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Diameter Control of Silver Nanowires by Chloride Ions and Its Application as Transparent Conductive Coating

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A simple method for the synthesis of silver nanowires (NW) in ethylene glycol is presented here with its diameter controlled by addition of chloride ions. The synthetic process consists of two separating steps, i.e., nucleation and growth. The resulting diameter, between 100 and 55 nm, becomes smaller when more chloride ions are added in the second step. Different silver nanowires are then coated on the glass substrate to fabricate transparent electrodes. A sheet resistance of 10 Ω/sq with optical transmittance of 80% can be obtained.

Silver has been widely used as a conductive material due to its high electrical conductivity. Different shapes of silver, such as nanoparticle, nanorod, etc. have been synthesized under different reaction conditions, and silver NW is also an example.[1,2] Various techniques had been attempted for the synthesis of silver NW, including hard-template and solution phase synthesis. Ju et al.[3] used anodic alumina oxide (AAO) membrane as template to prepare silver NWs array in solution phase by direct chemical reduction at room temperature. On the other hand, Huang et al.[4] utilized the nanoscale channels of mesoporous silica SBA-15 to synthesize Ag NWs. Yet more researchers adopted direct synthesis by polyol reduction. Here quite a few chemicals were used to facilitate the formation of silver NWs, for example, PbCl, CuCl, $CuCl_2$, KCl, KBr, and KOH, to name a few.[5–8] In some examples, precious metal such as Pd or Pt was also used to form seeds for the growth of NWs. Though this topic had been reported by many researchers, there are still subjects worth investigation. For example, in some cases, nanoparticles were still included as by-product to NWs especially when the NW was thinner than 100 nm in diameter. The control of NW diameter over a wide range still lacked clear demonstration.

As a conductive material, Ag NW was applied for transparent electrodes[9–13] or transparent conductive coatings (TCC), which are important for many optoelectronic devices such as touch panels, solar cells, and organic light-emitting diodes. In these applications, a number of oxide materials such as indium tin oxide (ITO), fluorine-doped tin oxide (FTO), and doped zinc oxide were common alternatives.[14–16] Furthermore, due to its unique microstructure, one-dimensional single-walled carbon nanotube also received attention[17,18] as a candidate in TCC application.

In this communication we will demonstrate a simple method to synthesize silver nanowires and to control its diameter by using an ordinary chemical, i.e., KCl. The silver NWs thus obtained will be used to form transparent conductive coating. The performance of the coating will then be rated by conductivity (or sheet resistance) and transmittance for NWs of different dimensions.

A two-step procedure was developed to synthesize Ag NWs by the polyol process. 110 mL of ethylene glycol (EG, boiling point: 197 °C) was used to dissolve poly(vinylpyrrolidone) (PVP, molecular weight: 360000) whose amount was fixed at 1.5 times the molar ratio of total silver in each experiment. The EG solution was magnetically stirred and maintained at 160 °C in an oil bath. Silver nitrate (0.6 g) and potassium chloride (2.25 mg) were mixed and dissolved in 10 mL of EG which was then injected into the PVP solution. The solution color turned dark gray in about 5 min suggesting the formation of nuclei. In the next step, silver nitrate (0.93 g) and different amounts of potassium chloride dissolved in 80 mL of EG were prepared and injected into the above solution, which totaled 200 mL. The very fast rate of addition of solution should also have some effect on the growth of these NWs. The solution temperature at this time would drop to about 130 °C and rose back to 160 °C in 3 min. The reaction was stopped after 30 min of growth time, and the solution was cooled to room temperature. The product was separated by acetone addition, thoroughly washed by deionized water, and redispersed in methanol for the following coating process.

The transparent conductive coating on glass substrate ($2.5 \times 2.5\,cm^2$) was prepared by a spray method using a commercial air spray gun.[10] After coating and thermal annealling at 200 °C for 20 min, the sheet resistance of the film was measured by a four-probe method, and its transmittance to light (550 nm wavelength) by UV–vis spectrometer. When the thermal treatment temperature was 300 °C and for 5 min, the electrical resistance of the film would increase instead of decrease, probably due to melting and then breaking of some fraction of nanowire microstructure.

When $AgNO_3$ was mixed with KCl, AgCl would naturally form, and it was involved in the formation of shapes of silver, including cubes, triangular bipyramids, and rods or wires. Yet, the same research group[19] also found that one could obtain uniform silver NW using air-assisted polyol method with chloride ions.[20] In our two-step procedure only NWs were obtained. Some samples are exhibited in Figure 1 in SEM pictures.

