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The photothermal effect of gold nanoparticles prepared by electrochemical method at different voltages

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Abstract

This paper was performed to evaluate the photothermal effect of pure gold nanoparticles (Au NPs) prepared by electrochemical method at different voltages, under laser irradiation in the safe wavelength range. The formation, morphological, and structural properties of Au NPs were analyzed by UV-Vis absorption spectroscopy, transmission electron microscopy (TEM), and X-ray diffraction (XRD). The stability and dispersion of Au NPs were investigated by dynamic light scattering (DLS) and Zeta potential measurements. The photothermal effect was evaluated by the temperature change of the sample under the green laser irradiated at a wavelength of 532 nm. The results showed the formation of the Au NPs has a spherical shape and high purity; the particle size distribution is in the range of 10 - 40 nm depending on the synthesis voltage, and the absorption peak is in the range of 530 to 556 nm. The temperature of the Au NPs solution increased by 1.3 to 6 °C, compared to that of bi-distilled water under the same conditions of laser irradiation. This paper shows the photothermal effect of Au NPs prepared by the electrochemical method at different voltages, it changed markedly when irradiated with a green laser in the safe wavelength range.

Keywords: Au NPs, photothermal effect, electrochemical method

1. Introduction

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Nowadays, nanomaterials technology is growing fast, especially precious metal nanomaterials have attracted a great deal of attention from researchers. Their unique properties include flexibility, confinement effect, quantum confinement effect, large surface area/mass ratio, and ability to deliver drugs or inhibit pathogens [1][2]. Gold nanoparticles are a topic of great interest to many research groups worldwide. Gold particles at the nanoscale, exhibit special properties compared to that of the bulk including electrical conductivity, thermal conductivity, high reflectivity and good compatibility [3]. Moreover, when illuminated, gold nanoparticles (Au NPs) have a surface plasmon resonance effect, generating local heat to the surrounding environment (also known as the photothermal effect) [4]. Gold nanoparticles have been widely studied and applied in biomedicine such as biosensors [3], bioimaging [3][5], disease therapies and drug delivery [6][7][8], etc. The synthesis of gold nanoparticles usually uses gold salt (HAuCl_4) via the reduction method [9][10]. This method is simple and can be produced in large scalability. However, the end product often still contains unwanted residues from the reduction process. These residues may have a certain influence on the activity of Au NPs. Recent articles also show that the evaluation of the photothermal effect of Au NPs mainly uses a laser with a wavelength in near-infrared (NIR) wavelength of 808 nm [11][12][13][7]. Rarely, there are few studies using lasers with wavelengths in the visible light region. This study was carried out to investigate the photothermal effect of pure Au NPs prepared by the electrochemical method using a green laser with a wavelength of 532 nm, which is close to the peak absorption spectrum of Au NPs. The results of the study are expected to contribute to giving a realistic view of the photothermal effects of Au NPs with high purity and different sizes through the fabrication by the electrochemical method using DC voltage varying from 6-18 V. Accordingly, this study aims to promote pure Au NPs applied in biomedicine.

2. Materials and Methods

2.1. Reagents

Gold foils (99.999%) with dimensions of 60 mm x 5 mm x 0.1 mm (length x width x height) were purchased from a jewellery store in Hanoi, Vietnam. Trisodium citrate ($\text{Na}_3\text{H}_5\text{O}_7$), and hydrogen peroxide (H_2O_2) were purchased from Sigma-Aldrich. Other chemicals were of analytical grade.

2.2. Electrochemical synthesis of Au NPs

The surface of the gold bars was cleaned with a 3% hydrogen peroxide (H_2O_2) solution and rinsed twice with bi-distilled water before use. Two gold bars were fixed (deeply submerged 5 cm) into a sealed electrochemical cell containing 60 ml of bi-distilled water, and connected to a DC source range 6 to 18V. Then, 0.1% sodium citrate was added to the electrochemical cell and the synthesis process was performed for 5 h under heated magnetic stirring conditions (80-100°C). Finally, the sample was cooled down at room temperature to obtain the Au NPs solution.

