

Effect of Reaction Driving Force on Copper Nanoparticle Preparation by Aqueous Solution Reduction Method

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Abstract

Copper nanoparticle was prepared by aqueous solution reduction method. Cu^{2+} was reduced to copper particle by using different types of reductant namely ascorbic acid ($\text{C}_6\text{H}_8\text{O}_6$), phosphinic acid (H_3PO_2), titanium sulfate ($\text{Ti}_2(\text{SO}_4)_3$) and sodium borohydride (NaBH_4). The effect of reaction driving force on the average size of the copper particle was investigated. An inversely proportional relationship between the reaction driving force and the average size of the copper particle was found, wherein the average size of the copper particle decreases as the reaction driving force increases.

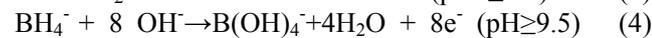
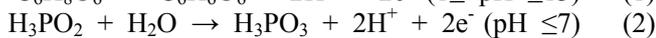
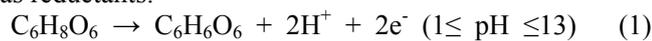
Keywords: Copper nanoparticle; Aqueous solution reduction method; Reaction driving force

Introduction

In recent years, the preparation of copper nanoparticles has received increasing attention from many researchers since copper nanoparticles are viewed as possible replacements for Ag and Au particles in some potential applications such as catalyst and conductive paste [1-3]. In previous research, much work has been done to explore the optimum conditions of copper nanoparticle preparation. However, the reaction mechanism has been seldom reported, which can help elucidate the reduction process. Therefore, the effect of different reductants on copper nanoparticle preparation was investigated to explore the reaction mechanism. $\text{C}_6\text{H}_8\text{O}_6$, H_3PO_2 , $\text{Ti}_2(\text{SO}_4)_3$ and NaBH_4 were used as the reductants, respectively.

Principle of experiment

The reduction of Cu^{2+} to Cu atom is the result of redox reaction, in which electrons are transferred from the reductant to Cu^{2+} . To discuss the reaction mechanism, reaction driving force (ΔE) was introduced in this paper. During the redox reaction process two half-cell reactions were taken place. One is the reduction of Cu^{2+} to Cu atom, and the other is the oxidation of reductant. The oxidation half-cell reaction equations are listed as follows when $\text{C}_6\text{H}_8\text{O}_6$, H_3PO_2 , $\text{Ti}_2(\text{SO}_4)_3$ and NaBH_4 are adopted as reductants:



Each one has a potential. Reaction driving force is the difference of the two half-cell reactions potential.

$$\Delta E = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Red}} \quad (5)$$

(In the equation, $E_{\text{Cu}^{2+}/\text{Cu}}$ represents the reduction potential of Cu^{2+} to Cu atom, and E_{Red} represents the oxidation potential of reductant.)

The value of ΔE determines the value of the reaction equilibrium constant (Ke), according to the following well-known equation:

$$\ln Ke = nF \Delta E / RT \quad (6)$$

where F, R, and T have the common meanings.

The reduction reaction is thermodynamically possible only if ΔE is positive, implying that the potential of a reductant must have a more negative value than that of Cu^{2+} . This difference should be larger than 0.3~0.4 V, otherwise, the reaction can not proceed, or will proceed too slowly to be of any practical significance. Furthermore, the larger the values of ΔE , the easier can the reaction take place.

According to Nernst equation,

$$E_{\text{Cu}^{2+}/\text{Cu}} = 0.337 + 0.0295 \lg [\text{Cu}^{2+}] \quad (7)$$

During the experiments, the potential – pH diagrams of the reductants were recorded. E_{Red} can be calculated by simulating the potential – pH equations. After then, the reaction driving force was calculated. This helped determine the relationship between the reaction driving force and the average size of the copper particle.

