

## Structural anomalies of hydrated $\text{Cu}^{2+}$ confined in slit-shaped carbon nanospace

Yohko NOBUHARA<sup>1</sup>, Takahiro OHKUBO<sup>3</sup>, Hiroshi NOGUCHI<sup>1</sup>, Yoshiyuki HATTORI<sup>2</sup>, Takehisa KONISHI<sup>2</sup>, Hirofumi KANO<sup>1,2</sup>, Tanaksi FUJIKAWA<sup>1,2</sup>, Katsumi KANEKO<sup>\*1,2</sup>

<sup>1</sup>Graduate school of science, Chiba Univ., Inage, Chiba 263-8522, Japan

<sup>2</sup>Department of chemistry, Faculty of science, Chiba Univ., Inage, Chiba 263-8522, Japan

<sup>3</sup>Research institute for Sci. & Tech., Tokyo Univ. of Sci., Noda, Chiba 278-8510, Japan

### Introduction

Molecules are confined in nanospace to form an ordered structure [1-3]. The structures of confined molecules in nanospace are of interest in variety of areas such as electrolytic solutions and electric double layer. Recently, Okubo et al. showed a characteristic hydration structure of Rb ion confined in slit-shaped solid nanospace by EXAFS analysis [4,5]. The understanding of hydration structure confined in nanospace has offered topics for research in nanospace science. In this work, we characterized the hydration structures of ionic solution of Cu in slit-shaped carbon nanospace by means of EXAFS technique and the structural anomalies of ionic solutions in nanospace will be discussed.

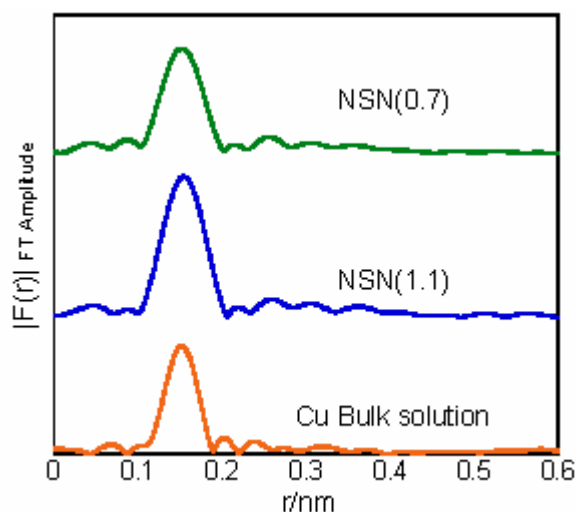
### Experimental

Pitch-based activated carbon fibers (A7 and A20) were used as a nanoporous carbon. The average width of slit-shaped nanospace in A7 and A20 was evaluated to be 0.7 and 1.1 nm, respectively. The Cu ionic solution was introduced into slit-shaped nanospace and dried in vacuo at 383 K for 2 h. After the dispersion of Cu ions, water vapor was adsorbed in the slit-shaped nanospace. In this report, we denote the hydrated Cu ions in the nanospace as "nanosolution". The XAFS measurements were performed on Cu *K*-edge at BL-7C beam line with transmission mode. Samples were adjusted in a sufficient quality to give an edge jump and installed in a glass cell with windows of Lumirror film. The program code FEFF8 was used to calculate the theoretical phase and amplitude for curve fitting.

### Results and Discussion

Figure 1 shows the radial distribution function of Cu nanosolutions and aqueous bulk solutions of 1 mol/l. The peak centered at 0.15 nm assigned to the first hydration shell of Cu ion. This figure shows that Cu-O distance of Cu nanosolution is almost the same as that of the bulk solution. Table 1 shows the best fits data of Fourier filtered EXAFS spectra for first hydration shell. The coordination number around a Cu ion in the nanosolution is quite small compared with that in the bulk solution. Also, the Debye-Waller factor of nanosolution decreased by 2.5% compared to the bulk solution. The change in the hydration structures of nanosolutions becomes remarkable with the decrease in the pore width, indicating that the hydration structures in the nanospace are strongly

affected by the pore walls. Water molecules confined in nanospace cannot form the hydration structure in the same as in the bulk solution. These results suggest that the anomalous hydration structure was stabilized by the molecular potential field in slit-shaped carbon nanospace.



**Figure 1.** The radial distribution functions of Cu bulk solution and nanosolutions. NSN(0.7) and NSN(1.1) denote nanosolutions formed in the nanospace of 0.7 and 1.1 nm, respectively.

**Table 1:** The local structural parameters around Cu ion.

	<i>N</i>	<i>R</i> /Å	$\sigma^2/\text{Å}^2$
NSN (0.7)	2.1	1.93	0.0017
NSN (1.1)	3.4	1.92	0.0028
Bulk	4.0	1.95	0.068

*N*: hydration number, *R*: Cu-O distance,  $\sigma$ : Debye-Waller factor

### References

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\*kaneko@pchem2.s.chiba-u.ac.jp