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Optimized Characteristics of Polyvinyl Alcohol Films Decorated with Silver Nanoparticles Synthesized via Chemical Reduction Method

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Abstract

This research shows how to prepare polyvinyl alcohol (PVA) films with silver nanoparticles and how different amounts of these nanoparticles affect the films' properties. The silver nanoparticles (AgNPs), featuring a uniform spherical shape, were synthesised using the chemical reduction method. The concentration of AgNPs and the amount of the reducing agent were found to influence the structural and optical characteristics of the prepared films. Higher volumes of the reducing agent have resulted in the formation of larger silver nanoparticles. These factors affected the size of the silver nanoparticles and the specific absorption peak, which was between 420 and 435 nm, with the nanoparticles measuring between 20 and 32 nm in size. The UV-visible spectroscopy of PVA film samples with silver nanoparticles showed that the silver nanoparticles had a peak absorption in the 420-435 nm range. The FTIR spectroscopy showed that the silver nanoparticles do not chemically attach to the PVA structure, but instead, they fit into the matrix as small flaws. Still, they integrate into the matrix as structural imperfections. The present work aims to study the structural behaviour and particle size effect of Ag NPs dispersed in a polymer network and select the best conditions for synthesizing such nanostructures.

Article Info.

Keywords:
Nobel metal Nanoparticles, Polymers, Surface Plasmon Resonance, Chemical Reduction, Concentration.

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1. Introduction

In the past decade, researchers have shown significant interest in nanoparticles composed of noble metals. These particles receive so much attention because of their remarkable properties at the nanoscale, which are so different from their bulk counterparts. Silver nanoparticles (AgNPs) are silver nanoparticles with typical sizes between 1 and 100 nm. They have wide applicability and have unique properties such as electrical, optical and magnetic [1].

AgNPs still continue to be manufactured with improved methods leading to more controlled manipulation of their size and shape. These nanostructures have been used to improve white light photoluminescence, and are promising for many medical applications. These can also be applied to therapeutic applications, diagnostic uses, and photothermal assisted drug delivery [2, 3]. Beyond their composition and morphology, these nanoparticles have value. Among them are notable stability, excellent optical and electrical properties, distinctive magnetic behaviours, high resistance to oxidation, and impressive structural properties. They are very widely applicable with such a combination of features [4, 5].

A number of methods have been used to produce nanoparticles, including chemical methods [6], electrochemical methods [7], reduction based synthesis [8] and metal salt reduction [9]. The chemical reduction technique is a commonly used, and important, method for the synthesis of colloidal silver, gold and copper nanoparticles [10-12].

AgNPs with localized surface plasmon resonance (LSPR) in the visible region of the electromagnetic spectrum and localized field effects have been the subject of considerable interest. AgNPs are attractive candidates for improving fluorescence performance and also a motivator for further scientific interest and exploitation of their potential [13-15].

Polymers are excellent matrices for encapsulating metal nanoparticles, such as silver, gold and copper, as dielectric materials. Agents are reducing and capping, and they provide environmental and chemical stability [16-18]. Due to their distinctive physicochemical properties, silver nanoparticles have been the subject of intense investigation. Due to its remarkable thermal stability, resistance to chemical degradation, robust mechanical properties, ability to dissolve in water, and tenable electrical conductivity, depending on the dopants, polyvinyl alcohol (PVA) has been selected as an excellent encapsulating matrix for these nanostructures. Establishing these properties has made PVA one of the most suitable polymeric hosts for silver nanoparticles [19, 20].

This research aims to improve synthesis methods of PVA-incorporated polymeric films with embedded silver nanoparticles. This research seeks to establish the structure of these nanoparticles and further understand how the characteristics of these dimensions affect the interaction or response of the nanoparticles within the polymer matrix.

2. Experimental Work

2.1. Liquid Samples

Chemical reduction method was employed to synthesize AgNPs. Silver nitrate ($AgNO_3$) (purity >98%) and trisodium citrate ($C_6H_5O_7Na_3$), as the reduction agent, (purity 99%) were utilized as the starting materials. All reactive material solutions were prepared with distilled water [21].

