

## A Comparison Method of Silver Nanoparticles Prepared by the Gamma Irradiation and in situ Reduction Methods

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Received March 25, 2010, Accepted May 25, 2010

Silver nanoparticles has been prepared by the  $\gamma$ -irradiation and in situ reduction methods. Based on the Raman spectra, TEM images, X-ray Diffraction (XRD) patterns and UV-vis spectra, the in situ reduction method is more stable and the average size of the silver nanoparticles is also smaller than by the  $\gamma$ -irradiation reduction method. It is identified that the silver ions interacting with nonbonding electrons of oxygen atom in the carbonyl group of polyvinylpyrrolidone (PVP) by the in situ reduction method. It is also found advantages of the in situ reduction method including no additional reducing agents, without  $\gamma$ -irradiations treatment and the room temperature treatment suitability.

**Key Words:** Composite materials, Irradiation effects, Polyvinyl pyrrolidone, Silver nanoparticles

### Introduction

Silver nanoparticles have received considerable attention because of their unique chemical and physical properties, which differ greatly from those of bulk materials, as well as their potential for technological applications.<sup>1-3</sup> During the past decades, various methods have been studied<sup>4-8</sup> in this regard. Recently, particular attention has been paid to metal-polymer nanocomposites because of their optical, electrical, and mechanical properties.<sup>9-11</sup> In general, silver nanoparticles are prepared by a typical procedure. Initially, silver ions exposed to  $\gamma$ -irradiation or any other reductants that can be reduced to silver atoms and then, the nearby silver atoms can aggregate at closer range. Finally, the aggregated silver atoms coalesce with other nearby silver atoms or interact with PVP in order to form larger aggregates, which form to spherical silver nanoparticles. Numerous researchers have paid attention to the mechanism for silver nanoparticle formation and its effect as a stabilizer. Generally, PVP is recognized as a good stabilizer in the making of silver nanoparticles.<sup>12-16</sup> They suggest a mechanism of PVP protection, in which PVP promotes the nucleation of metallic silver because silver ions are easily reduced by the lone pair electrons of PVP. In this study, we focus on principally effects of PVP and silver ions by the in situ reduction mechanism. Colloidal silver nanoparticles are synthesized by  $\gamma$ -irradiation and in situ reduction method using  $\text{AgNO}_3$ ,  $\text{H}_2\text{O}$  and PVP. Based on TEM images, UV-vis spectra, XRD patterns, Raman, and FT-IR spectra we observe few advantages of the in situ reduction method as compared with the  $\gamma$ -irradiation method. Therefore, we show a new PVP reduction mechanism for synthesizing silver nanoparticles by the in situ reduction method.

### Experimental

**Materials.** Silver nitrate ( $\text{AgNO}_3$ , 99.9%) was purchased from

Kojima Chemicals Co. Ltd. (Japan). Polyvinylpyrrolidone (PVP, MW. avg.=10,000) was obtained from Sigma-Aldrich Co. All chemical reagents were used without further purification.

**Preparation of silver nanoparticles by  $\gamma$ -irradiation reduction method.** Colloidal silver nanoparticles were prepared as follows: The solution was prepared by the addition of 0.3 M of  $\text{AgNO}_3$  and 5 wt% PVP in distilled water. Dissolved oxygen in the solutions was removed by bubbling with pure argon for 30 min, and then the solution was irradiated by  $^{60}\text{Co}$   $\gamma$ -ray source (in the field of a  $^{60}\text{Co}$   $\gamma$ -ray source with 25 kGy doses).<sup>17</sup>

