The power of polymer wrapping

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Summary

Electronic and optoelectronic device technology has been developing at a rapid pace in the last decades, and the high demand for this technology requires an unceasing pursuit of new materials to produce efficient field effect transistors, solar cells and light-emitting diodes, among others. To make these devices suitable for different needs and applications, the new materials should have properties such as an outstanding charge transport, and a high chemical and mechanical stability.

In the last years the desire of simplifying the production process by using solution processable materials also emerged. The use of inks in electronic and optoelectronic applications has allowed the fabrication of devices in the same fashion as printing newspapers. However, often these devices display properties far from the ones fabricated with traditional semiconductors. This is because there are very few semiconductors that display both solution processability and outstanding transport properties.

Single-Walled Carbon Nanotubes (SWNTs) are a unique example of a material with remarkable charge transport properties, high chemical and mechanical stability, and solution processability. However, SWNTs are synthesized as a mixture of semiconducting and metallic species, making their application in electronic and optoelectronic devices challenging. It has been estimated that purities of semiconducting SWNTs (s-SWNTs) above 99,99% should be reached to produce technologically relevant inks. For this reason, different techniques have been developed to separate semiconducting from metallic tubes.

In this thesis, I investigate the power of the polymer wrapping technique to sort s-SWNTs. While the technique is relatively well established, many questions are still to be answered. Among them are: i) what mechanism drives the sorting, ii) what is the nature of the interaction between the polymer chains and the SWNT, and iii) how to exploit the properties of the carbon nanotube-polymer hybrids for electronic and optoelectronic applications.

To address the first question I have used in chapter 2 three different polymers with very different backbone flexibility to sort two types of SWNTs of different diameters. The comparison of the s-SWNT yields obtained with either P12CPDTBT, P3DDT or PF12 has shown that for small diameter HiPCO tubes, higher flexibility of the polymer backbone leads to higher dispersion yields. Instead for larger diameter tubes (SO), higher dispersion yields were obtained with the bulkier and less flexible backbones of P12CPDTBT and PF12.

These results are rationalized by performing DFT calculations and analyzing the electronic and chemical structures of the carbon nanotube-polymer hybrids. The results show that for

small diameter tubes, the higher flexibility of the polymer allows a stronger binding energy with the SWNTs.The binding energy is less important for large diameter tubes, and the bulkier polymer showed higher dispersion yields as a consequence of the higher surface coverage of the SWNT walls.

In chapter 3 I identified two naphthalene diimide-based conjugated polymers (N2200 and PE-N-73) as a new class of macromolecules capable of efficiently selecting s-SWNTs.

Both these polymers have a narrow bandgap. However, the HOMO level of only PE-N-73 is similar to the HOMO level of (8,7) s-SWNTs, which is one of the dominant species of nanotubes in the sample.

The electron transport of field effect transistors fabricated with PE-N-73 and N2200 wrapped SWNTs are comparable. In contrast, a substantial difference is observed in the hole transport when an excess of free polymer is present in the solution. The excess of N2200 is detrimental for the hole transport, while the improved alignment of the HOMO level of PE-N-73 with the HOMO level of the nanotubes leads to outstanding p-type characteristics, even with a large amount of residual polymer between the tubes.

Not only high dispersion yields and the band alignment between the polymer and the carbon nanotubes are important for the application of the inks in electronics, but also the ability to control the polarity of the field effect transistors (FETs) fabricated with the s-SWNT inks.

In chapter 4, I showed that it is possible to achieve unipolar charge transport by mixing a highly purified ink of s-SWNTs with additives. Mixing s-SWNTs with benzyl viologen (BV) or with 4-(2,3-Dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzenamine (N-DMBI) gives rise to n-type field effect transistors, and mixing s-SWNTs with 2,3,5,6-Tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) gives rise to p-type transistors. This direct modification of the nature of the ink forms a new strategy that allows control over the FET polarity without extra fabrication steps.

We found that different mechanisms are causing this modification of the FET behavior. The BV additive modifies the Schottky barrier between the metal contact and the SWNT network, while N-DMBI increases the mobility of the FET by effective molecular doping. Interestingly, F4-TCNQ had an effect on both the work function and on the doping of the active material.

Highly conductive inks are not only relevant for the fabrication of FETs but can also be used in solar cells. In chapter 5, I demonstrated that s-SWNTs can be used as a transport and protective layer between the active layer and the anode of lead sulfide colloidal quantum dot (PbS CQD) solar cells (SCs). PbS CQD SCs including a thin layer of s-SWNTs wrapped with P3DDT can withstand harsh stability tests under constant solar illumination in ambient conditions for more than 100 hours, losing only 15% of their initial power conversion efficiency. Without the SWNTs interlayer the solar cell degrades more than 80% of the starting power conversion efficiency after 100 hours of illumination. The interlayer of SWNTs therefore has an impressive role in protecting the active layer.

This is a very important result as it increases the possibility of the application of polymer-wrapped SWNTs inks in solar cells and it increases the chance of expanding SC usage for renewable energy.

Finally, in chapter 6, I discuss how our results can be implemented in a practical way and I address the challenge of expanding the fruition of electronics technology in our society to enable the Internet of Things. Semiconducting SWNT inks present a massive opportunity for the Internet of Things, as they can enable low power consumption electronics which are simultaneously highly performing but also flexible and cheap. The first step is to ensure the scaling-up of s-SWNT inks. Finally, the inks need to be integrated in the fabrication process of different electronic components to produce smart labels.

In conclusion, with this thesis, I contribute to a deeper understanding of the power of the polymer wrapping technique for the selection of semiconducting carbon nanotubes and I show a way to implement s-SWNT inks in the production of electronic devices at the industrial scale.