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Description	

***In-Situ* Quick XAFS Study on the Formation Mechanism of Cu Nanoparticles Synthesized in Aqueous Phase**

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ABSTRACT

The formation process of Cu nanoparticles (NPs) capped by poly(*N*-vinyl-2-pyrrolidone) (PVP) using a wet-chemical reduction method was observed with *in-situ* time-resolved X-ray adsorption fine structure (XAFS) method in combination with other analytical techniques. XAFS analysis directly indicated that the Cu(OH)₂ and Cu⁺ species were formed as intermediates, and their life-time were extended by adding PVP capping agent. The morphology analysis and indicator method also supported that both reticulated Cu(OH)₂ structure and Cu⁺ intermediate remained for a long time with an increase in PVP capping agent. Our results suggested that the PVP capping agent plays an important role to the reaction kinetic resulting from extending the life-time of intermediates such as Cu(OH)₂ and Cu⁺ species.

Keywords: *in-situ* XAFS, Cu nanoparticles, formation mechanism, role of capping agent, reaction kinetic

1 INTRODUCTION

Wet-chemical reduction method has been used extensively for the synthesis of metal nanoparticles (NPs) because it makes highly dispersed NPs with narrow size distribution by a simple procedure. Many researchers already reported that the preparation conditions like temperature, pH, concentration, kinds of precursor, capping agents, additive sources, solvent, etc. can change the morphologies and properties of synthesized NPs.^[1,2] There were many reports to reveal the mechanism during the NPs formation, however, it was still remained to investigate dynamic changing directly with time resolution because of using *ex-situ* analysis (e.g., sampling, quench...).^[3,4]

Recently, with the development of *in-situ* observation techniques, the mechanisms for the highly dispersed NPs formation were gradually clarified with time variation. Harada et al. investigated the kinetics of Rh, Pd and Ag NPs prepared by photoreduction method, and they found that the induction periods occurred during reduction except for the case of Pd.^[5,6] Very recently, we succeeded in the observation of the formation process of Cu NPs synthesized with chemical reduction method, and suggested the poly(*N*-vinyl-2-pyrrolidone) (PVP) capping agent acts as not only

protector from overgrowth and aggregation, but also as a control agent over the reaction kinetics of NP formation.^[7]

In this study, we discuss the relationships between the concentration of PVP and the reaction kinetics during the Cu NPs formation process in more detail using *in-situ* X-ray adsorption fine structure (XAFS) method in combination with UV-vis spectroscopy, indicator method, TEM measurement, and so on.

2 EXPERIMENT

The synthesis of Cu NPs with wet-chemical reduction method was performed according to the previous reports^[8] with some modifications. In this procedure, the reducing agent (NaBH₄/NaOH) is injected into the aqueous solution containing Cu(II) acetate (Cu(OAc)₂) and PVP under stirring in N₂ atmosphere. The molar ratio of the mixture was Cu(OAc)₂/PVP/NaBH₄/NaOH/H₂O = 1.0/*x*/1.0/1.0/3.7 (*x* = 0.0033, 0.033, and 0.165). By using this procedure, highly dispersed Cu NPs were obtained.^[7] A plastic cell (PMMA, 1 × 1 × 4.5 cm³) was used as a reactor.

The fractions for each Cu species during Cu NPs formation process were characterized by *in-situ* XAFS at the Cu-K edge (8.98 keV) with quick scanning in fluorescence mode (SPRING-8, BL01B1, proposal No. 2008B1328 and 2010A1598). The beam size was approximately 1 × 5 mm², and each scan was carried out for every 68 seconds with interval. To evaluate time profiles of the fraction for each Cu species, the time-resolved X-ray absorption near-edge structure (XANES) spectra were fitted by a linear combination of the XANES spectra reference (Cu(OAc)₂ aq, Cu(OH)₂, Cu₂O, and Cu metal).^[9-11]

Morphology was analyzed by transmission electron microscopy (TEM) using a Hitachi H-7100 operated at 100 kV. Liquid samples were extracted by pipet, dropped onto a carbon-coated copper grid, and dried in vacuo before operation with TEM.