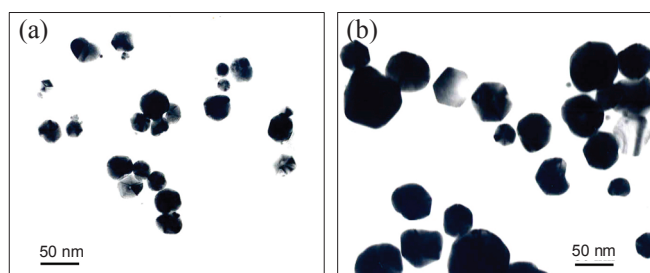
**Preparation of silver nanoparticles by in situ-reduction method.** Colloidal silver nanoparticles were prepared from the solutions of 0.3 M of  $\text{AgNO}_3$  and 5 wt% PVP in distilled water. The whole preparation procedure can be explained as the following: 12.50 g of PVP was dissolved in 250 mL of distilled water and afterwards 12.74 g of silver nitrate was added to the solution. Then, the solution changed in color from yellow to dark olive green. The chemical process was performed for 2 hour at room temperature.

**Characterization of silver nanoparticles.** The size of the silver nanoparticles was measured using a transmission electron microscope (Hitachi H-7100). The Raman spectra of the samples of PVP were measured by a Jobin-Yvon Horiva HR800 scanning single monochromator, a CCD 3000(V) detector and Labspec 4.01 software. A Coherent Innova 90C FredTM argon ion laser ( $\lambda = 514.5$  nm) was used as the excitation source. The laser power and confocal hole size were 10 mW and 400  $\mu\text{m}$ , respectively. The UV-vis spectra and XRD patterns of the silver nanoparticles were recorded with a SCINO UV S-2100 UV-vis spectrophotometer and Philips model X'Pert APD, respectively.

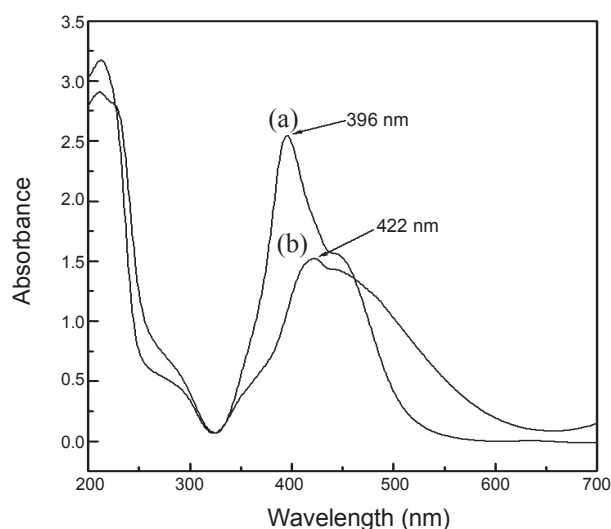
### Results and Discussion

Figure 1 shows the TEM images of silver nanoparticles prepared by the in situ reduction (Figure 1a) and  $\gamma$ -irradiation me-

thods [Figure 1(b)]. The average size of the silver nanoparticles is  $30 \pm 6.8$  nm and  $50 \pm 7.5$  nm by the in situ reduction [Figure 1(a)] and  $\gamma$ -irradiation methods, respectively. The in situ reduction method is found more stable and the average size of the silver nanoparticles is smaller than by the  $\gamma$ -irradiation synthesis method. The UV-vis spectra of the silver nanoparticles are presented in Figure 2, where the peaks (a) at 396 nm and (b) 422 nm are the surface plasmon band of the silver nanoparticles synthesized by the in situ reduction and  $\gamma$ -irradiation methods, respectively. It is well known that a surface plasmon band of spherical silver nanoparticles appears at around 400 nm region.<sup>18</sup> In the case of [Figure 2 (b)], the surface plasmon band of the silver nanoparticles around 390~450 nm is broad and shifts toward longer wavelengths. This indicates the size of an increase in the silver nanoparticles.<sup>19</sup> This result is considered to be an improvement over those obtained using the  $\gamma$ -irradiation syntheses of the silver nanoparticles. In order to have a general view of the time evolution of silver nanoparticles, the results of the 0.3 M of  $\text{AgNO}_3$  and 5 wt % PVP are presented in Figure 3. The peak at approximately  $\lambda_{\text{max}} = 396$  nm showed that the absorbance of silver nanoparticles gradually increased after one minute intervals. This means, that the silver ions converted to silver nanoparticles and the peak height are then directly in proportion to the number of silver nanoparticles present in the solution.<sup>20</sup>



