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Enhanced optical properties, wettability and antibacterial activity of PVP doped Au for optical applications

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A casting technique is used to create films of polyvinyl pyrrolidone (PVP) that contained different amounts of gold nanoparticles (Au 0.2, 0.4, 0.6, 0.8, and 1%). Fourier transform infrared (FT-IR) and Ultraviolet/Visible (UV/Vis.) including the optical energy gap (Eg). Using a contact angle system, the sessile drop method is utilized to measure the contact angle and antibacterial activity. It is observed in the UV spectra that a single-bond in the PVP backbone caused an n-π* transition and spectral peak is observed at a wavelength of 531 nm, which is believed to be caused by the surface Plasmon resonance of gold nanoparticles and appear two energy gaps decreased between (2.2-2 ev) and (3.1-2.9 ev) respectively that well-suited for utilization in electrochemical operations, such as polymer electrolytes and optoelectronic devices. The contact angle results showed an increase the contact angle between (43.85°- 55.98°) made this nanocomposite hydrophobic in surface. The antibacterial activity indicated that the inhibition zone measured approximately 12-16 mm and 8-10 mm against Escherichia coli and Staphylococcus aureus, respectively.

Keywords: PVP; Optical; Contact angle; Antibacterial activity.

1. INTRODUCTION

PVP is widely chosen as a polymeric material for encapsulating silver nanoparticles due to its non-toxic, biodegradable, biocompatible, and temperature-resistant properties [1]. In recent years, there has been a significant amount of interest in the design of metal nanoparticles/polymer composites. This is due to their wide range of applications, such as catalysts and in the field of biomedicine [2]. Gold nanoparticles are highly popular in various research fields due to their biocompatibility, lack of toxicity, and ease of production. In recent years, there has been a notable increase in the use of gold nanoparticles in various biological applications. Nanoparticles have been utilized in medications, photo thermal therapies, and medical diagnostics, often in conjunction with other forms of nanoparticles [3]. Adding nano-fillers of various sizes, types, and quantities to the host polymer often results in improved properties in polymer nanocomposites. This is because it combines the advantages of both the polymer and the nano-filler material [4]. Composite materials made from polymer/nanoclay are widely used in various manufacturing applications. These include construction, where they are used for building sections and structural panels, as well as in food and textile packaging. In the automotive industry, they are used for gasoline tanks, bumpers, and interior and exterior panels. Additionally, they find applications in pharmaceuticals, where they are used for flame agent panels and high-performance components, as well as in chemical processes [5]. A composite is a material composed of two or more substances, typically metals, ceramics, or polymers. The objective of composite synthesis is to generate a material that possesses characteristics that are not typically present in its individual components [6]. Understanding wettability involves examining how liquids interact with solid surfaces, with the contact angle being a commonly used measurement for this phenomenon [7]. When the energy of a solid surface is reduced, it results in higher contact angles with a specific liquid. Surfaces with a contact angle greater than 90 °C are considered hydrophobic, while surfaces with a contact angle less than 90 °C are considered hydrophilic [8]. Farah J. Kadhum et al. [9] variation of boundaries has been demonstrated. First, the plasmonic activity of the change of gold thickness (Au) and polyvinyl alcohol (PVA) is evaluated under different wavelengths from UV to near infrared. The goal of paper used Noble metal nanoparticles, whose average size falls in the range from some nanometers to micrometers, are considered, due their unusual optical properties, their size-dependent electrochemistry and their chemical stability, one of the leading materials in highly active fields such as catalysis, optoelectronics and biosensors, including drug and gene delivery and cancer treatment.

2. EXPERIMENTAL WORK

2.1 Materials

PVP (MW ≈ 72,000 g/mol, SICO Research Laboratories Pvt. Ltd, Mumbai, India) is used as basic polymeric materials and Sigma-Aldrich supplied Au with particle size that Synthesis the Gold Nanoparticles by Chemical Procedure known as Turkevich method. This method is simple and produced a spherical gold nanoparticle, the outline in the flow chart below summarized the procedure of synthesizing the gold nanoparticles. Prepare 50 ml of Chloroauric acid solution of molarity 0.177 mM. Withdraw 150 µl from 50 ml of deionized water and add 150 µl of Chloroauric acid stock solution instead of, or in another word, getting a different concentration of Chloroauric acid solution from Chloroauric acid stock solution, then heat the Chloroauric acid solution untill it boiled, stir the solution and add 500µl from Trisodium Citrate Dihydrate stock solution at once and still stirring, the solution changes its color until it becomes red-wine, after that stop heating and stirring and cool the solution.

