

**Ultra-uniform CuO/Cu in nitrogen-doped carbon nanofibers as a stable anode for Li-ion batteries**

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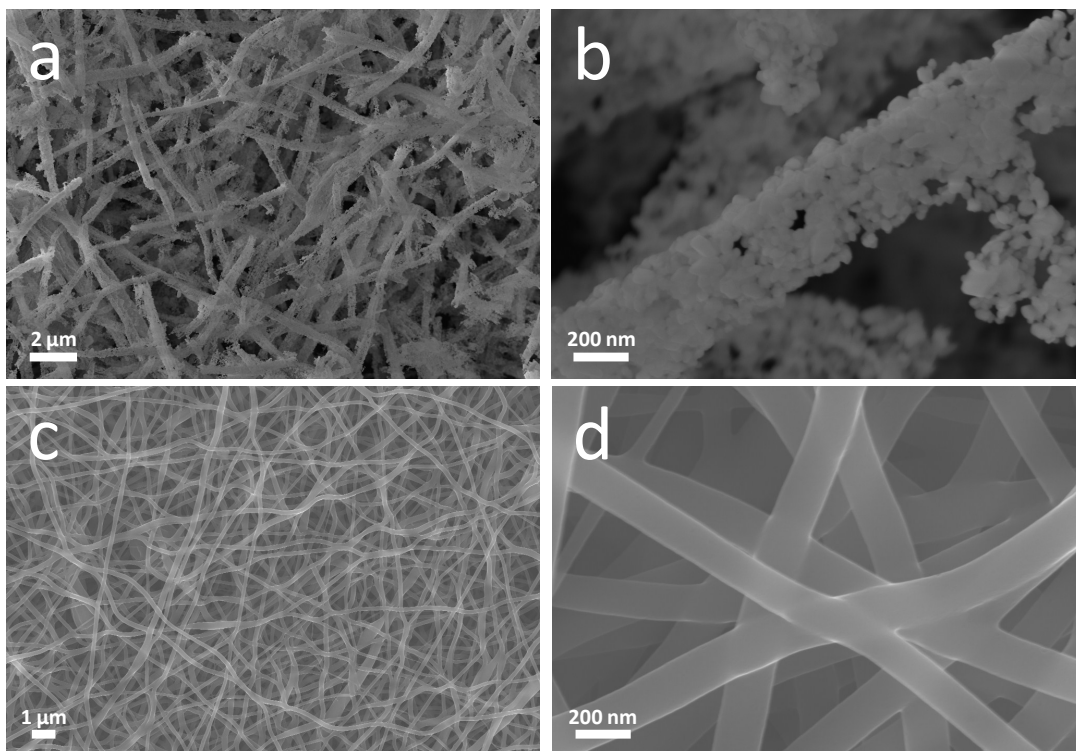
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**Fig. S10.** Photographs of a LED lighted by one coin cell prepared from CuO/Cu/C NFs electrode. a) Off-state; b) on-state; c) durable light in daylight; d) bright yellow light in darkness.

**Fig. S11.** a) SEM image and b) high magnification SEM image of flexible CuO/Cu/C NFs electrode before 100 cycles; c) SEM image and d) high magnification SEM image of flexible CuO/Cu/C NFs electrode after 100 cycles.

**Fig. S12.** Nyquist plots for CuO/Cu/C NFs, bare C NFs and pure CuO NFs.

**Table S1.** Comparison of the electrochemical properties of CuO/Cu/C NFs with recently reported carbon-based nanostructures and CuO/C composites anode materials for LIBs.



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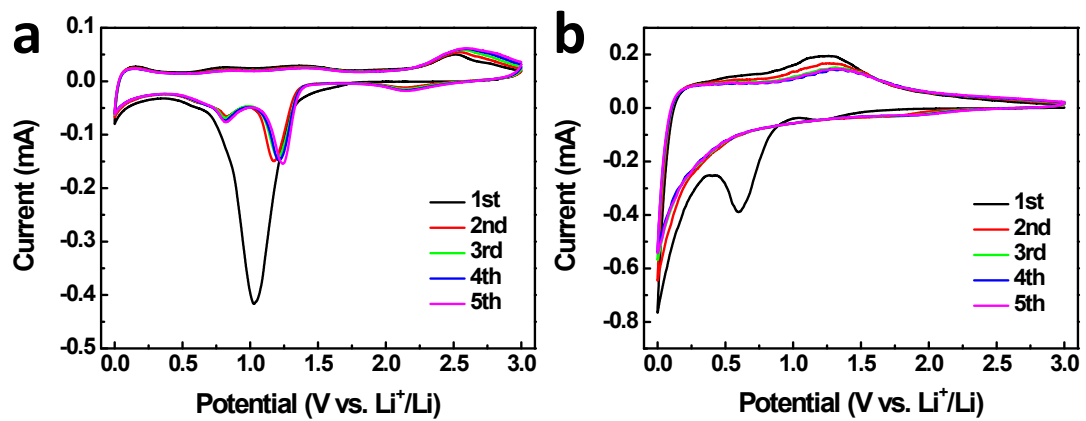
### Theoretical calculation of Cu in CuO/Cu/C NFs

