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A one-step route to Ag nanowires with a diameter below 40 nm and an aspect ratio above 1000†

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The synthesis of long and thin Ag nanowires is important to achieve high performance transparent conductive films. We report a one-step route to synthesizing Ag nanowires with an average diameter of ~25 nm and an aspect ratio larger than 1000 by utilizing a mixture of poly(vinylpyrrolidone) with different molecular weights as the capping agent in a polyol reduction reaction.

Silver nanowires (AgNWs) have been extensively investigated as the building blocks of new transparent conductive films (TCFs).[1–11] It has been theoretically predicted and experimentally demonstrated that thin and long AgNWs are conducive to the performance of the TCF, especially for high-end applications such as touch panel screens that require low sheet resistance and low haze under extremely high transparency conditions.[12–15] For example, Mutiso *et al.* modelled the light transparency characteristics of AgNW TCFs, and found that an aspect ratio as large as 800 was required for the high performance of AgNW TCFs with sheet resistance ~10 Ω □$^{-1}$ for a transparency of ~90% at 550 nm.[12] Sorel *et al.* predicted that AgNWs with a diameter of 25 nm could generate TCFs with sheet resistance as low as 25 Ω □$^{-1}$ for a transparency of 90%.[13] Khanarian and co-workers showed that to achieve a haze less than 1% AgNWs should have a diameter smaller than 50 nm.[14] Bergin *et al.* also independently showed that AgNWs with a diameter smaller than 40 nm would dramatically increase the performance of TCFs for high-transmittance networks in which the number of connections between nanowires limits the conductivity of the network, as in the case of touch panel screens.[15] As required by the transparent conductive electrodes in solar cells, the performance of the TCFs with sheet resistance smaller than 10 Ω □$^{-1}$ and transparency larger than 90% is favoured to achieve high efficiency of the solar cells.[16] Therefore, it is extremely important to utilize AgNWs with a small diameter and a large aspect ratio to fabricate TCFs.

AgNWs are mostly synthesized by a polyol reduction method with poly(vinylpyrrolidone) (PVP) as the capping agent.[17–20] Generally, AgNWs synthesized by the one-step route have an average diameter larger than 80 nm and a length shorter than 20 μm, transforming to an aspect ratio in the order of 200–300. Recently, synthesis of ultralong AgNWs with the length larger than 100 μm by the one-step or multistep method has been reported; however, the ultralong AgNWs usually have a diameter thicker than 80 nm, and it is difficult to lower the roughness and haze of TCFs using this kind of ultralong AgNWs.[21–23] The synthesis of AgNWs with diameters less than 40 nm is more difficult than the synthesis of long AgNWs. So far, there has been rather limited knowledge on how to synthesize AgNWs with a diameter less than 40 nm and an aspect ratio larger than 1000. It has been suggested that the longer the chain length of PVP molecules, the larger the aspect ratio of AgNWs.[24] However, there are also reports indicating that the capping efficiency is larger for PVP molecules with a shorter chain length.[25] There has been no consensus on the influence of the PVP chain length on the diameter of AgNWs. Although there has been much work regarding the effect of the experimental parameters, such as the molar ratio of PVP to Ag^+ ions in the precursor solution, the concentration of the polyol, the heating temperature and the growth time duration, on the growth behaviour of AgNWs, there is no report on the utilization of PVP with mixed molecular weight for controlling the growth of AgNWs to obtain AgNWs with a small diameter and a large aspect ratio.

