CHAPTER-2
SYNTHESIS AND CHARACTERIZATION OF Ag/PVA
NANOCOMPOSITES

2.1 Introduction

Ag/PVA nanocomposites are novel invention of nanocomposite materials which indicate a promising field in the frontiers of nanotechnology. These are promising nanocomposite materials for chemical and biological sensing applications [1] as well as high K materials [2]. Ag nanoparticles possess many interesting and unique properties. It is found in various applications, such as catalysis, electronics, non-linear optics, antimicrobial and biomaterial applications [3]. Several methods are reported for the synthesis of Ag nanoparticles, e.g., photochemical reduction [4, 5], microwave [6], chemical reduction [7, 8], and γ-irradiation [9]. The concept of green Ag nanoparticles preparation was first developed by Raveendran et al. [10], who used β-D-glucose as the reducing agent and starch as a capping agent to prepare starch Ag nanoparticles. A green method for nanoparticles preparation should be evaluated from three aspects: the solvent, the reducing agent and the stabilizing agent. The use of polyvinyl alcohol (PVA) as the host polymer for Ag nanoparticles is advantageous due to the reducing ability of the secondary alcohol groups, its excellent film forming properties and optical transparency [11-13].
2.2 Synthesis of Ag/PVA nanocomposites by thermal annealing process

2.2.1 The method

Polymer -metal nanocomposites can be obtained by two approaches, viz. *in situ* and *ex situ* techniques. In the *in situ* methods, metal particles are generated inside a polymer matrix of a metallic precursor dissolved in the polymer. In the *ex situ* approach, nanoparticles are first produced by soft-chemistry routes and then dispersed into the polymeric matrices. In our work the first method is employed.

In chemical route, polymer matrices play the central role in controlling the particle size. Physically the matrices provide some gaps in the polymer chain. These gaps are of nm range. During chemical reaction to produce small nano particle, the matrix is mixed with the reactants and then stirred. As soon as the nano structure is produced, it immediately enters into the gap provided by polymer matrix. Once the particle enters the gap, it can neither come out nor can enhance in size. During sample preparation, the particle size can be varied by controlling-

(i) Temperature of the reaction.

(ii) Time of reaction.

(iii) The molecular ratio of reactants to matrix.
In our work the silver nanoparticles are generated in the PVA matrix by thermal annealing process. The synthesis process of the present work of Ag/PVA nanocomposite by thermal annealing process is the modified form of the process used by S. Porel. et al.[14]. In their work thermal treatment is used after casting the reaction mixture on the substrate i.e. on the thin films. But in our work, heat treatment is used in the solution stage of the reaction mixture. The main advantage of the nanocomposites in solution form is its flexible applications. This type of nanocomposites can be used as coating on any symmetrical objects and surfaces where direct heat treatment is not possible.

In the present work, AgNO₃ and PVA of analytical grade purity are used without further purification. The general procedure involves the following steps-

(i) AgNO₃ solutions of different concentration (10 mmol/L to 50 mmol/L) are prepared by dissolving AgNO₃ powder in distilled water. The mixture is stirred at room temperature in magnetic stirrer (fig.2.1.1).

(ii) PVA solutions of different wt. % (1wt. % to 4wt. %) are prepared in distilled water. The mixture is stirred at 60°C for 3 hrs. in magnetic stirrer.

(iii) AgNO₃ solution and PVA solution is mixed in 1:1 ratio and thermal treatment of the solution is done at selected temperatures, for selected time in digital oven (fig.2.1.2) to generate the metal nanoparticles within the polymer matrix and,

(iv) The reaction nanocomposite material is dip coated to form thin film on chemically cleaned (in ultrasonic vibrator) (fig.2.1.3) glass substrate. The films are dried for several days at room temperature.
During sample preparation, the morphology of the films and the particle size can be varied by controlling the temperature of the reaction, time of reaction and the molecular ratio of reactants to matrix. These parameters are varied in the current investigation and the as-prepared nanocomposite materials are used as dielectric layer in the thin film capacitor and as sensitive material for fiber optic pH sensor. The fabrication process is limited to PVA weight up to 4% as for beyond 4%, the sample is obtained as a very thick gel, not suitable for application in the above mentioned fields.

