Supplementary Information

Quantitative analysis of nanoscale electrical properties of CNT/PVDF nanocomposites by current sensing AFM

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Results (Extended)

Absence of conductivity in pure PVDF samples

![Figure S1: Topography, deflection and current micrographs of blank PVDF at 0 and 10 V bias. Scan area is 20x20 µm² for all images. Z scale units are nm, mV and pA for the topography, deflection and current images respectively.](image)

More discussion on physical properties of CNTs

Table S1 lists the average length and diameter of synthesized CNTs. It was observed that Undoped CNTs showed larger length (1.7 µm vs 1.3 µm) and smaller diameter (15 nm vs 49 nm) than N-doped CNTs. The variation in the diameter of synthesized CNTs is owing to differences in the size of the catalyst growth nanoparticles. Thermal decomposition of precursor molecules in combination with high reaction temperature leads to sintering, liquefaction and coalescence of catalyst nanoparticles [1, 2]. Therefore, different types of synthesis gases (hydrogen versus ammonia) could account for dissimilar catalyst size distributions. Lower length of N-doped CNTs might arise from the influence of nitrogen in changing the morphology of synthesized CNTs. Indeed, the presence of nitrogen is conceived as a significant factor to bend, close and cap CNTs, thereby hindering their growth [3].

TGA analysis in air atmosphere was employed to investigate thermal stability and catalyst residue of synthesized CNTs. As presented in Table S1, Undoped and N-doped CNTs presented inflection points of 650 °C and 517 °C, respectively. Based on the inflection points, it can be said that the presence of nitrogen in the structure of CNTs makes them more susceptible to thermal degradation. These results are in consensus with the TEM micrographs and endorse the adverse impact of nitrogen doping on crystalline structure of CNTs. It was also observed that the catalyst residue of Undoped and N-doped CNTs was 14.6% and 19.6%, respectively. The catalyst particles comprised 80 wt% alumina and 20 wt% metallic particles. Alumina is insulative and metallic particles have much lower surface area than synthesized CNTs, and their surface area decreased further caused by sintering phenomenon at the synthesis temperatures. This explains that high catalyst residue drastically deteriorates electrical properties of CNT/polymer nanocomposites. The catalyst residue data demonstrate slightly better potential conductivity of Undoped CNTs compared to N-doped ones.

The inherent conductivity of filler is one of the influential factors determining the final electrical properties of nanocomposites. The compressed powder conductivity of Undoped and N-doped CNTs showed values of 1760 and 1350 S·m⁻¹, respectively. The
difference in conductivity of the compressed powders is not large and can be considered insignificant. This minor difference can be ascribed to the role of nitrogen atoms and their sequent defects, as polarization centers, in blocking nomadic charges and preventing them from moving along CNTs.

Table S1: Physical properties of Undoped and N-doped CNTs.

<table>
<thead>
<tr>
<th>Method</th>
<th>Undoped CNT</th>
<th>N-doped CNT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrogen Content (at. %)</td>
<td>XPS</td>
<td>-</td>
</tr>
<tr>
<td>Length (µm)</td>
<td>TEM</td>
<td>1.7</td>
</tr>
<tr>
<td>Diameter (nm)</td>
<td>TEM</td>
<td>15</td>
</tr>
<tr>
<td>Inflection Point (°C)</td>
<td>TGA</td>
<td>650</td>
</tr>
<tr>
<td>Catalyst Residue (%)</td>
<td>TGA</td>
<td>14.6</td>
</tr>
<tr>
<td>Powder Conductivity (S·m⁻¹)</td>
<td>ESP 4-pin-probe</td>
<td>1760</td>
</tr>
</tbody>
</table>

Scanning electron micrographs of nanocomposites

Figure S2: Scanning electron micrographs of (a) Undoped and (b) N-doped CNT/PVDF composites after surface etching.

Bulk electrical characterization of nanocomposites

Figure S3 compares the percolation curves of the generated nanocomposites. Employing the percolation theory [4, 5], we obtained an electrical percolation threshold equal to 0.44 vol% for the Undoped nanocomposites. In fact, the sharp upturn in the electrical conductivity in the loading range of 0.3 - 0.5 vol% is observable for the Undoped nanocomposites, indicating the advent of conductive network formation. Nevertheless, it was interestingly observed that N-doped nanocomposites were insulative up to 2.0 vol%, and could not match the electrical conductivity of their Undoped counterparts, even at high CNT loadings. The huge difference in the percolation threshold and electrical conductivity of the generated nanocomposites can be ascribed to the dissimilar physical and structural properties of synthesized CNTs in conjunction with their different states of dispersion. In fact, better electrical properties of Undoped nanocomposites are attributable to a combination of higher aspect ratio, higher crystallinity, higher powder conductivity, lower catalyst residue (higher carbon purity), and better dispersion state of Undoped CNTs compared to N-doped CNTs. It is well known that CNTs with higher aspect ratio (higher length and lower diameter) present lower percolation threshold and higher electrical conductivity [6-8]. Indeed, longer CNTs are more probable to neighbor or contact each other, and the diameter of a CNT has an inverse relationship with its surface area. Furthermore, the existence of more crystalline defects in N-doped CNTs, as confirmed by thermal analysis, could make them more susceptible to breakage and length loss during the melt mixing process. Better dispersion state of Undoped CNTs in microscale also contributes to enhanced conductive network.
Reference