Different concentrations (2, 3, 4, 5, 6 $\times 10^{-3}$) mol/L of $AgNO_3$ were dissolved in 125 ml of distilled water. A 62.5 ml starting solution of each concentration was prepared with 1:4 volume ratio of $AgNO_3$:H_2O. A dilute sodium citrate solution (1%) was created by combining 0.5 g of the compound with 50 mL of distilled water [22]. The $AgNO_3$ solution was heated to its boiling point of 98°C. Upon boiling, varying amounts (1, 1.5, 2, or 2.5 mL) of the sodium citrate solution were added dropwise. Continued heating resulted in color change to pale yellow, as depicted in Fig. 1. The chemical process underlying this reaction can be described as follows [23]:

$$4Ag + C_6H_5O_7Na_3 + 2H_2O \rightarrow 4Ag^0 + C_6H_5O_7H_3 + 3Na + O_2 + H \qquad (1)$$

Figure 1: Ag NPs at different concentration.

2.2. Film Samples

PVA (molecular weight: 10,000 g/mol) was obtained from BDH Chemicals in England. This polymer, characterized by specific viscosity, hydrolysis degree, and pH (all measured in 4% aqueous solutions), was dissolved in 10 ml of purified water. The resulting mixture underwent constant stirring for 15 hours using a magnetic stirrer, with temperatures maintained between 20-50°C. This process produced an appropriate transparent host for Ag.To produce PVA films embedded with AgNPs, 2.5 ml of reducing agent ($C_6H_5O_7Na_3$) was added to different concentrations of Ag NPs, doped with the polymer solutions at 4:2 ratios, and homogenized for 20 minutes on a magnetic stirrer. Finally, the final solution was kept in a Petri dish at 45°C for a minimum of 5 weeks, as shown in Fig. 2.

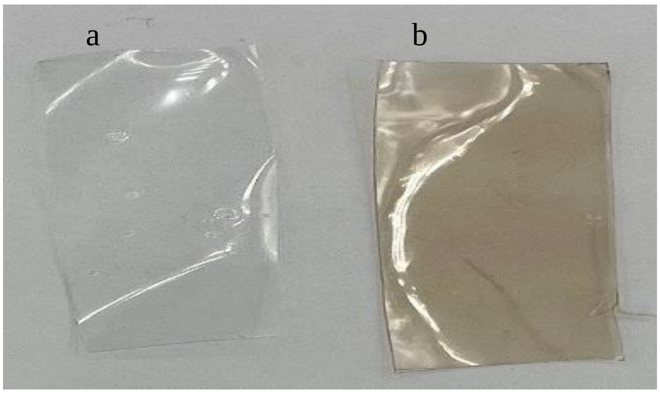

Figure 2: (a) pure PVA polymer film (b) PVA film embedded with Ag NPs.

2. 3. Characterization of the Synthesized Samples

A Field Emission-Scanning Electron Microscope (FE-SEM) (Inspect F50) was employed to probe the nanoscale dimensions and surface morphology of silver nanoparticles.

The transparency of PVA polymer as a host matrix was observed by recording the transmittance and absorption spectra using a UV-Vis spectrometer (Centra 5, manufactured by GBC Scientific Equipment Pty Ltd, Australia). This instrument employs tungsten and deuterium lamps as its light sources for spectral analysis.

Using Fourier transform infrared spectroscopy (FTIR) (Shimadzu, on KBr pellets of the samples, Mid-IR spectra, from 4000 to 400 cm^{-1}, were obtained for some pure samples and all doped samples.

3. Results and Discussion

The AgNPs particle size was determined with an FE-SEM, for the prepared samples at concentrations 5×10^{-3} mol/L and reduction period of 5 min [24]. The silver nanoparticles exhibited a homogeneous dispersion, adopting spherical shapes with diameters ranging from 20.40 to 31.52 nm, as depicted in Fig. 3. The irregularity in the particle size values with the $AgNO_3$ concentration (see Table 1) is related to the particle size distribution that gradually changes from small to large aggregations.

