

Controlling Size and Distribution of Silver Nanoparticles Generated in Inorganic Silica Nanofibers Using Poly(vinyl pyrrolidone)

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Abstract: Poly(vinyl pyrrolidone) was used successfully to control the size and distribution of silver nanoparticles generated on inorganic silica nanofibers. The inorganic nanofibers were electrospun using sol-gel chemistry of silicates, and the diameter of the prepared nanofibers was unaffected by adding up to 7% of poly(vinyl pyrrolidone). The silver ions, in the form of silver nitrate, were introduced into the silica nanofibers and reduced to metallic silver by ultraviolet irradiation with a subsequent thermal treatment. The size of the generated silver particles was decreased dramatically by adding poly(vinyl pyrrolidone). The size of the silver nanoparticles was 73 nm when no poly(vinyl pyrrolidone) was added but 23 nm with the addition of only 1% of poly(vinyl pyrrolidone). The extent of reduction could be checked by determining the concentration of silver ions leached into water from the silica nanofibers. After thermal treatment of the silica nanofibers, more than 99% of the silver remained in the nanofibers, indicating almost complete reduction of the silver ions to silver metal.

Keywords: electrospinning, silica nanofibers, silver nanoparticle, poly(vinyl pyrrolidone).

Introduction

Electrospinning technique has drawn a lot of interests from many researchers these days.¹⁻³ One of the advantages of this technique is in effectively preparing nano-size fibers from various organic and inorganic materials which do not form fibers by conventional methods. Nanofibers prepared using electrospinning have been used in many applications due to their large surface area and porous structure. Examples include filters, sensors, scaffolds for tissue engineering, and wound dressing materials.⁴⁻¹⁰

Filter materials with antibacterial and/or deodorizing properties would be very useful in some applications. Silver atom (Ag) has been known to render such properties. Ag has advantages of non-toxicity, high chemical and thermal stability, good antibacterial activity, and long active period.¹¹⁻¹³ These unique properties of Ag make it used in various biomedical applications.¹⁴⁻¹⁸ There have been sev-

eral reports of incorporating Ag nanoparticles into electrospun organic polymer nanofibers. Yang *et al.* prepared poly(acrylonitrile) nanofibers containing Ag nanoparticles using electrospinning of polymers/silver nitrate mixture, followed by chemical reduction of Ag⁺ ions.¹⁹ Park *et al.* also prepared cellulose acetate nanofibers with Ag nanoparticles using photoreduction of Ag⁺ ions.^{20,21} However, there has been no report of preparing inorganic nanofiber with Ag nanoparticles. Inorganic fibers, more specifically silica nanofibers, have drawn our interests because of their excellent thermal and mechanical properties. Inorganic nanofibers can be prepared using sol-gel chemistry, which can be applied to many metal oxide systems, including silicon oxide, iron oxide, titanium oxide, etc.²²⁻²⁶ Silicon oxide has been most extensively studied because of its unique reactivity. Since silicon is of relatively higher electron negativity value than other metals, it is possible to control the gelation reactions.

The antibacterial property and its durability of the silica nanofiber containing Ag nanoparticles should be affected by the size and distribution of the Ag nanoparticles. In our

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previous works, we prepared Ag nanoparticles embedded silica nanofibers by electrospinning silicates using sol-gel chemistry and then reducing the Ag^+ ions photochemically inside the silica nanofibers.²⁷ However, the generated Ag particles had an average size of more than 70 nm, which is much larger than those in other organic fibers. In many applications, nanoparticles are expected to have smaller size to be of larger surface area. The increased surface are beneficial in achieving high functionality, such as high antibacterial property of filtering materials, high sensitivity of sensors, and high efficiency of immobilized catalysts.

In this report, we used poly(vinyl pyrrolidone) (PVP) to reduce size of Ag nanoparticle on silica nanofibers. A mechanism has been reported that nitrogen and oxygen atoms in PVP coordinate with the Ag^+ ions.^{28,29} PVP coordinated with Ag^+ ions facilitates the reduction of Ag^+ ions and prohibits the excessive aggregation of the Ag atoms into larger aggregations. Based on this finding, we have reported use of PVP to control nanoparticles generated in organic nanofibers.³⁰ In those works, PVP was used as a matrix or as a additive in a concentration of 5% to PVA matrix, and could effectively reduce size of Ag nanoparticles generated in organic nanofibers.

