

## Effect of Surfactant Peptides on Electronic Properties of Single-Walled Carbon Nanotubes

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Understanding the electronic structure and properties of carbon nanotubes has attracted enormous interest due to their possible applications in nanodevice fabrication [1]. Since the electronic properties of carbon nanotubes are strongly connected to their delocalized  $\pi$ -electron system, these properties can be altered significantly by introducing various chemical modifications to the surface of the nanotube [2]. The focus of this study is to investigate how designed surfactant peptides with different electron-donating and electron-withdrawing capabilities may tailor the electronic properties of single-walled carbon nanotubes (SWNTs). Early studies have revealed that surfactant peptides show minimum folding and self-association properties resulting in a less complex system for understanding peptide/SWNT interactions [3]. Surfactant peptides designed for this study have an amphiphilic structure. The C-terminus of each peptide has two lysine residues forming a hydrophilic head, followed by five valine residues forming a hydrophobic tail. The N-terminus of the peptide consists of a test amino acid which has an aromatic side chain to facilitate  $\pi$ -stacking interactions between the SWNT and the peptide. For this study, three test amino acids were selected with i) a strong electron-donating group on the aromatic ring (*p*-amino phenylalanine), ii) a strong electron-withdrawing group on the aromatic ring (*p*-cyano phenylalanine) and iii) no functionality on the aromatic ring (phenylalanine). The corresponding peptides were named as SP-*p*NH<sub>2</sub>F, SP-*p*CNF and SPF, respectively.

Circular dichroism (CD) studies revealed that the surfactant peptides remain primarily as random coil structures in solution over a large concentration range (50-500  $\mu$ M). Also, CD data suggested that the peptides do not undergo any major structural changes upon interacting with SWNTs. Atomic force microscopy (AFM) and Ultraviolet-Visible-Near Infrared spectroscopy (UV-Vis-NIR) studies showed the ability of the surfactant peptides to disperse individual SWNTs (Fig. 1 and Fig. 2, respectively). Scanning tunneling microscopy (STM) images revealed the coating of surfactant peptides on SWNTs, however, the low intrinsic conductivity of peptides obscured the fine atomic structure of the SWNT (Fig. 3). In order to examine the effect of the peptides on SWNT electronic properties, Raman spectroscopy and scanning tunneling spectroscopy (STS) studies were performed. Raman G-band peak shifts for the peptide/SWNT composites demonstrated the potential of nanotube doping by the designed surfactant peptides. STS dI-dV spectra were used to compare the density of states (DOS) of SWNTs associated with different peptide/SWNT composites (Fig. 4). The dI-dV curves of bare SWNTs (Fig. 4a) and SPF-coated SWNTs (Fig. 4b) showed symmetrically positioned DOS about the Fermi level ( $E_f$ ). No additional features were observed near the  $E_f$ . A feature that appeared in the conduction band side of the dI/dV spectrum of SP-*p*NH<sub>2</sub>F/SWNT suggested an n-doping effect between the peptide and the nanotube (Fig. 4c). Conversely, the feature in the valence band side of the  $E_f$  for SP-*p*CNF/SWNT indicated a p-doping interaction (Fig. 4d). In conclusion, the STS and Raman data suggested that the SWNT electronic properties could be successfully altered using designed surfactant peptides.

## References

- [1] P. Avouris, *Acc. Chem. Res.* 35 (2002) 1026.
- [2] V.Z. Poenitzsch et al., *J. Am. Chem. Soc.* 129 (2007) 14724.
- [3] H. Xie et al., *J. Pept. Sci.* 14 (2008) 139.

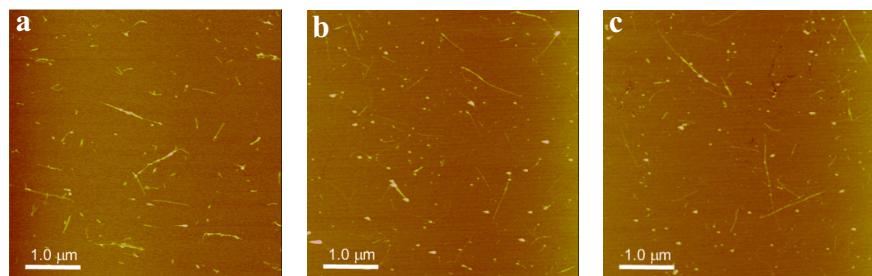


Figure 1. AFM images of (a) SPF/SWNT, (b) SP-*p*NH<sub>2</sub>F/SWNT, and (c) SP-*p*CNF/SWNT dispersions drop-cast onto mica.

