

Silver Immobilization on Honeycomb-patterned Polyvinylpyrrolidone thin Films *via* an Electroless Process

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Honeycomb-patterned polyvinylpyrrolidone (PVP) thin films coated with nanometer-sized silver particles were prepared using honeycomb-patterned polystyrene (PS) template films fabricated by casting a polystyrene solution under humid condition. Silver was first metallized on the patterned PS films *via* silver nitrate (AgNO₃) reduction using tetrathiafulvalene (TTF) and a small amount of PVP as the reductant and dispersing agent, respectively. The effects of AgNO₃, TTF, and PVP solution concentrations during the reduction process in acetonitrile were determined to obtain a uniform silver-coated honeycomb-patterned PS film. Second, the silver-metallized patterned porous PS films were filled with high PVP concentration solutions *via* the spin-coating process. Silver-coated patterned PVP films were obtained by peeling off the PVP layer from the template PS film after drying. The results show that the honeycomb-patterned PVP films uniformly coated with silver particles are conveniently obtained using the silver-coated patterned PS template, although the direct fabrication of these films using water droplets under humid conditions was not feasible because of the water solubility of PVP.

Key Words : Patterned PVP film, Silver reduction, PVP, Silver-immobilized PVP

Introduction

In recent years, composite thin films consisting of nanometer-sized metal or semiconductor particles dispersed in solid dielectric materials such as polymers or glass have been of great interest¹ not only for their novel properties but also for the continuously growing demand for further miniaturization of electronic components, optical detectors, chemical and biochemical sensors, and devices. Silver is typical among the metal nanoparticles because it has high optical excitation efficiency and strong three-order nonlinear optical susceptibility $\chi^{(3)}$.² Thus, silver-dispersed polymers have received considerable attention³ because the resulting nanocomposites can be used in catalysts, drug and wound dressings, as optical information storage, and in surface-enhanced Raman scattering, among others.⁴ Many different approaches, such as incorporation of metal particle to the polymerization process or *in-situ* gamma radiation-induced chemical polymerization method etc., have been used to prepare metal/polymer nanocomposites.⁵ Conventionally, metal nanoparticles are formed by first reducing a metal salt and then mixing the polymer and the nanoparticles to prepare the composites *via ex situ* methods.⁶ However, the formation of homogeneous dispersing silver nanoparticles on a polymer matrix is difficult because the nanoparticles easily agglomerate. Thus, convenient and effective ways of preparing silver nanoparticles in polymer materials are yet to be found.

Along with the composite thin polymer films with dispersed nanometer-sized metal particles, dimensionally organized

matrix structures with highly ordered porous polymer films have also attracted increased interest because of their potential applications in chemistry, biology, life science, and material technology. Porous films with ordered structures have been fabricated by a variety of methods such as lithography, the use of colloidal crystals, self-assembly, and a rod-coiled copolymers process.⁷⁻¹⁰ Microstructured materials can be prepared by downsizing engineering techniques in which micro-sized patterns are printed onto a material.¹¹ However, these lithographic methods are complicated and expensive. Self-organization and self-assembly of functional materials have been widely used along with the bottom-up process for the formation of a functional interface, whereas microporous structures can also be fabricated *via* the self-organization technique.^{12,13} Among many porous polymer film fabrication methods,¹⁴⁻¹⁶ breath figure formation is a simple and useful technique.¹⁷⁻¹⁹ The honeycomb films are generally fabricated using a hydrophobic polymer such as polystyrene together with an amphiphilic copolymer under a highly humid atmosphere; many kinds of substrates, including star polymers, block copolymers or proteins, and polymer composites, are fabricated using this method. The porous structure bases on the hexagonal packing of water microspheres are formed *via* the condensation of gaseous water at the air-polymer solution interface during solvent evaporation.

