

Molecular design for photoluminescence modulation of locally functionalized single-walled carbon nanotubes

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Near infrared photoluminescence (NIR PL) of semiconducting single-walled carbon nanotubes (SWNTs) is highly functionalized through chemical reactions of the tube walls, in which local functionalization is a key for partial doping of the sp² carbon network structures. Oxygen atom doping and sp³ defect doping have been conducted, and the resulting locally functionalized SWNTs (lf-SWNTs) show PL intensity enhancement with wavelength shifts. Recent studies are revealing that doped site structures are closely related to the PL functions of the lf-SWNTs. Based on our chemistry background, we synthesize new diazonium molecules for local functionalization of SWNTs, by which the doped site structures are molecularly designed towards modulation and functionalization of the NIR PL properties.

For example, bisdiazonium compounds (2Dz) were synthesized and the modification of (6,5) SWNTs using the 2Dz (lf-SWNTs/2Dz) provided new red-shifted PL.[1] Namely, the emission peak appeared at 1256 nm which was significantly red-shifted than those of pristine SWNTs (985 nm) and mono-functionalized SWNTs (lf-SWNTs/1Dz, 1129 nm). In another project, substituted aryl isomers were introduced as a moiety of the doped site structures of lf-SWNTs. The observed PL was varied with strong dependence on the isomeric substituent positions.[2, 3] Thus, these molecular structure-dependent spectral changes are expected to develop the lf-SWNTs whose PL appears in the wide wavelength range of NIR regions.

As another developed function of the lf-SWNTs, dynamic wavelength shifting is achieved through creation of the doped sites that selectively bind molecules and ions, etc. The local binding occurred by employing molecular recognition motives for the doped site design. The first example was phenylboronic acid-modified lf-SWNTs that showed PL wavelength shifts by attachment of saccharide molecules at the doped sites.[4] More recently, the modification of crown ether groups, which can capture cations such as metal ions, provided unique PL wavelength shifts depending on the difference in the bound cationic species. Therefore, the local events at the doped sites create PL shifting functions on the basis of the molecular systems that are driven by molecular interactions with selectivity and flexibility.

As described above, molecular design approaches are quite useful for modulation and functionalization of the NIR PL of the lf-SWNTs. The resultant functions are applicable to develop advanced applications such as bio/medical imaging and sensing, and nanodevices for telecommunication.

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[2] T. Shiraki, S. Uchimura, T. Shiraishi, H. Onitsuka and N. Nakashima, *Chem. Commun.* **53**, 12544-12547 (2017).

[3] T. Shiraishi, T. Shiraki and N. Nakashima, *Nanoscale* **9**, 16900-16907 (2017).

[4] T. Shiraki, H. Onitsuka, T. Shiraishi and N. Nakashima, *Chem. Commun.* **52**, 12972-12975 (2016).