

Adsorbed Structure of Iodine Species of CsI Restricted in Cylindrical Pore of Single-Walled Carbon Nanotube

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1 Introduction

To understand properties of hydrated ions under nano-confined conditions is a subject of great importance. We have, therefore, engaged in research works to unveil specific structure of hydrated metal ions confined in carbon nanopores. Through our investigations, we found surplus adsorption phenomena of anions in carbon micropores whose pore wall is constructed by π -electrons. Such specific adsorption of anion species was firstly investigated by the adsorption of aqueous RbBr solution on single-walled carbon nanotube (SWCNT) where the adsorbed amount of Br^- was 10-100 times larger than Rb^+ [1]. In addition, the solution pH, which is typically around 6 at the initial state, increased up to around 10 after the adsorption of ions indicating the strong adsorption of proton on SWCNT even though the concentration of proton in the aqueous solution is much smaller than that of both Br^- or Rb^+ . Herein, we briefly summarize specific structure formed around an iodine species of cesium iodide (CsI) confined in the nanospace of SWCNT to study dependence of anionic species to the surplus adsorption phenomena.

2 Experiment

CsI was impregnated into the cylindrical micropore of SWCNT (purchased from Meijo Nano Carbon Co., Ltd.; average pore width = 1.2 nm) by using CsI aqueous solution (0.5 M). Here, all CsI species can be successfully impregnated inside the cylindrical pore because the adsorbed amounts of iodine species on close- and open-ended SWCNT are 0.02 and 0.94 mmol g^{-1} , respectively meaning that no CsI species can be adsorbed outside the pore. Such CsI-deposited SWCNT (denoted as SWCNT-CsI) was obtained after drying in a desiccator. XAFS measurements were performed at KEK-PFAR (NW10A) around the I *K*-edge region.

3 Results and Discussion

Fig. 1 shows Fourier-transformed spectra of I *K*-edge EXAFS spectra of SWCNT-CsI, aqueous CsI solution (CsI aq.), and CsI crystal, respectively. The spectrum of SWCNT-CsI is obviously different from both CsI aq. and CsI crystal. Especially, the largest band around 0.27 nm for SWCNT-CsI is not observed in any other spectra, indicating an existence of unique structure initiated by the confinement of SWCNT pores. We carefully analyzed the band observed in SWCNT-CsI and were able to obtain an incredible result; the major species of iodine adsorbed on SWCNT was not I^- but I_3^- . We reached such an argument

because the distance between nearest I-I (0.289 nm) for SWCNT-CsI was similar to the literature value of I_3^- (0.290 nm) [2]. Generally, the oxidation reaction from I^- to I_3^- in aqueous solution needs three special conditions, *i.e.* (i) a highly concentrated I^- condition (ii) in an acidic solution and (iii) UV-light irradiation. However, I_3^- species was spontaneously synthesized through only a simple adsorption process in the present study. This is because a highly concentrated condition of iodine species was achieved by the confinement effect of SWCNT and SWCNT could also adsorb H^+ species from aqueous solution to balance between cation and anion species. Actually, the pH value of aqueous CsI solution increased from 6.6 to 10.1 by the adsorption of CsI. In addition, we already reported that a suitable nano-confinement condition can initiate a unique photoreaction [3], thus, the reaction to I_3^- must be launched under any room-light irradiated condition. Therefore, the three conditions mentioned above might be satisfied to produce I_3^- from I^- species inside the pore of SWCNT.

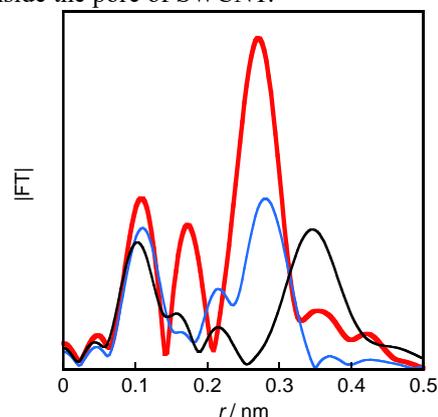


Fig. 1: Fourier-transformed spectra of I *K*-edge EXAFS spectra of SWCNT-CsI (red), aqueous CsI (blue), and CsI crystal (black).

Acknowledgement

This work was partially supported by the financial support from The Society of Iodine Science (SIS).

References

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