Here we tried to answer the following questions: 1) How would PVP affect the spinnability of the inorganic silicate mixture? 2) How would UV and thermal treatment affect reduction of Ag^+ ions to Ag nanoparticles? 3) Would PVP affect the formation of the Ag nanoparticles? If so, how much PVP would be needed for the effective stabilization of Ag nanoparticles in inorganic silica nanofibers?

Experimental

General. Tetraethyl orthosilicate (TEOS, 95%), nitric acid, ethanol, silver nitrate (AgNO_3), and PVP (MW=10,000) were purchased from Aldrich and used as received without further purification.

The morphologies of the prepared ultrafine silica fibers were observed on a scanning electron microscope (SEM) (Hitachi S-2350) after gold coating. Transmission electron microscope (TEM) images were obtained using a Philips CM 200 TEM for samples deposited on carbon coated copper grids. The average size of the nanofibers and Ag nanoparticles were determined by analyzing SEM or TEM images with a custom code image analysis program. In order to investigate the distribution of the Ag nanoparticles within the silica nanofibers, the latter were molded in an epoxy resin and microtomed to a thin section. Silver ions in silica nanofibers were extracted with water and their concentrations were monitored by a Direct Reading Echelle inductively coupled plasma (ICP) spectrometer (Leeman Labs Inc., DRE).

Electrospinning of Silicates Using Sol-Gel Chemistry. To a solution of TEOS in ethanol was added dropwise nitric

acid aqueous solution with continuous and vigorous stirring (TEOS/water/ethanol/nitric acid = 1/2/2/0.01). On adding nitric acid, hydrolysis and condensation reactions took place with generating heat. When the mixture was cooled to room temperature, AgNO_3 (0.05-0.5 wt% to silicate) was added. To this solution was added 5 wt% of PVP in ethanol dropwise with vigorous stirring. The mixture was aged for 70 min at 80 °C with continuous stirring, and then cooled to room temperature before spinning. The electrospinning setup used in this study consisted of a syringe with a needle (ID = 0.84 mm), an aluminum collecting plate, and a high voltage supply (Chungpa EMT). A syringe pump connected to the syringe controlled the flow rate. The solutions were electrospun at a positive voltage of 25 kV, a working distance of 10 cm (the distance between the needle tip and the collecting plate), and a solution flow rate of 3 mL/h. All electrospinning procedures were carried out at room temperature.

Photoreduction of Ag^+ Ion in the Silica Nanofibers. The silica nanofibers electrospun with 0.5 wt% of AgNO_3 on a glass slide were irradiated with UV light at 254 nm using a 500 W high-pressure Hg lamp system (StabiLight, NT-LS-HG50-SR). The glass slide was washed with deionized water in an ultrasonicator for 30 min and completely dried.

Thermal Treatment of Silica Nanofibers Containing Silver Nanoparticles. The silica nanofibers were baked at 600 °C to complete gelation reactions between silanols under N_2 atmosphere. Baking temperature was increased to 600 °C for 30 min, and held at that temperature for 30 min before cooling to room temperature.

Results and Discussion

A standard processing condition was applied in electrospinning silica nanofibers. The conditions were set to the one giving a good quality of nanofiber on electrospinning AgNO_3 -containing silicate mixtures without PVP in our previous work.²⁷ The selected conditions were an aging time of 70 min before spinning, a positive voltage of 25 kV, a working distance of 10 cm, and a solution flow rate of 3 mL/h. Using these processing parameters, the effect of PVP on the structures of the resulting nanofiber was studied. Figure 1 shows the SEM images of the silica nanofibers with different contents of PVP. From all samples with different PVP contents, it was possible to prepare nanofibers in good quality. The diameter of the prepared nanofiber was almost unchanged (560-610 nm) with up to 7% of PVP addition. However, a noticeable increase (1130 nm) was observed with 9% of PVP, probably because of the increased viscosity of the spinning solution.

