Semiconducting Polymer Assisted Separation of Semiconducting Carbon Nanotubes for High Efficiency Hybrid Photovoltaics

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Introduction

Currently, conventional silicon photovoltaics (PV) are too expensive to compete with fossil fuels due to their high temperature processing. Solution-processed organic and carbon nanotube photovoltaics, in contrast, exhibit advantages such as low cost, ready availability, light-weight, flexibility and stretchability. Carbon nanotubes, in addition, have also demonstrated ultra-high charge carrier mobility, strong light absorptivity as well as good temperature/environment stability in comparison to organic solar cells.

However, the as-synthesized SWNTs are typically mixtures of tubes with various chiralities, with approximately one- third metallic and the remaining two-third semiconducting. Only semiconducting SWNTs are needed for active layer in solar cells. SWNTs also have a wide range of diameters and bandgaps, which have significant impact on device performance. The central objective of this work to develop a scalable method to separate semiconducting SWNTs with a better purity and controlled bandgap distribution for solar cell applications.

Results

My colleagues (including myself) have developed a method to sort HiPco SWNTs using *regioregular* polythiophenes. It was a simple and low-cost process to effectively sort large quantity of semiconducting SWNTs. I then went on to 1) understanding the mechanism for polymer sorting of semiconducting SWNTs; 2) optimize the sorting yield and purity of semiconducting SWNTs with different diameters; 3) Apply sorted semiconducting SWNTs for solar cells applications.

In order to understand the mechanism of polymer sorting of semiconducting. I first investigated the effects of various solvents on the sorting of SWNTs by polythiophenes. In particular, I observed that the dispersion yield could be increased to over 40 wt% using decalin or o-xylene while maintaining high selectivity towards semiconducting SWNTs. Among all solvents explored for SWNT sorting, only non-polar solvents can result in selective dispersion of semiconducting SWNTs. In addition, I found that both p-type and n-type polymers can result in the enrichment of semiconducting SWNTs. Based on these results. I proposed a general mechanism to explain the selective dispersion of semiconducting SWNTs by conjugated polymers.

