# Seed-Mediated Synthesis of Gold Nanorods with Variation of Silver Nitrate ($AgNO_3$) Concentration

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***Abstract*—Gold nanostructures, such as gold nanorods (AuNRs) had been widely used in variety of utilization including disease detection, drug delivery, biomedical imaging, biosensing and many more. Many studies have been done by researchers due to its unique plasmon resonance properties as well as this research. This paper reports an investigation on the effects of Silver Nitrate ($AgNO_3$) concentration in producing AuNRs. In this study, AuNRs were synthesized using Seed Mediated Growth Method (SMGM) where the concentration of $AgNO_3$ was varied with 0.5 mM, 1.0 mM, 2.0 mM, 3.0 mM, 4.0 mM, 5.0 mM and 6.0 mM to optimize the aspect ratio, density and homogeneity of AuNRs using physical and optical characterization. The color changed from pale yellow to brownish when iced cold freshly prepared Sodium Tetraborohydride ($NaBH_4$) added to the seed solution. In addition, the color of solution changed from pale yellow to colorless as ascorbic acid added to growth solution. The final color of growth solution varied from pale blue to light violet as the concentrations of $AgNO_3$ used were different. Two parameters namely peak position and intensity obtained from transverse surface plasmon resonance (t-SPR) and longitudinal surface plasmon resonance (l-SPR) were analyzed. The optical spectra for all samples show two peaks. The first peaks in the range of 500 nm to 600 nm which are correspond to t-SPR and the second peaks are located in the range of 630 nm to 730 nm which correspond to l-SPR. The results show that the aspect ratio and the size of AuNRs increased as the concentration of $AgNO_3$ increased while the homogeneity decreased as the concentration of $AgNO_3$ increased. It was also found that the concentration of $AgNO_3$ affected the growth of gold nanostructures. Higher concentration of $AgNO_3$ resulted in larger size, higher aspects ratios and thus red shifted the surface plasmon resonance. Hence, the two peaks AuNRs is very suitable to be used in sensing application with the peak position as its sensing parameter.**

***Index Terms*—Localized Surface Plasmon Resonance; Gold Nanorods; Gold Nanoparticles; Silver Nitrate ($AgNO_3$) concentration; Seed Mediated Growth Method (SMGM).**

## I. Introduction

Metallic nanostructures, such as gold, had demonstrated exceptional radiative, nonradiative and optical properties, reasonable for an extensive variety of utilization including disease detection, diagnosis and therapy, drug delivery, biomedical imaging, biosensing and many more [1]. Apparently, gold nanospheres is the most commonly used due to its simple and easy preparation and synthesizing method [2]. However, the absorption strength of metal nanospheres is weak that dependent on its size, which limits its application in sensing. When anisotropy is added to the nanoparticles, such as nanorods or prisms, the surface plasmon resonance absorption will be enhanced and also strongly dependent on the size of such rods (tunable as a function of aspect ratio). Introducing anisotropy into the nanoparticles can also make a substantial change in their magnetic properties. This makes gold nanorods (AuNRs) potentially useful as sensing materials in plasmonic sensor.

Although there are numerous methods to produce high quality gold nanorods, the seed mediated growth methods is likely a potential approach for producing high quality gold nanorods due to the simplicity of the procedure for controlling the growth from the nanoseed. Seed Mediated Growth Method (SMGM) has been introduced by N. R. Jana and M. El-Sayed [1,2]. Thus far, many researches have been done in synthesizing AuNRs with variation of time [3], surfactant [4], temperature [5], pH [6] and other parameters [7].

Therefore, this study will review the effect of Silver Nitrate ($AgNO_3$) concentration in synthesizing AuNRs using SMGM as well as to optimize the aspect ratio when varying the concentration. The physical and optical properties of AuNRs have been analyzed and presented in this paper.

