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Formation of Anisotropic Gold Nanoparticles using Wet Chemical Method

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Abstract: This paper presents synthesized gold nanoparticles in nanorods shapes using wet chemical method. The gold nanoparticles forms are classified into spherical shapes and non-spherical shapes. The spherical shapes are basic and commonly synthesize due to its simplicity while non- spherical shapes have their own unique properties. Gold nanorods are one of the non-spherical shapes that highly compliant with the human body, have minimal toxicity, and are adaptable. In this project, wet chemical method namely seed-mediated growth has been used to synthesis gold nanorods. This method is preferred for producing gold nanorods in smaller size, higher yields, and cost less. In this process, during physical observation, the seed solution turned from yellow to light brown while after adding the seed solution into the growth solution, the colour changes to purple colour. Moreover, the molarity of surfactant named cetyl trimethylammonium bromide (CTAB) has been varied with the ranges from 0.1M to 1.0M. There are different colour observed with the variation of surfactant indicated the huge impact of this chemical on the synthesis process. This outcome has been supported by optical and morphological properties. The optical characterization has been observed using the UV-Vis-1800 Shimadzu (Japan) spectrophotometer. The morphology feature of gold nanoparticles was monitored using FESEM, Jeol JSM-7600F Schottky (Japan) with magnification of 100K and voltage acceleration of 5 kV.

Keywords: Nanoparticles, Nanorods, Seed-Mediated Growth Method

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1. Introduction

Gold is a chemical element called Aurum. Au is used as the symbol for gold. Among the elements with the highest atomic numbers, its atomic number is 79. It is often described to as a 'yellow nugget' because the metal in its raw state has a brilliant, slightly reddish yellow, dense, soft, malleable, and ductile appearance. In normal conditions, it is a solid substance.

Gold is found in bulk and nanoparticle form. In this project, the fabricated gold is in nanoparticles. A large range of nanoparticle classifications exists, ranging from less than 1 nm to over 100 nm in size [1]. Nanoparticles have distinctive characteristics as compared to the bulk substance. There are various shapes of nanoparticles which can be classified into two main groups; spherical shapes and non-spherical shapes [2]. The non-spherical shapes such as rods [3], plates [4], rice [5] and many more. These gold nanoparticles are widely used in many nanotechnology areas including biomedicine (medication distribution, cancer gene therapy, respiratory illness diagnostics and prevention, and infections), agriculture, and food processing - nano fertilizers, nanoagrochemicals, agro-pastoral reductions, and biofuels [6]-[7].

In this project, a Seed-Mediated Growth Method (SMGM) has been used to fabricate anisotropic gold nanoparticles with a rod form known as gold nanorods (GNRs). The GNRs have been characterized and analyzed and the surfactants' impact on the GNRs were investigated. The SMGM is the most common method for synthesizing gold nanorods is by growing gold nanorods in seeds. Gold nanoparticle seeds are added to the growing fluid to promote its development.

2. Methodology

Gold nanorods (GNRs) have been produced in this research. The procedure begins with pre-treatment. Before the treatment, all the contaminants need to be removed. The GNRs were synthesized using the SMGM wet chemical technique consists with two stages procedure; Seeding and Growth process. The physical observation has been performed to monitor color changes during these processes. After that, two characterization methods were used to verify GNR formation which are UV-Vis and FESEM. The effect of surfactant on the gold nanoparticle formation has been investigated after the entire procedure is done.

Materials; The materials used for synthesizing the GNRs are sodium borohydride (NaBH4, 98%), hexadecyltrimethylammonium bromide (CTAB, 99%), Lascorbic acid (AA, 98%) products from Sigma Aldrich USA while gold (III) chloride trihydrate (HAuCl4.3H2O) and silver nitrate (AgNO3) with purity 99.99% from Emory Chemicals.

Pre-treatment; The step that precedes conducting the experiment is the pre-treatment procedure. The contaminants and dust are no longer present as a result of the treatment. Figure 1 shows the entire pre-treatment method process. The vials were pre-soaked in ethanol before being placed in the ultrasonic bath for cleaning. After that, the vials were rinsed with DI water. Next, the acetone solution was put into vials and placed in an ultrasonic bath. For ultrasonic bath cleaning, the duration is just 5-10 minutes. Then, vials were washed with DI water. Finally, the vials were dried using convection ovens, utilizing ethanol and acetone solutions. 30 minutes is specified for drying the vials.

