Supplementary Information

Copper-assisted growth of high-purity carbon nanofiber networks with controllably tunable wettabilities

Xianglong Zhao,[a] Guowen Meng,* [b,c] Ping Wang,[d] Qijun Pan,[b] Bin Chen,[b] Haimin Zhang,[b] and Jong-Beom Baek* [e]

[a] School of Science, Shandong Jianzhu University, Jinan, 250101, P. R. China

[b] Key Laboratory of Materials Physics, and Anhui Key Laboratory of Nanomaterials and Nanotechnology, Institute of Solid State Physics, HFIPS, Chinese Academy of Sciences, Hefei 230031, P. R. China
Email: gwmeng@issp.ac.cn

[c] Department of Materials Science & Engineering, University of Science and Technology of China, Hefei 230026, P. R. China

[d] Key Laboratory of Energy Transforming Materials, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, P. R. China

[e] School of Energy and Chemical Engineering/Center for Dimension-Controllable Organic Frameworks, Ulsan National Institute of Science and Technology (UNIST), Ulsan 44919, Korea
Email: jbbaek@unist.ac.kr

Experimental Section

Growth of CNF networks on the outer surfaces of ceramic boats: Copper-nitrate-loaded aluminum (Al) foils were firstly placed in ceramic boats. The loading of the copper nitrates on the Al foils was achieved by dipping Al foils in 0.1 M aq. copper nitrate solution for a few seconds, followed by drying in air. Then, a chemical vapor deposition (CVD) process was conducted at 450 °C for 4-40 h with acetylene (80 sccm) as the carbon precursor and argon (10 sccm) as the carrying gas.

Growth of the CNF networks on the surfaces of other ceramic substrates: Copper-nitrate-loaded Al foils were firstly placed in ceramic boats. Then, various other

ceramic fragments (bowls, corundums, zirconias, bricks, and cement concretes) were placed over the ceramic boats. After that, a similar CVD process was carried out for 40-60 h.

Plasma modification: Plasma modification was conducted using a plasma cleaner (PDC-32G), with argon as the reactant gas.

Ammonia-annealing treatments: Ammonia-annealing treatments were conducted at 700-1000 °C for 5-15 min with 10 sccm of ammonia and 20 sccm of argon.

Characterization: The SEM was performed on a Hitachi SU8020, and the TEM and HRTEM were carried out on FEI Tecnai TF20. XRD patterns were recorded on a Philips X-Pert Pro X-ray diffractometer with Cu-Ka radiation. XPS spectra were recorded on a Thermo Fisher K-alpha XPS spectrometer. The water and diesel contact angles were measured using a contact angle meter (SL200B), and the compressive tests were performed using an Instron 5565A, which was equipped with two flat-surface compression stages.

Discussions

Recyclability tests of CNF networks for the absorption of various oils

Our CNF networks exhibit excellent recyclability for the absorption of various oils. For example, after combusting CNF networks to remove the absorbed ethanol, and then repeating the absorption/combustion cycles for 5 times, the CNF networks can still retained 89.6 % of their original absorption capacity for ethanol (Fig. S17a). In addition, our CNF networks also show good recyclability for the absorption of hexane.

As shown in Fig. S17b, their absorption capacity demonstrates no apparent deterioration even after 60 absorption/distillation cycles. Our CNF networks also have good recyclability for the absorption of octadecane. This can be observed in Fig. S17c, which shows that after squeezing out the absorbed octadecene in the CNF networks, and then repeating the absorption/squeezing cycles for 10 times, the absorption capacity of the CNF networks drops only by less than 10 %.

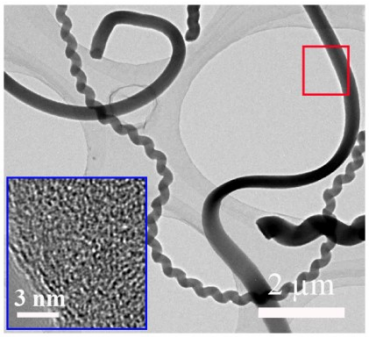

Fig. S1. TEM image of CNFs. Inset: HRTEM image of the CNF in the red rectangular area.

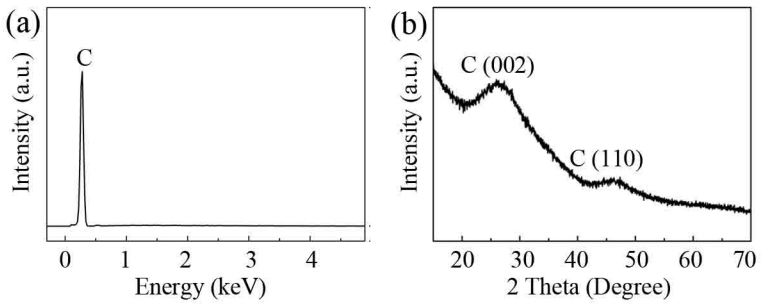

Fig. S2. EDS spectrum (a) and XRD pattern (b) of CNF networks grown on the outer surfaces of ceramic boats.

