

Synthesis and Purification of Silver Nanowires To Make Conducting Films with a Transmittance of 99%

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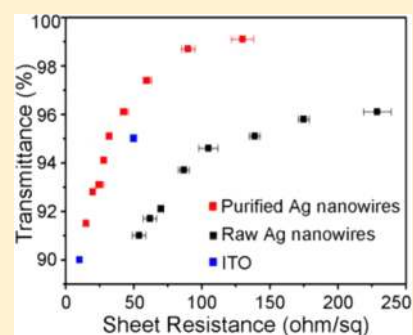
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S Supporting Information

ABSTRACT: Metal nanowire (NW) networks have the highest performance of any solution-coatable alternative to ITO, but there is as yet no published process for producing NW films with optoelectronic performance that exceeds that of ITO. Here, we demonstrate a process for the synthesis and purification of Ag NWs that, when coated from an ink to create a transparent conducting film, exhibit properties that exceed that of ITO. The diameter, and thus optoelectronic performance, of Ag NWs produced by a polyol synthesis can be controlled by adjusting the concentration of bromide. Ag NWs with diameters of 20 nm and aspect ratios up to 2000 were obtained by adding 2.2 mM NaBr to a Ag NW synthesis, but these NWs were contaminated by nanoparticles. Selective precipitation was used to purify the NWs, resulting in a transmittance improvement as large as 4%. At $130.0 \Omega \text{ sq}^{-1}$, the transmittance of the purified Ag NW film was 99.1%.

KEYWORDS: silver nanowires, sodium bromide, selective precipitation, transparent conductor



Transparent conductors (TCs) in large-area touch screens, thin-film solar cells, and organic light emitting diodes (OLEDs) are currently made from a sputtered film of indium tin oxide (ITO) due to its high transmittance (95%T) at low sheet resistances ($50 \Omega \text{ sq}^{-1}$).¹ However, the high-conductivity ITO used in these applications is particularly costly due to the slow coating rates involved with sputtering. This has motivated the search for solution-coatable alternatives to ITO that can be coated at high speeds and give comparable performance. There are several solution-coatable alternatives to ITO, including carbon nanotubes,^{2–4} graphene,^{5,6} conducting polymers,^{7,8} silver nanowires (Ag NWs),^{9–12} and copper nanowires (Cu NWs),^{13–15} but only commercially available Ag NWs have demonstrated optoelectronic performance that exceeds that of ITO.¹⁶ The processes required for production of metal NWs that, when coated onto a substrate, have optoelectronic performance that exceeds that of ITO have not been reported.

The performance of Ag NW-based TCs generally increases with decreasing diameter and increasing NW aspect ratio due to the fact that thin NWs scatter less light, and increasing aspect ratio decreases the number of high-resistance nanowire-nanowire contacts in the film.^{17,18} Although there have been many reported syntheses seeking to produce longer, thinner Ag NWs, none have demonstrated film performance that exceeds that of ITO.^{9,12,19} Ag NWs with a mean diameter of 20 nm and lengths up to 20 μm were prepared by a high-pressure polyol method.¹² These nanowires were used to produce films with a sheet resistance of $40 \Omega \text{ sq}^{-1}$ at a transmittance of 88%, performance below that of ITO. Lee and co-workers have developed a successive multistep growth method to obtain Ag

NWs with an average length of 95.1 μm and diameter of 160 nm. Although such long NWs exhibited optoelectronic performance that exceeds that of shorter NWs, their diameters are too large to match the properties of ITO.¹¹ Thus, there remains a need for a synthesis of Ag NWs that are both very thin (~ 20 nm in diameter) and very long ($> 50 \mu\text{m}$ in length) so as to achieve ITO-level performance.