Sodium bichoninic acid (BCA) was used as a color indicator method for detecting Cu⁺ species using the absorption peak at 562 nm. UV-vis absorption spectroscopy was carried out on a Perkin Elmer Lambda 35 UV-vis spectrometer in the range of 400-800 nm.

The zeta potential was measured with a Zetasizer Nano ZS ZEN 3600 (Malvern, UK) under alkaline conditions controlled by NaOH aqueous solution.

3 RESULTS AND DISCUSSIONS

The color of the solution immediately turned from light blue (absorption peak at ca. 750 nm) to an emerald green solution (ca. 650 nm) in the first step, then gradually changed to brownish-red (adsorption peak was extended to all wavelengths) for all samples. Moreover, the ratio of color change was also retarded for increasing PVP. These

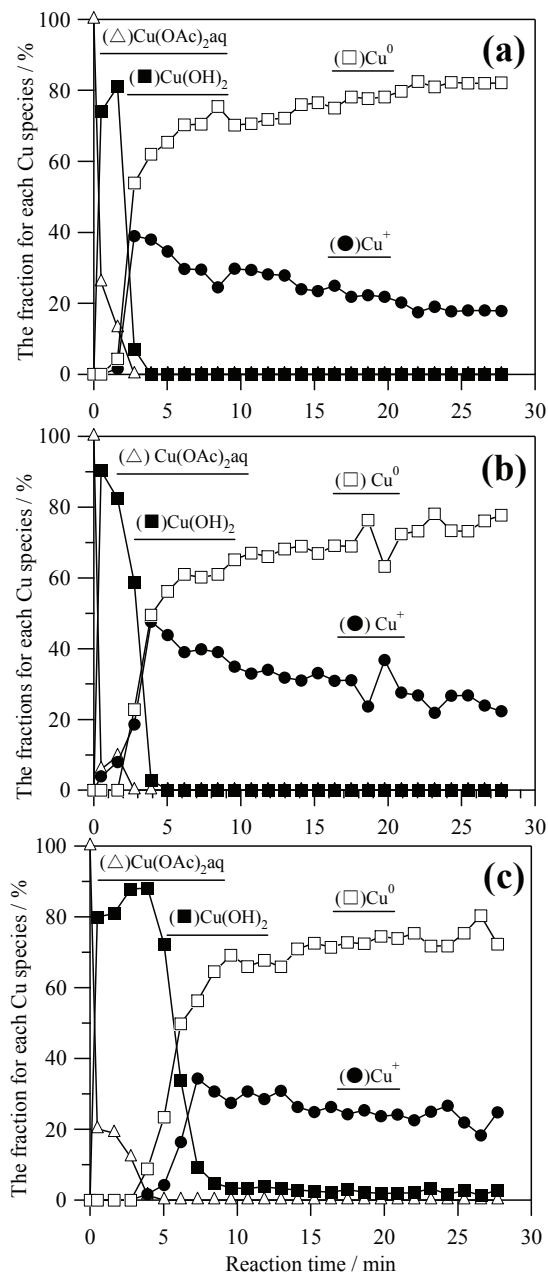


Figure 1. The time variation of the fraction for each Cu species at the condition of various amount of PVP, $x = 0.0033$ (a), 0.033 (b), and 0.165 (c), respectively.

changes implied that the PVP capping agent effected to the reaction kinetics.

Figure 1 shows the time variation of the fraction for each Cu species under conditions of various amounts of PVP, that calculated by using the time-resolved XANES spectra with a linear combination method. The transformations were as follows: the precursor of Cu(OAc)_2 drastically transformed to the Cu(OH)_2 in the first step, then Cu(OH)_2 gradually changed to Cu^0 through the Cu^+ species. All samples indicated the same pathway, however, the life-time of Cu(OH)_2 was clearly different. When small amounts of PVP was used ($x = 0.0033$), Cu(OH)_2 could only keep within ca. 4 min reaction. But when the case of more large amount of PVP ($x = 0.033$, and 0.165), the life-time of the Cu(OH)_2 became ca. 5 min and above 5 min, respectively. Additionally, the formation of Cu^+ species also became slower with following the life-time of Cu(OH)_2 . From the view point of the life-time of Cu^+ species behavior, it was indicated that the fraction of species existing with the peak during formation process under such strong reduction atmosphere. These results suggested the PVP capping agent was associated with slower reaction kinetics by elongating the life-time of the intermediates of Cu(OH)_2 and Cu^+ species.