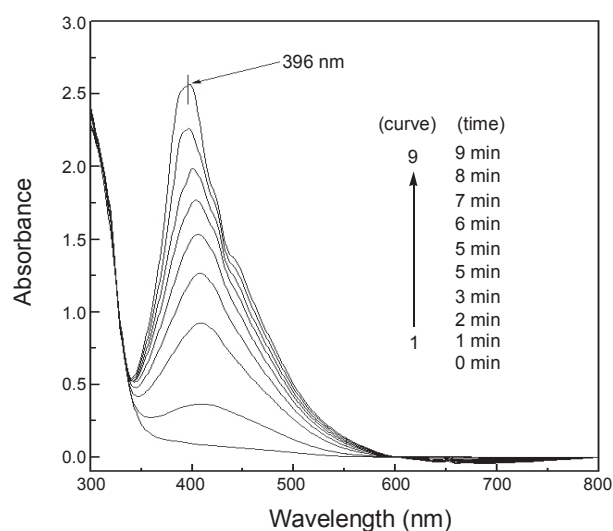
**Figure 1.** TEM images of silver nanoparticles prepared by the in situ reduction (a) and  $\gamma$ -irradiation (b).



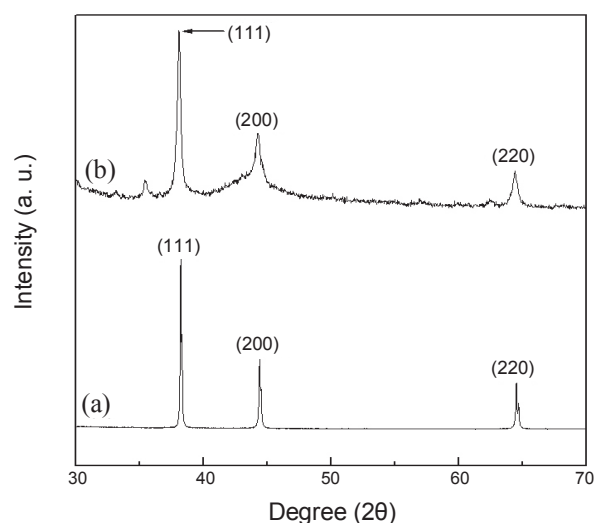
**Figure 2.** UV-vis spectra of silver nanoparticles prepared by the in situ reduction (a) and  $\gamma$ -irradiation method (b).

The powder XRD pattern of the silver nanoparticle is shown in Figure 4. Here, the three peaks can be seen at  $2\theta = 38.2$ ,  $44.3$  and  $64.5^\circ$ , which are characteristic diffraction peaks of metallic silver. These peaks correspond to the three d-spacing (111), (200), and (220), respectively. Crystallite size ( $D$ ) is calculated from Scherrer's equation<sup>21</sup>  $D = K\lambda/(\beta\cos\theta)$ , for peak broadening from size effects only. According to the equation of Scherrer's equation, the average diameter of silver nanoparticles prepared by the in situ reduction (a) and  $\gamma$ -irradiation method (b) are 26.7 and 52.5 nm, respectively.

The mesomeric structure of PVP is illustrated in Figure 5. PVP is known as a protective agent that plays a decisive part in controlling superfine silver particle size and distribution by reducing the silver nitrate with reducing agents. We use Raman spectra to investigate the effect of PVP with silver nanoparticles by the in situ reduction method. Figure 6 shows the Raman



**Figure 3.** Time evolution of UV-vis spectra after addition of 0.3 M  $\text{AgNO}_3$  on to 5 wt % PVP by the in situ reduction method.



**Figure 4.** X-ray diffraction patterns of silver nanoparticles prepared by the in situ reduction (a) and  $\gamma$ -irradiation method (b).

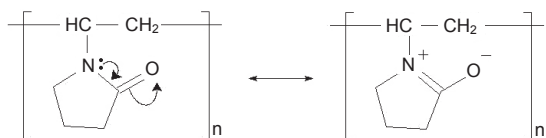


Figure 5. Schematic diagram of PVP mesomeric structure in water.

