Supporting Information

Hollow mesoporous ZnO/$ZnMnO_3$ microspheres: template-free formation process and enhanced lithium storage capability towards Li-ion batteries as a competitive anode

Yanru Zhang,[a, †] Zhengluo Wang,[a, †] Fakhr uz Zaman,[b] Zhiwei Zhao,[a] Xuan Sun,[b] Jinyang Zhang,[b] Linrui Hou,[b, *] Changzhou Yuan [a, b]*

[a] *School of Materials Science & Engineering, Anhui University of Technology, Ma'anshan, 243002, P.R. China*

[b] *School of Material Science & Engineering, University of Jinan, Jinan, 250022, P. R. China*

*E-mail: mse_houlr@ujn.edu.cn (*Prof.* L. R. Hou)

ayuancz@163.com; mse_yuancz@ujn.edu.cn (*Prof.* C. Z. Yuan)

† Theses authors contributed equally to this work

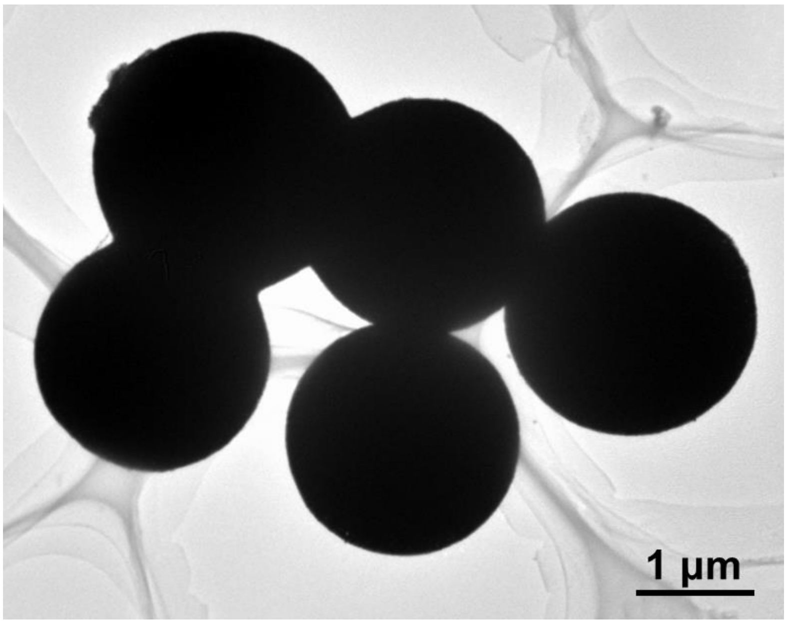

Fig. S1 TEM image of the ZnMn-glycolate-1 spheres.

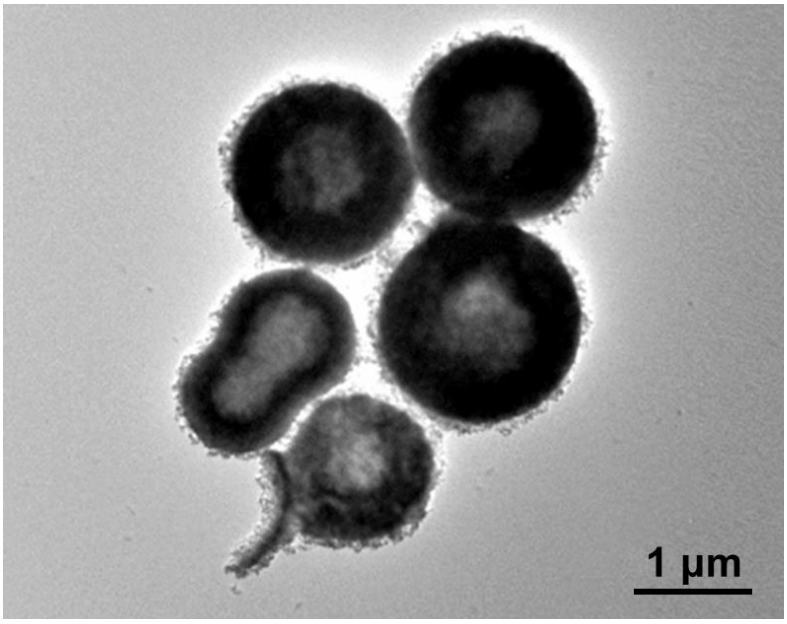

Fig. S2 TEM image of the ZnMn-glycolate-2 sphere.

