

Supplementary Information

Unique walnut-shaped porous MnO₂/C nanospheres with enhanced reaction kinetics for lithium storage with high capacity and superior rate capability

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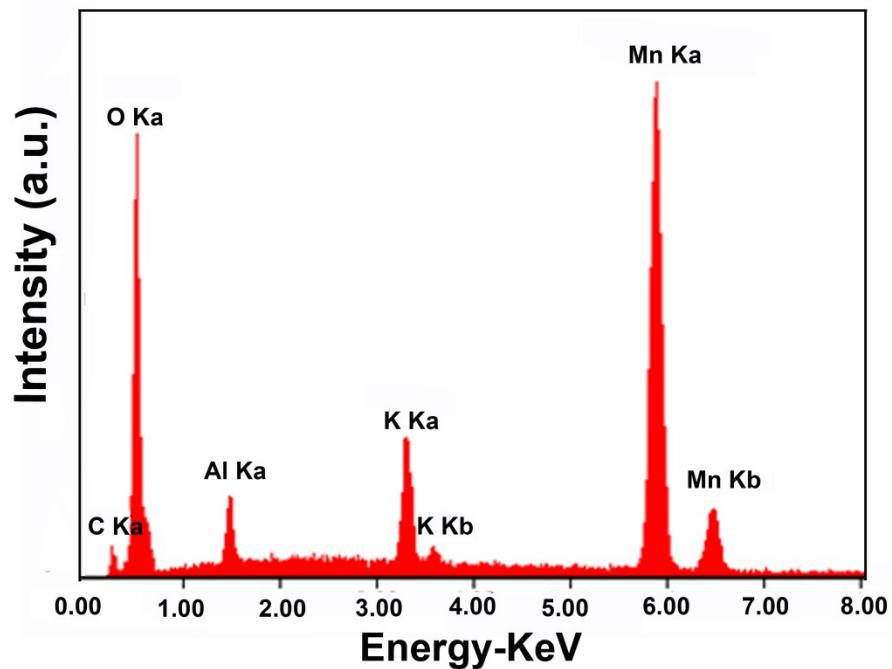


Fig. S1. EDX pattern of MO-NSs.

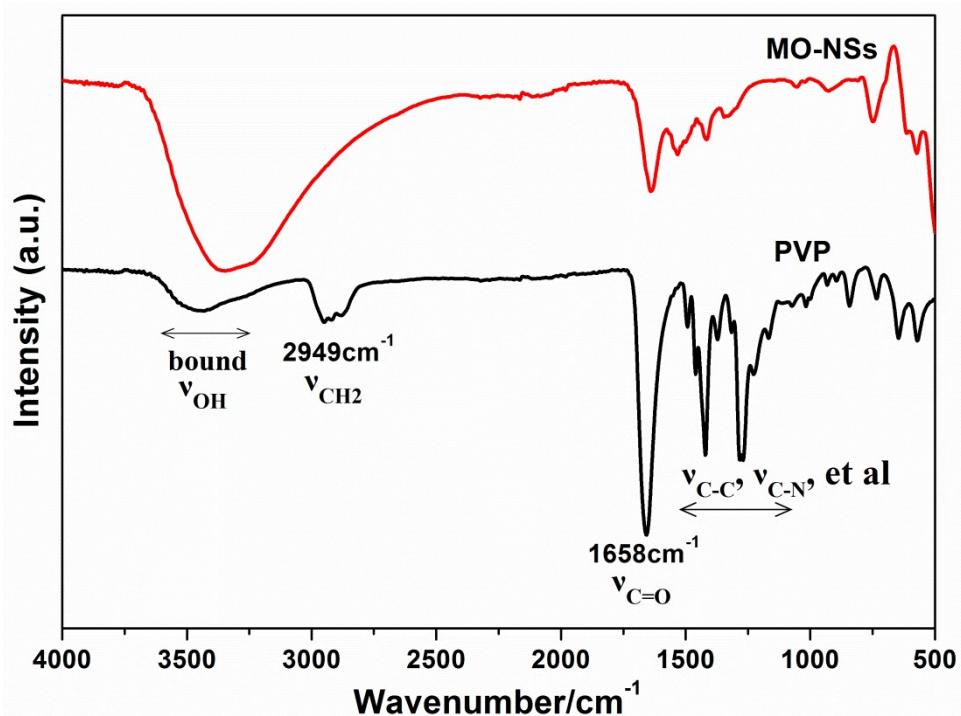


Fig. S2. FT-IR spectra of PVP and MO-NSs.

