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Research Article

The Effect of Hydrothermal Treatment on Silver Nanoparticles Stabilized by Chitosan and Its Possible Application to Produce Mesoporous Silver Powder

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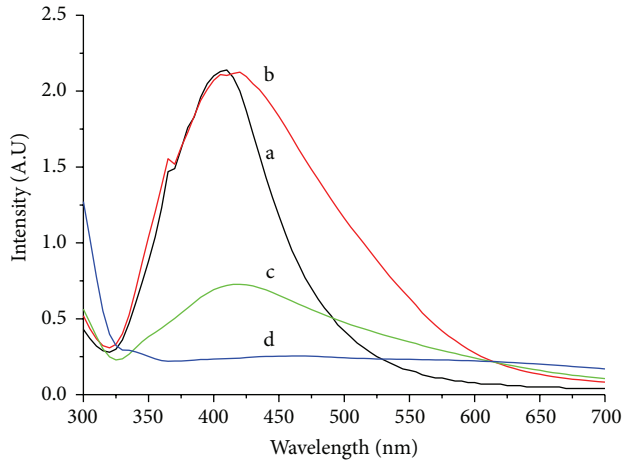
Aggregation state of silver nanoparticles dispersed in an aqueous solution greatly varies with storage and treatment conditions. In this study, silver nanoparticles synthesized in chitosan solution by a chemical reduction method were hydrothermally treated at different temperatures. The variation in the aggregation state of silver nanoparticles in the solution was observed by UV-Vis spectroscopy and field emission transmission electron microscopy. Results indicated that a phase transition occurred while silver nanoparticles were hydrothermally treated for 5 h at 100 and 120°C; however, they aggregated and completely precipitated at 150°C. Mesoporous silver powder obtained by hydrothermal treatment at 150°C was characterized by using X-ray diffraction technique, BET analyzer, and scanning electron spectroscope.

1. Introduction

Silver nanoparticles have become the most widely commercialized nanomaterials due to thier unique physicochemical and biological properties [1]. Silver nanoparticles can be synthesized and stabilized in the presence of polymers [2–7] in an aqueous solution or organic solvents. They can also be stabilized in the pores of porous materials where tiny spaces or channels act as spatial hindrance, which inhibits the growth of silver particles [8–11]. The size and shape of silver nanoparticles in porous materials depend on their pore diameters and are almost stable after synthesis, whereas that of silver nanoparticles in solutions is affected by various factors including storing conditions, the type and concentration of stabilizer, the concentration of silver nanoparticles, and synthetic routes. The properties, applicability and efficiency of final products are greatly related to the size, the shape, and the aggregation state of silver nanoparticles.

Silver powder has been widely used in catalysis, electronics, chemical industry, and biomedical application [12]. Electronic industry consumes large amounts of silver powder that is usually used as conductive paste [13–16]. Several studies have indicated that mesoporous silver powders with higher porosity and larger surface area engender higher application efficiencies such as reducing firing temperature of conductive film [17], enhancing the resistance of heat exchanger material at ultralow temperature [18], or increasing catalytic activity of an oxidation reaction [19, 20]. Recently, due to the rapid development of electronic industry, it demands a huge amount of high quality silver powder. Thus, scientists have investigated and proposed different methods such as spray pyrolysis [21–23], sonochemical synthesis [24], γ-radiation [25], and chemical reduction [13, 14, 26–28] to prepare silver powder.

Hydrothermal technique has been realized as an excellent and cost-effective method for the processing of nanostructural materials [29, 30]. It has been used to synthesize and control the growth and the phase transition of silver crystals [31–37]. However, the effect of hydrothermal treatment on presynthesized silver nanoparticles has been scarcely investigated. Therefore, the objective of this work is to investigate the stability of silver nanoparticles under the hydrothermal



a: As-synthesized solution
b: Solution treated at 100°C for 5 h
c: Solution treated at 120°C for 5 h
d: Solution treated at 150°C for 5 h

Figure 1: UV-Vis spectra of silver nanoparticle solution treated at various temperatures.

condition and to recover mesoporous silver powder from a silver nanoparticle/chitosan solution by hydrothermal treatment.

2. Method

2.1. Materials. Silver nitrate was purchased from DaeJung Chemical and Metals Co., Ltd. $NaBH_4$ was obtained from Duksan Pharmaceutical Co., Ltd. Chitosan (low molecular weight) supplied by Sigma-Aldrich was used to prepare a stock solution (10 g/L) in 1% acetic acid, which will be utilized for further experiments.

