

Supporting Information

Three-dimensional MnO₂ Ultrathin Nanosheet Aerogel for High-Performance Li-O₂ Batteries

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I. Experimental Section

1. Synthesis

Manganese chloride (MnCl₂·4H₂O, 99%), potassium permanganate (KMnO₄, 99%), and DMF (Dimethylformamide, 98%), were purchased from Sigma-Aldrich and directly used without further treatment or purification. In the first step, MnCl₂·4H₂O (0.18 g) was dispersed in DMF (50 mL) at 50 °C with vigorous stirring, where KMnO₄ aqueous solution (5 mL, 0.020 g mL⁻¹) was rapidly added. After reaction for 30 min, the product was centrifuged, washed with water for three times. In the second step, the as-resultant MnO₂ sample was dispersed in an aqueous solution at a concentration of 25 mg mL⁻¹. Then it was immersed in a liquid nitrogen bath to freeze for 0.5 h, and thawed in a freeze drier (Labconco Freezone) for 12 h. For comparison, the powder-like MnO₂ was prepared by directly drying of MnO₂ dispersion at 90 °C.

2. Characterization

X-ray diffraction (XRD) measurements were performed on a Philips 1130 X-ray diffractometer (40 kV, 25 mA, Cu K α radiation, $\lambda=1.5418$ Å); Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer; Ultraviolet–visible (UV-vis) spectra were recorded on a SHIMADZU UV-2550 spectrophotometer; Raman spectra were obtained on an WITEC alpha300R Raman microscope with a 532 nm solid laser as an excitation source; Thermogravimetric analysis (TGA) profiles were recorded on a TGA/SETARAM thermogravimetric analyzer from 100 to 800 °C with a heating rate of 10 °C min⁻¹ in N₂ flow; X-ray photoelectron spectroscopy (XPS) was performed on an

Axis Ultra (Kratos Analytical, UK) XPS spectrometer equipped with an Al Ka source (1486.6 eV). Morphologies of the samples were observed on transmission electron microscopy (TEM, Tecnai G2 Spirit and JEOL JEM-2100) and scanning electron microscope (SEM, QUANTA 450 and LEO-1550). Energy-dispersive X-ray spectroscopy (EDS) and elemental mapping patterns were acquired on the SEM (QUANTA 4500). The porosity of samples was evaluated by using nitrogen adsorption-desorption isotherm measured at 77 K on a TriStar II 3020 Micromeritics apparatus; pore size distribution was derived from the adsorption branch of the isotherm by using the Barrett-Joyner-Halenda (BJH) method.

3. Electrode preparation and electrochemical testing

Li-O₂ battery test was carried out in Swagelok TM cells composed of an Li metal anode, electrolyte (0.5 M lithium triflate (LiSO₃CF₃) in diethylene glycol dimethyl ether (DEGDME)) impregnated into a Celgard 3500 separator and a porous (3/8 inch diameter) cathode formed by casting a mixture of active carbon, the appropriate catalyst, and PVDF (poly-vinylidene fluoride) in molar ratio 85:7.5:7.5. The cells were sealed except for the stainless steel grid window that exposed the porous cathode to the 1 atm of O₂ pressure. The Swagelok cells were located within a chamber filled with 1 atm of O₂, which was itself thermostated at 30 °C.

