Supporting Information

Chemical Vapor Deposition of Carbon Nanocoils Three-Dimensionally in Carbon Fiber Cloth for All-Carbon Supercapacitors

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Figure S1. Images of a bare CFC (6.5 x 6.5 cm²). (A) Photograph and (B) magnified SEM view. Images of a CFC with coating of Au NPs (6.5 x 6.5 cm²). (C) Photograph and (D) magnified SEM view.

Figure S2. Photograph of an as-grown CNC-based electrode (2.5 x 1.0 cm²).

Figure S3. XRD patterns of an as-grown CNC-based electrode (red) and a bare CFC (black).

Figure S4. Raman spectra of a CNC-based electrode (red) and a pristine CFC (black).

Figure S5. TGA curves of an as-grown CNC-based electrode (red) and a bare CFC (black). The CNC-based electrode weighed 0.019 g. The mass loading of the CNCs was estimated to be 3.0 x 10⁻³ g.

Figure S6. Schematic illustration showing the growth steps of CNCs on CFC using the literature process. CNCs grew only on the surface of the CFC substrate. They did not grow inside the CFC.

Figure S7. Cross-sectional SEM images of different magnifications of a sample with CNCs grown on two surfaces of the CFC substrate. (A) Growth of CNCs was not observed inside the CFC substrate. (B) Enlarged view from the squared area in (A), and (C) enlarged view from the squared area in (B) showing partial CNC growth.

Figure S8. Cross-sectional SEM images of the interior of a CFC substrate. (A) Growth of CNCs was not observed inside the CFC substrate. (B) Image shows CFs partially covered by CNCs, the result of the shadow effect.

Figure S9. (A) Cross-sectional SEM images of a CFC substrate covered by PVD K metal. (B) EDS of the red squared region in the inset in (A). O atoms are attributed to the oxidation of K. Pt atoms are from the sputtered layer for increasing conductivity.

Figure S10. SEM images of CFs from a CFC substrate after PVD of Au. A penumbra generated by the shadow effect is indicated. (B) EDS results from the red squared regions in (A) indicating different quantities of Au deposited. Pt atoms are from the sputtered layer for increasing conductivity.

Experimental Parameter Optimization.

Figure S11. Schematic drawing of the specially designed quartz boat for loading the CFC substrate in the CVD process.

Figure S12. Experimental CVD system. The red rectangle region is enlarged in Figure S11.

Table S1. Summary of CVD of CNCs at 723 K. Metallic K was evaporated at 423 K.

Figure S13. SEM images of samples 1 - 3 listed in Table S1. PVD of Au 5 nm. H₂(g) flow rates
are (A) 50, (B) 40, and (C) 35 sccm.

Figure S14. SEM images of samples 4 and 5 listed in Table S1. PVD of Au 25 nm. H₂(g) flow rates are (A) 40 and (B) 30 sccm.

Figure S15. SEM images of samples 6 – 9 listed in Table S1. PVD of Au 25 nm. H₂(g) flow rates are (A) 20, (B) 15, (C) 10, and (D) 5 sccm.

Figure S16. SEM images of samples 11 and 12 listed in Table S1. PVD of Au 50 nm. H₂(g) flow rates are (A) 10 and (B) 5 sccm.

Figure S17. (A) Cross-sectional SEM image of the interior of a CFC substrate after it was immersed in HAuCl₄(aq) and further reduced by H₂(g) at high temperature and (inset) the high magnification view from the white squared region. (B) EDS of the red squared region in the inset of (A). Pt atoms are from the sputtered layer for increasing conductivity.

Electrochemical Active Surface Area (EASA) Measurements.

Figure S18. CV studies of bare CFC (black), samples 7 (blue) and 8 (red) in a solution of K₃[Fe(CN)₆]₆(aq) (5.0 mM) and KNO₃(aq) (1.0 M). (A) CV loops at 100 mV/s. (B) Plots of Iₚ (voltammetry peak current) versus v¹/₂ (square root of sweep rate). Sample 8 was selected as the CNC-based electrode.

Electrochemical Measurements.

Electrochemical Impedance Spectroscopy (EIS) Results.

Figure S19. Nyquist plots (10⁻² – 10⁵ Hz) of three samples by using three-electrode system in H₂SO₄(aq) (1.0 M) and (inset) the high-frequency region.

