Formation of Rod Shape Secondary Aggregation of Copper Nanoparticles in Aqueous Solution of Sodium Borohydride with Stabilizing Polymer

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Abstract. Morphological variations of copper nanoparticles synthesized by the reduction of copper acetate with sodium borohydride in the presence of poly(N-vinyl-2-pyrrolidone) (PVP) have been investigated. The results indicate that the specific rod shape secondary aggregation of copper nanoparticles are formed in the case that the oxygen is dissolved in the reacting solutions. Furthermore, it is also demonstrated that the copper nanorods with the aspect ratio of 2 – 20 and the average short axis length of 5 nm are synthesized in the weak oxidizing ambience with a medium amount of PVP. The anomalous variations of copper nanoparticles are explained by the alignments of precursor copper ions and their reducing rates, which are modified by the density of resolved oxygen and the amount of PVP.

1. Introduction
In recent years, metallic nanoparticles have been attracting many concerns for their tremendous industrial capabilities. It is expected that their anomalous optic, electromagnetic, and catalytic features lead to the innovative novel technology such as sensitive nonlinear optical sensors, sophisticated electrical devices, superdense magnetic storage media, and high-activated sustainable catalysts. Thus, numerous studies have been made to develop the available methods to control these properties. What has to be noticed here is that the physical and chemical properties of nanoparticles are strongly dependent on their shape as well as their size. It has been reported that the surface plasmon resonance (SPR) peaks observed in gold and silver nanoparticles varies depending on the particles shape and show red-shift with increasing the aspect ratio [1]. It has also been reported that the coercivity with ferromagnetic cobalt is strongly enhanced in the shape of vertical arrays of nanowires [2]. Furthermore, the catalytic activity for the cross-coupling reaction of arylboronic acids and haloarenes strongly depends on the shape of nanoparticles [3]. From these results, it follows that the establishment of useful and controllable synthetic procedure of non-spherical nanomaterials like nanowires and nanorods is peculiarly important. Previously, these 1-D nanostructures have been prepared by several ways, such as photo-reduction using UV irradiation [4], template-directing using membrane [5] or mesoporous silica [6], and solution-phase hydrothermal- reduction using various polymer surfactants [1,7-9]. Among these approaches, the structure-directing with polymer surfactants is a desired candidate on account of its simplicity and flexibility. Cao et al. reported that CuO nanowires and

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nanorods could be obtained through a solution-phase hydrothermal method using polyethylene glycol (PEG), and the lengths of the 1-D nanostructures were controlled by choosing different molecular weights of PEG [8]. In the same way, Murphy et al. reported that Au nanorods and Ag nanowires were synthesized through the reduction of metal salts by ascorbic acid in the presence of cetyltrimethylammonium bromide (CTAB) [1]. Added to these reports, further noteworthy is the structure-directing by using poly(N-vinyl-2-pyrrolidone) (PVP), which is commonly used surfactant polymer to prevent particle aggregations in colloidal particle dispersion. For silver, there have been many previous studies in these methods. Deivaraj et al. exhibited that the morphology of silver nanoparticles formed in the solution of AgNO₃ and PVP varies drastically depending on the ratio of silver-to-PVP [4]. Moreover, Wiley et al. studied the variations of silver nanostructure in a PVP mediated polyol process, and demonstrated that the various shapes, such as nanocubes, triangular nanoplates, nanowires, and nanospheres were obtained, depending on the synthesizing conditions [9].

In contrast, these shape variations for copper nanoparticles in the presence of PVP have not been elucidated well, with all the great industrial expectations to one-dimensional copper nanomaterials.

On the basis of above considerations, we have focused on the shape variation of copper nanoparticles in the aqueous solution of copper acetate and PVP with sodium borohydride, a typical reducing agent. The morphological and crystallographic features of these nanostructures were investigated by the transmission electron microscopy (TEM), high resolution TEM (HRTEM), and selected-area electron diffraction (SAED). In addition, the electrostatic conditions of the particles were evaluated by the zeta-potential obtained by phase analysis light scattering (PALS) and Laser Doppler Velo-city measurement (LDV). According to these experimental results, we demonstrate that anomalous variations of the agglutinative features and shapes for copper particles depending on the density of dissolved oxygen in the reacting solvent and the amount of PVP. Thus, we discuss the mechanism of these variations from the change of the reducing rates for precursor and their distributions depending on the experimental conditions.

