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Effect of $Na_4O_7P_2$ on Cu powder preparation from Cu_2O–water slurry system

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Abstract

A unique approach is presented for preparing highly dispersed ultrafine copper particles from cuprous oxide slurry using a wet chemical reaction with hydrazine (N_2H_4) as a reductant along with an appropriate addition of sodium pyrophosphate ($Na_4O_7P_2$) as a surfactant. It was found that very thin oxidized surfaces on the copper particles are formed during the reaction in the solution and subsequently sodium pyrophosphate plays an important role in the zeta potential of the particles, affecting their dispersion and growth significantly. The copper particles at low zeta potential easily aggregate and grow to bigger ones, whereas they at high zeta potential keep away each other and grew individually to ultrafine size. Additionally, a model for the copper particles growth in accordance with dispersion is proposed.
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1. Introduction

Uniform colloids have fascinated scientists for a long time. Generally, the particle growing model reported by Lamer [1,2] has been widely employed to generate monodispersed particle system, in which two requirements are considered [3,4]: first, a complete separation of nucleation and growth steps for the formation of particles; secondly, an avoidance of their aggregation during the nucleation and growth. The former would be fulfilled if a short burst nucleation is rapidly induced while the latter has been often achieved by either adding suitable protective organic agents or controlling the zeta potential.

Considerable attention has been paid to Cu powder in the past two decades due to their excellent electrical conduction properties and potential application in many fields [5–7]. A number of methods have been developed for the preparation of Cu powder. Among them, the chemical reduction of copper salts with hydrazine or hydrogen in an aqueous system has been well known [8–11]. However, this method characterized by a quick reaction rate suffers from agglomeration and chaotic

growth of copper particles. Later, copper oxide slurries in liquid polyols have been used to improve the uniformity and dispersion of copper particles [11–14].

The stability of particle dispersions in liquid has recently gained increases importance in powder preparation, and it has often been analyzed from an interaction energy standpoint between particles, known as the DLVO theory [15]. However, it is hardly found any reports to deal with how electrolytes in solution affect the mechanism of growth in association with dispersion of, especially, metal particles.

In this study, monodispersed ultrafine copper metal powder was prepared from the heterogeneous system of cuprous oxide (Cu_2O)–water slurry by chemical reduction with hydrazine as a reducing agent. The investigation also focused on knowing the electro-kinetic role of an inorganic electrolyte, sodium pyrophosphate ($Na_4O_7P_2$), in the size growth as well as dispersion of the particles.

2. Experimental procedure

All chemicals used in this study were in analytical grade. Cuprous oxide (Cu_2O), polyvinyl pyrrolidone (PVP k-30) and sodium pyrophosphate decahydrate ($Na_4O_7P_2·10H_2O$) were

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purchased from Junsei Chemical Co., Japan. Palladium chloride ($PdCl_2$) was from Kojima Chemical Reagents Inc., Japan and hydrazine monohydrate ($N_2H_4 \cdot H_2O$ 80%) from DC Chemical Co., Korea.

In a typical procedure, 5 ml of 0.614 g/L $PdCl_2$ solution was dissolved in 300 ml distilled water. Subsequently, 3 g PVP was added to the above solution and mixed under a magnetic bar stirring condition. Stable palladium seeds were formed by adding 1 ml hydrazine into the solution at 60 °C. This step can be understood as an attempt for achieving a short burst nucleation.

Separately prepared 3 g Cu_2O and $Na_4O_7P_2$ in the 0 to 8000 mg/L range were added into the above suspension and mixed in several minutes and then a hydrazine solution with N_2H_4/Cu_2O of 7 was slowly introduced drop by drop. Deriving from the $PdCl_2$ content as mentioned, the Cu^{2+}/Pd^{2+} weight ratio calculated is approximately equal to 1.5×10^3. The variation of bath pH was recorded with a pH meter (Orion 720A$^+$, THERMO Electron Corp.). The suspension was kept under agitation in atmospheric ambient air until the reaction completed. At the completion of each reaction, the precipitated solid particles were separated and subsequently washed with distilled water and ethanol several times. Finally, the powder were dried at 40 °C in nitrogen gas and kept in a desiccator to minimize oxidation.