Yellow ⟹ clear white ⟹ light gray ⟹ dark gray ⟹ dark violet ⟹ red-wine

After cooling the solution of gold nanoparticles, wash the solution two times in centrifuge at 13000 rpm about 15min. to get residual gold nanoparticles. In this step the gold nanoparticles can be used by adding deionized water for later use. TEM on left and SEM on right shows the size of gold nanoparticles (Fig1 a, b).

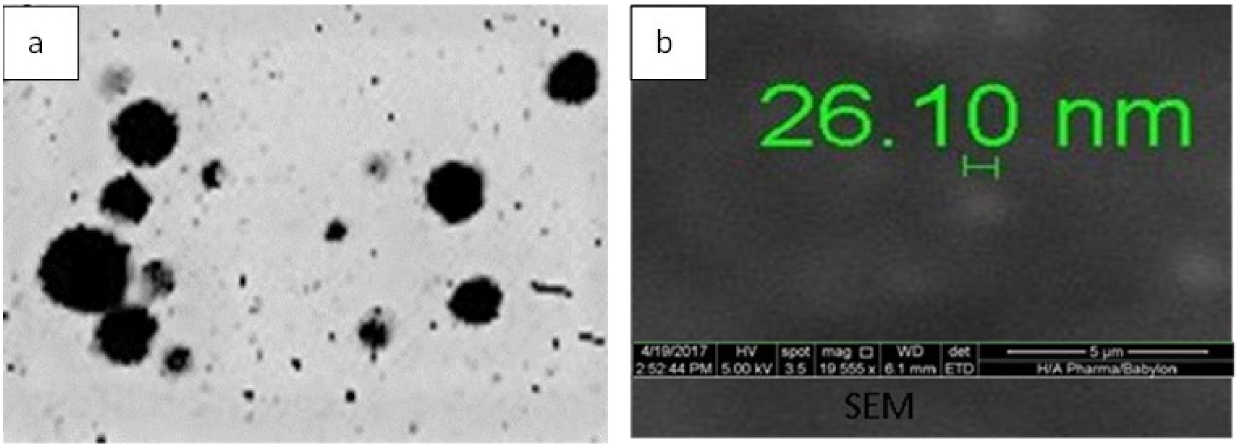

Figure 1 (a) TEM , (b) SEM.

2.2 PROCEDURE

2.2.1 Preparation of PVP and PVP/Au nanocomposite films

The polymer sample and its nanocomposite samples are prepared using the solution casting method. With continuous stirring at room temperature, a 3 gm quantity of PVP is dissolved in distilled water until complete dissolution occurred. Various amounts of Au (0.2, 0.4, 0.6, 0.8, and 1 wt.%) are introduced into the polymeric solution while stirring continuously for 24 hours. The solutions are poured onto polypropylene plates and underwent a drying process in an oven for 4 days at a temperature of 40 ◦C, allowing the solvent to gradually evaporate. After the drying process, the polymer films that are removed from the dishes are carefully placed in desiccators with a strong vacuum to ensure no moisture would be absorbed. The thickness of the prepared samples fell within the range of 0.03–0.05 *mm.*

2.2.2 Measurements

The films that are created are analyzed by obtaining FT-IR absorption spectra in the spectral range of 4000-400 cm−1 at room temperature using a single-beam Fourier transform-infrared spectrometer (Nicolet iS10, USA). An instrument for measuring contact angle is utilised to assess the wettability of the membrane. Deionized water is dropped onto the membrane at various locations, and the measurements are taken five times. The average value is then calculated. Testing for antimicrobial activity against E. coli and Staphylococcus aureus is conducted using an agar disc diffusion assay. For preservation, the bacteria culture is carefully stored in TSB broth with a 30% v/v glycerol solution at a frigid temperature of -80°C. Prior to use, the culture underwent two rounds of sub-culturing in broth. 0.1 mL samples of E. coli and Staphylococcus aureus suspensions, with a concentration of approximately 106–107 CFU mL-1, are evenly spread on an agar surface in a Petri dish. Three 6-millimeter film discs are carefully placed on top of the agar-filled Petri plate. The presence of a clearly defined area of inhibition surrounding the test films is utilized to ascertain whether the films demonstrated antibacterial activity. In order to ensure accuracy, the exam is conducted on three separate occasions. The spectrophotometer (V-570 UV/VIS/NIR, JASCO, Japan) is used to measure the absorption spectra of ultraviolet light and visible light. The measurements are taken within the wavelength range of (200-1000 nm).

