

Ag Nanowires Prepared by a Modified Polyol Method with 1,4-Benzoquinone Additives

Miseon Kang, Eunseon Chung, Sang-Ho Kim, and Seog Woo Rhee*

Department of Chemistry, Kongju National University, Kongju 314-701, Korea. *E-mail: jisanrhee@kongju.ac.kr
Received May 30, 2014, Accepted July 9, 2014

This paper describes a selective synthetic method of fabricating Ag nanowires by using a modified polyol process. To synthesize the Ag nanowire, an ethylene glycolic solution of silver nitrate and an ethylene glycolic solution of polyvinylpyrrolidone solution containing a small amount of organic oxidant, 1,4-benzoquinone, were slowly added to a hot ethylene glycol medium at 160 °C for 8 min using a syringe pump. The reaction mixtures were heated for an additional 45 min and cooled to room temperature. Finally, the silver nanomaterials were isolated from the mixture by centrifugation. The crystal structure of the nanomaterials was investigated by powder X-ray diffraction analyses, and their morphology was investigated by scanning electron microscopy. A small amount of organic oxidant, 1,4-benzoquinone, played a significant role in controlling the morphology during crystal growth. Consequently, Ag nanowires rather than Ag nanoparticles were selectively obtained.

Key Words : Ag nanowire, 1,4-Hydroquinone, Polyol process

Introduction

Silver nanomaterials have been actively used in material science, information, energy, and bioengineering fields, and recently even in medical and pharmaceutical fields.¹⁻⁴ The characteristics and applications of silver nanomaterials depend on their size, shape, composition, crystallinity, and microstructure.⁴⁻⁹ There are an extensive number of methods for synthesizing silver nanomaterials: mechanical, chemical, and electrochemical methods. A number of nanomaterials can be formed through various types of chemical reactions in solutions, and the chemical methods include solution reduction, hydrothermal, chemical precipitation, and polyol methods.^{5,10-14}

There have been various types of Ag nanomaterials synthesized *via* the application of the polyol method developed by Fievet.¹² In particular, Xia *et al.* reported the possibility of controlling the morphology of nanomaterials by controlling the reaction conditions, such as the molar ratio of the reactants, reaction temperature, reaction time, and the addition of additives in ethylene glycol (EG).^{5,9,15-17} In the polyol method, EG acts as a solvent and a reducing agent⁵, and polyvinylpyrrolidone (PVP) acts as a capping agent and a stabilizer.^{18,19}

It is possible to synthesize silver nanomaterials with various morphologies, including nanocubes, nanowires, nanospheres, nanoplates, and nanobelts by controlling the interaction between PVP and each facet of the seed crystal during crystal growth.⁹ Recent studies have tried to control the morphology of nanostructures formed by controlling the reaction with the addition of NaCl, CuCl/CuCl₂, Na₂S/NaHS, and Fe(II)/Fe(III) species.^{9,15-17,20,21} By controlling the reaction conditions, the crystal growth rates on each facet of the seed crystal could be controlled. As a result, it becomes possible to form uniquely shaped silver nano-

structures based on the growth of selective crystals in a specific direction.⁹

1,4-Hydroquinone (1,4-HQ) is used in the developing solutions of AgBr-based photographic film.²² 1,4-HQ is converted into 1,4-benzoquinone (1,4-BQ) after being oxidized reversibly under acidic conditions.²³ However, due to the lower oxidation potential of 1,4-HQ, it is not possible to reduce isolated silver ions.²⁴ When light is irradiated onto a AgBr-coated film by exposure, the photons reduce a small amount of silver ions to form silver clusters on the surface of the films, and then silver ions are reduced by 1,4-HQ during photo development.²⁴ Therefore, another reducing agent should be used in order to use the 1,4-HQ for the reduction of silver ions under solution conditions.

This paper describes a method for selective synthesis of silver nanowires based on the modification of a control polyol method by adding a small amount of 1,4-BQ. The effect of the 1,4-BQ on the nanowire formation process is also discussed. First, a glycolaldehyde was formed through the oxidation of EG, the reaction solvent, at a high temperature. Silver clusters were then generated by the reduction of the silver ions by the glycolaldehyde. Finally, Ag nanowires were obtained predominantly by the selective growth of silver on the surface of the clusters under the reversible 1,4-BQ/1,4-HQ redox reaction system.

Experimental

Reagent. All chemicals were purchased from Sigma-Aldrich Chemical Co.(MO, USA), Junsei Chemicals (Japan), and Samchun Chemicals (Korea). All chemicals were of reagent grade and used without further purification.

