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Study of photoluminescence quenching and DC conductivity measurements in polymer-SWNT composite films for various SWNT concentrations

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Abstract: Conducting polymer-SWNT composite films have a high potential in the area of Photovoltaic devices and Light emitting diodes (LEDs). SWNTs have high electron affinity and high mobility for electrons. As a result of this, the separation of photoinduced charges in the solar cell is very fast and efficient. For LEDs, the polymer-SWNT composite films act as efficient electron transporting layer (ETL). In the present work, composite solutions of P3HT and SWNTs were prepared in 1,2-dichlorobenzene with nanotube to polymer mass ratios varied from 0% to 30%. The films from this solution were spin coated on a glass substrate with the help of spinner keeping the film thickness ~100 nm. The photoluminescence (PL) of the film was observed with the help of Shimadzu Spectrofluorophotometer. It was found that the PL intensity decreases by ~90% as the concentration of the SWNT is increased from 0% to 30%. This decrease is due to the transfer of electrons from P3HT to SWNTs before the exciton in the polymer can decay radiatively to emit PL. DC conductivity of the composite films was measured with the help of Keithley sourcemeter in sandwich structures. It was found that conductivity increases by more than five orders of magnitude with the increase of SWNT concentration.

The composite films can therefore act as good electron transporter for LEDs and efficient electron acceptor for solar cells.

Keywords: SWNT; conducting polymer; composite; photoluminescence; dc conductivity; percolation limit; photovoltaics; LED.

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1 Introduction

Several workers have recently investigated the composite films of conducting polymers and carbon nanotubes (CNTs) [1–5] and have found considerable improvements in the electrical conductivity and mechanical strength of the film due to the association of CNTs [4–8]. Single walled carbon nanotubes (SWNTs) have high affinity and high mobility for electrons [9]. The semiconducting SWNTs have absorption in the near infrared region and their composite films with conducting polymers can harvest both visible and nIR regions [10]. The conducting polymer-SWNT composite films therefore have a high potential in the area of Photovoltaic devices [11,12]. Due to high Young's modulus of SWNTs (~1 TPa) and high tensile strength (~20 GPa) [13] it is possible to grow large area, mechanically strong and flexible composite films (>5 × 5 cm^2) using environment friendly processing techniques. Solar power therefore can be converted at a very low cost using photovoltaic devices based on conducting polymer-SWNT composite films grown by spin coating technique. The extremely high surface area of SWNTs and their high electron affinity enables very efficient dissociation of photoinduced excitons [14]. If the SWNTs are semiconducting enriched and are free from metallic portion, the percolation pathways are established in the composite films resulting in high performance of the photovoltaic device [13].

In the present work composite films of conducting polymer and SWNTs have been prepared using spin coating technique from a common solvent 1,2 dichlorobenzene. The optical absorption, photoluminescence (PL) and electrical conductivity of the films have been investigated. It has been observed that the PL of the composite films is quenched significantly with the increase of SWNT concentration. The electrical conductivity is found to increase by ~5 orders of magnitude as the concentration of the SWNTs is increased from 0% w/w to 30% w/w. The optical absorption of the conducting

polymer in composite films remains almost unaffected up to this concentration of SWNTs.

