

Facile fabrication of well-defined polyaniline microtubes derived from natural kapok fiber for supercapacitor with long-term cycling stability

Weibing Xu^{a,b}, Bin Mu^{a*}, Wenbo Zhang^{a,c} and Aiqin Wang^{a*}

^a *State Key Laboratory of Solid Lubrication, Center of Eco-Materials and Green Chemistry, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China.*

^b *University of Chinese Academy of Sciences, Beijing 100049, P.R. China.*

^c *School of Chemical Engineering, Northwest University for Nationalities, Lanzhou 730000, P.R.China.*

* Corresponding authors. Tel.: +86 931 4968118; fax: +86 931 8277088.
E-mail: mubin@licp.cas.cn (B. Mu), aqwang@licp.cas.cn (A. Wang).

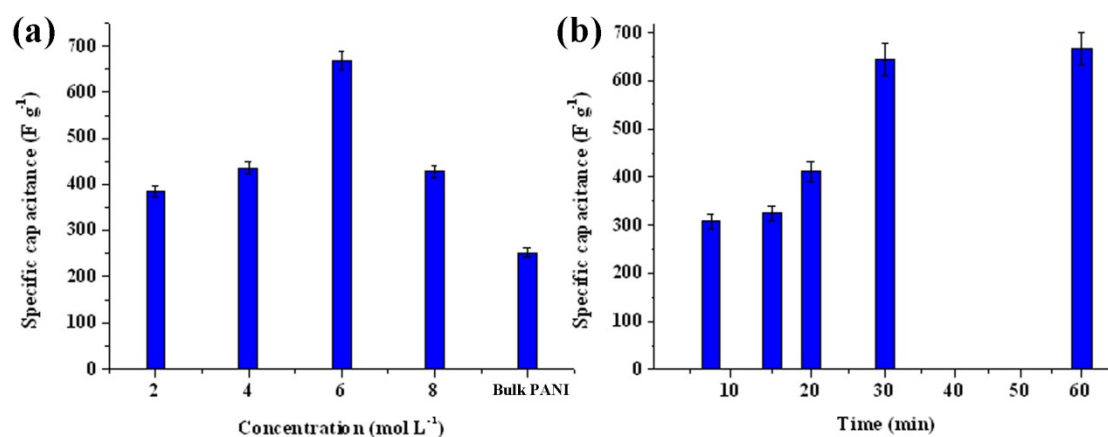


Fig. S1 The specific capacitance of bulk PANI and PANI microtubes prepared using different concentration of NaOH solution for 60 min (a), and (b) 6.0 M NaOH solution for different etching time.