As Cu element comes from copper acetate monohydrate, carbon is derived from pyrolysis of PAN with high carbon yields (about 70%<sup>1</sup>). The percentage content of Cu element is calculated as follows:

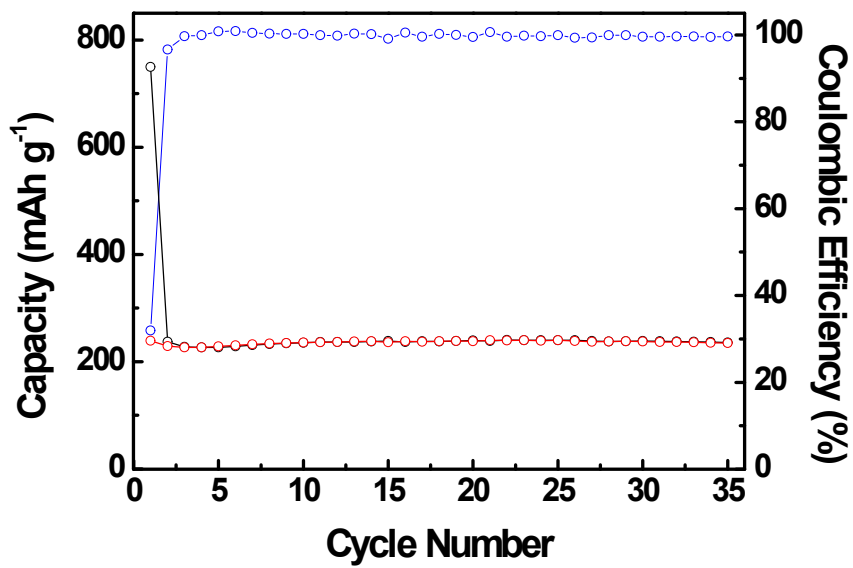
$$\begin{aligned} m_{Cu} &= n_{Cu(CH_3COO)_2 \cdot H_2O} \times M_{Cu} = \frac{m_{Cu(CH_3COO)_2 \cdot H_2O}}{M_{Cu(CH_3COO)_2 \cdot H_2O}} \times M_{Cu} & (1) \\ &= \frac{0.28 \text{ g}}{199.65 \text{ g} \cdot \text{mol}^{-1}} \times 63.55 \text{ g} \cdot \text{mol}^{-1} = 0.089 \text{ g} \end{aligned}$$

$$\begin{aligned} m_C &= m_{PAN} \times 70\% & (2) \\ &= 0.8 \text{ g} \times 70\% = 0.560 \text{ g} \end{aligned}$$

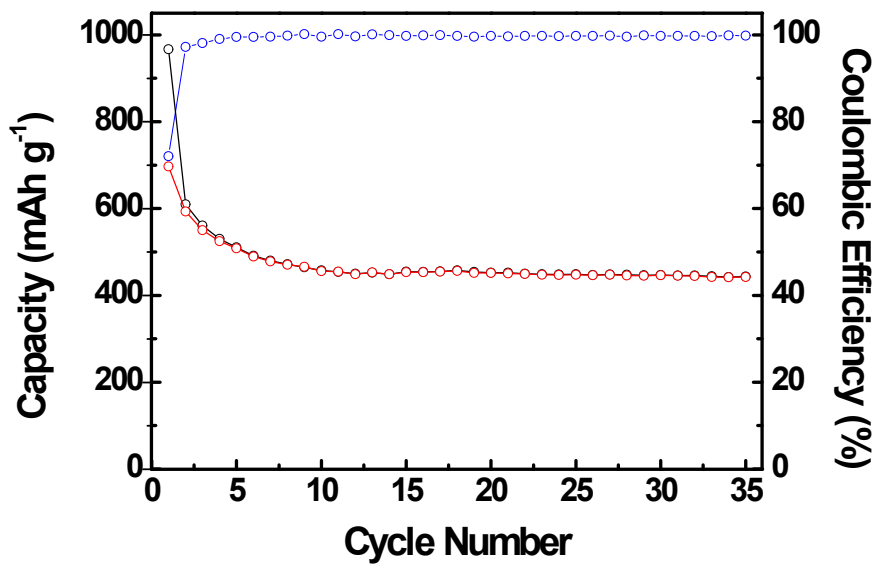
$$\begin{aligned} W_{Cu} \% &= \frac{m_{Cu}}{m_{Cu} + m_C} \times 100\% & (3) \\ &= \frac{0.089 \text{ g}}{0.089 \text{ g} + 0.560 \text{ g}} \times 100\% \approx 13.7\% \end{aligned}$$