2.3. Characterization of Au NPs

The formation and physicochemical properties of Au NPs were investigated by UV-Vis absorption spectroscopy (SP - 3000 nano, Optima), TEM (JEM1010, JEOL), and XRD (EQUINOX 5000, Thermo Scientific). Nanoparticle size distribution, identification and stability were studied by DLS, and Zeta potential (Zetasizer Nano ZS). The photothermal measurement was performed using an excitation source of a 532 nm green laser with the power of 100 mW, and a thermal sensor that recorded the temperature over time.

2.4. Investigation for the photothermal effect of Au NPs

A tube of 1 mL of prepared Au NPs solution was put into an ultrasonic vibration bath and vibrated at room temperature for 5 min. Then, the Au NPs solution was put into a glass tube with a

volume of 1.5 mL. The solution was illuminated by a 532 nm laser source for 15 min. The temperature of the solution was recorded every 5 seconds during illumination (Figure 1).

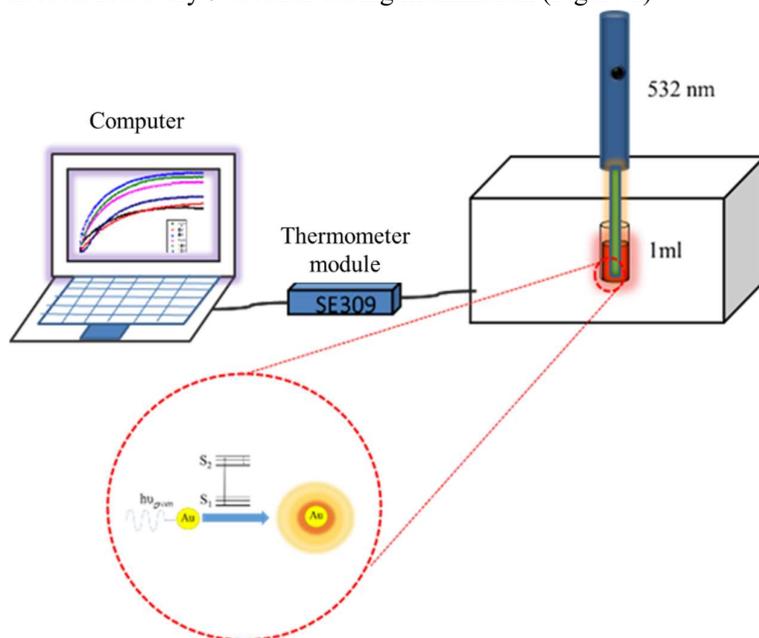


Figure 1: Photothermal measurement system

3. Results and Discussion

Physicochemical properties of Au NPs

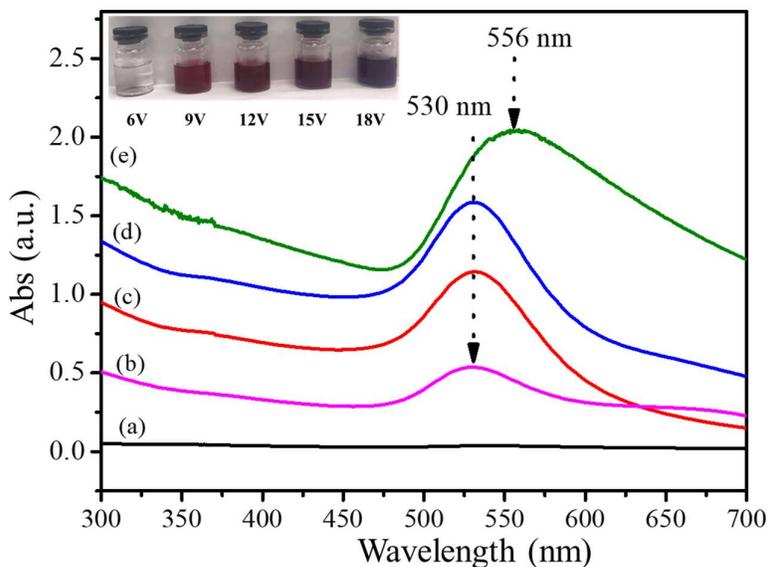


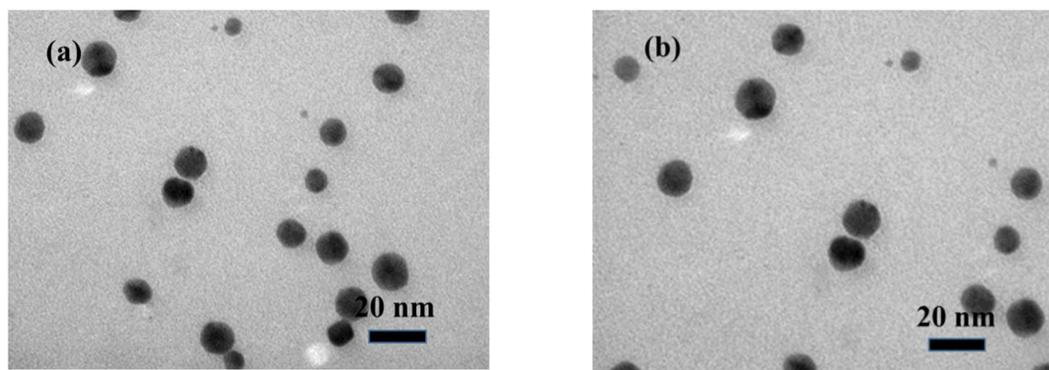
Figure 2: UV-Vis spectra of Au NPs (a) 6V; (b) 9V; (c) 12V; (d) 15V and (e) 18V

The Au NPs solution has been successfully prepared by electrochemical method from bulk gold. In this report, Au NPs were synthesized with DC voltage varying from 6-18V. With a voltage of 6V, the solution after the electrochemical process is transparent and the color does not change when

compared to that before. Therefore, Au NPs may have not been formed or are formed with very low concentrations at this voltage. For samples synthesized at 9 - 15V, the solution has a bright red color which is the characteristic color of gold nanoparticle solution. This shows the formation of Au NPs in the electrochemical solution[14]. With samples synthesized at 18 V, the color of the solution becomes dark red. Some studies show that the color of the Au NPs solution changes according to the change in the particle size of Au NPs [14][15].