Synthesis of Silver Nanomaterials by Polyol Method. The silver nanomaterials were synthesized by the similar method reported by Xia *et al.*⁵ After 5 mL of EG was heated

at 160 °C for 1 h, 3 mL of an ethylene glycol solution of 0.250 M silver nitrate and 3 mL of another ethylene glycol solution of 0.375 M PVP containing a small amount of 1,4-BQ (or without 1,4-BQ) were simultaneously injected into the hot EG media at a rate of 0.375 mL/min for 8 min by using a syringe pump. The reaction mixture was additionally heated at 160 °C for 45 min. The reaction mixture was cooled down to room temperature, washed three times with distilled water and once with ethanol, and the product was dried at room temperature.

The scale-up reactions were carried out under the same conditions with ten times higher concentrations of each reagent.

Physiochemical Analysis. The chemical composition of the surface of the nanomaterials was analyzed by energy dispersive spectrometry (EDS, Oxford, JEOL). The contents of the organic matter on the surface were measured by elemental analysis (EA, Thermo-Finnigan EA-1112) and thermogravimetric analysis (TGA, Setaram). The morphology of the synthetic solid materials was analyzed by using a scanning electron microscope (SEM, Mini-SEM, SNE-4000M, SEC). Powder X-ray diffraction (PXRD) patterns were recorded on an X-ray diffractometer (Mini flex-II, Rigaku) using Cu K α radiation with a scan rate of $2\theta = 4^\circ/\text{min}$ and a range of $2\theta = 3-90^\circ$. The size of spherical nanoparticles was measured by using a particle size analyzer (NanotractTM 150, Microtrac).

Results and Discussion

The silver nanomaterials were obtained with a high yield of over 90%. On the basis of the composition analyses of the silver nanomaterials, organic matter related to the PVP capping agent comprised only a small portion (~0.4%), whereas silver comprised a major portion of the materials. According to TGA (data not shown), the silver nanomaterials had a weight loss of 0.4% up to 400 °C. This loss is thought to be caused by the release of PVP.^{18,19} Detectable weight loss was not observed at temperatures between 400 and 800 °C.

Silver Nanomaterials Synthesized by Polyol Method without 1,4-BQ. Figure 1(a) shows the SEM image of the silver nanomaterials synthesized in this work according to the control polyol method without 1,4-BQ. As shown in the figure, the silver nanoparticles were mainly of quasi-spherical,

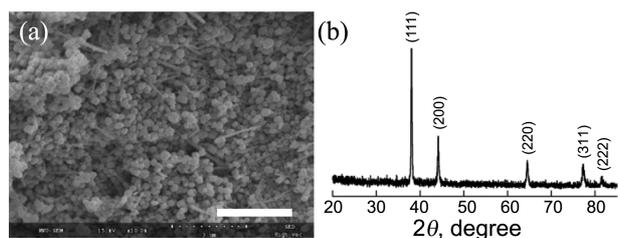


Figure 1. (a) SEM image and (b) PXRD pattern of silver nanomaterial synthesized without 1,4-BQ. Reaction conditions: $[\text{AgNO}_3] = 0.250 \text{ M}$; $[\text{PVP}] = 0.375 \text{ M}$; injection time: 8 min; additional heating: 45 min; reaction temperature of 160 °C. Scale bar: 3 μm .

although there were a few nanowires. The complete silver nanocubes reported by Xia *et al.*⁵ were not observed in this work. It was found that the particle sizes (data not shown) of the quasi-spherical silver nanoparticles were between 100 and 500 nm. The most frequent value was 410 nm, which accounted for approximately 41.8% of the particles.

Figure 1(b) shows the PXRD pattern of the silver nanomaterials synthesized without 1,4-BQ. Diffractions were identified on the (111), (200), (220), (311), and (222) planes, indicating that the crystals had a face-centered cubic (fcc) crystal system (JCPDS card No. 04-0783).

Silver Nanomaterials Synthesized by Polyol Method with 1,4-BQ. Figures 2(a)-(e) show the SEM images of silver nanomaterials synthesized by the modified polyol method with 1,4-BQ.

As can be observed in the SEM images, most of the particles are nanowires ranging from 190 to 250 nm in width and longer than 1 μm in length. It was observed that the thickness of the nanowires depended on the amount of 1,4-BQ: As the amount of 1,4-BQ increased, the thickness of the nanowires increased. The PXRD pattern of one sample of nanowires is shown in Figure 2(f). Like the PXRD pattern of the silver nanoparticles synthesized with no 1,4-BQ (Figure 1(b)), diffractions were identified on the (111), (200), (220), (311), and (222) planes, indicating a fcc crystal system.