II. Supplementary Results

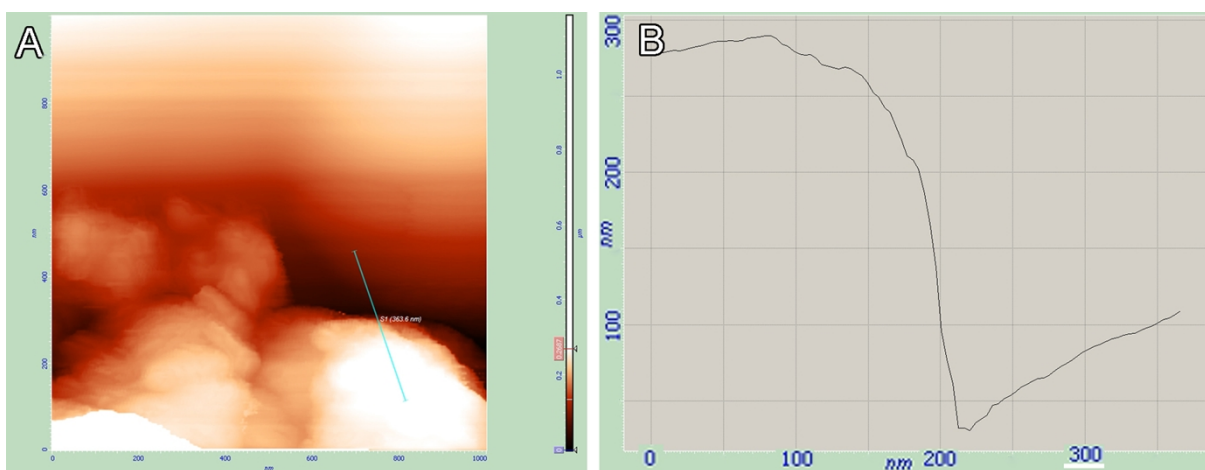


Figure S1. AFM analysis of MnO₂ nanoflowers.