3. RESULTS AND DISCUSSION

3.1 FTIR Analysis

The FTIR spectra of nanocomposites containing varying concentrations of Au (0.2, 0.4, 0.6, 0.8, and 1 wt.%) are shown in Figure 2. In this figure, the symbols A, B, and C represent different compositions: pure PVP, PVP with 0.2% Au, and PVP with 1% wt., respectively. A wide band at 3565 cm-1 is observed in all specimens of nanocomposites due to the presence of OH groups in the polymer matrix chain. The band at 2922 cm-1 suggests an asymmetric stretching mode of the CH2 group. The band at 1650 cm-1 corresponds to the C=O symmetric stretching, while the 1400 cm-1 band represents the CH2 scissoring vibrations. The spectra displayed distinct bands corresponding to the stretching and bending vibrations of the functional groups present in the prepared films. Which align with [10]. The presence of double bond segments in the structure of the studied materials provides optimal locations for the formation of polarons and/or bipolarons [11]. Fig. 2 b and c display the FT-IR experimental transmittance spectra of the pure polymer and other samples with varying concentrations of added Au. In addition, the spectra revealed a novel band at 1650 cm-1, indicating the formation of a complex between the Au nanoparticles and /PVP. There is a noticeable change in the peak shape at around 1300 cm^{-1} (C-O-C stretching) as the amount of Au nanoparticles increases. The peak becomes more distinct and defined.

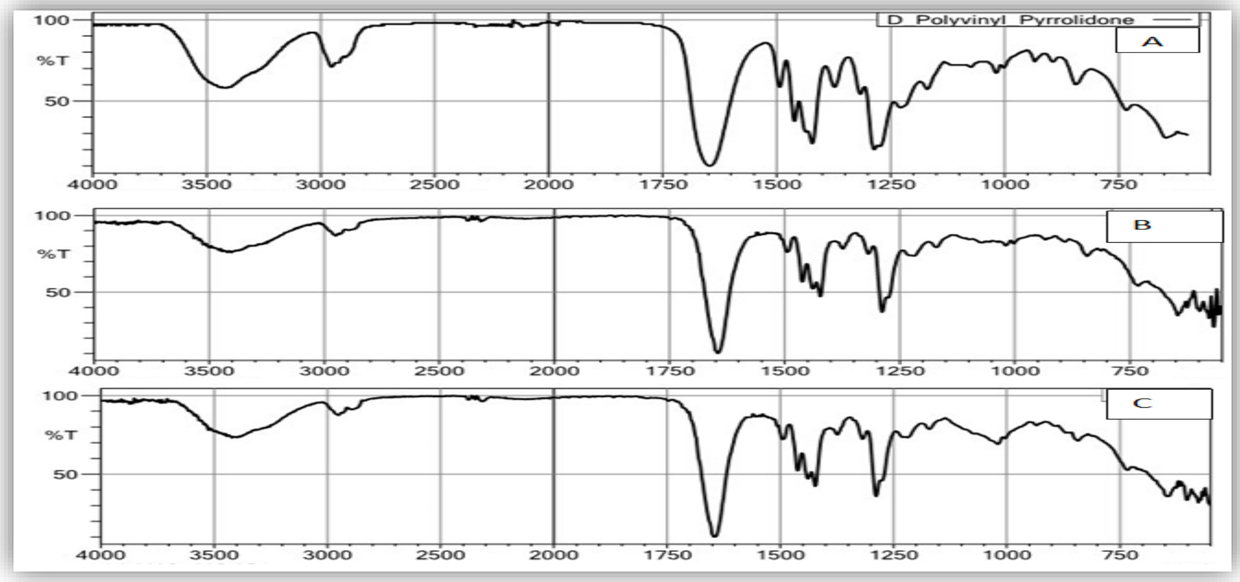

Figure 2 FTIR of PVP and PVP / Au nano composites.