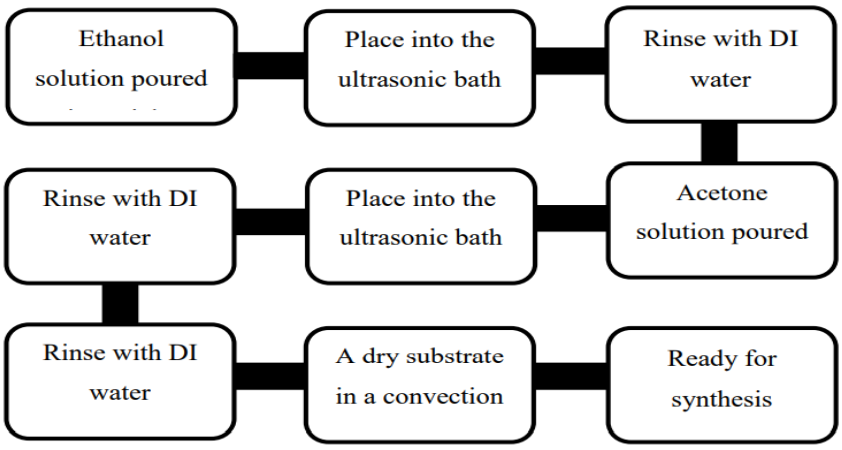


Figure 1: The pre-treatment procedure

Seed solutions for GNRs; The initial stage in generating the quasi-spherical seed solution needs three ingredients: gold(III), CTAB, and borohydride. Adding 15 ml of 0.2 M CTAB as the surfactant to 15 ml of 0.5 mM metal precursor gold(III) will produce the seed solution. Br- ions are displaced by Au3+ in CTAB micelles through a quantitative interaction between the surfactant agent and the precursor [8]. To begin, a fresh batch of ice-cold 0.01 M was added to a solution that contains CTAB, then added to the gold(III) solution. A drop in the concentration of the borohydride anion causes the stabilization of quasi-nanoparticles (NPs) with the CTAB bilayer. As a result, the colour of the seed solution changes from yellow to light brown.

Growth solutions for GNRs; The chemicals used in the growth process include gold(III), CTAB, silver nitrate, L-ascorbic acid, and the seed solution. In a vial, 1mM of gold(III) solution was added to 0.2M of CTAB solution and stored it at room temperature. The capping agents (CTAB) interaction with gold precursor resulted in quantitative displacement of Br– ions by Au3+ in CTAB micelles. Silver nitrate and L-ascorbic acid solution are then combined with the prepared solution. Thirty seconds after beginning mixing, the solution turns from yellow to colourless. The L-ascorbic acid reduces the Au3+ ions coupled to CTAB micelles to Au (I) and the outcome is Au (I). The seed solution was injected into a vial containing stable Au+ ions, and the solution is rapidly agitated for one minute.

Centrifuge process on GNRs; This centrifugation process was used to differentiate various nanoparticle morphologies and separate the precipitate from the supernatant. Firstly, the centrifuge tube contains 10 ml of GNR growth solution and the solution was then centrifuged for 60 minutes at 5000rpm using an Eppendorf Centrifuge 5804 from Germany. Centrifugation separates the growing fluid above the precipitate or sediment from the remainder of the solution. The precipitate is the development of a separate substance from a developing solution consisting of NPs. At the bottom of the centrifuge tube, a first layer of precipitate was visible. A pipette is used to remove the supernatant from the centrifuge tube holding the precipitate and 3 mL of DI water was added after the procedure has been performed. To ensure the full concentration of precipitates are collected and re-suspended in 3 mL of DI water, the second centrifugation step was performed. Figure 2 shows the centrifugation process to separate the growth solution with a speed 5000rpm for 1 hour and a sample of separation precipitate and supernatant.

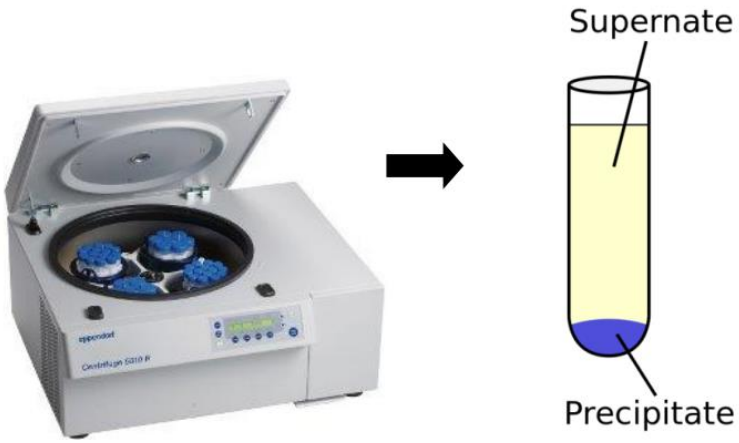


Figure 2: Centrifugation process to separate the growth solution with a speed 5000rpm for 1 hour and a sample of separation precipitate and supernatant.

