



Direct visualization of percolation paths in carbon nanotube/polymer composites



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ABSTRACT

Composites of single-walled carbon nanotubes (SWNT) and conjugated polymers are highly interesting as active semiconducting layers in solution-processable and flexible electronics. Understanding the percolation behavior and percolation threshold for electrical conductivity in these composites is a prerequisite for future applications. Here, we investigate the concentration and length dependence of on-currents and apparent mobilities for selectively dispersed, semiconducting (6,5) single-walled carbon nanotubes in a matrix of the dispersing polyfluorene-bipyridine copolymer (PFO-BPy) through field-effect transistor measurements. More importantly, we directly visualize the percolation paths at and above the percolation limit by near-infrared electroluminescence (EL) imaging with high spatial resolution. EL imaging reveals the various shapes of critical percolation paths at the threshold and the non-uniformity of charge transport even at high SWNT concentrations. We also find that percolation paths differ depending on the assignment of the injecting electrodes probably due to different injection barriers and variation of nanotube density at the electrodes.

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1. Introduction

Composites of multi- or single-walled carbon nanotubes (CNTs) and polymers have been an active area of research for many years with numerous practical applications such as mechanical reinforcement of thermoplastic polymers [1] and polymer fibres [2], electromagnetic shielding, flame retardants, anti-fouling coatings, etc. [3,4] In recent years the electrical conductivity [5] and thermal conductivity [6] of CNT/polymer composites have received increased attention, especially with regard to their application as thermoelectrics [7,8] and in flexible electronics [9,10]. At the same time, certain classes of conjugated polymers, in particular the polyfluorenes, were found to be highly efficient for the selective dispersion of only semiconducting single-walled carbon nanotubes (s-SWNTs) in organic solvents and even for specific diameters or chiralities [11,12]. These findings resulted in the search for and

discovery of many other conjugated polymers that are also able to efficiently separate semiconducting from metallic nanotubes in as-grown SWNTs [13]. For example, the polyfluorene-bipyridine copolymer PFO-BPy was found to result in almost monochiral dispersions of semiconducting (6,5) nanotubes when small-diameter CoMoCat nanotubes were dispersed with it in toluene [14]. After this long-standing hurdle for the investigation and application of semiconducting SWNTs as an electronic material was overcome, nanotubes were successfully integrated in (opto-)electronic devices such as solar cells [15] and field-effect transistors (FETs) [16]. FETs with dense, solution-processed (spincoated or printed) random networks of polymer-sorted s-SWNTs show excellent device characteristics with field-effect mobilities of about $5\text{--}50\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, high on/off ratios ($10^5\text{--}10^7$) and in some cases ambipolar transport, while also being flexible and highly stretchable [17–22]. They thus outperform many other solution-processable semiconductors, in particular semiconducting polymers, that can only reach carrier mobilities of less than $10\text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [23,24].

For the application of polymer-sorted s-SWNTs in FETs the excess polymer that remains from the dispersion process is usually removed in order to obtain a pure nanotube network. However, dispersions without this excess polymer are not very stable and

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quickly lead to reaggregation of the nanotubes. This instability results in processing non-uniformities and batch-to-batch variations. A possible approach to obtain better *s*-SWNT dispersion stability and processability while also reducing the amount of processing is to keep the dispersing polymer and create thin *s*-SWNT/polymer composite films with properties similar to the pure nanotube networks and considerably enhanced transport compared to the pure polymer. The resulting properties of the composite will depend on the concentration and length of the nanotubes with respect to the percolation limit. Adding small amounts of single-walled carbon nanotubes (SWNTs) to semiconducting polymer layers in FETs has been previously shown to have beneficial effects even below the percolation limit. Charge injection was improved for a wide range of different hole or electron conducting polymers [25,26] albeit without increasing the overall charge carrier mobility. By increasing the *s*-SWNT concentration above the percolation limit it should be possible to reach high on-conductances and high charge carrier mobilities in polymer/CNT composites and thus produce competitive devices with a minimum of processing steps.

To achieve carrier mobilities and on-conductances that are not limited by the polymer, the amount of *s*-SWNTs has to surpass the critical percolation concentration. At the percolation threshold the electrical conductivity of the composite will increase abruptly. Percolation theory describes this behavior and has been applied to pure CNT networks and CNTs in insulating polymers [5,27–29]. However, while the determination of the percolation threshold is straightforward from electrical measurements at different concentrations the actual percolation paths at the threshold and above are very difficult to investigate or to visualize experimentally. So far only few examples for pure SWNT networks [30–33] and none for SWNTs embedded within a polymer matrix exist. This lack makes the comparison of experiments to theoretical models that can predict and visualize percolation clusters impossible. Further, being able to visualize percolation pathways in *s*-SWNT/polymer composites would be very useful for further optimization of these materials and thin film devices in terms of uniformity and processing conditions.