2. Experimental

In this study, a series of copper nanoparticles were synthesized by the following liquid-phase reduction method. Initially, 0.2 g of copper acetate was dissolved into 10 mL of distilled water for copper precursor. As a reducing agent, we prepared 0.1 mol dm⁻³ of aqueous solution of sodium borohydride. After the respective amounts of PVP (Mₚ ~10,000) for each experimental condition was dissolved into 100 mL of the reducing agent, 10 mL of the prepared copper precursor was dropped in it. The mixed solution was refluxed under stirring for 60 min at 20 °C. Eventually, black colloidal dispersion of copper nanoparticles with no precipitations was obtained.

TEM, HRTEM, and SAED were performed with JEOL JEM-3000 transmission electron microscopy operated at 300 kV. For these observations, the samples were prepared by a dropping of the synthesized colloidal solutions onto a carbon-coated copper grid. Zeta-potential of each particle was derived from the electrophoresis mobility measured by Malvern Zetasizer Nano series ZS90. In addition, pH for the obtained colloids was measured by using HORIBA D-21 pH meter.

| Table 1. Summary of the experimental conditions and chemical properties for the samples. |
|-----------------------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Sample No. | Experimental amount of PVP (g) | Conditions ambiance | Features of synthesized samples | Features of synthesized samples | Features of synthesized samples |
|-------------|----------------------------------|-------------------|---------------------------------|---------------------------------|---------------------------------|
| 1-1         | 0.5                              | N₂ saturated⁴     | -29.9                           | 12.2                            | spherical or ellipse             |
| 1-2         | 0.5                              | Air               | -36.5                           | 12.7                            | rods                            |
| 1-3         | 0.5                              | O₂ saturated⁴     | -34.2                           | 11.7                            | spherical (small)               |
| 2-1         | 0.1                              | Air               | -34.5                           | 12.6                            | cubic                           |
| 2-2         | 2.0                              | Air               | -36.1                           | 12.3                            | spherical (small)               |

⁴Note: For the ambiance in No.1-1 and No.1-3, the reacting solvents were refluxed in advance for 60 min under N₂ and O₂ gas bubbling, respectively.
3. Results and Discussion

Fig.1(a)-(c) shows the typical TEM images of the synthesized copper nanoparticles for the samples of No.1-1 to No.1-3, which demonstrate the variation of morphology depending on the ambiance. In the case that the reacting solvent is refluxed for 60 min under N₂ gas bubbling (Fig.1 (a)), the shape of the synthesized particles are infinite. Spherical and ellipse nanoparticles with sizes in the range of 5 – 30 nm are coexisting. The particles are weakly aggregated each other, whereas the agglomeration shows no specific 1-D shapes. Added to this, highly anisotropic nanorods with high aspect ratio (>2) are not observed. In contrast, there are many nanorods for the samples synthesized in air (Fig.1 (b)). The aspect ratios of these nanorods are 2 – 20, with 5 nm average short axis length. It must be noted that these nanorods line up in several straight lines. It leads to the long particle chains by many nanorods with several joints and breaches. Similar trends are also observed on the particles synthesized in the oxygen saturated solvent, as shown in Fig.1(c). In this case, however, relatively small particles with average size of 3 nm are arranged to zonal. It forms particle collecting bands, whose dimensions of 100 – 500 nm in length and 10 – 30 nm in width. What is important is that the particles in these bands are entirely discrete each other, and do not form rod-like structures as seen in Fig.1 (b). From the SAED patterns, it is confirmed that the particles synthesized in N₂ saturated ambiance (No.1-1) and in Air (No.1-2) consist of metallic copper. On the other hands, the particles synthesized in oxygen saturated ambiance consist of copper (I) oxide (Cu₂O).

