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# Synthesis and Characterization of PVP embedded Silver Nanoparticles to Study their Structural and Optical Properties

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*Abstract:* **PVP embedded silver nanoparticles were prepared by using Polyol method in an Ethylene Glycol solution. Ethylene Glycol works as a solvent that has the potential to enhance the optical and electronic properties of the specimen. An absorption peak at 408.2nm in the UV/Vis- spectra resulted from the formation of nanoparticles with the calculated band-gap at 2.67eV. The morphology and size of these particles are confirmed with TEM, the nanoparticles are found to be spherical and oval. It shows the size of nanoparticles to be around 10-15nm. XRD peaks are in agreement with the literature and with its help, the d-spacing is calculated to be 0.23nm and confirms the presence of polymer as the capping agent of nanoparticles. The addition of silica facilitates the formation of nanoparticles further. These nanoparticles can be helpful in photoelectric devices and have an impact on our renewable energy technology**.

***Index Terms:*** **Nano-blends, Optical properties, Silver nanoparticles, TEM, XRD.**

## I. INTRODUCTION

Nanoparticles have become a very important tool for the advancement of technology and their unique characteristics have provided us with amazing opportunities to innovate and design new devices. One special characteristic of nanoparticles is that their optical and electrical properties are dependent on their physical properties i.e. size. In the case of their optical properties, size and shape determine their distinct surface plasmon absorption (Kerker, 1985; Hutter, E. & Fendler, J.H. 2004). Silver nanoparticles categorically exhibit these properties in each state, solid and liquid (Bohren, & Huffman 1998). There are various methods to prepare Silver nanoparticles but we have focused on green and bio-friendly methods (Khan et al. 2021). Silver nanoparticles have high optical properties and their polymer blends have high potential in the optical field. If nanoparticles can be embedded into polymers they could be used in various applications. Silver nanoparticles in water-soluble polymers such as PVP and PVA show absorption at 438nm and 410nm respectively (Khanna et al. 2005; Carotenuto 2001). Moreover, these nanoparticles exhibit absorption at 430nm for a water-insoluble polymer i.e. PVDF (Abou-alkheer 2015). Silver nanoparticle dispersion with such polymers opens a new avenue for the proliferation of optical information. The blend formed with these materials is monitored by keeping a tap on the surrounding conditions. Embedment of Silver nitrate in the solution of PVP and ethylene glycol determines the shape and size of nanoparticles. The size of nanoparticles can also be controlled by optimizing the chemical reduction method (Quintero-Quiroz et al., 2019). If the chemical process is accurate, the size of nanoparticles is quite homogeneous known as monodisperse particles. PVP is a flaky, water-soluble polymer that has been readily used with Silver nitrate to produce silver nanoparticles of different shapes (Silvert et al. 1996; Sun et al. 2002; Sun, Y et al. 2002). Ethylene glycol is a non-aqueous solvent that acts as an alternative to many other solvents (aqueous or non-aqueous) in such a reduction process since Ethylene glycol not only plays the role of a solvent but it also acts as a reducing agent of Ag (Silver), making colloidal

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solutions (Slistan-Grijalva et al., 2005). The use of polymer also helps in reducing the aggregation and spread in the distribution of nanoparticles. Under thermal energy PVP also helps in the formation of nucleation and the formation of silver nanoparticles (Gharibshahi et al., 2017).

The formation of nanoparticles is identified when the colour of the solution changes to reddish Brown because the properties of the material change when it transitions into the nano range. That change in properties is signified by the bright-coloured solutions. These extravagant colours of nanoparticles are due to a special characteristic of nanoparticles known as surface plasmon resonance.

SPR (Surface Plasmon Resonance) is a collective oscillation of free electrons at a resonant frequency that is augmented by Electromagnetic radiation. Among metal nanoparticles, silver nanoparticles in particular showcase the strongest plasmonic interaction with Electromagnetic radiation. The reason behind this enhanced plasmonic effect is a greater scattering cross section of Silver than other metal nanoparticles. This surface Plasmon Resonance is tunable by the size, shape, dielectric properties and temperature of the environment. Among these different sizes and shapes of nanoparticles, silver nanoparticles of anisotropic morphology show more LSPR bands since lesser symmetry plays a major role in increasing the number of bands.

The surface Plasmon resonance effect is responsible for some major optical properties of nanoparticles like photocatalysis, photoconductivity, electroluminescence, etc. (Liu et al., 2017; Matthew et al., 2002; Qian et al., 2002)

This paper is our humble effort to synthesise Silver nanoparticles in a non-toxic process after the chemical reduction of Silver nitrate with Ethylene Glycol and PVP along with Silica ($SiO_2$). This study shall help in amplifying the usage of silver nanoparticles in various optical and electrical properties. The addition of Ethylene Glycol has been made because it has been proven to enhance the stability of nanoparticles. (Chengcai Luo et al., 2005). This approach to manufacturing Silver-polymer nanocomposite gives an alternative to the green method to produce silver nanoparticles.