## II. Experimental

The synthesis process of gold nanorods (AuNRs) by Seed Mediated Growth Method (SMGM) was divided into two main parts which are seeding process and growth process. The seeding process is to plant nanoseeds whereas growth process is to grow the nanoseed, according to desired shapes. The chemicals used for the synthesis process were Hydrogen Tetrachloroaurate ($HAuCl_4.3H_2O$), Sodium Tetraborohydride ( $NaBH_4$), Cethyltrimethy Ammonium Bromide (CTAB), Ascorbic Acid (AA) and Silver Nitrate ($AgNO_3$). These chemicals were purchased from Sigma-Aldrich, St. Louis, USA except Ascorbic Acid (AA) and Silver Nitrate ($AgNO_3$). Ascorbic acid were obtained from Wako Pure Chemicals Ltd., Richmond, USA and Silver Nitrate ($AgNO_3$) were obtained from Emory Chemicals, Atlanta, Canada.

As mentioned, seeding process was carried out to plant nanoseeds in the solution. Three types of chemicals were used and mixed in the seeding process. 0.25ml of 5.0 mM $HAuCl_4.3H_2O$ and 5 ml of CTAB were mixed and the solution was shaken for 1 minute. The solution is referred as Solution A.

After that, 0.6 ml freshly prepared ice cold 0.01 M $NaBH_4$ was added into the solution. The color of solution changed from light yellow to brownish. The seed solution will be carried into growth process after the seeding process completed. Figure 1 shows the schematics of seeding process for AuNRs.

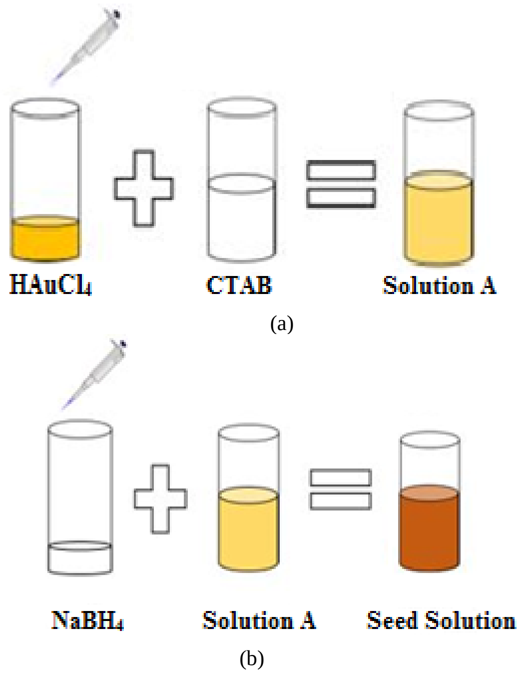



Figure 1: Preparation of Seeding Process for AuNRs. (a) $HAuCl_4$ mix with CTAB, (b) $NaBH_4$ added to the $HAuCl_4$ mix with CTAB

Then, the growth of gold nanoseeds into gold nanorods was determined and monitored in this process. Few chemicals were mixed to produce desired shaped of AuNRs. There were four chemicals used in growth solution preparation. The chemicals were 0.1 ml of 5.0 mM Hydrogen Tetrachloroaurate ($HAuCl_4.3H_2O$), 5 ml of 0.2 M CTAB, Silver Nitrate ($AgNO_3$) and 0.1ml of 0.1M Ascorbic Acid (AA). Firstly, the solution was prepared by mixing CTAB, $HAuCl_4$ and $AgNO_3$ (referred as Solution B). Then, 0.1 ml of AA was added to the Solution B and the solution color become colorless (referred as Solution C). The molarity of $AgNO_3$ was varied according to the listed concentrations as in Table 1 to study the effect of the aspect ratio and homogeneity of the produced AuNRs.

After that, 0.1 ml of the nanoseed solution was added to the Solution C followed by rigorously shaking for about 10 seconds to mix the reagents. The solution was left undisturbed in a controlled water bath at 28 $^{0}$C. After 2 hours of growth process, the reaction was stopped. The process which is shown in Figure 2 was repeated by changing the molarity of $AgNO_3$ according to the concentrations given in Table 1. Ultraviolet-Visible Spectroscopy (UV-Vis), UV-1800 from Shimadzu was used to investigate the optical AuNRs characterization.

