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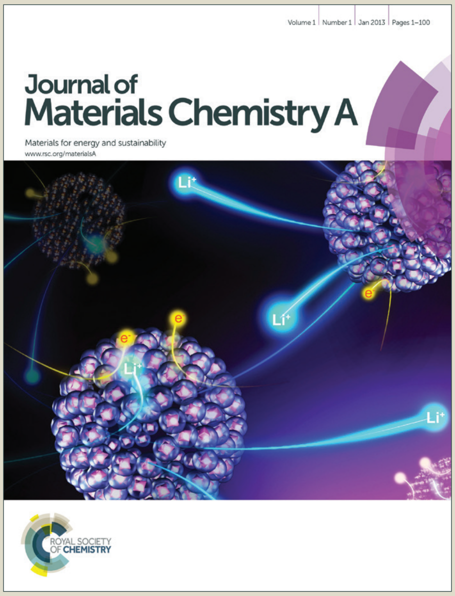

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Facile synthesis of very-long silver nanowires for transparent electrodes

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Silver nanowires >60 µm and even 100 µm in length have been synthesized using a polyol process by adjusting the stirring speed at 130°C. The length is over three times longer than those normal AgNWs. These wires have a uniform ~60 nm diameter, independent of the stirring speed. At 91% transmittance at 550 nm, AgNW films fabricated at room temperature achieved 25 Ω/sq sheet resistance, which is superior to that of expensive ITO films.

Future electronics will be bent, stretched, compressed, twisted, and deformed into complex, non-planar shapes. Meanwhile, they must still maintain a good performance, reliability, and integration. In many of these electronics, transparent electrodes are the core component for the touch screens, liquid crystal displays (LCDs), organic light emitting diodes (OLEDs), and solar cells that have been exhibiting a tremendous rapid growth over the years. Indium tin oxide (ITO), which is the dominant transparent conductor material, is now being substituted with the next generation of flexible transparent materials such as carbon nanotubes (CNTs), graphene, and metal nanowires.[1] Among these candidates, metal nanowires, especially silver nanowires (AgNWs), have gained attention as an alternative transparent conductor because it has the best conductivity, simple and large-scale preparation process, facial and inexpensive solution-based film manufacturing.[2-4] Although these AgNWs electrodes have achieved a high transmittance of over 90% and low sheet resistance of 49 Ω/sq, most of the methods only yield a high sheet resistance when different types of post-processes are used, such as thermal, mechanical, electrochemical, integration with other materials, plasmonic welding processes, and special fabrication conditions, because the current widely used AgNWs are relatively short (1–20 µm).[5-10]

The performance of the AgNWs electrodes mainly depends on a myriad of characteristics including the nanowire structure (length, diameter, size dispersity, and composition) as well as the overall network morphology.[11-13] Some conclusions have suggested that the length and diameter of the wires are critical factors for enabling the high transparency with a low haze, high electrical conductivity, and superior mechanical compliance and strength, which are usually hard to achieve simultaneously. This is because long wires with small diameters can form a more effective network with fewer wires number density by providing longer percolation paths and reducing the inter-nanowire junctions where the major contact resistance drop occurs. Therefore, extending the length of wires and keeping the diameter as low as possible is a simple solution process that has been a great challenge in the AgNWs field.

Over the past few years, the polyol process has been the most promising method for preparing AgNWs by using poly(vinylpyrrolidone) (PVP) as the capping agent and ethylene glycol (EG) as the solvent and reducing agent to reduce $AgNO_3$ into Ag nanowires.[14-16] In the polyol process, many factors such as additive agents, temperature, stirring speed, ratio of chemicals, reaction times, and injection speed of chemicals have always affected the yield and morphology of AgNWs.[13-16,18-24] However, very few studies attempted to synthesize long and thin AgNWs. Although Bergin *et al.*[13] claimed that low temperatures of 130°C and long reaction times of about 12 h can achieve long wires, the wires were below 25 µm and contained a broad distribution and large diameter. Coskun *et al.*[19] have experimentally shown that a slow stirring speed was conductive to growing long wires; however, the length is below 30 µm with diameter over 120 nm. Recently, Araki *et al.* [34] have prepared ultra-long AgNWs at low temperature of 110°C with low stirring speed. The length is in the range of 20-100 µm with a wide distribution and big diameter. Thus far, the most successful approach for the formation of very long AgNWs has been reported using a multistep repeating process, in which the pre-synthesized AgNWs play the role of nucleation sites for longer NW growth in an Ag ion-rich environment with polyol methods.[25-28] Although there has been some very long wires (over several hundred micrometers), which have been obtained using the multistep process, a broad AgNW length distribution was always observed owing to the process simultaneously including two growth models, i.e., the successive long AgNWs growth from the prior steps and fresh short AgNW growth from the seed nanoparticles. Also, the diameter of the AgNWs has been enlarged to over 150 nm, which is far bigger than the single-step polyol process that produces a width of only 60–70 nm. Therefore, the search for suitable synthesis methods capable of controlling the length and diameter of AgNWs are still an emerging strategy today.

