Supporting Information

General, Metal-free Synthesis of Carbon Nanofiber Assemblies from Plant Oils
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## Supporting Information

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Material-S1. Synthesis of carbon nanostructures

Vegetable oil (briefly oil) is from supermarket nearby the Max Planck Institute of Colloids and Interfaces. P₂O₅ anhydrous is from Sigma-Aldrich (99%). In typical, 10 mL of oil was put into a graphite bottle. Then, 10.0 g of P₂O₅ powder was added into the vegetable oil. The mixture was stirred by a glass rod for 10 min at room temperature to allow a thorough mixing. The color of the mixture changes slightly from light yellow to light brown. After that, the graphite bottle with cap on it was put into an autoclave, which was transferred into a convection oven at 180 °C. The reaction time last for 12 h. In this step, the mixture would turn into dark brown soft material, which served as intermediate for carbon nanofibers. The dark brown intermediate was heated in a tube furnace in N₂ atmosphere to 600 °C with isothermal time of 1 h. Finally, the dark brown intermediate changed to black carbon material. The carbon material was rinsed with deionized water to remove the impurity. For the synthesis of the carbon materials in Figure S9, S10 and S11, the whole procedures and formula are identical to the ones illustrated above.

NOTE:
Graphite bottle as a reaction vessel might introduce graphitic impurity into the final product. Therefore, it is recommended to pretreat the graphite bottle before the oil-P₂O₅ reaction. For instance, carbonization of glucose in the graphite bottle would introduce amorphous crosslinked carbonaceous materials, firmly sticking on the inner wall of graphite bottle, which could prevent the falling out of impurity from graphite body.

Another option. Glassy carbon bottle could be used to replace the graphite bottle since glassy carbon is of crosslinking feature, too, and no carbon impurity would come from it. The main problem is that glassy carbon bottle is terribly expensive.

Commonly, quartz bottle or corundum bottle is the popular choice for carbonization. However, in our experiment, these options are not suitable because P₂O₅ can potentially react with them. We use corundum bottle as an example to illustrate this problem and the details can be found in Figure S17.
Material-S2. Materials characterizations

Scanning electron microscopy (Hitachi S4800 FEG SEM) was used to examine the morphology of the samples with an accelerated voltage of 5 kV. The samples were coated by Au layer (5 mA, 60 s). Transmission Electron Microscopes (TEM, JEOL 2010F USA) was further applied to investigate the morphology and the element distribution of the samples with accelerated voltage of 200 kV. The sample was dispersed by ultrasonication before TEM preparation. Fourier transform infrared spectroscopy (Nicolet IS10) was conducted with the range of 800-3200 cm\(^{-1}\) with 64 times of scanning and the resolution is 4 cm\(^{-1}\). Raman spectroscopy (LABRAM-HR 800 spectrometer) was used to study the graphitization. The acquisition time is 5 s (accumulated times: 5) with laser wavelength of 512 nm. X-ray photoelectron spectroscopy (ESCALAB 250Xi spectrometer) was taken to evaluate the composition of materials. The dual anode (Mg/Al) X-ray source is of 400 W power with a chamber pressure at $\sim$10\(^{-10}\) Torr. Surface charging effects was compensated by referencing all binding energies to the C1s neutral carbon peak at 284.8 eV. X-ray diffractometer (XRD, SIMENS D500 Bruker) was carried out to investigate the crystallinity of the carbon material by operating at 40 kV and 40 mA using Cu K\(\alpha\) radiation ($\lambda = 0.15406$ nm) in the range of 10-80° (2\(\theta\)) with a step size of 1 °/min. The physisorption system (Micromeritics ASAP 2460) was adopted to measure the specific surface area and porosity of the carbon materials. The sample was firstly vacuum dried at 200 °C for 12 h. Then, the N\(_2\) and CO\(_2\) adsorption & desorption isotherm was acquired at 77 K and 273 K, respectively. Elemental analysis (Elementar Vario MICRO_cube) was applied to quantitatively measure the content of C, H, and O in the carbon material. Zetasizer Nano-ZS instrument (Malvern Instruments Co., England) was used to measure the zeta potential of the carbon material. Thermo Gravimetric Analysis (TGA, NETZSCH STA 449F3) was done to
investigate the thermal stability of the carbon nanofibers by using air as the atmosphere, and the ramp is 10 °C/min. Atomic force microscope (Bruker Dimension Icon system) was conducted to measure the thickness. Nuclear magnetic resonance (^1H-NMR) spectra were recorded by using Bruker 400 MHz spectrometer. Gas chromatography–mass spectrometry (450-GC & 320-MS, Bruker) was used to measure the chemicals from the side products in the synthesis of the intermediate-180C.
Material-S3. Electrochemical performance and electro-adsorption evaluation

