

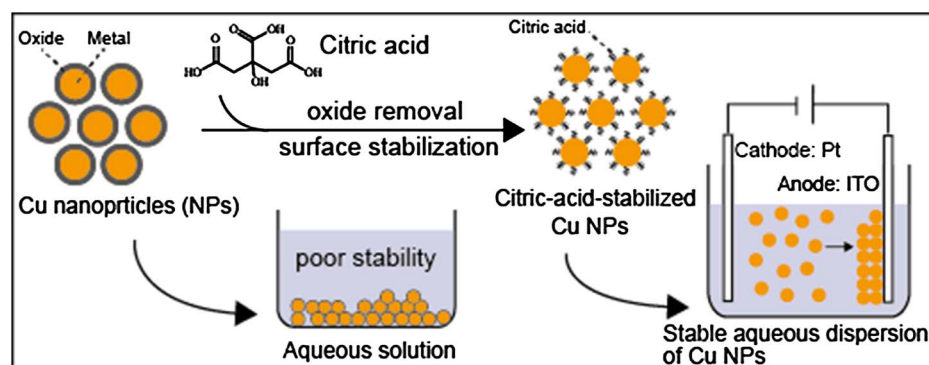
Aqueous electrophoretic deposition of citric-acid-stabilized copper nanoparticles

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GRAPHICAL ABSTRACT



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ABSTRACT

Citric-acid-stabilized copper (Cu) nanoparticles (NPs) were deposited on indium tin oxide (ITO) substrates using aqueous electrophoretic deposition (EPD). Usually, Cu NPs are unstable in aqueous solution because they oxidize and aggregate easily, which is why aqueous EPD has not been used before to deposit them on substrates. However, we showed that treating Cu NPs using citric acid in aqueous solution removed surface oxides and stabilized the surfaces sufficiently. After the treatment, the Cu NPs remained highly stable in aqueous solution even after one week, and this stability was sustained under an electric field in aqueous solution. The Cu NPs were deposited rapidly on ITO substrates by aqueous EPD at a deposition rate that increased with current density (0.25, 0.46, and 0.96 mg/cm²/min at 0.10, 0.20, and 0.30 mA/cm², respectively). The Cu NP films obtained by the rapid deposition at 0.30 mA/cm² contained too much water, leading to cracked and low density films. Instead, we demonstrated that a current density of 0.20 mA/cm² resulted in uniform and high density Cu NP films.

1. Introduction

Because of their high conductivities and low sintering temperatures, silver (Ag) and copper (Cu) nanoparticles (NPs) have attracted considerable interest as a means of forming conductive patterns on various electronic devices [1–3]. Ag NPs have been studied and used most

extensively because of their high stability in air and various solvents. Cu NPs are expected to be among the next generation materials because Cu is much cheaper than Ag. Nevertheless, it remains expensive to synthesize Cu NPs and form conductive patterns with them because they oxidize and aggregate easily in aqueous solution and then require organic solvent. Recently, we developed a green synthesis of Cu NPs

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based on aqueous chemical reduction of Cu citric acid complexes using ascorbic acid [4]. After heat treatment at 200 °C, Cu NPs show low resistivity (7.6 $\mu\Omega$ cm) [5]. Next, for low-cost Cu conductive patterns, we require a deposition method based not on organic solvent but on aqueous solution. Aqueous electrophoretic deposition (EPD) is widely used to deposit metal oxide particles on various substrates because of its low cost, simple equipment, fast deposition rates, and wide range of applications [6–13]. In EPD, charged particles dispersed in aqueous solution migrate under electric fields and are deposited on oppositely charged electrodes. Because this method requires particles that are highly stable in aqueous solution, EPD has been unsuitable for depositing metal NPs, especially Cu. Indeed, we found that the aqueous EPD of Cu NPs obtained from our synthesis method failed because the Cu NPs oxidized, aggregated, and precipitated immediately after being dispersed in aqueous solution. To realize the many potential advantages of using aqueous EPD with Cu NPs, we must make such particles highly stable in aqueous solution. Herein, we use citric acid to remove surface oxides and stabilize the surfaces of Cu NPs obtained from our green synthesis. Citric acid is reported not only to remove the oxides on bulk metal surfaces but also to stabilize such surfaces [14–17]. We vary the pH and reaction time to control oxide removal and surface stabilization for Cu NPs, and we show that the Cu NPs are stable in aqueous solution. We then use aqueous EPD to deposit the treated Cu NPs on indium tin oxide (ITO) substrates. We also discuss the effects of reaction time and current density on the formation of Cu NP films by aqueous EPD.