The chemical reactions occurred during thermal annealing process is complex. But the possible reaction can be explained by ‘polyol route’ [14] as follows-

\[
R_2CHOH + AgNO_3 \rightarrow R_2CO + H_2O + NO_2 + Ag
\]

The purpose of heating is to supply the reduced silver ions with enough kinetic energy to penetrate the polymer layer [Cao, 2004] [15].

Fig. 2.1.1: Photograph of magnetic stirrers (INSIF make, No. H-359)
Fig. 2.1.2: Photograph of digital oven [Imperial Lab. Equipments, IL931].

Fig. 2.1.3: Photograph of ultrasonic cleaner [IKON Instruments].
2.2.2 Characterization Techniques

2.2.2.1 UV-VIS Characterization

Ultraviolet-Visible spectroscopy is used to analyze materials in the UV (200 to 400 nm) and visible (400 to 800 nm) region of the electromagnetic spectrum. Figure 2.2.1 shows the block diagram of UV-VIS spectrometer. The absorption in these regions corresponds to electronic transitions between different molecular orbitals of the systems. In particular, UV-VIS spectroscopy is of most use for identifying conjugated systems since transitions involving $\pi$ orbital and lone pairs tend to have stronger absorptions. The absorption of radiation in a sample follows the Beer-Lambert law which states that the concentration of a substance in a sample (thin film/solution) is directly proportional to the absorbance “A” i.e-

\[
\text{Absorbance (A) = Constant} \times \text{Concentration} \times \text{Cell length}
\]

This law is true for monochromatic light, provided that the physical and chemical state of the substance does not change with the concentration.
When a monochromatic radiation passes through a homogeneous sample, the intensity of the emitted radiation depends upon the thickness (L) and concentration (c) of the sample. If \( I_0 \) is the intensity of the incident radiation and \( I \) is that of the transmitted radiation then the ratio \( I_0/I \) is known as transmittance and is expressed as a percentage and referred to...
as % transmittance (T). Mathematically, the relation between “A” and “T” can be expressed as-

$$A = \log_{10} \left( \frac{I_0}{I} \right) = \log_{10} \left( \frac{100}{T} \right) = kcL$$

Where “k” is the extinction coefficient that depends upon the nature of the molecule and wavelength of incident radiation, “L” is the length of the radiation path through the sample and “c” is the concentration of absorbing molecules in that path.

UV-VIS absorption characterization is used on Ag/PVA nanocomposite to investigate their optical properties. In such cases, absorption of incident radiations takes place due to Surface Plasmon Resonance (SPR) of Ag nanoparticles. SPR is the coherent oscillation of the surface conduction electrons of metal nanoparticles excited by electromagnetic radiation (As discussed in section 1.2.2 of chapter 1).

When the wavelength of an incident radiation is comparable with the mean free path of the conduction electrons of a metal nanoparticle, the electric component of the electromagnetic incident field induces the polarization of the conduction electrons, giving rise to the surface plasmon absorption [25, 26]. When metal-polymer nanocomposites like Ag/PVA are exposed to the electromagnetic radiation, SPR absorption band is observed at a specific wavelength depending upon the nature of the metal, matrix, size of the particles as well as distribution.

A Perkin-Elmer Spectrophotometer (LAMDA 950 UV/Vis/NIR Spectrophotometer) is employed in this work to characterize the optical properties of the fabricated samples. The working range of this equipment is 190-3200 nm, but in this work it is used to scan the samples in the wavelength range of 300-650 nm as the SPR absorption of Ag nanoparticles
is near 400 nm. The recording and analysis of data are done through “UV Winlab” which is an integral part of the spectrophotometer. The recorded data for different samples are plotted in “Origin 6.5” software.

For absorption spectra characterization we have prepared dozens of samples by varying the fabricating parameters as follows-

(i) Concentration of AgNO₃ from 10 m mol/L to 50 m mol/L, keeping temperature, annealing time and PVA weight % constant.
(ii) Annealing temperature from 70 °C to 150 °C keeping concentration, annealing time and PVA weight % constant.
(iii) Annealing time from 10 to 30 minutes, keeping concentration, annealing temperature and PVA weight % constant.
(iv) PVA weight % from 1 % to 4 %, keeping concentration, annealing time and annealing temperature constant.

