Supporting Information

Vacuum-assisted layer-by-layer superhydrophobic carbon nanotubes films with electrothermal and photothermal effects for deicing and controllable manipulation

Xiaojing Su,[a] Hongqiang Li,*[a,b] Xuejun Lai,[a,b] Zhipeng Yang,[a] Zhonghua Chen,[a] Wenjian Wu[c] and Xingrong Zeng*[a,b]

[a]School of Materials Science and Engineering, South China University of Technology, Guangzhou 510640, China

[b]Key Lab of Guangdong Province for High Property and Functional Polymer Materials, Guangzhou 510640, China

[c]School of Environmental and Civil Engineering, Dongguan University of Technology, Dongguan 523808, China

***E-mail: lihq@scut.edu.cn, psxrzeng@gmail.com**

1. Preparation and characterizations of MWCNTs-COOH and MWCNTs-NH_2

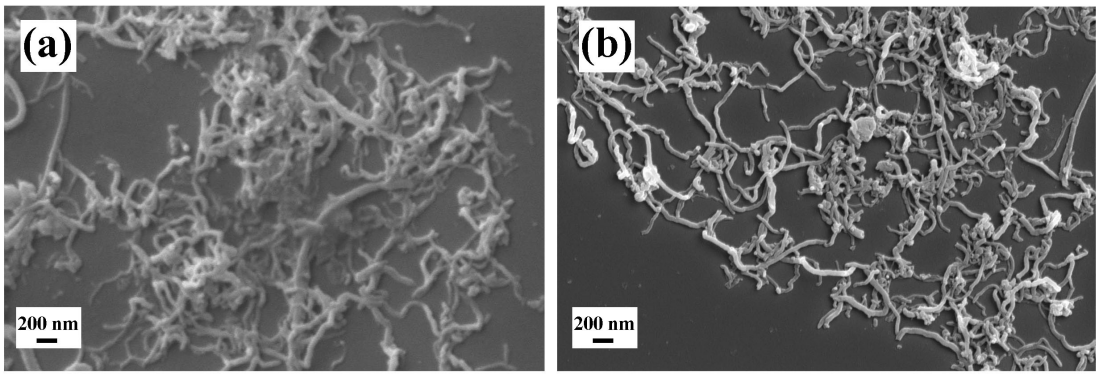

Fig. S1 SEM images of (a) MWCNTs and (b) MWCNTs-COOH.

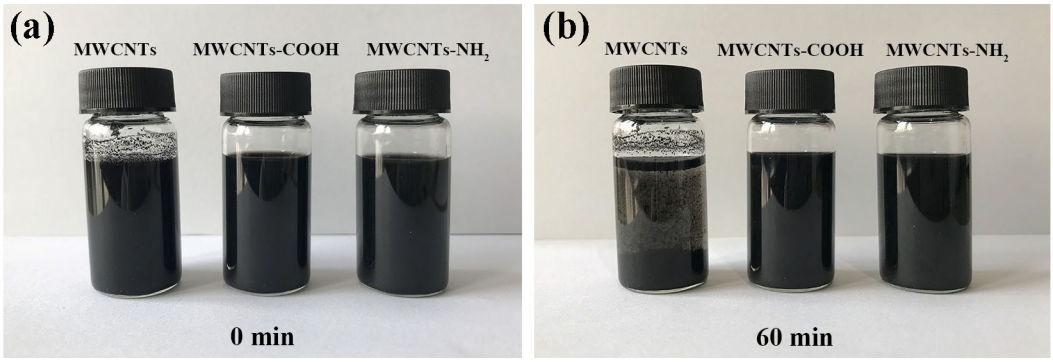

Fig. S2 Dispersion of MWCNTs and modified MWCNTs in water after settling for 0 min and (b) 60 min.

For the existence of hydrophilic polar groups, the dispersibility of MWCNTs-COOH and MWCNTs-NH_2 in water was remarkably improved comparing to that of the as-received MWCNTs. After sonication for 10 min, the MWCNTs with high surface energy were still difficult to disperse in water. However, the MWCNTs-COOH and MWCNTs-NH_2 quickly formed a stable dispersion in water (0.04 mg/mL), and no obvious precipitation and agglomeration was observed after 60-minute settle.