We have performed an extensive literature search and carefully distinguished and summarized the parameters that affect the morphology of AgNWs in the polyol process. We found that, except for the reaction temperature, it appears that the stirring speed is crucial. This reminded us of the phenomenon of crystal growth. In order to guarantee the growth of crystal, the number of nucleation sites, mechanical agitation of the system, and time should be controlled. Thinking of the one-dimension growth behavior of AgNWs, it is reasonable and necessary to keep the synthesis system still to avoid disturbing the oriented growth of the wires.

Therefore, a simple and straightforward polyol process method is proposed to grow very-long AgNWs by only adjusting the stirring speeds. Long AgNWs of over 60 µm with a small diameter of about 60 nm have been successfully synthesized. In contrast with the above-mentioned methods, the single-step and one-pot polyol process is significant in science and industry. At last, the prepared long AgNWs have been applied to form transparent conducting films using a straightforward drop-coating method at room temperature and discussed the transmittance and sheet resistance of the film.

For a typical synthesis of very-long AgNWs, a one-pot reaction was employed to mix all compounds and solvents. Briefly, 0.2 g of PVP (M_W = 360000) was first added to 25 mL of ethylene glycol (EG) and completely dissolved using magnetic stirring at room temperature, Afterwards, 0.25 g of silver nitrate ($AgNO_3$) was added to the PVP solution. Complete dissolution was required to obtain a transparent and uniform solution. Finally, 3.5 g of a $FeCl_3$ salt solution (600 µM in EG) was dumped into the mixture and stirred for one or two minutes. The mixture was then immediately transferred into a preheating to 130°C reactor to grow AgNWs for 5 h until the reaction was complete. Afterwards, acetone and ethanol were used to wash the precipitate with centrifugation of 4000 rpm for 5 mins. Finally, the AgNWs were re-dispersed in ethanol for future use.

During the polyol process, the molar ratio of $AgNO_3$/PVP, the concentration of additives such as HCl, NaBr, NaCl, $FeCl_3$ or $CuCl_2$ have been studied in detail in References 13-19. Therefore, these parameters will not be discussed in this work. Moreover, the reaction temperature affected the reducing power of EG; therefore, AgNWs were generally synthesized at about 150°C, which is a moderate and soft reaction condition for the growth of the Ag nucleus to achieve nanowires that are 10–20 µm in length and 70 nm in diameter.[5-10,14-16] In order to extend the length of the AgNWs, low reaction temperatures of 130°C[13], and no agitation[19] have been proposed to extend the length of AgNWs. Hence, in present work, the stirring speed and temperature have been discussed and shown to affect wire lengths.

