

## ARTICLES

## Dissolution of Pristine Single Walled Carbon Nanotubes in Superacids by Direct Protonation

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Strong tube–tube van der Waal attractions that hinder the dissolution of single walled carbon nanotubes (SWNTs) as individuals have been overcome by the direct protonation of the tubes by superacids. The pristine nanotubes disperse as individuals in 100% H<sub>2</sub>SO<sub>4</sub>, oleum, trifluoromethanesulfonic acid, and chlorosulfonic acid to varying solubility levels. Optically homogeneous solutions with concentration as high as 45 g/L (2.5 wt %) at room temperature have been observed in the case of chlorosulfonic acid, the strongest among the series of superacids investigated. A dissolution model is proposed wherein the solubilized tubes exist as protonated polycarbocations, charge balanced by corresponding conjugate base anions. The removal of electrons from the SWNT, leading to a fractional positive charge on the carbons in the protonated state, is reversible upon deprotonation. With increasing concentration of the solubilized nanotubes, anion-mediated attractions at lower concentrations and spatial constraints at high concentrations guide the transformation of the SWNT–acid system into a nematic mesophase. Highly anisotropic, nematic mesophases formed in the dissolution process are promising precursors for the fabrication of macroscopic forms of SWNTs with high alignment of the carbon nanotubes.

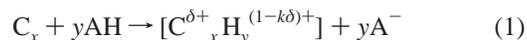
## Introduction

Solubilization of pristine single walled carbon nanotubes (SWNTs) as individual molecular entities remains the single largest obstacle to the realization of their application potential.<sup>1–3</sup> Various attempts<sup>4,5</sup> to disperse the SWNTs as individuals have centered on the covalent derivatization of the tube side wall with suitable organic modifier groups. While the derivatization approach is successful in solubilizing the SWNT, interesting electronic and optical properties of the SWNT are lost with extensive derivatization. Although surfactant-assisted suspensions preserve the electronic structure of the singly suspended pristine carbon nanotube,<sup>6</sup> the concentrations are low and the surfactant often remains as an impurity in downstream processes. A high cohesive energy of more than 0.5 eV/nm arising from tube–tube van der Waal interactions,<sup>7</sup> coupled with the larger *L/D* ratio (ca. 1000) of the SWNT, is a formidable force to overcome for any solvent.

Our preliminary investigations<sup>8</sup> on the solubility of SWNT in superacids have shown evidence for the dissolution of SWNT in higher concentrations and the formation of intrinsically aligned nematic-like phases in superacids, generically the group

of acids with acidity higher than 100% sulfuric acid. The dissolution behavior of conformationally analogous stiff-chain polymers in superacids is enhanced by the presence of nitrogen- or oxygen-containing groups on the polymeric backbone serving as specific centers for protonation.<sup>9,10</sup> Since pristine single walled carbon nanotubes lack such specificity, it is not clear if the superacids will exhibit the same solvation behavior as in the case of conventional rod-like polymers. However, the amphoteric nature of carbon nanotubes suggests that they will behave as a weak base and be protonated, directly resulting in the delocalization of positive charge over the entire nanotube.

The process leading to the formation of a polycarbocation can be viewed as



where  $k = x/y$  and  $\delta$  is the fractional positive charge carried by each carbon atom. The formation and stability of the polycarbocation is dependent on the stability of the conjugate base anion, A<sup>−</sup>. This is a significant difference, compared to the conventional rigid rod polymeric molecules which have very specific localized sites for protonation. In this paper, we address the dissolution of single walled carbon nanotubes in superacids such as 100% sulfuric acid, oleum (20% free SO<sub>3</sub>), methanesulfonic acid, trifluoromethanesulfonic acid (triflic acid), and chlorosulfonic acid.

