Evaluation of substituent effects on the potential levels of locally-functionalized single-walled carbon nanotubes using *in situ* photoluminescence spectroelectrochemistry

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Recently, single-walled carbon nanotubes (SWNTs) with local chemical functionalization were reported to produce the photoluminescence (PL) with red-shifted PL wavelengths by over 100 meV and enhanced quantum yields compared to those of pristine SWNTs [1]. Interestingly, the PL wavelengths of locally-functionalized SWNTs (lf-SWNTs) shift based on the difference in the chemical structures of the modified groups on the lf-SWNTs [2]. As another structural factor, we reported the proximal modification using bisdiazonium compounds for the synthesis of the lf-SWNTs and observed a largely red-shifted PL by 250 meV from E_{11} PL of the pristine SWNTs [3]. These finding are of importance in view of the new PL phenomena of the SWNTs but the effect of the defect structures on the lf-SWNTs has been mainly discussed based on the optical band gaps of the SWNTs and their PL dynamics.

In this study, we conduct an *in situ* PL spectroelectrochemical analysis to evaluate potential levels (HOMO and LUMO) of the lf-SWNTs [4]. Four types of lf-SWNTs with aryl groups that had different substituents (-MeO, -H, -Br and $–NO_2$) were synthesized and characterized in order to investigate the substituent effect on their electronic states. As shown in Fig. 1, the HOMO and LUMO levels shifts occurred by the local functionalization and a substituent dependence was observed specifically in the HOMO level. The observed negative potential shift in the HOMO level largely occurred according to the increase in the electron-accepting natures of the substituents. Regarding the LUMO level, on the other hand, negligible change was observed. In this presentation, we will discuss more details in terms of factors of the level shifting and, differences in chiral indices and family patterns of the nanotubes.

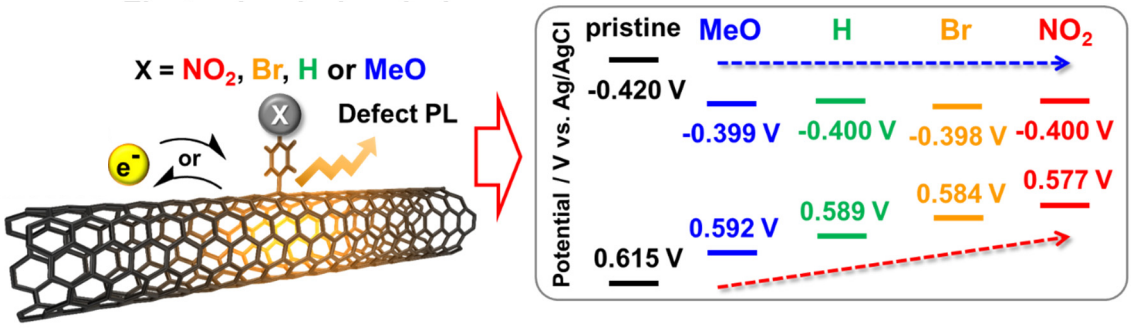

Fig. 1 (Left) Schematic illustration for the reduction/oxidation of lf-SWNTs using the *in situ* PL spectroelectrochemical method. (Right) The evaluated HOMO and LUMO levels of the pristine and lf-SWNTs with different substituents.

[1] Y. Miyauchi *et al.,* Nat. Photonics. **7**, 715 (2013). [2] Y. Wang *et al.,* Nat. Chem. **5**, 840 (2013). [3] T. Shiraki *et al.,* Sci. Rep. **6**, 28393. (2016). [4] T. Shiraki *et al.,* Nanoscale **9**, 16900 (2017).