The results obtained are shown in table 2.1 to table 2.4 and fig. 2.4.1, fig. 2.4.2, fig. 2.4.4 and fig.2.4.6.
2.2.2.2 SEM Characterization

SEM provides high resolution images of the surface of a sample. The image in an SEM is produced by scanning the sample with a focused electron beam and detecting the secondary and/or backscattered electrons. Practically the scattering processes (figure 2.2.2.) experienced by electrons during their passage through specimen determine the kind of information obtained [15]. The resolution of the SEM approaches a few nanometers, and the instruments can operate at magnifications that are easily adjusted from ~10 to over 100,000 [15]. Not only does the SEM produce topographical information as optical microscopes do, it also provides the chemical composition information near the surface.

In a typical SEM (figure 2.2.3), electrons emitted from gun is focused into a beam, with a very fine spot size of ~5nm and having energy ranging from a few hundred eV to 50KeV, that is rastered over the surface of the specimen by deflection coils [15]. As the electrons strike and penetrate the surface, number of interactions occur that result in the emission of electrons and photons from the sample (figure 2.2.2), and SEM images are produced by collecting the emitted electrons on a cathode ray tube (CRT). Various SEM techniques are differentiated on the basis of what is subsequently detected and imaged, and the principal image is of three types: secondary electron images, backscattered electron images and elemental X-ray maps. When a high energy primary electron interacts with an atom, it undergoes either inelastic scattering with atomic electrons or elastic scattering with the atomic nucleus. In an inelastic collision the primary electron, transfers part of its energy to
the other electron. When the energy transfer is large enough the other electron will be emitted from the sample. If the emitted electron has energy less than 50eV, it is known as secondary electron. Backscattered electrons are the high-energy electrons that are elastically scattered and essentially possess the same energy as the primary electrons. The probability of backscattering increases with atomic number of the sample material.

Although backscattering images cannot be used for elemental identification, useful contrast can develop between the regions of the specimen that differ widely in atomic number. An additional electron interaction in the SEM is that the primary electron collides with and ejects a core electron from an atom in the sample. The excited atom will decay to its ground state by emitting a characteristic X-ray photon, which are used for chemical characterization (EDS).

![Diagram of electron scattering phenomena](http://www.tu-chemnitz.de/physik/AFKO/eml/praktika/HREM_AN.pdf)

Fig. 2.2.2: Various scattering phenomena [M. Karlik, Available at: http://www.tu-chemnitz.de/physik/AFKO/eml/praktika/HREM_AN.pdf]
In our work, Scanning Electron Microscopy (SEM) (LEO 1430VF and LEO 435VP, IITG) at different resolutions is used for SEM characterization. The results obtained are shown in fig. 2.4.1 to fig. 2.4.7.
2.2.2.3 AFM Characterization

The AFM is an instrument capable of measuring the topography of a given sample. The advantage of the AFM over SEM is the ability to make topographical measurements for detection and investigation of the size and shape of nanoparticles in three dimensions.

An AFM is a lens-free microscope where a tip is mounted on the end of a micro-fabricated cantilever, as seen in Fig. 2.2.4. [24] It makes use of the deflection of the cantilever caused by the small force of interaction between the tip and the sample surface to reveal the sample’s topography in a 3D way, and its typical lateral resolution is about 10 nm, down to the atomic level. The AFM generally has three operation modes: Contact Mode, Non-contact mode and Tapping Mode. The mode used mainly in this study is the Tapping Mode for its higher resolution than the Non-contact Mode and less damage to the sample than the Contact Mode. The Tapping Mode AFM operates by scanning a very fine tip attached to the end of an oscillating cantilever across the sample surface. The cantilever is oscillated at or near its resonance frequency with the amplitude ranging typically from 20 nm to 100 nm. The frequency of oscillation can be at or on either side of the resonant frequency. During scanning, the tip slightly “taps” on the sample. The feedback loop maintains constant oscillation amplitude by maintaining a constant root-mean-square (RMS) of the oscillation signal acquired by the split photodiode detector, so that a constant tip and sample interaction can be maintained during imaging.
In the present work an AFM (Molecular Imaging PICOSCAN TM 2500 USA) is used in this study to retrieve three-dimensional (3D) profiles of interested patterns.
2.3 Theoretical estimation of nanoparticle size

