Formation of anisotropic gold nanoparticles on indium tin oxide substrates as a plasmonic sensing material

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Abstract
A simple technique of seed-mediated growth has been successfully performed to grow anisotropy gold nanoparticles on solid substrates. The growth of the gold nanoparticles has been carried out in the presence of a binary surfactant mixture of hexadecyltrimethylammonium bromide with two different molecular weights of a capping agent, namely polyvinylpyrrolidone: 40,000 and 55,000. In this study, the effect of process parameters, growth time and molecular weight of capping agent was investigated. The growth time shows a significant impact on the shape and size of nanoparticles. The shorter growth time produced small spherical to square-like shape particles, whereas bigger particles including nanorods, nanosquares and nanotriangles were formed with longer growth time. The shape controlling agent, polyvinylpyrrolidone, was used to synthesis gold nanoparticles. It was found that monodisperse gold nanoparticles with uniform shape and size are hardly obtained when polyvinylpyrrolidone 40,000 was used as capping agent. Polyvinylpyrrolidone 55,000 produced more uniform shape and size of gold nanoparticles. Thus, these process parameters were found affected to the size, shape, surface density and uniformity of gold nanoparticles. This sample was further applied as a sensing material in the detection of toxic fungicide, namely chlorothalonil. The sensitivity of the sensor system was determined by the changes in peak positions and intensities of the transverse and longitudinal surface plasmon resonance peaks on different medium, that is, air, deionized water and chlorothalonil solution. The sensor response of gold nanoparticles thin film in 30 mM chlorothalonil showed two resonance peaks in comparison to the control experiment without gold nanoparticle thin film. The gold nanoparticles thin film sensor was successfully synthesized and potentially useful as a sensing material for fungicide detection.

Keywords
Localized surface plasmon resonance, seed-mediated growth method, gold nanoparticles, plasmonic sensor

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Introduction

Throughout the last decade, size and shape-dependent metal nanoparticles (NPs) have exhibited properties that are beneficial for applications ranging from drug delivery, diagnosis and therapy, sensor, disease detection and biomedical imaging. Typical metals used are gold, silver, platinum and palladium. These metal NPs are popular and widely used because of their chemical and physical properties such as nanometre (nm) in size and having good conductivity. Among these metals, gold and silver are commonly used metal because gold has the properties of corrosion resistance and binding capability while silver has low dielectric loss at different optical frequencies. Metal NPs have a unique optical properties obtained from the interaction of light and electron on the surface called localized surface plasmon resonance (LSPR). The characteristics of LSPR adsorption are highly dependent on the particle size, shape, composition and the dielectric constant of the surrounding medium and have a potential in plasmonic sensing applications. The most commonly used are isotropic NPs, namely nanospheres, due to their simple and easy preparation and synthesizing method. However, the application of metal nanospheres in plasmonic sensing is limited due to their weak and size-dependent absorption strength. Nanostructures of larger diameters also have the effect of producing broader spectra, yielding lower sensitivity. As the size of the NPs increases, the damping frequencies also increase, resulting in a broader optical spectrum. This peak broadening can be classified as either homogeneous or inhomogeneous. Hence, the diameter of the nanostructure will depict the wavelength at which the LSPR signal will be observed. Intrinsic properties of the nanostructure cause homogeneous broadening, whereas inhomogeneous broadening is the result of an averaging of the individual spectrum from a group of differing NPs. Alternatively, an anisotropic NPs exhibit distinctive optical and electronic properties, improved mechanical properties and specific surface-enhanced spectroscopy compared to isotropy NPs. Anisotropic gold nanoparticles (GNPs) have dual-band surface plasmon resonance peaks corresponding to the transverse and the longitudinal plasmon mode. The absorption and scattering of light along the short axis of the NPs results in transverse surface plasmon resonance (t-SPR), which occurs at the shorter wavelength, while the longitudinal surface plasmon resonance (l-SPR) lays along the long axis. In plasmonic sensing properties, the dual plasmon resonance contributes to an additional parameter compared with the single plasmon from the isotropic nanoparticle. Therefore, in this research, anisotropic GNP was fabricated as a thin film to manipulate their benefits for plasmonic sensing application.

