Supplementary Information

"One-for-All" Strategy to Design Oxygen-Deficient Triple-Shelled MnO_2 and Hollow Fe_2O_3 Microcubes for High Energy Density Asymmetric Supercapacitors

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Calculations. The specific capacitance was calculated from GCD curves the following equation by integrating discharge current *I* [1]

$$C = \frac{I \times \Delta t}{m \times \Delta v}$$

where *m* is the weight of active materials (g), I is the discharge current (A), *Δt* is the discharge time (S). The power density (*P*, KW Kg^{-1}) and energy density (*E*, W h Kg^{-1}) were calculated from GCD curves [2],

$$E = \frac{0.5CV^2}{3.6}$$

$$P = \frac{3600E}{t}$$

where C is capacitance (F g^{-1}), V is the sweep potential range, t is the discharge time (s).

Experimental Section

Synthesis of the $MnCO_3$ microcubes: Typically, 0.169 g $MnSO_4 \cdot H_2O$ was fully dissolved in a premixed solution composed of 70 mL of water and 7 mL of ethanol. Afterwards, NH_4HCO_3 (0.84 g) and $(NH_4)_2SO_4$ (1.321 g) was dissolved in H_2O (70 mL) to form another uniform solution. The solution of NH_4HCO_3 and $(NH_4)_2SO_4$ was added into the solution of $MnSO_4$ under stirring, and the obtained mixture was maintained at room temperature for 3 h. Finally, the obtained $MnCO_3$ microcubes was washed and dried at 60 ^oC.

Synthesis of triple-shelled MnO_2 microcubes: Triple-shelled MnO_2 microcubes were synthesized from three controlled steps. Step I, the as-obtained $MnCO_3$ sample (0.017 mol) was redispersed in 40 mL of DW under ultrasonication for 10 min. 19.5 mL of $KMnO_4$ aqueous solution (0.032 M) was poured into the $MnCO_3$ dispersion and stirred for another 30 min. Next, the black precipitate was filtered and washed with DW. Then, the sample was redispersed in 0.15 M HCl solution with ultrasonication and stirred for 15 min. Step II, the obtained samples were reacted with $KMnO_4$ (0.016 M) for 25 min and HCl (0.075 M) for 15 min. Step III, the samples were reacted with $KMnO_4$ (0.008 M) for 25 min and HCl (0.15 M) for 1 h. The obtained samples were washed with water, ethanol and then dried at 60 ^oC for 8 h. Hollow MnO_2 microcubes were synthesized according to step I and prolong the HCl treatment to 1h. Double shell MnO_2 microcubes were synthesized according to step I and step II and prolong the HCl treatment in step II to 1h.

Synthesis of ov-MnO_2 microcubes: The ov-MnO_2 microcubes were further synthesized through room temperature reduction in $NaBH_4$ solution with ethanol as

solvent. In detail, the ov-MnO_2 microcubes were immersed in 1 M $NaBH_4$ solutions for 30 min at room temperature. After reduction process, the obtained samples were cleaned and dried in the vacuum oven at 60 ^oC for 2 h.

Synthesis of hollow Fe_2O_3 microcubes: The 0.6 g $MnCO_3$ sample was redispersed in 100 mL of DW under ultrasonication for 10 min. 100 mL of Fe_2SO_4 aqueous solution containing 1.08 g $Fe_2SO_4 \cdot 7H_2O$ was poured into the $MnCO_3$ dispersion and stirred for 5 min. Then, the solution was transferred to the Teflon-lined stainless steel autoclave and kept at 90 ^oC for 3h. The obtained sample was rinsed in distilled water, dried in the vacuum oven, and further annealed at 350 ^oC for 1 h in air to obtain hollow Fe_2O_3 microcubes.

Synthesis of ov-Fe_2O_3 microcubes: Similar to the synthesis of ov-MnO_2 microcubes, only change the triple-shelled MnO_2 microcubes to hollow Fe_2O_3 microcubes.

