Shape Control of Silver Tree by Pulse Electro-deposition Method in AgNO$_3$ Aqueous Solution

Junichi NISHINO$^a$* and Yoshinori KANNO$^b$

$^a$Department of Chemistry, Nagaoka University of Technology (1603-1 Kamitomioka-machi, Nagaoka 940-2188, Japan) [Present Address: Department of Chemistry and Biology Engineering, Fukui National College of Technology (Geshi-cho, Sabae 916-8507, Japan)]
$^b$Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi (4-3-11 Takeda, Kofu 400-8511, Japan)

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Dendrite silver was synthesized on the carbon fiber by pulse electro-deposition method in AgNO$_3$ aqueous solution. The morphology of the silver changed from dendrite to plate-like crystal, and the formation mechanism was investigated by using continuous wave (CW) potential and rectangular wave potential. The fractal dimension of the silver tree deposited at 10 Hz showed the highest value in the each low of the potential, $V_L$, of rectangular wave. The shape of the silver tree is able to control by adjusting the frequency of the rectangular wave that applied for electro-deposition.

Key Words: Silver Tree, Dendrite, Shape Control, Pulse Electro-deposition

1 Introduction

The ordered nanostructure of metals has been attracting keen attention in view of nanotechnology.$^{3,4}$ The dendrite silver of nanoscale is the base material whose specific surface is large and the silver possess a surface enhanced Raman scattering (SERS) effect.$^{2,3}$

Nakato et al. reported that the strikingly well-ordered metal latticeworks,$^4$ under a constant current-density condition, standing perpendicular to the substrate, are spontaneously formed in oscillatory electro-deposition through the cooperation of various processes with long-range spatiotemporal synchronization.

We assume that the shape of the silver tree can be controlled when three parameters composed of an electric potential oscillation, a diffusion determining condition, and an electronic supply determining condition are made to appear alternately growth pattern by applying the pulse potential.

A carbon fiber is stable in AgNO$_3$ aqueous solution, and easily obtained fine fiber and good substrate for cold cathode of field emission display. The purpose of this work is to prepare the controlled shape of silver tree on the carbon fiber by pulse electro-deposition method in AgNO$_3$ aqueous solution.

2 Experimental

2.1 Materials and preparation method

AgNO$_3$ (99.8%) was purchased from Nacalai Tesque Inc. Japan, carbon fiber (Toray Industries Inc., M60JB) was used as a substrate. A carbon fiber that was bonded slide glass with reentrant part was mounted in a three-electrode glass cell containing a platinum wire as a counter electrode and an Ag/AgCl 3M-NaCl a potentiostat and a function generator. The schematic diagram of apparatus and a list of the deposition conditions are

![Schematic diagram of apparatus]
shown in Fig. 1 and Table 1, respectively.

2.2 Evaluation methods
The morphology of the silver tree that obtained from the each sample was observed by scanning electron microscope (SEM, JEOL-5310LVB). The fractal dimensions D were determined by box counting method from these SEM 2D images using PopImaging and Fractal3 of fractal analysis system for MS-Windows.

An X-ray diffraction apparatus using CuKα radiation (MacScience M03XHF22) was used for determines the crystal structure of the silver tree.

3 Results and Discussions
Figure 2 shows the X-ray diffraction patterns of silver tree deposited at various frequency of applied potential rectangular wave from \( f = 1 \) Hz to 1000 Hz under the conditions of \( V_L = -0.4 \) V and \( V_H = 0 \) V (vs. Ag/AgCl). The preferred orientation of the \([111]\) direction of the silver metal was observed. It suggests that the cubic Ag nucleation and growth take place as well as deposited layer by layer of \([111]\) close-packed planes.

Figure 3 shows the morphology of the silver tree prepared at various frequency of applied potential rectangular wave from \( f = 1 \) Hz to 100 Hz under the conditions of \( V_L = -0.1 \) V and \( V_H = 0 \) V (vs. Ag/AgCl) and CW at \( V = -0.1 \) V. The fine dendrite shaped silver tree is only observed at CW applied potential condition.