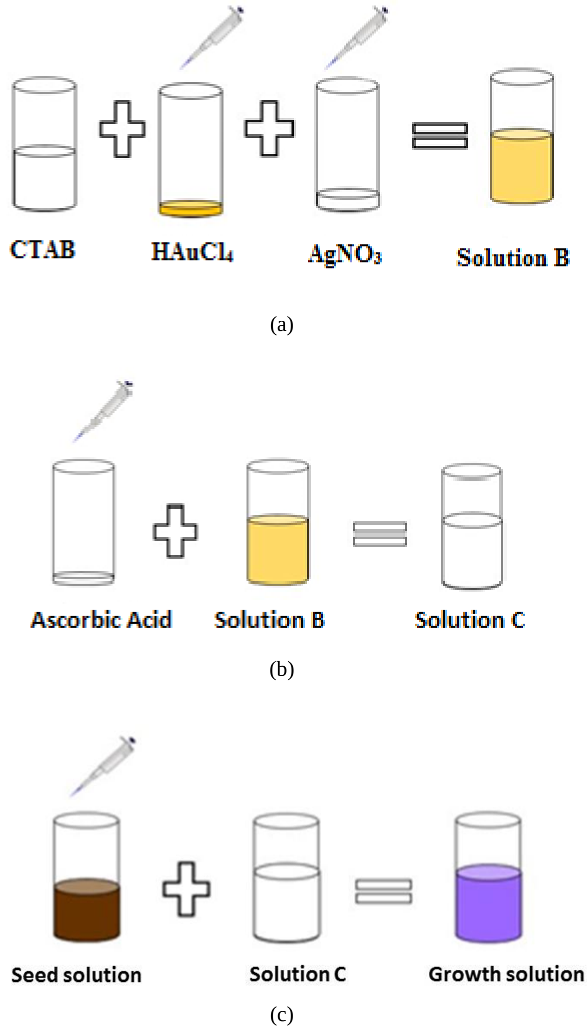



Figure 2: Preparation of growth process for AuNRs. (a) Mixture of CTAB, $HAuCl_4$ and $AgNO_3$ (Solution B), (b) Ascorbic acid added to the Solution B (Solution C) and (c) Seed solution added to the mixture of Solution C.

Table 1
The Molarity of $AgNO_3$

| *Sample* | *$AgNO_3$ (ml)* |
|---|---|
| 1 | 0.5 |
| 2 | 1.0 |
| 3 | 2.0 |
| 4 | 3.0 |
| 5 | 4.0 |
| 6 | 5.0 |
| 7 | 6.0 |

## III. RESULT AND ANALYSIS

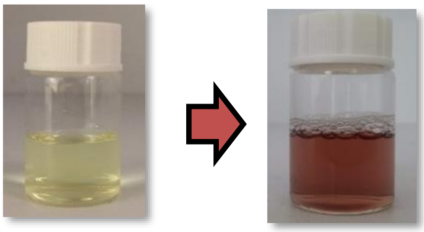
The gold nanorods (AuNRs) was successfully grown in the solution. It was observed using two characterization methods, physical and optical observation. The details of the results as discussed below.

### *A. Physical Observation*

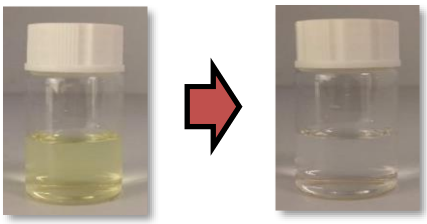
Physical observation is performed to monitor changes during synthesizing AuNRs. During the seed solution preparation, CTAB was mixed with $HAuCl_4$ and the color of the solution turned to light yellow. When the ice cold freshly prepared $NaBH_4$ was added to the seed solution, the color changed from light yellow to brownish indicating the formation of nanoseeds in the solution. The result is shown in

Figure 3(a). The change of solution color is similar as reported by Akrajas et. al [9, 13].