Herein we report the synthesis of AgNWs of high aspect ratio with a mixture of PVP molecules of different molecular weight. PVP is well-known to selectively passivate on {100} planes of Ag seeds, leaving the unpassivated {111} planes to grow longitudinally (Scheme S1, ESI†).[25,26] The passivation of PVP on the surface of Ag is believed to be a steric effect by blocking the

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† Electronic supplementary information (ESI) available: Details of the experiments, SEM and TEM images of AgNWs under different conditions, the XRD pattern and optical transmittance spectrum of AgNWs, tables and statistical diameter and length dispersion data of AgNWs. Scheme of the nucleation and growth of AgNWs. See DOI: 10.1039/c4cc04698f

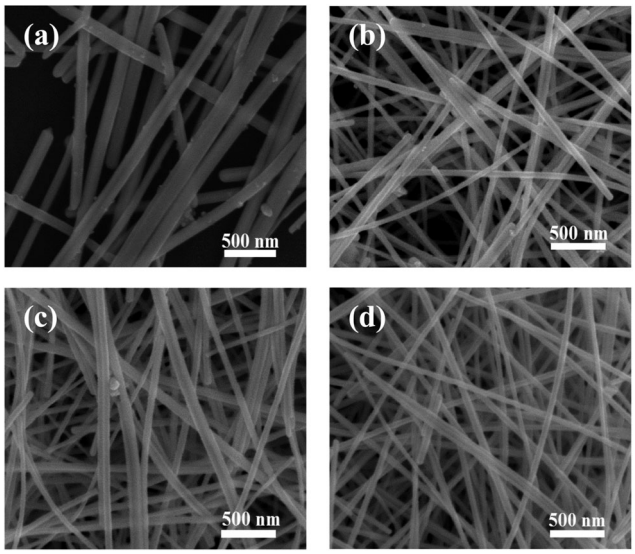

Fig. 1 FE-SEM images of AgNWs synthesized with PVP molecules of different chain lengths (a) PVP-55 000, (b) PVP-360 000, (c) PVP-1 300 000, and (d) PVP-1 300 000 + PVP-55 000 (a weight ratio of 1 : 1).

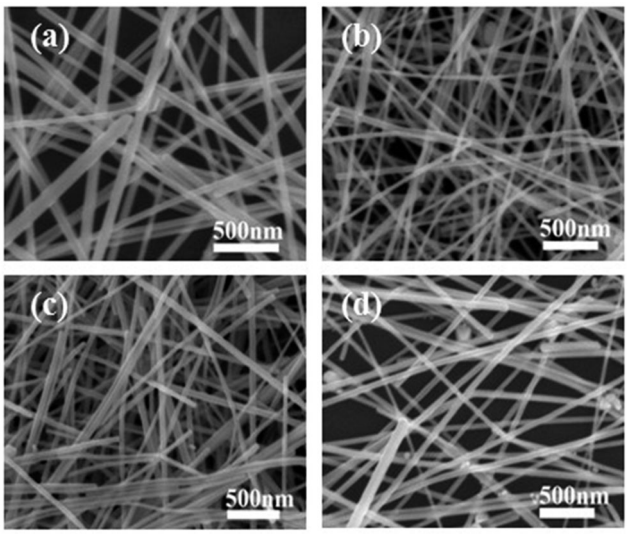

Fig. 2 FE-SEM images of AgNWs synthesized with PVP-360 000 and PVP-55 000 of different weight ratios of (a) 1 : 1, (b) 2 : 1, (c) 3 : 1, and (d) 4 : 1.

access of Ag^0 to {100} planes of Ag seeds. Using a mixture of PVP molecules with different chain lengths, the passivation could be improved through insertion of the shorter chain molecules in between large chain molecules (Scheme S1, ESI†). Consequently, thin AgNWs could be produced with fine Ag seeds in the following growth process, since the diameter of AgNWs will not deviate much from the size of Ag seeds at the point of the initiation of elongation of the seeds, as will be discussed in the following sections. In this work, we will show that we can synthesize AgNWs of aspect ratio larger than 1000, with an average diameter of ~40 nm and an average length of ~40 μm *via* a one-step route by using mixed PVP molecules of different chain length. Furthermore, with the optimization of the weight ratio between PVP molecules of different chain length and the growth temperature, we can further reduce the diameter of AgNWs to ~25 nm with length ~35 μm.