Theoretical estimation of nanoparticle size is made utilizing software “Mieplot 4203” which is based on classical Mie scattering theory [16]. Mie theory describes the scattering or absorption of electromagnetic radiation from a spherical particle depending on its size [17]. Mie’s classical solution is described in terms of absorption cross section ($\sigma_{abs}$) and scattering cross section ($\sigma_{sca}$) which can be normalized as-

$$Q_{abs} = \frac{\sigma_{abs}}{\pi a^2}, \quad Q_{sca} = \frac{\sigma_{sca}}{\pi a^2}$$ (1)

Where $Q_{abs}$ and $Q_{sca}$ are referred to as the efficiencies of light absorption and scattering, respectively. The surface plasmon polariton modes excited in the metal nanoparticles contributes towards total light extinction $Q$, which is the sum of $Q_{abs}$ and $Q_{sca}$ [18].

The absorption and scattering efficiencies for sufficiently small particles (comparable with the wavelength $\lambda$ of the incident light) with a dielectric permittivity $\varepsilon$ can be expressed as follows:

$$Q_{abs} \equiv \frac{8\pi a}{\lambda} \text{Im} \left( \frac{\varepsilon - 1}{\varepsilon + 2} \right)$$ (2)

$$Q_{sca} \equiv \frac{128\pi^4 a^4}{3\lambda^4} \frac{|\varepsilon - 1|^2}{|\varepsilon + 2|}$$ (3)

Hence $Q_{abs} \gg Q_{sca}$. 
In general, light absorption dominates in the extinction spectrum for particles of relatively small radius (< 20 nm) and light scattering becomes the dominate process for large particles [19]. For small particles, $Q_{abs}$ and $Q_{sca}$ include contributions only from the dipolar modes of surface plasmon excitation. However, for large particles, the contribution of higher order modes to the absorption and scattering efficiencies becomes significant [17].

The algorithm of the “Mieplot software” is the calculation of $Q_s$, $Q_{abs}$ and $Q_{sca}$ as functions of wavelength. The main ingredients of this calculation are refractive indices ($n_p$) of the sphere and the surrounding medium ($n_{med}$). To determine the particle size we performed several calculations changing the radius of particles and compared absorption dependence on wavelength with the experimental UV-VIS absorption spectrometry results. In our theoretical calculations the radius of particles is changed from 1 nm to 100 nm and the best fit between the experimental and theoretical results are considered as the size of the particles. An example of this calculation for the sample no. a5 and d1 are shown in fig.2.3.1 and 2.3.2 respectively. The standard deviation used in the calculation is 10 %. For the sample number a5, $\lambda_{max}= 413$ nm and the best fit between the experimental and theoretical results is obtained when for theoretical absorption dependence calculations radius of particle as 47 nm is used. Similarly for the sample no. d1, $\lambda_{max}= 418.4$ nm and at 50 nm of particle size, the experimental and theoretical SPR peak coincide.
Fig. 2.3.1: Comparison of theoretical and experimental absorption dependence on wavelength for the sample $a_5$ of table 2.1.

Fig. 2.3.2: Comparison of theoretical and experimental absorption dependence on wavelength for the sample $d_1$ of table 2.4.
2.4 Results and discussions

2.4.1 UV-VIS Spectroscopy

2.4.1.1 Effect of annealing temperature

UV-VIS spectrometry can confirm formation of silver nanoparticles prepared following in situ approach because silver nanoparticles can show an intense absorption peak around 400 nm originating from Surface Plasmon Resonance (SPR). In the present study, when annealing temperature of the composite films are varied from $70^\circ$C to $120^\circ$C, no prominent SPR peak is found [fig. 2.4.1]. At $130^\circ$C, recorded spectra shows the presence of a SPR peak at 412 nm which is characteristics of the surface plasmon resonance of silver nanoparticles. When the heating temperature is $150^\circ$C, a SPR peak at 423nm is obtained but the spectrum is comparatively broader than that obtained at $130^\circ$C which indicates the larger size distribution of the silver nanoparticles [17] at high temperatures.