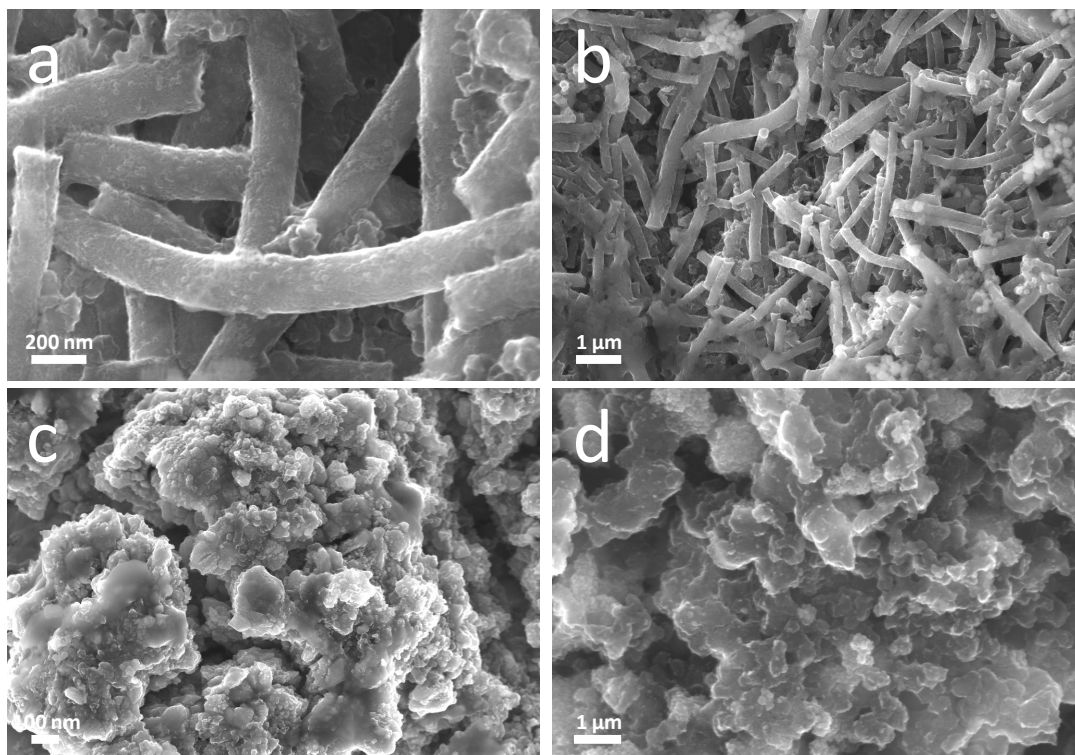
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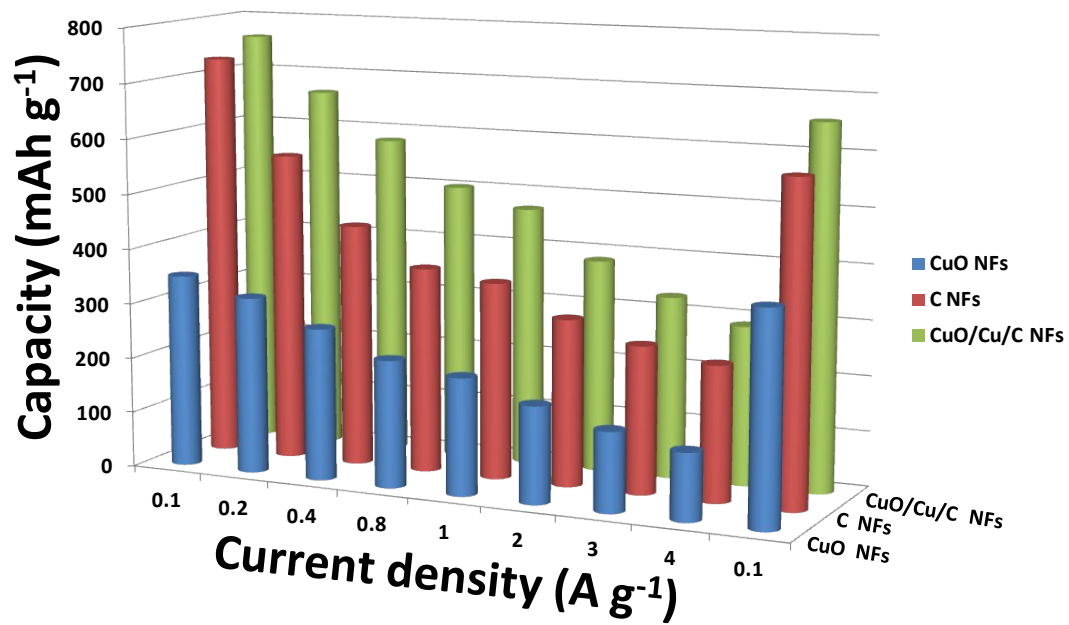
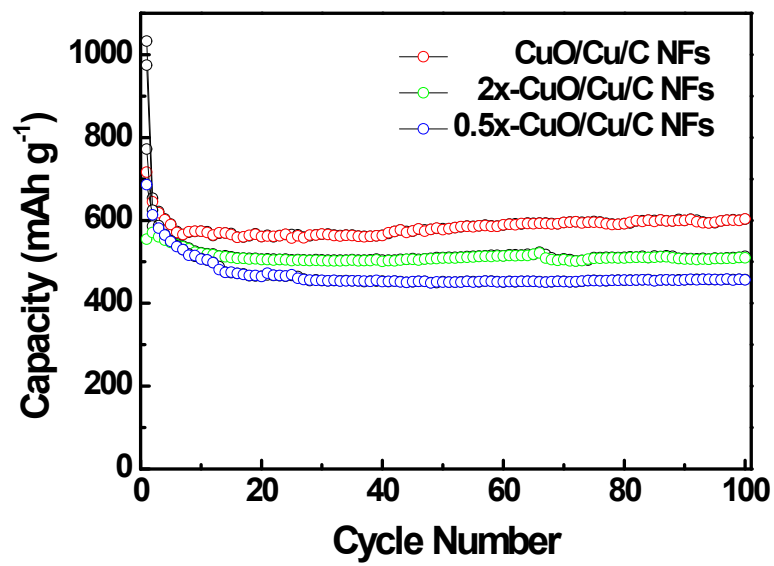
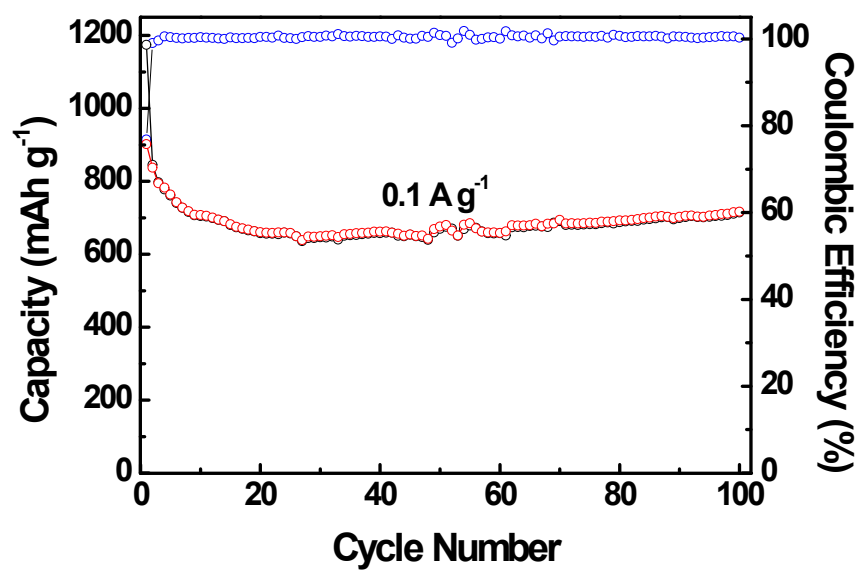