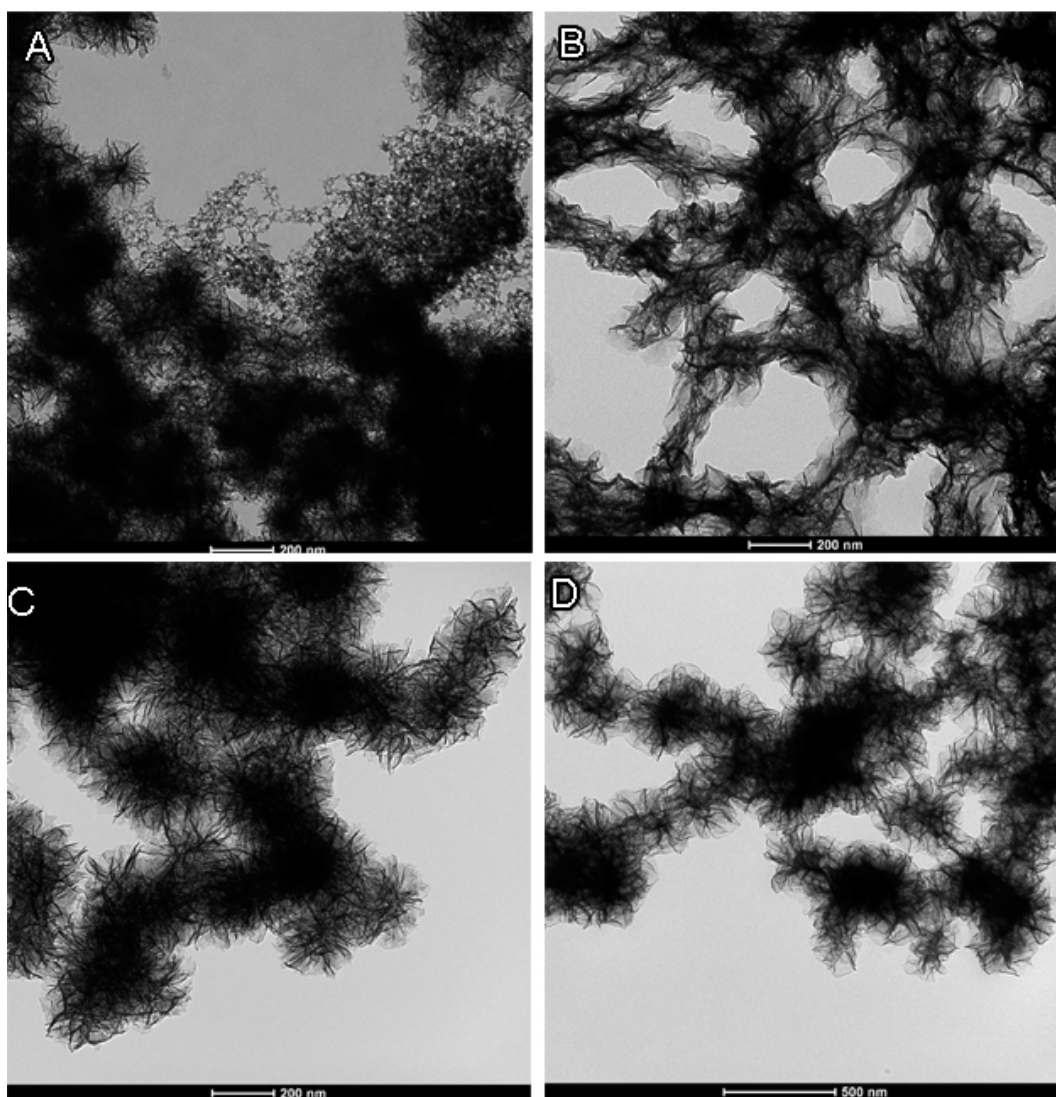


Figure S2. TEM image of MnO₂ dispersions taken directly from reaction solution at different time intervals: (A) 1 min; (B) 3 min; (C) 10 min; (D) 30 min.

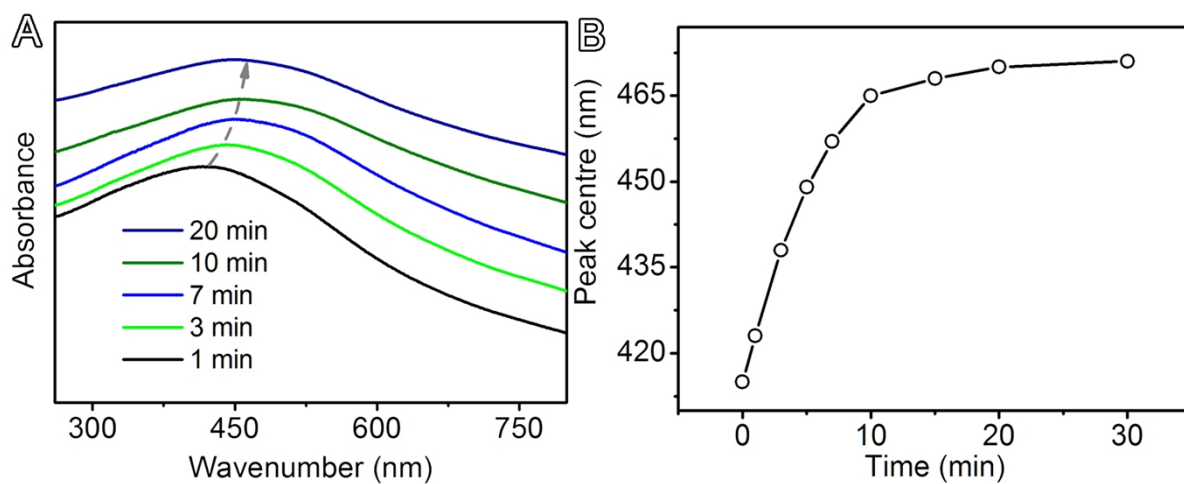


Figure S3. (A) UV-vis spectra of MnO₂ dispersions taken directly from reaction solution at different time intervals; (B) the corresponding plots of peak centre wavenumbers vs. reaction time.

