

## NEXAFS analysis of a P-doped carbon alloy with two-dimensional anisotropy

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### Introduction

“Carbon alloys” prepared by hetero-atom doping attract much attention as Pt alternative catalysts, because B- and/or N-doped carbon electrodes and nanotubes were recently reported to have high catalytic property [1,2]. However, study of carbon alloys with other dopants is behind those prepared with typical B and N dopants. P is an interesting dopant, because this is one of the group V elements as well as N. Although some precedent works on P-doping have been reported [3, 4], experimental study of chemical bonding and structure at dopant sites is very limited. In this work, we attempted P doping in graphite and confirmed formation of a P-doped carbon alloy that had two-dimensional anisotropic structure using polarization dependence of NEXAFS spectroscopy.

### Experimental

Experiments were performed at the BL27A.  $\text{PCl}_3$  was used for P doping. Fragment ions of  $\text{PCl}_3$  were formed by a cold cathode ion gun and irradiated on a highly oriented pyrolytic graphite (HOPG) heated at 700 °C with an acceleration energy of 3 keV. After the ion doping, the HOPG was annealed at 800 °C by a YAG laser. The fluence of the total fragment ions was  $3.5 \times 10^{15}$  ions/cm<sup>2</sup>. P content was estimated to be 2.0 % from intensities of P 1s and C 1s photoelectron peaks. P K-edge NEXAFS spectra were measured by total electron yield. Polarization dependence of NEXAFS was obtained by measuring NEXAFS spectra at various incidence angles  $\theta$  that is defined by the angle between the electric field vector of the linearly polarized X-ray and the surface normal of the HOPG.

### Results and discussion

Figure 1 shows polarization dependence of P K-edge NEXAFS spectra of the sample measured at  $\theta = 20, 55,$  and  $90^\circ$ . The peak **a** at 2144 eV was enhanced at less grazing angle and the peak **b** at 2148 eV was enhanced at more grazing angle. This suggests that P sites had two-dimensional configuration in graphite matrix, and the peaks **a** and **b** are assigned to out-of-plane and in-plane transitions, respectively.

To interpret these peaks, we calculated electronic structure of a model cluster of  $\text{C}_{63}\text{PH}_{20}$  using discrete variational (DV)- $X\alpha$  method. The structure of the model cluster is shown in the inset of Fig.2. Partial density of state (PDOS) at the P site of the model cluster was calculated with minimal basis set and core-hole effect, and photoabsorption cross section (PACS) was obtained from the PDOS based on the electric dipole transition.

The PACS spectrum in Fig.2 shows out-of-plane and in-plane transition peaks appeared at 2148.3 and 2151.6

eV, respectively. This theoretical result qualitatively explains opposite polarization dependences between the peaks **a** and **b** in Fig.1. Therefore, we conclude that graphite-like structure was formed by this method and P sites had  $sp^2$  hybridized chemical bonding in the sample.

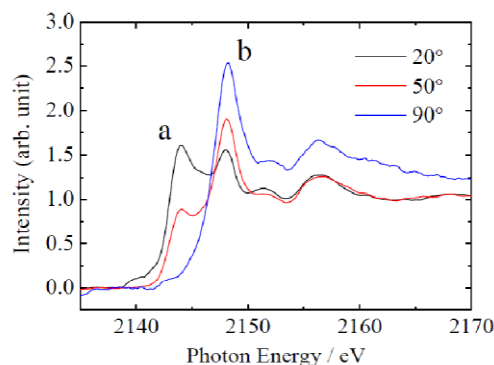


FIG.1. Polarization dependence of P K-edge NEXAFS spectra of the P-doped HOPG. Solid, broken, and dotted curves show spectra at  $\theta = 20, 55,$  and  $90^\circ$ , respectively.

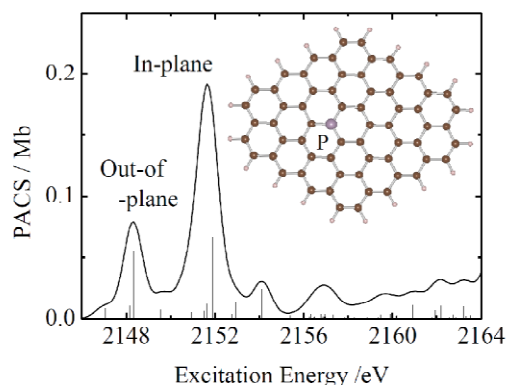


FIG.2. Theoretical PACS spectrum for P1s core excitation of the  $\text{C}_{63}\text{PH}_{20}$  model cluster calculated by the DV- $X\alpha$  method.

### References

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