There are two approaches in fabricating gold nanostructures: physical and chemical approaches. Examples of the physical method are lithography, thermal evaporation and evaporation–condensation method. The evaporation–condensation method is implemented for not only gold but also other metal such as silver, palladium and fullerene. This method requires high cost equipment, longer preparation time and a great deal of energy that raises the furnace’s surrounding temperature. The chemical approach, meanwhile, is simpler but controlling the chemical reactions requires meticulousness. One of the wet chemical synthesis approaches is the seed-mediated growth method (SMGM), which can produce high yield NPs with various sizes, shapes and structures. Furthermore, compared with the physical method, SMGM can be performed at room temperature and has simple experiment preparation at a lower cost.

Anisotropic GNPs such as nanorods, nanorices and nanopyramids are colloidal NPs that, due to their difficulty in attaching onto the substrate surface, are synthesized typically as solutions. Although these colloidal GNPs have dual-band responses, maintaining their stability is crucial since they are in solution form. Therefore, there is a need to fabricate anisotropic GNPs as a thin film. The advantages of GNPs in a thin film are that it can be used multiple times and it is more stable than in solution form as the shape will not change over time. Thus far, only a few anisotropic GNPs have been fabricated as a thin film for plasmonic sensing, such as nanoplates, nanospherical and nanorods. These GNPs thin films have been widely used in plasmonic sensors to detect a variety of pesticides, diseases and many more.

In this research, we have been working in the synthesizing of the GNPs using wet chemical SMGM. The work was started by Umar et al. with the formation of two-dimensional structure of gold on the indium tin oxide (ITO) surface with maximum yield as high as approximately 30%. The polymer capping material, namely polyvinylpyrrolidone (PVP), was used to shape the NPs. The study was further extended to synthesize the GNPs with variation concentration of hexadecyltrimethylammonium bromide (CTAB) and PVP. As a result, the GNPs formation strongly depended on the PVP concentration, while the GNPs size depended on the CTAB concentration. Then, in producing highly thin and electron transparent GNPs, poly(ethylene glycol) was used in the growth process. Subsequently, Morsin et al. successfully fabricated the gold nanoplates on the substrates with high density and produced product as high as approximately 63%. Then, the GNPs on the substrate have been deposited using single-step procedure with the surface density in the range of 14.47% to 48.99%. However, the absorption spectrum shows no strong surface plasmon resonance band observed at ultraviolet–visible (UV-Vis) and infrared region. Besides, process parameters effect such as growth time, seeding time and many others onto the formation of GNPs also been studied. Thus far, there are no studies have been conducted onto the effect of molecular weight (MW) in the growth of GNPs. Thus, in this study, the GNPs were
synthesized as a thin film using SMGM with variation of growth time and MW of PVP to study the effect to the shape and density. Therefore, by having anisotropic structure, it might increase the sensitivity of the LSPR sensor. The aim of this study is to fabricate anisotropic structure with size less than 100 nm which is suitable to be used as a sensing material specifically for the localized plasmonic sensor.

**Experimental work**

**Materials**

CTAB with purity ≥98% and l-ascorbic acid were purchased from Sigma Aldrich (China). Trisodium citrate dihydrate, sodium borohydride (NaBH₄) with purity of 98%, gold (III) chloride trihydrate (HAuCl₄·3H₂O) and PVP with an average MW of 40,000 were purchased from Sigma Aldrich (St. Louis, USA). PVP with an average MW of 55,000 was purchased from Emory Chemicals. All the solutions of these chemicals were prepared using deionized (DI) water with resistivity around 18.2 MΩcm from ELGA PURE LAB UHQ (Land End, UK).

**Analytical instrumentation**

The elemental composition of NPs was analysed with the X-ray diffraction (XRD) methods using X’Pert Powder X-Ray Diffractometer from PANalytical (Netherland) with monochromatic CuKα radiation at a wavelength (λ) of 0.1540 nm with a step size of 0.03°. The detected data were taken in a 2θ range of 20° to 60°. The morphology of the gold nanocrystals growth was characterized using field-emission scanning electron microscopy (FESEM, JSM-7600F, JEOL, Peabody, Massachusetts, USA) with high vacuum at 5-kV accelerating voltage. UV-Vis optical absorption spectroscopy was performed using UV-1800 Spectrophotometer from Shimadzu (Japan) with baseline from 400 nm to 800 nm.

