Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Porous ternary $TiO_2/MnTiO_3$@C hybrid microspheres as anode materials with enhanced electrochemical performances

Shimei Guo,[ac] Jiurong Liu,*[a] Song Qiu,[a] Wei Liu,*[b]

Yiran Wang, [d] Nannan Wu,[a] Jiang Guo,[d] and Zhanhu Guo *[d]

[a] Key Laboratory for Liquid–Solid Structural Evolution and Processing of Materials, Ministry of Education and School of Materials Science and Engineering, Shandong University, Jinan 250061, China

[b] State Key Laboratory of Crystal Materials, Shandong University, Jinan 250100, China

[c] College of Physics and Electronic Engineering, Qujing Normal University, Qujing, Yunnan 655011, China

[d] Integrated Composites Laboratory (ICL), Department of Chemical & Biomolecular Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States

* E-mail: jrliu@sdu.edu.cn (J. L.); weiliu@sdu.edu.cn (W. L.); zguo10@utk.edu (Z. G.).

Tel.: +86-531-88390236 (J. L.); (865) 974-2933 (Z. G.).

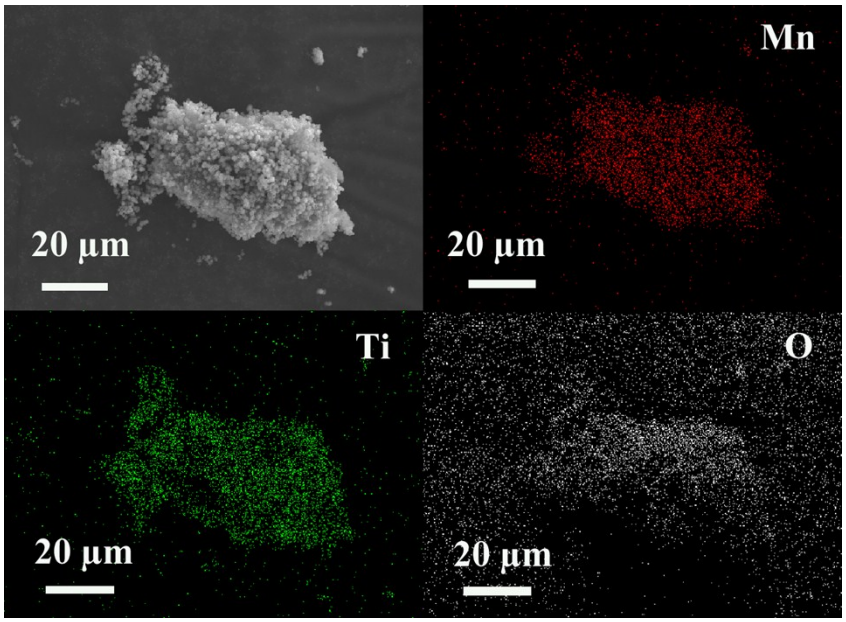

Fig. S1 SEM and EDX mapping images (Mn, Ti, O) of $TiO_2/MnTiO_3$@C.

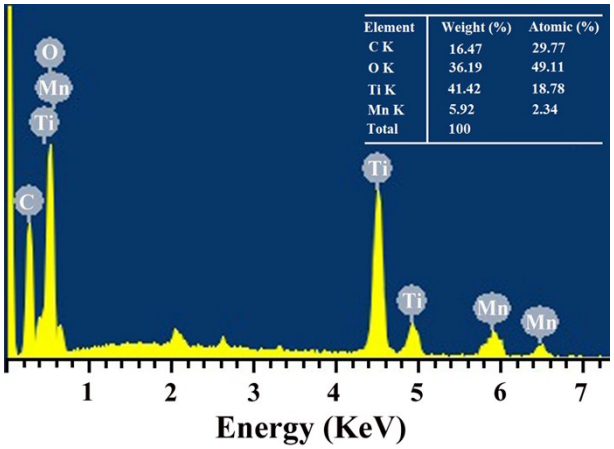

Fig. S2 EDS spectrum of $TiO_2/MnTiO_3$@C microspheres.

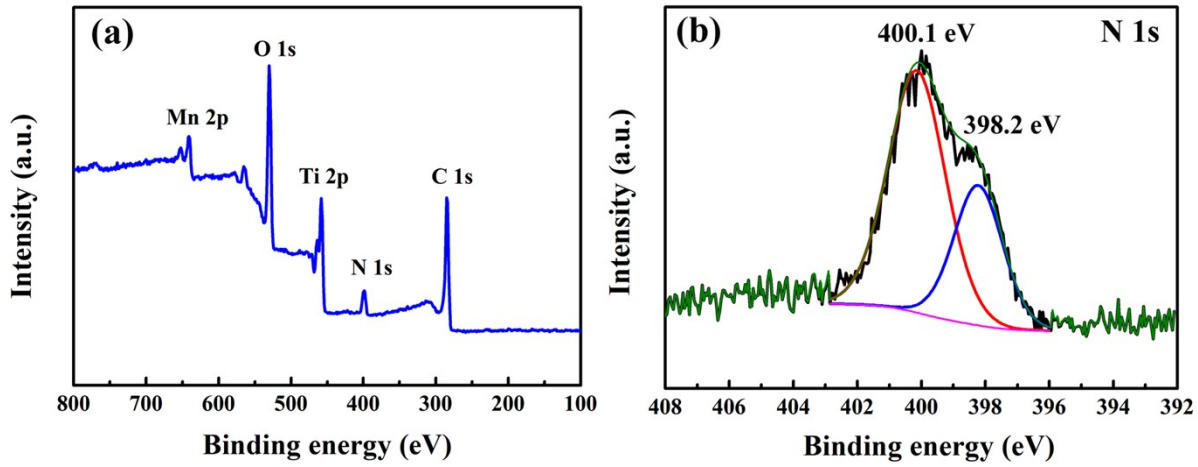

Fig. S3 XPS survey scan (a) and N 1s (b) spectra of $TiO_2/MnTiO_3$@C microspheres.

