Ion Adsorption Mechanism of Bundled Single-walled Carbon Nanotubes

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Abstract. In order to elucidate ion adsorption mechanism of bundled single-walled carbon nanotubes (SWCNTs), *in situ* synchrotron XRD measurements of SWCNT electrode in alkali halide aqueous electrolyte at several applied potentials were performed. It was found that the surface inside SWCNT is the important ion adsorption site.
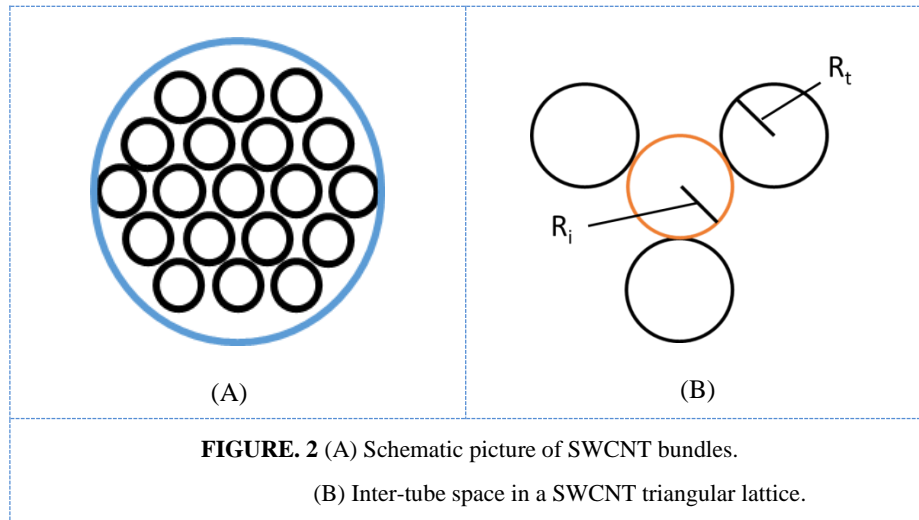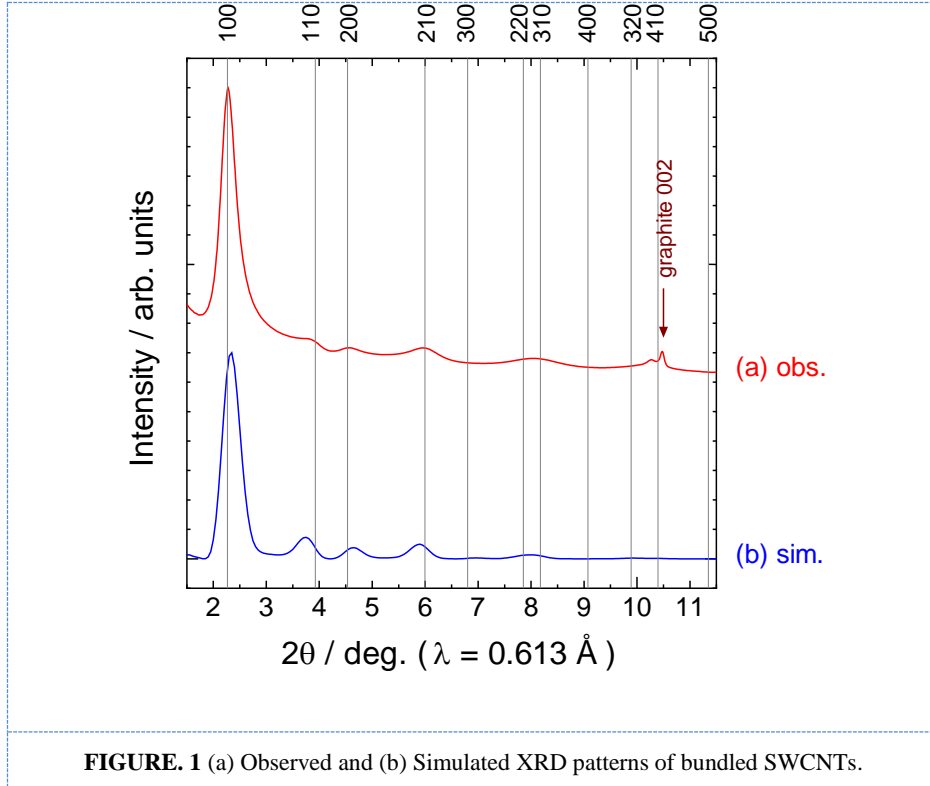
INTRODUCTION