First, the stirring speed was adjusted to observe the effect on the length and diameter of AgNWs. Fig. 1 SEM images show the effect of stirring speeds on the length of AgNWs. It is clear that the length of wires largely depends on the stirring speed. In addition, a high speed of 700 rpm produced short wires as well as a greater amount of irregular particles and big rods (Fig. 1a). However, a lower speed of 300 rpm produced long wires and decreased the amount of nanoparticles (Fig. 1b). Furthermore, no shaking solution produced very-long AgNWs without separate nanoparticles (Fig. 1c). The clear length distribution photos have been obtained using optical microscopy at a low magnification (VH-Z500, VHX-600, Keyence Co.) and were shown in supporting information (Fig. S1). The length distribution is summarized in Fig. 1d by counting 500 wires. Most of the wires produced at 700 rpm had lengths between 15 and 20 µm; however, wire lengths below 5 µm and over 30 µm were observed. When the stirring speed was decreased 300 rpm, the wire length increased to 25–30 µm. In fact, more than 10% of the wires had lengths exceeding 40 µm. Without any mechanical agitation, i.e., no stirring, the length of the wires were drastically increased to over 60 µm. The main distribution in length was in the range of 65–75 µm with a narrow range, which is twice as long as that prepared at low speeds of 300 rpm and over four times as that prepared at high speeds of 700 rpm. Some wires were even longer than 100 µm. Therefore, by only adjusting the mechanical agitation, the growth of very-long AgNWs in the one-pot simple polyol process has been achieved. The results indicate that the growth of long wires require an environment without any interference and agitation. The AgNWs may be spontaneous growth and free assemble after those seeds of AgNWs have been formed in the nucleation stage, which is very similar to the growth of crystals that requires a completely stationary solution environment and a sufficient growth time. Moreover, the yield of Ag product is over 90% in every condition with the polyol process. In this work, the low reaction temperature of 130°C and no-agitation have provided a suitable and effective growth environment for the formation of very-long AgNWs. It can be hypothesized that long wires will be obtained when the reaction temperature is further decreased with longer reaction time, and vice versa, which is similar to that of crystal growth.

In order to verify this hypothesis, AgNWs have been synthesized at 180 and 110°C without stirring, respectively (Fig. 2). At 110°C, it took over 12 h to complete the reaction because of the slow growth of the AgNWs, which is longer than that at 130°C. On the contrary, at high temperatures of 180°C, the reaction was completed in only 45 min. At lower temperatures, the majority of the AgNWs had a length greater than 80 µm; in fact, some had a length of 150 µm (Fig. 2a). When the temperature was increased to 180°C, however, the length of the AgNWs was only 20–30 µm, although several wires had a length greater than 40 µm (Fig. 2b). These results support the above conclusion that a low-temperature and long-time correspond to the formation of very-long AgNWs in the polyol process.

Moreover, in previous reports, low reaction temperatures and low stirring speeds always corresponded to large diameters in these AgNWs.[13,19] In our case, these synthesized AgNWs have been observed and counted to confirm the diameter distribution. Fig. 3 shows some interesting SEM images of these AgNWs at different stirring speeds. As previously mentioned, high speed stirring always caused a large number of nanoparticles and large rods (Fig. 1a), in order to assess the diameter of the AgNWs, these irregular nanoparticles and large rods are not shown in the SEM images. It is evident that these AgNWs have nearly same diameters, i.e., the diameter is independent of the stirring speeds. Comparing these SEM images, they indicate that the diameter distribution appears slightly more uniform at high speed stirring compared to the low speed. The dominant diameter is about 60 nm with a small distribution of other diameters. Moreover, it can be determined that the diameters between some small and big wires have multiple relationships. For example in Fig. 3c, the wires marked by white arrows have a diameter that seems twice as large as the wires marked by black arrow. The result may imply that those AgNW seeds are different in size in the nucleation stage. Once these seeds have been formed that can be evolved into suitable wires according to the morphology of seeds, which are agree with those reports in References 5-10, 14–16.

To establish the average diameter of the AgNWs, the diameters of 100 wires were measured and analyzed (Fig. 3d). Excluding the irregular nanoparticles and big rods, the AgNWs prepared with different stirring speeds exhibited a very narrow and mono-distribution. The percentage of wires containing a 60 nm diameter was over 97 % at the 700 rpm speed. When the speed was decreased to 300 rpm, the number of wires containing a diameter of 60 nm was about 92% with another 6% of the wires containing a diameter greater than 90 or even 120 nm. This result implies that slow agitation corresponded large diameter wires. Without agitation, the distribution of wire diameters is as follows: 86% are 60 nm, 11% are 90 or 120 nm, and 3% are 30 nm. These results imply that the agitation favors a uniform AgNW diameter. It is well known that chemical reactions are always performed with agitation to ensure a uniform solution. In this work, the agitation may facilitate the uniform distribution of AgNW seeds in the early reaction stage, which corresponds to the uniform growth of AgNWs in the later stage with high stirring speeds. No large differences in the diameter with these agitations indicate that the nucleation and growth of Ag were dominant factors in controlling the diameter of AgNWs in the polyol process. However, when the temperature is decreased to 110°C, the diameter of AgNWs has slowly increased to 75–85 nm (not shown here), which has same trend in References 13 and 19. It implied the temperature is crucial to determine the diameter of wires on the polyol process.

