Effect of plasma exposure on silver nanoparticles embedded in polyvinyl alcohol

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Abstract. Silver nanoparticles embedded in polyvinyl alcohol (6.2 nm in size) were synthesized by simple polyol process. Silver nanoparticles were deposited on glass plates by dip coating method and exposed to DC glow discharge plasma for 10 minutes and 60 minutes. Samples were characterized by UV-Vis absorption spectra, energy dispersive x-ray spectrogram (EDX), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). UV-Vis spectrum showed a single peak at 415 nm due to the surface plasmon resonance (SPR) of silver nanoparticles embedded in polyvinyl alcohol. Position of surface plasmon resonance (SPR) peak changed after the samples were exposed to DC glow discharge plasma, which reveals that the DC glow discharge plasma can be used as a size controlling agent for the silver nanoparticles embedded in polyvinyl alcohol.

Keywords: Glow discharge plasma, silver nanoparticles, surface plasmon resonance (SPR), polyvinyl alcohol.

1. Introduction

Cold plasma can be used to modify the surface properties of macromolecular materials [1] because plasma treatment enhances the surface energy by polar contributions to the solid surfaces and the plasma surface activation takes place by the formation of polar groups such as carbonyl, carboxyl and hydroxyl groups [2]. Silver metal nanoparticles have been the focus of intense research in the past several decades due to their potential applications in electronic industries such as in inkjet printing [3and 4] and in medical fields to inhibit the growth of bacteria such as E. coli, Pseudomonas [5]. Nowadays, polymer nanocomposites play major roles in biomedical, electronic and optical devices [6-8]. Presence of metal nanoparticles can be confirmed by the surface plasmon resonance (SPR) in the absorption spectrum and the surface plasmon absorption bands of very small silver particles are located in the near UV domain and it shifts to higher wavelength as the diameter of the nanoparticles is increased [9-11]. The formation of silver nanoparticles with the help of polyvinyl alcohol and the effect of low pressure DC glow discharge plasma on the prepared silver nanoparticles are reported in this paper. The samples were characterized by UV-Vis- NIR spectrogram, x-ray diffractogram (XRD), energy dispersive x-ray spectrogram (EDX), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

2. Experimental

2.1. Materials
Silver nitrate solution of 0.01 M was prepared in 5 ml of de-ionized water by magnetic stirring in a beaker covered with black cloth to avoid the photo degradation of the silver nitrate. Another beaker with 50 ml of de-ionized water had been used to prepare 0.03g/ml of polyvinyl alcohol solution and the temperature of polyvinyl alcohol solution was maintained between 60°C – 70°C while continuing...
magnetic stirring. The solution transformed into a transparent liquid when the polyvinyl alcohol completely dissolved and then the silver nitrate solution was added drop by drop (one drop per second) by using a syringe while the temperature was maintained between 60°C – 70°C (with continuous stirring). Magnetic stirring continued (temperature was maintained between 60°C – 70°C) until the solution became a faint brownish viscous liquid. Silicate glass slides were then dipped into this viscous solution to form a fine thin film of silver nanoparticles embedded in polyvinyl alcohol for characterizing the silver nanoparticles.

2.2. Plasma exposure
A cylindrical stainless steel chamber used as plasma chamber in this experiment was 50 cm in length and 24 cm in diameter with four view ports. The electrodes were fixed at 5 cm apart from each other and a pressure of 0.3 torr was maintained inside the chamber. The sample was fixed with the coated side facing the cathode at a distance of 2 cm apart from the cathode and a voltage of 350 V was applied between the electrodes. Samples were exposed to the low pressure glow discharge plasma for 10 minutes and 60 minutes.

2.3. Characterization
UV – VIS-NIR absorption spectra were obtained from ‘JASCO UV-VIS Spectro-Photometer V-570’. Surface and compositional analysis were studied using scanning electron microscope (SEM) and energy dispersive X-ray spectrum in conjunction with the scanning electron microscope (JEOL model JSM-5800). The transmission electron microscope (TEM) image was obtained by JEOL 3010 instrument and the X-Ray diffractogram was recorded by Bruker AXS D8 Advance.

3. Results and Discussion
Presence of silver in the as synthesized and 10 minutes plasma exposed samples (Figure 1) were confirmed from JCPDS card No. 41-1402 (hexagonal) and from JCPDS card No. 04-0783 (cubic). Some unknown peaks were also observed in the x-ray diffractogram. The ‘d’ values are tabulated in the Table 1 and compared with JCPDS values.

![Figure 1. X-ray diffractogram of 10 minutes plasma exposed sample](image)

**Table 1.** Comparison of ‘d’ spacing of as synthesized and 10 minutes plasma exposed samples.
X-ray diffraction of 60 minutes plasma exposed samples (Figure 2) confirms the presence of AgO (JCPDS card No. 84-1108 for tetragonal structure) against the presence of Ag in the as-synthesized and 10 minutes plasma exposed samples. The ‘d’ spacing for 60 minutes plasma exposed sample is shown in Table 2.