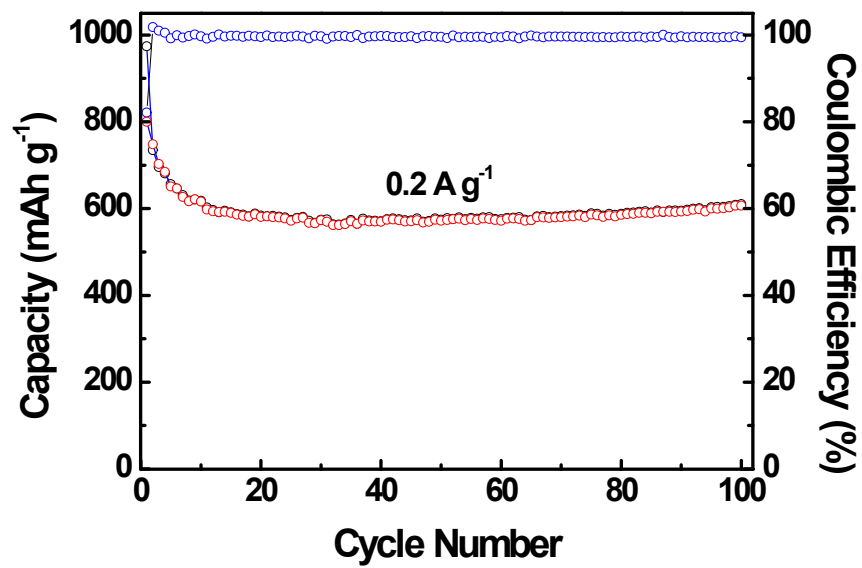
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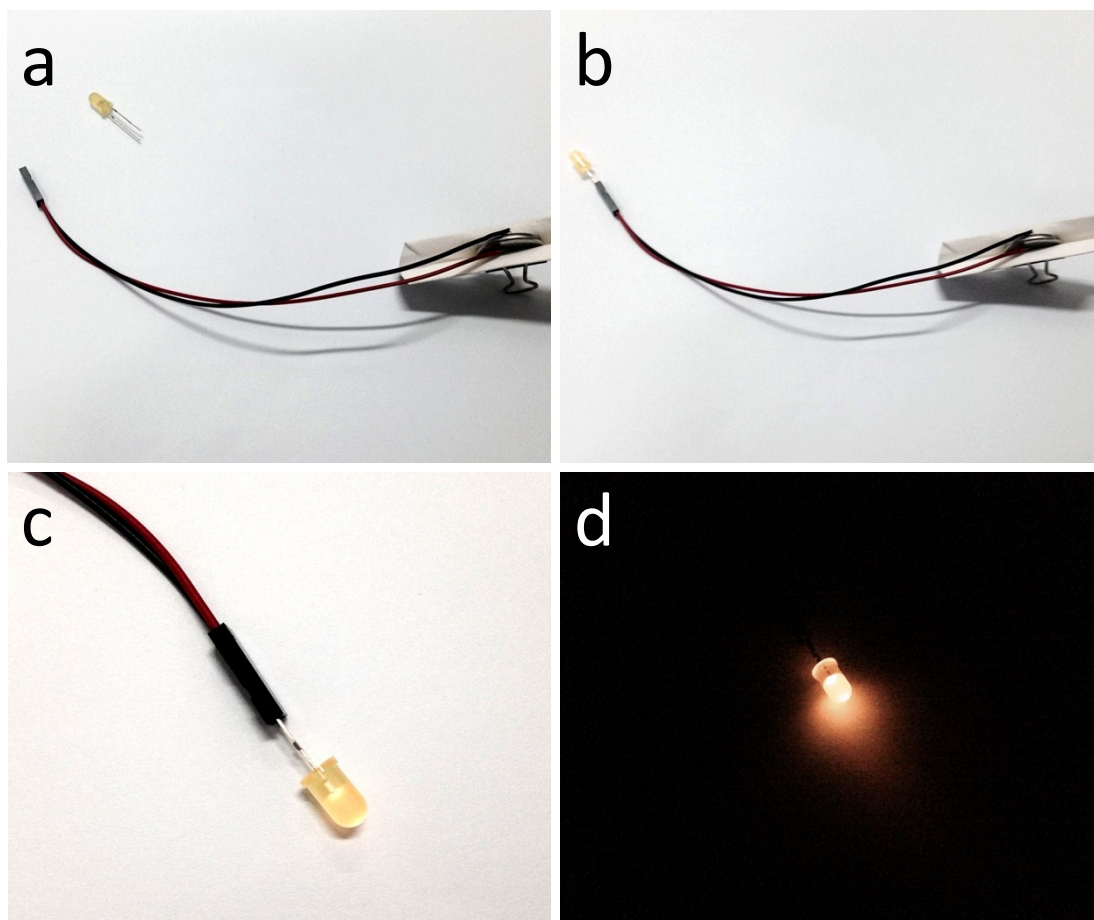
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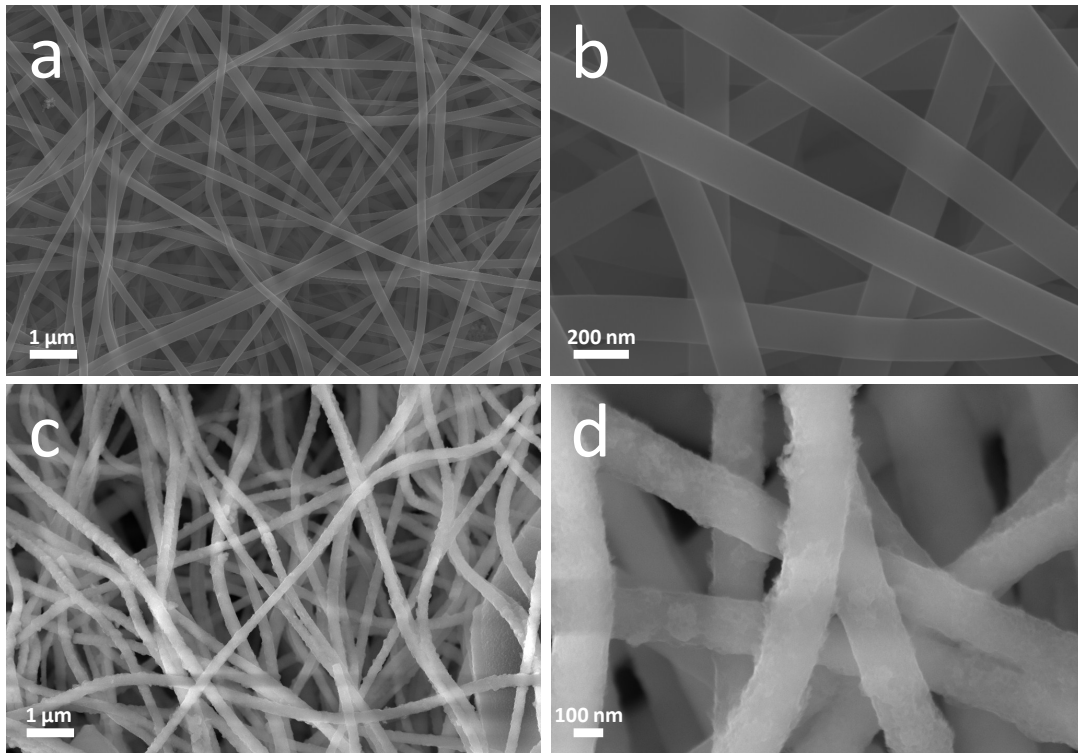
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