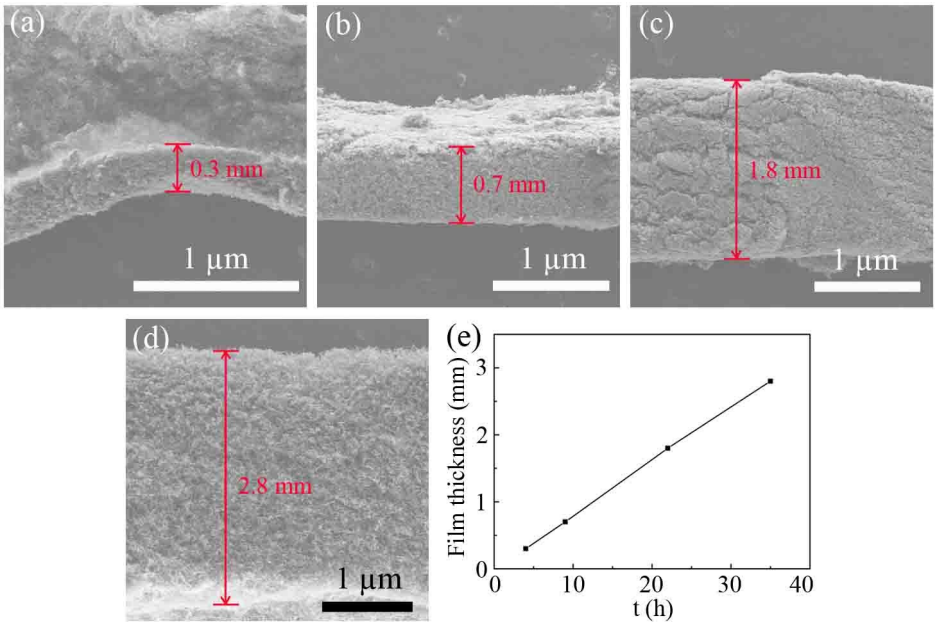

Fig. S3. (a)-(d) SEM images of CNF networks when the CVD process was conducted for 4, 9, 22, and 35 h, respectively. (e) Variation in the thickness of the CNF networks with CVD time (t).

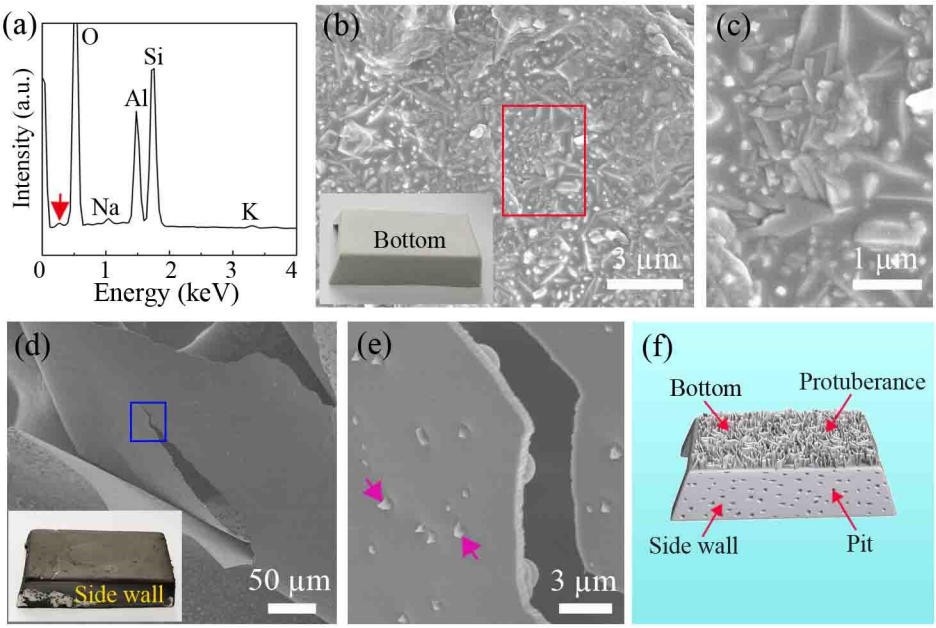

Fig. S4. (a) EDS spectrum of pristine ceramic boats. The red arrow indicates Ca element. (b) SEM image of the outer bottom surface of a pristine ceramic boat. The inset shows a photograph of the pristine ceramic boat. (c) High-magnification SEM

image of the red rectangular area in (b). (d) SEM image of carbon layers grown on the outer sidewall surfaces of a ceramic boat *via* CVD (acetylene: 6 sccm; argon: 60 sccm) at 650 °C for 2 h. The inset shows a photograph of the ceramic boat after CVD. (e) High-magnification SEM image of the blue rectangular area in (d). As carbon materials can be synthesized within the pores of substrates, hence they can replicate the morphologies of the substrate's pores.[1,2] Therefore, the protuberances (as indicated by purple arrows) on the carbon layers should be from the pits on the outer side walls of the ceramic boat. (f) Schematic of a pristine ceramic boat, showing that there are protuberances and pits on its outer surfaces.

