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X-ray absorption fine structure spectroscopy studies of thiol-capped copper nanoparticles

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Abstract. Monodisperse Copper nanoparticles with controllable sizes of 0.6 and 1.8nm were synthesized via modifying Brust-Schiffrin two-phase method. This route involves a slow reduction of \([\text{TOA}]_2[\text{CuBr}_4]\) precursor in toluene, with particles sizes rationally controlled by the S/Cu ratio. Size-dependent inter-atomic distance contraction in the thiol-capped copper nanoparticles was investigated by Extended X-ray Absorption Fine Structure (EXAFS). The analysis revealed a shortened Cu-Cu inter-atomic distance, indicating strong surface interaction, in accord with the larger effect expected for ultrasmall particlals (<2nm).

1. Introduction

Synthesizing nanoparticles with desired sizes is important in exploring their either unusual or different properties from corresponding bulk materials [1]. Nanostructured copper particles have been found to possess fascinating properties in catalysis [2], optics [3-5] and sensors [6,7]. Thus, the synthesis of copper nanoparticles with controllable sizes and electronic properties is vital to both fundamental science and technical applications.

Although there are a number of approaches available to synthesize copper NP, few methods have been established to obtain stable and size controllable copper nanoparticles as they undergo rapid oxidation in air and aqueous media. In previous reports, copper nanoparticles have been synthesized with molecularly capped surface to keep them stable. Most of the strategies are performed by the manipulation of reaction temperature or concentration of precursor and reducing agent or other extreme condition for the synthesis of copper nanoparticles in two-phase liquid/liquid system or in a specific single-phase solvent in the presence of capping agents [8,9]. However, few reports provide even smaller (<2 nm) Cu NPs that behave more like a molecule. It is expectable that ultrasmall nanoparticles possess special characters such as strong surface interaction and lattice contraction [10].

This work describes an investigation of synthesizing thiol capped copper nanoparticles with controlled sizes. X-ray absorption fine structure (XAFS) was used to investigate the atomic structures. With the advantage of the sensitivity of the XAFS spectroscopy to the local structure around Cu atoms, combined with the theoretical calculations, we aim to reveal the local structure of the Cu atoms in ultrasmall nanoparticles (0.5-2 nm).

2. Experimental
The synthesis of DT-capped copper nanoparticles was achieved by the procedure modified Brust-Schiffrin two-phase method as illustrated schematically in figure 1 [11]. 

CuCl$_2$·2H$_2$O was dissolved in water in the presence of potassium bromide to convert Cu$^{2+}$ to CuBr$_4^{2-}$. This solution was then mixed with a solution of TOABr in toluene under vigorous stirring to induce a phase transfer of the CuBr$_4^{2-}$ from the aqueous phase to the organic phase. After being stirred for 45 min, the aqueous solution was removed. The copper toluene solution was stirred under argon for 30 min purge to eliminate all oxygen from the system. Then, different amount of decanethiol was added. Next, a solution of sodium borohydride in water was added dropwise. The solution became a deep cloudy orange, indicating the formation of copper nanoparticles. The solution was stirred under argon for 5 h before further analysis. The Cu k-edge XANES and EXAFS measurements were conducted at U7C stations of the National Synchrotron Radiation Laboratory, China. High Resolution Transmission Electron Microscopy (HRTEM) measurements were carried out using a JEOL 2010 system. The calculations were performed with the Feff 8.2 code [12].

3. Results and Discussion

The TEM images of the Cu nanoparticles with tailored sizes are shown in Figure 2(a)-(b), where the insets display their corresponding size distributions. Ultrasmall Cu nanoparticles of ~0.6 nm in size are obtained when S/Cu ratio is 5. By reducing the amount of dodecanethiol, the size of Cu nanoparticles increases to ~1.8 nm. As illustrated in Figure 1, before the addition of the reductant NaBH$_4$, the copper atom is in the state of [TOA]$^2^-$[CuBr$_4$] with the absence of Cu-S bond [13]. Upon the addition of NaBH$_4$, the complex was reduced slowly, due to the stronger steric hindrance. Thus, the initial naked, micelle-encapsulated NP distribution is narrow. Then the thiolate generated from the reduction of thiol diffuses through the TOA shell and forms the Cu-S bonds, and the ligand-protected copper NPs were formed. The increase of the concentration of thiol is expected to increase the probability of collision between thiolate and the initial NPs. With more Cu-S bonds formed, further growth of first formed Cu core inside the micelles would be impeded, as indicated in Figure 2.

