Size/shape control of gold nanoparticles synthesized by alternating current glow discharge over liquid: the role of pH

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Keywords: AC glow discharge, pH, reduction reaction, gold nanoparticles, morphology, reducing species, plasma-liquid interaction

Abstract
In this study, we report the influence of pH level in HAuCl\textsubscript{4} solution on the size and shape of gold nanoparticles synthesized by an alternating current glow discharge on liquid. The results indicate there have three distinct groups in the size/shape of gold nanoparticles due to varying pH, one at pH \(\leq 8\), one at pH 9 and the other at higher than 9. At pH \(\leq 8\), single spherical gold nanoparticles with an average size of 5.7 nm and coral-shaped clusters aggregated from these gold nanoparticles were formed after 10 min of alternating current glow discharge on liquids. In the case of pH 9, spherical AuNPs with the size of 120 nm and coral-shaped clusters with the size up to 100 nm were generated after 10 min of discharge. At pH \(\geq 10\), roughly spherical gold nanoparticles with an average size of 100 nm (at pH 10) to 30.6 nm (at pH 13) were generated after 10 min of discharge. There has a decrease in the average size of gold nanoparticles when pH increases from 10 to 13. Our findings open a new way to control the size/shape of gold nanoparticles synthesized by plasma over liquid via pH control in the precursor solution.

1. Introduction
Gold nanoparticles (AuNPs) have been used in numerous applications of optical process\textsuperscript{1}, sensor technique\textsuperscript{1,2}, biomedicine\textsuperscript{2,3}, chemical analysis\textsuperscript{4}, and catalysis\textsuperscript{5}. The success of AuNPs in practical applications and nanoscience is due to their unique properties related to surface plasmons\textsuperscript{6}, high chemical and physical stability\textsuperscript{6}, and the ease of surface functionalization\textsuperscript{7}. Therefore, the improvement in the synthesis performance and control of the size/shape of AuNPs is still an attracted area of research activities.

Plasma-liquid interactions have been considered as a powerful instrument in nanotechnology. The process of synthesis nanoparticles via the interactions is based on the reduction reaction between reducers from plasma and metal ions in liquids\textsuperscript{8,9}. The interactions provide a variety of reducing species such as electrons, H, OH, and H\textsubscript{2}O\textsubscript{2} in a bulk liquid\textsuperscript{8}. These active species reduce metal ions into neutral atoms before growing to the nanoscale. This process in AuNPs synthesis has also been investigated using a direct current power supply to generate plasma over liquid. The liquid alternatingly plays as anode and cathode electrodes to study the synthesis mechanism of each reducing species\textsuperscript{10}. The effect of other factors such as reduction current\textsuperscript{11}, liquid-stirring\textsuperscript{11}, pressure and temperature conditions\textsuperscript{11,12} on the characterization of AuNPs have been studied. However, the influence of pH level of liquid and behavior of these reactive species from plasma on the synthesis process, and the characterization of AuNPs has not been considered.

In this study, our aim is to experimentally investigate the influence of pH level in HAuCl\textsubscript{4} solution on the size/shape of AuNPs synthesized by AC glow discharge on liquid.
2. Experimental methods

Figure 1 shows the schematic of the experimental setup used in the study. The experimental setup in this study is similar to the setup used in the previous study [13]. AC power supply was kept at 18 kV of voltage and 38 kHz of frequency. Helium gas with a rate of 5 l min$^{-1}$ was injected into the anode electrode. The anode electrode with its outer diameter of 6 mm and inner diameter of 4 mm was kept at 15 mm above the liquid's surface.

The solutions of sodium hydroxide (NaOH) 1 M and chloroauric acid (1 mg Au ml$^{-1}$, HAuCl$_4$ in 1 M HCl) (Hayashi Pure Chemical Ind., Ltd) were used without further purification. Deionized water was used during the preparation of samples. Each sample was prepared as follows: 98 ml of deionized water and 1 ml of HAuCl$_4$ solution were put into a glass beaker ($\Omega^{53}\times70$ mm). Then the solution of NaOH 1 M was added to each sample to keep the pH of the sample at an initial designed value from 2 to 13.

The pH measurement was performed using a pH meter (TOA WM 32-EP) with automatic temperature compensation feature. Characterization of the synthesized particles was monitored using transmission electron microscopy (TEM) (HT7700, Hitachi, Tokyo, Japan) with 100 kV of accelerating voltage. The size distribution was also analyzed using a dynamic light scattering (DLS) spectrophotometer (Zeta-potential & Particle size Analyzer ELSZ-2ND). UV–VIS spectra of all samples were observed using a spectrophotometer (JASCO V-570). After the irradiation of AC glow discharge, each solution was stirred to diffuse all particles in bulk liquid before UV–VIS observation. Deionized water was used as a reference during UV–VIS operation.