3.2 Contact angle

The wettability of reinforcing materials significantly affects their surface characteristics. One of the basic equations which describes the behavior of a liquid phase in contact with a solid surface. Determining the wettability of modified materials can be effectively done by using the water contact angle approach and know that surface become hydrophobic or hydrophilic. Imagine that contact angle values below 90° are connected to excellent wettability, while those above 90° are linked to subpar wettability. Understanding the contact angle provides insights into the water-loving and water-repelling properties of polymer and nano composites. Performing the contact angle test on all samples of PVP and PVP/Au is crucial in assessing the surface's wettability. The contact angle results for PVP and PVP/Au nanocomposites can be observed in Figure 3 and Table 1. The figure clearly shows that as the weight ratio of Au increases, the contact angle values of the nanocomposites also increase because that nature of gold is hydrophobic and the contact angle of water on gold at room temperature is about 62◦[11] and the contact angle values are given for Au, Ag, Cu, and Zn, on graphite , vitreous silica, .These types of ceramic materials, prevalently covalent, have a close electronic configuration with strong inter-atomic bonds, and are therefore chosen for evaluation as crucible materials for melting gold alloys. [12] . The wetting behavior of water on metal surfaces is important for a wide range of industries, for example, in the metallurgical industry during the preparation of metallic nanoparticles or electrochemical or electroless coating preparation from aqueous solutions, as well as in the construction industry (e.g., self-cleaning metal surfaces).

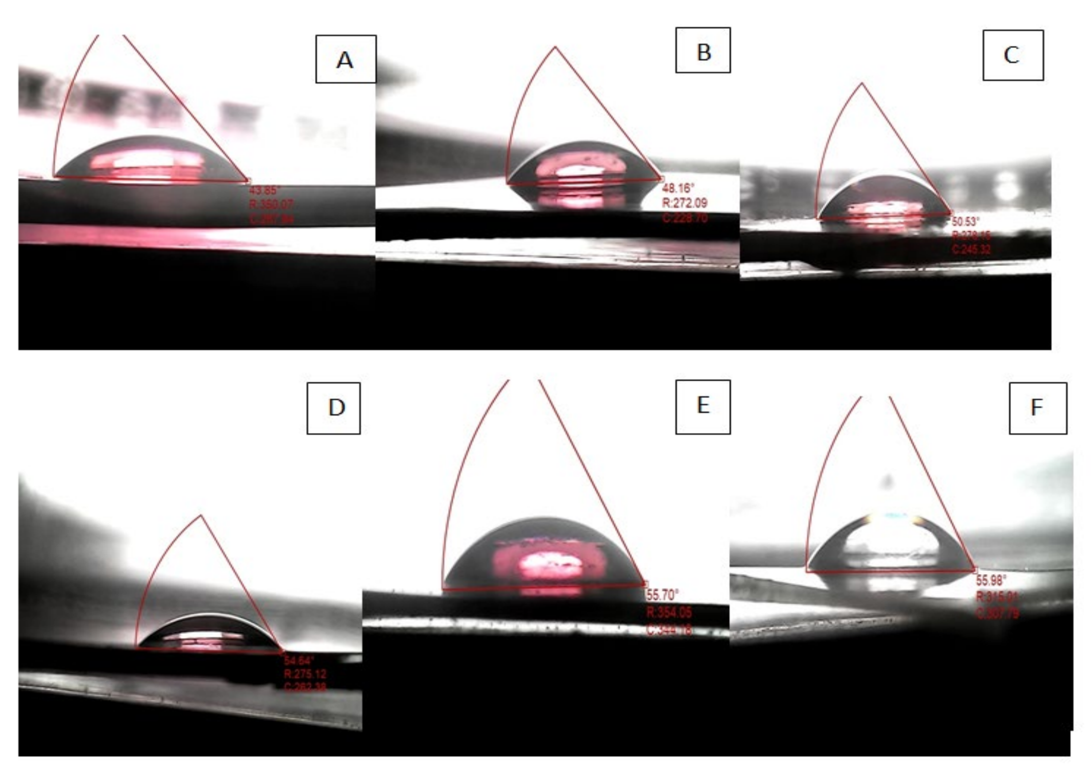

Figure 3 Contact angle values of PVP and PVP/Au A. PVP B. 0.2% Au C.0.4%Au D. 0.6%Au E. 0.8% Au F. 1% Au.