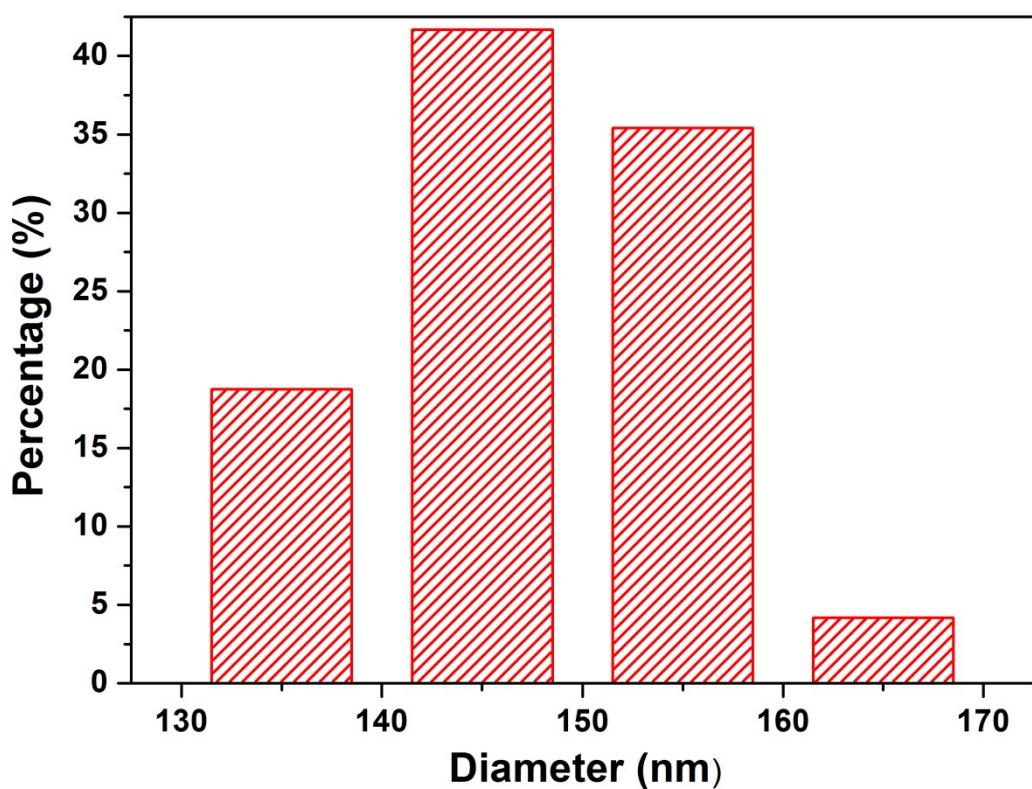


Fig. S3. Size distribution of MO-NSs. Size distribution measured based on the SEM images.

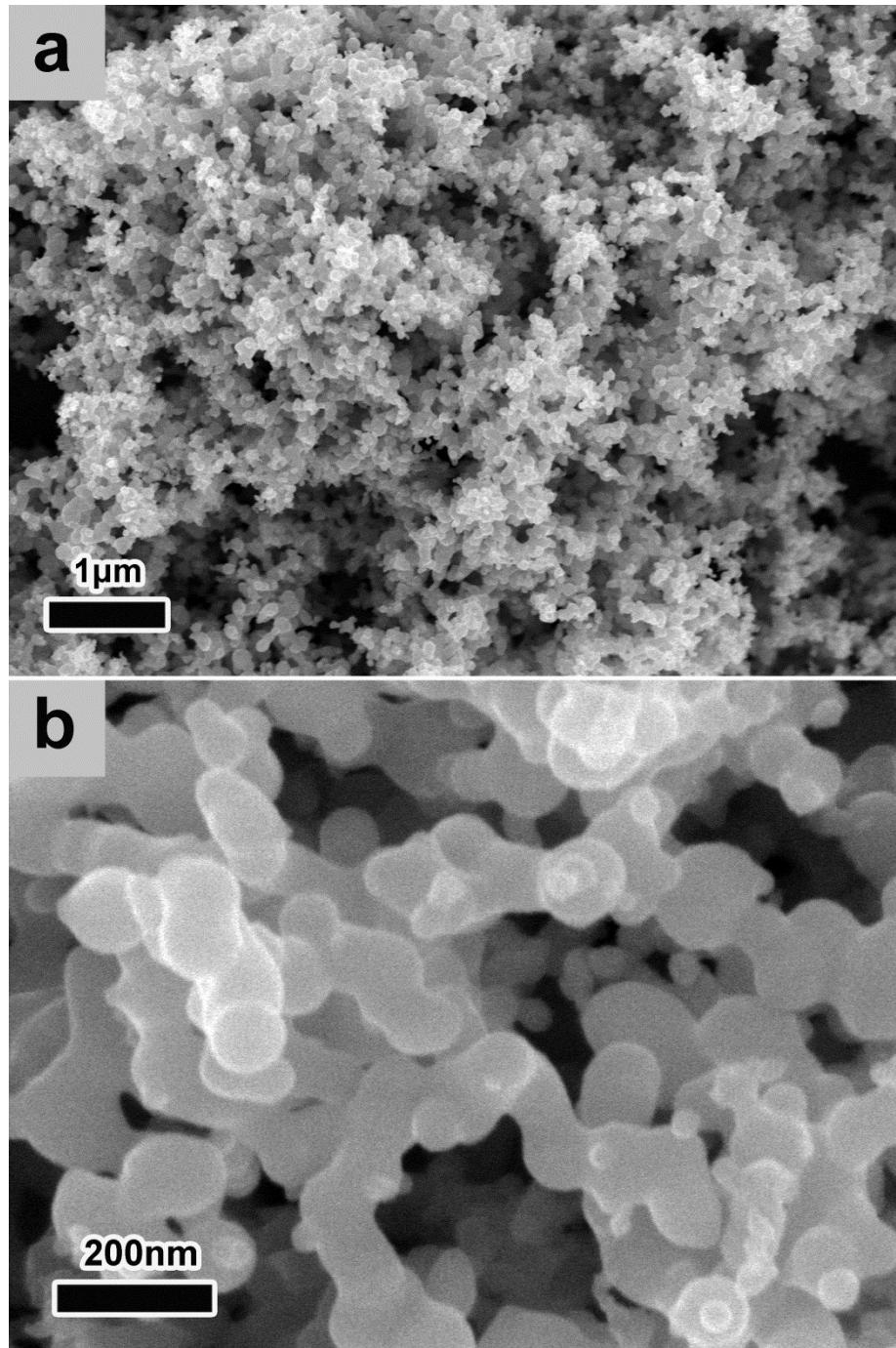


Fig. S4. SEM images of the non-uniform MnO_2 nanoparticles without PVP: (a) low and (b) high magnification.