For evidence, UV-Vis absorption was used to analyze the samples. Figure 2 shows the UV-Vis absorption spectra of Au NPs solutions after the electrochemical process with different voltages. Figure 2(a) is the absorption spectrum of the electrochemical sample at a voltage of 6V; as there is no absorption peak, the particle formation has not been determined. This is completely consistent with the results observed by the naked eye. Figures 2(b), 2(c), and 2(d) are the UV-Vis absorption spectra of the electrochemical solution at the voltages of 9V, 12V, and 15V, respectively. From the UV-Vis spectra, it was shown that all solutions had an absorption peak at 538 nm, which is believed to be the plasmon absorption peak of Au NPs. Furthermore, the three samples have the same absorption peak, and the widths of the absorption peaks are quite similar. This proves that the size range of gold nanoparticles is slightly changed in the voltage range from 9-15V. Figure 2e is the UV-Vis absorption spectrum of the electrochemical solution at 18V. From the absorption spectrum, the absorption peak at 556 nm can be seen. Compared with samples at lower voltages, the absorption peak shifts to longer wavelengths, which means that the particle size has changed [15]. Specifically, the particle size of Au NPs can be large with the samples synthesized at 18V. In addition, the spectral width extends towards the longer wavelength compared to that of the samples synthesized at lower voltages, indicating that the size range also widens when the sample is synthesized at the voltage. Therefore, the particle size of Au NPs synthesized at this voltage may be less uniform than that in the voltage range of 9-15V. To confirm the formation of Au NPs, samples were prepared for TEM observation.

TEM images can help clarify the morphology and size of the particles formed.