However, Bergin *et al.*[13] only obtained AgNWs with a length smaller 25 μm at 130°C; Coskun *et al.*[19] have also achieved AgNWs with a lengths in the range of 7–30 μm and a diameter greater 120 nm at 170°C when the stirring speeds were set to 1000 rpm. In our case, the diameter was constant (about 60 nm), while the length was controlled using the temperature. In fact, length up to 120 μm, which is much greater than 30 μm, was achieved without stirring. The main difference between our case and the previous works is the addition of reaction agents. For their cases, $AgNO_3$ and PVP were added with an injection rate or in a different order than our one-pot. The addition order may cause the nucleation and growth of Ag nuclei at different stages, which corresponded to a wide distribution in length and diameter of AgNWs. In our case, all agents have been added together at room temperature and react at the desired temperature, which contributed to the nucleation and growth of Ag nuclei during same stage. This is similar to the crystal growth process and environment, which promoted the formation of very-long wires with a stationary solution. With the polyol process, therefore, low stirring speeds and low temperatures are an excellent method to synthesize long AgNWs.

AgNWs prepared at 130°C have been used to fabricate a transparent film using a straightforward drop-coating method on glass substrates and drying at room temperature. Fig. 4 shows the relationship between the transmittance of the AgNW films and sheet resistances at room temperature. The transmittance depended upon the amount of AgNWs on the substrates. With AgNWs prepared at 0 rpm, the sheet resistance and transmittance at 550 nm was 566 Ω/sq and 97%, respectively. The sheet resistance has been drastically decreased by the decreasing transmittance. A very low resistance of about 25 Ω/sq at 91% and 9.2 Ω/sq at 85% have been achieved for the very-long AgNWs, which is the best record for AgNWs electrodes without any extra treatment to our knowledge. These values are superior to traditional ITO film. Also, the resistance and transmittance values are much lower than the AgNW films formed by the polyol process using a heat treatment, i.e., a sheet resistance of 20 Ω/sq with a transmittance of only 80% transmittance at 550 nm. [33] A possible explanation for this is that the very long wires produce a random network with only a few contact points, which correspond to an unavoidable contact resistance in the film per unit area compared to the short wires. [11,34] For the AgNWs prepared at 300 and 700 rpm, the sheet resistance also decreased with decreasing transmittance. The resistance value is about 359 and 492 Ω/sq at 85% for the 300 and 700 rpm speeds, respectively. The high sheet resistance was related to short length as well as some large diameter rods and irregular nanoparticles inside the two films (Fig. 4). It was difficult to measure the resistance when the transmittance was over 90% in the two films, which agree with those reports with short length wires. [11] Thus, pure long wires are an important parameter for high performing AgNW films[35].

In conclusion, very-long and thin AgNWs have been synthesized by mixing all reaction agents and reacted at the desired temperatures without any agitation in the famous polyol process by simulating the mechanism of crystal growth in still solution. The diameters of these AgNWs were nearly constant at 60 nm with a length of 65~75 μm which is three as long as those normal use AgNWs now. The length distribution is narrow comparing those methods due to the uniform nucleation growth. In addition, low temperatures and long reaction times also have been confirmed to contribute to the formation of longer AgNWs in this work. The very-long AgNWs have been used to fabricate transparent conductive AgNW films, which achieved a resistance of 9.2 Ω/sq with 85% transmittance at only room temperature, which is superior to the ITO film.