## II. Materials and Methods

All the chemicals used in our experiments are of high quality and used without further purification. Silver nitrate (99%) was purchased from *Qualigens*, Ethylene Glycol (MW 62) was purchased from *Rankem*, PVP (Polyvinylpyrrolidine, MW 10,000) was purchased from *Alfa Aesar*, and Silicon dioxide (99.99%) from *Umicore*. De-Ionized water was used to clean the glassware and prepare aqueous solutions. The ambient temperature during all the processes of the experiment is 24±2° C.

100mg Silver nitrate is added to 10 ml de-ionised water (about 58.8 mM) solution is prepared. 2ml of this solution is added to another solution of PVP (0.5gm) and Ethylene Glycol (20 ml). This mixture was heated at 45° C with a consistent magnetic stirring at 500 RPM. $SiO_2$ is gradually added to the solution after putting it on the burner with magnetic agitation for 10-15min. After the addition of $SiO_2$, this solution is left to heat at this continuous stirring for 24 hours. After 24 hours of mixing the solutions, the mixture was extracted and part of it is dried in a vacuum oven whereas the solution is put under the UV-Vis spectroscope.

## III. Results and Discussion

Polyvinylpyrrolidone (PVP) is a whitish powdered polymer that has a high propensity to make thin films. It is readily used as a protective colloid and a stabilizer for hydrophobic materials like Silver. [16] The silver colloid was prepared with the incorporation of PVP and Silver nitrate in ethylene glycol solvent with thermal heating and magnetic stirring. Its optical properties were studied by plotting a graph of wavelength vs absorbance as shown in figure 1.

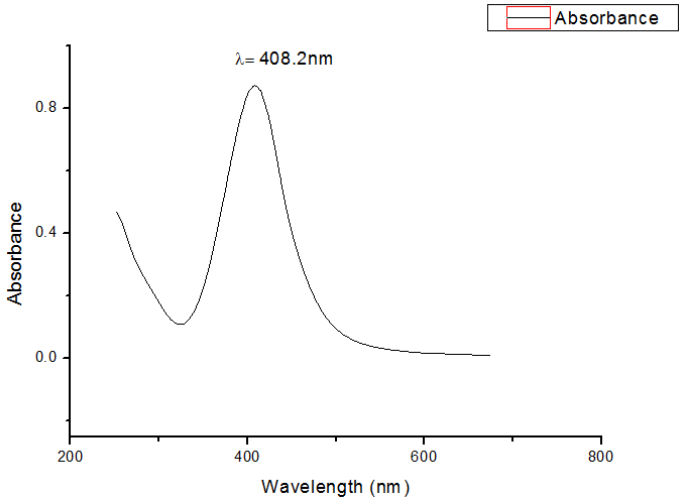


Fig. 1. UV-vis spectrum of PVP-silver nanoparticles prepared in ethylene glycol with the addition of silica.

A broad peak at 408.2 nm is observed in the UV-Vis spectrum which is the result of the surface plasmon resonance effect in the Silver-PVP-Silica-Ethylene Glycol colloid because of the formation of silver nanoparticles. Similar absorption peaks were detected for silver nanoparticles synthesized using chitosan (a kind of sugar obtained from the skeleton of crustaceans like shellfish) extract via green synthesis (Maragoni et al., 2012) or using various organic agents including ethylene glycol in the absorption region of 408-410 nm (Das et al., 2009). The size and shape dependence of LSPR (Localised Surface Plasmon Resonance) effect signifies that the broad absorption peak is the result of an uneven distribution of nanoparticles in terms of size and shape (Coronado et al., 2011).

The absorption peak or the region where surface plasmon resonance of spherical silver nanoparticles depends upon the refractive index of the medium, the size of the nanoparticle, and the nature of the capping agent on the nanoparticles. We can

notice that the absorption peak is observed at a significantly lower wavelength in the range of 310–320 nm by comparing the absorption spectrum of silver nanoparticles prepared by green synthesis.

This red-shift of the surface plasmon absorption in our (PVP-silicon- AgNPs) sample can be attributed to the presence of PVP as a reducing and a capping agent. The role of PVP as a reducing agent of Silver nitrate has been reported by Silvert, Herrera-Urbina et al. 1996 & Zheng et al. 2001.

Further, the band of the prepared specimen can be calculated based on the calculations of some specific parameters like wavelength, Absorbance, Energy, Molar absorptivity ~ a, and $(ahv)^{1/2}$ then a graph is plotted between E (at x-axis) and the value $(ahv)^{1/2}$ (at y-axis) which is given in Fig. 2.

