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Research paper

Lustrous copper nanoparticle film: Photodeposition with high quantum yield and electric conductivity

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ABSTRACT

Cu nanoparticle (NP) film has attracted much attention due to its high electric conductivity. In the present study, we prepared a Cu NP film on a TiO_2-coated substrate by photoreduction of copper acetate solution. The obtained film showed high electric conductivity and metallic luster by the successive deposition of Cu NP. Moreover, the film was decomposed on exposure to fresh air, and its decomposition reaction mechanisms were proposed. Hence, we concluded that the obtained lustrous film was composed of Cu NP, even though its physical properties was similar to bulk copper.

1. Introduction

Metal nanoparticle (NP, hereafter) has been investigated because of its optical and electric properties since the 20th century. In particular, Ag NP has been studied, focused on surface plasmon resonance (SPR, hereafter) and its high electric conductivity [1–3]. However, growing demand of the Ag NP for electronics in the 21st century has resulted in a rising cost of silver. Thus, Cu NP is becoming a promising alternative metal due to its large amount of reserve and cost-effectiveness [4–6]. From these backgrounds, Cu NP has recently much attention especially for printable electronics [5,7]. Even though the Cu NP has a problem with its low oxidation resistance, selection of appropriate capping agents and the silica-coating method has recently solved this problem [8,9].

In contrast, our research group has previously developed a method to synthesize regenerative Cu NP from copper acetate solution in the presence of polyvinylpyrrolidone by a photoreduction method [10]. The obtained colloidal Cu NP has reacted with oxygen, producing copper acetate solution again. Our photoreduction method is simple and environmentally friendly since the Cu NP is synthesized at room temperature without any hazardous chemicals. To apply our Cu NP for an inhomogeneous catalyst or a device, deposition of the Cu NP on a substrate is needed. However, it requires multiple-step processes, which ruin the facile synthesis of the Cu NP. Hence, we assume that the Cu NP film can be obtained directly on a substrate if it is immersed in the copper acetate solution and irradiated by UV light. Furthermore, it is rather curious whether or not a Cu film obtained by the successive deposition of the Cu NP will show bulk copper-like properties at the expense of characteristics of the Cu NP, which can be revealed by the decomposition reaction by the air exposure.

In the present study, we have synthesized the Cu NP film directly on a glass substrate so that the Cu NP can be separated from the solution without centrifugation. We have also investigated the relation between the electric conductivity and the morphology, and tested the decomposition of the obtained film on exposure to fresh air. To synthesize the Cu NP film on the substrate efficiently, the glass was coated with TiO_2 preliminarily. Similar syntheses of the Cu NP have been reported in colloidal TiO_2 solutions [11,12].

2. Experimental

Copper nanoparticle was synthesized by a photoreduction method, similar to that reported previously [10,13]. In brief, copper(II) acetate monohydrate (purity >99.0%) was purchased from Wako Pure Chemical Industries, and 10 mmol L^{-1} aqueous solution of copper acetate containing 10% ethanol was prepared. Anatase-type TiO_2 nanoparticle with a diameter of less than 25 nm was purchased from Sigma-Aldrich, and 1 g of the powder sample was grinded in 33 μL of acetylacetone and 2 mL of water for 5 min. Then, 330 μL of the obtained TiO_2 dispersion was dropped on a fluorine-doped tin oxide (FTO) glass (Aldrich, 735167-1EA), and dried under ambient temperature. The FTO glass was then sintered at 450 °C. The obtained TiO_2-coated substrate was immersed in 15 mL of the copper acetate solution in 20 mL of a glass tube. As

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the schematic instrumental picture is illustrated in Fig. S1, the substrate was irradiated by LED light from the reverse side of the TiO_2 thin film. The irradiation wavelength was 365 ± 5 nm, and an LED head unit (Hamamatsu Photonics, L11921-400) was used combined with an LED controller (C11924-101). The distance between the head unit and the substrate was 60 mm, and the optical intensity was 150 mW cm^{-2}.

The photoirradiated substrate was washed by ethanol. X-ray diffraction (XRD) measurement of the substrate was performed with an X-ray diffractometer (Rigaku, Smartlab) using CuKα radiation (0.154 nm). The photoirradiated substrate was also measured by X-ray photoelectron spectroscopy (XPS, AXIS-His, Kratos Analytical) using monochromatic X-ray AlKα radiation (1486.6 eV).

Electric conductivity of the Cu NP film was measured with a four-point probe (Mitsubishi Chemical, MCP-T410). Volume resistivity [Ω m] was calculated by using the obtained resistance [Ω] and the film thickness [m]. The latter value was estimated from the weight of the Cu film [g], the density of Cu metal [g cm^{-3}], and the area of the film [cm^2].

Scanning electron microscopy (SEM) images of the substrate were observed with a field-emission SEM (Hitachi High-Technologies, S-5500). The accelerating voltage was 2 kV. UV–vis–NIR absorption spectra of the copper acetate solution were measured with an UV–vis–NIR spectrometer (Shimadzu, UV-3600) using a rectangular quartz cuvette with an optical length of 10 mm. To test the back reaction from Cu film to Cu^{2+}, the cap of the glass tube was opened after the UV irradiation, and the substrate immersed in the photoirradiated solution was exposed to fresh air.