2. Experimental

2.1. Surface modification of Cu nanoparticles for aqueous electrophoretic deposition

We obtained all the chemicals used herein from Wako Pure Chemical Industry, Ltd., in Japan. In all the experiments, we used deionized water (18 M Ω) obtained from a water purifier system (WT101UV; Yamato Scientific Co., Ltd., Japan). We synthesized Cu NPs using Cu nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; purity $\geq 99.9\%$) as a Cu salt, trisodium citrate dehydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$; purity $\geq 99.0\%$) as a complexing/capping agent, and L(+)-AA ($\text{C}_6\text{H}_8\text{O}_6$, purity $\geq 99.6\%$) as a reducing agent. A detailed description of the synthesis method is given in [4]. To modify the surfaces of the Cu NPs, we prepared citric acid aqueous solutions by dissolving citric acid ($\text{C}_6\text{H}_8\text{O}_7$; purity $\geq 98.0\%$) in deionized water. Subsequently, we adjusted the pH values of the solutions to 1.6–9.0 by adding an NaOH solution. The final solution volume and concentration were 30 ml and 0.5 M citric acid, respectively. We dispersed 0.35 g of the Cu NPs in the solution at different pH values under ultrasonication (W-113MK; Honda Electronics Co., Ltd., Japan) for 30 min, whereupon the Cu NPs were filtrated, rinsed with methanol, and dried under vacuum at room temperature for 1 h. We analyzed the crystal structure, morphology, and chemical state of the Cu NPs using X-ray diffraction (XRD, R-wing, CuK α , Rigaku Corp., Japan); electron microscopy (S-4200 field emission scanning electron microscope (FE-SEM), Hitachi High-Technologies Corp., Japan); HD-2700 scanning transmission electron microscope (STEM, Hitachi High-Technologies Corp., Japan); and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Fisher Scientific Inc., USA), respectively. To analyze the surface species of the particles, we recorded Fourier transform infrared (FT-IR) spectra using a spectrometer (Frontier FT-NIR/MIR, Perkin Elmer, USA) operating at a resolution of 4 cm^{-1} . The spectra were collected in transmission mode using KBr pellets. The amount of the Cu NP dissolution in the citric acid aqueous solutions was measured using an inductively coupled plasma (ICP; SPECTRO ARCOS, AMETEK, Inc., USA).

2.2. Stability evaluations of Cu nanoparticles in aqueous solution

After treating the Cu NPs using citric acid, we prepared a Cu NP

dispersion (1 wt% Cu) by adding the treated Cu NPs to deionized water under ultrasonication for 5 min. We measured the size distribution of the 10 times diluted Cu dispersion by dynamic light scattering, using an NP analyzer (SZ100; HORIBA, Ltd., Japan) to analyze the dispersibility of the Cu NPs.

To evaluate the electrochemical stability of the Cu NPs, we performed cyclic voltammetry in a three-electrode cell using a potentiostat/galvanostat (Reference 600, Gamry Instruments, USA) under atmospheric conditions at 25 ± 2 °C. The potential was scanned from open circuit potential to positive direction at a scan rate of 10 mV/s. The electrolyte was 0.10 M NaNO_3 solution. The mixture of Cu NPs, deionized water, and 5% Nafion dispersion (DE521; Nafion in a mixture of ethanol, 1-propanol, and water) was drop-cast onto a glassy carbon (GC) electrode as the working electrode. Nafion was used as the binder. The reference electrode was an Ag/AgCl electrode, and the counter electrode was a platinum (Pt) wire. The area of the Cu NPs on the GC electrode was 0.79 cm^2 . After the cyclic voltammetry, the working electrode surface was characterized using XPS. In addition to the Cu NPs on the GC electrode, we obtained cyclic voltammograms (CVs) of a glass electrode covered with ITO (8–12 Ω /sq surface resistivity; purchased from Sigma-Aldrich) and a Cu plate (purity = 99.96% from Nilaco corporation). From the CVs of the ITO, electrochemical stability of the ITO was evaluated because the ITO was used as a substrate for EPD. The CVs of the Cu plate were obtained to compare with the Cu NPs on the GC electrode.

2.3. Aqueous electrophoretic deposition of Cu nanoparticles

We conducted aqueous EPD of the treated Cu NPs in a two-electrode cell using the potentiostat/galvanostat under atmospheric conditions at 25 ± 2 °C. We used the glass electrode covered with ITO as the anode and a Pt plate as the cathode after rinsing the electrodes with acetone and deionized water. The distance between the electrodes was 2 mm in the two-electrode cell. The area of the electrodes was 1.81 cm^2 . The Cu NP dispersion for aqueous EPD was prepared by dissolving the treated Cu NPs (1 wt%) in deionized water. During the deposition, we recorded the current and voltage in constant current mode. We varied the current to increase the thickness of the Cu NP films, and we measured their thickness and weight using a digital micrometer (Litematic VL-50B, Mitutoyo Corp., Japan) and an electronic microbalance (XS205 Dual Range, Mettler Toledo, LLC, Switzerland).

3. Results and discussion

3.1. Surface modification of Cu nanoparticles

We used our green synthesis method to synthesize Cu NPs with a mean diameter of 77.8 nm. The XRD profile of the Cu NPs shows that they consisted of only Cu metal (JCPDS No. 04-0836), and the FT-IR spectrum reveals that citric acid was adsorbed on their surfaces (Fig. S1). Because we used citric acid to form stable Cu complexes and stabilize the surfaces in our synthesis method, citric acid already existed on the Cu NPs surface before surface modification using citric acid. When the Cu NPs were dispersed in aqueous solution for EPD, they aggregated and precipitated. Although citric acid is widely used as a surface stabilizer for aqueous stable NPs [16,17], the Cu NPs are unstable in aqueous solution. Since the dispersibility of NPs depends on their surface conditions, we conducted XPS measurements of the Cu NPs to evaluate any surface impurities and the extent of surface oxidation. Fig. 1 shows XPS profiles from (a) the Cu 2p region and (b) the Cu LMM region of the Cu NPs, as well as from a Cu plate for comparison. We removed the surface oxides from the Cu plate by argon ion etching before the XPS measurement. XPS (Cu 2p) and Auger (Cu LMM) spectroscopy were utilized to evaluate the extent of oxidation on the Cu NP surfaces. Although the peak corresponding to Cu (932.6 eV) and/or Cu_2O (932.5 eV) was observed in the Cu 2p region, the peak did not

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