The growth solution was prepared by mixing Hydrogen Tetrachloroaurate ($HAuCl_4.3H_2O$), CTAB and Silver Nitrate ($AgNO_3$). This solution's color is light yellow and turned to colorless as ascorbic acid added to it. The result is shown in Figure 3 (b). After that, 0.1 ml of nanoseed solution was added to growth solution and the color of these solutions gradually changed within 60 minutes. Figure 4 shows the different concentration of $AgNO_3$ in the growth solution. The color of the final solutions for each concentrations are different, indicating a different plasmon band for each reaction [3–4].



(a)



(b)

Figure 3: (a) The seed solution (b) The growth solution

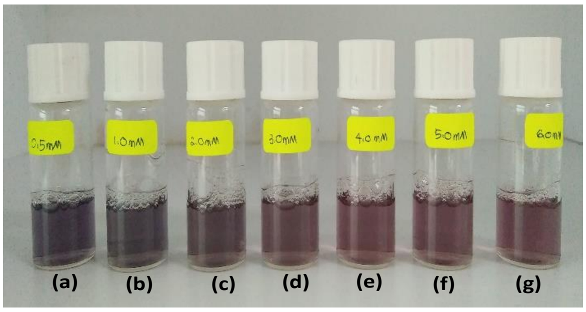



Figure 4: The different colors for different concentrations of $AgNO_3$ added into the growth solution. (a) 0.5 mM $AgNO_3$ (b) 1.0 mM $AgNO_3$ (c) 2.0 mM $AgNO_3$ (d) 3.0 mM $AgNO_3$ (e) 4.0 mM $AgNO_3$ (f) 5.0 mM $AgNO_3$ (g) 6.0 mM $AgNO_3$

*B. Morphological and Optical Characterization*

The sample with 4.0 mM $AgNO_3$ was observed using Field Emission Scanning Electron Microscopy (FESEM) to confirm the formation of nanorods on the substrate surface. Figure 5 shows the FESEM images of AuNRs on the ITO glass substrate with aspect ratio W/L= 5 (W~ 20 nm, L~ 100nm).

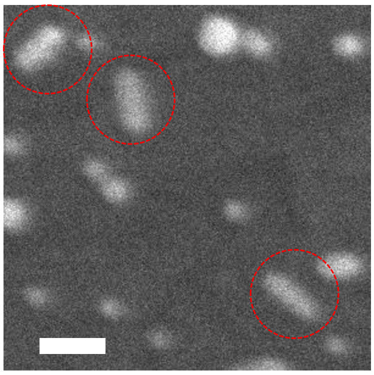


Figure 5: The formation of AuNRs on ITO substrate. Scale: 100 nm

The AuNRs will have two resonance bands as shown in Figure 6 and it will be obtained during the optical characterization process.

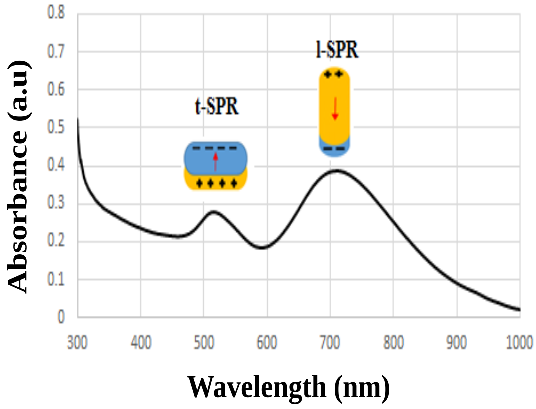



Figure 6: An example of AuNRs surface plasmon resonance with schematic describing the electron oscillations along the two axes within the nanorods [10].

