

## **Supplementary Materials**

**Binder-free, multidentate bonding-induced carbon nano-oligomer assembly for boosting charge transfer and capacitance of energy nanoparticle-based textile pseudocapacitors**

## Experimental Section

*Synthesis of OA-MnO<sub>x</sub> NPs:* OA-MnO<sub>x</sub> NPs with an average diameter of ~10 nm were synthesized following a previously reported method [S1]. Briefly, 40 mmol of manganese(II) chloride tetrahydrate (MnCl<sub>2</sub>·4H<sub>2</sub>O; Sigma-Aldrich) and 80 mmol of sodium oleate (TCI Co. Ltd) were mixed in a solution containing ethanol (30 mL), deionized water (40 mL), and *n*-hexane (70 mL). This mixture was then stirred at 70 °C for 12 h. After the completion of reaction, the organic phase was separated from the aqueous phase, washed with deionized water, and evaporated to obtain a pink-colored Mn-oleated complex powder. Subsequently, 1.24 g of Mn-oleated complex was dissolved in 1-hexadecene (12.8 mL; Alfa Aesar) and stirred at 70 °C for 1 h under an Ar atmosphere. The reaction mixture was then heated up to 280 °C with a constant heating rate of 1.9 °C min<sup>-1</sup> and kept at that temperature for 10 min. The resultant solution was cooled to room temperature and purified through several times of centrifugation with excess acetone and ethanol. The obtained OA-MnO<sub>x</sub> NPs were dispersed in toluene for further use.

*Synthesis of CNOs:* 0.5 g of pristine carbon blacks (EQ-Lib-Super P; MTI Korea) underwent surface treatment in a mixture of H<sub>2</sub>SO<sub>4</sub> (30 mL, 98%) and HNO<sub>3</sub> (10 mL, 60%) at 70 °C for 3 h with stirring. After the reaction, the resultant solution was cooled to room temperature and slowly neutralized by adding deionized water. Then, the CNOs were separated through centrifugation and subjected to vacuum filtration to remove residual acid. The filtrated CNO films were dried in a vacuum oven and dispersed in ethanol for further use.

*Synthesis of OA-Fe<sub>3</sub>O<sub>4</sub> NPs:* OA-Fe<sub>3</sub>O<sub>4</sub> NPs with an average diameter of ~10 nm were synthesized by referring to a previously reported method [S2], and all chemicals were purchased from Sigma-Aldrich. Briefly, a mixture of iron(III) acetylacetonate (Fe(acac)<sub>3</sub>, 2.0 mmol), 1,2-hexadecandiol (10 mmol), oleic acid (OA, 6.0 mmol), oleylamine (OAm, 6.0

mmol), and benzyl ether (20 mL) was stirred under an Ar atmosphere. Subsequently, the mixture solution was heated at 200 °C for 2 h and then at 300 °C for 1 h. After cooling the resultant solution to room temperature, centrifugation with excess acetone and ethanol was repeated to precipitate the OA-Fe<sub>3</sub>O<sub>4</sub> NPs. These precipitants were redissolved in toluene containing OA (0.05 mL) and OAm (0.05 mL). After several additional centrifugation processes, the final OA-Fe<sub>3</sub>O<sub>4</sub> NPs were dispersed in toluene for further use.

*Preparation of NTCs:* First, bare cotton textiles was thoroughly cleaned with deionized water and dried in a vacuum oven at room temperature. Under a continuous N<sub>2</sub> gas flow, they were carbonized by heating up to 950 °C at a constant heating rate of 3.0 °C min<sup>-1</sup> and holding for 3 h in a tube furnace, followed by cooling to room temperature. For the Ni electroplating of the carbonized textiles, a Watts bath was prepared by dissolving nickel(II) sulfate hexahydrate (NiSO<sub>4</sub>·6H<sub>2</sub>O, 240 g L<sup>-1</sup>; Alfa Aesar), nickel(II) chloride hexahydrate (NiCl<sub>2</sub>·6H<sub>2</sub>O, 45 g L<sup>-1</sup>; Sigma-Aldrich), and boric acid (H<sub>3</sub>BO<sub>3</sub>, 30 g L<sup>-1</sup>; Alfa Aesar) in deionized water [S3]. The carbonized textiles (as a cathode) and high-purity Ni plates (as an anode) were immersed in the Watts bath and electroplating was conducted at a current density of 100 mA cm<sup>-2</sup> for 20 min using a power supply. The formed NTCs were washed with deionized water and completely dried in a vacuum oven at room temperature.

*Direct Multidentate Assembly of (MnO<sub>x</sub> or Fe<sub>3</sub>O<sub>4</sub> NP/CNO)<sub>n</sub> Multilayers:* Substrates, including Si wafers, Au-sputtered Si wafers, QCM electrodes, quartz glasses, ITO glasses, and Ni plates, were irradiated to UV-ozone cleaning for 30 min. In the case of NTCs, they were used without further treatment. After then, all substrates were dipped in a polyethyleneimine (PEI, M<sub>w</sub> ~800; Sigma-Aldrich) solution (in ethanol, 5.0 mg mL<sup>-1</sup>) for 30 min to generate a robust underlayer and rinsed with pure ethanol to remove loosely attached PEI molecules. The PEI-coated substrates were then dipped into a metal oxide NP (MnO<sub>x</sub> or Fe<sub>3</sub>O<sub>4</sub> NP) solution (in toluene, 10 mg mL<sup>-1</sup>) for 10 min and rinsed with pure toluene to remove loosely attached

NPs. Subsequently, they were dipped into a CNO solution (in ethanol, 2.0 mg mL<sup>-1</sup>) for 10 min and rinsed with pure ethanol, resulting in the formation of one bilayer of (MnO<sub>x</sub> or Fe<sub>3</sub>O<sub>4</sub> NP/CNO) film. These procedures were repeated until the desired bilayer number (*n*) was achieved.

*Preparation of (MnO<sub>x</sub> slurry)-NTCs:* The slurry was prepared by physically blending 80 wt% of MnO<sub>2</sub> powder (average particle size ~10 μm; Sigma-Aldrich), 10 wt% of pristine carbon blacks, and 10 wt% of poly(acrylic acid) (PAA, M<sub>v</sub> ~450,000; Sigma-Aldrich) binder in ethanol. The as-prepared slurry was casted on NTCs and then dried in a vacuum oven at 120 °C for 8 h to produce (MnO<sub>x</sub> slurry)-NTCs with a MnO<sub>x</sub> loading mass of ~5.0 mg cm<sup>-2</sup>.

*Preparation of NTC-AFCs:* (MnO<sub>x</sub> NP/CNO)-NTCs and (Fe<sub>3</sub>O<sub>4</sub> NP/CNO)-NTCs were used as positive and negative electrodes for NTC-AFCs, respectively. The area ratio of the electrodes was precisely controlled based on the following charge balance equations [S4]:

$$q = C \times \Delta E \times m \quad (1)$$

$$\frac{m^+}{m^-} = \frac{C^- \Delta E^-}{C^+ \Delta E^+} \quad (2)$$

where *q*, *C*, *ΔE*, and *m* represent the stored charge, areal capacitance (mF cm<sup>-2</sup>), potential window (V) during CV scans, and area (cm<sup>2</sup>) of the positive/negative electrodes, respectively. Based on these equations, the area ratio of positive (MnO<sub>x</sub> NP/CNO)-NTCs and negative (Fe<sub>3</sub>O<sub>4</sub> NP/CNO)-NTCs was adjusted to 1:1.3.

*Characterization:* The morphology and crystal structure of the NPs were investigated through HR-TEM (Tecnai 20, FEI). The crystallinity of the NPs was also examined by XRD

using a SmartLab instrument (Rigaku) with Cu K $\alpha$  radiation (45 kV, 200 mA). The electrical properties of CNOs films on SiO $_2$ /Si wafers were measured with a four-probe method using a Loresta-GP MCP-T610 (Mitsubishi Chemical Analytech). For interfacial chemistry analysis, FTIR spectra was acquired using a Cary 600 (Agilent Technology) with a resolution of 4 cm $^{-1}$ . The obtained FTIR data were baseline-corrected and smoothed through spectrum analysis software (OMNIC, Thermo Fisher Scientific). The contact angles of the multilayers on Si wafers were monitored through a Phoenix-300 instrument (SEO Corp.) using water droplets with a pH of  $\sim$ 5.8. The qualitative growth of the multilayers was investigated through UV-vis spectroscopy (Lambda 365, Perkin Elmer) within the scan range of 800 to 250 nm. The mass change ( $\Delta m$ ,  $\mu\text{g cm}^{-2}$ ) of each layer were quantitatively calculated from the frequency change ( $\Delta F$ , Hz) in QCM measurements (QCM 200, SRS) using a simplified equation derived from the Sauerbrey equation [S5].

$$\Delta F = 56.6 \times \Delta m \quad (3)$$

The film thickness, surface morphology, and EDS images were observed through FE-SEM (S-4800, Hitachi). The current ( $I$ )-voltage ( $V$ ) profiles of the multilayers were measured through a semiconductor parameter analyzer (Agilent 4155B, Agilent Technology) using two gold wires (diameter  $\sim$ 0.5 mm) as the top and bottom electrodes, respectively.

**Electrochemical measurements.** Electrochemical performance was evaluated through a Ivium-n-Stat workstation (Ivium Technology). For a three-electrode system, Pt mesh and Ag/AgCl (saturated with 3.0 M NaCl) electrode were used as counter and reference electrodes, respectively. For a two-electrode system, the NTC-AFCs (consisting of (MnO $_x$  NP/CNO)-NTCs as positive electrodes and (Fe $_3$ O $_4$  NP/CNO)-NTCs as negative electrodes) were evaluated using an aqueous Na $_2$ SO $_4$  electrolyte (for aqueous AFCs) and a Na $_2$ SO $_4$ /PVA

gel electrolyte (for solid-state AFCs). In this case, the Na<sub>2</sub>SO<sub>4</sub>/PVA gel electrolyte was obtained by mixing 1.0 M Na<sub>2</sub>SO<sub>4</sub> with polyvinyl alcohol (PVA, 6.0 g) in 60 mL of deionized water at 90 °C for 1 h. CV and GCD tests were measured in the range of 0 to 0.8 V (for the positive electrodes) and 0 to -0.8 V (for the negative electrodes) vs. Ag/AgCl. EIS measurements were carried out in the frequency range of 10<sup>5</sup> to 0.01 Hz with a perturbation amplitude of 0.01 mV. The areal, specific, and volumetric capacitance (*C*) values of electrodes were obtained from GCD curves using the following equation:

$$C = \frac{I\Delta t}{S\Delta V} \quad (4)$$

where *I*,  $\Delta t$ , and  $\Delta V$  are the discharge current density (A), discharge time (s), and operating potential window (V), respectively. The variable (*S*) indicates the active area (cm<sup>2</sup>) for the areal capacitance, the active mass (g) for the specific capacitance, or the active volume (cm<sup>3</sup>) for the volumetric capacitance of the electrodes. To separate capacitive- (*k*<sub>1</sub>*v*) and diffusion-controlled (*k*<sub>2</sub>*v*<sup>1/2</sup>) currents in the scan rate-dependent CV curves, we used the Dunn's method [S6].

