Supporting Information

Built-up Superhydrophobic Composite Membrane with Carbon Nanotubes for Water Desalination

Bowu ZHANG^{*a*}, Lixia LIU^{*b,c*}, Siyuan XIE^{*a,c*}, Fei SHEN*^{*b*}, Hui YAN^{*b*}, Huanhuan WU^{*b,c*}, Yinhua WAN^{*b*}, Ming YU^{*a*}, Hongjuan LI^{*a*}, Linfan LI^{*a*} and Jingye LI*^{*a*}

^a TMSR Research Center and CAS Key Lab of Nuclear Radiation and Nuclear Energy Techniques, Shanghai Institute of Applied Physics, Chinese Academy of Sciences. Shanghai 201800, P. R. China. Fax: (+) 86-21-39194505; E-mail: jingyeli@sinap.ac.cn

^b The National Key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, P.R. China. Tel: (+) 86-10-82544991; E-mail: <u>fshen@home.ipe.ac.cn</u>

^c University of the Chinese Academy of Sciences, Beijing 100049, P.R. China.

Dr. B.W. Zhang and Miss L.X. Liu contributed equally to this work.

Experimental Part

Materials

Multi-walled carbon nanotube (L-MWNT-4060, 95%) were purchased from Shenzhen Nanotech Port Co., Ltd., (Shenzhen, China); Nitric acid (65 wt%), vinyl acetate (99%) and other chemical reagents (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China); All chemicals were used as received without any purification process. Double distilled water was used for all experiments unless stated.

Graft Polymerization of Vinyl Acetate onto CNT

30 mg of dry pristine CNT were dispersed in 30 mL of vinyl acetate/acetone solution by 30 minutes ultrasonication. Following dry nitrogen-bubbling and second ultrasonication (10 minutes), the black dispersion was irradiated by γ -ray in the field of ⁶⁰Co source for presetting doses at the given dose rate. After irradiation, glue or gel-like mixtures were obtained. The mixtures were diluted respectively with excessive acetone and then sonicated for 15 minutes. For the sake of separating indissoluble black sediment, the mixtures were subjected to centrifugation at 1000 rpm for 10 minutes. After removal of the homogeneous black supernatant, the black sediment was redispersed in acetone by sonication and centrifuged for 10 min again. This operation cycle was repeated 3 times, and the black supernatant was collected every time.

The collected black supernatant was vacuum-filtered with 0.45 µm PVDF microfiltration membrane, and the collected black solids were thoroughly washed 5 times with fresh acetone. The black filter-cake was then redispersed in fresh acetone by sonication for 15 min, filtered, and washed with superabundant fresh acetone again. After 3 times repeated operation, the obtained black solids, *i.e.* poly (vinyl acetate) functionalized CNT (F-CNT) were scraped off from PVDF membrane and dried overnight in a vacuum oven at 60 °C. The amount of poly (vinyl acetate) on CNT (degree of grafting, DG) was determined by thermogravimetric analysis (TGA), and we can control the DG by altering the feed ratio of vinyl acetate in acetone.

Build-up of superhydrophobic F-CNT/PVDF composite membrane

15 mg F-CNT powder was dispersed in 100mL acetone and after sonication 10 minutes, a stable black dispersion was obtained. The stable black dispersion was filtered through a PVDF membrane (0.45 μ m) to produce an F-CNT coating. After washed with acetone several times, the coating was dried overnight in vacuum oven at 60°C.

Contact angle measurements

Static contact angle (CA) was measured for water drops placed on the sample surface using a KSV ATTENSION Theta Optical Tensiometer. A 4 μ L liquid drop from a stainless steel needle was stroked onto the membrane surface. Shape of the droplet was recorded by a digital camera and static contact angle was calculated according to the image taken by evaluation software provided from the instrument manufacturer. 5 different points of every sample and 3 samples for every membrane were measured and the CA was the average of these 15 measurements. All measurements were carried out at room temperature (25 °C) and the relative humidity of air was 30~60%.

Characterization and method

The FT-IR spectra of samples were collected in the form of potassium bromide (KBr) tablets using a Thermo Nicolet Avatar 370 FTIR Spectrometer at a resolution of 4 cm⁻¹ and 32 scanning. A Renishaw inVia plus laser Raman spectrometer was used to investigate the structural changes of powder samples using an excitation wavelength of 514.5 nm. XPS analysis was carried out on a SHIMADZU Kratos AXIS Ultra DLD XPS instrument equipped with a monochromated Al K α X-ray source. The TGA curves were recorded using a PerkinElmer PyrisTM 1 Thermogravimetric Analyzer at a heating rate of 10 °C/min under a nitrogen atmosphere (20 mL/min). The surface feature of F-CNT coating was observed through a JEOL JSM-6700F Field-Emission Scanning Electron Microscope.