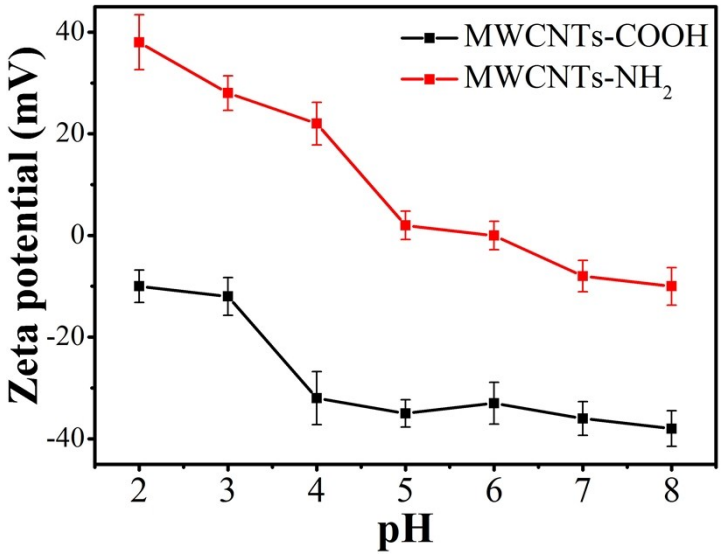

Fig. S3 pH-dependent zeta potential of MWCNTs-COOH and MWCNTs-NH_2.

It was found that the ionization of modified MWCNTs was closely correlated with pH values. Partial carboxylic groups (-COOH) of MWCNTs-COOH existed as carboxylate anions (COO^-) in aqueous solution of pH at 2 to 8, and the zeta potential gradually decreased with increasing pH values. Moreover, amine groups (-NH_2) of MWCNTs-NH_2 appeared as amino cations (NH_3^+) in aqueous solution of pH at 2 to 4, but the ionization changed to negatively charged with increasing pH values. To achieve a better assembly of functionalized MWCNTs, the MWCNTs-COOH suspension kept pH at 4.5 (zeta potential: approximately -33 mV), and the MWCNTs-NH_2 suspension kept pH at 2.5 (zeta potential: approximately +34 mV).

2. Fabrication of vacuum-assisted layer-by-layer superhydrophobic MWCNTs films

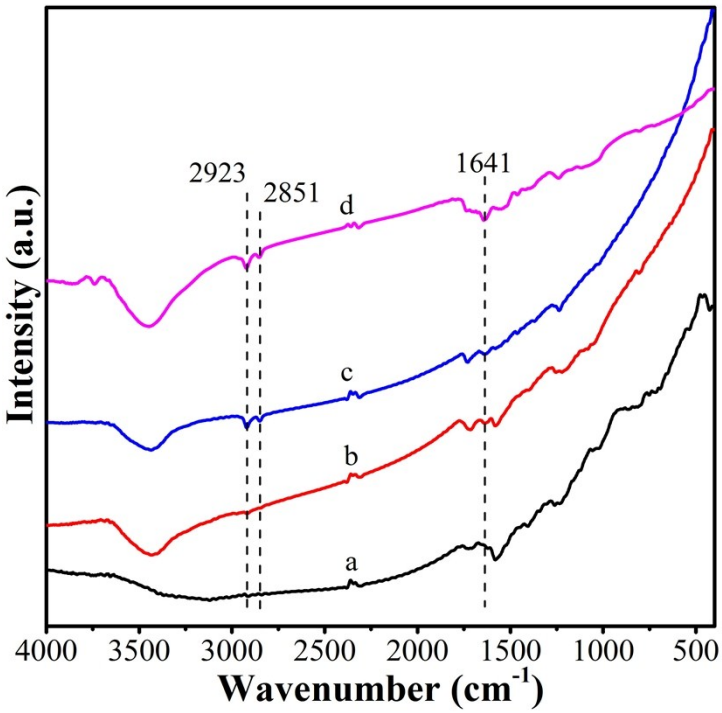

Fig. S4 FT-IR spectra of (a) the vacuum-assisted assembled (MWCNTs-COOH/MWCNTs-NH_2)$_6$ film, (b) the thermally crosslinked (MWCNTs-COOH/MWCNTs-NH_2)$_6$ film, (c) the superhydrophobic ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film, and the (d) ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film after immersing in ethanol for 36 h.

