

Ni K-Edge XANES Analyses of Residual Ni Catalyst in Carbon Nanofiber Using Full Multiple Scattering Theory

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Abstract. Residual Ni species after Ni removal treatment of carbon nanofibers have been investigated by use of XAFS analyses. Most of the Ni impurities are in Ni monomer which is located on defects in carbon nanofibers. The XAFS analyses combined with the multiple scattering theory give useful information on nano-structures of small amount species. Molecular orbital calculation also support the results from the XAFS analyses.

Keywords: XAFS, XANES, Ni trapped in graphene sheet, multiple scattering calculations

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INTRODUCTION

Carbon nanotubes (CNTs) and carbon nanofibers (CNFs) can be applied to electric devices, hydrogen reservoir, medical usages and so on. There are some preparation methods to produce CNTs/CNFs, and metal catalysts such as Ni play an important role in their synthesis processes. Although most of Ni in the CNTs/CNFs can be removed by an acid (*e.g.* HCl) treatment, a small amount of Ni impurities are still left in the CNTs/CNFs. Furthermore, the residual Ni is toxic for living body. Therefore information on the structure and the chemical state of the residual Ni species is important in the medical application of CNTs/CNFs.

Recently, Asakura *et al.* reported that the K-edge X-ray absorption fine structure (XAFS) spectrum after the Ni removal treatment is different from that of Ni foil and that before the treatment [1]. The X-ray absorption near edge structure (XANES) spectrum after the treatment has two specific peaks in the absorption edge region, whereas the XANES spectrum before the treatment is quite similar to that of Ni foil. This suggests that the residual Ni species in CNFs after the treatment (a few hundred ppm) should not be metal Ni particles or simple Ni oxides.

Although XANES contains more information than EXAFS, XANES analysis requires a complex multiple scattering theory to obtain some information on the three-dimensional stereochemical structures.

Main purpose of this paper is to understand the local geometric and the electronic structure around the residual Ni species in CNFs after the Ni removal treatment by use of full multiple scattering XANES analyses [2, 3, 4] and *ab initio* molecular orbital theory. The molecular orbital theory gives us some useful information about

the electronic and the geometric structure of Ni species trapped in CNFs.

EXPERIMENT

CNF is synthesized by a CVD method using Ni catalyst following a previous literature [5]. The CNF used here is hat-stacked carbon nanofiber (HSCNF) that is composed of graphene hats stacked toward the needle axis [6]. The diameter and the length of the CNF is 25-100 nm and 0.1-5.0 μm , respectively. It is purified by a calcination in atmosphere followed by 6 M HCl treatment for 6 hours in order to remove the carbon nanoparticles and Ni catalysts.

XAFS measurements are carried out at BL9A in the Institute for Structure Material Science's Photon Factory (KEK-PF) using a Si(111) double crystal monochromator (99G280, 2001G117, 2003G247).

THEORY

The XANES theory used in this paper is based on the full multiple scattering theory proposed by Fujikawa *et al.* [2]. The X-ray absorption intensity σ from the core orbital $\phi_c(\mathbf{r}) = R_{l_c}(r)Y_{L_c}(\hat{\mathbf{r}})$, $L_c = (l_c, m_c)$ at site A (X-ray absorbing atom) is given by Eq.(1) for photoelectron kinetic energy $\varepsilon_k = k^2/2$. We assume excitation by a linearly polarized X-ray in the z -direction [3],

$$\sigma = -\frac{8}{3}\text{Im}\left\{\sum_{L,L',m_c} i^{l-l'} \exp\{i(\delta_l^A + \delta_{l'}^A)\} \rho_c(l) \rho_c(l')\right\}$$

$$\times G(L_c 10|L) G(L_c 10|L') (t^{-1})_{LL'}^{AA} [(1-X)^{-1}]_{LL'}^{AA} \Big\}, \quad (1)$$

where $G(LL'|L'')$ is a Gaunt's integral and $\rho_c(l)$ is a radial dipole integral between the radial part of $\phi_c(\mathbf{r})$ and a l th partial wave of photoelectrons $R_l(r)$ at site A. The phase shift of the l th partial wave at site A is represented by δ_l^A . The inverse matrix $(1-X)^{-1}$ includes an infinite order of the multiple scatterings inside the cluster we are considering. The clusters used in the present work include all surrounding atoms up to about 7 Å around an X-ray absorption atom.

