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Preparation of silver nanowires for transparent conductive films

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Silver nanowires with various aspect ratios were successfully synthesized using a polyol method. The diameter and length of the silver nanowires were controlled by changing the reaction variables of initial reaction temperature, injection rate, and molecular weight of poly(vinyl) pyrrolidone (PVP). Silver nanowires with small diameters were synthesized by lowering the initial reaction temperature, while those with longer length were obtained when PVP with a large molecular weight was used. In addition, silver nanowires with a high aspect ratio greater than 3000 were produced by controlling the injection rate of the silver source. For transparent conductive films, silver nanowire ink with a resistance of 10 Ω/square and a transmittance of 80% were produced using a mixture of silver nanowires with high and low aspect ratios.

Key words: Silver nanowires, Aspect ratio, Transparent conductive films, Poly(vinyl)pyrrolidone.

Introduction

Silver has been one of the most favored conductive materials due to its high electrical conductivity and stability. For this reason, silver has been used in various areas of industrial applications such as transparent flexible displays, solar cells, and electronic patterning [1, 2]. The performance of silver in the above applications is significantly enhanced by processing silver into nanostructures with well controlled dimensions, including nanoparticles, nanocubes, nanoplates, nanorods, nanobelts, and nanowires [3-5]. Among these nanostructures, silver nanowires with a one-dimensional structure have been favored for a wide range of applications such as transparent electronic devices and displays due to their low resistance and high transmittance [6-9]. To date, indium tin oxide (ITO) has been extensively used for transparent conducting devices with greater than 80% transmittance and less than 100 Ω/square of resistance. However, the high cost, brittleness, and high deposition temperature prevent ITO from being widely applied in industrial applications [10, 11]. Recently, silver nanowires have received great attention as a substitute for ITO [12-14]. The performance characteristics of silver nanowires have been optimized up to 90% transmittance with 10 Ω/square [15, 16], which could be attributed to their small diameter and long length.

For wider industrial applications of silver nanowires, a simple and scalable preparation process is required. Various synthetic methods for silver nanowires have been investigated over the past decade. In this study, silver nanowires with various aspect ratios were successfully synthesized using a polyol method. The diameter and length of the silver nanowires were controlled by changing the reaction variables of initial reaction temperature, injection rate, and molecular weight of poly(vinyl) pyrrolidone (PVP). For transparent conductive films, silver nanowire ink with a resistance of 10 Ω/square and a transmittance of 80% were produced using a mixture of silver nanowires with high and low aspect ratios.

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Experimental

Materials

The following materials were purchased commercially and were used without further purification. Silver nitrate ($AgNO_3$, JUNSEI, 99.8%), poly(vinyl)pyrrolidone (MW 58,000 g/mol, Acros-Organics, MW 360,000 g/mol, MW 1,300,000 g/mol, Sigma-Aldrich), and copper (II) chloride ($CuCl_2$ anhydrous, 99.0%, Sam-Chun Chemicals) were used for the preparation of silver nanowires. Ethylene glycol (99.0%, Dae-Jung Chemicals) was used both as a solvent and reducing agent. Ethyl alcohol (99.5%, Sam-Chun Chemicals) and acetone (99.5%, Sam-Chun Chemicals) were used as washing solvents. De-ionized water was used for re-dispersion of silver nanowires. For preparation of silver nanoparticles, silver acetate (99%, KOJIMA Chemicals) was used as a silver source, and octylamine (99.8%, JUNSEI) and phenylhydrazine (99%, JUNSEI) were employed as reducing agents. Toluene (99.5%, Dae-Jung Chemicals) was used as a solvent, and methyl alcohol (99.5%, Sam-Chun Chemicals) was used for washing.

Preparations

Preparation of silver nanowires

A three-neck round flask was charged with 100 ml of ethylene glycol and heated to the initial reaction temperature. The initial reaction temperature is known to be one of the main factors influencing silver seed formation. When the initial reaction temperature was reached, 1.15 ml of a copper chloride solution (4 mM, 4.6×10^{-6} mol in ethylene glycol) was added to the flask. Copper(II) chloride has been used to etch silver atoms to form multi-twinned structural particles for the growth of wires. After 3 min, a silver nitrate solution (0.4 M, 25 ml in ethylene glycol) and a poly (vinyl)pyrrolidone solution (PVP, 0.4 M, 25 ml in ethylene glycol) were injected simultaneously at different feed rates. After injection, the reaction flask was maintained at this temperature for 20 min to assure seed formation and was then heated to 180 °C within 15 min. for the growth of nanowires. Silver nanowires were produced in a flask at a final temperature of 180 °C, and the flask cooled to room temperature. The product was centrifuged and washed several times with ethanol and acetone. After washing, silver nanowires were re-dispersed in DI water.

