Abstraction of Nano Copper in a Room Temperature Ionic Liquid

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Abstract. Speciation of copper in the abstraction of nano copper with a room temperature ionic liquid (RTIL) (1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6]) has been studied by X-ray absorption near edge structural (XANES) and extended X-ray absorption fine structural (EXAFS) spectroscopies in the present work. The least-square fits of the XANES spectra suggest that nano CuO (79%) and Cu(II) complex (Cu(II)-IL) (21%) are the main copper species in the RTIL. The fitted EXAFS spectra show that the Cu-O (1st shell) bond distance is 2.08 Å with a coordination number (CN) of 2.6. In the second shells of copper, the average bond distance of Cu-Cu is 2.99 Å with a CN of 5.1.

Keywords: Nano Copper, Ionic Liquid, XANES and EXAFS.
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INTRODUCTION

Nano size materials with extraordinary electronic, light-emitting and catalytic properties have been applied to many fields including catalysts, fuel cells, glues, paints, solar cells, intelligent drugs and optical systems [1]. Most nanoparticles that are currently in use have been made from transition metals, metal oxides (zinc dioxide and titanium dioxide), silicon and carbon (singlewalled carbon nanotubes and fullerenes) [2]. However, their unique physical characteristics raise concerns that tiny metals, ceramics, and organics could be uniquely toxic as well. Currently, information describing the relative health and environmental risk assessment of manufactured nanoparticles or nanomaterials is severely lacking. Concerns about nanoparticles' or nanomaterials' toxicity must be addressed while the field is still young.

How to treat these discharged nanoparticles effectively is another important issue. Once these very fine particles are emitted into the environment, they are difficult to be collected for further treatments. Currently, potential treatment methods are coagulation/flocculation, flotation, and microfiltration/ ultrafiltration [3]. However, the efficiency is, in fact, very limited.

Ionic liquids are composed entirely of ions and are similar to molten metallic ionic melts such as NaCl at 1073 K. Molten salts are generally thought to refer to a high-melting, high viscous and very corrosive medium. On the contrary, ionic liquids are already liquid at low temperatures and have relatively low viscosity [4]. Ionic liquids also exhibit special characteristics such as water immiscibility, moisture stability, miniscule volatility, thermal stability and non-flammability. Because of their unique chemical and physical properties, ionic liquids have received much attention in applications of synthesis, catalysis, electrochemistry and extractions [5]. By suppressing conventional solvation and solvolysis phenomena, ionic liquids provide capability of dissolving a wide range of inorganic molecules to very high concentrations [6]. Wei and coworkers employed an ionic liquid to abstract gold nanoparticles and nanorods from the aqueous phase [7]. However, speciation of nanosize species abstracted with ILs is not well understood. Thus, the main objective of this work was to study speciation of nano copper abstracted with a room temperature ionic liquid (RTIL) (1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6]) by X-ray absorption near edge structural (XANES) and extended X-ray absorption fine structural (EXAFS) spectroscopies.

EXPERIMENTAL

To synthesis of the organic cation (1-butyl-3-methylimidazolium chloride ($[C_4mim]^+$)), equal amounts (0.3 mol) of 1-chlorobutane (Riedel-deHaën) and 1-methylimidazole (Fluka) were mixed in a 250 mL round-bottom flask fitted with a reflux condenser at 353 K for 96 h till the formation of a golden viscous liquid. The ($[C_4mim]^+[Cl]^-$) liquid was washed three times with 30 mL of ethyl acetate (J.T. Baker) in a separation funnel. The lower liquid portion ($[C_4mim]^+[Cl]^-$) was then slowly added to a 200 mL potassium hexafluorophosphate (SHOWA) solution and then stirred at 298 K for 24 h. After washed with dichloromethane (Merck), the solvent was evaporated by vacuum at 343 K. Nano CuO (Kanto, dp=27.2-95.3 nm) (~3.3%) was added into the RTIL ($[C_4mim][PF_6]$) with shaking.

XANES and EXAFS spectra of copper were collected on the Wiggler beamline at the Taiwan Synchrotron Radiation Research Center (SRRC). A Si(111) double-crystal monochromator was used for providing highly monochromatized photon beams with energies of 1-9 keV. The electron storage ring was operated with energy of 1.3 GeV (current = 100-200 mA). Data were collected in the fluorescence mode. The raw absorption data in the region of 50 to 200 eV below the edge feature were fitted to a straight line by the least-square algorithms. The fitted pre-edge background curves were extrapolated throughout all data ranges and subtracted and normalized to minimize the effect of sample thickness. The near-edge structure in an absorption spectrum covers the range between the threshold and the point at which the EXAFS begins. The XANES spectra extend to an energy of 50 eV above the edge. The k^2-weighted and EXAFS spectra were Fourier transformed to R space over the range between 1.5 and 11.5 $Å^{-1}$. The Fourier transforms were not phase-shift corrected, and thus the peak positions were 0.3-0.5 Å less than the true bond distance. The EXAFS data were analyzed using the UWXAFS 3.0.