The effect of $[Cl^-]/[Ag^+]$ molar ratio on resulting diameter of silver NW is summarized in Figure 2. The diameter decreased from 100 nm when no chloride ion was added in the second step

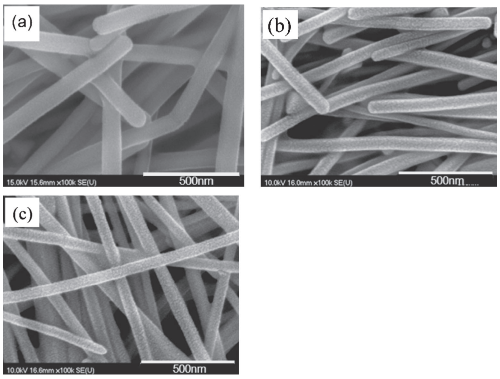

Figure 1. SEM images of silver NWs synthesized with different molar ratios of $[Cl^-]/[Ag^+]$ in second step. (a) 0, (b) 0.0061, and (c) 0.122.

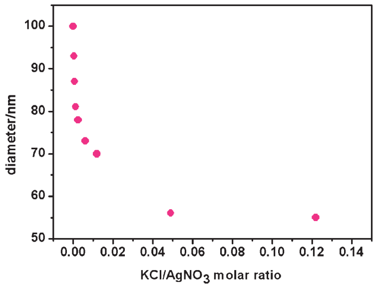

Figure 2. The relation between the molar ratio of $[Cl^-]/[Ag^+]$ (in the second step) and diameter of silver NW.

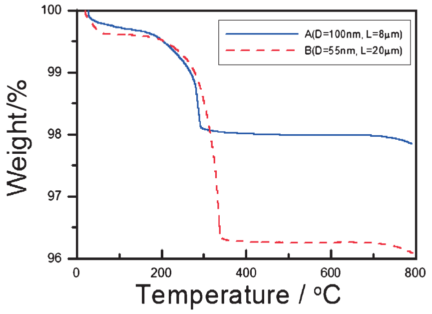

Figure 3. TGA results for two different nanowires showing quantities of residual PVP.

to about 55 nm when the extra chloride ion was more than 0.05 times the concentration of $AgNO_3$. The effect was very significant when the quantity of chloride addition was small, and it became negligible when the molar ratio was above 0.05. The inhibition of growth in Ag NW diameter by chloride ion seemed to suggest preferential adsorption onto the ⟨100⟩ surface of silver. Sun et al.[5] proposed strong interaction between PVP molecules and ⟨100⟩ face of silver to assist the subsequent formation of NWs. The possible interaction (or competition) between PVP and chloride ion required further studies. The NW diameter stopped decreasing when the molar ratio of $[Cl^-]/[Ag^+]$ was above 0.05, suggesting the saturation of adsorption.

TGA analysis, Figure 3, indicated that the residual PVP on silver NW after washing was between 2 and 4%. Here we noticed that PVP molecules started to decompose around 200 °C and completed the decomposition before 350 °C. If we assumed monolayer adsorption, the thickness of PVP adsorption was estimated to be between 5–4 nm based on the dimension of wires. For comparison, the PVP adsorption (MW: 40000) on nanosized silver colloids was estimated to be around 4.2 nm[21] which was consistent with the current finding. Furthermore, potassium contamination in the product was also analyzed by atomic absorption (AA) technique. Our results indicated that the potassium contents were positively correlated with the quantities of added KCl in each experiment and that it changed from about 2 ppm in the 100 nm NW to 55 ppm in 55 nm NWs. Finally, the increased addition of chloride ion showed adverse effect on the yield of silver NW due to the binding power of chloride to silver ion making it unavailable for the growth of these NWs. Our data showed that the yield to silver NW was about 93% for the case of 100 nm NW and dropped to 90% for the case of 55 nm NW, where more chloride ions were added in its synthesis.

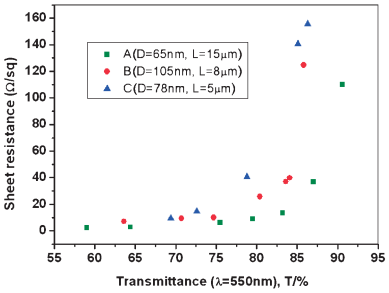

Figure 4. The relation between sheet resistance and transmittance of coatings with silver NWs of different scales.

Next, we used three different NWs to fabricate transparent electrodes on the glass substrate by spray method. A concentration of 250 ppm in silver NW was used after preliminary test runs. The respective scales of silver wires were $\varphi = 65\,\text{nm}$, $L = 15\,\mu\text{m}$ for coating A; $\varphi = 105\,\text{nm}$, $L = 8\,\mu\text{m}$ for coating B; and $\varphi = 78\,\text{nm}$, $L = 5\,\mu\text{m}$ for coating C. Figure 4 showed the transmittance and resistance behavior of these coatings. When the coating was thin, both transmittance and sheet resistance were high. Both data decreased when the coating became thick as shown in this figure. Also from this figure, we could conclude that the best result was obtained from coating A, i.e., when the wires were thin and long. A transmittance of 80% and sheet resistance of $10\,\Omega/\text{sq}$ were obtained when the NW loading was about $70\,\text{mg}\,\text{m}^{-2}$.

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