The Testing of DCMD

The DCMD set-up used to evaluate the flat-sheet F-CNT/PVDF composite membranes was presented in **Figure S1**. The membrane module was composted by two stainless steel cylindrical chambers. One of the chambers was connected to a heating system while the other chamber was connected to a cooling system. The membrane was placed between the two chambers. The hot feed solution was brought into contact with the hydrophobic CNTs layer of the membrane and the cold permeate solution is in contact with the supporting membrane (PVDF). Pure water, sodium chloride solutions with 3.5 wt% and 10.0 wt% were employed as feed sequentially. Deionized water was used at cold side. The effective membrane area of the DCMD system is 8.5487×10^{-4} m². The feed solution and cold water were circulated in counter-current operation. The flow rates on both sides were set to be 500 ml/min. The inlet and outlet temperatures of the feed and permeate were measured by sensors connected to a digital meter. The permeate flux was collected in an overflow tank located on one digital balance. The DCMD flux was calculated according to

$$J_{w} = \frac{\Delta m}{At} \tag{1}$$

Where $J_w, \Delta m$, A, t representing the water flux (kg/m²h), amount of permeate (kg), effective membrane area (m²), and the time duration (h), respectively. The sodium chloride concentration of both permeates and feed solution was determined by a conductivity meter. The salt rejection rate R was calculated using the following expression:

$$R = (1 - \frac{C_p}{C_f}) \times 100\%$$
⁽²⁾

Where C_p and C_f are the sodium chloride concentration of permeate and bulk feed solution, respectively.

Table S1 DCMD performances of the reported flat-sheet MD membranes for desalination: feed temperature (T_f) , permeate temperature (T_p) , feed flow rate and permeate flow rate are the same.

Membrane	Permeate Flux	Salt rejection Feed	process operating property			Ref.	
	(Kg/m ² h)	(%)	solution	T _f (°C)	T _p (°C)	Flow rate	
PVDF-HFP electrospun membrane	20-22	98	10g/L NaCl solution	50	20	0.25L/s	[1]
PVDF electrospun membrane	15	99.7	12 g/L NaCl solution	80	20	500rpm	[2]
PVDF-clay nanofiber membrane	5.2	99.9	3.5 wt% NaCl solution	65	17±2	1.8L/min	[3]
CF4 plasma- modified PVDF membrane	32	99.98	4.0 wt% NaCl solution	65	21	600ml/m in	[4]
PVDF electrospun membrane	20.4	99.98	3.5 wt% NaCl solution	50	20	0.4m/s	[5]
CNT Bucky- Paper membrane	8~9	95~97	35 g/L NaCl solution	65	5	300ml/m in	[6]
Silane- functionalise d CNT Bucky-Paper membrane	9.3	97	35 g/L NaCl solution	65	5	300ml/m in	[7]
PTFE coated CNT Bucky- Paper membrane	7.5	97	35 g/L NaCl solution	65	5	300ml/m in	[8]
CNT Bucky- Paper membrane	6	90	35g/L NaCl solution	65	5	300ml/m in	[9]
F-CNT-2M membrane	25	99.5	3.5 wt% NaCl solution	80	20	500ml/m in	Curre nt



Figure S1 Schematic diagram of the experimental DCMD set-up.



Figure S2 (a) the water contact angle stability of PVDF membrane with 0.45 μ m pore size before and after 1 hour DCMD testing by 3.5% NaCl solution; (b) the relationships of permeate flux and salt rejection of PVDF membrane with 0.45 μ m pore size to testing time of DCMD by 3.5% NaCl solution.



Figure S3 the TGA curves of pristine CNT and F-CNT with different DG.



Figure S4 The dispersibility of CNT before and after grafting with PVAc.



Figure S5 (a) the photo of CNT/PVDF composite membrane; (b) the photo of F-CNT/PVDF composite membrane.



Figure S6 (a) the relationships of permeate flux and salt rejection of F-CNT-1M to testing time of DCMD by 3.5% NaCl solution; (b) the relationships of permeate flux and salt rejection of F-CNT-3M to testing time of DCMD by 3.5 wt% NaCl solution. (Temperature of feed solution: 70 °C; temperature of permeate solution: 20 °C)



Figure S7 the surface micro-morphology of (a) F-CNT-1M; (b) F-CNT-2M and (c) F-CNT-3M.



Figure S8 the water contact angle stability of F-CNT-1M, F-CNT-2M and F-CNT-3M before and after 2 hour DCMD testing by 3.5% NaCl solution at 70 °C.



Figure S9 the contact angle of water droplet on the surface of PVAc film which prepared by casting the PVAc solution on class slide.

Video S1 The water drop on the F-CNT-1M surface with a slope of 1.6°

Video S2 The water drop on the F-CNT-1M surface with a slope of 2°

Video S3 The water drop on the F-CNT-1M was completely taken in by syringe needle

Video S4 The water drop on the F-CNT-1M was completely sopped up with drinking paper

Video S5 stroking water drop on syringe needle onto the surface of F-CNT-1M

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