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Building better rechargeable Zn-Mn batteries with highly active Mn_3O_4/carbon nanowires cathode and the neutral $Na_2SO_4/MnSO_4$ electrolyte

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Experimental Details:

Synthesis of long MnO_2 NWs: The starting materials of MnO_2 NWs were prepared in advance via a simple hydrothermal process. 1.51 g $(NH_4)_2S_2O_8$, 1.12 g $MnSO_4·H_2O$ and 2.85 g $(NH_4)_2SO_4$ were dissolved in deionized (DI) water (30 mL) aided by the ultra-sonication (time: 15 min). The obtained solution was then transferred to a Teflon-lined stainless autoclave, heated to 200 °C and kept for 12 h. When cooled down to room temperature naturally, the products were collected by filtration, washed with DI water for three times and dried at 60 °C in a vacuum oven.

Synthesis of MnO@C NWs intermediates: 0.5 g MnO_2 NWs and 0.15 g dopamine (DA) powders were successively dispersed into 300 mL *Tris* buffer solution (pH 8.5) and subjected to an ultrasonication treatment for 1 h. Then, the as-formed mud-like MnO_2@PDA products were treated by vacuum filtration, washed with deionized water several times and dried at 60 °C in a vacuum oven for 12 h. Later, the samples were annealed at 600 °C under Ar flow (50 sccm) for 0.5 h to evolve into MnO@C NWs intermediates.

Synthesis of Mn_3O_4@C NWs: 10 mL H_2O_2 was slowly dropped into a glass container (50 mL) wherein 0.5 g MnO@C NWs were involved. The mud-like mixtures were transferred into a Teflon-lined stainless autoclave, heated to 120 °C and kept still for 1 h. Afterwards, the samples were harvested by vacuum filtration, washed with deionized water several times and dried at 60 °C in a vacuum oven for 12 h.

Synthesis of Zn$\subset$CB matrix: The Zn and CB powders were mixed in a mass ratio of 9:1 and carefully grinded. Then, such powder mixtures were annealed at 500 °C for 1 h in Ar atmosphere. When cooled down naturally, the samples were collected and grinded into fine powders for later electrode fabrications.

Characterization Techniques and Battery Testing: Sample Characterizations were conducted using field emission scanning electron microscope (FESEM, JEOL JSM-7800F) with energy dispersive X-ray spectroscopy (EDS), transmission electron microscope (TEM, JEM 2010F), X-ray powder diffraction (XRD), X-ray photoelectron spectroscopy (XPS; Thermo Electron, VG ESCALAB 250 spectrometer). Raman spectrum was made with a 532 nm diode laser as the excitation source. The working electrodes were fabricated by a conventional slurry-coating method. For Mn_3O_4@C cathodes, the active Mn_3O_4@C hybrid powders, poly(vinylidene fluoride) (PVDF) binder and CB were mixed in a mass ratio of 70:15:15 and evenly dispersed in N-methyl-2-pyrrolidone (NMP) to form slurries. Then, the obtained homogeneous slurry was pasted onto a graphite rod (thickness: 2 mm) and dried at 60 °C for 12 h under a vacuum condition. The mass loading on each current collector was controlled to be 2.5–4.0 mg cm^{-2}. The fabrication of Zn⊂CB counter electrode was achieved by the same method except that the slurry mixture was pasted onto a Ni foam (thickness: 1.5 mm). For single electrode testing, the electrochemical properties were measured in a three-electrode system, with a Pt foil as counter electrode and an Ag/AgCl as reference electrode in 1 M $ZnSO_4$+0.5 M Na_2SO_4+0.1 M $MnSO_4$ aqueous. Full-cell batteries were assembled with pre-activated Zn@C anodes, Mn_3O_4@C NWs cathodes and the aqueous solution (1 M $ZnSO_4$+0.5 M Na_2SO_4+0.1 M $MnSO_4$). To balance the charge storage between electrodes, the cathode/anode mass ratio is eventually determined to be ~1.1:1 by referring to rate behaviors of both electrodes. Electrochemical impedance spectroscopy (EIS) measurements were performed by applying an AC voltage with 5 mV amplitude in a frequency range from 0.1 Hz to 100 kHz at open circuit potential. The specific capacities were calculated from galvanostatic charge/discharge curves by using

$$Q_{spec} = I \times t/3.6m$$

wherein I, t, and m represent the discharging current (A), the discharging time (s), and the mass of actives on electrode (g), respectively. The specific energy and power densities (E and P) based on the total mass of actives on electrodes were calculated according to equations of

$$E = \int_0^{\Delta t} IV(t)dt$$

$$P = E/\Delta t$$

wherein I is the discharging current (A), V is discharging voltage (V), dt is the time differential and Δt is the discharging time (s).

