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Direct writing of copper-based electrodes using femtosecond laser reductive sintering of copper (II) oxide nanoparticles

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Abstract

Specific surface area of the electrodes is an important feature for electrochemical detection. We investigated the porous nature with specific surface area of the copper-based electrodes fabricated by femtosecond laser reductive sintering using two copper (II) oxide nanoparticle inks with different grain size distributions, Gaussian and bimodal distributions. Although the electrode fabricated using the ink with bimodal distribution exhibited high density, the higher current was obtained by using the electrode fabricated using the ink with Gaussian distribution for electrolysis reaction. These results suggest the advantage of the large surface area of the electrodes by comparing to the resistance of the electrodes. In the presentation, we will introduce the cobalt-added copper-based electrodes for nonenzymatic glucose detection.

Keywords: femtosecond laser reductive sintering; coppe (II) oxide nanoparticle; electrode; nonenzymatic glucose; nanoparticle distribution;

1. Introduction

Microsensors are generally fabricated using well-established semiconductor technology such as lithography and vacuum deposition process. These techniques enable to form precise patterns using photomasks which are fabricated for the designed patterns. In addition, metal deposition process is performed under vacuum atmosphere such as sputtering methods. In contrast, laser direct writing of metals is a promising tool for

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printing devices because of its vacuum-free simple process [1,2]. We have reported a femtosecond laser direct writing technique in air by reducing and sintering metal oxide nanoparticles such as copper (II) oxide nanoparticles mixed with a reducing agent [3,4]. The density, surface area of the metal patterns, and compositions of metal/metal oxides can be controlled by laser irradiation conditions. However, the size effect of the nanoparticles was not clarified. In this study, we investigated the effect of particle size on patterning in femtosecond laser reduction using copper (II) oxide nanoparticles of different particle sizes distributions as raw materials. First, two copper (II) oxide inks with different particle size distributions were prepared. Then,

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2. Experimental methods

2.1. Preparation of copper (II) oxide nanoparticle ink

First, bimodal distribution of copper (II) oxide nanoparticles were prepared by a chemical method. 0.2 M copper nitrate pentahydrate ($Cu(NO_3)_2 2.5H_2O$) solution and 0.2 M urea solution were prepared. 25 mL of these two solutions were added to a round bottom flask and mixed [5]. The reaction was carried out using a microwave in atmospheric pressure, and the solution was heated until it evaporated to synthesize a nanoparticles of copper nitrate hydroxide ($Cu_2(OH)_3(NO_3)$), the precursor of copper (II) oxide. The resulting nanoparticles was centrifuged and washed with DI water, ethanol, and acetone. Finally, the copper nitrate hydroxide nanoparticles were placed in a mortar and heated at 300 °C for 60 minutes in an electric furnace at atmospheric pressure to prepare a black copper (II) oxide nanoparticles.

Two types of inks were prepared to compare the effect of the particle size: gaussian distribution ink containing commercially available copper (II) oxide nanoparticles (average diameter: ⩽50 nm Sigma-Aldrich) and bimodal distribution ink containing the prepared copper (II) oxide nanoparticles with a different particle size distribution. Table 1. shows the composition of the prepared copper (II) oxide nanoparticle inks. copper (II) oxide ink was prepared by mixing ethylene glycol and polyvinylpyrrolidone (PVP, ~M_w10000) using an ultrasonic homogenizer, adding copper (II) oxide nanoparticles to the stirred solution, and mixing and stirring again.

Table 1. Composition of copper (II) oxide ink

Component of copper (II) oxide nanoparticle ink	Gaussian type	Bimodal type
Copper (II) oxide nanoparticles (<50 nm) (wt%)	60	-
Copper (II) oxide nanoparticles (prepared) (wt%)	-	60
Ethylene glycol	27	
Polyvinylpyrrolidone (M_w~10000)	13	

2.2. Fabrication of copper patterns using femtosecond laser reductive sintering

Fig. 1. shows a diagram of the Cu pattern writing process. First, a copper oxide nanoparticle ink was spin-coated on glass substrates. Then, femtosecond laser pulses were focused on the surface of the ink films and

irradiated to form the patterns. Finally, non-sintered and melted nanoparticles were removed by rinsing the samples in ethylene glycol and ethanol.

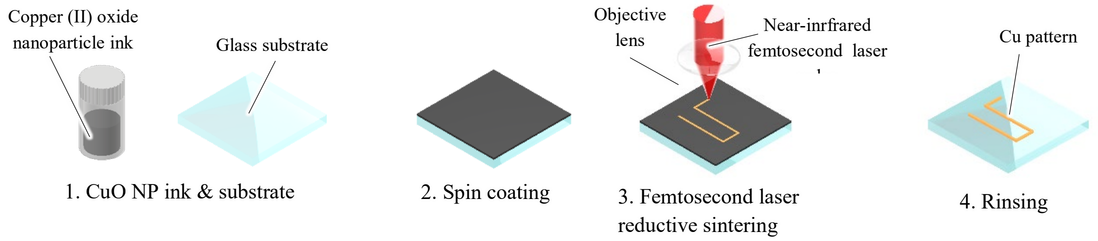

Fig. 1. Schematic of Cu writing process.

2.3. Evaluation methods

The crystal structure of the prepared copper (II) oxide nanoparticles was characterized by x-ray diffraction (XRD) analysis, and the particle size distribution was analyzed by field emission scanning electron microscope (FE-SEM). The line widths of the line patterns fabricated by laser reductive sintering were measured from the optical microscope images.

