The effect of nitric acid and Hexadecyltrimethylammonium Bromide (CTAB) concentration on the morphology and plasmonic properties of gold nanorods

V Fauzia and H E Permana

Department of Physics, Fakultas MIPA, Universitas Indonesia, Depok 16424, Indonesia

E-mail: vivi@sci.ui.ac.id

Abstract. Metal nanoparticles have unique optical properties called Localized Surface Plasmon Resonance (LSPR). Gold nanorods have better plasmonic property for sensor application due to its longitudinal resonance mode is more sensitive to environment dielectric properties changes. Controlling the aspect ratio during the synthesis process becomes important because it would determine the plasmonic properties of the gold nanorods. In this study, gold nanorods have been successfully synthesized in the solution with three different concentrations of HNO$_3$ and CTAB. Increasing the concentration of HNO$_3$ and CTAB tends to increase the length, diameter, aspect ratio and yield of gold nanorods. All samples appeared to have a peak of transversal mode at the wavelength of 510 nm. However, the longitudinal mode peaks could not be seen in this observation.

1. Introduction

Nanoparticles have attracted much attention among researchers. It is well known that the size and shape of nanoparticles produced the unique physical and chemical properties which are very different from those in the bulk size, due to the high fraction of the atoms or molecules on the surface of nanoparticles. Unique characteristic of metal nanoparticles that has attracted many attentions is the effect of Localized Surface Plasmon Resonance (LSPR), which was then shortened as a plasmonic effect. This optical property arises as an effect of the resonance between the collective oscillations of conduction electrons of the metal nanoparticles with the electric field oscillation of the incoming light. In the case of gold and silver nanoparticles, this effect could be observed by the occurrence of absorption peaks in the visible light [1]. Metal nanorods show two plasmonic peaks, longitudinal and transversal peaks, where both have its own wavelength characteristic depends on the aspect ratio of nanorods [2]. Therefore, controlling the aspect ratio of nanorods during the synthesis process becomes important to study, since it would determine the plasmonic properties later on.

In general, the nanoparticles which were produced in solution would have relatively less homogeneous in shape and size. Seed-mediated growth method developed by Murphy was able to produce the gold nanorods with aspect ratio of 18 [3]. Some other studies has reported the effect of the NaOH, AgNO$_3$, HCl, H$_2$SO$_4$, H$_3$PO$_4$, and HNO$_3$ addition on the morphology of the nanoparticles [4]. It has been known that the surfactant plays an important role as a soft micellar template which could control the length and yield of nanorods [5]. Therefore, in this study we want to learn the effect of
HNO₃ and Hexadecyltrimethylammonium bromide (CTAB) addition as surfactant on the shape and yield of the produced gold nanorods.

2. Experiment

The synthesis method used in this research was conducted by modifying the seed-mediated growth method that was developed in our previous work [4]. In this method there are four kinds of solutions, i.e a seed solution A, consisting of 0.2 mL C₆H₅Na₃0.2H₂O 0.025M and 19.8 mL HAuCl₄·3H₂O 0.00025M. Then 0.6 mL of iced cold 0.1M NaBH₄ was added into seed solution and was left for 60 minutes at room temperature. Meanwhile, the growth solution consisted of three solutions, i.e. 4.5 ml solution B and C (4.5 mL of 0.01M HAuCl₄·3H₂O 0.1125 mL, 25 mL of 0.1M and 25 μL C₆H₅O₆ 0.1M and 4.3875 ml CTAB 0.1M) and 45 ml solution D (1.1125 mL HAuCl₄·3H₂O 0.01M, 250 μL C₆H₅O₆ 0.1M and 43.875 mL CTAB 0.1M). In order to study the effect of the concentration of HNO₃, 300 μL HNO₃ was added into solution D with three variations of concentration i.e. 0M, 0.02M and 0.05M. Meanwhile, to study the effect of the CTAB concentration, solution D containing 0.05M HNO₃ was made with three different CTAB concentrations, i.e. 0.05M, 0.1M and 0.2M.

The gold nanorods synthesis process was started by injecting 0.4 mL of solution A into solution B, and 0.4 mL of this mix solution was then injected into solution C. Afterwards, 4 mL this mixture was injected into solution D and then left it for 24 hours at room temperature to get the precipitation. In order to reduce the contamination of non-rod shaped particles and to get rid of the excess surfactant, the final solution was centrifuged twice for 20 minutes in 2000 rpm. The last precipitate was then dispersed in 1 mL deionized water.

