Electronic Supplementary Material (ESI) for RSC Advances.

Gas-Switchable Carbon Nanotube/Polymer Hybrid Membrane for Separation of Oil-in-Water Emulsions

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1. Experimental Section

1.1 Materials:- 2-(Diethylamino)ethyl methacrylate (Aldrich, 99%) was purified by passage through basic alumina and vacuum distillation. Thionyl chloride ($SOCl_2$, EMD, 99%), ethylene glycol (Fisher, 97%), 2-bromoisobutryl bromide (Aldrich, 97%), *N,N,N′,N″,N″*-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), CuCl (Aldrich, 99.99 %) Sulfuric acid (Anachemia, 98%), Nitric acid (J.T.Baker, 90%), anhydrous methanol (Aldrich, 99.8 %) and anhydrous dichloromethane (DCM, Aldrich 99 %,) were used as received. Triethylamine (TEA) was dried over anhydrous $MgSO_4$. Nitrogen gas (99.998 %) and Carbon Dioxide (CO_2, 99.9%) were purchased from Praxair. Milli-Q water with resistivity of 18 MΩ was used as the medium for the gas switchable experiments. Carbon nanotubes based mat were generously provided from Tortech Inc, Tarshiha, Israel and powdered CNTs are purchased from Carbon Nanotechnologies Inc., Houston, TX (HiPco, batch CM260015-6).

1.2 Carbon nanotube (CNT) Functionalization:- The CNTs are functionalized with carboxylic acid groups by oxidation with mixture of H_2SO_4/HNO_3 at room temperature. Briefly, 250 mg of carbon nanotube mat/powder was mixed with 50 mL of H_2SO_4/HNO_3 (3:1) and then ultrasonicated at room temperature for 10 hours. Subsequently, this solution was neutralized with ammonium hydroxide and filtered with a 0.22 μm cellulose acetate membrane in the case of CNT powder. The CNT mat/powder were washed several times using deionized water until the pH 5.5 was reached and are vacuum dried at 75 °C for 20 hrs.

1.3 Synthesis of 2-Hydroxyethyl 2′-Bromopropionate:- A 500 mL three-neck round-bottomed flask was charged with 31 g (0.50 mol) of ethylene glycol, 250 mL of anhydrous THF, and 8.0 mL (0.057 mmol) of triethylamine (TEA). The flask was cooled to 0 °C by placing in ice bath, and a solution of 10.8 g (0.050 mol) of 2-bromopropionyl bromide and 100 mL of THF was added dropwise under nitrogen. The mixture was stirred overnight, warming to room temperature of its own accord. Solids were removed by filtration, and the solvent was evaporated. The remaining liquid was dissolved in 200 mL of deionized water and extracted with chloroform. The organic phase was dried over anhydrous $MgSO_4$, and the solvent was removed. The remaining liquid was vacuum-distilled (bp 86°C at 2.1 mmHg) to yield 4.24 g (43%) of colorless liquid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.92 [3H, CH($\mathbf{CH_3}$)$_3$Br]; 1.99 (1H, **HO**-CH_2CH_2O); 3.91 (2H, HO-$\mathbf{CH_2}$-CH2O-), 4.28 (2H, HO-CH_2-$\mathbf{CH_2}$-O-), 4.33 [1H, -**CH**-(CH_3)Br].

1.4 CNT Macro initiator:- A 100 mL round-bottomed flask was charged with 500 mg of the carboxylic acid-functionalized CNT mat/powder, 80 mL of $SOCl_2$, and 10 mL of dichloromethane. The flask was fitted with a water condenser, and the mixture was stirred at 65 °C for 30 h. The solvent was removed under vacuum in the case of CNT powder. The remaining solid was washed three times with anhydrous THF and was vacuum dried at 25 °C for 2 hrs. The CNT mats were thoroughly washed with anhydrous THF, and vacuum dried for 2 hrs at RT. Then the acid chloride CNTs mat/powder was then mixed with ethylene glycol (~60 mL) and stirred for 2 days at 120 ^{o}C. The resulting solid powder was separated by vacuum filtration using 0.22 µm polycarbonate membrane filter and finally washed with anhydrous THF. The resulting solid was dried in a vacuum to generate hydroxy terminated (CNT-OH) CNTs. Then, in a 250 mL round bottom flask, 500 mg of CNT mat/powder and 50 mL of anhydrous THF was cooled to 0^{o}C by placing in ice bath then 8.0 mL triethylamine (TEA) (0.057 mmol) was added and stirred the solution for 30 minute. Then 10.8 g (0.050 mol) of 2-bromopropionyl bromide and 10 mL of anhydrous THF was drop-wise added into the CNT solution under nitrogen atmosphere. The resulting solid powder was separated by centrifugation and several times washed with anhydrous THF, finally dried under high vacuum.