Electroless plating is a widely used method for surface metallization and is a purely chemical process that involves the reduction of metal ions on solid surfaces *via* chemical adsorption, sputtering, or vapor deposition.²⁰ A major advantage of electroless plating is on its applicability to a wide

variety of materials, including insulating surfaces such as glass, silicon oxide surfaces, and organic polymers, without the need for any electrical equipment. Yabu *et al.* recently used this technique for silver metallization on a honeycomb-patterned polystyrene film prepared *via* the simple breath figure process²¹ and using polymer films bearing Pt/Pd catalysts on their surfaces. Before electroless plating, the Pt/Pd catalyst was sputtered onto the surface of a honeycomb-patterned or pincushion film for 50 s, depositing a *ca.* 10 nm thick Pt/Pd layer. The film was soaked in an aqueous solution of silver nitrate (AgNO₃) after the deposition of the catalyst layer. Ag was deposited onto the Pt/Pd catalyst sites according to the hydrazine reduction reaction. Basically, the surface of the polystyrene is hydrophobic, but the formation of the Pt/Pd catalyst layer hydrophilized the surface. As a result, the plating solution penetrated into the pores and the metal layer was formed.

On the other hand, for the electroless metal plating, water-soluble polymers such as polyvinylpyrrolidone (PVP) or polyvinyl alcohol (PVA) are also effective in particle dispersion²² because they are absorbed on the metal surface and protect the ultrafine particles from coagulation caused by electric or steric repulsion between the absorption layers. PVP is one of the best polymers for metal nanoparticle immobilization because of the strong affinity of the pyridyl group to metals and its ability to undergo hydrogen bonding with polar species. Some metal and semiconductor nanoparticles have successfully been prepared in the presence of PVP in solution.²³ However, a direct preparation of honeycomb-patterned film *via* PVP solution casting under humid conditions is not possible because of the low solubility of PVP in chloroform.

In the current study, a simple and effective process for Ag immobilization on the honeycomb-patterned PVP films using an electroless method is presented. Ag immobilization of the patterned PVP polymer film was performed in two steps. First, Ag was metallized onto the honeycomb-patterned polystyrene (PS) films *via* AgNO₃ reduction in acetonitrile solution using tetrathiafulvalene (TTF) and dilute PVP as the reductant and dispersing agent, respectively. The honeycomb-patterned PS films were prepared by casting a PS solution under humid condition. Second, the Ag-metallized honeycomb-patterned PS films were filled with high concentrations of PVP solution *via* the spin-coating method and dried at room temperature. The metallized Ag particles were adsorbed onto the PVP film when the PVP layer was peeled from the Ag-metallized honeycomb-patterned PS film.

Experimental

Materials. The PS standard (average M_w 400,000 g mol⁻¹, Aldrich Co. product No. 330353) and TTF were purchased from John Matthey Co. AgNO₃, PVP (average MW 40,000 g mol⁻¹), chloroform (99.8%), and acetonitrile (99.8%) were all obtained from Aldrich Co.

Procedure.

Preparation of a Patterned PS thin Film as a Template:

The procedure for the preparation of patterned PS thin films was introduced in a previous report.²⁴ A solution of PS in chloroform was cast on a glass Petri dish. The solution was allowed to completely evaporate under humid condition, and an opaque film was obtained. Evaporated water was applied on the solution surface through an air pump at a flow rate of 0.6 L/min to acquire a highly ordered honeycomb-patterned structure. The microporous film was formed *via* the condensation and deposition of water droplets on the solution surface resulting from evaporative cooling. The solution was cast on a glass dish with a 90 mm diameter at a 20 °C temperature and a 60% relative humidity. Well-ordered honeycomb-patterned PS films were obtained *via* the addition of an amphiphilic copolymer (P₁) to the PS solution. The copolymer was prepared *via* the copolymerization of dodecylacrylamide and 6-hexaamido acrylic acid.²⁵ For the preparation of the honeycomb-patterned PS film, the total amount of polymer used was kept constant at 0.25 g in 4 mL chloroform.

Preparation of Convex-structured PVP Films Using the PS Film Template:

Before obtaining the Ag-metallized honeycomb-patterned PVP film, a pure-patterned PVP film was fabricated by casting the PVP solution on the porous patterned PS films. The patterned PS films were filled with a highly concentrated PVP solution (3.52 mM) in acetonitrile through the spin-coating (1000 rpm, 30 seconds) method. Patterned PVP films were obtained by separating the PVP layer from the PS film after drying for 24 h at room temperature. The obtained film structure was observed under an optical microscope (Olympus BX-51), and the images were processed using the Motic Image Plus 2.0 image acquisition software. The detailed patterns of the obtained structures were observed under a scanning electron microscope (SEM; COXEM CX-100s).