3. Results and discussion

3.1. Size distribution of copper (II) oxide nanoparticles

Fig. 2. Show the size distribution of the prepared copper (II) oxide nanoparticles and nanoparticles with an average diameter of ⩽ ϕ 50 nm. The bimodal size distribution and a median particle size of 14 nm. The commercially available particles had a gaussian size distribution and a median particle size of 18 nm. This indicates that the 14 nm particles have a surface area 1.25 times larger than the 18 nm particles.

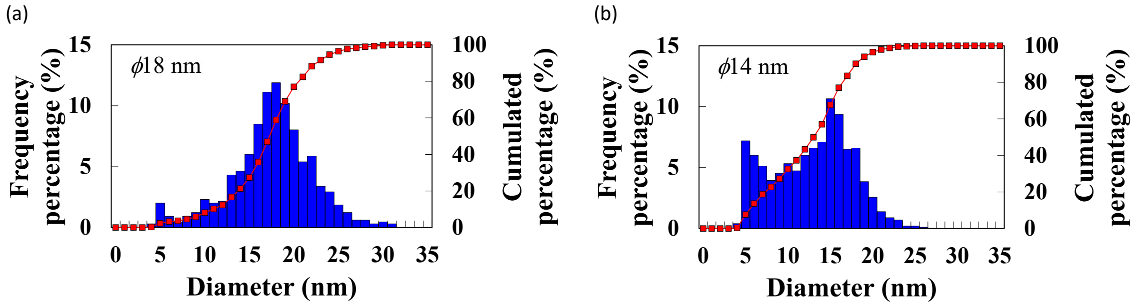

Fig. 2. Size distribution of (a) Gaussian type and (b) bimodal type.

3.2. Size effect of the nanoparticle distributions on patterns

Fig. 3. shows the cross-sectional FE-SEM images of the fabricated patterns using Gaussian and bimodal distribution types of the inks. The densities of the patterns fabricated using the Gaussian and bimodal types of inks were 82.2 % and 87.5 %, respectively. In addition, the resistivity of the patterns fabricated using Gaussian distribution ins was 16.1 μΩm, which lower than that fabricated using the bimodal distribution inks, 59 μΩm, under the condition that the scanning speed, raster pitch, and pulse energy were 5 mm/s, 5 μm, and

0.56 nJ, respectively. These results suggest that the optimal pores formed by the nanoparticles filled by the reducing agents, resulting that copper (II) oxide nanoparticles were well-reduced and sintered even though its low density.

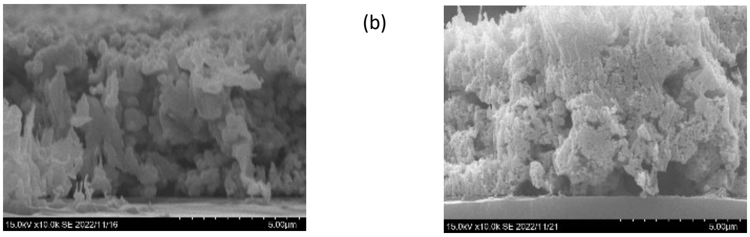

Fig. 3. Cross-sectional FE-SEM images of the patterns fabricated using (a) Gaussian and (b) bimodal types of inks.

3.3. Electrochemical properties of the electrodes

Fig. 4. shows the cyclic voltammograms of the patterns fabricated with each ink. The Gaussian particles were found to have a higher redox peak. This is because that Cu patterns provide higher reaction currents.

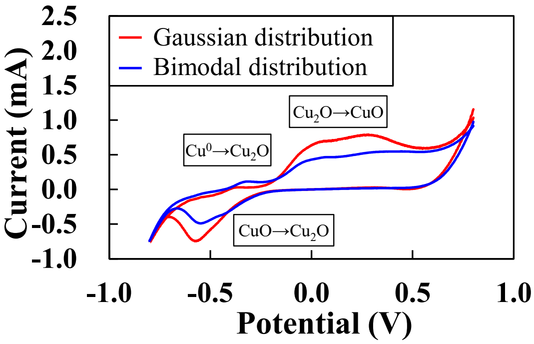

Fig. 4. Cyclic voltammetry.

4. Conclusions

We evaluated size effects of copper (II) oxide nanoparticles on femtosecond laser reductive sintering.

- Combination of large and small particles expected to increase sintering density.
- The resistivity of the patterns fabricated using Gaussian typed ink was lower than that using the bimodal one, even though their densities were lower. Optimal pores between the nanoparticles were filled by reducing agents, resulting that the nanoparticles were well-reduced and sintered.
- The electrode fabricated using Gaussian type inks was found to have a high redox peak.

Acknowledgements

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References

[1] B. Kang, S. Han, J. Kim, S. Ko, M. Yang, "One-step fabrication of copper electrode by laser-induced direct local reduction and agglomeration of copper oxide nanoparticle", Journal of Physical Chemistry C, 115, (2011) 23664.
[2] D. Lee, D. Paeng, H. K. Park, C. P. Grigoropoulos: "Vacuum-free, maskless patterning of Ni electrodes by laser reductive sintering of NiO nanoparticle ink and its application to transparent conductors", ACS Nano, 8 (2014) 9807.
[3] M. Mizoshiri, S. Arakane, J. Sakurai S. Hata : "Three-dimensional Cu microfabrication using femtosecond laser-induced reduction of CuO nanoparticles", Appl. Phys. Express., 10 (2017) 017201
[4] S. Arakane, M. Mizoshiri, J. Sakurai S. Hata : "Direct writing of three-dimensional Cu-based thermal flow sensors using femtosecond laser-induced reduction of CuO nanoparticles", J. Micromech. Microeng., 27, (2017) 055013.
[5] N. M. Shaalan, M. Rashad, M. A. Abdel-Rahim. "CuO nanoparticles synthesized by microwave-assistedmethod for methane sensing", Opt Quantum Electron, 48, (2016) 531.