2.2. Synthesis of Silver Nanoparticles. Silver nitrate (787 mg) was weighed and transferred into 3 L beaker containing 880 mL of chitosan solution (500 ppm) and mixed for 1 h using a magnetic stirrer. Then, 120 mL of $NaBH_4$ (0.05 M) was dropwise added at room temperature (25°C) while the solution was vigorously stirred. The solution changed from transparent to yellow when $NaBH_4$ added indicated the formation of silver nanoparticles.

2.3. Hydrothermal Treatment. To investigate the effect of hydrothermal treatment on silver nanoparticles, 200 mL of as-synthesized silver nanoparticles solution was taken into a 500 mL Teflon-lining stainless steel autoclave. After being tightened, it was heated at various temperatures for 5 h and slowly cooled down. The solution in autoclave was decanted and precipitated silver was collected and washed with deionized water and then filtered. The obtained precipitated silver was dried at 105°C for 2 h for further characterization.

2.4. Characterization. UV-Vis absorption spectra were acquired at room temperature using UV-Vis spectrophotometer Optizen 2120 UV over the wavelength ranging from 300 nm to 700 nm. The morphologies of samples were investigated using field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800) with an accelerating voltage of 15 kV. Field emission scanning transmission electron microscopy (FE-STEM) pictures were acquired using a JEOL 2000 FX instrument. X-ray diffraction (XRD) was carried on XRD-6000 (Shimazu) operating at 40 kV, 100 mA with the Cu/Kα radiation (γ = 1.54059 Å). The Brunauer-Emmett-Teller (BET) surface area and the porosity of the samples were studied by using a nitrogen adsorption instrument (Micrometrics ASAP 2020). All the samples measured were degassed at 105°C for 3 h before analyzing.

3. Results and Discussion

3.1. Morphology and Structure of Silver Nanoparticles. UV-Vis spectra of silver nanoparticle solution treated at different temperatures are shown in Figure 1. As seen in this figure, adsorption band at 415–425 nm was observed on the spectra of the as-synthesized solution and solution treated at 100 and 120°C for 5 h. The observation of this adsorption band is attributed to the characteristic surface Plasmon resonance of silver nanoparticles, which indicated the presence on silver nanoparticles in the solution. In this study, the absorption band of as-synthesized sample is sharp and intensive, but its intensity and sharpness decreased after hydrothermal treatment at 100 and 120°C. Moreover, the position of adsorption peak shifted toward longer wavelength. The reduction in its intensity may refer to the decrease in the concentration of silver nanoparticles. The red shift implies the increase in size and transition in the shape of silver nanoparticles. Shoulders around 370 nm and broad peaks at 420–425 nm observed on their spectra suggest the occurrence of anisotropic particles [31]. Those anisotropic particles may cause the structural transition during hydrothermal treatment, which results in the formation of silver particles with different shape. This observation can be further affirmed by TEM analysis shown in Figure 2. The intensity of the adsorption band was rapidly

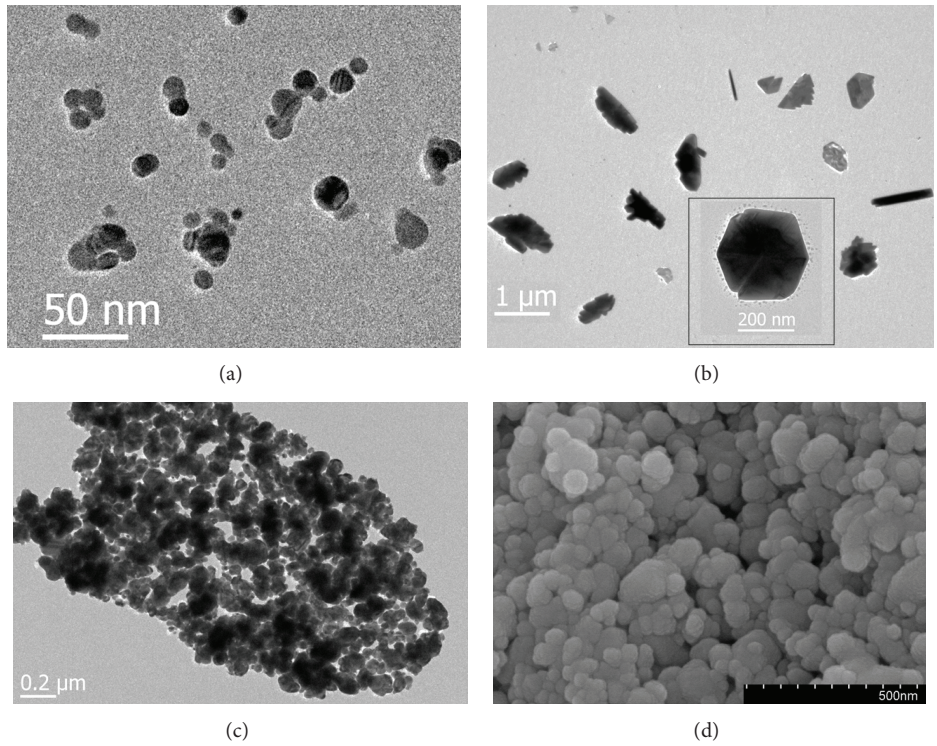


Figure 2: TEM images of as-synthesized silver nanoparticles (a) treated at 100°C (b) and 150°C (c) and an SEM image of silver powder (d).