![Figure 1. Schematic presentation of the Cu NPs formation process](image-url)

**Figure 2.** The TEM images (a)-(c) of copper nanoparticles with tailor sizes as 0.6 and 1.8 nm by adding dodecanethiol with varied S/Cu ratio (5 and 2.5) and corresponding size distributions. The scale bar is the same.

Figures 3(a) and (b) displays the Cu K-edge extended XAFS $k^3\chi(k)$ functions and their Fourier transform (FT) for as-prepared Cu NPs and Cu foil. We have also performed quantitative curve-fitting for the XAFS spectra, and the obtained structural parameters are summarized in Table 2. First of all,
the oscillatory functions of prepared Cu nanoparticles shown in Fig. 3(a) are significantly different with that of Cu foil. Owing to the reduced particle size, an overall attenuation and broadening is observed over the whole XAS spectra. It is mainly due to the decrease of the mean coordination number and the absence of higher order coordination shells as indicated in Table 2. The presence of the ligand on the surface may also contribute to the oscillation damping at high $k$-values. Fig. 3(b) presents two peaks at about 1.2 and 1.9 Å corresponding to the Cu-S shell and Cu-Cu shell. With high S/Cu ratio, the smaller Cu NP show stronger oscillation in Cu-S shell, in accordance with the increase of the Cu-S coordination numbers. The obvious shift of the second peak for Cu NP compared to bulk Cu is also probably resulting from the size effect of lattice contraction, as significantly shortened Cu-Cu distance ($R_{\text{Cu-Cu}}$) is observed in Table 2. The Cu-Cu Debye-Waller factor ($\sigma^2$) indicates that the system disorder increases for smaller particles, as expected due to the larger surface/volume ratio. Generally, the prepared nanoparticles process obvious lattice contraction effect and strong surface interaction.

![Figure 3](image-url)

**Figure 3.** (a) Experimental EXAFS $k^2\chi(k)$ functions of prepared Cu NPs and Cu foil. (b) Experimental Fourier transforms (FT) curves of prepared Cu NPs and Cu foil.

**Table 2.** Structure parameters around Cu atoms for prepared Cu NPs and Cu foil.

| Sample | Bond type | N  | $R(\text{Å})$ | $\sigma^2(10^{-3}\text{Å}^2)$ |
|--------|-----------|----|--------------|-----------------------------|
| Bulk   | Cu-Cu     | 12 | 2.56         | -                           |
| 1.8 nm | Cu-Cu     | 5.2±0.2 | 2.25±0.01     | 11.7±0.1                     |
|        | Cu-S      | 1.1±0.2 | 1.91±0.01     | 12.3±0.3                     |
| 0.6 nm | Cu-Cu     | 4.9±0.3 | 2.24±0.01     | 13.2±0.2                     |
|        | Cu-S      | 1.4±0.2 | 1.92±0.01     | 8.9±0.2                      |

The XANES spectra of the two Cu nanoparticles samples reveal similar features to the bulk one in general (Figure 4). Nevertheless, their main oscillations show obvious attenuation and broadening, especially for the white line (arising from $p\rightarrow d$ dipole transition). The intensity of white line is very strong for elements with unoccupied d orbital. Although the d band is nominally fully filled in Cu atoms, a small white line can still be detected in the XANES of bulk Cu due to s-p-d hybridization.
[14,15]. The size effect of small nanoparticles leads to an increase of d electron density. Meanwhile, in the Cu-SR system, the electronegativity of Cu- and SR- is different leading to an electrical potential, which induces the d-charge transfer from copper to sulfur atoms. Then the d-hole counts at the copper site of the nanoparticles would increase [16]. In despite of the strong surface interaction, there is still a significant decrease in the XANES spectra of the Cu K-edge. It is indicated a strong size effect in the samples, as reflected by the much shorter Cu-Cu distance.

4. Conclusions
Stable Cu NPs have been prepared with controllable size in the range of 0.6 and 1.8 nm by varying the S/Cu molar ratio in the two-phase system, and the XAS spectra (XANES and EXAFS regions) have been analyzed in detail. The thiol-capped Cu NPs show rather strong surface interaction. Furthermore, we have demonstrated that copper nanoparticles smaller than 2.0 nm present a much strong size-dependent inter-atomic distance contraction. These results reinforce importance of even smaller size effect on nanoparticles, which should not be neglected for research of nanometer science.

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