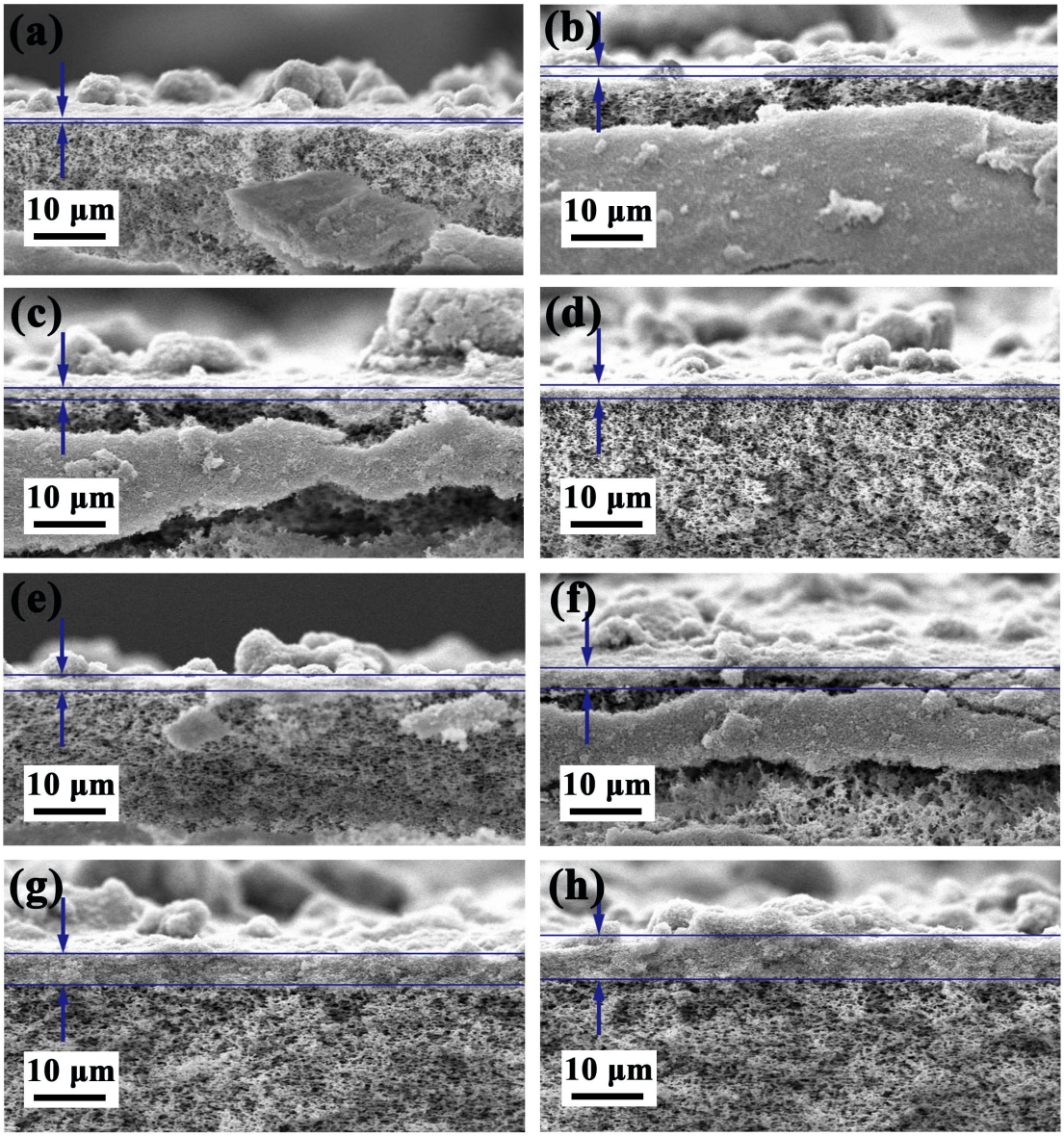

Fig. S5 Cross-sectional images of the thermally treated (MWCNTs-COOH/MWCNTs-NH_2)$_n$ film at different *n*: (a) 0.5, (b) 1, (c) 1.5, (d) 2, (e) 3, (f) 4, (g) 5, and (h) 6.

