

## Supporting Information

### Controlled Formation of Uniform Nanoshells of Manganese Oxide and their Potential in Lithium Ion Batteries

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#### Experimental section

**Materials.** Manganese Acetate Tetrahydrate, urea, ethyl alcohol were of analytical pure and purchased from Sinopharm Chemical Reagent Co. Ltd. Mili-Q water(resistance > 18 M $\Omega$ ) was used for all experiments.

**Preparation of 3-AF@Mn<sub>3</sub>O<sub>4</sub>.** 0.1494g Mn(Ac)<sub>2</sub>·H<sub>2</sub>O, 0.108g urea were slowly dissolved in 30 mL ethyl alcohol under mechanical magnetic stirring. Subsequently, 1mL(100 mg/mL) the obtained 3-AF nanospheres solution were added to the coating solution. Finally, the resultant solution was incubated at 80°C for 5h under vigorously stirring. The obtained product was centrifuged at 10800 rpm for 3min, which was followed by washing with water and ethanol and drying at 80°C for 10h, respectively. The reaction time was varied to control the thickness of Mn<sub>3</sub>O<sub>4</sub> coating layer.

**Preparation of Mn<sub>2</sub>O<sub>3</sub> hollow spheres.** The obtained powder was annealed at 400°C for 2h in air to remove the core and obtain manganese oxide hollow spheres.

**Preparation of SiO<sub>2</sub>@Mn<sub>3</sub>O<sub>4</sub>.** 0.1494g Mn(Ac)<sub>2</sub>·H<sub>2</sub>O, 0.108g urea were slowly dissolved in 30 mL ethyl alcohol under mechanical magnetic stirring. Subsequently, 0.02g SiO<sub>2</sub> powder were added to the coating solution. Finally, the resultant solution was incubated at 80°C for 5h under vigorously stirring. The obtained product was centrifuged at 10800 rpm for 3min, which was followed by washing with water and ethanol and drying at 80°C for 10h, respectively.

**Electrochemical measurement.** Charge-discharge tests were performed with CR2032 coin cells assembled in an argon-filled glove box, which consisted of a lithium metal as the counter and reference electrode, a anode as the working electrode, 1M LiPF<sub>6</sub> in ethylene carbonate (EC)/ethyl methyl carbonate (EMC)/4-fluoroethylene carbonate (FEC) (1:4:2, in wt %) as the electrolyte, and polypropylene membrane (Celgard) as a separator. The anode was prepared as a mixed slurry of 70 wt % active materials, 15 wt% of Super P carbon black, 7.5 wt % of Polymerized Styrene Butadiene Rubber (SBR, Aldrich) , and 7.5 wt % of Carboxymethylcellulose sodium (CMC, Aldrich) binder in a water solvent, casting onto Cu foil (99%, Goodfellow) and cutting into circular electrodes of 1.13 cm<sup>2</sup> area after drying under a vacuum at 80 °C for 10h. Galvanostatic tests of the assembled cells were performed with a Land CT2001A battery test system with a voltage window of 0.01-3V at room temperature.

Electrochemical impedance spectral (EIS) measurements are acquired on an Autolab PGSTAT 302N electrochemical workstation by applying a sine wave with amplitude of 10.0 mV over the frequency range from 100 kHz to 100 mHz at room temperature. The EIS test is before cycling.

**Characterization.** Scanning electron microscopy (SEM) was collected on Field Emission Scanning Microscopy (FE-SEM, Hitachi S-4800). Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) images were recorded on a JEOL-2100F and FEI Tecnai F20 operated at 200kV. X-ray

diffraction (XRD) data was collected on a Rigaku D/MAX-2500 with Cu K $\alpha$  radiation at 50 kV and 250 mA. X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab250Xi using 200 W monochromated Al K $\alpha$  radiation.