Figure S20. Nyquist plot (10⁻² – 10⁵ Hz) of a liquid-state CFC electrode by using two-electrode system in H₂SO₄(aq) (1.0 M). The Rₛ and Rₑt values are estimated directly from the plot and listed in Table S2.

Figure S21. EIS studies (10⁻² – 10⁵ Hz) of the SCs by using two-electrode system. (A) Nyquist plots of a liquid-state CNC-based SC in H₂SO₄(aq) (1.0 M) (red) and an equivalent electrical circuit model in the inset (black). (B) Nyquist plots of a solid-state CNC-based SC in H₂SO₄/PVA gel and an equivalent electrical circuit model in the inset (black). Estimated Rₛ, Rₑt, Rₓ, CₓDL, and CₓL are listed in Table S2.

Table S2. Fitted values from Nyquist plots.

Figure S22. GCD curves of a CNC-based electrode (red) and a bare CFC electrode (black) in three-electrode system.

Figure S23. (A) Schematic illustration of the configuration of solid-state CNC-based SC. (B)
Photographs of a solid-state SC (red rectangle in (B)). (C) Bending test of the SC in (B).

**Table S3**  Summary of Performance of Solid-State All-Carbon SCs.

**Reference**
Figure S1. Images of a bare CFC (6.5 x 6.5 cm²). (A) Photograph and (B) magnified SEM view. Images of a CFC with coating of Au NPs (6.5 x 6.5 cm²). (C) Photograph and (D) magnified SEM view.
Figure S2. Photograph of an as-grown CNC-based electrode (2.5 x 1.0 cm$^2$).
Figure S3. XRD patterns of an as-grown CNC-based electrode (red) and a bare CFC (black).
Figure S4. Raman spectra of a CNC-based electrode (red) and a pristine CFC (black).
Figure S5. TGA curves of an as-grown CNC-based electrode (red) and a bare CFC (black). The CNC-based electrode weighed 0.019 g. The mass loading of the CNCs was estimated to be $3.0 \times 10^{-3}$ g.
Figure S6. Schematic illustration showing the growth steps of CNCs on CFC using the literature process. CNCs grew only on the surface of the CFC substrate. They did not grow inside the CFC.
Figure S7. Cross-sectional SEM images of different magnifications of a sample with CNCs grown on two surfaces of the CFC substrate. (A) Growth of CNCs was not observed inside the CFC substrate. (B) Enlarged view from the squared area in (A), and (C) enlarged view from the squared area in (B) showing partial CNC growth.
**Figure S8.** Cross-sectional SEM images of the interior of a CFC substrate. (A) Growth of CNCs was not observed inside the CFC substrate. (B) Image shows CFs partially covered by CNCs, the result of the shadow effect.
Figure S9. (A) Cross-sectional SEM images of a CFC substrate covered by PVD K metal. (B) EDS of the red squared region in the inset in (A). O atoms are attributed to the oxidation of K. Pt atoms are from the sputtered layer for increasing conductivity.
Figure S10. (A) High resolution SEM image of CFs from a CFC substrate after PVD of Au. A penumbra generated by the shadow effect is indicated. (B) EDS results from the red squared regions in (A) indicating different quantities of Au deposited. Pt atoms are from the sputtered layer for increasing conductivity.
Experimental Parameter Optimization.