Materials characterization: The morphology and structure of the samples were characterized by SEM (Helios Nanolab 600i) and TEM (Tecnai G2 F30), respectively. XRD was performed using a D/max 2550 with graphite monochromatized Cu Kα radiation. Raman spectra were collected on a Renishaw inVia Raman Microscope with laser excitation at 532 nm. Surface chemical states were investigated by XPS (Thermo Fisher) with a base pressure of 2×10^{-9} mbar.

Electrochemical Performance Measurements: Electrochemical measurements were conducted in a typical three-electrode cell. The samples were used as working electrodes. Pt foil as the counter electrode and a saturated calomel electrode (SCE) electrode as reference electrode in 1 M Na_2SO_4 electrolyte. The working electrodes were prepared by mixing 70 wt% of active material, 20 wt% of carbon black, and 10 wt% of polyvinylidene fluoride (PVDF) in an N-methyl-2-pyrrolidone (NMP) solution to make a slurry. Then, it was coated onto the Ni foam substrate and dried in a vacuum

oven at 60 ^{o}C for 12 h. CV curves and the galvanostatic cycling test were carried out on a CHI 760D electrochemical workstation. EIS measurements were performed on PARSTAT 4000A electrochemical workstation, over a frequency range from 10^{5} to 10^{-1} Hz, at an amplitude of 5 mV. Further, an asymmetric supercapacitor using ov-MnO_2 electrodes as positive electrode and ov-Fe_2O_3 electrodes as negative electrode were tested in a two-electrode configuration. The mass ratio of two electrodes were balanced by the following relationship:

$$m_+/m_- = (C_- \times \Delta E_-)/(C_+ \times \Delta E_+)$$

where m (g) is the mass of the electrode materials (anode or cathode), C (F/g) is the specific capacitance, and ΔE is the potential window.

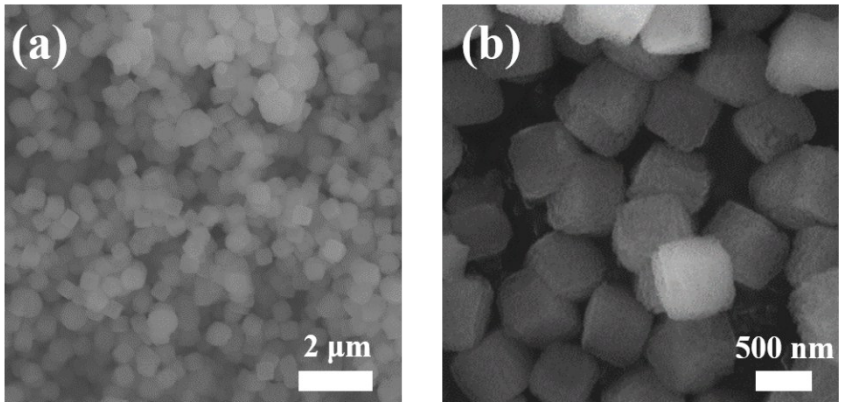

Figure S1. SEM images of the $MnCO_3$ microcubes.

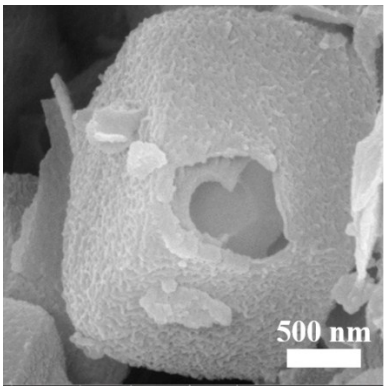

Figure S2. SEM images of the broken tips of triple-shelled MnO_2 microcubes revealing its multi-shell structure

