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# EFFECT OF ULTRAVIOLET IRRADIATION ON THE OPTICAL AND STRUCTURAL CHARACTERISTICS OF IN-SITU PREPARED PVP-Ag NANOCOMPOSITES

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Silver nanoparticles dispersed Polyvinylpyrrolidone (PVP) nanocomposites were prepared by in-situ chemical reduction of silver nitrate ($AgNO_3$) from an ethanolic solution of PVP. The prepared nanocomposite films were subjected to ultraviolet (UV) irradiation at room temperature for different times. The effect of UV-irradiation has been studied through electron microscopy, optical spectroscopy and FTIR spectroscopy. The appearance of Surface Plasmon Resonance (SPR) band at ~ 420 nm in the UV-Visible absorption spectra indicates the presence of the silver nanoparticles. The optical band gap values were found to reduce from 4.90 eV in pure PVP to 4.11 eV for PVP-Ag nanocomposite prior to irradiation. This value is further reduced to 3.55 eV after UV irradiation for 180 minutes. Such a reduction in optical band gap may be linked to the increased conjugation in PVP matrix as an effect of embedding of silver nanoparticles followed by UV-irradiation, as observed through FTIR analysis.

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*Keywords:* Ag nanoparticles, UV irradiation, Optical band gap, Urbach's energy

## 1. Introduction

The polymers embedded with metal nanoparticles are of current research interest because of their some novel properties generated from quantum size effect of the embedded metal nanoparticles. Polymer metal nanocomposites with varying nano-particle size, shape and concentration are significantly used in many potential optical, electrical and optoelectronic applications [1-3]. The role of Polyvinylpyrrolidone (PVP), with monomer structure shown in figure 1, as a host matrix is important because of its excellence as a good reducing and capping agent for metal and semiconductor nanoparticles [4-5]. Further, it is well quoted in the literature [6-12] that size, shape and dispersity of the embedded particles can be tuned through gamma, ultraviolet and charged particle irradiation.

In the present work, after synthesizing PVP-Ag nanocomposites through in-situ chemical reduction method, a systematic study of the effect of ultraviolet irradiation on the optical and structural properties of this nanocomposite has been carried out. The induced optical and structural changes have been investigated using UV-Visible and Fourier Transform Infrared (FTIR) spectroscopy.

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## 2. Experimental

### 2.1. Synthesis

After procuring PVP (MW: 40,000 amu) from HiMedia Laboratories Pvt. Ltd. (INDIA), Silver nitrate ($AgNO_3$) from Loba Chemical Pvt. Ltd. (INDIA) and ethanol from Changshu Yangyuan Chemical (CHINA), the synthesis of PVP-Ag nanocomposites were carried out. For this purpose, PVP (1gm) was dissolved in ethanol (20 ml) followed by addition of $AgNO_3$ (50 mg) under continuous stirring for half an hour. This resulted in the change of the colour of the solution from transparent to light yellow. This solution was then poured into plastic petri-dishes for sufficient time (~ 24 hrs) to convert it into film. Afterwards, the prepared films were subjected to ultraviolet irradiation at room temperature for different times with maximum upto 180 minutes. For this purpose, Handheld UV lamp (UVGL-58) was used with 254 nm wavelength and at intensity of 58000 $\mu J/cm^2$ per minute.

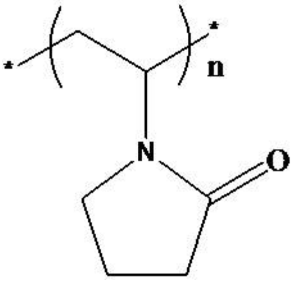

*Fig. 1 Monomer structure of PVP.*

### 2.2 Characterization

Transmission electron microscopy (TEM) was performed using Hitachi “H-7500” electron microscope operated at 80kV by re-dissolving the small piece of composite film in ethanol and dropping it onto carbon coated gold grid. After evaporation of the ethanol, the grid was inserted into the TEM.

For the optical characterization of the casted films, Shimadzu Double Beam Double Monochromator, UV-Visible Spectrophotometer (UV-2550) with the Integrating Sphere Assembly ISR-240A in the wavelength range 190 – 900 nm with a resolution of 0.5 nm was used. The FTIR analysis of the films was carried out using the Perkin Elmer RX1 FTIR spectrophotometer.

