

Supporting Information

Two-way CO₂-responsive dispersions of carbon nanotubes in water

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Experimental section

Materials

All materials were used as received unless otherwise stated. Multi-walled carbon nanotubes (CNTs) of 10-20 nm in diameter and 5-15 μm in length was supplied by Taiwan Conjutek Corp. and used as received. 2-(Dimethylamino)ethyl methacrylate (DMAEMA, 97%) purchased from Alfa Aesar and *N,N,N',N'',N''*-pentamethyl diethylene triamine (PMDETA, > 98 %) purchased from Acros Organics were purified by vacuum distillation before use. Methyl α-bromoisobutyrate (MBIB, > 99%), copper (I) bromide powder (CuBr, 99.999%), deuterium oxide (D₂O, 99.9% D), and ethanol (HPLC grade) were purchased from Sigma-Aldrich. The 40% w/w sodium deuterioxide solution in D₂O (NaOD, 99.5% D) was purchased from Alfa Aesar and deuterated chloroform (CDCl₃, 99.8% D) was purchased from Acros Organics. Iodomethane (CH₃I, > 95 %) was purchased from SHOWA. Tetrahydrofuran (THF, 99.5%) was purchased from J. T. Baker. n-Hexane (HPLC grade) was purchased from Duksan Reagents. Sodium hydroxide pellets (NaOH, ≥ 97 %) were purchased from UniRegion. 37 % Hydrochloric acid aqueous solution (HCl) was purchased from Honeywell FLUKA. Dialysis membranes with a molecular weight cut-off of 3,500 or 6,000-8,000 g/mol were purchased from Membrane Filtration Products Inc.

Instrumentation and Characterizations

¹H Nuclear Magnetic Resonance (¹H NMR)

Proton NMR spectra were recorded at 25 °C on a JEOL ECZ600R (600 MHz) spectrometer. For the measurements, PDMAEMA sample (10~20 mg) was dissolved in CDCl₃ (0.8~1 mL), qPDMAEMA sample (10~20 mg) was dissolved in D₂O (0.8~1 mL), and PMAA sample (10~20 mg) was dissolved in D₂O (0.8~1 mL). All chemical shifts are reported in ppm (δ).

Fourier Transform Infrared Spectroscopy (FT-IR)

FT-IR spectra were recorded using a Perkin Elmer Spectrum Two spectrometer in the mid-infrared range ($4000 - 1000 \text{ cm}^{-1}$) at room temperature. The number of scans was set at 16, and the resolution was 2 cm^{-1} . PDMAEMA sample was obtained via casting from the acetone solution onto a KBr disk. qPDMAEMA and PMAA samples were obtained via casting from the deionized water onto CaF_2 disks. CNT-g-PDMAEMA, CNT-g-qPDMAEMA, and CNT-g-PMAA samples were obtained by grounding with KBr powders and made into disks. All samples were dried under vacuum at $60 \text{ }^\circ\text{C}$ for 24 h prior to the measurements.

Thermogravimetric Analysis (TGA)

The amounts of grafting of CNT-g-PDMAEMA-*h* and CNT-g-PDMAEMA-*l* were determined by subtraction of the residual weights of CNT-g-PDMAEMA-*h* and CNT-g-PDMAEMA-*l* at $550 \text{ }^\circ\text{C}$ from that of pure CNT at $550 \text{ }^\circ\text{C}$ as heated in a TA Instruments SDT-Q600 thermogravimetric analyzer at $20 \text{ }^\circ\text{C}/\text{min}$ from 30 to $800 \text{ }^\circ\text{C}$ in N_2 .

Raman spectrometry

Raman spectrometer (i-Raman plus, B&W TEK) was used to examine D band at near 1350 cm^{-1} to characterize carbons with sp^3 hybrid structure or defective carbons with sp^2 hybrid structure and G band at near 1580 cm^{-1} to characterize carbons with graphitic sp^2 hybrid structure in CNT-g-PDMAEMA. The ratio of the intensities of D and G bands (i.e., I_D/I_G) was used to indicate the content of defect structure on the nanotube sample.

Field emission scanning electron microscopy (FESEM)

Field emission scanning electron microscopy (FESEM; Hitachi S-4800) was used to examine the morphology of CNT, CNT-g-PDMAEMA, and CNT-g-PMAA powders. These powders were placed on a copper tape attached to the special metal stage using a carbon tape. The specimen was sputtered with gold to increase electrical conductivity before SEM measurements at 3 kV. SEM was also used to examine the morphology of CNT-g-PMAA cast films from 0.01 wt% aqueous solutions of pH 4, 7, and 10.