**Seeding process**

The seeding process of GNPs on the substrates was done by immersing the ITO substrates into vial that contained 0.5 ml of HAuCl₄·3H₂O, 2 ml of trisodium citrate, 0.5 ml of ice-cold NaBH₄ and 18 ml of DI water for 2 h at room temperature before further use. The colour of solution changed from light yellow to reddish orange indicating the formation of gold nanoseeds. The samples were then removed, gently washed with DI water, dried and finally transferred to vacuum oven for annealing process at 150°C for 1 h to strengthen the gold nanoseeds on the surface.

**Growth process**

The growth of GNPs was determined and monitored in this study to observe their shapes and density. There were four chemicals used in growth solution preparation. In this process, the chemicals used were hydrogen tetrachloroaurate (HAuCl₄·3H₂O), CTAB, PVP and l-ascorbic acid (AA). The growth time was varied from 2 h to 8 h.

Firstly, 8 ml of CTAB was mixed with 10 ml of PVP. Then, 2 ml of DI water was added to the solution followed by 0.5 ml of HAuCl₄·3H₂O and 0.1 ml of AA. Then, the solution was rigorously shake for about 10 s to mix the reagents. After complete mixing, the solution colour changed from light yellow to colourless. The solution was left undisturbed in a controlled surrounding temperature at 28°C.

In this experiment, the MW of PVP was manipulated using two different MWs, 40,000 and 55,000 (PVP 40 k and PVP 55 k), to investigate the effect on shape formation. Same as previous study, these 2 MW of PVP were used in three different growth time, which are 2 h, 5 h and 8 h. The samples using PVP 40 k were labelled as GA 2.0, GA 5.0 and GA 8.0, respectively. While, the sample using PVP 55 k were labelled GB 2.0, GB 5.0 and GB 8.0, respectively.

**Plasmonic sensor system set-up**

The optimized GNPs thin films were tested as a sensing material in the optical LSPR sensor system. In this study, the sensor was used to detect chlorothalonil in liquid form. The absorbance spectrum corresponding to the sensing response was recorded. Figure 1 shows the set-up of a LSPR-based sensor with GNPs as its sensing material. There were five components required to set up the sensor: a light source, spectrometer, sensor chamber, computer and fibre optic.

According to previous study, four design modes were used to set up the plasmonic sensor. The configuration with reflectance mode was chosen as sensor operation mode. This mode allows the reflected light from the sensing material to be collected by the fibre optics probe and converted into optical absorption data. In this operation, a halogen light source excites the plasmon resonance properties of GNPs by transmitting the light from the light source towards the GNPs thin film via the duplex fibre optic. Subsequently, the reflected light from the thin film was transmitted to the spectrometer. The sensing parameters were based on the change of resonance peak position and peak intensity. The light absorption data were then analysed using spectrum analysis OceanView Software (Shanghai, China).

To ensure a stable operation of the sensor during testing, the sensor system needs to be warmed up and stabilized for at least 10 min prior to sensor testing. After stabilization, the sensor testing was performed by recording the LSPR properties of the GNPs thin film in air (Figure 2(a) and DI water (Figure 2(b)), which then was further used as the reference. Then, the LSPR properties of GNPs thin film was recorded again with the presence of the targeted analyte (Figure 2(c)). The spectrum responses for both medium (DI water and chlorothalonil) were recorded for 600 s. For testing purposes, the volume of analyte and DI water...
Results and discussion

The GNPs have been successfully synthesized using SMGM. The schematic of chemical reaction in seeding process is shown in Figure 3. Seeds are small nuclei\(48\) which serve as a base to develop more complex (anisotropic) structure. High-quality seed solution is needed to obtain high-quality NPs. In this process, Au\(^{3+}\) ions capped with COO\(^-\)/C0\(^-\) head group were produced once Au\(^{3+}\) ions and trisodium citrate were mixed and initiated the formation of Au complex as shown in Figure 3(a). As a weak reducing agent, sodium borohydride was added to the Au complex, then the solution turned to reddish-orange, indicates the formation of gold seeds.\(^49\) Figure 3 shows the reaction occurs in this condition.