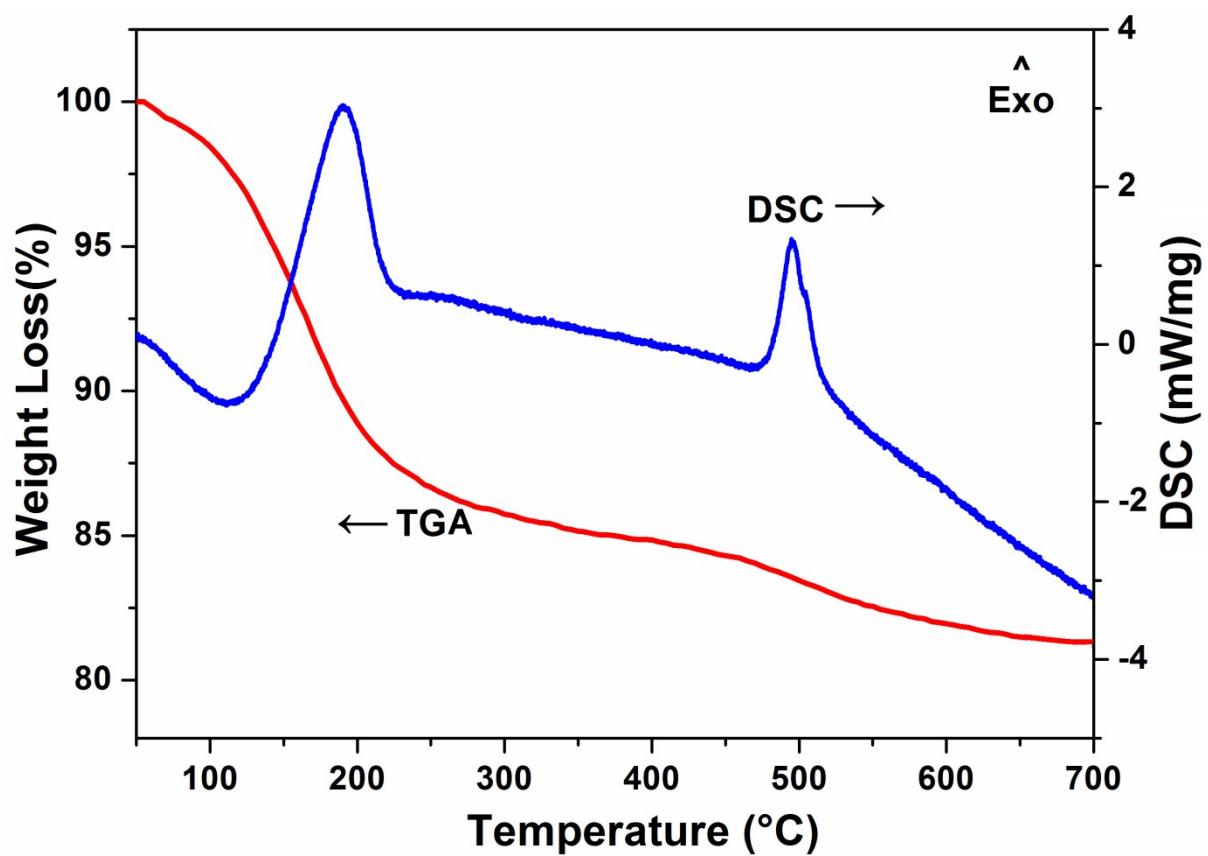


Fig. S5. TGA/DSC plots of MO-NSs under argon at a rate of $5\text{ }^{\circ}\text{C min}^{-1}$ from 50 to $800\text{ }^{\circ}\text{C}$.