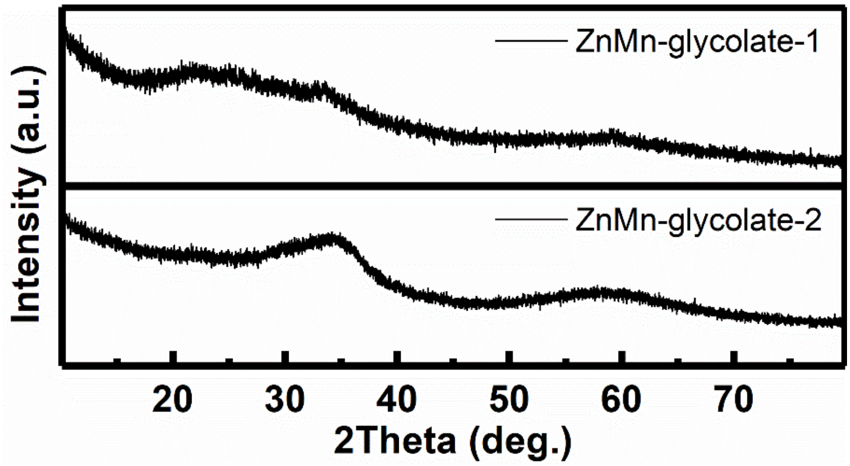

Fig. S3 XRD patterns of ZnMn-glycolate-1 and ZnMn-glycolate-2.

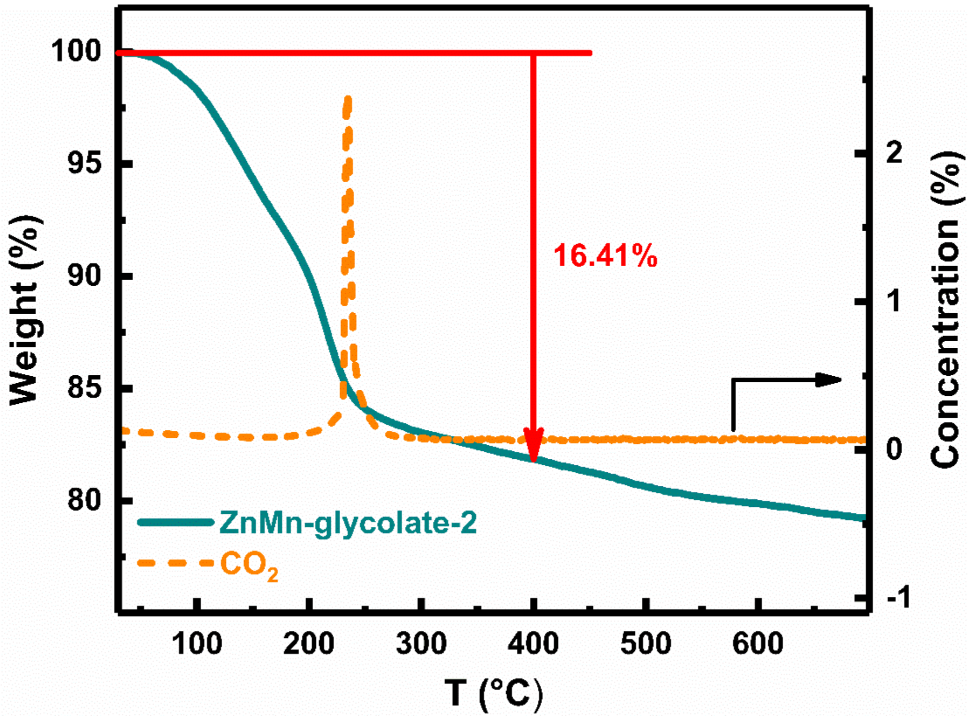

Fig. S4 TG-MS analysis of the ZnMn-glycolate-2 precursor under air flow with a temperature ramp of 10 ºC min^{-1}.

