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Effect of semiconductor polymer backbone structures and side-chain parameters on the facile separation of semiconducting single-walled carbon nanotubes from as-synthesized mixtures

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ABSTRACT

Semiconducting single-walled carbon nanotubes (SWNTs) show promise as core materials for next-generation solar cells and nanoelectronic devices. However, most commercial SWNT production methods generate mixtures of metallic SWNTs (m-SWNTs) and semiconducting SWNT (sc-SWNTs). Therefore, sc-SWNTs must be separated from their original mixtures before use. In this study, we investigated a polymer-based, noncovalent sc-SWNT separation approach, which is simple to perform and does not disrupt the electrical properties of the SWNTs, thus improving the performance of the corresponding sc-SWNT-based applications. By systematically investigating the effect that different structural features of the semiconductor polymer have on the separation of sc-SWNTs, we discovered that the length and configuration of the alkyl side chains and the rigidity of the backbone structure exert significant effects on the efficiency of sc-SWNT separation. We also found that electron transfer between the semiconductor polymers and sc-SWNTs is strongly affected by their energy-level alignment, which can be tailored by controlling the donor-acceptor configuration in the polymer backbone structures. Among the polymers investigated, the highly planar P8T2Z-C12 semiconductor polymer showed the best sc-SWNT separation efficiency and unprecedentedly strong electronic interaction with the sc-SWNTs, which is important for improving their performance in applications.

1. Introduction

Single-walled carbon nanotubes (SWNTs) have been regarded as one of the most promising next-generation materials for more than 20 years. This is mainly because the one-dimensionally quantized SWNTs exhibit a wide variety of unique chemical, electrical, and optical properties that make them suitable for a variety of applications, such as in transparent electrodes [1,2], biological [3,4] and chemical sensors [5], and optoelectronic devices [6–8]. In recent years, SWNTs have been actively investigated as core materials for solar cells and flexible/stretchable nanoelectronic devices [9,10]. Semiconducting SWNTs (sc-SWNTs), as opposed to metallic SWNTs (m-SWNTs), are required for these applications [11–14]. For example, high-purity sc-SWNTs are required for the fabrication of active layers in solar cells, as m-SWNTs act as recombination sites and promote nonradiative emission, even at trace levels, thus negatively impacting charge separation at the interfaces of electron-donor and electron-acceptor substances [15].

However, most commercial SWNT production methods produce mixtures of m- and sc-SWNTs, and therefore, they need to be separated before application. A number of post-treatment techniques have been reported for effectively separating sc-SWNTs from m-SWNTs using either covalent or noncovalent functionalization, including electrophoresis [16], ultracentrifugation [17–19], selective chemistry [16,20–24], DNA wrapping [25,26], gel chromatography [27,28], and polymer wrapping [29,30].

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Recently, high-efficiency polymer-based separation approaches have been reported. For example, Lee et al. reported the isolation of a selective dispersion of high-purity sc-SWNTs with relatively small diameters (0.8–1.0 nm) using polythiophene derivatives bearing C12 alkyl chains [31], and Gomulya et al. demonstrated the selective wrapping of sc-SWNTs with a relatively large average diameter (1.4 nm) using polyfluorene derivatives bearing longer alkyl side chains [29]. It has been concluded that an appropriate length, density, and configuration of the polymer side chains are critical for the polymer to wrap around the sc-SWNTs in a helical fashion. The selective separation of the sc-SWNTs by the optimized polymer was also confirmed by the improved efficiency of the device in which they were employed, which would have been much lower if even a small amount of m-SWNTs were present.

These polymer-based approaches are simple and do not disrupt the electronic structure of the SWNTs during separation because they involve noncovalent functionalization. Furthermore, the resultant sc-SWNT/polymer mixture can be used in its hybrid form for certain applications, including in solar cells, avoiding the need for additional post-processes and allowing these approaches to be commercially scalable.

However, these previous studies mainly focused on the effects of side-chain length and density on polymer-SWNT interactions, despite polymer backbone structures also being a significant factor in these interactions and, consequently, the performances of the corresponding devices. It has been previously suggested that a rigid backbone enables a polymer to form a highly ordered supramolecular conformation around an SWNT.

We have previously investigated the effect of polymer structure in alkyl-chain-substituted thiophene/thiazole semiconductor polymers (i.e., their backbone and side-chain lengths) on charge transfer and binding energy in their nanohybrids with SWNTs [10]. We reported that longer side chains interact with sc-SWNTs more effectively, but that electrostatic interactions between the polymer backbone and m-SWNTs hinder effective interaction between the polymer and sc-SWNTs. Furthermore, we found that side-chain length affects the efficient dispersion of sc-SWNTs in the polymer matrix, and the polymer backbone controls its density of states (DOS), i.e., the charge transfer between the polymer and the sc-SWNTs. Therefore, it is important to investigate the effect of polymer backbone structure as well as side-chain length, because the former controls the performance and the latter controls the separation efficiency of the polymer/sc-SWNT hybrid.

