Supplementary Information

Manganese Dioxide Nanowires on Carbon Nanofiber Frameworks for Efficient Electrochemical Device Electrodes

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Analysis of Specific Capacitance.

The capacitance, C, of electrode was determined as follows:

$$C = \frac{i \cdot \Delta t}{\Delta V} \qquad \text{(S1)}$$

where i is the applied current, and $\Delta V / \Delta t$ is the slope of the discharge curve after the initial iR drop.

The specific gravimetric capacitance for total electrode mass (C_g) and deposited MnO_2 NWs (C_g-MnO_2), and the specific volumetric capacitance for apparent volume of electrode (C_v) were calculated through dividing C to the mass of the total electode, the mass of the MnO_2 NWs and the apparent volume of the electrode, respectively.

Evaluation of Asymmetric Supercapacitors.

The energy density, E, and power density, P, of the ASC device were determined as follows:

$$E = \frac{CV^2}{2m} \tag{S2}$$

$$P = \frac{V^2}{4Rm} \tag{S3}$$

$$R = \frac{\Delta V_{iR}}{2i} \tag{S4}$$

where m is the total electrode mass of ASC, C is the capacity of total electrode of ASC, V is the operating voltage, R is the inner resistance of ASC, ΔV_{iR} is the voltage of the iR drop, and i is the applied current.