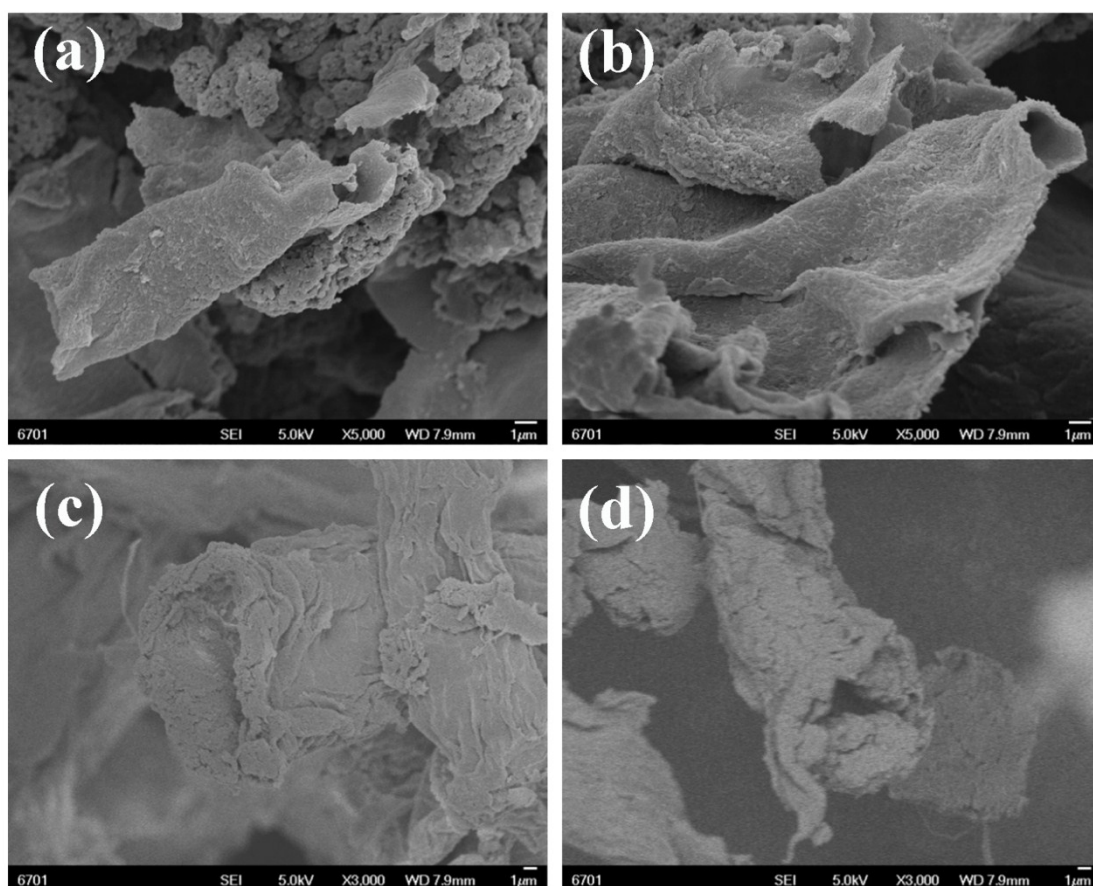


Fig. S2 SEM images of PANI microtubes prepared using NaOH solution with different concentrations of (a) 2.0 M, (b) 4.0 M, (c) 6.0 M and (d) 8.0 M.

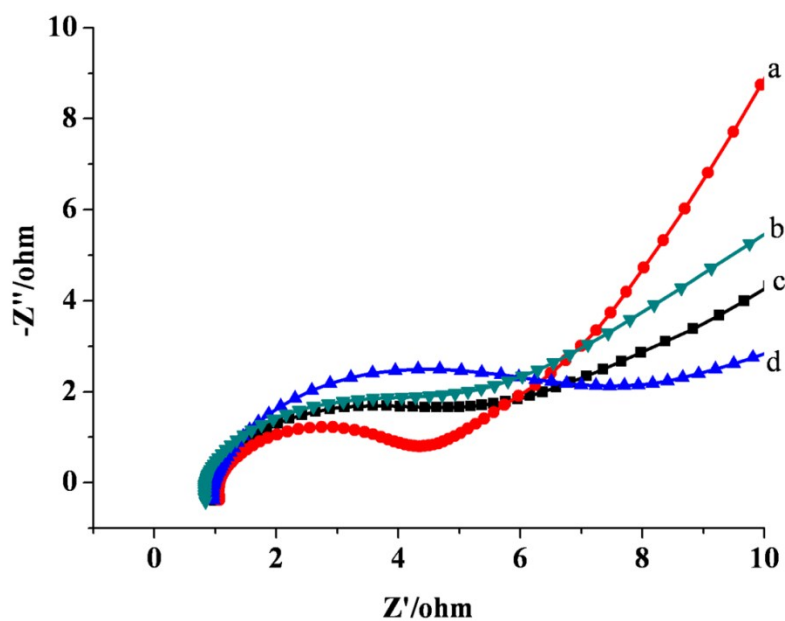


Fig. S3 EIS spectra of PANI microtubes prepared using different concentrations of NaOH solution for 60 min: (a) 2.0 M, (b) 4.0 M, (c) 6.0 M and (d) 8.0 M.