There is much interest in electric double layer capacitors (EDLCs) due to the quick response for charge and discharge processes. EDLCs store electric energy just by physical adsorption of electrolyte ions on the surface of electrodes. Since an electrode having larger specific surface area can store higher energy, single-walled carbon nanotubes have been expected as a good electrode material for EDLC because the theoretical specific surface area of SWCNTs is very large (2630 m^2/g) [1-4]. However, the reported EDLC capacity values of SWCNTs are not so high comparing to the values of the normal EDLC electrodes (e.g. activated carbon). One of the reasons why the expected high value could not be obtained is SWCNT aggregation form (bundle structure), whereby SWCNTs are gathered by van der Waals interaction. Due to this aggregation form, the actual specific surface area of the aggregated SWCNTs is much lower than that of an isolated single SWCNT. On the other hand, interestingly, it is also known that the EDLC capacitance of the bundled SWCNTs per unit surface area is much higher than that of activated carbons [1]. However, the ion adsorption mechanism of the bundled SWCNTs has not been understood well. In order to elucidate the mechanism, we performed *in situ* synchrotron XRD measurements of the bundled SWCNTs during adsorption of electrolyte ions.

EXPERIMENTAL

In the present study, we used high quality SWCNT sample (Meijo Nano Carbon Co Ltd., SO type). The quality and the purity of the SWCNT sample were characterized by TEM, XRD, and Raman measurements [5-7]. Ion adsorption process, that is the main topic in the present study, was investigated by *in situ* synchrotron XRD measurements of SWCNT electrode under applied potential. The XRD measurements were performed on a synchrotron radiation beam line BL-18C at the Photon Factory in High-Energy Accelerator Research Organization (KEK), Tsukuba, Japan. The beam was monochromatized by Si(111) double monochromators and collimated by a pinhole collimator of 100 mm in diameter. The incident X-ray wavelength was set to $\lambda = 0.0613$ nm. For the *in situ* XRD measurements, we fabricated three electrode configuration cell which consists of SWCNT working, Pt counter, and Ag/AgCl reference electrode. Several kinds of alkali halide aqueous electrolytes were used.

RESULTS & DISCUSSION

Figure. 1 shows the observed and simulated XRD patterns of the bundled SWCNTs having 2-dimensional hexagonal structure (Fig. 2) [8]. As shown in Fig. 1, the simulated pattern reproduced the observed pattern very well. The mean tube diameter of 1.47 nm and the tube-center distance a of 1.79 nm were used for the simulation. Therefore, the distance between surfaces of the nearest neighbor tubes is evaluated to be 0.32 nm which is in good agreement with the van der Waals radius of carbon atom.
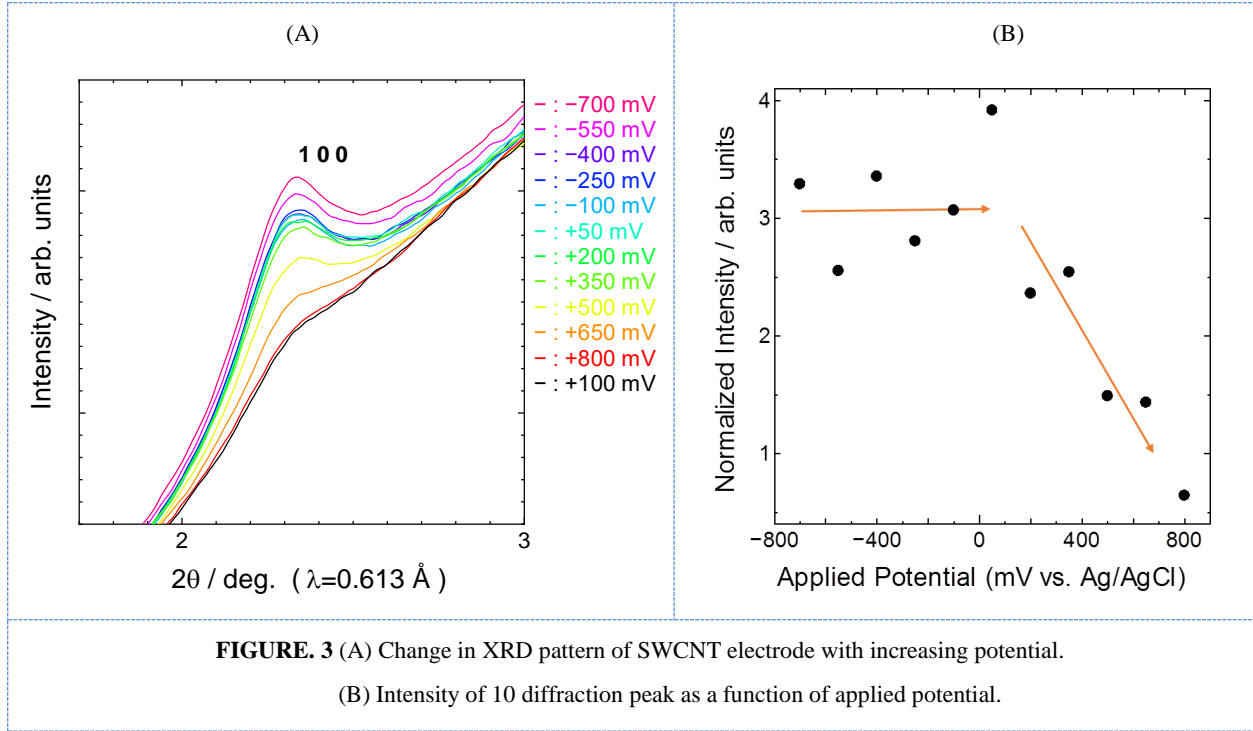

FIGURE. 1 (a) Observed and (b) Simulated XRD patterns of bundled SWCNTs.