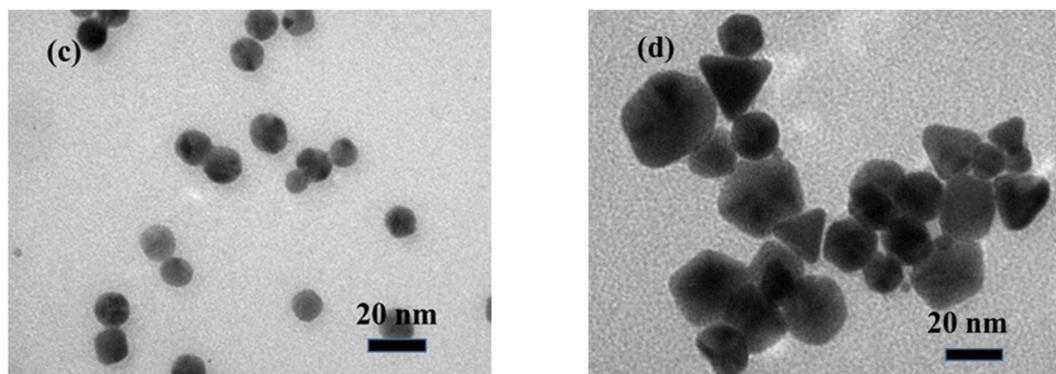


Figure 3: TEM images of gold nanoparticles fabricated at different voltages: (a) 9V; (b) 12V; (c) 15V and (d) 18V

Figure 3 shows TEM images of Au NPs synthesized at different voltages. In samples synthesized at 6V, we evaluated their size and morphology in our previous report [16]. At this voltage, Au NPs formed with low concentration and irregular size are completely consistent with the analysis of the UV-Vis spectra. Figure 3(a), 3(b), 3(c) present TEM images of Au NPs synthesized at 9V, 12V and 15V. TEM images show that these gold nanoparticles are similar in shape and size at these voltages. Specifically, at these voltages, Au NPs are spherical, with sizes ranging from 10 to 18 nm. Moreover, grain boundaries are very clear, which proves that Au NPs are well dispersed in water. Figure 3(d) is a TEM image of Au NPs synthesized at a voltage of 18V. TEM images show spherical particles similar to the sample synthesized at the lower voltage, there are also Au NPs with different shapes such as pyramids, cubes, and particle sizes ranging from 20-40 nm. Thus, the plasmon absorption peak of this sample shifted to a longer wavelength compared to that of the sample synthesized at the lower voltage. It can be explained by two reasons: (i) the increase of particle size at high voltage; and (ii) the appearance of anisotropic Au NPs. Furthermore, all the observed Au NPs have the same density, indicating that Au NPs have crystallized well and uniformly.

