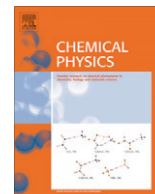


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## Enhancing extraction of photogenerated excitons from semiconducting carbon nanotube films as photocurrent

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## ABSTRACT

We study the effect of residual polymer on exciton transport and the external quantum efficiency (EQE) of photocurrent generation in thin film semiconducting single walled carbon nanotube (s-SWCNT)/C<sub>60</sub> heterojunction diodes. Specifically, increasing the s-SWCNT film content from 22% to 43% increases peak EQE from absorption by s-SWCNTs from 15% to 23%. We monitor intertube exciton energy transfer via steady state photoluminescence spectroscopy and determine the length scale for exciton migration via s-SWCNT film thickness dependence of EQE. We observe increased intertube exciton transfer in photoluminescence spectra with increased polymer removal, and EQE-thickness dependence suggests increased intratube exciton transport along isolated pathways. Our results extend the state of the art with respect to the use of s-SWCNT thin films as photoabsorbers in photovoltaics, describe exciton migration in s-SWCNT films, and provide a framework for the design of high efficiency s-SWCNT photovoltaic and photodetector devices.

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### 1. Introduction

Semiconducting single-walled carbon nanotubes (s-SWCNTs) are promising materials for light detection and photovoltaic energy conversion, owing to their unique ensemble of photophysical properties [1]. For example, s-SWCNTs have optical and electronic bandgaps which can be tuned from 0.5 to 2.0 eV [2], optical absorption cross-sections in excess of  $1 \times 10^{-17} \text{ cm}^{-2}$  per atom [3], charge carrier mobilities up to  $10^5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  [4], and can be processed in both organic and aqueous solvent systems. Like in organic polymers and small molecules, photogenerated charges in s-SWCNTs are bound as excitons with binding energies  $> k_B T$  at room temperature, of order 0.2–0.5 eV [5,6]. Consequently, photogenerated excitons must be dissociated into free carriers in order to harvest their potential energy for solar photovoltaics or photo-detection. This splitting is accomplished by creating a donor/acceptor semiconductor heterojunction with energetic offsets greater than the exciton binding energy, inducing charge transfer from photoexcited s-SWCNTs to the acceptor material. The overall incident-photon-to-collected-electron conversion efficiency of the photovoltaic device and/or sensitivity of the photodetector is determined not only by the quantum efficiencies of light absorption and exciton dissociation, but also by how efficiently excitons

are channeled to this active interface. For these reasons, a deep understanding of intertube and intratube exciton diffusion rates and mechanisms, exciton lifetimes, recombination pathways, recombination kinetics and the morphological influences of all of the above in thin film samples containing many s-SWCNTs is critical to realizing technologically relevant photovoltaic devices.

Recently, we demonstrated efficient power conversion and photocurrent generation from optically excited s-SWCNTs using C<sub>60</sub> as an acceptor [7–9]. Bilayer photovoltaic heterojunction diodes were created by depositing a thin film of s-SWCNTs onto a transparent indium tin oxide (ITO) anode, followed by the thermal evaporation of a film of C<sub>60</sub> on top of the s-SWCNTs followed by the cathode contact. The diodes were rectifying with a  $10^4$  rectification ratio at  $\pm 1 \text{ V}$ . Optical excitation of the s-SWCNTs in the near-infrared was observed to result in a photovoltaic effect, with a generated photocurrent at zero-bias and light-to-electrical power conversion in the 4th quadrant of the current–voltage characteristics of the diode. In diodes with thin layers of s-SWCNTs, approaching roughly one monolayer of s-SWCNTs, the electron transfer efficiency from the photoexcited s-SWCNTs to the overlying film of C<sub>60</sub> approached 100% for s-SWCNTs with optical bandgaps  $> 1 \text{ eV}$ , indicating that the s-SWCNT/C<sub>60</sub> materials pair is highly promising for use in light harvesting devices. Using tailored polydisperse mixtures of s-SWCNTs, it should be possible to capture the majority of the solar photon flux  $> 1.1 \text{ eV}$  in films of 100–200 nm in thickness. If we could route excitons through such a film implemented in a bilayer heterojunction to the interface with the C<sub>60</sub> layer, then it would be possible to realize high-efficiency solar cells and

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photodetectors with broadband EQE approaching unity. In consideration of the many reports placing the exciton diffusion length along isolated s-SWCNTs in the range 200–600 nm, this exciton channeling problem seems trivial [10–12].