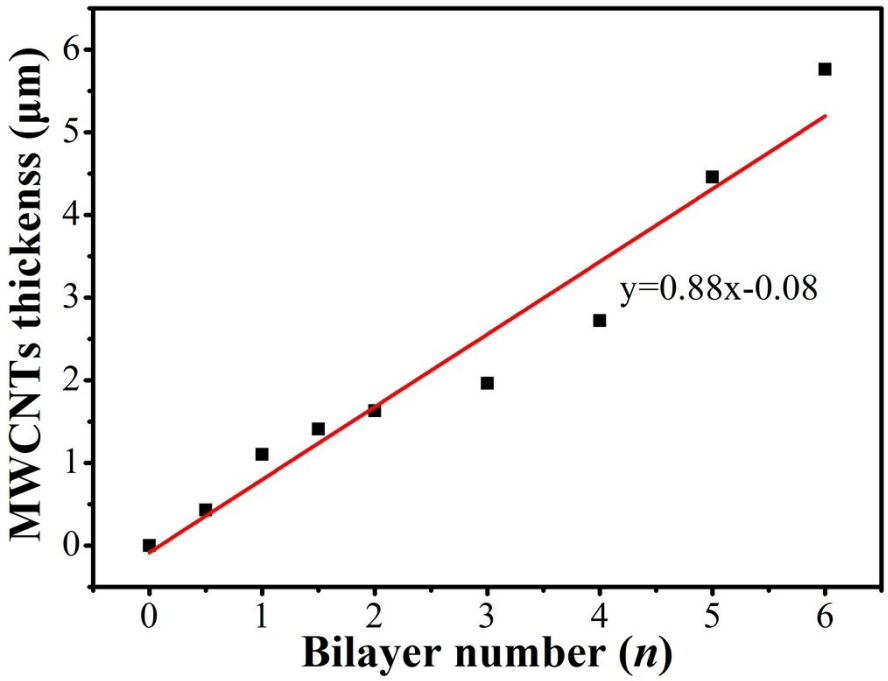

Fig. S6 MWCNTs thickness changes of the heated (MWCNTs-COOH/MWCNTs-NH_2)$_n$ film with bilayer number (n).

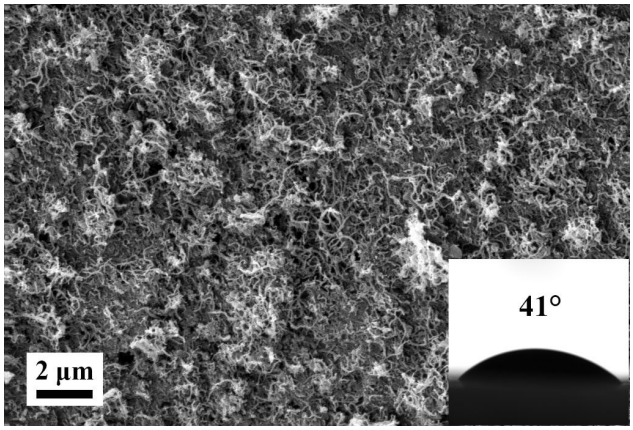

Fig. S7 SEM image of the transferred (MWCNTs-COOH/MWCNTs-NH_2)$_6$ film on substrate (inset on the bottom right was the CA optical image).