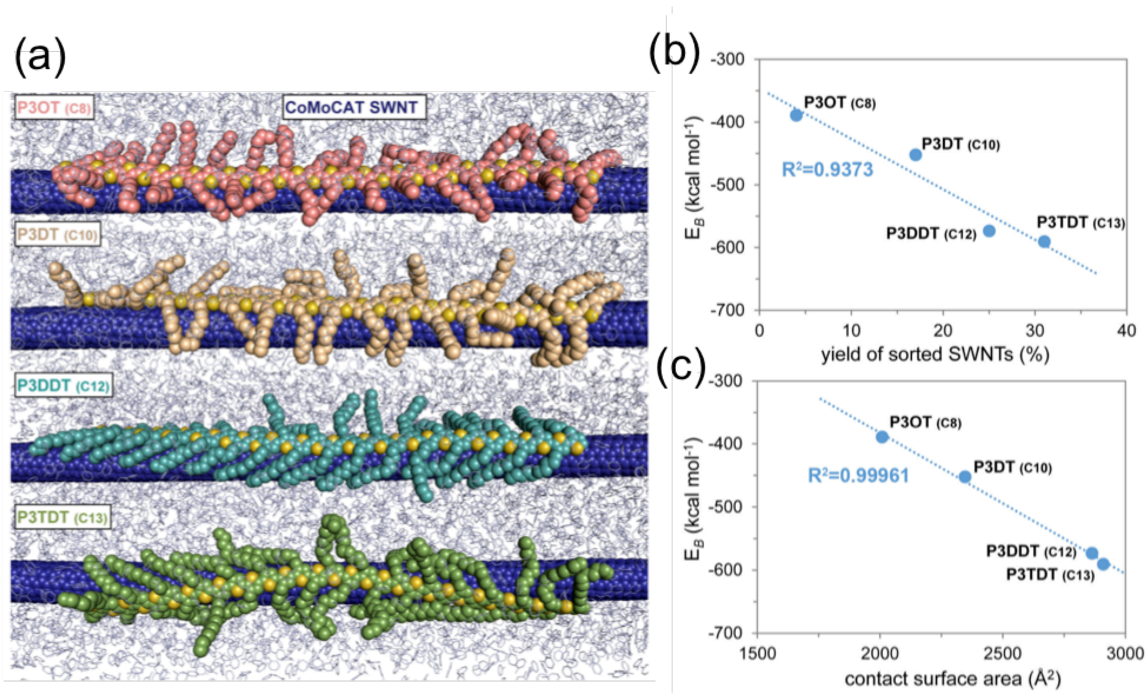

Figure 1 (a) Representative snapshots of the MD simulations for (6,5) SWNT with P3OT, P3DT, P3DDT, and P3TDT in explicit toluene. (b) Calculated binding energies (E_B) *vs.* yield of sorted (6,5) SWNTs. (c) Calculated binding energies (E_B) *vs.* contact surface area (CSA) between the polythiophene polymers and (6,5) SWNTs.

Large-diameter arc-discharged semiconducting SWNTs (1.2~1.7 nm) are reported to have higher charge carrier mobility than HiPco SWNTs (0.8nm~1.1nm) but the sorting of these large-diameter SWNTs has been difficult due to the strong van der Waals interactions between the lower curvature walls of the tubes. In order to achieve the sorting of large-diameter SWNTs, we designed large-plane dithiafulvalene/thiophene copolymer, with fused rings in dithiafulvalene to enable stronger interaction between the flatter walls of large-diameter SWNTs. We indeed found that higher dithiafulvalene to thiophene ratio copolymers results in better dispersion yield with SWNTs. By modifying polymer/SWNT ratio used in the sorting process further, we have achieved very high purity of semiconducting large-diameter SWNTs.

I also found that polythiophenes could sort small-diameter diameter CoMoCAT SWNTs (0.7nm~0.9nm) in a similar manner as sorting of HiPco SWNTs (0.8nm~1.1nm). I observed that the dispersion yield was directly related to the length of the polythiophene alkyl side chains. Molecular dynamics simulations (Figure 1a) in explicit toluene indicate that polymers with longer alkyl side chains bind more strongly to SWNTs due to the increased overall surface contact area with the SWNTs (Figure 1b and 1c).

Finally, I compared the effects of SWNTs with various diameters on the performance of SWNT based solar cells. The solar cell device structure and the corresponding energy band level diagrams are shown in Figure 2a and 2b. As predicted from Figure 2b, we indeed found that solar cells fabricated from small-diameter CoMoCAT SWNTs had higher open-circuit voltage (V_{OC}) than solar cells fabricated from HiPco SWNTs (Figure 2c). In addition, we found the better infrared external quantum efficiency (EQE) of polymer-sorted CoMoCAT SWNTs in comparison to polymer-sorted HiPco SWNTs (Figure 2d). This is as a result of improved type-II heterojunction formation with C60 acceptors as the active materials for solar cells.