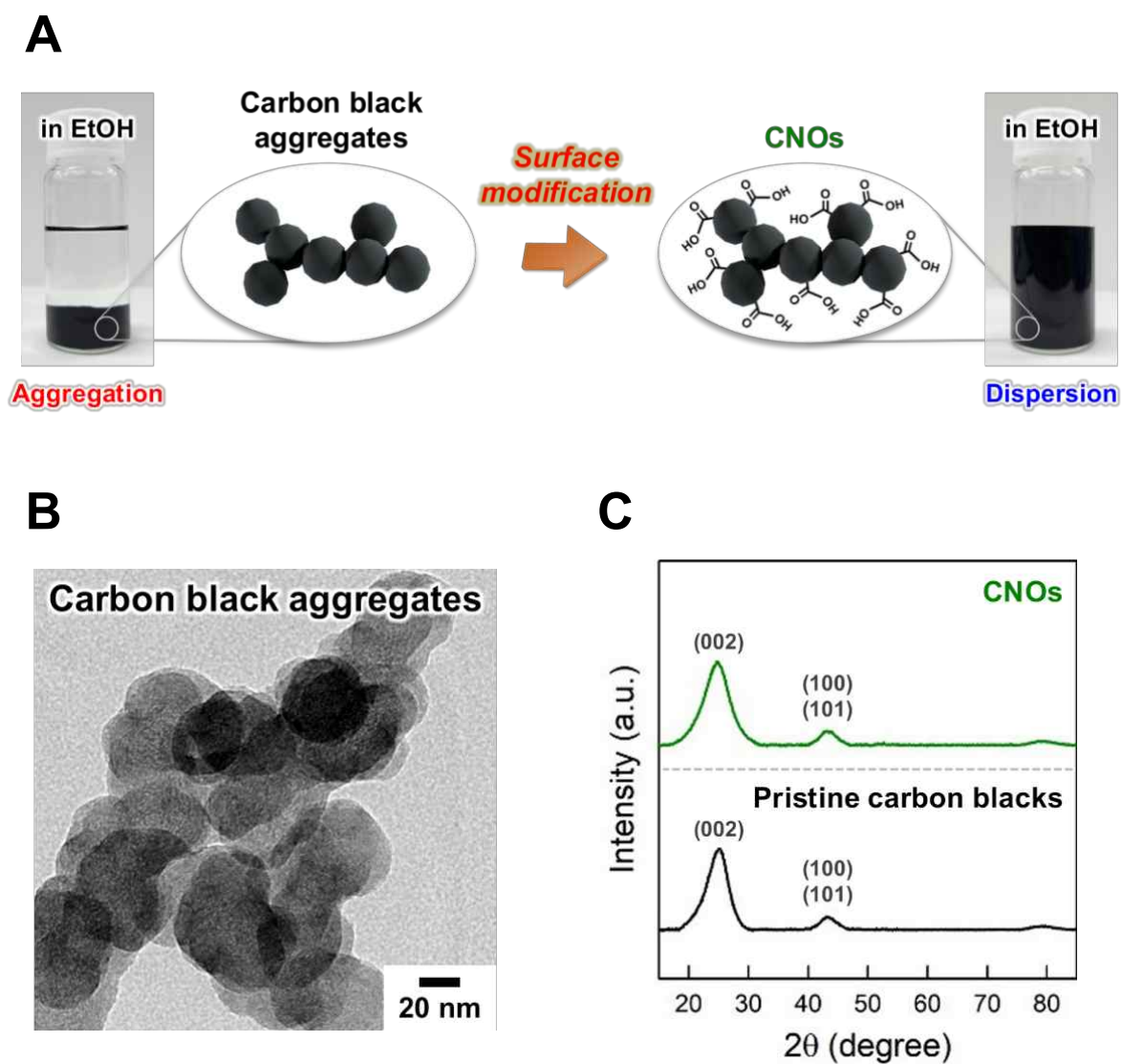
$$i(V) = k_{1(V)}v + k_{2(V)}v^{1/2} \quad (5)$$

Here, *k*<sub>1</sub> and *k*<sub>2</sub> are constants at a certain potential (*V*). The values of *k*<sub>1</sub> and *k*<sub>2</sub> can be obtained by plotting *i(V)/v*<sup>1/2</sup> vs. *v*<sup>1/2</sup>, where *k*<sub>1</sub> and *k*<sub>2</sub> are the slopes and y-intercepts, respectively. The areal energy density (*E*, mWh cm<sup>-2</sup>) and power density (*P*, mW cm<sup>-2</sup>) values of the NTC-AFCs were calculated from GCD curves based on previously defined relationships.

$$E = \frac{CV^2}{7200} \quad (6)$$

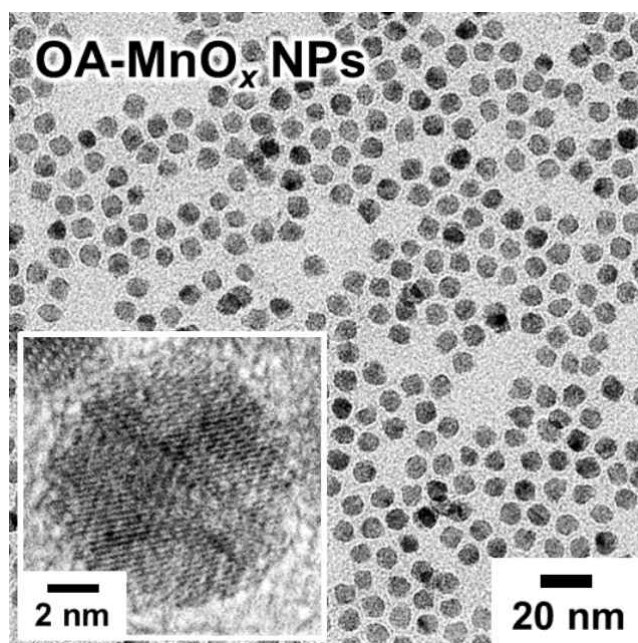
$$P = \frac{E \times 3600}{\Delta t}$$

(7)

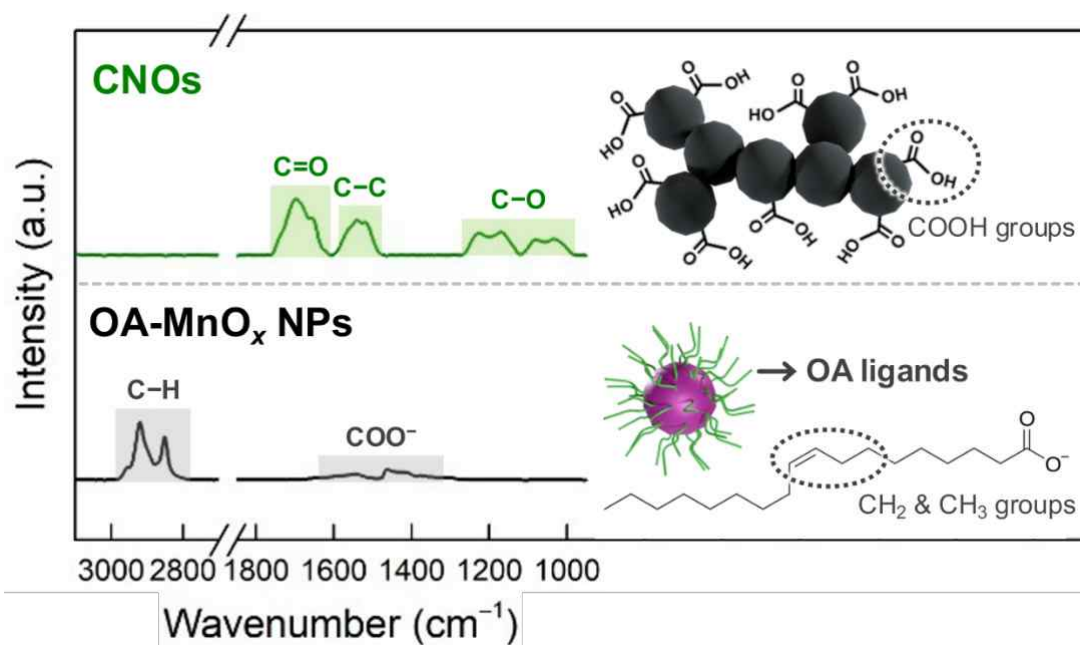


**Fig. S1.** (A) Schematic illustrations and digital images of pristine carbon black aggregates and CNOs in ethanol. Notably, the pristine carbon blacks were aggregated in ethanol, whereas the surface-modified CNOs exhibited an excellent dispersion stability in the same solvent. (B) HR-TEM image of carbon black aggregates. (C) XRD patterns of CNOs (top) and pristine carbon blacks (bottom).

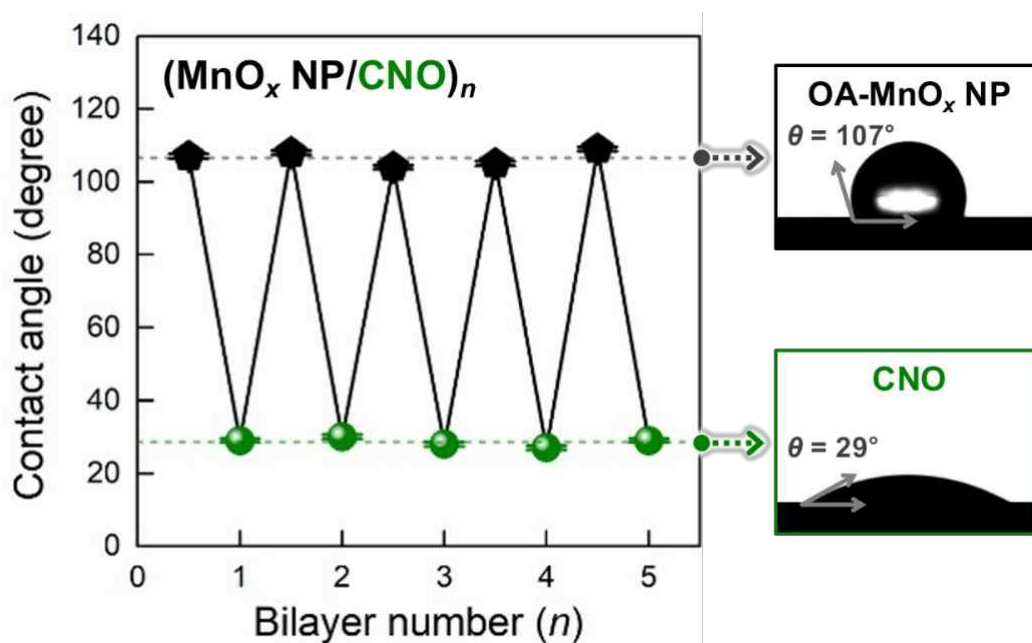




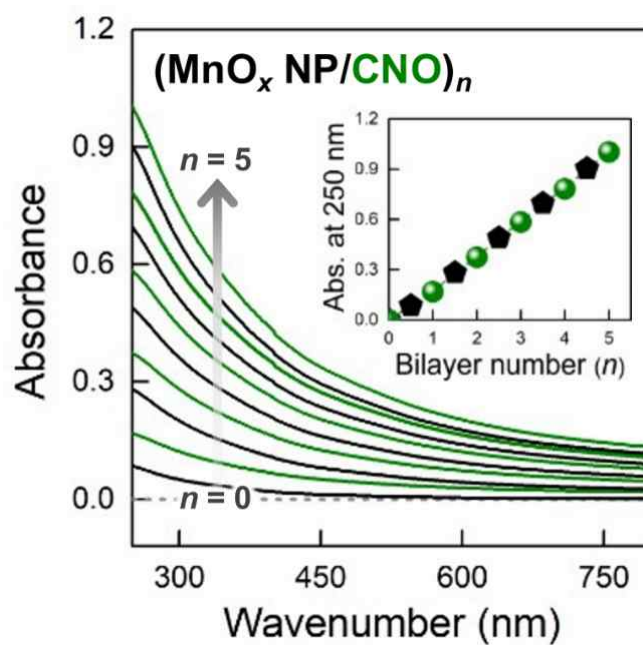
**Fig. S2.** HR-TEM images of OA-MnO<sub>x</sub> NPs with an average diameter of ~10 nm.



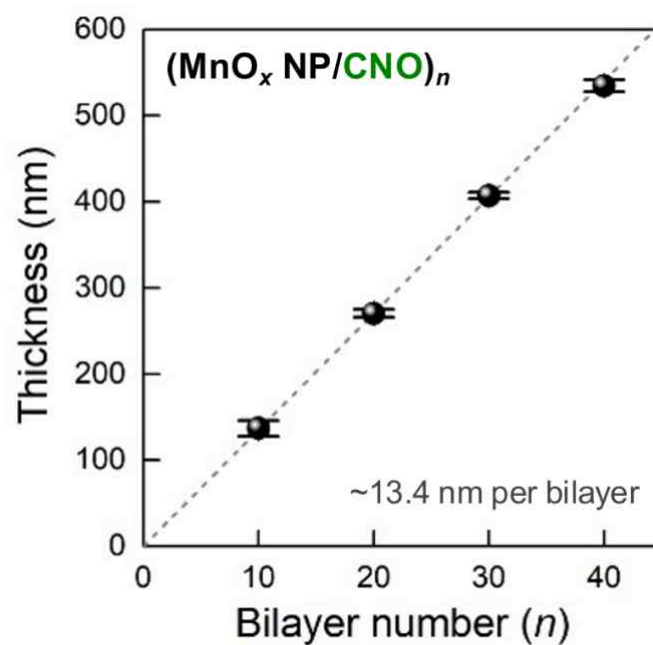
**Fig. S3.** FTIR spectra of CNOs (top) and OA-MnO<sub>x</sub> NPs (bottom). The OA-MnO<sub>x</sub> NPs showed distinctive C–H stretching peak (at 3000–2800 cm<sup>-1</sup>) derived from the long alkyl chains (CH<sub>2</sub> and CH<sub>3</sub> groups) of native OA ligands. On the other hand, the CNOs did not exhibit any notable absorption in the same wavelength region.