RESULTS AND DISCUSSION

Multiple Scattering Analyses

The results of EXAFS analyses show that after the treatment Ni-C distance is 1.83 ± 0.05 Å with coordination number 2.4 ± 0.8 and Ni-Ni distance is 2.48 ± 0.05 Å with coordination number 0.8 ± 0.3 [8]. We draw upon the results of the EXAFS analyses when we calculate the models of the residual Ni species in CNFs after the treatment. In these calculations, we use a flat graphene sheet for simplicity and the Ni atoms are assumed to be neutral as supported by our DFT calculations [7].

First, we study the edge model shown in Fig.1 (a). Ni atoms can adsorb on the edge of a graphene sheet because of having dangling bonds at the site. In this model, Ni-C distance is 1.8 Å with coordination number 1. Figure 2 shows the calculated Ni K-edge XANES spectra of the models shown in Fig.1 compared with the experimental spectrum. The calculated spectrum of the edge model (a) has too small shoulders at 7 and 16 eV where the experimental data has specific peaks, and above 30 eV it decrease rapidly. We thus reject the edge model.

Next, we investigate two substitution models shown in Figs.1 (b) and (c), because Ni can be bound to carbon atoms at crack-like defect site of CNFs. In the model (b), a Ni atom is bound to the nearest neighbor three carbon atoms at crack-like defect site (monomer model). In the model (c), each of two Ni atoms binds to two carbon atoms, where Ni-Ni distance is 2.5 Å (dimer model). In both models, Ni-C distances are 1.8 Å: These values are consistent with the EXAFS results [8]. The calculated XANES spectra of the two models are shown in Figs.2 (b) and (c). Both of the two calculated spectra have two characteristic peaks in the absorption edge region (7 and 16 eV) where the experimental spectrum has the specific peaks. The dimer model, however, gives too small two characteristic peaks and rapid decrease above 30 eV

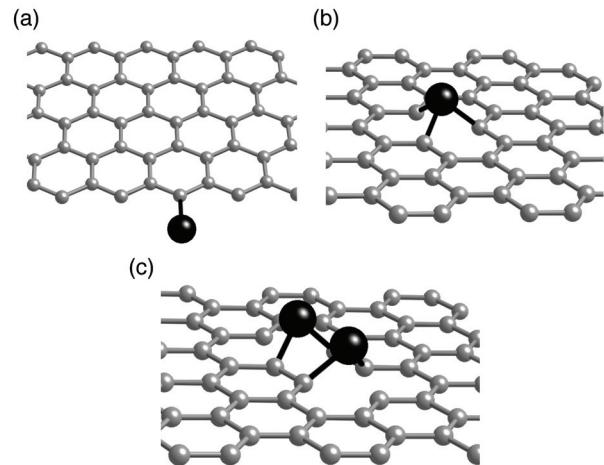


FIGURE 1. An edge model (a) and two substitution models (b) and (c), where black (gray) balls are Ni (C) atoms. In the model (a), a Ni atom bind to a carbon atom at the nearest edge site. In the model (b), a Ni atom replaces a carbon atom of a graphene sheet (monomer model), and in the model (c) two Ni atoms replace two carbon atoms (dimer model).

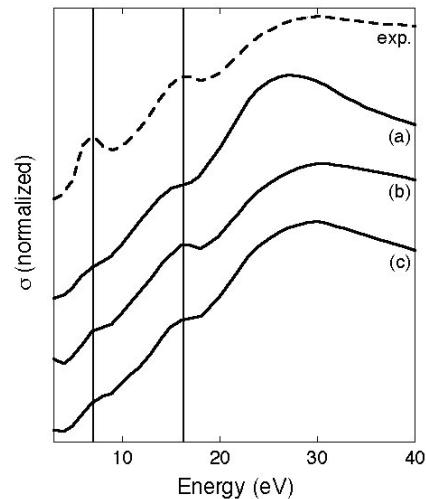


FIGURE 2. The calculated Ni K-edge XANES spectra of the three models shown in Fig.1 compared with the experimental data after the treatment (broken line). The energy is measures from the onset of the K-edge absorption.

compared with the monomer model. The first peak at 7 eV is located just at the beginning of the edge rise and should have a contribution from atomic bound state that cannot be fully taken into account by present method. We thus expect that the monomer model can be a good candidate for the residual Ni species in CNFs.