Table 1 contact angle values of PVP /Au nanocomposites.

Samples	Contact angle (°)
PVP	43.85
PVP / 0.2 % Au	48.16
PVP/ 0.4% Au	50.53
PVP/0.6% Au	54.54
PVP/ 0.8% Au	55.70
PVP/ 1% Au	55.98

3.3 Antibacterial activity

Testing the antibacterial activity of Polymer PVP and PVP/Au is done using the agar-well diffusion method, a commonly used technique for evaluating the effectiveness of plant or microbial extracts. Figure 4 showcases the results of evaluating the zones of inhibition for the PVP and PVP/Au samples against both Gram-positive and Gram-negative bacteria, specifically E. coli and S. aureus. These bacteria are selected for their impact on food, distinguishing them from other options. Figure 4 and Table 2 show that pure PVP, E. coli, and S. aureus have inhibitory zones on both pure PVP and PVP/Au samples.

However, only the PVP/Au sample exhibits an inhibitory zone for E. coli, while S. aureus does not. It is worth mentioning that PVP and PVP/Au possess antibacterial properties due to the unique characteristics of PVP and Au nanoparticles, which enable them to effectively eliminate bacteria [13]. It is widely known that when an antimicrobial material comes into contact with a bacterial strain, it creates a distinct area around the antibacterial material known as the inhibition zone. One of the main properties that allows these particles to be employed in different biomedical applications is the scattering and absorption of light at resonant wavelengths. This phenomenon is known as due to the excitation of plasmon oscillations (Surface Plasmon Resonance, SPR). The resonant wavelength depends on the size, shape and geometry of the nanostructures, thus providing important information and making them the model system of choice in a wide range of biomedical applications depending in absorption light [14].

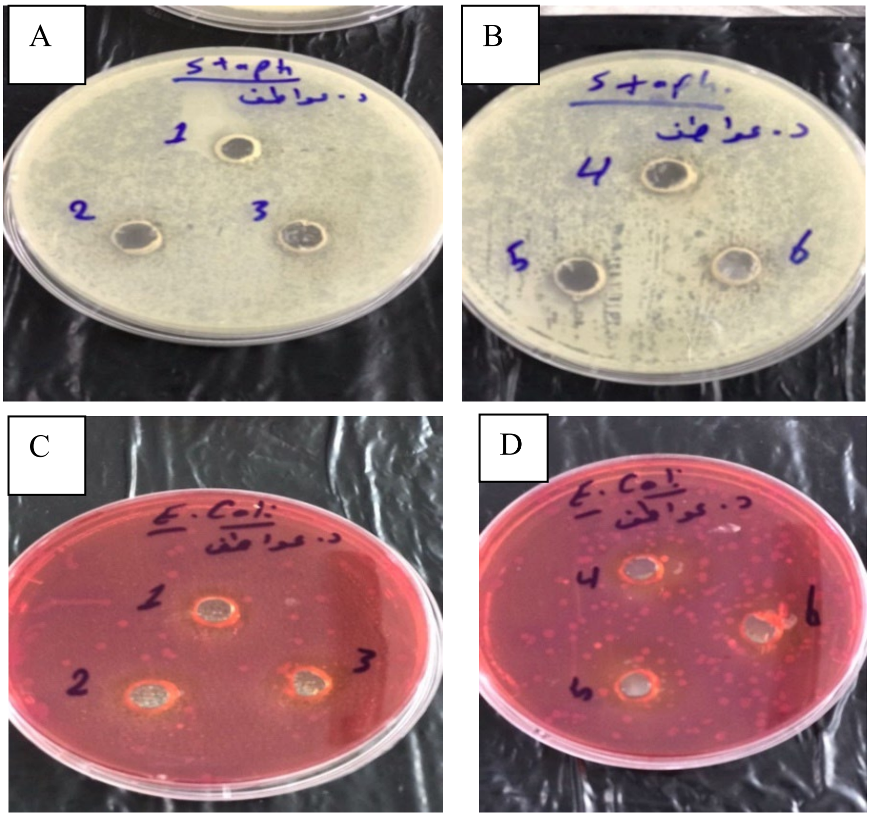

Figure 4 (A, B, C and D) show antibacterial activity of PVP and PVP/Au nanocomposites.