Electroless Ag metallization on the PVP films: Ag metallization on the patterned PVP films was attained in two steps, namely, Ag metallization on the PS film and Ag-PS film deposition on the PVP film. For Ag metallization, AgNO₃ was reduced using TTF and PVP as the reducing and dispersing agents, respectively. TTF derivatives are known to act as electron donors and form stable charge-transfer complexes with a variety of organic and inorganic acceptor species.²⁶

AgNO₃ was dissolved in 25 mL acetonitrile, and a small amount of PVP was added to the solution to inhibit the aggregation of the reduced Ag particles. TTF was then added to the solution under vigorous stirring at room temperature, and the PS template film was soaked in the solution for 24 h. The color of the reaction mixture gradually changed from yellow to dark brown under continuous stirring. The Ag nanoparticle-coated PS template film was then dried at room temperature for 24 h, and then Ag nanoparticle-coated porous PS template was filled with a high concentration PVP solution (3.52 mM) to prepare the Ag-metallized patterned PVP film. After drying, the PVP layer was detached from the PS template. The Ag particle

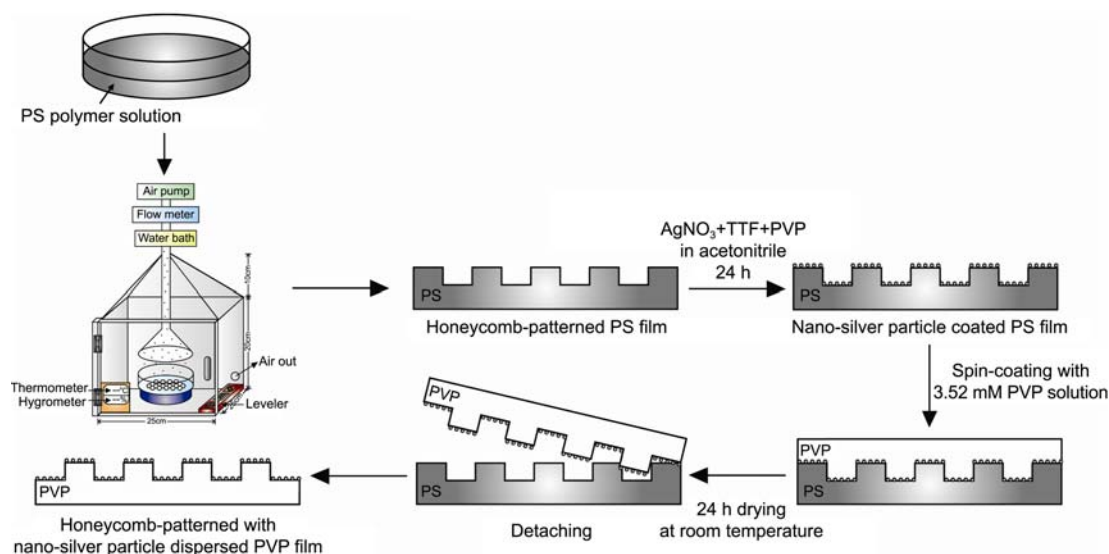


Figure 1. Overall experimental scheme, from the preparation of the honeycomb-patterned PS film to the formation of the Ag-coated patterned PVP film.

coating was analyzed using SEM (COXEM CX-100s). The overall experimental scheme is shown in Figure 1.

Results and Discussion

Patterned PVP Film Depending on the Structure of PS Template Film. Figures 2(a) and (b) show typical surface of PS films. Figure 2(a) shows an irregularly ordered pattern obtained without the addition of any amphiphilic copolymer, whereas Figure 2(b) shows a typical well-ordered honeycomb-patterned film obtained *via* the addition of the amphiphilic copolymer of P₁. The left-side images in both figures are the surface images and on the right are the cross-sectional images. A 10% P₁ solution was added to the casting solution to obtain a well-ordered pattern. Figures 2(c) and (d) show patterned thin PVP films obtained by casting the PVP solution on the patterned PS films shown in Figures 2(a) and 2(b), respectively. The patterned PVP films have a convex structure because the films were obtained by peeling off the PVP film from the porous PS film.