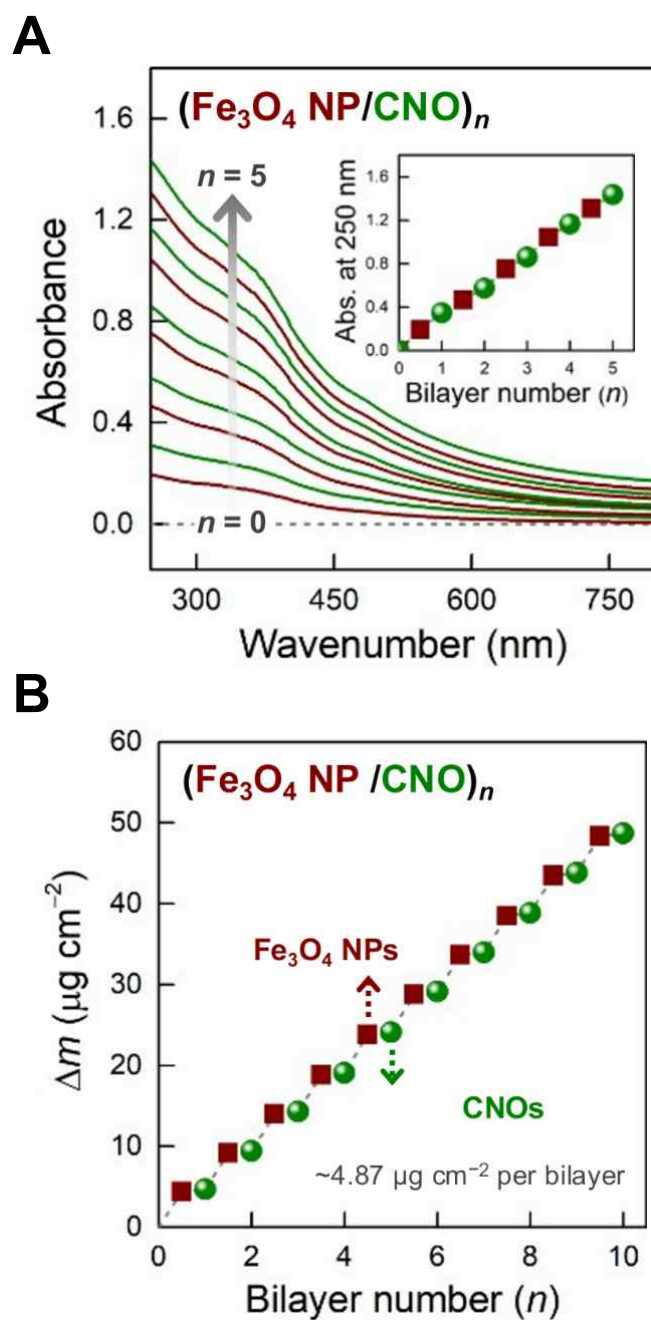
**Fig. S4.** Water contact angle changes of  $(\text{MnO}_x \text{ NP/CNO})_n$  multilayers as a function of bilayer number ( $n$ ), along with digital images for the outermost layer of OA- $\text{MnO}_x$  NPs (top) and CNOs (bottom). The average water contact angles were measured to be  $\sim 107^\circ$  for the outermost layer of OA- $\text{MnO}_x$  NPs ( $n = 0.5, 1.5, 2.5 \dots$ ) and  $\sim 29^\circ$  for the outermost layer of CNOs ( $n = 1.0, 2.0, 3.0 \dots$ ).



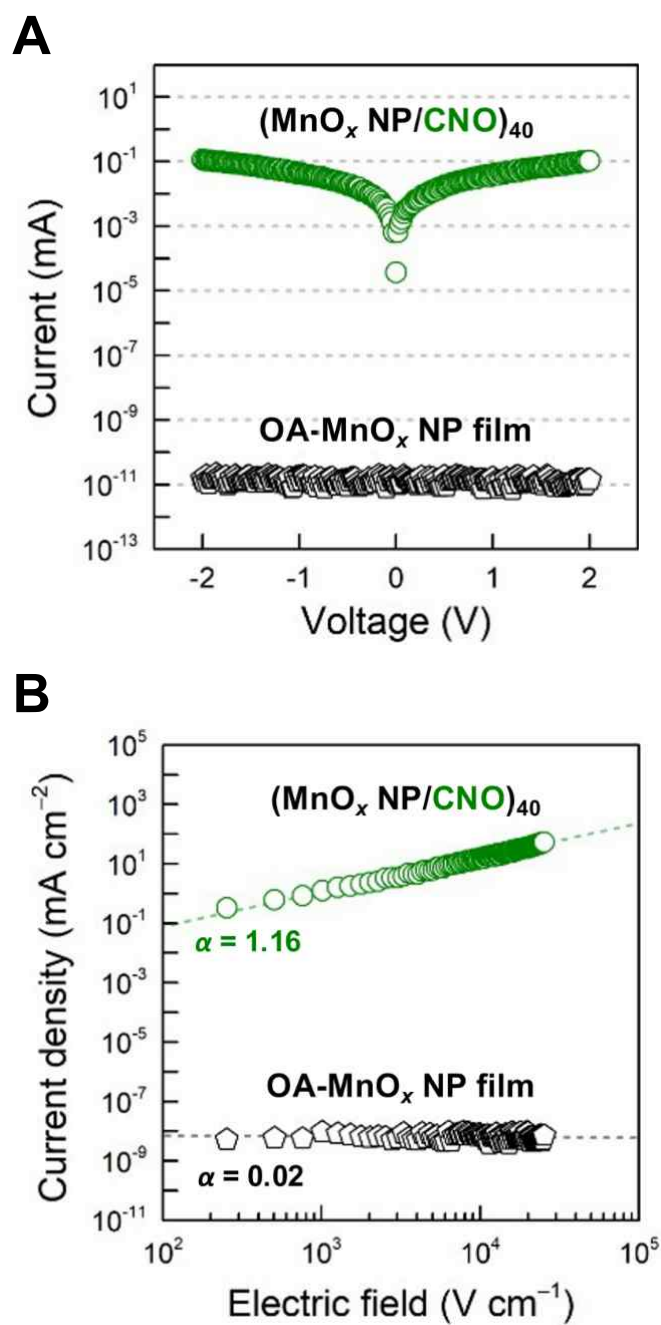
**Fig. S5.** UV-vis absorbance spectra of  $(\text{MnO}_x \text{ NP/CNO})_n$  multilayers with increasing the bilayer number ( $n$ ) from 0 to 5 in the wavelength from 800 to 250 nm. The inset represents the absorbance values at the wavelength of 250 nm, indicating a linear growth of the multilayers.



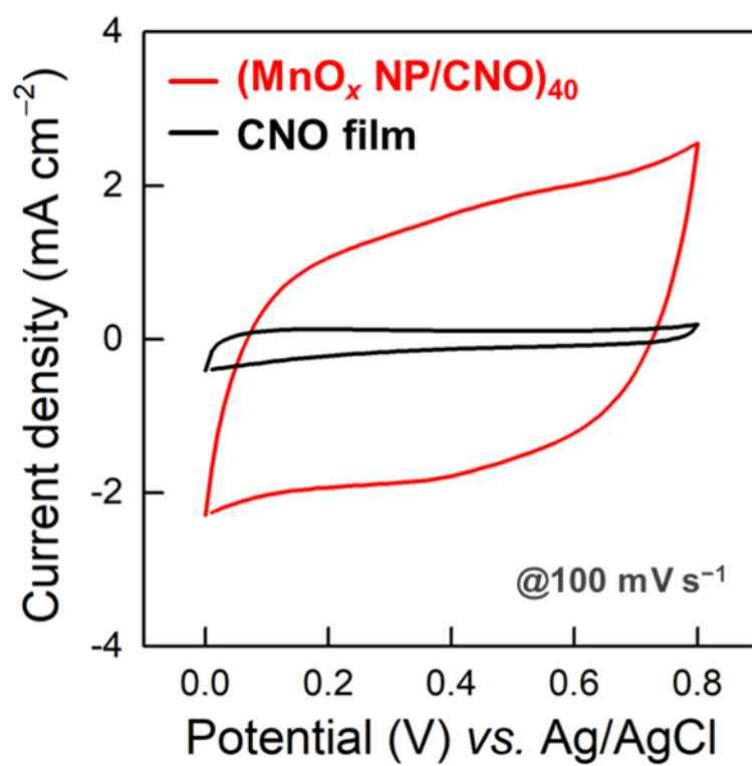
**Fig. S6.** Film thickness changes of  $(\text{MnO}_x \text{ NP/CNO})_n$  multilayers with increasing the bilayer number ( $n$ ) increased from 0 to 40 (average film thickness per bilayer  $\sim 13.4$  nm).



**Fig. S7.** (A) UV-vis absorbance spectra and (B) mass changes ( $\Delta m$ ) (obtained from QCM measurement) of  $(\text{Fe}_3\text{O}_4 \text{ NP/CNO})_n$  multilayers with increasing the bilayer number ( $n$ ).

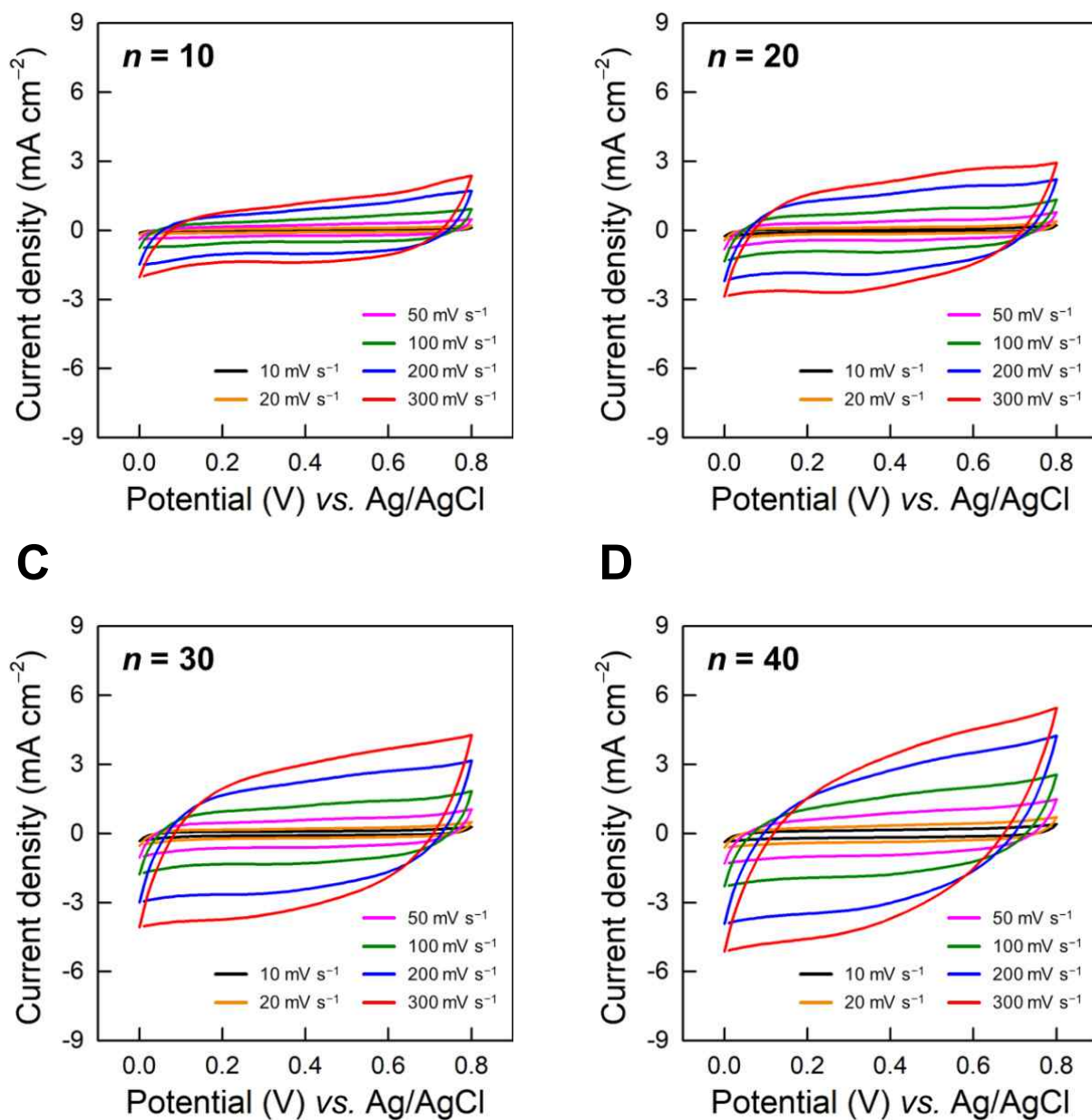


**Fig. S8.** (A) Current ( $\log I$ ) vs. voltage ( $\log V$ ) and (B) current density ( $\log J$ ) vs. electric field ( $\log E$ ) profiles of  $(\text{MnO}_x \text{ NP/CNO})_{40}$  multilayers and pristine OA- $\text{MnO}_x$  NP films.