In addition, we postulate CNTs with 14 Å in diameter to check how the curvature of CNTs has some influence on the XANES spectra by use of the multiple scattering

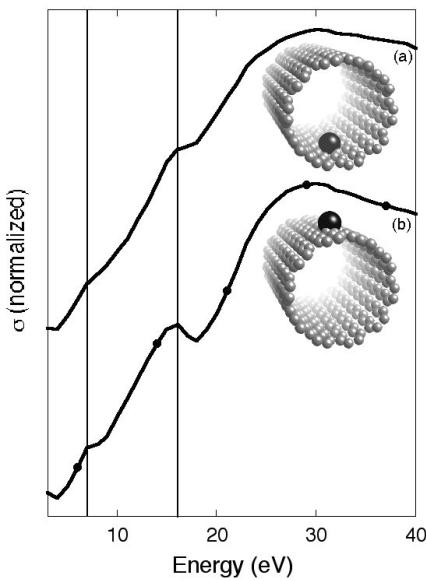


FIGURE 3. The calculated Ni K-edge XANES spectra of two CNT models. In the (a), a Ni atom is located in inside of the tube, whereas in the (b) outside.

calculations. Figure 3 shows the calculated Ni K-edge XANES spectra of two CNT models. In the model (a), a Ni atom is located on inside of the tube and in the model (b) outside. Comparing the two spectra, we can find small difference between them. The difference may be caused by the different distances to the second nearest carbon atoms. This result shows that the Ni adsorption on the inside or outside of the tube can be distinguished from the present XANES analyses.

Molecular Orbital Analyses

We apply the *ab initio* molecular orbital theory to obtain useful information on the electronic and the bonding character of the Ni impurities in CNFs.

We have optimized the structures of the two substitution models by using Gaussian 03 code [9]. We use a density functional theory (DFT) method employed the B3LYP type exchange-correlation potential and LanL2MB basis set. As the initial models for optimization, we use the flat structures as shown in Figs.1 (b) and (c). The results of the optimization show that the flat sheets are unstable and the Ni atoms of both models locate on the outside of the curved graphene sheet. In the monomer model, the Ni-C distances are 1.85 Å, while in the dimer model, the Ni-C distances are 1.89 Å and the Ni-Ni distance is 2.99 Å which is longer than EXAFS result 2.4 ± 0.8 Å.

We also study the bonding character of the Ni-C bonds

by use of natural population analyses [10]. The bond orders of the Ni-C bonds are 0.78 for the monomer model and 0.67 for the dimer model: The bond order of Ni-C in the monomer model is larger than that in the dimer model, which suggests that Ni dimers are rarely formed on CNFs in comparison with Ni monomers. These results are consistent with the results obtained from the XANES analyses.

CONCLUSION

We carry out Ni K-edge XANES analyses to determine the local electronic and geometric structures of the residual Ni species in CNF by applying multiple scattering calculations. After the treatment most of the Ni impurities are in Ni monomer species: A carbon atom in CNF is substituted by the Ni atom.

The XAFS analyses combined with the multiple scattering theory can provide unique information on the nanosystems.

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REFERENCES

1. K. Asakura, W. J. Chun, K. Tohji, Y. Sato and F. Watari, *Chem. Lett.* **34**, 382–383 (2005).
2. T. Fujikawa, T. Matsuura and H. Kuroda, *J. Phys. Soc. Jpn.* **52**, 905–912 (1983).
3. T. Fujikawa, *J. Phys. Soc. Jpn.* **62**, 2155–2165 (1993).
4. T. Fujikawa, K. Nakamura, S. Nagamatsu and J. J. Rehr, *J. Phys. Soc. Jpn.* **71**, 357–362 (2002).
5. N. M. Rodriguez, *J. Mater. Res.* **8**, 3233–3250 (1993).
6. Y. Sato, K. Shibata, H. Kataoka, S. Ogino, F. Bunshi, A. Yokoyama, K. Tamura, T. Akasaka, M. Uo, K. Motomiya, B. Jeyadevan, R. Hatakeyama, W. Fumio and K. Tohji, *Mol. BioSyst.* **1**, 142–145 (2005).
7. M. Ushiro, K. Asakura, K. Ohminami, S. Nagamatsu and T. Fujikawa, *e-J. Surf. Sci. Nanotech.* **3**, 427–432 (2005).
8. M. Ushiro, K. Uno, Y. Sato, K. Tohji, F. Watari, W. J. Chun, Y. Koike, K. Asakura and T. Fujikawa, *Phys. Rev. B* **73**, 144103-1–11 (2006).
9. Gaussian 03, J. A. Pople et al. (Gaussian, Inc., Wallingford CT, 2004).
10. NBO Version 3.1, E. D. Glendening, A. E. Reed, J. E. Carpenter and F. Weinhold.