However, it is not enough to obtain Ag NWs with the right dimensions; they must also be highly pure and uncontaminated by the presence of nanoparticles. Nanoparticle impurities dramatically decrease the electrical conductivity and transparency of NW networks.^{20,21} Given the fact that the polyol methods most widely used for production of Ag NWs inevitably produce nanoparticles as a side product, this remains an important issue for the production of high-purity Ag NWs.^{12,19,22–24} The traditional purification process of performing many tedious cycles of centrifugation is time-consuming and, at least for the authors, has not produced Ag NWs with sufficient purity.^{10,22} Pradel and co-workers developed a cross-flow filtration method to purify NWs, but the success of this method depends on many parameters, such as NW size, pore size of the fiber membrane, flow rate, and pressure, and is not easily scalable.²¹ Thus, there remains a need for a simple, convenient, and scalable method for separating nanoparticles from NWs.

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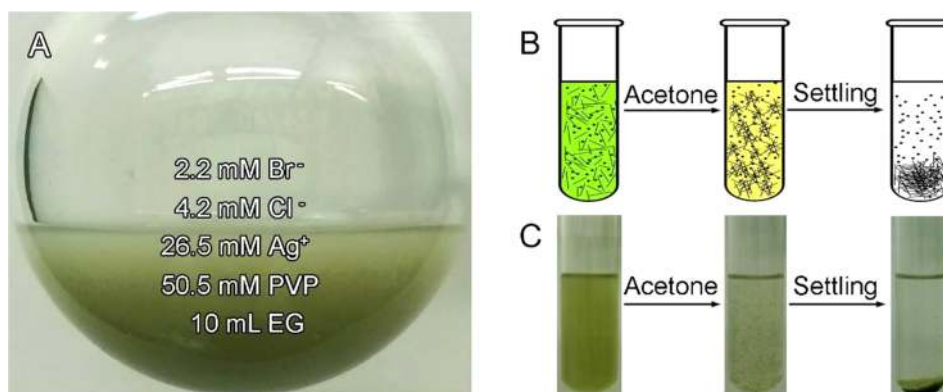


Figure 1. (A) Camera picture of the reaction flask after the growth of Ag NWs at 170 °C for 1 h. (B) Scheme demonstrating the process for purification of Ag NWs. (C) Pictures showing the stages of the purification process.

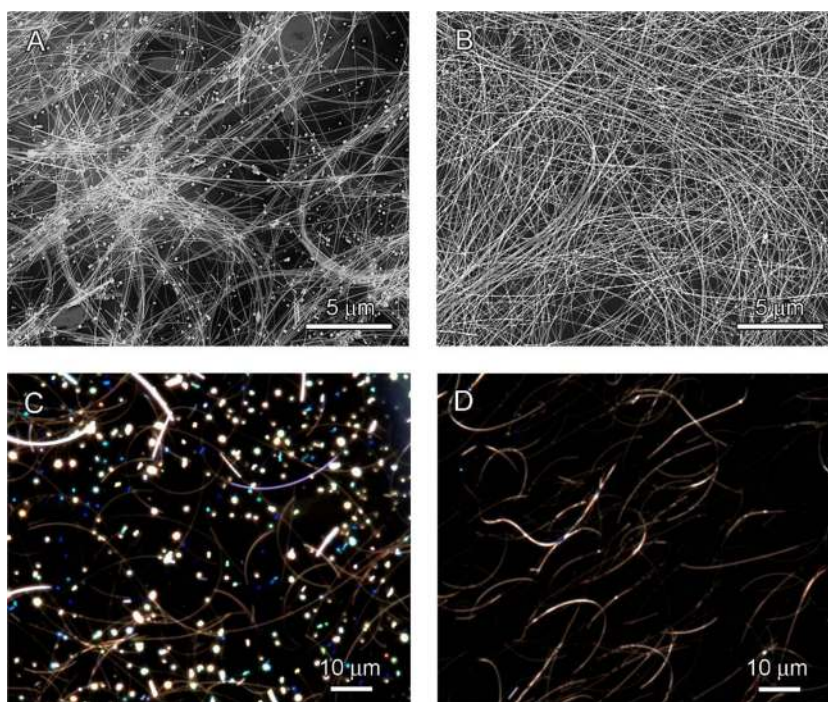


Figure 2. SEM images of Ag nanowires before (A) and after (B) purification. Dark field optical microscope images of Ag nanowires before (C) and after (D) purification.