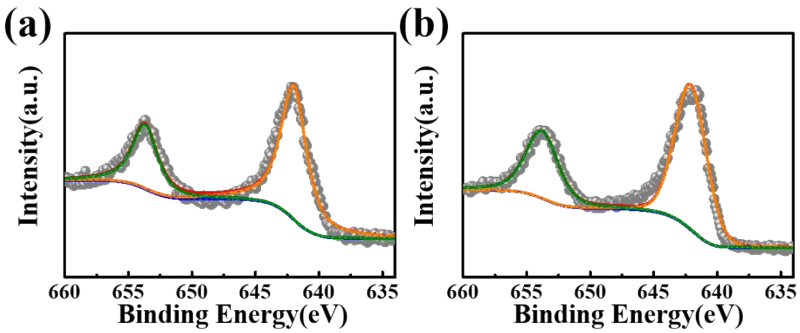

Figure S3 High-resolution XPS spectrum of Mn 2p in a) triple-shelled MnO_2 microcubes and b) ov-MnO_2 microcubes.

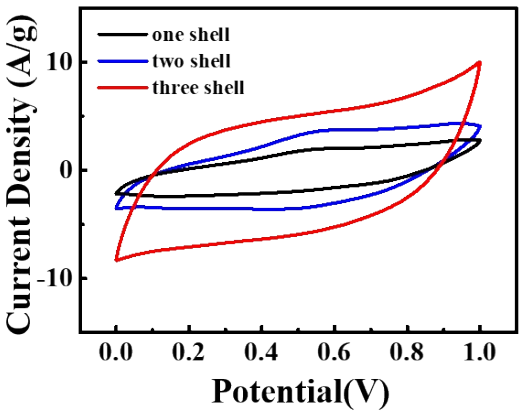

Figure S4. CV curves of MnO_2 microcubes with different shell numbers of 1, 2 and 3.

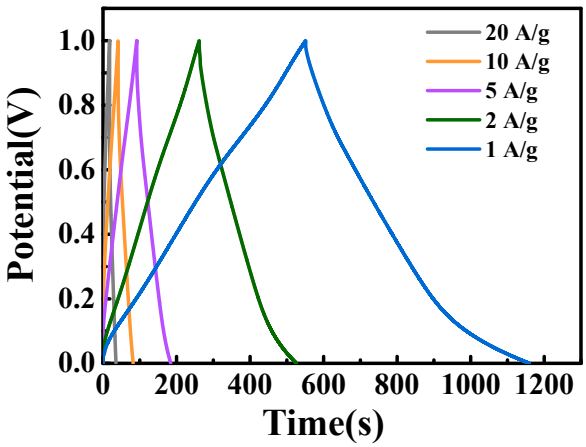

Figure S5. GCD curves of ov-MnO_2 microcubes at different current dencities.

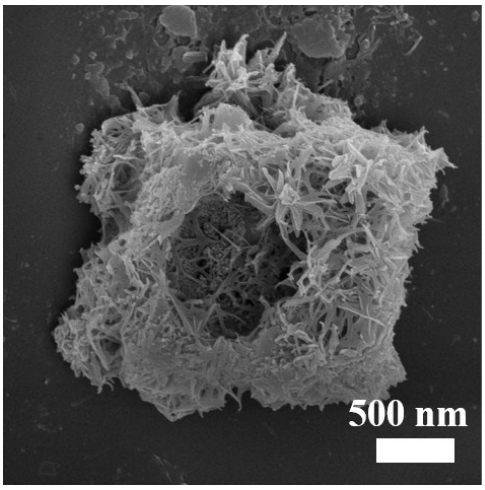

Figure S6. SEM image of the cracked hollow Fe_2O_3 microcube.