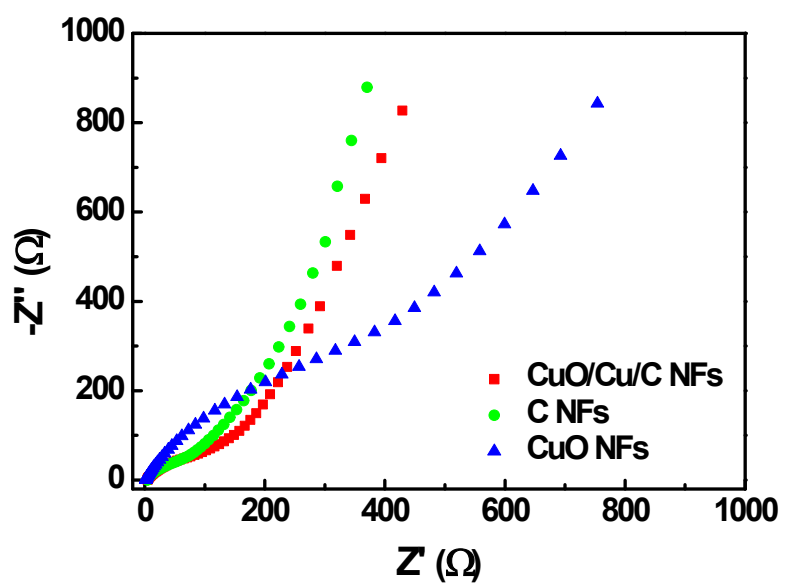
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**Table S1.** Comparison of the electrochemical properties of CuO/Cu/C NFs with recently reported carbon-based nanostructures and CuO/C composites anode materials for LIBs.

