Electronic Supplementary Material (ESI) for New Journal of Chemistry.
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Supporting Information

Metal organic frameworks induced formation of core-shell $ZnCo_2O_4$ spheres composed by nanoparticles with Enhanced Lithium Storage Properties

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Experimental section

Typical synthesis of hollow sphere ZCO

All reagents used were of analytical grade and used without any purification. In a typical process, $Zn(NO_3)_2 \cdot 6H_2O$ (1 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (2 mmol), 2-methylimidazole (8 mmol) and citric acid (0.5 g) were dissolved in 3 mL methanol, respectively under ultrasound for 20 min at room temperature. Subsequently, the solution of $Zn(NO_3)_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and citric acid in methanol was slowly added to 2-methylimidazole solution. After forming a pink solution, the as-prepared mixture was transferred into a Teflon-lined stainless autoclave (20 mL volume) and then maintained at 120 ^oC for 18 h. After the autoclave cooled down to room temperature, the precipitate was washed and collected via centrifugation at 10000 rpm for 5 min with alcohol for several times. The samples were dryed with vacuum at 100 °C over 12 h. Ultimately, in order to acquire $ZnCo_2O_4$, the samples were annealed at 600 ^oC for 2 h in N_2 gas with a heating rate of 2 $^oC\ min^{-1}$. For comparation, polyhedral ZCO were prepared without citric acid through the above method.

Materials characterizations

X-ray diffraction (XRD) patterns were obtained by a Rigaku-D/MAX-2550PC diffractometer using Cu-Kα radiation (λ=0.1542). Scanning electron microscopy (SEM) images of the as-prepared materials were collected by employing an FEI Quanta 200F field emission scanning electron microscope. The microstructures of synthesized samples were observed transmission electron microscopy (TEM, FEI Tecnai G2 S-Twin, 300 kV).

Electrochemical measurements

For preparing the working electrode, the synthesized $ZnCo_2O_4$, carbon black and polyvinylidene fluoride (PVDF) at a weight ratio of 7 : 2 : 1 was dissolved in N-methylpyrrolidinone (NMP). In order to form a homogeneous slurry, it was stirred at a constant speed for 12 h. Finally, the slurry was coated onto a copper foil current collector and dried in a vacuum at 120 ^oC for 12 h. The average mass loading of active material with the mass of 0.5-1.2 mg. The electrolyte comprised a solution of 1 M $LiPF_6$ in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) according to the volume ratio of 1 : 1. The cells are assembled in an argon-filled glove-box. The discharge-charge performance was evaluated by using a NEWARE BTS-610 (Neware Co., Ltd., China) battery instrument at a galvanostatic current density with a voltage window of 0.01 - 3.0 V at room temperature. The cyclic voltammetry (CV) measurements was carried out in the range of 0.01-3.0 V (*vs* Li^+/Li) at a scan rate of 0.2 mV s^{-1}, and electrochemical impedance spectroscopy (EIS) were recorded in the frequency range of 0.01 Hz to 100 kHz at an open circuit potential, both of them were measured on a CHI604C (Shanghai Chenhua Instrument Company, China) electrochemical workstation. The full battery was fabricated with commercial $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ cathode and discharged hollow sphere ZCO with a mass ratio (including conductive agent) of 4:1. The full cells were assembled under inert atmosphere in an Ar-flled glove box, and galvanostatic measurements were performed at constant current densities 0.2 C in the range from 1.5 to 3.5 V on NEWARE BTS-610.