In fig. 2.4.1, it is found that the absorbance increases with increasing temperature indicating higher number of Ag nanoparticles generated at higher temperatures [20].
Fig. 2.4.1: Absorption spectra of Ag/PVA nanocomposite thin film (Concentration, PVA wt. %, and annealing time are kept Constant at 40 mmol/L, 4%, 20 minutes respectively). (a₁ at 70 °C, a₂ at 90 °C, a₃ at100 °C, a₄ at110 °C, a₅ at120 °C, a₆ at130 °C, a₇ at150 °C)

The particle sizes for different samples (a₁ to a₇) calculated on the basis of classical Mie Scattering theory along with the experimental conditions are listed in table 2.1-
Table 2.1: Variation of particle size with annealing temperature.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Annealing temperature in °C</th>
<th>Annealing time in minutes</th>
<th>Concentration in mmol/L</th>
<th>PVA weight in %</th>
<th>λ\text{max} (nm)</th>
<th>Particle size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a₁</td>
<td>70</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>a₂</td>
<td>90</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>a₃</td>
<td>100</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>a₄</td>
<td>110</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>a₅</td>
<td>120</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>413</td>
<td>47</td>
</tr>
<tr>
<td>a₆</td>
<td>130</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>414</td>
<td>48</td>
</tr>
<tr>
<td>a₇</td>
<td>150</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>422.2</td>
<td>52</td>
</tr>
</tbody>
</table>
2.4.1.2 Effect of annealing time

Effects of annealing time on the optical property of the composite films and on the size of Ag nanoparticles are studied by varying the annealing time from 10 minutes to 30 minutes in the interval of 5 minutes. The absorption spectra obtained are shown in fig.2.4.2.

Fig. 2.4.2: Absorption spectra of Ag/PVA nanocomposite thin film (Concentration, PVA wt. %, and annealing temperature are kept Constant at 40 mmol/L, 4%, 130 °C respectively). (b_1 for 10 mints., b_2 for 15 mints., b_3 for 20 mints., b_4 for 25 mints., b_5 for 30 mints.)
The particle sizes for different samples (b₁ to b₅) calculated on the basis of classical Mie Scattering theory along with the experimental conditions are listed in table 2.2.

Table 2.2: Variation of particle size with annealing time.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Annealing temperature in °C</th>
<th>Annealing time in minutes</th>
<th>Concentration in mmol/L</th>
<th>PVA weight in %</th>
<th>λ_max. (nm)</th>
<th>Particle size in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>b₁</td>
<td>130</td>
<td>10</td>
<td>40</td>
<td>4</td>
<td>456.2</td>
<td>68</td>
</tr>
<tr>
<td>b₂</td>
<td>130</td>
<td>15</td>
<td>40</td>
<td>4</td>
<td>457.2</td>
<td>68.5</td>
</tr>
<tr>
<td>b₃</td>
<td>130</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>408</td>
<td>41</td>
</tr>
<tr>
<td>b₄</td>
<td>130</td>
<td>25</td>
<td>40</td>
<td>4</td>
<td>407.2</td>
<td>42.5</td>
</tr>
<tr>
<td>b₅</td>
<td>130</td>
<td>30</td>
<td>40</td>
<td>4</td>
<td>460</td>
<td>69</td>
</tr>
</tbody>
</table>

Variation of particle size and absorption with annealing time are depicted in fig. 2.4.3.
It is observed that as annealing time increases, the wavelength of SPR is blue shifted up to ~ 20 minutes and then red shifted beyond 20 minutes of annealing time. The observed variation of absorbance calls for further experimental as well as theoretical investigations.

Fig. 2.4.3: Dependence of particle size and absorption of SPR on annealing time.
2.4.1.3 Effect of AgNO₃ Concentration

In fig. 2.4.4, it is found that the absorbance increases with increasing concentration indicating higher number of Ag nanoparticles generated at higher concentration and the increasing concentration resulted in larger particles indicating red shift in the SPR wavelength [11].

Fig. 2.4.4: Absorption spectra of Ag/PVA nanocomposite thin film (PVA wt. %, annealing temperature and annealing time are kept Constant at 4%, 130 °C and 20 mints. respectively). (c₁ for 10 mmol/L, c₂ for 20 mmol/L c₃ for 30 mmol/L, c₄ for 40 mmol/L and c₅ for 50 mmol/L)
Variation of particle size and absorption with concentration are shown in fig. 2.4.5.