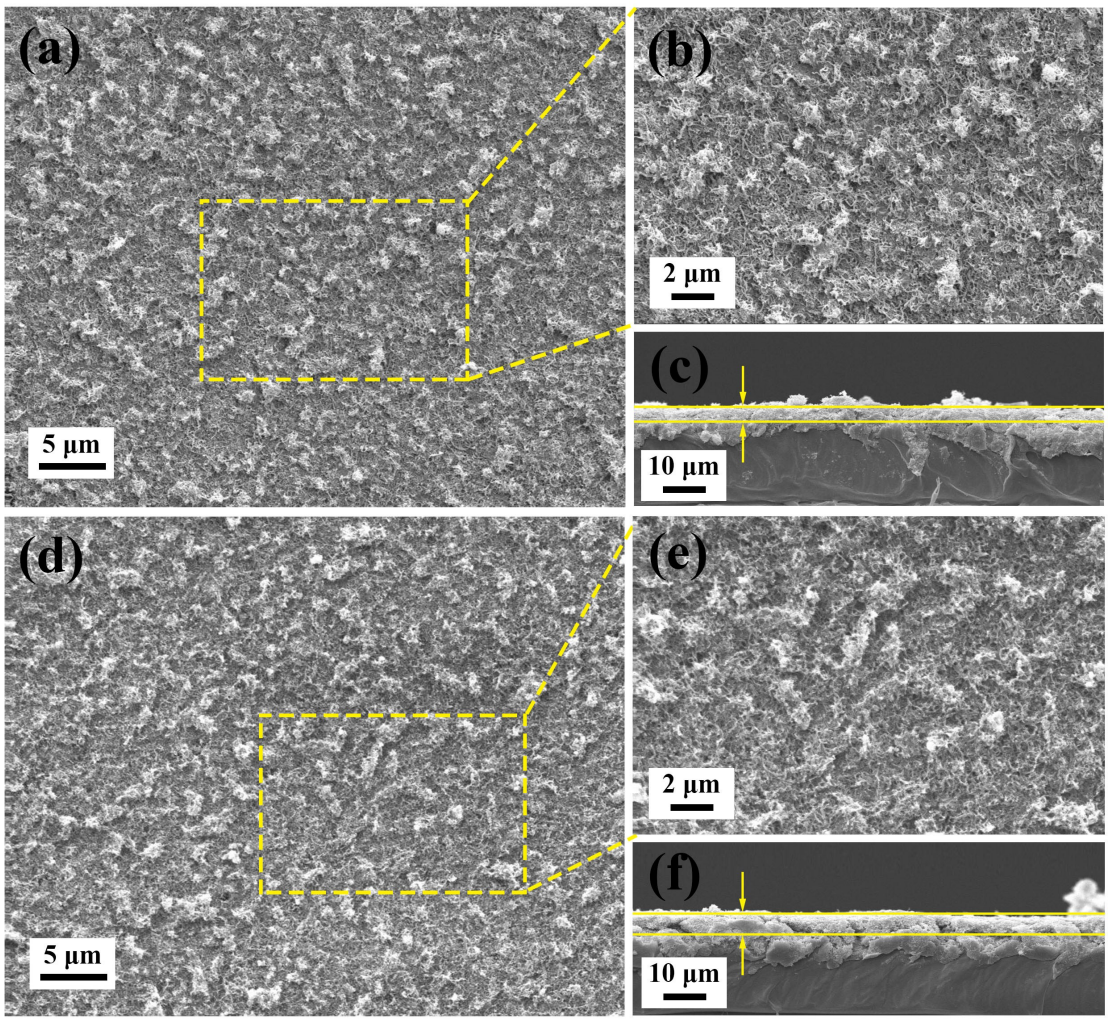

Fig. S8 SEM images, corresponding higher-magnification images, and cross-sectional images of (a, b, c) the ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_2$ film and (d, e, f) ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_4$ film.

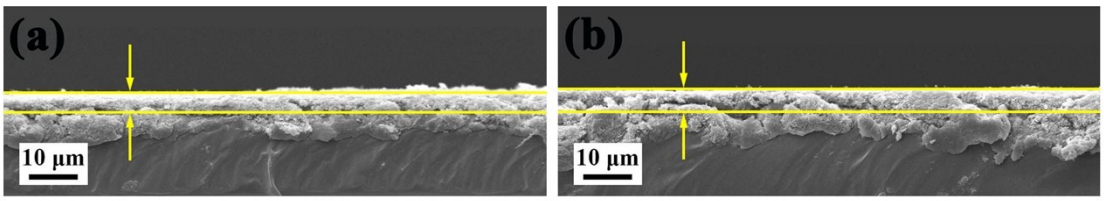

Fig. S9 Cross-sectional images of (b) the ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_3$ film and (b) ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_5$ film.