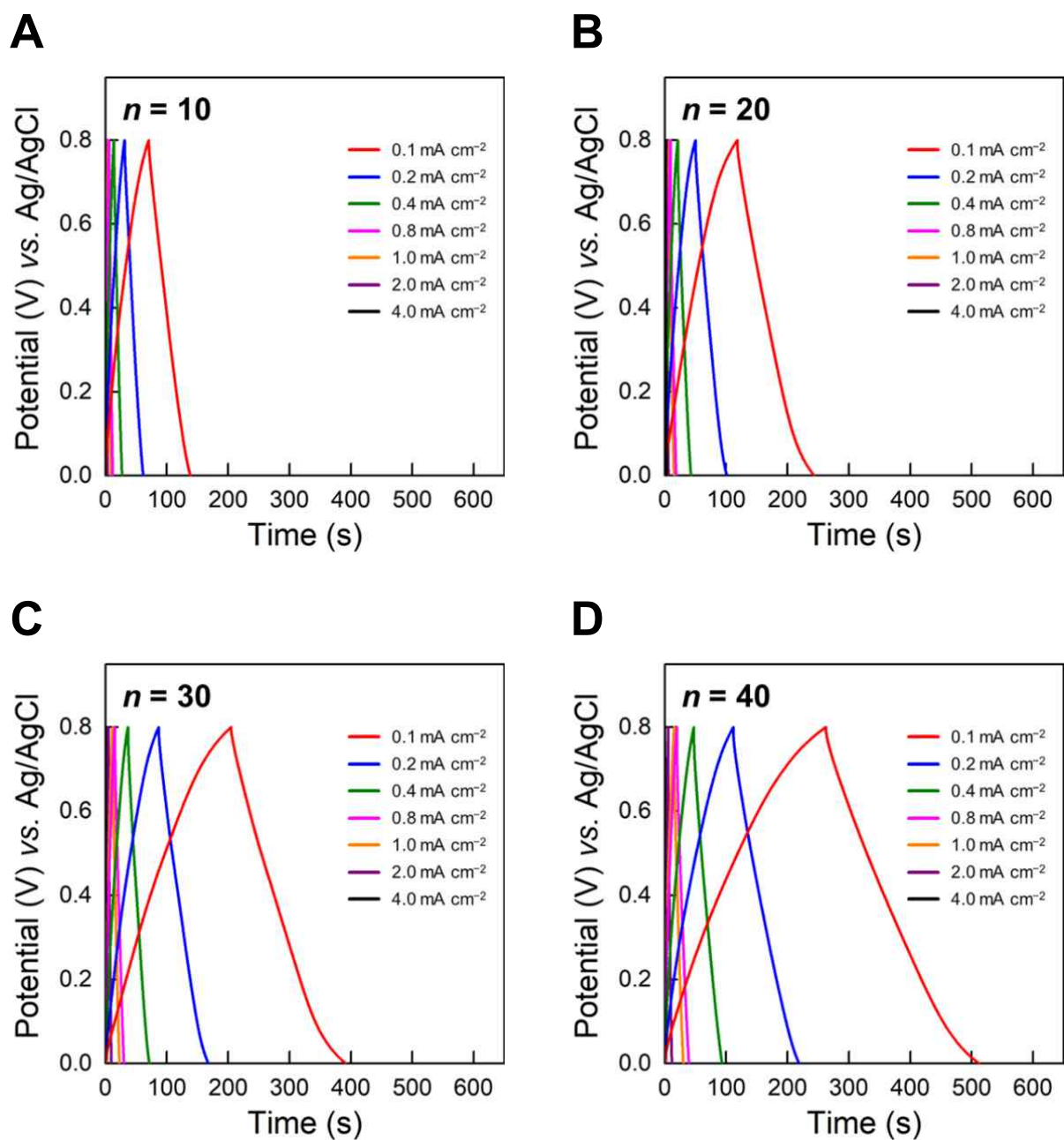


**Fig. S9.** Comparison of CV curves between (MnO<sub>x</sub> NP/CNO)<sub>40</sub> electrodes and CNO films with the same loading mass of CNOs at 100 mV s<sup>-1</sup>.

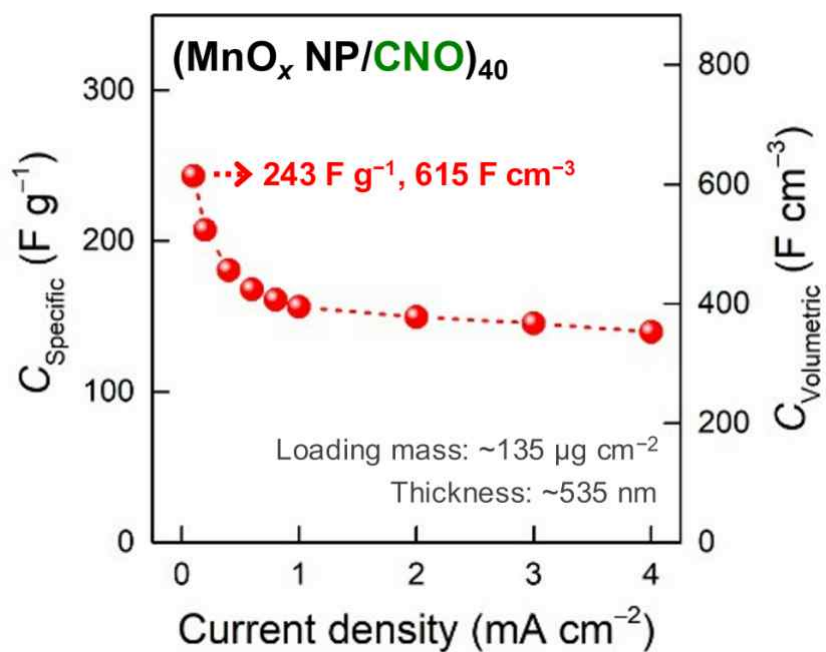




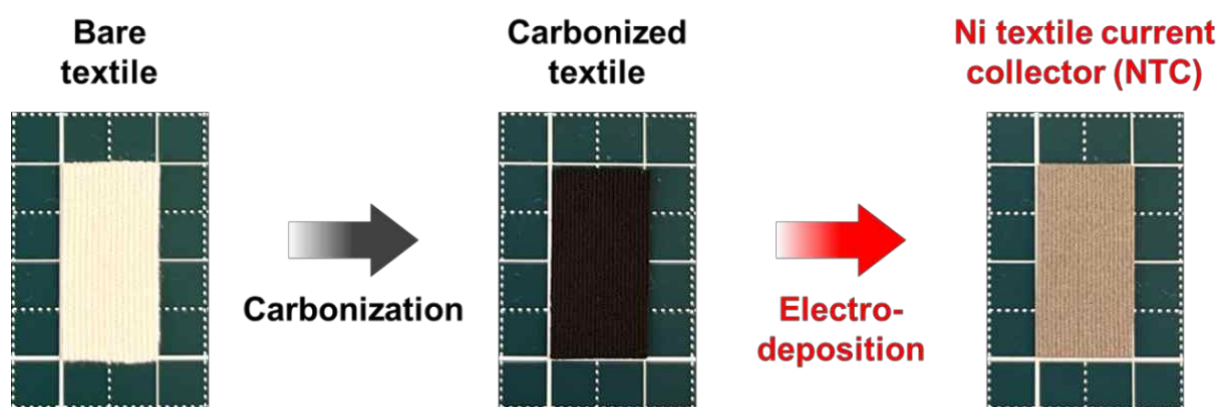
**Fig. S10.** Scan rate-dependent CV curves of  $(\text{MnO}_x \text{ NP/CNO})_n$  electrodes at different bilayer number ( $n$ ): (A)  $n = 10$ , (B)  $n = 20$ , (C)  $n = 30$ , and (D)  $n = 40$ .



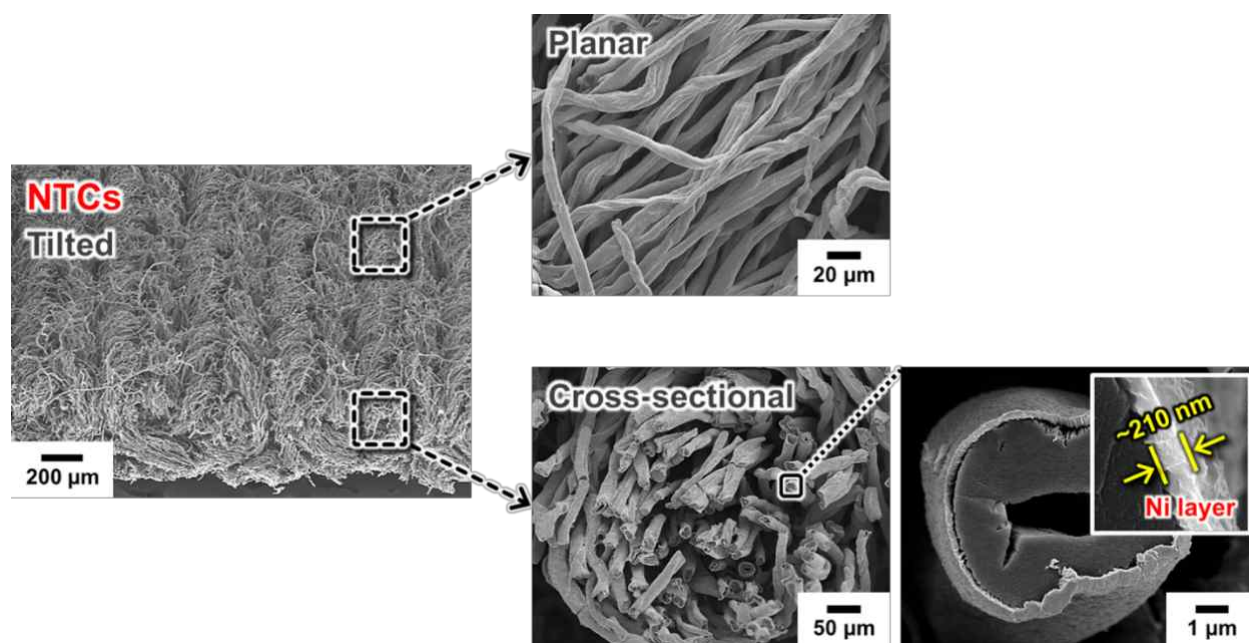
**Fig. S11.** Current density-dependent GCD curves of  $(\text{MnO}_x \text{ NP/CNO})_n$  electrodes at different bilayer number ( $n$ ): (A)  $n = 10$ , (B)  $n = 20$ , (C)  $n = 30$ , and (D)  $n = 40$ .



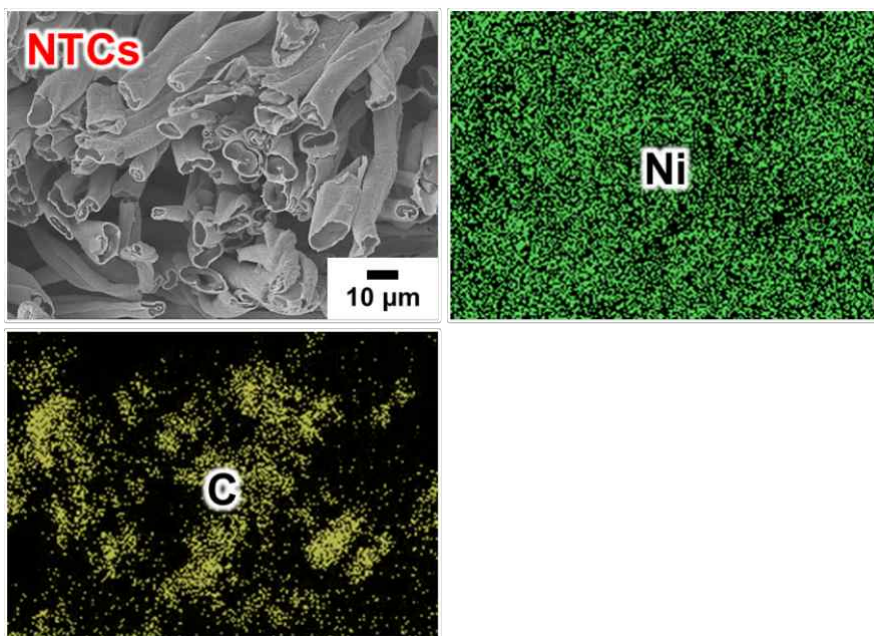
**Fig. S12.** Specific ( $C_{\text{Specific}}$ , left axis) and volumetric ( $C_{\text{Volumetric}}$ , right axis) capacitance values of  $(\text{MnO}_x \text{ NP/CNO})_{40}$  electrodes at various current densities in the range of 0.1 to 4.0 mA  $\text{cm}^{-2}$ .