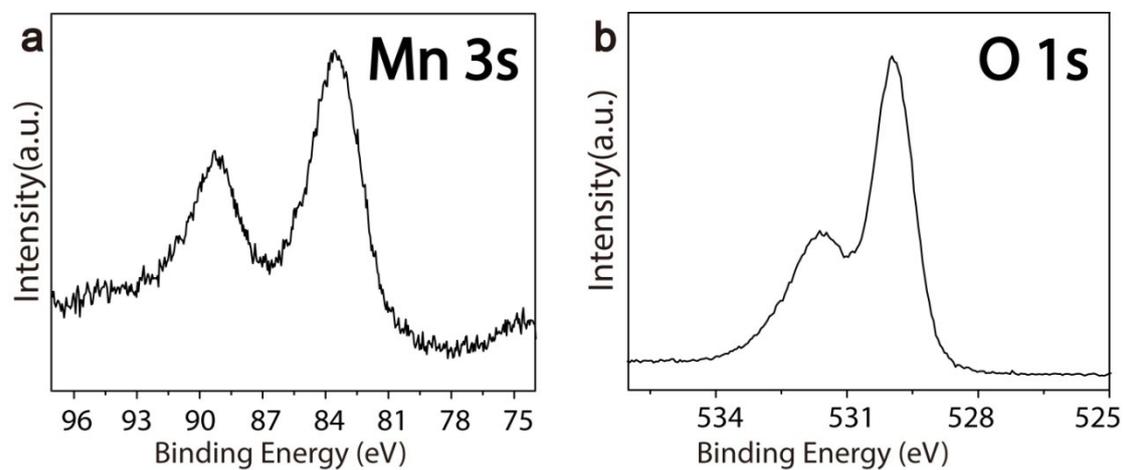


Fig. S1 XPS of surface coated samples: (a) Mn; (b) O.

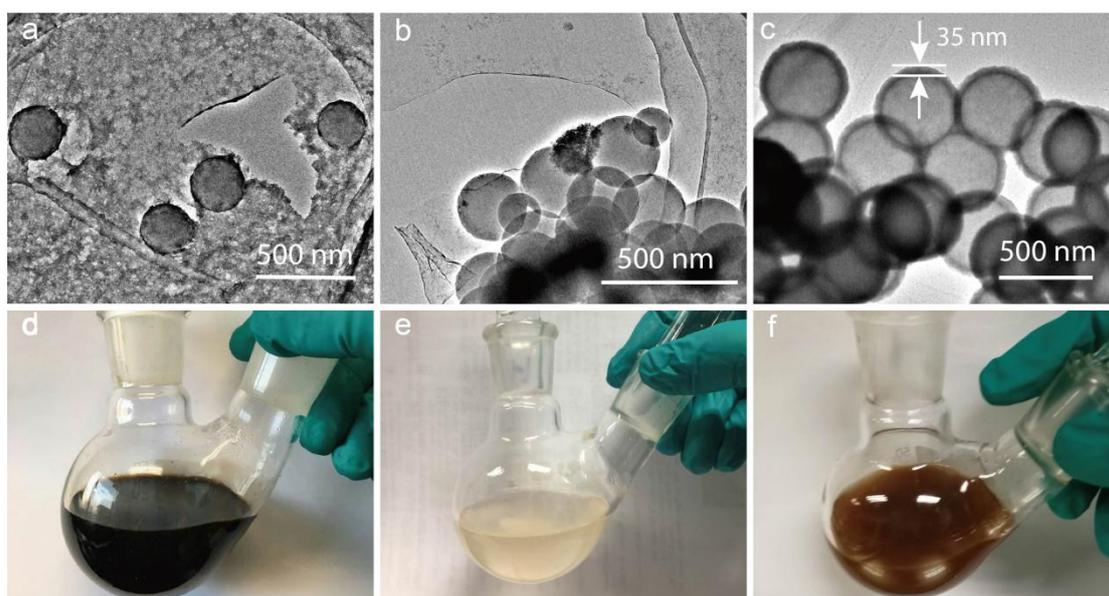


Fig. S2 TEM images (a-c) and experimental photos (d-f) of samples prepared at different precipitation conditions: a,d) urea is replaced by NaOH, under Air; b,e) urea as the precipitate, Ar protection; c,f) urea as the precipitate, under air.

