Supplementary material (ESI) for Journal of Materials Chemistry

Supporting Information:

Microcapsules Containing Suspensions of Carbon Nanotubes

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Experimental Procedures

Chlorobenzene, ethyl phenylacetate, single-walled carbon nanotubes (50-70% carbon basis, diam. × L 1.2-1.5 nm × 2-5 μm, bundle dimensions), formaldehyde solution, resorcinol were purchased and used as-received from Sigma-Aldrich. Urea and ammonium chloride were obtained from Fisher Chemicals. ZeMac® ethylene-maleic anhydride (EMA) copolymer was donated by Vertellus® (formerly Zeeland Chemicals), and mixed with deionized water to produce a 2.5 wt% surfactant solution. Silicon wafers (2" in diameter, 228-330 nm thick, resistivity: 0.001 – 100, P/Boron type <100> orientation) were purchased from Montco Silicon Technologies.

The *in situ* polymerization method for encapsulation of hydrophobic solutions[1-4] was modified to encapsulate SWNTs. Briefly, a core solution consisting of 60 mL solvent (PhCl or EPA) and 30 mg CNTs (SWNTs) was sonicated for 30 minutes using a Fisher Scientific Mechanical Ultrasonic Cleaner (FS20, without heater) that operates at 40 Hz. Pictures in Figure S1 show the increased dispersion of the SWNTs in EPA initially (S1a) and after sonication (S1b). This solution was added to a stirring mixture of 100 mL deionized H_2O, 25 mL EMA, 2.5 g urea, 0.25 g ammonium chloride, 0.25 g resorcinol at a pH of 3.5 in a 600 mL beaker. The concentration of SWNTs was changed in the core solution by adding 15, 45, or 60 mg to 60 mL EPA in place of 0.5 mg/mL CNTs in EPA. After the emulsion stabilized for 10 minutes, 6.33 g formalin (37 w/v% formaldehyde) was added to the beaker and the reaction stirred for 4 h at 55C. The

resulting capsules were washed with water and dried by vacuum filtration for 2 days. Figure S1c is an actual image of the resulting 0.05 wt% SWNT in EPA microcapsules.

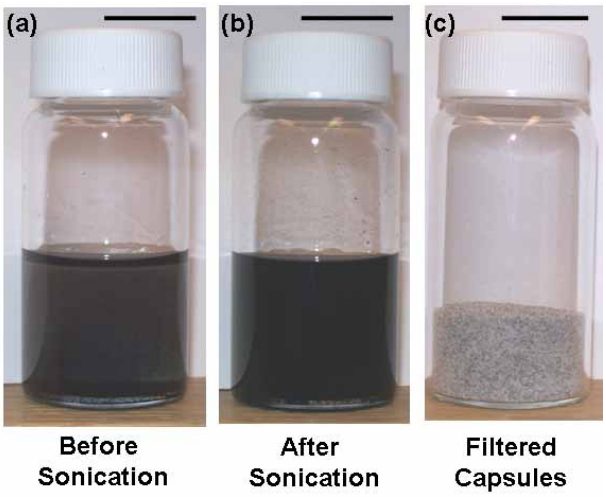

Figure S1. Photographs of vials containing CNT suspensions before (a), and after sonication (b), as well as dried, filtered microcapsules (c).

Capsule diameters were determined through optical microscopy using a Leica DMR Optical Microscope at various magnifications. ImageJ software was used measure the diameters and an average of 100 capsules were used to determine the size distribution. Capsules were also imaged using an environmental scanning electron microscope (ESEM). A Philips XL30 ESEM-FEG instrument was used after sputter-coating the sample with a gold-palladium source. The released CNT suspensions were prepared by rupturing the microcapsules on a silicon wafer mounted on top of a carbon tape-coated stage, sputter-coated, and then imaged by SEM. Transmission electron microscopy (TEM) was performed using a Philips CM200 instrument with an operating voltage of 120 kV. The solutions containing CNTs were mounted onto carbon-coated copper grids (Ted Pella, Inc.). To determine the thermal stability of the microcapsules, thermogravimetric analysis (TGA) was performed on a Mettler-Toledo TGA851^{e}

instrument, calibrated by indium, aluminum and zinc standards. The mass loss was recorded during a heating cycle over the temperature range of 25˚C to 650˚C at a constant rate of 10˚C/min in an atmosphere of nitrogen. For each experiment, approximately 2-5 mg of sample was accurately weighed (± 0.02 mg) into an alumina crucible.

To prepare the solutions for conductivity measurements, 0.1 g of microcapsules were added to 1 mL of the respective core solvent (EPA or PhCl) in a 20 mL scintillation vial. For the "destructive" method of mixing, the vials were stirred with a magnetic stir bar for 30 minutes. For the "non-destructive" method of mixing, the vials were agitated with a vortex mixer for 30 minutes. To demonstrate the conductivity of CNTs in solution, 2 drops of each suspension were pipetted onto a glass slide from the vials and the current was measured using a two-point measurement technique at a Signatone table-top probe station customized with a standard S725 manipulator (see Figure S2). The voltage was swept from -50V to +50V continuously 5-7 times for each solution using an Agilent 4155C Semiconductor Parameter Analyzer. This same method was used to analyze the control solutions containing SWNT in EPA and PhCl (0.05 wt% SWNT, or 1.0 mg in 2.0 mL solvent) as a comparison and their conductivities were recorded at +50 V.

