Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Electronic Supplementary Information

Photochemical fabrication of 3D hierarchical Mn_3O_4/H-TiO_2 composite films with excellent electrochemical capacitance performance

Shasha Zhu, Peipei Zhang, Ling Chang, Yuan Zhong, Kai Wang, Haibo Shao, Jianming Wang*, Jianqing Zhang, Chu-nan Cao

Department of Chemistry, Zhejiang University, Hangzhou 310027, PR China

*Corresponding author.

Tel.: +86-571-87951513; Fax: +86-571-87951895.

E-mail address: wjm@zju.edu.cn (J.M. Wang)

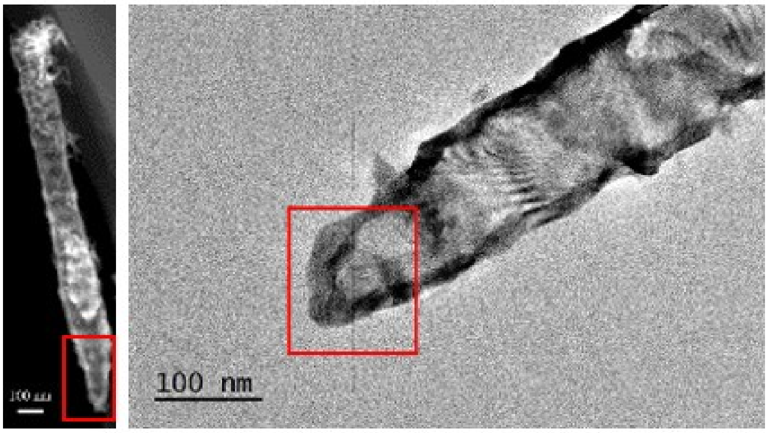

Fig. S1 TEM images of single TiO_2 nanotube

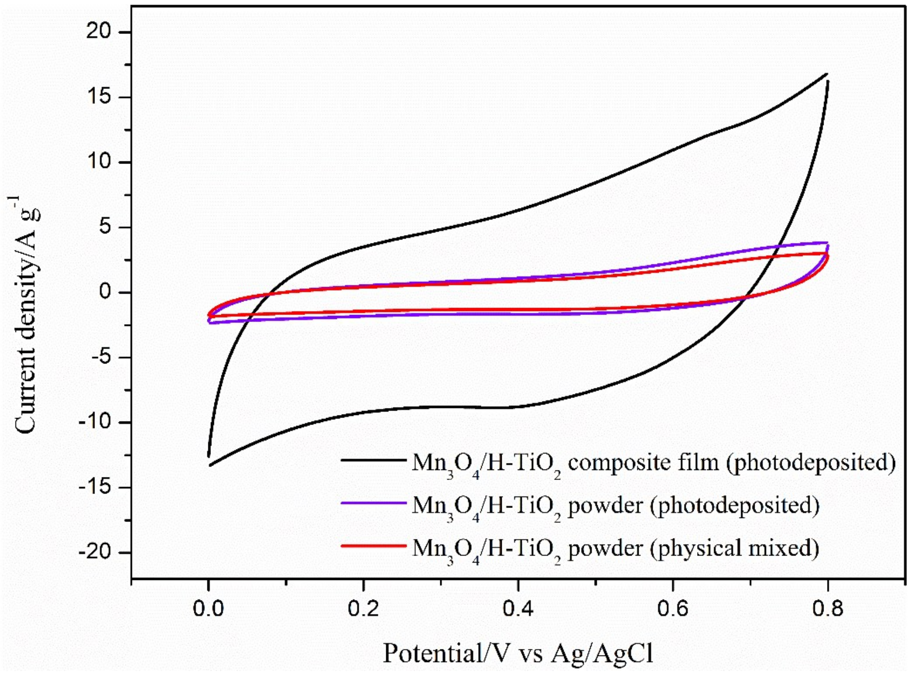

Fig. S2 CV curves of Mn_3O_4/H-TiO_2 composite film electrode and two pasted electrodes in 0.5 M Na_2SO_4 aqueous solution at a scan rate of 50 mV s^{-1}. The two pasted electrodes using as-photodeposited Mn_3O_4/H-TiO_2 powders peeled from substrate and Mn_3O_4/H-TiO_2 powders physically mixed were fabricated by coating a slurry containing 70 wt% active materials, 15 wt% acetylene black (Super-P), and 15 wt% polyvinylidene fluoride (PVDF) dissolved in N-methyl-2-pyrrolidinone onto Ti foil, and dried at 80℃ in vacuum for 12 h.