Electron spectroscopy for chemical analysis (ESCA)

Electron spectroscopy for chemical analysis (ESCA, PHI 5000 VersaProbe, ULVAC-PHI) or X-ray photoelectron spectroscopy (XPS) was used to characterize elemental identity, chemical state and quantity of an element on surface of CNT, CNT-

g-PDMAEMA, and CNT-*g*-PMAA.

Results and discussion

3-1 Characterization of PDMAEMA, qPDMAEMA and PMAA

$^1\text{H-NMR}$ spectroscopy was used to characterize PDMAEMA, qPDMAEMA and PMAA; recorded spectra are shown in Figure S1. From Figure S1a for PDMAEMA, the peaks at 2.34, 2.6, and 4.06 ppm correspond to N-CH₃, N-CH₂, and O-CH₂ in the side group, respectively. The integrated areas of the 1.25 ppm peak for C-CH₃ in MBIB and the 2.6 ppm peak for N-CH₂ and the 4.06 ppm peak for O-CH₂ in side group of PDMAEMA were used to calculate molecular weights of PDMAEMA being 15,600 g/mol for PDMAEMA-*h* and 5200 g/mol for PDMAEMA-*l*. These calculated molecular weights were consistently close to the theoretical values. From Figure S1b for qPDMAEMA, due to quaternization of the tertiary amine, the peaks for N-CH₂, O-CH₂, and N-CH₃ have shifted to downfield. In the spectra for PMAA (Figure S1c), the peaks at 0.91~1.04 ppm and 1.8~1.93 ppm correspond to C-CH₃ and C-CH₂ in the backbone of PMAA, respectively.

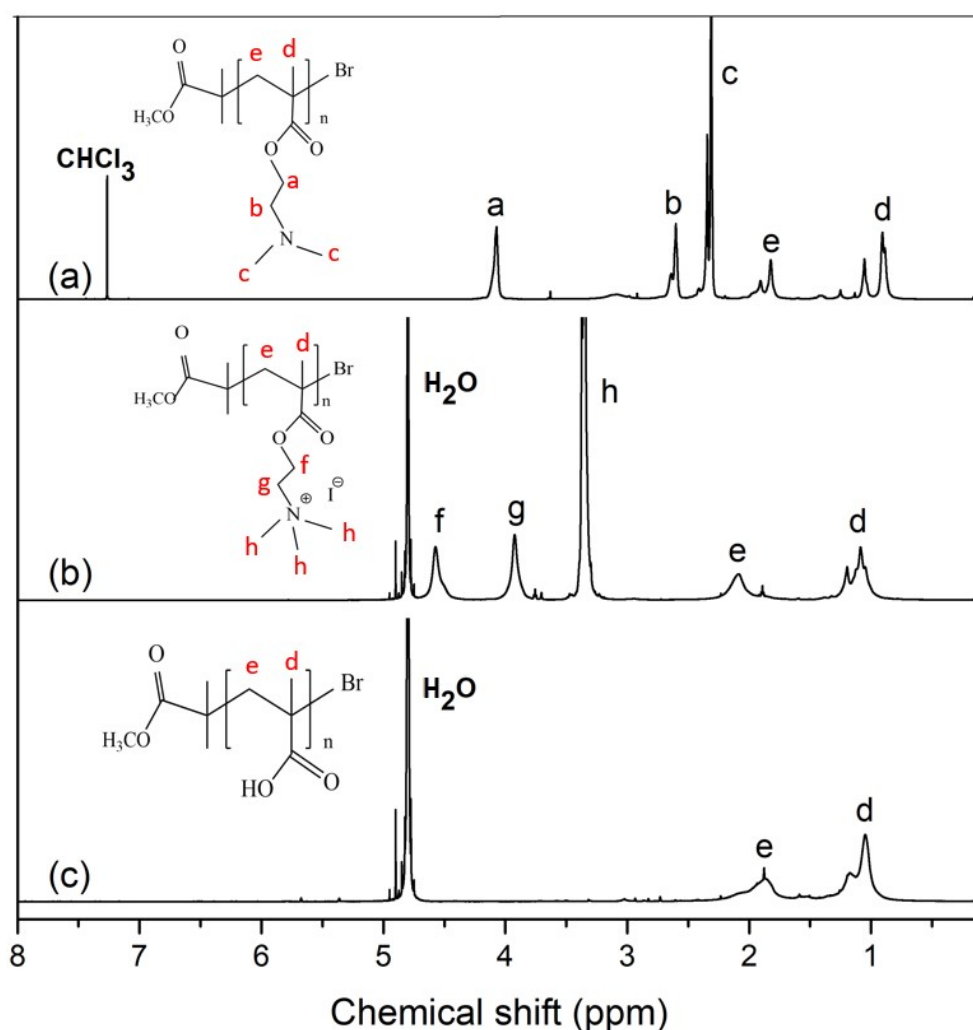


Figure S1 $^1\text{H-NMR}$ spectra of (a) PDMAEMA in CDCl_3 , (b) qPDMAEMA and (c) PMAA in D_2O .