Preparation of silver ink for a transparent conductive film

A hydroxy(propyl)cellulose (HPC) solution (6 wt% in DI-water, 100 μl), used to improve adhesion with the glass substrate, and 300 μl of silver nanowires with a small aspect ratio (1 wt% in DI-water) were blended. Then, a given composition (0.1 wt% ~ 0.5 wt%) of silver nanowires with high aspect ratio was added. Finally, a glass substrate was coated with silver ink by spin coating and was sintered at 200 °C for 30 min.

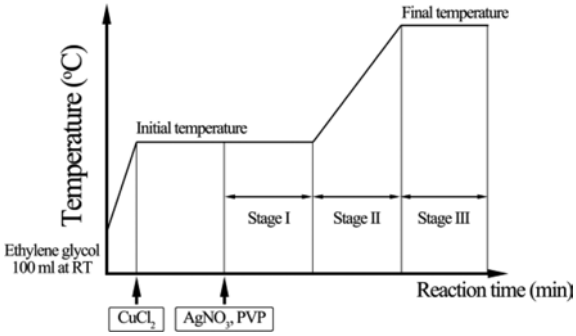
Characterization

Crystallographic structures of the silver nanoparticles and silver nanowires were determined by XRD (X-ray diffractometer, Rint-2000, Rigaku) using Cu-Kα radiation at 40 kV and 60 mA. The size and morphology of the silver nanowires were investigated with TEM (transmission electron microscopy, JEM-2000 EXIT Jeol), SEM (scanning electron microscopy, Model JSM-2010, Jeol), and OM (optical microscopy, BX-21, Olympus). The evolution of silver nanowires and the transmittance of the conductive film were monitored by UV-Vis spectroscopy (S-4100, Scinco). The conductivity of the transparent, conductive samples was measured using a four-point probe (CMT-SR2000N, Jandel).

Results and Discussion

Preparation of silver nanowires

The reaction temperature is one of the most important parameters in the preparation of silver nanowires via a polyol process [17]. In this study, the reaction temperature was divided into an initial temperature and a final temperature of 180 °C.



Scheme. 1. Overall procedure for the preparation of silver nanowires.

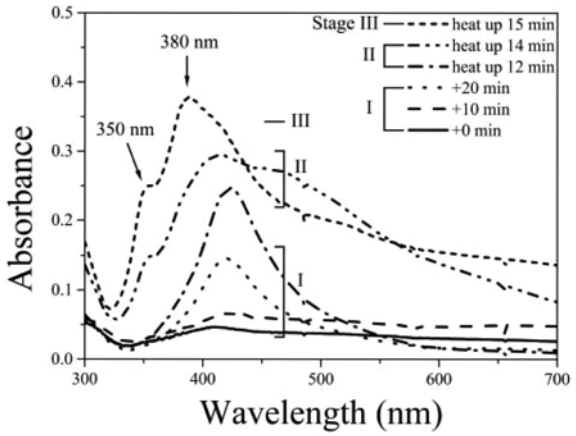


Fig. 1. Changes in UV-Vis spectra during the formation of silver nanowires. Section (a): from 0 min. to 20 min. after injection; Section (b): from 5 min. to 10 min. after heating; Section (c): 15 min. after heating.

The overall preparation procedure for silver nanowires is shown in Scheme 1. In this study, the preparation procedure was divided into three stages, each being maintained at different reaction temperature. In the schematic, Stage I represents silver seed formation after simultaneous injection of silver nitrate and PVP into ethylene glycol containing $CuCl_2$ at the initial temperature. Stage II is the temperature increase from the initial temperature to the final 180 °C. In this stage, silver nanowires with small diameters started to grow along the vertical axis. In Stage III, the vertical axial growth rate of silver nanowires was accelerated by heat energy.

