Electronic Supplementary Information (ESI)

Mechanism analysis of the capacitance contributions and ultralong cycling-stability of the isomorphous MnO_2@MnO_2 core/shell nanostructures for supercapacitors

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Part I: Calculations

The specific capacitance of the electrode was calculated from the C-V curves according to the following equation, $C = Q/(\Delta V \cdot m)$, where C ($F\ g^{-1}$) is the specific capacitance, m (g) is the mass of the MnO_2 in the electrodes, Q (C) is an average charge during the charging and discharging process, and ΔV (V) is the potential window. The discharge specific capacitance is calculated from the discharge curves using the following formula, $C = I \cdot \Delta t / (\Delta V \cdot m)$, where I (A), Δt (s), m (g), and ΔV (V) are the discharge current, discharge time consumed in the potential range of ΔV, mass of the active materials (or mass of the total electrode materials), and the potential windows, respectively.

Part II: Supplementary Figures

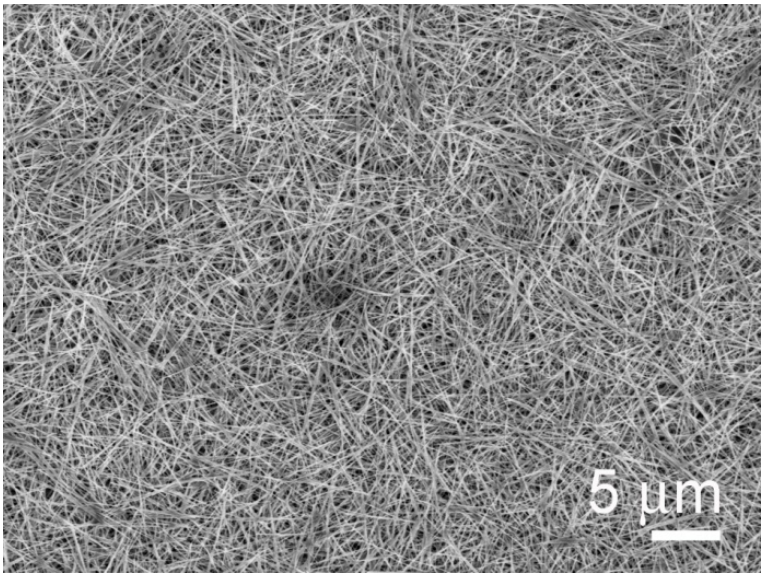

Fig. S1 Low magnification SEM images of MnO_2 nanowires.