3. Results

3.1. Change in color and pH value of solutions during AC glow discharge

Firstly, we observed the color change in all solutions of pH values from 2 to 13 during AC glow discharge. We found that there were three tendencies in color change of these solutions during the discharge as shown in figure 2. The color in the solution for pH value of 2 almost did not change during the discharge. For solutions of pH values from 4 to 9, the color of the liquid below the plasma–liquid interface changed from colorless to blue after four minutes of discharge. In the case of solutions with pH values from 10 to 12, the color changed from colorless to violet and then shifted to red. The color change of the solution for pH value of 13 during the discharge was similar to the solution for pH value of 9.

Figure 3 shows the change in the pH value of all solutions during AC glow discharge. The results show a decrease in pH values of all solutions during the discharge excepting solutions at pH 2 and pH 4. The reduction in the pH value of the solutions at the pH from 10 to 13 was continuous during the discharge. In the case of the solutions at pH 6 to pH 9, the pH value decreased significantly and stabilized at approximately 5.0 after 1 min of discharge. For the solutions at pH 2 to 4, the pH value did not change during the discharge.
3.2. Change in the size/shape of AuNPs due to the change in pH value and during the discharge

TEM analysis was performed to characterize the synthesized particles in these solutions. Several TEM images of each patch of particles in each solution were also taken. We confirmed by using energy-dispersive X-ray spectroscopy (EDS) analysis that these particles are AuNPs. The diameter, i.e., the longest Feret diameter, of these particles measured by ImageJ software \[14\] was determined to characterize the size distribution of AuNPs. We found that the morphology of AuNPs synthesized separates into three distinct groups due to varying pH, one at less than or equal to 8, one at pH 9, and the other at higher 9.

**Figure 2.** The color change in solutions with pH in the range of 2 to 13 (top-down) during 10 min of AC glow discharge. The spots in samples are air bubbles.
Figure 4 shows TEM images of AuNPs synthesized in all solutions after 1 and 10 min of discharge. In the solution of pH 8, AuNPs synthesized after 10 min of discharge were found as single spherical with an average size of 5.7 ± 1.9 nm (mean ± SD). The coral-shaped clusters aggregated from these small particles were also detected with the size up to 100 nm. We also found that the morphology of AuNPs generated in the solutions of pH 2 to pH 6 is similar to in the solution of pH 8. In the case of the solution at pH 9, the synthesized particles after 10 min of the discharge were found as coral-shaped clusters with the size up to 100 nm and spherical with a size of approximately 120 nm. AuNPs in solutions at high pH (pH 10−13) after 10 min of discharge exhibited a distinct characterization. The shape of AuNPs in these solutions was mainly spherical of which the aspect ratio, i.e., the ratio of the long to short Feret diameters, of the synthesized particles in these solutions was under 1.3. There also were nanoparticles like triangle, hexagon, and rod with an aspect ratio up to 2.0. In the case of higher pH value, the shape of AuNPs was more homogeneous.

Figure 5 shows the size distribution of AuNPs in solutions of pH 9 to 13 after 10 min of discharge. The size distributions were produced from TEM images. Note that the size distribution of AuNPs in the solution pH 9 was counted from single particles (excluding coral-shaped clusters). It was found that the average size (blue triangle points) in these solutions can be fitted with a linear regression (blue dash line) over pH values (R² = 0.9, p-value = 0.0013 by Pearson’s correlation test). It can be concluded that the AuNPs synthesized in higher pH solutions of the range from 9 to 13 have a smaller size.

The change in the size of AuNPs was also analyzed using DLS technique. Figure 6 shows the size distribution of from DLS measurement of AuNPs synthesized in the solutions of pH 9−13 after 10 min of discharge. It shows that the results of TEM and DLS analysis were similar for the solutions of pH 10 and pH 11. However, there has the difference between TEM and DLS results for the solutions at pH 9, pH 12 and pH 13, of which the particle size from DLS measurement is higher than from TEM analysis. In the case of pH 9, TEM result for the average size of 120.6 nm was counted from only single particles. While DLS result for the average size of 101.7 nm was determined from both of single particles and coral clusters. This results in the difference in the result between the two techniques.

We found the aggregation of AuNPs in the solution of pH 12 after stopping the discharge. Figure 7 shows the color change from red to colorless after 10 min of stopping the discharge in the solution pH 12. This behavior was well explained in [15], in which the aggregation of AuNPs caused by H₂O₂ at high pH results in the change in the color of solutions. In this study, the existence of H₂O₂ in solutions also occurs due to the impact of the positive ions from AC glow discharge with water molecules [13]. TEM images also indicate that small particles (figure 7(c)) aggregated into a large cluster (figure 7(d)) after stopping the discharge. It is reasonable to consider that the aggregation of AuNPs in the solution pH 12 after stopping the discharge is caused by H₂O₂. It takes time to perform the DLS measurement after the discharge because of the distance between the experimental apparatus and the DLS device. The single AuNPs in the solutions pH 12 and pH 13 could aggregate into a large size before the DLS measurement. Therefore, the result from DLS measurement in the solutions of pH 12 and pH 13 is larger than from TEM analysis.
3.3. Time evolution of UV-VIS absorption spectra for samples

Understanding the optical properties of AuNPs is a reliable way to determine the properties of AuNPs in a solution [16]. In this work, we also observed UV-VIS spectra of all samples by a spectrophotometer without dilution. Figure 8 shows the evolution of UV-VIS absorbance spectra in all solutions for 10 min of discharge. It indicates that the absorbance in the 500-800 nm region expanded over plasma irradiation time and pH at each solution. In comparison to the TEM analysis results, it is possible to consider that the evolution of the absorbance was caused by the change in the formation process and the transformation of AuNPs morphology in these solutions during the discharge [6, 16].