Here, we use almost monochiral dispersions of semiconducting (6,5) SWNTs with the conjugated polymer PFO-BPy (poly[(9,9-dioctylfluorenyl-2,7-diyl)-*alt*-co-(6,6'-(2,2'-bipyridine))]) in toluene, that give composite thin films with excellent optical properties [34,35] and are thus interesting for future optoelectronic applications that also require efficient charge transport. We demonstrate direct visualization of the percolation paths in these nanotube/polymer composites at and above the percolation threshold with micrometer resolution by using the near-infrared electroluminescence of the semiconducting SWNTs in ambipolar light-emitting field-effect transistors (LEFETs). Ambipolar LEFETs have been previously employed to visualize charge transport in polycrystalline semiconducting polymers and pure SWNT networks [33,36,37]. By varying the nanotube concentration we are able to identify single percolation paths close to the threshold and survey the uniformity of percolation well above the percolation limit. The charge transport characteristics of the investigated SWNT/polymer composites, such as high carrier mobility, high on/off ratio and low onset voltages, are promising for future applications in solution-processed and flexible electronics.

2. Materials and methods

2.1. Dispersions

High quality dispersions of long and semiconducting SWNTs in polymer solution were produced as previously described [38].

Briefly, 70 mg PFO-BPy (poly[(9,9-dioctylfluorenyl-2,7-diyl)-*alt*-co-(6,6'-(2,2'-bipyridine))]), for molecular structure see inset in Fig. 1a) were dissolved in 140 ml toluene and 49.8 mg of as-received CoMoCat SWNT powder (diameter 0.7–0.9 nm, Sigma-Aldrich, Lot#MKBV6100V) were added. Shear force mixing was applied for several days, using a Silverson L5M-A mixer at maximum speed, while keeping the temperature at 20 °C. (6,5) SWNTs were selectively dispersed by the PFO-BPy as described by Ozawa et al. [14]. Subsequent centrifugation with a Beckman Coulter Avanti J26XP centrifuge at 74200 g resulted in a supernatant only containing the polymer-wrapped (6,5) SWNTs. The supernatant was collected and centrifuged at 284600 g for 15 h (ultracentrifuge Optima MAX-XP (Beckman Coulter) with a swinging bucket rotor). The resulting (6,5) SWNT-pellets were redispersed in 1 ml of toluene in an ultrasonic bath for 15 min. From the absorption spectrum (see Fig. 1a) of this dispersion the residual PFO-BPy content was estimated to be lower than 0.03 mg/ml. 9 mg of PFO-BPY were added to this dispersion leading to a polymer concentration of ~9 mg/ml and a (6,5) SWNT concentration of 4.09 µg/ml. Portions of this SWNT/polymer stock dispersion were combined with different volumes of a solution of 9 mg/ml PFO-BPy in toluene to keep the polymer concentration constant while creating a dilution series of the nanotubes with (6,5) SWNT E_{11} absorbances from 0.16 to 2.41. These SWNT/polymer dispersions were immediately used for spincoating (see below). Absorption spectra of the dispersions were recorded (cuvette with 1 cm path length) with a Cary 6000i spectrometer (Varian Inc.). To ensure linearity of the detector response

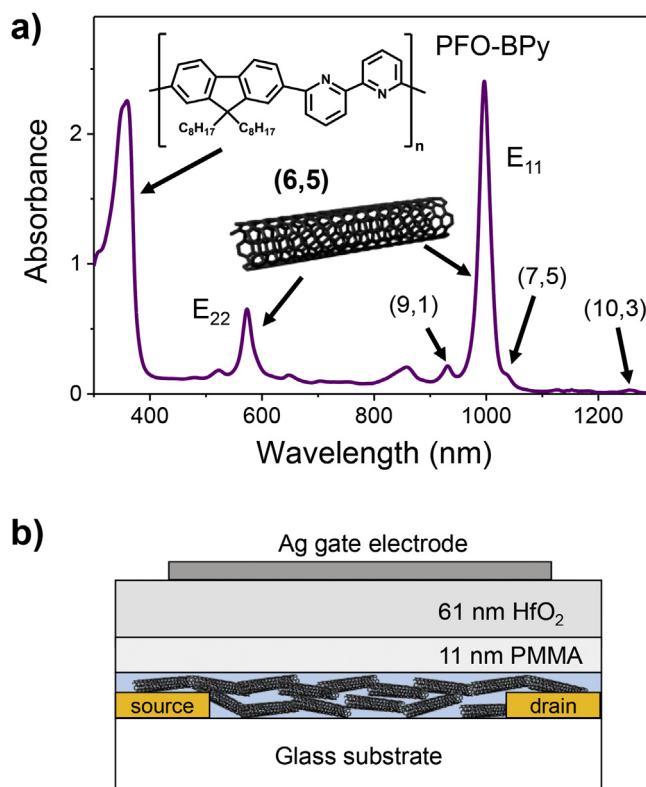


Fig. 1. a) Absorption spectrum of redispersed polymer-sorted SWNTs with clearly visible E_{11} and E_{22} absorption peaks of the (6,5) nanotubes and their phonon side band as well as absorption by residual PFO-BPy (359 nm). The spectrum was acquired for a diluted dispersion (1:19) and scaled to display the spectrum of the undiluted dispersion (concentration of (6,5) SWNTs: 4.09 µg/ml). Small absorption peaks by (7,5), (9,1) and (10,3) nanotubes are also visible. The insets show the molecular structures of the polymer and (6,5) SWNTs. b) Schematic bottom contact/top gate transistor structure with a 40 nm thick SWNT/PFO-BPy composite film and a PMMA/HfO_x bilayer dielectric.

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