Here, we show that the diameter of Ag NWs in a polyol synthesis can be controlled by adjusting the concentration of bromine. Ag NWs with diameters of 20 nm and aspect ratios up to 2000 were obtained by adding 2.2 mM NaBr to a Ag NW synthesis. We also demonstrate a simple selective precipitation process to purify the Ag NWs. Purified Ag NWs were transferred to an ethyl cellulose-based ink formulation and coated onto glass with a Meyer rod to produce films with a transmittance of 99.1% at $130 \Omega \text{ sq}^{-1}$.

Ag NWs were synthesized through a modified polyol process.^{25,26} To start, three stock solutions were prepared: (A) 220.0 mM NaBr, (B) 210.0 mM NaCl, and (C) 505.0 mM PVP (56.0 g/L, MW = 130,000) in ethylene glycol (EG, J.T. Baker). Next, 7.7 mL of EG, 0.1 mL of solution A, 0.2 mL of solution B, 1.0 mL of solution C, and 1.0 mL of freshly prepared 265.0 mM AgNO₃ in EG were added into a 50 mL round-bottom flask placed in an oil bath at room temperature. The flask was stirred vigorously for 30 min, and then heated to

170 °C with stirring for 15 min. During heating, nitrogen gas was bubbled through the reaction solution. Once it reached 170 °C, the flask was capped and allowed to react for 1 h without stirring. After 1 h, the flask was removed from the oil bath and 30 mL of water was added to the reaction solution to cool it to room temperature, thereby stopping the reaction. Figure 1A shows a picture of the reaction flask after Ag NW growth.

After the synthesis, the Ag NWs were purified by selective precipitation (Figure 1B and C). This process simply involved the slow addition of acetone to the mixture of the reaction solution and water. Because the Ag NWs were coated with PVP, and PVP is not soluble in acetone, the Ag NWs aggregated and settled to the bottom of the vessel. As the aggregation involved a change in the color of the suspension from green to yellow (Figure 1C), it could be observed visually. This color change occurred when 80–160 mL of acetone was added, at which point no additional acetone was added and the NWs settled to the bottom of the vessel. The aggregated NWs