We report here the solubilization of SWNT in significant quantities (up to ~45 g/L) in chlorosulfonic acid. Dispersion

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of rigid rod-like carbon nanotubes in superacids at high concentrations predictably leads to molecular level spatial constraints<sup>11</sup> resulting in the percolation of the tubes followed by the formation of an anisotropic nematic mesophase. This paper presents the results of an experimental investigation addressing the nature of solvation, intertubular interactions, and the spontaneous intrinsic alignment of the SWNT, studied by UV-vis-NIR absorption spectroscopy, polarized light microscopy, laser Raman spectroscopy, and scanning electron microscopy.

### Experimental Section

Single walled carbon nanotubes produced by the HiPco process<sup>12</sup> were purified by a process described elsewhere,<sup>13</sup> finely ground with a mortar and pestle, and dried under vacuum at 110 °C. Dilute solutions for UV-vis-NIR absorption spectroscopy were made by dispersing about one milligram of the dry SWNT in 10 mL of the appropriate acid at room temperature. A few drops of the resulting dark solutions were transferred to a quartz cell and diluted further with the acid to adjust the optical density to obtain a light colored solution. UV-vis-NIR absorption spectra of the dilute solutions of SWNT-superacid dilute solutions were recorded with a Shimadzu UV3101PC spectrophotometer. The corresponding pure acids were used as a baseline reference.

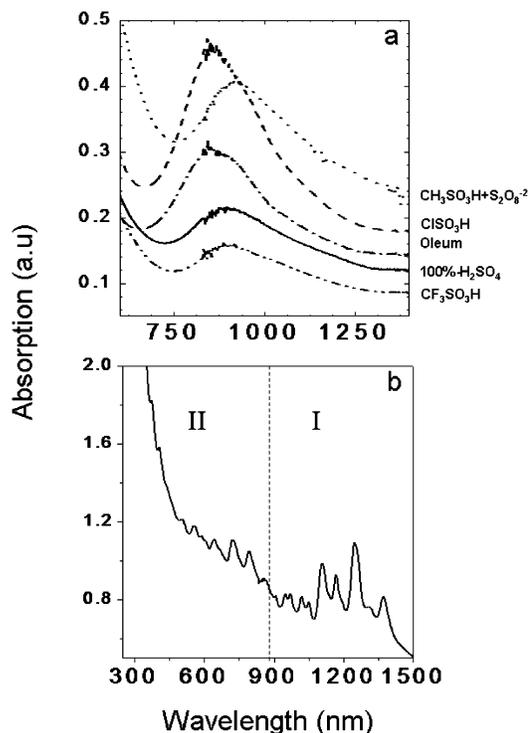
Higher concentration solutions of SWNTs in superacids (up to 4 wt %) were prepared for microscopic examination in a custom-designed all glass mechanical mixer with Teflon seals running under a blanket of argon and then were hermetically sealed between a dry microscopic slide and a glass cover slip. The samples were examined by polarized Raman spectroscopy in the reflection geometry employing a Renishaw micro-Raman spectrometer. Two different lasers of wavelengths respectively at 513 nm ( $\text{Ar}^+$  ion) and 780 nm (diode) were used as exciting sources.

The samples were also examined by polarized light microscopy in the differential interference contrast (DIC) mode employing a Zeiss polarized light microscope equipped with an oil immersion objective (63X, 1.4 NA), a rotatable sample holder mounted between the polarizer and analyzer, and a piezo motor. Scanning electron microscopy (SEM) of the coagulated solids was carried out employing a Philips Electroscan XL30 environmental scanning electron microscope.

### Results and Discussions

The room temperature solubility of SWNTs in 100% sulfuric acid, oleum, and triflic acid was limited compared to the immediate and quantitative dissolution of SWNTs in chlorosulfonic acid. Solutions ranging in color from golden yellow to pale brown were obtained in each case, except for methanesulfonic acid in which SWNTs were found to be insoluble even after prolonged sonication. However, the SWNTs could be readily dispersed at room temperature and a colored solution obtained in methanesulfonic acid in the presence of potassium persulfate (500 mg in 10 mL of methane sulfonic acid).