Fig. 4 illustrates the room temperature absorption and transmission of PVA polymer. The high transparency of 89% can be noted with no spectral activity in the spectral range of 400-800 nm. The high transparency is assumed to be a suitable property for the PVA films as a host matrix for some dopants, including noble metal nanoparticles.

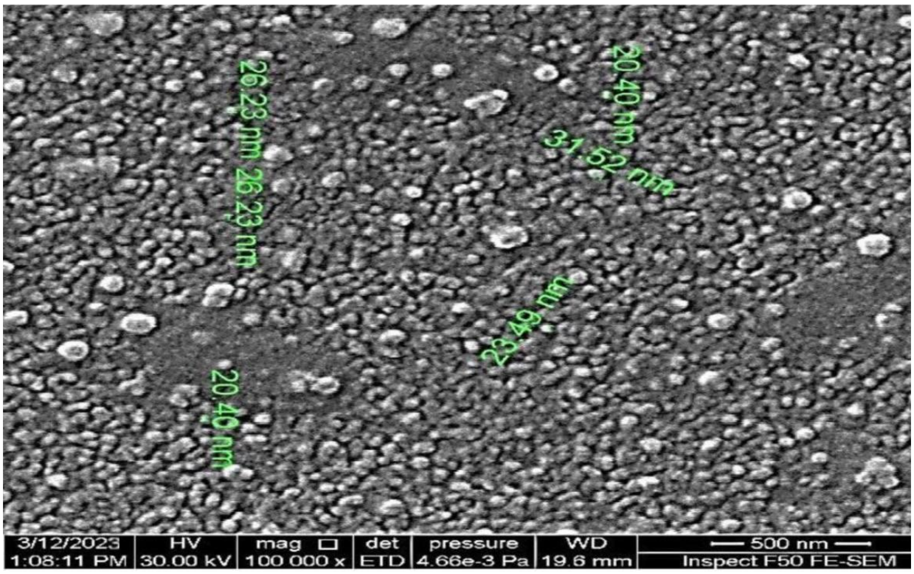

Figure 3: FE-SEM image of Ag NPs synthesized at $5\times10^{-}$ mol/L concentration and reduction period of 5 min.

Table 1: The particle size of AgNPs as a function of concentrations.

Concentration mol\L	Particle size (nm)
2.0×10^{-3}	30.15 – 50.20
3.0×10^{-3}	16.80-35.24
4.0×10^{-3}	14.38-39.00
5.0×10^{-3}	20.40 -31.52

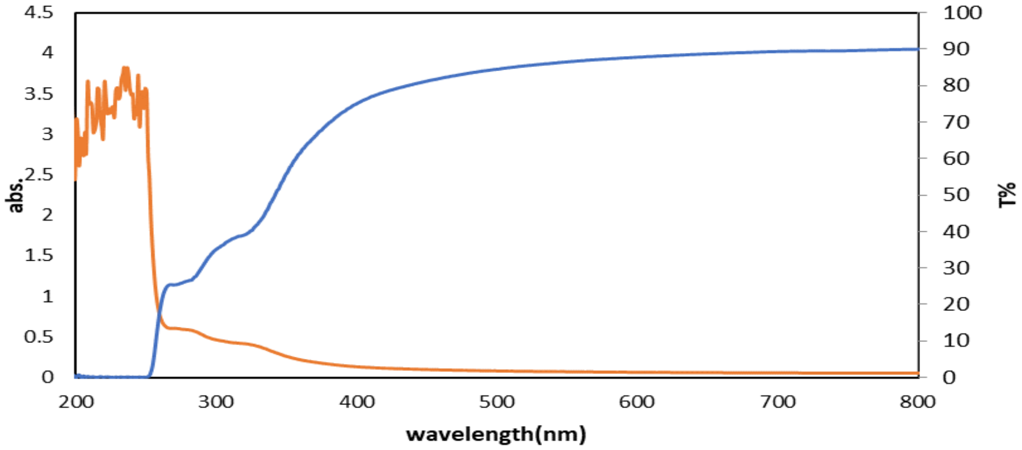

Figure 4: Absorption and transmission spectra for pure PVA polymer.