The reaction occurs in growth process is illustrated in Figure 4. During this process, when the Au\(^{3+}\) ions, PVP and CTAB surfactant were mixed, the solution turned into light yellow, indicating the formation of AuBr\(^-\). In sequence, ascorbic acid which work as reducing agent was added into the same mixed solution. Then, the solution turned colourless indicates that Au\(^{3+}\) ion was successfully reduced to Au\(^+\) as described in Figure 4.

Physical observation

Physical observation is a process performed to monitor changes during synthesizing GNPs such as colour changes of the solution and the final colour of the substrates. During seed solution preparation, when hydrogen tetrachloroaurate
Figure 3. The schematic diagram of chemical reaction during seeding process: (a) reduction process of $\text{Au}^{3+}$ ions to Au complex in the presence of trisodium citrate and (b) reduction of Au complex to Au nanoseeds in presence of sodium borohydride.

Figure 4. The schematic of GNPs growth process: (a) reduction process of $\text{Au}^{3+}$ ions to $\text{Au}^{+}$ complex ions in the presence of ascorbic acid and (b) reduction of $\text{Au}^{+}$ complex ions to $\text{Au}^0$ (Au NPs) assist by Au nanoseeds. GNP: gold nanoparticle.
(HAuCl₄·3H₂O) added into trisodium citrate, the colour of the solution turned to light yellow. As mentioned in experimental work, the seeding solution shows the colour of the solution turned into reddish-orange as weak reducing agent (NaBH₄) added into the solution, indicated the formation of gold nanoseeds (Figure 5(a)). Figure 5(b) shows the growth solution turned colourless as all the chemicals mixed together and Figure 5(c) shows the colour of these solutions gradually changed after 8 h growth time.

Initially, the ITO substrate is colourless and the colour changed to blue violet after the growth process completed. The purple colour indicates the formation of GNPs. Figure 6 shows the colour of the ITO substrate after 8 h growth time.

**Structural properties**

The XRD was used to examine the structure of the GNPs film. The sample with 8 h growth time was chosen to represent all samples due to its similar structural properties. As shown in Figure 7, the sample exhibits two diffraction peaks from angle 20° to 60°. The first peak appeared in the plane (111) in position 38.215° with intensity of 349.839 a.u., while the second peak is seen in the plane (200) at 44.614° and 109.293 a.u. intensity. The obtained result is matched with data for bulk material gold standard of JCPDS 006-4701. Comparing the height and sharpness of both peaks, it can be clearly seen that the (111) place is the dominant. This indicates that majority of the GNPs have grown in parallel to the surface of the substrate, which coincide to the formation of GNPs and nanosphericals. From diffraction graph obtained, there is no appearance of additional peaks, indicating a pure crystalline has been formed on substrate surface.

Then, the sample was analysed using FESEM to observe the morphological properties of GNPs produced on the substrate surface. The samples were captured at 50,000 magnification at 5-kV accelerating voltage. Next, the optical properties of the GNPs were investigated using UV-Vis spectroscopy. As shown in Figure 8(a), a majority of the grown shapes on the substrate surface were anisotropic structures such as square, rod and triangular. However, other shapes, such as spherical and irregular shapes, also appeared and were referred to as the by-products. The optical responses of GNPs exhibited two resonance peaks at wavelengths of 550 and 651 nm (Figure 8(b)). As previously mentioned, the first band of surface plasmon resonance

![Figure 5](image-url)

**Figure 5.** Colour changes of solution: (a) seeding process, (b) initial condition growth solution, and (c) after 8 h growth time.