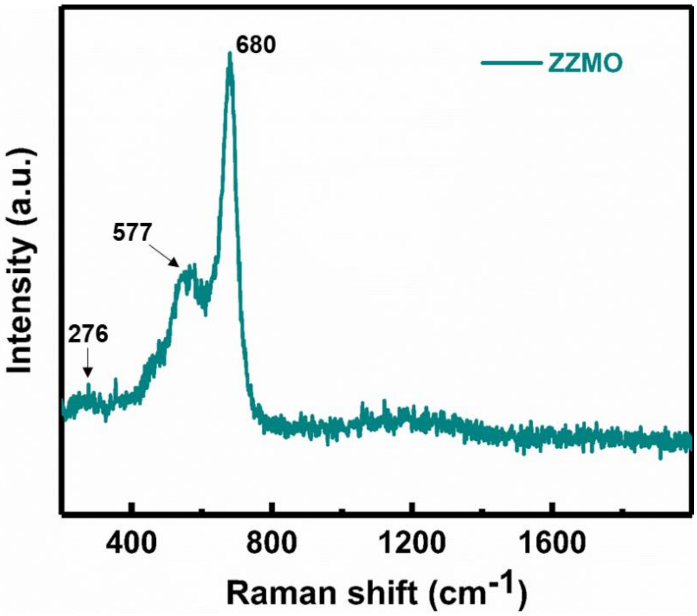

Fig. S5 Raman spectra of the hollow ZZMO microsphere.

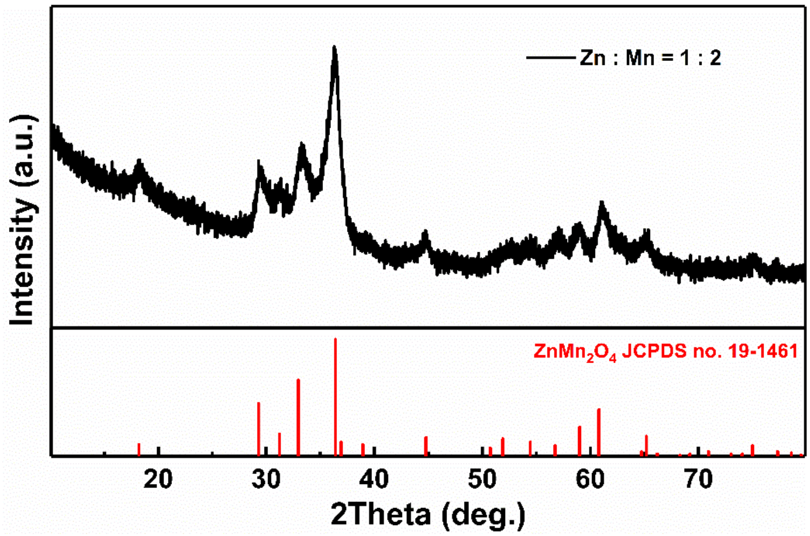

Fig. S6 XRD patterns of the sample for the radio of Zn to Mn for 1 : 2.