To generate Ag particle in the silica nanofiber, the silica nanofiber was irradiated with UV lamp at 254 nm. On UV treatment, Ag^+ ion from silver nitrate was reduced to Ag metal, which aggregated to nanoparticles and migrated to the surface of the nanofibers.²¹ Again, the condition for UV

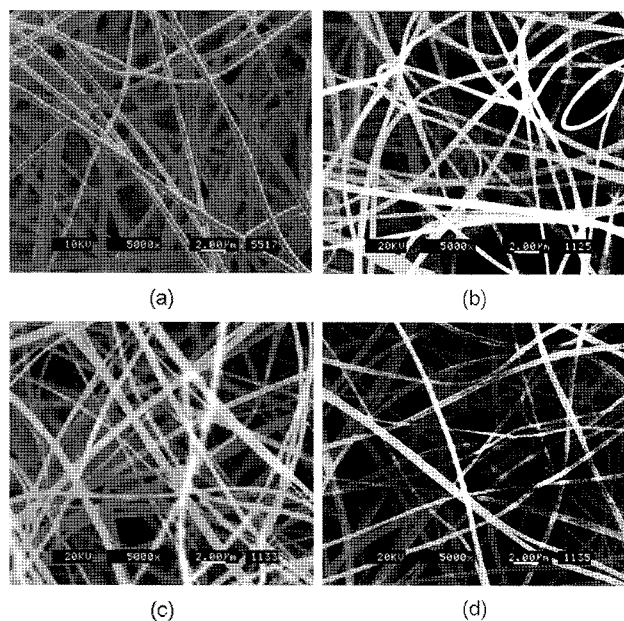


Figure 1. SEM images of 0.5 wt% AgNO_3 -containing silica nanofibers with different PVP contents: (a) 0%, (b) 3%, (c) 5%, and (d) 7%. The scale bars correspond to 2 μm .

treatment was determined with the samples without PVP. When PVP was not added, the generated Ag particles had an average size of 73 nm after 4 h of irradiation, which is much bigger than Ag particles on organic nanofiber. TEM images of the UV-treated fiber showed that Ag particles were formed predominantly on the surface of the fiber. With an addition of PVP, on the other hand, the generated Ag particles had much smaller size with more homogeneous distribution. It was because the added PVP coordinated with Ag^+ ions to prohibit the reduced Ag particle aggregation and grain growth as a result of steric effect.²⁵ Interestingly enough, size of the Ag particle dropped dramatically to 23 nm with only 1% of PVP addition, indicating very efficient and selective coordination of PVP with Ag particles. With up to 7% of PVP addition, size of the Ag nanoparticles continuously decreased to 17 nm and there was no further decrease with 9% of PVP (Figure 2). Like samples without PVP, the generated Ag particles located predominantly on the surface of the silica fiber.

The silica nanofiber was then baked at 600 °C to complete the reactions between silanols. FT-IR measurements showed that silanol groups presented in the as-spun nanofiber disappeared after thermal treatment, indicating the prepared nanofiber was composed of inorganic silicon oxides only. At that temperature, though, PVP was decomposed completely as evidenced with TGA measurements. Figure 3 is the SEM images of the resulting nanofibers. The diameter of the baked fibers was similar to or slightly smaller than unbaked ones (410–560 nm), because the baking process completed the gelation between silanols to make the struc-

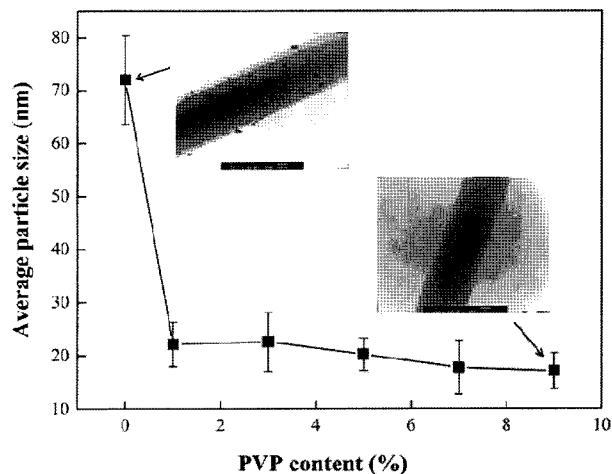


Figure 2. Change in average size of Ag particles on the silica nanofibers with different PVP contents. Insets are the SEM images of the nanofibers containing Ag particles. The scale bars correspond to 100 nm.