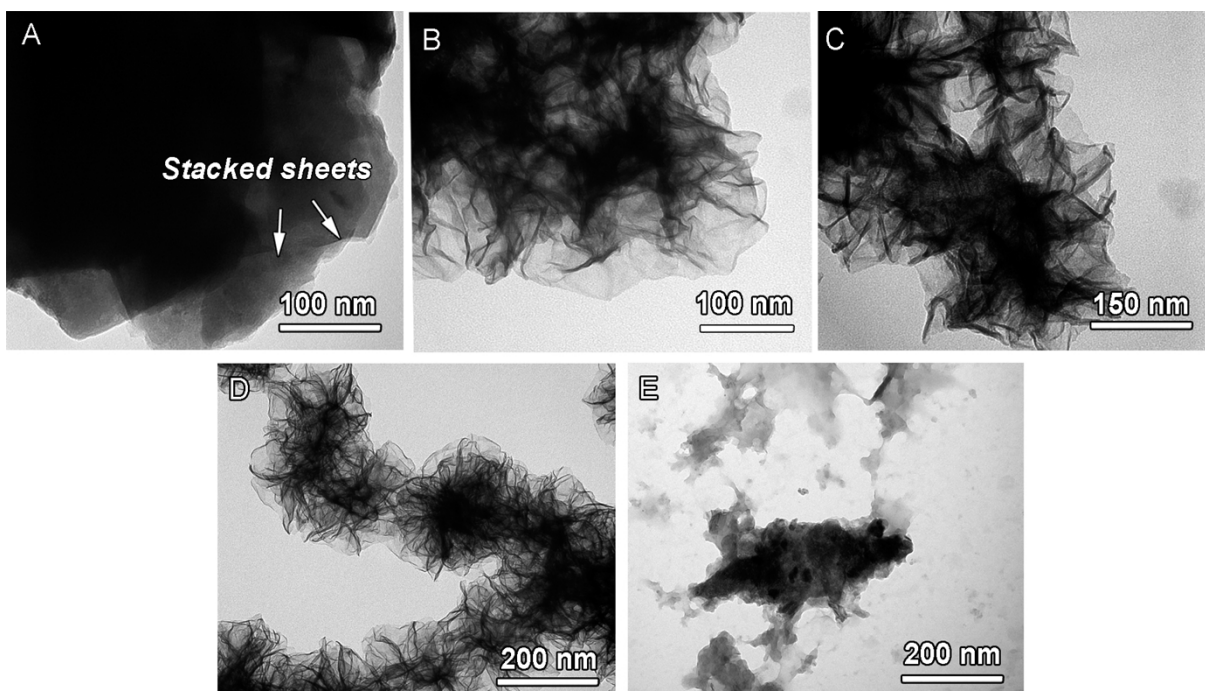


Figure S4. TEM images of 3D MnO₂ prepared with different water/DMF ratios: (A) only water; (B) 45/10; (C) 35/20; (D) 15/40; (E) only DMF.