Table 2 The inhibition zone values.

Samples	E.coli	S. aureus
1 PVP	12	10
2 (PVP / 0.2%Au)	14	8
3 (PVP / 0.4%Au)	16	10
4 (PVP / 0.6%Au)	14	8
5 (PVP / 0.8%Au)	14	8
6 (PVP / 1%Au)	12	8

3.4 Ultraviolet and visible analysis

Figure 5 displays the absorption spectra of the PVP/Au nanocomposites, covering a range of 200-1000 nm. In this configuration, the absorption edge of the spectra of the PVP films containing Au shifts towards longer wavelengths when the concentration of Au NPs in the pure PVP solution increases. The nanocomposite samples exhibit a red shift in the absorption edge, suggesting that the optical energy gap of PVP may have been altered as a result of a complexation between the Au and the polymeric matrix. The presence of a peak at the wavelength of maximum absorption (max = 531 nm) in the visible area is a clear indication of the primary characteristic associated with the creation of gold nanoparticles (Au) [15]. Another characteristic of PVP with Au is the appearance of a peak that shifts towards the red end of the spectrum. The intensity of this peak increases consistently as the amount of Au nano-filler in the PVP increases. The red shift signifies an increase in the maximum absorption wavelength (max), indicating a rise in the concentration of Au in the PVP nanocomposites. This shift causes a movement towards longer wavelengths.

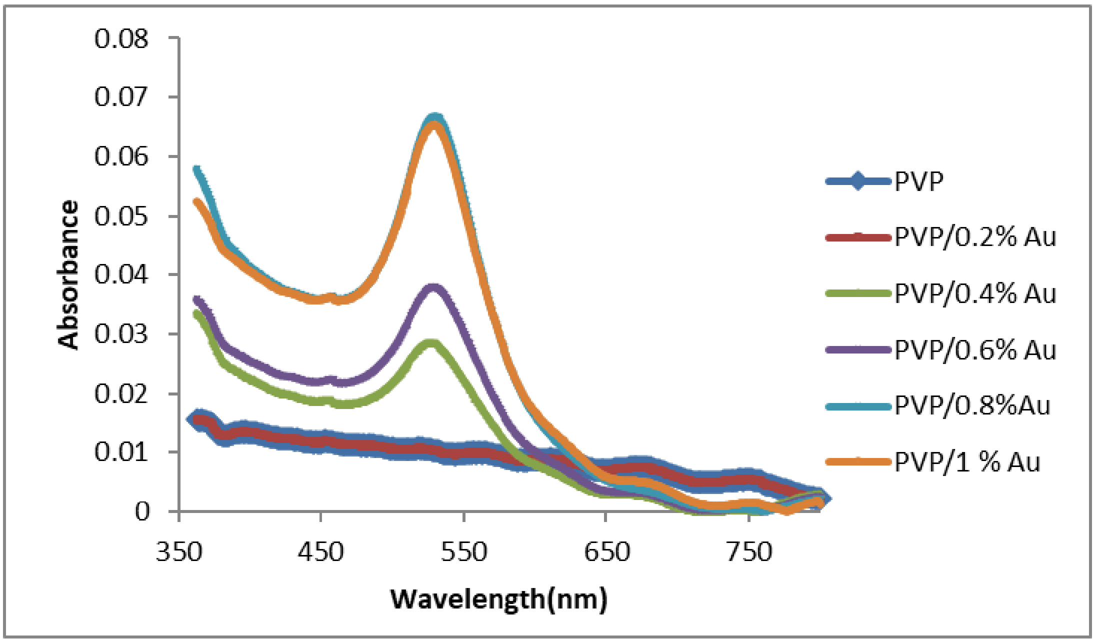

Figure 5 UV/Vis. spectra for pure PVP and PVP /Au nanocomposites.