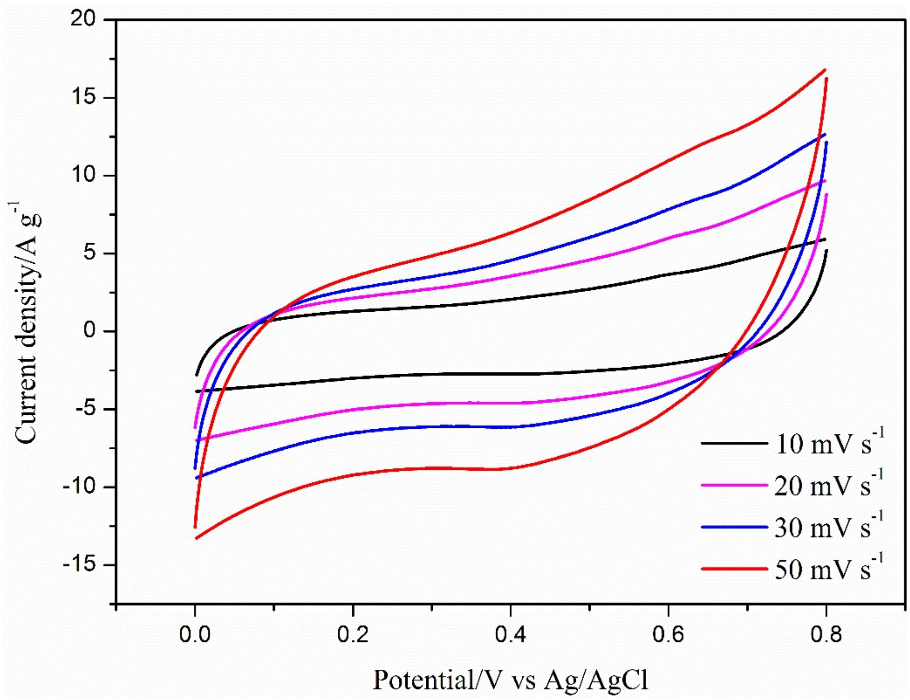

Fig. S3 CV curves of Mn_3O_4/H-TiO_2 composite films at different scan rates

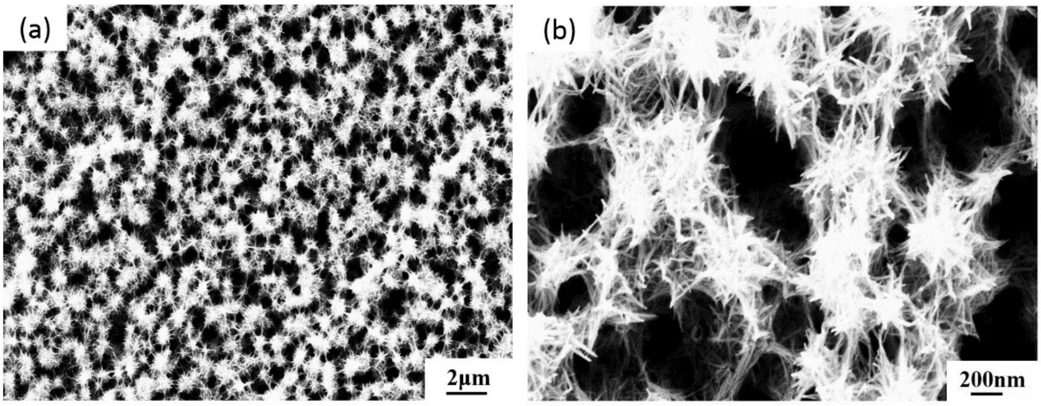

Fig. S4 SEM images of Mn_3O_4/H-TiO_2 composite film electrode after 10000 cycles at a current density of 3.6 A g^{-1}

Table S1 Comparison of the pseudocapacitive performance of MnO_x based materials in this work and some references

