

CARBON NANOTUBE - POLYANILINE COMPOSITES: SYNTHESIS AND PROPERTIES

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ABSTRACT

Several methods for preparation of carbon nanotube and polyaniline composites have been reported. However, it is important to understand how those methods affect structure and properties of the nanocomposites, in order to use the best materials for each application. In this study, recent advances on the *in situ* polymerization of aniline with different kinds of carbon nanotubes are presented. Results from studies of morphology and properties are evaluated, trying to correlate composite nanostructure with polymerization conditions.

INTRODUCTION

Polyaniline (PAni), an important conducting polymer with good environmental stability, can be changed from a semiconducting form to a conducting one by acid doping. PAni can be synthesized as the conducting emeraldine salt form in an acidic solution (e.g. 1M HCl) of aniline by adding an oxidant (e.g. ammonium persulfate). It can also be synthesized as nanofibers by a simple interfacial polymerization reaction [1], nanostructured PAni has advantages over the bulk polymer in sensors [2] and other applications, such as templates for composites [3].

Carbon nanotube (CNT) PAni composites have been reported by Cochet *et al.* [4], they dispersed multi-walled carbon nanotubes (MWCNT) in the typical 1 M HCl aqueous solution used for oxidative synthesis of polyaniline; even though CNTs were irregularly mixed with large PAni particles conductivity was improved. Yan *et al.* [5] sonicated MWCNTs for 10 hs in concentrated H₂SO₄/HNO₃ 3:1 to be able to suspend them in water; by mixing with an aqueous solutions of PAni nanofibers they obtained composites with improved conductivity. CNT-PAni composites may have applications in sensors, conducting inks [6] and artificial muscles [7].

In this study we used interfacial polymerization to produce nanostructured CNT-PAni composites in one step, testing the effect of dispersing CNTs in either the aqueous or the organic phase, type of solvent and other variables.

EXPERIMENTAL

MWCNT were synthesized by CVD of an aerosol of ferrocene (2.5 wt.%) solution in toluene [8] and nitrogen doped carbon nanotubes (CN_x-MWNT) from a ferrocene (2.5 wt.%) solution in benzylamine [9]. Aniline functionalized nanotubes (Af-MWCNT) were made via a Birch reduction reaction [10,11], using a 1:1:1 weight ratio of MWCNTs/Aniline/Lithium, with ~0.5 mg/mL of MWCNT in liquid NH₃.

CNTs were dispersed in ~200 mL of solvents (1,2-dichloroethane, tetrachloroethylene, toluene, benzene, 1,2-dichlorobenzene) by sonication in a bath (Fisher, model FS-20) for at least 2 and up to 7 hs. Aniline, typically 1 g, was added to these solutions, then they were mixed with acid solutions (2M HCl) of (NH₄)₂S₂O₈ (1:1, 2:1, 4:1 molar ratios aniline/persulfate)

CNTs were dispersed in the aqueous phase by sonicating 1-2 hs in 50% sulfuric acid, then distilled water was added to make a 6 M acid solution, and sonicated for 3 hs more. For comparison the CNTs were also dispersed by 3 hs sonication with HCl or acetic acid (CH₃COOH). Ammonium persulfate was added to the aqueous phase just before mixing with aniline in the organic phase (tetrachloroethylene or toluene).

After bringing together both solutions the interfacial polymerization was allowed to proceed for at least 3 hours, and up to 48 hs, in most cases with magnetic stirring. The products were

filtered through PTFE membranes (45 μm pore), and washed with ethanol and acetone to remove the organic solvent, unreacted substances and impurities, and finally dried in vacuum.

Morphology of the materials was examined with a FEI-Phillips XL-30-SFEG Scanning Electron Microscope, equipped with an optional STEM detector for transmission images. The samples were also characterized by Raman spectroscopy and four point probe resistivity measurements.

RESULTS AND DISCUSSION

We tested the effect of ammonium persulfate on yield, with 1 g aniline in tetrachloroethylene as one phase, and 2M HCl as the aqueous phase, for a reaction time of 6 hs. Based on the results, shown in Table 1, we decided on a 2:1 ratio aniline/persulfate for all further reactions.

Table 1: Effect of aniline/ $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ratio on PANi yields in interfacial polymerization, for pure PANi and in situ polymerization with MWCNT.

