Formation of 13-atom Cu cluster revealed by XANES

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Introduction

In order to control the properties of nanoparticles and clusters through their size, the mechanism of nucleation and growth needs to be clarified. In this work, we studied the local structure of Cu nanoparticles and clusterss by XANES spectra taken at reaction steps (dissolving with solvent, ligand exchange and reduction) and compared with the data for reference materials and multiple scattering (MS) calculation, taking the Cu system as a model system.

Methods and results

Cu nanoparticles and clusters were synthesized by a wet-chemical reduction method in organic solution[1]. The copper stock solution, denoted as Cu-(hfac)$_2$ was prepared by dissolving Cu(II) hexafluoroacetylacetonate [Cu(hfac)$_2$] with diethylene glycol diethyl ether (DEGDEE). The Cu-(hfac)$_2$ solution was reacted with oleylamine (OLA) as a ligand and finally mixed with a reductant, diphenylsilane (DPS). The Cu K-XANES spectra were sequentially taken at each step, *i.e.*, i) after the dissolving with a solvent, ii) after a ligand exchange reaction and iii) after adding DPS. We also measured reference compounds CuO (Cu^{2+}) and Cu metal (Cu^0) in both transmission and fluorescence modes. All XANES measurements at the Cu *K*-edge were performed at the NW2A station of AR, High Energy Accelerator Research Organization, Tsukuba.

The incidence angle of the x ray irradiation and the fluorescence take-off angle were both 45°. For the calculation of XANES with *n*-atom clusters, we used the *ab initio* multiple-scattering code FEFF8.20. For the MS calculations, model structures with 13-135 atoms assuming a fcc structure starting from a 13-atom NC with a cubo-octahedron symmetry with a constant Cu-Cu distance (2.52 Å) of the fcc structure.

Figure 1 summarizes the calculated XANES spectra for the model *n*-atom clusters (*n*=13-135) compared to the experimental data. The results for a fcc metal reproduces the characteristic near-edge features (B, C) around 9000 eV which appear only when *n* exceeds 43. As smaller clusters (*n* 19) have a single peak at this energy, the presence/absence of the first peak around 9000 eV can serve as a signature of a small cluster (*n* 19). Focusing on small *n*-atom clusters (*n* 19), the density functional theory (DFT) calculation is in progress aimed at the symmetry-dependent MS calculation.
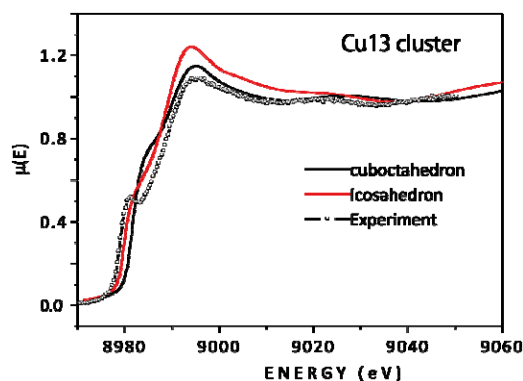

Fig.1 Symmetry dependence of XANES spectra

Our XANES calculation was based on imaginary cubo-octahedron pathway which smoothly connect to a fcc structure neglecting the size-dependent bond length. Although other polymorphs (hcp and icosahedron) are less likely in terms of total energy and packing fraction, conclusion on symmetry must be reserved [2]. A study on symmetry-dependent stability with the presence of ligand interaction will appear elsewhere. Consideration of geometrical stability with the presence of ligand molecules would correctly describe stability and chemical affinity of small magic clusters around Cu$_{13}$. Symmetry dependence of the MS calculation for DFT coordinates is illustrated in Figure 1.

References
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