Table S1 Charge/discharge capacities (mA h g^{-1}) at 1st and 100th cycle at 100 mA g^{-1}, and discharge capacities of the 10th cycle at different current densities (mA g^{-1}).

Materials	Capacities (charge/ discharge)		Capacities of the 10th cycle at various densities					
	1st cycle	100th cycle	100	200	400	800	1600	100 (last)
TiO_2	121/319	100/101	105	67	49	30	21	100
$MnTiO_3$@C	208/574	102/ 104	212	161	114	74	28	201
TiO_2@C	300/541	233/235	258	220	189	153	111	254
TiO_2/Mn_3O_4	231/525	201/204	—	—	—	—	—	—
$TiO_2/MnTiO_3$@C	310/579	304/308	260	237	201	154	106	324

Table S2 List of the recent researches on TiO_2-based anodes for lithium ion batteries

Materials	Current density	Last cycle number	Reversible capacity (last cycle)	Capacity retention	Ref.
TiO_2@C	30 mA g^{-1}	90	143 mA h g^{-1}	86.6%	[1]
TiO_2/Co_3O_4	50μA cm^{-2}	70	280 μAh cm^{-2}	60.2%	[2]
TiO_2–SiO_2@C	30 mA g^{-1}	200	272 mA h g^{-1}	72.7%	[3]
MoO_2–TiO_2@CNT	33.6 mA g^{-1}	100	249.5 mAh g^{-1}	89.5%	[4]
TiO_2–MnO/C	100 mA g^{-1}	100	377 mA h g^{-1}	93%	[5]
$TiO_2/MnTiO_3$@C	100 mA g^{-1}	300	402.6 mAh g^{-1}	130%	this work

Supplementary Experimental Section

Synthesis of Carbon Coated $MnTiO_3$ ($MnTiO_3$@C) particles

In a typical synthesis, 0.989 g $MnCl_2.4H_2O$ was dissolved in 25 mL absolute ethanol to form a transparent solution A, while 1.7 mL TBT was added to another 25 mL absolute ethanol to form a transparent solution B. Afterwards, solution B was mixed with solution A under magnetic stirring for 30 min. The light brown precipitate appeared immediately when 9 mL $NH_3.H_2O$ was added dropwise to the mixing solution of solution A and B with vigorous stirring. After being stirred constantly for 2 hours at room temperature, the color of precipitate changed to dark brown. The resultant dark brown precipitate was centrifuged and washed using ethanol for five times, and then dried in an oven at 60 ºC for 12 h. Ti-Mn oxides were obtained by annealing the as-prepared precipitate at 500°C for 1 h. Carbon coating was conducted by mixing 1.5 g as-prepared Ti-Mn oxides with 0.5 mL pyrrole in a stainless steel autoclave, followed by carbonizing the mixed products at 550 ºC for 5 h in 30 mL autoclaves made of 316 L stainless steel (without

lining). After the reaction, $MnTiO_3$@C particles were obtained (as shown in Fig.S4).

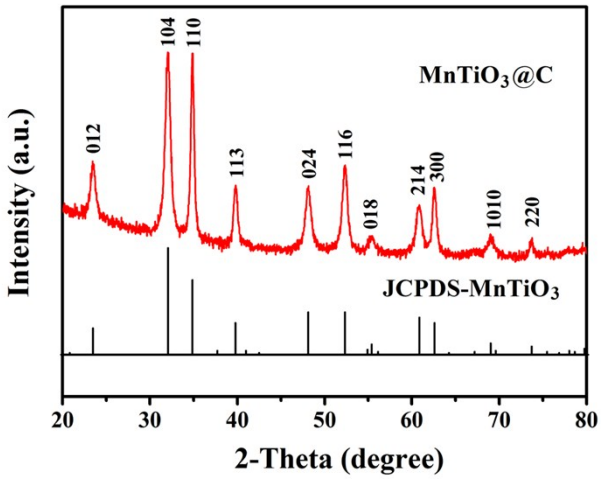

Fig. S4 XRD patterns of $MnTiO_3$@C

Notes and references

1 Z. Liu, J. Liu, J. Liu, L. Wang, G. Zhang, X. Sun, *Phys. Chem. Chem. Phys*., 2014, 16, 8808.

2 Y. Fan, N. Zhang, L. Zhang, H. Shao, J. Wang, J. Zhang, C. Cao, *Electrochim. Acta,* 2013, 94, 285.

3 J.-J. Zhang, Z. Wei, T. Huang, Z.-L. Liu, A.-S. Yu, *J. Mater. Chem. A,* 2013, 1, 7360.

4 D. Yuan, W. Yang, J. Ni, L. Gao, *Electrochim. Acta,* 2015, *163*, 57.

5 N. Zhao, T. Li, L. Jiao, Y. Qi, H. Zhu, J. Liu, R. Fan, N. Lun,Y. Bai. *J. Alloys Compd*., 2015, 640, 15.