Figure 2. X-ray diffractogram of 60 minutes plasma exposed sample

Table 2. ‘d’ spacing of 60 minutes plasma exposed sample from X-ray diffractogram (Figure 2.)

| Planes | Measured ‘d’ values of 60 minutes plasma exposed sample (Å) | Structure |
|--------|-------------------------------------------------------------|-----------|
| (103)  | 1.9995                                                      | Hexagonal |
| (104)  | 1.7308                                                      | Hexagonal |
| (311)  | -                                                           | Cubic     |
| (200)  | -                                                           | Cubic     |

SEM and EDX spectra for the three samples are shown in Figures 3 to 8. From the SEM analysis of the as synthesized film (Figure 3) it was seen that polyvinyl alcohol capped silver nanoparticles form
island structures and when the samples were exposed to plasma it was seen that all the island structures have been joined together (Figure 5). This agglomeration may be a reason for the increase in size of the silver nanoparticles as seen in the optical absorption spectrum (Figure 9 & Table 4). Surface roughness has increased and many of the materials have been etched out when the samples were exposed for 60 minutes to plasma (Figure 7). This etching may result in the reduction of the particle size and more information about the physical nature of the samples is explained with the help of optical absorption spectra (Figure 9). The EDX spectrum confirms the elemental composition of polyvinyl alcohol capped silver particles and the presence of Si in the EDX is due to the silicon glass substrate and the appearance of carbon and oxygen is due to polyvinyl alcohol. The variation in the weight percentages of silver in the EDX (Table 3) occurred due to the variation in the thickness and the non-uniform coating of the film.

Figure 3. SEM image of as-synthesized sample.

Figure 10 shows TEM image of the as synthesized sample and the average size of the particle calculated was 6.2 nm (Figure 11). HRTEM image is shown in Figure 12, and lattice spacing ‘d’ measured as 0.16 nm and 0.15 nm. SAED picture (Figure 13) shows that the silver nanoparticles in the unexposed sample are polycrystalline in nature and aligned in the (103) and (104) planes.
Figure 4. EDX spectrum of as synthesized sample

Figure 5. SEM image of 10 minutes plasma exposed sample.
Figure 6. EDX spectrum of 10 minutes plasma exposed sample.

Figure 7. SEM image of 60 minutes plasma exposed sample.
Optical absorption spectra of as synthesized and plasma exposed silver nanoparticles embedded in polyvinyl alcohol films (Figure 9) shows surface plasmon resonance (SPR) peak at 415 nm with a band width of 75 nm for as synthesized sample. This intense absorption band is observed due to the collective excitation of all the free electrons in the surface of the metal nanoparticles and the weak peak observed around 310 nm may be due to the carbonyl groups in polyvinyl alcohol [12].

Particle size was calculated using Mie theory equation 1 [9 and 13] and tabulated in Table 4.

\[
2R = \frac{\lambda_{\text{max}}^2 V}{\pi c \omega}
\]

where \(\lambda_{\text{max}}\) is the wavelength at maximum intensity of the SPR, \(V\) is the velocity of the electron at Fermi levels (1.4 x 10^6 ms\(^{-1}\) for silver), \(c\) is the velocity of light in free space and \(\omega\) is the FWHM.

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**Table 3. Elemental composition from EDX**

| Element line | As synthesized sample | 10 min exposed sample | 60 min exposed sample |
|--------------|-----------------------|-----------------------|-----------------------|
|              | Weight % | Atoms % | Weight % | Atoms % | Weight % | Atoms % |
| C K          | 70.37         | 77.89       | 42.18 | 51.09 | 30.44 | 41.08 |
| O K          | 24.49         | 20.39       | 52.56 | 47.80 | 53.55 | 55.08 |
| Si           | 3.18          | 1.51        | 1.05  | 0.55  | 1.81  | 1.06  |
| Ag L         | 1.98          | 0.24        | 4.21  | 0.57  | 14.20 | 2.17  |

Figure 8. EDX spectrum of 60 minutes plasma exposed sample.
Figure 9. Absorption spectra of as synthesized and plasma exposed samples.

Table 4. Particle size calculated from Mie theory

| Plasma exposure time (minutes) | SPR peak (nm) | FWHM (nm) | Particle size (nm) |
|-------------------------------|--------------|-----------|-------------------|
| Un exposed                    | 415          | 75        | 3.41              |
| 10                            | 418          | 64        | 4.03              |
| 60                            | 410          | 92        | 2.72              |

Surface plasmon resonance is observed at 418 nm in the case of 10 minutes exposed sample. The red shift with decreased FWHM from 75 nm to 64 nm may be due to the increase in the size of the diameter of the particles [9] and the same result is observed from equation (1) and shown in Table 4.

Mulvaney [14] reports that the surface plasmon resonance (SPR) spectrum depends upon the refractive index of the surrounding medium, particle size, shape of particle and absorption substance of their surface. Dependence of the surface plasmon resonance (SPR) on the particle size and also the dependence of full width at half maximum (FWHM) with reciprocal of the particle diameter is clearly seen from the Table 4. The increase in the intensity of the 10 minutes plasma exposed sample when compared to the as synthesized sample is also due to the increase in the size of the particle.

It is seen that the absorption spectrum of the sample (Figure 9) exposed for 60 minutes is entirely different from the other samples and when the intensity is decreased, the peak is broadened (FWHM is 92 nm) with a shift to blue region (410 nm). This blue shift and broadening of the peak may be due to the reduction in the size of silver nanoparticles because of the formation of AgO [15] owing to the longer exposure to low pressure glow discharge plasma. The presence of AgO is confirmed from Figure 2 and Table 2.
**Figure 10.** TEM image of as synthesized sample

**Figure 11.** Particle size distribution from TEM image of as synthesized sample.
Figure 12. HRTEM image of as synthesized sample.
4. Conclusions
Silver nanoparticles embedded in polyvinyl alcohol films were prepared by polyol method and exposed to low pressure DC glow discharge plasma to understand its effect on the prepared silver nanoparticles. The samples were analyzed by different characterizing methods and it is confirmed that the prepared silver particles are in nano size. Optical absorption studies of the plasma exposed samples support that the plasma treatment can be used to alter the size of the particles and also the plasma treatment of the silver nanoparticles can be used to synthesize silver oxide nanoparticles.

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