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Research Article

An Influence of Concentration of Polyvinylpyrrolidone on the Morphology of Silver Metal Formed from $AgNO_3$ Aqueous Solution

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Metal silver rods having a partly regular direction on the substrate are synthesized from the fine copper particles on acrylic plastic plate immersed in 50 μM-PVP and 0.1 M-$AgNO_3$ aqueous solution. An increase of PVP concentration in the $AgNO_3$ aqueous solution inhibits the growth of the string-shaped silver and dendrite-shaped silver as well as polyol method. The absorbance of the plasmon peak around 410 nm immersed in 0.1 M-$AgNO_3$ aqueous solution at 25°C for 24 hours increased with an increase of the PVP concentration.

1. INTRODUCTION

In the past years, as for the silver nanoparticles, a research on the particle diameter and the form is active in the application field of catalyst, optical material, nanodevice material, and so on. While the silver nanowire and the nanorod play an important part as a machine for the mutual connection in the electronic device of nanoscale, nanostructure silver has been synthesized by polyol method [1–8], electron beam irradiation under high vacuum [9], and template method [10–14]. When silver nanorod is synthesized by the polyol method, polyvinylpyrrolidone (PVP) is added as a protecting agent in silver nitrate ethylene glycol solution [1–3, 5, 8]. However, when we use it for catalysts and antibacterial materials, it is important to fix the nanosilver on the substrate from the viewpoint of the environmental protection.

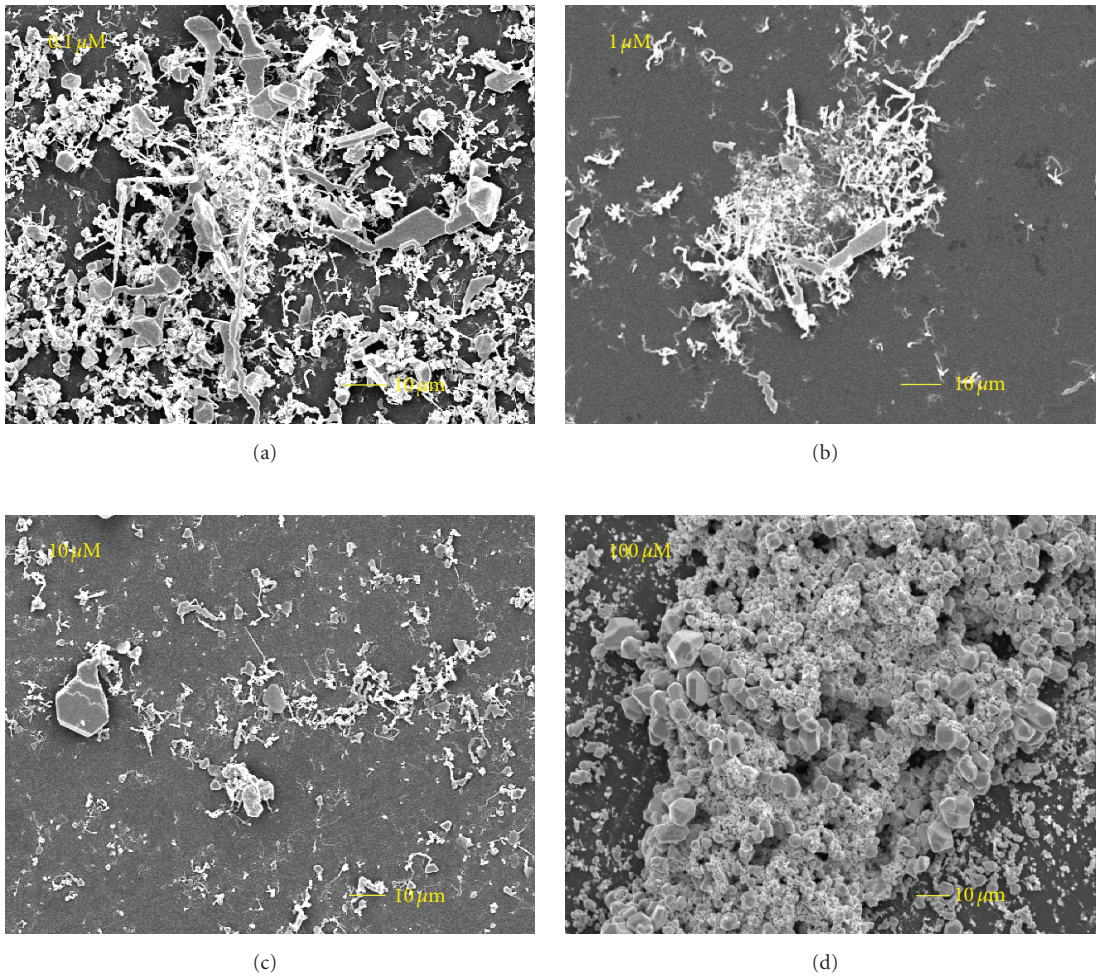
This study concerns the formation of nanostructure silver from $AgNO_3$ aqueous solution with PVP and the substitution technique to change from copper fine particles to silver on a substrate, based on the displacement plating and PVP reduction effect [15].

