

Supplementary Information

Experimental Section

Material synthesis

The cubic MnCO_3 was synthesized via a precipitation reaction in a microemulsion. Typically, 4 g cetyltrimethyl ammonium bromide (CTAB) was dissolved in a mixture of 100 mL cyclohexane, 5 mL of n-pentanol and 5 mL of 0.8 M NH_4HCO_3 aqueous solution. The solution was stirred until it became transparent. Then 5 mL of 0.4 M MnSO_4 was added dropwise under stirring and a white emulsion was obtained. Finally, the white MnCO_3 was filtered, washed several times with ethanol and distilled water, and dried under vacuum at 90 °C.

The synthesized MnCO_3 (1 g) was dispersed into the KMnO_4 aqueous solution (0.032 M). The mixed solution was treated with sonication for 2 minutes and then under stirring for 10 minutes. The unreacted carbonate cores were removed by the subsequent excess addition of aqueous HCl (1.2 M). The obtained MnO_2 boxes were collected through centrifugation, washed for three times with deionized water and dried under 100 °C.

The conductive polymer coating process was conducted from the polymerization of the 3,4-ethylenedioxythiophene monomer. Typically, 50 μL 3,4-ethylenedioxythiophene was added into the HCl solution (0.1 M, 40 mL) and under stirring for 30 minutes. Then 200 mg MnO_2 and 100 mg $(\text{NH}_4)_2\text{S}_2\text{O}_8$ were dissolved into the solution respectively. The obtained solution was stirring for 10 hours. To get the final product, the obtained powder was collected through centrifugation, then washed for three times with deionized water and ethanol separately and dried under 80 °C.

Materials characterization

The morphology of the samples was observed by field-emission scanning electron microscopy (FESEM, JEOL JSM-6380), transmission electron microscopy (TEM, JEOL JEM-2100HR) and high-resolution TEM (HRTEM). The surface area

was determined by the Brunauer-Emmett-Teller method (BET, Micromeritics V-Sorb 2800 P) at liquid nitrogen temperature (77K). The crystal structure of the samples was analyzed by X-ray diffraction (XRD, Bruker D8 ADVANCE, Germany) with Cu K_{α} radiation. The X-ray photoelectron spectroscopy (XPS) spectra was obtained on ESCALAB 250 using a focused monochromatized Al K_{α} radiation ($h\nu=1486.6$ eV) under ultra-high vacuum. The spectra obtained were fitted using XPS Peak 4.1.

Electrochemical measurements

The electrode for electrochemical tests was prepared by mixing 70 wt% of active material with 20 wt% of acetylene black and 10 wt% of polyvinylidene difluoride (PVDF) binder, coating the mixture on a copper sheet and then cutting the sheet into pieces of 12.5 mm in diameter. The typical mass of loaded active material was 5–8 mg. A CR2025 coin cell was used and assembled in an Ar-filled MBraun glove box by using the prepared electrode as working electrode and the lithium foil as counter and reference electrode, Celgard 2400 as a separator and 1 M LiPF_6 in EC:DMC (1 : 2 by volume) as electrolyte. Charge/discharge test was performed using a Land cell test system (Land CT2001A, China) with various current rates between 0.01 V and 3.0 V (vs. Li/Li^+) at 25 °C. Cyclic voltammetry was performed using a Solartron 1470E Cell Test at 25 °C between 0.01 V and 3.0 V at a sweep rate of 0.1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) were tested on a PGSTAT-30 electrochemical station on the cells at open circuit potential after 10 cycles at 100 mA g^{-1} .