UV-Vis was used to test the absorption of light in ultraviolet-visible, visible and adjacent (near-UV and near-infrared [NIR]) spectral region ranges of the synthesized sample. This testing also known as optical characterization. In the formation of AuNRs using UV-Vis, the pattern shall shows two absorption bands that represented transverse and a longitudinal surface plasmon resonance (t-SPR and l-SPR). The t-SPR is typical for gold nanoparticles with strong absorbance band in visible region of 500 – 600 nm [9]. For AuNRs, the t-SPR is referred to the width of the nanorods and l-SPR is referred to the length of the nanorods. These two parameters were used to analyze the aspect ratio of AuNRs [10]. The concentration of $AgNO_3$ were varied in this study thus tuned the aspect ratio of AuNRs [1,10, 14].

AuNRs exhibit two distinct plasmon resonance bands arising from their anisotropic configuration, transverse bands and longitudinal bands, which correspond to the oscillation of electrons in the shorter and longer axis respectively. The longitudinal band is extremely sensitive to changes in local environment and interparticle distance that depends on the aggregation and dispersion status [6–8]. Figure 7 show the individual optical spectra for all samples and it can be seen that all samples have two distinct plasmon resonance bands with different peak positions and intensities. Next, the overall optical spectrum for all concentration is shown in Figure 8. The results for all samples were tabulated as in Table 2. From the data, it can be seen that the peak for 0.5 mM $AgNO_3$ are sharper than other samples. While 6.0 mM $AgNO_3$ has the broadest peak among all samples. The width of spectrum is related with homogeneity of the AuNRs [8, 11]. Sample 1 with 0.5 mM silver nitrate ($AgNO_3$) has the sharpest peak indicating that the samples are the most homogenies sample. In contrast, sample 7 with 6.0 mM $AgNO_3$ has the broadest peak, which mean-it is the least homogeny sample.

