Electronic Properties of SWNT Fabric/Conducting Polyaniline Interface

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Introduction

In recent years there has been an increasing interest in organic materials and carbon nanotubes (CNTs) for use in carbon based electronic device applications. Much has been invested in creating better performing conducting polymers, as well as CNTs. Scientists have made much progress in using CNTs for bulk or fabric memory devices [1], photovoltaics [2], or as single tubes in transistors and other types of MEMS devices [3]. In the fabrication of flexible and efficient electronic devices these materials have been typically used in a multi-layer or "sandwich" geometry [2]. The functionality of the devices depends largely on the surface chemistry of the interfaces between these dissimilar materials.
This work explores on one type of these interfaces; the interface between a conducting polymer and a dense CNT thin fabric. Using ultraviolet photoelectron spectroscopy (UPS) the energy level alignment at the interface of a conducting polyaniline and SWNT fabric film is investigated.

Experimental

Materials preparation

As-produced HiPco SWNT from Unidym, Inc. (formerly Carbon Nanotechnologies, Inc.) was dispersed in solution similar to work by O'Connell et al. [4]. HiPco SWNT (10mg) was weighed out and dispersed in 100 ml of deionized water with 0.5wt% of sodium docedyl benzene sulfonate (SDBS). The solution was then sonicated for 30min.
Polyaniline, emeraldine salt from p-toluenesulfonic acid (PANI-PTSA) and toluene were purchased from Alfa Aesar along with dodecyl benzene sulfonic acid (DBSA), which was purchased from Sigma Aldrich. PANI-PTSA (1wt%) was dispersed in a 5wt% of DBSA in toluene mixture. The solution was simultaneously stirred and heated at 50^{o}C for at least 48hrs until a consistent nearly soluble mixture was achieved.

Sample preparation

The SWNT samples used for UPS and voltage-current (VI) characterization were prepared using vacuum filtration on a 47mm anodisc such that a dark buckypaper-like fabric was formed. The SEM and AFM images, shown in Figure 1, indicate the general morphology of the films.

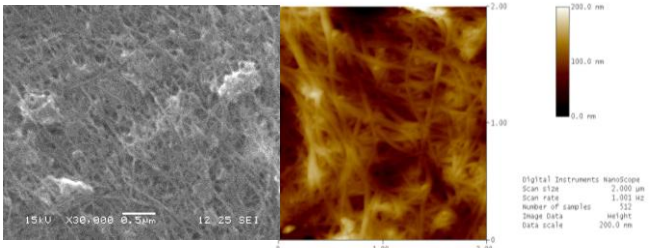

Figure 1: SEM image (left) and AFM image (right) of HiPco fabric on a filter disc.

The conducting polyaniline was spincoated at 4000 rpm for 30sec with a static volumetric dispense of 0.5ml on a 25mm x 25mm glass slide. The film was then baked at 95^{o}C for 5min to remove as much of the solvent (toluene) as possible. The SEM image in Figure 2 shows the surface morphology of the conducting polyaniline film after spincoating onto a glass slide.

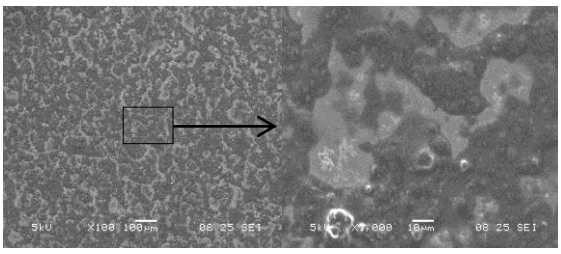

Figure 2: SEM iamge of PANI-PTSA thin film.

Instrumentation

The UPS analysis instrument used for this study is a custom assembled system with a Thermo Electron Alpha 110 hemispherical electron energy analyser and the UVL high intensity ultra-violet discharge light source. Photoemission measurements were performed at room temperature in a Mu-metal analysis chamber with 2.0x10^{-9}Torr base pressure. Discharge line from HeI gas was used, which gives hν=21.2eV photon energy. In order to measure the work function, the samples were biased at -9V to

accelerate secondary electrons and overcome the analyser work function. The Fermi edge (E_F) position was calibrated using a 100nm polycrystaline Au film thermally deposited on a polished Si substrate. The Fermi edge resolution of the UPS system was 90meV, using the 20%-80% definition, measured from the same Au sample.