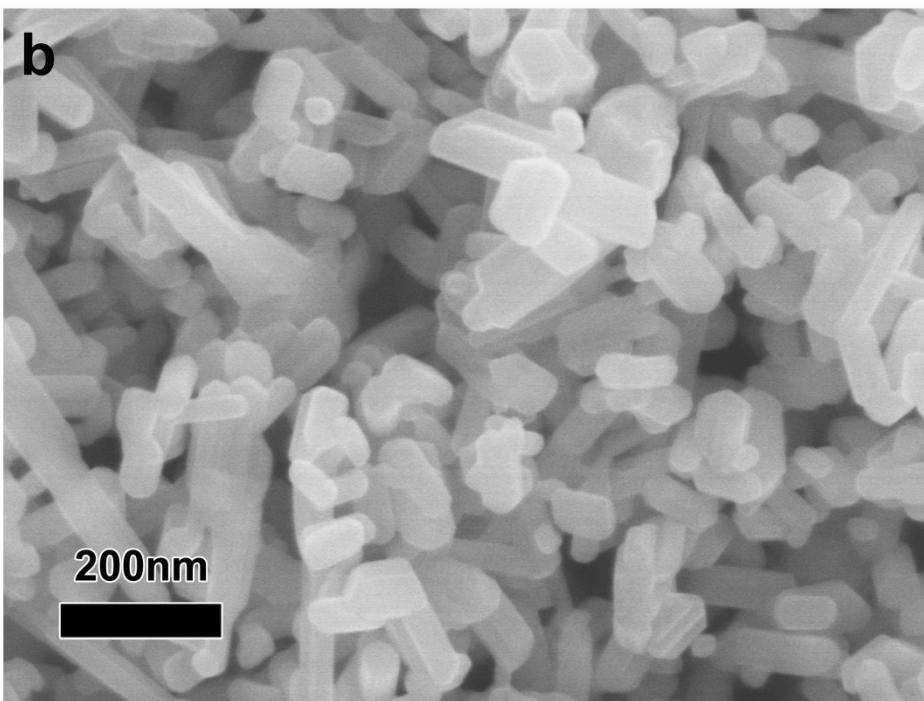
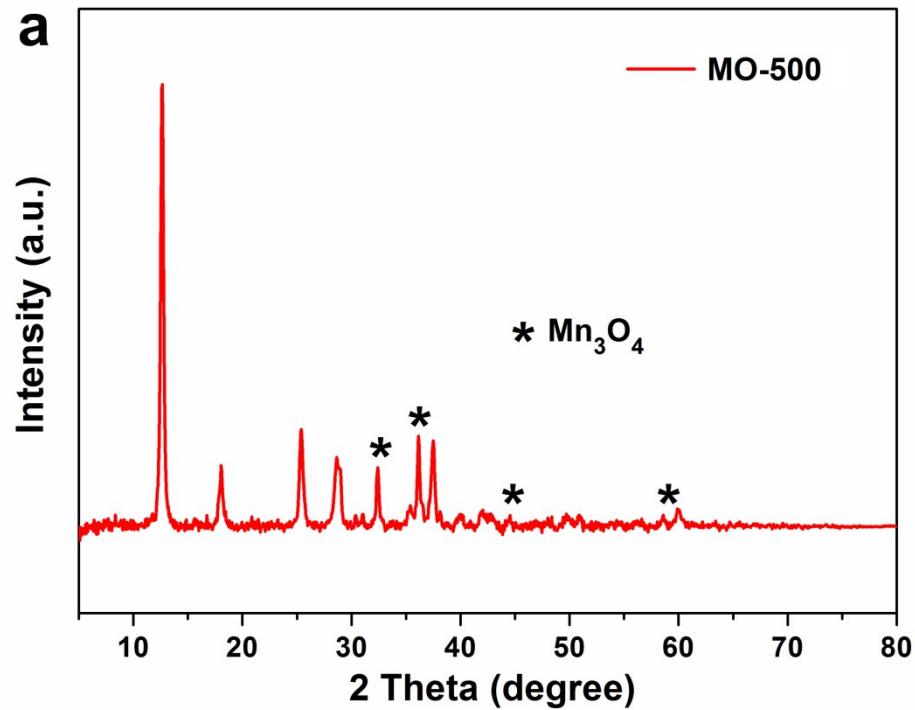


Fig. S6. (a) XRD pattern and (b) SEM image of the sample after annealing under argon at 500 °C, showing the presence of Mn_3O_4 .