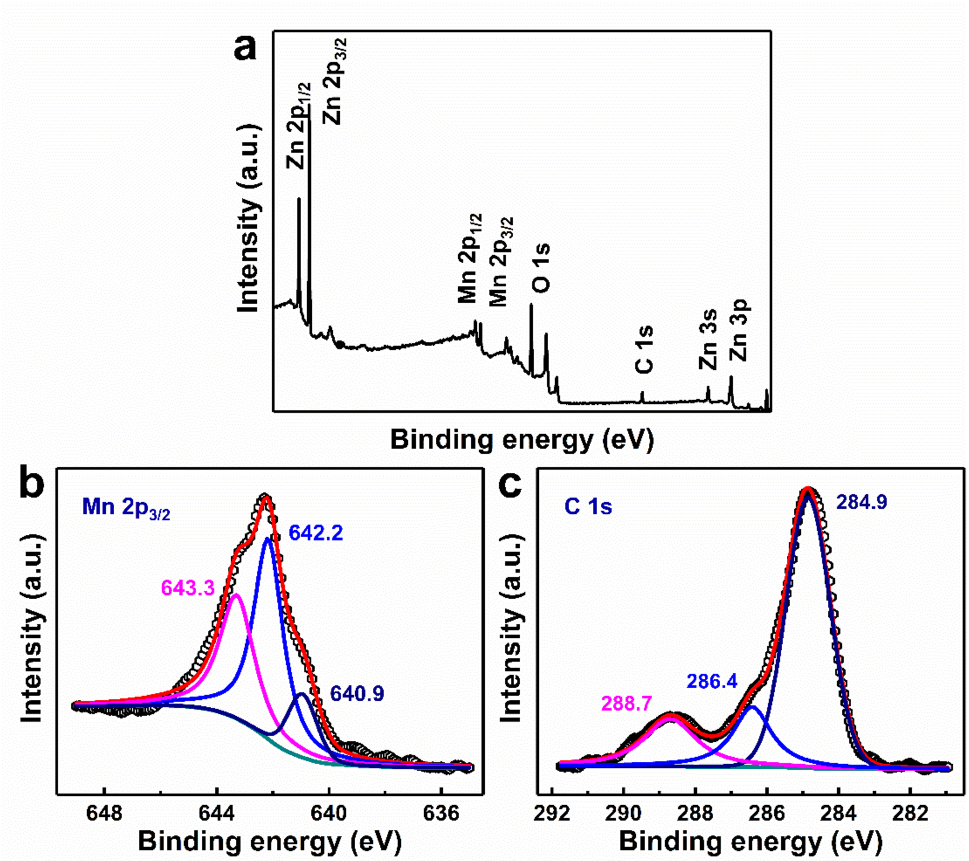

Fig. S7 (a) Full scan XPS spectrum and high-resolution elemental (b) Mn $2p_{3/2}$ and (c) C 1s spectra along with the fitted profiles for the ZZMO specimen.

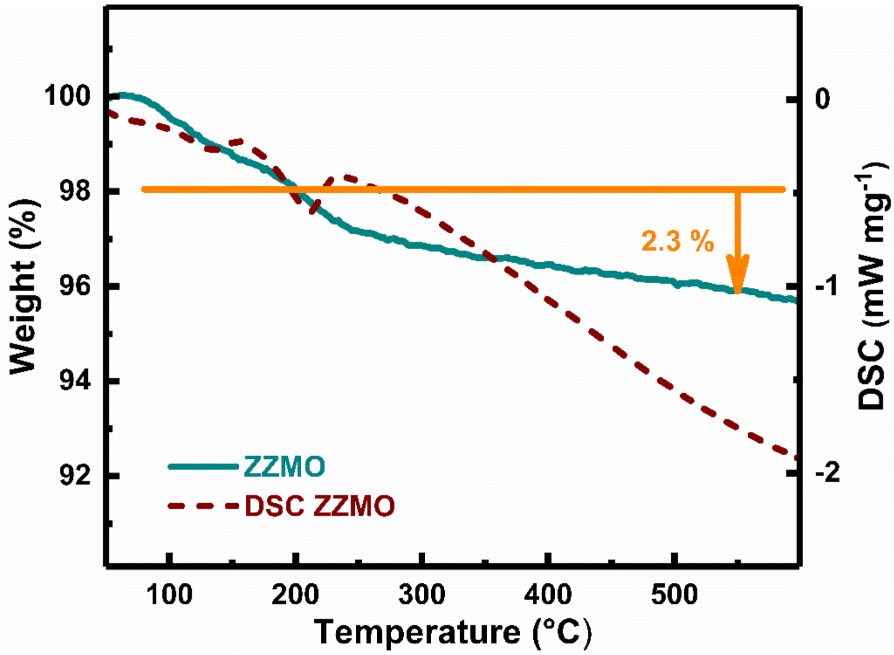

Fig. S8 TG analysis of the ZZMO under O_2 flow with a temperature ramp of 10 ºC min^{-1}.

Table S1 The C 1s XPS data of ZZMO sample.

Element	Binding/eV	Function	Ratio (%)
	284.9	C-C	66.1
C	286.4	C-O	17.0
	288.7	C=O	16.9