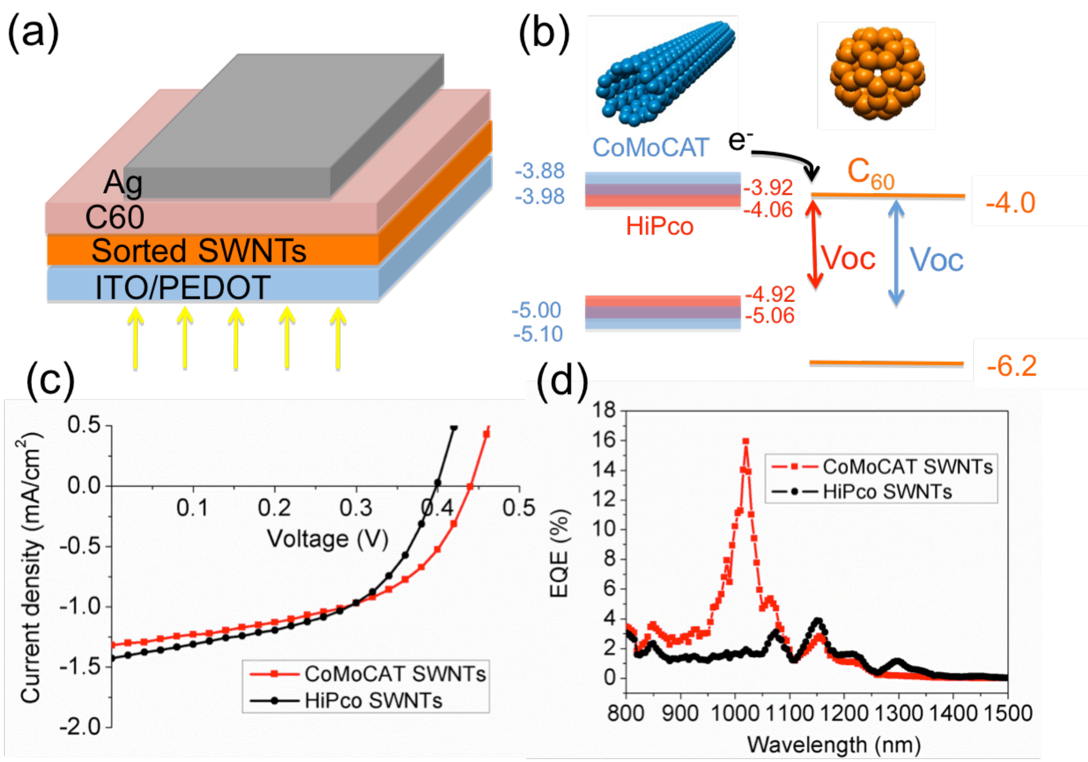

Figure 2. (a) Device structure of the carbon based solar cell structure. (b) Schematic diagram showing the band structure, predicted open circuit voltage and charge transfer of SWNTs/C_{60} heterojunction. (c) J-V characteristics of the devices measured under standard illumination AM1.5 for CoMoCAT SWNTs and HiPco SWNTs dispersed by polythiophenes. (d) External quantum efficiency for the comparison of HiPco and CoMoCAT SWNTs in the IR regime.

Significance, impact and future direction

The works reprted here demonstrate that we can tune the purity, yield and bandgap of sorted semiconducting carbon nanotube by applying various solvents, polymers, carbon nanotube types and sorting procedure. As a result, the final solar cell performances can be enhanced. The research leads to both better fundamental understanding on sorting of carbon nanotubes by conjugated polymers as well as their engineering applications in solar cell devices.

The technology of sorting semiconducting SWNTs with conjugated polymer will not only lead to better SWNT based solar cells but also lead to their applications in a range of other solution-processed electronic devices such as flexible electronic circuits, photodetectors, and thermoelectrics.

List of publications that have acknowledged link foundation support

1. H. Wang, J. Mei, P. Liu, K. Schmidt, G.J.Oses, S. Osuna, L Fang, C.J. Tassone, A.P. Zoombelt, A.N.Sokolov, K.N.Houk, M.F.Toney, Z. Bao. *Scalable and Selective Dispersion of Semiconducting Arc-Discharged Carbon Nanotubes by Dithiafulvalene/Thiophene Copolymers for Thin Film Transistors*. ***ACS Nano***, 26, 2659-2668 (2013)

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5. H. Wang, B. Hsieh, G. Jiménez-Osés, P. Liu, C.J. Tassone, Y. Diao, T. Lei, K.N. Houk, Z. Bao, *Solvent effects on polymer sorting of carbon nanotubes with applications in printed electronics,* ***Small***, 11,126-133 (2015)

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7. H. Wang, Y. Wang, B.T.C. Keong, K. Kim, J. Lopez, C. Wei, Z. Bao, *Shape-Controlled, Self-Wrapped Carbon Nanotube Electronics*, ***Advanced Science****,* 2, 1500103, (2015)

8. H. Wang, Z. Bao, *Sorting of semiconducting carbon nanotubes by conjugated polymers and their electronic applications*, ***Nano Today***, 10, 737-758 (2015)

Usage of discretionary funds

The funds were mainly used to compensate my stipend during 2012~2014. In addition, the funds support me to go to various scientific meetings to present my research findings such as MRS 2013, MRS 2014 and NT14 (The Fifteenth International Conference on the Science and Application of Nanotubes). I also used the funding to order supplies for my research projects.

Impact of the link fellowship

The fellowship was a very important encouragement for me during the early years of my graduate work since it is a demonstration of my capability to raise funding for my research. In addition, the fellowship allowed me to travel to various places for conferences, where I can develop my professional network and make friends in the research field outside my lab. All of these are important for my current career path.