1.5 Synthesis of surface-initiated PDEAEMA Brush on CNTs:- In a 100 mL Schlenk flask charged with DEAEMA (8.96 g; 63.0 mmol) monomer and 15 mL of anhydrous methanol and was degassed with nitrogen bubbling for 20 minutes. Then 10.4 mg of CuCl (0.105 mmol) and 2.34 mg of $CuCl_2$ was added, followed by 10 minute bubbling with nitrogen gas. Then add 32.8 mg (0.210 mmol) of PMEDETA was added via syringe, and the reaction mixture was degassed by three freeze-pump-thaw cycles. In a separate sealed 100 mL of Schlenk flask containing 500 mg of CNT-initiator (mat/powder) (contains 0.0042 mmol of initiator groups) were vacuumed for 1 hour then filled with nitrogen gas. The monomer mixtures were then injected into flask containing CNT-initiator through a syringe. The reaction mixtures were then heated to 80^{o}C for 24 h. After polymerization (Figure S1), the CNTs (mat/powders) were washed (centrifugation in the case of CNT powder) with THF and methanol, and dried under vacuum.

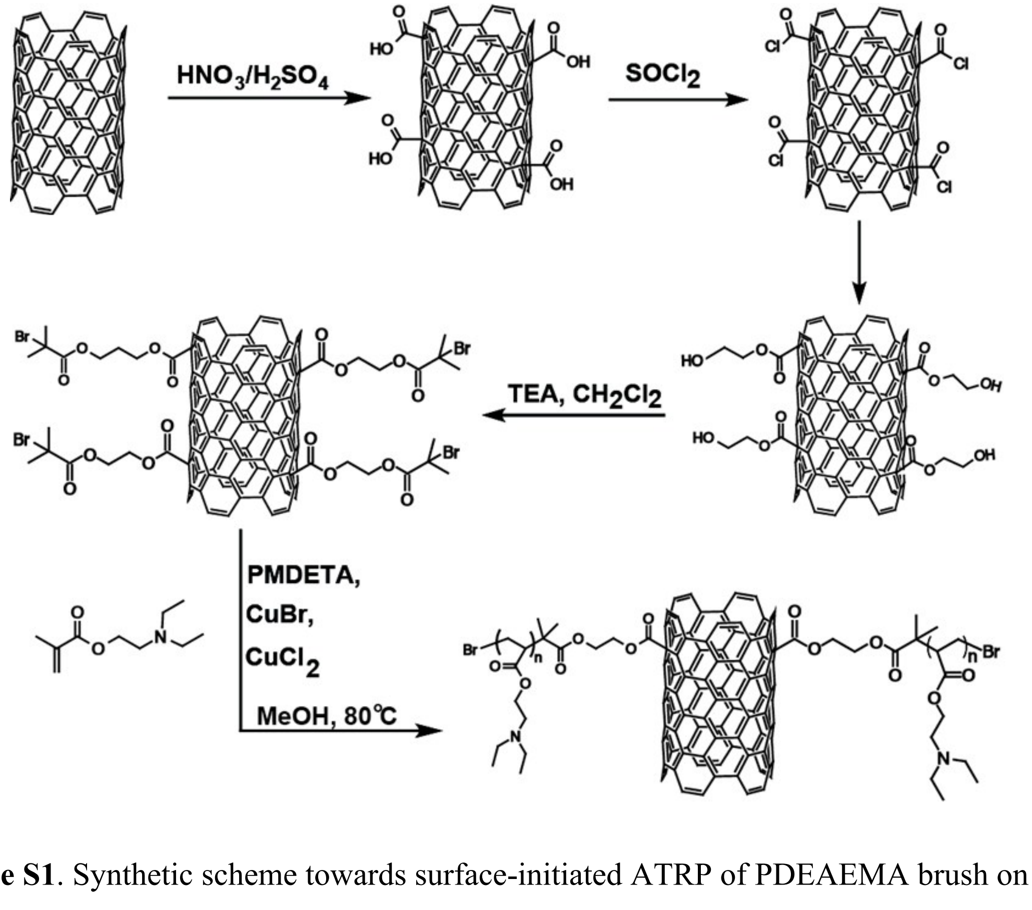

Figure S1. Synthetic scheme towards surface-initiated ATRP of PDEAEMA brush on CNTs.

2. Instruments and Measurements:- The chemical compositions of PDEAEMA grafted on CNTs was determined from 500 MHz ^{1}H NMR spectra by use of $CDCl_3$ as solvent. Thermal behaviors of polymer/CNT hybrid membrane were performed on a TA instruments Q50 thermo-gravimetric analyzer from 25^{o}C to 650^{o}C at heating rate 10^{o}C min^{-1} under nitrogen atmosphere. The characteristic temperature and residual weight were determined for hybrid membrane and only CNT were determined by analyzing ~5mg of samples. Raman spectra were recorded on a Nicolet Almega XR Raman spectrometer equipped with a charge-coupled device (CCD) detector and 532 nm (laser power 24 mW) laser excitation. Raman spectra were acquired with 100× objective, which resulted in a spatial resolution down to 1 μm and for each sample at least 3 scans were performed. The Fourier transform infrared analysis of polymer hybrid membranes were performed using Varien FTS 7000 series equipped with single reflectance ATR unit, DTGS detector (DIGILAB, Randolph, MA). The spectrum for each sample was recorded at absorbance mode from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} with 128 scans. X-ray photoelectron spectroscopy (XPS) measurements are performed on an ULTRA (Kratos Analytical) spectrometer using monochromatic Al-Kα radiation (hν = 1486.6 eV) run at 210 W. Before XPS analysis, the samples were dried under vacuum to remove any absorbed water on to hybrid membrane. The spectra were recorded in ultra high vacuum ($<10^{-9}$ Torr) and analyzer having pass energy of 20 eV. The data were collected for a takeoff angle of 60° with respect to the surface normal. No charge neutralization current was applied during the sample analysis. High-resolution