Then, the GNR growth solution is available for drop-drying on the substrate surface, prior to characterization. Drop-drying methods was used to put the GNRs sample onto substrate in order to identify the optical and morphological features of GNRs. In this process, 30 mL of the growth solution was dropped onto a 1 cm × 1 cm area of the substrate surface and allowed to dry at room temperature as shown in Figure 3. In order to be used as the sample material in the characterization process, it must be fully dried.

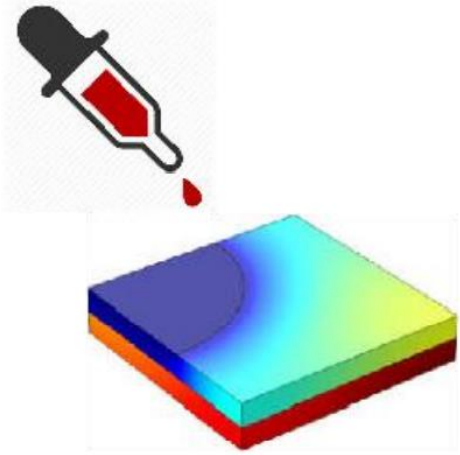
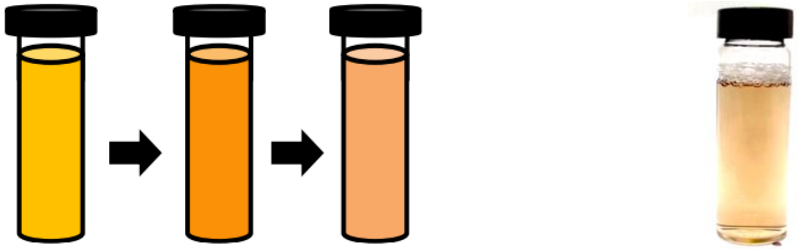


Figure 3: A drop-drying of a growth solution after centrifugation on a thin film substrate.

3. Results

3.1 Physical Colour Changes on the Seed Solution

The seed solution became orange following the addition of the CTAB. After a little while, the solution was added to the ice-cold $NaBH_4$. The color of the seed solution fades to a pale brown. All the solutions are shown in Figure 4.



(a) (b)

Figure 4: (a) After mixed with three materials: $HAuCl_4$. $3H_2O$, CTAB, and $NaBH_4$ (b) After mixing the three ingredients, the seed solution changes colour to a light brown

3.2 Physical Colour Changes on the Growth Solutions of GNRs

The $AgNo_3$ was mixed with the 0.1M CTAB surfactant as a first sample. Then, after both materials have been mixed up, HAuCl4. 3H2O was added to the solution. The colour starts to change from a colourless solution into orange colour. The L-ascorbic acid was added, and the solution starts to change into a colourless solution. This condition happens due to Au3+ ions bound to CTAB micelles reduced to Au (I) by the L-ascorbic acid. After a few seconds, the seed solution was added to the solution. The growth solution will slowly change into purple in a few minutes, as shown in Figure 5.

