X-ray Absorption Fine Structure Studies on the Local Structures of Ni Impurities in a Carbon Nanotube

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Local structure around Ni impurities in a carbon nanotube was studied by X-ray absorption fine structure (XAFS). The Ni was present in the form of Ni particles before the purification process. After the purification Ni content was decreased to a few hundreds ppm. The Ni K-edge XAFS could be measured by a 19 element solid-state detector. The Ni species was strongly bound to the carbon of the carbon nanotube with a Ni–C covalent bonds at 0.173 nm.

Carbon nanotubes draw much attention as new materials, which have wide applications to many fields such as electric devices, hydrogen storage materials, field emission display, AFM tip, and so on.[1] Since carbon nanotubes are composed of only carbon atoms and are expected to have biocompatibility, the researches for the biological application have been started such as a drag delivery system, scaffolds for cell engineering, artificial bones, dental roots, and cell culture media.[2] Chemical vapor deposition (CVD) synthesis method using catalysts such as Ni, Fe, Fe–Ni, and Ni–Mo is one of promising methods for large-scale production of carbon nanotubes.[3] Ni is one of the best catalysts to produce carbon nanotubes but it often shows toxic properties to a living body. Although most of Ni in the carbon nanotube can be removed by the HCl treatment, it is important to know the metabolism, chemical state, and structure of Ni impurity left in the carbon nanotubes after the HCl treatment in order to apply the nanotubes to medical and biological fields safely. In this paper, we report the characterization of the chemical state of residual Ni species before and after the purification processes of a carbon nanotube by XAFS (X-ray absorption fine structure) technique. Because the amount of Ni species after the purification is about a few hundred ppm, it is difficult to estimate the Ni chemical state by conventional techniques. We carried out fluorescence XAFS analysis of Ni impurity in the carbon nanotube. We found that the Ni species was strongly fixed to the carbon of a carbon nanotube through a Ni–C covalent bond.

Carbon nanotube was synthesized by a CVD method using Ni catalyst. It was purified by a calcination followed by 6 M HCl treatment for 6 h in order to remove the carbon nanoparticles and Ni catalysts.

XAFS measurements were carried out at BL9A of the Photon Factory in Institute for Structure Material Science (KEK-PF) using a Si(111) double crystal monochromator.[4] (99G280, 2001G287) The incident and transmitted X-rays were monitored by ionization chambers filled with nitrogen. The fluorescence X-ray was detected by a 19 element SSD (solid state detector) (Camberra Co.) The dead times of SSD were corrected according to the literature.[5] The XAFS analyses were carried out by REX2000 (Rigaku Co) using phase shift and amplitude functions derived from FEFF8.[6,7]

Figure 1 showed the Fourier transforms of Ni K-edge XAFS oscillations before the purification over $k = 30\text{–}150\,\mathrm{nm}^{-1}$. We measured the XAFS oscillation in a transmission mode because we had an enough edge jump. We found several peaks. The first and main peak appeared at 0.25 nm, which corresponded to that of the Ni–Ni distance in the first shell of Ni metal. The longer Ni–Ni peaks clearly appeared, which were corresponding to the 2nd, 3rd and 4th shells in the Ni fcc structure. The curve fitting analysis showed that the coordination number and bond distance of the first shell Ni–Ni bond were 12 and 0.248 nm, respectively, indicating that the Ni was present in a metal particle larger than 5 nm judging from the coordination numbers of the first and the higher shells which were almost equal to that of the bulk Ni species.[8]

When the Ni metal particles were removed by the HCl treatment, we could not observe Ni K-edge in a transmission mode any more. Thus we used a fluorescence mode to obtain Ni XAFS oscillations. According to the Ni Kα fluorescence peak intensity, the amount of Ni can be estimated to be about a few hundred ppm. Figure 2 shows the X-ray near edge structure of Ni species in the carbon nanotube before and after the HCl treatment to-

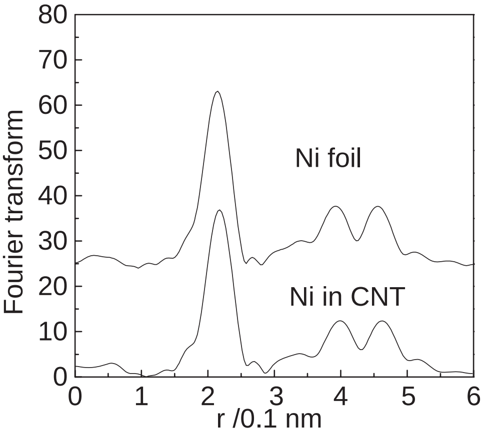

Figure 1. Fourier transforms of XAFS oscillations for Ni catalysts in the carbon nanotube and Ni foils.