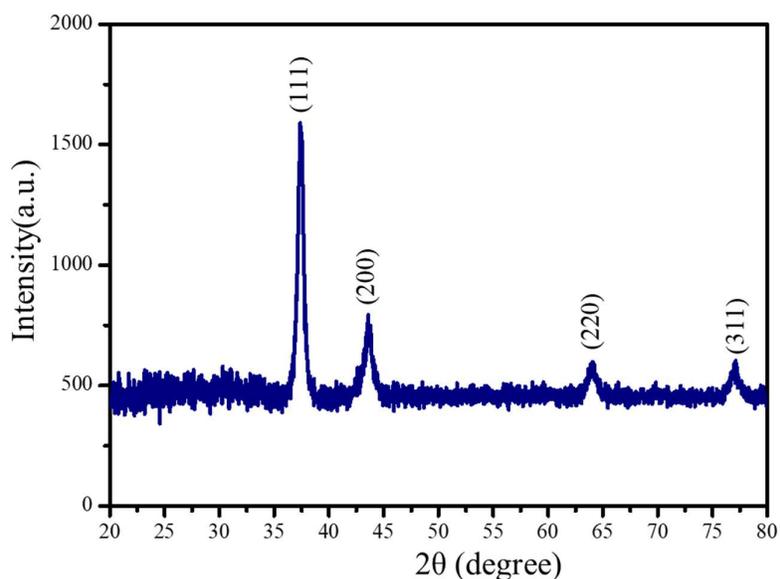


Figure 4: XRD pattern of Au NPs synthesized at 12V for 5 h

The crystal structure and purity of Au NPs were investigated XRD. The samples are synthesized under the same conditions but differ in voltages, so a representative sample is taken for XRD analysis. Figure 3 is the XRD pattern of Au NPs synthesized by the electrochemical method from two bulk gold. The XRD pattern showed the diffraction peaks of the crystal face families (111), (200), (220) and (311), corresponding to the 2θ angle positions of 37.38°, 43.52°, 63.94° and 77.22°, respectively, which are characteristic of the face-centered cubic structure of gold (JCPDS no. 00-004-0784). There is no diffraction peak characteristic of impurities. So, the formation of Au NPs in the electrochemical solution revealed good crystallinity and single-phase crystallization. This proves that Au NPs can be easily synthesized with good crystallinity and high purity via the electrochemical method from bulk gold.