Sample	Current density	Cycles	Capacity	Ref.
Nanographene-constructed hollow carbon spheres	0.2 C/0.074 A g <sup>-1</sup>	30	600 mAh g <sup>-1</sup>	2
Vertically aligned carbon Nanotubes/graphene paper	0.03 A g <sup>-1</sup>	40	290 mAh g <sup>-1</sup>	3
Graphene nanosheets-carbon nanotubes composite	0.2 C/0.074 A g <sup>-1</sup>	30	518 mAh g <sup>-1</sup>	4
Nitrogen-doped carbon nanotubes	0.1 A g <sup>-1</sup>	100	397 mAh g <sup>-1</sup>	5
Graphene-multiwalled carbon nanotubes hybrid nanostructure	0.09 A g <sup>-1</sup>	100	768 mAh g <sup>-1</sup>	6
Graphene-carbon nanotube hybrid materials	0.5 C/0.372 A g <sup>-1</sup>	100	429 mAh g <sup>-1</sup>	7
	1 C/0.744 A g <sup>-1</sup>	100	330 mAh g <sup>-1</sup>	
Folded structured graphene paper	0.1 A g <sup>-1</sup>	100	568 mAh g <sup>-1</sup>	8
Nitrogen-doped graphene	0.1 A g <sup>-1</sup>	80	460 mAh g <sup>-1</sup>	9
Two-dimensional mesoporous graphene	0.2 A g <sup>-1</sup>	10	540 mAh g <sup>-1</sup>	10
	0.5 A g <sup>-1</sup>	10	430 mAh g <sup>-1</sup>	
	1 A g <sup>-1</sup>	10	370 mAh g <sup>-1</sup>	
Vertically aligned Graphitic carbon nanosheets	0.5 A g <sup>-1</sup>	680	648 mAh g <sup>-1</sup>	11
Nitrogen-doped double-shelled hollow carbon spheres	1.5 C/0.558 A g <sup>-1</sup>	500	512 mAh g <sup>-1</sup>	12
Hierarchical porous carbon microspheres	0.05 A g <sup>-1</sup>	70	480 mAh g <sup>-1</sup>	13
Core-shell structured porous carbon-graphene composites	0.1 A g <sup>-1</sup>	100	680 mAh g <sup>-1</sup>	14
	0.1 A g <sup>-1</sup>	100	620 mAh g <sup>-1</sup>	



