Optical Properties of Oxidized Single-Wall Carbon Nanotubes

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Optical properties of oxidized single-wall carbon nanotubes (SWCNTs) have attracted much attention because of the greater luminescence quantum yield than that of pristine CNTs [1]. To advance the fundamental understanding of the optical properties of oxidized SWCNTs, we theoretically investigated the energetics and the optical transitions for complex oxygen (O) adsorption structures on (6,5) CNTs, including adsorption of two O atoms [2]. Further O diffusion simulations considering the energetics provide a possible mechanism for significant emission at lower energy in recent bioimaging experiments.

As shown in Fig. 1, we obtained four groups of optical transition levels below E_{11} for CNTs adsorbed by isolated O atoms, including the levels known as E_{11}^{*} and E_{11}^{*-}. The most stable O-adsorption structure is ether structure, which corresponds to the E_{11}^{*} level; however the epoxy structure that produces the E_{11}^{*-} level is much less stable than the ether structure, which is unlikely to expain the experimentally observed E_{11}^{*-} emission. To address this issue, we considered adsorption of two O atoms. The most stable adsorption structure for two O atoms is two parallel ether structures, whose transition energy appear between E_{11}^{*} and E_{11}^{*-}, and more stable than two isolated ether structures. The second most stable structure is neighboring ether and epoxy structures, whose O-adsorption energy is also much stronger than the sum of those of isolated ether and epoxy structures. The transition energy is only 0.02eV lower than the E_{11}^{*-} level that is produced by the isolated epoxy structure. According to the O diffusion simulations considering the energetics we had found, we found that a certain number of O atoms maintain the epoxy structure at higher O concentrations, providing a possible mechanism for significant brightening of E_{11}^{*-} in the recent bioimaging experiments.

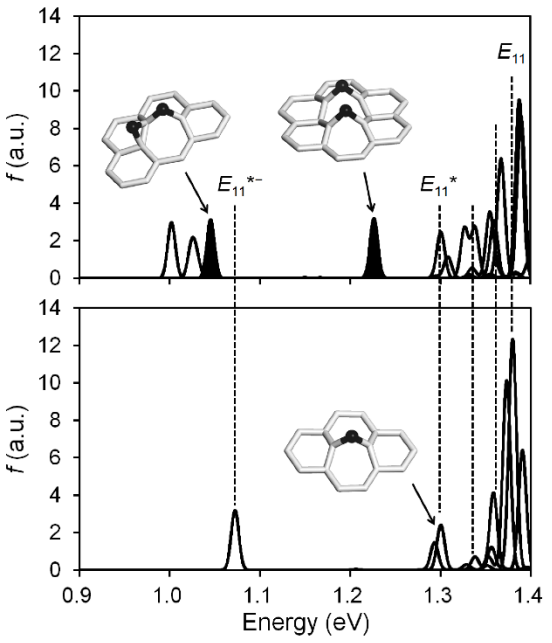

Fig.1: Optical transitions for (6,5) CNTs adsorbed by one O atom (lower panel) or two O atoms (upper panel). The oscillator strengths are plotted with 5-meV width around the transition energies. The insets are the schematic diagrams for the related O-adsorption structures. The gray sticks and black spheres represent C−C bonds and O atoms, respectively.

These results explain the multiple emission peaks in the low-temperature PL measurements of SWCNTs oxidized by O_3 and those in the PL spectra of SWCNTs oxidized by O_2 molecules during single chirality separation processes. Our comprehensive understanding is essential for further applications of oxidized SWCNTs.

[1] S. Ghosh *et al.*, Science **330**, 1656 (2010).
[2] M. Ohfuchi, Y. Miyamoto, Carbon **114**, 418 (2017).