Ag Metallization on the Patterned PS Film. Reaction 1 shows the mechanism of AgNO₃ reduction by TTF and PVP in acetonitrile. PVP assists in the reduction of Ag and acts as a dispersing agent of the reduced Ag particles.²⁶ Therefore, Ag metallization on the patterned PS film should be considered by varying the concentration of each reactant (*i.e.*, AgNO₃, TTF, and PVP). Figure 3 shows the typical SEM images of the Ag-metallized honeycomb-patterned PS film obtained from AgNO₃ and TTF in acetonitrile without the addition of PVP. The SEM images in Figures 3(a)-3(c) were obtained from different [TTF]/[AgNO₃] ratios, namely, 0.5, 1.0, and 1.5, respectively, at constant [AgNO₃] as 0.704 mM.

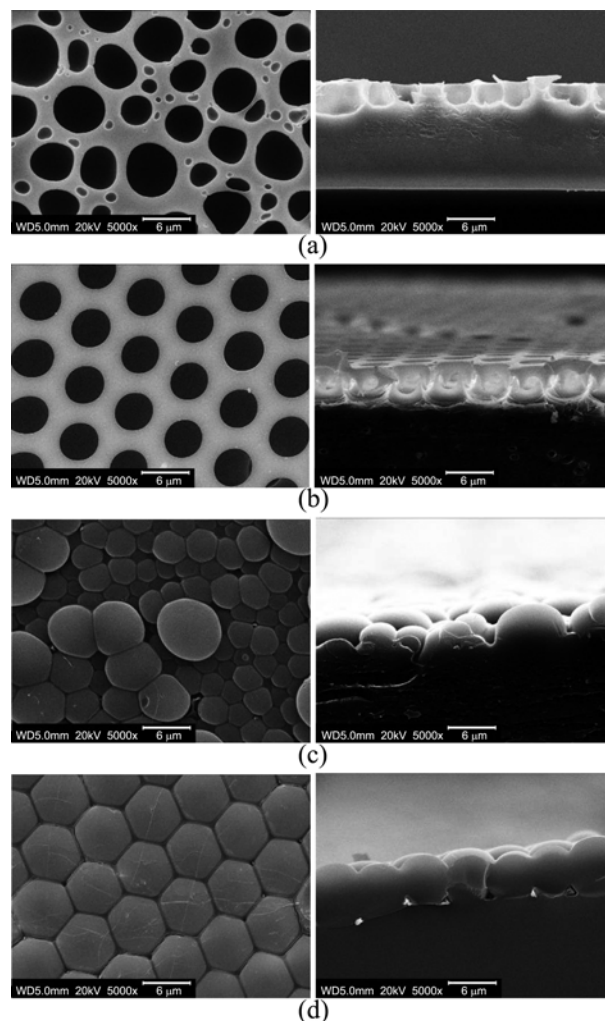
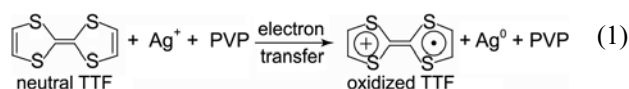


Figure 2. Typical SEM images of PS and PVP film surfaces. (a) Irregularly ordered PS film obtained without amphiphilic copolymer P₁, (b) Well-ordered honeycomb patterned PS film by addition of P₁. (c) PVP film obtained by using the irregularly ordered template PS film given (a), (d) PVP film obtained by using the well-ordered template PS film given (b).

