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Supplementary Information

The Synthesis of Core-shell MnO_2/3D-Ordered Hollow Carbon Sphere Composite and Its Superior Electrochemical Capability for Lithium Ion Battery

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Experimental

Synthesis of hollow carbon sphere (HCS). The hollow carbon sphere (HCS) was obtained by templating against hard particles. Typically, 5.5 g resorcinol (R) and 9.5 ml formaldehyde (F) were dissolved in 30 mL water. The amount of PMMA emulsion was added into the solution. After hermetic in the 85 °C oven for 72 h, the precursor was sintered at 800 °C for 1 h under nitrogen atmosphere to get HCS. The PMMA template was prepared by emulsifier-free emulsion polymerization of methyl methacrylate monomer (MMA) at 76 °C with potassium persulfate (KPS) as an initiator.

Synthesis of MnO_2/HCS composites. MnO_2/HCS composites were prepared by a facile redox method. Typically, 30 mg of HCS and 100 mg of P123 were dispersed in 30 mL water. After stirring for 3 h, 39, 79, 158 and 600 mg (excess) of $KMnO_4$ were added into the solution, respectively. The solutions were incubated at 80 °C with continuous magnetic stirring for 3 h in a water bath, then filtrated and rinsed to get the final products.

Materials characterization. The crystal structure of the products was characterized by X-ray powder diffraction (Philips Panalytical X-pert, using Cu Kα1 radiation λ=1.5405 Å). The morphology of the products was observed by field-emission scanning electron microscopy (SEM Hitachi S-4800, 10 KV) and transmission electron microscopy (TEM Hitachi JEM-2100, 200 KV). Compositional investigation of samples was carried out by X-ray photoelectron spectroscopy (XPS, PHI Quantera-2000). TGA was carried out on a Pyris Diamond TG-DTA (PE Co., US) to investigate the mass loading of MnO_2 in a constant flow of dry air (50 ml min^{-1}) and a heating/cooling rate of 5 °C min^{-1}. Alumina crucibles were loaded with 5-10 mg of sample powder. The as-prepared products were named MnO_2/HCS-68%, MnO_2/HCS-47%, MnO_2/HCS-35% and pure MnO_2.

Electrochemical measurements. Electrochemical measurements were carried out in CR2016 type coin cell. The working electrode was made up by 80wt% active materials, 10wt% super P and 10wt% water soluble polymer n-lauryl acrylate (LA Chengdu, China). The mass loading of the working electrode is about 1 mg (~0.8 mg cm^{-2}). Cu foil was used as current collector and Li foil was used as counter electrode. 1 M $LiPF_6$ in ethylene carbonate, dimethyl carbonate and diethyl carbonate (EC/DMC/DEC, v/v/v=1:1:1) solution was used as the electrolyte.

Galvanostatic charge and discharge measurements were carried out in the voltage range between 0.01 and 3.0 V vs. Li/Li$^+$ at different current densities using a Neware battery system (Shenzhen NEWARE Co., China). All the capacities calculated in this work are based on the whole mass of composites.

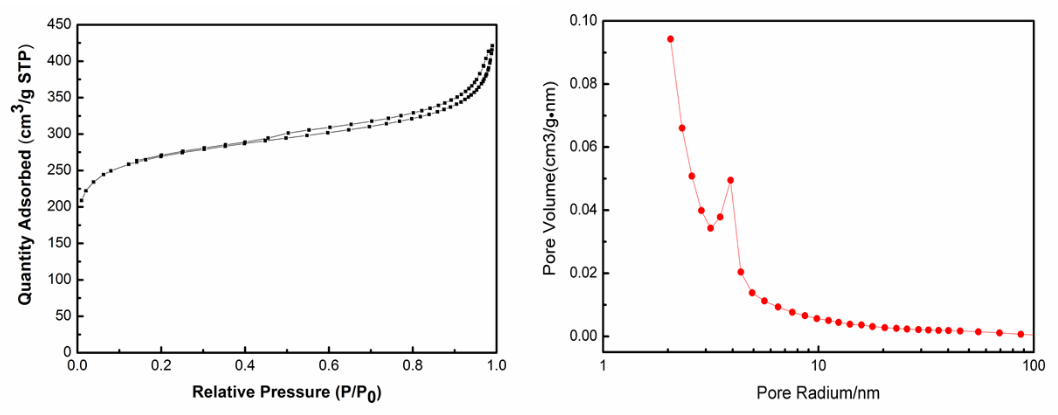

Fig. S1 N_2 adsorption-desorption isotherm and pore-size distribution of HCS.