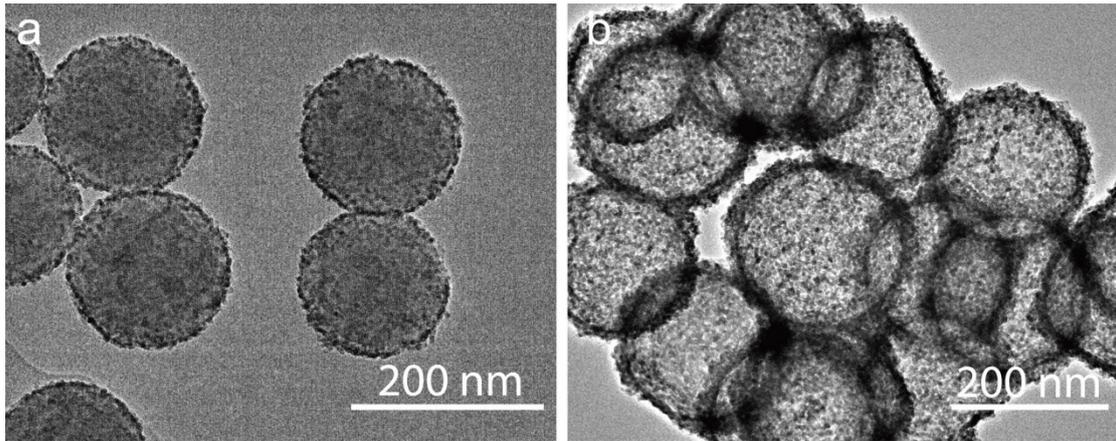


Fig. S3 TEM images of the a) surface coated  $\text{SiO}_2$  samples; b) hollow samples after removing  $\text{SiO}_2$ .

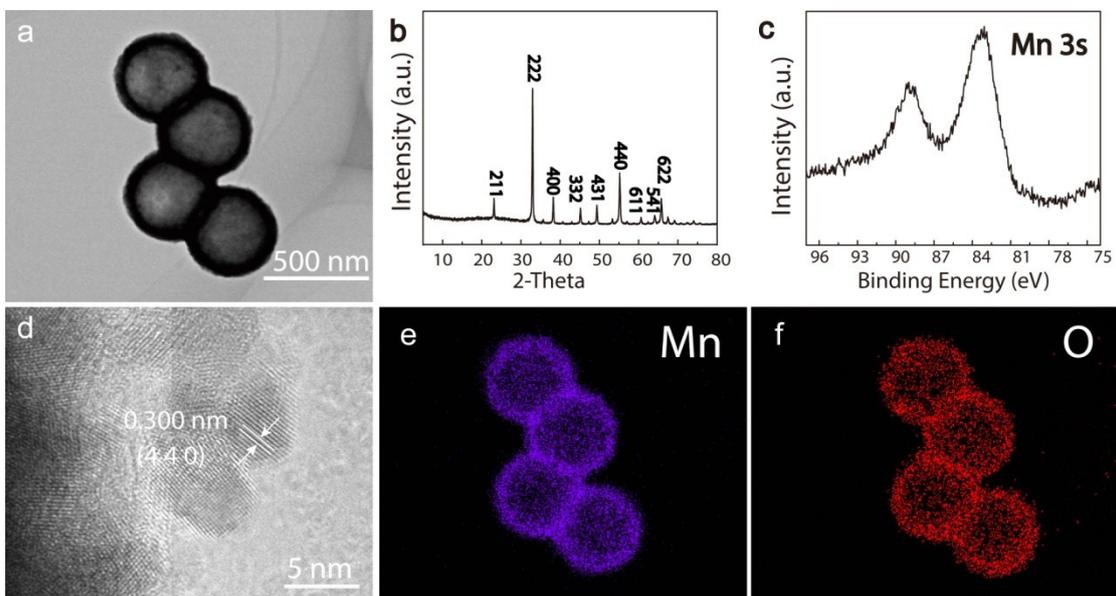


Fig. S4 Hollow nanospheres characterized by different methods: a) TEM, b) XRD, c) XPS, (d) HRTEM, e-f) elemental mappings

