Review—Photophysics of Trions in Single-Walled Carbon Nanotubes

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The photophysics of trions in single-walled carbon nanotubes (SWCNTs) is reviewed briefly. The trion state is observed energetically below the exciton state in hole-doped SWCNTs, and shows a single exponential decay. The decay dynamics of trions depends on the photoexcitation condition. The optical responses of trions can be discussed by considering the energy relaxation of the optically accessible trion state. Detailed studies of excitons, trions, and biexcitons provide a deep understanding of the material properties of SWCNTs, and exciton states are required for the design of photonic devices.

The discovery of C60 fullerenes1 and carbon nanotubes2 has opened up a new active research field concerning carbon nanomaterials and nanostructures from the viewpoints of both fundamental science and technological applications. Semiconductor single-walled carbon nanotubes (SWCNTs) are regarded as one-dimensional materials. Isolated semiconducting SWCNTs, which are synthesized by simple chemical techniques, exhibit efficient room-temperature photoluminescence (PL),3,4 which has led to accelerated experimental studies on various optical properties of SWCNTs. Electrons and holes are strongly spatially confined to diameters on the order of 1 nm, resulting in room temperature stable excitons with large binding energies in the range of 200–400 meV.5–11 The exciton dynamics thus dominates the optical properties of semiconducting SWCNTs.5,6 High-quality carbon nanomaterials provide an excellent experimental stage for studies on photophysics of excitons and exciton complexes.

The exciton structures in SWCNTs are complicated due to the intrinsic properties of graphene, their unique helical structures, and coulomb interactions.3 The origin of the optical absorption and PL is ascribed to the dipole-allowed (bright) exciton states, and their dynamics are affected by the interplay with the dipole-forbidden (dark) exciton states. Single nanotube spectroscopy has revealed details of the intrinsic exciton properties. For example, magneto-optical studies showed that the even-parity singlet dark exciton state is located energetically below the bright exciton state.12,13 Thermalization between the bright and dark exciton states determines the temperature-dependent PL properties12,13 and the exciton diffusion length14,15. Furthermore, strong spatial confinement accentuates the exciton-exciton and exciton-electron interactions. Time-resolved transient absorption (TA) and PL spectroscopy measurements have revealed that multiple exciton states show rapid decays due to nonradiative Auger recombination.16–19 Nonradiative Auger recombination, which competes with exciton diffusion, determines the PL efficiency of semiconducting SWCNTs.16,20–24 It ensures nonclassical PL by preventing the occupation of identical exciton states.25

Carrier doping is one of the most important techniques in semiconductors, which controls their electrical and optical properties. In SWCNTs, carrier doping has been actively studied using chemical modifications26–31 and gate-voltage techniques.32–34 Carrier doping can modify the exciton dynamics through the exciton-carrier interactions. Carrier doping causes quenching of exciton absorption and PL,35–39,40–42 exciton peak shifts,39,41–42 reduction in the band-gap energy,26 and rapid exciton decay.39–42 In addition, a bound trion (a charged exciton), is discovered energetically below the E11 exciton state in hole-doped SWCNT samples.34 Since our first observation of the trion states in 2011,34 theoretical and experimental studies on trions have been carried out extensively.43–52

Trion states are confirmed by various doping methods such as chemical doping,43,44,45 photoexcitation,45 electrochemical technique,46 and electrostatic gating.47 Under strong photoexcitation conditions, dissociated carriers resulting from Auger recombination can create trion states with a subsequent absorbed photon.43 Positive and negative trion states show almost the same binding energies.44 Time-resolved TA and PL measurements have revealed fast formation of the trion state through the exciton-hole interaction.48,49 Active experimental studies on trions have led to the observation of an exciton complex, a biexciton state in nanotubes,52,53 and encourage further studies of trions in atomic monolayer materials such as MoS2 and MoSe2.54,55 Moreover, considerable experimental efforts have been devoted to improve the luminescence quantum yield of semiconducting SWCNTs by coupling them to photonic crystal cavities,56,57 applying electric fields,58 and introducing luminescent local defects.59–62 Similar to the case of quantum dot nanocrystals,61–63 a deep understanding of trion states is essential for development of photonic and optoelectronic devices based on SWCNTs.

Here, we briefly discuss the recombination dynamics of trions in hole-doped SWCNTs. The trion decay shows a single-exponential profile, while the exciton decay exhibits complicated behavior. The trion state under the resonant trion photoexcitation exhibits faster decay than that under high-energy photoexcitation. These trion decay dynamics are discussed by considering the energy relaxation of the optically accessible trion state. This short review provides several perspectives for understanding the trion dynamics in SWCNTs.