However, when tracking the quantum efficiency by which photogenerated excitons in s-SWCNT films migrate to the hetero-interface with  $C_{60}$  as a function of s-SWCNT film thickness, we extracted a short effective exciton diffusion length of order 3 nm [7]. We understood this discrepancy in diffusion length partly by determining that the s-SWCNT film morphology consisted of s-SWCNTs overwhelmingly “lying-down” on the ITO, requiring that exciton migration to the  $C_{60}$  interface occur through the slower process of tube–tube exciton hopping. Developing a complete understanding of the mechanisms of exciton migration in our poly-disperse films and identifying extrinsic factors which influence this migration will be critical to realizing the full potential of s-SWCNTs as photoabsorbers.

In the case that exciton hopping from tube to tube dominates exciton migration, increasing the electronic coupling between s-SWCNTs should enhance exciton migration. In our films, the coupling between s-SWCNTs is modulated by the coexistence of poly(9,9 dioctylfluorene 2,7-diyl) (PFO), which we use for its selective affinity for small diameter s-SWCNTs in toluene and toluene-like solvents [13–15]. While these polymers are critical for obtaining samples of s-SWCNTs with low concentrations of metallic species and aggregates, the quantity of residual polymer present in cast films influences inter-tube coupling and therefore inter-tube exciton migration. In this manuscript, we examine the effects of excess PFO on the extraction of excitons and charges from s-SWCNT films. Specifically, we have created s-SWCNT films with varying amounts of PFO and have employed spectrally resolved photoluminescence and thickness-dependent measurements of photocurrent evolution as tools to characterize the migration of excitons.

## 2. Methods

Device quality solutions of s-SWCNTs were prepared by dispersing 1 mg mL<sup>-1</sup> HiPco® single walled carbon nanotubes (Unidym) with 1 mg mL<sup>-1</sup> PFO (American Dye Source) in toluene using a titanium sonotrode for 1 h, utilizing a water bath to cool the solution [13]. The resulting suspension was then centrifuged for 15 min at 50,000g over an 11 cm pathlength in a swing-bucket rotor, the supernatant collected and the pellet discarded. The supernatant was then filtered through a 5 µm Millex Millipore-SV® syringe filter. The resulting, dilute, solution was concentrated while simultaneously removing excess PFO by pelleting the s-SWCNTs out of solution at 50,000g in 11 cm long fluoropolymer centrifuge tubes in a 30 deg fixed angle rotor held at 4 °C over a period of time approaching 90 h for high extraction yields. The pellet was then redispersed, and dissolved in fresh tetrahydrofuran (THF) by heating on a hotplate set to 90 °C for iterative pelleting, or redispersed into chlorobenzene to yield a stable solution. The resulting solutions consisted of primarily the (7, 5), (7, 6), (8, 6), (8, 7), and (9, 7) chiralities of semiconducting nanotubes – typical of the HiPco PFO/toluene system [13,16] – wrapped by tunable amounts of PFO, with minimal quantities of metallic nanotubes, amorphous carbon, aggregates, or residual catalyst.