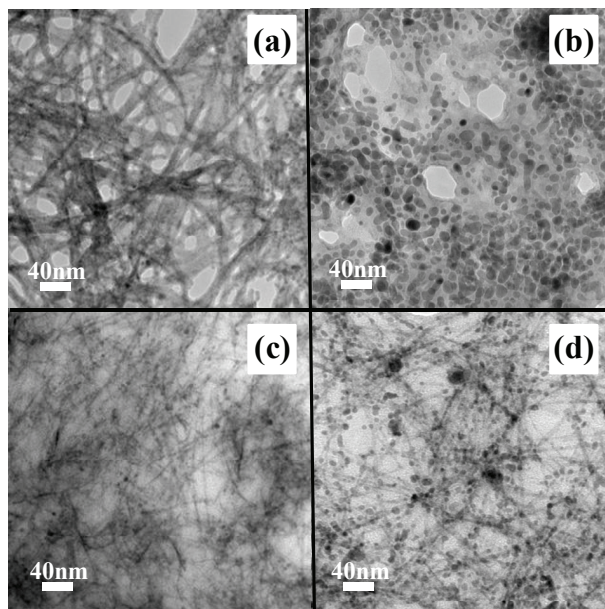


Figure 2. The TEM images of the solution after 2 min (left side) and 15 min (right side) reaction in the case of adding different amounts of PVP, $x = 0.0033$ (a, b), and 0.165 (c, d).

To compare the morphology change of Cu(OH)_2 , the TEM images are shown in Figure 2. After 2 min reaction, the reticulated structure was obtained in both conditions with size differences. Using small amount of PVP (Fig. 2(a)) caused larger reticulated structure, and a large amount caused smaller ones (Fig. 2(c)). In addition, the large

reticulated structures were consumed and disappeared (Fig. 2(b)), however the small reticulated structure remained after 15 min reaction (Fig. 2(d)). Generally, the morphology of $\text{Cu}(\text{OH})_2$ prepared with simple pH control is known as a nanostrand.^[12-14] In addition, the concentration of capping agent to metal precursor, relating to the average size of synthesized NPs was reported.^[15-18] Therefore, it is possible that the PVP capping agent acts as a stabilizer to the $\text{Cu}(\text{OH})_2$ intermediate, and the reaction kinetics become slower.

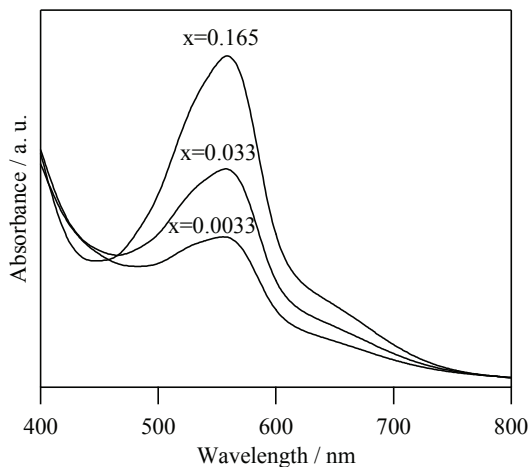


Figure 3. The UV-vis spectra after the addition of BCA in the case of varying the amount of PVP after 30 min reaction.