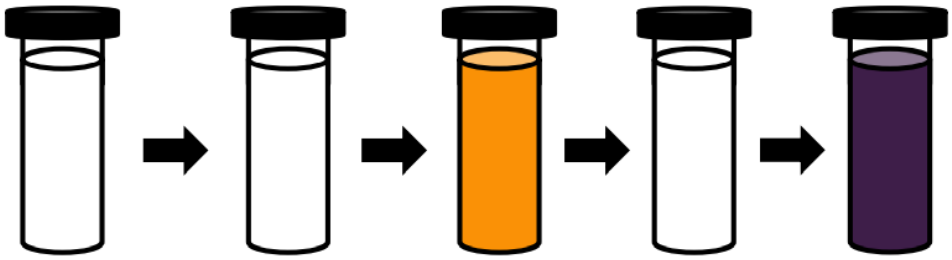


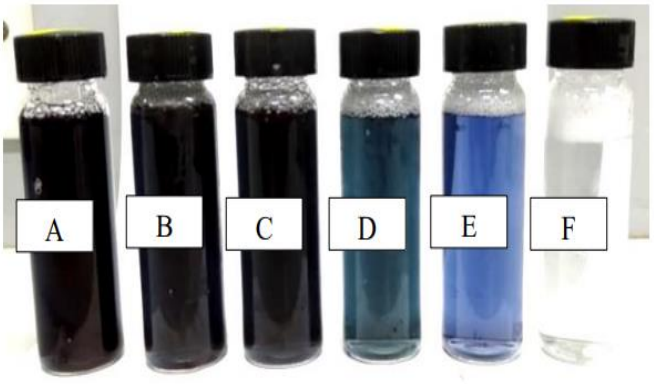
Figure 5: The growth solution after adding AgNo3, CTAB, HAuCl4. 3H2O, L-ascorbic acid, and seed solutions.

3.3 Effect of Centrifugation Process to the Growth Solution

The samples had been observed in the centrifugation process. From the observation, the varied colors changed in the growth solution due to the separation of nanoparticles that spin after two centrifugations at a speed of 5000 rpm for 60 minutes each. Before the centrifugation process, the dark purple solution colour was the original colour. All six samples have changed colour from dark purple to light purple. Thus, it visualized that this NPs rod is a low aspect ratio and surface density. Since GNRs are known to have their intrinsic stimulation of surface plasmon vibrations, changes in the colour of the solution may be linked to the production of high-density GNRs.

3.4 Effect of CTAB Surfactant on the Growth Solution

The effect of CTAB surfactant has been studied by examined six samples of growth solution with different range of molarity in CTAB material. The CTAB molarity range start from 0.1M, 0.2M, 0.4M, 0.6M, 0.8M and 1.0M. The CTAB concentration became viscous. Thus, this condition will affect the growth solution's colour changing, as shown in Figure 6. In the physical observation, the color for lower molarity of CTAB seems darker compared to higher molarity of CTAB.

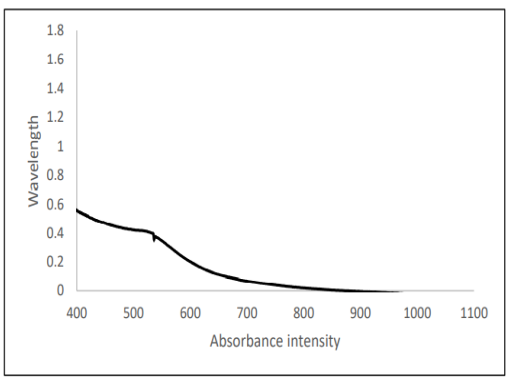


(a)

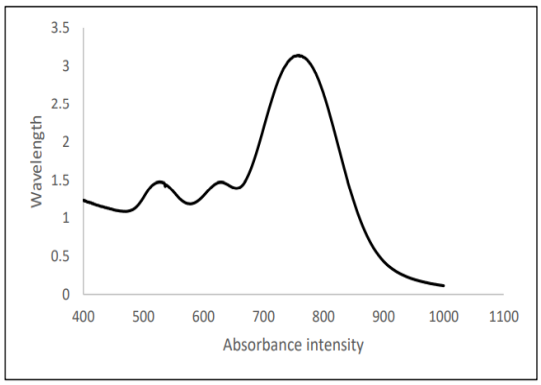
(b)

Figure 6: The growth solution with different molarity of CTAB. Vial A to F contain of 0.1M, 0.2M, 0.4M, 0.6M, 0.8M, and 1.0M molarity CTAB surfactant. (a) Before the growth process (b)The growth solution colour changing after 20 hours. The colour changing depends on the CTAB surfactant, which is the more viscous CTAB solution, the paler colour of the growth solution.

Then, the extinction coefficients of the seed and growth solutions of the GNRs are measured using the UV-Vis spectrophotometer to show the details in the wavelength and absorption intensity function as shown in Figure 7.



(a)



(b)

Figure 7: The wavelength and absorbance intensity of (a) seed solution and (b) growth solution.

The resulting for all data are plotted into a graph, as illustrated in Figure 8. It shows dual-band (transverse and longitudinal axis) peaks throughout the visible and near infra-red spectrum. Table 1 lists all the readings for the results.

