Effects of chloride ions and poly (vinyl-pyrrolidone) on morphology of silver particles in solvothermal process

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ABSTRACT

Silver particles with various morphologies including cubic, spherical, and rod-shaped have been synthesized by a facile solvothermal procedure using poly (vinyl pyrrolidone) (PVP) as an adsorption agent and architecture soft template. Preparation conditions such as the molar ratio and concentration of starting materials were optimized for studying the growth kinetics of silver particles. The amount of chloride ions and PVP plays an important role for the morphology of silver particles during synthesis. Chloride ions as a stabilizer against the aggregation of particles could sufficiently retard particle growth. The selected bounding of PVP molecules on the silver particle is a key for morphological controlling. The morphological evolution of the silver particle was investigated by adjusting systematically preparation parameters. Because of PVP molecules are easily bounded to the (100) facet of silver crystals, the growth of the silver particle occurred around (111) plane. Silver particles with a series of morphologies were created via such anisotropic growth. Copyright © 2011 VBRI press.

Keywords: Silver; morphology; PVP; solvothermal; chloride ions.

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Introduction

Many kinds of morphological noble metallic particles such as rods and other one-dimensional (1D) nano- and micro-structures (wires, belts, and tubes) have been extensively studied in last decade due to their potential applications in catalysis [1], photonics and plasmonics [2], information storage [3], surface-enhanced Raman scattering (SERS) [4], microelectronics, biological devices [5], and sensing [6]. For example, Ag particles as ulta-sensitive biosensors were excellent analytical tools for pollution monitoring [7]. Because the morphologies of the particles alter their physical and chemical properties, shape- and size-dependent optical properties have already been demonstrated theoretically by several groups. Both of Ag and Au are having outstanding optical properties because of the strong surface plasmon resonances (SPRs), which depend strongly on their size, morphology, composition, and structure [8]. In particularly, the morphology plays an important role for SPRs. It is worth to point out that metallic silver has exhibited excellent SERS effects compared with other metals to a certain degree due to its' diverse morphologies [9].

One-dimensional structures can be created chemically by a hard or soft template synthesis [10, 11]. However, the removal of these templates by either thermal (sintering) or

chemical (etching) methods is complicated [**12**]. Even though hard templates such as tracketched polycarbonate [**13**], pores within zeolite [**14**], and meso-porous silica [**15**] were effective for fabricating nanowires uniformly, many of them needed to be selectively dissolved under harsh conditions in order to harvest the nanowires [**16**]. DNA chains [**17**], rod-shaped micelles of cetyltrimethylammonium bromide (CTAB) [**18**], and liquid crystalline phases of oleate [**19**] as soft templates have been used for the synthesis of metallic nanowires. They also confronted with the difficulties in removing the templates in order to recover the individual nanowires. Compared with template approaches, wet-chemical strategies involving the use of capping agents such as surfactants, polymers, and some ionic species have been proven to be sufficient enough in the controlled synthesis of large-scale 1D silver nano- and micro-structures [**20**]. The building-up procedure and the sample acquisition process are facile in the wet-chemical synthesis. Even if the synthesis of 1D silver nanostructure like nanobar, nanorice, nanorods, and nanobeam, has made great progress [**21–24**], novel SERS substrates are still requested to further get high SERS activities which base on a kind of novel silver structures. In this regard, we synthesized 1D silver rod with extraordinary structure because there are few reports relating to the synthesis process from cubic particles to rods.

A lot of methods have been devoted to prepare silver nano- and micro-structures with various morphologies. For example, single-crystal silver with dendritic supramolecular nano- and micro-structures has been prepared via an ultraviolet irradiation photoreduction technique at room temperature using poly (vinyl alcohol) as a protecting agent [**25**]. We have developed a facile solvothermal approach in the presence of poly (vinyl pyrrolidone) (PVP), $AgNO_3$, and NaCl in ethylene glycol (EG). Silver particles with various kinds of morphologies were fabricated by adjusting reaction time as well as the concentration and ratio of starting materials. Furthermore, PVP and chloride ions play important roles for the evolution of silver morphology [**26, 27**].