![Figure 6](image-url)

**Figure 6.** Colours of ITO substrates after 8 h growth time. ITO: indium tin oxide.

![Figure 7](image-url)

**Figure 7.** Structural properties of GNPs. GNP: gold nanoparticle.

![Figure 8](image-url)

**Figure 8.** (a) FESEM image of GNPs at 50,000 magnification and (b) optical property of GNPs. FESEM: field-emission scanning electron microscopy; GNP: gold nanoparticle.
refers to the width of the NPs, namely the t-SPR, and the other band refers to the length of the NPs, called the l-SPR.

As a comparison, gold nanosphericals (GNSs), which exhibit only one resonance peak of t-SPR at wavelength of 545 nm, were also fabricated. Figure 9(a) shows the morphological image of small GNSs, while Figure 9(b) shows the optical properties of GNSs. Therefore, anisotropic GNPs have an additional sensing parameter due to the l-SPR band compared to GNSs, which improves the detection analysis in the plasmonic sensor.

The study was extended by investigating two process parameters: variation of MW of PVP and growth time to achieve optimum surface density and homogeneity.

**Effect of different MW of PVP with variation of growth time**

Referring to current studies on the formation of triangular and rod GNPs with the present of PVP, nanotriangles shapes were produced from the transformation of spherical NPs, while the nanorods were formed via multiply twinned NPs.\(^{50-52}\) MW of PVP plays a critical role in the shape control of GNPs. When a short chain PVP used, that is, 40 k, it was found that nanotriangles and nanosphericals were dominantly formed, while nanorods and nanosquares shapes were preferentially synthesized using longer chain PVP (55 k). The formation mechanism of triangular and rod NPs with the assistance of PVP is shown in Figure 10. Initially, seeding process produced seed NPs. Next, the \(\text{Au}^+\) ions were reduced to Au spherical atom as it capped with NCO group of PVP. The function of PVP on the shape control can be classified into two different roles: adsorption and steric effect. When using PVP with small MW (40 k), transformation from nanospherical to NP occurred because PVP (40 k) adsorbed dominantly on the \{111\} facets of spherical particles.\(^{53}\) Therefore, crystal growth occurred on \{100\} direction, resulting to the formation of 2D triangular NPs. In contrast, for the case of long-chain PVP (55 k), crystal has grown from multiply twinned NPs to nanorods due to adsorption mainly on the \{100\} facets side compared to \{111\} facets.\(^{54}\)

Hence, the effect of different MWs of PVP with the variation of growth time was investigated via FESEM images of GNPs as shown in Figure 11, and Table 1 shows the analysis of the shape distribution for each sample. As can be seen in Figure 11, the growth time increment affects the size and shape of the NPs. Referring to the morphological image for 2 h of growth time using PVP 40 k, the dominant shape formed was the spherical-square shape. Bigger square particles were formed with 5 h of growth time, along with a small number of by-products. For 8 h of growth time, it produced the biggest particle size among all samples. However, the increment of growth time also

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**Figure 9.** (a) FESEM images of GNSs and (b) optical property of GNSs. FESEM: field-emission scanning electron microscopy; GNP: gold nanoparticle.

**Figure 10.** Growth mechanism of gold nanostructures by SMGM in the presence of two different MW of PVP: 40 k and 55 k. Modified from Tsuji et al.\(^{54}\) SMGM: seed-mediated growth method; MW: molecular weight; PVP: polyvinylpyrrolidone.
increased the number of by-products and formed bigger size of NPs of more than 100 nm, which is not suitable to be used as a sensing material specifically for the localized plasmonic sensor. The average surface density for all samples is listed in Table 1.

For PVP 55 k, the FESEM image for 2 h of growth time shows that the shape formed was the small spherical-square shape with some by-products. In comparison, GNPs using PVP 5000 with 8 h was the optimum growth time as it produced smaller (lower than 100 nm) size of NPs. Although using PVP 40,000 for 8 h produced the highest surface density of 48.99 ± 1.43%, the size was larger than 100 nm, which was not localized compared to particles formed using PVP 55 k. High surface density was barely obtained because it is hard to control the attachment process of the GNPs onto the substrates surface.