Experimental details

All reagents used in the experiment were guaranteed reagents from Nacalai Tesque (Kyoto). The flow chart of the experiment process is shown in Fig. 1. A 50 mL 0.2M CuSO_4 solution and a 50 mL 0.4M reductant solution were prepared before the reaction was induced. Ar gas was bubbled into the two solutions for 30 minutes, and these solutions' pH value was adjusted to the same value by H_2SO_4 or NaOH solution, respectively. 0.75mMPVP (polyvinylpyrrolidone) was added into the CuSO_4 solution as dispersant. Then this solution was mixed with the reductant in a beaker under a temperature of 333K, with the mixture stirred continuously with a magnetic rod. The color of the mixture changed from blue to brown after the brown precipitate appeared. When the reaction was completed, a small amount of slurry was taken out to measure its size distribution using an electrophoretic light scattering spectrophotometer (model: ELS-8000NS, made by Otsuka Electronics, Japan). The precipitate was separated from the turbid liquid by centrifugation and subsequently washed several times with distilled water and alcohol. It was then dried in a vacuum stove at room

temperature for one or two days.

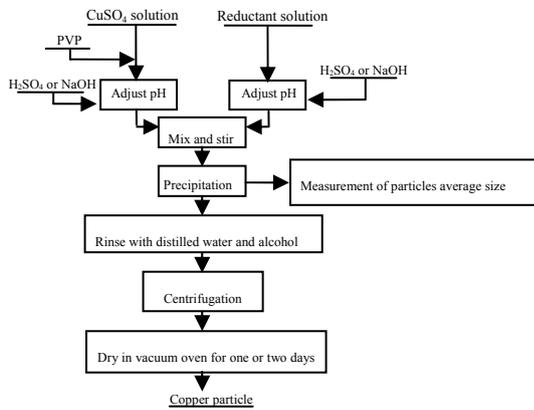


Fig. 1 Flow chart of the experiment process

In another experiment, the potential – pH diagrams of the reductants were measured. The experiment apparatus is shown in Fig. 2. Pt wire, Pt coil and Ag/AgCl sat. KCl electrodes were used as the working, counter, and reference electrodes, respectively. A 0.4M reductant solution was kept bubbling by Ar gas and stirring with a magnetic rod. The temperature of the water bath was set at 333K. The potential – pH diagrams of the reductants were recorded by a computer.

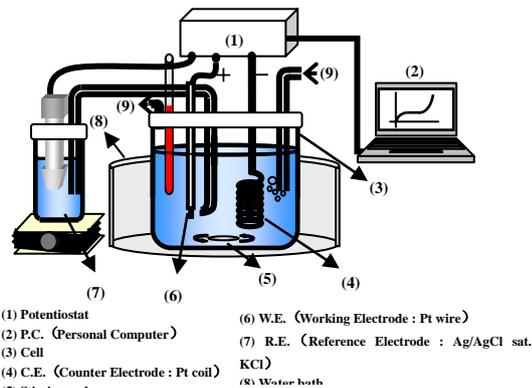


Fig. 2 The apparatus for potentiodynamic analysis

Result and discussion

The redox potential – pH diagrams of Cu and the reductants are shown in Fig. 3, in which the Cu diagram refers to the theory data [4]. The Cu diagram is described in red line in the figure.

The diagrams of the reductants can be similarly expressed as the following equations:

$$E(\text{C}_6\text{H}_8\text{O}_6) = 0.46 - 0.07 \text{ pH [V]} \quad (1 \leq \text{pH} \leq 13) \quad (8)$$

$$E(\text{H}_3\text{PO}_2) = 0.19 - 0.065 \text{ pH [V]} \quad (\text{pH} \leq 7) \quad (9)$$

$$E(\text{Ti}^{3+}) = -0.20 - 0.088 \text{ pH [V]} \quad (\text{pH} \leq 1.7) \quad (10)$$

$$E(\text{BH}_4^-) = -0.413 - 0.0591 \text{ pH [V]} \quad (\text{pH} \geq 9.5) \quad (11)$$

On the other hand, when the solution pH is less than 2, $E(\text{Cu}^{2+}/\text{Cu}) = 0.31 \text{ [V]}$ (12)