The structural behavior of silver nanoparticles within the PVA matrix was investigated by Fourier transform infrared (FTIR) spectroscopy. Fig.5 below shows FTIR spectra of pure PVA and silver nanoparticle-doped PVA samples. The vibrational bands at around 3441.88, 2905.64 and 1639.43 cm^{-1} are assigned to O–H, C–H and C = C stretching vibrations, respectively [25]. Moreover, vibration bands of AgNPs could arise at wavenumbers around 1100, 1364.39, 1629.5 cm^{-1} [26]. These results give primarily impression that AgNPs do not form any links with the PVA network structure, and, instead, they may tend to take positions within the structure as defects.

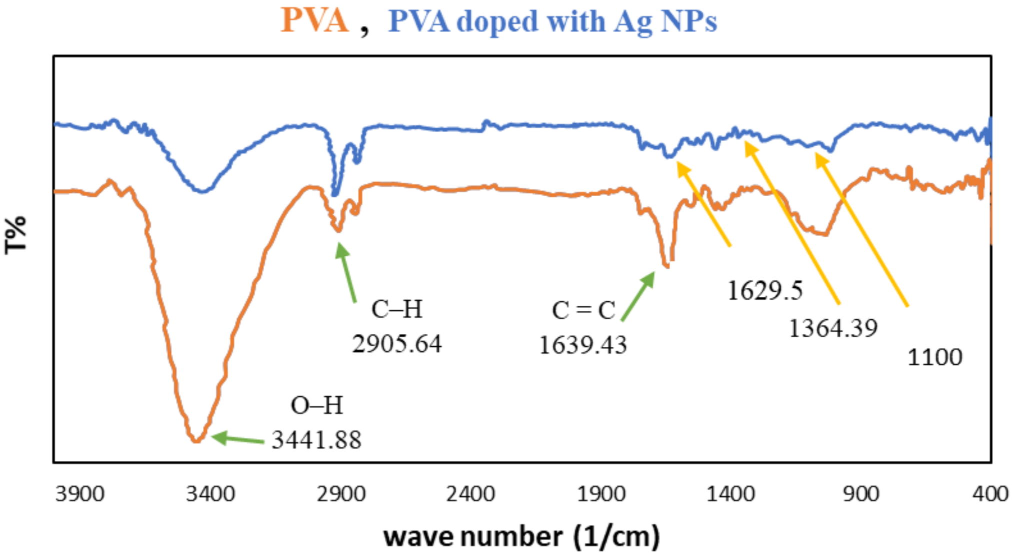

Figure 5: FTIR spectra of pure polymer and polymer embedded with Ag NPs.

Figs. 6 and 7 depict the absorbance spectra of Ag colloidal produced by heating after boiling point for various $AgNO_3$ concentrations at a reduction period of 5 min. Increasing the concentration of silver nanoparticles led to increased absorption. Notably, the SPR band shows a slightly shift towards longer wavelengths (420-435 nm) as the concentration increases, which is consistent with Beer-Lambert law [22].