The particle sizes for different samples (b₁ to b₅) calculated on the basis of classical Mie Scattering theory along with the experimental conditions are listed in the following table (table 2.3)-

Table 2.3: Variation of particle size with concentration.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Annealing temperature in °C</th>
<th>Annealing time in minutes</th>
<th>Concentration in mmol/L</th>
<th>PVA weight in %</th>
<th>λ_{max.} (nm)</th>
<th>Particle size in nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>c₁</td>
<td>130</td>
<td>20</td>
<td>10</td>
<td>4</td>
<td>392</td>
<td>27</td>
</tr>
<tr>
<td>c₂</td>
<td>130</td>
<td>20</td>
<td>20</td>
<td>4</td>
<td>422.4</td>
<td>52</td>
</tr>
<tr>
<td>c₃</td>
<td>130</td>
<td>20</td>
<td>30</td>
<td>4</td>
<td>414.4</td>
<td>48</td>
</tr>
<tr>
<td>c₄</td>
<td>130</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>427.6</td>
<td>55.5</td>
</tr>
<tr>
<td>c₅</td>
<td>130</td>
<td>20</td>
<td>50</td>
<td>4</td>
<td>419.6</td>
<td>51</td>
</tr>
</tbody>
</table>
Fig. 2.4.5: Concentration dependence of particle size and absorption of SPR.
2.4.1.4 Effect of PVA weight %

The absorption spectra for the variation of PVA wt. % for Ag/PVA nanocomposites are shown in fig. 2.4.6. The figure reveals sharp blue shift of SPR wavelength and increase in absorption with increase in PVA wt. %. The variation of particle size and absorption with PVA wt. % are shown in fig. 2.4.7.

Fig. 2.4.6: Absorption spectra of Ag/PVA nanocomposite thin film (Concentration, annealing temperature and annealing time are kept Constant at 40 mmol/L, 130 °C and 20 mints. respectively). (d₁ for 1 wt. %, d₂ for 2 wt. %, d₃ for 3 wt. %, d₄ for 4 wt. %)
The particle sizes for different samples (b₁ to b₅) calculated on the basis of classical Mie Scattering theory along with the preparative conditions are listed in the table 2.4.

Table 2.4: Variation of particle size with PVA wt. %.

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Annealing temperature in °C</th>
<th>Annealing time in minutes</th>
<th>Concentration in mmol/L</th>
<th>PVA weight in %</th>
<th>Λₘₐₓ (nm)</th>
<th>Particle size In nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>d₁</td>
<td>130</td>
<td>20</td>
<td>40</td>
<td>1</td>
<td>418.4</td>
<td>50</td>
</tr>
<tr>
<td>d₂</td>
<td>130</td>
<td>20</td>
<td>40</td>
<td>2</td>
<td>418</td>
<td>50</td>
</tr>
<tr>
<td>d₃</td>
<td>130</td>
<td>20</td>
<td>40</td>
<td>3</td>
<td>415.2</td>
<td>48.5</td>
</tr>
<tr>
<td>d₄</td>
<td>130</td>
<td>20</td>
<td>40</td>
<td>4</td>
<td>413.6</td>
<td>47</td>
</tr>
</tbody>
</table>
Comparison of fig. 2.4.1, 2.4.2, 2.4.4 & 2.4.6 points towards the possibility of narrower size distribution in the samples d\(_1\) to d\(_4\) compared to the other sets i.e. a\(_1\) to a\(_7\), b\(_1\) to b\(_5\) and c\(_1\) to c\(_5\). Moreover, the SPR peaks in the UV-VIS spectra for the samples d\(_1\) to d\(_4\) are more prominent than those of the rest of the samples. The preparative parameters for this set of samples (i.e. d\(_1\) to d\(_4\)) are chosen by selecting the optimized parameters corresponding to the best SPR peaks from the other sets of samples. More precisely, annealing temperature at 130 °C from the set a\(_1\) to a\(_5\), annealing time at 25 minutes from the set b\(_1\) to b\(_5\) and AgNO\(_3\) concentration at 40 mmol/L from the set c\(_1\) to c\(_5\) are selected for the preparation of the samples d\(_1\) to d\(_4\). The SPR peak of d\(_4\) is more prominent with higher absorption than d\(_2\), d\(_3\) and its SPR position is less in comparison to the others indicating blue shift of
wavelength which results in smaller particle size. Hence the optimized conditions for generating smaller and homogeneous nanoparticle based nanocomposites are achieved at \( d_4 \). As a result, the characterizations results presented are mostly confined to \( d_4 \).