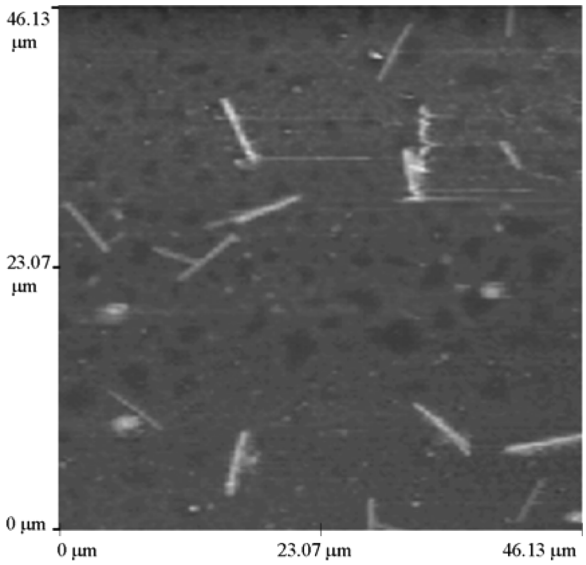
2 Experimental details

The conducting polymer (poly(3-hexylthiophene)), P3HT and as produced SWNT powder was commercially procured from Sigma Aldrich, USA. The SWNT diameter was in the range 0.7–1.2 nm and their length was up to 20 μm. The procured SWNT powder was purified by refluxing process [15] to remove metal catalyst and amorphous carbon impurities. For this SWNT powder was boiled in distilled water for ~12 h and was subsequently dried at 60°C in vacuum. The dried powder was heated in air for about 20 min. at 500°C. Later the powder was heated with 6M HCl for about 1 h in a water bath sonicator. This process is repeated four times to ensure the removal of amorphous carbon and metal catalyst impurities. Conducting polymer P3HT was dissolved in 1,2-dichlorobenzene in concentration 5 mg/ml. SWNTs were dispersed in this solution with varying concentrations from 0 to 30% w/w. Dispersion was achieved by ultra sonicating the suspension for about 5 minutes followed by a constant shaking in a shaker for about 4 h. After this the solution was kept undisturbed for two days to allow other impurities to settle down and the upper 50% of the dispersion was decanted off. The upper solution containing homogeneous dispersion of SWNT in the polymer solution was used for spin coating the composite films on a glass substrate. The thickness of the films was kept around 100 ± 10 nm. The samples were kept in vacuum oven for 1 h at 100°C to remove the remaining solvent. The composite films were characterised using Atomic Force Microscopy (AFM, Veeco instruments Inc., USA). The absorption and PL spectra were recorded using Shimadzu UV-VIS Spectrophotometer Model UV 2450 and Shimadzu Spectrofluorophotometer Model RF 5301PC respectively. For conductivity characterisation, a sandwich structure Al-film-Al was made in which, Al was patterned by vacuum evaporation on a glass substrate to act as anode and the composite film was spin coated over it. Again Al electrodes were deposited on the upper surface of the film by the same technique for taking the cathode contacts keeping the cell area 0.25 cm^2. The conductivity of the composite films was studied using Keithley Sourcemeter Model 2400.

3 Results and discussion

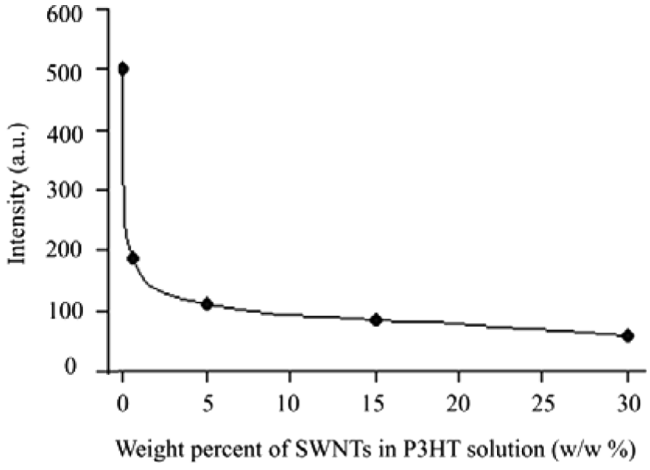
The morphology of the composite film as studied by AFM is shown in Figure 1. It is observed that the length of the nanotubes varies from 4.8 μm to 7 μm and the nanotubes are found to be present in rope like bundles with bundle diameter ranging from 310 nm to 440 nm. The absorption spectra of the composite films were studied in the wavelength range 400–900 nm. The absorption of P3HT is found to remain almost unchanged by the presence of SWNTs up to concentration of 30% w/w. Further addition of SWNTs results in the decrease of optical absorption of conducting polymer, which should be avoided in the interest of the efficiency of the photovoltaic devices.