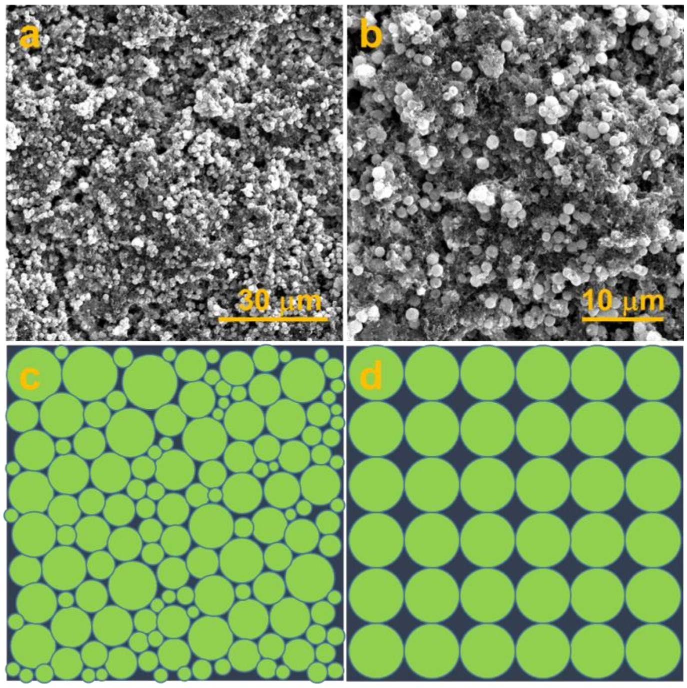

Fig. S9 (a, b) FESEM images of ZZMO electrode, and schematic illustration for (c) uneven size distribution and (d) the uniform size distribution of the electrodes.

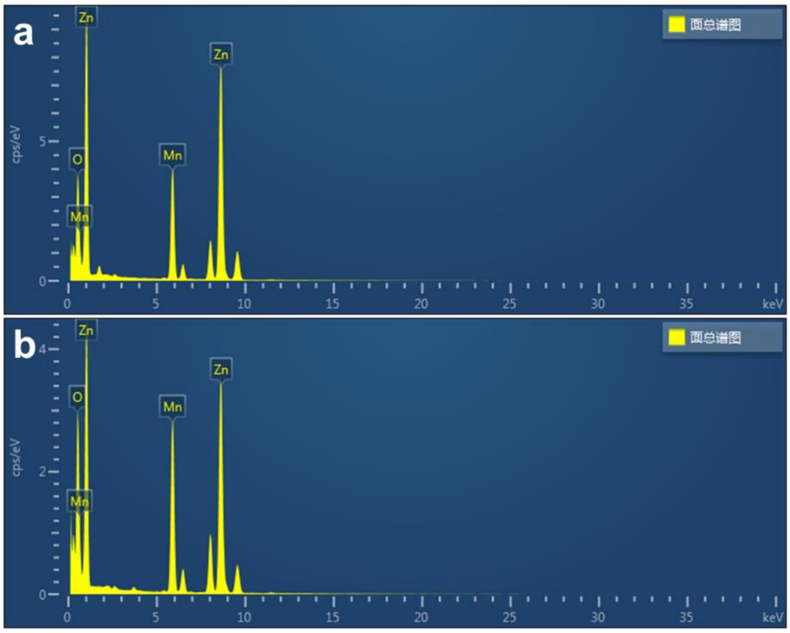

Fig. S10 EDX spectra of (a) ZZMO and (b) ZMO.