XPS spectra for C, O and N elements were collected with pass energy of 20 eV, step size of 0.1 eV, and sweep time of 200 s. The measured binding energies were calibrated with respect to C1s hydrocarbon bond at 284.6 eV. Peak fitting and quantification analysis were performed using the software package Casa XPS to deconvolute the spectral envelopes into their constituent chemical states. Atomic force micrographs (AFM) of Hybrid membranes and CNT mats were acquired using Bruker Dimension FastScan, operated at ambient conditions by use of SiN cantilevers with a spring constant of ca. 20 N/m and a resonance frequency of about 265 kHz. The hybrid composite membranes were cut in to small piece and mounted on 1x1 cm^2 Si wafer using double sided tape. An area of 10x10 μm^2 of the hybrid membranes was scanned three times using tapping mode at scan rate of 1.0 Hz at ambient conditions of temperature and humidity. Nanoscope analysis software V.1.40 was used for processing the AFM data, removing the noise and calculating the roughness values. Scanning electron microscopy (SEM) images were obtained on a Hitachi S-4800 Magellan scanning electron microscope (FEI Company, Hillsboro, OR, USA) operating at a voltage of 10-25 kV. The membrane samples were stick on Aluminum Cambridge stubs using double sided carbon tape and then tightly mounted on flat-based holder. The images were taken at 80000x magnification under high-resolution mode. The surface wettability and contact angle (CA) measurement of the hybrid membranes were measured using Rame-hart model 400-goniometer instrument (Rame-hart Instrument Inc). A sessile drop of ultra-pure water was placed on the surface of hybrid membrane in air at RT and the static contact angle was measured using DROPimage standing software. The water contact angles were calculated using Yong's equation and were obtained by measuring the each sample at five different positions in order to minimize the experimental error. The Transmission Electron Microscopy (TEM) analyses were conducted with Philips/FEI (Morgagni) microscope. A Gatan Digital Camera captured image acquisition and microscope control occurs through the Morgagni user interface and integrated image analysis software. The hybrid membranes were dispersed in water using ultra sonication and TEM samples were prepared by casting on a carbon coated copper grid and vacuumed for an hour. The dynamic light scattering of oil water emulsions and zeta potential analysis of the powdered PDEAEMA grafted CNTs were conducted by using Malvern Zetasizer (Nano ZS 90). The DEAEMA was polymerized on powdered CNT by using surface initiated ATRP. Zeta potential reversibility of hybrid PDEAEMA/CNT composite was dispersed in Millipore water by bubbling with CO_2 for 10 minute followed by bubbling with N_2 for 10 minutes.