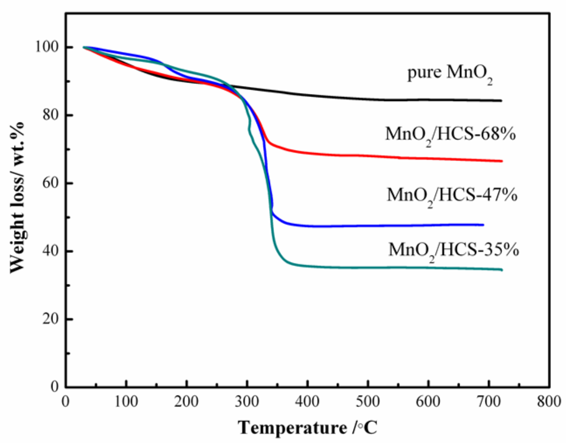

Fig. S2 TG curves of MnO_2/HCS composites.

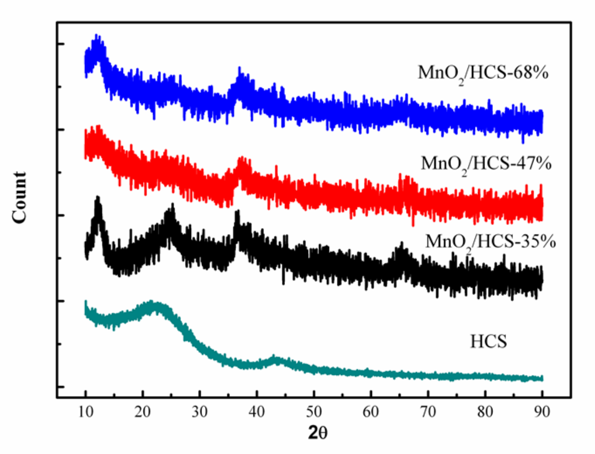

Fig. S3 XRD patterns of hollow carbon sphere (HCS) and MnO_2/HCS composites.

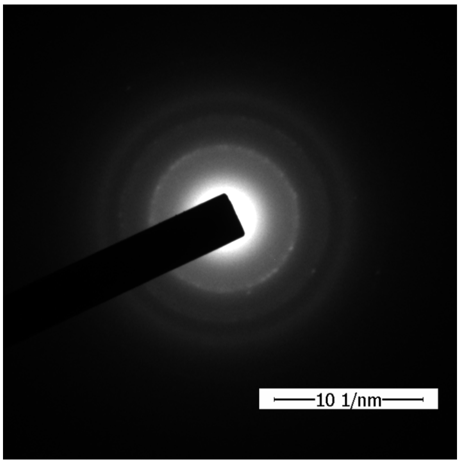

Fig. S4 SAED pattern of MnO_2/HCS-47% composite.

The battery performances were tested by galvanostatic method in CR2016 coin cell. The theoretical capacity of MnO_2/HCS composites can be described as following equation:

$Q_{capacity} = a*Q_{MnO2} + (1-a)*Q_{HCS}$

Where the theoretical capacity Q_{MnO2}=1233 mAh g^{-1}, Q_{HCS}=372 mAh g^{-1} and *a* is the mass ratio of MnO_2 in MnO_2/HCS composites.

Table S1 comparative study of the stable capacity versus different MnO_2 mass loading at a current density of 0.1 A g^{-1} after 100 cycles.

	a, MnO_2 mass loading (%)	theoretical capacity of MnO_2/HCS composites	real capacity of MnO_2/HCS composites	real capacity based on MnO_2
MnO_2/HCS-68%	68	957.5 mAh g^{-1}	330 mAh g^{-1}	332.6 mAh g^{-1}
MnO_2/HCS-47%	47	776.7 mAh g^{-1}	692.5 mAh g^{-1}	1107.5 mAh g^{-1}
MnO_2/HCS-35%	35	673.4 mAh g^{-1}	615 mAh g^{-1}	1154 mAh g^{-1}