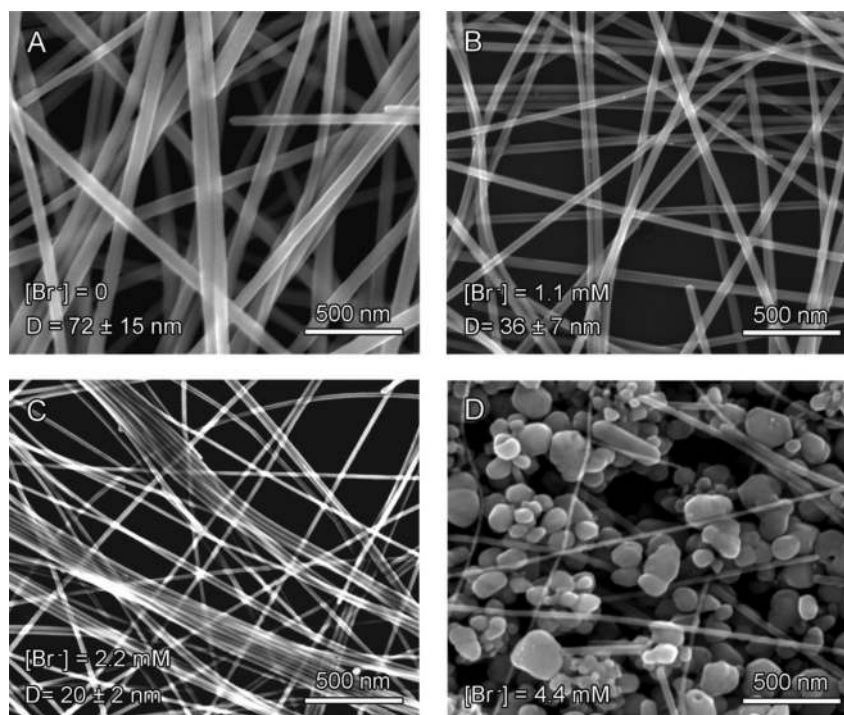


Figure 3. Typical high-resolution SEM images of purified products obtained from different concentrations of NaBr: (A) 0, (B) 1.1, (C) 2.2, and (D) 4.4 mM. The concentrations of AgNO₃, PVP, and NaCl in each of these reactions was 26.5, 50.5, and 4.2 mM, respectively, and the reaction temperature was 170 °C.

settled to the bottom of the cylinder within 10 min, at which point the supernatant containing short NWs and nanoparticles was removed with a pipet. The aggregated NWs were redispersed in 20 mL of DI water containing 0.5 wt % PVP. The redispersed NWs were purified again by adding 40–80 mL of acetone, allowing the NWs to settle for 10 min, and removing the supernatant. NWs with high purity were obtained after 2–4 cycles of this purification process.

Figure 2 shows the images of Ag NWs with diameters of 20 ± 2 nm and lengths of $40 \pm 15 \mu\text{m}$ before and after four cycles of selective precipitation (see Figure S1 in Supporting Information for histograms). There is clearly a dramatic decrease in the number of particles after the purification process. This same process could be applied to purify nanowires with larger diameters without modification (Figures S2 and S3 in Supporting Information).

Halide ions play an important role in the polyol synthesis of Ag NWs.^{9,19,25–28} We varied the concentration of NaBr added to the synthesis to gain additional insight into how it affects nanowire diameter. When there was no bromine present in the polyol synthesis, it produced Ag NWs with a mean diameter of 72 ± 15 nm and lengths of $63 \pm 17 \mu\text{m}$ (Figure 3A and Supporting Information Figure S2). Addition of 1.1 mM NaBr reduced the diameter of the NWs to 36 ± 7 nm (Figure 3B and Supporting Information Figure S3), with lengths of $48 \pm 15 \mu\text{m}$. Addition of 2.2 mM NaBr reduced the diameter of the NWs further to 20 ± 2 nm (Figure 3C and Supporting Information Figure S1), with lengths of $40 \pm 13 \mu\text{m}$. Further increasing the concentration of NaBr to 4.4 mM resulted in many more nanoparticles in the reaction product (Figure 3D). If 8.8 mM NaBr was added, the main products were nanoparticles (Supporting Information Figure S4).

Experimental results presented in Table S1 in Supporting Information suggest that the decrease in diameter upon

addition of NaBr was primarily caused by an increase in the number of nucleation events, with a smaller contribution from a decrease in the conversion of Ag⁺ to Ag. Increasing the concentration of NaBr from 0 to 2.2 mM increased the number of NWs produced in the reaction by a factor of 13, from 5.6×10^{12} to 73.5×10^{12} , whereas the average nanowire volume decreased by a factor of 20, primarily due to the decrease in nanowire diameter. The increase in the number of NWs produced by the reaction suggests that there was an increase in the number of nucleation events upon addition of NaBr. We attribute this increase in nucleation events to the presence of a silver halide nanoparticle precipitate. In our experiment, the chemicals were mixed at room temperature before heating. In the absence of NaCl or NaBr, the reaction solution was clear after mixing at room temperature (Figure S5A in Supporting Information). In contrast, the solution with NaCl was a translucent white, and the solution with NaBr was a more opaque white or pale yellow (Figures S5B–D), indicating the formation of AgCl and AgBr. The extinction spectrum peak intensity for solutions with NaBr was ~ 2.4 times greater than for NaCl alone (Figure S6 in the Supporting Information), indicating more precipitate formed after addition of NaBr. Figure S7 in Supporting Information shows TEM images of the silver halide nanoparticles and histograms of the nanoparticle diameters. TEM imaging of the precipitate showed that the diameter of the AgCl nanoparticles (180 ± 57 nm) was about 5 times greater than the diameter of the AgBr nanoparticles (35 ± 13 nm). When both the nanoparticle size and change in absorption were taken into account, the number of silver halide nanoparticles increased by ~ 12 times after addition of NaBr relative to the number of nanoparticles present with NaCl alone. Both AgBr and AgCl have been shown to act as heterogeneous nucleants for growth of Ag NWs.^{9,29,30} Thus, the 13-fold increase in the number of nanowires upon addition