Experimental

Preparation of silver particles

In a typical solvothermal synthesis, EG, silver nitrate, PVP (Mw ~ 40000, the concentration was calculated in terms of the repeating unit), and NaCl were as starting materials. $AgNO_3$ (2 mmol) was added in 3 mL of EG with vigorous stirring for getting solution A. PVP (0.13 mmol) and NaCl (0.03 mmol) were added in 3 mL of EG with vigorous stirring for getting solution B. Solution A was added in 5 mL of EG and mixed with solution B with vigorous stirring until the color of the solution changed into light blue. After that, the solution was put into an agitated reactor (a Teflon-sealed autoclave). The agitated reactor with seal can supply a high temperature and pressure environment. The agitated reactor was put in an oven maintained the temperature at 120ºC for 24 h, followed by natural cooling to room temperature. The resulting samples were washed with ethanol by centrifuging at 16000 rpm for 8 min for three

times to remove EG, PVP, and other unreacted materials. Finally, samples were re-dispersed in ethanol for further characterization. To investigate the influence of preparation conditions on the morphology of silver particles, preparation parameters were optimized. **Table 1** illustrates the preparation conditions of silver particles.

Characterization

The microstructures images were taken using a scanning electron microscope (SEM, S-2500, Hitachi, Japan) with a link energy dispersive X-ray (EDX) system with an ultra-thin detector window for local chemical analysis. The phase composition of the silver particles was identified by using X-ray diffraction (XRD, D8-Advance, Bruker, Germany).

Results and discussion

For the synthesis of Ag particles without high pressure as well as without PVP and chloride ions, Ag atoms are generated and diffused at a sufficiently high rate. The resulting Ag particles have no choice but to take the thermodynamically favored shapes (multiply twinned decahedron) and give the most stable (111) face on the top surface of Ag particles. Under high pressure provided by a solvothermal process, atomic diffusion is constrained, which makes atomic mobility more difficult. In this case, the growth kinetics of these Ag particles became complicated. In current experiments, the morphology and dimension of these Ag particles depended on the molar ratio of $PVP/AgNO_3/Cl^-$, the concentration of starting materials as well as reaction temperature and time. The formation of silver rods by a solvothermal approach consisted of three steps. In **step 1**, the Ag^+ ions were first reduced into small Ag seeds by EG and PVP. At the beginning, EG serves as a reducing agent and PVP serves primarily as a stabilizer against aggregation. Furthermore, PVP also serves as a reductant and even plays a role in controlling the shape of Ag seeds [**28**]. In **step 2**, the Ag seeds grew with increased edge lengths of the side faces by the template direction of PVP. In **step 3**, the anisotropic growth of Ag particles occurred, where Ostwald ripening was most likely the driving force for the shape evolution. EG is both as a solvent and a reducing reagent [**27, 29**]. Chloride ions play important roles to prevent the quick growth of Ag particles during synthesis. **Fig. 1** shows the formation scheme of silver rods in solvothermal synthesis.
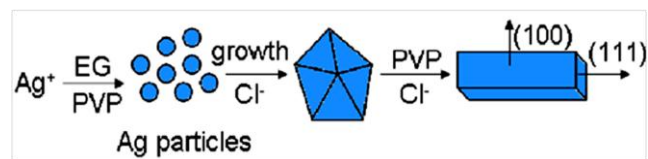
Fig. 1. Formation scheme of silver rods in solvothermal synthesis.

