## **Supporting Information**

## Ultrahigh Capacity and Superior Stability of Three-Dimensional Porous Graphene Networks Containing In Situ Grown Carbon Nanotube Clusters as Anode Material for Lithium-Ion Batteries

Shizhi Huang, Jingyan Wan, Zhiyi Pan, Jinliang Zhu\* and Pei Kang Shen\*

Guangxi Key Laboratory of Electrochemical Energy Materials, Collaborative Innovation Center of Renewable Energy Materials, and State Key Laboratory of Processing for Non-ferrous Metal and Featured Materials, Guangxi University, Nanning, 530004, PR China

\* Corresponding author. Tel.: +86 07713237990; E-mail: jlzhu85@163.com (Jinliang Zhu); pkshen@gxu.edu.cn (Pei Kang Shen).



Fig. S1 XRD patterns of CNTs@3DG fabrications at different temperatures.



**Fig. S2** (a-c) SEM and (d-f) TEM images of 3DG, marked region in e is corresponding to f.



Fig. S3 SEM images of (a) CCNTs and (b) 3DG+CCNTs.



Fig. S4 XPS spectra of (a) CNTs@3DG and (b) C1s.

In this XPS analysis, the atomic percentages of C1s and O1s are 92.57 and 6.34%, respectively.



**Fig. S5** Voltage profiles of (a) 3DG, (b) 3DG+CCNTs, and (c) CCNTs at a current rate of 0.1 A  $g^{-1}$  with the voltage range from 0.01 V to 3 V (*vs.* Li/Li<sup>+</sup>).



**Fig. S6** Voltage profiles of CNTs@3DG at current rates of (a) 1 A g<sup>-1</sup>, (b) 2 A g<sup>-1</sup> with the voltage range from 0.01 V to 3 V (*vs.* Li/Li<sup>+</sup>).



Fig. S7 Cyclic properties of highly CNTs@3DG anode masses of 2.8, 3.2 and 4.6 mg from 0.01 V to 3 V (*vs.* Li/Li<sup>+</sup>) at a current of 100 mA  $g^{-1}$ .



**Fig. S8** Electrochemical impedance spectroscopies (EIS) of CNTs@3DG, 3DG, 3DG+CCNTs and CCNTs after 200 cycles. The insertion in (a) is corresponding to the equivalent circuit.



**Fig. S9** SEM images of (a, a1) 3DG, (b, b1) 3DG+CCNTs, and (c, c1) CCNTs after discharge/charge 200 cycles.

**Table S1.** Performance comparisons of CNTs@3DG and other typical carbon-based

 anode materials for lithium ions batteries.

Materials	Current	Reversible	Decay rate	Ref.
	Densities	Capacity	of per cycle	
	(mA g <sup>-1</sup> )	$(mA h g^{-1})$		
Nanoporous carbon	50	375	0.2%	[1]
nanotube				
Graphene-multiwalled	90	813	0.41%	[2]
carbon nanotubes hybrid				
Graphene	100	1172.5	0.17%	[3]
oxide/graphite/carbon				
nanotube composites				
Graphene-winged carbon	100	644	0.28%	[4]
nanotubes				
N-doped Graphene Sheets	50	1043	0.54%	[5]
Nitrogen and	100	1073	0.57%	[6]
fluorine co-doped				
graphene				
Graphite/Graphene	744	500	0.025%	[7]
Nanosheets				
Graphene/N-doped	100	1100	0.19%	[8]
carbon				
Hierarchical carbon	100	1021	0.50%	[9]
nanocages				
Biomass derived carbon	100	742	1.11%	[10]
nanoparticle				
	100	1132	0.03%	
CNTs@3DG	1000	720	0.017%	This
				work
	2000	663	0.025%	

## References

- 1 X. Li, J. Yang, Y. Hu, J. Wang, Y. Li, M. Cai, R. Li and X. Sun, *J. Mater. Chem.*, 2012, **22**, 18847–18853.
- 2 B. P. Vinayan, R. Nagar, V. Raman, N. Rajalakshmi, K. S. Dhathathreyan and S. Ramaprabhu, *J. Mater. Chem.*, 2012, **22**, 9949–9956.
- 3 B. Li, N. Zhang and K. Sun, Small, 2014, 10, 2039–2046.
- 4 M. Ye, C. Hu, L. Lv and L. Qu, J. Power Sources, 2016, 305, 106–114.
- 5 Z. -S. Wu, W. Ren, L. Xu, F. Li, and H. -M. Cheng, ACS Nano, 2011, 5, 5463–5471.
- 6 S. Huang, Y. Li, Y. Feng, H. An, P. Long, C. Qin and W. Feng, *J. Mater. Chem. A*, 2015, **3**, 23095–23105.
- 7 M. Agostini, S. Brutti and J. Hassoun, ACS Appl. Mater. Interfaces, 2016, 8, 10850–10857.
- 8 X. Liu, J. Zhang, S. Guo and N. Pinna, J. Mater. Chem. A, 2016, 4, 1423-1431.
- 9 Z. Lyu, L. Yang, D. Xu, J. Zhao, H. Lai, Y. Jiang, Q. Wu, Y. Li, X. Wang and Z. Hu,

Nano Res., 2015, 8, 3535–3543.

10 R. R. Gaddam, D. Yang, R. Narayan, K. Raju, N. A. Kumar and X. S. Zhao, *Nano Energy*, 2016, 26, 346–352.