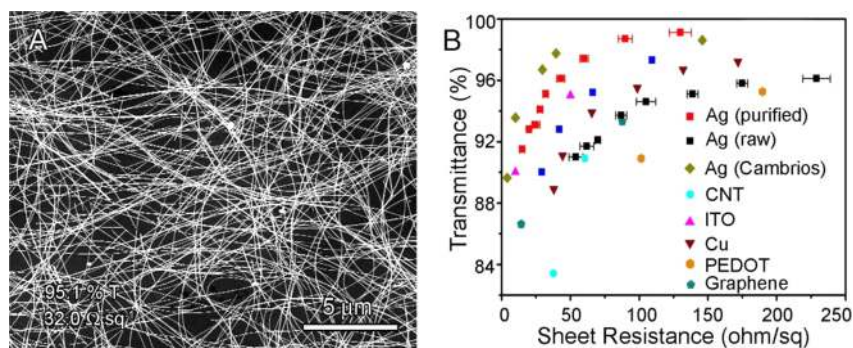


Figure 4. (A) Typical SEM image of a Ag NW film. (B) Plot of specular transmittance ($\lambda = 550$ nm) vs sheet resistance for Ag NW films before and after purification. Error bars show one standard deviation for five measurements. The performance of ITO, Ag NWs,¹⁶ CNT,³³ Cu NWs,³⁴ PEDOT,⁷ and graphene⁶ are shown for comparison.

of NaBr may have been caused by the ~ 12 -fold increase in the number of silver halide nanoparticles that could serve as heterogeneous nuclei.

The remaining contribution to the 20-fold decrease in NW volume can be attributed to the decrease in the % conversion of Ag^+ to Ag from 77.7 to 58.6% upon addition of 2.2 mM NaBr to the reaction. At present it is not entirely clear why the presence of NaBr reduced the reduction rate of Ag^+ to Ag. Hu et al. have suggested that the addition of Br^- and subsequent formation of AgBr decreased the concentration of dissociated Ag^+ ions and thereby reduced the reduction rate of Ag^+ , leading to the formation of thinner nanowires.⁹ An alternative hypothesis is that Br^- adsorbed on the surfaces of the Ag NWs reduced the rate of atomic addition to the Ag NWs.³¹

Reactions were also carried out using PVP with different molecular weights to see if the molecular weight was an important factor in determining NW diameter. When the molecular weight of PVP was 55 K instead of 130 K, the diameter of the NWs was 25 ± 2 nm (Figures S8A and B in the Supporting Information), slightly larger than the 20 ± 2 nm obtained for PVP with a molecular weight of 130 K. The diameter could be decreased to 21 nm in the presence of 2.75 mM NaBr with a molecular weight of PVP = 55 K (Figure S9 in the Supporting Information). If the PVP molecular weight was reduced to 29 K, nanoparticles were the dominant product (Figure S8C in the Supporting Information). Thus, as demonstrated previously in similar reactions, the molecular weight of PVP is important in determining the yield of NWs relative to nanoparticles, but it does not have a very significant effect on nanowire diameter.^{22,24,32}