Figure 1 (a) shows the UV-vis-NIR absorption spectra of dilute solutions of pristine SWNTs in various superacids in the 500–1400 nm range. The spectra are characterized by a broad absorption ranging from 700 to 1100 nm. Chlorosulfonic acid and oleum registered maximum absorptions at 855 nm and 852 nm, respectively. The triflic acid and 100% sulfuric acid showed maximum absorptions at 900 nm and 895 nm, respectively, whereas the solution of SWNTs in methanesulfonic acid-persulfate solution showed a maximum absorption at 925 nm. The UV-vis-NIR absorption spectra of an SDS aided suspen-

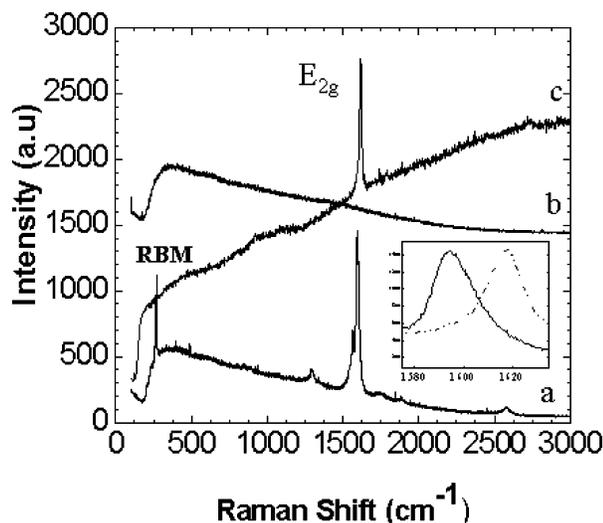


**Figure 1.** UV-vis-NIR absorption spectra of (a) dilute solutions of pristine SWNTs in various superacids; (b) a surfactant aided aqueous suspension of pristine SWNTs. The first and the second van Hove transition regions are marked accordingly. The dotted vertical line is the approximate region where the division is observed.

sion of pristine SWNTs in water<sup>6</sup> is given in Figure 1b for comparison. The first van Hove features arising from transitions involving the  $v_1 \rightarrow c_1$  transitions of the SWNT (marked as I in Figure 1b) are sensitive to adsorption of any species on the surface of the nanotube, whereas the second van Hove transitions arising from deeper lying  $v_2$  states (marked as II in Figure 1b) are less sensitive to the chemical environment of the nanotube.

When compared to the spectra of the SWNTs in SDS,<sup>6</sup> the broad absorption feature observed in the case of superacid solutions does not appear to originate from a possible shifting of the interband transitions. Rather, they appear to arise from a charge-transfer process similar to a broad charge-transfer band at 1.07 eV (1158 nm) observed in the case of SWNTs solubilized in carbon disulfide<sup>14</sup> or when doped with  $\text{Br}_2$ .<sup>15</sup> Also, in comparison with the reported UV-vis-NIR absorption spectra of  $\text{C}_{60}$  in oleum,<sup>16</sup> the absorption bands in the case of oleum and chlorosulfonic acid can be attributed to a charge transfer complex with free sulfur trioxide (available only in these two acid systems in the current study). The correlation of this band with protonation and associated charge-transfer process is further strengthened with the shifting of this broad band with the acid strength. The wider span of the polycarocation band in all the superacids, compared to sharper absorption features in the  $\text{C}_{60}$ -oleum system can be understood in terms of the distribution of tube diameters in the SWNT sample. Superacids based on an oxyacid functionality also serve as oxidizers in addition to protonating the SWNTs.