Thin films of the s-SWCNTs were deposited by doctorblade casting on a hotplate with a surface temperature of 100 °C in a dry nitrogen glovebox. Droplets (5–20 µL) of s-SWCNT containing solution were placed at one end of the heated substrate and immediately drawn across the substrate using a doctorblade (casting knife) with a substrate clearance between 0.1 and 0.25 mm. Films of increasing thickness were built up by iterative casting. Quartz

substrates were used for optical characterization and ITO-coated glass substrates (Prazisions Glas & Optik, <20 Ω/sq.) were used for device manufacture. Both quartz and ITO substrates were previously cleaned in a typical solvent degreasing process involving acetone, trichloroethylene, and isopropanol; following solvent baths, the substrates were UV/ozone exposed for 20 min at 100 °C.

Bilayer heterojunction devices were fabricated by transferring s-SWCNT coated ITO to a thermal evaporator and depositing 120 nm  $C_{60}$ , applying shadow-masks to define independent 1 mm diameter cathodes, and sequentially depositing 10 nm bathocuproine (BCP) and 100 nm silver cathodes. All evaporations were conducted with a background pressure <5 × 10<sup>-7</sup> torr.

## 3. Results and discussion

In order to study exciton migration in films of s-SWCNTs with varying amounts of PFO, films were cast from three different s-SWCNT solutions, which were taken after the second, third and fourth pelleting iterations. Solution absorbance was measured to quantify PFO content and chirality distributions (Fig. 1A). The (7, 5), (7, 6), (8, 6), (8, 7), and (9, 7) s-SWCNTs were present in abundances of 23%, 28%, 29%, 19%, 2%, respectively, (determined from fit  $E_{11}$  full-width-half-maximum-amplitude products, assuming optical cross section chirality family dependences directly proportional to exciton oscillator strength family dependences calculated by Ando [17]. Relative chirality abundance remained constant among the three samples studied by extracting solutions 1, 2, and 3 from the same master-batch during processing. The PFO concentration in each solution was determined by analyzing the PFO spectral weight at 390 nm, having subtracting off broad background absorption and expected absorption arising from the  $E_{33}$  and  $E_{44}$  optical transitions of the s-SWCNTs in their pre-determined abundance. A measured PFO solution optical cross-section of 1.69 × 10<sup>5</sup> cm<sup>2</sup>/g, (assumed to remain constant whether free in solution or wrapping a s-SWCNT) was used to quantify PFO concentrations in solution. s-SWCNT concentrations were determined by using the  $E_{11}$  optical cross-section of Hertel and coworkers of 1.02 × 10<sup>7</sup> cm<sup>2</sup>/mol C with a width of 44 meV for the (6, 5) chirality, [3] and the exciton oscillator strength family dependences of Ando [17]. The change in s-SWCNT optical cross-section from the work of Hertel and coworkers to ours due to changes in the external dielectric constant is expected to be minor (<10%) and was thus ignored [17]. Accordingly, the s-SWCNTs were estimated to represent 22%, 36%, and 43% of the solute by weight, for solutions 1, 2, and 3, respectively. Full analysis of the optical fitting and determination of the relative abundances of nanotubes and PFO is presented in the Supplementary Information, with the fit of the 43% s-SWCNT solution displayed in Fig. S1. Solutions containing roughly 43% by weight s-SWCNTs are consistently the lowest PFO:s-SWCNT ratio we can achieve using our approaches. It is unclear from our analysis whether successive removal of PFO from solution is due to desorption of PFO from the s-SWCNT surface, or whether PFO-wrapped s-SWCNT hybrids exist in this PFO:s-SWCNT ratio inherently.

The line-width of the  $E_{11}$  optical transitions in solution was fairly narrow, independent of the relative concentration of PFO. For example, the linewidth of the (7, 5) chirality in absorption was 23 meV in solution. However, this line-width increased to 42, 53, and 54 meV in films cast from solutions 1, 2, and 3, respectively (Fig. 1B). This increased broadening with increased removal of PFO suggests an increase in heterogeneity of the dielectric landscape and increased tube–tube coupling. The ratio of PFO peak absorbance at 390 nm to integrated absorbance across the  $E_{22}$  s-SWCNT transitions from 600–780 reduced significantly from

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