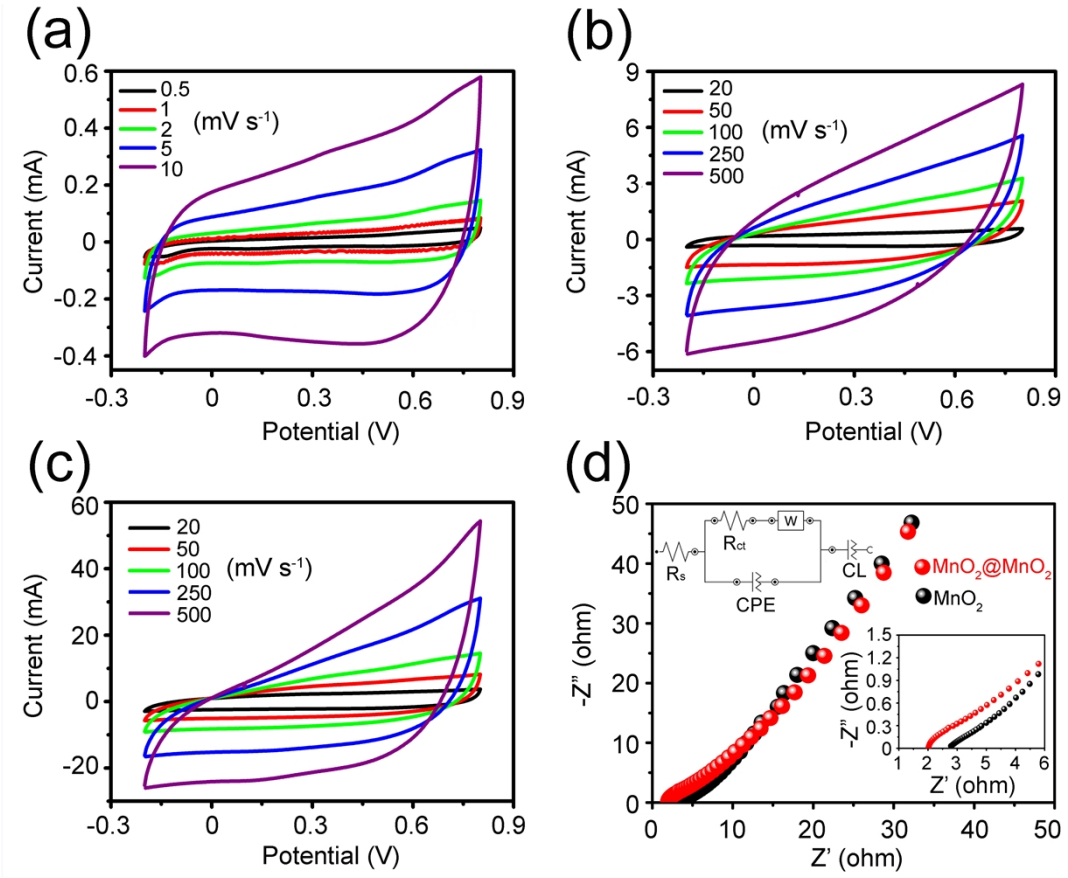

Fig. S2 CV curves of MnO_2 electrode at low scan rates (a) and high scan rates (b), respectively. (c) CV curves of MnO_2@MnO_2 electrode at different high scan rates. (d) Nyquist plots of the MnO_2@MnO_2 and MnO_2 electrodes, inner lower right corner is

corresponding enlarged spectra, and the top left corner is the corresponding quivalent fitting circuit.

