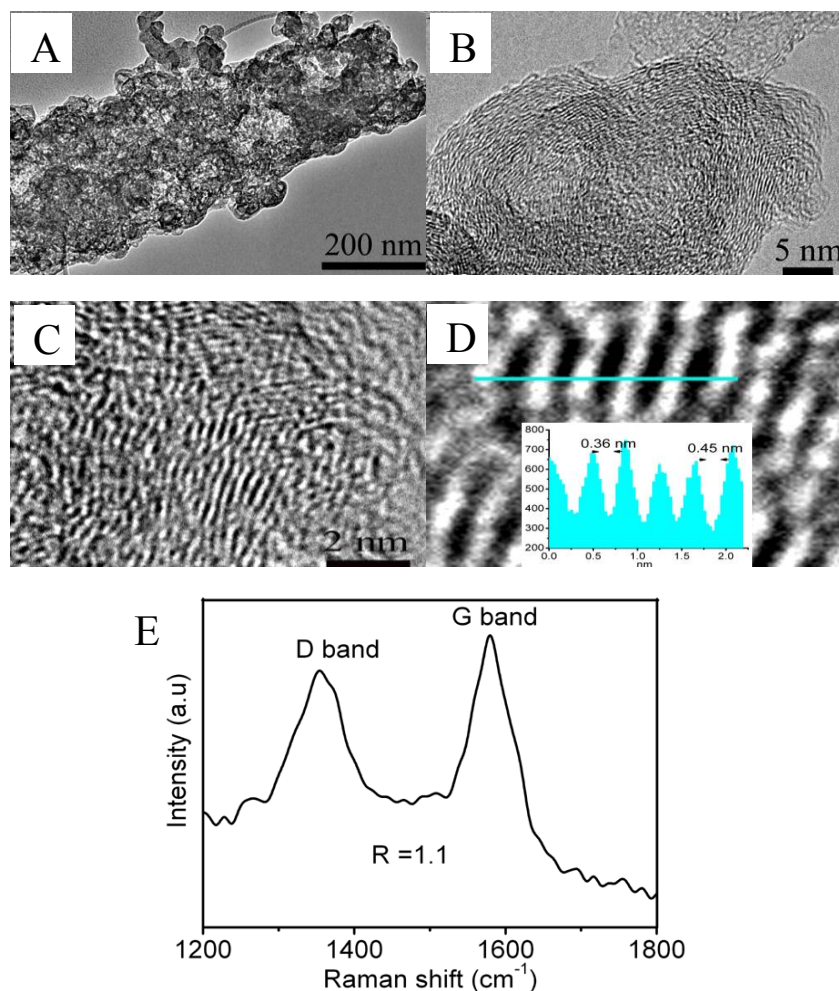


Figure S9. Characterization of ANHTGCNs after full lithiation. (A) TEM image of ANHTGCNs. (B) HRTEM image of the hollow structure, showing a little disorder. (C) HRTEM image of the wall of the hollow structure, indicating more disordered graphene sheets and defects. (D) HRTEM image of enlarged d -spacing distribution of the (002) plane of carbon and line profiles (inset) extracted from the image. (E) Raman of the ANHTGCNs after lithiation.

Figure S9 shows the morphology and structure of ANHTGCNs after full lithiation. It can be seen that the morphology of the hollow graphitic carbon structure becomes a little vague after full lithiation (Figure S9A, B). The R value decreases from ~ 1.84 to 1.1, indicating a decrease of crystallinity of ANHTGCNs after lithiation (Figure S9E). The wall of the hollow structure shows more disordered graphene sheets and defects (Figure S9C). Figure S9D shows the increased d -spacing distance of the (002) plane of the inter-wall carbon. These show that the lithium ions have diffused from the outer space of ANHTGCNs into the inner space of the ANHTGCNs through the defects.

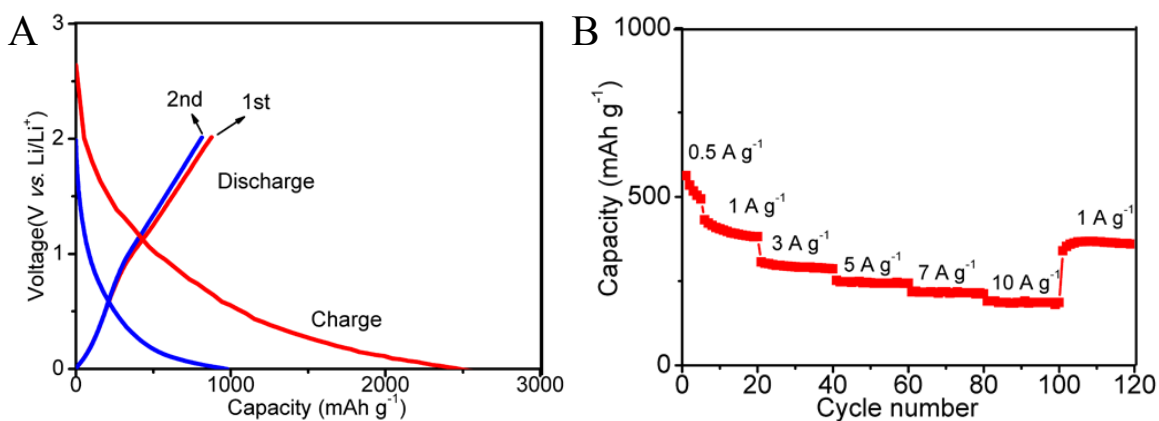


Figure S10. (A) Charge-discharge voltage profiles of the ANHTGCN electrode at 0.1 A g⁻¹ and (B) capacity of the ANHTGCN electrode at various rates from 0.5 A g⁻¹ to 10 A g⁻¹, tested between 2 and 0 V *versus* Li⁺/Li.

References

- 1 H. B. Wang, C. J. Zhang, Z. H. Liu, L. Wang, P. X. Han, H. X. Xu, K. J. Zhang, S. M. Dong, J. H. Yao and G. L. Cui, *J. Mater. Chem.*, 2011, **21**, 5430-5434.
- 2 A. L. M. Reddy, A. Srivastava, S. R. Gowda, H. Gullapalli, M. Dubey and P. M. Ajayan, *ACS Nano*, 2010, **4**, 6337-6342.
- 3 L. L. Zhang, X. Zhao, M. D. Stoller, Y. W. Zhu, H. X. Ji, S. Murali, Y. P. Wu, S. Perales, B. Clevenger and R. S. Ruoff, *Nano Lett.*, 2012, **12**, 1806-1812.