The effect of the concentration of the stabilizer in the formation of a silver nanoparticle on the phenomenon of Surface Plasmon Resonance (SPR) as an active material for biosensor

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Abstract. It has been successfully synthesized silver nanoparticles by chemical reduction methods. Silver nitrate (AgNO$_3$) is used as a metal precursor and trisodium citrate as a reducing agent with varying concentrations of the stabilizer PVA. The UV-Vis spectrometer shows that increasing the mass concentration of the stabilizer can sharpen the surface plasmon maximum absorption band and there is a shift in the maximum absorption band towards a larger wavelength. This shift occurred from a wavelength of 428.79 nm at a PVA concentration of 0.85 ppm shifted to a wavelength of 429.01 nm, 430.93 nm and 434.13 nm for each PVA concentration of 1.70 ppm, 2.55 ppm and 4.25 ppm. The observation results of the SPR phenomenon showed a shift in the SPR angle when a thin layer of silver as the active ingredient of the sensor was coated with silver nanoparticles. This addition also sharpens the reflectance value. The SPR angle shift and the increase in reflectance value are caused by changes in the surface plasmon wave constant, which becomes a reference that the SPR phenomenon by modifying the sensing surface using an additional layer of silver nanoparticles can increase its sensitivity.

1. Introduction
In conventional Surface Plasmon Resonance (SPR) biosensors, the biosensor's performance is determined by the Surface Plasmon Polariton (SPP), which is excited on a thin film of metal and propagates along the surface. The metal nanoparticle structure's addition allows for rigid coupling between the incident light and the plasma oscillations of electrons in the nano metallic structure [1]. This mechanism will amplify the signal because of its capability to generate waves simultaneously.

The addition of metal nanoparticles on top of a thin film has been previously carried out by Singh et al. [2]. It was reported that the occurrence of metal nanoparticles in the BSA (bovine serum albumin) detection experiment could shift the ATR curve by 1.037° in comparison with conventional SPR, which only shifted by 0.716°. A technique to elevate the sensitivity of biomolecule sensing by utilizing nanoparticles entrenched in the SiO$_2$ matrix has been developed as well [3]. Apart from that, the nanoparticles were selected because of their very high binding ability to the material, considering that the surface area that interacts with the material in contrast to its bulk phase is extensive. With a very high absorption capacity, the analyte's mobility can also be suppressed to enhance the biosensor's accuracy and sensitivity. We develop a conventional SPR model-based biosensor by incorporating a silver nanoparticle structure into a silver thin film. The sensitivity of the SPR biosensor is aimed to be elevated by silver nanoparticle incorporation[4].
Diverse methods related to developing silver nanoparticles such as ultrasonic irradiation, electrochemical synthesis, thermal decomposition, radiolysis, and the chemical reduction of metal salts have been reported [5], [6], [7], and [8]. In the present study, we synthesized silver nanoparticles from silver nitrate salt solution with trisodium citrate as the reducing agent and supported with a stabilizer to control nanoparticles' growth by chemical reduction method.

2. Experimental methods
2.1 Materials
Silver nitrate (AgNO₃), reducing agent trisodium citrate (Na₃C₆H₅O₇·2H₂O), and stabilizing agent PVA.

2.2 Preparation and characterization
The synthesis was performed at a temperature of 90 °C by varying the stabilizer PVA at a concentration of 0.85 ppm, 1.70 ppm, 2.55 ppm, and 4.25 ppm by observing the color change to get a dark yellow solution. Metal ion reduction was monitored by measuring the absorbance of the silver nanoparticle solution using UV-Vis spectroscopy. Measurements were performed with a Shimadzu dual-beam spectrophotometer (model UV-1650 PC) operating at a resolution of 1 nm and wavelengths ranging from 350 to 800 nm. Observation of the introduction of silver nanoparticles to the SPR biosensor system was carried out by the Attenuated Total Reflection (ATR) method in the Kretschmann configuration. The thin layer of silver nanoparticles' deposition is deposited on the silver thin layer's surface using the spray method. The BK7 type prism was used as a prism with a refractive index of 1.51.