From above experimental results, it is clear that the shapes of synthesized particles and their agglomerations are markedly influenced by the ambiances of the reacting solutions. As the ratio of oxygen in the ambiance increases, the size of generated particles becomes smaller. It seems that the variations in scale relates to that of reducing strength for the reductant. It is noteworthy to mention that the rate of reduction for precursors becomes slow as the ratio of oxygen increase. In the nitrogen saturated solution, the reduction occurs just immediately after the mixing of precursor and reducing agents, and the color of reacting solution turns into black within 1 min. In the oxygen saturated solution, on the other hands, it takes about 30 min for the color to be black, and the obtained particles are oxidized. With strong reducing conditions, the particles nucleate and grow quickly. It will lead to the generation of spherical and ellipse nanoparticles with sizes in the range 5 – 30 nm as shown in the sample of No.1-1. With weak reducing conditions, the nucleation occurs slowly and the growth is little, which results in the small and oxide particles with average size of 3 nm for sample No.1-3. The specific nanorods with high

Figure 1. TEM images of the synthesized copper nanoparticles in various ambiances, (a) N₂ saturated, (b) in air, (c) O₂ saturated.
aspect ratio are generated in the medium condition of above two extreme cases. It is considered that the nanorods are derived from the small nanoparticles that locate linearly in the solutions. We can confirm the growing process of nanorods in the other TEM image for the sample of No.1-2, as shown in Fig.2. In this image, we can find several nanorods locating in the zonal agglomerations of small nanoparticles. These nanorods most likely have grown from the aggregated small nanoparticles. Fig.3 shows the HRTEM image of one of these nanorods. We know from the image that the nanorods are made of single phase monocrystal. Thus, it is supposed that these nanorods have grown in accordance with the Ostwald ripening with re-dissolutions of smaller particles and the growths of larger particles, rather than the simple coalition of small particles.

Let us consider the role of PVP in the generation of nanorods. PVP is one of the most popular stabilizing polymers for the nanoparticles. As we mentioned in this introduction, there are several studies referring the shape variations of nanoparticles in the presence of PVP [3-4,9,11]. On the basis of the reports for colloidal silver nanoparticles with PVP by Shin et al. [10], metallic ions interact with PVP and gather closely through this interaction. In the case that the metallic ions are reduced to metal atoms by the reducing agents, these atoms aggregate in accordance with the assembly formation. Therefore, the shape of obtained particles markedly depends on the initial formation of the ion distributions fixed by the condensed state of PVP. From the results shown in Fig.1, it is supposed that the PVP takes linear formation, which leads to the rod shape aggregations of copper nanoparticles.

For the further understandings of the role of PVP, we have also examined the influence of amount of PVP on the variation of particles shapes. Fig.4 (a), (b) shows the TEM images of the synthesized particles with a small (0.1 g) and a large (2.0 g) amount of PVP in air. In the case that the amount of PVP is small (Fig.4 (a)), rectangular nanocubes with average size of 30 nm are formed. These nanocubes are discrete each other. The particles generated with the large amount of PVP (Fig.4 (b)), meanwhile, are all spherical and quite small with average size of 2 nm. These particles are mutually aggregated to form large agglomerations. It is possible to discuss the variations of particles shapes in different amount of PVP by the difference in the condensed state of PVP. For the samples with small amount of PVP, the copper ions gather densely in the several small regions with a little amount of PVP. The particles grow independently in each region. It will lead to the growth of cubic nanoparticles. For the samples with large amount of PVP, the copper ions gather in large regions tenuously with many PVP, which results in the generation of the large agglomerations of small nanoparticles.

We also measured the zeta potentials and pH for each sample, for the purpose of identifying the relation between the variation of particle aggregation and electrostatic conditions. They are summarized in the table 1. With all the drastic variation of aggregation features, the variation of the zeta potential and pH is a little, and there is no obvious tendency between them. Accordingly, it seems
that the shape variation of aggregations in this system does not have strong relation to its electrostatic conditions.

4. Conclusion
We have studied the morphological variations of copper nanomaterials synthesized by the reduction of copper acetate with sodium borohydride in the presence of PVP. The results indicate that the rod shape secondary aggregations of copper nanoparticles, which lead to the generation of copper nanorods, are formed in the weak oxidizing ambiance with a medium amount of PVP. It implies that the PVP can act as a template to generate copper nanorods as well as a stabilizing surfactant. It is concluded that the shape variations of copper nanomaterials are determined by the alignments of precursor copper ions and their reduction rate depending on the density of dissolved oxygen and the amount of PVP.

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