Supporting information

Self-Assembled Three-Dimensional Hierarchical Graphene Hybrid Hydrogels with Ultrathin β -MnO₂ Nanobelts for High Performance Supercapacitors

Sheng Zhu^a, Hui Zhang^b, Ping Chen^a, Lin-Hui Nie^a, Chuan-Hao Li^{*c}, Shi-Kuo Li^{*a}

[a] Innovation Lab for Clean Energy and Green Catalysis, School of Chemistry and Chemical Engineering, Anhui University, Hefei 230601, P. R. China

[b] School of Physics and Materials Science, Anhui University, Hefei 230601, P. R.

China

[c] Department of Chemical & Environmental Engineering, Yale University, New

Haven, US 06511

E-mail: chuanhao.li@yale.edu; lishikuo@ahu.edu.cn



Figure S1. SEM image (a), TEM graph (b) of the as-obtained ultrathin β -MnO₂ nanobelts



Figure S2. SEM images of the as-obtained MnO_2 nanorods (a), the 3D typical rGO/MnO₂ nanorod hybrid aerogel (b), nanorod-nanobelt heterostructure (c), and 3D typical rGO/MnO₂ heterostructure hybrid aerogel (d).



Figure S3. EDX spectrum of the typical 3D rGO/β -MnO₂ nanobelt hybrid sample, the inset is the table of the corresponding element content.

Samples	Mass (g)	Volume (cm ³)	Density (g/cm ³)
rGO	0.0084	1.092	0.007692
18.9% β-MnO ₂ NBs/rGO	0.0107	1.240	0.008629
30.7% β-MnO ₂ NBs/rGO	0.0186	1.286	0.01446
54.2% β-MnO ₂ NBs/rGO	0.0242	1.442	0.02526
80.9% β-MnO ₂ NBs/rGO	0.0345	1.366	0.01678

Table S1. The mass, volume and density of the 3D rGO/ β -MnO₂ nanobelt hybrid aerogels

Numb	er Composite electrodes	Highest capacitance (F/g)	Current density or scan rate
1	MnO ₂ nanosheets/grapher	ne 236	0.25 A/g
2	MnO ₂ nanosheets/grapher	ne 380	0.1 mA/cm^2
3	MnO ₂ nanopaticles/rGO	312	2 mV/s
4	urchin-like MnO ₂ /GNS	263	10 mA/cm ²
5	MnO ₂ nanoflower/grapher	ne 195	77 A/g
6	nanostructured MnO ₂ /GC) 280	0.5 A/g
7	MnO ₂ nanobelts/rGO	362	1 A/g

Table S2. The comparisons of the as-obtained specific capacitance with the reported values under different current densities or scan rates.

References

- 1 Y. He, W. Chen, X. Li, Z. Zhang, J. Fu, C. Zhao and E. Xie, *ACS nano*, 2012, **7**, 174-182.
- G. Yu, L. Hu, N. Liu, H. Wang, M. Vosgueritchian, Y. Yang, Y. Cui and Z. Bao, *Nano Letters*, 2011, 11, 4438-4442.
- 3 J. Yan, Z. Fan, T. Wei, W. Qian, M. Zhang and F. Wei, *Carbon*, 2010, **48**, 3825-3833.
- 4 W. Yang, Z. Gao, J. Wang, B. Wang, Q. Liu, Z. Li, T. Mann, P. Yang, M. Zhang and L. Liu, *Electrochimica Acta*, 2012, **69**, 112-119.
- 5 H. Zhang, G. Cao, Z. Wang, Y. Yang, Z. Shi and Z. Gu, *Nano letters*, 2008, **8**, 2664-2668.
- 6 C. J. Jafta, F. Nkosi, L. le Roux, M. K. Mathe, M. Kebede, K. Makgopa, Y. Song, D. Tong, M. Oyama and N. Manyala, *Electrochimica Acta*, 2013, **110**, 228-233.

Samples	C (F/g)	E (Wh/kg)	E (kW/kg)	
rGO	118	61	14.50	
45.9% β-MnO ₂ NRs/rGO	242	121	25.64	
48.7% β-MnO ₂ NRs-NBs /rGO	326	163	33.97	
54.2% β-MnO ₂ NBs/rGO	362	181	49.57	

Table S3. The detailed comparison of the specific capacitance (C), energy density (E) and power density (P) for the typical hybrid hydrogels with various nanostructures.



Figure S4. CV curves of the typical 3D hybrid hydrogels under the voltage scan rate of 500 mV/s in 6.0 M KOH electrolyte.



Figure S5. The comparison of the CV, GCD and EIS curves of the rGO/β -MnO₂ nanobelt hybrid hydrogel before and after using under the voltage scan rate of 5 mV/s in 6.0 M KOH electrolyte.

Samples	R _{ct} [ohm]
rGO	19.5
18.9% β-MnO ₂ NBs/rGO	5.2
30.7% β-MnO ₂ NBs/rGO	5.1
54.2% β-MnO ₂ NBs/rGO	4.6
80.9% β-MnO ₂ NBs/rGO	22.8

Table S4. The detailed ESR values of different electrodes