Notes and references

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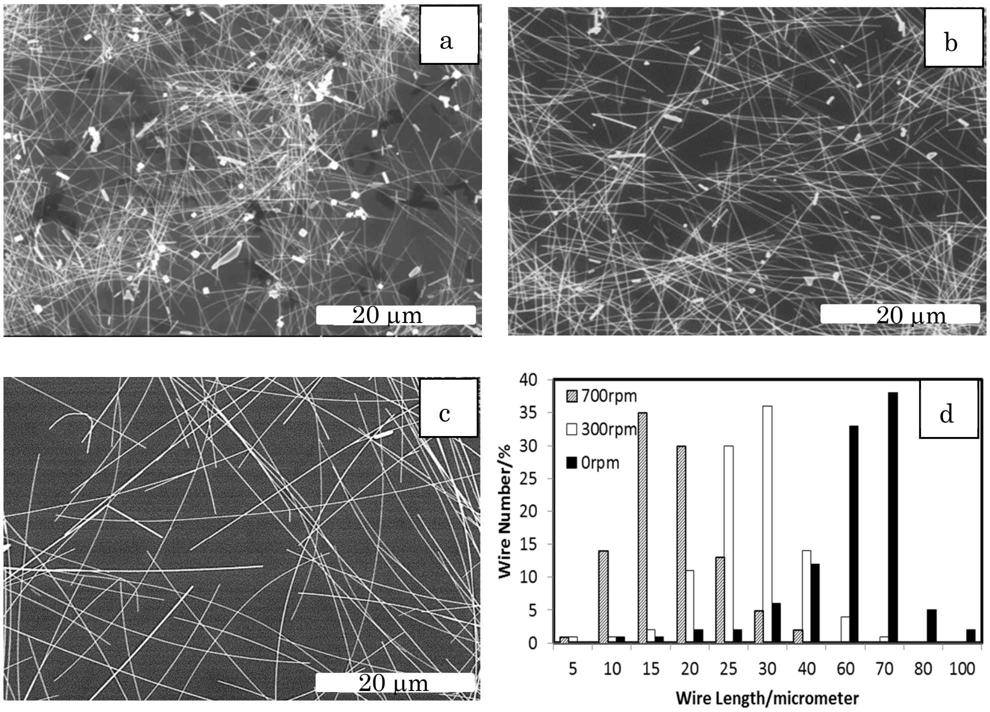


Fig.1. The SEM images of AgNWs prepared at 130 ^{0}C with stirring speeds of (a) 700, (b) 300 and (c) 0 rpm (those inserted photos have a scale bar of 30μm), and the length distribution of AgNWs with different stirring speeds (d).

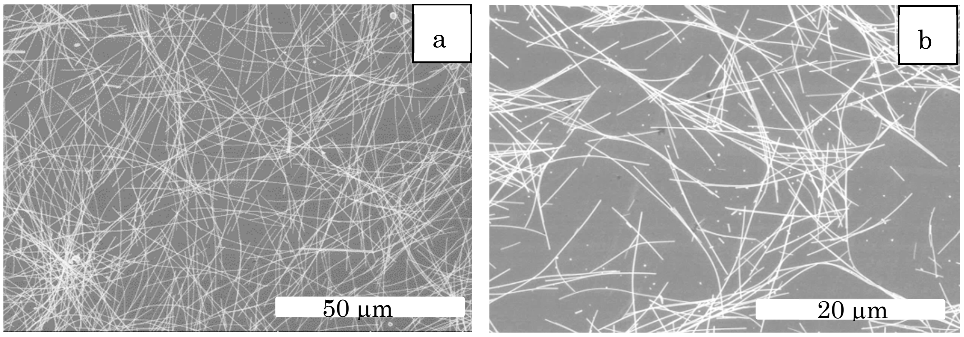


Fig.2. The SEM images of AgNWs prepared at 110 (a) and 180 ^{0}C (b) without agitation.

