

Supporting Information:

**Synthesis of mesoporous $\text{TiO}_2@\text{C}@\text{MnO}_2$ multi-shelled hollow nanospheres
with high rate capability and stability for lithium-ion batteries**

Li Liu,^{‡a} Jun Peng,^{‡a} Gang Wang^{a*}, Yanqing Ma^a, Feng Yu^{a*}, Bin Dai^a, Xu-Hong Guo^{a,b} and Ching-Ping Wong^{c,d}

^a School of Chemistry and Chemical Engineering, Key Laboratory of Materials-Oriented Chemical Engineering of Xinjiang Uygur Autonomous Region, Shihezi University, Shihezi, P.R. China. Email: gwangshzu@163.com, yufeng05@mail.ipc.ac.cn

^b State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, P. R. China

^c Department of Electronic Engineering, The Chinese University of Hong Kong, Shatin, New Territories, HongKong, SAR, China

^d School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, GA, 30332, United States

[‡]These authors contributed equally to this work.

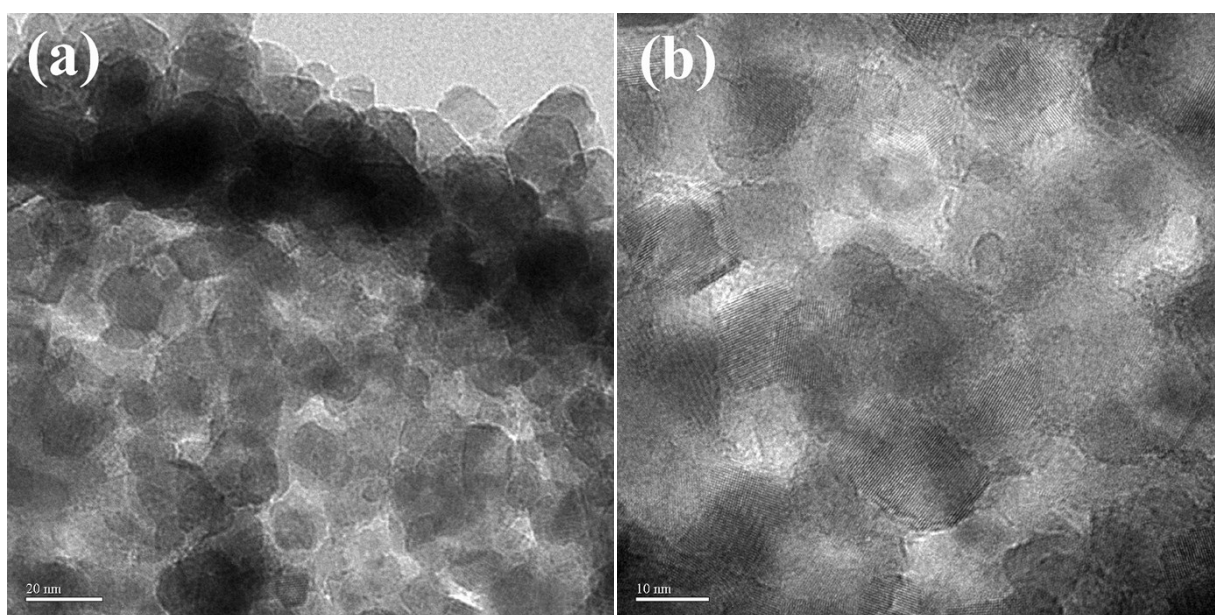


Figure S1 (a) Magnified TEM image of a single TiO_2 HNSs; (b) HRTEM image of the shell of TiO_2 HNSs