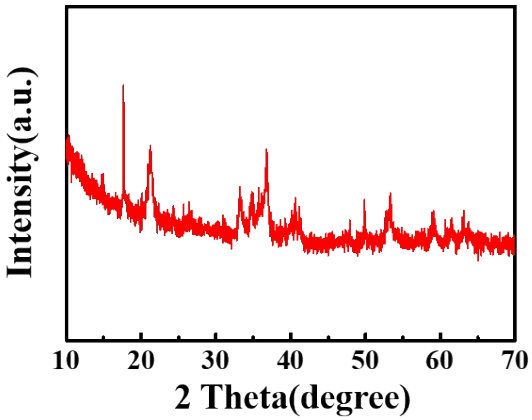

Figure S7. XRD pattern of the hollow Fe_2O_3 microcubes before annealing.

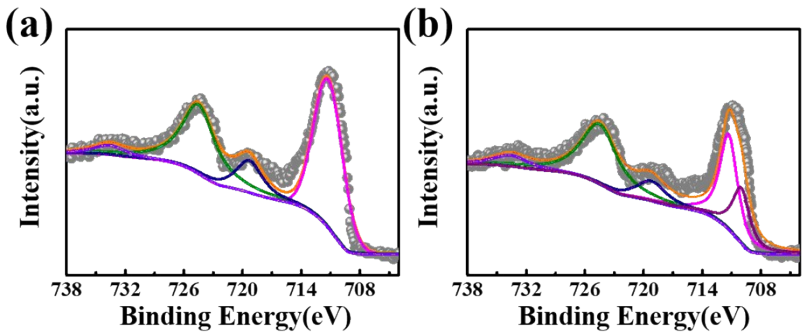

Figure S8. High-resolution XPS spectrum of Fe 2p in a) hollow Fe_2O_3 microcubes and b) ov-Fe_2O_3 microcubes.

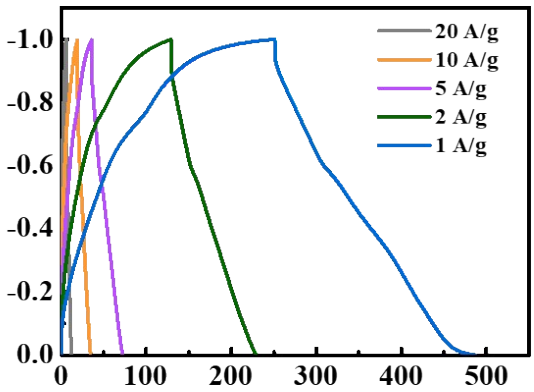

Figure S9. the GCD curves of Fe_2O_3 hollow microcubes.

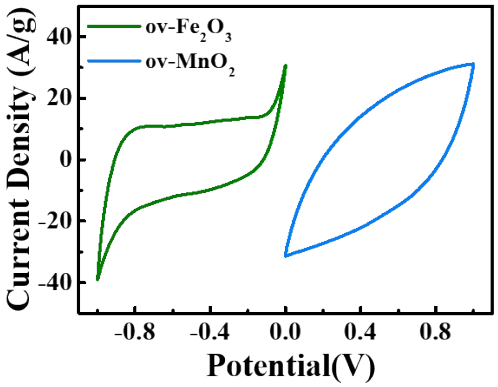

Figure S10. CV curves of the ov-MnO_2 and ov-Fe_2O_3 electrodes at the scan rate of 50 mV s^{-1}.

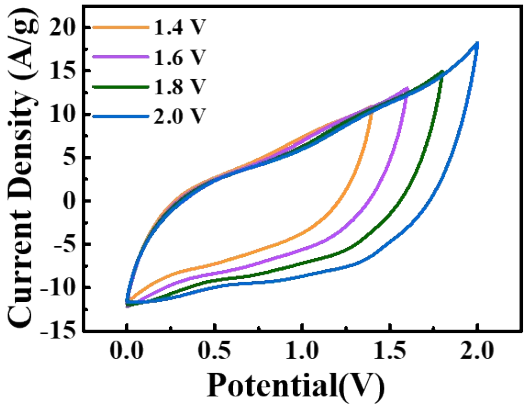

Figure S11. CV curves of the ov-MnO_2//ov-Fe_2O_3 ASC in different voltage window.