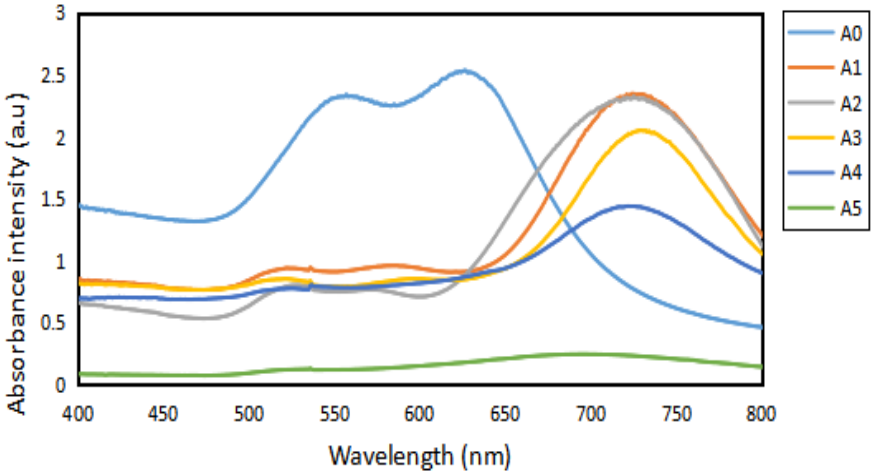


Figure 8: The optical response for various CTAB surfactant of GNRs

Table 1: The transverse and longitudinal band peaks at different CTAB surfactants on GNRs

Sample	Δ Peak Position(nm)		Absorbance Intensity (a.u)	
	t-SPR	***l-SPR***	***t-SPR***	***l-SPR***
A0	561	632	2.236	2.508
A1	585	728	0.96	2.345
A2	575	727	1.253	2.34
A3	596	733	0.854	2.04
A4	587	726	0.804	1.439
A5	538	700	0.118	0.244

In this studies, 6 variances of CTAB surfactant are prepared with various molarity of the surfactant agents. The Mie theory [9]-[10] used to compute the UV-visible absorption spectra of a relatively dilute dispersion of colloidal particles, and this method is a reliable tool for characterizing metal nanoparticles. Resonant peak absorbance magnitude may show the concentration of nanoparticles. The sample of A0 showing the peak of t-SPR at 561 slightly different from other sample peak position that are following the trend. This condition occurs because of the small amount of CTAB surfactants, where the roles of surfactant is to stabilize the nanoparticles. The relationship between surface area and volume increases with increasing size, progressively decreasing trend.

Finally, the FESEM image for GNRs with 0.1M CTAB surfactant confirmed the gold nanorods have been successfully synthesize in this study with density 58.6% as shown in Figure 9.

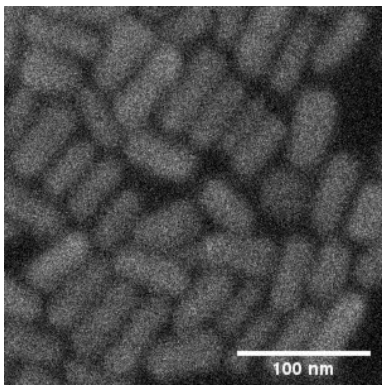


Figure 9: The FESEM image for GNRS with 0.1M CTAB

4. Conclusion

One of the most interesting and promising golden nanomaterials is gold anisotropic nanoparticles. The nanoparticles have diameters ranging from one to one hundred nanometers. Metal nanoparticles are primarily controlled by many different optical, catalytic, electrical, chemical sensing, and therapeutic uses. This study seeks to synthesize anisotropic gold nanoparticles using a wet chemical technique that is a seed-mediated growth method. Two types of characterization were used: optical, and morphological. The UV-Vis spectrophotometer evaluated the seed and growth solution of the GNRs as an extinction function. Surfactant seems to affect the gold nanoparticles' anisotropy while varying the concentration of CTAB. Recording the colour of the growth solutions has shown that the surfactant has an impact on the GNRs. In minutes, the CTAB surfactant becomes purple in colour. Au reduces the CTAB micelles, allowing L-ascorbic acid to get into solution (I). The solution will progressively become purple. After two centrifugations, the solution becomes purple. It is possible that the high-density GNRs were responsible for generating the surface plasmon vibrations. The optical response shows dual-band (transverse and longitudinal axis) peaks throughout the visible and near infra-red spectrum. The FESEM images confirmed the formation of gold nanorods in this process.

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