N-doped herringbone carbon nanofibers	0.5 C/0.186 A g <sup>-1</sup>	110	> 300 mAh g <sup>-1</sup>	15
Hard carbon/graphene	0.4 A g <sup>-1</sup>	500	205 mAh g <sup>-1</sup>	16
CuO/C microspheres	0.1 A g <sup>-1</sup>	50	440 mAh g <sup>-1</sup>	17
CuO/CNT nanocomposites	0.1 C/0.067 A g <sup>-1</sup>	100	650 mAh g <sup>-1</sup>	18
Core-shell CuO/polypyrrole nanocomposites	0.2 A g <sup>-1</sup>	80	613 mAh g <sup>-1</sup>	19
CuO nanosheets/r-GO paper	0.067 A g <sup>-1</sup>	50	736.8 mAh g <sup>-1</sup>	20
CuO/GNS nanocomposite	0.1 A g <sup>-1</sup>	60	650 mAh g <sup>-1</sup>	21
CuO/graphene nanocomposite	0.2 C/0.122 A g <sup>-1</sup>	30	500 mAh g <sup>-1</sup>	22
Porous CuO/C submicron spheres	0.2 C/0.134 A g <sup>-1</sup>	100	681 mAh g <sup>-1</sup>	23
N-GO/CuO nanocomposite	0.372 A g <sup>-1</sup>	100	472 mAh g <sup>-1</sup>	24
CuO nanorods/graphene nanocomposites	0.1 C/0.067 A g <sup>-1</sup>	50	692.5 mAh g <sup>-1</sup>	25
CuO-Cu <sub>2</sub> O/graphene composite	0.2 A g <sup>-1</sup>	60	487 mAh g <sup>-1</sup>	26
Nanoleaf-on-sheet CuO/graphene composites	0.1 A g <sup>-1</sup>	50	600 mAh g <sup>-1</sup>	27
CuO-graphene hybrids	0.2 A g <sup>-1</sup>	120	532 mAh g <sup>-1</sup>	28
Nanoporous CuO/Cu composite	0.5 A g <sup>-1</sup>	200	600 mAh g <sup>-1</sup>	29
Hierarchical branching Cu@Cu <sub>2</sub> O@CuO NWs	0.1 A g <sup>-1</sup>	50	345 mAh g <sup>-1</sup>	30
Ultra-uniform CuO/Cu/C composites	0.1 A g <sup>-1</sup>	100	714.5 mAh g <sup>-1</sup>	Our work
	0.2 A g <sup>-1</sup>	100	610.4 mAh g <sup>-1</sup>	
	0.5 A g <sup>-1</sup>	500	572.0 mAh g <sup>-1</sup>	
	1 A g <sup>-1</sup>	400	441.9 mAh g <sup>-1</sup>	
CuO/Cu/C NFs paper	0.1 A g <sup>-1</sup>	100	569.4 mAh g <sup>-1</sup>	