The plasmonic effect characterization of the gold nanorods was conducted using Thermo Fisher Scientific GENESYS 10S UV Visible spectrometer. FESEM Inspect F50 was also employed to characterize the morphology of the gold nanorods.

3. Results and discussion

3.1. The effect of HNO₃

The SEM images of gold nanorods synthesized without and with three different HNO₃ concentrations were shown in figure 1. By observing these three figures, it was confirmed that the gold nanorods appeared as the white rods. Generally, HNO₃ influenced the number, length and the aspect ratio of the gold nanorods produced. The increase of HNO₃ concentration tends to increase the length and yield of gold nanorods.

![Figure 1. The FESEM images of gold nanorods synthesized (a) without and with HNO₃ concentration of (b) 0.02M, (c) 0.05M.](image-url)
To obtain the quantitative data of the gold nanorods dimension, SEM images were taken for 70 pieces of gold nanorods and the length of each nanorod was measured manually. The summary of calculation is presented in table 1. The gold nanorods synthesized without HNO₃ has the average diameter of 20 nm, the average length of 118 nm, and the average aspect ratio of 5.9. It looks less homogeneous; it is reflected in the widening of length distribution (118 ± 37 nm). Gold nanorods synthesized with HNO₃ 0.02M and 0.05M has the average diameter of 24 and 29 nm, the average length of 205 and 247 nm, respectively, and it has the same average aspect ratio of 8.5. They are relatively homogeneous in length, which is reflected from the narrow length distribution. From table 1, the increase of HNO₃ concentration tends to increase the length, the diameter and the aspect ratio of gold nanorods. It has similar trend with the previous results, however the formation of the high aspect ratio of gold nanorods, which was assisted by nitrate ions, still could not be explained clearly. [4]. From table 1, we also observe that the pH of the solution shows only minor change from 3.11 to 3.02. The pH of growth solution with addition of HNO₃ may not be the major factor for the increase of nanorods length.

| HNO₃ (M) | pH     | Diameter (nm) | Length (nm) | Aspect Ratio |
|----------|--------|---------------|-------------|-------------|
| 0        | 3.11   | 20 ± 3        | 118 ± 37    | 5.9 ± 1.8   |
| 0.02     | 3.04   | 24 ± 3        | 201 ± 54    | 8.5 ± 2.0   |
| 0.05     | 3.02   | 29 ± 5        | 247 ± 60    | 8.5 ± 2.7   |

The plasmonic property of the gold nanorods which was obtained by using the UV-VIS absorption spectrum could be seen in figure 4. All samples appear to have a peak at a wavelength of 510 nm, which is confirmed as the transversal mode of the gold nanorods as reported by previously results [4, 6, 7]. All samples are seen to have only one peak at 510 nm. If we use the discrete dipole approximation method to predict the position of the longitudinal peak, the gold nanorods with aspect ratios of 5.9 and 8.5 should have longitudinal peak at the wavelengths of 984 nm and 1234 nm, respectively. In figure 4, the peak at 984 nm is not clearly seen, it could be caused by little amount of gold nanorods. Meanwhile, the peak at 1234 nm could not be observed because it is beyond the spectrum range of the instrument.
3.2. The effect of CTAB

Figure 3 shows the SEM images of gold nanorods synthesized with three different CTAB concentrations. It shows that the higher CTAB concentration, the longer gold nanorods were produced. However, the nanosphere and nanoplates also presented besides nanorods. Table 2 shows the quantitative data of the average of diameter, length, and aspect ratio of gold nanorods synthesized with three variations of CTAB concentrations. It is clearly seen that by increasing CTAB concentration the length of nanorods were also increased significantly from 273 nm to 526 nm, in the other side slightly the diameter were slightly reduced from 26 nm to 29 nm. This result corresponded to the aspect ratio, which increased from 10 to 18. These results are similar to those reported on previous researches, where the similar research was conducted by varying the CTAB concentration from 0.1M to 0.6M. Yoshiko et.al. reported that increasing the CTAB concentration leads to the enhancement of gold atoms number which was bonded with CTAB, therefore the longer gold nanorods could be produced [8]. Another analysis suggested that the surfactant concentration plays an important role to maximize the dissociation of bromide ions, so that much more formation of AuBr$_4^-$ ion complexes, which act as precursors for the gold nanorods, could be growth [5].