Xia *et al.* proposed several possible mechanisms based on the reaction conditions and roles of the materials involved in the reaction, especially regarding the morphology control of silver nanomaterials synthesized on the basis of the polyol

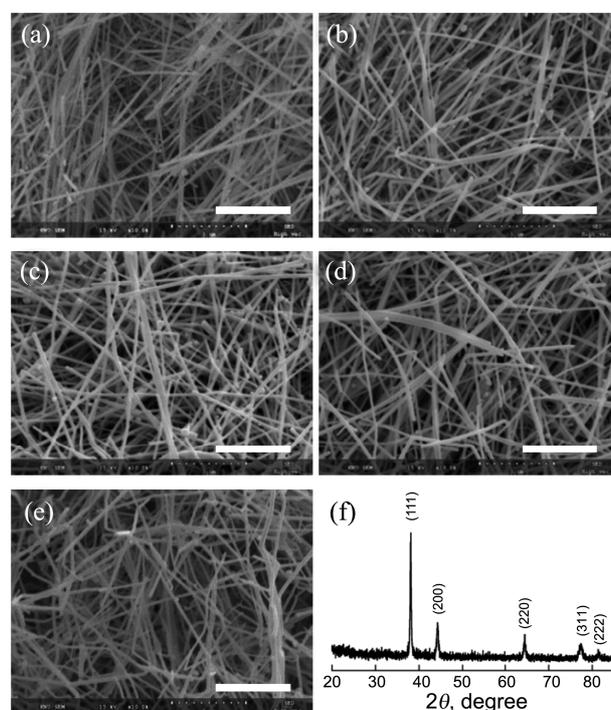


Figure 2. SEM images of silver nanomaterials synthesized with $[\text{1,4-BQ}]/[\text{Ag}^+]$ of (a) 0.030, (b) 0.060, (c) 0.10 (d) 0.13, (e) 0.15. (f) PXRD pattern of sample (a). Reaction conditions: $[\text{AgNO}_3] = 0.250 \text{ M}$; $[\text{PVP}] = 0.375 \text{ M}$; injection time: 8 min; additional heating: 45 min; reaction temperature of 160 °C. Scale bar: 3 μm .

method.⁹ Silver nanocubes were obtained as a major product and nanowires were obtained as a minor product under the reaction conditions used in this study: a reaction temperature of 160 °C, the total number of moles of $\text{AgNO}_3 = 7.5 \times 10^{-4}$ mol, the total number of moles of PVP repeating units = 1.125×10^{-3} mol, [number of moles of PVP repeating units]/[number of moles of AgNO_3] = 1.50, injection time of 8 min, and additional reaction time of 45 min.⁵ According to the literature, some parts of the solvent EG were oxidized into glycolaldehyde by heating in air, which then reduced the silver ions in the solution to form silver clusters or silver nuclei.²⁶ The seed crystals were grown by the subsequent reduction of silver ions on the silver clusters.⁹ At the same time, the seed crystals were etched in an anisotropic manner by HNO_3 , which was generated as a side product. Therefore, the rate of crystal growth decreased and the crystals grew in a specific facet direction. As a result, cube-shaped crystalline nanomaterials could be obtained in the single crystal seed.^{12,15} Also, owing to differences in the binding affinity between the facets of the silver nanomaterials and PVP, the rate of crystal growth differs between the $\{100\}$ and $\{111\}$ facets of the polyhedral nuclei. Consequently, anisotropic growth on the $\{111\}$ facet with a high crystal growth rate takes place in the nanocube.²⁷

In order to synthesize nanowires based on the polyol method reported by Xia *et al.*, the concentration of silver ions should be lowered to the conditions of $[\text{Ag}^+] < 0.1$ M, or [number of moles of PVP repeating units]/[number of moles of AgNO_3] ~ 1.50 , or additional additives should be used under the similar conditions.^{5,9,19,20,25,27} In this study, however, we used an organic oxidant, 1,4-BQ, such that [number of moles of 1,4-BQ]/[number of moles of AgNO_3] = 0.03-0.30 for the selective synthesis of nanowires. In the initial step of the reaction, silver ions can be reduced to form silver seed clusters by the glycolaldehyde that is generated from the oxidation of EG by heating. At the same time, the 1,4-BQ present in solution can also be reversibly reduced to 1,4-HQ by the glycolaldehyde. Moreover, as H^+ is consumed in the 1,4-BQ reduction reaction, the etching reaction of the initial nuclei by HNO_3 is inhibited. Because the 1,4-HQ might be bound only on the $\{111\}$ facet of the multi-twinned seed crystal and because it has a lower reducing power, the crystal is grown selectively on the $\{111\}$ facet where PVP is weakly bound.¹² It is thought that anisotropic crystal growth

is preferred due to the influence of 1,4-BQ/1,4-HQ redox system, as like $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox system,²¹ and thus the silver nanowires are formed.