(A)

(B)

FIGURE. 2 (A) Schematic picture of SWCNT bundles.

(B) Inter-tube space in a SWCNT triangular lattice.

FIGURE. 3 (A) Change in XRD pattern of SWCNT electrode with increasing potential.

(B) Intensity of 10 diffraction peak as a function of applied potential.

Figure. 3 shows the change in XRD pattern of SWCNT electrode with increasing potential. Since the open-circuit voltage was 0.13 V, cation and anion adsorption potential ranges correspond to -800 - 200 mV and 200 - 800 mV, respectively. The probable ion adsorption sites of the bundled SWCNTs are i) bundle outside surface, ii) tube inside surface, and iii) inter tube sites. If ions are intercalated in inter-tube site, the tube-center distance should be enlarged. However, as shown in Fig. 3, since the 10 peak position did not change with ion adsorption, ions were not intercalated between tubes.
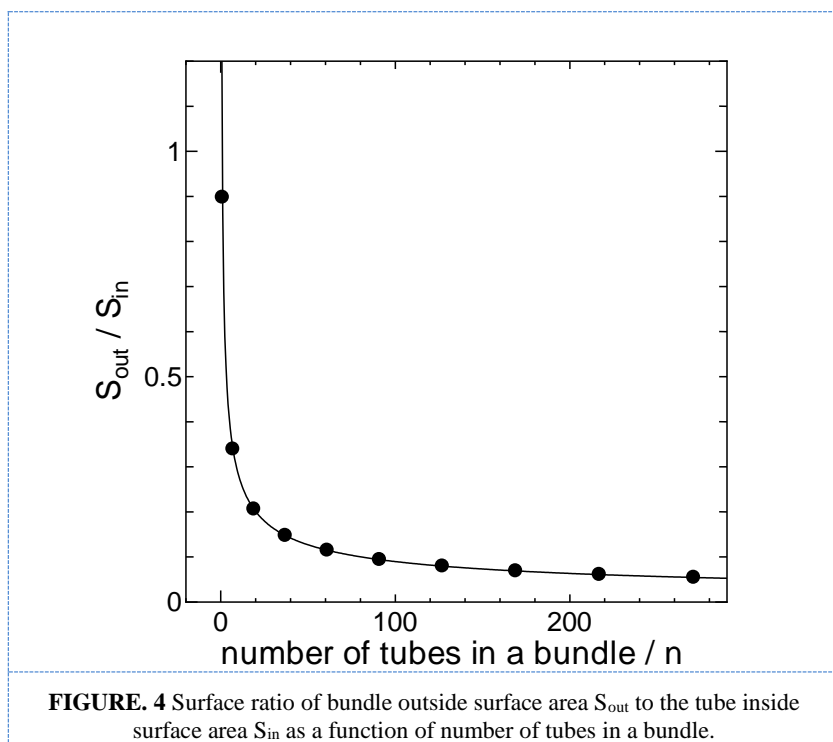
The radius R_i of the inter-tube space shown in Fig. 2 is expressed by the following equation

$$R_i = \frac{1}{\sqrt{3}} a - R_t \quad (1)$$

where R_i corresponds to the tube radius. In the present experiment, the tube radius R_t is 0.74 nm, R_i is calculated to be 0.29 nm which is too small for solvated ions to be intercalated. On the other hand, the peak intensity of the 10 diffraction changed with applied potential. The intensity change indicates that ions are adsorbed inside the tubes. Therefore, it was found that the tube inside is the important adsorption site. Equation. 2 expresses the surface ratio of bundle surface area S_{out} to the tube surface area S_{in} as a function of number n of tubes in a bundle.

$$S_{out}/S_{in} = \left(3^{\frac{1}{4}}\sqrt{n\pi}a\right)/(2R_t n\pi) \quad (2)$$

According to Eq. 2, tube inside becomes the dominant surface with increasing bundle size. The bundle size of the present SWCNT sample was several tens of nanometers, which was estimated by the diffraction line width. Assuming the bundle size is 50 nm, the tube inside surface area is about 7 times greater than the bundle outside surface area (Fig. 4). Therefore, the main adsorption site of the bundled SWCNTs used in the present study would be tube inside surface site.

FIGURE. 4 Surface ratio of bundle outside surface area S_{out} to the tube inside surface area S_{in} as a function of number of tubes in a bundle.

ACKNOWLEDGMENTS

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