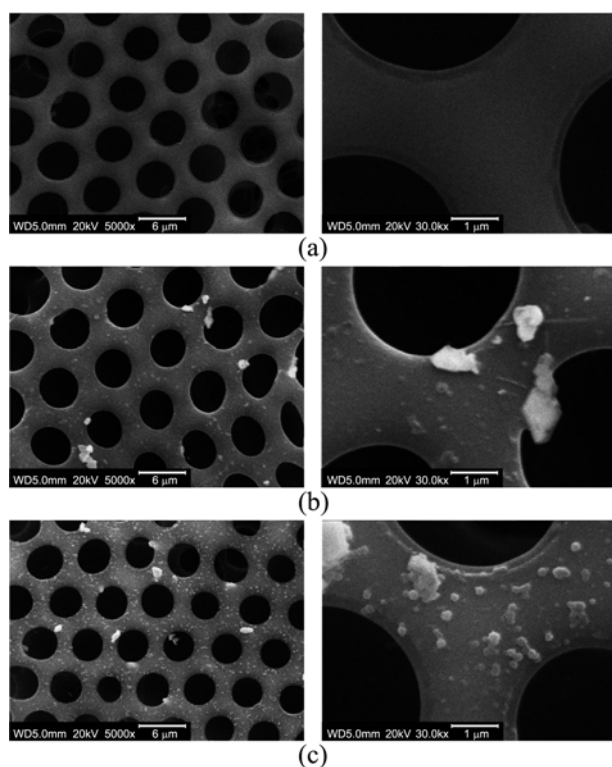


Figure 3. SEM images showing typical Ag-metallized honeycomb-patterned PS films obtained from AgNO_3 and TTF at different TTF concentrations. $[\text{TTF}]/[\text{AgNO}_3]$ is (a) 0.5, (b) 1.0, and (c) 1.5, with $[\text{AgNO}_3]$ kept constant at 0.704 mM.

Reduced Ag particle was not easily detected at a low TTF concentration as shown in Figure 3(a). The reduced Ag particles were appeared on the patterned PS film by increasing [TTF] as shown in Figure 3(b) and 3(c). However, the reduced Ag particles show an irregular size distribution, from 50 nm to an aggregated lump. This result well agrees with the general experimental results that the electroless chemical metallization without surfactants may produce aggregated metal particles than well-distributed particles.²²

Figure 4 shows the effect of PVP as a dispersing agent on AgNO_3 reduction. Figures 4(a)–(c) show the typical SEM images when the $[\text{PVP}]/[\text{TTF}]$ ratios was changed as 0.5, 1.0, and 1.5, respectively, at constant $[\text{AgNO}_3]$ and [TTF] which were kept as 0.704 mM. The results clearly show that PVP facilitates Ag metal reduction and Ag particle dispersion. In the low concentration of PVP, reduced silver was not complete particles rather shows lump as shown in Figure 4(a). By increasing the concentration of PVP, homogeneous Ag particles without aggregation were obtained as shown in Figure 4(b). The effect of PVP is well shown in Figure 4(c), in which uniformly distributed small-sized silver particles are obtained. Figure 5 more clearly shows the role of PVP as a dispersing agent. Figures 5(a) and 5(b) are the typical SEM images for the coated PS film obtained by increasing $[\text{AgNO}_3]$ to 1.5 and 2.0 times higher than the condition to obtain the coated PS film shown in Figure 4(c) at the same [PVP] and [TTF]. The inset image in Figure 5(b) shows the

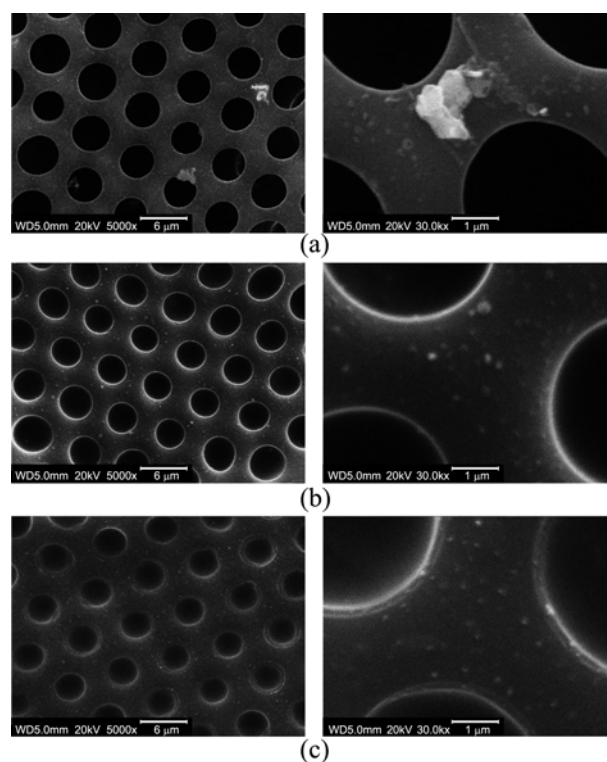


Figure 4. SEM images showing the effect of PVP as a dispersing agent on AgNO_3 reduction. $[\text{PVP}]$ was increased *via* $[\text{PVP}]/[\text{TTF}]$ at (a) 0.5, (b) 1.0, and (c) 1.5, with $[\text{AgNO}_3]$ and [TTF] kept constant at 0.704 mM.

