

Supporting Information

Highly efficient oil–water separators based on dual superhydrophobic and superoleophilic properties of multiwall- carbon nanotube filtration films

Experimental Section

Preparation of alkyl-pyrene:

A new compound (alkyl-pyrene) had been synthesized by classic aldehyde and amine coupling reactions. 1-pyrenecarboxaldehyde (0.23 g) and octadecylamine (0.27 g) were mixed in dichloromethane, and then the mixture was stirred at room temperature for 12 h. The mixture was filtered to obtain alkyl-pyrene (0.47 g) then the as-prepared alkyl-pyrene was recrystallized from ethanol (20 mL) to obtain a pure compound (0.38 g, 76% yield). Mass spectrum (m/e) calculated for $C_{35}H_{47}N = 481.7$. Found 482.3. 1H NMR (300 MHz, d_6 -DMSO) $\delta=0.80$ – 0.85 (m, 3H, $-CH_3$), $\delta=1.15$ – 1.39 (m, 30H, $-CH_2-$), $\delta=1.73$ – 1.77 (m, 2H, $-CH_2-$), $\delta=3.77$ – 3.82 (m, 2H, $-CH_2-$), $\delta=8.11$ – 8.55 (m, 8H, Ar–H), $\delta=9.11$ – 9.15 (d, 1H, Ar–H), $\delta=9.37$ (s, 1H, $-CH=N$). FTIR (KBr, cm^{-1}): 2920, 2849 and 1633.

Preparation of Free-Standing MWCNT Films:

MWCNT (50 mg) was suspended in NMP (20 mL) then sonicated for 1 h to obtain a homogeneous MWCNT suspension. Alkyl-pyrene (2.5 mg) was then dissolved in the MWCNT solution and stirred (1000 RPM) for 12 h at room temperature. The MWCNT film was prepared by filtering the solution through a filter paper (ADVANTECH NO. 1 qualitative filter paper, the pore size and thickness of it is 6 μm and 0.2 mm, respectively.) and washed thoroughly with NMP (20 mL) and acetone (20 mL) to get rid of the remaining alkyl-pyrene. The film was easily peeled off without displaying any visible damage. Finally, the MWCNT film was dried under vacuum at 40 °C for 24 h.

Materials and Characterization

The commercial MWCNTs was purchased from Golden Innovation Business Co. Ltd, Taiwan (AC tube, the diameter is 10~20 nm, the length >30 μm). Octadecylamine (97%), 1-pyrenecarboxaldehyde (99%), N-methyl-2-pyrrolidone (NMP, anhydrous, 99.5%) and ethanol (for HPLC, $\geq 99.8\%$) were purchased from Sigma-Aldrich and used as received. Mass spectrum was run on a Bruker Daltonics IT mass spectrometer model Esquire 2000 (Leipzig, German) with an Agilent ESI source (model G16076001). Fourier transform infrared spectra of all chemicals were collected using an FTIR spectrometer (JASCO FT-IR-4100) at room temperature. Fourier-transform infrared attenuated total reflectance (FTIR-ATR) characterization was performed on the pristine and functionalized MWCNT films directly. The chemical structure of the alkyl-pyrene was determined by ^1H NMR spectroscopy on a Bruker 300 spectrometer, using deuterated dimethyl sulfoxide (DMSO) as the solvent. The dynamic mechanical analysis (DMA) was performed with a TA Instrument DMA 2980 at a frequency of 1 Hz, at 30 $^\circ\text{C}$. Contact angle (CA) of samples were measured using a First Ten Angstroms FTA 175. The metering of the individual water droplets was controlled at 5 μL . Optical microscopy images were taken on a Zeiss LSM 510 Meta microscope. The field emission scanning electron microscope (FE-SEM, JEOL JSM-7100F) was performed at an acceleration voltage of 10 kV to observe the morphology of MWCNT films.