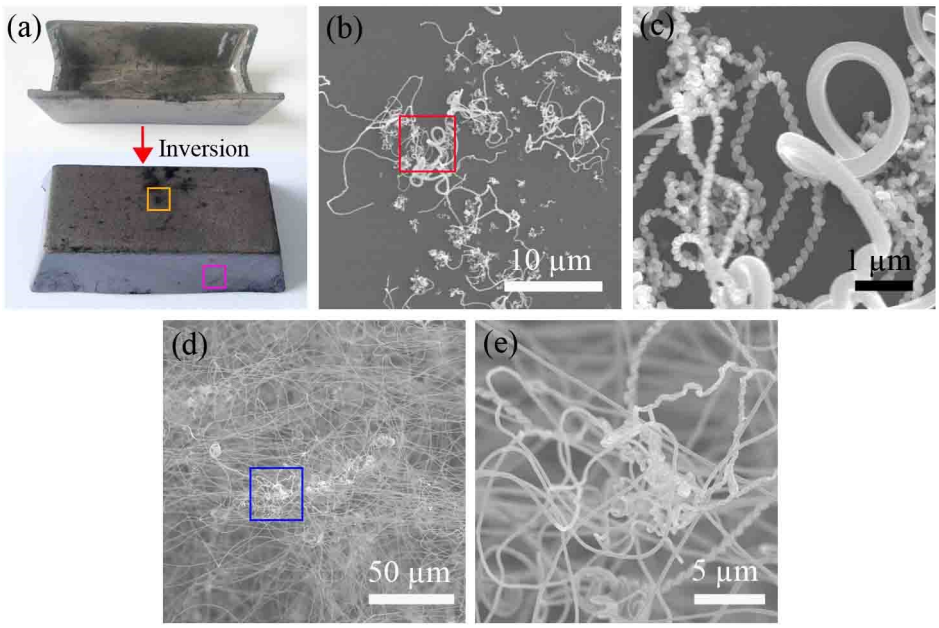

Fig. S5. (a) Photographs of a bare ceramic boat after the CVD process. (b) SEM image of the purple square area in (a). (c) High-magnification SEM image of the red square area in (b). (d) SEM image of the area inside the brown square in (a). (e) High-magnification SEM image of the area in the blue square in (d). From (b) to (e), we can see that a small quantity of CNF networks was grown on the outer surfaces of the bare ceramic boat.

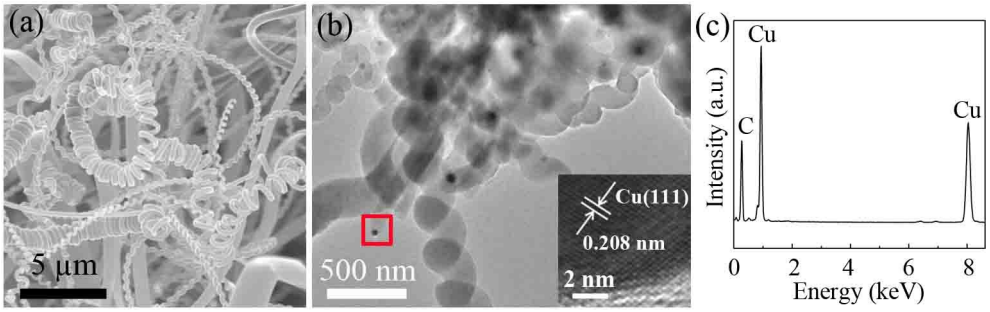

Fig. S6. (a)-(c) SEM image, TEM image and EDS spectrum of the Cu@CNF networks, respectively. Inset in (b) is a HRTEM image of the Cu@CNF in the area within the red square.