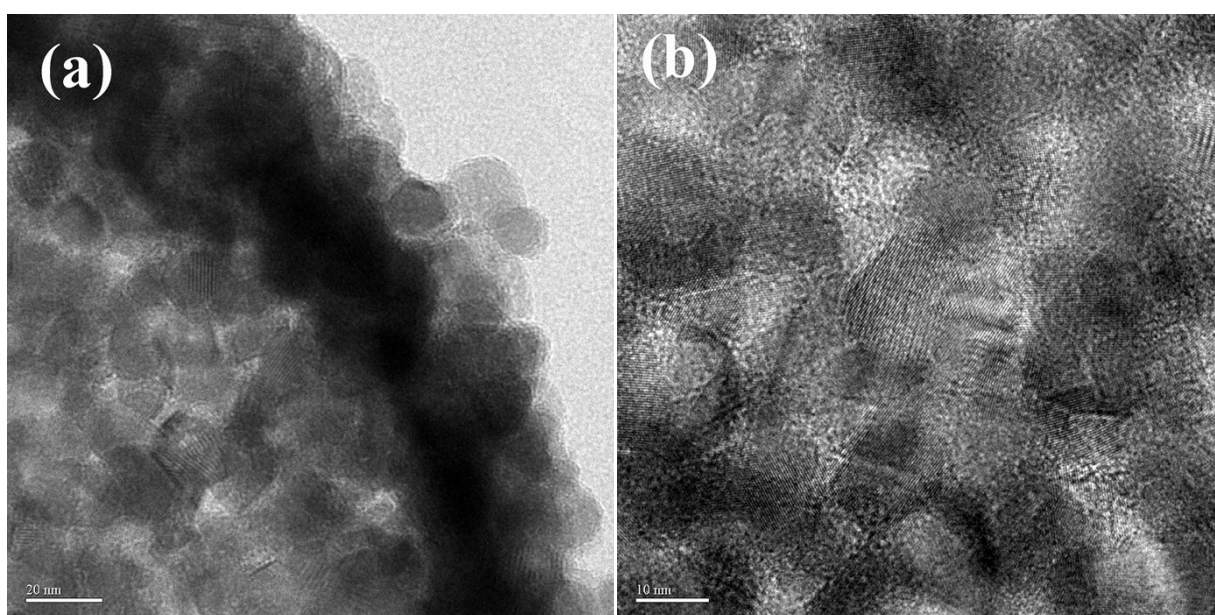


Figure S2 (a) Magnified TEM image of a single $\text{TiO}_2@\text{C}$ HNSs; (b) HRTEM image of the shell of $\text{TiO}_2@\text{C}$ HNSs

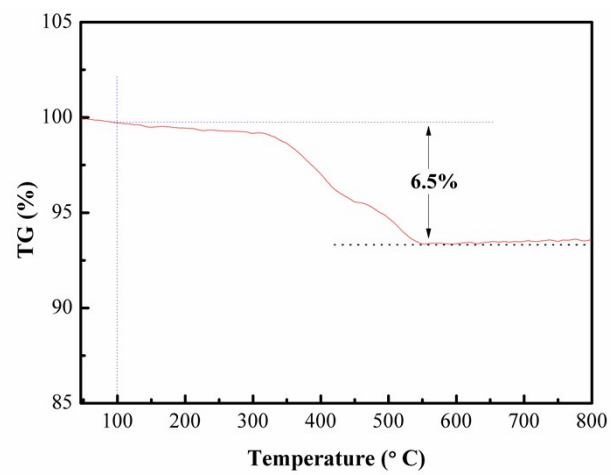


Figure S3 Thermogravimetric analysis of $\text{TiO}_2@\text{C}$ HNSs.

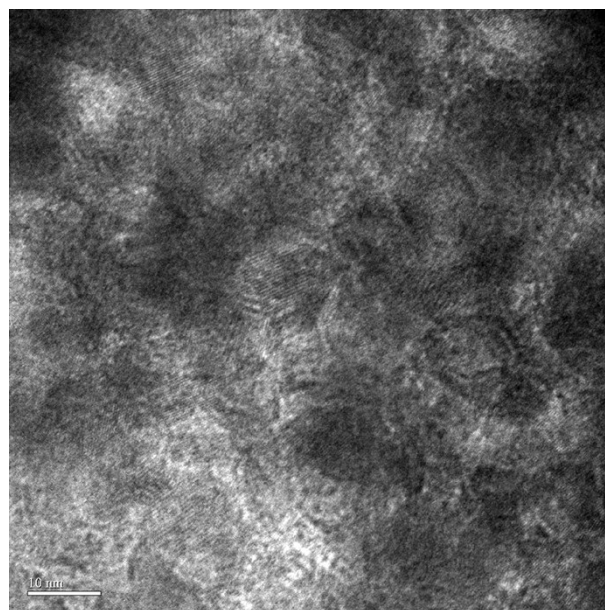


Figure S4 HRTEM image of the shell of $\text{TiO}_2@\text{C}@\text{MnO}_2$ HNSs

Table S1. The relative MnO₂ composition of TiO₂@C@MnO₂ HNSs samples.