Purified Ag NWs were transferred into an ink containing ethyl cellulose, ethyl alcohol, isopropyl alcohol, ethyl acetate, pentyl acetate, and toluene for coating with a Meyer rod. We have previously used a nitrocellulose-based ink for making Cu NW films, but this ink requires the use of acetone to dissolve nitrocellulose, and Ag NWs are not easily dispersed in acetone because they are coated with PVP (which is not soluble in acetone). Figure 4A shows a SEM image of a Ag NW film coated with a Meyer rod from the ethyl cellulose ink. Figure 4B shows a plot of specular transmittance (%T) versus sheet resistance (R_s) for films of 20 nm Ag NWs before and after purification, along with some of the best previous literature results for solution-coatable transparent conductors. The transmittance of films made from purified NWs was up to 4% greater than films made from NWs without purification. The performance of the purified NWs exceeds the performance of any other transparent conductor at sheet resistances $>75 \Omega$

sq^{-1} . Only Ag NWs from Cambrios have higher values at lower sheet resistance. These results further demonstrate the importance of the aspect ratio, diameter, and purity on the performance of NW-based transparent conductors.¹

In conclusion, the introduction of NaBr into a polyol synthesis enables the production of Ag NWs with aspect ratios >2000 , and diameters of 20 nm. The reduction in NW diameter obtained through the addition of NaBr was primarily due to an increase in the number of nucleation events, and secondarily due to a reduction in the % conversion of Ag^+ to Ag. The nanoparticles that inevitably contaminate the NWs produced by a polyol synthesis can be removed with a simple, scalable selective precipitation process. When coated from an ethyl cellulose-based ink to make a transparent conducting film, purified Ag NWs exhibited a transmittance of 99.1% at $130.0 \Omega \text{sq}^{-1}$. Purification of the NWs improved the transmittance at a given sheet resistance by as much as 4%. Variations of the selective precipitation process can likely enable the purification of a wide variety of NWs. The synthesis and purification process demonstrated here is expected to be very useful for researchers in industry and academia seeking to produce NW-based films with performance that exceeds that of ITO.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.nanolett.5b02582](https://doi.org/10.1021/acs.nanolett.5b02582).

Detailed description of experimental methods and additional figures. (PDF)