In this study, we investigated the effects of polymer backbone structure (in terms of donor-acceptor configuration) and side-chain parameters on the separation of sc-SWNTs from SWNT mixtures and the electron-transfer behavior of the resultant hybrids. We found that when the side-chain length is C12 and the energy levels of the polymer match well with those of the sc-SWNTs, highly efficient sc-SWNT separation is achieved by means of an unprecedented strength of interaction between the polymer and sc-SWNTs.

2. Material and methods

2.1. SWNT dispersions

As-produced HiPco (Unidym), CoMoCAT (SG65, SWeNT) or arc-discharged SWNTs (Hanwha Chemical) were used for functionalization and separation. The reference SWNTs were suspended in H_2O with 2% (w/v) sodium cholate (Sigma-Aldrich) and sonicated (Vibra-Cell™ Ultrasonic Liquid Processor VCX-750, Sonics & Materials, USA) followed by ultracentrifugation (Optima™ L-100 XP Ultracentrifuge, Beckman-Coulter Optima, USA) to remove SWNT bundles and other impurities following a previously reported method [32].

For the separation experiments, 5 mg of HiPco, CoMoCAT, or arc-discharged SWNTs and 10 mg of semiconductor polymer (regioregular poly(3-hexylthiophene-2,5-diyl) (rr-P3HT, Sigma-Aldrich), poly(didodecyl quaterthiophene alt-didodecyl bithiazole) (PQTBTz-C12) [10], regioregular poly(3-dodecylthiphene) (rr-P3DDT, Sigma-Aldrich), or poly(tetryldodecyl octathiophene alt-didodecyl bithiazole) (P8T2Z-C12) [33]) were suspended in 25 mL of toluene (Sigma Aldrich) (We used toluene as a solvent rather than chlorinated solvents such as chloroform or 1,2-dichlorobenzene because the use of chlorinated solvents has been known to hamper selective interaction between SWNTs and semiconductor polymers [31,34]). This suspension was kept in a temperature-controlled cooling bath and sonicated (Vibra-Cell™ Ultrasonic Liquid Processor VCX-750, Sonics & Materials, USA) for 30 min at 0 °C and an amplitude level of 70%. The solution was subsequently centrifuged (Eppendorf™ 5424 Microcentrifuge, Eppendorf, Germany) for 90 min at 14,680 rpm to remove SWNT bundles and insoluble materials. The supernatant was carefully collected for further analysis. The absorption spectra of SWNTs and polymer-SWNT complex solution were obtained by UV–vis spectrometer (Lamda 750 UV/vis/NIR Spectrophotometer, Perkin-Elmer, USA) and photoluminescence (PL) contour plots of the samples were characterized by a spectrofluorometer (HORIBA Jobin Yvon, Nanolog, 450 W xenon short-arc excitation, emission resolution 4.2 nm, InGaAs linear array detector with scanning range from 800 to 1700 nm, HORIBA Scientific, Japan).

2.2. Film preparation

We fabricated SWNT films from HiPco, CoMoCAT, or arc discharged SWNT using a vacuum filtration method. We used Anodisc 25 alumina membranes (Whatman, 0.2 μm pore size, 25 mm diameter). The membranes were placed on a glass frit and washed with 20 mL of H_2O under vacuum. Then, 20 mL of the diluted SWNT solution was slowly drawn through the vacuum filtration membrane, followed by 20 mL H_2O to remove remaining surfactants from the SWNT film. The film was then allowed to dry in an oven at 70 °C for 20 min. To dissolve the alumina membrane underlying the SWNT film, we placed the film on 3 M NaOH solution in a petri dish for 20 min. The NaOH solution was then completely removed by flushing several times with deionized water. The SWNT film was then carefully placed onto a glass slide. The film on the slide glass was left to dry in an oven at 70 °C for 2 h and then annealed in a furnace (Lindberg/Blue M™ Tube Furnace, Thermo Scientific, USA) at 450 °C for 1 h under nitrogen atmosphere to remove any residual water and organic surfactants. We prepared hybrid films (semiconductor polymer (rr-P3HT, PQTBTz-C12, rr-P3DDT, or P8T2Z-C12) + SWNTs (HiPco, CoMoCAT, or arc-discharged)) using the same vacuum filtration method as that used for preparation of the SWNT films but using toluene as a solvent instead of water. The hybrid films were also annealed in a furnace at 450 °C for 1 h to see which type of SWNT selectively interacted with the semiconductor polymers. The absorption spectra of the prepared film samples were characterized by UV–vis spectrometer (Lamda 750 UV/vis/NIR Spectrophotometer, Perkin-Elmer, USA).

3. Results and discussion

Fig. 1 shows (a) the chemical structures of the semiconductor polymers utilized in this study and (b) their absorption spectra when dispersed in toluene. For semiconductor polymers to form a supramolecular structure around SWNTs, several structural conditions should be fulfilled. Lee et al. suggested that alkyl-side-chain length, density, and regioregular configuration are critical for polymers to properly wrap around sc-SWNTs [31]. In

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