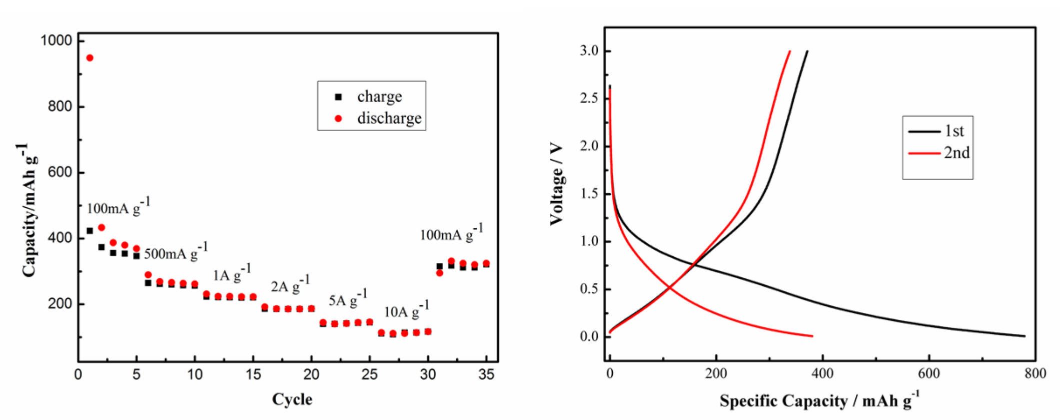

Fig. S5 Rate performance and discharge-charge curves of HCS.

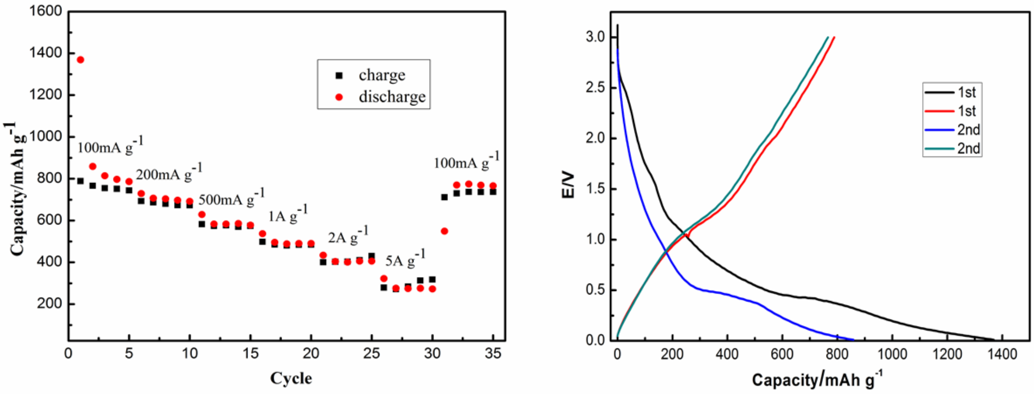

Fig. S6 Rate performance and discharge-charge curves of MnO_2/HCS-47%.

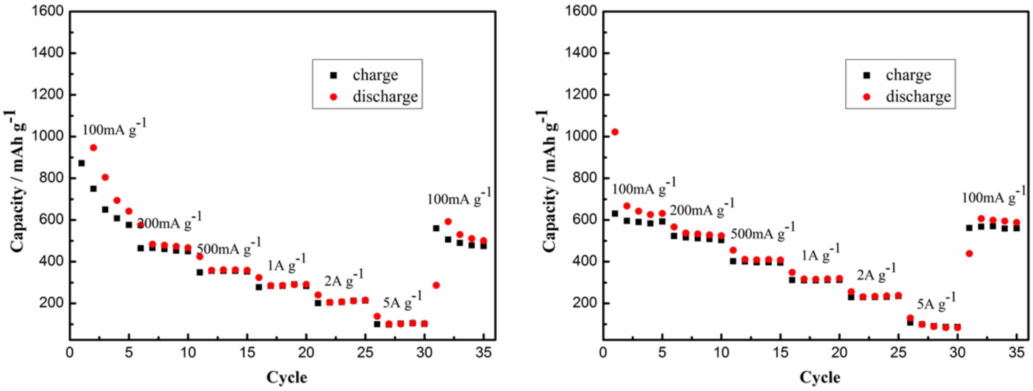

Fig. S7 Rate performances of MnO_2/HCS-68% and MnO_2/HCS-35%.