3. Results and discussion
We successfully synthesized nanoparticles by chemical reduction methods. The yellowish color that forms in the sample indicates that silver nanoparticles dominate the nanoparticle colloid produced in this synthesis process.

This research is focalized on studying the action of PVA as a stabilizer in the formation of colloidal silver nanoparticles. To obtain information on the role of preventing agglomeration, we analyzed the surface plasmon band focusing on the absorption spectrum of silver nanoparticles which produced with varied PVA concentrations. PVA can be used very well as a stabilizer in the formed nanoparticle colloids because it provides a more stable nanoparticle size distribution. As is known, the growth of nanoparticles, which are stabilized by the polymer in solution, consists of the reduction of metal ions and stabilization of metal polymers. This reduction process can occur before or after the interaction between metal ions and polymers. If the reduction precedes the interaction, then the polymer may not correctly control the nanoparticles' growth, and, therefore, the second case is more favorable. In this way, a yellow solution was obtained, and with increasing intensity lead to a dark yellow solution.

The absorption band of maximum surface plasmon for the colloidal spectrum of silver nanoparticles that was synthesized with 0.04 M trisodium citrate at 90°C with varied concentrations of the stabilizer PVA was shown in Figure 1. Furthermore, a colloidal spectrum of silver nanoparticles synthesized with a PVA stabilizer concentration of 0.85 ppm exhibiting maximum absorption at 428.79 nm. The incorporation of mass stabilizer concentration within the synthesis process sharpened the maximum absorption band of surface plasmon and created a shift in the maximum absorption band towards a larger wavelength. The shift occurred from a wavelength of 428.79 nm at a PVA concentration of 0.85 ppm shifted to a wavelength of 429.01 nm, 430.93 nm, and 434.13 nm for each PVA concentration of 1.70 ppm, 2.55 ppm, and 4.25 ppm.

In general, the increase in absorption at larger wavelengths can generally be ascribed to the aggregation process, and the larger colloidal particles can cause the shift towards larger wavelengths. Furthermore, the study will focus on the weight aggregation process of reducing trisodium citrate in the sample by using an additional stabilizer (PVA). As shown in Fig. 1, The UV-Vis spectrum displays a crucial change in the maximum absorption band of the silver nanoparticle solution synthesized with the addition of PVA. According to the literature, the amount of PVA in solution dramatically affects the resulting particles' size and shape [9]. Besides, the adsorption of stabilizers such as PVA has been shown to cause a shift in the maximum absorption peak due to an increase in the particle environment's
dielectric constant [10]. However, a shift in the maximum absorption band towards a smaller wavelength was observed in the obtained spectrum compared to the synthesis without PVA.

Our study confirmed that to obtain stable colloid silver nanoparticles; we can use a low stabilizer PVA concentration. The relationship between the surface plasmon absorption band and the full width at half the maximum (FWHM) to the concentration of the PVA stabilizer is given in Table 1. Table 1 shows that the increase in the mass concentration of the PVA stabilizer causes a shift in the surface plasmon band to a larger wavelength also reduces FWHM. It shows that increasing the concentration of PVA will increase the more dispersive particle distribution nanoparticles' size. The effect of variations in PVA concentration on the wavelength of the maximum surface plasmon absorption band is shown in Figure 2. Figure 2 shows an almost linear relationship between the maximum surface plasmon absorption band's wavelength and the PVA stabilizer concentration.

![Absorption Spectrum](image)

**Figure 1.** The absorption spectrum (UV-Vis) of silver nanoparticles synthesized with various concentrations of the stabilizer PVA

| Concentration (ppm) | Surface plasmon band (nm) | FWHM (nm) |
|---------------------|---------------------------|-----------|
| 0.85                | 428.79                    | (135.0 ± 0.9) |
| 1.70                | 429.01                    | (117.3 ± 0.8) |
| 2.55                | 430.93                    | (112.2 ± 0.6) |
| 4.25                | 434.13                    | (121.0 ± 0.5) |
Figure 2. The effect of variations in the concentration of PVA on the wavelength of the maximum surface plasmon absorption band.