To search for the best set of experimental conditions to grow CNCs on CFC substrates, the following experiments were carried out. A generalized procedure is presented below as an example. To a cleaned CFC (6.5 cm x 6.5 cm, CeTech), a layer of 5 nm Au was uniformly deposited on both sides by e-gun PVD (Figure S1). The as-processed CFC substrate was further cut into rectangles 2.5 x 1.0 cm² and loaded on a specially designed quartz device (Figure S11) to be placed in a hot-wall CVD reactor (Figure S12). After the reactor was purged by Ar(g) (100 sccm) for 15 min, the quartz device was pushed downstream to 20 cm away from the center of the furnace. Then, KH powder (0.25 g, Sigma-Aldrich) was loaded on another quartz tube and placed at the center of the furnace. The KH powder was thermally decomposed at 623 K under Ar(g) flow (20 sccm, 1 atm) for 1 h to from K(l). K(l) was evaporated at 2.0 x 10⁻³ torr, 443 K, for 30 min to deposit K(l) uniformly on the fibers of the CFC substrate at 373 K. After the K(l) was deposited, the quartz tube loader was removed under Ar(g) (100 sccm). Then, the substrate was placed at the center of the furnace and ramped under 1 atm of Ar(g) (20 sccm) to 723 K. C₂H₂(g) (11 sccm) and H₂(g) (50 sccm) were introduced to deposit carbon for 1 h. After the reaction was completed, the furnace was cooled down to room temperature under 1 atm of Ar(g) (20 sccm). The substrate turned to brown and was washed by ethanol and DI water several times to remove potassium containing byproducts. After dried in an oven at 333 K, Sample 1 was obtained. Other samples (samples 2 – 12) prepared under different sets of conditions are summarized in Table S1. Their SEM results of the samples are displayed in Figure S13 - 16. The CNCs in samples 7 (Figure S15B) and 8 (Figure S15C) appear to be the densest and longest ones. Their electrochemical active surface areas (EASAs) were further examined (see below). Sample 8 with the higher EASA was selected for further device studies.
**Figure S11.** Schematic drawing of the specially designed quartz boat for loading the CFC substrate in the CVD process.
Figure S12. Experimental CVD system. The red rectangle region is enlarged in Figure S11.
Table S1. Summary of CVD of CNCs at 723 K. Metallic K was evaporated at 423 K.\textsuperscript{a}

| Sample | Au coating thickness (nm)\textsuperscript{b} | C\textsubscript{2}H\textsubscript{2} (sccm) | H\textsubscript{2} (sccm) | Product Morphology | CNC Density | CNC Length (μm) |
|--------|---------------------------------|----------------|----------------|------------------|-------------|-----------------|
| 1      | 5                               | 11             | 50             | Nanowire         | Low         | < 5             |
| 2      | 5                               | 11             | 40             | Nanowire + Nanocoil | Medium     | < 5             |
| 3      | 5                               | 11             | 35             | Nanowire + Nanocoil | Medium     | < 5             |
| 4      | 25                              | 11             | 40             | Nanowire         | High        | 5               |
| 5      | 25                              | 11             | 30             | Nanowire         | High        | 5               |
| 6      | 25                              | 11             | 20             | Nanowire + Nanocoil | High       | 10              |
| 7      | 25                              | 11             | 15             | Nanowire + Nanocoil | High       | 20              |
| 8      | 25                              | 11             | 10             | Nanocoil         | High        | > 50            |
| 9      | 25                              | 11             | 5              | Cluster          | Low         | < 5             |
| 10     | 25                              | 5.5            | 10             | -c               | -           | -               |
| 11     | 50                              | 11             | 10             | Nanowire         | Medium      | < 5             |
| 12     | 50                              | 11             | 5              | -c               | -           | -               |

\textsuperscript{a}: The CNCs only grew on the surface of the CFC substrates. Because there was no Au NP catalyst inside the CFC, CNCs did not grow within the CFC.

\textsuperscript{b}: The Au layer was transformed into Au NPs during the CVD process.

\textsuperscript{c}: Growth of nanostructures was not observed.
Figure S13. SEM images of samples 1 - 3 listed in Table S1. PVD of Au 5 nm. H$_2(g)$ flow rates are (A) 50, (B) 40, and (C) 35 sccm.
**Figure S14.** SEM images of samples 4 and 5 listed in Table S1. PVD of Au 25 nm. H$_2$(g) flow rates are (A) 40 and (B) 30 sccm.
Figure S15. SEM images of samples 6 – 9 listed in Table S1. PVD of Au 25 nm. H₂(g) flow rates are (A) 20, (B) 15, (C) 10, and (D) 5 sccm.
Figure S16. SEM images of samples 11 and 12 listed in Table S1. PVD of Au 50 nm. H$_2$(g) flow rates are (A) 10 and (B) 5 sccm.
**Figure S17.** (A) Cross-sectional SEM image of the interior of a CFC substrate after it was immersed in HAuCl$_4$(aq) and further reduced by H$_2$(g) at high temperature and (inset) the high magnification view from the white squared region. (B) EDS of the red squared region in the inset of (A). Pt atoms are from the sputtered layer for increasing conductivity.
Electrochemical Active Surface Area (EASA) Measurements.

