Preparation of netted silver metal from fine copper particle in silver nitrate aqueous solution

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1. Introduction

Many diffusion-limited aggregation (DLA) patterns are naturally seen in the dendrite, the bacteria colony, and so on. There are reported many computer simulations about DLA. Most of the experimental knowledge about the dendrite, however, has been obtained from the electro-deposition technique. Then, the other experimental research about the DLA pattern formation is anticipated to understand the growth of dendrite. Silver crystal can also be formed by electro-less reduction of silver ions at the surface of dissolving copper particle. However, there is no report about the silver metal dendrite formation from fine copper particles. In the present study, we investigated the morphology of the silver metal tree by changing the size of copper particles, which were served to the reduction of silver ions in aqueous solution. To prepare fine copper particles, we examined the condition of electro-deposition of copper on a glass substrate, which was aimed to a transparent silver electrode with large surface area.

2. Experimental

Fluorine doped tin oxide (FTO) coated glass was used as a substrate. The substrate was sonicated in the aqueous suspension of alumina powder to obtain rough surface and then it was cleaned by sonication in acetone and then in water purified with milliQ system. The FTO coated glass substrate was mounted in a three-electrode glass cell containing a platinum wire as a counter electrode and an Ag/AgCl reference electrode. To improve adhesion of copper on the FTO coated glass electrode[1)], the FTO surface was treated before the deposition in a 0.1M-H_2SO_4 aqueous solution (MilliQ+) at –1.1 V (vs Ag/AgCl) for 15 s. The galvanostatic electro-deposition of the sparse copper particles was carried out from a 0.72M-$CuSO_4$ and 0.65M-H_2SO_4 aqueous solution system in the same three-electrode glass cell. The optical absorbance for the sparse copper particles deposited on the FTO coated glass substrate was measured at room temperature by a UV-VIS spectrophotometer and the density and average diameter of copper particles were measured from the observation with a scanning electron microscope (SEM).

The silver metal trees were grown at 25°C by the copper-deposited sample in a 0.1M-$AgNO_3$ aqueous solution (MilliQ+) for 24 hours. The morphology of the obtained metallic silver was observed using SEM. The average diameter of the silver metal strings was measured from SEM pictures.

In order to extend the size of particles to that could not be obtained by electro-deposition, copper particles embedded in an acrylic plastic plate were employed as well. Copper particles were allotted by the average particle diameters at 40 and 17μm by appropriate sieves. Each size of powder was daubed by friction on the plastic plate to be fixed. Then the silver metal trees were grown at 25°C by this plate in a 0.1M-$AgNO_3$ aqueous solution for 24 hours. The morphology of the silver metal from the each sample was also observed using SEM.

3. Results and Discussion

The prepared copper particles with constant charges were placed in $AgNO_3$ aqueous solution to grow silver crystals. The dendrite silver metal was not formed from the copper particles when the current density of electro-deposition was low, but the string-shaped silver tree was formed from copper particles deposited at a higher current density. Netted silver metal formed at the current density of 3.8 mA cm^{-2} were crowded and stuck on the FTO coated glass as shown in the Figure 1 because the density of particles became higher. Dendrite-shaped silver tree in the morphology was partly observed when copper particles were prepared in the higher current density.

The average diameter of the silver metal strings was increased with increasing the concentration of silver nitrate aqueous solution. Significant change in the diameter was not observed for the silver strings prepared in the concentration region examined.

The dendrite shape was formed when silver metal was grown where the size of original copper particles was larger than 40 μm. On the other hand, strings of silver metal were formed from copper particles of the size of 17 μm. It is noticeable that the morphology of the silver metal tree depends on the size of copper particles used as the reactant. This observation suggests that the dendrite structure could be formed only at the enough size of copper particle to release Cu^{2+} and receive Ag^{+} ions at the solid-solution interface. It is reported that string-shaped zinc metal grows at an electrode only in the reaction conditions with a higher Zn^{2+} concentration and a higher reduction potential[2)]. In the present study, since Ag^{+} concentration is relatively high and the copper elution from a small copper particle is fast, the string-shaped silver metal tree was formed.

References

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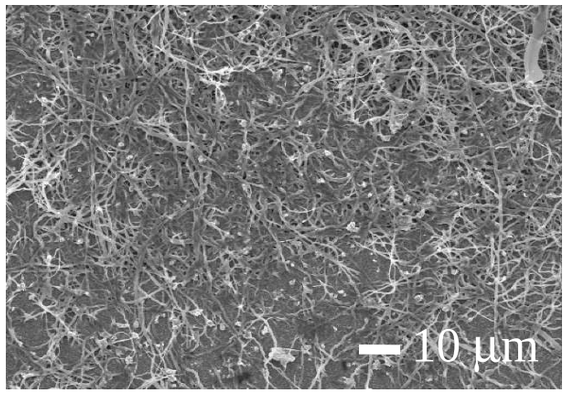

Fig. 1 SEM image of the silver metal tree obtained from copper particles those were deposited with various reduction current densities at 3.8 mA cm^{-2} for 72 s.