Aniline/Persulfate molar ratio	Pure PANi yield	In situ polymerization with MWCNT	
		PANi yield	Wt. % MWCNT
8:1	7.7 %	-----	-----
4:1	17.6 %	16.5 %	1.16
2:1	36.6 %	33.5 %	1.87
1:1	-----	44.2 %	3.12

Polymerization times of 3 hs yield ~7% polymerization, with 12 hs the yield increases to 25-30%, producing thicker nanofibers and some PANi agglomerates. Polymerization times of 48 hs gave about 50% yield of polyaniline but the PANi fibers thickened and formed agglomerates, approaching “bulk” morphology. Polymerization yields are relatively stable for the same synthesis conditions, thus concentration of nanotubes in the composite can be controlled easily.

Huang and Kaner [1] suggest that no stirring is better to obtain nanofibrous PANi, however, without stirring the CNTs were not well dispersed in PANi (Fig. 1A). We could obtain nanofibrous polymer when stirring (Fig. 1B) as well as composites with well dispersed CNTs in nanofibrous PANi (Fig. 1C, D). There were no noticeable improvements in CNT dispersion with sonication times longer than 2 hs, and all the solvents tested gave good dispersions, tetrachloroethylene was used for all the reactions reported below unless otherwise noted.

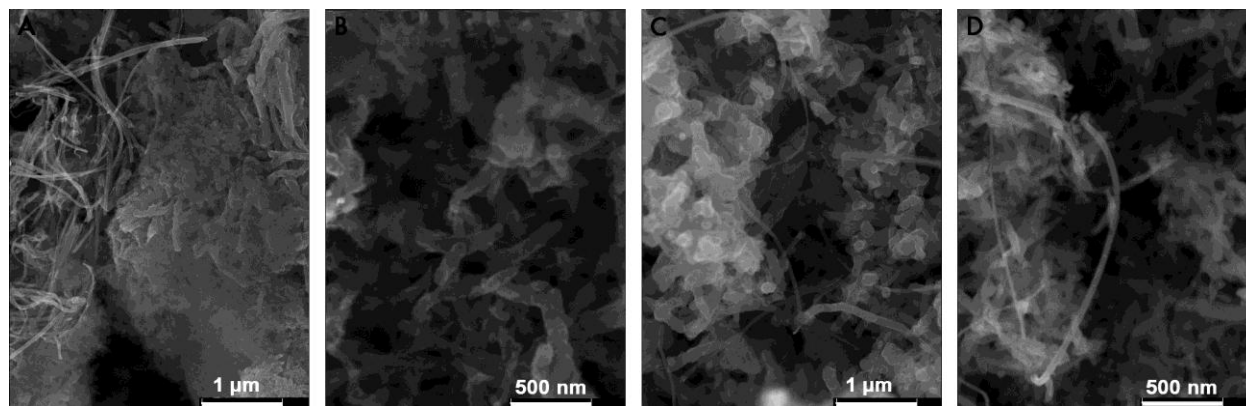


Figure 1: A) CN_x (7 wt.%) composite showing bad dispersion when stirring is not used in the interfacial polymerization. B) Nanofibrous morphology of pure PANi from a stirred polymerization. Well dispersed composites are obtained when stirring is used for both C) MWCNT (3 wt.% composite) and D) CN_x (2 wt.% composite).

Compared to the one step synthesis of Cochet et al. [4] we obtain better dispersions and nanostructured PANi. We think that as polymer chains grow, stirring helps to mix them with the

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nanotubes achieving a good dispersion. Yan *et al.* [5] suggest that electrostatic interactions between negatively charged oxidized MWCNTs favor interaction with positively charged doped PANi. We achieve a good dispersion, and a better nanofibrous morphology without needing to rely on such interaction. CNTs are not oxidized when dispersed in organic solutions, thus they are expected to be less damaged. Also, for dispersions in water we used 50% H_2SO_4 , not concentrated acids, and shorter sonication times; so we expect less damage to the nanotube surface.

Aqueous suspensions of CNTs were relatively stable for several minutes, and stirring during interfacial polymerization helped to keep the nanotubes in suspension. The stability of the dispersion of CN_x -MWCNT in acid solutions depended on the acid concentration used. For example, with a 1 M CH_3COOH solution, suspensions were stable for several hours, while with 0.5 and 2M CN_x flocculated within 2 hours.

A striking difference was found when CN_x were in the aqueous phase: most of the nanotubes were coated with PANi, as shown in figure 2. This morphology occurs for all three acids tested. We propose that this is due to a strong interaction of PANi with functional groups on the nanotube surface; possibly even a reaction of the functional groups occurs with oligomers or PANi chains.