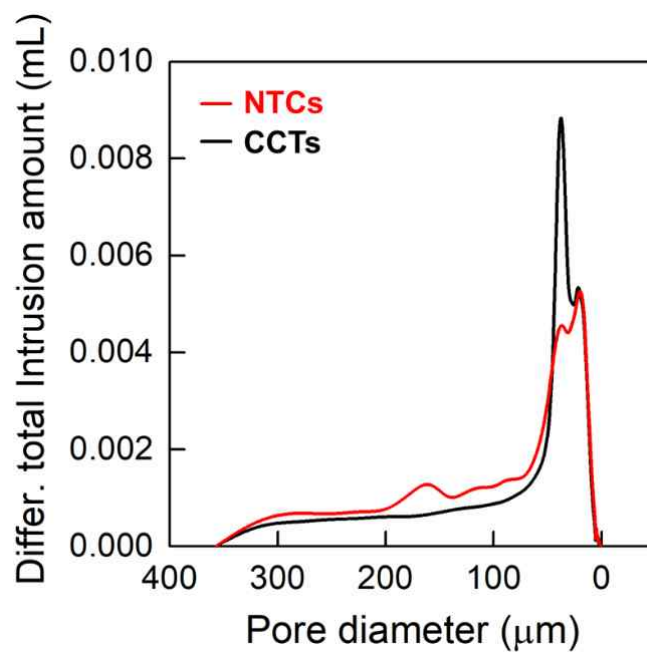
**Fig. S13.** Procedure of preparing Ni textile current collectors (NTCs) and digital images of each step (see the details in Experimental Section).



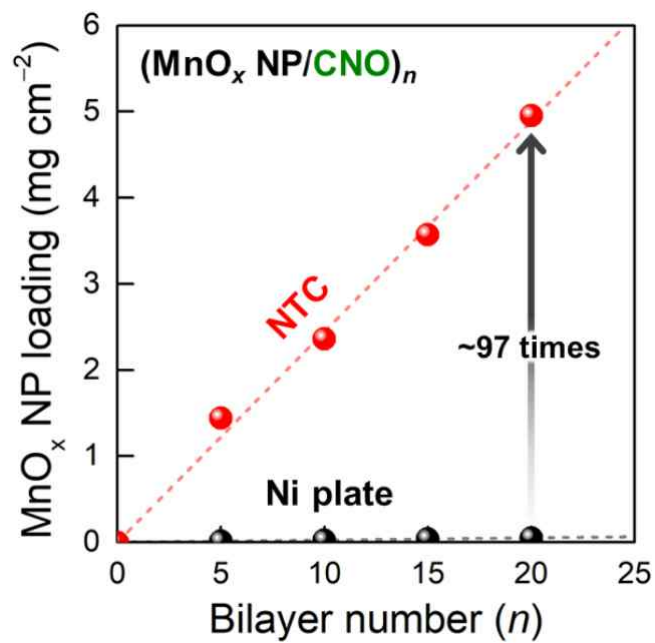
**Fig. S14.** Tilted, planar, and cross-sectional FE-SEM images of porous NTCs. A thin Ni layer of ~210 nm was uniformly coated all outer/inner fibrils within the NTCs without blocking the pores.



**Fig. S15.** EDS mapping images of porous NTCs.

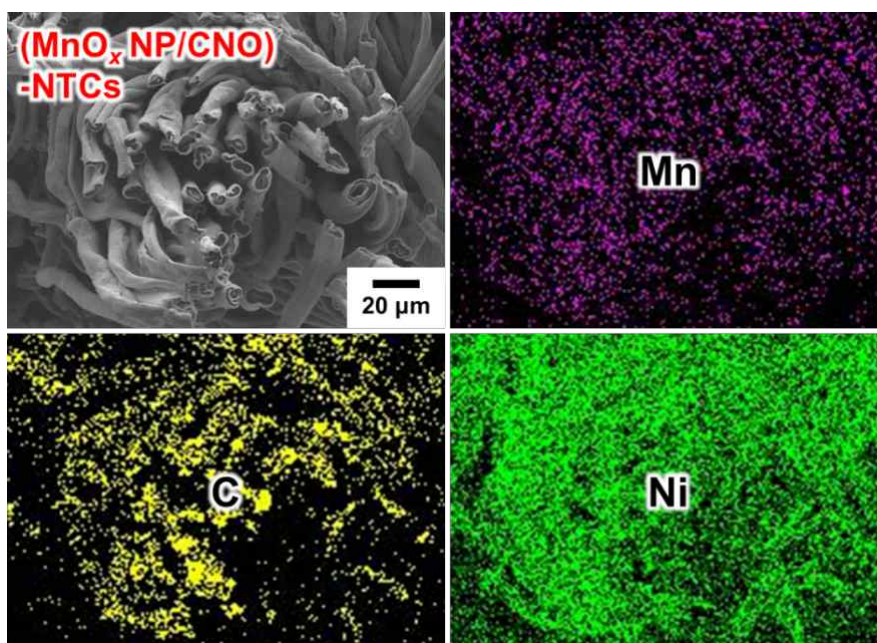


**Fig. S16.** MIP analysis for CCTs and NTCs. The total surface area of the CCTs was determined to be  $\sim 225.2 \text{ cm}^2$  (at an electrode size of  $1 \text{ cm} \times 2 \text{ cm}$ ), which was relatively higher than that of the NTCs ( $\sim 173.3 \text{ cm}^2$ ). This decrease in surface area of the NTCs was mainly attributed to the overall reduction in pore size within the textiles due to the electrodeposition of the Ni layer.

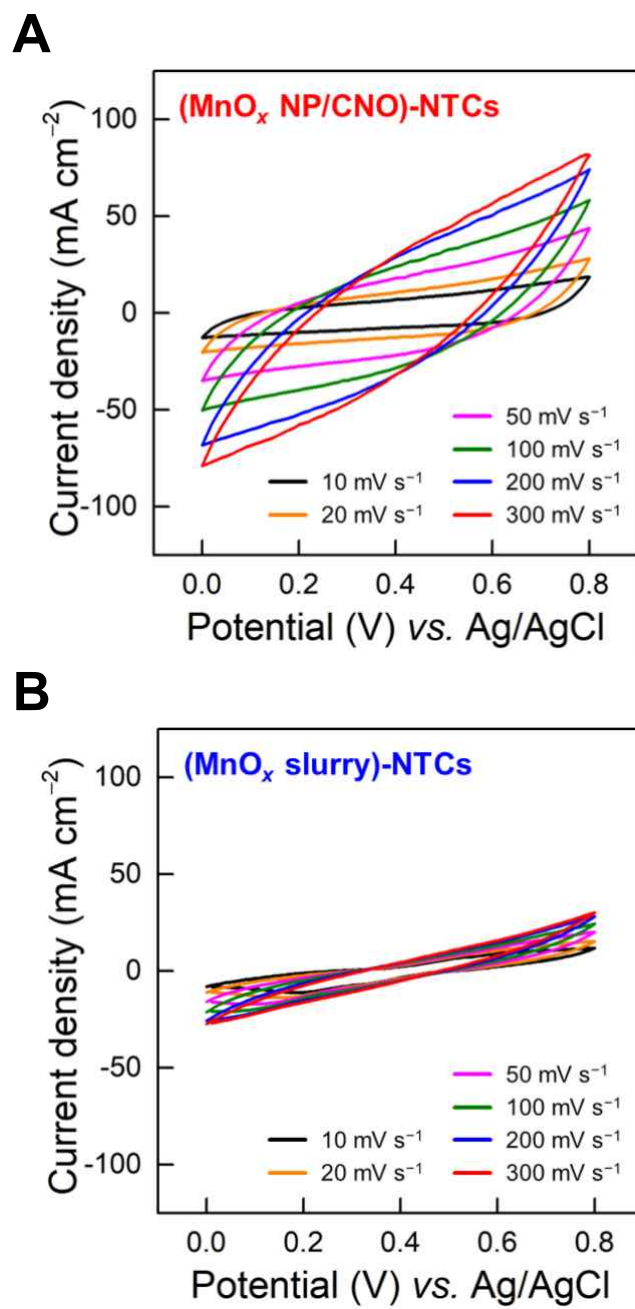


**Fig. S17.** Loading mass of MnO<sub>x</sub> NPs on porous NTCs and flat Ni plates with increasing the bilayer number ( $n$ ) from 0 to 20.

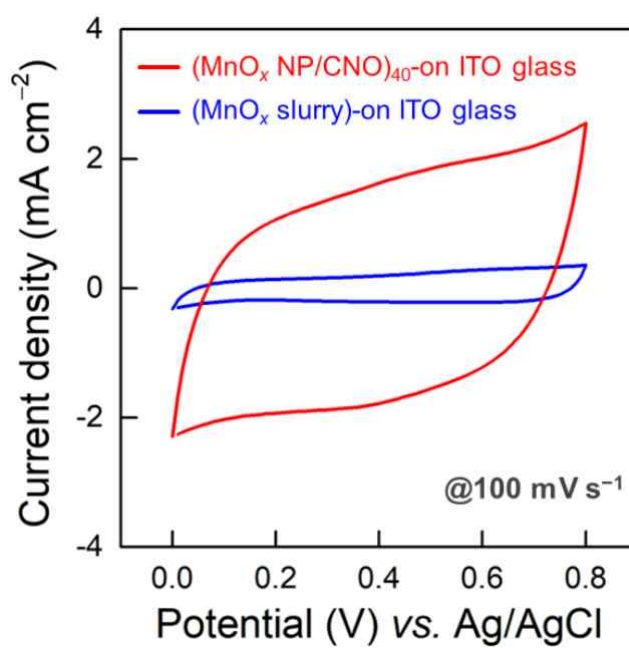




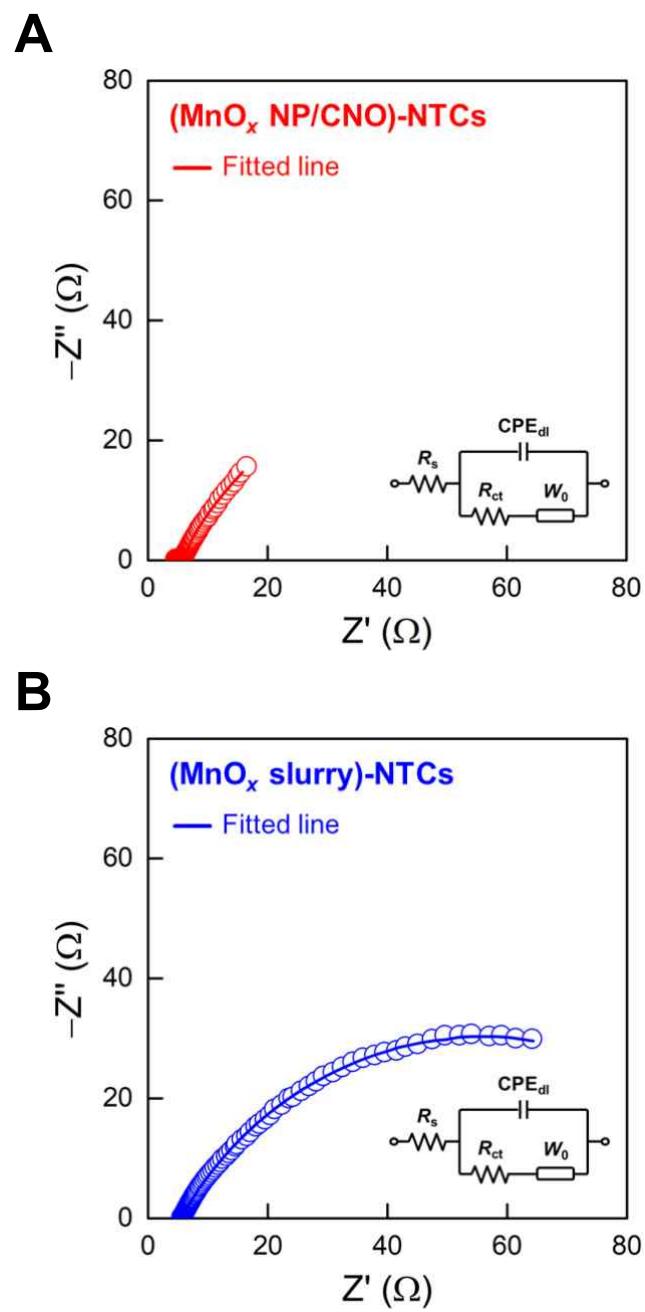
**Fig. S18.** Cross-sectional FE-SEM and corresponding EDS mapping images of (MnO<sub>x</sub> NP/CNO)-NTCs.