Figure 5 shows a decrease in the breadth of the restricted band as the Au NPs content increases. One can determine the absorption coefficient (α) by utilizing the Beer–Lambert's relation [14].

$$\alpha = 2.303\ A / L \qquad (1)$$

Where absorbance (A) and film thickness (L) are explicitly defined. The optical band gap which is the another feature of film is calculated from absorption coefficient data as a component of wavelength as given by [4];

$$\alpha (h\nu) = B(h\nu - Eg)r \qquad (2)$$

Where (r) is the power factor that determines the kind of transition and it can get the quantities 1, 2, 3, 1/2 and 3/2, depending on the method of the electron moves that is responsible for the optical retention. It is necessary to understand that (r) can get the value of 1/2 in case of direct electronic transition transversely over direct energy gap in the k space. However, (r) takes the value 2, if there should be an occurrence of indirect electronic transition crosswise over roundabout energy gap. Both of the direct and indirect transtions happen and can be seen by plotting (αhν) 2 and (αhν) 1/2 versus photon vitality (hν)

[15,16]. Fig. 6 shows the plot of the (αhv)2 as a function of photon energy (hv), The energy gap is computed of the evaluating of the erect partition as show in figure below.

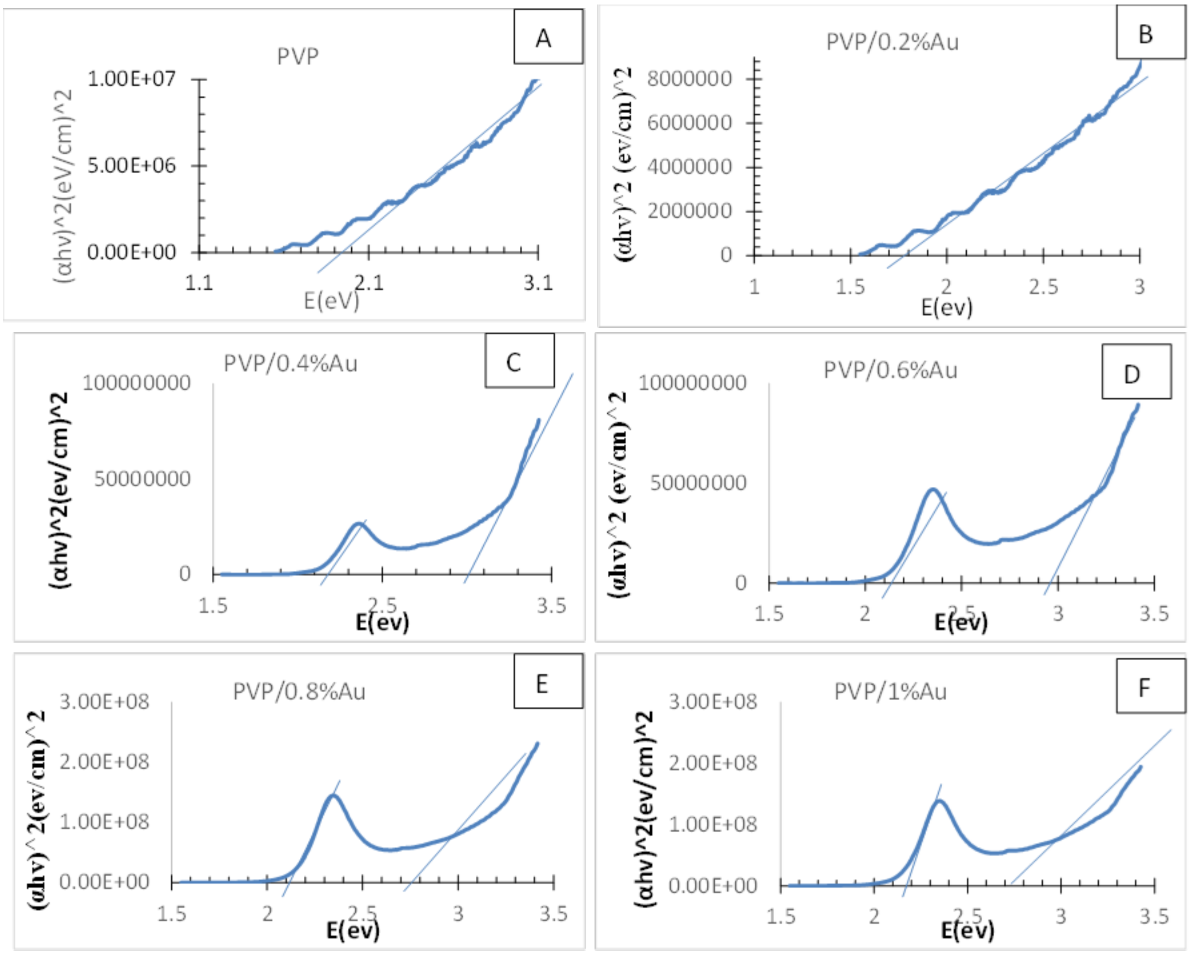

Figure 6 (A, B, C, D, E, and F) show (αhv)^{2} versus photon energy for PVP and PVP/Au nanocomposites.