Samples	The concentrations of KMnO ₄	MnO ₂ contents in the TiO ₂ @C@MnO ₂	The ration of TiO ₂ /MnO ₂
	[mol L ⁻¹]	[wt.%]	
a	0.008	9.1	9.43
b	0.016	17.8	4.82
c	0.04	29.7	2.89

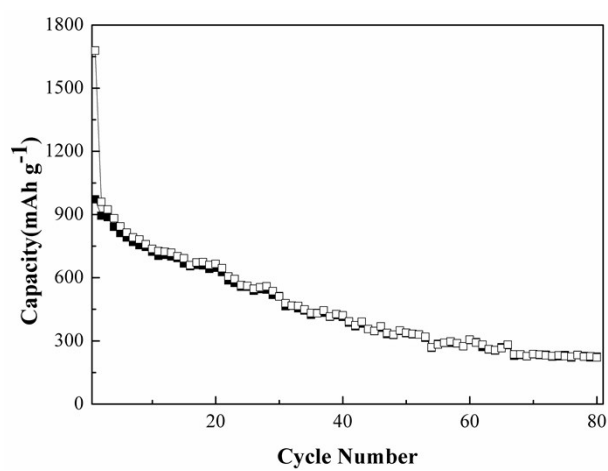


Figure.S5 Cycling performance of the bare MnO₂ HNSs at a current density of 100mA g⁻¹

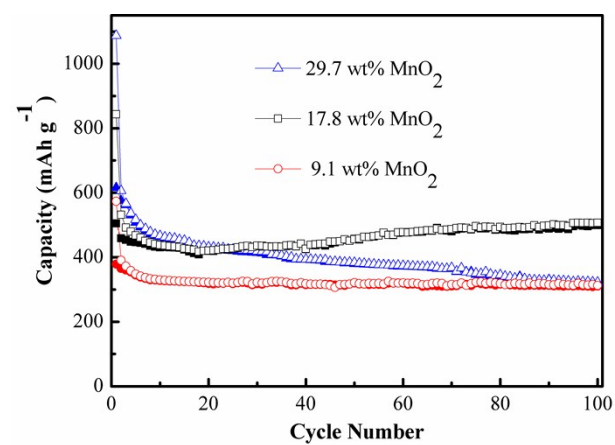


Figure S6 Cycling performance of $\text{TiO}_2@\text{C}@\text{MnO}_2$ with different account of MnO_2 at a current density of 100 mA g^{-1}

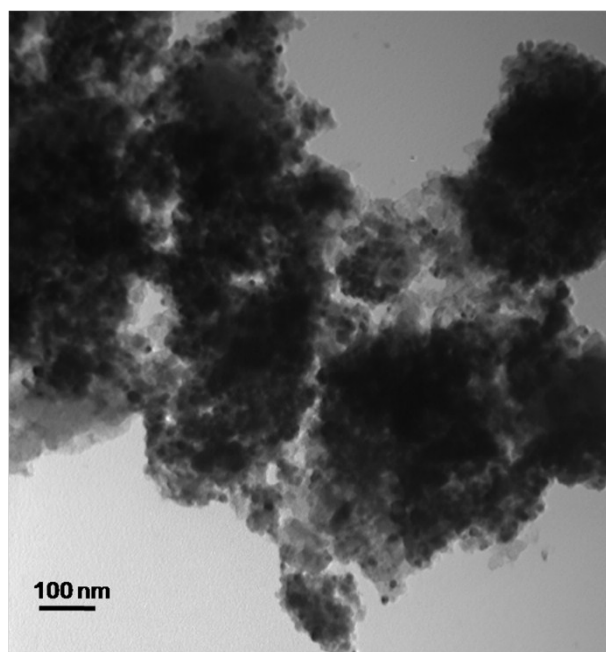


Figure S7 TEM image of the $\text{TiO}_2@\text{C}@\text{MnO}_2$ (29.7 wt% MnO_2) after 100th cycles.

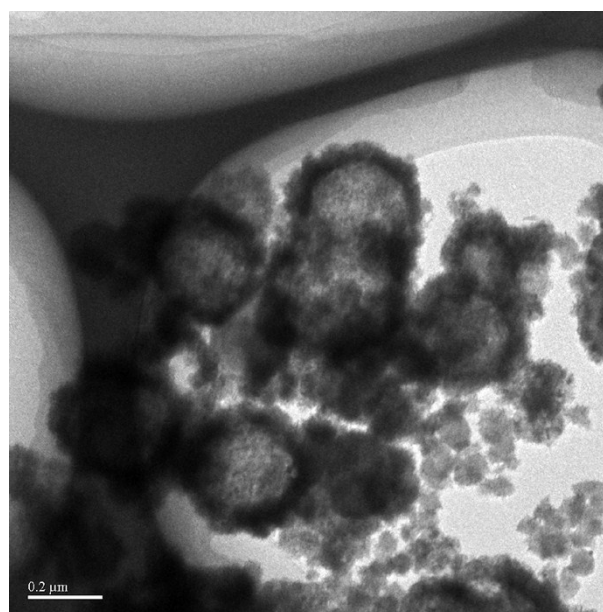


Figure S8 TEM image of the $\text{TiO}_2@\text{C}@\text{MnO}_2$ (17.8 wt% MnO_2) after the rate cycling test.