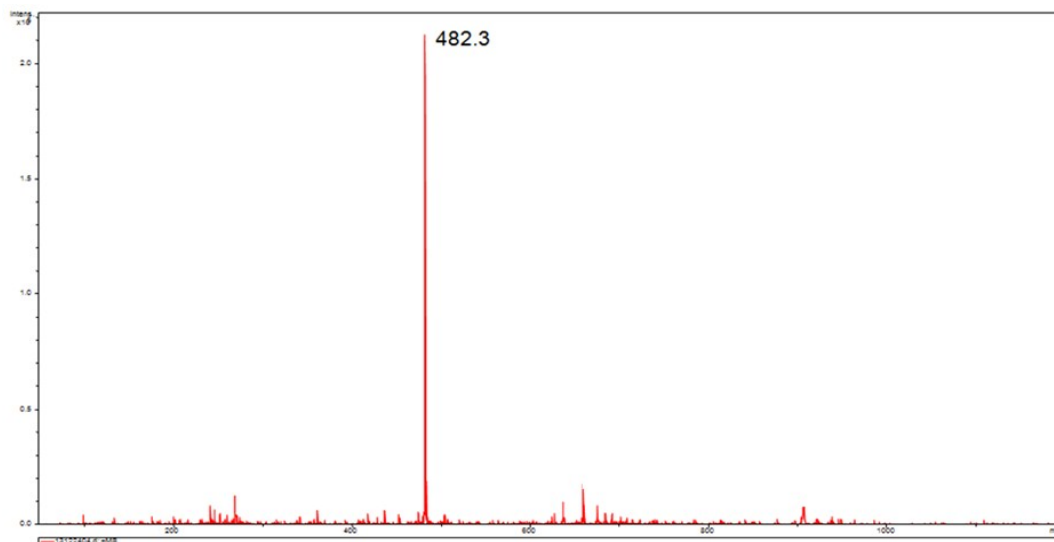


Fig. S1 LC-mass of the alkyl-pyrene.

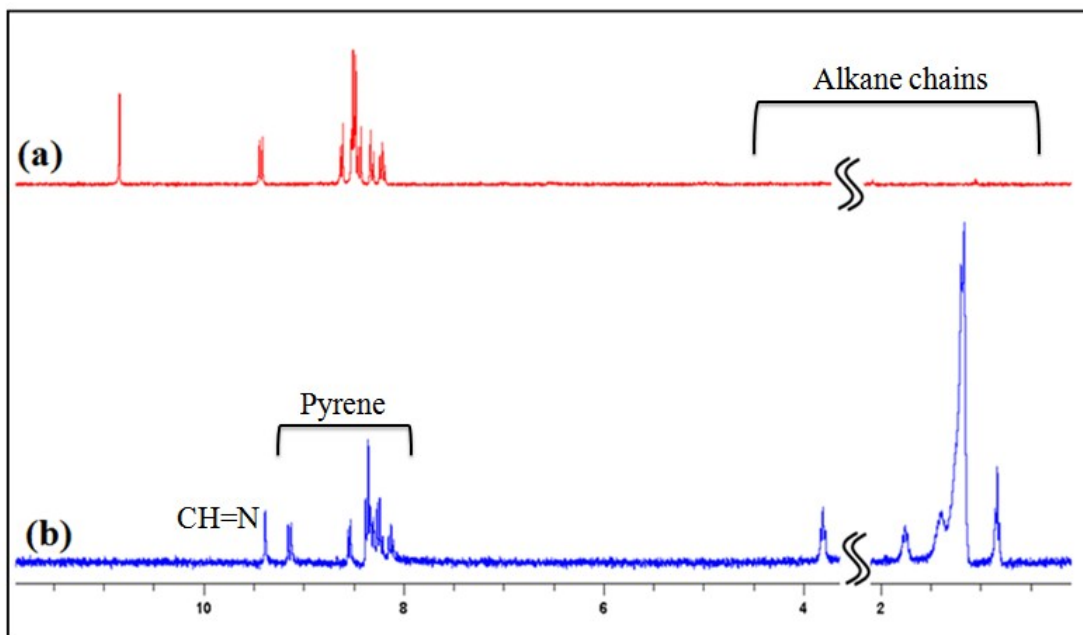


Fig. S2 ^1H NMR of (a) 1-pyrenecarboxaldehyde, (b) alkyl-pyrene.