FTIR spectra were used to characterize PDMAEMA before and after quaternization and hydrolysis. Figure S2a shows characteristic peaks at 2768 and 2830 cm^{-1} for CH_3 stretching in $\text{N}-(\text{CH}_3)_2$ of PDMAEMA and 1720 cm^{-1} for $\text{C}=\text{O}$ stretching in COO of PDMAEMA. The characteristic peaks of PDMAEMA (2768 and 2830 cm^{-1}) disappear in quaternized sample (qPDMAEMA) as can be seen in Figure S2b. Due to the presence of strongly hydrophilic quaternary ammonium cations in qPDMAEMA, the adsorbed moisture gives OH absorption at near 3455 cm^{-1} in spectrum of qPDMAEMA. After hydrolysis, a broad peak for the OH stretching appears in the range of 2500~3500 cm^{-1} in the spectrum of PMAA in Figure S2c.

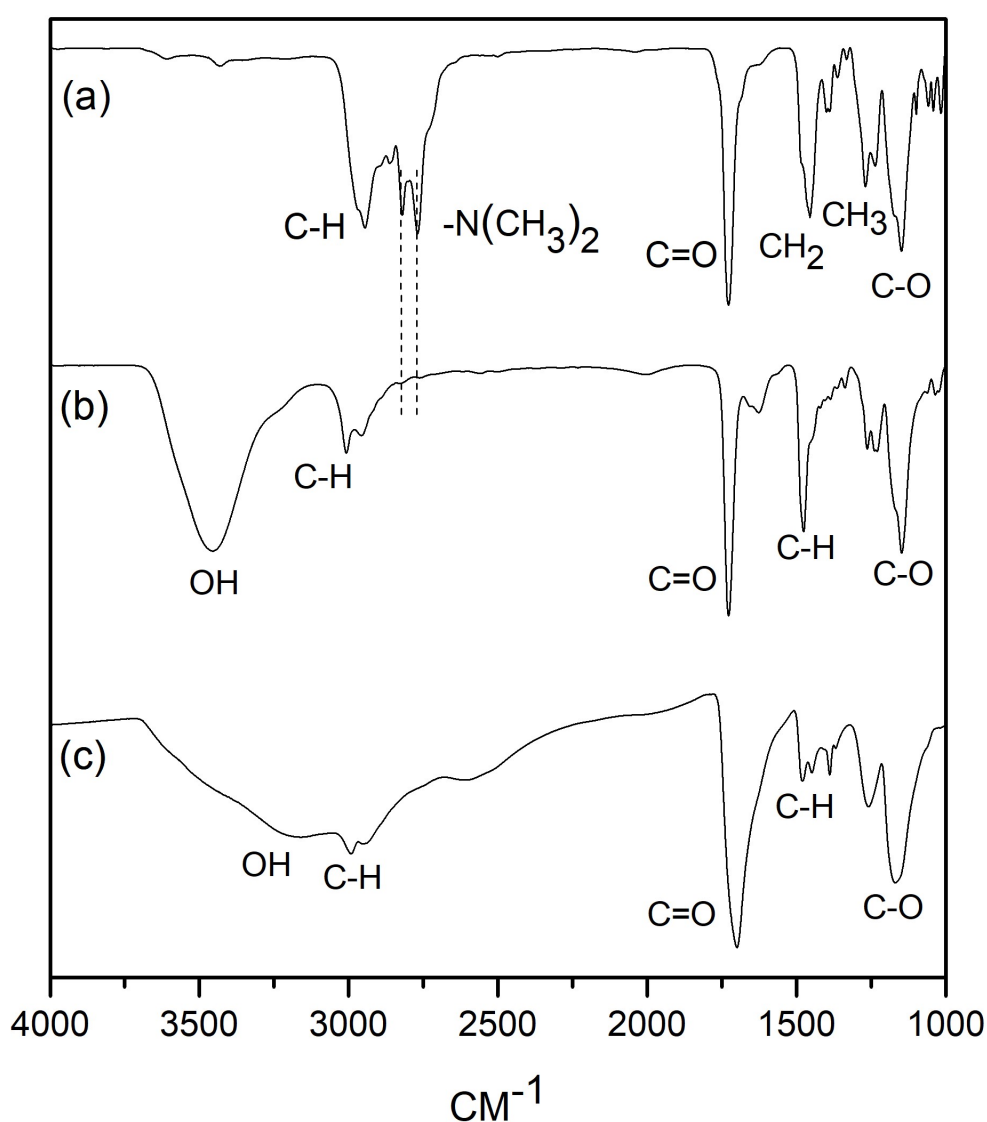


Figure S2 FT-IR spectra of (a) PDMAEMA, (b) qPDMAEMA, and (c) PMAA.

