Understanding and Engineering Interfacial Charge Transfer of Carbon Nanotubes and Graphene for Energy and Sensing Applications

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Graphene is a one-atom thick planar monolayer of sp²-bonded carbon atoms organized in a hexagonal crystal lattice. A single walled carbon nanotube (SWCNT) can be thought of as a graphene sheet rolled up into a seamless hollow cylinder with extremely high length to diameter ratio. Their large surface area, and exceptional optical, mechanical and electronic properties make these low-dimensional carbon materials ideal candidates for (opto-)electronic and sensing applications. In this thesis I studied the charge transfer processes that occur at their interface, and developed applications based on the discovered properties.

When light is incident on a semiconducting SWCNT, it can excite an electron from the valence band to the conduction band, thereby creating a Coulombically bound electron-hole pair, also known as an exciton. Excitons can decay via radiative or non-radiative recombination or by colliding with other excitons. They can diffuse along the length of a SWCNT or hop from larger band gap SWCNTs to lower band gap SWCNTs, a process known as exciton energy transfer (EET). We studied their behavior as a function of temperature in SWCNT fibers and showed that at room temperature the rate constant for EET is more than two orders of magnitude larger than that of each of the different recombination processes. This led us to construct a core-shell SWCNT fiber, which consists of a core of smaller band gap SWCNTs, surrounded by a shell of larger band gap SWCNTs, essentially forming what is known as a type I heterojunction. In agreement with a model that describes exciton behavior in the SWCNT fibers, we found that upon illumination all the energy (in the form of excitons) was quickly transferred from the shell to the core, faster than the excitons would otherwise recombine. The SWCNT fiber proved to be an efficient optical and energetic concentrator.

We showed that SWCNTs and poly(3-hexylthiophene) (P3HT) form a type II heterojunction, which implies that excitons generated in the P3HT can easily dissociate into free charge carriers at the interface with the SWCNTs. Despite this, the efficiency of a P3HT/SWCNT bulk heterojunction (BHQ) photovoltaic is subpar. We developed a planar heterojunction (PHJ) and achieved efficiencies that were 30 times higher, which showed that the formation of bundled aggregates in BHJs was the cause: metallic SWCNTs can quench the excitons in an entire bundle.

Another interesting feature of our SWCNT/P3HT PHJ is that a maximum efficiency was reached when ~60 nm of P3HT was used, which is surprising since in a planar photovoltaic a maximum is expected for ~8.5 nm of P3HT, the value of the exciton diffusion length. A Kinetic Monte Carlo simulation revealed that bulk exciton dissociation was responsible for the lower efficiencies observed for devices with low P3HT thickness.

Next we created and studied a junction between SWCNTs and a monolayer of graphene, an ideal one-dimensional / two-dimensional carbon interface. We used Raman spectroscopy to probe the degree of charge transfer at the interface and based on a shift in the G peak position of the graphene Raman signal at the junction deduced that a typical metallic (semiconducting) SWCNT dopes the graphene with $1.12 \times 10^{13}$ cm$^{-2}$ ($0.325 \times 10^{13}$ cm$^{-2}$) electrons upon contact, in agreement with the fact that the Fermi level of the SWCNTs is more shallow than that of the
A molecular dynamics simulation ruled out that the observed Raman peak shifts are due to strain, although it did show that SWCNTs are being compressed radially by the graphene sheet, resulting in a widening of their Raman peaks.

We studied charge transfer between diazonium molecules and graphene, to better inform transistor and sensor design. The reaction rate depends on the degree of overlap between the filled energy levels in graphene and the unoccupied ones in the diazonium molecule. We showed that with increasing degree of functionalization the charge transfer characteristics of a graphene field effect transistor (FET) alter in the following ways: the minimum conductivity decreases, the Dirac point upshifts, the conductivity plateau at high carrier density decreases and the electron-hole conduction asymmetry increases. We developed a theoretical model of charge transport in graphene FETs that takes into account the effect of both short-range and long-range scatterers. Fitting it to the charge-transport data reveals quantitative information about the number of impurities in the substrate supporting the graphene, about the number of defects created as a result of the reaction, and about the degree of electron-hole conduction asymmetry.

Graphene functionalization also affects the graphene Raman signal. After reaction, the D to G intensity ratio increases, which is a sign of covalent modification of the graphene lattice. Additionally, the G peak and 2D peak positions increase while the 2D/G intensity ratio decreases, which are signs of hole-doping.

Based on a Raman analysis, we were also able to show that the end group of the diazonium salt can affect both the degree of chemisorption (covalent modification) as well as the degree of physisorption (doping).

Finally, we studied the effects of charge transfer between graphene and biological cells on the graphene Raman signal and designed a fundamentally new type of biosensor. Graphene can be thought of as a continuous array of information units (sensor units). The Raman signal collected in each unit can report on its local environment. In contrast to graphene FET biosensors, the graphene Raman biosensor offers subcellular spatial resolution.

The graphene Raman signal was shown to display a strong dependence on pH. Metabolically active cells acidify their local environment; therefore, pH is a proxy for cellular metabolism. We placed both human embryonic kidney (HEK) cells that were genetically engineered to produce mouse antibodies and control HEK cells that were not genetically modified onto the graphene. Based on the change in the graphene Raman signal we deduced the former have a metabolic rate that is 4 times higher than that of the control cells. Increased cellular adhesion allows the cells to interact more closely with the graphene monolayer and intensifies the observed Raman effects.