2. EXPERIMENTAL DETAILS

2.1. Materials and methods

PVP-K30 ($(C_6H_9NO)_n$ molecular weight av. 40 000), $AgNO_3$ (99.8%), and fine copper particles (99.99%, ca. 1 μm in size, protected from oxidation) were purchased from Tokyo Chemical Industry Co., Ltd. (Japan), Nacalai Tesque Inc. (Japan), and Kojundo Chemical Laboratory Co., Ltd. (Japan), respectively, and used as received. Distilled and deionized water was used as the solvent. Acrylic, polystyrene, and polyethylene plates were used as a substrate.

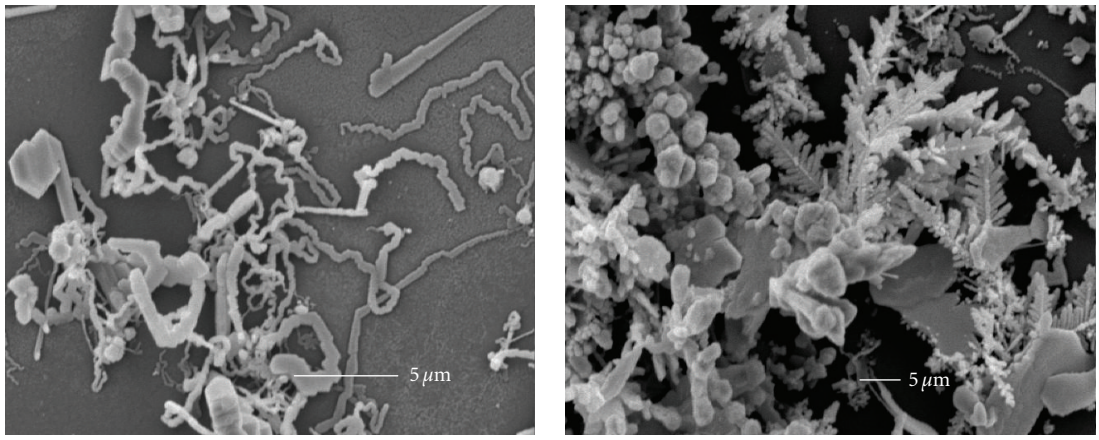
Plastic plates were ultrasonically cleaned in distilled and deionized water for 5 minutes, and dried by air splay as a substrate. Copper particles were daubed by pressing to be a support between the plastic plates, and then the weak contact particles were brown off by gas splaying. The plastic plate was hung by nylon yarn with sticking the side of copper particles into the solution, and set on parallel to the bottom of beaker. Then the silver was grown at 25°C on this plate in a 0.1 M-$AgNO_3$ aqueous solution with 0 to 100 μM-PVP for 24 hours.



(a) (b)

(c) (d)

Figure 1: SEM images of the silver metal obtained by ionic exchange from fine copper particles on acrylic plastic plate in the various concentrations of PVP and 0.1 M-$AgNO_3$ aqueous solutions at 25°C for 24 hours.