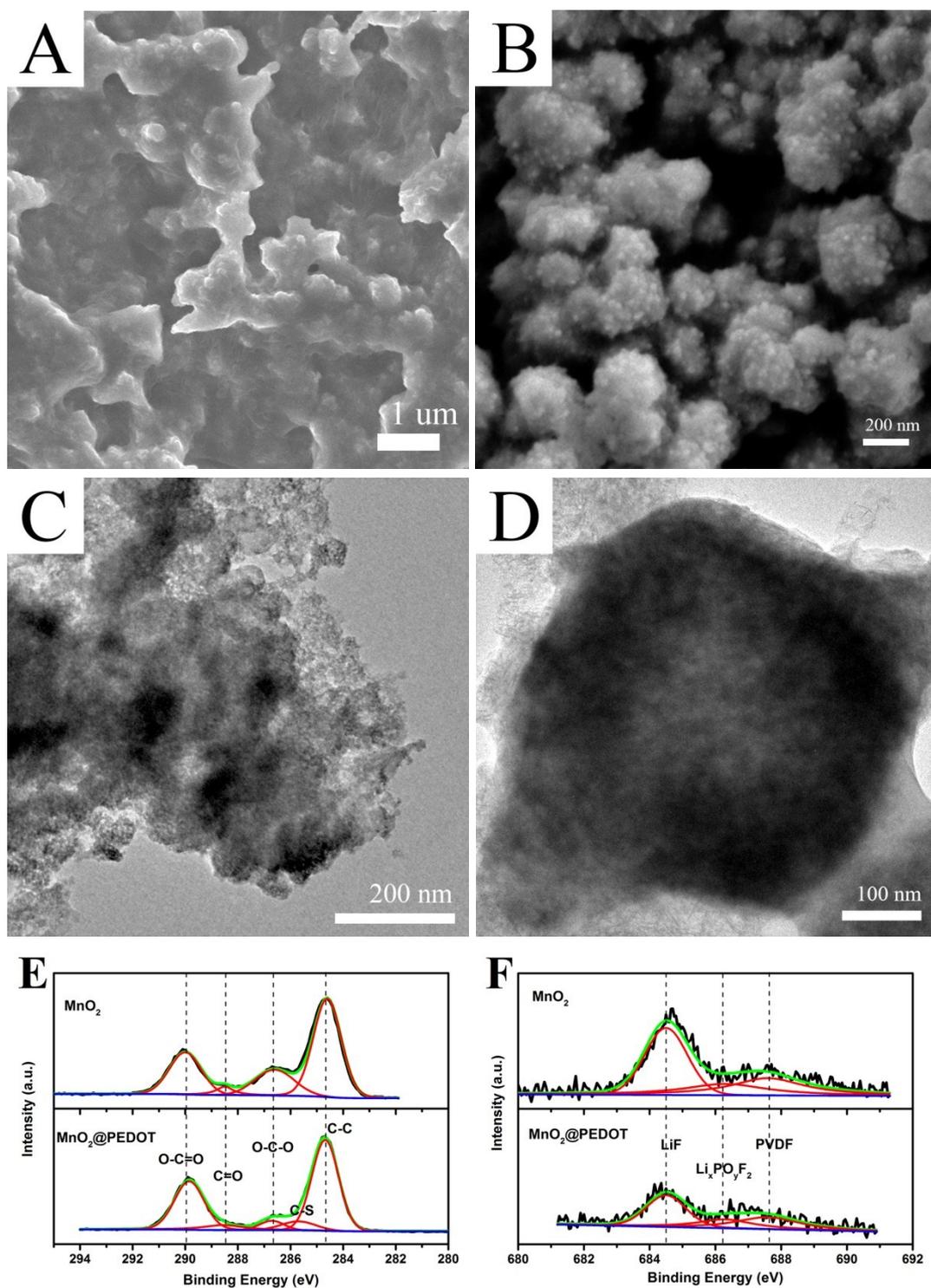


Figure S1. FESEM images (A and B), TEM images (C and D) and XPS spectra of C 1s (E) and F 1s (F) for MnO₂ and MnO₂@PEDOT nanoboxes after 300 cycles.