With increasingly higher concentrations of 1,4-BQ, the glycolaldehyde is consumed faster. As a result, the formation rate of the seed silver clusters decreases and the size of the seeds increases as compared to the control synthesis case. Moreover, the etching of seed silver is inhibited as the HNO_3 generated by the reduction of silver ions is consumed by the reduction of 1,4-BQ. Therefore, the anisotropic crystal growth based on larger seeds results in thicker nanowires.

Figures 3(a)-(c) show the SEM images of silver nanomaterials that resulted from the reaction with the addition of 1,4-BQ after the control polyol method-based synthesis with no 1,4-BQ added. The particles are mainly of quasi-spherical with a few nanowires to the silver nanoparticles obtained by the control polyol method. It was found that adding 1,4-BQ after the complete formation of the silver nanoparticles had no effect on the silver nanoparticle morphology.

Figures 4(a)-(b) show the SEM images of silver nanomaterials that resulted from reactions with ten times higher concentrations of reactants.

As shown in Figure 4(a) in the case of the reaction without 1,4-BQ, the silver nanoparticles were mainly quasi-spherical, with a few nanowires. The particle size of the quasi-spherical silver nanoparticles was *ca.* 1 μm , which is much bigger than that of nanoparticles obtained from the control polyol method. As shown in Figure 4(b) in the case of the reaction with 1,4-BQ, most of the obtained silver nanoparticles con-

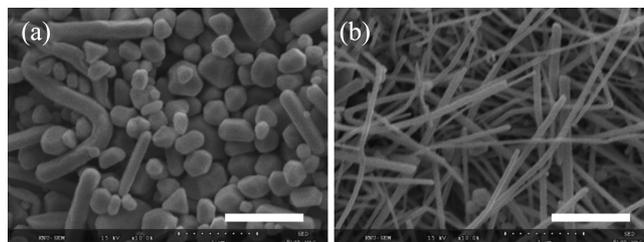


Figure 4. SEM images of silver nanomaterials synthesized using ten times higher concentrations of the reactants: $[\text{AgNO}_3] = 2.50$ M; $[\text{PVP}] = 3.75$ M, injection time: 8 min; additional heating: 45 min; reaction temperature of 160 °C. (a) Silver nanomaterials synthesized without 1,4-BQ. (b) Silver nanomaterials synthesized with 1,4-BQ ($[\text{1,4-BQ}]/[\text{Ag}^+] = 0.10$). Scale bar: 3 μm .

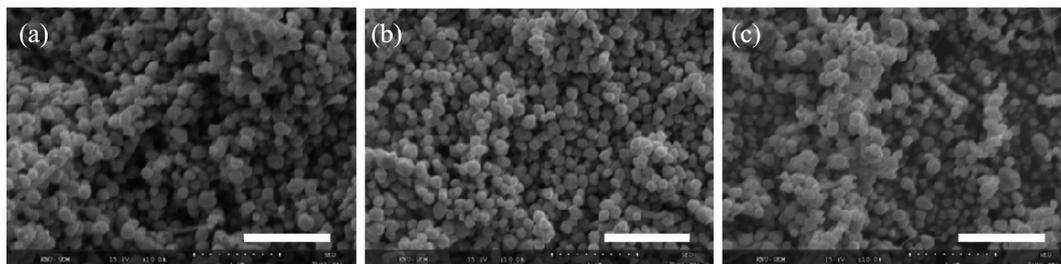


Figure 3. SEM images of silver nanomaterials synthesized without 1,4-BQ, and then further heated with 1,4-BQ ($[\text{1,4-BQ}]/[\text{Ag}^+] = 0.10$) for (a) 30 min, (b) 45 min, and (c) 60 min. Reaction conditions: $[\text{AgNO}_3] = 0.250$ M; $[\text{PVP}] = 0.375$ M; injection time: 8 min; additional heating: 45 min; reaction temperature of 160 °C. Scale bar: 3 μm .

sisted with nanowires. In other words, even when the reaction concentration increased ten times, nanowires were obtained due to the effect of 1,4-BQ.