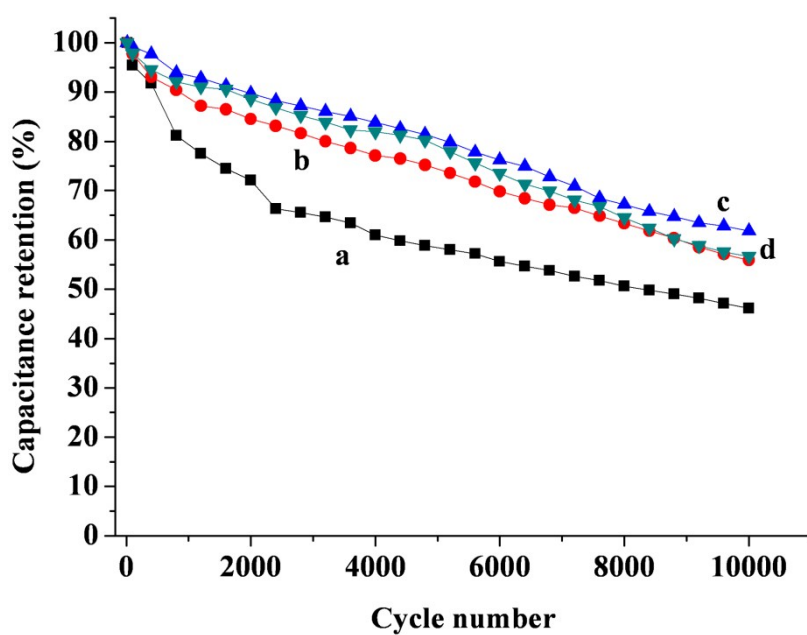


Fig. S4 Cycle stability of PANI microtubes prepared using different concentrations of NaOH solution for 60 min: (a) 2.0 M, (b) 4.0 M, (c) 6.0 M and (d) 8.0 M.

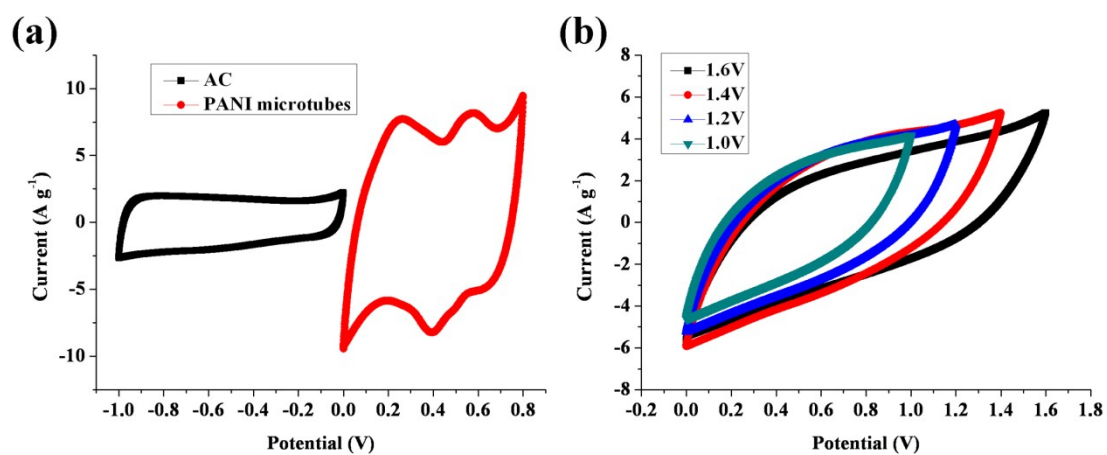


Fig. S5 CV curves of the negative (AC) and positive (PANI microtubes) electrodes in a three-electrode configuration at a scan rate of 10 mV s^{-1} and (b) CV curves of the PANI microtubes//AC asymmetric supercapacitor at a scan rate of 100 mV s^{-1} within different potential windows in $1.0 \text{ M H}_2\text{SO}_4$.

Table S1 Comparison of the diameter and the cycling stability of various micro/nanostructured PANI materials.