XANES spectroscopy can be combined with principal component analysis (PCA) and least-squares fitting (LSF) as a quantitatively analytical tool for speciation of dilute and/or amorphous multicomponents, which is not easily attainable with conventional methods. Semi-quantitative analyses of the XANES spectra were conducted by the least-square fitting of linear combinations of standard spectra to the spectrum of the sample. XANES spectra of copper model compounds such as nano CuO (Kanto), $Cu(CH_3COO)_2$ (Hanawa), and Cu(II) complex (Cu(II)-IL) were also measured on the Wiggler beamline.

RESULTS AND DISCUSSION

The Cu K-edge XANES spectra and their first derivatives of nano CuO abstracted in the RTIL are shown in Fig. 1. The 1st derivative feature of XANES spectra appeared at 8985 and 8992 eV indicated the existence of Cu(II) species. A shoulder at 8985-8988 eV and an intense band at 8994-9002 eV can be attributed to the 1s-to-4p transition.

The XANES spectra were also expressed mathematically in a LC XANES fit vectors, using the absorption data within the energy range of 8970-9040 eV. XANES spectra of copper model compounds such as nano CuO, $Cu(CH_3COO)_2$, and Cu(II) complex (Cu(II)-IL) were also measured on the SRRC Wiggler beamline. Relative contents of the copper species in the RTIL with an over 90% reliability in the fitting process. We found that abstraction of nano CuO in the RTIL for 2 min, nano CuO (79%) and Cu(II)-IL (21%) were the main copper species in the RTIL. It is clear that within 2 min of abstraction with the RTIL, about 21% of nano CuO were dissolved and formed complex with the RTIL.

Generally, EXAFS spectroscopy can provide the information on the atomic arrangement in terms of bond distance, coordinate number and kind of near neighbors, thermal and static disorder. An over 99 % reliability of the EXAFS data fitting for copper species was obtained. In all EXAFS data analyzed, the Debye-Waller factors (σ^2) were less than 0.01 $Å^2$. The structural parameters obtained from the best fit to the EXAFS data are shown in Table 1. In the 1st shell, copper species in the RTIL possessed a Cu-O bond distance of 2.08 Å with a coordinate number (CN) of 2.6. It should be noted that due to the axial distortion of the CuO_6 octahedron caused by the Jahn-Teller effect, the bond distances between the central copper ion and the equatorial (2.00 Å) and axial (2.14 Å) oxygens were not identical [8]. The bond distance of Cu-(O)-Cu in the 2nd shell was 2.99 Å with a CN of 5.1.

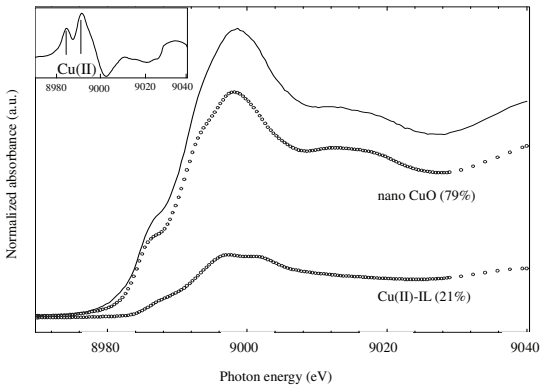

FIGURE 1. Normalized Cu K-edge XANES spectra of nano CuO abstracted in the RTIL ($[C_4mim][PF_6]$).

TABLE 1. Speciation parameters of copper abstracted in the RTIL ([C_4mim][PF_6]).

Shell	Bond Distance (Å)	Coordination Number	σ^{2a} (Å^2)
Cu-O	2.08	2.6	0.008
Cu-(O)-Cu	2.99	5.1	0.009

[a]σ^2: Debye-Waller factor.

CONCLUSIONS

The least-square fits of the XANES spectra indicate that nano CuO (79%) and Cu(II)-IL (21%) are the main copper species in the RTIL ([C4mim][PF6]). The existence of the Cu(II)-IL species in the RTIL suggests that dissolutions of nano CuO may occur during abstraction of nano CuO with the RTIL. The fitted EXAFS spectra show that the average Cu-O (1st shell) bond distance was 2.08 Å. In the second shells of copper, the average bond distance of Cu-(O)-Cu was 2.99 Å with a CN of 5.1.

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