We studied the absorption spectra of trions and their decay dynamics in hole-doped SWCNT ensemble samples.34,35,40 Figure 1 shows the absorption spectra of the undoped and hole-doped CoMoCAT SWCNTs dispersed by poly[9,9-diocylfluorenyl-2,7-diyl] in toluene solutions.64 The absorption intensities imply that these samples were highly enriched in (7,5) SWCNTs (95% or more). Hole doping was chemically achieved using 2,3,5,6-tetracyanoquinodimethane (F4TCNQ).65 In the undoped sample, strong absorption peaks ascribed to E11 and E22 exciton states were clearly observed at 1.18 eV and 1.90 eV, respectively. When F4TCNQ was added for hole doping, the E11 and E22 exciton absorptions drastically reduced and exhibited small redshifts. As shown in the inset of Fig. 1, a new absorption peak ascribed to the trions...
appeared at 1.01 eV.\textsuperscript{34} In chemical methods, hole doping of SWCNTs occurs inhomogeneously, and SWCNTs with a different hole number coexist in the sample.\textsuperscript{35} Thus, the optical spectrum is the ensemble of optical responses from SWCNTs with a different hole number. Doping with two holes decreases exciton absorption to one-tenth of that in undoped SWCNT.\textsuperscript{35} As a result, in hole-doped SWCNT samples, trion absorption is mainly contributed from SWCNTs doped with multiple holes, while the exciton absorption is mainly determined by undoped and one-hole doped SWCNTs.\textsuperscript{35,49}

Figure 2 shows temporal changes in the population of the trion and $E_{11}$ exciton states under $E_{22}$ photoexcitation observed in femtosecond pump-probe TA experiments. Trion formation occurs immediately after the $E_{22}$ photoexcitation. This fast trion formation is also observed under $E_{11}$ photoexcitation,\textsuperscript{39} and it is much faster than the exciton-hole interactions in one- and two-hole doped SWCNTs.\textsuperscript{35,49} In SWCNTs doped with three or more holes, the exciton-hole interaction is strong enough to form a trion within a pump pulse duration of 150 fs.\textsuperscript{40} The trion shows a simple decay profile: a single exponential behavior.\textsuperscript{22} The complicated decay profile of the exciton state reflects on the exciton fine structures.\textsuperscript{37,65-67}

The exciton decay dynamics depends on the photoexcitation condition. A high-energy photon creates multiple $E_{11}$ excitons through multiple-exciton generation\textsuperscript{68-70} or $E_{11}$ excitons and free carriers through exciton spontaneous dissociation.\textsuperscript{71} In addition, the $E_{11}$ exciton under the resonant $E_{11}$ photoexcitation shows a faster decay than that under the $E_{22}$ photoexcitation, as shown in the inset of Fig. 3. We have reported that this observation is well explained by the thermalization within the $E_{11}$ exciton band.\textsuperscript{72} The resonant $E_{11}$ photoexcitation populates only the exciton states with nearly zero momentum (hereafter referred to as the optically accessible excitation) due to the momentum selection rule, followed by the thermalization within the exciton band.\textsuperscript{73} This thermalization process is observed as the fast decay only under the resonant $E_{11}$ photoexcitation.\textsuperscript{37} Here, we briefly comment on the excitation energy dependence of trion decay dynamics. Figure 3 shows the trion decay curves under the photoexcitation of trion and $E_{22}$ states. The resonant trion photoexcitation leads to faster trion decay than in the $E_{22}$ photoexcitation. Because the exciton-hole interaction generates trions rapidly, the trion formation does not affect significantly the trion decay behavior on a few picoseconds time region. In analogy to the exciton case, this fast component can be ascribed to the energy relaxation of the optically accessible exciton states. Assuming the thermalization within the trion band, we calculated the decay curves with expanding the previous simple model proposed in Ref. 37. The solid curves in Fig. 3 are the calculated results (details not shown). The thermalization rate within the trion band is comparable with that within the excitation band in the undoped SWCNT sample, which is caused by the exciton-phonon scattering.\textsuperscript{74} This result indicates that the transition within the trion band can be also determined by scattering with phonons. The excitation energy dependence of exciton and exciton complexes provides several insights into the details of their energy structures.

In conclusion, we briefly discussed the excitons and exciton complexes in SWCNTs and focused on the recombination dynamics of trions in hole-doped SWCNTs. The trion and exciton decay dynamics shows a similar dependence on the excitation energies, which is well explained by a simple model considering the energy relaxation of the optically accessible trion and exciton states. Our discussion on trions provides several insights into the photophysics of SWCNTs. Finally, we would like to appreciate Prof. Kroto for opening up the unique nanocarbon research field.

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