The electrochemical behavior was evaluated by a three-electrode system with 1 M NaCl solution as electrolyte, where carbon paper coated with active material serving as working electrode, Ag/AgCl as reference electrode, and platinum sheet electrode (2 cm²) as counter electrode. Cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) were performed on an electrochemical workstation (CHI 760e) and electrochemical impedance spectroscopy (EIS) was tested by Autolab M204 electrochemical workstation. The voltage window for CV and GCD was -0.4-0.6 V. The test frequency for EIS was 100KHz to 0.01Hz at 5mv amplitude. The specific capacitance (Cs, F g⁻¹) of electrodes were calculated from the GCD curves according to the following equation:

\[ Cs = \frac{I \times \Delta t}{m \times \Delta U} \]  

(1)

where Cs (F g⁻¹) is corresponds to the specific capacitance of the electrodes calculated from GCD curves, I (A), \(\Delta t\) (s), m (g), \(\Delta U\) (V) stand for discharging current, discharge time, mass of electrodes and discharge voltage difference, respectively.

The capacitive deionization performance of the electrodes was evaluated in batch mode electrosorption experiments. The electrodes of CDI were prepared by mixing the sample, Polyvinylidene fluoride and conductive carbon black in the weight ratio of 8:1:1 to form a mixed slurry. The slurry was uniformly coated onto titanium plates (collector electrodes) by drying at 120 °C for 12h. During the CDI test, the standard table of the relationship between conductivity (mS cm⁻¹) and solution concentration (mg L⁻¹) was established. The salt adsorption capacity (SAC) and average salt adsorption rate (SAR) of the electrodes were calculated by the following formula:

\[ SAC = \frac{(C_0 - C)V}{m} \]  

(2)
ASAR = SAC/t \quad (3)

where SAC (mg g\(^{-1}\)) and ASAR (mg g\(^{-1}\) min\(^{-1}\)) are electrosorption capacity and average salt adsorption rate, respectively, \(C_0\), \(C\), \(V\), \(m\) and \(t\) are the initial NaCl solution concentrations, final NaCl solution concentrations, the total volume of NaCl solution, and the total mass of the active material brush on titanium plate, total electrosorption time, respectively.
Figure S1. Characterization of the side-product in the formation process of intermediate-180C

The side product condensed from vapor phase. Figure S1 shows the GC-MS characterization of the side product. As seen in Figure S1, the side products are mostly alkane and alkenes, with some cyclization products due to the high temperature.
The oily organic substance contains abundant C-H groups that can be detected by IR technique in the range of 3100-2800 cm⁻¹ (Figure 3a). From the FTIR spectrum above, however, we could not find out the stretching vibration of C-H groups. This suggests that the organic substance transforms into carbonaceous materials in the carbonization process under elimination of hydrocarbon species.
Figure S3. SEM images of CNb-oil1.5