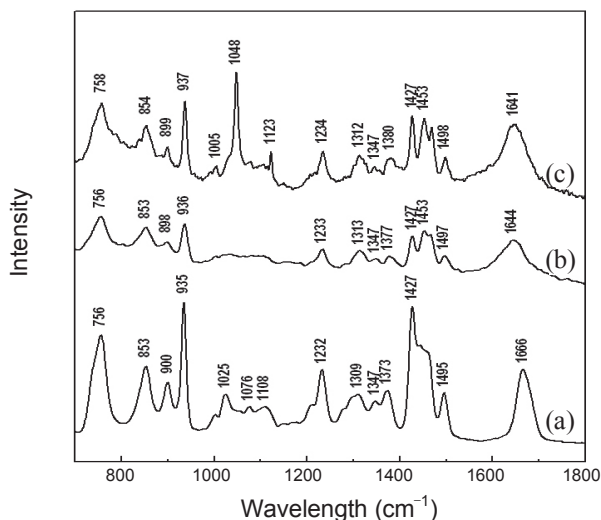


Figure 6. Raman data of (a) solid PVP and (b) 5 wt % PVP in H<sub>2</sub>O; (c) SERS spectrum of 0.1 M silver nanoparticles in 5 wt % PVP.

spectra (a) solid PVP, (b) 5 wt % PVP in H<sub>2</sub>O, and (c) SERS spectrum of 0.1 M of silver nanoparticles in 5 wt % PVP within the frequency range of 1800 ~ 700 cm<sup>-1</sup>. Significant Raman frequencies are shown in Table 1. For solid PVP peaks, they are assigned as follows:<sup>22</sup> 1666 (C=O stretch), 1427 (CH<sub>2</sub> scissors), 1230 (C-N-C asymmetrical stretch), 1025 (C-N-C symmetrical stretch), and 750 cm<sup>-1</sup> (C-N-C symmetrical stretch).

The spectral pattern of 5 wt % of PVP in H<sub>2</sub>O spectrum differs from that of 0.1 M silver nanoparticles in aqueous solution. The significant change in 0.1 M silver nanoparticles in 5 wt % of PVP in aqueous solution is the intensity increases of 1048, 1427 modes, respectively. From above result, it may conclude about the orientation of PVP molecules to the silver surface has been made by applying the results of "surface selection rules". As it is well known that if the reaction occurs *via* lone pair electrons of oxygen atom, the plane of the PVP ring would lie perpendicular to the silver surface and the totally symmetric in-plane stretching modes would be expected to show surface enhancement. Therefore, it is thought that the intensity of the 1048 and 1427 modes are increased [Figure 6(c)]. Also, the absorption peak of the C=O bond at 1666 cm<sup>-1</sup> [Figure 6 (a)] for solid PVP is shifted to 1641 cm<sup>-1</sup> for 0.1 M silver nanoparticles in the 5 wt % PVP aqueous solution [Figure 6 (c)]. This decrease in wavenumber for C=O absorption may result from bond weakening *via* partial donation of oxygen lone pair electrons of PVP to the vacant orbitals of the silver surface. The FT-IR data of 0.1 M silver nanoparticles in the 5 wt % of PVP is demonstrated in Figure 7. The peak at 3420 and 1366 cm<sup>-1</sup> are correspond to O-H bond vibration and NO<sub>3</sub><sup>-</sup> group, respectively. Therefore, it is

Table 1. Proposed assignments of significant peaks in the Raman and SERS spectra of solutions for PVP