(a) (b)

Figure 2: SEM image of the silver metal obtained by ionic exchange from fine copper particles on acrylic plastic plate in 0.1 M-$AgNO_3$ aqueous solutions without PVP at 25°C for 24 hours.

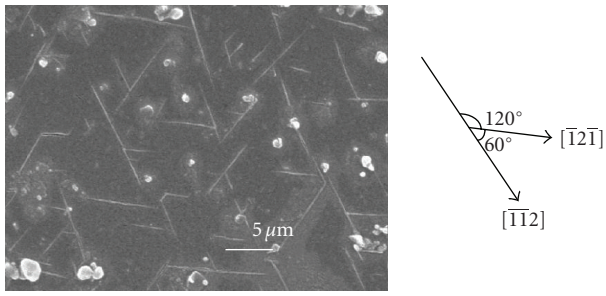
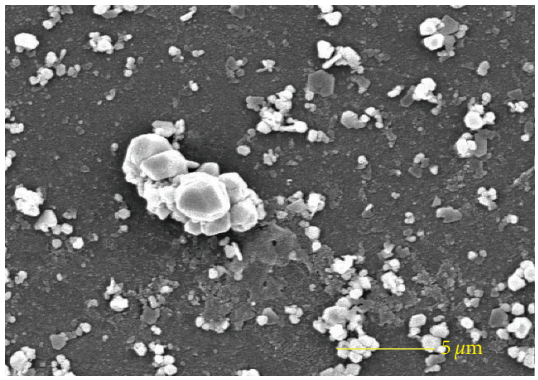
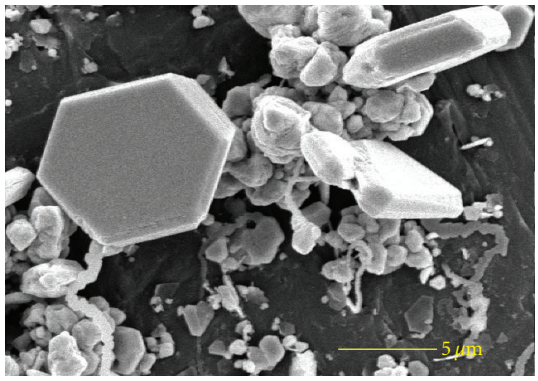


Figure 3: SEM image of the silver rod, which was focused on substrate, obtained from the fine copper particles on acrylic plastic plate in 50 μM-PVP and 0.1 M-$AgNO_3$ aqueous solution at 25°C for 24 hours.



(a)



(b)

Figure 4: SEM images of the silver on polystyrene (a) and polyethylene (b) substrates which were synthesized by being immersed in 50 μM-PVP and 0.1 M-$AgNO_3$ aqueous solution at 25°C for 24 hours.

The electron transfer reaction from copper metal particle to silver metal is a simple reduction-oxidation reaction of

$$Cu + 2Ag^{+} \longrightarrow Cu^{+} + 2Ag, \quad (1)$$

where the reaction takes place at the surface of copper metal and proceeds from the difference in the redox potential between $Cu/Cu^{2+}$and Ag/Ag^{+}.