Morphology	Diameter	Templating	Max capacitance	Retention(cycles)	Ref
Nanofibers	400-550nm	PAA	601	62%(500)	1
Nanotube	400nm	ZnO	650	65%(400)	2
Nanowire	50nm	Free	950	88%(500)	3
Nanowires	30-60nm	Free	775	90%(1500)	4
Nanofibers	100nm	Free	278	53%(2000)	5
Nanofibers	200nm	Free	267	86%(1000)	6
Nanotubes	100nm	MnO ₂	533	65%(1000)	7
Nanofibers	110nm	PPD	548	75%(1000)	8
Irregular	-	Free	323	89%(1300)	9
Nanorods	50nm	Free	455	65%(1300)	10
Particles	100nm	Free	358	95%(1000)	11
Nanofibers	50-100nm	SA	2093	74%(1000)	12
Nanorods	150nm	Free	658	65%(250)	13
Nanotubes	80nm	MnO ₂	661	63%(1000)	14
Nanotubes	100nm	MnO ₂	896	57%(6000)	15
Nanobelts	2μm	Free	873	96%(1000)	16
Nanorods	1-2μm	Free	757	90%(1000)	17
Nanofibers	70-100nm	Free	480	75%(1000)	18
Microtube	20-25μm	KF	667	60%(10000)	This

1. Y. E. Miao, W. Fan, D. Chen and T. X. Liu, *ACS applied materials & interfaces*, 2013, **5**, 4423-4428.
2. Z. L. Wang, R. Guo, G. R. Li, H. L. Lu, Z. Q. Liu, F. M. Xiao, M. Q. Zhang and Y. X. Tong, *Journal of Materials Chemistry*, 2012, **22**, 2401-2404.
3. K. Wang, J. Y. Huang and Z. X. Wei, *The Journal of Physical Chemistry C*, 2010, **114**, 8062-8067.
4. V. Gupta and N. Miura, *Materials Letters*, 2006, **60**, 1466-1469.
5. H. L. Xu, X. W. Li and G. C. Wang, *Journal of Power Sources*, 2015, **294**, 16-21.

6. S. Chaudhari, Y. Sharma and P. S. Archana, *Journal of Applied Polymer Science*, 2013, **129**, 1660-1668.
7. L. R. Wang, F. Ran, Y. T. Tan, L. Zhao, L. B. Kong and L. Kang, *Chinese Chemical Letters*, 2011, **22**, 964-968.
8. H. Guan, L. Z. Fan, H. C. Zhang and X. H. Qiu, *Electrochimica Acta*, 2010, **56**, 964-968.
9. X. Wang, D. Liu, J. X. Deng, X. J. Duan, J. S. Guo and P. Liu, *RSC Advances*, 2015, **5**, 78545-78552.
10. X. Wang, J. X. Deng, X. J. Duan, D. Liu, J. S. Guo and P. Liu, *Journal of Materials Chemistry A*, 2014, **2**, 12323-12329.
11. J. X. Deng, X. Wang, J. S. Guo and P. Liu, *Industrial & Engineering Chemistry Research*, 2014, **53**, 13680-13689.
12. Y. Z. Li, X. Zhao, Q. Xu, Q. H. Zhang and D. J. Chen, *Langmuir*, 2011, **27**, 6458-6463.
13. H. Xu, J. L. Li, Z. J. Peng, J. X. Zhuang and J. L. Zhang, *Electrochimica Acta*, 2013, **90**, 393-399.
14. L. J. Ren, G. N. Zhang, J. F. Wang, L. P. Kang, Z. B. Lei, Z. W. Liu, Z. T. Liu, Z. P. Hao and Z. H. Liu, *Electrochimica Acta*, 2014, **145**, 99-108.
15. W. Chen, R. B. Rakhi, H. N. Alshareef, *The Journal of Physical Chemistry C*, 2013, **117**, 15009-15019.
16. G. R. Li, Z. P. Feng, J. H. Zhong, Z. L. Wang and Y. X. Tong, *Macromolecules*, 2010, **43**, 2178-2183.