decreased as temperature increased and it disappeared when sample treated at 150°C for 5 h. The disappearance of the adsorption band refers to the attenuation of surface Plasmon resonance of silver nanoparticles. In other words, it indicated the absence of silver nanoparticles in the solution. In fact, brown precipitate was found at the bottom and on the wall of autoclave after treated at 150°C. It is evident that silver nanoparticles in the solution were aggregated and precipitated.

As-synthesized silver nanoparticles have quasi-spherical shape with the size ranging from 5 to 20 nm (Figure 2(a)). After treatment at 100°C, silver particles with various sizes and shapes were obtained (Figure 2(b)). The existence of rod and plate in this sample implies the anisotropic growth of silver nanoparticles. In this system, extremely small particles with higher surface energy tend to merge into larger ones to make them larger, while the small particles get smaller and disappear. This is well characterized in Figure 2(b) (inset), where a large particle is surrounded by numerous small ones, which would be likely to deposit on the surface of the larger particles. The stronger interaction of chitosan with a preferential facet of silver nanoparticles can be attributed to the anisotropic growth, resulting in the formation of different shapes such as nanoplate and nanorod [38]. However, as treated at 150°C, we obtained aggregates by the random flocculation of silver nanoparticles (Figures 2(c) and 2(d)). In fact, the growth in the size of nanoparticle and their flocculation in solution are natural processes, which simultaneously occur to reduce surface energy of small particles. Depending on the thermodynamic condition, one process can be faster and dominant over another. In this work, it is likely that the rate of random flocculation dominated the growth rate of silver nanoparticles at 150°C, which resulted in the aggregation and precipitation of silver clusters.

3.2. Mesoporous Silver Powder. Figure 3 presents the XRD pattern of silver powder obtained by hydrothermal treatment at 150°C. The peaks at 37.84°, 44.04°, 64.23°, and 77.20° are assigned to the diffraction of (111), (200), (220), and (311) planes of the face centered cubic phases of silver, respectively. The analysis of XRD indicated that the powder comprises pure metallic silver.

The porous properties of the silver powder were studied by nitrogen adsorption-desorption method. Sorption isotherm of silver powder shown in Figure 4 is corresponding to type IV of IUPAC classification of sorption isotherms [39]. The hysteresis loop implies the occurrence of pore condensation, indicating that silver powder is associated with a mesoporous structure. An indistinguishable inflection point at the initial part of the isotherm may refer to a slightly weak interaction between silver powder and nitrogen atoms. The specific surface area of the silver powder (8.5 m^2/g) was determined by the BET method. The Barret, Joyner, and Halenda (BJH) method was applied to the calculation of total pore volume and pore size distribution. Result indicates that the powder has the total pore volume of 0.12 cm^3/g. The pore size distribution of silver powder is displayed in Figure 4 (inset), indicating that the product is a mesoporous material with pore sizes mostly ranging from 7 to 30 nm. This result

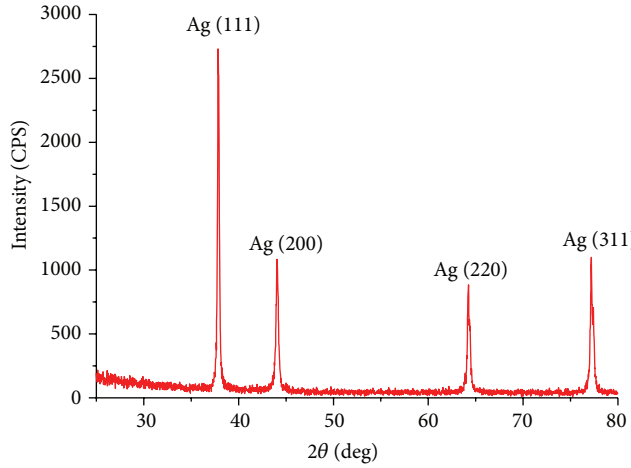


Figure 3: XRD pattern of porous silver powder obtained by hydrothermal precipitation at 150°C.