Figure S3 shows the SEM images of CNb-oil1.5. As seen, the major morphology of the nanobelt-based assembly changes to spindles when the relative dosage of $\text{P}_2\text{O}_5$ was increased to 15.0 g.
Figure S4 shows the SEM images of CNb-oil0.5. As seen, the morphology of the assemblies changes obviously as compared with the CNb-oil1 and CNb-oil1.5. Typically, the assemblies exhibited not only the spindles-like morphology but also the wall-like morphology. The typical wall-like
assemblies were marked by the yellow circles. Actually, they are uniformly mixed with the nanobelts-based spindles.
Based on the AFM, we can confirm that nanofibers are of collapsed nanotubes and/or partially hollow structures.
Based on the TEM images, the carbon nanofibers assemblies exhibit similar morphology and elemental distribution to CNb-oil1.
Figure S7. FTIR spectra of the intermediates synthesized from the reaction between other chemical agents and P₂O₅

| Full name                  | Brief name |
|----------------------------|------------|
| diethyl hexanedioate       | DH         |
| 1,2-tetradecylene oxide    | TDO        |
| polyethylene glycol        | PEG        |

Figure S8 presents the FTIR spectra of the raw materials and the corresponding intermediates. These control experiments were designed to further confirm the possible mechanism illustrated in Figure 2 (main text).

The DA possesses similar structural feature to the vegetable oil that has long tail and ester group. The possible reaction between ester group and P₂O₅ was given in Figure 3 (main text).

EPx possesses long tail and epoxy group. Different from ester group, the chemical reaction between epoxy and P₂O₅ would possibly bring about an intermediate with highly cross-linked structure.⁵¹
The epoxy group disappears and the -P-O-C- group emerges after the chemical reaction. The possible reaction pathway was illustrated in the following image.

PEG possesses short aliphatic chain and ether group. PEG is composed of repeated -O-CH₂-CH₂-O- unit. It would produce the cross-linked structure, too.
Figure S8. SEM characterizations of carbon nanobelts synthesized by using diethyl hexanedioate as carbon source

In this control experiment, diethyl hexanedioate was used to replace vegetable oil as carbon source. The synthetic process is completely identical to the ones shown in Material-S1. Figure S9 presents the SEM images of this product, which is similar to the ones shown in Figure 1 in main text. This possibly indicates the similar morphology evolution mechanism illustrated in Figure 1.
Figure S9. SEM characterization of carbon nanostructures synthesized using 1,2-tetradecylene oxide

In this control experiment, 1,2-tetradecylene oxide was used to replace vegetable oil as carbon source. Special Note: the reaction between 1,2-tetradecylene oxide and P₂O₅ is highly exothermic, and it is strongly recommended to carry out this experiment in inert atmosphere.

Figure S10 provides the SEM images of the final product. As seen, there is no 1d nanostructures as well as the corresponding assemblies in the final carbon materials. The major morphology is the 3d nanoparticles. This means the highly cross-linked structure from epoxy and P₂O₅ completely changes the morphology evolution process, although there is a long tail in 1,2-tetradecylene oxide for assembly.
Figure S10. Photo image and SEM characterization of carbon material synthesized using polyethylene glycol as carbon source

As seen in the left part of the above image in Figure S8, the final product is a macroscopic solid but not nanomaterials. Based on the SEM image on the right part in Figure S11, the morphology of the surface of the solid is irregular.
Figure S11. XPS spectra of CNb-oil0.5 and CNb-oil1.5

CNb-oil0.5

CNb-oil1.5
Based on the comparison of the XPS spectra of CNb-oil0.5/1/1.5, the relative content of P element increased but the relative content of C-P to C-O-P decreased, when the P$_2$O$_5$ dosage increased.
Figure S12. XRD patterns of the CNb-oily synthesized by using graphite bottle as reaction vessel

![XRD patterns](image)

Figure S13 presents the XRD patterns of the CNb-oil series. Noticeably, these materials were synthesized using the pretreated graphite bottle as vessel (Material-S1). The XRD pattern of the CNb-oil series synthesized using the corundum crucible as vessel was given in Figure S18 by taking CNb-oil1 as a typical example.