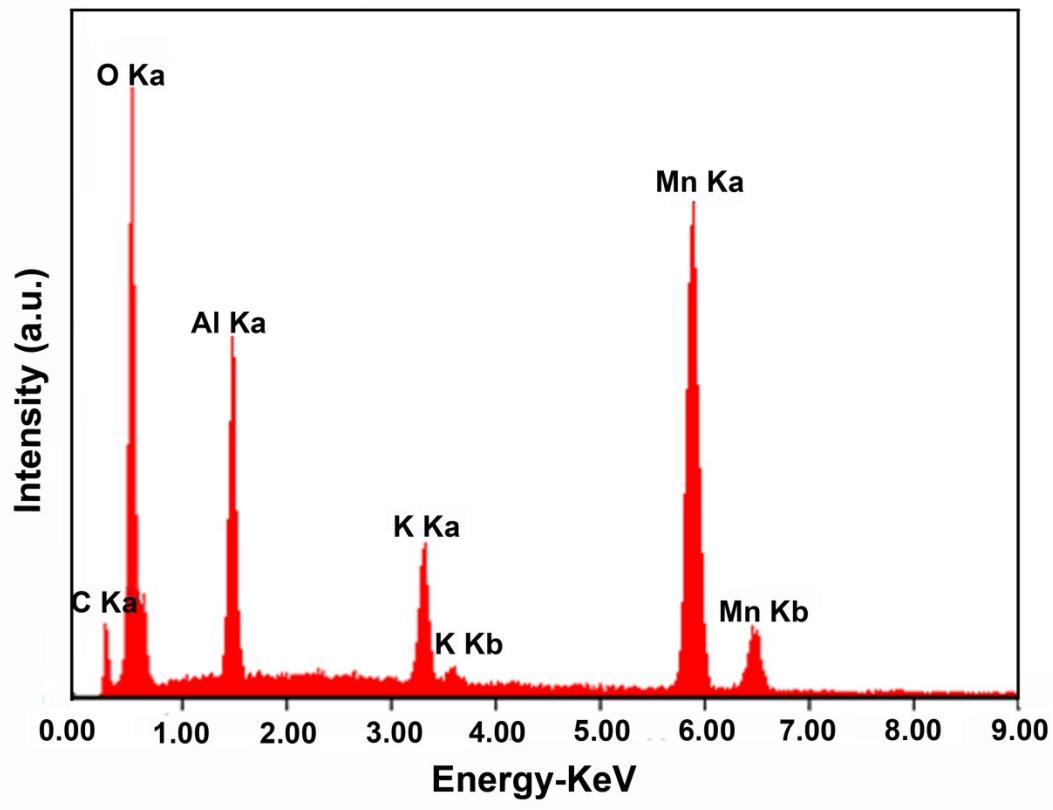


Fig. S7. EDX pattern of MO/C-NSs.

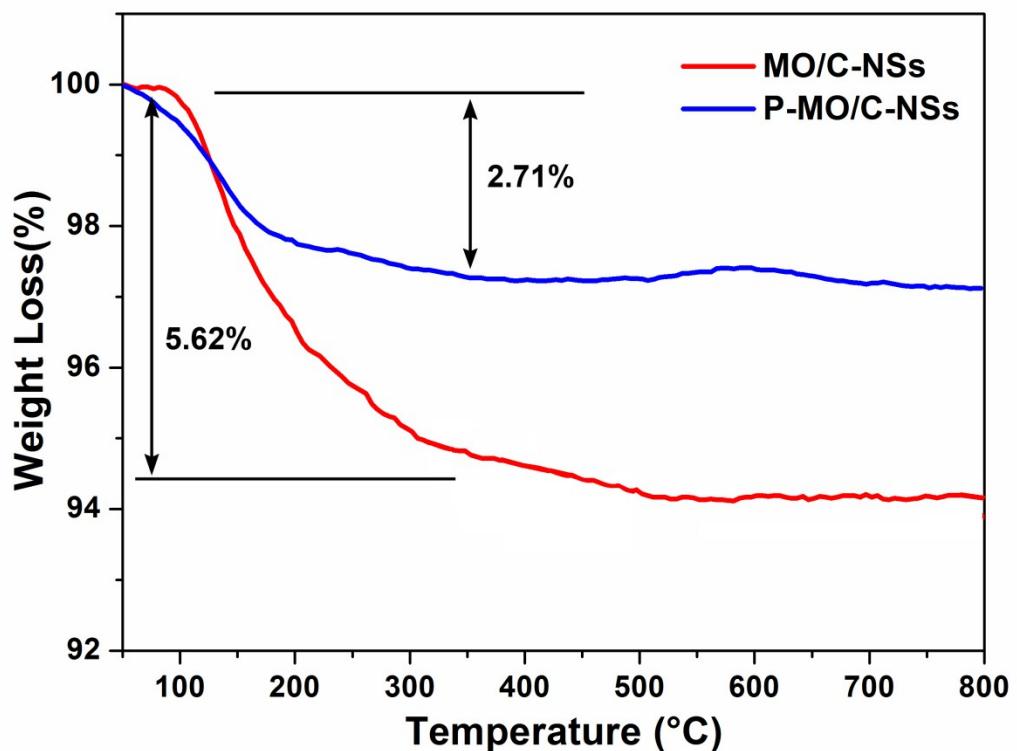


Fig. S8. TGA plots of MO/C-NSs and P-MO/C-NSs under air at a rate of $5\text{ }^{\circ}\text{C min}^{-1}$ from 50 to 800 $^{\circ}\text{C}$.