## 3. Results and discussion

### 3.1. Transmission electron microscopy (TEM)

According to the procedure detailed above, composite films of PVP-Ag were prepared and then irradiated to UV radiation for different times. These composite films were re-dissolved in ethanol to record the TEM images (Figure 2a and 2b). It is clearly depicted from TEM micrographs that before UV-exposure, Ag nanoparticles dispersed in PVP matrix are of low concentration with almost spherical shape and about 3-5 nm in size (figure 2a). After exposure to 180 min, concentrations of embedded nanoparticles increased and are uniformly distributed within the PVP matrix.

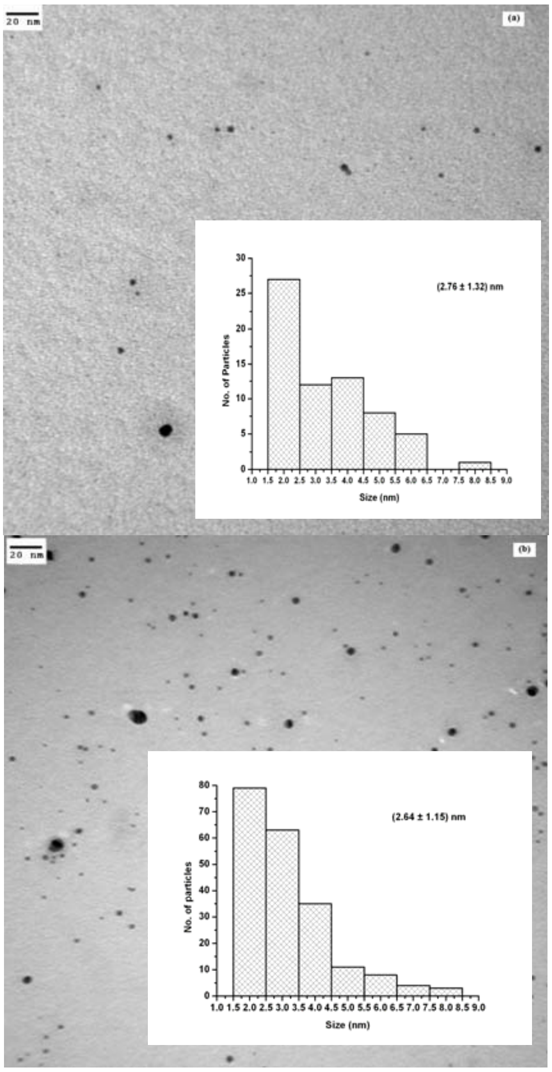

*Fig. 2 Transmission electron micrographs with particle size distribution of embedded Ag nanoparticles in PVP (a) before exposure to UV radiation; (b) after exposure to UV radiation for 180 minutes.*

### *3.2. Absorption spectroscopy*

Fig. 3 (curves ‘a’ to ‘e’) represents the UV-Visible absorption spectra for pure PVP and PVP-Ag composites exposed to ultraviolet radiations for different times varying from 0 to 180 minutes. It is clearly observable from curve ‘a’ in this figure that there is no absorption in visible region for pure PVP sample. However, a small absorption band at ~ 420 nm starts appearing in the absorption spectra of the prepared composite film (curve ‘b’). This small absorption band starts growing and red shifted continuously (curves ‘c’ to ‘e’) with increase in exposure time to UV radiations. This absorption band in the visible region (curves ‘b’ to ‘e’) corresponds to the characteristic SPR bands for polymer embedded Ag nanoparticles [13]. This observation clearly indicates the formation of Ag nanoparticles in the PVP matrix with their increasing concentration as a result of increasing dose to UV radiation. The formation of Ag nanoparticles prior to the UV irradiation is due to the reducing action of PVP itself, converting silver ions into the metallic silver and further enhanced through the photo-reduction process of remaining silver ions as a result of UV irradiation.

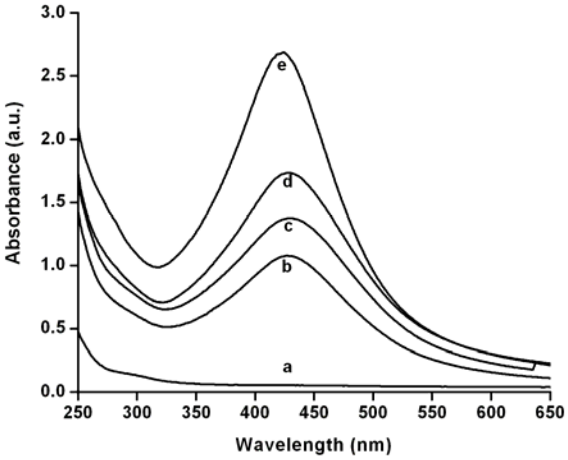

*Fig. 3 UV-Visible absorption spectra for (a) pure PVP and PVP-Ag nanocomposites (b) without exposure; with exposure to ultraviolet radiations for (c) 30; (d) 90 and (e) 180 minutes.*