Table S2 List of recent work on TiO_2 based composites as the lithium-ion battery electrode.

Typical examples	Cycling Performance	Rate Performance	Ref
$\text{TiO}_2@\text{C}@\text{MnO}_2$	506.8 mAh g^{-1} at 100 mA g^{-1} (100 cycles)	242.5 mAh g^{-1} at 3.35 A g^{-1}	This work
multi-shelled HNSs	284.6 mAh g^{-1} at 1.0 A g^{-1} (200 cycles)	196.6 mAh g^{-1} at 6.7 A g^{-1}	
		149.9 mAh g^{-1} at 10 A g^{-1}	
$\text{TNAs}@\text{MnO}_2$	610 mAh g^{-1} at 0.35 A g^{-1} (100 cycles)	695 mAh g^{-1} at 0.14 A g^{-1}	[53]
nanosheets	320 mAh g^{-1} at 0.7 A g^{-1} (100 cycles)	400 mAh g^{-1} at 0.7 A g^{-1}	
	385 mAh g^{-1} at 0.7 A g^{-1} (700 cycles)	55 mAh g^{-1} at 3.5 A g^{-1}	
$\text{TiO}_2\text{-MnO}_2/\text{MnO}_2$	888 mAh g^{-1} at 0.1 A g^{-1} (50 cycles)	347 mAh g^{-1} at 1 A g^{-1}	[17]
heterostructures	185 mAh g^{-1} at 2 A g^{-1} (400 cycles)	212 mAh g^{-1} at 2 A g^{-1}	
		122 mAh g^{-1} at 4 A g^{-1}	
$\text{TiO}_2\text{-C}/\text{MnO}_2$	352 mAh g^{-1} at 0.335 A g^{-1} (100 cycles)	332 mAh g^{-1} at 0.67 A g^{-1}	[12]
core-double-shell	218 mAh g^{-1} at 3.35 A g^{-1} (150 cycles)	235 mAh g^{-1} at 3.35 A g^{-1}	
nanowire arrays		130 mAh g^{-1} at 10 A g^{-1}	
$\text{TiO}_2/\text{SnO}_2/\text{C}$	589.3 mAh g^{-1} at 0.2 A g^{-1} (550 cycles)	438.7 mAh g^{-1} at 0.4 A g^{-1}	[16]
hollow microspheres	403.6 mAh g^{-1} at 0.8 A g^{-1} (500 cycles)	371.3 mAh g^{-1} at 1 A g^{-1}	
	323.9 mAh g^{-1} at 2 A g^{-1} (500 cycles)	298.3 mAh g^{-1} at 3 A g^{-1}	
TiO_2 nanotube @ SnO_2	450 mAh g^{-1} at 1.6 A g^{-1} (50 cycles)	1400 mAh g^{-1} at 0.4 A g^{-1}	[56]
nanoflake		1000 mAh g^{-1} at 0.8 A g^{-1}	
		400 mAh g^{-1} at 3.2 A g^{-1}	
$\text{TiO}_2/\text{SnO}_2/\text{Carbon}$	438.9 mAh g^{-1} at 0.03 A g^{-1} (100 cycles)	313.9 mAh g^{-1} at 0.5A g^{-1}	[10]
hybrid nanofibers		198.36 mAh g^{-1} at 1 A g^{-1}	
		165 mAh g^{-1} at 2 A g^{-1}	
$\text{TS}@\text{G}$	617 mAh g^{-1} at 0.4 A g^{-1} (700 cycles)	600 mAh g^{-1} at 0.5A g^{-1}	[19]
		481 mAh g^{-1} at 1 A g^{-1}	