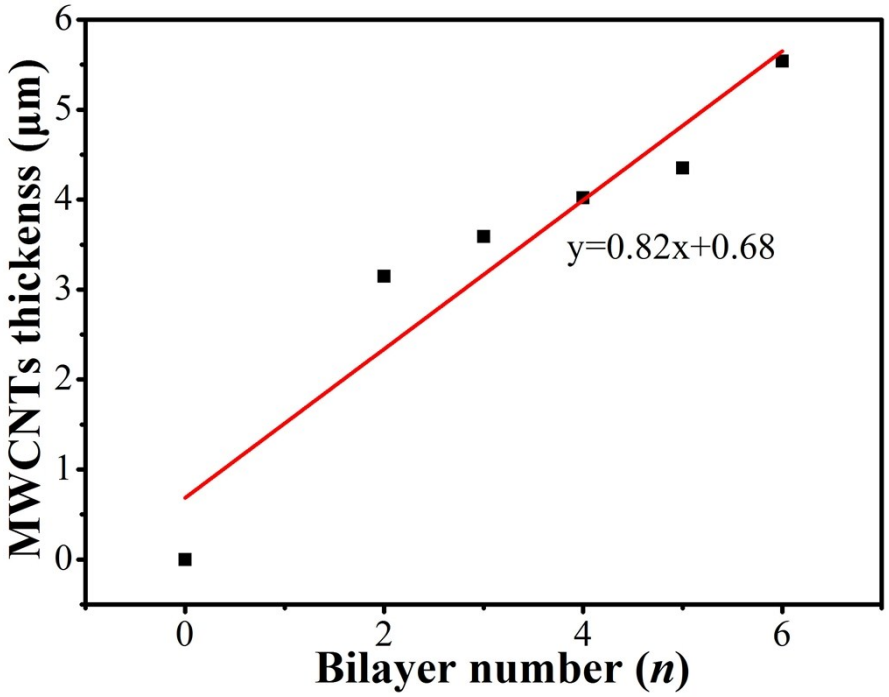

Fig. S10 MWCNTs thickness changes of the ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_n$ film with bilayer number (*n*).

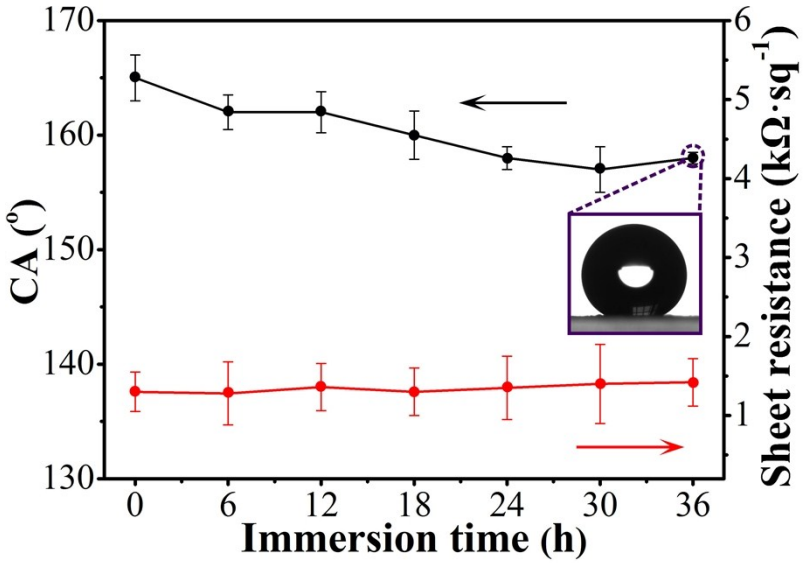

Fig. S11 CAs and sheet resistances of the ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film with different immersion time in ethanol.

To evaluate the chemical stability, a ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film was immersed in ethanol to observe the change of wettability and conductivity.

With immersion time increasing to 36 h, the ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film kept superhydrophobic with CA at 158^o and highly conductive with sheet resistance at 1.42 kΩ·sq^{-1}. The presence of peaks at 2923, 2851, and 1641 cm^{-1} in FT-IR spectrum of the treated ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film proved the preservation of covalently grafted ODA molecules and thermally crosslinked amide groups (Fig. S4d).