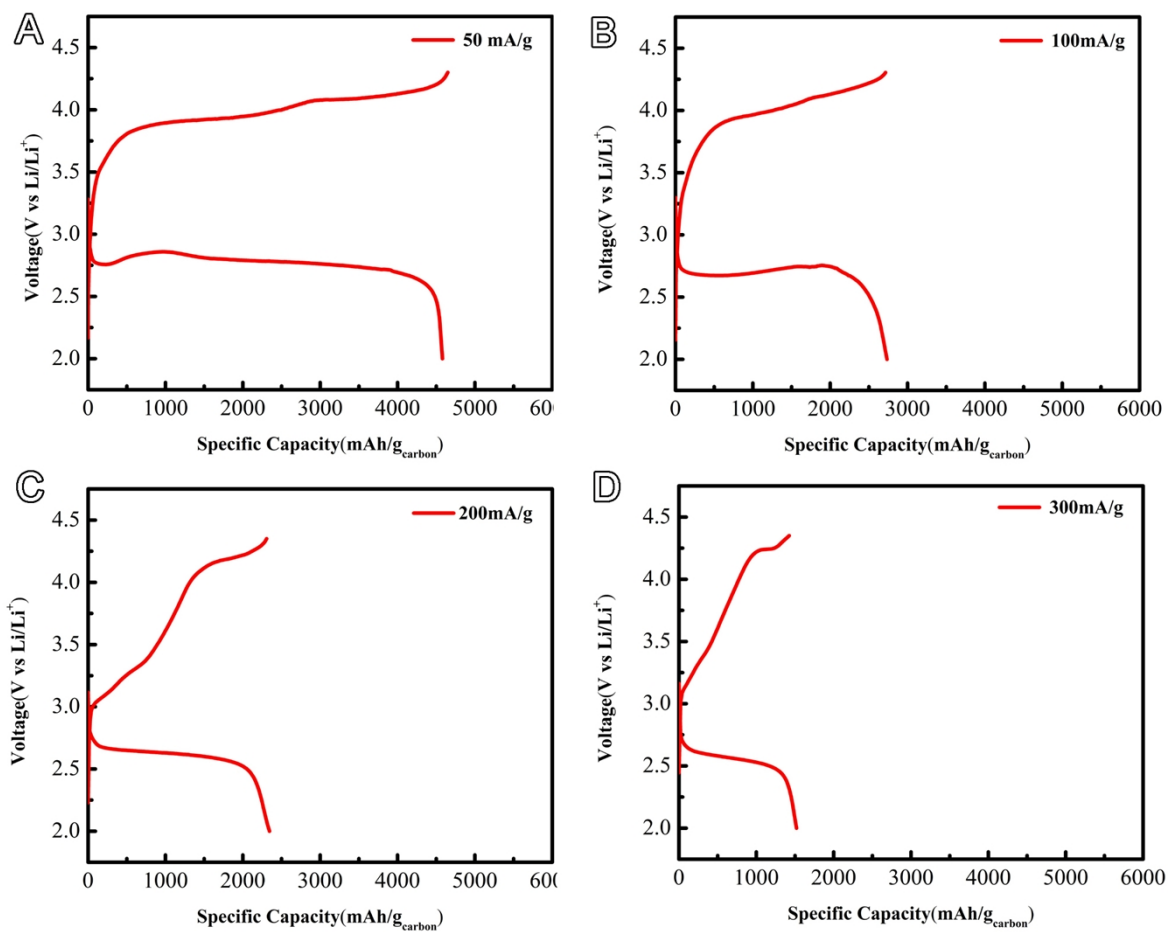


Figure S5. Charge-discharge plots of Li-O₂ batteries with 3D MnO₂ catalyst at different current densities.

Table S1. Comparison of Li-O₂ battery performances of 3D MnO₂ with some representative transition metal oxide/hydroxide nanostructures recently reported in the literature.

Materials	Discharge capacity	Cycling stability	Samples
3D MnO₂	4581 mAh g⁻¹	Stable after 25 cycles	This work
α-MnO ₂ nanowires	3000 mAh g ⁻¹	Stable after 10 cycles	S1
MnO ₂ -CNTs hybrid	2247 mAh g ⁻¹	Stable after 6 cycles	S2
Fe ₂ O ₃	2700 mAh g ⁻¹	Stable after 10 cycles	S3
carbon supported-MnO ₂ hybrid	4750 mAh g ⁻¹	Stable after 10 cycles	S4
MnO ₂ nanotubes	not available	Stable after 30 cycles	S5
Flower-like MnO ₂ /graphene hybrid	3660 mAh g ⁻¹	Stable after 132 cycles	S6

References.

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- S2. J. Li, N. Wang, Y. Zhao, Y. Ding and L. Guan, *Electrochem. Commun.*, 2011, **13**, 698-700.
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- S6. S. Liu, Y. Zhu, J. Xie, Y. Huo, H. Y. Yang, T. Zhu, G. Cao, X. Zhao and S. Zhang, *Adv. Energy Mater.*, 2014, **4**, DOI: 10.1002/aenm.201301960.