The growth of silver nanowires was monitored by UV-Vis spectroscopy. As shown in Figure 1, changes in UV-Vis spectra were also divided into three different time regions. Figure 1 shows the UV-Vis spectra of a reaction mixture containing PVP with MW of 360,000 g/mol-prepared with Stage I temperature of 100 °C and silver nitrate injection rate of 3 ml/min-at the three different stages. Stage I is a region of initial temperature, where an absorption peak at 410 nm was produced without any wavelength shift, indicating the increase in the number of silver seeds [18]. Stage II

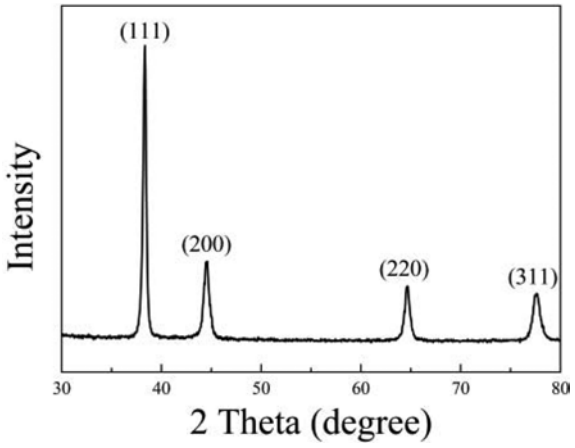


Fig. 2. XRD pattern of silver nanowires.

corresponds to the temperature increase, where the intensity of a peak around 410 nm increased, and the wavelength was blue-shifted due to the growth of nanowires. Two weak peaks were observed at 350 nm and 380 nm, which corresponded to the diameter and length of silver nanowires, respectively. In Stage III, peaks at 350 nm and 380 nm were clearly evolved with the formation of silver nanowires [18]. XRD patterns in Figure 2 exhibited intense peaks centered at 2Θ values of 38.3 º, 44.4 º, 64.6 º, and 77.5 º, indicating the face-centered cubic (fcc) phase of silver nanowires, which were indexed to (111), (200), (220), and (311), respectively [19].

These results confirmed the successful growth of silver nanowires by the suggested Scheme 1 procedure. In below, the effects of reaction parameters of initial temperature and injection rate of silver nitrate as well as molecular weight of PVP on the morphology and aspect ratio of silver nanowires were investigated in detail.

Effect of initial reaction temperature on the formation of silver nanowires

Initial reaction temperature was an important reaction variable for the formation of silver seeds, and the size and crystallinity of the silver seed also strongly influenced the formation. Therefore, the effect of initial reaction temperature on the morphology and aspect ratio of the final silver nanowires was investigated first. SEM and OM images in Figure 3 show changes in diameter and length of silver nanowires prepared at various initial reaction temperatures. As the initial reaction temperature was increased from 80 to 90, 100, and 110 ºC, the average diameter of silver nanowires increased from 34(± 3) nm to 58(± 11), 78 ± 12, 80(± 11) nm, while the length of the silver nanowires increased from 11(± 5) μm to 28(± 5), 34(± 6), and 43(± 5) μm, respectively. The standard deviation and average values were calculated from 50 silver nanowires randomly selected from OM and SEM images. The

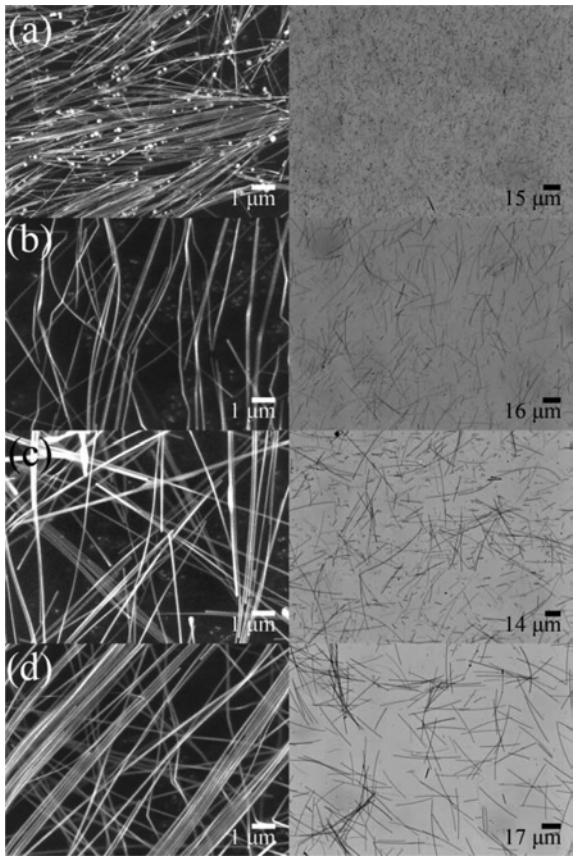


Fig. 3. Effects of initial reaction temperature on the diameter and length of silver nanowires: a) 80 ºC, b) 90 ºC, c) 100 ºC, and d) 110 ºC. Right: SEM images, Left: OM images.

aspect ratio of silver nanowires was also increased from 323 to 540. The differences in diameter and length of silver nanowires were attributed to the morphology and size of the original silver seeds, which was strongly affected by initial reaction temperature. We postulated that a reaction temperature greater than 90 ºC provided sufficient energy to form multi-twinned silver seeds, which were used for the growth of silver nanowires. As can be seen in Fig. 3a, silver nanowires with a low aspect ratio and a large amount of silver nanoparticles were observed at the initial reaction temperature of 80 °C.