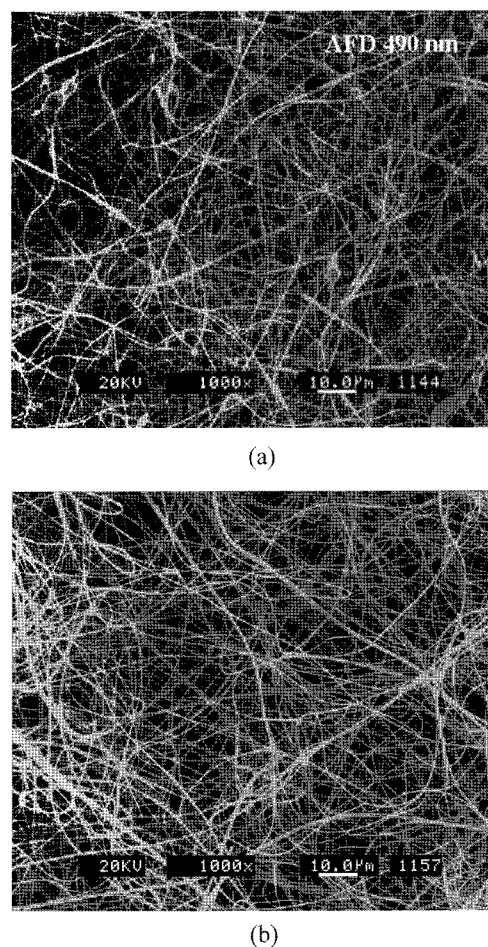


Figure 3. SEM images of 0.5 wt% AgNO_3 containing silica nanofibers with different PVP contents after heat treatment at 600 °C under N_2 atmosphere: (a) 3% and (b) 7%. The scale bars correspond to 10 μm .

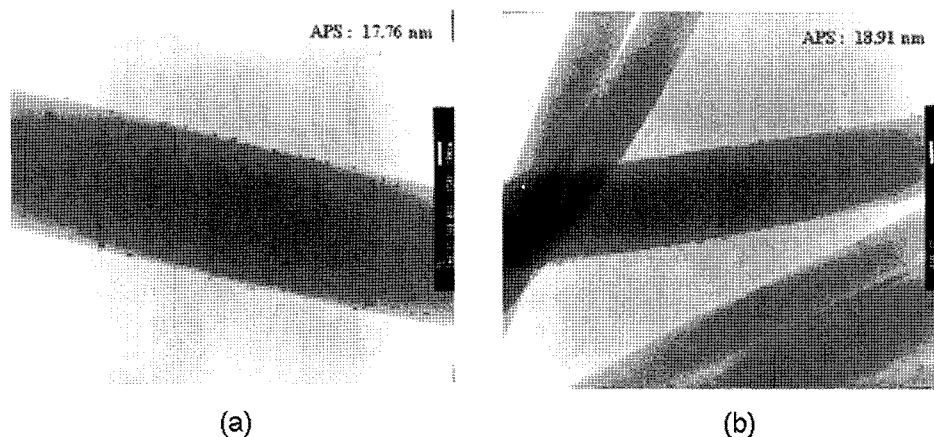


Figure 4. TEM images of silver particles: 0.5 wt% AgNO_3 containing silica nanofibers with 7 % PVP (a) before and (b) after heat treatment at 600 °C under N_2 atmosphere. The scale bars correspond to 100 nm.