The optical bandgap of the specimen is calculated to be 2.67eV which is lower than the normal bandgap observed for PVP polymer. Hence, it shows that the recombination of electron-hole is decreased with the addition of Silver which can be utilised to increase the efficiency of photochemical cells. This decrease in the optical band gap also signifies the increase in the metallic character of the specimen.

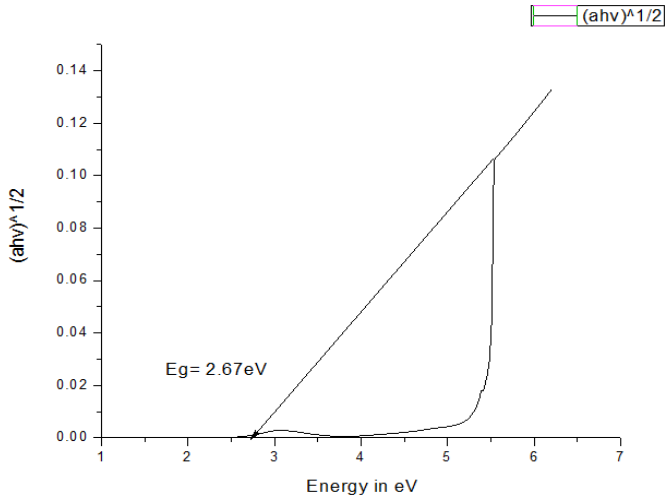


Fig. 2 Graph of the bandgap of PVP-AgNP-Silica using UV-Visible spectroscopy

XRD spectrum confirms the formation of crystalline metal nanoparticles with the presence of capping agents on the surface of nanoparticles (Cherukuri et al. 2022). X-ray diffraction is a very useful tool to study the characteristics, crystallization, and structure of the polymer nanostructure. Fig. 3 shows the peaks of XRD diffraction pattern at 2θ= 38.24°, 44.2°, 68.73° and 77.7° that correspond to cubic structure of miller indices (111), (200), (220), and (311) hkl values (JCPDS file no. 04-0783) respectively which represent the diffractions of fcc structure characteristic of metallic Silver.

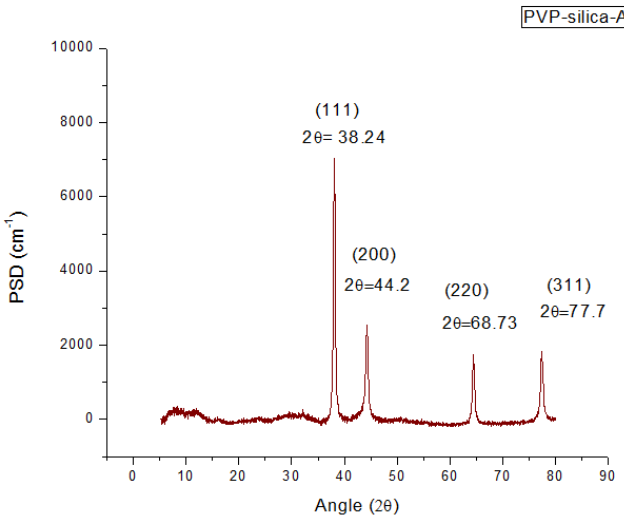


Fig. 3 XRD pattern for PVP augmented silver nanoparticles with silica in ethylene glycol giving peaks at 38.24 °, 44.2 °, 68.73 °, 77.7 ° (JCPDS file no. 04-0783).

The size of the crystallite can be calculated by using the Scherrer equation (Tawfiq 2021).

$D = 0.9 \lambda/\beta \cos\theta$

where, λ represents the wavelength of Cu X-ray that has the wavelength of 0.1541 nm, β represents FWHM (full width at half maximum) of the peak, θ represents the diffraction angle and D represents the crystallite diameter size.

Results of the sample characterised through XRD diffraction pattern to measure the size of the prepared nanoparticles.

Table 1.

| θ (Angle) in degrees | Cosθ | β (FWHM) in radians | Λ (wavelength) in nm | D size of crystallite in nm |
|---|---|---|---|---|
| 19.12 | 0.945 | 0.0068296820423719 | 0.1541 | 21.49 |

After calculation of FWHM of the curve by origin software, the mean size of nanoparticles is obtained to be around 21.49 nm which is quite similar to the size of nanoparticles observed through TEM as we shall see further in this paper.

Similarly, d spacing between these planes can also be calculated by using Bragg's law as given in Table 2.

$2d \sin\theta = n\lambda$ (Beiser, 1979)

At n=1

Results showing the d spacing of the crystal

Table 2.

| θ (Angle) | Sin θ | λ (wavelength) in nm | d (spacing) in nm |
|---|---|---|---|
| 19.12 | 0.327 | 0.1541 | 0.23 |

TEM study is particularly useful in confirming the production of nanoparticles. Fig. 4 shows us the size, shape, and extent of dispersion of the manufactured PVP-AgNP-Silica nanoparticles.