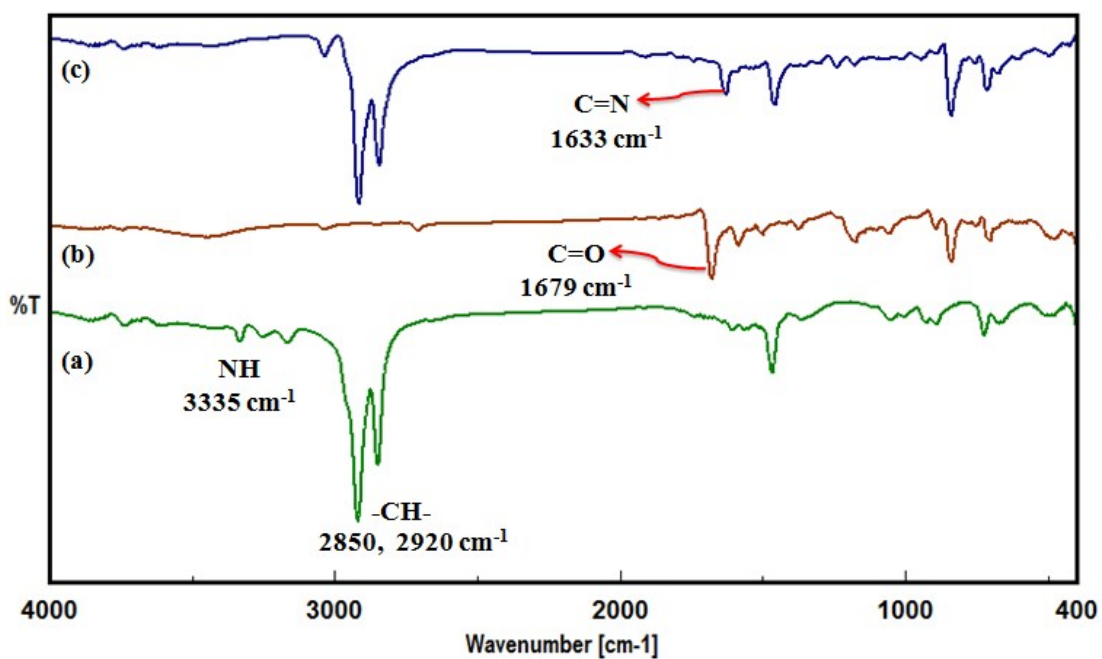


Fig. S3 FTIR spectra of (a) octadecylamine, (b) 1-pyrenecarboxaldehyde, and (c) alkyl-pyrene.