By using the three-electrode system, the CV loops of the CFC substrate, samples 7 and 8 are measured (Figure S18). The EASAs ($A$) are determined from the Randles-Sevcik equation:¹

$$I_p = 2.69 \times 10^5 \times n^{3/2} \times A \times D_0^{1/2} \times C_0 \times \nu^{1/2}$$

Where $I_p$ (A) is voltammetry peak current, $n$ is the number of electrons transferred in the rate determining step, $D_0$ (cm$^2$ s$^{-1}$) is diffusion coefficient, $C_0$ (M) is the concentration of active species in solution and $\nu$ (mV s$^{-1}$) is applied scan rate. The measurement was applied using electrolyte consisted of $K_3[Fe(CN)_6]_{(aq)}$ (5.0 mM, J. T. Baker, 99.0%) and $KNO_3_{(aq)}$ (1.0 M, Fluka 99.9%). Where $n = 1$, $D_0 = 7.5 \times 10^{-6}$ cm$^2$ s$^{-1}$ in $K_3[Fe(CN)_6]_{(aq)}$. $A$ values of the CFC substrate, samples 7 and 8 are 5.84 cm$^2$, 12.1 cm$^2$ and 16.5 cm$^2$, respectively. Sample 8 with the highest EASA was selected as the CNC-based electrode for further supercapacitor device studies.
Figure S18. CV studies of bare CFC (black), samples 7 (blue) and 8 (red) in a solution of K$_3$[Fe(CN)$_6$]$_{(aq)}$ (5.0 mM) and KNO$_3$(aq) (1.0 M). (A) CV loops at 100 mV/s. (B) Plots of $I_p$ (voltammetry peak current) versus $\nu^{1/2}$ (square root of sweep rate). Sample 8 was selected as the CNC-based electrode.
**Electrochemical Measurements.**

By utilizing the two-electrode system, the specific capacitances of supercapacitors were determined from CV tests using the following formula:²

\[
C_{sp} = \frac{\int_{V_i}^{V_f} I \times V \, dV}{m \nu (V_f - V_i)}
\]

Where \( C_{sp} \) (F/g) is the specific capacitance, \( I \) (A) is the instant current of the CV loop, \( m \) (g) is the total mass of the loaded active materials on both electrodes, \( \nu \) (V/s) is the potential scan rate, and \( V_i \) and \( V_f \) are the switching potentials in the CV loop.

Specific capacitance of the supercapacitor can be calculated from the GCD curve referring to the following equation also:²

\[
C_{sp} = \frac{I \times \Delta t}{m \times \Delta V}
\]

Where \( C_{sp} \) (F/g) is the specific capacitance, \( I \) (A) is the constant discharge current, \( \Delta t \) (s) is the discharging time, \( m \) (g) is the sum of the mass of the loaded active materials on both electrodes, and \( \Delta V \) is the discharge potential window.

The specific energy density of the supercapacitor is calculated from the following relationship:²

\[
E_{sp} = \frac{C_{sp} (\Delta V)^2}{2 \times 3.6}
\]

And the specific power density of the supercapacitor is calculated according to the equation:²

\[
P_{sp} = \frac{E_{sp}}{t}
\]

Where \( E_{sp} \) (Wh/kg) is the specific energy density, \( P_{sp} \) (W/kg) is the specific power density, \( \Delta V \) is the potential window and \( t \) (h) is the discharge time.
Electrochemical Impedance Spectroscopy (EIS) Results.

From the Nyquist plots in Figure S19, EIS data (10^{-2} - 10^5 Hz utilizing the three-electrode system) of CFC, CNC-based, and surface-only CNC-based electrodes are shown. For the last one, CNCs were grown only on the surface of the CFC (see Figure S7). As observed in Figure S19, the pristine CFC electrode shows the highest resistance among three. With CNCs grown on the surface of the substrate, the resistance drops dramatically to tens of Ω. The resistance minimizes to 3.7 Ω for the CNC-based electrode. This huge improvement is attributed to the growth of crisscrossing CNC networks inside the CFC.
Figure S19. Nyquist plots ($10^{-2} – 10^5$ Hz) of three samples by using three-electrode system in H$_2$SO$_4$ (aq) (1.0 M) and (inset) the high-frequency region.
The Nyquist plot of the bare liquid-state CFC is shown in Figure S20. Because an adequate equivalent electrical circuit was yet to be found to fit the profile of the CFC SC, another way is employed to estimate $R_s$ (serial resistance) and $R_{ct}$ (charge transfer resistance). $R_s$ is usually described as the sum of the resistance of the electrolyte and the internal resistance of the electrode. Its value is determined from the intersection of the manifested semicircle with $Z'$ axis. $R_{ct}$ is related to the diameter of the semicircle at the high frequency region.$^{3,4}$ As found in Figure S20, the CFC shows large resistance values of $R_s$ ($1.2 \times 10^2 \ \Omega$) and $R_{ct}$ ($7.5 \times 10^2 \ \Omega$).
Figure S20. Nyquist plot ($10^{-2} – 10^5$ Hz) of a liquid-state CFC electrode by using two-electrode system in H$_2$SO$_4$(aq) (1.0 M). The $R_s$ and $R_{ct}$ values are estimated directly from the plot and listed in Table S2.
On the other hand, the experimental profiles of the liquid-state and the solid-state CNC-based SCs (Figure S21A and S21B) are fitted by using the Randle’s equivalent electrical circuit diagram (inset of Figure S21A and S21B) with a $R_s$, a $R_{ct}$, a double-layer capacitance ($C_{DL}$) at the interface between the electrode and the electrolyte, a pseudocapacitive component ($C_L$) from some oxygen-contenting functional groups on the surface groups, and a leakage resistance ($R_L$). All the data are summarized in Table S2.