As shown in Fig. 1a–c, AgNWs synthesized with PVP molecules of molecular weight (M_W) 55 000, 360 000, and 1 300 000 (denoted as PVP-55 000, PVP-360 000, and PVP-1 300 000, respectively) have an average diameter of 100, 60, and 80 nm, and an average length of 25, 46, and 50 μm, respectively. It is clear that if the chain length of PVP molecules is too short, thick and short AgNWs are obtained. PVP molecules with a very large chain length (PVP-1 300 000) work better than those with a very short chain length (PVP-55 000), albeit not as well as those with a median chain length (PVP-360 000). The synthesis conditions, the yield (number percentage of nanowires to sum of nanoparticles and nanowires), and the size of products are shown in Table S1 (ESI†). We have investigated the effect of temperature on the growth of AgNWs, and found that 140 °C is the optimum temperature for growing relatively thin and long AgNWs with long chain PVP molecules (Table S2, ESI†). In addition, the yield of nanowires against nanoparticles is also high at 140 °C, and synthesis at higher or lower temperatures will not only produce AgNWs thicker and shorter in dimension, but also generate more nanoparticles.

When mixing PVP-360 000 or PVP-1 300 000 with PVP-55 000 at a weight ratio of 1 : 1, AgNWs with average diameters of 30 and 60 nm and average lengths of 29 and 40 μm, respectively, were obtained (Fig. 1d and 2a). From the above observations, we can reach the conclusion that using a mixture of PVP with different chain lengths could indeed decrease the diameter of AgNWs. When we mix PVP-360 000 and PVP-55 000 with a weight ratio of 1 : 1, the diameter of AgNWs could be reduced to ~30 nm. For the synthesis of AgNWs with mixed PVP molecules, growth at 130 °C generates AgNWs with slightly larger dimensions (Fig. S1 and Table S3, ESI†).

Although PVP-55 000 alone is not efficient enough to produce AgNWs with a small diameter, the mixture of PVP molecules of larger chain length with smaller ones is far more efficient in reducing the diameter of AgNWs. We found that by adjusting the weight ratio between PVP-360 000 and PVP-55 000, we can even reduce the diameter of AgNWs to ~25 nm when the weight ratio is close to 2 : 1. Further increasing the weight ratio causes the increase of the diameter of AgNWs as shown in Fig. 2. The diameter and length distributions are exhibited in Fig. S2 (ESI†). For a weight ratio of 2 : 1, more than 80% of AgNWs have diameters smaller than 30 nm, and more than 50% with lengths larger than 40 μm.

The morphology and microstructure of AgNWs are characterized by transmission electron microscopy (TEM) and shown in Fig. 3a and c. From these images, the as-synthesized AgNWs are thin and uniform in diameter. Fig. 3d exhibits a high-resolution transmission electron microscopy (HRTEM) image of an AgNW with lattice fringes corresponding to {111} planes of the face-centered cubic phase of Ag. AgNWs grow along the $[01\bar{1}]$ direction, the same as the observations in the literature.[17,18] The selected area electron diffraction (SAED) pattern along the ⟨011⟩ zone axis in Fig. 3b further exhibits the single crystallinity of