To investigate the morphological evolution of silver particles against preparation conditions such as time and

starting material concentrations, the solvothermal reaction was conducted under a few different durations together with various molar ratios of starting materials. Our experiments demonstrated that the morphology of Ag particles depended on the preparation conditions during the solvothermal process. **Fig. 2** shows the SEM images of sample 1 shown in **Table 1**. Most of Ag particles exhibited a cubic morphology. In contrast, very little amount of Ag particles exhibited a hexagonal morphology. To further clarify the composition and crystal structure of Ag particles, we employed EDX and XRD analysis for the characterization. The EDX analysis indicated that the particles contained Ag components. Typical EDX analysis patterns are shown in the lower part of **Fig. 2**. The EDX analysis from all selected points such as 1 and 2 exhibited very similar composition. The EDX analysis for point 3 shows the components of the background of the substrate. As a result, no Cl component was detected from EDX analysis. Possible reason is that AgCl was not formed during synthesis because of the existence of EG and PVP [**27**]. Since a specimen was put on a cover glass, Al, Si, K, and Na components were detected as shown in **Fig. 2**. **Fig. 3** shows the XRD pattern of Ag particles (sample 1 shown in **Table 1**). The diffraction peaks of Ag particles were match well with a face-centered-cubic (fcc) silver. Four peaks are corresponding to the diffractions from (111), (200), (220), and (311) facets.

Table 1. Preparation conditions of silver particles.

* Concentration of starting materials during reaction.

Sample	EG amount (ml)	AgNO$_3$ (M)*	PVP (M)*	NaCl (M)*	Reaction time (h)	Reaction temperature (℃)
1	11	0.67	0.0417	0.0103	24	120
2	11	1.34	0.0834	0.0205	24	120
3	11	1.34	0.0834	0.0307	24	120
4	11	1.34	0.0834	0.0307	12	120
5	11	1.34	0.0834	0.0307	38	120
6	22	0.67	0.0417	0.0154	38	120

In a solvothermal process, EG was as both solvent and reducing agent. Thus, the nucleation of Ag first occurs in a EG solution. When Ag nanoparticles were formed, PVP was adsorbed on the surface of the nanoparticle through the connection of the N-C=O of PVP and the particle [**26, 28**]. Ag seeds can be formed in the next growth process, which finally yields Ag products. A similar mechanism was used in the case of fractal silver nanostructures generated with high yields via a self-organized process that uses PVP as the adsorption reagent [**30**]. According to the wet etching model, chloride ions play a role as a coordination ligand in the oxidative dissolution process. Namely, the chloride ions could coordinate to Ag nuclei, thereby stabilizing them against aggregation, a primary mechanism for nanoparticle growth [**31**]. In our case, chloride ions as a stabilizer against aggregation could also sufficiently retard particle growth. Two kinds of morphologies were obtained for sample 1. This is ascribed to the kinetic balance between the coordination of chloride ions and the inhomogeneous

adsorption of PVP. To verify the concentration dependent of the morphology of Ag particles, the concentrations of starting materials were increased as explained as follows.
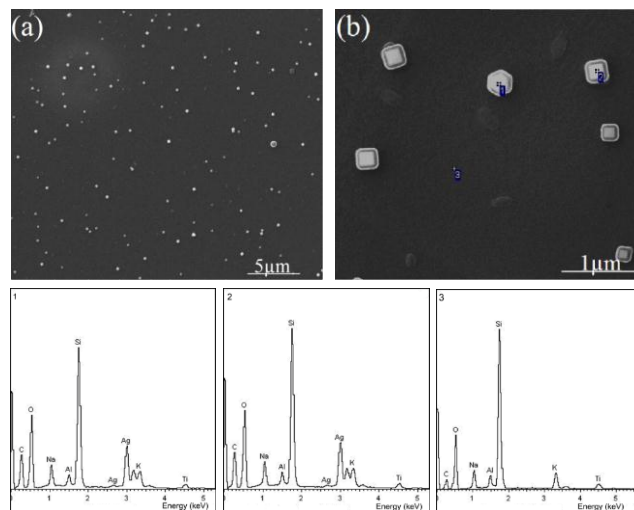
Fig. 2. SEM images of silver particles (sample 1 shown in Table 1 (a) and (b), images taken for same specimen in different area. EDX analysis of detection points 1, 2, and 3 in (b) are shown in lower part. From the EDX analysis of points 1 and 2, Ag component was detected. The EDX analysis for point 3 shows the component of the background.
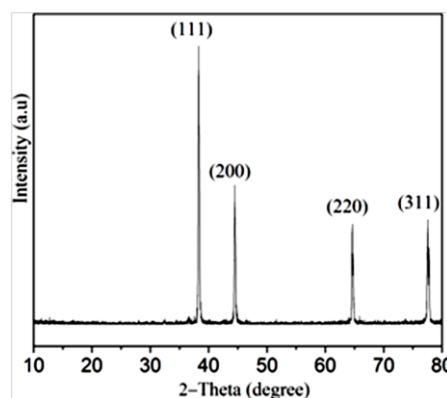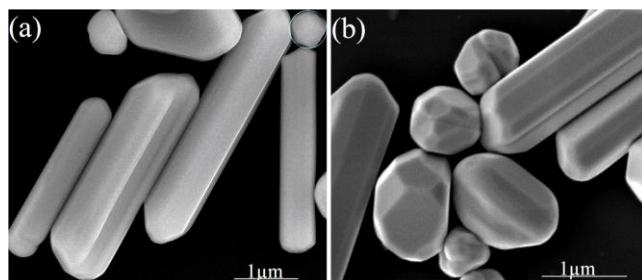