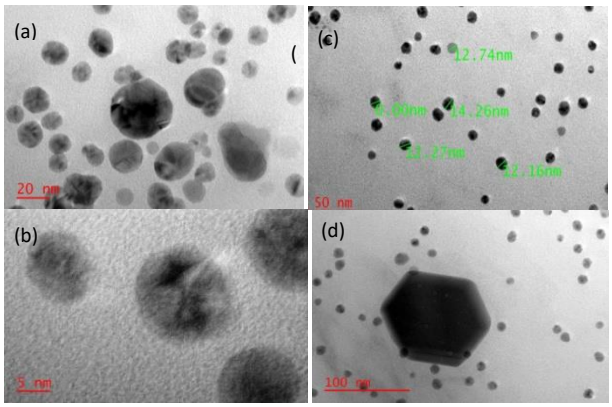


Fig. 4 TEM images of AgNPs formed in the PVP blend with silica dispersed in ethylene glycol at (a) scale of 20nm (b) scale of 5nm (c) 50nm (d) 100nm

The particles are well distributed in the solvent and well mixed in with the Polymer matrix. We can see in the images that the nanoparticles are around the 10-20 nm range. They are spherical and clearly visible. The selected SAED pattern of the sample [fig.5] & Table 3 shows the crystalline nature of the nanoparticles and with Image J software, we can see the crystal structure of (111), (200), (220), (311) similar to the structure observed in XRD graph earlier. It confirms the coating of capping polymer on the nanoparticles.

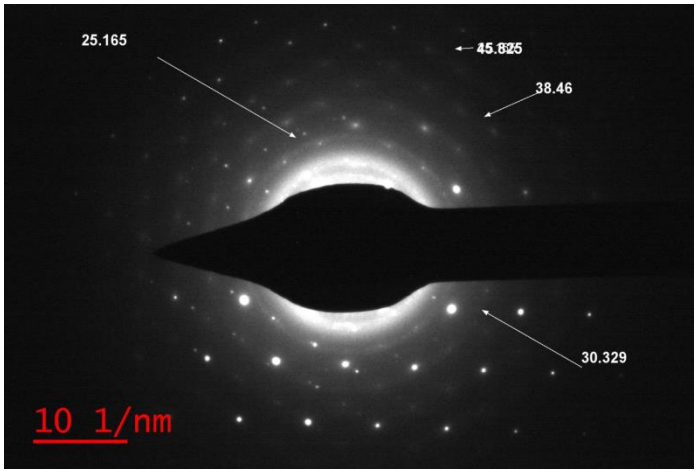


Fig. 5 SAED pattern of PVP-AgNPs-Silica with the radial distance from the centre in the reciprocal space with the unit $nm^{-1}$.

SAED pattern studied through ImageJ software[22]

Table 3.

| S.No. | 1/2r ($nm^{-1}$) | 1/r($nm^{-1}$) | r ($nm^{-1}$) | d-spacing (Å) | hkl value |
|---|---|---|---|---|---|
| 1 | 25.165 | 12.5825 | 0.079475 | 0.794755 | (111) |
| 2 | 30.329 | 15.1645 | 0.065943 | 0.659435 | (200) |
| 3 | 38.463 | 19.2315 | 0.051998 | 0.51998 | (220) |
| 4 | 45.825 | 22.9125 | 0.043644 | 0.436443 | (311) |

## CONCLUSION

AgNps (Silver nanoparticles) were successfully prepared using PVP as a reducing agent and silica as a coating agent in ethylene glycol as a solvent. The indication of the formation of silver nanoparticles is given by the UV-Vis spectroscopy where the band-gap of the specimen was calculated at about 2.67eV. As per the observation using TEM, the size of the nanoparticles was found to be in the range of 10-15nm. Most of the nanoparticles that were captured in TEM were 12-15nm in diameter and the confirmation of their crystalline structure was achieved by the SAED pattern. In comparison, the calculated size of nanoparticles was 21.49nm from XRD data. We also calculated the d-spacing of the crystalline nanoparticles at 0.23nm. These data of Polymer augmented silver nanoparticles are compared to silver nanoparticles prepared by the green method and we observe that capping agents of nanoparticles differ as we change the reducing agent in the reaction. Hence we can control the specific characteristics of our nanoparticles by controlling the kind of capping agent and the kind of preparation technique we are employing. These nanoparticles should prove to be beneficial in photoelectric devices such as Solar collectors as they have great electrical conductivity and capacitance due to their metallic properties as well as the optimal tunability of nanoparticles.

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