Electronic Supplementary Material (ESI) for RSC Advances

Supplementary Information - Creating Supersolvophobic Nanocomposite Materials

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Experimental Section

Preparation of free-standing polymer films: Both polysulfone (PSF) and polyimide powders were dissolved in tetrahydrofuran (THF) and drop-casted onto glass slides. To control the rate of evaporation, an inverted funnel was placed on top of the slide, and left overnight at room temperature. When making N-methylpyrrolidone (NMP)-based films, solutions were drop-casted on slides and left overnight at 100^{o}C in a vacuum oven.

CNT growth conditions: Multi-walled carbon nanotubes (MWNTs) were synthesized via floating catalyst aerosol-assisted chemical vapor deposition onto silicon substrates with a 100 nm oxide layer. The synthesis procedure and apparatus is similar to that published elsewhere [12,13,14]. The substrates were placed within a 46 mm I.D. quartz tube furnace (30 cm heating zone) and brought to a temperature of 800 ºC in an inert environment and atmospheric pressure conditions. The precursor solution was prepared using toluene (Aldrich, ≥ 99.9%) and ferrocene (Alpha Aesar, 99%) at a concentration of 60 mg mL^{-1}. During growth, the argon carrier gas flow rate was set to 4.00 L min^{-1} which carried the precursor solution into the reactor in the form of an aerosol generated at a feed rate of 0.8 ml min^{-1} using a 2.4 MHz ultrasonic generator device (Model 241PGT by Sonaer Ultrasonics Inc., Farmingdale, NY).

Perfluoro-functionalization of CNTs and spray-painting on substrates: Carbon nanotubes were functionalized by combining 1 mL of perfluorosulfonic acid-PTFE copolymer solution (5%

w/w, Alfa Aesar) with 50 mg of pristine multi-walled nanotubes (MWNTs) in ethanol. The mixture was bath sonicated for 2 hours, followed by tip sonication for 5 minutes. All spraying procedures were carried out using an airbrush spray gun (Deluxe Airbrush Kit, Central Pneumatic). No vacuum drying was required due to the volatile nature of ethanol.

Isolation of functionalized CNTs and fabrication of composite, supersolvophobic films: The CNT ink described above was vacuum filtered using a 0.45 μm Fluoropore membrane to isolate perfluoro-functionalized CNTs which showed super-solvophobicity in the solid state. These were mixed with 5 – 12 wt% solutions of either PSF or polyimide in solvent (THF or NMP) and bath-sonicated overnight to form composite solutions. These solutions were drop-casted on a substrate. Free-standing films were obtained by drop-casting on glass substrates, followed by immersing in a water bath, which resulted in films that were readily removable from the substrate. For comparison, identical procedures were followed to prepare composite films comprising of PTFE-PSF and PTFE-polyimide.

Characterization: Scanning electron microscopy (SEM) images were obtained on a high-resolution field-emission scanning electron microscope (FEI Quanta 400) and solid fCNTs were used directly for X-ray photoelectron spectroscopy (XPS, PHI Quantera). Contact angle measurements were performed at laboratory conditions using the standard sessile drop technique. 5 drops of solvent were measured at different places on the film and the average value is reported. The contact angles of both de-ionized water and 30 wt% monoethanolamine (MEA) were measured to characterize the surfaces. For all experiments, 99% purity MEA was used.

Additional Characterization

Additional SEM and XPS of both PSF-fCNT and Polyimide-fCNT composites have been presented in Figures S1 and S2.