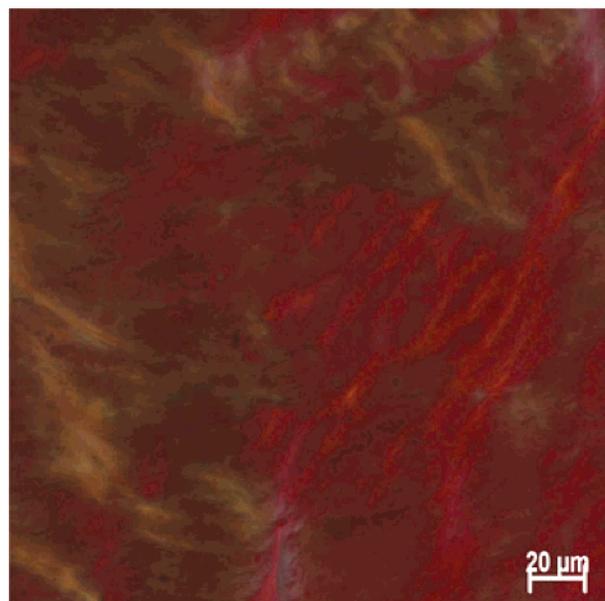
In fact, only in those rare instances where the conjugate base provides for extreme delocalization, as in the case of a larger carborane cage anion, does a superacid directly protonate elemental carbon without oxidation.<sup>17</sup> The absence of hydrogen evolution during the dissolution of the SWNT in superacids suggests that protonation is reversible and that fractional removal of electrons from the SWNT represents a polarization in the



**Figure 2.** (a) Raman spectrum of the dry SWNT sample before dissolution in chlorosulfonic acid ( $\lambda_{\text{exc}} = 780$  nm). The radial breathing modes (RBM) and the  $E_{2g}$  stretching mode at  $1596\text{ cm}^{-1}$  are marked accordingly. (b) Raman spectrum of the SWNT–chlorosulfonic acid paste (2.5 wt/wt %) recorded with the same excitation source. The radial breathing modes and the  $E_{2g}$  mode vanish completely, leaving only the background scattering. (c) Raman spectrum of the SWNT–chlorosulfonic acid solution (2.5 wt/wt %) recorded with the argon ion laser ( $\lambda_{\text{exc}} = 514$  nm) as exciting source. The  $E_{2g}$  mode is observed at  $1619\text{ cm}^{-1}$  registering a shift of  $23\text{ cm}^{-1}$  (shown enlarged in the inset).

C:H<sup>+</sup> moiety rather than a permanent removal of electrons from the SWNT. In this context the SWNT–superacid system may be represented by  $[\text{C}^{\delta+}_x\text{H}_y^{(1-k\delta)+}]_y\text{A}_y^{-1}$  where  $\delta$  is the fractional positive charge carried by a single carbon atom,  $x$  is the number of carbon atoms in a given nanotube,  $y$  the number of protons solvating the carbon nanotube,  $\text{A}^{-1}$  is the conjugate base anion and  $k = x/y$ .

Trace (a) of Figure 2 shows the Raman spectrum of the dry SWNT sample before dissolution in chlorosulfonic acid ( $\lambda_{\text{exc}} = 780$  nm). The radial breathing modes (RBM) and the  $E_{2g}$  stretching mode at  $1596\text{ cm}^{-1}$  are marked accordingly. Trace (b) of Figure 2 shows the Raman spectrum of the SWNT–chlorosulfonic acid paste (2.5 wt/wt %) recorded with the same excitation source. The radial breathing modes and the  $E_{2g}$  mode vanish completely leaving only the background scattering. This is not surprising considering the dependence of resonance enhancement of the Raman scattering in SWNT on their electronic structure.<sup>18</sup> The excitation energy from a 780 nm laser source is in resonance with the  $v_1 \rightarrow c_1$  transitions. There will be no contribution to the Raman scattering cross section from the  $v_1$  valence electrons as they largely become depleted in the protonation process. On the other hand, the excitation source at 514 nm (2.2 eV) that resonates with the  $v_2 \rightarrow c_2$  transition shows little dependence of the scattering cross section on the depletion of the  $v_1$  levels. Trace (c) of Figure 2 shows the Raman spectrum of the SWNT–chlorosulfonic acid solution (2.5 wt/Wt %) recorded with the argon ion laser ( $\lambda_{\text{exc}} = 514$  nm) as the exciting source. The  $E_{2g}$  mode is observed at  $1619\text{ cm}^{-1}$  registering a shift of  $23\text{ cm}^{-1}$  (see inset of Figure 2). From the reported value of Eklund et al. of  $320\text{ cm}^{-1}$  per hole per carbon,<sup>19</sup> a shift of  $23\text{ cm}^{-1}$  observed in SWNT–chlorosulfonic acid system corresponds to a single positive charge being shared by approximately 14 carbon atoms. Oxidative exfoliation of SWNT bundles by various oxidizers including  $\text{H}_2\text{SO}_4$  has been reported by Kovtukovha et al.,<sup>20</sup> wherein the authors have formed highly viscous hydrogels under certain oxidative, hydrous conditions. The gels are formed in a very slow,