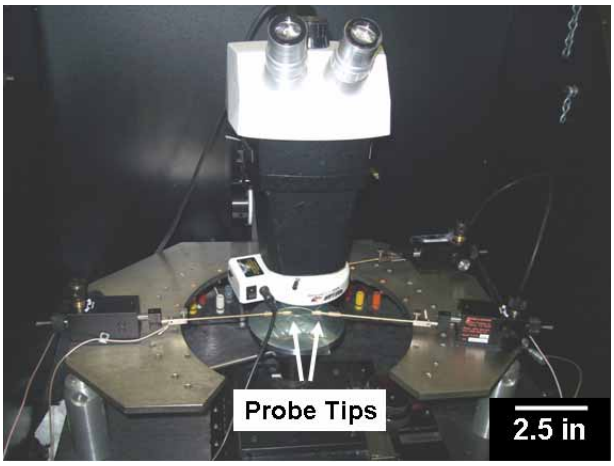

Figure S2. Experimental setup for conductivity measurements at a table-top probe station.

Additional Figures

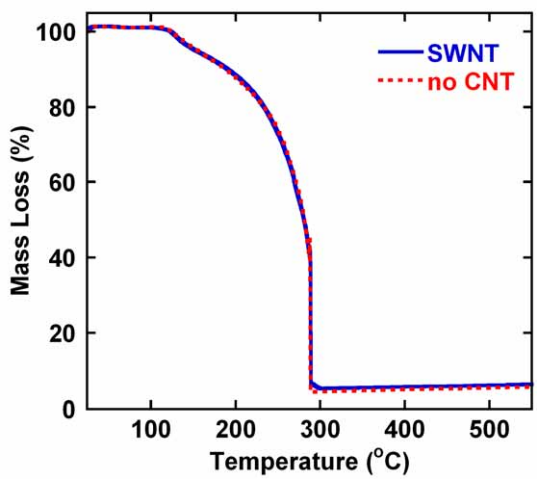

Figure S3. TGA scans of microcapsules containing 0.05 wt% CNTs in EPA and pure EPA (no CNT).

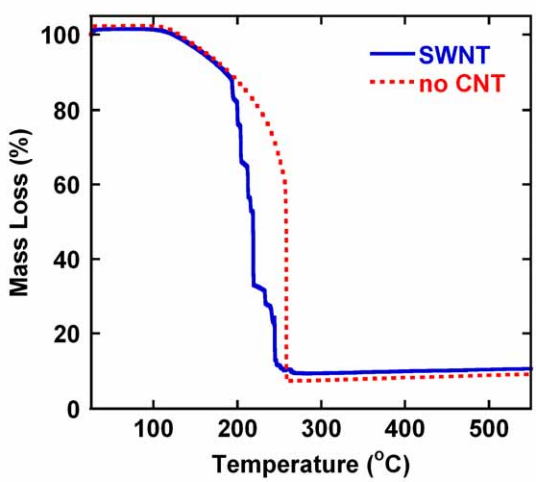

Figure S4. TGA scans of microcapsules containing 0.05 wt% CNTs in PhCl and pure PhCl (no CNT).

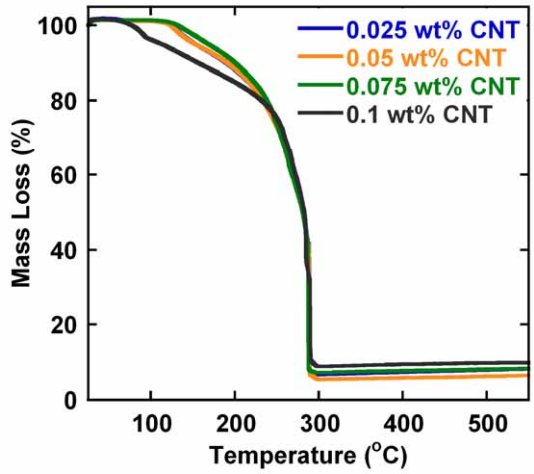

Figure S5. TGA scans of microcapsules containing various weight fractions of CNTs in EPA.

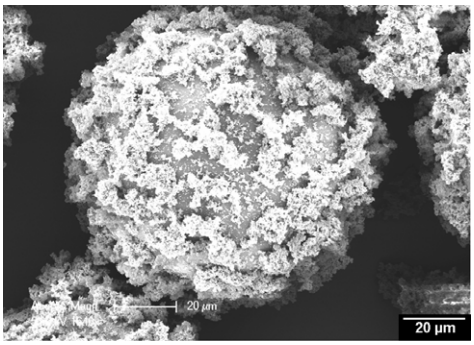

Figure S6. SEM of microcapsule containing SWNTs in PhCl prepared with *in situ* polymerization method[1] showing excess wall material.

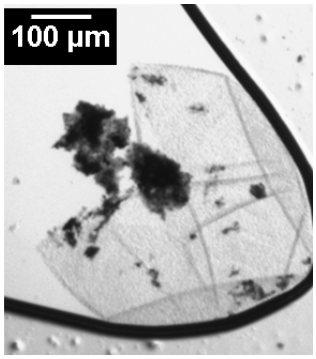

Figure S7. Optical micrograph of ruptured capsule containing a SWNT-EPA suspension (0.05 wt%) on a glass slide showing the released liquid and CNT bundles.

References

(1) Brown, E. N.; Kessler, M. R.; Sottos, N. R.; White, S. R. *J. Microencapsulation* **2003**, *20*, 719-730.
(2) Caruso, M. M.; Delafuente, D. A.; Ho, V.; Sottos, N. R.; Moore, J. S.; White, S. R. *Macromolecules* **2007**, *40*, 8830-8832.
(3) Caruso, M. M.; Blaiszik, B. J.; White, S. R.; Sottos, N. R.; Moore, J. S. *Advanced Functional Materials* **2008**, *18*, 1898-1904.
(4) Blaiszik, B. J.; Caruso, M. M.; McIlroy, D. A.; Moore, J. S.; White, S. R.; Sottos, N. R. *Polymer* **2009**, *50*, 990-997.