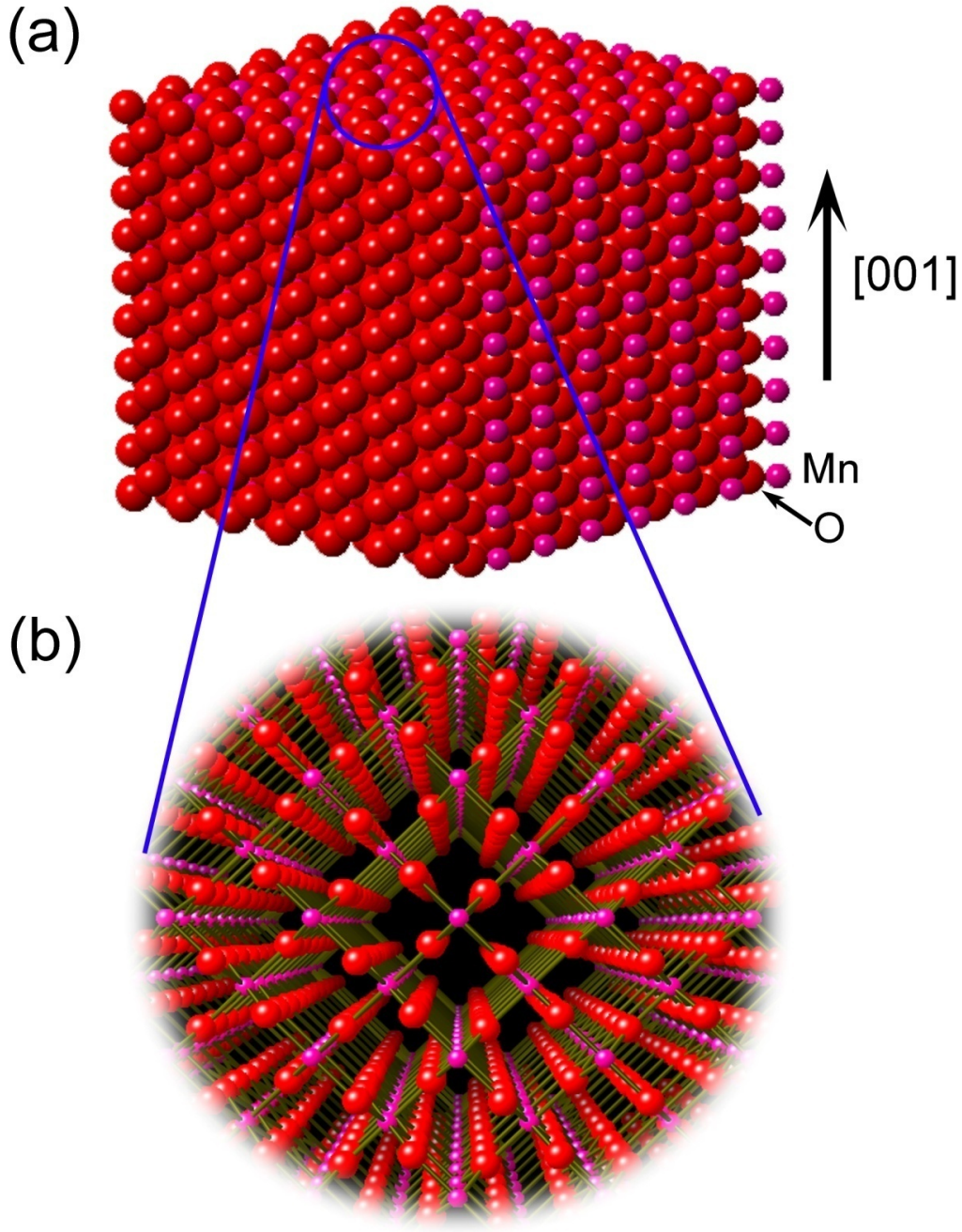

Fig. S3 Graphical representation of the atom positions comprising, structure of the nanoparticles: (a) model representation showing the stacking of the Mn and O plans along the [100]; (b) segment of the nanoparticles, cut from (a) illustrating more clearly the related migration paths, ball and stick representation. Red spheres are oxygen, purple manganese.

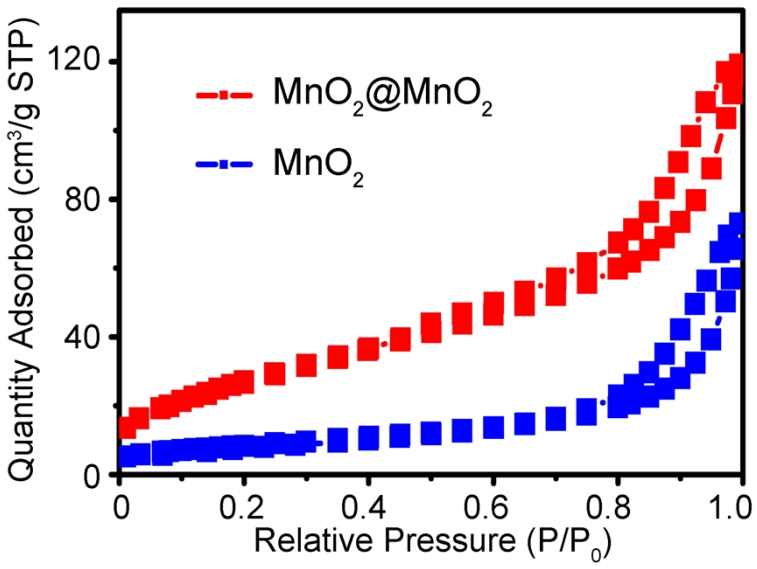

Fig. S4 Nitrogen adsorption and desorption isotherms of the isomorphous MnO_2@MnO_2 core/shell nanostructure and MnO_2 nanowires.

Part III: Supplementary Table

	MnO_2@MnO_2			MnO_2		
Scan rate (mV/s)	Capacitance (F/g)	$\propto V$ (F/g)	$\propto V^{1/2}$ (F/g)	Capacitance (F/g)	$\propto V$ (F/g)	$\propto V^{1/2}$ (F/g)
Trassati Method	208.3	151.8	56.5	43.5	31.5	12.0
0.5	190.4	144.7	45.7	41.6	30.6	11.0
1	180.5	147.5	33.0	38.5	30.8	7.7
2	172.8	149.3	23.5	36.2	30.6	5.6
5	165.2	150.2	15	34.3	30.8	3.5
10	161.9	151.2	10.7	32.7	30.2	2.5

Table S1 Capacitance of the pristine MnO_2 and MnO_2@MnO_2 in a 0.5 M Na_2SO_4 solution at different scan rates $\propto V$ and $\propto V^{1/2}$ correspond to the current contributions

from the surface capacitive effects and the diffusion-controlled intercalation process, respectively. The capacitance fluctuation of capacitive processes ($\propto v$) for MnO_2@MnO_2 core/shell nanostructures maybe caused by continuously activation process of the electrodes during the CV test.