### 3.2.1 Determination of optical band gap

The observed shift in the fundamental absorption edge of UV-Visible spectra can be correlated with the optical band gap $E_g$ by Tauc's expression [14]

$$(\alpha h\nu)^{1/2} = B\,(h\nu - E_g) \tag{1}$$

where, $\alpha$ is the absorption coefficient corresponding to the fundamental absorption edge, $h\nu$ is the photon energy and $B$ is the constant of proportionality. The values of optical band gap $E_g$ can be deduced from the intercept of the linear fitted lines in the plots of *sqrt (αhν)* versus *hν*, as shown in Fig. 4.

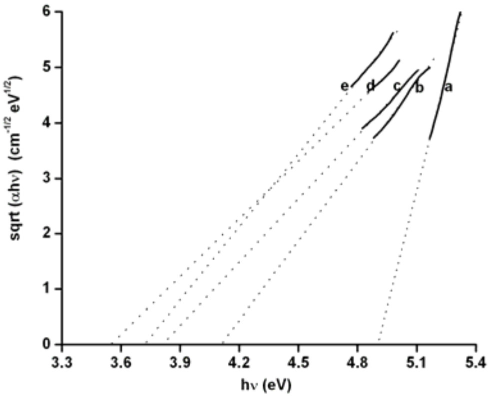

*Fig. 4 Plots of sqrt (αhν) versus hν for (a) pure PVP and PVP-Ag nanocomposites (b) without exposure; with exposure to ultraviolet radiations for (c) 30; (d) 90 and (e) 180 minutes.*

The values of optical band gap so determined are listed in Table 1. It is clear from the table that the value of $E_g$ decreases from 4.90 eV (pure PVP) to 4.11 eV for PVP-Ag nanocomposite (unexposed). Such a decrease in the value of $E_g$ can be attributed to be due to the formation of bonds between silver nanoparticles and PVP molecules, which form the trap levels between the HOMO and LUMO energy states, making the lower energy transitions feasible and results in the reduction of optical band gap. Furthermore, the value of $E_g$ for PVP-Ag nanocomposites decrease to 3.55 eV as the irradiation time increases to 180 minutes. This decrease in optical band gap after ultraviolet irradiation can be correlated to the enhanced lower energy optical transitions through the traps owing to the increase in the concentration of embedded silver nanoparticles.

Further, the values of the optical band gap, $E_g$, can be correlated to the number of carbon atoms per molecule through the expression [15]:

$$E_g = 34.3/\sqrt{M} \tag{2}$$

where, $M$ is the number of carbon atoms in carbonaceous cluster. The calculated values of $M$ for PVP and its composites are tabulated in Table 1. The value of M for PVP, which is around 49, increases to 70 in PVP-Ag nanocomposite (unexposed). Such an increase can be correlated to the increased conjugation in monomer units [15] of PVP matrix after the embedding of silver nanoparticles. The number of carbon atoms taking part in carbonaceous cluster in PVP-Ag nanocomposite further rises to 94 after the UV irradiation for 180 minutes, which may be attributed to the supplement increased in complexity of conjugation in monomer units of PVP as a result of ultraviolet irradiation.

*Table 1. Values of optical band gap ($E_g$), Urbach's energy ($E_u$) and number of carbon atoms (M) per carbonaceous cluster for pure PVP and PVP-Ag nanocomposite films without & with exposure to ultraviolet radiation for different times.*

| Sample | Optical band gap $E_g$ (eV) | Urbach's energy $E_u$ (eV) | M |
|---|---|---|---|
| Pure PVP | 4.90 ± 0.02 | 0.39 ± 0.02 | ~ 49 |
| PVP-Ag nanocomposite (30 min) | 3.81 ± 0.02 | 0.92 ± 0.01 | ~ 81 |
| PVP-Ag nanocomposite (90 min) | 3.72 ± 0.03 | 1.11 ± 0.02 | ~ 85 |
| PVP-Ag nanocomposite (180 min) | 3.55 ± 0.02 | 1.25 ± 0.01 | ~ 94 |