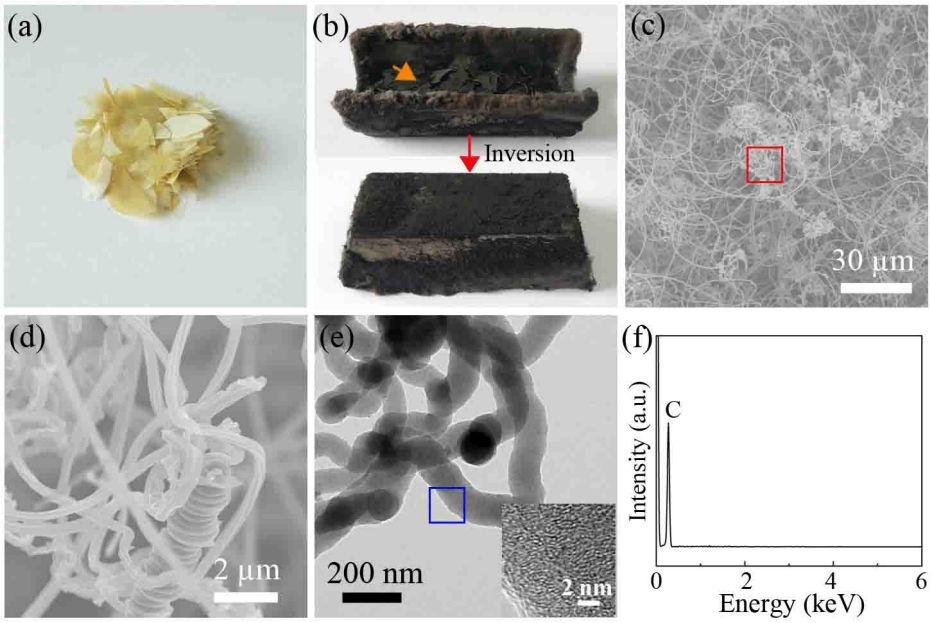

Fig. S7. (a) Photograph of stacked anodic aluminum oxides. (b) Photographs of CNF networks grown on the outer surfaces of a ceramic boat. Before the CVD process, some anodic aluminum oxides were placed in the ceramic boat. The brown arrow indicates that the original anodic aluminum oxides turned black after CVD due to the deposition of carbon within their pores.[2] (c)-(f) Characterization results of CNF networks grown on the outer surfaces of the ceramic boat in (b). (c) SEM image. (d) High-magnification SEM image of the area in the red square in (c). (e) TEM image.

The inset is an HRTEM image of the CNF in the blue square. (f) Corresponding EDS spectrum.

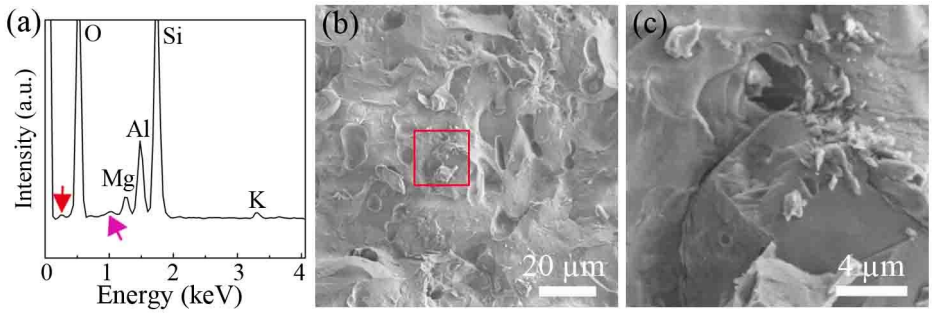

Fig. S8. (a) EDS spectrum of ceramic bowl fragments. The red and purple arrows indicate Ca and Na elements, respectively. (b) SEM image of the fracture surface of a ceramic bowl fragment. (c) High-magnification SEM image of the red square area in (b).

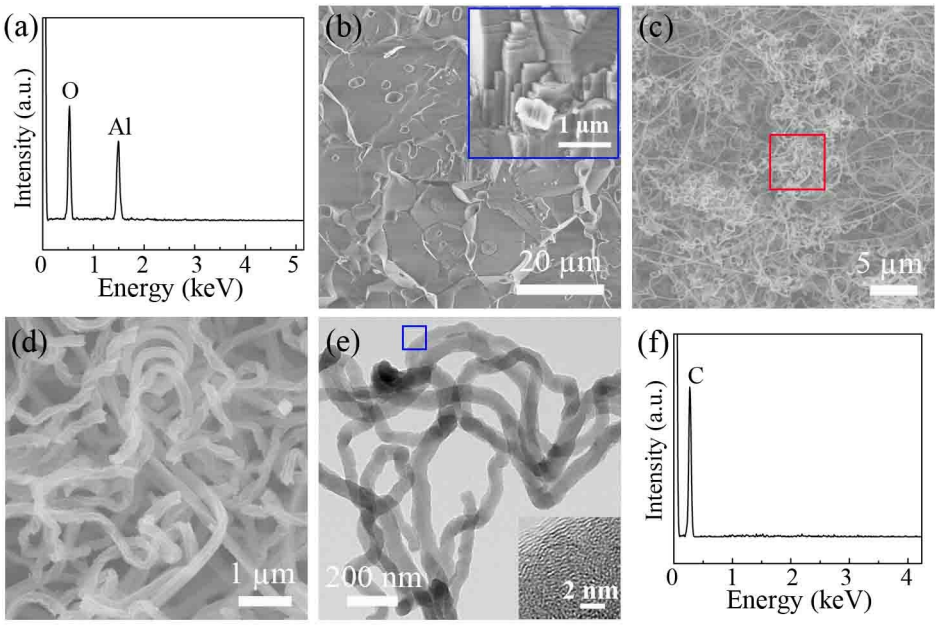

Fig. S9. (a) EDS spectrum of corundum fragments. (b) SEM and high-magnification SEM (Inset) images of the fracture surface of a corundum fragment. (c)-(f) Characterization results of CNF networks grown on the surfaces of corundum fragments. (c) SEM image. (d) High-magnification SEM image of the red square area