PVP solid (Raman: cm <sup>-1</sup> )	5 wt % PVP in H <sub>2</sub> O (Raman: cm <sup>-1</sup> )	0.1 M AgNO <sub>3</sub> in 5 wt % PVP (SERS: cm <sup>-1</sup> )
756 CNC sym str	756 CNC sym str	758 CNC sym str
853, 935 ring brth.	853, 936 ring brth.	854, 937 ring brth.
1025 CN vibration	-	1048 CN str
1232 CNC asy str	1233 CNC asy str	1234 CNC asy str
1427 CH <sub>2</sub> sci	1427 CH <sub>2</sub> sci	1427 CH <sub>2</sub> sci
1452 CH <sub>2</sub> sci	1453 CH <sub>2</sub> sci	1453 CH <sub>2</sub> sci
1666 C=O str	1644 C=O str	1641 C=O str

sym = symmetrical; str = stretching; brth = breathing; asy = asymmetrical; sci = scissors

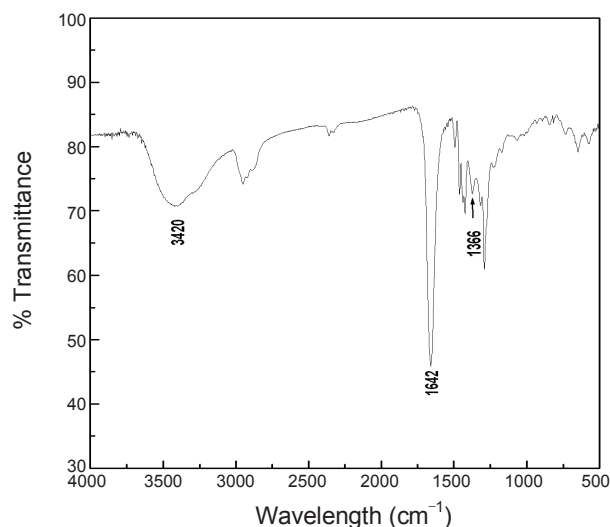


Figure 7. FT-IR data of 0.1 M silver nanoparticles in 5 wt % PVP.

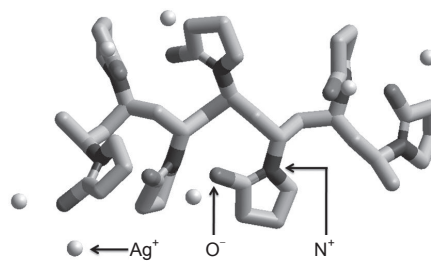


Figure 8. Schematic model for the charge transfer interaction of seven repeating units of PVP and silver ions (geometry optimized by PM3 methods).

assumed that a charge transfer interaction is responsible for Ag<sup>0</sup> formation, the possible bonding site is lone pair electron of carbonyl group.<sup>23-28</sup>

From the above results, we suggest that the reduction of silver cation with PVP could be prepared by the in situ reduction method. The mechanism consists of three steps. Firstly, silver ions interact with the nonbonding electrons of oxygen atom in the PVP carbonyl group. Secondly, silver ions are reduced by charge transfer interaction. Finally, they aggregate to become

large silver nanoparticles. Figure 8 shows a schematic model for the charge transfer interaction of the seven PVP repeating units and silver cation which is calculated by HyperChem7.0 PM3 methods.

### Conclusion

Silver nanoparticles has been prepared by using both of the  $\gamma$ -irradiation and in situ reduction methods. A comparison of silver nanoparticles synthesized from the above two methods can be summarized that by the in situ reduction method a uniform shape with smaller particles size could be prepared. Also, here is observed few advantages by the in situ reduction methods; (i) room temperature treatment suitability, (ii) no additional reducing agents, and (iii) no  $\gamma$ -irradiation process. Moreover, we deduce the following three steps mechanism for the reduction of silver ions with PVP prepared by the in situ reduction method; (i) silver ions interact with the nonbonding electrons of the oxygen atom in the carbonyl group of PVP, (ii) silver ions is reduced by charge transfer interaction, and (iii) finally, they aggregate to become a larger silver nanoparticles.

**Acknowledgments.** This research was supported by Kyungpook National University Research Fund, 2007 and by Korea Research Foundation Grant No. KRF-2006-005-J02401. Prof. T. Vasudevan thanks the Korean Federation of Science and Technology Society (KOFST) for sanction of Brainpool Professorship.

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