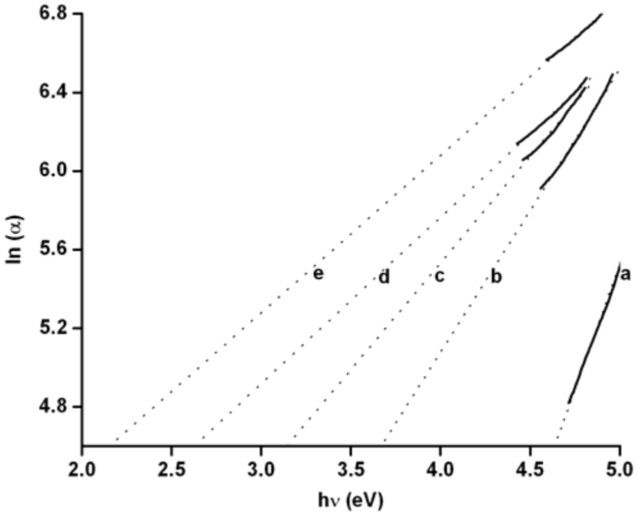

*Fig. 5 Plots of ln (α) versus hν for (a) pure PVP and PVP-Ag nanocomposites (b) without exposure; with exposure to ultraviolet radiations for (c) 30; (d) 90 and (e) 180 minutes.*

### 3.2.2 Determination of Urbach's energy

The Urbach's energy corresponds to the width of the tail of localised states within the optical band gap. It is linked to the absorption coefficient in the lower energy region of fundamental edge and can be described by the relation [16]:

$$\alpha(\nu) = \alpha_0 \exp\left[h\nu/E_u\right] \tag{3}$$

where, $\alpha_0$ is constant and $E_u$ is the Urbach's energy. From equation (3), it is obvious that the plot of $\ln(\alpha)$ versus $h\nu$ should follow the linear behaviour. Figure 5 presents such plots for pure PVP and PVP-Ag nanocomposite films exposed to UV radiations for different times. The determined values of Urbach's energy are listed in Table 1. It is evident from this table that $E_u$ increases from 0.39 eV (pure PVP) to 0.69 eV in PVP-Ag nanocomposite without irradiation to UV radiation. This value gradually increases with increasing exposure time to UV radiations and approaches to 1.25 eV after an exposure time of 180 minutes. The linkage between the optical band gap values and Urbach's energy is shown in figure 6. It is apparent from the figure that the increase in Urbach's energy corresponds to the decrease in optical band gap. Such an observation supports the increase in the number of traps as a result of increasing concentration of embedded silver nanoparticles with increasing exposure time to ultraviolet irradiation, which results in the lower energy transitions feasible and thus, reducing the values of optical band gap.

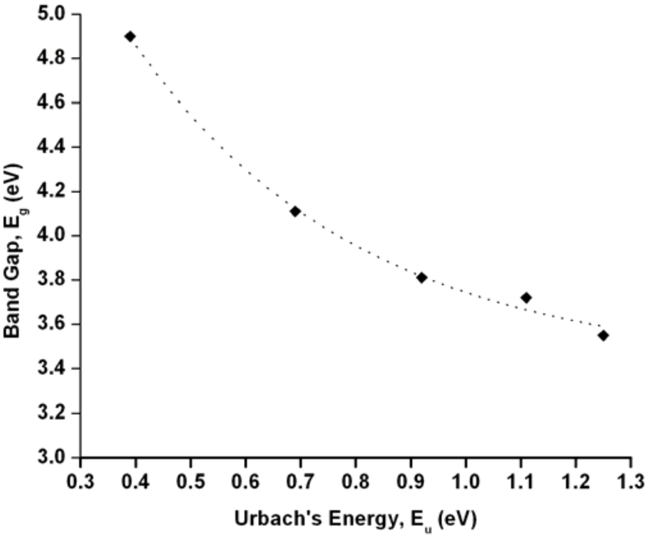

*Fig. 6 Variation of the Urbach's energy ($E_u$) versus Optical band gap ($E_g$) values.*

### *3.3. FTIR Analysis*

As discussed above, the optical behavior of PVP matrix changes on embedding the silver nanoparticles followed by ultraviolet irradiation and an attempt has been made to correlate such changes with the induced structural changes. Figure 7 (curves 'a' to 'c') represents the FTIR spectra for pure PVP, PVP-Ag nanocomposite (without UV exposure) and PVP–Ag nanocomposite (with 180 minutes UV exposure) films.