2.1. Preparation of oil-in-water emulsions:- Surfactant-stabilized oil-in-water emulsions were prepared by using Tween-80 surfactant. The oil-in-water emulsions of n-n-dodecane/H_2O was prepared by mixing 1mg mL^{-1} of Tween-80 with 2 g of n-dodecane (oil) and followed by sonication of oil and water (v/v=1/100) mixture for 30 minutes and stirring (2500 rpm) for one day and finally diluted to 25 times. The emulsions before use were kept stabilized for 2 hours in laboratory environment. The size of emulsion was measured by dynamic light scattering (Malvern Zen 3600).

2.2. CO_2 responsive Oil-in-water emulsion separation

The separation process was carried out on a vacuum filter assembly apparatus (Figure **4** main text) connected to 250 mL Erlenmeyer flask. A round piece of membrane (area of 4.3 cm^2) was mounted in between supportive glass membrane with epoxy glue and finally the flanges were tightened with spring clamp. Then, 10 mL of dichloromethane (stained with oil red dye) and 1o mL of water (stained with methylene blue dye) were poured into the upper glass tube, the dichloromethane (oil phase) rapidly passed through the membranes while water could not, due to the hydrophobic/oleophilic surfaces (Supporting Information Video I). By contrast, when the water phase was bubbling with CO_2, the water permeation was observed. The water and oil phase flux was calculated based on the average water volume permeating through the PDEAEMA/CNT membranes. Similarly oil-in water emulsion was permeating through the hybrid CNT membranes was studied by pouring the oil-in water emulsion into the upper glass cell and bubbled with CO_2 for the entire experiment. The water permeate flux were calculate based on the average water volume permeating through the membranes.

3.1. Thermo gravimetric analysis (TGA) of membranes:- Thermal behaviors of polymer/CNT hybrid membrane were performed at $10^oC\ min^{-1}$ at N_2 atmosphere. Figure **S2** shows the TGA curves of the CNT mat and PDEAEMA/CNT. The weight loss of pristine CNTs was about 26.5% when the temperature was 600 °C. Here it is worth to note that the manufacturing process for large CNT mat is based on a gas-phase catalytic reaction creating a dense cloud of very long carbon nanotubes probably contains some loosely bound amorphous carbons. The weight loss of CNTs was significantly increased to about 88.2% after modification with PDMAEMA under the same temperature, confirming that polymer was successfully grafted to the CNTs' surface via surface-initiated atom transfer radical polymerizations.

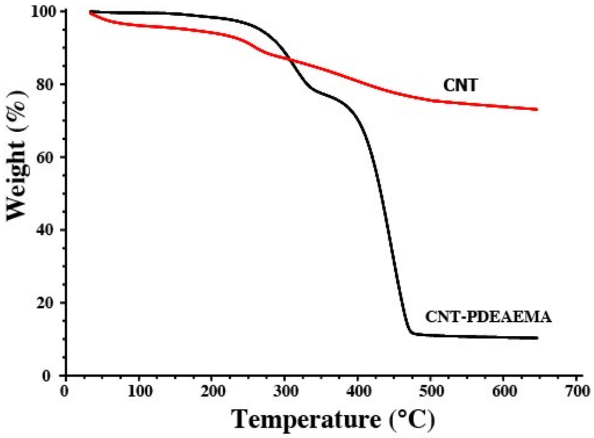

Figure S2: Thermal gravimetric analysis of CNT mat (-) and PDEAEMA/CNT (-) membrane.