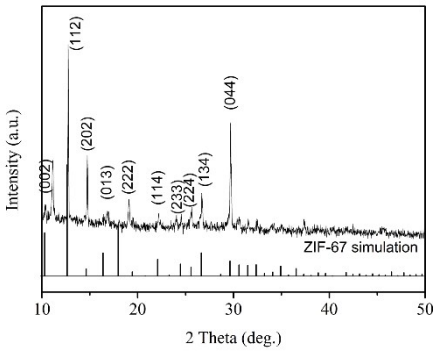

Fig. S1 XRD pattern of ZIF obtained at 120 ^{o}C for 18h with citric acid

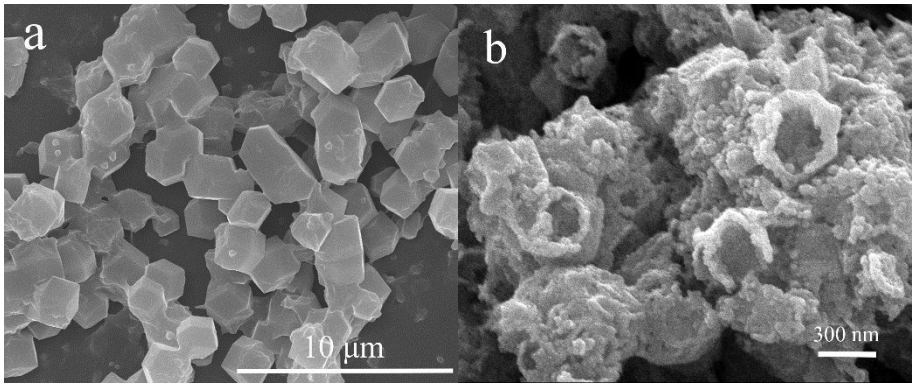

Fig. S2 SEM image of (a) ZIF and (b) ZCO synthesized without citric acid

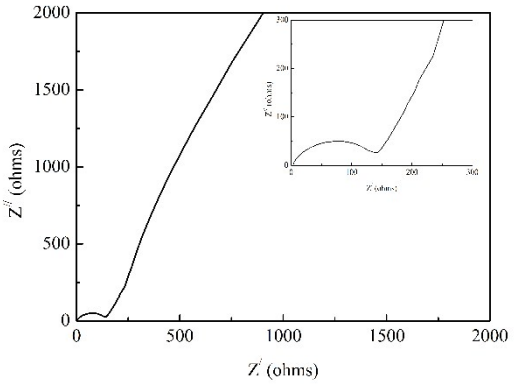

Fig. S3 Nyquist plot of the hollow sphere ZCO

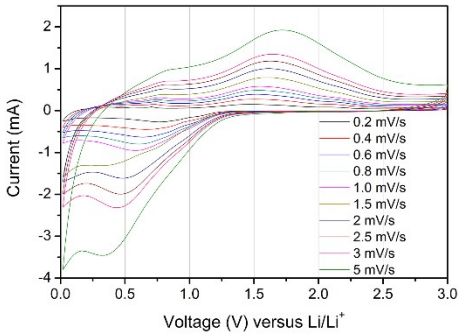

Fig. S4 CV curves of hollow sphere ZCO at the scan rates of 0.2mV/s, 0.4mV/s, 0.6 mV/s, 0.8mV/s, 1.0 mV/s, 1.5mV/s, 2 mV/s, 2.5 mV/s, 3 mV/s, and 5mV/s over the voltage range 0.01 ~ 3 V.

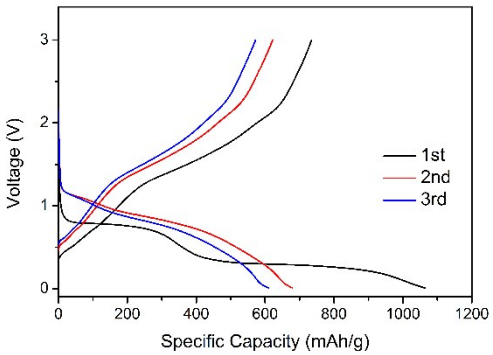

Fig. S5 Charge-discharge curves of hollow sphere ZCO.

