

Energy Modulation of Localized Excitons in Single-walled Carbon Nanotubes by Molecular Chemistry Approaches

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Single-walled carbon nanotubes (SWNTs) are one dimensional (1D) nanocylinders with the diameter of ca. 1 nm and the length of a few hundred nm or $\sim\mu\text{m}$. [1] SWNTs consist of rolled-up single graphene whose structures are identified by chiral indices and show the structure-dependent properties, such as metallic and semiconducting features. Owing to their unique nanostructures, quantum confinement and weak dielectric screening clearly appear, which allows strong Coulombic interactions. [2] Thus, photoexcitation of the SWNTs generates the excitons (electron-hole bound states) that are stable even at room temperature and migrate along the tubes because of their high binding energies (a few hundred meV). Consequently, such excitonic properties determine optical properties of the SWNTs, exemplified by the notable near infrared (NIR) photoabsorption and photoluminescence (PL).

Local chemical functionalization of the SWNTs has achieved defect (e.g. sp^3 carbon) doping into their crystalline sp^2 carbon networks. As a result, the doped sites emit E_{11}^* PL that is redshifted and bright compared to the original E_{11} PL from the pristine sites in the locally functionalized SWNTs (lf-SWNTs). That is due to the narrow bandgap formation and the exciton trapping (localization) function by the functionalization-induced electronic structure changes at the doped sites. [3,5] In particular, the functionalized molecules on the doped sites play important roles for the wavelength modulation of E_{11}^* PL from the lf-SWNTs. [4-9] Namely, the lf-SWNTs enable the excitons to be localized at the doped sites and be efficiently employed to the NIR PL whose energies (wavelengths) can be flexibly modulated based on the molecular designs of their doped sites.

Our proximal defect doping approach using bis-aryldiazonium salts (bA), which have two reactive groups in the molecular structures, allows to create largely redshifted PL (E_{11}^{2*} PL) from the lf-SWNTs. [4,9] When the SWNTs with (6,5) chiral index were used, the obtained lf-SWNTs showed E_{11}^{2*} PL at 1256 nm which was significantly redshifted than E_{11} PL (985 nm) and E_{11}^* PL (1129 nm) from the pristine SWNTs and the mono-aryl functionalized lf-SWNTs, respectively. Interestingly, the wavelength shifts of E_{11}^{2*} PL showed a clear relationship with the distance between the proximal defects, which was confirmed by changing the linker lengths and positions connecting the two diazonium groups in the bA molecules.

We have found unique microenvironment responses of E_{11}^* PL of the lf-SWNTs. [8] The environmental PL energy shifts of the SWNTs is well-known phenomena. In the lf-SWNTs, however, the E_{11}^* PL showed larger shifts than those of E_{11} PL when various organic solvent environments were created by solvent injection in the hydrophobic domain between the lf-SWNTs and the coating surfactant micelles in aqueous media. Density functional theory calculations suggested electron localization at the doped sites, which would enhance interactions with solvent molecules. Moreover, the energy shift trends with respect to a polarity parameter were found to change remarkably depending on the doped site structures of the lf-SWNTs.

In the lf-SWNTs, therefore, the exciton localization and energy modulation can be achieved based on the molecular functionalization, which provides promising ways to control and utilize the generated excitons in this material. The functionality is applicable to develop bio/medical imaging and sensing [6,7] using NIR II windows and photonic nanodevices for quantum communication.

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