

Self-assembly of SWCNT in P3HT matrix

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Abstract

We explore the possibility of the formation of efficient electron-conducting percolative network in an efficient hole conducting polymer matrix, a desirable combination for novel polymer electronic devices. A network of carbon nanotubes (CNTs), an efficient electron conductor, has been achieved by self-assembling of nanotubes during solution evaporation on poly(3-hexylthiophene) known to be an efficient hole conducting polymer matrix. The revelation of a viable nanotube network and its strong interaction with polymeric chains have been accomplished through characterization of composite matrices by UV–visible, photoluminescence spectroscopy, thermal gravimetric analysis, scanning electron microscopy and atomic force microscopy. The idea of gross evolution of nanotube network is accomplished in terms of more than six fold (10^{-7} – 10^{-1} S/cm) increase in conductivity of the present composite at insertion of merely ~4% CNTs content in P3HT matrix. The formation of such a strong percolative network will be of immense importance for the development of electronic devices.

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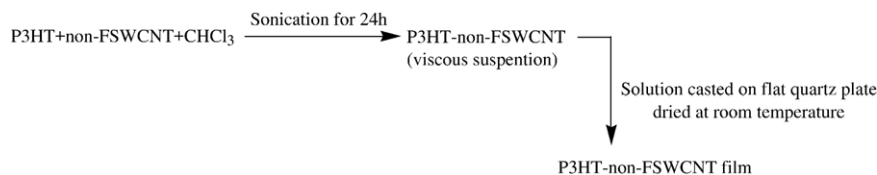
1. Introduction

Carbon nanotubes (CNTs) [1] imbedded in semiconducting polymers [2,3] constitute an emerging electronic composite [4–12] due to the desired combination of the hole conducting π -conjugated polymers especially polythiophenes with electron-conducting inorganic semiconductors such as CNTs. However, the main obstacles in using CNTs based composite materials as electronic devices are: (i) the wettability of the CNT surface [13] and (ii) the ability to disperse CNTs homogeneously into the polymer matrix [14]. These obstacles can be overcome by making single-walled CNTs (SWCNTs) soluble [4] in either polar or nonpolar solvents, through chemical functionalization. SWCNTs, once in solution, get effectively incorporated in a polymer matrix with high extent of dispersion [15–20], and form a strong percolative nanotube network, essential for effective electron transfer. However, there are merits and demerits of the nanotube's functionalization. The common drawback in both

cases is the loss of π -conjugation of the nanotubes with its magnitude depending on the extent of functionalization. If nanotubes are soluble in a polar solvent like water, the resultant composite is hygroscopic in nature. The advantage of this type of functionalization is that π -conjugation of the host polymer does not get disturbed and the added groups are generally small and also easily removable. In case nanotubes are soluble in organic solvents through covalent attachment of non- π -conjugated chemical groups, the result is an effective loss in chromophore density.

Many efforts have been made for chemical functionalization [4,21–23] of CNTs, which will not only assist in the preparation of the composite but also open new prospects in aligning and forming molecular devices, and generating nanoscale architectures. The first step of functionalization of CNTs involves reactions of CNTs with different oxidants, known as acidic treatment. It results in the opening and shortening of nanotubes with insertion of new functional groups such as carboxyl, hydroxyl, sulphonic groups, etc. With further functionalization of these groups, the dispersability of CNTs in different solvents gets considerably improved. While the ultraviolet–visible (UV–vis.) spectra confirm the covalent modification of SWCNTs [24–26], the thermal gravimetric analysis (TGA) gives the amount of

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Scheme 1.

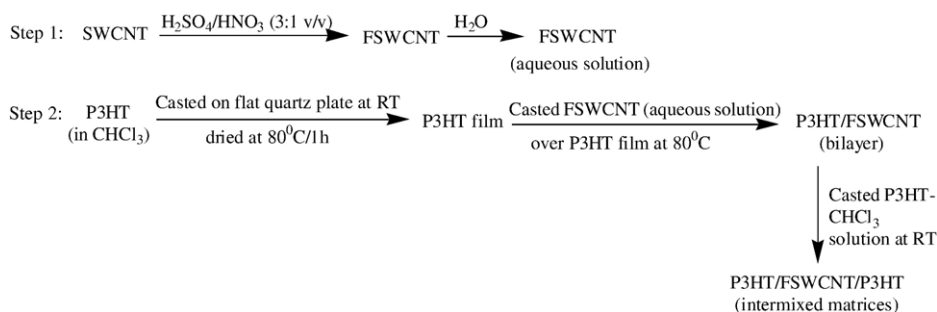
functional moieties covalently attached to the sidewalls of the SWCNTs [27]. Notably, the effect of moisture on the properties of this type of composite has not been studied so far.