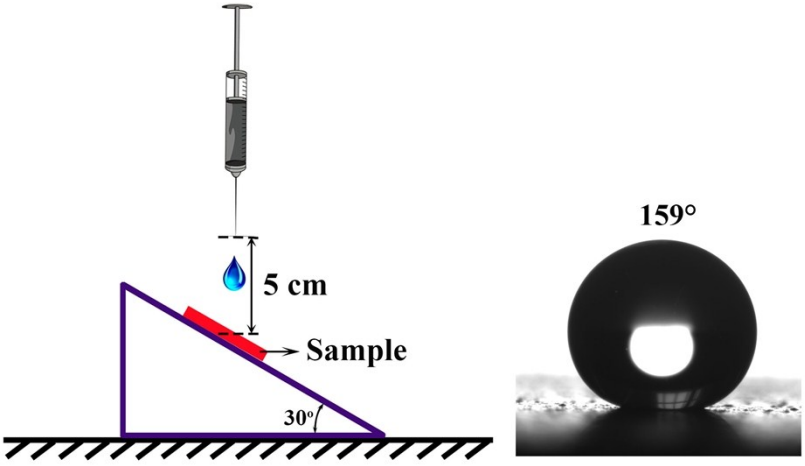

Fig. S12 Schematic illustration of water droplet impact test and the CA optical image after water droplet impinging the superhydrophobic ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film for 1 h.

The mechanical durability of the superhydrophobic ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film was examined by continuous water droplets with a volume of 7 μL impinging the surface from a height of 5 cm (Fig. S12). The film was put at a tilting angle of 30^o, and the falling speed of water was 40 drops per minute. After water droplets impacting for one hour, the surface remained water-repellent with a CA of 159^o and highly conductive with a sheet resistance of 1.36 kΩ·sq^{-1}.

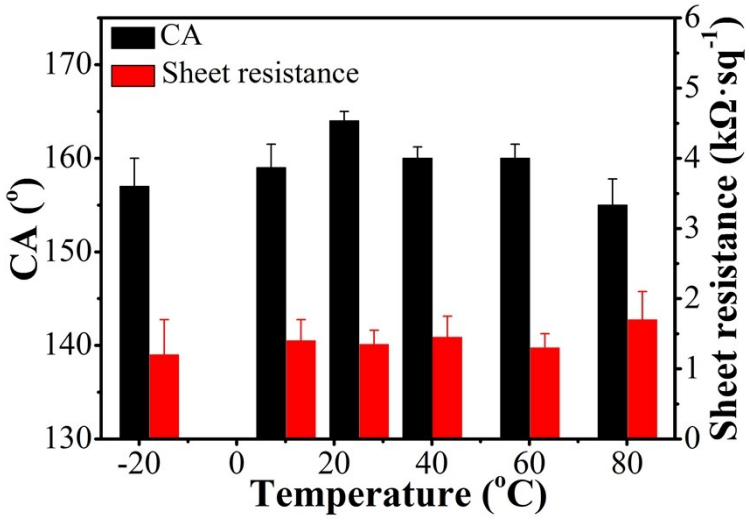

Fig. S13 CAs and sheet resistances of the ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film under different temperatures for 12 h.

In addition, temperature resistance was evaluated by separately putting superhydrophobic ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ films into freezer and oven with temperature varying from -18 to 80 °C for 12 h. The superhydrophobicity and electrical performance of the films were only slightly reduced after subzero and thermal treatment. Clearly, the covalent connection played a crucial role to maintain superhydrophobicity and high conductivity.

3. Electrothermal effect of superhydrophobic ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_n$ films for deicing

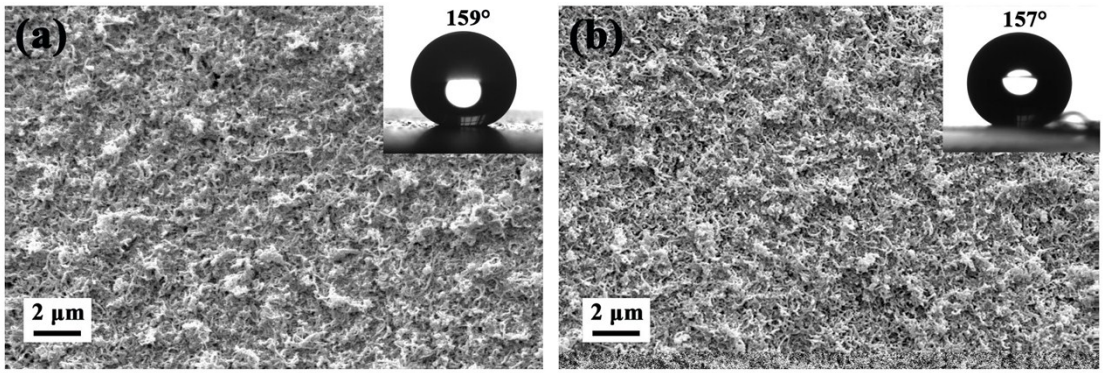

Fig. S14 SEM images of the superhydrophobic (MWCNTs-COOH/MWCNTs-NH_2)$_5$ films after deicing (a) without voltage and (b) with a voltage of 30 V (inset on the bottom right was the CA optical image).