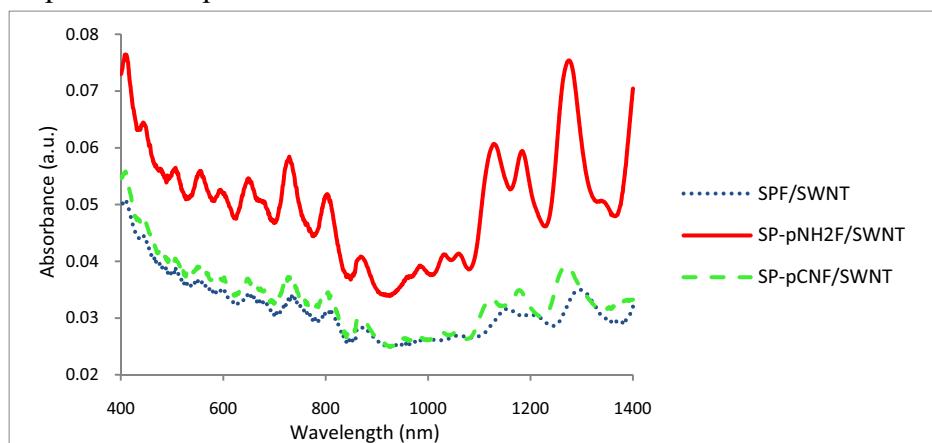


Figure 2. Absorption spectra of SPF/SWNT, SP-*p*NH<sub>2</sub>F/SWNT, and SP-*p*CNF/SWNT dispersions.

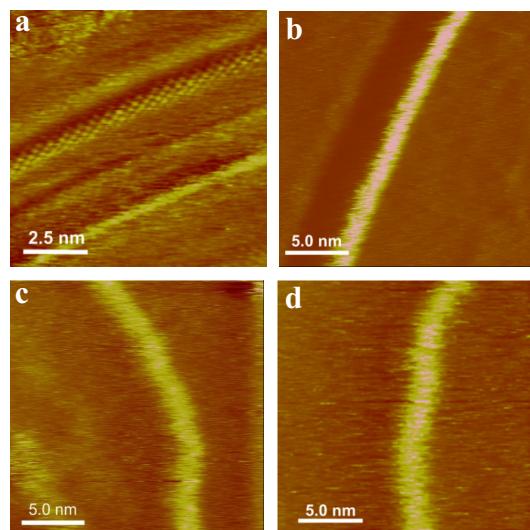


Figure 3. STM images of (a) bare SWNT, (b) SPF/SWNT, (c) SP-*p*NH<sub>2</sub>F/SWNT, and (d) SP-*p*CNF/SWNT.

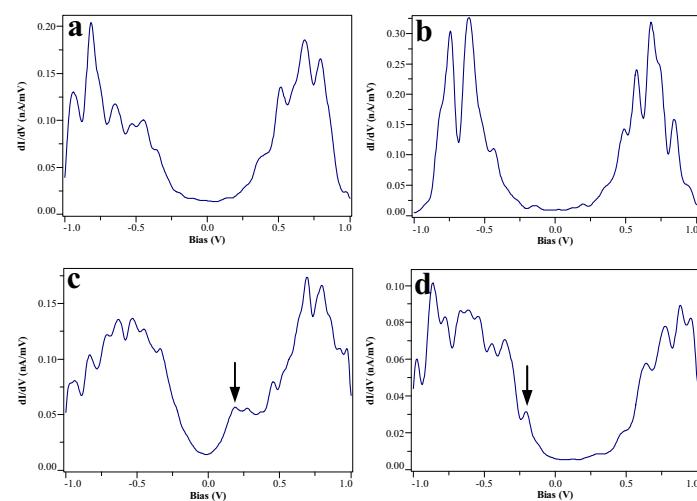


Figure 4. STS dI/dV spectra of (a) bare SWNT, (b) SPF/SWNT, (c) SP-*p*NH<sub>2</sub>F/SWNT, and (d) SP-*p*CNF/SWNT.