For MWCNT, the annular composite morphology is more common when they are dispersed in oxidizing acids (H_2SO_4), but rare with HCl or CH_3COOH solution. With the non-oxidizing acids possibly the coated nanotubes were oxidized by ammonium persulfate.

To minimize the possibility of oxidation of CN_x by persulfate, it was added slowly and in small portions after mixing the organic and aqueous solution. A coaxial morphology is still found under these conditions.

Dispersing aniline functionalized MWCNT in the aqueous phase produced composites with the same annular morphology as with CN_x . It is likely that this morphology is due to reaction of the aniline moieties on the surface of the Af-MWCNT. All of this supports the hypothesis that the nitrogen atoms on the CN_x surface, and not oxidative functionalization of the doped nanotubes; are responsible for the good interaction that results in a uniform coating of CN_x by PANi.

Since MWCNTs in the organic phase are not functionalized by oxidation, and solvation of CN_x by the organic solvent may prevent their nitrogen groups from interacting with the PANi chains; it is rare to see them coated with PANi when they are dispersed in the organic phase. In such case both nanomaterials only get physically mixed.

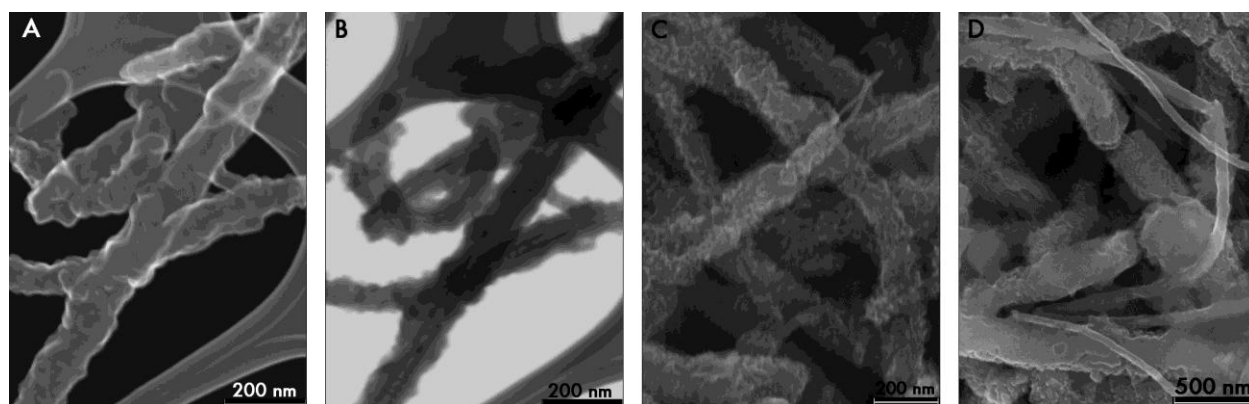


Figure 2: SEM (A) and STEM (B) images of a CN_x composite, showing the radial coating of PANi over the nanotubes. The same type of coating can be observed for Af-MWCNT (C) and for some MWCNT dispersed in oxidizing acid solutions (D).

We attempted to use Raman spectroscopy (633 nm excitation source) to examine if more persulfate in the reaction induced greater functionalization of the nanotubes. However, the

Raman peaks of PANi overlap the positions of the D (sp^3 carbon) and G (sp^2 carbon) peaks of CNTs, preventing us from seeing changes in the D/G relative intensities or shifts of the CNT peaks.

To measure resistivity, the powdery samples were hot pressed (150 °C) giving very fragile sheets. 4-point probe tests showed surface resistivity on the order of $10\text{-}10^2 \Omega$, with variations in surface resistivity not correlated to type of nanotubes or even to amounts of CNTs in the composite. Given the need for temperature at pressing some of the dopant may also be lost. We consider these results preliminary only, and better processing is needed to get better resistivity measurements.

CONCLUSIONS

We have designed an *in situ* polymerization method that allows us to obtain well dispersed composites of carbon nanotubes and polyaniline. We have also identified conditions that yield a nanocomposite composed of polymer coated nanotubes. We believe that the nitrogen atoms in CNx-MWNT favor this morphology and showed that other types of functional groups can be created in MWCNT to achieve this same type of nanostructured composite. More studies are needed to see the differences in the properties of the PANi coated CNT nanocomposites versus the uncoated CNT composite morphology.

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