Fig. 3. XRD pattern of silver particles (sample 1 shown in Table 1).

Fig. 4 shows the SEM images of as-synthesized Ag particles shown in **Table 1**: (a) sample 2; (b) sample 3. Except for Ag rods, an Ag particle with pentagonal shape was found out in **Fig. 4a**. Compared with sample 1 shown in **Fig. 2**, the concentration of starting materials became into two times high for sample 2. Such high concentrations resulted in the formation of Ag particles with pentagonal morphology. Ag rods were then created because the anisotropic growth of Ag seeds (pentagonal Ag particles) occurs. Furthermore, the growth of Ag particles was controlled through the kinetics of the adsorption and desorption of PVP on the different facets of Ag seeds. This process resulted in the anisotropic growth of the crystal. The key to the formation of silver rods was supposed to be the use of PVP as a polymer capping reagent. The rods were fabricated by the evolution from a decahedral multiply twinned particle. That is ascribed that the ends of the rods are terminated by (111) facet while the side faces

are terminated by (100) facet. With the side faces are completely passivity by capping agents (PVP) which can be effectively covering and stabilizing on the (100) facet, the rods are gained. The pentagonal structure Ag particles and PVP with a proper concentration play important roles for limiting the growth of silver rods into the 1D mode. If the interaction between PVP and the (100) facet become weak, other morphologies will appear such as cubic and spherical.

To investigate the effect of chloride ions on the formation of Ag rods, the concentration of chloride ions was increased as shown in **Fig. 4b** (sample 3 shown in **Table 1**). Compared with sample 2, the ratio of spherical particle/rod increased for sample 3. This is ascribed to the effect of chloride ions on the growth of Ag particles. Because chloride ions as a stabilizer against aggregation sufficiently retard particle growth, the amount of spherical polyhedron increased for sample 3 as shown in **Fig. 4b**. In the case of large amount of chloride ions, two kinds of growths occur at the same time. Single crystal was grown into a spherical polyhedron while twinned crystal was developed into a rod.
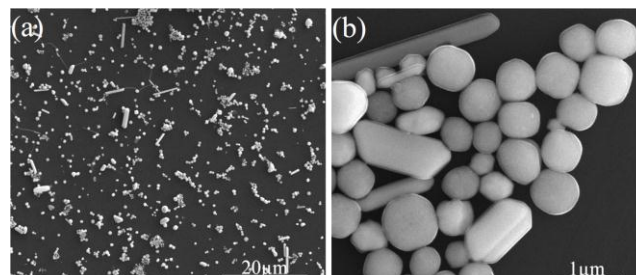

Fig. 4. SEM images of as-synthesized Ag particles shown in Table 1: (a), sample 2; (b), sample 3.