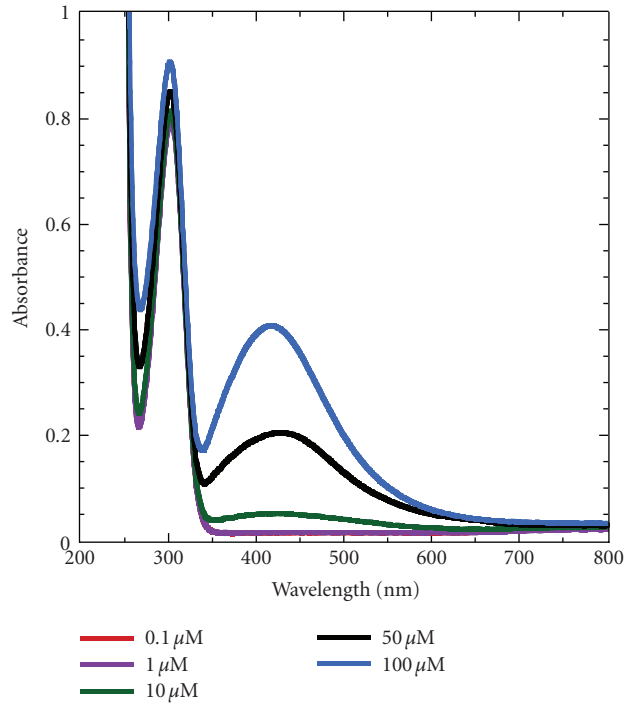


Figure 5: Absorbance spectra of various concentrations of PVP and 0.1 M-$AgNO_3$ aqueous solutions after 24 hours at 25°C.

2.2. *Evaluation methods*

The morphology of the silver metal obtained from each sample was observed by scanning electron microscope (SEM, JEOL-5310LVB). The absorbance of solution containing nanoparticles silver was measured with a Shimadzu UV-3150 spectrometer at room temperature in the wave length ranging from 200 to 800 nm.

3. RESULTS AND DISCUSSION

SEM images of the silver metal obtained by ionic exchange from fine copper particles on acrylic plastic plate in the various concentrations of PVP and 0.1 M-$AgNO_3$ aqueous solutions are shown in Figure 1.When the silver was grown in the region from 1.0 μM to 10 μM PVP concentration solution, the silver composed of needle-shaped, string-shaped, and board- shaped was grown on the acrylic substrate. It is understood that the string-shaped silver being twisted has a tendency to decrease in comparison with the case of no addition of PVP as shown in Figure 2. In this case, a growth direction was unified, because PVP molecules had a coordination place around the silver [16].

Particle-shaped silvers were observed in the $AgNO_3$ aqueous solution with PVP concentration of 100 μM. Even if the silver particles had been aggregated, dendrite-shaped silver would not have been formed. We can consider that the silver grows uniformly, because the reducing PVP molecules, which have a reduction effect [15], are fully coordinated around the silver particles in the region of high PVP concentration.

