NEUROELECTRONIC COMPOSITES CONTAINING CONDUCTING POLYMERS AND CARBON NANOTUBES

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Introduction

Composites based on conductive polymers and carbon nanotubes (CNT) offer the advantage of generating functional materials with superior bionic properties. CNTs proved to be highly useful substrate for growth and electronic interface neuron with neurons. Polyaniline (PANI) on the other hand can be assembled as 2D-conducting polymer on solid templates.[1] Neuron outgrowth on such nanometric layers containing surfaces have created an intimate interface for neurons outgrowth manifested in lamellipodia formation.[2] The combinations of positively charged polymer with rough interface led to very strong cell adhesion to this substrate. Additionally, multielectrode array (MEA) containing PANI coated CNT showed substantial reduction in the electrodes impedance.[3] The two last developments suggested the potential of creating a composite material based on SWCNT/PANI complexes as a promising neuroelectronic hybrid.

Experimental

PAN electrochemically wrapped on SWCNT: ITO coated with purified SWCNT –1ml of 0.026mg/ml purified SWCNT solution in DMF was deposited dropwise on an ITO slide; next the solvent was evaporated in air. Samples were coated by cyclic voltammetry with PANI, polycarbazole and melanin. The working electrode in the preparations is an ITO coated with SWCNT the reference electrode is Ag/AgCl and Pt used as counter electrode. The electrolyte in each preparation is 0.01 M carbazole in 0.1 M sodium perchlorate in Acetonitrile, 0.1 M aniline in distilled water solution at pH 3.5 and .4 mM dopamine in 0.1 M phosphate buffer solution and 0.5 M potassium chloride at pH 7.

Preparation of SWCNT/SDS/PANI by In-situ chemical polymerization: 5.2 mg of clean SWCNT suspended in 10 ml of distilled water by sonication then 0.12 g of SDS were added. The SWCNT was precipitated and the residue was washed and dried in vacuum. The dried SWCNT/SDS were dispersed in about 5 ml of hydrochloric acid solution pH 2 then 2.8 µl of aniline were added, and finally 10 mg of ammonium persulphate were added. The product was precipitated, washed and dried in vacuum.

Result and discussion

Electrochemical polymerization yields nanotubes wrapped by the conducting polymers - polyaniline (PANI), polycarbazole and polydopamine. From the attenuation of in-plane vibrations in the infrared spectra in Fig. 1, which is the part of the spectrum containing molecular vibrations of the polymer coating materials (in this region, the CNT spectrum is featureless). Compared to the pure polymers, we observe some distinct changes. For the carbazole hybrid, although the vibrational mode of the ClO_4^- ion at 1080 cm^{-1} indicates the presence of the polymer, the carbazole modes[4] are much weaker. The effect is even more outspoken for PANI-wrapped tubes: the PANI vibrations are considerably weaker than expected from the infrared spectrum of the pure material; some vibrations completely disappear. The latter, disappearing bands (at 1150, 1500 and 1590 cm^{-1}) have been assigned as benzenoid or quinoid modes, all in-plane polarized.[5] In the melanin hybrid the spectra are much more similar before and after coating.

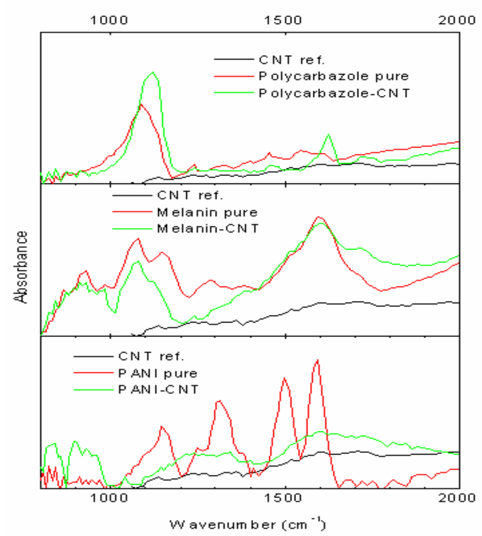

Fig.1: IR spectra of the hybrid materials (conducting polymers coated SWCNT) and their constituents.

This effect, was previously seen on poly(*p*-phenyleneethynylene) adsorbed on nanotube surfaces by Setyowati et al[6] and was termed SAIRA (surface attenuated infrared absorption). The effect originates in the image dipoles on the polarizable surface of the nanotube, which cause a vibrational motion of charges opposite to that of the molecule adsorbed on the tube. As a result, the net dipole change during the vibration weakens and can become close to zero.

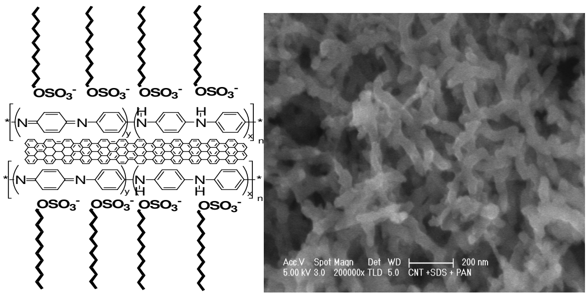

Fig.2: Schematic description [left] and SEM image [right] of the composite SWCNT/SDS/PANI synthesized by *in situ* chemical polymerization.

The key strategy in our synthesis is the use of an anionic surfactant (SDS) containing ion-exchangeable sodium cation that can be replaced by the monomer, anilinium ion. This kind of template synthesis was exemplified in 2D.[7] The SEM image shows clearly that the carbon nanotubes are wrapped with PANI. XPS spectra show PANI's quaternary and tertiary nitrogen and that all of hybrids contain sulphour in the same amount including the final hybrid (SWCNT/SDS/PANI). Thus we suggest that during polymerization polyaniline is replacing SDS in contact with the SWCNT due to π-π interaction with the aromatic surface of SWCNT. Having the idea of integrating these new types of SWCNT conjugates into advanced biomedical tools, we explored their potential impact on the viability and function of cells from the immune system. In particular, we have compared the cytotoxic effects on mouse spleen cells and macrophages. The results in Fig. 3 indicate that biocompatibility of the different SWCNT conjugates is dependent both on the doses used and the type of cells. We have observed significant cell mortality induced by SWCNT/SDS/PANI at the concentration of 100 µg/ml, particularly for macrophages (data not shown). However, at the doses typically used for biological applications (i.e. 1 or 10 µg/ml), SWCNT/SDS/PANI did not show cytotoxicity neither towards spleen cells nor macrophages. On the other hand, TEM images show that macrophages are capable to phagocyte the different nanotubes telling the possibility of their elimination. These results suggest that a certain attention is needed to guarantee low level of release of CNT hybrids once deposited on electrodes conceived for interfacing with neurons.

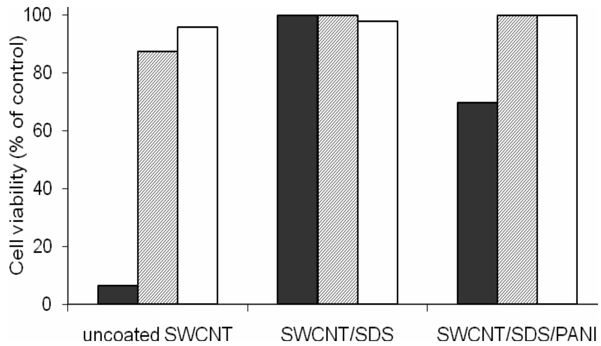

Fig. 3: Effect of uncoated and coated SWCNT on cell viability. Mouse spleen cells were either left untreated or incubated with 1 µg/ml (white), 10 µg/ml (grey) or 100 µg/ml (black) of the indicated SWCNT.

Conclusion

In conclusion we introduce the preparation of SWCNT/conductive polymers composites by electrochemical polymerization of PANI, PCz and Polydopamine (melanin) on ITO coated SWCNT. The HRSEM shows a uniform layer of conductive polymer whose thickness can be controlled. The impedance measurements show that wrapping the nanotubes with polymers increases their conductivity and facilitates electron transfer from the electrolyte to the electrode. From the attenuation of in-plane vibrations in the infrared spectra, we infer that the strongest interaction occurs between PANI and the nanotube surface. We also have found that SWCNT coated with the electro-active polymer polyaniline by chemical polymerization are compatible with primary immune cells such as spleen cells in a dose-dependent manner.

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References

1. R. Sfez, L. De-Zhong, I. Turyan, D. Mandler, S. Yitzchaik, *Langmuir* **2001**, 17, 2556-2559.
2. R. Oren, R. Sfez, N. Korbakov, K. Shabtai, A. Cohen, H. Erez, A. Dorman, H. Cohen, J. Shappir, M. E. Spira, S. Yitzchaik, *J. Biomater. Sci. Polymer Edn.* **2004**, 15, 1355-1374.
3 David-Pur, M.; Benvalid, S.; Yitzchaik, S.; Hanein, Y., Eurosensors, **2008**, XXII, 354.
4. Macit, H.; Sen, S.; Saçak, M.: *J. Appl. Polym. Sci.* **2005,** 96, 894-898.
5. Quillard, S.; Louarn, G.; Lefrant, S.; Macdiarmid, A.G.: *Phys. Rev. B* **1994,** 50, 12496-12508.
6. Setyowati, K.; Piao, M.J.; Chen, J.; Liu, H. *Appl. Phys. Lett.* **2008,** *92,* 043105.
7. R. Sfez, N. Peor, S. Cohen, H. Cohen, S. Yitzchaik, *J. Mater. Chem.* **2006**, *16*, 4044 - 4050.