To confirm the mechanism we discussed above, SEM observation was employed to observe the morphological evolution of Ag particles with time. **Fig. 5** shows the SEM images of Ag particles prepared with a short reaction time (sample 4 shown in **Table 1**). Even though little amount of rods was still observed, most of Ag particles revealed torispherical morphology. This is ascribed that PVP cannot be fully attached to the (100) facet of Ag particles within a short time. When the reaction time was increased to 38 h, Ag particles with torispherical morphology were further grown into rods. **Fig. 6** shows the SEM images of these rods (sample 5). Because of the Ostwald ripening mechanism, particles with large size were directly grown into rods and small particles were dissolved.

For further explaining the co-effect of chloride ions and PVP on the morphology of Ag particles, the concentration of starting materials was adjusted. **Fig. 7** shows the SEM images of Ag particles (sample 6 shown in **Table 1**). These Ag particles exhibited rod morphology. Compared with sample 1, the concentration of chloride ions increased and reaction time was prolonged. For sample 1, most of Ag particles revealed cubic morphology. In contrast, the Ag rods in the SEM images of sample 5 did not show cubic cross section. This means the growth process of sample 5 is different from sample 1. Therefore, the high concentration

of chloride ions affected the growth kinetic of Ag particles. The growth process of sample 5 was similar to that of sample 3. Namely, Ag particles with pentagonal morphology were first formed. Ag rods were then created due to the anisotropic growth of these Ag particles. Therefore, our experiments suggest that the solvothermal process is utilizable to form anisotropic Ag particles and PVP and chloride ions play critical roles for Ag particles with various morphologies.

Fig. 5. SEM images of as-synthesized Ag particles (sample 4 shown in **Table 1**): (a) and (b), images taken for same specimen in different area.
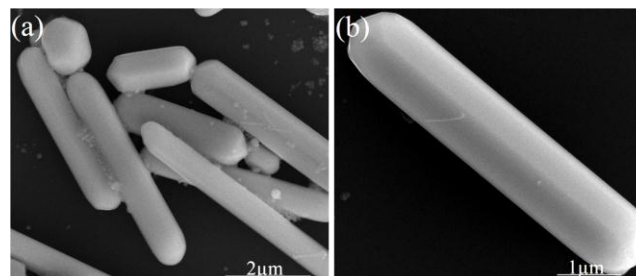
Fig. 6. SEM images of silver particles (sample 5 shown in **table 1**): (a) and (b), images taken for same specimen in different area.
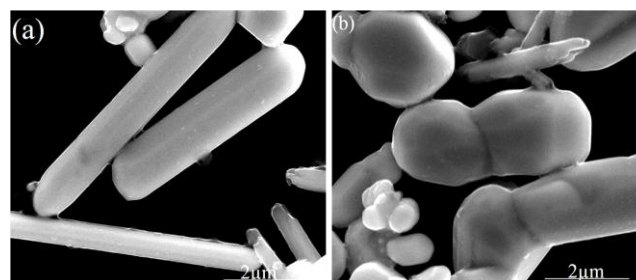
Fig. 7. SEM images of as-synthesized Ag particles (sample 6 shown in **Table 1**): (a) and (b), images taken for same specimen in different area.

Conclusion

A sufficient solvothermal process has been developed to create Ag particles with various morphologies such as cubic particles, rods, and spheres. The morphologies of theses Ag particles depended strongly on the concentration of starting materials and reaction time. Especially, chloride ions and PVP play important roles in the controlling of morphology. PVP was as an adsorption agent and architecture soft template because PVP is easily bonding to the (100) facet of Ag particles. Chloride ions as a stabilizer

against aggregation could also sufficiently retard particle growth. The co-effect of PVP and chloride ions affected the growth kinetics of Ag particles in solvothermal process. It was worth to point out the solvothermal process is useful to form anisotropic Ag particles by optimizing the preparation conditions. Current results should be utilizable for the synthesis of metal particles with different morphologies.

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