in (c). (e) TEM image. The inset is an HRTEM image of the CNF in the blue square. (f) Corresponding EDS spectrum.

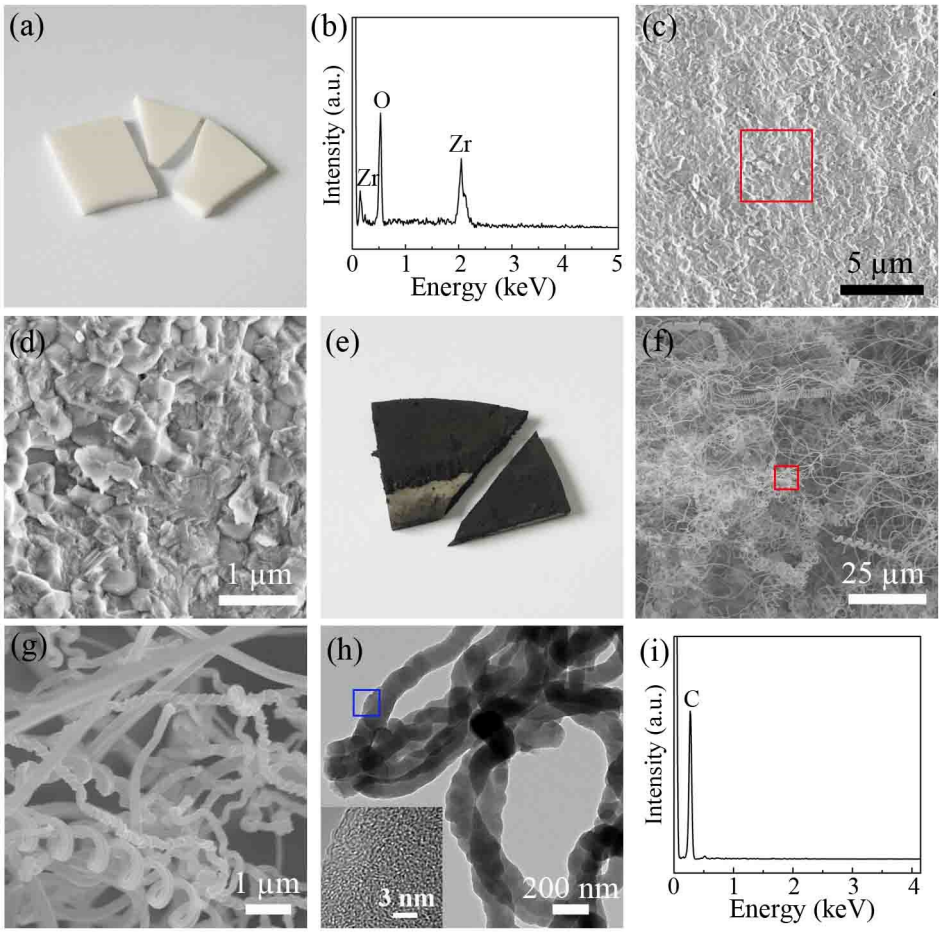

Fig. S10. (a) and (b) Photograph and EDS spectrum of zirconia fragments, respectively. (c) SEM image of the fracture surface of a zirconia fragment. (d) High-magnification SEM image of the red square area in (c). (e) Photograph of the CNF networks grown on the surfaces of the zirconia fragments. (f)-(i) Characterization results of the CNF networks grown on the surfaces of the zirconia fragments. (f) SEM image. (g) High-magnification SEM image of the red square area in (f). (h) TEM image. The inset is an HRTEM image of the CNF in the blue square. (i) Corresponding EDS spectrum.