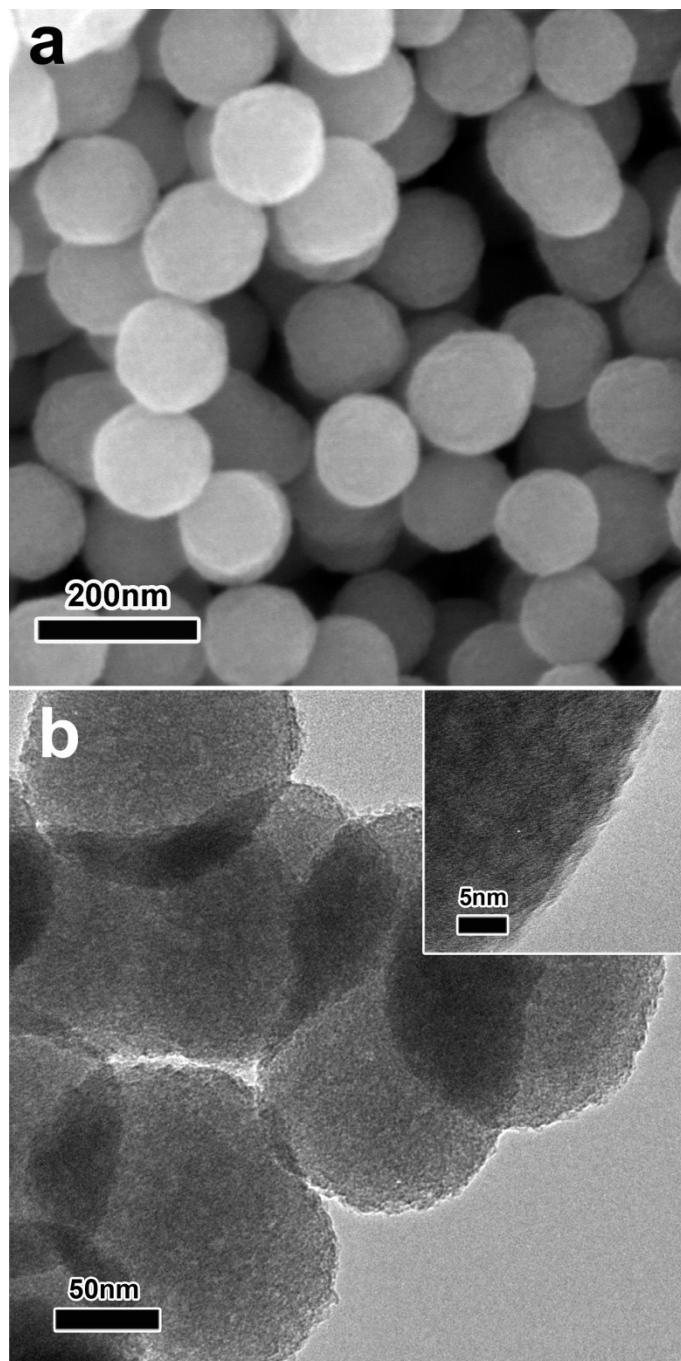


Fig. S9. (a) SEM and (b) TEM images of MO/C-NSs. The inset in (b) is an HRTEM image of the edge of a MO/C-NS sphere.

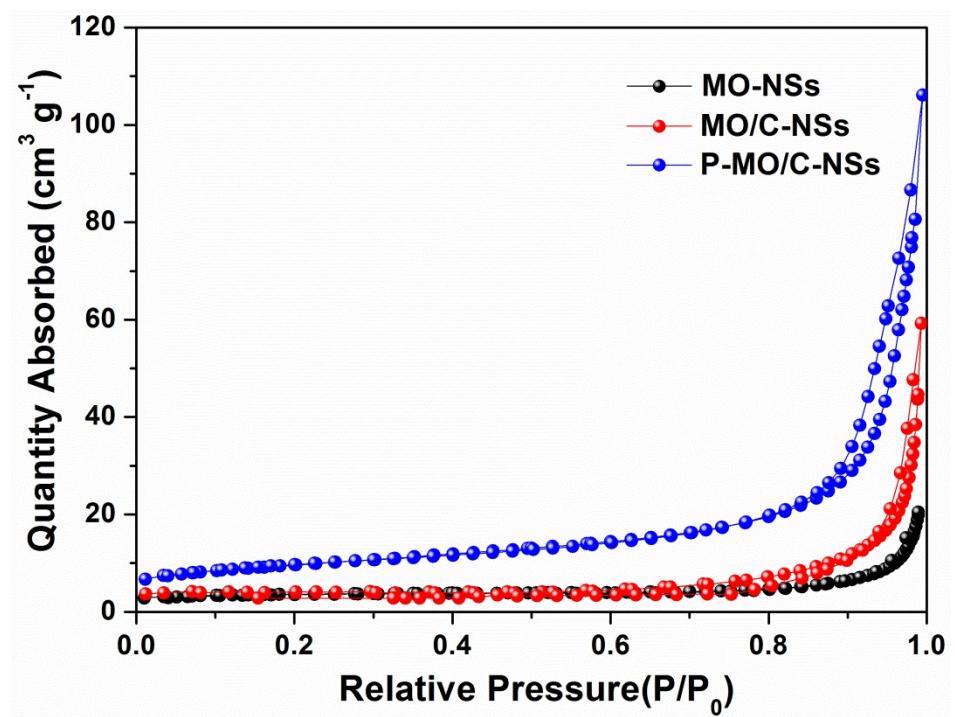


Fig. S10. Nitrogen adsorption-desorption isotherms of MO-NSs, MO/C-NSs and P-MO/C-NSs.