Table 4 presents the Eg values of the films. The table demonstrates that the energy values often decrease as the concentration of Au increases, when compared to PVP. If the induced states formed by loading PVP with Au alter Eg, then the shift in optical gap behavior could be attributed to the filling level mode. The presence of Au NPs in the polymer has a substantial impact on the optical band gap. The presence of Au may be responsible for the formation of defects in the filled samples. These imperfections result in a higher level of disorder in the nano-composite samples by creating localized states inside the optical band gap. The optical energy gap value of a 1% Au sample is 2.0 eV, which is lower than the 2.6 eV value for pure PVP. The formation of localized states within the energy bands between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) is a consequence of the bonding between the mixed chains and gold nanoparticles (Au). This bonding is responsible for the observed decrease in energy [17]. Au show a SPR, with values in the range 400–800 nm depending on the size and shape of the nanoparticles. This resonance is also useful for the development of optoelectronic devices because the tunability of the SPR peak position allows the feasibility of highly sensitive surface-enhanced Raman scattering (SERS)-active substrates for molecular identification and for SPR biosensors, sensitive to the refractive indices of surface-bonded species [18]. Assuming that Eg to be influenced by the induced states due to Au filling of PVP, one may attribute the optical gap behavior to the change of the filling level (FL) mode. The increment of Au into polymer blend causes a resultant effect on the optical band gap. Au is responsible for defects formation within the filled samples. These defects create localized states in the optical band gap. The localized states density is proportional to the defect's concentration. The nanofiller may make the changes in the localized states to overlap. These overlaps give a proof for decreasing the gap of optical band when the content of Au is increased in the polymeric matrix and appear two energy gap . Also, this decrease can be understood by the increase in the disorder degree in the nano-composite samples agree with [19].

Au is of great importance due to their ability to interact with light efficiently by dint of surface plasmon resonance (SPR). SPR is the collective oscillations of the conduction electrons in the metal when the wavelength for incident light is much larger than the size of nanoparticle. Also, it has catalytic activity due to high surface area to bulk atoms ratio. Thus, Au NPs surely have the potential to be the building blocks of future plasmonic and photonic devices as the nanotechnology field matures [20-23].

Table 3 Optical energy gap of PVP/Au nanocomposites.

Samples	Eg1	Eg2
PVP	2.6	-
(PVP / 0.2Au)	2.3	-
(PVP /0.4%Au)	2.2	3.1
(PVP / 0.6%Au)	2.1	3.01
(PVP / 0.8%Au)	2.1	3.0
(PVP / 1%Au)	2.0	2.9

4. CONCLUSIONS

PVP was used to prepare a composite material with Au nanoparticles using the casting technique. The interaction between PVP and Au has been confirmed using FT-IR analysis, indicating that the polar groups of the PVP polymer engage with the Au. Based on the contact angle results, it was observed that the contact angle values of the nanocomposites increased as the weight ratio of Au expanded. Testing the antibacterial activity of PVP and PVP/Au was conducted using the agar-well diffusion method, a commonly used technique for evaluating the antimicrobial properties of plant or microbial extracts. The PVP/Au nanocomposites exhibited a prominent peak in the UV/vis absorption spectra within the visible region, indicating the presence of Au nanoparticles. The intensity of this peak increased as the content of Au nanoparticles increased, resulting in a shift towards longer wavelengths and a reddish color. When Au is added to the polymeric matrix, the energy gap values for nanocomposite films were decreased and enhanced. Au is of great importance due to their ability to interact with light efficiently by dint of surface plasmon resonance (SPR). SPR is the collective oscillations of the conduction electrons in the metal when the wavelength for incident light is much larger than the size of nanoparticle [8,9]. Also, it has catalytic activity due to high surface area to bulk atoms ratio. Thus, Au NPs surely have the potential to be the building blocks of future plasmonic and photonic devices as the nanotechnology field matures.

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