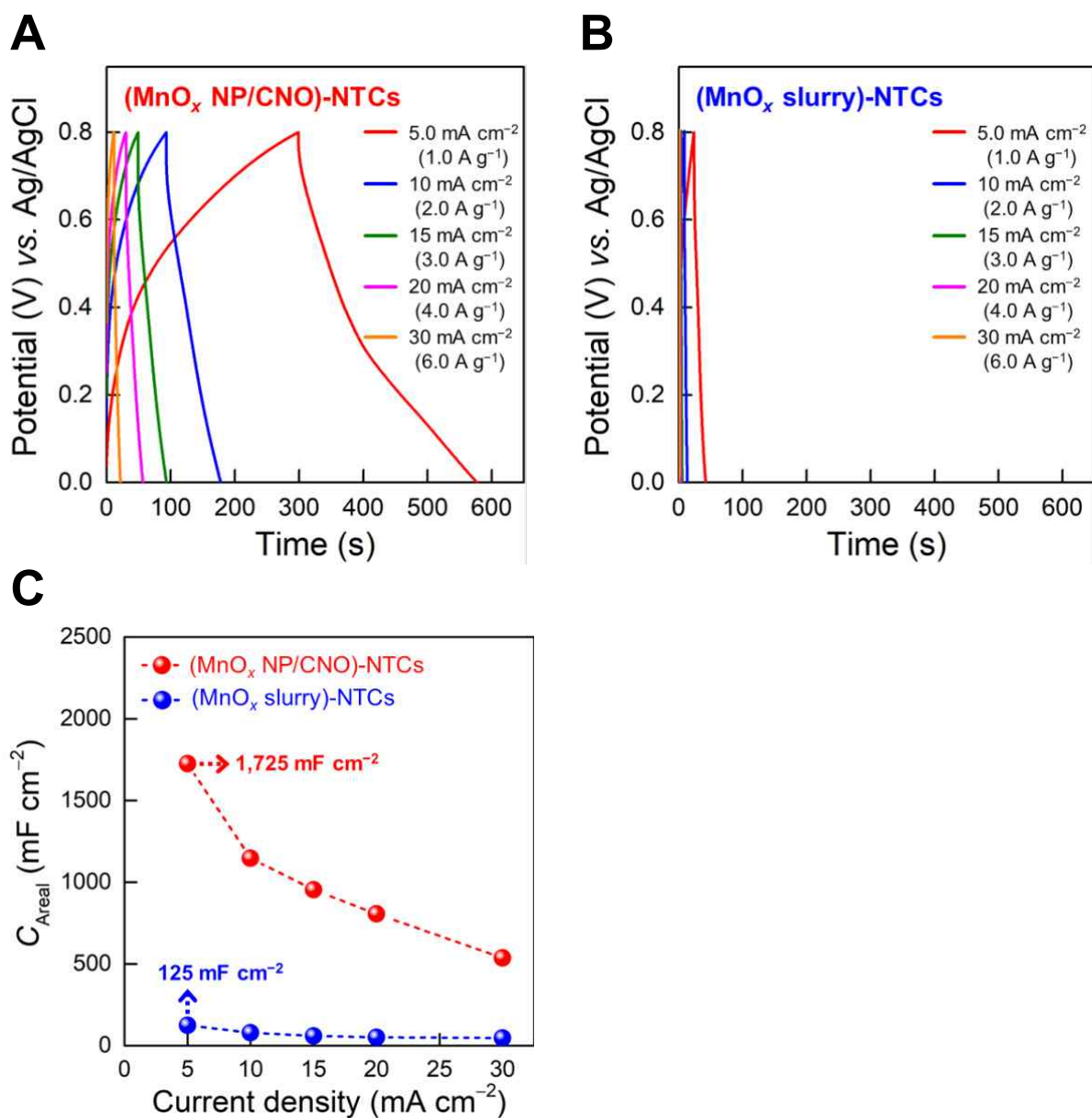
**Fig. S19.** CV curves of (A) (MnO<sub>x</sub> NP/CNO)-NTCs and (B) (MnO<sub>x</sub> slurry)-NTCs at various scan rates in the range of 10 to 300 mV s<sup>-1</sup>.



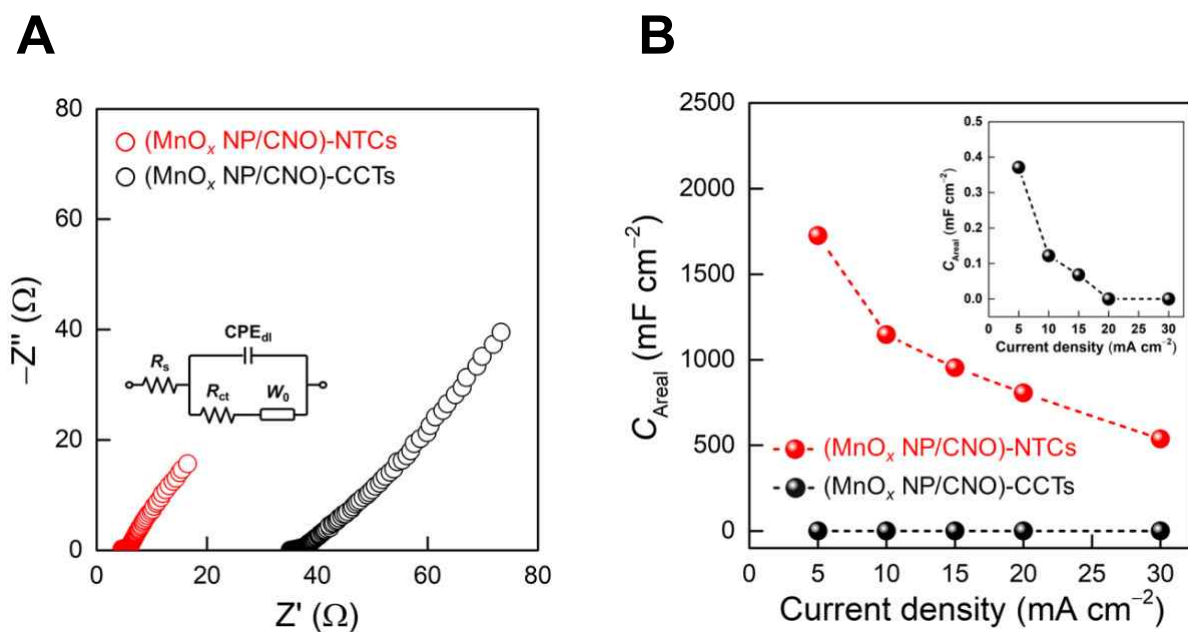
**Fig. S20.** Comparison of CV curves between the electrode layers of (MnO<sub>x</sub> NP/CNO) and (MnO<sub>x</sub> slurry) using the 2D flat ITO current collectors at 100 mV s<sup>-1</sup>.



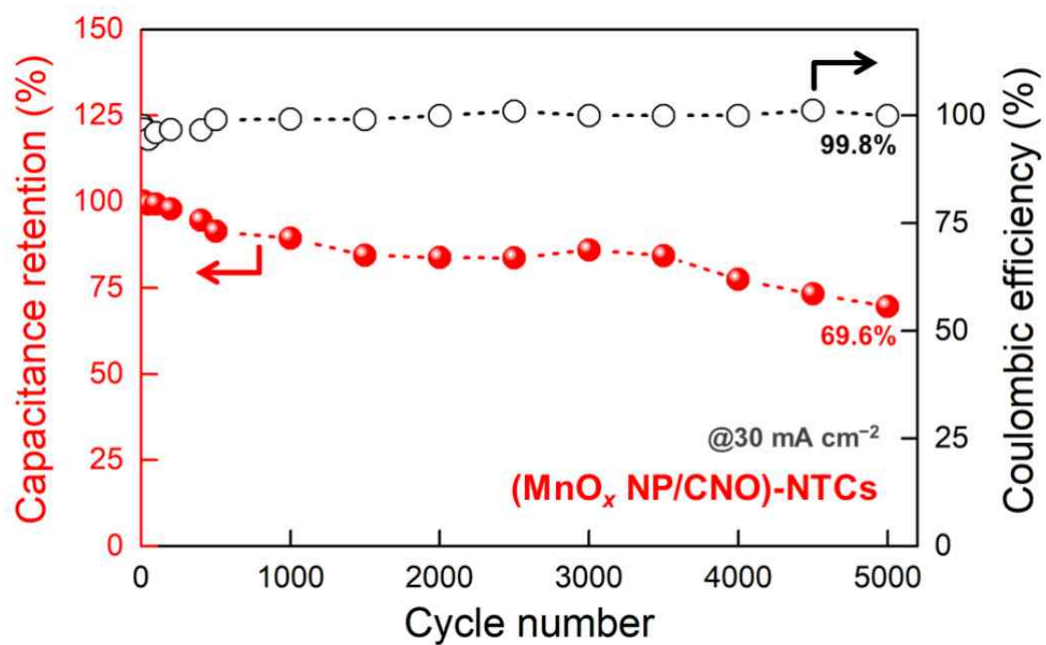
**Fig. S21.** Nyquist plots and fitted lines using a Randle circuit model (inset) of (A) (MnO<sub>x</sub> NP/CNO)-NTCs and (B) (MnO<sub>x</sub> slurry)-NTCs.



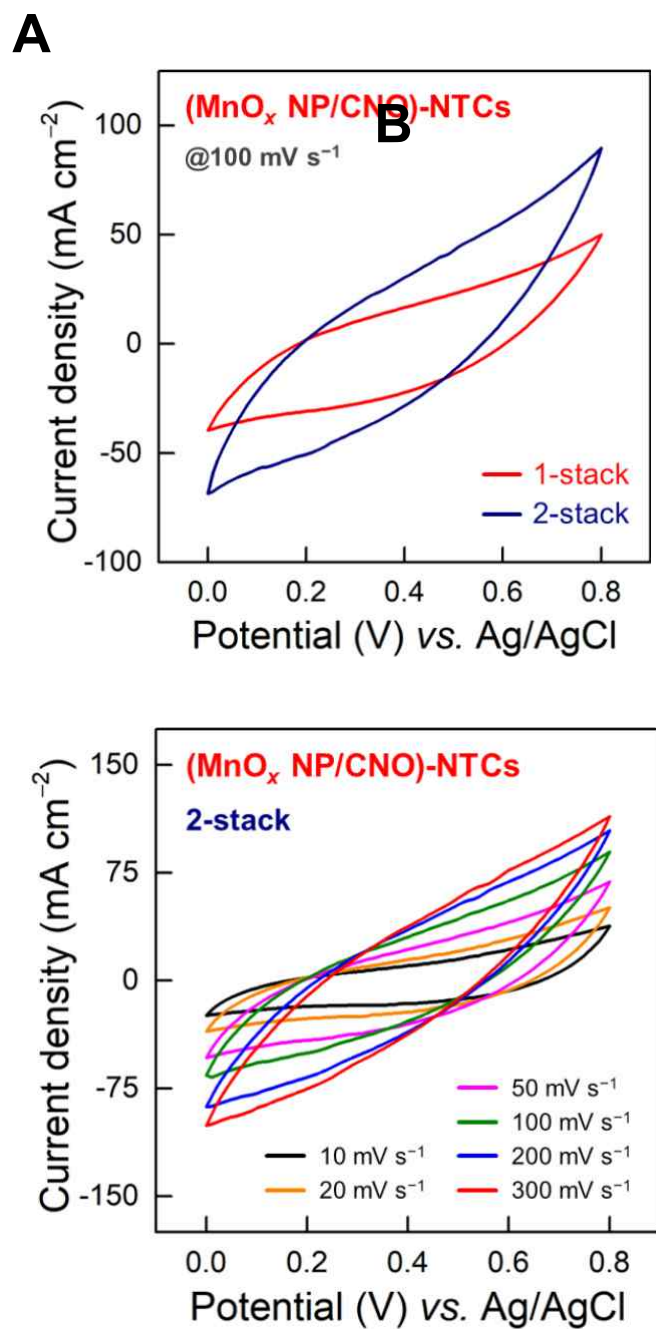
**Fig. S22.** Current density-dependent GCD curves of (A) (MnO<sub>x</sub> NP/CNO)-NTCs and (B) (MnO<sub>x</sub> slurry)-NTCs. (C) Areal capacitance (C<sub>Areal</sub>) values of (MnO<sub>x</sub> NP/CNO)-NTCs and (MnO<sub>x</sub> slurry)-NTCs at various current densities in the range of 5 to 30 mA cm<sup>-2</sup>.