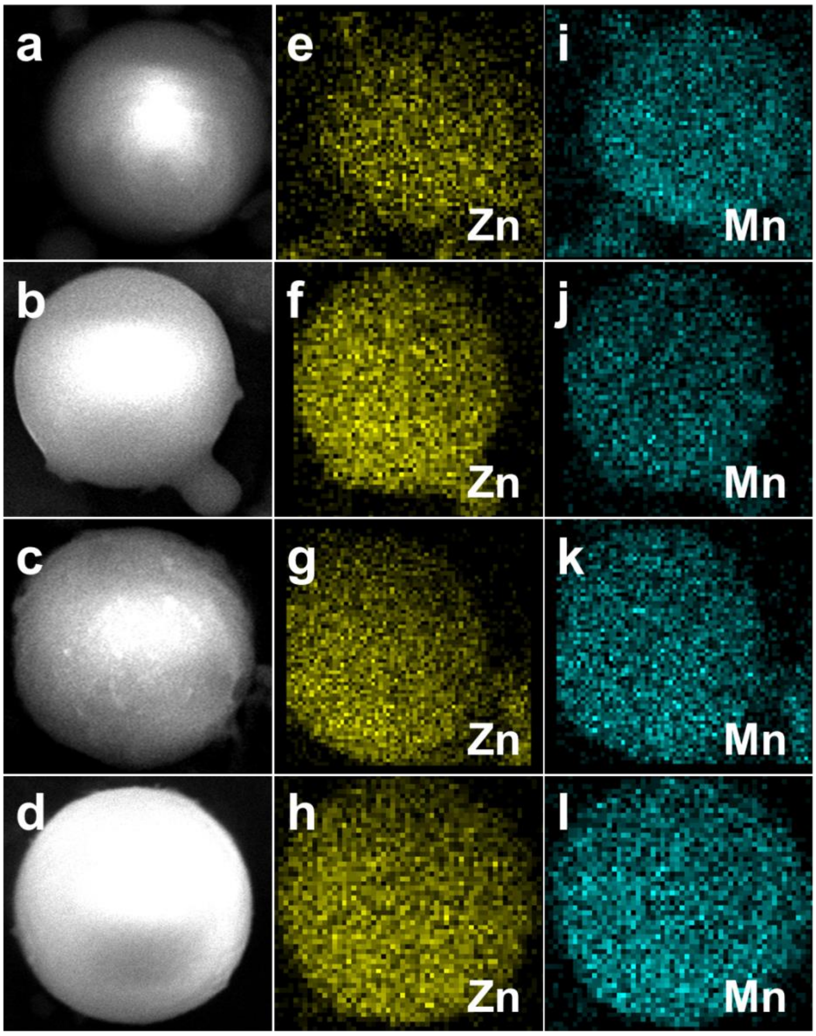

Fig. S11 (a-d) FESEM images and elemental (e-h, Zn and i-l, Mn) mapping images for the ratio of Zn to Mn as (a, e, i) 1 : 3, (b, f, j) 3 : 2, (c, g, k) 1.5 : 2 and (d, h, l) 1 : 1

Table S2 The EDX data of the different ratio of Zn to Mn samples.

The molar ratio of zinc acetate to manganese acetate	Content (at.%) of Zn in the polymer spheres	Content (at.%) of Mn in the polymer spheres	The atomic Zn/Mn ratio in the polymer spheres
Zn : Mn = 1 : 3	3.79	10.41	Zn : Mn = 1 : 2.75
Zn : Mn = 3 : 2	6.57	4.01	Zn : Mn = 1.64 : 1
Zn : Mn =1.5 : 2	5.14	6.28	Zn : Mn = 1 : 1.22
Zn : Mn = 1 : 1	6.63	5.93	Zn : Mn = 1.12 : 1

Table S3 BET results for the ZZMO and ZMO samples.

ZZMO		ZMO	
SSA (m^2 g^{-1})	115.9	SSA (m^2 g^{-1})	132.7
Pore volume (cm^3 g^{-1})	0.29	Pore volume (cm^3 g^{-1})	0.35
Average pore diameter (nm)	4.5	Average pore diameter (nm)	9.2

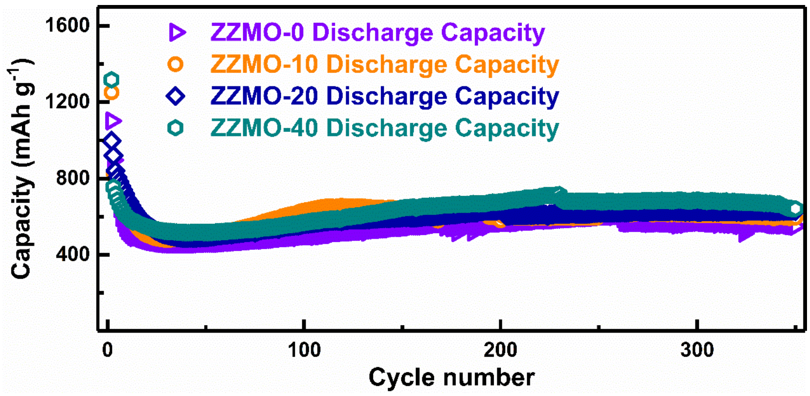

Fig. S12 Cycling behaviors of the ZZMO-0, ZZMO-10, ZZMO-20 and ZZMO-40 anodes measured at current density of 0.5 A g^{-1}

Table S4 Comparison of electrochemical performance reported previously and in this work.