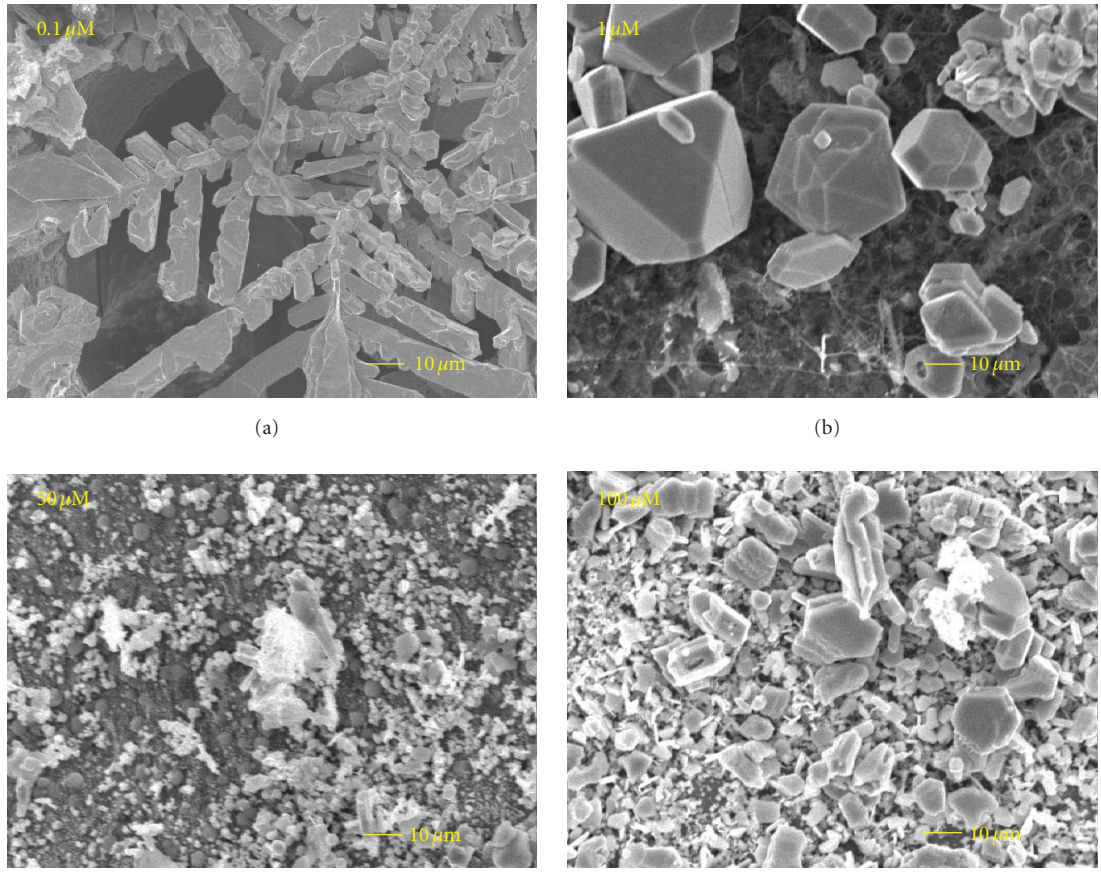


FIGURE 6: SEM images of the silver obtained by ionic exchange from copper plate for TEM sample grid to silver metal in the various concentrations of PVP and 0.1 M-$AgNO_3$ aqueous solution at 25°C for 5 minutes.

Figure 3 shows the SEM image of the silver rod, which was focused on the substrate, obtained from the fine copper particles on acrylic plastic plate in 50 μM-PVP and 0.1 M-$AgNO_3$ aqueous solution at 25°C for 24 hours. An average diameter of silver rods was 119 ± 25 nm in size. As the angle of branching is 60 degrees between branch and trunk, we can consider that the silver crystal growth direction is (211) direction.

To see the influence of the substrate on the grown particles, the copper particles supported by polystyrene and polyethylene were used as a substrate with the combination of 50 μM-PVP and 0.1 M-$AgNO_3$. The SEM images of the silver, on polystyrene and polyethylene substrates, which was synthesized by being immersed in the aqueous solution at 25°C for 24 hours are shown in Figure 4.

Regular arranged needle-shaped silver was not formed on the polystyrene and the polyethylene substrates. In the present work, we can assume that a strong electronegativity of CN groups composed of acrylic substrate significantly affects the growth of nanosize silver, that is, it contributes to attract the PVP molecules.

The absorbance of UV-visible light for various concentrations of PVP and 0.1 M-$AgNO_3$ aqueous solution, which is the samples after 24 hours, is shown in Figure 5. The absorbance of the plasmon peak around 410 nm increased with increasing the PVP concentration in 0.1 M-$AgNO_3$ aqueous solution. The peak position means that the silver in nanoparticles size is formed and the size is 20–30 nm [1]. The position of these plasmon peaks was shifted to shorter wavelength with an increase of the PVP concentration. This blue shift suggests that the size of silver particles decreased by protective effect with increasing the PVP concentration.

Figure 6 shows the SEM images of the silver obtained by ionic exchange from copper plate for TEM sample grid on in the various concentrations of the PVP and 0.1 M-$AgNO_3$ aqueous solution. Dendrite-shaped silver was observed at low concentration of PVP in 0.1 M-$AgNO_3$ aqueous solution, but not observed in high PVP concentration. It suggests that PVP protective effect increases with increasing the PVP concentration as well as fine copper particles as a reducer.

4. CONCLUSIONS

The silver rods having a partly regular direction on the substrate were obtained from the fine copper particles on acrylic plastic plate immersed in 50 μM-PVP and 0.1 M -$AgNO_3$ aqueous solution at 25°C for 24 hours.

An increase of the PVP concentration in the $AgNO_3$ aqueous solution inhibits the growth of the string-shaped silver and dendrite-shaped silver as well as polyol method.

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