When the solution pH is greater than 2, the potential of Cu half reaction is as follows:

$$E(\text{Cu}_2\text{O}/\text{Cu}) = 0.45 - 0.066 \text{ pH} \quad (13)$$

The reaction driving force can be calculated as follows according to Equations (5) and (8) ~ (13).

$$\text{C}_6\text{H}_8\text{O}_6: \Delta E = -0.01 + 0.004 \text{ pH [V]} \quad (2 \leq \text{pH} \leq 13) \quad (14)$$

$$\text{H}_3\text{PO}_2: \Delta E = 0.26 - 0.001 \text{ pH [V]} \quad (\text{pH} \leq 7) \quad (15)$$

$$\text{Ti}_2(\text{SO}_4)_3: \Delta E = 0.51 + 0.088 \text{ pH [V]} \quad (\text{pH} \leq 1.7) \quad (16)$$

$$\text{NaBH}_4: \Delta E = 0.863 - 0.0069 \text{ pH [V]} \quad (\text{pH} \geq 9.5) \quad (17)$$

The maximum reaction driving force can be calculated according to Equations (14) ~ (17). The maximum reaction driving force of $\text{C}_6\text{H}_8\text{O}_6$ is 42 mV

when the pH is 13; that of H_3PO_2 is 258mV when the pH is 2; that of $\text{Ti}_2(\text{SO}_4)_3$ is 660 mV when the pH is 1.7; and that of NaBH_4 is 797 mV when the pH is 9.5. Therefore, the sequence of maximum reaction driving force is: $\text{NaBH}_4 > \text{Ti}_2(\text{SO}_4)_3 > \text{H}_3\text{PO}_2 > \text{C}_6\text{H}_8\text{O}_6$.

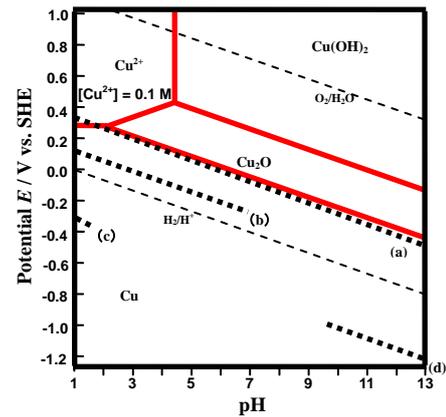


Fig. 3 Redox potential - pH diagrams for Cu - H₂O system and reductants at 333K (a) 0.4 M C₆H₈O₆ (b) 0.4 M H₃PO₂ (c) 0.4 M Ti₂(SO₄)₃ (d) 0.4 M NaBH₄

The relationship between the reaction driving force and the average size of the copper particles prepared in the experiments is shown in Fig. 4. The average size of the copper particles decreases as the reaction driving force increases. According to the classical theory of nucleation, the formation of copper particles usually undergoes three periods: pre-nucleation, nucleation and growth of the crystal nucleus. The reaction driving force represents the nucleation capability of the reductants, and it can influence the nucleation period. For the reaction with strong driving force, a large amount of nuclei was formed at the beginning of the nucleation period. Because the majority of Cu^{2+} is consumed to form the nucleus, the particles encounter difficulty as they grow and undergo aggregation. Thus, copper particles with very small size can be obtained.

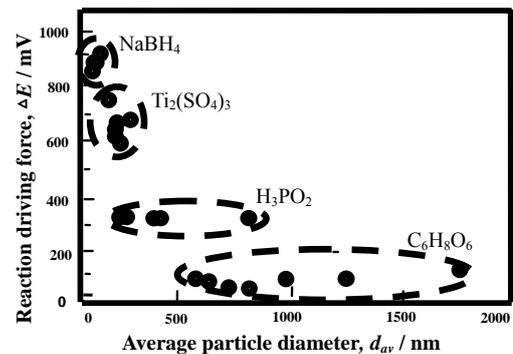


Fig. 4 Relation of reaction driving force and average particle diameter

Conclusions

The reaction driving force can influence the average size of copper particles. The stronger the reaction driving force, the smaller the average size of the copper particles that can be prepared.

References

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