Effect of injection rate of silver nitrate on the formation of silver nanowires

Figure 4 exhibits the changes in diameter and length of silver nanowires prepared with different injection rates at an initial reaction temperature of 100 ºC and a final temperature of 180 ºC. As the injection rate of the silver source was increased from 1 ml/min. to 3 ml/min. and 8 ml/min., the diameter of silver nanowires decreased from 65(± 12) nm, to 51(± 7) and 42(± 5) nm, respectively, while the length of the silver nanowire also decreased from 35(± 6) μm to 28(± 7) and 20(± 2) μm, respectively. However, the aspect ratio did not change significantly (from 538 to 549 and 476).

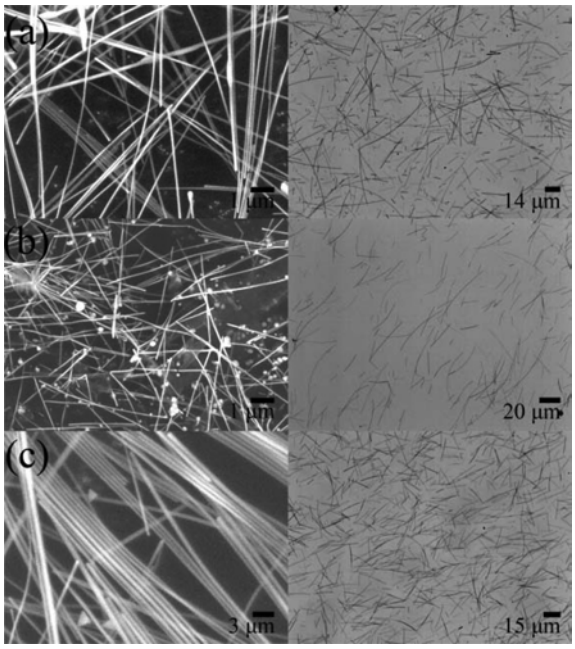


Fig. 4. Effects of injection rate on the diameter and length of silver nanowires: (a) 1 ml/min., (b) 3 ml/min., and (c) 8 ml/min. Right: SEM images, Left: OM images.

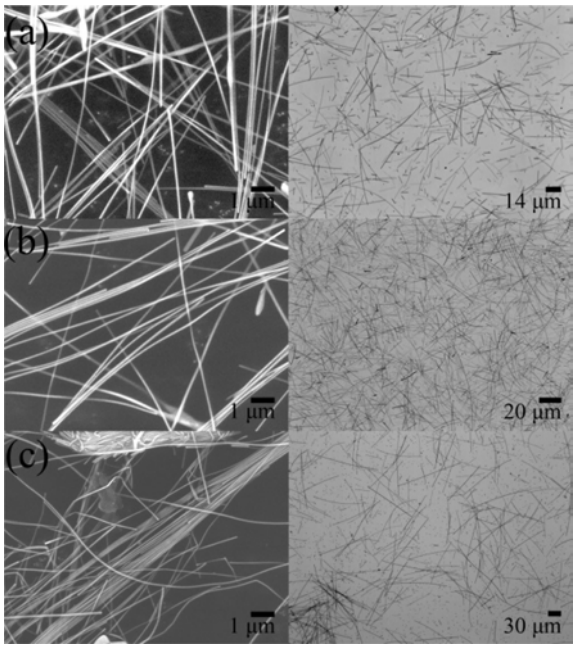


Fig. 5. Effects of molecular weight of PVP on the diameter and length of silver nanowires. (a) MW of 58,000 g/mol, (b) MW of 360,000 g/mol, (c) MW of 1,300,000 g/mol. Right: SEM images, Left: OM images.

It is known that, as the nucleation process becomes dominant, the growth process is slowed. With a high injection rate, large amounts of silver seeds were initially formed by the abrupt nucleation process, resulting in silver nanowires with relatively smaller diameter and length.