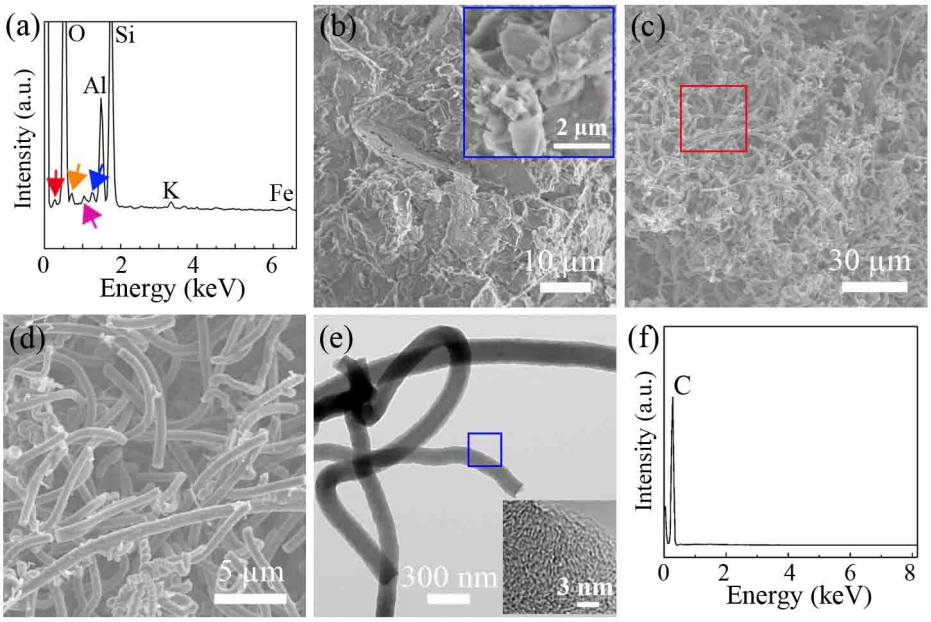

Fig. S11. (a) EDS spectrum of brick fragments. The red, brown, purple and blue arrows indicate Ca, Fe, Na and Mg elements, respectively. (b) SEM and high-magnification SEM (Inset) images of the fracture surface of a brick fragment. (c)-(f) Characterization results of the CNF networks grown on the surfaces of the brick fragments. (c) SEM image. (d) High-magnification SEM image of the red square area in (c). (e) TEM image. The inset is an HRTEM image of the CNF in the blue square. (f) Corresponding EDS spectrum.

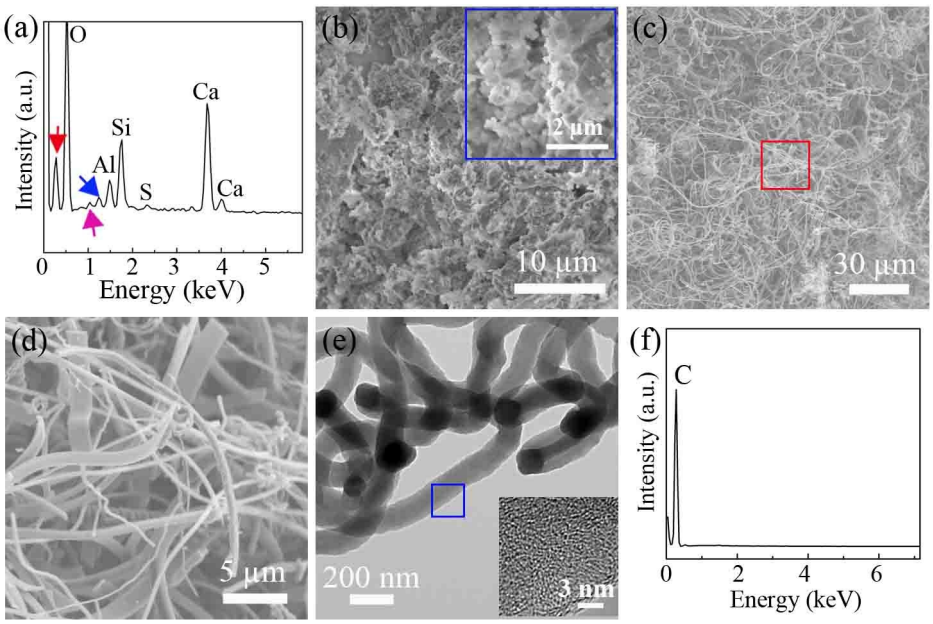

Fig. S12. (a) EDS spectrum of cement concrete fragments. The red, purple and blue arrows indicate Ca, Na and Mg elements, respectively. (b) SEM and high-magnification SEM (Inset) images of the fracture surface of a cement concrete fragment. (c)-(f) Characterization results of the CNF networks grown on the surfaces of the cement concrete fragments. (c) SEM image. (d) High-magnification SEM image of the red square area in (c). (e) TEM image. The inset is an HRTEM image of the CNF in the blue square. (f) Corresponding EDS spectrum.