Conclusion

This study proposed a way of synthesizing silver nanomaterials by reducing silver ions with the addition of a small amount of oxidant, 1,4-BQ, to the polyol method. It was observed that the shape of the silver nanomaterials was dependent on the addition of 1,4-BQ. The 1,4-BQ/1,4-HQ system reduced the silver ions by a reversible redox reaction under the reaction conditions, enabling crystal growth in one specific direction of the seed crystal, resulting in the fabrication of nanowires. Moreover, in spite of scaling the reaction concentration up by a factor of ten, the structure, shape, and size of nanomaterials remained almost unchanged, indicating very good reproducibility. Therefore, the results of this study will make a contribution to applications related to the morphology control of silver nanoparticles.

Acknowledgments. This study was supported by the Research Supporting Program of Kongju National University in 2012.

References

1. Tolaymat, T. M.; El Badawy, A. M.; Genaidy, A.; Scheckel, K. G.; Luxton, T. P.; Suidan, M. *Sci. Tot. Environ.* **2010**, *408*, 999-1006.
2. Kim, S. H.; Choi, B. S.; Kang, K.; Choi, Y.-S.; Yang, S. I. *J. Alloys Compd.* **2007**, *433*, 261-264.
3. Marambio-Jones, C.; Hoek, E. M. V. *J. Nanopart. Res.* **2010**, *12*, 1531-1551.
4. Reidy, B.; Haase, A.; Luch, A.; Dawson, K. A.; Lynch, I. *Materials* **2013**, *6*, 2295-2350.
5. Sun, Y.; Xia, Y. *Science* **2002**, *298*, 2176-2179.
6. Albanese, A.; Tang, P. S.; Chan, W. C. W. *Ann. Rev. Biomed. Eng.* **2012**, *14*, 1-16.
7. Saion, E.; Gharibshahi, E.; Naghavi, K. *Int. J. Mol. Sci.* **2013**, *14*, 7880-7896.
8. Burda, C.; Chen, X.; Narayanan, R.; El-Sayed, M. A. *Chem. Rev.* **2005**, *105*, 1025-1102.
9. Wiley, B.; Sun, Y.; Xia, Y. *Acc. Chem. Res.* **2007**, *40*, 1067-1076.
10. Khaydarov, R. A.; Khaydarov, R. R.; Gapurova, O.; Estrin, Y.; Scheper, T. *J. Nanopart. Res.* **2009**, *11*, 1193-1200.
11. Krutyakov, Y. A.; Kudrinskiy, A. A.; Olenin, A. Y.; Lisichkin, G. V. *Russ. Chem. Rev.* **2008**, *77*, 233-257.
12. Fievet, F.; Lagier, J. P.; Figlarz, M. *MRS Bull.* **1989**, *14*, 29-34.
13. Zou, J.; Xu, Y.; Hou, B.; Wu, D.; Sun, Y. *China Particuology* **2007**, *5*, 206-212.
14. Chou, K.-S.; Ren, C.-Y. *Mater. Chem. Phys.* **2000**, *64*, 241-246.
15. Im, S. H.; Lee, Y. T.; Wiley, B.; Xia, Y. *Angew. Chem. Int. Ed.* **2005**, *44*, 2154-2157.
16. Wiley, B.; Herricks, T.; Sun, Y.; Xia, Y. *Nano Lett.* **2004**, *4*, 1733-1739.
17. Siekkinen, A. R.; McLellan, J. M.; Chen, J.; Xia, Y. *Chem. Phys. Lett.* **2006**, *432*, 491-496.
18. Wang, H.; Qiao, X.; Chen, J.; Wang, X.; Ding, S. *Mater. Chem. Phys.* **2005**, *94*, 449-453.
19. Sun, Y.; Xia, Y. *Adv. Mater.* **2002**, *14*, 833-837.
20. Korte, K. E.; Skrabalak, S. E.; Xia, Y. *J. Mater. Chem.* **2008**, *18*, 437-441.
21. Wiley, B.; Sun, Y.; Xia, Y. *Langmuir* **2005**, *21*, 8077-8080.
22. James, T. H. *J. Am. Chem. Soc.* **1939**, *61*, 648-652.
23. Radel, R. J.; Sullivan, J. M.; Hatfield, J. D. *Ind. Eng. Chem. Prod. Res. Dev.* **1982**, *21*, 566-570.
24. Gentry, S. T.; Fredericks, S. J.; Krchnavek, R. *Langmuir* **2009**, *25*, 2613-2621.
25. Chen, J.; Wiley, B. J.; Xia, Y. *Langmuir* **2007**, *23*, 4120-4129.
26. Skrabalak, S. E.; Wiley, B. J.; Kim, M.; Formo, E. V.; Xia, Y. *Nano Lett.* **2008**, *8*, 2077-2081.
27. Wiley, B.; Sun, Y.; Mayers, B.; Xia, Y. *Chem. Eur. J.* **2005**, *11*, 454-463.