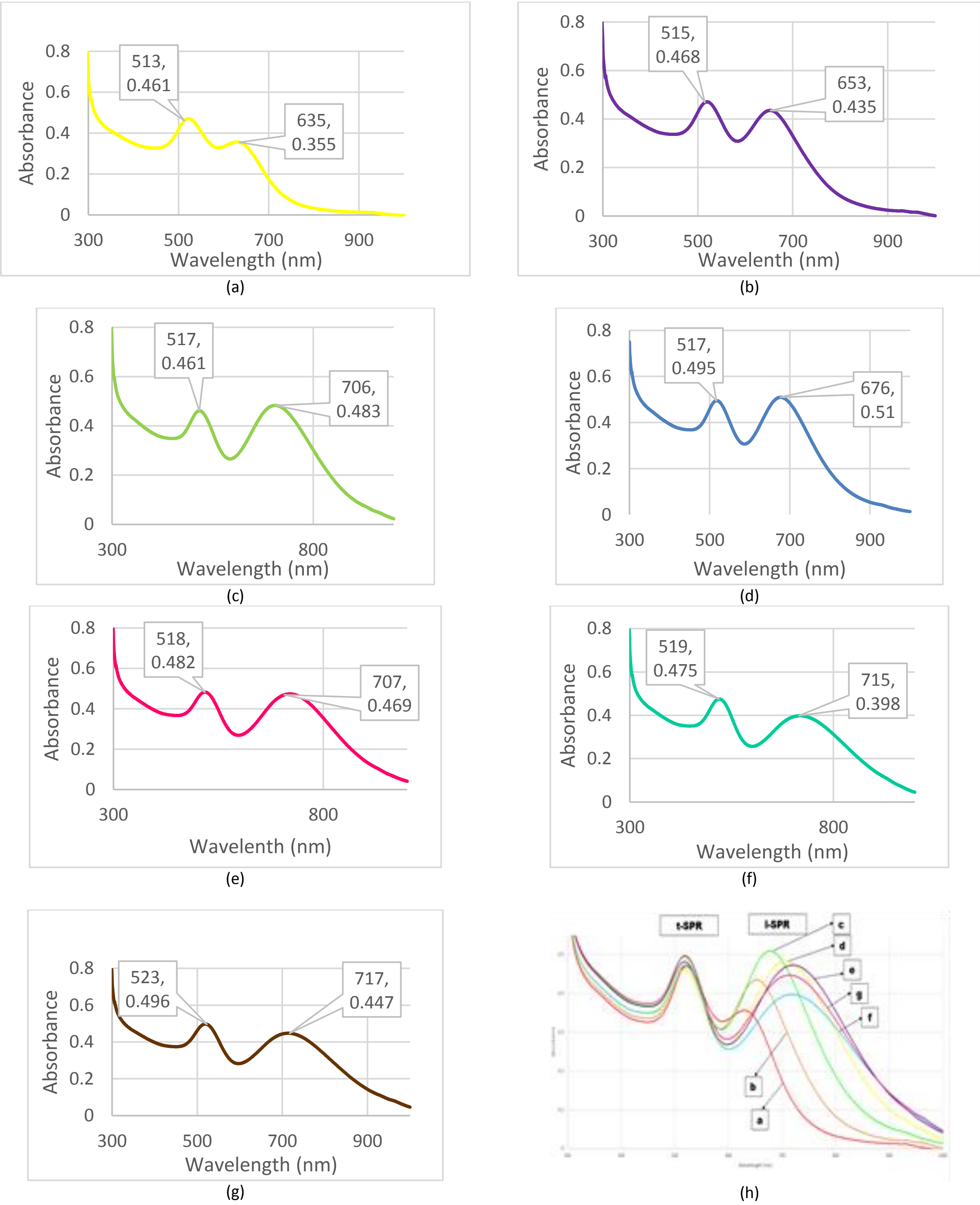



Figure 7: The UV-Vis absorption spectra by using different molarity of $AgNO_3$. (a) 0.5 mM $AgNO_3$ (b) 1.0 mM $AgNO_3$ (c) 2.0 mM AgNO3 (d) 3.0 mM AgNO3 (e) 4.0 mM AgNO3 (f) 5.0 mM AgNO3 (g) 6.0 mM AgNO3 (h) All concentration of $AgNO_3$

Moreover, increasing the amount of silver ions (by increasing the molarity of $AgNO_3$) leads to higher aspect ratios of AuNRs [1], which is consistent with the shifting of surface plasmon resonance to right side [8 - 9]. The prominent red shift of the longitudinal plasmon band in the optical spectra of noble metal particles with increasing aspect ratio is a well-known phenomenon [15]. As the aspect ratio increases, the long wavelength plasmon band shifted to the right or called red shifted. From our observation, the variation of $AgNO_3$ concentration does not affect the intensity. Thus, it was found that the AuNRs using 3.0 mM of $AgNO_3$ have optimum aspect ratio and sharp peak.

Table 2
Tabulated Data of the UV-Vis Results.

| Molarity $AgNO_3$ (mM) | Wavelength (nm) | | Intensity | |
|---|---|---|---|---|
| | l-SPR | t-SPR | l-SPR | t-SPR |
| 0.5 | 513 | 635 | 0.461 | 0.355 |
| 1.0 | 515 | 653 | 0.468 | 0.435 |
| 2.0 | 517 | 676 | 0.461 | 0.483 |
| 3.0 | 517 | 706 | 0.495 | 0.510 |
| 4.0 | 518 | 707 | 0.482 | 0.469 |
| 5.0 | 519 | 715 | 0.475 | 0.398 |
| 6.0 | 523 | 717 | 0.496 | 0.447 |

## IV. CONCLUSION

In this study, the physical and optical properties of gold nanorods (AuNRs) were investigated. The concentration of silver nitrate ($AgNO_3$) were varied into six different concentrations which are 0.5 mm, 1.0 mm, 2.0 mm, 3.0 mm, 4.0 mm, 5.0 mm and 6.0 mm during growth process. According to the results, it was found that, increasing the amount of silver ions leads to higher aspect ratios of gold nanorods which is consistent with red shifting of surface plasmon resonance. The sharp and narrow peak of transverse surface plasmon resonance (t-SPR) and longitudinal surface plasmon resonance (l-SPR) response are very important in plasmonic sensing applications for good sensitivity and repeatability

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## REFERENCES

[1] X. Huang, S. Neretina, and M. A. El-Sayed, “Gold nanorods: From synthesis and properties to biological and biomedical applications,” *Adv. Mater.*, vol. 21, no. 48, pp. 4880–4910, 2009.