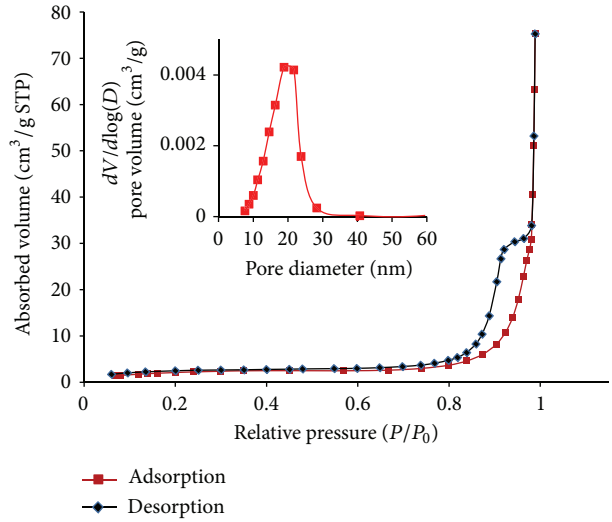


Figure 4: Nitrogen adsorption and desorption isotherms and pore size distribution (inset) of mesoporous silver powder.

is also in congruence with the observation of TEM and SEM images (Figures 2(c) and 2(d)).

Although hydrothermal process has been widely utilized to synthesize and grow anisotropic silver crystals, its influence on preprepared silver nanoparticles in an aqueous solution has been scarcely investigated. This short communication indicates that hydrothermal technique provide not only a good method to synthesize anisotropic silver particles but also to control the anisotropic transition of preprepared silver nanoparticles. Moreover, by increasing temperature to 150°C, we can obtain mesoporous silver powder that could be desired for various applications.

4. Conclusion

This work demonstrates that hydrothermal treatment has a great effect on presynthesized silver nanoparticles. At 100 and 120°C, silver nanoparticles undergo a transition from quasi-spherical shape to rod and plate. When temperature increases to 150°C, they flocculate and precipitate to form mesoporous silver. The results obtained in this research suggest a new route to control the size and shape of presynthesized silver nanoparticles. This study also provides a novel method to produce a mesoporous silver powder with relative high surface area and large pore diameter from an aqueous solution of silver nanoparticles.

Acknowledgment

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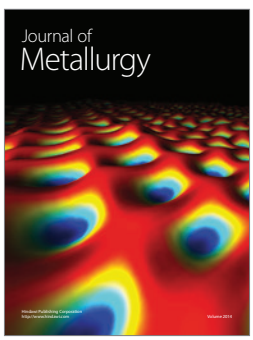

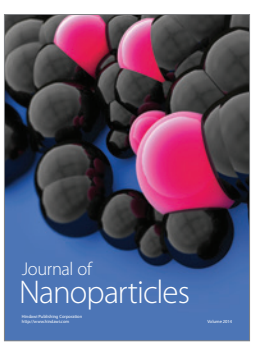

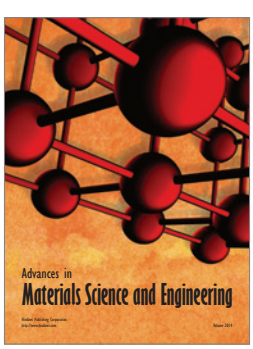

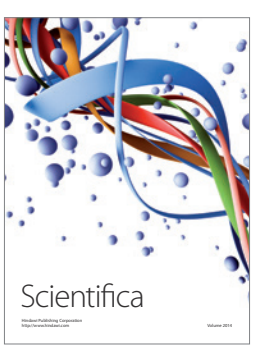

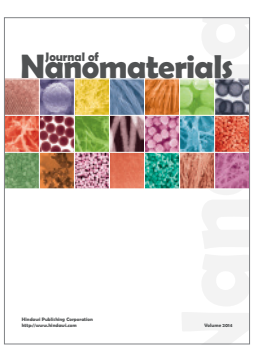

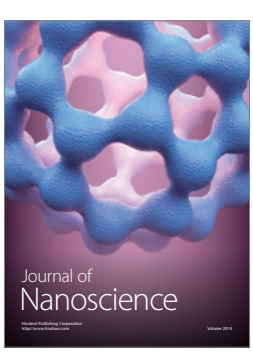

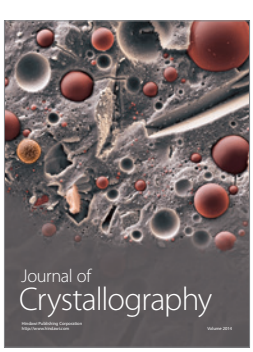

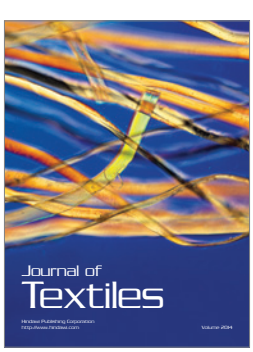

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