UV-VIS characterizations for sample no. a\(_1\), b\(_2\) and b\(_5\) having more than one SPR peak indicates possibilities of non spherical shape of the particles whereas for others having single peak, the particle shape may be spherical. It is because when particles have non symmetrical shapes, the electrons begin to demonstrate resonances associated with each of the dimensions. For instance, while a spherical nanoparticle may have a single resonant frequency related to its singular dimension, i.e. its radius, an ellipsoidal particle may have two or three resonance frequencies related to its two or three axes. These differences arise from different orientations and magnitudes of the dipoles on the ellipsoidal particles and results in distinct resonance frequencies for each dimension [21-23]. Although two SPR peaks are observed for the above mentioned samples, only the peak of maximum absorption is adopted for estimating particle size. This estimation regarding the shape of the nanoparticles is further confirmed from AFM characterization results.
2.4.2 SEM characterization

SEM photograph (WL= 300 nm, EHT=10KV, WD=13mm, SIGNAL A=SE1) for sample no. b₃ and b₄ are given in fig. 2.5.1 and 2.5.2.

Fig. 2.5.1: SEM picture for the sample b₃.

Fig. 2.5.2: SEM picture for the sample b₄.
The minimum particle diameter for the sample no b3 and b4 from SEM characterization is found to be ~75 nm and 88 nm respectively and the diameters estimated from Mie Scattering theory is 82 and 85 nm respectively. Therefore the experimental and theoretical observations are in almost good agreement.

The SEM investigation on the sample with optimized parameters i.e d4 is shown in fig. 2.5.3. The general morphology for d4 as observed in SEM characterization is shown in fig.2.5.4.

Fig. 2.5.3: SEM picture for the sample d4 (particle size)
Fig. 2.5.4: SEM picture for the sample d₄ (morphology).

Fig. 2.5.5: SEM picture for sample a₄ at 520X magnification
Fig. 2.5.6: SEM picture for sample a₄ at 2.81 KX magnification.

Fig. 2.5.7: SEM picture for sample a₄ at 8.92 KX magnifications.
In the UV-VIS spectrum for the sample number a_4 (fig. 2.4.1), there is no prominent SPR peak. This observation reveals the absence of silver nanoparticles in that sample. The SEM photographs for this sample [(fig.2.5.5 –fig. 2.5.7) at different resolutions confirm the non-formation of nanoparticles for that sample.
2.4.3 AFM characterization

The UV-VIS spectrum for the sample no. b$_2$ having double resonance peak [inset of fig. 2.6.1] reveals non-spherical shape of the particles. The AFM characterization for b$_2$ confirms the formation of elliptical shaped particles (i.e. non-spherical) as shown in the following figure [fig. 2.6.1]-

![AFM picture for the sample b$_2$.](image-url)
Similarly the AFM characterization for the sample nos. d$_1$ [fig. 2.6.2] and d$_4$ [fig. 2.6.3] having singular SPR peak in UV-VIS spectrum [inset picture], reveals spherical shape of the particles.

Fig. 2.6.2: AFM picture for the sample d$_1$. (Inset: corresponding UV-VIS spectra)
Fig. 2.6.3: AFM picture for the sample d$_4$. (Inset: corresponding UV-VIS spectra)
The general morphology in AFM characterization for d₄ is shown in the following figure (fig. 2.6.4)-

Fig. 2.6.4: AFM picture for the morphology of sample d₄
2.5 Conclusions

In summary, UV-VIS spectrometry confirms in situ generation of Ag nanoparticles in PVA matrix by simple thermal annealing process, with modifications introduced by the author, the main advantage of the modified process being the flexible applications of the so-formed nanocomposites. The wavelength corresponding to maximum absorption ($\lambda_{\text{max}}$) and hence the particle size are successfully controlled by controlling the physical parameters like concentration, annealing time, annealing temperature and PVA wt. %. The fabrication conditions confined to the range of the physical parameters adopted in the present investigation for generating homogeneous nanoparticles are optimized. Particle size is estimated by comparing theoretical (calculations according Mie Scattering theory) and experimental UV-VIS absorption spectra. The results are in good agreement with those obtained from SEM characterization. The AFM characterization confirms the shape as indicated by UV-VIS characterizations.
2.6 References


[16]. The “Mieplot 4203” software is available from Philip Laven, available at:


