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Polyaniline/multi-walled carbon nanotubes films prepared by two-phase polymerization: synthesis and characterization

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Abstract – Free-standing films of polyaniline/multi-walled carbon nanotubes have been obtained by an *in situ* approach involving oxidative polymerization in a toluene dispersion of carbon nanotubes, in an aqueous-toluene two phase system. The composites are self-assembled at water/toluene interface and can be easily removed and deposited on any surface. The films containing different amounts of nanotube were characterized by FTIR, UV-Vis, SEM, TEM, cyclic voltammetry and Raman spectroelectrochemistry. Results show carbon nanotubes embedded in a conductive-form of PANI, with an effective interaction between PANI and CNTs.

Carbon nanotubes have been widely studied as fillers for polymeric composites aiming new composite materials with mechanical reinforcement or, in case of conducting polymers, changes in electronic properties arising from interaction between nanotube sidewalls and polymeric chains.¹ Polyaniline has remarkable features among other conducting polymers, as facility to the synthesis, controllable doping process and environmental stability. Recently, new strategies have been developed in order to attain superior properties and nanostructured morphologies (e.g., nanofibers, nanorods), ² allowing the possibility to enhance interaction of this material in novel nanocomposites.

Nanocomposites were obtained in this work by an *in situ* oxidative polymerization in a two phase system giving rise to self-assembled composite films of NTC/PAni (emeraldine salt) at the interface water/toluene. The green film can be easily removed from interface and deposited on any kind of surface (e.g., glass, FTO glass) (Figure 1). The preparation route should be summarized as following: multi-walled carbon nanotubes were synthesized by CVD method (ferrocene pyrolysis) and present their cavities filled with iron and iron oxide crystals. Carbon nanotubes were ultrasonically dispersed in a toluene solution of aniline and the dispersion were added to an aqueous H_2SO_4 /ammonium persultate solution. Different nanocomposites varying CNT:PAni proportion were synthesized by changing the aniline/CNT ratio in the precursors.

The nanocomposites were characterized by FTIR, UV-Vis, SEM, TEM, cyclic voltammetry and Raman spectroelectrochemistry. The FTIR spectra show preferential interaction of carbon nanotubes sidewalls with polyaniline chains as indicated by intensity of characteristic quinoid and benzoid bands. TEM images showed polymer nanofibers along with structures consisting of carbon nanotubes surrounded by polyaniline nanofibers (figure 2), representative morphology of the two phase polymerization, as already seen in previous work. ³ Also, it was observed by cyclic voltammetry a reduction in the potentials for leucoesmeraldine/esmeraldine oxidation according the increases in the carbon nanotubes content. Resonant Raman spectroelectrochemical experiments using 632.8 nm excitation line have been performed in order to investigate this interaction.



Figure 1: SEM image of two superposed films of nanocomposite NTC:PANI (1:100) deposited on FTO substrate. The sample was tilted to visualize the films edge.



Figure 2: TEM images of nanocomposite NTC:aniline (1:16), showing multi-walled carbon nanotubes wrapped by polyaniline fibers.

References

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