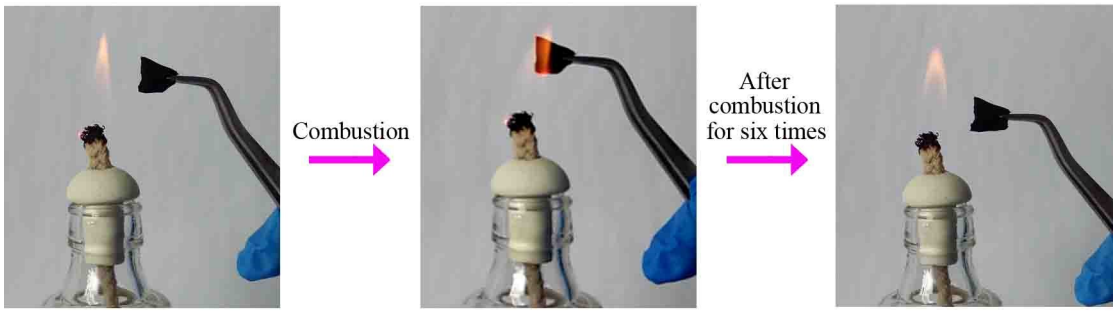

Fig. S13. Photographs of combustion of the CNF networks.

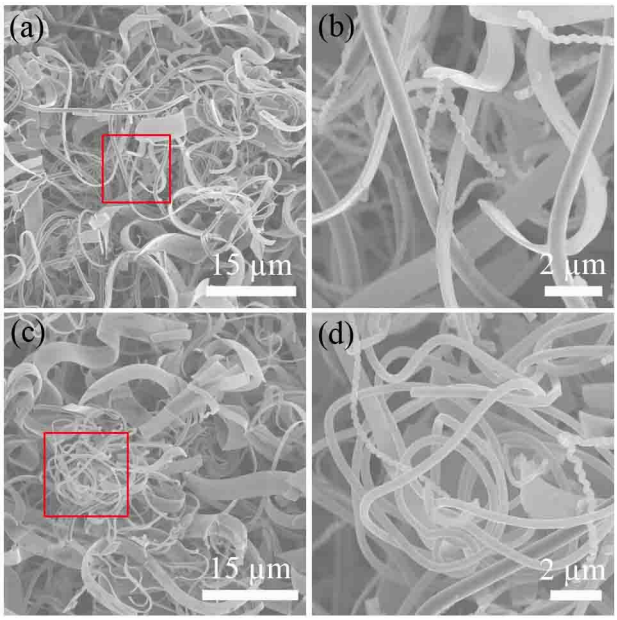

Fig. S14. (a) and (c) SEM images of CNF networks before and after compression (compressive strain is 80%), respectively. (b) and (d) High-magnification SEM images of the red square areas in (a) and (c), respectively.

Fig. S15. Diesel contact angle of 0° on the surface of the CNF networks.

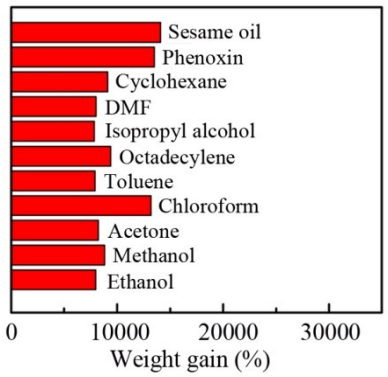

Fig. S16. Absorption capacity of CNF networks for various oils.