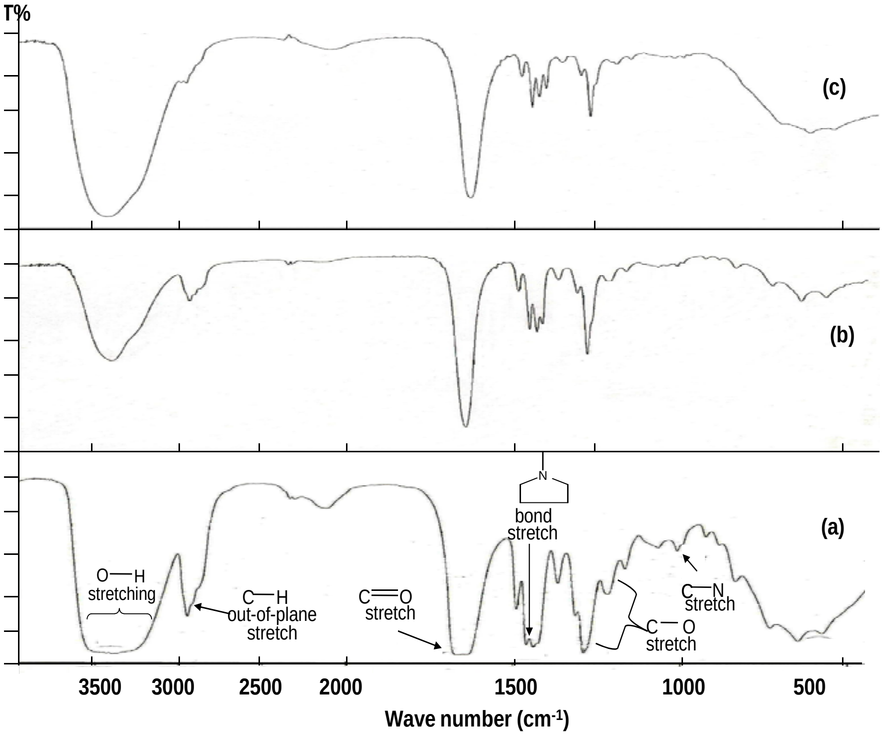

*Fig. 7 FTIR spectrum for (a) Pure PVP; PVP-Ag nanocomposite (b) without exposure and (c) for 180 minutes exposure to ultraviolet radiation.*

The FTIR spectrum for pure PVP (curve 'a') clearly indicates that the observed absorption peaks correspond to the characteristic chemical bonds present in PVP [17]. The peak at 1019 $cm^{-1}$ (curve 'a') represents the functional unit C-N present in PVP, shifts to 1035 $cm^{-1}$ (curve 'b') after embedding of silver nanoparticles. After UV exposure for 180 minutes, this peak again shifts to 1049 $cm^{-1}$ (curve 'c'). The peak shifting corresponding to C-N bond towards higher wavenumber may be attributed due to chemical coordination of Ag nanoparticles with C-N bond, which increases with increase in exposure to ultraviolet radiation. Another peak at 1665 $cm^{-1}$ in pure PVP (curve 'a') due to C=O bonds becomes narrower and shifts to 1657 $cm^{-1}$ (curve 'b') after the formation of Ag nanoparticles within PVP matrix, which further shifts to 1648 $cm^{-1}$ (curve 'c') after UV exposure for 180 minutes. Such a decrease in wavenumber ($cm^{-1}$) of C=O bond may occur due to the bond weakening as a result of back bonding via partial donation of lone pair electrons from oxygen in PVP to vacant orbital of Ag. No appreciable change has been observed for other peaks marked in figure 7 (curve 'a'). This confirms the coordination and conjugation of embedded Ag nanoparticles with N and O atoms of C-N and C=O bonds, respectively of this polymer, which results in the observed changes in optical behavior of host PVP matrix.

## 4. Conclusions

Poly (vinylpyrrolidone) capped silver nanoparticles were prepared by in-situ chemical reduction method. The concentration of embedded silver nanoparticles has been found to increase with increased exposure time to ultraviolet radiations, as clearly depicted from TEM and UV-Visible absorption spectroscopy. Change in optical band gap values and Urbach's energy values on embedding silver nanoparticles followed by ultraviolet irradiation have been found as an outcome of formation of conjugated structure between functional groups of PVP and embedded silver nanoparticles, as confirmed through FTIR analysis.

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