Figure 4 shows the morphology of the silver tree prepared at various frequency of applied potential rectangular wave from \( f = 1 \) Hz to 100 Hz under the conditions of \( V_L = -0.4 \) V and \( V_H = 0 \) V (vs. Ag/AgCl) and CW at \( V_L = -0.4 \) V. The fine dendrite shaped silver tree is observed at CW applied potential condition and rectangular wave at \( f = 1 \) Hz.

Figure 5 shows the morphology of the silver tree prepared at various frequency of applied potential rectangular wave at various conditions.

![Fig. 2 X-ray diffraction patterns of the silver tree deposited at various frequency of applied potential rectangular wave from \( f = 1 \) Hz to 1000 Hz under the conditions of \( V_L = -0.4 \) V and \( V_H = 0 \) V (vs. Ag/AgCl).](image2.png)

![Fig. 3 SEM images of silver tree on carbon fiber deposited at various frequency of applied potential rectangular wave, (a) CW, (b) 1 Hz, (c) 10 Hz, and (d) 100 Hz under the conditions of \( V_L = -0.1 \) V and \( V_H = 0 \) V (vs. Ag/AgCl).](image3.png)

![Fig. 4 SEM images of silver tree on carbon fiber deposited at various frequency of applied potential rectangular wave, (a) CW, (b) 1 Hz, (c) 10 Hz, and (d) 100 Hz under the conditions of \( V_L = -0.4 \) V and \( V_H = 0 \) V (vs. Ag/AgCl).](image4.png)

![Fig. 5 SEM images of silver tree on carbon fiber deposited at various frequency of applied potential rectangular wave, (a) CW, (b) 1 Hz, (c) 10 Hz, and (d) 100 Hz under the conditions of \( V_L = -0.8 \) V and \( V_H = 0 \) V (vs. Ag/AgCl).](image5.png)
lar wave from $f = 1$ Hz to 100 Hz under the conditions of $V_c = -0.8$ V and $V_m = 0$ V (vs. Ag/AgCl) and CW at $V = -0.8$ V. The fine dendrite shaped silver tree is observed at CW applied potential condition and rectangular wave from $f = 1$ Hz to 10 Hz.

We can consider that the amount of nucleation increased remarkably under the high applied potential, because of the number of nuclei increased with increasing an overpotential$^{[57]}$, the dendrite shaped silver grows at high applied potential and lower frequency range of rectangular wave. Because the growth of silver tree was determined by diffusion control of Ag$^+$ at low frequency potential wave, but the mass transfer of reduction was controlled by the growth of silver tree at high frequency of applied potential wave. To control the growth of dendrite silver, an overpotential must be higher than some critical value. K. I. Popov et al. reported that the critical overpotential value for dendritic growth becomes higher$^{[49]}$ upon increasing the Ag$^+$ ion concentration in the electrolyte. By applying the CW potential, the critical overpotential becomes low as time advances. When the applied pulse is more high frequency, on the other hand, the dendrite critical overpotential becomes higher value. Therefore the critical electric potential becomes high, the dendrite growth is restrained because Ag$^+$ ion concentration around the carbon fiber is with being high as much as pulse width is short at applied high frequency pulse wave.

Figure 6 shows the fractal dimensions ($D$) of the silver tree as a function of frequency of the rectangular wave. The $D$ of the silver tree deposited at 10 Hz showed the highest value in the each $V_c$. The values of $D$ are independent at the various frequency of applied rectangular wave. The value of $D$ at $V_c = -0.8$V under various frequency of applied rectangular wave is constant in high value and the average gives around 1.78. While shape influence strength of electricity examination, we will be examined it from now on.

4 Conclusions

The morphology of the silver changed from dendrite to plate like crystal with scanning the applied rectangular wave from low frequency to high frequency. This work demonstrates that the shape of the silver tree is able to control by adjusting the frequency of the rectangular wave that applied for pulse electro-deposition.

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