The products were characterized by X-ray diffraction (XRD, RTP 300PC, Rigaku, Japan) in reflection mode (Cu$K\alpha$ radiation), scanning electron microscopy (SEM, JSM-6400, JEOL, Japan), and X-ray photoelectron spectroscopy (XPS, JEOL JPS-9010, Japan). Particle size distributions of the resulting Cu powders were measured by counting 100 particles in three different SEM pictures taken from each powder. Measurements of zeta potential were performed using a zeta-potential analyzer (ELS-8000, Otsuka, Japan). The produced copper powders were dissolved by nitric acid (HNO_3 60%) and its purity was determined by atomic absorbance spectroscopy (A.A.S., Varian Techtron A.A-1475, USA).

3. Results and discussion

3.1. Preparation of Cu powder

A reaction in metal oxide slurries-metal powders conversion system proceeds via dissolution and crystallization processes rather than solid phase transformation [11–13]. Therefore, copper particles are likely synthesized from Cu_2O through chemical reduction in aqueous systems as the following plausible scheme:

(i) Formation of Pd seeds

$$N_2H_4 + 4OH^- \rightarrow N_2 + 4H_2O + 4e^-, \tag{1}$$

$$Pd^{2+} + 2e^- \rightarrow Pd. \tag{2}$$
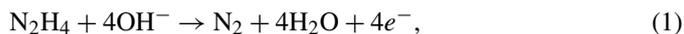
(ii) Progressive dissolution of Cu_2O through the complex form

$$Cu_2O + 4N_2H_4 + H_2O \rightarrow 2[Cu(N_2H_4)_2]^+ + 2OH^-. \tag{3}$$
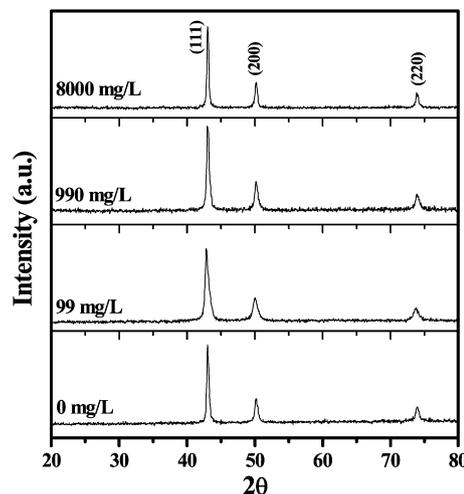
Fig. 1. XRD patterns of copper powders prepared at different concentrations of $Na_4O_7P_2$.

(iii) Reduction in solution and subsequent growth of copper on Pd nuclei

$$[Cu(N_2H_4)_2]^+ + e^- \rightarrow Cu^0 + 2N_2H_4. \tag{4}$$
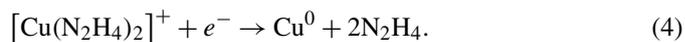
The reactions in Eqs. (1) and (2) are strongly promoted in basic media [16] meanwhile the others in Eqs. (3) and (4) are in accordance with that reported elsewhere [17].

The seeds of metallic palladium formed in (i) will act as nuclei for the subsequent growth of the Cu particles. The copper metal contributed to the particle growth on Pd nuclei is slowly generated by the progressive dissolution of Cu_2O in (ii) and a subsequent reduction process in (iii).

Fig. 1 includes XRD patterns of the powder samples obtained at 0, 99, 990, and 8000 mg/L $Na_4O_7P_2$. They give rise to the well-defined copper crystalline peaks only, but no phosphate and oxide compound forms in the particles are found. Therefore, according to the XRD data, it can be said that the Cu_2O–Cu powder conversion was clearly completed by chemical reduction.

3.2. Formation of oxide layers

In order to analyze any phosphates or oxides possibly formed during the powder preparation processes, X-ray photoelectron spectroscopy analyses were done.

Fig. 2 shows XPS patterns of the Cu powder prepared with and without the addition of $Na_4O_7P_2$. Essentially, no differences between them are found. The peaks at 77.2, 932.50, and 952.1 eV corresponding to the binding energies of Cu $3p_{1/2}$, Cu $2p_{3/2}$, and Cu $2p_{1/2}$, respectively, are in good agreement with the data observed for Cu_2O. Especially, the spectrum of 2p band as shown in the inserted figures match completely with that of Cu_2O reported by Wang et al. [18]. The peak at 530.3 eV indicates O^{2-} in Cu_2O, while the peak at 122.2 eV corresponds to the binding energy of Cu 3s referring to Cu metal. Moreover, the peak at 286.1 eV corresponding to the binding energy of C 1s is referred to the absorption of residual PVP on the surface of Cu particles [19,20]. The groups of peaks denoted with