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One-pot synthesis of silica-coated copper nanoparticles with high chemical and thermal stability

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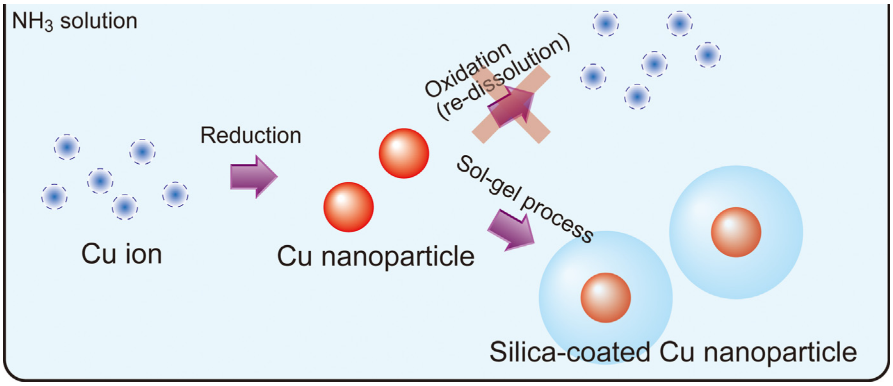
GRAPHICAL ABSTRACT



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ABSTRACT

With the recent development of nanotechnology, enhancement of the stability of nanomaterials is becoming ever more important for their practical applications. We studied the silica-coating of Cu nanoparticles and the enhanced stability of silica-coated Cu nanoparticles to oxidation. The metallic nanoparticles are easily oxidized and agglomerated compared with the bulk metals because the nanoparticles possess large specific surfaces. The Cu nanoparticle is one of the most difficult nanoparticles to be handled due to its absence of the oxidation stability. In the synthesis of silica-coated Cu nanoparticles via a sol–gel process using tetraethyl orthosilicate, the addition of NH_3 as a catalyst of sol–gel reaction yielded homogeneous silica-coating. However, a large amount of Cu nanoparticles is instantly dissolved by forming complex ions in a NH_3 solution during and before the silica-coating process. This is the difficulty in the silica-coating of Cu nanoparticles. In the present work, the dissolution behavior of Cu nanoparticles was electrochemically examined. This electrochemistry-based optimization of reducing power of a reaction bath enabled us to synthesize the silica-coated Cu nanoparticle via a consecutive liquid-phase reaction which requires only basic equipment and involves no separate centrifuging or extraction step. Cu nanoparticles coated by silica shells had the remarkable stability even in the presence of a strong oxidizing agent. Furthermore, we demonstrated that the highly stable Cu nanoparticles can be applied to a red pigment using a unique red color of Cu nanoparticles because of its surface plasmon resonance.

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1. Introduction

Noble metal nanoparticles show various characteristic properties, such as high catalytic activities, surface plasmon resonance, good electrical and thermal conductivities and low-temperature sintering [1–8]. These unique properties have led to the use of such materials in wide applications, for example, optical sensors [1–3], biosensors [4], electronic materials [5,6], or colorants [7]. However, as nanoparticles possess large active surface areas, they can agglomerate and oxidize more easily than their respective bulk materials [9,10]. The difficulty of handling nanoparticles in ambient atmosphere and at room temperature is a barrier to applications of metal nanoparticle systems. To overcome this problem, nanoparticles are often used in composite structures, for example as "supported" structures [11,12], "endohedral" structures [13,14], or "core–shell" structures [15–20]. Moreover, the synthesis technique of "yolk–shell" structures [21,22] is also recently developed. Among those structures, the core–shell structure has been widely investigated because it provides high stability and the materials can be easily dispersed in solution. Silica, as a coating layer, is remarkably chemically and thermally stable, and silica-coatings maintain the unique color and optical properties of the metal core because of silica's high optical transparency. In the electronic application, the silica-coating certainly has a weakness, because the silica shell shows strong electric insulation and prevent the agglomeration of metallic nanoparticles. However, from another viewpoint, the silica shell can give the insulation property to the metallic material with keeping the thermal conductivity of metal by improving the oxidation resistance. This type of material, for example, may have a potential for use as a filler of a molding compound for semiconductor packaging that needs both electrical insulation and high thermal conductivity. Moreover, silica can be fabricated by the sol–gel procedure which is a relatively simple chemical procedure [23]. Mine et al. successfully synthesized Au@SiO_2 nanoparticles using tetraethylorthosilicate (TEOS) and NH_3 solutions, with the latter acting as a catalyst for the sol–gel process [18]. Kobayashi et al. produced Ag@SiO_2 nanoparticles with various SiO_2 shell thicknesses by a simple sol–gel process [19]. The fabrication of Ag nanowires with a silica-coating by using a polyol method and the TEOS-based sol–gel process has also been reported [24]. In a similar fashion, uniform silica shells have been successfully fabricated on noble metal nanostructures in a solution using NH_3 as a catalyst for the TEOS-based sol–gel process. This silica-coating method is applicable for Ag which is not as stable as Au, because the sol–gel process proceeds in a solution at room temperature. However, the silica-coating of base metals is much more difficult because of the instability of such metal particles.