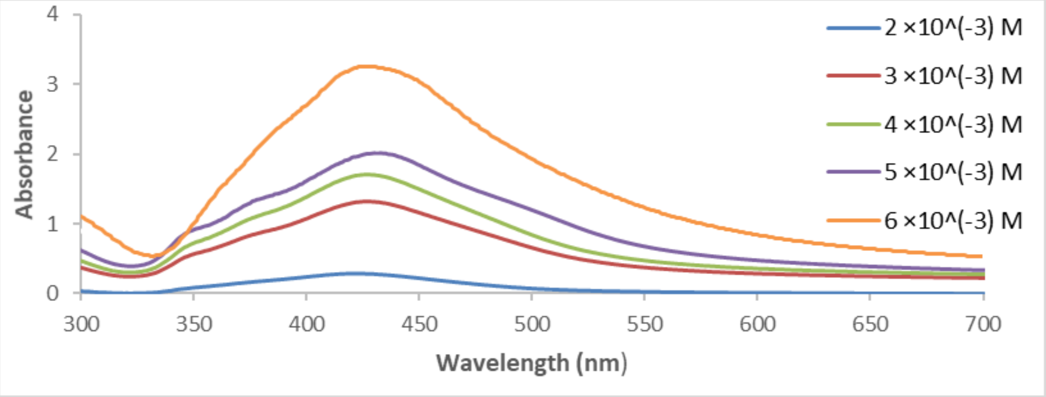

Figure 6: Absorbance spectra of Ag colloidal as a function of concentrations at 5 min reduction period.

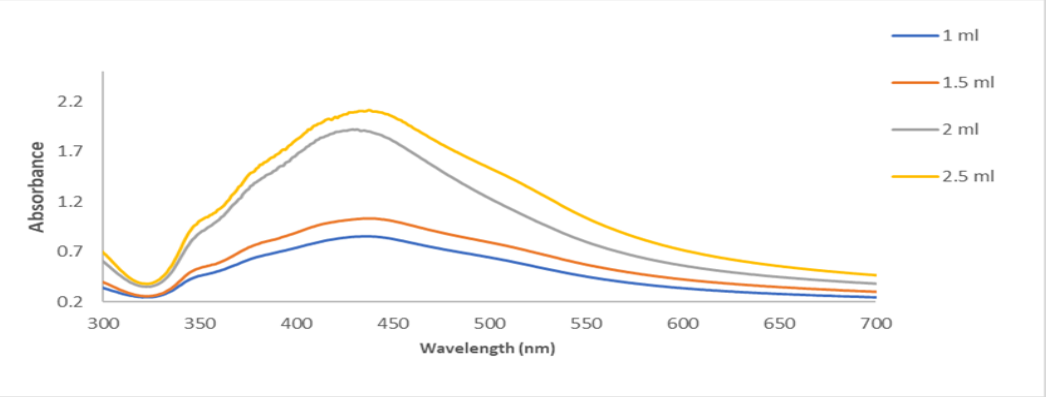

Figure 7: Absorption spectra of Ag colloidal material as a function of the reducing agent.

This section aims to elucidate the impact of silver on the absorption spectra of both the AgNPs solution and pure PVA samples, providing a basic understanding of silver's behavior within PVA. Fig.8 shows the absorption spectra of PVA samples doped with varying concentrations of Ag NPs. After identifying the nanoscale of AgNPs, it can be seen that the spectral activity of AgNPs is clearly observed through the band of SPR that is located at around 432 nm. Also, the absorbance at SPR band increased with the increasing of AgNPs concentration according to Beer-Lambert law.