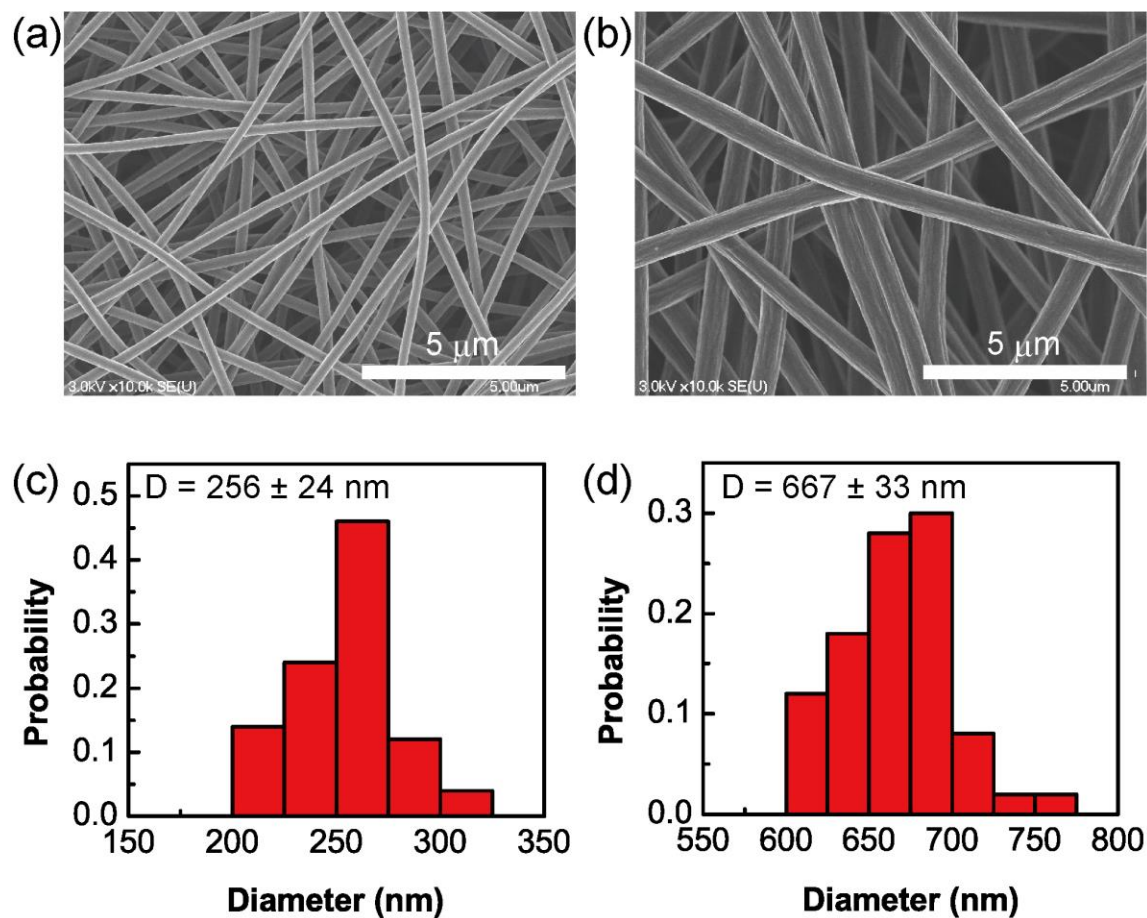**Characterization of CNF webs.**

Fig. S1. SEM images and diameter distributions of the prepared CNF webs. SEM images of (a) C-250 and (b) C-650 nanofibers. Diameter distributions of (c) C-250 and (d) C-650 nanofibers.

Table S1. Properties of the prepared CNF webs.

CNF	Thickness (μm)	Surface electrical conductivity (S/cm)
C-250	32.0 ± 10	7.51
C-650	33.5 ± 2	6.16

XPS analysis of Mn-3.7/C-250 electrode.

The Mn 3s and O 1s core level spectra are known to be useful to assess the oxidation state of MnO_2[1–4]. Fig. S2 and Table S2 show XPS spactra and the peak analysis of Mn-3.7/C-250 electrode, respectively. As shown in Fig S2 (b), the O 1s spectra could be deconvolated into three oxygen-containing chemical bonds such as oxide (Mn-O-Mn) at 529.3-530.0 eV, hydroxide (Mn-O-H) at 530.5-531.5 eV and water molecule (H-O-H) at 531.8-532.8 eV[1]. The relatively higher content of the hydroxide oxygen (41.8%) in the MnO_2 NWs, which is close in value to the content of the oxide oxygen (49.8%), indicates that MnO_2 NWs contain a large number of hydroxide. The Mn 3s core level peak splitted due to the parallel spin coupling of the 3s level electron with the 3d level electron during the photoelectron ejection[1–4]. The energy separation between the two peaks is related to the mean valence number of Mn. For the MnO_2 NWs, the energy separation of peak 1 and peak 2 of Mn 3s is 5.55 eV (Table S2). The empirical linear relation is known between the energy separation of Mn 3s and the valence number of Mn[4]. From this relation, the mean valence number of Mn can be established at about 2.55 for the MnO_2 NW. From the XPS results, MnO_2 NWs contain a large number of manganese hydroxide with the mean valence number of about 2.55, which agrees with the existence of the microtwinning as shown in XRD and TEM results. In general, microtwinningincludes chemical defects or Mn vacancies which are compensated by OH^-/O^{2-} in twinned boundaries. Therefore, the electrochemically-prepared MnO_2 NWs contain large amount of structural water[5].
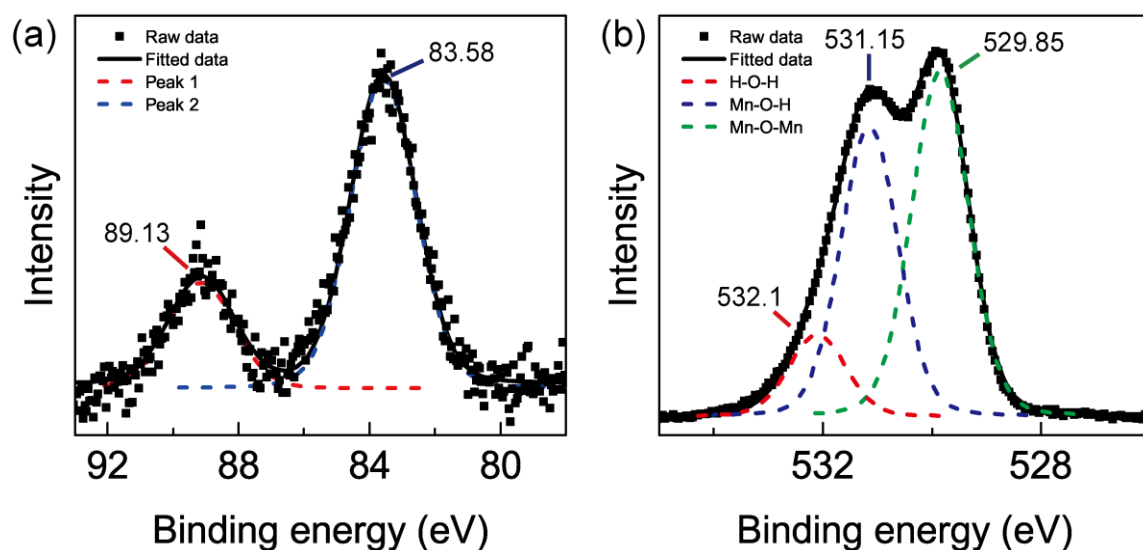
Fig. S2. XPS spectra of (a) Mn 3s and (b) O 1s from Mn-3.7/C-250 electrode after peak deconvolution. The raw and fitted data are represented by dots and lines, respectively.