As shown above, the CNb-oil exhibited a classical characteristic of amorphous materials. The broad peak at ~26 ° is related to the (002) plane of graphite, which indicates the poor crystallinity of the graphite.
Figure S13. Raman spectra of the CNb-oily

Figure S14 presents the Raman spectra of CNb-oil series. The G peak is at 1596 cm$^{-1}$ while the D peak is at 1335 cm$^{-1}$. The $I_G/I_D$ ratio gradually decreased with the increased dosage of P$_2$O$_5$. 
Figure S14. Zeta potential of the CNb-oily

Figure S15 presents the zeta potential of CNb-oil series. It is interesting to see that the potential maintained below -30 mV when the pH is higher than 5.
Figure S15. Thermal stability of the carbon nanofibers (CNb-oil1) and single-walled carbon nanotubes

Based on the TGA profile above, it is clear that the CNb-oil1 possesses much better thermal stability than the SWCNTs.
Control experiments were conducted to confirm the superior performance of the CNb-oilI. In the main experiment, CNb-oilI was used to remove the Na\(^+\) while the activated carbon was adopted to remove the Cl\(^-\). As shown in Figure S17, when replacing the CNb-oilI with activated carbon to build the CDI system with both electrodes consisting of activated carbon, the adsorption capacity drops obviously to \(~20\) mg g\(^{-1}\). In turn, we also tried CNb-oilI-based electrode for Cl\(^-\) with activated carbon-based electrode for Na\(^+\). As given in Figure S17 (red line), the adsorption capacity further decreases to \(~16.8\) mg g\(^{-1}\). These two control experiments further proved the specific function of CNb-oilI for cation removal. This is possibly due to the negative charged surface of the CNb-oilI, which is caused by the -P-O-C- functionalization in the carbon structure.
Figure S17. XRD pattern of CNb-oil/1 synthesized by using corundum crucible as reaction vessel

Figure S18 shows the XRD patterns of CNb-oil/1. The CNb-oil/1 was synthesized by using corundum crucible as vessel. As seen, the broad peak of the CNb-oil/1 is identical to that synthesized using graphite bottle as reaction vessel. However, there are several typical sharp peaks in the pattern. Based on the PDF indexing, it could be found that there are Al(PO₃)₃ crystals in the carbon product. This is due to the reaction between P₂O₅ and corundum (Al₂O₃).
Table S1. Yield, elemental composition, and texture properties of carbon nanobelts (CNb-oily)

| CNb-oily | Yield (%)\(^a\) | C (%)  | H (%)  | O (%)  | SSA (m\(^2\)g\(^{-1}\))\(^b\) | Pore volume (cm\(^3\)g\(^{-1}\))\(^b\) | Area in pore (<1 nm / m\(^2\)g\(^{-1}\))\(^c\) |
|----------|------------------|--------|--------|--------|-----------------------------|--------------------------------|----------------------------------|
| 0.5      | 7.96             | 72.7   | 2.2    | 12.8   | 171.8                       | 0.103                          | 45.4                             |
| 1.0      | 18.50            | 73.3   | 2.1    | 13.3   | 780.9                       | 0.688                          | 189.9                            |
| 1.5      | 32.99            | 71.1   | 2.2    | 15.5   | 459.5                       | 0.358                          | 102.6                            |

\(^a\) Yield was calculated based on equation below:

\[ Y = \frac{m_{CNb}}{M} \times 100\% \]

where \(m_{CNb}\) is the mass (g) of the carbon nanobelts, \(M\) is the mass (g) of vegetable oil.

\(^b\) The specific surface area (SSA) and pore volume was calculated based on N\(_2\) adsorption-desorption isotherm.

\(^c\) The specific surface area in micropores with size less than 1 nm was calculated based on CO\(_2\) adsorption-desorption isotherm.
Ref.

[S1] W. B. Woodstock (US) US2568784A, 1951.