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Size distribution of silver nanoparticles in polyvinyl alcohol composite film: Impact on photoluminescence spectra

Deepali Sarkar*, Sulochana Deb
Department of Physics, Gauhati University, Guwahati - 781 014, Assam, (INDIA)
E-mail : sarkardeepali@gmail.com

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ABSTRACT

Silver- polyvinyl alcohol (Ag-PVA) nano composite dispersion have been synthesized by facile chemical reduction method. The film obtained from this dispersion shows to have particle size varying from 10-50 nm. This wide range of variation is supported by broadening of UV-Vis spectra also by the red shift in photoluminescence (PL) peak with the increase in excitation wave length. The observed effect may be assigned to contribution of particle size towards optical transition.

KEYWORDS

Size distribution;
Ag-PVA nanocomposite;
Chemical reduction;
Plasmon resonance;
Electron microscopy;
Photoluminescence.

INTRODUCTION

Synthesis of metal nanostructure has been an active area of research because of the importance of these materials to catalysis, photography, electronics, photonics, information storage, optoelectronics, biological labelling, imaging and sensing[1-6]. Size of the metal nanoparticles play a dominant role as their intrinsic properties can be tailored by controlling the size in association with the shape, crystalinity and structure[7]. A major difficulty arises in the process of synthesis of such low dimensional particles. With the elapse of time these coalesce to larger sized particles due to electrostatic interaction across the Debye double layer. There are ways to improve the stability of metal nanoparticles, one by polyol synthesis[8], other by bioreduction[9] and the most common and convenient, is by dispersing them in a synthetic high polymer matrix[10]. The choice of such polymer may be polyvinyl alcohol (PVA) polymethyl methacrylate (PMMA), polyacryl amide (PAA) and may be many more. Among them PVA has the advantage of being water soluble, transparant and has capability of uniform dispersion of nanoparticles. Also, this polymer simultaneously acts as reducing agent to form silver nanoparticles from its salt. So that one obtains homogeneous, transparent film of Ag-PVA nanocomposite. Optical properties of these composite films, viz; UV-Vis absorption and photoluminescence spectra depend strongly on the particle size of the noble nanoparticles[11-13]. So, it becomes of immense importance to control the size of silver nanoparticles to tailor their optical properties for specific need[14]. In a single composite film also, the particle size may not be uniform. The in-situ size distribution can also be manifested in its photoluminescence behaviour[10]. In the present paper, we show this in-situ size selective behaviour of photoluminescence and correlate this with the other studies, such as UV-Visible absorption, crystal structure and SEM micrographs. In one of our earlier papers[15], we have reported synthesis and characterization of Ag-PVA composite taking different concentration of silver nitrate ($AgNO_3$) solution. The result suggested minimum sized grains for 1mM $AgNO_3$ concentration. Keeping that in mind, we are restricting ourselves to that particular concentration of $AgNO_3$ in the present work.

EXPERIMENTAL

Materials

PVA (1700-1800) is obtained from Sigma chemical Co. and is of very high purity (99.9%). Silver nitrate of 99.9% purity is obtained from E. Merk, Germany. These are used without any further purification.

Preparation of composite

Silver nano dispersion in PVA is achieved by chemical reduction method. To be particular, Silver nitrate (1mM) solution is added to PVA solution (3 wt%) with constant stirring at 90^0C. The solution is maintained at that temperatute for 1hr. for the formation of silver nano, indicated by the change in colour of the solution to light yellow. This solution is spin cast and dried in vacuum for further investigations.

Structural and optical characterization

UV-Vis spectra for optical absorption study are taken by Cary 300 scan UV-Visible spectrophotometer. Field emission scanning electron microscope (FESEM) images for morphology and particle size determination are taken by FESEM (JSM-6700F, JEOL, Japan). XRD data for structure study are collected by Scifert XRD 3000 pd diffractometer with Cu-K_α (0.15418 nm) radiation and Photoluminescence (PL) are recorded by F-2500FL spectrometer.

RESULTS AND DISCUSSION

In figure 1, we show the UV-Visible absorption spectra of silver nano dispersed in PVA. This shows strong Plasmon resonance peak at 441nm which is a clear consequence of formation of nanosized particles[16]. It has been reported that for narrow particle size distribution of silver nano in SiO_2 matrix the absorption spectra homogeneous broadening whereas for wide particle size distribution the broadening is predicted to be inhomogeneous[17]. In our study, we notice that the absorption curve broadens more towards red region indicating distribution of particle size of little wide range and the absorption peak corresponds to the value for average particle size.