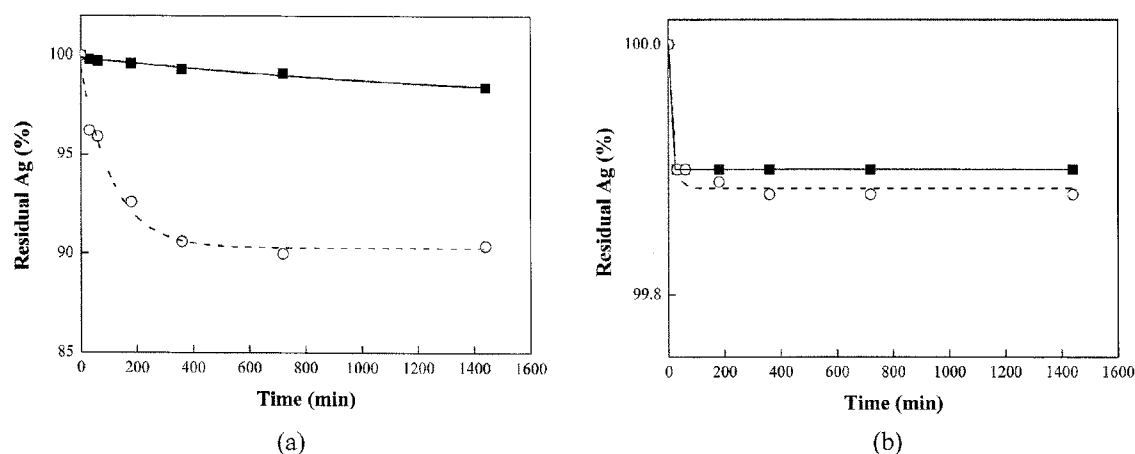


Figure 5. Residual Ag contents in silica nanofibers after extraction in water; (a) samples before heat treatment and (b) after heat treatment at 600 °C in N_2 atmosphere. (■) Silica nanofibers with PVP, (-○-) silica nanofibers without PVP.

ture more compact. All the PVP containing nanofiber possessed similar diameter, regardless of PVP content. Even though all PVP was removed by thermal treatment, Ag particles retained their small size and homogeneous distribution on the fiber surface (Figure 4).

For filtering applications in long-term use, not only the antibacterial activity of silica nanofibers but its durability is also important. Since most of the generated Ag particles located on the nanofiber surface, the degree of extraction of Ag^+ ions from the nanofiber into water should be checked. The silica nanofiber was immersed into water, and the amount of the extracted Ag^+ ion was determined by inductively coupled plasma analysis. The residual amount of Ag in the silica fiber was calculated from the concentration of the extracted Ag^+ ions in water (Figure 5). The residual amount of Ag in the silica nanofiber was more than 90% after UV treatment, indicating most of Ag^- ion reduced to Ag nanoparticles. The residual amount of Ag in silica nanofiber was increased by adding PVP. PVP has been

known to facilitate the reduction of Ag^- ions to metallic Ag by forming the Ag^+ ions-PVP complex which is more easily reduced than Ag^+ ions alone.^{28,29} Moreover, some portion of the remaining Ag^+ ions might be coordinated with PVP, which further suppress the migration of Ag^+ ions out of the silica nanofiber.

After thermal treatment, leakage of Ag^+ ions into water was further suppressed and more than 99% of Ag remained in the silica nanofiber. It was probably due to the completed reduction of remaining Ag^+ ions to Ag particles by the thermal treatment.³¹ Also more compact and hydrophobic structure of the silica nanofibers as gelation reaction becomes completed by the thermal treatment would be another reason for the lower leakage of the silver ions. Even though PVP-containing silica nanofibers made the Ag particle have larger surface area, there was very low level of Ag^+ leakage into water. These results indicated that PVP could decrease size of the generated Ag particles without harming durability of the particles.

Conclusions

Using PVP, it was possible to control size and distribution of Ag nanoparticles in inorganic silica nanofiber. PVP didn't harm the spinnability of silica fiber in electrospinning technique using sol-gel chemistry. PVP was very effective on controlling nanoparticle size, and with only 1% addition of PVP, the size of the generated Ag nanoparticle had decreased to about 30% to the one without PVP. The increased surface area of the Ag nanoparticle achieved with the decreased size, though, did not deteriorate the durability of the particle in nanofibers. When the UV and heat treated silica nanofiber was immersed into water, more than 99% of Ag nanoparticles remained in the nanofiber. Therefore, the prepared silica nanofiber web containing Ag nanoparticles may find its uses in filtering applications where good thermal stability and antibacterial activity are required.

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