3-2 Characterizations of CNT-g-PDMAEMA, CNT-g-PDMAEMA and CNT-g-PMAA

To further support TGA data, Raman spectroscopical analysis was performed. Recorded Raman spectra of CNT, CNT-g-PDMAEMA-*h*, and CNT-g-PDMAEMA-*l* are displayed in Figure S3. A ratio of intensity of D band (1350 cm^{-1}) and G band (1580 cm^{-1}) (i.e., I_D/I_G) was used to evaluate a level of CNTs structural defects for each sample. An increase in the I_D/I_G ratio indicates a higher number of defects occurring due to the disruption of sp^2 hybridized graphitic carbon atoms vibrations. Expectedly, pristine CNTs had the least defected structure with the I_D/I_G ratio of 0.84, whereas CNTs with PDMAEMA-*l* and PDMAEMA-*h* attached to the surface displayed the I_D/I_G ratios of 0.90 and 0.92, respectively (Table S1). It is evident that the polymer grafting treatments damaged the graphitic structure of CNTs, which lead to the formation of sp^3 bonded carbon atoms and/or non-graphitic sp^2 hybrid structures.

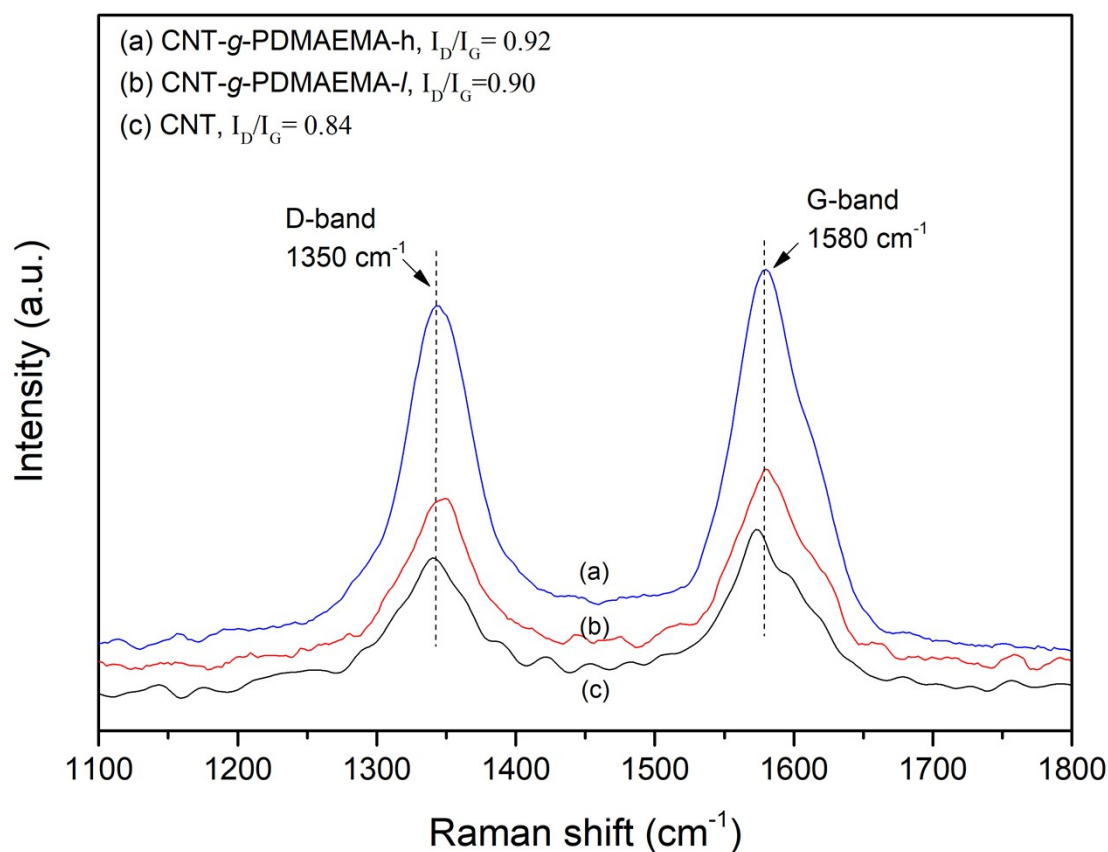


Figure S3 Raman spectra of (a) CNT-g-PDMAEMA-*h*, (b) CNT-g-PDMAEMA-*l*, and (c) CNTs.