Figure S1a and Figure S4c showed the XPS patterns for  $\text{Mn}_2\text{O}_3$  and  $\text{Mn}_3\text{O}_4$ , respectively. The distance between two Mn3s peaks are different for Mn at different oxidation states, which is in good agreement with the observed values for  $\text{Mn}_3\text{O}_4$  and  $\text{Mn}_2\text{O}_3$  reported in the references.<sup>1</sup>

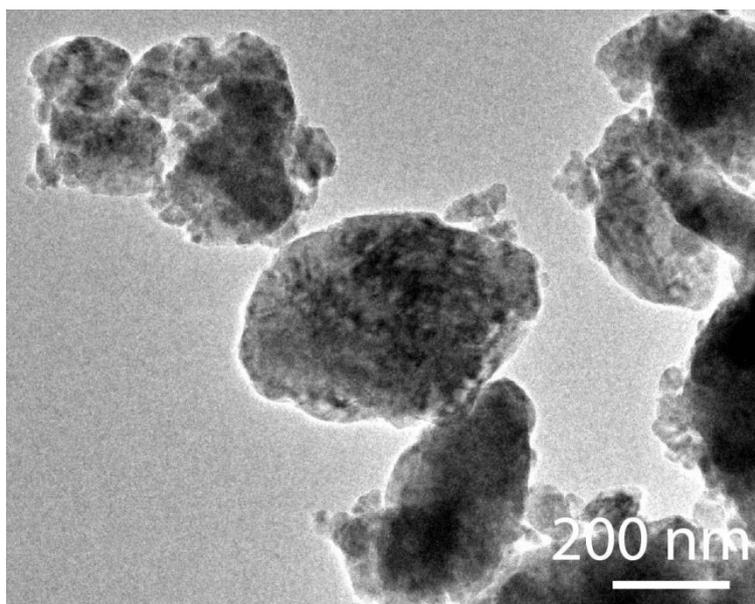


Fig. S5 TEM images of the solid samples

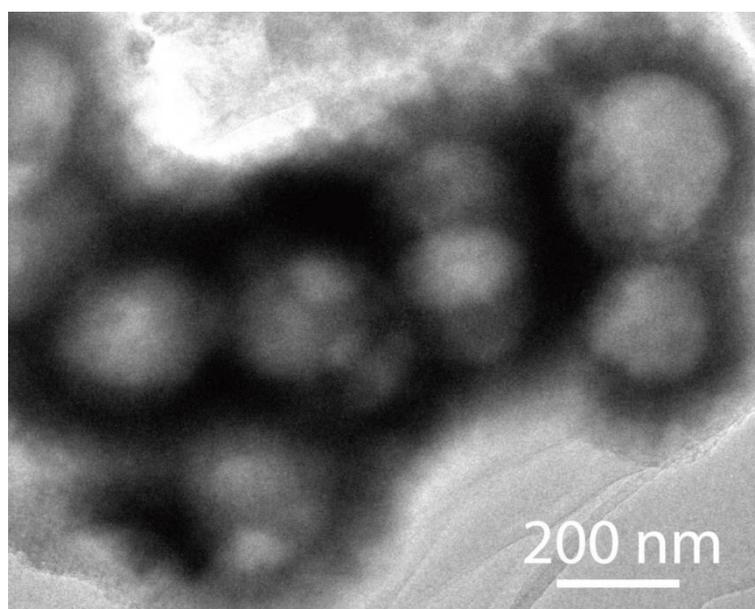


Fig. S6 TEM images of the  $\text{Mn}_2\text{O}_3$  hollow nanospheres after 50 cycles at 0.1C.

#### References

1. M. Toupin, T. Brousse and D. Bélanger, *Chem. Mater.*, 2004, **16**, 3184.