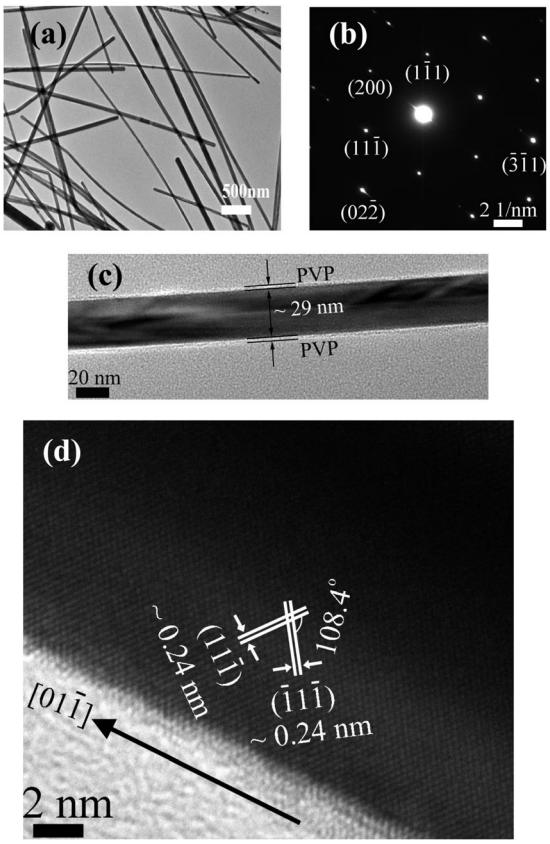

Fig. 3 Microstructure of AgNWs synthesized with PVP-360 000 + PVP-55 000 (a weight ratio of 2 : 1) at 140 °C. (a) TEM image, (b) SAED pattern along the ⟨011⟩ zone axis, (c) TEM image of a 29 nm-thick AgNW, and (d) HRTEM image.

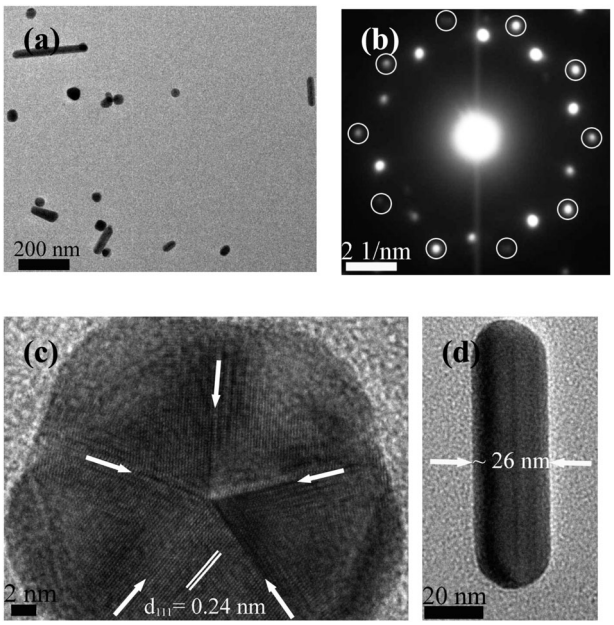

Fig. 4 TEM characterization of AgNWs synthesized with PVP-360 000 + PVP-55 000 (a weight ratio of 2 : 1) at 140 °C for 9 min. (a) TEM image, (b) SAED pattern, and (c) HRTEM image of well-crystallized decahedral seeds, and (d) HRTEM image of elongated grains with a diameter below 26 nm.

AgNWs. The x-ray diffraction (XRD) pattern in Fig. S3 (ESI†) also indicates that the as-synthesized AgNWs are highly crystalline.

To explain the exact formation mechanism of thin and long AgNWs by the mixed PVP method, systematic TEM characterization of AgNWs from the nucleation to the growth stages has been carried out, and the results are shown in Fig. 4 and Fig. S4–S11 (ESI†). From morphology evolution of AgNWs synthesized with PVP-360 000 + PVP-55 000 (weight ratio of 2 : 1), nuclei appeared within 3 min and grew to well-crystallized decahedral seeds within ~9 min, followed by the elongation of the seeds. With the elongation into nanowires, it was noticed that the diameter of the nanowires only slightly increased from the size of the starting seeds at the point of the initiation of elongation. Compared with samples prepared by using mixed PVP molecules, the size of Ag seeds is larger when using single type PVP molecules of the same concentration (Fig. S8 and S9, ESI†), leading to the formation of thicker AgNWs. These facts implied that mixed PVP molecules played a role from the very beginning of nucleation to form smaller Ag seeds by confining their growth. The confining effect could be varied by the mixing ratio of different PVP molecules, leading to slightly different sizes of nanowires (Fig. S10 and S11, ESI†). It appears that the shape of the seeds does not noticeably affect the formation of thin AgNWs, considering that the number ratio of nanowires in the final product is as high as more than 90%.

