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Hydrated Structure of Copper Acetate Restricted in Micropore of Single-Walled Carbon Nanotube

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1 Introduction

We have studied specific structure of hydrated ions such as Zn^{2+} [1, 2], Cu^{2+} [3], and Co^{2+} [4] confined in carbon nanospaces with X-ray absorption fine structure (XAFS) technique, because nano-restricted ions in solid space can play an important role in various phenomena such as catalytic reaction and energy storage. Nanospace can also initiate some chemical reactions which cannot be observed in any bulk phases. For instance, we have succeeded in synthesizing cuprous oxide (Cu_2O) nanoparticles from copper acetate ($Cu(OAc)_2$) confined in the micropore of single-walled carbon nanotube (SWCNT) under the visible-light irradiated condition [5]. Herein, we report the possibility to form unique structure of copper acetate, which is a candidate of the precursor to initiate the specific reaction, in the cylindrical micropore of SWCNT.

2 Experiment

$Cu(OAc)_2$ was impregnated into the micropore of SWCNT (MEIJO eDIPS (EC2.0); average pore width = 1.7 nm). The $Cu(OAc)_2$-deposited SWCNT was evacuated at 423 K followed by the adsorption of water under the dark condition to obtain the hydrated precursor of $Cu(OAc)_2$. *In-situ* XAFS measurements were performed at KEK-PFAR (NW10A) on the *K*-edge of Cu as a function of vapor pressure of water.

3 Results and Discussion

Fig. 1(a) shows XANES spectra on Cu *K*-edge of $Cu(OAc)_2$ deposited on SWCNT during the adsorption process of water. The adsorption-desorption isotherm of water on $Cu(OAc)_2$-deposited SWCNT is also shown in Fig. 1(b). The band intensities around 8984.0 eV under the water-adsorbed conditions were smaller than that in the evacuated state. The decrease in the band intensity can be observed from P/P_0 = 0.2 where adsorbed water molecules hydrate to the Cu atoms of $Cu(OAc)_2$. Actually, the band around 8984.0 eV can be assigned to the planner formation of Cu compounds [6]; non-planner structure of $Cu(OAc)_2$ in the micropore tends to be formed by the hydration of water. On the other hand, the band intensities around 8981.5 eV were obviously elevated with the vapor pressure after finishing the hydration process of water to Cu atoms ($P/P_0 \geq 0.5$). The clear uptake in the adsorption isotherm shown in Fig. 1(b) can be typically observed because of the clustering of water molecules in the cylindrical micropore. Therefore, the increase in the band intensities around 8981.5 eV should be assigned to structural variation of hydrated $Cu(OAc)_2$ initiated by the formation of water clusters in the micropore. Actually, the band around 8981.5 has never been observed in any bulk conditions such as crystal or aqueous solution of $Cu(OAc)_2$. Thus, we could find a possibility on the specific formation of hydrated $Cu(OAc)_2$ confined in the micropore of SWCNT whose structure must relate to the unique photoreduction reaction. We are now trying to identify the actual structure of hydrated $Cu(OAc)_2$ formed in the micropore of SWCNT from both experimental and theoretical methods.

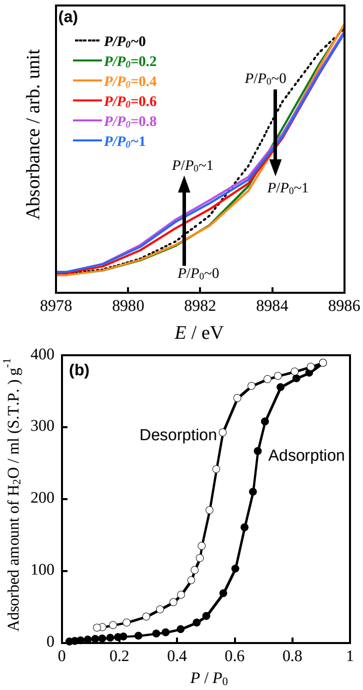

Fig. 1: (a) XANES spectra on Cu *K*-edge of $Cu(OAc)_2$ deposited on SWCNT at different vapour pressure conditions and (b) adsorption-desorption isotherm of water on $Cu(OAc)_2$-deposited SWCNT at 303 K.

References

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