		388 mAh g ⁻¹ at 1.5 A g ⁻¹	
TiO ₂ -SnO ₂ /C	354.3 mAh g ⁻¹ at 0.5 A g ⁻¹ (120 cycles)	350.3 mAh g ⁻¹ at 1 A g ⁻¹	[20]
double-shell nanotubes	256 mAh g ⁻¹ at 1 A g ⁻¹ (710 cycles)	100 mAh g ⁻¹ at 2 A g ⁻¹	
		77 mAh g ⁻¹ at 5 A g ⁻¹	
TiO ₂ @Fe ₂ O ₃ core-shell	430.2 mAh g ⁻¹ at 0.2 A g ⁻¹ (103 cycles)	401.6 mAh g ⁻¹ at 0.4 A g ⁻¹	[54]
nanoframework arrays		268.4 mAh g ⁻¹ at 0.8 A g ⁻¹	
		168.3 mAh g ⁻¹ at 1.6 A g ⁻¹	
TiO ₂ /Fe ₂ O ₃ fiber-in-tube	642.5 mAh g ⁻¹ at 0.1 A g ⁻¹ (240 cycles)	261.8 mAh g ⁻¹ at 2 A g ⁻¹	[21]
hierarchical heterostructures		143.3 mAh g ⁻¹ at 4 A g ⁻¹	
		85.3 mAh g ⁻¹ at 6 A g ⁻¹	
TiO ₂ @Fe ₂ O ₃	530 mAh g ⁻¹ at 0.2 A g ⁻¹ (200 cycles)	490 mAh g ⁻¹ at 0.4 A g ⁻¹	[13]
hollow nanostructures		440 mAh g ⁻¹ at 0.8 A g ⁻¹	
		300 mAh g ⁻¹ at 1.6 A g ⁻¹	
TiO ₂ /Fe ₃ O ₄ -PG	703 mAh g ⁻¹ at 0.5 A g ⁻¹ (200 cycles)	264 mAh g ⁻¹ at 3 A g ⁻¹	[22]
ternary heterostructures	524 mAh g ⁻¹ at 1 A g ⁻¹ (200 cycles)	219 mAh g ⁻¹ at 5 A g ⁻¹	
		192 mAh g ⁻¹ at 8 A g ⁻¹	
TiO ₂ nanowire@MoS ₂	544 mAh g ⁻¹ at 0.1 A g ⁻¹ (100 cycles)	500 mAh g ⁻¹ at 0.4 A g ⁻¹	[23]
nanosheet		440 mAh g ⁻¹ at 0.8 A g ⁻¹	
		414 mAh g ⁻¹ at 1 A g ⁻¹	
TiO ₂ /MnTiO ₃ @C	402.6 mAh g ⁻¹ at 0.1 A g ⁻¹ (300 cycles)	200.4 mAh g ⁻¹ at 0.4 A g ⁻¹	[19]
porous microspheres		150.5 mAh g ⁻¹ at 0.8 A g ⁻¹	
		103.3 mAh g ⁻¹ at 1.6 A g ⁻¹	
G-TiO ₂ @Co ₃ O ₄	437 mAh g ⁻¹ at 0.1 A g ⁻¹ (190 cycles)	345 mAh g ⁻¹ at 0.2 A g ⁻¹	[11]
nanobelt arrays		250 mAh g ⁻¹ at 0.4 A g ⁻¹	
		204 mAh g ⁻¹ at 0.8 A g ⁻¹	
TiO ₂ @NiO core/shell	376.5 mAh g ⁻¹ at 0.2 A g ⁻¹ (100 cycles)	410 mAh g ⁻¹ at 0.4 A g ⁻¹	[49]
nanosheet arrays		250 mAh g ⁻¹ at 0.8 A g ⁻¹	
		199.2 mAh g ⁻¹ at 1.6 A g ⁻¹	
TiO ₂ @ZnO array	340.2 mAh g ⁻¹ at 0.2 A g ⁻¹ (100 cycles)	330 mAh g ⁻¹ at 0.4 A g ⁻¹	[15]
		253 mAh g ⁻¹ at 0.8 A g ⁻¹	
		205.2 mAh g ⁻¹ at 1.6 A g ⁻¹	

Table S3 Kinetic Parameters of the TiO₂ HNSs, TiO₂@C HNSs and TiO₂@C@MnO₂ HNSs.

Materials	SEI film resistance (R _f)	Charge-transfer resistance (R _{ct})
TiO ₂ HNSs	2.9 Ω	116.9 Ω
TiO ₂ @C HNSs	4.7 Ω	81.4 Ω
TiO ₂ @C@MnO ₂ HNSs	3.7 Ω	51.8 Ω