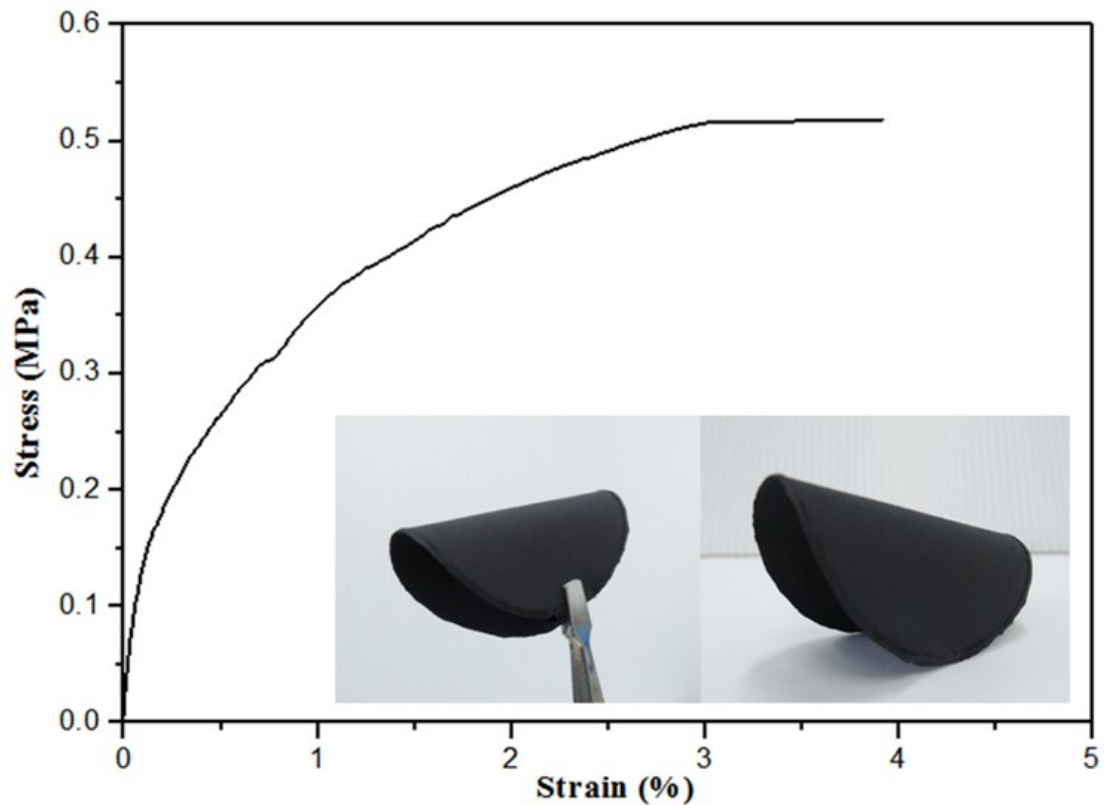


Fig. S4 Stress-strain curve of MWCNT films. The inset shows the photograph of flexible MWCNT films.

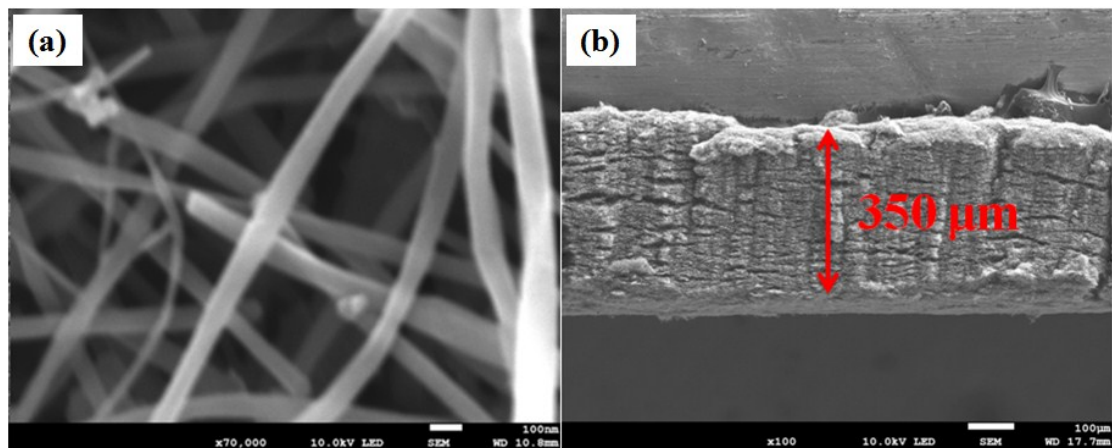


Fig. S5 SEM images of (a) the surfaces and (b) cross-section of the MWCNT film.

Water breakthrough pressure testing

The water breakthrough pressure (P), is calculated by using the equation:

$$P = \rho gh$$

ρ is the density of water, g is acceleration of gravity, and h is the height of water the membrane can support. As a result, CNT films with an area of 2.009 cm^2 can support 2 m water column. The P is calculated to be 20 kPa. There was no water drop passing

through after three days. This means the breakthrough pressure of the MWCNT films is higher than 20 kPa.