17. J. Ma, Y. F. Liu, Z. H. Hu and Z. J. Xu, *Ionics*, 2013, **19**, 1405-1413.
18. H. R. Ghenaatian, M. F. Mousavi, S. H. Kazemi and M. Shamsipur, *Synthetic Metals*, 2009, **159**, 1717-1722.

Table S2 Comparison of energy density (ED) and power density (PD) of supercapacitor based on various micro/nano-structured PANI materials.

Material	Electrolyte	ED ^a	PD ^b	Ref
Polyaniline nanofibers	1 M HCl	9.4 Wh kg ⁻¹	436W kg ⁻¹ 289 KW kg ⁻¹	1
Polyaniline nanotubes	1 M H ₂ SO ₄	8.7 Wh kg ⁻¹	¹	2
Polyaniline powder	1 M LiPF ₆	14.8 Wh kg ⁻¹	48W kg ⁻¹	3
Graphene/Polyaniline Nanofiber	1 M HCl	18.5 Wh kg ⁻¹	100W kg ⁻¹	4
Polyaniline-MnO ₂ nanotube	1 M H ₂ SO ₄	17.8 Wh kg ⁻¹	600W kg ⁻¹	5
Graphene-mesoporous polyaniline	1 M H ₂ SO ₄	11.3 Wh kg ⁻¹	107W kg ⁻¹	6
Polyaniline-MnO ₂ nanofibrous	1 M NaNO ₃	6.6 Wh kg ⁻¹	100W kg ⁻¹	7
RGO-PANI	1 M H ₂ SO ₄	17.6 Wh kg ⁻¹	10W kg ⁻¹	8
Graphene/PANI nanofibers	1 M H ₂ SO ₄	4.9 Wh kg ⁻¹	300W kg ⁻¹ 3.1KW kg ⁻¹	9
Graphene nanoribbon/PANI	1 M H ₂ SO ₄	7.6 Wh kg ⁻¹ 21.1 Wh kg ⁻¹	¹	10
Graphene/MWCNT/PANI	1 M H ₂ SO ₄	kg ⁻¹	25KW kg ⁻¹	11
Polyaniline microtubes	1 M H ₂ SO ₄	14.1 Wh kg ⁻¹	250W kg ⁻¹	This work

^a ED is the highest value in literature. ^b PD corresponding to highest energy density.

1. H. R. Ghenaatian, M. F. Mousavi, S. H. Kazemi and M. Shamsipur, *Synthetic Metals*, 2009, **159**, 1717-1722.
2. W. Chen, R. B. Rakhi and H. N. Alshareef, *Journal of Materials Chemistry A*, 2013, **1**, 3315-3324.

3. K. S. Ryu, K. M. Kim, N. G. Park, Y. J. Park and S. H. Chang, *Journal of Power Sources*, 2002 **103**, 305-309.
4. Q. Wu, Y. Xu, Z. Yao, A. Liu and G. Shi, *ACS nano*, 2010, **4**, 1963-1970.
5. J. R. Jaidev, A. K. Mishra, S. Ramaprabhu, *J Mater Chem*, 2011, **21**, 17601-17605.
6. Q. Wang, J. Yan, Z. Fan, T. Wei, M. Zhang and X. Jing, *Journal of Power Sources*, 2014, **247**, 197-203.
7. L. J. Sun, X. X. Liu, K. K. T. Lau, L. Chen and W. M. Gu, *Electrochimica Acta*, 2008, **53**, 3036-3042.
8. P. Yu, X. Zhao, Z. Huang, Y. Li and Q. Zhang, *Journal of Materials Chemistry A*, 2014, **2**, 14413-14420.
9. P. J. Hung, K. Chang, Y. F. Lee, C. C. Hu and K. M. Lin, *Electrochim. Acta*, 2010, **55**, 6015–6021.
10. L. Li, A. R. Raji, H. Fei, Y. Yang, E. L. Samuel and J. M. Tour, *ACS Appl. Mater. Interfaces*, 2013, **5**, 6622–6627.
11. J. Shen, C. Yang, X. Li and G. Wang, *ACS Appl. Mater. Interfaces*, 2013, **5**, 8467–8476.