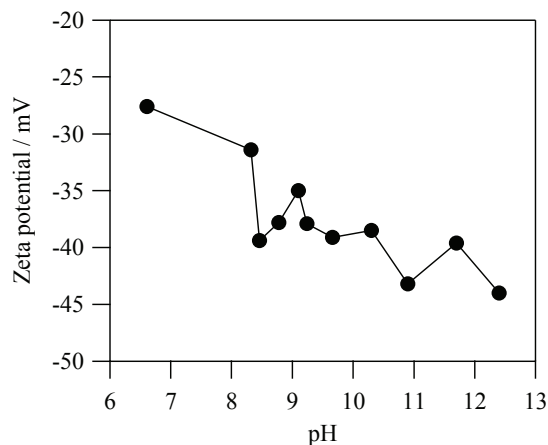
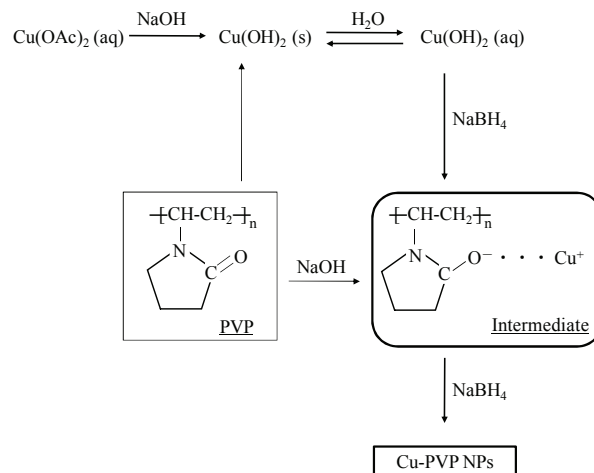


Figure 4. The zeta potential of PVP as a function of various pH conditions controlled with NaOH.

To verify the presence of the Cu^+ species despite a strong reducing atmosphere, an indicator method with BCA was performed. BCA is a well known reagent possessing the capacity to selectively-form an intense purple complex (adsorption peak at 562 nm) with Cu^+ ion.^[19-21] Figure 3

shows the UV-vis spectra after the addition of BCA to the reaction solution after 30 min reaction. Every sample shows a sharp absorbance peaks at 562 nm, this indicates the stable Cu^+ species exist during Cu NPs formation process despite the PVP amount. Furthermore, the intensity of the specific peak was progressively increased by the PVP amount. It suggests the PVP could make the life-time of Cu^+ species longer. To consider this assumption, the zeta potential of PVP as a function of pH variation was graphically-illustrated in Figure 4. Under alkaline condition similar to the reaction conditions, PVP with a negative charge was observed.



Scheme 1: Reaction pathway of Cu NPs formation

Scheme 1 illustrates the reaction pathway of Cu NPs formation using liquid chemical reaction. First, the precursor $\text{Cu}(\text{OAc})_2$ reacted with NaOH (containing with NaBH_4 reductant), and reticulated $\text{Cu}(\text{OH})_2$ was formed. This reaction occurs immediately (within a few minutes). Secondly, the slightly-soluble $\text{Cu}(\text{OH})_2$ gradually reduced to Cu^0 by strong reductant of NaBH_4 through stable Cu^+ intermediate states. Finally, after consumption of almost all of $\text{Cu}(\text{OH})_2$, the Cu^+ intermediates transformed to Cu^0 step by step. The PVP capping agent acts as a stabilizer to not only the synthesized Cu NPs but also intermediate such as $\text{Cu}(\text{OH})_2$ and Cu^+ species. This proposed pathway agrees with the above experimental observations.

4 CONCLUSIONS

In summary, we succeeded to reveal the Cu NPs formation process under various amounts of PVP capping agents using the *in-situ* time-resolved XAFS observation in combination with several analytical techniques. It was observed that the life-times of $\text{Cu}(\text{OH})_2$ and Cu^+ species were gradually extended with increasing the PVP capping agent. From investigation on the morphology changes of $\text{Cu}(\text{OH})_2$ against the amount of PVP and zeta potential under alkaline condition, it is suggested that PVP capping

agent can potentially coordinate with $\text{Cu}(\text{OH})_2$ and Cu^+ species. These results indicated that the PVP capping agent plays an important role not only to stabilize the synthesized NPs, but also to control the reaction kinetics by acting as the stabilizer of intermediates.

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