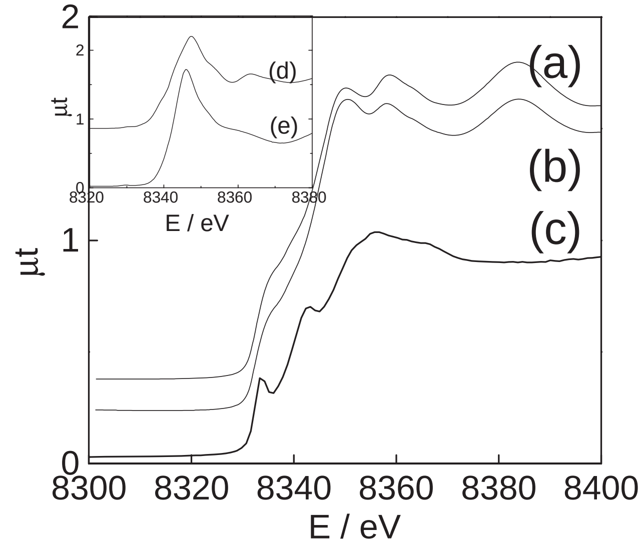

Figure 2. Ni K-edge XANES of (a) Ni foil, (b) Ni species in the carbon nanotube before purification, and (c) that after the purification. (d) and (e) in the inset showed XANES spectra for NiO and $Ni(NO_3)_2 \cdot 9H_2O$.

gether with reference compounds. The XANES (X-ray absorption near edge structure) spectrum after the HCl treatment was completely different from that before the HCl treatment and Ni foil, indicating that the metallic Ni particles were completely removed by the HCl treatment. The XANES spectrum of the sample after the HCl treatment was different from those of NiO and $Ni(NO_3)_3 \cdot 9H_2O$. The residual Ni species was not simple oxide or aquo complex ions. Peaks in the XANES spectrum appeared at the similar positions as in the spectrum of the deactivated Ni catalyst after the CH_4 decomposition reaction though the peak heights were much stronger in the present spectrum.[9]

Figure 3 shows the Fourier transforms of Ni K-edge XAFS of Ni species in the carbon nanotube after the HCl treatment. Peaks appear at 0.16 and 0.22 nm. We carried out curve fitting analysis for the first shell assuming Ni–C bond. The bond distance and coordination number were 0.177 nm and 1.5, respectively. The second shell peak could be assigned to Ni–Ni at 0.247 nm with its coordination number 0.8. Ni–C distance 0.177 nm was smaller than 0.186 and 0.184 nm found in Ni_3C and $Ni(CO)_4$, respectively. Thus the Ni species was fixed strongly to carbon nanotube through a covalent bond. Since carbon nanotubes were stable in the living body, Ni impurity may stay there for a long time and may bioaccumulate. We recommend that the Ni catalyst should not be used to the production of the carbon tube if it is used as a biomaterial.

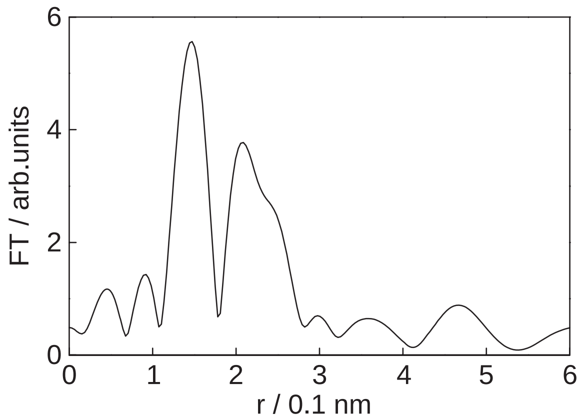

Figure 3. Fourier transform of Ni K-edge EXAFS for the Ni species in the carbon nanotube after the HCl treatment.

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