Effect of PVP molecular weight on the formation of silver nanowires

Figure 5 shows the changes in diameter and length of silver nanowires prepared using PVP with different molecular weights. As the molecular weight of PVP increased from 58,000 g/mol. to 360,000 g/mol. and 1,300,000 g/mol., the diameter of silver nanowires increased from 65(± 12) nm to 80(± 12) and 100(± 30) nm, and the length of the silver nanowire increased from 35(± 6) μm to 100(± 6) and 300(± 40) μm, respectively. The aspect ratio also increased significantly (from 538 to 1250, and 3000, respectively). Thus, selective adsorption of PVP seemed to block the (100) plane of silver atoms, resulting in deposition of silver atoms on the (111) plane along the (110) axis. With the use of long-chain PVP, which has a higher degree of polymerization, more silver nuclei can coordinate along the vertical axis, producing very long silver nanowires [26].

Preparation of silver nanowire ink for transparent conductive film

In this study, silver nanowires with a wide range of aspect ratios from 350 to greater than 3000 were prepared by controlling various reaction parameters. Two types of silver nanowires with a large difference

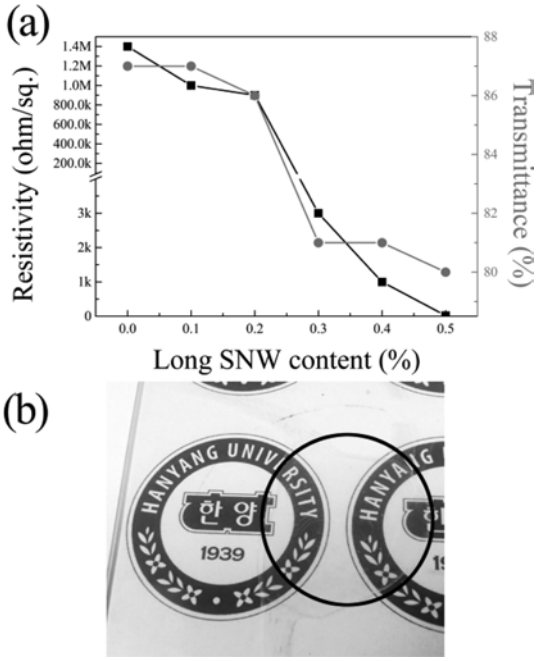


Fig. 6. (a) Resistivity change and (b) transparency of transparent conductive films prepared with a mixture of long and short silver nanowires.

in aspect ratio were used either separately or together to investigate the performance characteristics of conductive ink. First, the film coated with silver nanowires having small diameter and length (40 nm, 20μm) showed a transmittance of 90% and a resistivity of 2 MΩ//square. The surface resistivity of this film was too high to be used for conductive devices even though

the transmittance was suitable for transparent electrodes in a display panel. On the other hand, the film coated with silver nanowires having a long length (over 300 μm) exhibited a transmittance of 40% and a resistivity of 5 Ω/square. In this case, the surface resistivity of a film was low enough for conductive devices, but the transmittance was not sufficient for display panels. Therefore, a mixture of silver nanowires with low and high aspect ratios was used.

As shown in Figure 6, the surface resistivity was decreased to 10 Ω/square and transmittance was reduced to 80% with an increase in the relative amount of silver nanowires having a high aspect ratio. The symbol of Hanyang University was clearly seen through the transparent conductive film coated with 99.5 wt% silver nanowires with small aspect ratio (40 nm, 20 μm) and 0.5 wt% long wires (100 nm, over 300 μm). These results indicate that the silver nanowires prepared in this study can be used as an alternative to ITO.

Conclusions

Silver nanowires with controlled aspect ratios were successfully synthesized via a polyol method. The crystalline structures of silver nanowires were characterized by XRD and UV-Vis spectroscopic analysis, and the morphologies and aspect ratios of silver nanowires were confirmed by SEM and OM. The diameter and length of the silver nanowires were controlled by changing the initial reaction temperature, injection rate, and MW of PVP. Silver nanowires with small diameters were synthesized by lowering the initial temperature. Nanowires with a longer length were obtained using PVP with a large molecular weight. In addition, silver nanowires with a high aspect ratio greater than 3000 were produced by controlling the injection rate. For transparent conductive patterns, silver nanowire ink with a resistance of 10 Ω/square and a transmittance of 80% were produced using a mixture of silver nanowires with small and large aspect ratios.

Acknowledgments

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