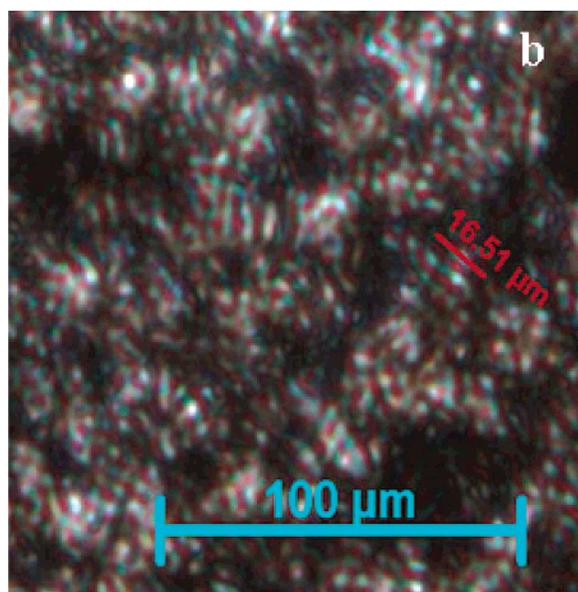
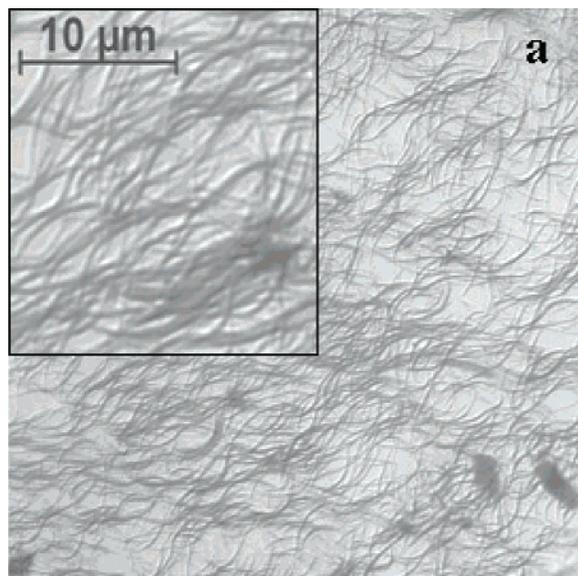
**Figure 3.** Optical micrograph of the 0.5 wt% solution of SWNTs in chlorosulfonic acid observed between crossed polarizers.

hydrogen bonded cross-linking of SWNTs. These kind of gels are formed at relatively low concentration of SWNTs and more importantly lack the anisotropic optical properties that are dominant in a nematically ordered collection of SWNTs.

The transmission optical micrograph of the 0.5 wt % solution of SWNTs in chlorosulfonic acid placed between crossed polarizers is shown in Figure 3. A direct consequence of the electrostatic repulsion between individually solubilized SWNTs is the molecular level spatial constraints that lead to alignment of the solute species to form a nematic mesophase. The micrograph shown in Figure 3 shows evidence for the formation of a highly anisotropic nematic solution and compares very well with the optical micrographs of nematic phases formed by rigid rod polymers in 100% sulfuric acid.<sup>21</sup> The domains with different orientations with respect to the polarization direction were observed to change their color with the rotation of the sample between the crossed polarizers.