The role of PVP molecules having different chain lengths and their mixing ratio on the size of Ag seeds and the diameter of Ag nanowires could be explained preliminarily according to Scheme S1 (ESI†). Firstly, PVP molecules of single type and longer chain length could indeed block the access of Ag^0 to the surfaces of Ag nuclei and nanowires at a relatively large distance due to their long chains. However, these long chain molecules could not passivate the surface sufficiently owing to the repulsion between adjacent PVP molecules; therefore Ag^0 could reach the surfaces of Ag nuclei by diffusion through the gap between adjacent PVP molecules, and large seeds and thick AgNWs could be anticipated. Secondly, PVP molecules of a single type and a smaller chain length could not passivate sufficiently the surface of Ag nuclei because of the rigidity and less bulky size compared to long-chained PVP molecules;[27] therefore Ag^0 still has a large probability to reach the surface of Ag nuclei and nanowires, again leading to large seeds and thick AgNWs. Thirdly, if PVP molecules having different chain lengths were mixed, short-chained molecules could adsorb on the surface of Ag seeds and fill the gap between long-chained molecules. Consequently, Ag^0 could be blocked more efficiently, and, by adjusting the mixing ratio of PVP molecules, successful passivation of the surfaces of Ag nuclei and nanowires could be realized, leading to smaller Ag seeds and thin AgNWs. So far, it has been not known if it is possible to further reduce the diameter of AgNWs by the combination of PVP molecules of more suitable chain length. Work is underway toward ultrathin AgNWs by this experimental route. The size distribution of the AgNWs synthesized by the mixed PVP method (Fig. S2, ESI†) is still somewhat wide. In future work, effort will be invested to improve the diameter and length uniformity of AgNWs, for

example, by controlling the nucleation process to obtain Ag seeds with a narrow size distribution before injecting the nuclei precursor into the growth solution. The exact role of mixed PVP molecules on the formation of thin Ag nanowires will be further investigated. Results of our experiments through replacing $FeCl_3$ by $Fe(NO_3)_3$ salt and halide contaminants indicate that they could not contribute to the selective formation of AgNWs with the reported aspect ratio (Fig. S12, ESI†).

It is known that the thinner the diameter of AgNWs, the weaker the visible light scattering and the larger the visible light transmittance.[28] We have measured the optical transmittance of AgNW dispersions with different dimensions, with average diameters of <35 nm, ~60, ~80, and ~100 nm, respectively. As shown in Fig. S13 (ESI†), the dispersions of thin AgNWs transmit more visible light than those of thick ones. It is expected that TCFs fabricated with thin AgNWs of high aspect ratios will generate low haze,[28] and our preliminary experimental results support the idea (Fig. S14, ESI†), which needs further investigation in future work.

In summary, we have synthesized thin AgNWs with an aspect ratio larger than 1000 by a facile method using PVP molecules of a mixed chain length as the capping agent. We found that by adding a suitable amount of PVP-55 000 in PVP-360 000, the diameter of AgNWs could be reduced to ~25 nm. Systematic studies reveal the importance of the mixed PVP molecules in controlling the size of the initial Ag seeds and the diameter of AgNWs in a later growth stage. The ability to synthesize AgNWs with a diameter smaller than 40 nm and an aspect ratio larger than 1000 will readily find application in the fabrication of high-performance transparent conductive films.