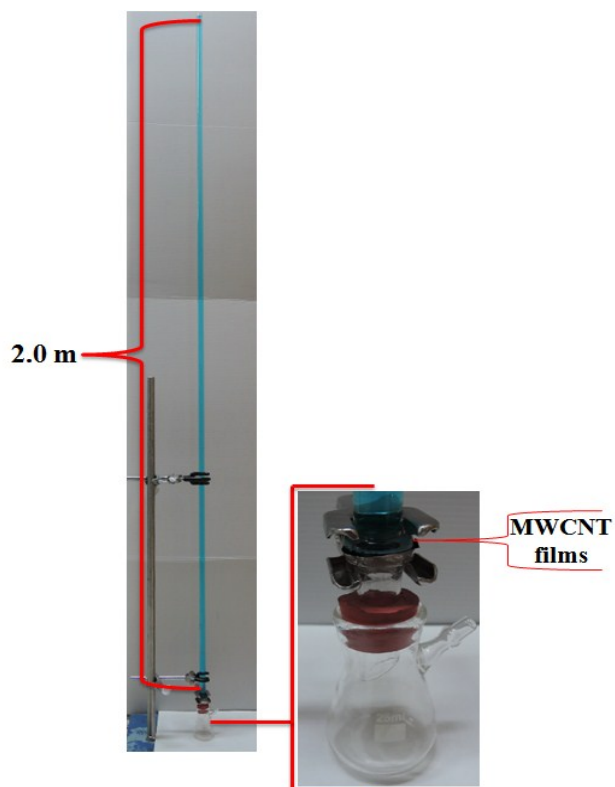


Fig. S6 Optical image of 2.0 meter height of water on MWCNT films.

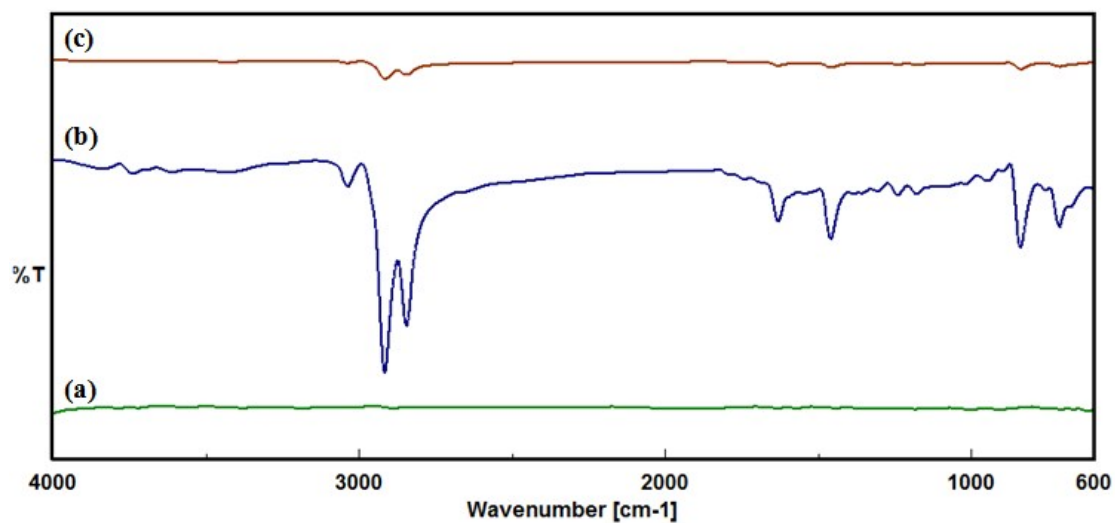


Fig. S7 FTIR-ATR spectra of the CNT films (a) pristine CNT, (b) alkyl-pyrene, and (c) modified CNT films

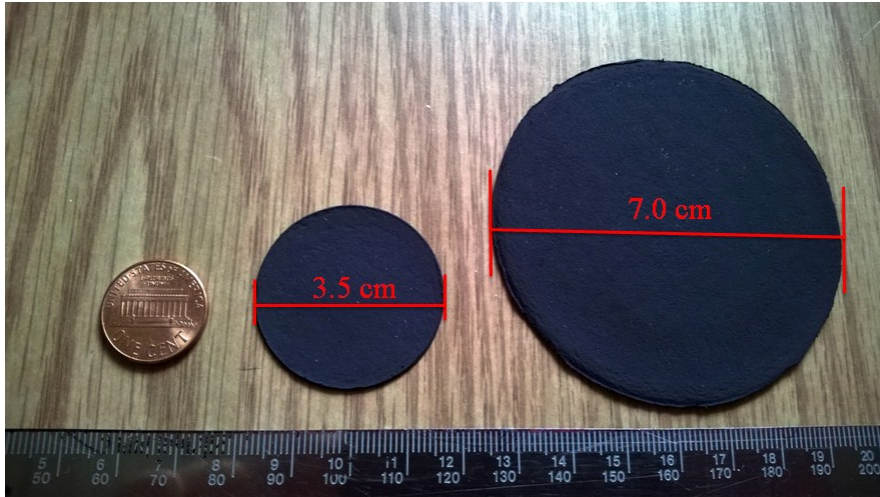


Fig. S8 Photograph of large-scale CNT films.