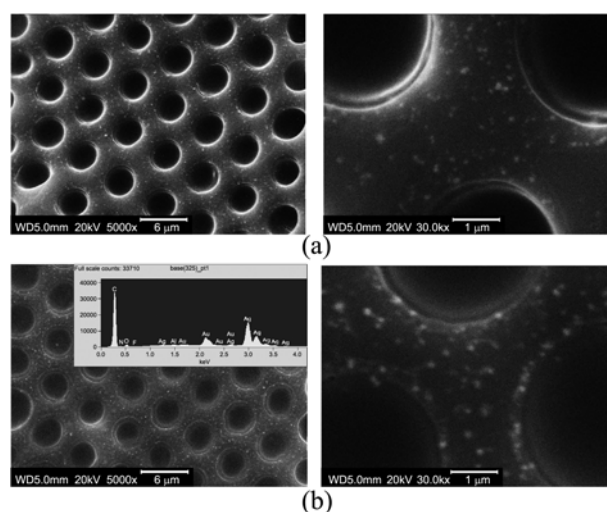


Figure 5. Typical SEM images showing well-dispersed silver particles in the patterned PS films obtained by the increased $[\text{AgNO}_3]$. (a) $[\text{AgNO}_3]$ was increased by 1.5 times, (b) $[\text{AgNO}_3]$ was increased by 2.0 times comparing to $[\text{AgNO}_3]$ used for Fig. 4(c) without changing [PVP] and [TTF].

SEM-EDX for the existence of silver nanoparticles distributed in the films. Au peak in the image should be obtained in the pretreatment process to obtain the SEM image. This result shows that the number of Ag particles coated onto the PS film were increased without aggregation in spite of increased concentration of AgNO_3 in the reduction process,