Biphasic systems, where an isotropic solution of nanotubes in superacids coexists with a nematic phase, were observed at lower concentrations whereas complete nematic phases were formed at higher concentrations. This was also the case for SWNT solutions in triflic acid, 100% sulfuric acid and oleum which exhibit a lower solubility for SWNT compared to chlorosulfonic acid.

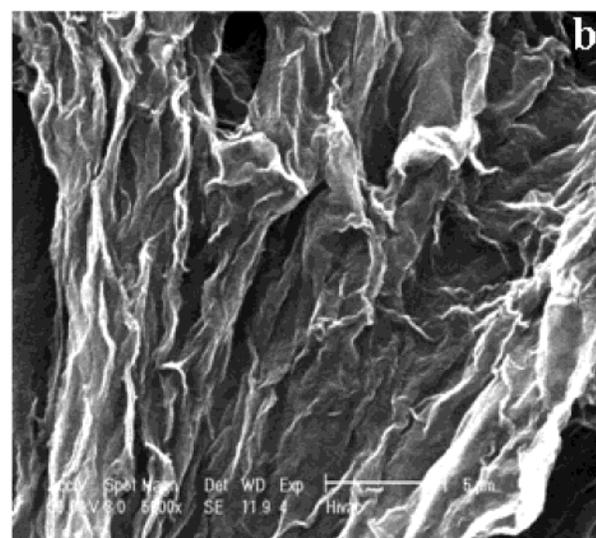
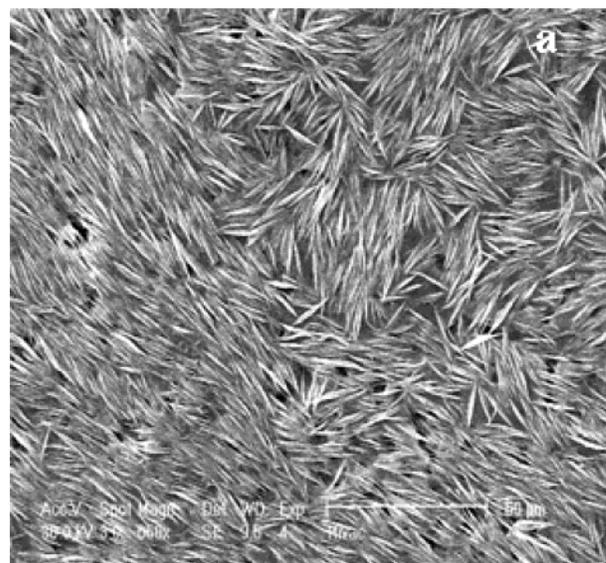
However, one of the salient features of the SWNT–superacid interactions at lower concentrations, the hierarchical ordering of SWNT, arising likely from its limited solubility, is presented here in the context of the SWNT– $\text{H}_2\text{SO}_4$ – $\text{SO}_3$  system. The transmission optical micrograph in the differential interference contrast mode of a 0.25 wt % solution of SWNT in 100% sulfuric acid is shown in Figure 4a. The sample consists of continuous and uniform bundles of thickness 600–700 nm composed of single walled carbon nanotubes. At lower concentrations of SWNT in 100% sulfuric acid, the anion mediated attraction of the protonated SWNTs causes their alignment into uniformly thin strands of SWNTs which we call “SWNT spaghetti”. The protonated SWNTs have an unrestricted mobility along the axis direction of the SWNT spaghetti and hence grow from relatively shorter lengths to long continuous strands by the continuous adsorption of protonated nanotubes from the solu-



