Introducing New Optical Functions to Semiconducting Carbon Nanotubes

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Carrier doping in single-walled carbon nanotubes enables manipulation of their optical spectra and dynamics and provides a possible route toward quantum computing.

During the last half-century, low-dimensional semiconductor nanostructures have been extensively studied due to the advantages they provide when compared with bulk crystals (3D structures). High optical gain and ultrafast electrical response are among the advantages provided by these low-dimensional structures. Because the electrons and holes (i.e., charge carriers) are spatially confined by the electrostatic potential in semiconductor nanostructures, their Coulomb interactions—attraction or repulsion—become stronger than is the case within bulk crystals. Due to these strong Coulomb interactions, excitons (i.e., the bound state of an electron and a hole) are stable in nanostructures. These stable excitons have unique optical properties.

Intensive studies have been conducted on the fundamental physics and possible device applications of 2D quantum wells and 0D quantum dots. However, due to the difficulty in fabricating high-quality 1D structures, the optical properties of 1D quantum wires remain unclear. In the past, sophisticated techniques—e.g., the use of molecular-beam epitaxy—were required to fabricate 1D quantum wires with atomically smooth interfaces.[1] However, in 2002, efficient photoluminescence was observed in single-walled carbon nanotubes (SWCNTs) that had been fabricated using simple chemical methods.[2,3] This observation illustrated the high-quality 1D structure of SWCNTs and demonstrated their ability to provide an excellent platform for experimental studies of optical processes in 1D nanostructures.

In our work, we focused on the dynamics of excitons and trions in hole-doped SWCNTs. To realize optical and optoelectronic devices based on SWCNTs, a detailed understanding of exciton and trion dynamics in carrier-doped SWCNTs is essential. We have studied the dependence of exciton and trion dynamics on dopant concentration by femtosecond pump-probe transient absorption (TA) spectroscopy,[7] and clarified the exciton- and trion-relaxation processes in SWCNTs.

The angle at which a carbon lattice is rolled to create a nanotube is described by its chirality. We used SWCNTs synthesized by the CoMoCAT (cobalt-molybdenum catalytic) method, which predominantly includes (7,5) and (6,5) chiralities, as the sample. The SWCNTs were dispersed in toluene with poly[9,9-dioctylfluorenyl-2,7-diyl] (PFO).[8] Due to the high selectivity of PFO, the sample included only the (7,5) chirality. This avoids SWCNTs with different chiralities making a contribution to the obtained experimental data and provides essential information on the optical properties of (7,5) SWCNTs. The SWCNTs were doped with holes by the addition of a solution of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4TCNQ, a p-dopant).[9] The energy of the pump pulse was set to the exciton resonance energy, and the energies of the probe pulse were chosen in tune with whether we were measuring the exciton or trion dynamics.

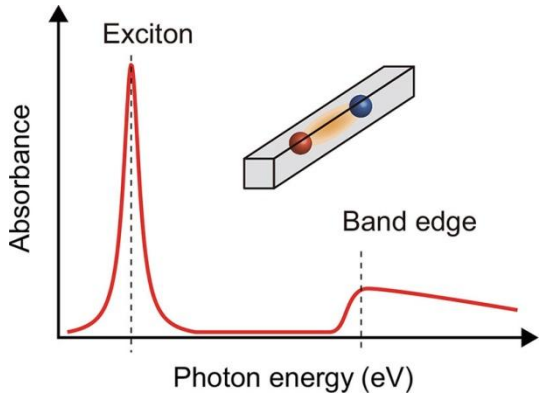

Figure 1. Schematic view of the optical absorption spectrum in 1D structures. Band-edge absorption is extremely weak and optical transitions are concentrated at the lowest exciton state.

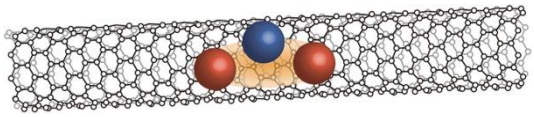

Figure 2. Schematic view of a positively charged exciton (a trion)—the bound state of an electron (blue) and two holes (red)—in a single-walled carbon nanotube (SWCNT).