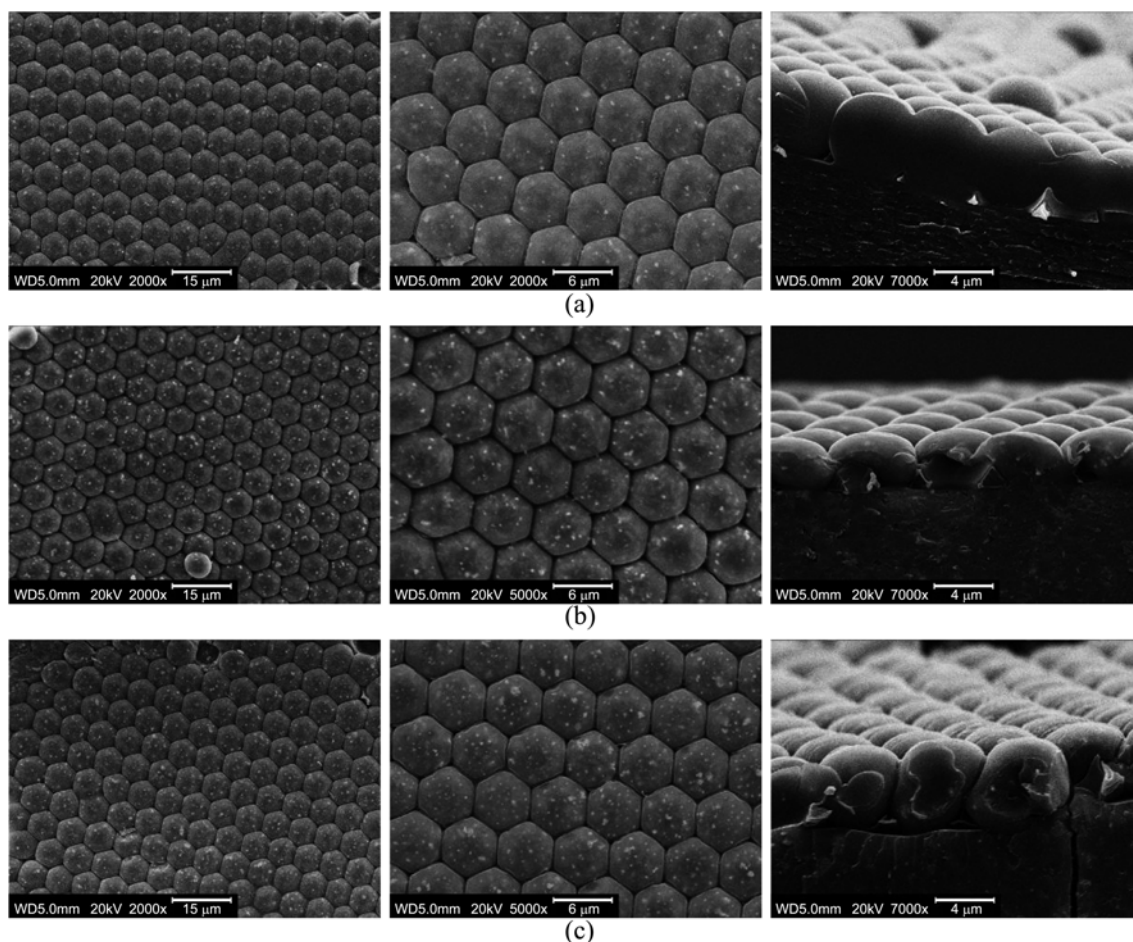


Figure 6. Typical SEM images showing silver-coated PVP films obtained by varying $[\text{AgNO}_3]$ during AgNO_3 reduction for PS film preparation. $[\text{AgNO}_3]$ = (a) 0.704, (b) 1.056, and (c) 1.408 mM. $[\text{PVP}]$ and $[\text{TTF}]$ were kept constant at 1.056 and 0.704 mM, respectively.

and therefore well proves that PVP is a good dispersing agent in the chemical reduction of AgNO_3 .²²

Formation of Ag-immobilized Patterned PVP Films. The patterned PS film coated with Ag particles was filled with the PVP solution through spin-coating to prepare the Ag-immobilized patterned water-soluble PVP film. The PVP concentration used for the spin-coating was 3.52 mM, which is 5 to 10 times higher than the concentration used in AgNO_3 reduction as a dispersing agent. The higher PVP concentration was used to obtain a stable thin film after solvent evaporation by drying the casting solution on the porous PS film. Figure 6 shows typical SEM images of Ag-immobilized patterned PVP films obtained by peeling off the PVP layer from the Ag-metallized honeycomb-patterned PS films after drying. The PVP films shown in Figures 6(a)-6(c) were prepared from the Ag-metallized PS template films using different $[\text{AgNO}_3]$, namely, 1:1.5:2.0, respectively (here, 1 means 0.704 mM), and in the constant $[\text{PVP}]/[\text{TTF}]$ as 1.5 at 0.704 mM of TTF. Figure 6 clearly shows that the Ag particles originally reduced in the PS template films were adsorbed well in the PVP films. The migration of the Ag particles from the PS template to the PVP films may be due to the high adhesive property of PVP. In addition, the Ag nanoparticles shown in the convex-structured PVP films

indicate that the reduced Ag particles originally existed in the pore insides of the honeycomb-patterned PS film were completely migrated into the PVP film although the pore size was not large.

Conclusion

A new process of immobilizing Ag particles on honeycomb-patterned PVP films was introduced. The honeycomb-patterned PVP polymer film was prepared by indirectly since a direct formation of honeycomb patterned PVP film by casting of PVP solution under humid condition was infeasible because of water solubility of PVP. PVP has mainly been used as a dispersing agent for the formation of metal nano-particles such as silver and gold by reduction of the metal ions. Therefore, the formation of metal immobilized PVP films was not feasible by simple reduction process in aqueous solution. After metallization of Ag onto the honeycomb-patterned PS films *via* AgNO_3 reduction in acetonitrile solution using TTF as the reductant, high concentration PVP solution was poured onto the patterned PS film *via* the spin-coating method, dried at room temperature, and peeled off. For the immobilization of uniform-sized silver particles, the concentration effect of used reagents for the reduction pro-

cess was studied in detail. The proposed procedure for the preparation of Ag-dispersed honeycomb-patterned PVP films may have many potential applications including drug delivery and for medical applications.

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