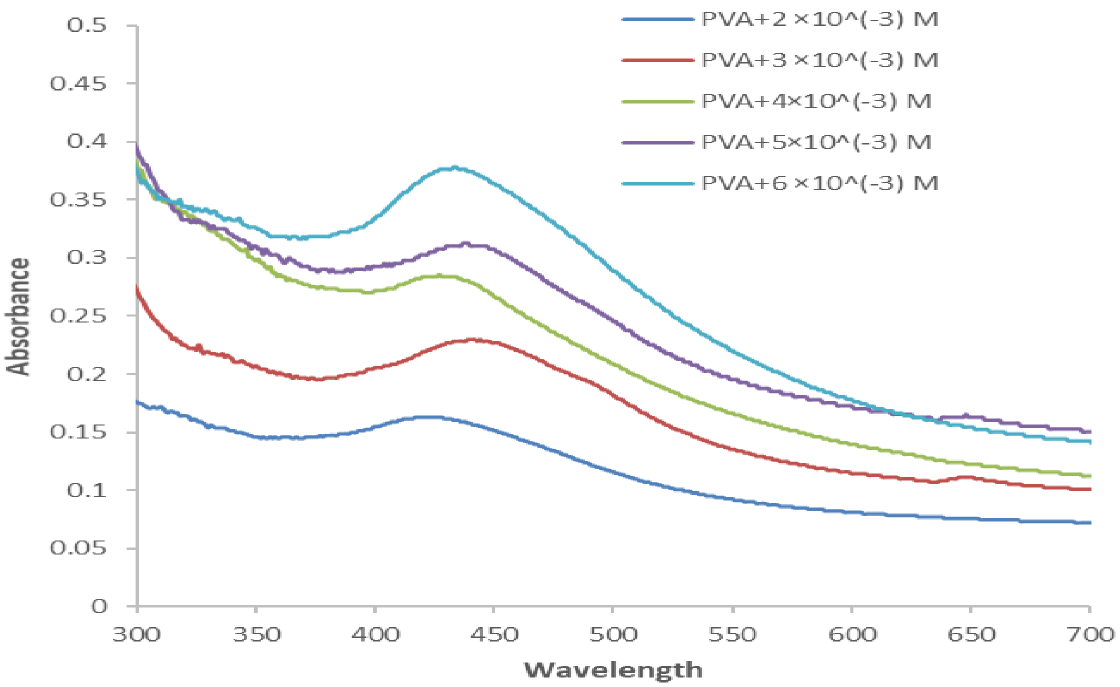

Figure 8: Absorption spectra of PVA polymer doped with different concentrations of AgNPs and a reducing agent of 2.5 ml.

4. Conclusions

The study revealed that the chemical stability of silver nanoparticles produced through chemical reduction and the surface plasmon resonance band's intensity show direct proportionality with the quantity of reducing agent added post-reduction, particularly at lower concentrations. AgNPs cannot form links with the PVA network structure; instead, they may take positions within the structure as defects. It can be observed that the peak of each band of the absorbance spectra increased somewhat with the increase in concentration of silver nanoparticles.

Conflict of interest

The authors state that there is no conflict of interest associated with this research.

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تحسين خصائص افلام بولي كحول الفينيل المطعمة بجسيمات الفضة النانوية والمحضرة بطريقة الاختزال الكيميائي

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الخلاصة

يعرض هذا البحث عملية تحضير افلام بولي كحول الفينيل (PVA) المطعمة بجسيمات الفضة النانوية ودراسة تأثير التراكيز المختلفة لهذه الجسيمات على خصائص الافلام المحضرة. ان جسيمات الفضة النانوية (AgNPs) والتي تم تحضيرها بطريقة الاختزال الكيميائي ظهرت بالشكل الكروي المنتظم. وجد ان تركز جسيمات الفضة النانوية وكذلك كمية عامل الاختزال تؤثر على الخصائص التركيبية والبصرية للأفلام المحضرة. اذ ان حجم العالية من عامل الاختزال تؤدي الى تكون جسيمات الفضة النانوية بحجم أكبر. هذه العوامل اثرت على كل من حجم الجسيمات وحزمة امتصاص رنين بلازمون السطح المميزة، والتي ظهرت في المدى 420-435 نانومتر، وحجم الجسيمات كان ضمن المدى 20-32 نانومتر. اظهرت مطيافية الامتصاص في المنطقتين المرئية والفوق بنفسجية لجسيمات الفضة المطعمة ضمن افلام الـ(PVA) وجود امتصاص رنين البلازمون السطحي وبقيمة عظمى لجسيمات الفضة المتضمنة داخل مصفوفة PVA ضمن المدى 420-43 نانومتر. اثبتت نتائج مطيافية تحت الحمراء بتحويلات فورير لجسيمات الفضة النانوية ضمن شبكة PVA ان هذه الجسيمات لم ترتبط كيميائيا مع هيكلية البوليمر ولكن ارتباطه كان بشكل شوائب تركيبية داخل المصفوفة. هدف العمل الحالي هو دراسة تأثير السلوك التركيبي وحجم جسيمات الفضة النانوية على توزيع الجسيمات ضمن شبكة البوليمر واختيار شروط التحضير الامثل لهذه التراكيب النانوية.

الكلمات المفتاحية: الجسيمات النانوية المعدنية النبيلة، البوليمرات، رنين بلازمون السطح، الاختزال الكيميائي، التركيز.