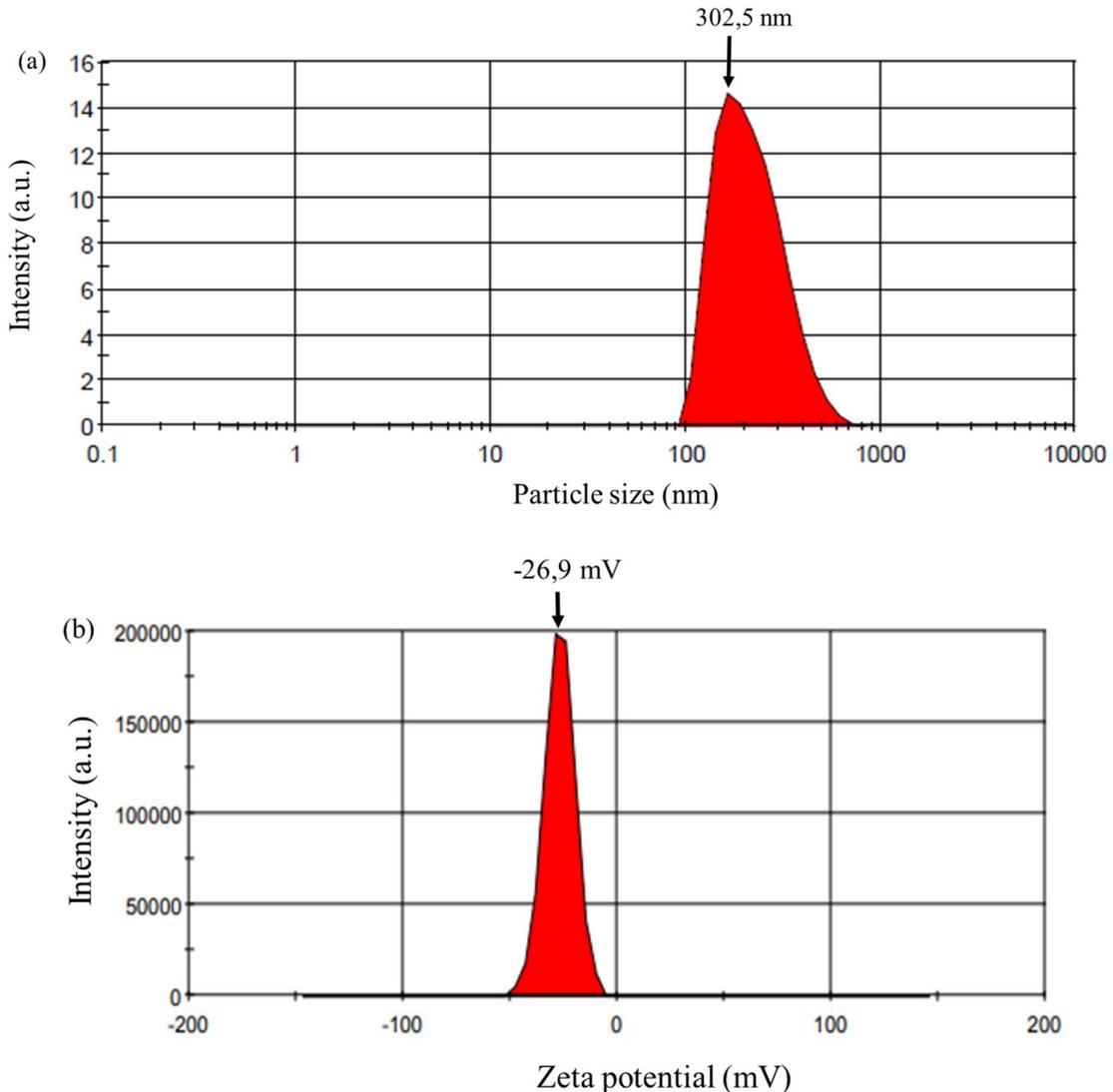


Figure 5: Illustration of DLS (a) and zeta potential (b) analysis of Au NPs synthesized at 12V

The dispersion ability and size distribution range of the Au NPs solution were investigated by dynamic light scattering (DLS) measurement. Figure 5(a) is the dynamic light scattering spectrum of the Au NPs solution synthesized at 12 V. The DLS spectrum shows that there is only a single peak at the size of 302.5 nm. The peak has a narrow width and high intensity, which validates the uniform particle size distribution. The single-dispersion index of Pdi of Au NPs solution synthesized at 12V is 1. The monomeric index at this level shows that Au NPs are likely to begin to agglomerate.

Zeta potential measurements were performed to investigate the stability and dispersibility of the Au NPs solution. The result of the surface potential (Zeta potential) of Au NPs synthesized at 12V is shown in Figure 5(b). From the graph, it can be seen that there is a peak potential at -26.9 mV, which is lower than the threshold of -30 mV; so the stability of the Au NPs solution after electroporation is at an average level [17]. Hence, there is still the possibility of agglomeration. Moreover, the potential peak is in the negative direction, indicating that the surface charge layer of Au NPs is negatively

charged. This is because citrate-based negative ions add to the surface of Au NPs [18]. Thus, sodium citrate salt takes a role as a reducing agent and a surfactant.

The photothermal effect of Au NPs

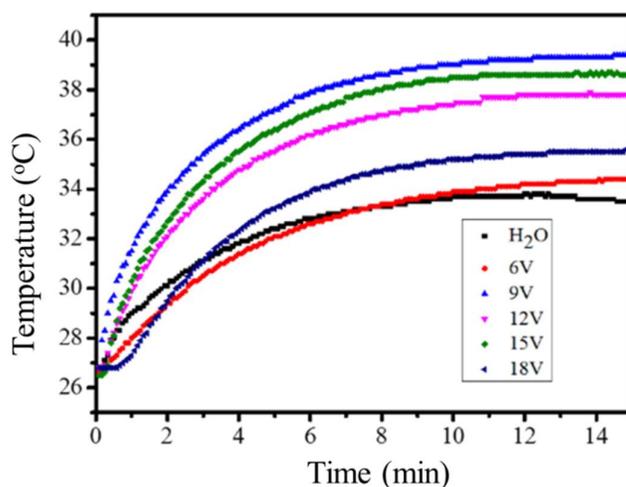


Figure 6: Photothermal curves of Au NPs synthesized at different voltages (6 to 18V) under green light irradiation laser of 532 nm

The photothermal effect was investigated based on the temperature change of bi-distilled water, Au NPs synthesized at different voltages of 6V, 9V, 12V, 15V and 18V. The temperature of the Au NPs solution depends on the time of irradiation of a green laser source with a wavelength of 532 nm. The Au NPs solution was laser irradiated at a stable temperature of 26.5°C the temperature of all solutions increased and reached the saturation status after 90 seconds. The saturation temperature (T_{max}) after 90 seconds of irradiation and the difference in the temperature between Au NPs solutions and bi - distilled water under the light of 532 nm are shown in Table 1.