Figure S21. EIS studies ($10^{-2} – 10^5$ Hz) of the SCs by using two-electrode system. (A) Nyquist plots of a liquid-state CNC-based SC in $\text{H}_2\text{SO}_4$ (aq) (1.0 M) (red) and an equivalent electrical circuit model in the inset (black). (B) Nyquist plots of a solid-state CNC-based SC in $\text{H}_2\text{SO}_4$/PVA gel and an equivalent electrical circuit model in the inset (black). Estimated $R_s$, $R_{ct}$, $R_L$, $C_{DL}$, and $C_L$ are listed in Table S2.
**Table S2.** Fitted values from Nyquist plots.

| Sample                   | $R_s$ (Ω) | $R_{cl}$ (Ω) | $R_L$ (Ω) | $C_{DL}$ (F) | $C_L$ (F) |
|--------------------------|-----------|--------------|-----------|--------------|-----------|
| CFC (liquid)$^a$         | $1.2 \times 10^2$ | $7.5 \times 10^2$ | -         | -            | -         |
| CNC-based SC (liquid)    | 6.5       | 4.9          | 526.0     | $1.3 \times 10^{-1}$ | $3.3 \times 10^{-4}$ |
| CNC-based SC (solid)     | 10.3      | 41.5         | 6236.0    | $1.5 \times 10^{-1}$ | $1.5 \times 10^{-4}$ |

$^a$: The listed resistance values are interpreted directly from the data shown in Figure S18.
Figure S22. GCD curves of a CNC-based electrode (red) and a bare CFC electrode (black) in three-electrode system.
Figure S23.  (A) Schematic illustration of the configuration of solid-state CNC-based SC. (B) Photographs of a solid-state SC (red rectangle in (B)). (C) Bending test of the SC in (B).
Table S3 Summary of Performance of Solid-State All-Carbon SCs.

| Materials                              | Electrolyte       | Potential window (V) | Capacitance (F/g) | Energy density (Wh/kg) | Power density (W/kg) | Reference |
|----------------------------------------|-------------------|----------------------|-------------------|------------------------|----------------------|-----------|
| N, B doped 3D graphene                 | PVA-H$_2$SO$_4$   | 1                    | 62                | 8.7                    | -                    | 5         |
| 3D graphene foam                       | PVA/KOH           | 1                    | 82.1              | 11.4                   | 255                  | 6         |
| 3D graphene hydrogel film              | PVA-H$_2$SO$_4$   | 1                    | 186               | 0.61                   | 0.67                 | 7         |
| Porous graphene on carbon fibers       | PVA-H$_2$SO$_4$   | 1                    | 11.8              | 1.64                   | 670                  | 8         |
| Au NPs-embedded graphene hydrogel      | PVA-H$_2$SO$_4$   | 1                    | 135               | 18.5                   | -                    | 3         |
| CNT sheet                              | PVA/H$_3$PO$_4$   | 1                    | 59                | 1.88                   | 755.9                | 9         |
| Pristine CNCs                          | 3M KOH$_{(aq)}$   | 0.9                  | 40                | -                      | -                    | 10        |
| CNC-based SC                           | PVA-H$_2$SO$_4$   | 1                    | 163               | 15.3                   | 510                  | This work |
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