Figure 1 Typical AFM image of the composite film



For studying the PL spectra of the composite films, the excitation wavelength 550 nm was used (maximum absorption of P3HT is at 550 nm) and the emission spectra were studied in the wavelength range 400–800 nm. The variation of PL peaks obtained from the PL spectrum is shown in Figure 2. It can be observed that with increase in concentration of SWNTs, the intensity of PL emission peak decreases and as the concentration of SWNTs reaches 30% w/w, about 90% of the PL intensity is quenched. This indicates that the rate of transfer of photoinduced electrons from the donor polymer to acceptor SWNTs increases tremendously as the SWNT concentration is increased.

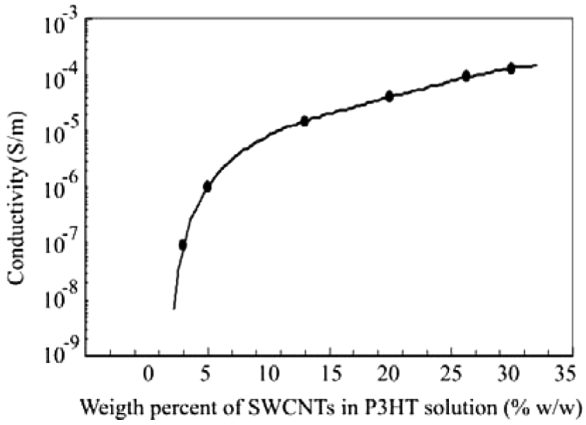
Figure 2 Quenching of PL emission from the polymer P3HT with variation in SWNT concentration in the composite



A fast transfer of photoinduced charges from donor to acceptor is very essential for an efficient photovoltaic device [16]. If the electron is not transferred within few femto seconds, the photo generated exciton will decay to ground state emitting PL resulting in an inefficient photovoltaic device.

The variation in dc conductivity of the composite film with increase in SWNT concentration is shown in Figure 3. It is found that the value of conductivity increases rapidly with increase of SWNT concentration and it increase by about five orders of magnitude as the concentration reaches 30% w/w. The high conductivity of composite films helps in collection of photo induced charges by the electrodes. For LEDs, therefore polymer-SWNT composite films can be used as electron transporting layer (ETL). In general the mobility for electrons in conducting polymers is much lower than that for holes due to efficient trapping of electrons by the impurities and traps in the polymers. Due to high mobility of electrons in SWNTs, use of polymer-SWNT composite film as ETL is a good alternative.

Figure 3 Change in conductivity of the P3HT-SWCNT composite films with variation in SWCNT concentration



For low weight fraction of SWNTs, the nanotubes are isolated and it is the conductivity of P3HT, which governs the conductivity of the composite films. The observed electrical response of the composites for higher SWNT concentration can be described by percolation theory [17] and is given by

$$\sigma = C\,(f - f_c)^t \tag{1}$$

where σ is the composite conductivity, f is the weight percent of nanotubes in the composite, f_c is percolation limit, C is a constant and t is the critical exponent. Our experimental data fits with the equation for a value of f_c as ~1% and t as 1.5. It has been shown by Stuffer [18] that for a three dimensional percolation systems the value of exponent t should be close to 2. A value lower than 2, can mean that the percolation system network deviates from a classical random network and has a large number of dead arms [19]. The low percolation threshold observed in the present experiment is due to high aspect ratio (~10^3) of our samples. A low percolation threshold is desirable for the photovoltaic devices because the absorption spectrum gets affected at higher concentrations of SWNTs.

4 Conclusions

The conducting polymer-SWNT composite films have a high potential for fabrication of large area, mechanically reinforced and flexible photovoltaic devices at extremely low cost. In the present experiment it has been shown that incorporation of SWNTs with conducting polymer P3HT results in an increase of conductivity by ~5 orders of magnitude and quenching of PL by 90%, showing efficient transfer of photoinduced charges from donor polymer to acceptor SWNTs. These are highly desirable requirements for fabricating photovoltaic devices from these composite films. Also the high conductivity of the composite films makes them usable in LED to act as ETL.

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