[2] M. Morsin, M.M. Salleh, A.A Umar, Burhanuddin Yeop Majlis, " High sensitivity localized surface plasmon resonance sensor of gold nanoparticles: Surface density effect for detection of boric acid "*Semiconductor Electronics (ICSE), 2012 10th IEEE International Conference on*, pp .352 - 356, 2012

[3] M. A. El-Sayed, “Some interesting properties of metals confined in time and nanometer space of different shapes,” *Acc. Chem. Res.*, vol. 34, no. 4, pp. 257–264, 2001.

[4] N. R. Jana, L. Gearheart, C. J. Murphy, L. Gearheart, and C. J. Murphy, “Seed-Mediated Growth Approach for Shape-Controlled Synthesis of Spheroidal and Rod-like Gold Nanoparticles Using a Surfactant Template,” *Adv. Mater.*, vol. 13, no. 18, pp. 1389–1393, 2001.

[5] H. N. Verma, P. Singh, and R. M. Chavan, “Gold nanoparticle: Synthesis and characterization,” *Vet. World*, vol. 7, no. 2, pp. 72–77, 2014..

[6] M. S. El-Deab, “Electrocatalysis by nanoparticles: Oxidation of formic acid at manganese oxide nanorods-modified Pt planar and nanohole-arrays,” *J. Adv. Res.*, vol. 1, no. 1, pp. 87–93, 2010.

[7] S. Eustis and M. a el-Sayed, “Why gold nanoparticles are more precious than pretty gold: noble metal surface plasmon resonance and its enhancement of the radiative and nonradiative properties of nanocrystals of different shapes.,” *Chem. Soc. Rev.*, vol. 35, no. 3, pp. 209–217, 2006

[8] Y. Sun and Y. Xia, “Shape-controlled synthesis of gold and silver nanoparticles.,” *Science*, vol. 298, no. 5601, pp. 2176–9, 2002.

[9] Akrajas, M. Mat Salleh, and M. Yahaya, “Enriching the selectivity of metalloporphyrins chemical sensors by means of optical technique,” *Sensors Actuators, B Chem.*, vol. 85, no. 3, pp. 191–196, 2002.

[10] B. Grillo, “Synthesis and Alignment of Gold Nanorods for Optical Applications,” *Igarss 2014*, no. 1, pp. 1–5, 2014.

[11] J. Cao, T. Sun, and K. T. V Grattan, “Gold nanorod-based localized surface plasmon resonance biosensors: A review,” *Sensors Actuators, B Chem.*, vol. 195, pp. 332–351, 2014.

[12] L. B. Sagle, L. K. Ruvuna, J. a Ruemmele, and R. P. Van Duyne, “Advances in localized surface plasmon resonance spectroscopy biosensing.,” *Nanomedicine (Lond).*, vol. 6, no. 8, pp. 1447–62, 2011.

[13] S. Nengsih, A. A. Umar, M. M. Salleh, and M. Oyama, “Detection of formaldehyde in water: A shape-effect on the plasmonic sensing properties of the gold nanoparticles,” *Sensors (Switzerland)*, vol. 12, no. 8, pp. 10309–10325, 2012.

[14] C. J. Huang, P. H. Chiu, Y. H. Wang, C. F. Yang, and S. W. Feng, “Electrochemical formation of crooked gold nanorods and gold networked structures by the additive organic solvent,” *J. Colloid Interface Sci.*, vol. 306, no. 1, pp. 56–65, 2007.

[15] N. R. Jana, L. Gearheart, and C. J. Murphy, “Wet chemical synthesis of high aspect ratio cylindrical gold nanorods,” *J. Phys. Chem. B*, vol. 105, no. 19, pp. 4065–4067, 2001.