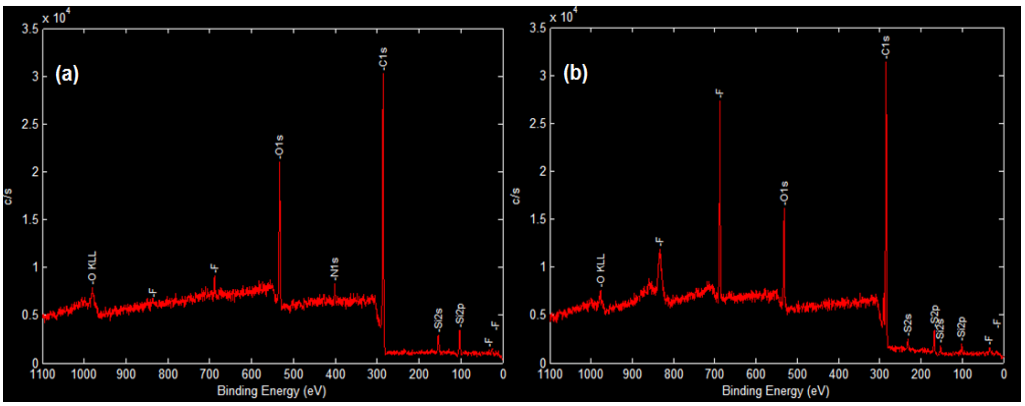

Figure S1| XPS Spectra of composite films. Survey scans show characteristic carbon, fluorine and oxygen peaks in both polyimde (a) and PSF (b) based composite films. Evaluating the actual atomic % of each element is challenging, but the presence of fluorine along with carbon is similar to that observed for pristine perfluoro-fucntionalized carbon nanotubes.

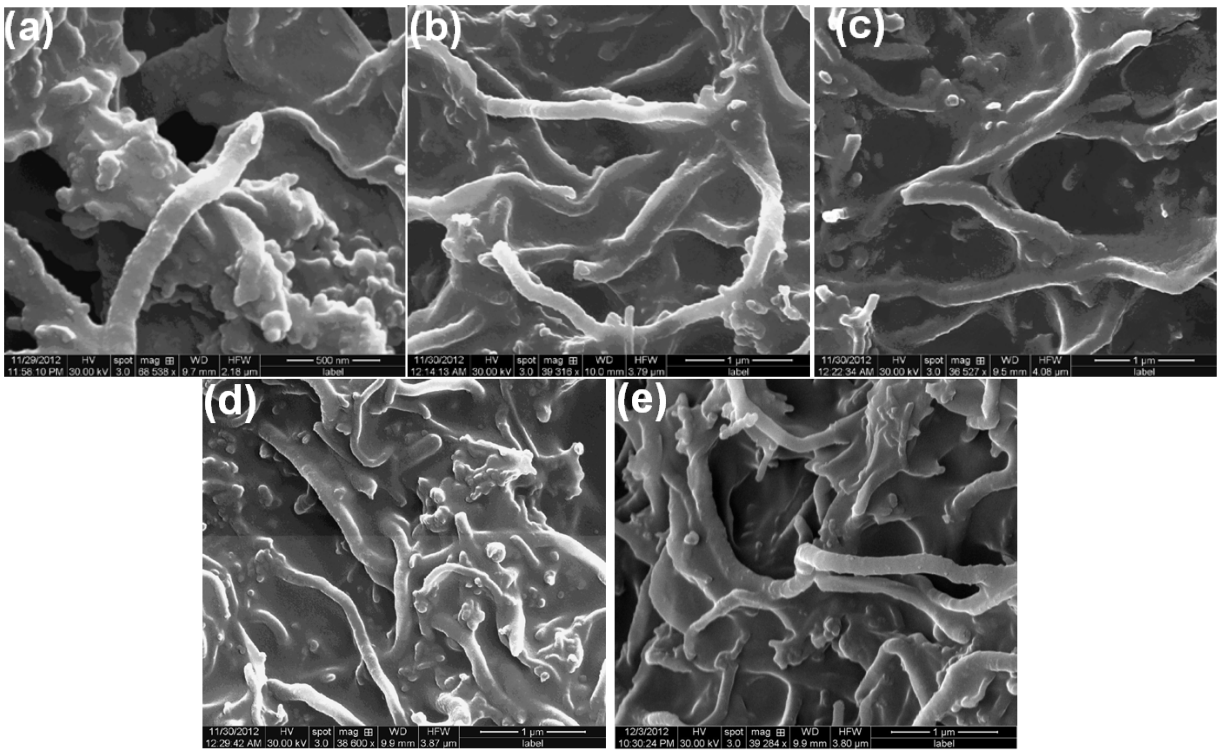

Figure S2| Additional SEM of composite films. A closer look at the SEM of composite films confirm dispersion of fCNTs inside the polymer matrix which is responsible for intrinsic supersolvophobicity. PSF-fCNT composites of ratios 2:1, 6:1 and 8:1 (a, b, c) and polyimide-fCNT composites of ratios 3:1 and 5:1 (d, e) are shown above.