3.2. Transmission electron microscopy images of CNTs:- Figure **S3** depicts the TEM image of pristine and PDEAEMA grafted on CNTs. From the TEM morphology analysis, the pristine CNTs (Figure **S3a**) shell is quite shallow. Figure **3Sb** clearly shows the surface grafted CNTs are thicker than pristine one. The average thickness d, of the polymer layer is ~13.8 nm, and about 2-fold of its precursor CNT. These results indicate that the PDEAEMA can be effectively grafted on CNT by surface-initiated atom transfer polymerization and the outcome obtained from TEM effectively accords with that resulting from TGA.

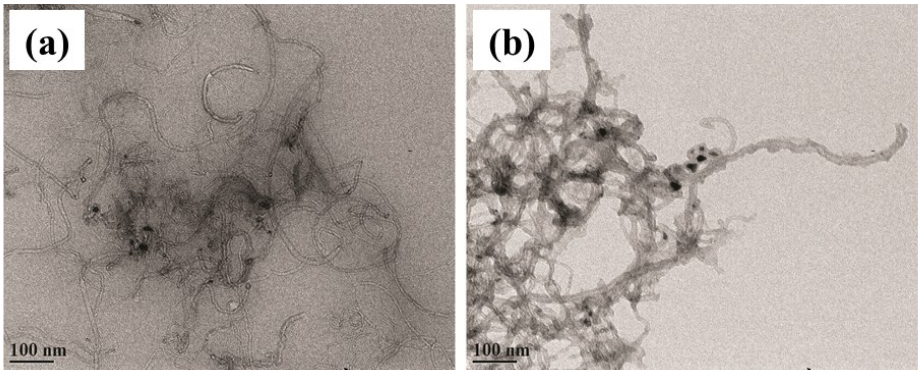

Figure S3: Transmission electron microscope (TEM) analysis of pristine CNT mat (a) and PDEAEMA/CNT membrane (b).

3.3. Raman analysis of hybrid membranes:- Figure **S4** shows the Raman spectra of pristine CNTs, CNT-initiator and PDEAEMA/CNT. After the surface grafting of initiator and PDEAEMA, prominent band at 1580 cm^{-1} (G band) is associated with the vibration of sp^2-bonded carbon atoms (in-plane stretching E_{2g} mode), 1320 cm^{-1} (D band) the disorder mode band which is related to the presence of defects in the CNTs and 1605 cm^{-1} (D′ band). To understand the relative extended of structural defects in the CNT due to surface modification, the intensity ratio of the D and G and (I_D/I_G) were calculated. For the pristine CNTs, this value was found to be 0.30. However, this value increased to 0.47 and 0.71 for the CNT initiator and PDEAEMA/CNTs, membranes respectively. These increments of the I_D/I_G ratio clearly indicated a formation of more defects in the structure of the nanotubes and also an increase in polymer functional groups.

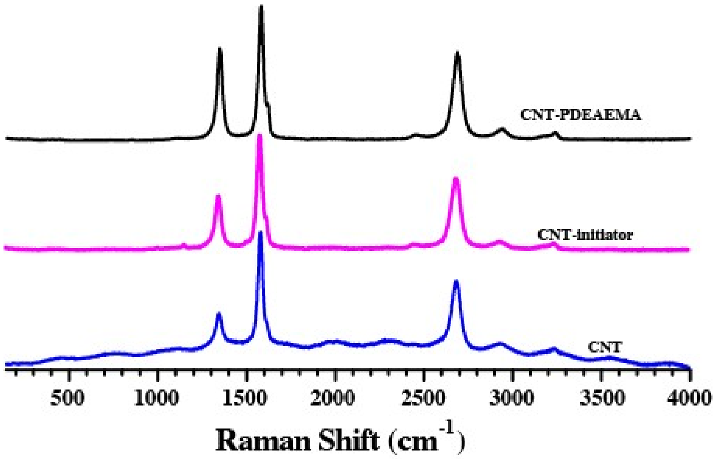

Figure S4:- Raman spectra of CNT mat (-), CNT-initiator (-) and PDEAEMA/CNT (-) membrane.