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B.L. and S.Y. contributed equally to this work.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Ye, S.; Rathmell, A. R.; Chen, Z.; Stewart, I. E.; Wiley, B. J. *Adv. Mater.* **2014**, *26*, 6670.
- (2) Zhang, D.; Ryu, K.; Liu, X.; Polikarpov, E.; Ly, J.; Tompson, M. E.; Zhou, C. *Nano Lett.* **2006**, *6*, 1880.
- (3) Wu, Z.; Chen, Z.; Du, X.; Logan, J. M.; Sippel, J.; Nikolou, M.; Kamaras, K.; Reynolds, J. R.; Tanner, D. B.; Hebard, A. F.; Rinzler, A. G. *Science* **2004**, *305*, 1273.
- (4) Geng, H. Z.; Kim, K. K.; So, K. P.; Lee, Y. S.; Chang, Y.; Lee, Y. H. *J. Am. Chem. Soc.* **2007**, *129*, 7758.
- (5) Wassei, J. K.; Kaner, R. B. *Mater. Today* **2010**, *13*, 52.
- (6) Lee, J. H.; Shin, D. W.; Makotchenko, V. G.; Nazarov, A. S.; Fedorov, V. E.; Kim, Y. H.; Choi, J. Y.; Kim, J. M.; Yoo, J. B. *Adv. Mater.* **2009**, *21*, 4383.
- (7) Elschner, A.; Lovenich, W. *MRS Bull.* **2011**, *36*, 794.
- (8) Na, S. I.; Kim, S. S.; Jo, J.; Kim, D. Y. *Adv. Mater.* **2008**, *20*, 4061.
- (9) Hu, L.; Kim, H. S.; Lee, J.; Peumans, P.; Cui, Y. *ACS Nano* **2010**, *4*, 2955.
- (10) Mayousse, C.; Celle, C.; Moreau, E.; Mainguet, J. F.; Carella, A.; Simonato, J. P. *Nanotechnology* **2013**, *24*, 215501.
- (11) Lee, J.; Lee, P.; Lee, H.; Lee, D.; Lee, S. S.; Ko, S. H. *Nanoscale* **2012**, *4*, 6408.
- (12) Lee, E. J.; Chang, M.-H.; Kim, Y.-S.; Kim, J.-Y. *APL Mater.* **2013**, *1*, 042118.
- (13) Guo, H.; Lin, N.; Chen, Y.; Wang, Z.; Xie, Q.; Zheng, T.; Gao, N.; Li, S.; Kang, J.; Cai, D.; Peng, D. L. *Sci. Rep.* **2013**, *3*, 2323.
- (14) Rathmell, A. R.; Bergin, S. M.; Hua, Y. L.; Li, Z. Y.; Wiley, B. J. *Adv. Mater.* **2010**, *22*, 3558.
- (15) Rathmell, A. R.; Wiley, B. J. *Adv. Mater.* **2011**, *23*, 4798.
- (16) Cambrios Technologies. <http://www.cambrios.com/> (accessed May 2015).
- (17) Mutiso, R. M.; Sherrott, M. C.; Rathmell, A. R.; Wiley, B. J.; Winey, K. I. *ACS Nano* **2013**, *7*, 7654.
- (18) Bergin, S. M.; Chen, Y. H.; Rathmell, A. R.; Charbonneau, P.; Li, Z. Y.; Wiley, B. J. *Nanoscale* **2012**, *4*, 1996.
- (19) Chang, Y.-H.; Lu, Y.-C.; Chou, K.-S. *Chem. Lett.* **2011**, *40*, 1352.
- (20) Tao, A.; Sinsermuksakul, P.; Yang, P. *Angew. Chem., Int. Ed.* **2006**, *45*, 4597.
- (21) Pradel, K. C.; Sohn, K.; Huang, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 3412.
- (22) Sun, Y. G.; Yin, Y. D.; Mayers, B. T.; Herricks, T.; Xia, Y. N. *Chem. Mater.* **2002**, *14*, 4736.
- (23) Sun, Y. G.; Xia, Y. N. *Adv. Mater.* **2002**, *14*, 833.
- (24) Zhu, J. J.; Kan, C. X.; Wan, J. G.; Han, M.; Wang, G. H. *J. Nanomater.* **2011**, *2011*, 1.
- (25) Wiley, B. J.; Sun, Y. G.; Xia, Y. N. *Langmuir* **2005**, *21*, 8077.
- (26) Wiley, B. J.; Sun, Y. G.; Xia, Y. N. *Acc. Chem. Res.* **2007**, *40*, 1067.
- (27) Wiley, B. J.; Herricks, T.; Sun, Y. G.; Xia, Y. N. *Nano Lett.* **2004**, *4*, 1733.
- (28) Wiley, B. J.; Im, S. H.; Li, Z. Y.; McLellan, J.; Siekkinen, A.; Xia, Y. N. *J. Phys. Chem. B* **2006**, *110*, 15666.
- (29) Liu, S.; Yue, J.; Gedanken, A. *Adv. Mater.* **2001**, *13*, 656.
- (30) Schuette, W. M.; Buhro, W. E. *ACS Nano* **2013**, *7*, 3844.
- (31) Foresti, M. L.; Kobayashi, H.; Pezzatini, G.; Guidelli, R. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 3747.
- (32) Zeng, X.; Zhou, B.; Gao, Y.; Wang, C.; Li, S.; Yeung, C. Y.; Wen, W. *Nanotechnology* **2014**, *25*, 495601.
- (33) Hecht, D. S.; Heintz, A. M.; Lee, R.; Hu, L.; Moore, B.; Cucksey, C.; Risser, S. *Nanotechnology* **2011**, *22*, 075201.
- (34) Ye, S.; Rathmell, A. R.; Stewart, I. E.; Ha, Y. C.; Wilson, A. R.; Chen, Z.; Wiley, B. J. *Chem. Commun.* **2014**, *50*, 2562.