**Figure 4.** (a) The transmission optical micrograph in the differential interference contrast mode of a 0.25 wt % solution of SWNT in 100% sulfuric acid. Inset shows a magnified view of the same sample. (b) Transmission optical micrograph of a 4 wt % solution of SWNT in 100% sulfuric acid (mixed at 110 °C) placed between crossed polarizers.

tion coupled with their mobility along the axis direction of the bundle. In this arrangement the individual tubes are suggested to have unrestricted diffusional mobility along the entire length of the spaghetti phase. We have recently presented elsewhere detailed results on the phase behavior of SWNT–sulfuric acid system, derived from rheometric and optical microscopic investigations.<sup>22</sup>

As in the case of chlorosulfonic acid, at higher concentrations of SWNT in 100% sulfuric acid, the restricted relative mobility of the nanotube bundles favors the alignment of the bundles themselves leading to nematic-like phases. A transmission optical micrograph of a 4 wt % solution of SWNT in 100% sulfuric acid (mixed at 110 °C) placed between crossed polars is shown in Figure 4b. Anisotropic phases similar to the one shown in Figure 4b were obtained at high concentrations of SWNT in triflic acid as well as oleum (20% SO<sub>3</sub>). The existence of an aligned mesophase in the SWNT–oleum system was evidenced further by the precipitation of the nematic mesophase



**Figure 5.** (a) Scanning electron micrograph of a collection of SWNT alewives precipitated from a solution of 4 wt % solution of SWNT in oleum (20% SO<sub>3</sub>) by slow exposure to moisture. The remaining acid in the carbon alewives was removed by quenching the solution in diethyl ether. Scale bar is 50 μm. (b) Scanning electron micrograph of a solid obtained by quenching an 1 wt % suspension of SWNT–96% sulfuric acid in diethyl ether. Scale bar is 5 μm.

phase into monodispersed, acicular shaped particles on slow exposure to moisture.

The particles, which we named as “SWNT alewives”<sup>23</sup> for their striking resemblance to a school of Great Lakes fish (*Alosa pseudoharengus*) bearing the same name, are constituted of single walled carbon nanotubes intrinsically aligned along the long axis of the carbon alewife as determined by polarized Raman spectroscopy. Figure 5a shows the scanning electron micrograph of a collection of SWNT alewives obtained by the slow exposure to moisture of a solution of 4 wt % solution of SWNT in 20% oleum kept stirring at 110 °C. Alewives could be obtained from lower concentration solutions (e.g., 1 wt %) of SWNT in oleum and 100% sulfuric acid, as well.

Water, which plays the role of a competing base, deprotonates the nanotubes and precipitates them as carbon alewives. On the other hand, concentrated sulfuric acid (96%) could not disperse SWNTs to give even a slightly colored solution. The syrupy black slurry of 1 wt % SWNT in 96% sulfuric acid was quenched in diethyl ether and the product examined by scanning

electron microscopy. The scanning electron micrograph given in Figure 5b reveals that the morphology rather resembles the SWNT buckypapers obtained from surfactant-assisted suspensions. This observation rules out the existence of an aligned mesophase in SWNT–96% H<sub>2</sub>SO<sub>4</sub> suspension prior to quenching and goes further to strengthen our notion that direct protonation of the SWNT by a superacid and their alignment is possible only in the absence of a competing base.

### Conclusions

Single walled carbon nanotubes, conformationally analogous to stiff-chain polymers, are solubilized in superacid solutions by direct protonation. The solubilized SWNTs exist in solution as individual polycarbonocations in an isotropic phase only at very low concentrations and transform to a nematic mesophase at high concentrations. Deprotonation takes place in the presence of a competing base (such as water), resulting in the precipitation of the solubilized SWNT. The intrinsic alignment of SWNTs in the liquid crystalline mesophase is preserved in the solid SWNT aggregates upon precipitation followed by removal of the acid. The anhydrous SWNT–superacid mesophases hold great potential as precursors for the fabrication of macroscopic materials such as fibers and thin films.

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