In the present work, we synthesized Cu nanoparticles in NH_3 solution by an electroless deposition method [25,26], and formed a silica shell layer for Cu nanoparticles by a sol–gel method with TEOS. Because Cu nanoparticles are much less stable than Au and Ag, it is highly required to prevent the Cu nanoparticles from the oxidation or redissolution during the silica-coating process. If we can understand the oxidation and dissolution mechanism of Cu nanoparticles in the NH_3 solution during the silica-coating process, the appropriate reaction bath condition can be determined to obtain the uniform core–shell structure. Thus, we investigated and clarified the oxidation and dissolution mechanism of the Cu nanoparticles from the electrochemical viewpoint, which enables us to optimize the reaction bath condition and synthesize the silica-coated Cu nanoparticles without the oxidation or dissolution of the Cu nanoparticles by the simple process involving no complicated equipment or steps such as centrifuging or extraction steps for the separation of Cu nanoparticles.

2. Experimental

CuO powder was purchased from Kanto Chemical, Inc. Aqueous ammonia (NH_3, 28%), hydrazine monohydrate ($N_2H_4{\cdot}H_2O$, 98%), gelatin fine powder, ethanol (C_2H_5OH, 99.5%), tetraethylorthosilicate ($Si(OC_2H_5)_4$, (TEOS), 95%) and nitric acid (HNO_3, 60%) were purchased from Nacalai Tesque, Inc. and used without further purification.

Fig. 1 shows the synthesis procedure used to obtain Cu@SiO_2 nanoparticles. CuO powder (0.25 g) was dispersed in aqueous NH_3 solution (28%, 19 ml) and gelatin (0.20 g) was added as a dispersing agent. Hydrazine (2.0 ml) was mixed with NH_3 solution (28%, 19 ml) and gelatin (0.20 g) added. These two solutions were stirred separately at a rate of 500 rpm using a magnetic stirrer. To minimizing the effect of dissolved oxygen, nitrogen gas was bubbled at a rate of 50 $cm^3\ min^{-1}$ for more than 30 min. The temperature of the solutions was maintained at 323 K throughout the synthesis of the Cu nanoparticles. The two solutions were mixed to start the reaction and had a total volume of about 40 ml. In parallel to the above process, ethanol (32 ml) and TEOS (8 ml) were mixed and nitrogen gas was bubbled through the solution at a rate of 50 $cm^3\ min^{-1}$ for more than 30 min. This TEOS/ethanol solution was added to the suspension of synthesized Cu nanoparticles at room temperature and stirred for more than 20 min. The TEOS/ethanol solution was added about 30 min after the Cu nanoparticle deposition. Nitrogen gas was bubbled continuously throughout the entire process. The as-synthesized product was also annealed in Ar at 973 K for 10 h.

During the reaction, a copper-sputtered quartz crystal microbalance (QCM) electrode (SEIKO EG&G, QA-A9M-CU) was immersed in the solution and its frequency change was monitored [27–29]. The weight change of the electrode was calculated from the frequency of the quartz substrate using the Sauerbrey equation;

$$\Delta m = -\frac{A\sqrt{\rho_q \mu_q}}{2f_0^2}\Delta f$$

where f_0 is the frequency of the QCM substrate before the weight change, A is the active area of the QCM substrate (0.196 cm^2), ρ_q is the density of quartz (2.648 g cm^{-3}), and μ_q is the shear modulus of quartz (2.947×10^{11} g $cm^{-1}\ s^{-2}$).

A copper red glass (glaze) was prepared by mixing low-melting-temperature glass frit, Raku frit [30], (1.0 g) and Cu@SiO_2 nanoparticles that had been annealed at 1173 K (0.04 g), painting the mixture on a white ceramic test piece, and heating the test piece at 1073 K in air. The color of the product was measured by a colorimeter (Nippon Denshoku, NF333 spectrophotometer).

3. Results and discussion

3.1. Synthesis of Cu@SiO_2 nanoparticles

Fig. 2a shows a scanning electron microscopy (SEM) image of the as-synthesized Cu nanoparticles having a diameter of about 30 nm which was determined by an image analysis for randomly selected 300 particles. The silica-coating was applied to the Cu nanoparticles by adding a TEOS/ethanol solution to the Cu nanoparticles dispersed in an aqueous NH_3 solution immediately after the completion of Cu nanoparticle formation. In this work, the addition of TEOS/ethanol solution was suggested to be completed within 30 min after the Cu nanoparticle formation. Here, NH_3 acts as a catalyst for the production of a continuous and homogeneous silica-coating in the sol–gel process. Therefore, only adding a TEOS/ethanol solution to the Cu nanoparticles suspension