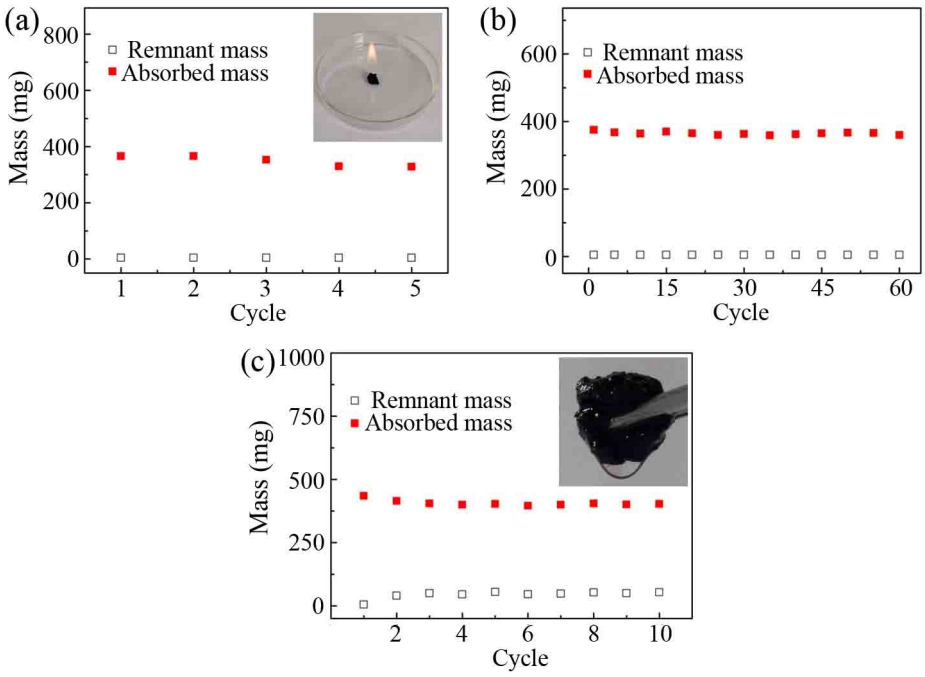

Fig. S17. Recyclability tests of CNF networks for the absorption of ethanol (a), *n*-hexane (b) and octadecene (c). Accordingly, the CNF networks were recycled by combustion (a), distillation (b) and squeezing (c). The insets in (a) and (c) are photographs of the combustion and squeezing of the CNF networks, respectively.

Fig. S18. Photograph of a CNF network (plasma modification time: 5 min) immersed in water.

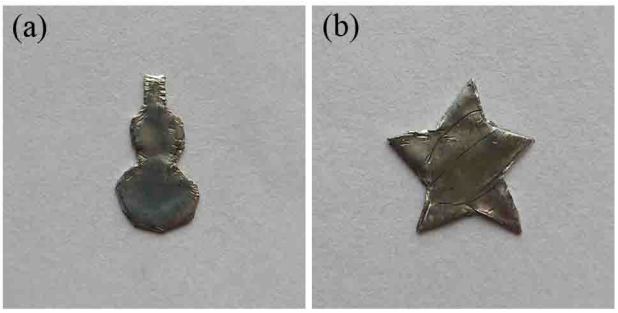

Fig. S19. Photographs of Al foils with calabash-like (a) and star-like shapes (b).

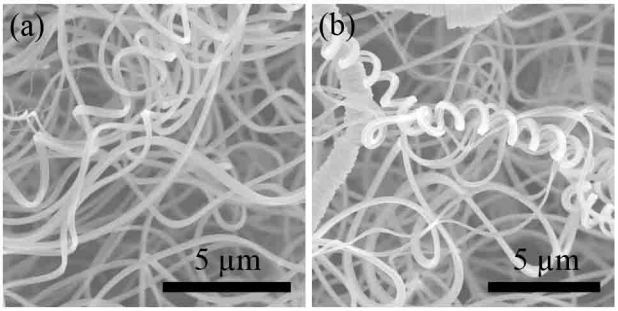

Fig. S20. SEM images of CNF networks before (a) and after (b) plasma modification.

Fig. S21. Photographs of the Janus CNF networks (shown in Fig. 4f) after one year, showing that water was dropped on their obverse and reverse surfaces. Their originally superhydrophilic areas (indicated by brown arrows) were still hydrophilic, and their hydrophobic areas (indicated by red arrows) also remained unchanged.

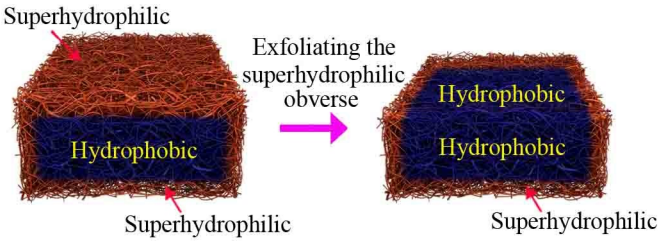

Fig. S22. Schematics of cross-sections of a CNF network with ammonia annealing at 900 °C (Left) and a Janus CNF network (Right). The Janus CNF network was fabricated by exfoliating the superhydrophilic obverse surface of the CNF network using a razor blade.

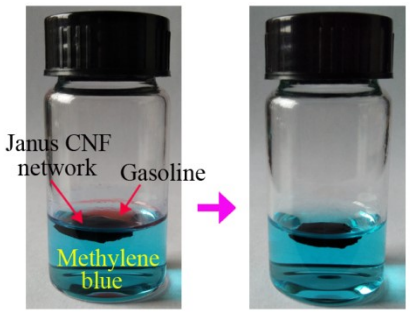

Fig. S23. Photographs showing the Janus CNF networks absorbing only gasoline at the interface of gasoline (dyed with Sudan III) and aqueous methylene blue solution.

Fig. S24. Photographs of Janus CNF networks removing both oils floating on water surfaces and dyes dissolved in water. The oils in (a) and (b) are toluene (dyed with solvent green 3) and olive oil (dyed with oil blue N), respectively, and the dyes in (a) and (b) are methyl orange and rhodamine 6G, respectively.

References

1. J. Lee, S. Yoon, S. M. Oh, C. Shin, T. Hyeon, *Adv. Mater.*, 2000, **12**, 359.
2. T. T. Xu, F. T. Fisher, L. C. Brinson, R. S. Ruoff, *Nano Lett.*, 2003, **3**, 1135.