Summary

Electronic devices are ubiquitous in everyday life. Almost every aspect of human life relies on some form of electronic devices, from a portable phone to a super computer. Especially in the last decade, the use of electronic devices has become pervasive. Nowadays, we can use our phones as small computers, owing to powerful processing units inside them. At present, all transistors used in integrated circuits are silicon based, and they have nearly reached the limit of downscaling as projected by Moore's law; which predicted that the number of transistors that can be packed into a given unit of space will double every two years. As a result, non-silicon materials, such as III-V semiconductors or nanotubes/nanowires have been proposed to replace silicon with the purpose to continue to increase the computational power and decrease the dimensions of the microprocessors.

Single-walled carbon nanotubes (SWNTs) have demonstrated their potential as a *post-silicon material*, due to their unique properties, such as small dimensionality (they can be less than 1 nm in diameter and several microns long), high carrier transport in 1-D, high mechanical and thermal stability, and also high chemical stability. The small dimensions of SWNTs could allow to overcome the limits of the downscaling of the current transistor generation. Carbon nanotubes also show balanced hole and electron transport, showing mobilities more than 100 times higher than that of silicon. Furthermore, the robustness of SWNTs allows device fabrication using the same lithographic processes used in Si-based technology. Despite all the advantages they have, SWNTs also possess a major drawback: the coexistence of semiconducting and metallic species in the as grown SWNTs remains a big challenge, since the latter causes significant degradation in device performance.

Polymer wrapping-assisted semiconducting-SWNT separation, in this respect, has shown its ability to solve this issue, by allowing separation of semiconducting tubes from the metallic ones. The progress obtained in developing this purification method in these last 8 years has given the possibility to extract s-SWNTs with the highest purity (reported in this thesis as higher than 99.9%) compared to other separation techniques, and with a very high extraction yield, which is suitable for large scale production with low processing cost. The electronic devices fabricated utilizing s-SWNT obtained by this purification process, especially field-effect transistors (FETs),

demonstrated superior performance compared to other SWNT-FETs. They show balanced ambipolar properties, high on/off ratio (more than 10^8), and high carrier mobility (up to 50 cm^2/Vs for random network devices, and more than 2000 cm^2/Vs for single carbon nanotubes devices). The investigation of the separation process, the discovery of new polymers that discriminate more effectively the s-SWNTs, and the optimization of the deposition of the s-SWNTs on a substrate in ordered arrays, are still desired to understand the physical mechanism of the polymer-wrapping technique and to further obtain better device performance. The aim of this thesis is to investigate the above mentioned aspects, which are extremely important to make of SWNTs the silicon of the future.

In **chapter 2**, we explored the photophysical properties of s-SWNTs dispersed in different solvents with various dielectric constants. We found that an increase of the dielectric constant results in a red-shift of the PL peak and in a lower photoluminescence intensity. The homogeneity of the photoluminescence lifetimes shows that the semiconducting SWNT dispersions are stable and the nanotubes remain individualized in most organic solvents.

Temperature is another crucial factor that determines the selection of s-SWNTs, which is the main subject of **chapter 3**. The interaction mechanism between polymer chains and SWNTs is studied by controlling the polymer aggregation via variation of the processing temperature. Optical absorption and photoluminescence measurements including time resolved photoluminescence spectroscopy are employed to study the degree of interaction between Poly(3-dodecylthiophene-2,5-diyl) in different aggregation states and the carbon nanotubes. The formation of small clusters of tubes is due to the inter-digitation of alkyl tails between neighboring polymer-wrapped SWNTs, as experimentally evidenced and investigated by molecular dynamics simulations. Furthermore, the sonication temperature plays an important role in determining the extraction yield of the SWNTs in the final dispersions, where the optimum temperature for the highest extraction yield is between 10 °C and 20 °C.

The introduction of new conjugated polymers to disperse SWNTs is reported in chapter 4 and 5. We showed in **chapter 4** that the alkyl side chains have a big influence on the selection of carbon nanotubes of different diameters. Increasing the number of carbon atoms from 6 to 12 in the alkyl side chains leads to a broader selection of s-SWNTs diameters, i.e. from 0.75 nm to 1.51 nm. The interaction mechanism of the polymer with long alkyl side chains was studied by performing molecular dynamics simulations, confirming the importance of the van der Waals

interaction between the alkyl side chains and SWNTs in promoting the separation of large diameter SWNTs. We found that polyfluorene containing 12 carbon atoms in the alkyl side chains shows the best selection of s-SWNTs, as evidenced by steady state and time-resolved spectroscopy measurements. Field effect transistors fabricated with this large diameter SWNTs using ion-gel gating demonstrate ambipolar behavior, and mobilities higher than 14 $cm^2/V{\cdot}s$ for both electrons and holes.

Inks containing a high density of carbon nanotubes are necessary to achieve high performance solution processable devices. **Chapter 5** shows how to obtain high extraction yield of small diameter SWNTs by using a new type of polymer, namely polyazine and polyazomethine derivatives that containing heteroatoms in their main backbone. The polyazomethines show strong adsorption to the s-SWNTs, resulting in high extraction yield, while polyazines show the tendency to interact with the m-SWNTs due to unbounded electron lone pairs in the diimine ligands and more flexible backbones of the polymer, as observed by absorption and photoluminescence spectroscopy. Field-effect transistors fabricated from polyazomethine-dispersed SWNTs show record mobility (33 $cm^2/V{\cdot}s$) for small diameter random network FETs. This evidence opens the path to new tailored polymers with direct coordinative atoms to improve the extraction yield for large-scale separation of s-SWNTs.

The placement of SWNTs on substrates in a certain direction is expected to improve the output performance of the SWNT-FETs. In **chapter 6**, we exploited the possibilities of SWNT self-deposition onto substrate using polyfluorenes derivatives with side chains containing thiol groups. We show that the inclusion of thiol groups in each monomer of the polymer disrupts the s-SWNTs selection. However, the metallic nanotubes content can be reduced either by adjusting the number of thiol groups in the polymer, or by fine-tuning the polymer to SWNT ratio. We demonstrated that the polymer containing 2.5% thiol groups gives the best s-SWNT purity, as confirmed by photoluminescence measurements. Field-effect transistors fabricated by direct self-assembly of the SWNTs/thiolated-polyfluorenes on gold patterned substrates show superior performances (mobility up to 16 $cm^2/V{\cdot}s$) with 3 orders of magnitude higher on-current compared to transistors fabricated with SWNTs wrapped with the same polymer without thiol functionalization.

To conclude, we investigated the mechanism of semiconducting SWNT selection using the polymer wrapping method by varying the chemical structures of polymers and physical parameters of the process supported by molecular dynamics simulations. Highly pure and concentrated solutions have been achieved, which allowed to apply

these solutions for the fabrication of highly performing field effect transistors, showing the prospects of this nano-objects as a candidate for low-cost and high performance electronics.