Table 1. Shape distribution of each sample.

| Sample | Rod      | Triangular | Square    | Others    | Yield     |
|--------|----------|------------|-----------|-----------|-----------|
| GA 2.0 | 0.65 ± 0.19 | 2.49 ± 1.47 | 4.41 ± 2.21 | 6.92 ± 0.06 | 14.47 ± 0.98 |
| GA 5.0 | 2.08 ± 0.10 | 3.80 ± 0.23 | 12.47 ± 3.28 | 11.37 ± 2.35 | 29.72 ± 1.49 |
| GA 8.0 | 6.82 ± 1.17 | 7.83 ± 0.92 | 20.59 ± 0.27 | 13.75 ± 3.34 | 48.99 ± 1.43 |
| GB 2.0 | 2.03 ± 0.41 | 1.28 ± 0.22 | 5.11 ± 0.29 | 7.80 ± 2.32 | 16.22 ± 0.81 |
| GB 5.0 | 6.19 ± 1.68 | 2.58 ± 1.11 | 13.20 ± 0.91 | 9.06 ± 0.99 | 31.03 ± 1.17 |
| GB 8.0 | 7.79 ± 0.48 | 4.69 ± 0.77 | 19.38 ± 2.85 | 11.80 ± 0.80 | 43.66 ± 1.23 |

The average aspect ratio and surface density for all samples are calculated and respectively listed in Table 1. In this study, the surface density data for all shapes were analysed using ImageJ software (USA) and Microsoft Excel. In ImageJ, the line selection tool was used to measure the length and width of the particles following its shape. The analysis was done by selecting three different areas from the FESEM images and then the average of surface density with standard deviation error was calculated.

Figure 12 and Table 2 show the optical spectrum and analysis of all GNP samples with different MWs of PVP and growth times. GA 2.0 with 2 h of growth time produced only one resonance peak as the shape formed was likely spherical. Thus, 2 h of growth time was not enough to form anisotropic NPs. Next, GA 5.0 and GB 5.0 with 5 h of growth time produced broad resonance peaks for both t-
SPR and l-SPR with a weak l-SPR response. GA 8.0 had higher intensities by comparing the peak positions of 2 and 5 h of growth time. In addition, for PVP 40 k, as the size of GNPs increased, the longitudinal and transverse plasmon resonances were both affected; however, the longitudinal axis was more polarisable and more sensitive to size changes.

The samples with PVP 55 k showed similar optical response trend as PVP 40 k. The absorbance for GB 2.0, GB 5.0 and GB 8.0 were 0.021, 0.185 and 0.299, respectively. It was related to the amount of particle density, as previously calculated. GB 2.0 had a single resonance peak, while GB 5.0 had a broad resonance response with weak l-SPR peak. GB 8.0 had higher intensities with almost clear t-SPR and l-SPR peak responses. Also, it is observed that both t-SPR and l-SPR for GB 5.0 and GB 8.0 were right-shifted, or called as red-shifted, indicating that larger NP size and anisotropic nanostructures formed.

**Implementation of GNPs as sensing material thin film on the detection of chlorothalonil**

The sample with optimum synthesis parameters was further used as a sensing material for the developed sensor set-up to detect a fungicide, namely chlorothalonil. In this section, sensor testing was carried out in four different media, that is, air, DI water, bare GNPs and 30.0-mM chlorothalonil solution. The sensitivity of the sensor was investigated with observation onto the changes in peak positions (wavelength shift) and intensities.

From Figure 13, all responses with GNPs as a sensing material showed two peaks referring to t-SPR and l-SPR response bands. It was clearly seen that the sensor response in pure chlorothalonil without GNPs showed almost consistent intensity with no significant peaks of both l-SPR and t-SPR.