Materials	Preparation method	Specific capacitance/rate	Cycle performance Final capacity/cycle number/rate
Mn_3O_4/H-TiO_2 nanotube arrays (this work)	Photodeposition	508 F g^{-1}/0.7 A g^{-1} 228 F g^{-1}/35.7 A g^{-1}	329 F g^{-1}/10000/3.6 A g^{-1}
Mn_3O_4/graphene nanocomposites[1]	Precipitation	238 F g^{-1}/0.1 A g^{-1} 146 F g^{-1}/2 A g^{-1}	137 F g^{-1}/1000/2 A g^{-1}
TiO_2 nanobelts@MnO_2 arrays[2]	Hydrothermal method	455 F g^{-1}/0.2 A g^{-1} 54 F g^{-1}/2 A g^{-1}	~450 F g^{-1}/900/0.2 A g^{-1}
Mn_3O_4 nanosheets[3]	Chemical deposition	398 F g^{-1}/5 mV s^{-1} ~290 F g^{-1}/100 mV s^{-1}	~238 F g^{-1}/2000/100 mV s^{-1}
Mn_3O_4/CNT composite arrays[4]	Dip-casting method	299 F g^{-1}/2 mV s^{-1} ~150 F g^{-1}/200 mV s^{-1}	~180 F g^{-1}/1000/50 mV s^{-1}
MnO_2 /PDDA/ONCNO composites[5]	Chemical deposition	219 F g^{-1}/2 A g^{-1}	~177 F g^{-1}/1000/2 A g^{-1}
MnO_2/TiN nanotube coaxial arrays[6]	Electrodeposition	486 F g^{-1}/2 mV s^{-1} 267 F g^{-1}/2000 mV s^{-1}	~359 F g^{-1}/1000/200 mV s^{-1}
Mn_3O_4 nanocubes/graphene[7]	Chemical decomposition	131 F g^{-1}/0.5 A g^{-1} 86 F g^{-1}/5 A g^{-1}	~85 F g^{-1}/500/5 A g^{-1}
MnO_2 nanoneedles/graphene[8]	Dipping coating	367 F g^{-1}/10 mV s^{-1} ~290 F g^{-1}/500 mV s^{-1}	~311 F g^{-1}/1000/10 mV s^{-1}
Mn_3O_4 nanoparticles/ITO[9]	Chemical deposition	403 F g^{-1}/10 mV s^{-1} 202 F g^{-1}/200 mV s^{-1}	~264 F g^{-1}/5000/100 mV s^{-1}
Mn_3O_4/graphene[10]	Hydrothermal synthesis	367 F g^{-1}/5 A g^{-1}	337 F g^{-1}/3000/5 A g^{-1}
Porous MnO/Mn_3O_4 nanocomposite[11]	Thermal decomposition	207 F g^{-1}/1 A g^{-1} 172 F g^{-1}/20 A g^{-1}	143 F g^{-1}/3000/20 A g^{-1}

3D Mn_3O_4 hierarchical architecture[12]	Hydrothermal synthesis	229 F g^{-1}/0.1 A g^{-1} 82 F g^{-1}/0.5 A g^{-1}	87 F g^{-1}/1000/0.5 A g^{-1}

References

1. F. Gao, J. Qu, Z. Zhao, Q. Zhou, B. Li and J. Qiu, *Carbon*, 2014, **80**, 640–650.
2. Y. Luo, D. Kong, J. Luo, S. Chen, D. Zhang, K. Qiu, X. Qi, H. Zhang, C. M. Li and T. Yu, *RSC Adv.*, 2013, **3**, 14413–14422.
3. D. P. Dubal and R. Holze, *J. Power Sources*, 2013, **238**, 274−282.
4. X. Cui, F. Hu, W. Wei and W. Chen, *Carbon*, 2011, **49**, 1225–1234.
5. R. Borgohain, J. P. Selegue and Y.-T. Cheng, *J. Mater. Chem. A*, 2014, **2**, 20367–20373.
6. S. M. Dong, X. Chen, L. Gu, X. H. Zhou, L. F. Li, Z. H. Liu, P. X. Han, H. X. Xu, J. H. Yao, H. B. Wang, X. Y. Zhang, C. Q. Shang, G. L. Cui and L. Q. Chen, *Energy Environ. Sci.*, 2011, **4**, 3502–3508.
7. K. Subramani, D. Jeyakumar and M. Sathish, *Phys. Chem. Chem. Phys.,* 2014, **16**, 4952–4961.
8. M. Kim, Y. Hwang and J. Kim, *Phys. Chem. Chem. Phys.,* 2014, **16**, 351–361.
9. I. Ryu, G. Kim, D. Park and S. Yim, *J. Power Sources*, 2015, **297**, 98–104.
10. H. M. Lee, G. H. Jeong, D. W. Kang, S. W. Kim and C. K. Kim, *J. Power Sources*, 2015, **281**, 44–48.
11. J. H. Yang, X. F. Yang, Y. L. Zhong and J. Y. Ying, *Nano Energy*, 2015, **13**, 702–708.
12. Z. X. Liu, Y. Xing, S. M. Fang, X. W. Qu, D. P. Wu, A. Q. Zhang and B. Xu, *RSC Adv.*, 2015, **5**, 54867–54872.