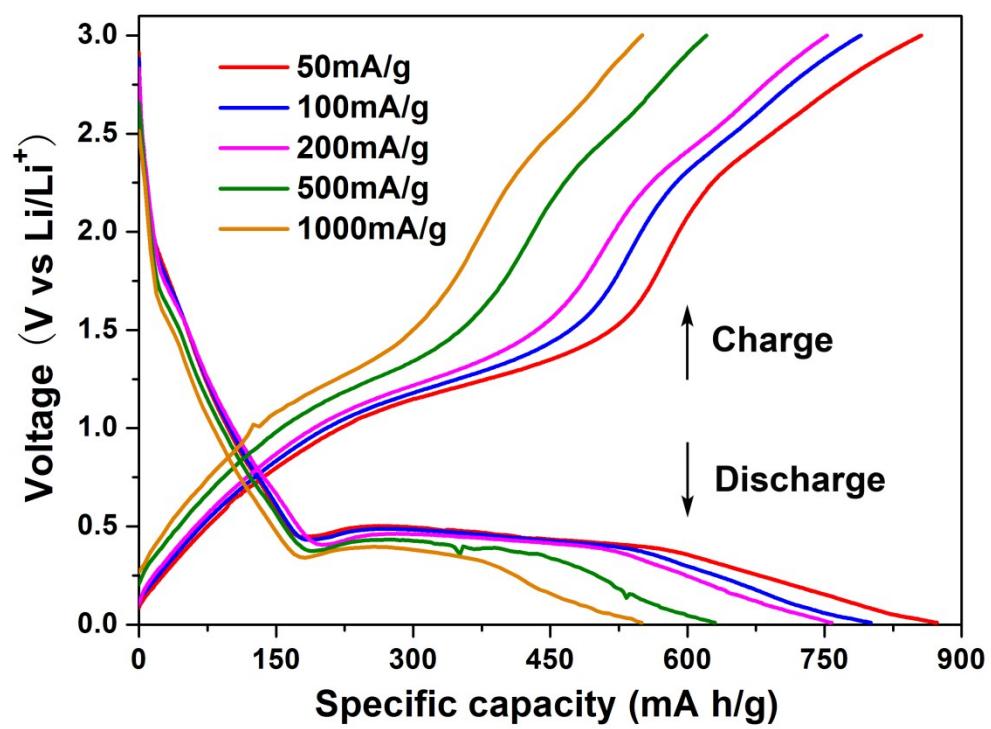


Fig. S11. Discharge/charge profiles of the P-MO/C-NSs electrode at various current densities.

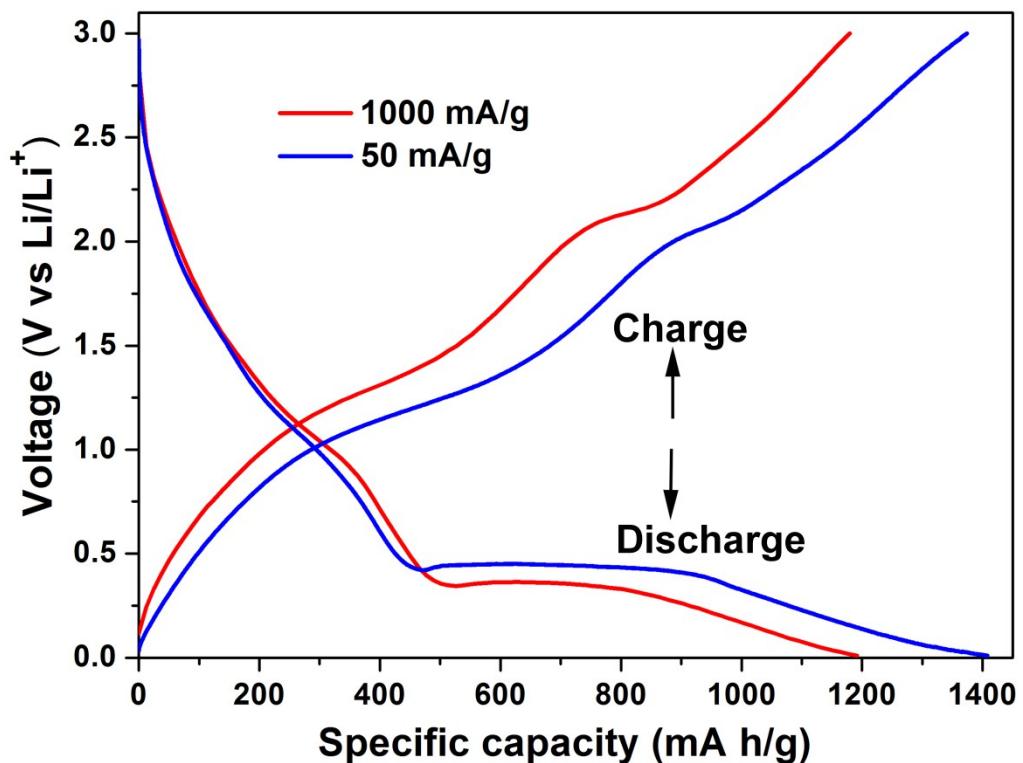


Fig. S12. Discharge/charge profiles of the P-MO/C-NSs electrode at 50 mA g^{-1} and 1000 mA g^{-1} (the 85th cycle), respectively.