Table 1: Temperature T_{max} and temperature difference ΔT between bi-distilled water and Au NPs synthesized at different voltages

Samples	$T_{max}(^{\circ}C)$	$\Delta T=T_{Au}-T_{H2O}(^{\circ}C)$
H ₂ O	33.4	0
6V	34.7	1.3
9V	39.4	6
12V	37.8	4.4
15V	38.7	5.3
18V	35.6	2.2

From Table 1, it can be seen that the change in temperature between bi - distilled water, and Au

NPs solution synthesized at 6V when illuminated for 90 seconds, increases by 5.9°C and 7.2°C, respectively. Its saturation temperature increases significantly by 1.3°C in comparison with that of bi-distilled water. This is completely consistent with the results analyzed from UV-Vis and TEM measurements of Au NPs formed after electrochemical synthesis with low concentrations. Meanwhile, the temperature in Au NPs samples synthesized at 9V, 12V and 15V increased by 11.9°C, 10.3°C and 11.2°C, respectively, compared with the saturation temperature of bi-distilled water (increased by 6°C, 4.4°C and 5.3°C, respectively). For the sample synthesized at 18V, the temperature increased by 8.1°C compared to the initial temperature; and 2.2°C compared with that of bi-distilled water illuminated under the same conditions. This could explain why Au NPs absorb light with a wavelength of 532 nm corresponding to the surface plasmon resonance frequency of Au NPs. The process of converting light energy into heat has occurred (photothermal effect)[4]. This process causes an increase in the local temperature in the solution. The highest temperature rise is the models with voltage from 9 - 12V. Au NPs synthesized at these voltages are uniformly sized spherical particles and have a plasmon absorption peak at 530 nm close to that of the incident light. Samples synthesized at 6V have the lowest temperature rise due to the very low concentration of Au NPs in the solution. Similarly, the sample synthesized at 18V does not have a high-temperature rise because of the large particle size, in addition to the spherical particles, anisotropic heterogeneous particles also appear. Therefore, the plasmon absorption peak shifts to a long wavelength (556 nm), that is different from that of the incident light. In some recent publications, Au NPs prepared by the chemical reduction method are illuminated by NIR near-infrared light with wavelengths from 800 nm to 808 nm. The saturation temperature can increase by 15-25°C compared to distilled water in the same period of irradiation [11][19]. However, if Au NPs are used *in vivo* for drug delivery or disease treatment, an increase in local temperature that is too high compared to body temperature (about 37°C) can also affect other healthy tissues in the surrounding area, harmful to living organisms. In this paper, a laser with a wavelength of 532 nm was used in the safe wavelength region. Although the temperature of the Au NPs solution is not as high as that previously reported, it is still enough to weaken or kill the target cells without affecting the surrounding healthy cells. This local and intrinsic temperature rise is safer and is expected to stimulate the surface properties of Au NPs, especially when these particles are surface functionalized with biologically active substances.

3. Conclusions

The photothermal effect of electrochemically synthesized Au NPs depending on the input voltage has been investigated. The Au NPs solution is illuminated with light in the visible region with a wavelength of 532 nm, and the solution temperature increases from 7.2°C to 11.9°C depending on the voltage. Corresponding to the temperature difference compared with bi-distilled water in the same lighting time from 1.3°C to 6°C. The samples with the highest temperature rise from the corresponding spherical particles of size 20-40 nm were synthesized in the voltage range from 9-15V. The temperature increase is at least at 6V due to the low concentration of Au NPs. In addition, at a voltage of 18V, the solution temperature did not increase as high due to the large particle size and appearance of heterogeneous nanoparticles. Thus, the photothermal effect of Au NPs synthesized by the electrochemical method depends on the voltage.

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Conflict of interest

The authors have no competing interests or personal relationships that could have appeared to influence the work reported in this paper.

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