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Notes and references

1 L. B. Hu, H. Wu and Y. Cui, *MRS Bull.*, 2011, **36**, 760.
2 L. B. Hu, H. S. Kim, J.-Y. Lee, P. Peumans and Y. Cui, *ACS Nano*, 2010, **4**, 2955.
3 V. Scardaci, R. Coull, P. E. Lyons, D. Rickard and J. N. Coleman, *Small*, 2011, **7**, 2621.
4 S. De, T. M. Higgins, P. E. Lyons, E. M. Doherty, P. N. Nirmalraj, W. J. Blau, J. J. Boland and J. N. Coleman, *ACS Nano*, 2009, **3**, 1767.
5 A. R. Madaria, A. Kumar and C. W. Zhou, *Nanotechnology*, 2011, **22**, 245201.
6 C. Preston, Y. L. Xu, X. G. Han, J. N. Munday and L. B. Hu, *Nano Res.*, 2013, **6**, 461.
7 J. Lee, P. Lee, H. B. Lee, S. Hong, I. Lee, J. Yeo, S. S. Lee, T.-S. Kim, D. Lee and S. H. Ko, *Adv. Funct. Mater.*, 2013, **23**, 4165.
8 C. H. Chung, T. B. Song, B. Bob, R. Zhu and Y. Yang, *Nano Res.*, 2012, **5**, 805.
9 D. Langley, G. Giusti, C. Mayousse, C. Celle, D. Bellet and J.-P. Simonato, *Nanotechnology*, 2013, **24**, 452001.
10 J. Jiu, T. Araki, J. Wang, M. Nogi, T. Sugahara, S. Nagao, H. Hoga, K. Suganuma, E. Nakazawa, M. Hara, H. Uchida and K. Shinozaki, *J. Mater. Chem. A*, 2014, **2**, 6326.
11 M.-S. Lee, K. Lee, S.-Y. Kim, H. Lee, J. Park, K.-H. Choi, H.-K. Kim, D.-G. Kim, D.-Y. Lee, S. Nam and J.-U. Park, *Nano Lett.*, 2013, **13**, 2814.
12 R. M. Mutiso, M. C. Sherrott, A. R. Rathmell, B. J. Wiley and K. I. Winey, *ACS Nano*, 2013, **7**, 7654.
13 S. Sorel, P. E. Lyons, S. De, J. C. Dickerson and J. N. Coleman, *Nanotechnology*, 2012, **23**, 185201.
14 G. Khanarian, J. Joo, X. Q. Liu, P. Eastman, D. Werner, K. O'Connell and P. Trefonas, *J. Appl. Phys.*, 2013, **114**, 024302.
15 S. M. Bergin, Y. H. Chen, A. R. Rathmell, P. Charbonneau, Z. Y. Li and B. J. Wiley, *Nanoscale*, 2012, **4**, 1996.
16 M. W. Rowell and M. D. McGehee, *Energy Environ. Sci.*, 2011, **4**, 131.
17 Y. G. Sun, Y. D. Yin, B. T. Mayers, T. Herricks and Y. N. Xia, *Chem. Mater.*, 2002, **14**, 4736.
18 Y. G. Sun, B. Gates, B. Mayers and Y. N. Xia, *Nano Lett.*, 2002, **2**, 165.
19 Y. G. Sun, B. Mayers, T. Herricks and Y. N. Xia, *Nano Lett.*, 2003, **3**, 955.
20 S. Coskun, B. Aksoy and H. E. Unalan, *Cryst. Growth Des.*, 2011, **11**, 4963.
21 J. H. Lee, P. Lee, D. Lee, S. S. Lee and S. H. Ko, *Cryst. Growth Des.*, 2012, **12**, 5598.
22 P. Lee, J. Lee, H. Lee, J. Yeo, S. Hong, K. H. Nam, D. Lee, S. S. Lee and S. H. Ko, *Adv. Mater.*, 2012, **24**, 3326.
23 T. Araki, J. T. Jiu, M. Nogi, H. Koga, S. Nagao, T. Sugahara and K. Suganuma, *Nano Res.*, 2014, **7**, 236.
24 J. J. Zhu, C. X. Kan, J. G. Wan, M. Han and G. H. Wang, *J. Nanomater.*, 2011, 982547.
25 X. H. Xia, J. Zeng, L. K. Oetjen, Q. G. Li and Y. N. Xia, *J. Am. Chem. Soc.*, 2012, **134**, 1793.
26 N. Murshid and V. Kitaev, *Chem. Commun.*, 2014, **50**, 1247.
27 K. Din, U. S. Siddiqui and G. Ghosh, *J. Dispersion Sci. Technol.*, 2009, **30**, 1310.
28 C. Preston, Y. L. Xu, X. G. Han, J. N. Munday and L. B. Hu, *Nano Res.*, 2013, **6**, 461.