**Fig. S23.** Comparison of (A) Nyquist plots and (B) areal capacitance ( $C_{Areal}$ ) values (at different current densities in the range of 1.0 to 6.0 A g<sup>-1</sup>) between the NTC-based electrodes and the CCT-based electrodes with the same loading mass of electrode layers (*i.e.*, (MnO<sub>x</sub> NP/CNO)<sub>n</sub> multilayers).

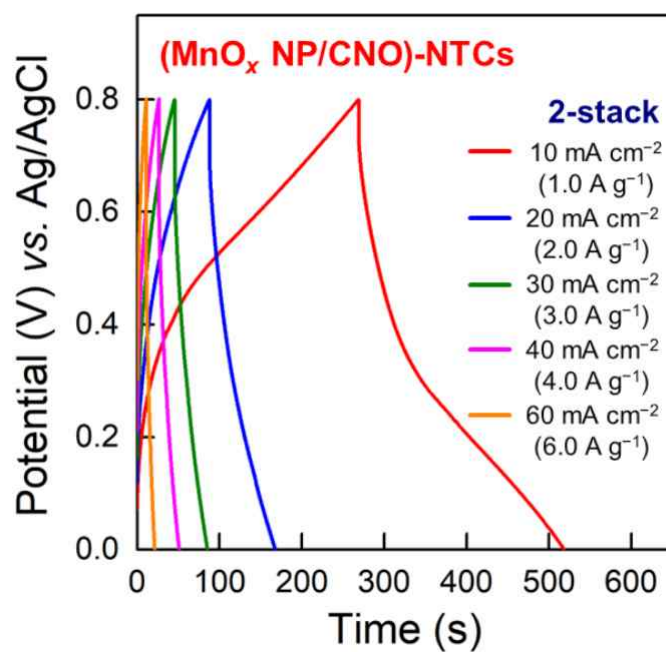


**Fig. S24.** Cycling stability of (MnO<sub>x</sub> NP/CNO)-NTCs, showing a capacitance retention of ~69.6% after GCD 5,000 cycles at 30 mA cm<sup>-2</sup>.

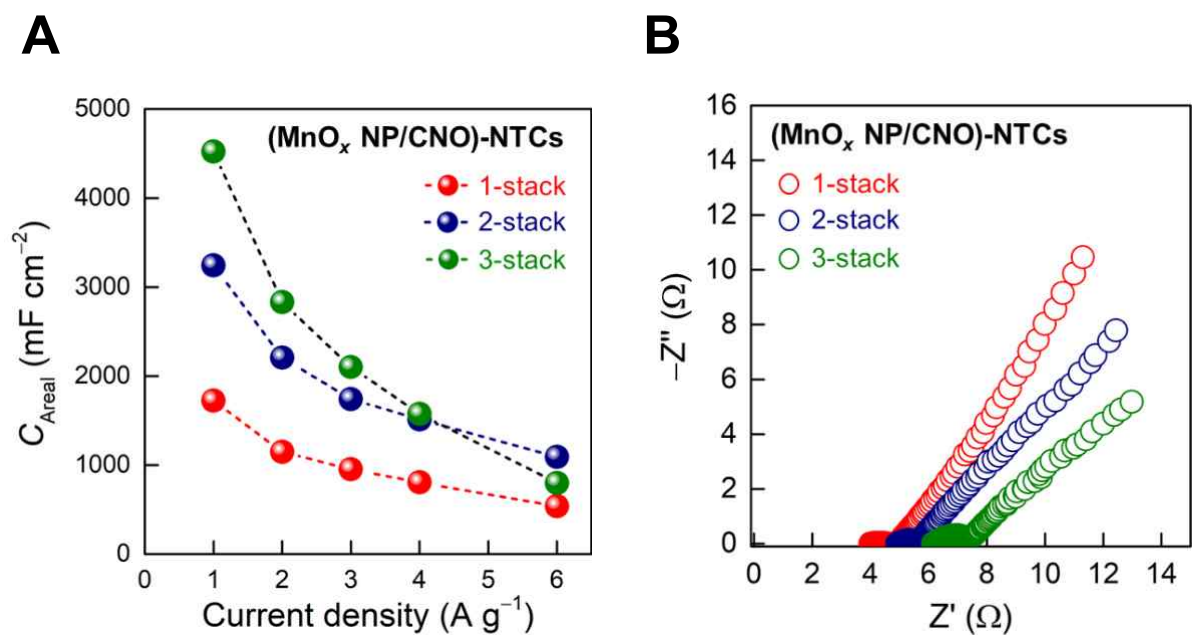


**Fig. S25.** (A) CV curves of non-stacked and two-stacked (MnO<sub>x</sub> NP/CNO)-NTCs at 100 mV s<sup>-1</sup>. (B) CV curves of two-stacked (MnO<sub>x</sub> NP/CNO)-NTCs at various scan rates in the range of 10 to 300 mV s<sup>-1</sup>.



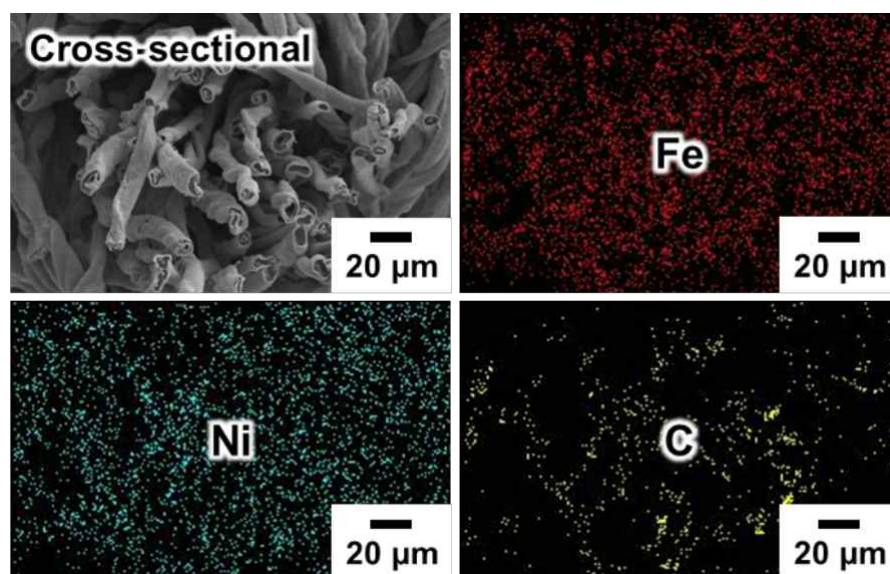
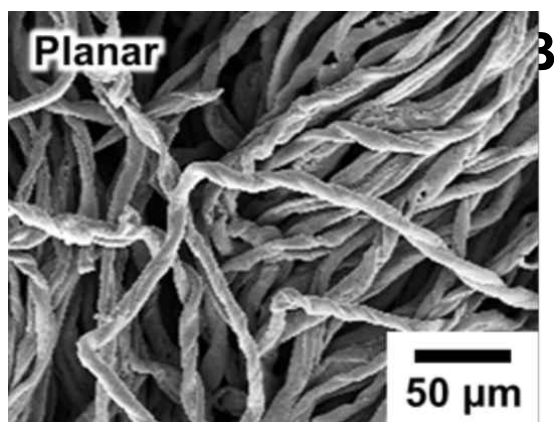


**Fig. S26.** GCD curves of two-stacked (MnO<sub>x</sub> NP/CNO)-NTCs at various current densities in the range of 10 to 60 mA cm<sup>-2</sup> (1.0 to 6.0 A g<sup>-1</sup>).

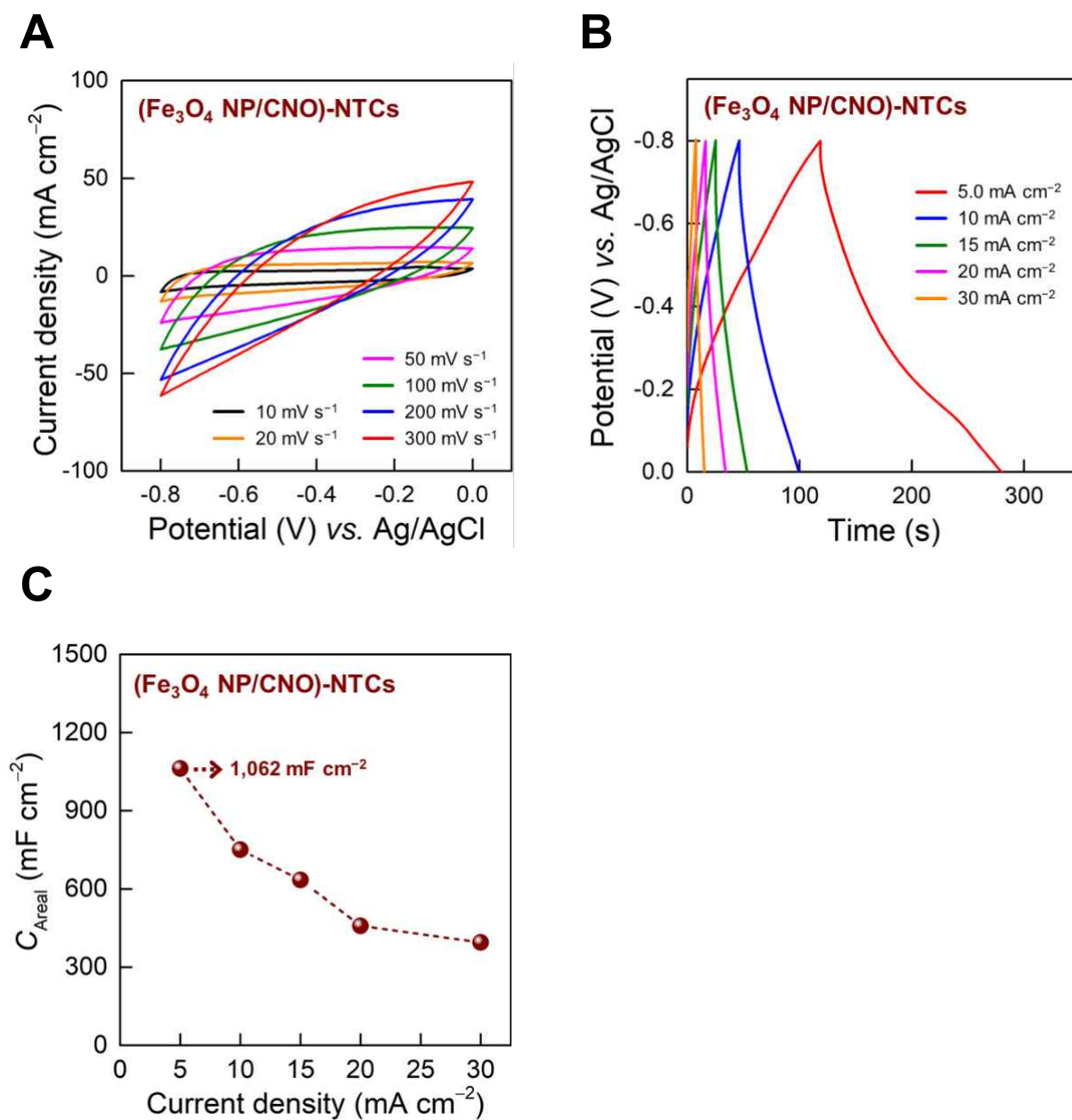


**Fig. S27.** (A) Areal capacitance ( $C_{\text{Areal}}$ ) values of ( $\text{MnO}_x$  NP/CNO)-NTCs as a function of the multi-stacking number at different current densities in the range of 1.0 to 6.0 A g<sup>-1</sup>. (B) Nyquist plots of ( $\text{MnO}_x$  NP/CNO)-NTCs as a function of the multi-stacking number.