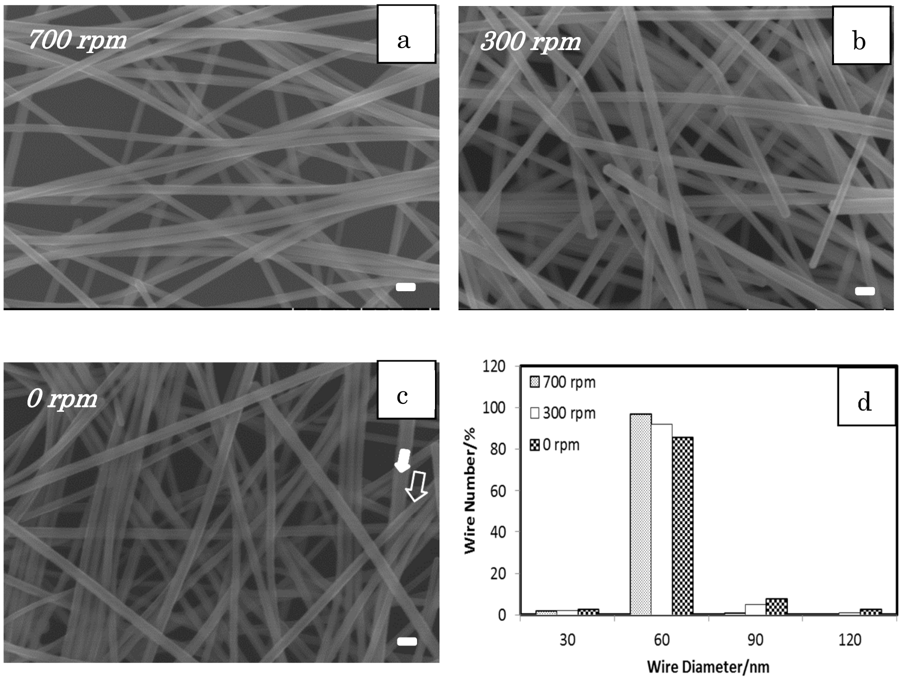


Fig.3. The SEM images of AgNWs prepared at 130 ^{0}C with stirring speeds (a, b and c with the scale bar of 100 nm), and related diameter distribution (d).

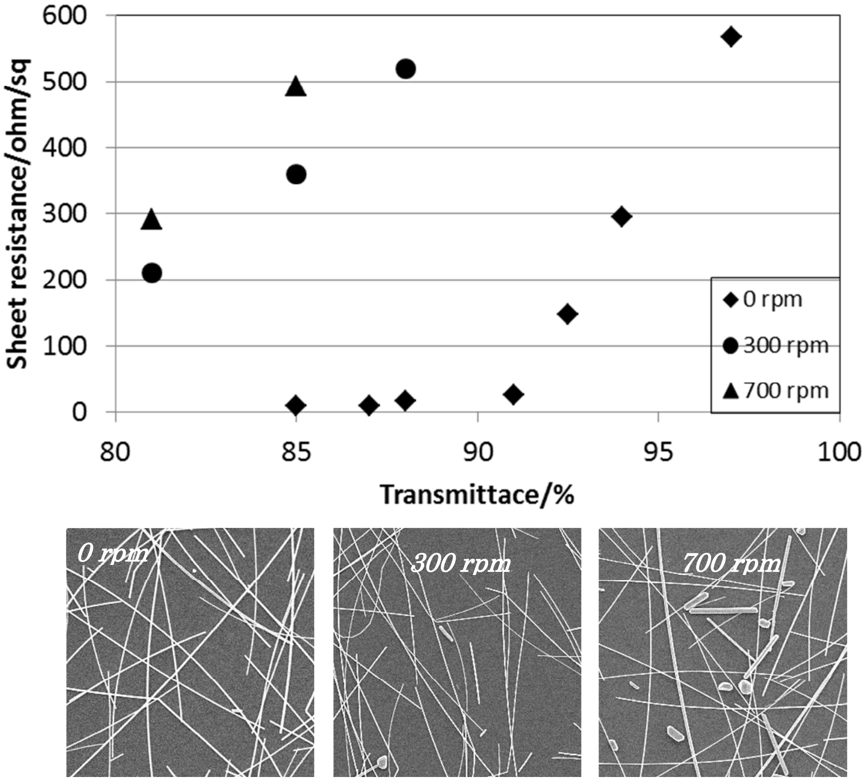
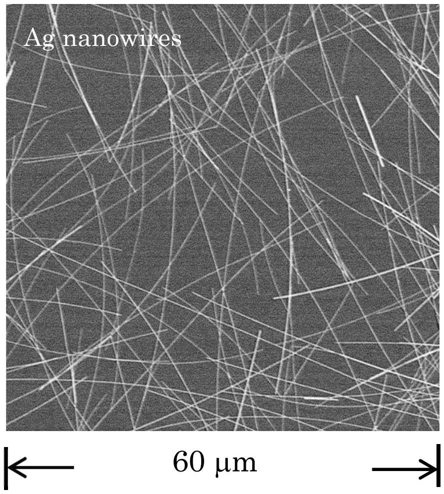


Fig.4 The relationship between sheet resistance and transmittance of AgNWs film on glass substrate and film SEM images with transmittance of 85 % at 550 nm (the side length is 15 μm).



Silver nanowires >60 μm have been synthesized using a polyol process without stirring speed at 130°C.