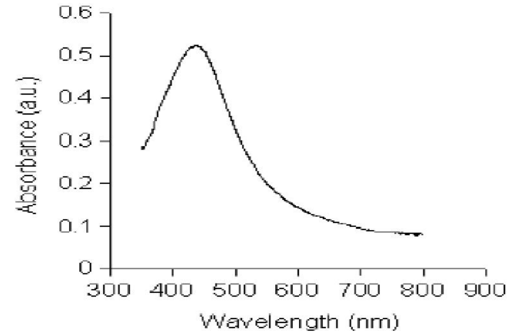

Figure 1 : UV-Visible absorption spectra of composite film

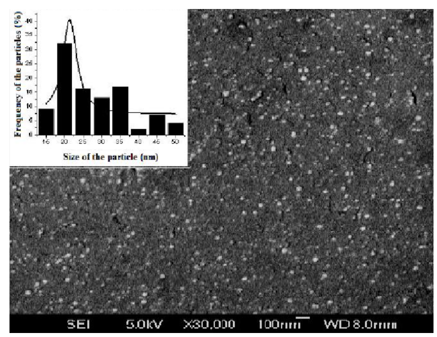

Figure 2 : SEM image of the composite film. Inset shows size distribution histogram

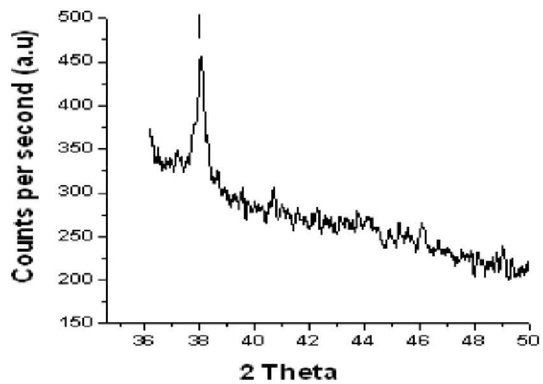

Figure 3 : XRD of the composite film

The film morphology and particle size distribution of Ag-PVA nanocomposite is studied by FESEM image which is shown in figure 2. The picture shows the uniform distribution of nanoparticles throughout the film.

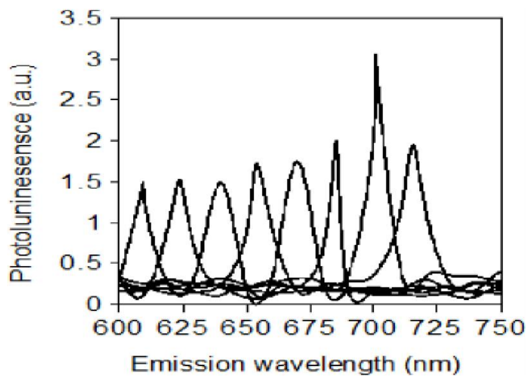

Figure 4(a) : Photoluminescence spectra of composite film

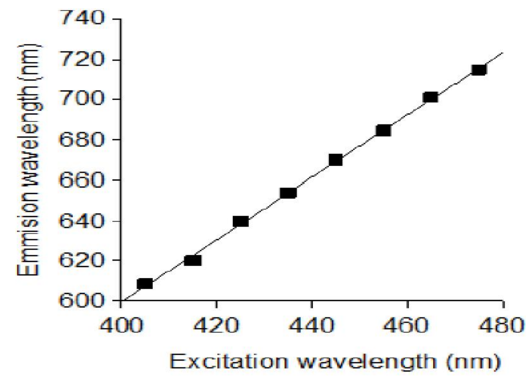

Figure 4(b) : Plot of emission wavelength vs excitation wavelength

Further the particles are of various sizes ranging from 10nm to 50 nm and the particles are nearly uniformly spherical in shape. The size distribution frequency (among 100 particles taking interval of 5nm) is calculated and plotted in a histogram. This shows that the frequency of occurrence is maximum for the particle size in the range 15-20 nm. In the inset of the SEM picture we show this histogram.

The structure of as prepared silver colloid is investigated by XRD analysis. The XRD pattern of the nanocomposite film is shown in figure 3. This shows characteristic peak of silver nano at $2\Theta = 38.02°$ for (111) crystalline plane[18]. The broad nature of the XRD peak could be attributed to the nanosize of the particles.

The room temperature (300K)PL spectra of Ag-PVA nano composite film for different excitation wavelengths ranging from 405nm to 475 nm are shown in figure 4a. The PL position is observed to red shift in a regular manner with increase of excitation wavelength. Similar result has been reported for silver nano in PMMA (polymethyl methacrylate)[10] and the phenomena has been considered as size selective excitation effect.

In figure 4b, we plot the PL peak position vs excitation wavelength and it is found that with the increase in excitation wavelength, the PL peak position increases linearly.It is also found that the PL intensity is dependent on excitation wavelength. The intensity is maximum for excitation wavelength of 465nm. However this is little more than the peak position in UV-Vis spectra observed by us which is 441nm. This is justified as our surface plasmon resonance peak is much broader. The change in peak position and intensity of PL can be attributed to various particle sizes so that different set of particles of definite size range is active for a particular excitation wavelength.

CONCLUSION

Silver-PVA nanocomposite film fabricated chemically shows distribution of various particle sizes. Silver nano formation is further confirmed by UV-Vis absorption and XRD study. FESEM picture further confirms the nanosized particle formation with a wide range of particle size variation in the single film. This is in conformity with the broadening of UV-Vis absorption spectra and subsequent shift of PL peak with gradual change in excitation wavelength.

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