3.3. X-ray photoelectron spectroscopy (XPS) analysis of hybrid membranes:- The chemical composition and binding energy of the PDEAEMA/CNT membranes were determined from XPS data. Figure **S5** shows that high-resolution XPS spectra for the C 1s peak was at 285 eV, the N 1s peak was at 400 eV, and the O 1s peak was at 532 eV. The Figure **S5a** shows the high-resolution C 1s signals fitted with using Gaussian/Lorentzian curves, which correspond to the aliphatic carbon atoms of the polymer backbone (C-C) at 285 eV, the ester groups (C-C=O) at 285.5 eV, the C-N moieties at 286.6 eV, and the carbonyl (C=O) ester group at 289 eV). The high-resolution N 1s peak corresponds to the tertiary amine group (C-**N**-C) at 399 eV shown in the Figure **S5b**. Finally the high-resolution spectra corresponding to the O 1s carbonyl oxygen at (C=O) 532 eV and carboxyl oxygen (O-C=O) at 534 eV are shown in the Figure **S5c**.

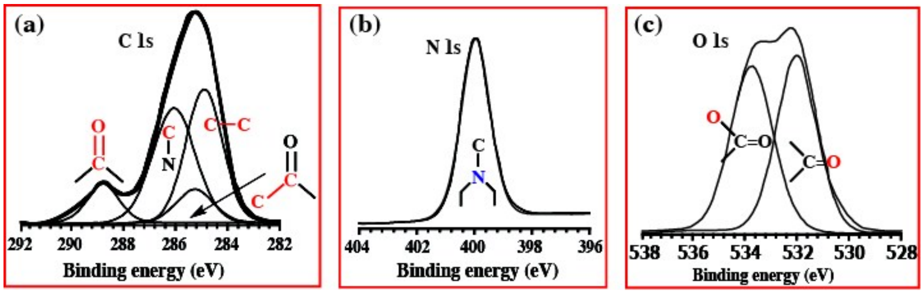

Figure S5: High-resolution X-ray photoelectron spectroscopy spectra of the PDEAEMA/CNT membranes (a) C1s, (b) N1s and (c) O1s.

3.4. Zeta potential analysis and reversible transition of PDEAEMA/CNT upon bubbling with CO_2 and N_2:-

Figure S6 depicts the reversible transitions of PDEAEMA/CNT powder dispersion on bubbling with CO_2 and N_2 for 10 minutes. In Figure **S6a**, the PDEAEMA grafted on powdered CNTs initially exhibited a negative ~-24 mV at the initial condition due to the partial hydrolysis of diethylaminoethyl group. Upon bubbling of CO_2, the zeta potential changed to ~+33 mV (Figure **S6b**), indicating the carbamate structure was formed.

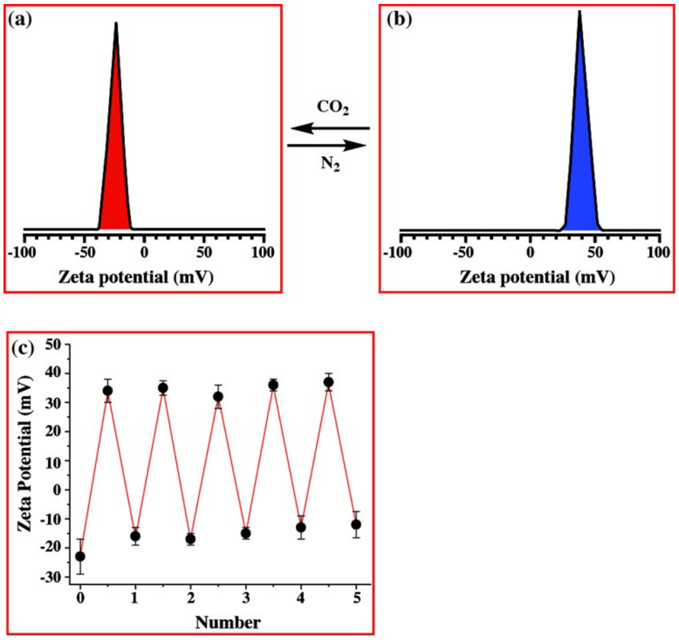

Figure S6: Zeta potential analysis of powdered PDEAEMA/CNTs on bubbling with CO_2 (a) N_2 (b), and zeta potential change during several CO_2/N_2 cycles (c).