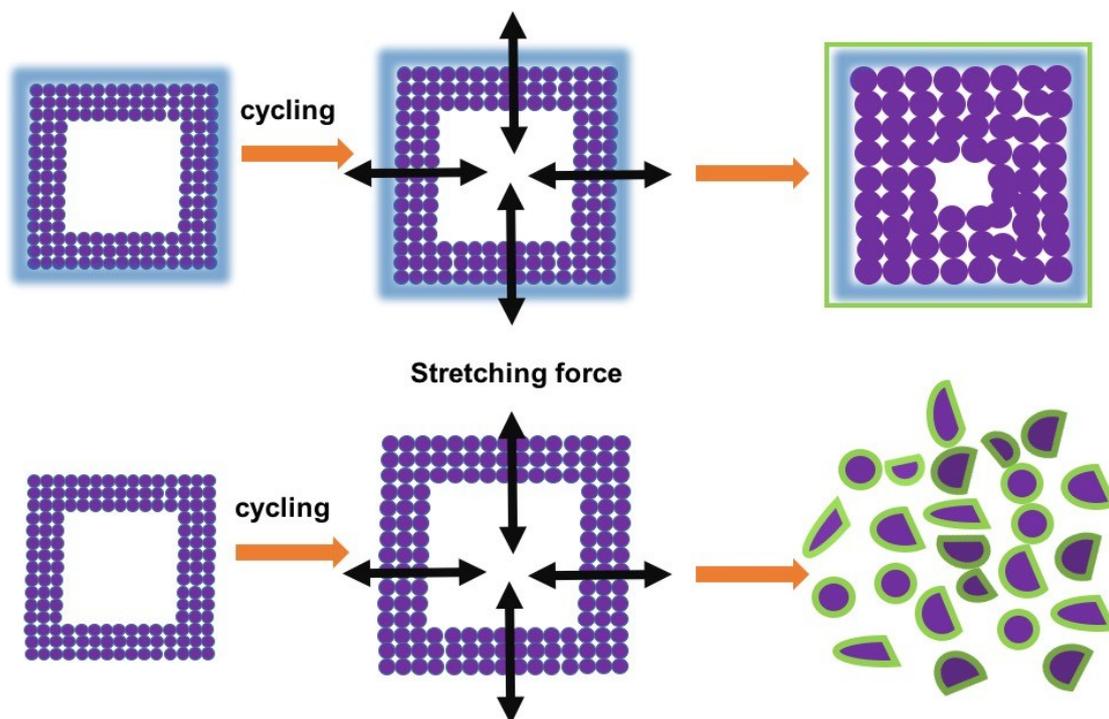


Figure S2. Schematic illustration of the structural failure of MnO₂ nanobox and the protection that PEDOT provides during cycling process.

Table S1 Comparison in electrochemical performance of MnO₂@PEDOT as anode of lithium ion battery with other other MnO₂ materials reported in literature

References	Highest Capacity	Cyclic Stability	Rate capability
1	816 mAh g ⁻¹ (200 mA g ⁻¹)	620 mAh g ⁻¹ after 50 cycles	250 mAh g ⁻¹ (4000 mA g ⁻¹)
2	840 mAh g ⁻¹ (100 mA g ⁻¹)	840 mAh g ⁻¹ after 60 cycles	225 mAh g ⁻¹ (1000 mA g ⁻¹)
3	1105 mAh g ⁻¹ (50 mA g ⁻¹)	948 mAh g ⁻¹ after 15 cycles	698 mAh g ⁻¹ (400 mA g ⁻¹)
4	909 mAh g ⁻¹ (400 mA g ⁻¹)	909 mAh g ⁻¹ after 200 cycles	636 mAh g ⁻¹ (1500 mA g ⁻¹)
5	1421 mAh g ⁻¹ (50 mA g ⁻¹)	\	341 mAh g ⁻¹ (500 mA g ⁻¹)
This work	1152 mAh g ⁻¹ (300 mA g ⁻¹)	1152 mAh g ⁻¹ after 300 cycles	367 mAh g ⁻¹ (3000 mA g ⁻¹)

References

1. H. Xia, M. Lai and L. Lu, *J. Mater. Chem.*, 2010, 20, 6896-6902.
2. J. Yue, X. Gu, L. Chen, N. Wang, X. Jiang, H. Xu, J. Yang and Y. Qian, *J. Mater. Chem. A*, 2014, 2, 17421.
3. C. X. Guo, M. Wang, T. Chen, X. W. Lou and C. M. Li, *Adv. Energy Mater.*, 2011, 1, 736-741.

4. Z. Sui, C. Wang, K. Shu, Q. Yang, Y. Ge, G. G. Wallace and B. Han, *J. Mater.*

Chem. A, 2015, 3, 10403.

5. X. Li, H. Song, H. Wang, Y. Zhang, K. Du, H. Li and J. Huang, *J. Appl.*

Electrochem., 2012, 42, 1065-1070.