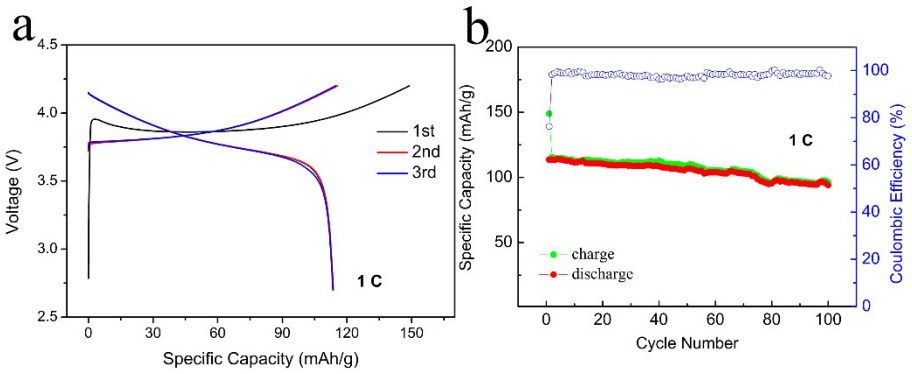

Fig.S6 (a) Charge-discharge curves of commercial LNCM for the first three cycles at 1 C. (b) Cycling performance of commercial LNCM for 100 cycles at 1 C.

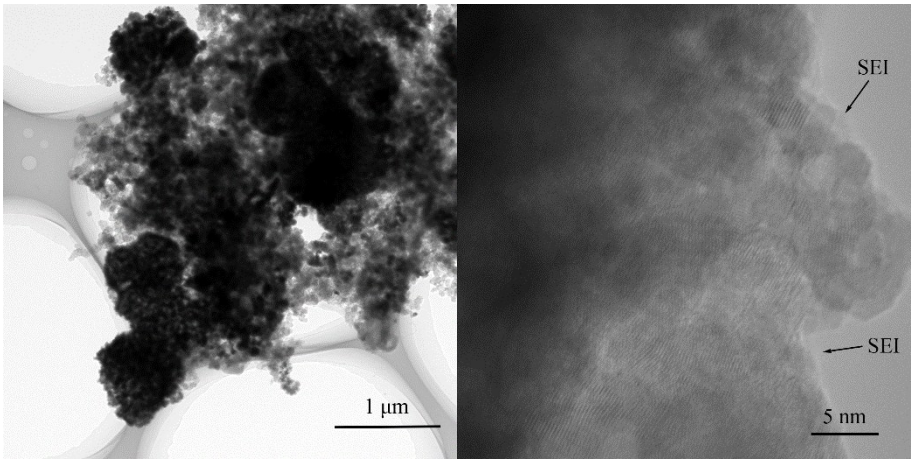

Fig. S7 (a) TEM and (b) HRTEM images of hollow sphere ZCO after cycling at 1 A/g for 200 cycles

Table S1 Summary of recent studies on MOF/ZIF-derived metal oxides anode materials for lithium ion battery

Active materials	MOF	Cycling capacity (mAh/g)	Rate capacity (mAh/g)	Reference
Sphere $ZnCo_2O_4$	ZIF-67	511 mAh/g after 400 cycles at 1 A/g	351 mAh/g at 5 A/g	This work
Porous Fe_2O_3 nanostructures	MIL-53(Fe)	744 mAh/g after 500 cycles at 1 A/g		[1]
porous $ZnO/ZnCo_2O_4$	Zn–Co-MOF	1016 mAh/g after 250 cycles at 2 A/g	630 mAh/g at 10 A/g	[2]
CuO–G composite	Cu-MOF	700 mAh/g at 60 mA/g	425 mAh/g at 600 mA/g	[3]
mesoporous $Ni_{0.3}Co_{2.7}O_4$ nanorod	Co/Ni-MOFs	1410 mAh/g after 200 cycles at 100 mA/g	656 mAh/g at 5 A/g	[4]
NiO/Ni/Graphene composites	Ni-MOFs	1144 mAh/g after 1000 cycles at 2 A/g	805 mAh/g at 15 A/g	[5]
ZnO@ZnO QDs/C	ZIF-8	699 mAh/g after 100 cycles at 500 mA/g	530 mAh/g at 1 A/g	[6]
porous MWCNTs/Co_3O_4 nanocomposites	ZIF-67	813 mAh/g at 100 mA/g after 100 cycles	514 mAh/g at 1 A/g	[7]
CuO@NiO microsphere	Cu-Ni-BTC MOF	1061 mAh/g at 100 mA/g after 200 cycles		[8]
porous $NiCo_2O_4$/NiO	ZIF-67	1497 mAh/g after 100 cycles at 0.2 A/g	689 mAh/g at 10 A/g	[9]

Reference

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