Charge transfer analysis by EELS

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In Ref.1, we investigate the structure of Tetracyano-*p*-quinodimethane (TCNQ) attached to oxidized SWNH. TCNQ is an interesting compound because of its high electron affinity and formations of charge-transfer (CT) complexes with various donor molecules. Spectroscopic characterization using X-ray photoemission spectroscopy and near-edge X-ray-absorption fine structure spectroscopy supported the possibility of a CT between single wall carbon nanohorn (SWNH) and TCNQ. To create defects in the SWNH, they have been oxidized and then heat treated to open holes in the graphene.

To elucidate chemical states of the adsorbed TCNQ, we performed EELS experiments. The STEM image of TCNQ/SWNH and its nitrogen mapping are shown in Figs. 1a and b. The white and light blue points of Fig. 1b represent higher and lower concentrations of nitrogen, respectively. It should be noted that the nitrogen was distributed uniformly over the entire aggregate, which was further confirmed from the N/C density ratio shown in Fig. 1c.

The EELS spectrum measured from TCNQ/SWNHh and TCNQ(pristine) crystal, showing K-shell ionization peaks of nitrogen atoms are shown in Figs. 1d and e, respectively. The π^* transition at 401 eV was assigned to trivalent N atoms of TCNQ. The intensity ratio of the π^*/σ^* of TCNQ/SWNHh was considerably smaller than that of TCNQ(pristine) crystal. This may be caused by doped TCNQ. In such a case, some electrons transferred from the graphene walls to the TCNQ molecule will be localized in the LUMO of the TCNQ, i.e., around the N atoms and the quinoid ring. These extra electrons populate the π^* band of the nitrogen atoms and so reduce the probability of transition for core electrons

Ab initio calculations and Mulliken population analysis reveals that the total charge of TCNQ increased after this reaction (Figs. 2c and d), which were consistent with those inferred from EELS spectra. Mainly, the extra-charge get localized around the carbon atom between the TCNQ and the graphene and at the other

extremity of the molecule.

Therefore EELS fine structure analysis can be used to compare the structure expected by ab-initio calculation and the actual sample.

References

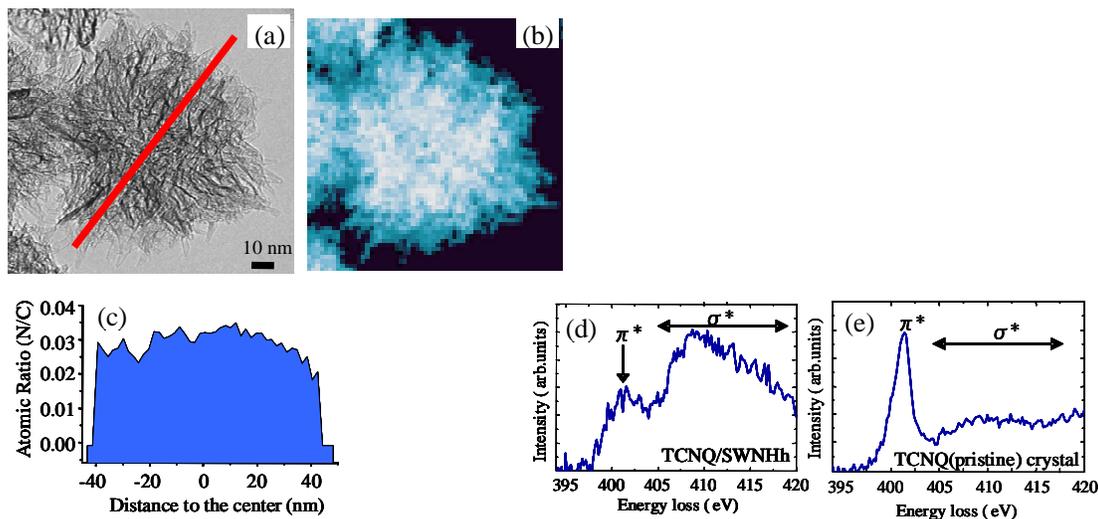[1] Yuge et al. J. Phys. Chem. C 2008, 112, 5416-5422

FIG.1. Bright field STEM image of TCNQ/SWNHh (a), its elemental map of the nitrogen measured by EELS (b), atomic ratio of N/C along the indicated red line (c), EELS spectra of TCNQ/SWNHh (d), and TCNQ(pristine) crystal (e).
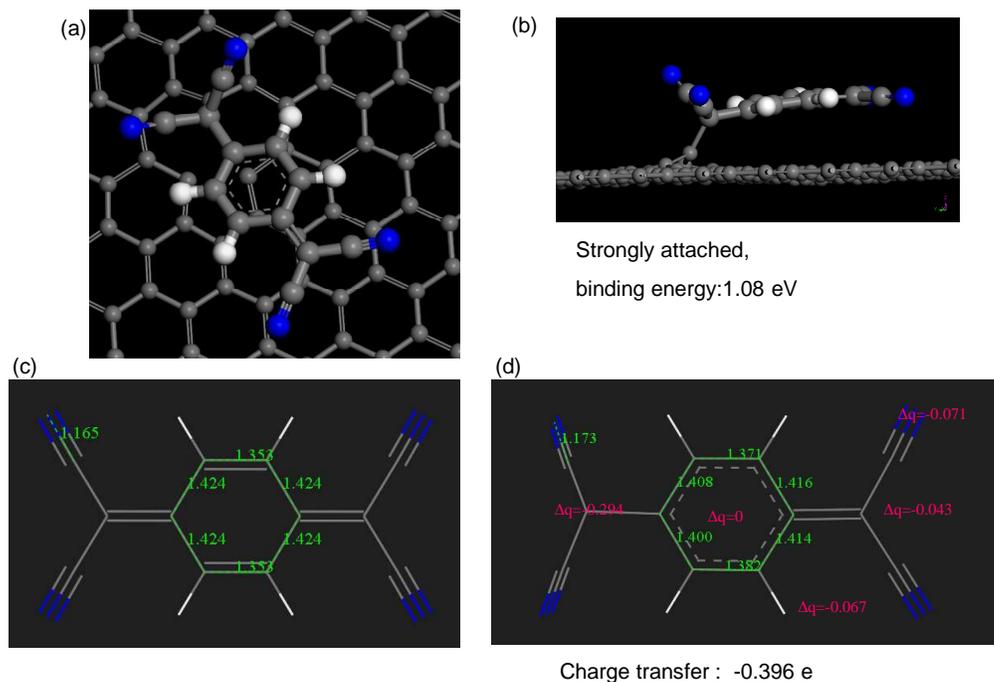

FIG. 2. The grey, white, and blue balls or segments indicate carbon, hydrogen, and nitrogen, respectively. DFT geometrical optimization shows that TCNQ molecule get bended through attaching to the defected graphene as it is shows in (a) and (b). This structure is the most stable with a binding energy of 1.08 eV . Comparing the main bond lengths (expressed in nm) of TCNQ molecule physisorbed on a perfect graphene sheet, those of TCNQ molecule in (c) are different as shown in (d) where the carbon atom