In 1D nanostructures, optical transitions are concentrated at the lowest exciton state, and the band-to-band absorption is either extremely weak or not observed in the linear absorption spectra (see Figure 1). In SWCNTs, excitons are stable at room temperature due to large binding energies of several hundred millielectron volts.[4] This means that even at room temperature, an exciton dominates the optical and electronic properties of SWCNTs.[5] The impact of excitons on these optical properties has been studied extensively over the past decade. Our group recently discovered positive trions (positively charged excitons) in hole-doped SWCNTs: see Figure 2.[6] Trions are also stable at room temperature and strongly affect the optical properties of hole-doped SWCNTs.[6,7] This finding shows that carrier doping in SWCNTs can manipulate the optical spectra and dynamics via strong interactions between excitons and holes.

Because trions have a spin degree of freedom different from that of excitons, they are potential candidates for quantum bits ('qubits') in quantum computing applications. However, the effects of carrier doping on the optical properties of SWCNTs, including the formation of trions, are still under investigation.

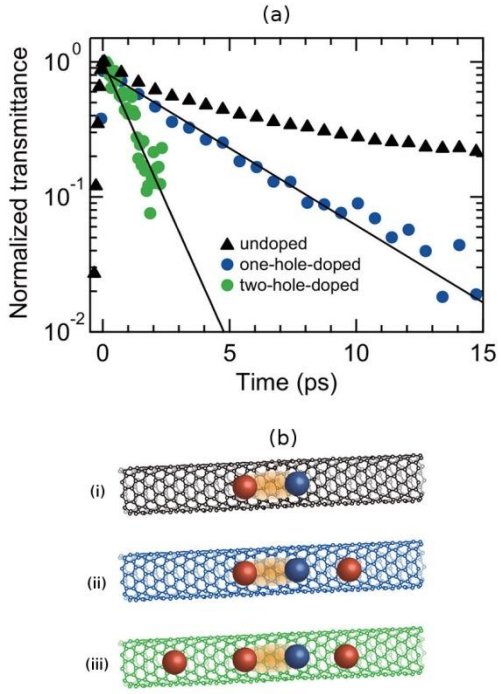

Figure 3. (a) Exciton dynamics in doped and undoped SWCNTs, obtained by a simple subtractive procedure. Blue and green circles correspond to the exciton dynamics in one- and two-hole-doped SWCNTs.[7] (b) Schematic view of an exciton in (i) undoped, (ii) one-hole-doped, and (iii) two-hole-doped SWCNTs.

We found that the doped holes per SWCNT followed a Poisson distribution (on the basis of the dopant-concentration dependence of the TA decay dynamics). This finding enabled us to estimate the number of holes introduced by various chemical doping methods. Figure 3 shows the exciton dynamics in undoped, and one- and two-hole-doped SWCNTs.[7] These dynamics were extracted from dopant-concentration-dependent TA decay using a simple subtractive procedure.[10] The exciton decay dynamics become faster as the number of doped holes is increased. The exciton decay times we obtained for one- and two-hole-doped SWCNTs were about 4 and 1ps, respectively. Based on the measurements of trion dynamics, we also found that rapid energy relaxation occurs from the exciton state to the trion state. We have therefore demonstrated that a small number of holes can modulate the exciton dynamics. These results indicate strong interactions between excitons and holes, suggesting that exciton dynamics can be controlled by hole doping.

In summary, we have revealed that the hole doping of semiconducting SWCNTs accelerates exciton decay due to strong interactions between excitons and doped holes. We were also able to develop a method to estimate the number of doped holes using the Poisson distribution. These results may open up new frontiers in both fundamental physics and the development of ultrafast optical and optoelectronic devices. Our next step will be to realize deliberate modulation of the exciton dynamics.

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