# Study of Negative and Positive Trions in the Electrochemically Carrier-doped Single-walled Carbon Nanotubes 

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The optically generated electron-hole pair in a $1-\mathrm{nm}$ cylinder structure of single-walled carbon nanotubes (SWNTs) forms exciton as the strongly bound state, such as the hydrogen atom (H)-like state. Due to the strong Coulomb interaction, the formation of a charged exciton, called as trion, has been expected in carrier-doped SWNTs. The trion is the three-particle bound state of a doped carrier (electron or hole) and an optically generated electron-hole pair, such as $\mathrm{H}^{-}$or $\mathrm{H}^{2+}$. Recently, the positive trion (bound state of two holes and an electron) has been experimentally observed by the chemically holedoped SWNTs [1], however, the negative trion (bound state of two electrons and a hole) in the SWNTs has not yet been observed. We here report the direct observation of negative trions as well as positive trions on the SWNTs by the electrochemical doping method.

We observed the electrochemical PL spectra of CoMoCAT SWNTs at the non-doped $(0 \mathrm{~V})$, hole-doped $(+0.5 \mathrm{~V})$ conditions. The new peaks are appeared below the emission energies of the $E_{11}$ bright exciton peaks at the hole-doped conditions, which come from the positive trion [1]. The electrochemical PL spectra of CoMoCAT SWNTs are also observed at the electron-doped ( -0.7 V ) conditions. The similar new peaks are also appeared at the electron-doped conditions, which can be assigned as the negative trion peaks [2]. The positive trion peaks at a hole-doped condition and the negative trion peaks at an electron-doped condition are at around 1.07 eV in the $(6,5)$ SWNTs and at 1.03 eV in the $(7,5)$ SWNTs, respectively. The energy separations, $\Delta E^{+}\left(\Delta E^{-}\right)$, defined as the difference between the $E_{11}$ exciton and the positive (negative) trion energy, are very high values of 140-170 meV , depending on the diameter of SWNTs. In both cases, the energy separations of the positive and negative trions are very similar to each other, which suggest the similar binding energy of positive and negative trions in the SWNTs. Moreover, we will discuss the spatial localization nature of trions from the information on the temperature dependence of PL spectra of trions.

## References:

[1] R. Matsunaga, K. Matsuda, and Y. Kanemitsu, Phys. Rev. Lett. 106, 037404 (2011).
[2] J. Park, Y. Hirana, S. Mouri, Y. Miyauchi, N. Nakashima, and K. Matsuda, J. Am. Chem. Soc. 134, 14461 (2012).
[3] S. Mouri, Y. Miyauchi, M. Iwamura, and K. Matsuda, submitted for publication.