Table S2. XPS analysis of Mn-3.7/C-250 electrode.

Mn 3s			O 1s		
BE of Peak 1 (eV)[a]	BE of Peak 2 (eV)[a]	DE (eV)[b]		BE (eV)[c]	Area (%)
89.13	83.58	5.55	Mn-O-Mn	529.85	49.8
			Mn-O-H	531.15	41.8
			H-O-H	532.1	8.4

[a]Biding energies of Mn 3s split peaks. [b]Difference between the binding energies of peak 1 and peak 2. [c]Binding energies of deconvoluted peaks of O 1s.

Characterization of CNF webs and MnO₂ NW/CNF composite electrodes.
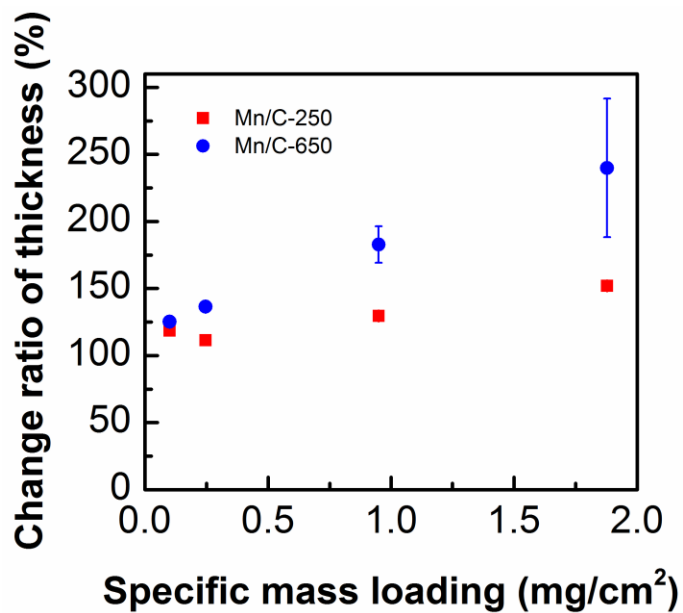

Fig. S3. The change ratio of electrode thickness before and after electrodeposition.

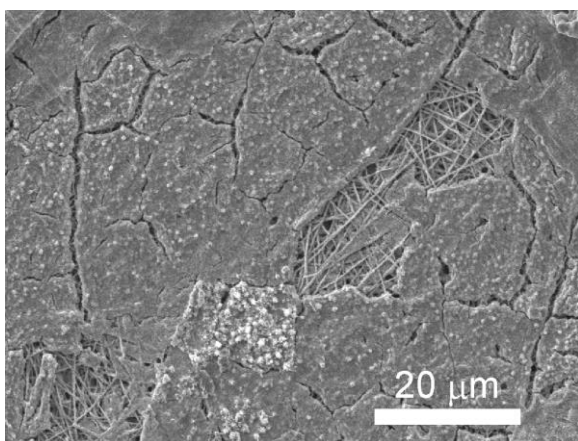**Evaluation of the asymmetric supercapacitor.**

Fig. S4. SEM image of the positive electrode for the ASC device after 2000 cycles.

Refference

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