Results and Discussion

Subsequent UPS analysis of as produced HiPco SWNT fabric on a filter disc shows (Figure 3) the metallic nature of the fabric. The valence band of the fabric is aligned with the E_F, as Figure 3 (inset) illustrates. The secondary electron cutoff of HiPCO fabric is at 16.1eV, which indicates a work function of 5.1eV, where $\Phi=h\nu-E_{cutoff}$. While high, this value falls in the 4.7-5.2eV range, established by theoretical and experimental studies of SWNT networks [2].

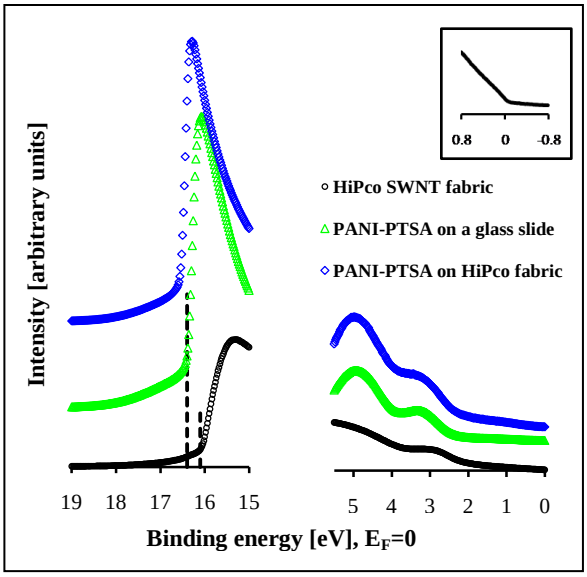

Figure 3: UPS spectra of HiPco SWNT fabric (bottom spectra), PANI-PTSA on glass slide (middle spectra), PANI-PTSA on SWNT fabric (top spectra). Inset represents the Fermi edge of the HiPco SWNT fabric.

Although the ratio of semiconducting to metallic nanotubes has a theoretical value of around 2:1 [5], the concentration of metallic CNTs is high enough to dominate the electric properties in the bulk fabric. This is verified by the VI analysis.

Figure 3 also shows a UPS spectra of PANI-PTSA on a glass slide. Again, it indicates metallic electronic properties. The valence band is pinned to the E_F and the VI curve (Figure 4) is linear. The work function of PANI is 4.8eV, according to measurements.

Based on the analysis above, the Fermi levels of the two materials align at the interface and only an interfacial dipole of 0.3eV exists. The spectra of PANI, coated on the HiPco fabric is also shown in Figure 3. As expected for the spectra of a metallic material, it has stayed virtually the same regardless of change of the substrate. Change in the cutoff value falls within the experimental margin of error ±0.1eV.

Four-probe VI measurements (Figure 4) were conducted to obtain resistance values as well as determine a correlation between the VI curves and UPS data for the samples that were studied.

By taking the inverse of the slope of the curve in Figure 4a, a resistance of 3.96Ω is calculated for the HiPco thick fabric. Note that the curve is linear which is contrary to literature [5] for HiPco material. Figure 4a (inset) shows this semiconducting trend due to HiPco having ~33% metallic SWNTs and ~66% semiconducting SWNTs. Thinner films of HiPco SWNT show semiconducting behavior compared to thick fabrics.

The resistance of conducting polyaniline (PANI-PTSA) measured 2.73kΩ, and again showing a linear trend.

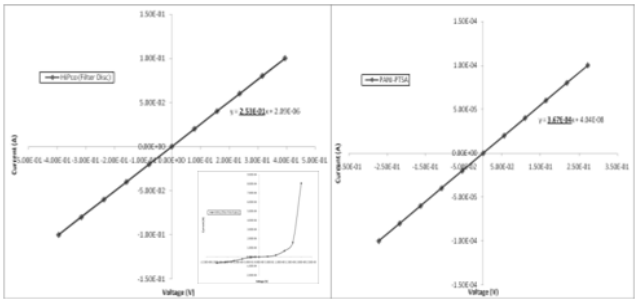

Figure 4: (a) VI curve of HiPco on filter disc and VI curve of HiPco thin film (inset) and (b) VI curve of PANI-PTSA thin film.

Conclusion

To study the electronic properties of SWNT fabric, conducting PANI, and their interface, we have employed UPS and other techniques. The results show a metallic electronic nature for both materials and therefore their interface. This suggests the interface of these materials may have viable applications, such as thermocouples and thermopiles.

References

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