| CTAB (M) | Diameter (nm) | Length (nm) | Aspect Ratio |
|----------|---------------|-------------|--------------|
| 0.05     | 27 ± 3        | 273 ± 43    | 10.3 ± 2.9   |
| 0.1      | 28 ± 3        | 323 ± 83    | 11.6 ± 2.9   |
| 0.2      | 29 ± 3        | 526 ± 164   | 18.0 ± 5.4   |

Figure 2. The absorbance spectrum of gold nanorods synthesized without and with HNO$_3$ concentration of 0.02M and 0.05M.
Figure 3. The FESEM images of gold nanorods synthesized with CTAB concentration of (a) 0.05M, (b) 0.1M, (c) 0.2M.

Figure 4 shows the UV-VIS absorption spectrum of the gold nanorods synthesized with three different CTAB concentrations. Similar with the result in figure 3, the transversal mode peak of the gold nanorods appears at the wavelength of 510 nm. For the sample with CTAB 0.05M there are other two peaks at the wavelength of 700 nm and 940 nm, the sample with CTAB 0.1M there are also two other peaks at the wavelength of 800 nm and 1000 nm and the sample with CTAB 0.2 M there is only one peak at 510 nm. The longitudinal mode peak position was also predicted using the discrete dipole approximation method. The gold nanorods with the aspect ratio of 10.3, 11.6 and 18.0 is predicted to have another peak at the wavelength of 1407 nm, 1532 nm, and 2146 nm, respectively. All these peaks position are beyond the measurement tool range, hence the peaks at wavelengths of 700, 800, 940 and 1000 nm could not be judged as the longitudinal mode peak, but those might appears as the resonance effect of nanoparticles besides nanorods.

Figure 4. The absorbance spectrum of gold nanorods synthesized with CTAB concentration of 0.05M, 0.1M and 0.2M.
4. Conclusions
In this study, gold nanorods have been successfully synthesized in the solution with three different concentrations of HNO\textsubscript{3} and CTAB. Generally, the increase of HNO\textsubscript{3} concentration tends to increase the length and diameter; therefore the aspect ratio also increases from 5.9 to 8.5. All samples appear to have a transversal mode peak at the wavelength of 510 nm. However, the longitudinal peaks could not be seen in all samples. The mechanism formation of gold nanorods high aspect ratio, which was assisted by nitrate ions, also could not be explained clearly. Meanwhile, the increase of CTAB concentration significantly enhanced the length of gold nanorods from 273 nm to 526 nm which corresponded to the increase of aspect ratio from 10 to 18. The CTAB concentration plays an important role to enhance the number of gold atoms bonded with CTAB and to maximize the formation of AuBr\textsubscript{4}\textsuperscript{-} ion complexes which act as precursors for the gold nanorods growth.

Acknowledgment
This work was funded by Hibah PUPT 2016 from Ministry of Research, Technology and Higher Education Indonesia. The authors also would like to thank Prof. Dr. Muhamad Mat Saleh and Assoc. Prof. Dr Akrajas Ali Umar from Organic and Printed Electronic Laboratory (OPEL) IMEN Universiti Kebangsaan Malaysia for this beneficial research collaboration.

References
[1] Chen H, Kou X, Yang Z, Ni W and Wang J 2008 Langmuir 24(10) 5233
[2] Lohse SE and Murphy CJ 2013 Chem. Mater. 25(8) 1250
[3] Jana NR, Gearheart L and Murphy C 2001 J. Phys. Chem. C 105(19) 4065
[4] Wu H, Chu H, Kuo TJ, Kuo C and Huang MH 2005 Chem. Mater. 17(25) 6447
[5] Toussi SM, Zanella M, Abdelrasoul GN, Athanassiou A and Pignatelli F 2015 J. Photochem. Photobiol. A 311 76
[6] Rioux D and Meunier M 2015 J. Phys. Chem. C 119(23) 13160
[7] Cheng J, Ge L, Xiong B and He Y 2011 J. Chin. Chem. Soc. 58(6) 822
[8] Takenaka Y, Kawabata Y, Kitahata H, Yoshida M, Matsuzawa Y and Ohzono T 2013 J. Colloid Interface Sci. 407 265