Matrials	Cycling Stability (mAh g^{-1})	Ref. no
Porous ZMO spherulites	~ 879 at 0.5 A g^{-1} (150 cycles)	1
ZMO nanotube arrays	~ 815 at 0.5 A g^{-1} (550 cycles)	2
Triple-shelled ZMO	~ 290 at 0.4 A g^{-1} (150 cycles)	3
$ZnMn_2O_4$ hollow microspheres	~ 607 at 0.4 A g^{-1} (100 cycles)	4
Triple-shelled $ZnMn_2O_4$	~ 537 at 0.4 A g^{-1} (150 cycles)	3
$ZnMn_2O_4$ ball in ball hollow microspheres	~ 750 at 0.4 A g^{-1} (120 cycles)	5
$ZnMn_2O_4$-ZnO-C nanohybrids	~ 620 at 0.1 A g^{-1} (100 cycles)	6
ZZMO	~ 695 at 1 A g^{-1} (100 cycles)	In this work
ZZMO	~ 1045 at 0.5 A g^{-1} (350 cycles)	
ZMO	~ 743 at 0.5 A g^{-1} (350 cycles)	

Reference:

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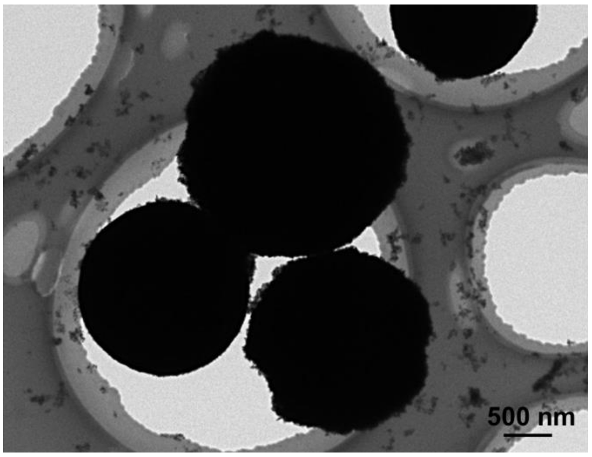

Fig. S13 The TEM image of bulk ZZMO material.

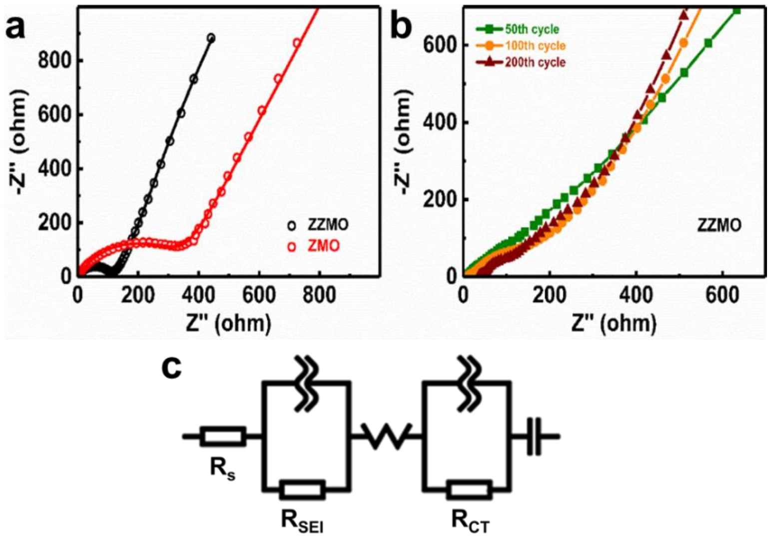

Fig. S14 (a) Electrochemical Impedance Spectra (EIS) of ZZMO and ZMO electrodes before cycling, (b) EIS of ZZMO electrode measured after total cycles of 50, 100, 200 respectively and (c) fitting mode for EIS data of ZZMO after cycling.

Table S5 The R_s and R_{ct} values for the ZZMO and ZMO electrodes before cycling, and the cycled ZZMO electrode after the 50th, 100th and 200th cycles as indicated.

Electrodes	Cycle number	R_s (Ω)	R_{ct} (Ω)
ZMO	0	3.01	338.5
ZZMO	0	5.8	115.8
	50th	6.8	97.3
	100th	10.7	82.4
	200th	32.6	72.5