In the present investigation, we have solubilized SWCNTs in water by ‘acidic treatment’ and formed a composite with π -conjugated pristine poly(3-hexylthiophene) (P3HT) polymer in the nanotube’s functionalized and non-functionalized states. We report here a comparative study of both types of composites to see the effect of solubilization of SWCNTs in terms of homogeneity of composite and conductivity of the respective matrix. We have observed a manifold ($\sim 10^6$ times) increase in room temperature dc electrical conductivity (σ_{dc}) with merely $\sim 4\%$ functionalized SWCNTs (FSWCNTs) inclusion to the P3HT matrix, whereas even with more than $\sim 20\%$ addition of non-functionalized SWCNTs (non-FSWCNTs) into P3HT the increase in conductivity is only $\sim 10^4$ times. The conductivity enhancement is explained in terms of largely homogeneous morphological evolution of composite with appreciably less quantity of FSWCNTs over non-FSWCNTs, a consequence of the formation of finite-sized nanotubes percolative network with viable inter-nanotubes interaction. In this work, we demonstrate, for the first time, a percolative network of efficient electron transporting nanotubes in a hole transporting π -conjugated polymer, forming homogeneous heterostructure required for polymer electronic devices such as organic field-effect transistor (OFET), organic photovoltaic (OPV), etc. [12]. We have also studied the effect of moisture on the properties of FSWCNT–P3HT composite and the possibility of thermal de-functionalization (after composite formation) to restore the inherent properties of carbon nanotubes about which very little is known to date.

2. Experimental section

P3HT was synthesized in our laboratory as reported earlier [2]. Molecular weights of pristine P3HT are typically

$M_w = 39,278$ and $M_n = 27,298$ with a polydispersity (PD) index of 1.44. SWCNTs were purchased from Sigma Aldrich and used as received and in functionalized form. The covalent functionalization was carried out in our laboratory by suspending raw SWCNTs in a concentrated sulphuric acid/nitric acid mixture (3:1 v/v) and sonicated for 2 h. The acid-treated nanotubes, after filtration, was thoroughly washed with a dilute sodium hydroxide aqueous solution and then with distilled water till the filtrate became colorless as reported elsewhere [28,29]. The non-FSWCNTs–P3HT composite films were formed at room temperature by solution casting of viscous non-FSWCNTs–P3HT–chloroform (CHCl₃) suspension, obtained after sonification for longer duration of time (24 h), on a specially designed cell having an inbuilt flat quartz plate. In the case of FSWCNTs–P3HT composite films, the film formation consisted of multi-steps: (a) the first layer was self-assembled P3HT film casted on the above-mentioned flat quartz plate from P3HT–CHCl₃ solution and subsequently dried, (b) the second layer of FSWCNTs was formed on the P3HT layer by casting an aqueous solution of FSWCNTs at 80 °C, and (c) the third layer was obtained by pouring the P3HT–CHCl₃ solution over a semi-permeable nanotube network that resulted into diffusion limited intermixing of constituents without harming the nanotube layer. It is worthwhile to mention here that the steps (a)–(c) give ample opportunity to form this kind of matrix with full control over the thickness of the individual layer and quantity of individual constituents. The most interesting aspect of this process is that the final step gives a composite film without the formation of distinct layers. In fact, once the solution of P3HT–CHCl₃ is poured over a non-interacting nanotube network, it diffuses to an inner polymer layer and forms a matrix of P3HT in which a nanotube network is imbedded without agglomeration of nanotubes as in the case of composite with non-functionalized nanotubes. Thus prevention of agglomeration of nanotubes in a polymer matrix is responsible for the formation of a strong network of nanotubes, a highly desirable combination for



Scheme 2.

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