3. Results and discussion

3.1. Formation of lustrous Cu nanoparticle film

When a TiO_2-coated substrate immersed in the copper acetate solution was irradiated by UV light, appearance of the substrate gradually changed, as shown in Fig. 1. At 0.5 h of UV irradiation, the color of the substrate was reddish brown, which is characteristic of the SPR of Cu NP [10]. Thus, formation of a thin Cu NP film was suggested by photoreduction of copper acetate. Upon the prolonged irradiation, the film got brighter. At 5 h of UV irradiation, the film took on metallic luster like bulk copper. These observations suggest that the successive deposition of the Cu NP on the substrate induced the metallic luster. It is noted that the luster did not faded away in 1 week even when the film was placed under air at the ambient temperature, suggesting that the film is stable. Also, no significant difference was observed when the temperature of the sample was slightly changed because the reduction occurs with the photocatalytic activity of TiO_2, which will be described in Section 3.4. We also tried to irradiate the UV light from the side of the TiO_2 thin film. However, the obtained Cu film was not uniform probably because the TiO_2 film was partially covered with the produced Cu NP and could not absorb the UV light.

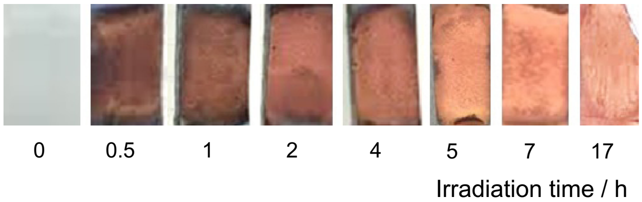

Fig. 1. Color changes of the TiO_2-coated substrate in copper acetate solution by UV irradiation.

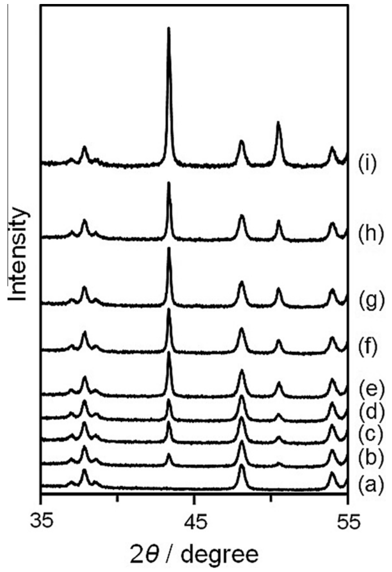

Fig. 2. Changes of XRD patterns of the TiO_2-coated substrate against the UV irradiation time: (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h, (f) 5 h, (g) 6 h, (h) 7 h and (i) 17 h, respectively.

Fig. 2 shows XRD patterns of the Cu NP film on the TiO_2-coated substrate. According to JCPDS card No. 4-0836, two strong peaks at 43.3° and 50.5° correspond to the Miller planes (111) and (200) of the crystalline Cu metal, respectively. All other peaks originate from anatase-type TiO_2 (JCPDS card No. 21-1272). During any photoirradiation time, no peaks assignable to Cu_2O or CuO were observed, for example at 36.4° and 48.7° (JCPDS cards No. 5-0667 and 48-1548, respectively), indicating that Cu^{2+} was reduced to Cu^0 directly by UV irradiation. The fact that only metallic Cu NP was produced without oxides by UV irradiation is notable since Cu NP generally gets oxidized easily [13–15]. Also, FWHM values at 43.3° were almost constant, suggesting that the diameter of the Cu NP did not change significantly during the UV irradiation. Additionally, when the distance between the LED head unit and the substrate gets longer, the obtained film took on dark brown, and Cu_2O was detected by XRD measurement. This result supports that Cu^{2+} was reduced to Cu^0 efficiently when the distance is 60 mm.

One may suspect that a very thin oxide layer or amorphous oxides possibly exist, neither of which can be detected by the XRD measurement. To clarify this, we measured an XPS spectrum of a Cu NP film obtained by 5-h UV irradiation, as shown in Fig. 3. Two peaks were observed at 932.6 and 952.6 eV. The former peak is consistent with that of metallic Cu $2p_{3/2}$ reported previously [16], but inconsistent with those of Cu_2O and CuO appearing at

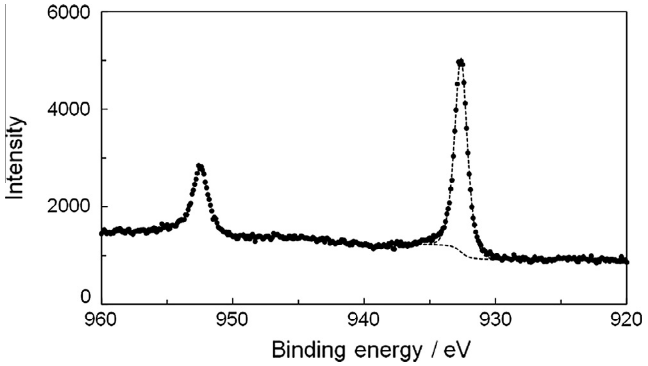

Fig. 3. An XPS spectrum of the Cu NP film at 5 h of UV irradiation.