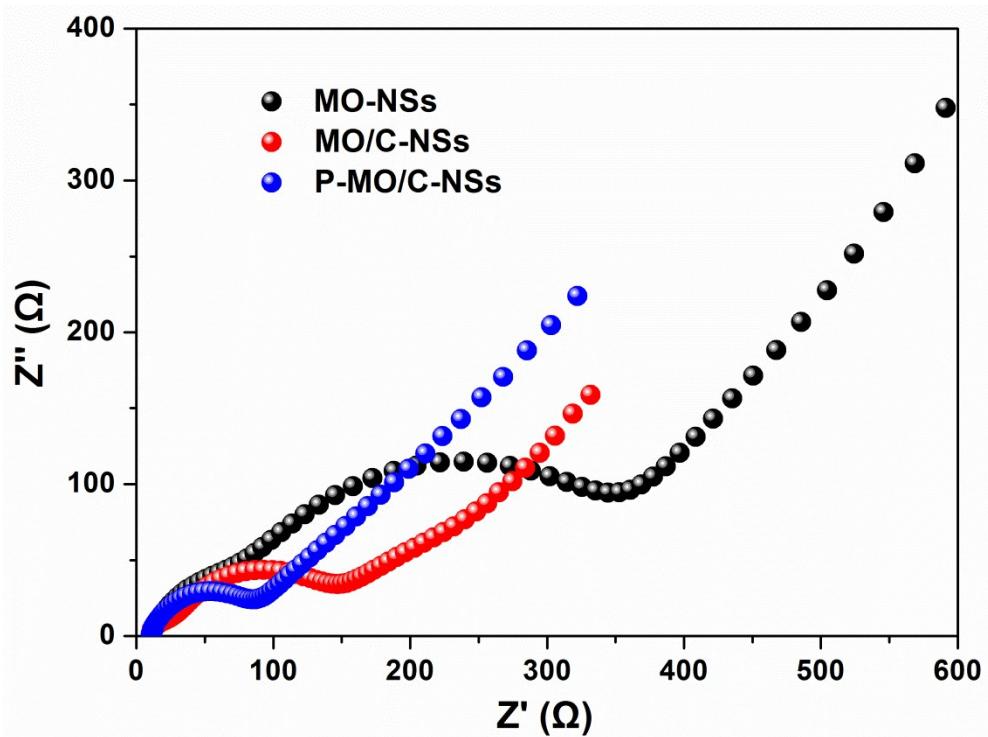


Fig. S13. Electrochemical impedance spectra of the three electrodes after 10 full cycles at 100 mA g⁻¹.

Table S1. The electrochemical performance comparison between our work and other published works

MnO ₂ materials	Reversible capacity [mAh/g], cycle numbers	Current density [mA/g]	Initial coulombic efficiency	Ref.
Porous MnO₂/C nanospheres	1110, 100	1000	75.2%	This work
MnO ₂ hollow urchins	481, 40	270	-	1
MnO ₂ nanotubes	656.5, 20	100	50%	2
MnO ₂ /carbon nanotube array	500, 15	50	<50%	3
Nanoflaky MnO ₂ /carbon nanotube	620, 50	200	58.3%	4
PTh-coated MnO ₂ nanosheets	500, 100	500	-	5
MnO ₂ /conjugated polymer/graphene	948, 15	50	59%	6
Graphene-MnO ₂ nanotube	495, 40	100	~50%	7
Carbon nanohorns/MnO ₂	565, 60	100	70%	8
MnO ₂ nanotubes	618, 300	200	-	9
Polymorphic MnO ₂	220.7, 30	100	<50%	10
Mesoporous MnO ₂ nanosheet arrays	900, 200	1000	-	11
Onion-like carbon/MnO ₂	600, 100	200	<50%	12
Porous graphene-like MnO ₂	836, 200	100	64%	13
Hollow MnO ₂ nanospheres	637, 150	100	<50%	14
MnO ₂ nanoflakes/graphene foam	1200, 300	500	~65%	15
Nitrogen-doped graphene/MnO ₂	750, 200	300	50%	16

Reference:

1. B. Li, G. Rong, Y. Xie, L. Huang and C. Feng, *Inorg. Chem.*, 2006, **45**, 6404.
2. J. Zhao, Z. Tao, J. Liang and J. Chen, *Cryst. Growth Des.*, 2008, **8**, 2799.
3. A. L. M. Reddy, M. M. Shaijumon, S. R. Gowda and P. M. Ajayan, *Nano Lett.*, 2009, **9**, 1002.
4. H. Xia, M. Lai and L. Lu, *J. Mater. Chem.*, 2010, **20**, 6896.
5. W. Xiao, J. S. Chen, Q. Lu and X. W. Lou, *J. Phys. Chem. C*, 2010, **114**, 12048.
6. C. X. Guo, M. Wang, T. Chen, X. W. Lou and C. M. Li, *Adv. Energy Mater.*, 2011, **1**, 736.
7. A. Yu, H. W. Park, A. Davies, D. C. Higgins, Z. Chen and X. Xiao, *J. Phys. Chem. Lett.*, 2011, **2**, 1855.
8. H. Lai, J. Li, Z. Chen and Z. Huang, *ACS Appl. Mater. Interfaces*, 2012, **4**, 2325.
9. L. Li, C. Nan, J. Lu, Q. Peng and Y. Li, *Chem. Commun.*, 2012, **48**, 6945.
10. K. Chen, Y. Dong Noh, K. Li, S. Komarneni and D. Xue, *J. Phys. Chem. C*, 2013, **117**, 10770.
11. M. Kundu, C. C. A. Ng, D. Y. Petrovykh and L. Liu, *Chem. Commun.*, 2013, **49**, 8459.
12. Y. Wang, Z. J. Han, S. F. Yu, R. R. Song, H. H. Song, K. Ostrikov and H. Y. Yang, *Carbon*, 2013, **64**, 230.
13. Y. Li, Q. Zhang, J. Zhu, X. L. Wei and P. K. Shen, *J. Mater. Chem. A*, 2014, **2**, 3163.
14. J. Yue, X. Gu, L. Chen, N. Wang, X. Jiang, H. Xu, J. Yang and Y. Qian, *J. Mater. Chem. A*, 2014, **2**, 17421.
15. J. Deng, L. Chen, Y. Sun, M. Ma and L. Fu, *Carbon*, 2015, **92**, 177.
16. T. Yang, T. Qian, M. Wang, J. Liu, J. Zhou, Z. Sun, M. Chen and C. Yan, *J. Mater. Chem. A*, 2015, **3**, 6291.