According to Mie theory, the peak resonance wavelength of the NP plasmon resonance is influenced by the local refractive index, \( \eta \). In this study, when the particles were in air (\( \eta = 1.00 \)), the peak wavelength of the plasmon resonance was 860.16 nm, while in water (\( \eta = 1.33 \)), the peak resonance of GNPs was 909.70 nm; there was a right-shift (red-shift) of the peak position, which was 49.54 nm. Similar changes were also observed when DI water was replaced with 30.0-mM concentration of chlorothalonil solution. The change in the response can be related to the change of the refractive index of the surrounding medium.

|          | t-SPR | l-SPR |
|----------|-------|-------|
|          | Wavelength (nm) | Absorbance (a.u.) | Wavelength (nm) | Absorbance (a.u.) |
| GA 2.0   | 555    | 0.021 | –        | –        |
| GA 5.0   | 555    | 0.185 | 628      | 0.141    |
| GA 8.0   | 555    | 0.299 | 657      | 0.282    |
| GB 2.0   | 545    | 0.052 | –        | –        |
| GB 5.0   | 549    | 0.146 | 623      | 0.118    |
| GB 8.0   | 550    | 0.284 | 651      | 0.286    |

t-SPR: transverse surface plasmon resonance; l-SPR: longitudinal surface plasmon resonance.

**Figure 13.** Optical responses spectra of GNPs in four different medium: (A) pure GNPs, (B) pure chlorothalonil, (C) GNPs in DI water and (D) GNPs in 30.0 mM chlorothalonil. GNP: gold nanoparticle; DI: deionized.
water ($\eta = 1.33$) and chlorothalonil ($\eta = 1.633$). As the refractive index of the surrounding medium is increased, the SPR red-shifts to longer wavelengths.\(^5\)\(^6\) This effect allows plasmonic NPs to be used as an efficient plasmonic sensor. Hence, when molecules adsorb to or desorb from the particle surface, the local refractive index changes, resulting in an SPR wavelength shift. Furthermore, the optical spectra showed that absorbance intensity changes when the medium changes. The intensity of GNPs in the air was higher compared to GNPs in solution due to low refractive index of air. The results are summarized in Table 3.

Therefore, the implementation of GNPs as a sensing material proves to increase the sensitivity of this sensor due to the plasmonic effect. The NP’s optical properties are highly reliant on material composition and size and the medium in which the particles are surrounded, caused by electron vibration from the interaction between light and free electrons on the nanogold surface.\(^5\)\(^7\)

### Conclusion

GNPs was successfully synthesized on the substrate using SMGM. All samples exhibit two distinct surface plasmon resonance bands, t-SPR and l-SPR, which correspond to the oscillation of electrons in the shorter (t-SPR) and longer axis (l-SPR), respectively, except for 2 h growth time. Varying the growth time will affect the size of NPs. The size and surface density of GNPs increased as the growth time increased. Although the size increased, the preferred size of GNPs must not be exceeding 100 nm as it is not suitable to be used as localized plasmonic sensing materials. Besides, the shape of GNPs can be controlled by manipulating the MW of PVP, shorter chain (40 k) PVP will mainly produce triangular and square shape while using longer chain (55 k) PVP will produce square and rod shape. Furthermore, the sensitivity of GNPs as sensing material in different surrounding medium, that is, DI water and 30 mM chlorothalonil, was successfully tested. At first, bare GNPs in air medium shows two peaks referring to t-SPR and l-SPR response band. The same results obtained for GNPs in DI water and chlorothalonil but with different peak intensities and positions. Meanwhile, the sensor response in pure 30.0 mM chlorothalonil without GNPs shows almost consistent intensity with no significant peaks of both l-SPR and t-SPR. Therefore, the implementation of GNPs as sensing material proves to increase the sensitivity of this sensor due to its plasmonic effect.

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| Medium                  | t-SPR Wavelength (nm) | t-SPR Absorbance (a.u.) | l-SPR Wavelength (nm) | l-SPR Absorbance (a.u.) |
|-------------------------|-----------------------|-------------------------|-----------------------|-------------------------|
| Pure GNPs (air)         | 450.46                | 0.50                    | 860.16                | 0.48                    |
| Chlorothalonil          | 399.36                | 0.34                    | 909.70                | 0.34                    |
| GNPs + DI water         | 463.99                | 0.45                    | 907.84                | 0.47                    |
| GNPs + chlorothalonil   |                       |                         |                       |                         |

GNP: gold nanoparticle; DI: deionized; t-SPR: transverse surface plasmon resonance; l-SPR: longitudinal surface plasmon resonance.
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