Based on this description, it can be concluded that increasing the concentration of stabilizer will increase the size of the nanoparticles and produce almost spherical or round silver nanoparticles with a fairly dispersive particle distribution even though there is a tendency for clumping to occur. This level of dispersibility of nanoparticles is potential as an active material for SPR sensors.

Moreover, we have observed the SPR phenomenon in the prism/LT-silver/nanosilver-VarPVA coating system using the ATR method in the Kretschmann configuration. As displayed in Figure 3, a deposited thin film of silver with silver nanoparticles shift the SPR angle. The coating system of silver prism/LT has a surface plasmon wave constant of 1.01. It has a 42.8° SPR angle, reflectance value of 0.35, and wave constant of $1.011 \times 10^7$ m$^{-1}$. After completing the thin film coating process from silver to synthesized silver nanoparticles with a PVS concentration of 0.85 ppm, the SPR angle shifted from 0.1° to 42.9°, with the reflectance value sharpened to 0.267. The surface plasmon wave constant was changed to $1.013 \times 10^7$ m$^{-1}$ as well.

Meanwhile, the use of a PVA with a concentration of 1.70 ppm in colloidal silver nanoparticles synthesis shifted SPR angle from 0.2° to 43.0° with a reflectance value of 0.263 and a surface plasmon wave constant to $1.015 \times 10^7$ m$^{-1}$. Furthermore, the use of 2.55 ppm PVA concentration shifted the SPR angle from 0.4° to 43.2° with a reflectance value of 0.331 and the surface plasmon wave constant to $1.018 \times 10^7$ m$^{-1}$. Addition of silver nanoparticles layer on the silver thin film's surface and utility of varied concentrations of PVA stabilizer change dielectric constant, which alter surface plasmon wave constant.

Based on the observation results of the SPR phenomenon, the surface plasmon wave constant value can be determined for each additional layer, as presented in Table 2. The surface plasmon wave constant value was calculated from the experimental results. Table 2 described that the SPR angle shifts as wave constant value increases. SPR angle defines as an angle in which resonance between evanescent waves and surface plasmon waves occurs when $k_{sp}$ and $k_{ew}$ values are the same. Alterations at the surface plasmon wave constant shift SPR angle and increase reflectance value because of dielectric constant changes of the silver nanoparticle thin film. The SPR angle shift and the increase in reflectance value
are caused by changes in the surface plasmon wave constants due to changes in the silver nanoparticle thin film's dielectric constant. Higher the wave constant, resulting in a higher SPR angle.

Figure 3. Observed SPR curve on SPR phenomenon from silver nanoparticles synthesized with varied PVA stabilizer concentration.

Table 2. The value of surface plasmon wave constants, reflectance, and resonance angle for each addition of the synthesized nanoparticle thin film with variations in the concentration of the stabilizer PVA

| Parameters Layer | SPR angle (°) | Reflectance | $K_x (10^7 \text{ m}^{-1})$ |
|------------------|--------------|-------------|-----------------------------|
| Silver thin film | 42.8         | 0.350       | 1.0113                      |
| Silver nanoparticles + PVA (0.85 ppm) | 42.9 | 0.267 | 1.0132 |
| Silver nanoparticles + PVA (1.70 ppm) | 43.0 | 0.263 | 1.0151 |
| Silver nanoparticles + PVA (2.55 ppm) | 43.2 | 0.331 | 1.0189 |

4. Conclusion
The increase in the stabilizer's mass concentration causes a shift in the surface plasmon band towards a larger wavelength and reduces the FWHM. It shows that the size of the nanoparticles is enlarging with an increasingly dispersive particle distribution. This level of dispersibility of nanoparticles is potential as an active material for SPR sensors.

Silver nanoparticles with varying stabilizer concentrations coating a thin film of silver will shift SPR angle and sharpen the reflectance value. Changes or alterations in surface plasmon wave constant cause SPR angle shift and increase in reflectance value. These results can be used as a reference that the SPR
phenomenon, by adding a layer of silver nanoparticles to modify the sensing surface will increase its sensitivity.

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