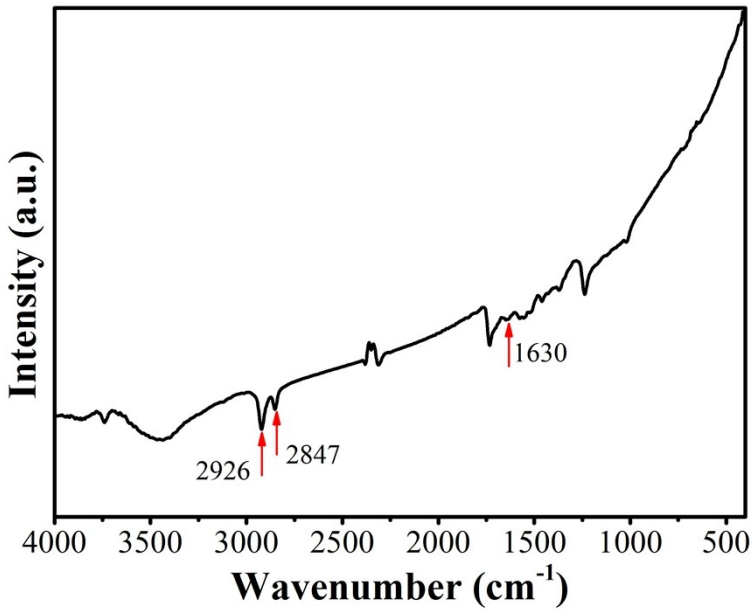

Fig. S15 FT-IR spectrum of the superhydrophobic (MWCNTs-COOH/MWCNTs-NH_2)$_5$ film after deicing with voltage of 30 V.

4. Photothermal effect of superhydrophobic ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_n$ films for controllable manipulation

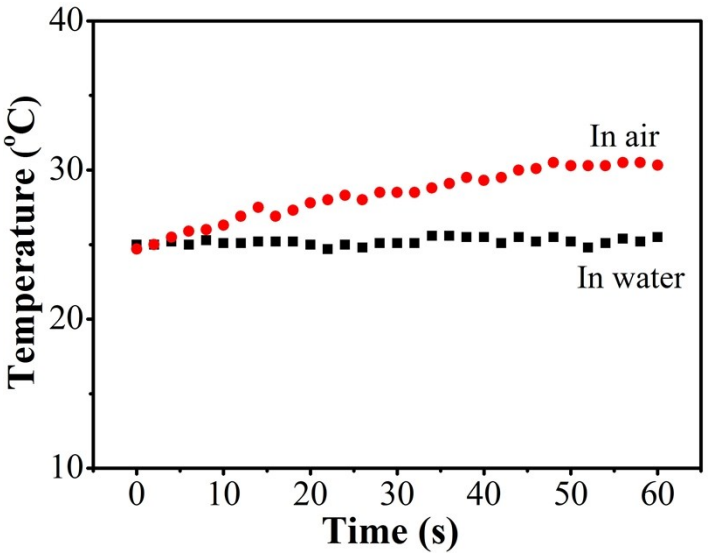

Fig. S16 Temperature change of the untreated glass in water and air with irradiation time of NIR light at 2 W·cm^{-2}.

With a NIR light of 2 W·cm^{-2} irradiating the untreated glass floating on water for 60 s, the surface temperature presented no obvious variation. Comparatively, when being irradiated in air, the temperatures reached 30 °C at 60 s, which was still far smaller than the ODA-(MWCNTs-COOH/MWCNTs-NH_2)$_6$ film. The results illustrated the highly light-absorptive MWCNTs layer was capable of efficiently converting light energy to heat.