## References

- 1 M. Wu, Q. Wang, K. Li, Y. Wu and H. Liu, *Polym. Degrad. Stabil.*, 2012, **97**, 1511-1519.
- 2 S. Yang, X. Feng, L. Zhi, Q. Cao, J. Maier and K. Mullen, *Adv. Mater.*, 2010, **22**, 838-842.
- 3 S. Li, Y. Luo, W. Lv, W. Yu, S. Wu, P. Hou, Q. Yang, Q. Meng, C. Liu and H.-M. Cheng, *Adv. Energy Mater.*, 2011, **1**, 486-490.
- 4 S. Chen, P. Chen and Y. Wang, *Nanoscale*, 2011, **3**, 4323-4329.
- 5 X. Li, J. Liu, Y. Zhang, Y. Li, H. Liu, X. Meng, J. Yang, D. Geng, D. Wang, R. Li and X. Sun, *J. Power Sources*, 2012, **197**, 238-245.
- 6 B.P. Vinayan, R. Nagar, V. Raman, N. Rajalakshmi, K.S. Dhathathreyan and S. Ramaprabhu, *J. Mater. Chem.*, 2012, **22**, 9949.
- 7 S. Chen, W. Yeoh, Q. Liu and G. Wang, *Carbon*, 2012, **50**, 4557-4565.
- 8 F. Liu, S. Song, D. Xue and H. Zhang, *Adv. Mater.*, 2012, **24**, 1089-1094.
- 9 C. Zhang, N. Mahmood, H. Yin, F. Liu and Y. Hou, *Adv. Mater.*, 2013, **25**, 4932-4937.
- 10 Y. Fang, Y. Lv, R. Che, H. Wu, X. Zhang, D. Gu, G. Zheng and D. Zhao, *J. Am. Chem. Soc.*, 2013, **135**, 1524-1530.
- 11 J. Zhu, K. Sakaushi, G. Clavel, M. Shalom, M. Antonietti and T.P. Fellingner, *J. Am. Chem. Soc.*, 2015, **137**, 5480-5485.
- 12 K. Zhang, X. Li, J. Liang, Y. Zhu, L. Hu, Q. Cheng, C. Guo, N. Lin and Y. Qian, *Electrochim. Acta*, 2015, **155**, 174-182.
- 13 F. Wang, R. Song, H. Song, X. Chen, J. Zhou, Z. Ma, M. Li and Q. Lei, *Carbon*, 2015, **81**, 314-321.
- 14 R. Guo, L. Zhao and W. Yue, *Electrochim. Acta*, 2015, **152**, 338-344.
- 15 X.-B. Cheng, Q. Zhang, H.-F. Wang, G.-L. Tian, J.-Q. Huang, H.-J. Peng, M.-Q. Zhao and F. Wei, *Catal. Today*, 2015, **249**, 244-251.
- 16 X. Zhang, S. Han, P. Xiao, C. Fan and W. Zhang, *Carbon*, 2016, **100**, 600-607.
- 17 X.H. Huang, C.B. Wang, S.Y. Zhang and F. Zhou, *Electrochim. Acta*, 2011, **56**, 6752-6756.
- 18 S. Ko, J.-I. Lee, H.S. Yang, S. Park and U. Jeong, *Adv. Mater.*, 2012, **24**, 4451-4456.
- 19 Z. Yin, Y. Ding, Q. Zheng and L. Guan, *Electrochem. Commun.*, 2012, **20**, 40-43.
- 20 Y. Liu, W. Wang, L. Gu, Y. Wang, Y. Ying, Y. Mao, L. Sun and X. Peng, *ACS appl. Mater. Interfaces*, 2013, **5**, 9850-9855.
- 21 D. Qiu, B. Zhao, Z. Lin, L. Pu, L. Pan and Y. Shi, *Mater. Lett.*, 2013, **105**, 242-245.
- 22 S.-D. Seo, D.-H. Lee, J.-C. Kim, G.-H. Lee and D.-W. Kim, *Ceram. Int.*, 2013, **39**, 1749-1755.
- 23 H. Kim, H.-S. Lim, Y.-J. Kim, Y.-K. Sun and K.-D. Suh, *RSC Adv.*, 2014, **4**, 60573-60580.
- 24 Y. Pan, K. Ye, D. Cao, Y. Li, Y. Dong, T. Niu, W. Zeng and G. Wang, *RSC Adv.*, 2014, **4**, 64756-64762.
- 25 Q. Wang, J. Zhao, W. Shan, X. Xia, L. Xing and X. Xue, *J. Alloys Compd.*, 2014, **590**, 424-427.
- 26 X. Zhou, J. Shi, Y. Liu, Q. Su, J. Zhang and G. Du, *J. Alloys Compd.*, 2014, **615**, 390-394.
- 27 X. Zhou, J. Zhang, Q. Su, J. Shi, Y. Liu and G. Du, *Electrochim. Acta*, 2014, **125**, 615-621.
- 28 W. Zhou, F. Zhang, S. Liu, J. Wang, X. Du, D. Yin and L. Wang, *RSC Adv.*, 2014, **4**, 51362-51365.
- 29 X. Xu, M. Han, J. Ma, C. Zhang and G. Li, *RSC Adv.*, 2015, **5**, 71760-71764.
- 30 Y. Zhao, Y. Zhang, H. Zhao, X. Li, Y. Li, L. Wen, Z. Yan and Z. Huo, *Nano Res.*, 2015, **8**, 2763-2776.