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Hydration Structure around a Zinc Ion Restricted in Cylindrical Carbon Nanospace

Masayasu Nishi, Mitsuhiro Ushio, Kazuma Tsurusaki, Tomoko Kusudo, Masaya Akiyama,
Hiroe Torigoe, Akira Oda, Yuusuke Sogawa, Naoya Matsushima, Atsushi Itadani,
Takahiro Ohkubo*, and Yasushige Kuroda
Okayama University, Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

1 Introduction

It has been studied that hydration structure around a metal ion restricted in carbon nanospace is different from that in bulk solution [1]. Recently, we reported the dehydrated structure around a zinc ion confined in slit-shaped carbon micropore of activated carbon fiber [2]. In addition, a lot of recent papers predict the characteristics of structure, nanofluidics, or dynamics of water or ions restricted in quasi-one dimensional nanospaces [3, 4]. In this report, we briefly summarize the hydration structure around a zinc ion restricted in cylindrical micropore of single-wall carbon nanotube (SWCNT) [5].

2 Experiment

We used open-ended SWCNT whose average pore width is 0.87 nm. SWCNT was dispersed in aqueous solution of zinc acetate ($Zn(OAc)_2$) to impregnate zinc ions into the micropore followed by washing and drying at 353 K. SWCNT adsorbed by zinc ion were evacuated at 423 K (denoted by SWCNT-Zn-evac) followed by the adsorption of water vapor (denoted by SWCNT-Zn-H_2O). Both XAFS and QXAFS spectra on Zn *K*-edge were obtained and analyzed by IFEFFIT code.

3 Results and Discussion

Figure shows XANES spectra of SWCNT-Zn-H_2O. The spectrum of SWCNT-Zn-H_2O was analyzed by linear least-squares fitting of each spectrum from SWCNT-Zn-evac and that from bulk aqueous solution of $Zn(OAc)_2$. The results of the linear combination were well agreed with the experimental ones, indicating that it is enough for SWCNT-Zn-H_2O to assume only the dissolved and insoluble species [1, 5]. Moreover, the coefficients of the linear combination analysis obviously reflect the ratio of dissolved or insoluble zinc species in the nanospace at saturated vapor pressure condition. We could estimate the proportion of the dissolved species formed inside the nanospace of SWCNT as 44% even at the saturated vapor-pressure region. Here, to estimate the structural information only from the dissolved species restricted in the nanospaces, we assume that such structural parameters are the linear combination of dissolved and insoluble species. Consequently, the hydration number around a zinc ion restricted in SWCNT is 5.5 which is smaller than that of bulk $Zn(OAc)_2$ solution. Moreover, SWCNT includes a little amount of multi-wall carbon nanotube (MWCNT) whose pore size is in mesopore region. Because the hydration number around a zinc ion confined in mesopore of MWCNT was 6.0 [5], the effective hydration number around a Zn^{2+} formed only in the micropore of SWCNT is evidently smaller than 5.5.

In addition, the square of Debye-Waller factor of SWCNT is 9.56×10^{-5} nm^2 which is smaller than that of slit-shaped carbon micropore (average pore width=0.63 nm). The present results significantly suggest that statistically ordered and/or thermally compressed hydration structure around a Zn^{2+} having smaller number of hydrated molecules must be formed by the strong confinement effect of cylindrical pore of SWCNT.

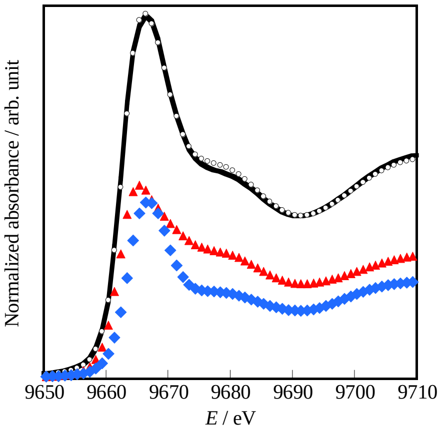

Figure: Zn *K*-edge XANES spectra of SWCNT-Zn-H_2O: experimental data (solid line), component in evacuated condition (red triangle), bulk aqueous solution of $Zn(OAc)_2$ (blue diamond), and sum of the components in both evacuated condition and bulk aqueous solution (open circle).

References

[1] T. Ohkubo et al., *J. Am. Chem. Soc.* **124**, 11860 (2002).
[2] T. Ohkubo, M. Nishi, and Y. Kuroda, *J. Phys. Chem. C* **115**, 14954 (2011).
[3] J. K. Holt et al., *Science* **312**, 1034 (2006).
[4] T. Ohba et al., *Langmuir* **29**, 1077 (2013).
[5] M. Nishi et al., *Nanoscale* **5**, 2080 (2013).

Research Achievement

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* ohkubo@okayama-u.ac.jp