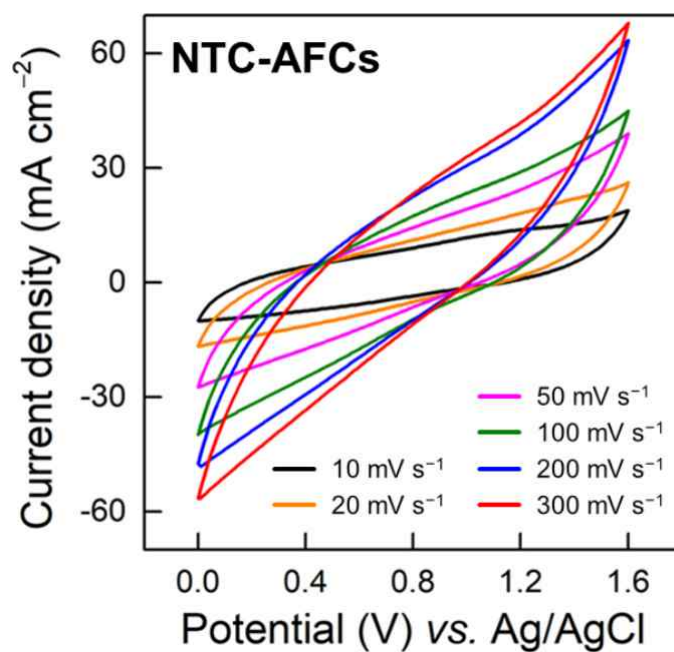
**A**



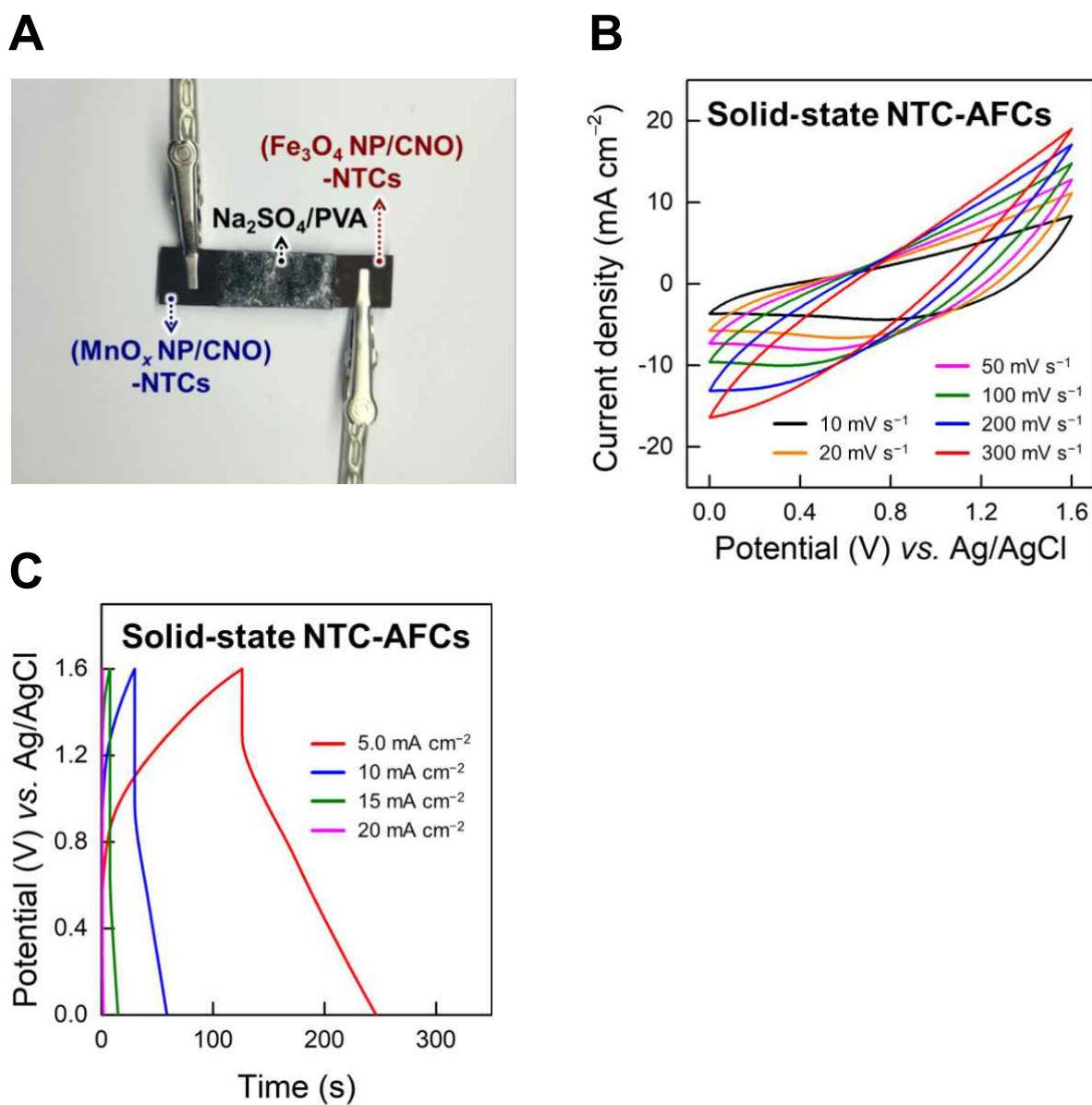
**Fig. S28.** (A) Planar and (B) cross-sectional FE-SEM and corresponding EDS mapping images of  $(\text{Fe}_3\text{O}_4 \text{ NP/CNO})\text{-NTCs}$ .



**Fig. S29.** (A) Scan rate-dependent CV curves, (B) current density-dependent GCD curves, and (C) areal capacitance ( $C_{\text{Areal}}$ ) values (at various current densities in the range of 5.0 to 30 mA cm<sup>-2</sup>) of (Fe<sub>3</sub>O<sub>4</sub> NP/CNO)-NTCs.



**Fig. S30.** CV curves of NTC-AFCs at various scan rates in the range of 10 to 300 mV s<sup>-1</sup>.



**Fig. S31.** (A) Digital image of solid-state NTC-AFC. (B) Scan rate-dependent CV and (C) current density-dependent GCD curves of solid-state NTC-AFCs.

**Table S1.** Comparison of areal capacitance values between our work and other studies using active MnO<sub>x</sub> and 3D porous current collectors.

| Electrode materials                   | Methods                              | Substrates       | Electrolytes                        | Potential window  | Areal capacitance (mF cm <sup>-2</sup> )   | Reference       |
|---------------------------------------|--------------------------------------|------------------|-------------------------------------|-------------------|--|-----------------|
| <b>MnO<sub>x</sub> NP/<br/>CNO</b>    | <b>LbL assembly</b>                  | <b>NTC</b>       | <b>Na<sub>2</sub>SO<sub>4</sub></b> | <b>0 to 0.8 V</b> | <b>1-stack<br/>1,725 (@1 A g<sup>-1</sup>)<br/>2-stack<br/>3,244 (@1 A g<sup>-1</sup>)</b> | <b>Our Work</b> |
| MnO <sub>2</sub> /PPy                 | Electrodeposition/<br>Polymerization | Carbon cloth     | Na <sub>2</sub> SO <sub>4</sub>     | 0 to 1.0 V        | 1,240 (@0.3 A g <sup>-1</sup> )  | S7              |
| MnO <sub>2</sub> -TEA <sup>a)</sup>   | Slurry casting                       | Carbon cloth     | Na <sub>2</sub> SO <sub>4</sub>     | 0 to 1.0 V        | 418 (@1 A g <sup>-1</sup> )  | S8              |
| MnO/CNF                               | Electrospinning/<br>Carbonization    | Carbon nanofiber | Na <sub>2</sub> SO <sub>4</sub>     | -0.4 to 0.8 V     | 533 (@0.3 A g <sup>-1</sup> )  | S9              |
| H-MnO <sub>2</sub> -TEA               | Slurry casting                       | Ni foam          | Na <sub>2</sub> SO <sub>4</sub>     | 0 to 1.0 V        | 475 (@0.5 A g <sup>-1</sup> )  | S10             |
| MnO <sub>2</sub>                      | Electrodeposition                    | Paper            | Na <sub>2</sub> SO <sub>4</sub>     | 0 to 0.8 V        | 636 (@0.3 A g <sup>-1</sup> )  | S11             |
| MnO <sub>2</sub>                      | Electrodeposition                    | Ni mesh          | Na <sub>2</sub> SO <sub>4</sub>     | 0 to 0.8 V        | 1,150 (@0.05 A g <sup>-1</sup> )   | S12             |
| MnO <sub>2</sub> /graphene            | Slurry casting                       | Carbon cloth     | Na <sub>2</sub> SO <sub>4</sub>     | 0 to 0.8 V        | 1,490 (@0.5 A g <sup>-1</sup> )  | S13             |
| Mn <sub>3</sub> O <sub>4</sub> /rGO   | Slurry casting                       | Carbon cloth     | Na <sub>2</sub> SO <sub>4</sub>     | -0.1 to 1.2 V     | 432 (@0.7 A g <sup>-1</sup> )  | S14             |
| α-MnO <sub>2</sub> /AEG <sup>b)</sup> | Slurry casting                       | Ni foam          | Na <sub>2</sub> SO <sub>4</sub>     | 0 to 1.0 V        | 408 (@1 A g <sup>-1</sup> )  | S15             |

<sup>a)</sup>TEA: triethanolamine; <sup>b)</sup>AEG: activated expanded graphite.

**Table S2.** Comparison of areal energy/power densities between our work and other studies using active MnO<sub>x</sub> and 3D porous current collectors.

| <b>Positive materials (substrates)</b>                        | <b>Negative materials (substrates)</b>          | <b>Methods</b>      | <b>Potential window</b> | <b>Areal energy density (<math>\mu\text{Wh cm}^{-2}</math>)</b> | <b>Areal power density (<math>\text{mWh cm}^{-2}</math>)</b> | <b>Reference</b> |
|---|---|---------------------|-------------------------|---|--|------------------|
| <b>MnO<sub>x</sub> NP/CNO (NTC)</b>                           | <b>Fe<sub>3</sub>O<sub>4</sub> NP/CNO (NTC)</b> | <b>LbL assembly</b> | <b>0 to 1.6 V</b>       | <b>188</b>  | <b>30.1</b>  | <b>Our work</b>  |
| MnO <sub>2</sub> -TEA <sup>a)</sup><br>(Carbon cloth)         | MoO <sub>3-x</sub><br>(Carbon cloth)            | Slurry casting      | 0 to 1.8 V              | 115   | 0.90   | S8               |
| H-MnO <sub>2</sub> -TEA<br>(Ni foam)                          | AC <sup>b)</sup><br>(Ni foam)                   | Slurry casting      | 0 to 2.0 V              | 51.6  | 30.0   | S10              |
| MnO <sub>2</sub> -AC<br>(Ni foam)                             | MnO <sub>2</sub> -AC<br>(Ni foam)               | Slurry casting      | 0 to 1.8 V              | 43.2  | 2.20   | S16              |
| MnO/Mn <sub>3</sub> O <sub>4</sub><br>(Carbon cloth)          | AC<br>(Carbon cloth)                            | Slurry casting      | 0 to 2.0 V              | 40.6  | 1.00   | S17              |
| Mn <sub>2</sub> O <sub>3</sub> /MnO <sub>2</sub><br>(Ni foam) | AC<br>(Ni foam)                                 | Slurry casting      | 0 to 1.8 V              | 54.0  | 0.20   | S18              |
| Mn <sub>3</sub> O <sub>4</sub> /C/rGO<br>(Ni foam)            | CNT/rGO<br>(Ni foam)                            | Slurry casting      | 0 to 1.8 V              | 42.4  | 0.70   | S19              |
| Mn <sub>3</sub> O <sub>4</sub> /rGO<br>(Carbon cloth)         | VO <sub>2</sub> /rGO<br>(Carbon cloth)          | Slurry casting      | 0 to 2.2 V              | 53.4  | 0.40   | S14              |
| MnO <sub>2</sub> /GQD <sup>c)</sup><br>(Ni foam)              | NG <sup>d)</sup><br>(Ni foam)                   | Hydrothermal        | 0 to 2.3 V              | 156   | 1.23   | S20              |

<sup>a)</sup>TEA: triethanolamine; <sup>b)</sup>AC: activated carbon; <sup>c)</sup>GQD: graphene quantum dot; <sup>d)</sup>NG: nitrogen-doped graphene.



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