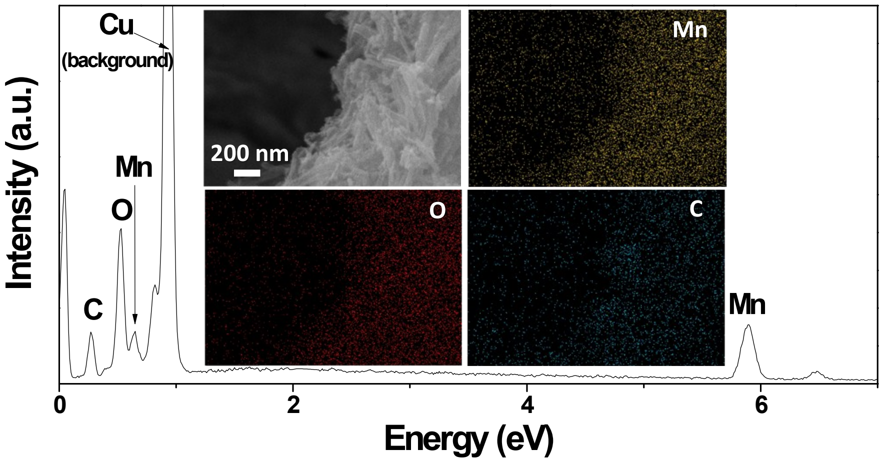

Fig. S1. EDS spectrum and the elemental mappings of Mn_3O_4@C hybrid NWs.

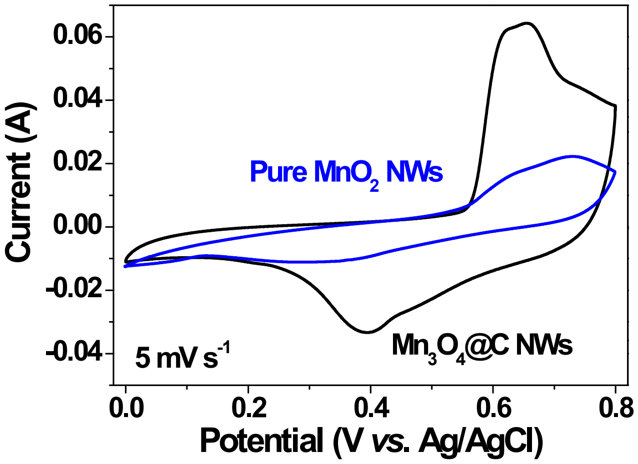

Fig. S2. CV testing comparisons between Mn_3O_4@C and pure MnO_2 NWs.

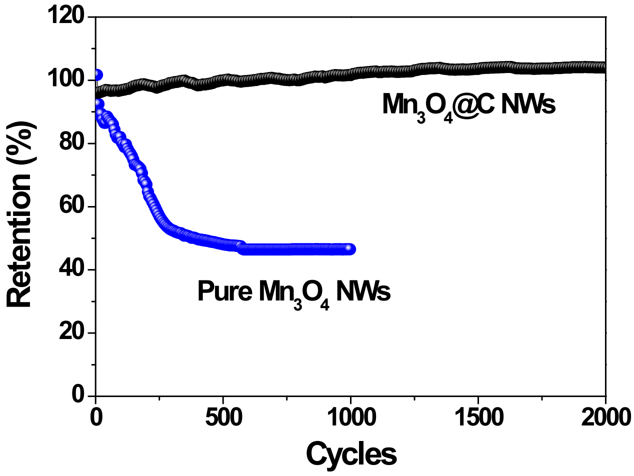

Fig. S3. Cyclic comparisons between Mn_3O_4@C and pure Mn_3O_4 NWs.

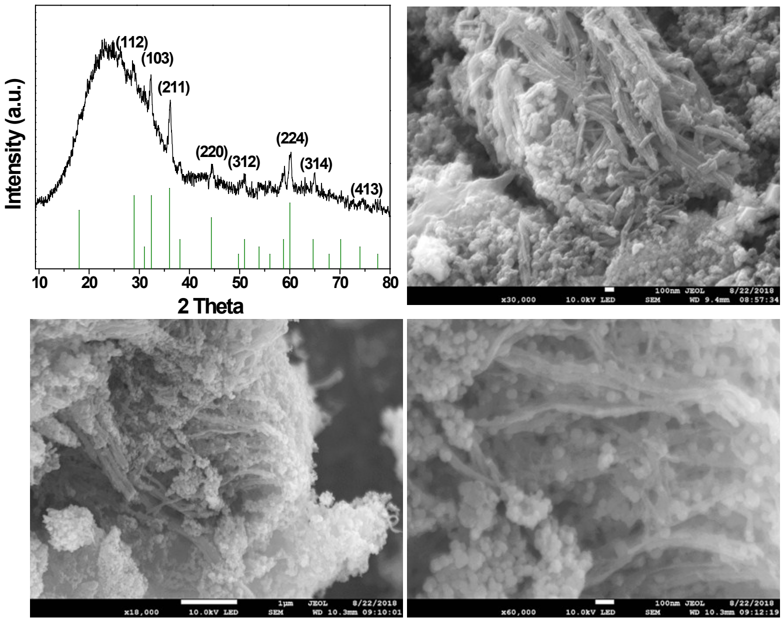

Fig. S4. XRD pattern and SEM images of cycled Mn_3O_4@C NWs electrodes.