The absorbance difference in the solution of pH 2 was negligible. For solutions of pH 4 to pH 8, the change of the absorbance in the range 500–800 nm was clear during 10 min of discharge. The bandwidth of the absorbance covered a large region, and it is not clear to determine the peak of maximum absorbance in these solutions. For solutions of pH 9 to pH 13, the absorbance intensively increased and reached a maximum in the solution of pH 11 before decreasing in solutions pH 12 and 13. The peak of maximum absorbance in solutions of pH 9 to pH 12 can be clearly determined in the 500–650 nm region.

We found that there was a blue-shift in the absorption of these solutions during the discharge. Many studies have reported that the blue-shift in the absorption light of AuNPs is caused by two main reasons: the reduction of size and fine-tuning in shape from anisotropic to isotropic [16, 17]. In this study, we also found the size reduction and fine-tuning in the shape of AuNPs during the discharge. Figure 4 shows the transformation in the shape of AuNPs from branched (left - after 1 min of discharge) to roughly spherical (right - after 10 min of discharge). Figure 4 also indicates the size reduction of AuNPs during the discharge (left to right).

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Figure 5. Box plot of size distribution of AuNPs synthesized in the solutions of pH 9 – 13 after 10 min of discharge. Each box describes the median and interquartile range (IQR) with whiskers representing 1.5 times IQR. The table summarizes the values of mean ± standard deviation (SD), median and number of particles counted. The blue triangle points indicate the mean of distribution, the dotted line illustrates the regression line ‘Y-value = 336 – 24.4 × X-value’.

Figure 6. Size distribution from DLS measurement of AuNPs synthesized in the solutions of pH 9 – 13 after 10 min of discharge. The histogram (black) and blue line show the frequency and the cumulative frequency of size distribution, respectively.
average size of AuNPs in pH 10 solution after 1 and 10 min of discharge was evaluated as 123.8 ± 35.6 nm (as shown in figure 9) and 100.6 ± 36.6 nm, respectively.

4. Discussion

4.1. Change in the form of ions gold Au3+ due to pH value
Many studies have indicated that AuCl4− ions dissociated in aqueous HAuCl4 take the form [AuCl4(OH)x]−, where x ≥ 2 at low pH values, and x < 2 at high pH values [8, 18, 19]. There has the complete transformation of ions [AuCl4−] generated in aqueous HAuCl4 at pH 3 to ions [Au(OH)4]− at pH 12 [20]. Goia et al indicated the decrease in the redox potential due to the transformation, in which the redox potential of AuCl4−/Au° and Au(OH)4−/Au° are 0.95 and 0.6 V [20], respectively. Wang et al have also shown a decrease in the reduction potential of aqueous HAuCl4 due to the pH increase [18]. This transformation leads to a decrease in the formation rate of gold atoms from these ions, resulting in decreasing the rate of nucleation and change in the growth route of AuNPs. Many reports have investigated that pH affects the morphology of AuNPs synthesized via citrate reduction [19] or H radical [21] reduction caused by the transformation as discussed above.

4.2. Role of charged particles from AC glow discharge during the synthesis process
In this study, we used the AC power supply at kHz range to generate the AC glow discharge on liquids. In the previous study [13], we investigated that the AC glow discharge generates both the positive ions and free electrons colliding and impacting onto the liquids. The impact of positive ions leads to the generation of H+ cations and OH radicals transforming to H2O2 in liquid. Meanwhile, free electrons directly solve into liquid and become solvated electrons (eaq) in the penetration of 10 nm below the plasma-liquid interface. Thus, the AC glow discharge provides strong reactive species eaq,H2O2, which have the possibility to reduce AuCl4− to AuNPs according to reactions N1-N2 in table 1. To the best of our knowledge, reactions between [Au(OH)4]− ions and eaq,H2O2 species have not been reported. Note that reaction N1 occurs only in the penetration depth of eaq, while the reaction N2 possibly occurs in the bulk liquid where H2O2 can diffuse. The AuNPs also could be synthesized via reactions N5 to N8. However, the reaction N5 is low with a rate constant [22] of 103 s−1 and low redox potential of (−2.93 V) [23]. Therefore, the AuNPs synthesized by the reduction of H radical is negligible.

When the AC glow discharge irradiates on the solution at low pH (pH < 8), there are available H+ ions in the solution. Thus, the species eaq and H2O2 not only react with AuCl4− ions to generate Au atoms as reactions N1-N2 but also are captured by available H+ ions as reactions N3-N4. This results in only a small amount of Au
Figure 8. The evolution of UV-VIS absorption spectra of AuNPs in solutions during 10 min of AC glow discharge.

Figure 9. TEM image of AuNPs synthesized in pH 10 solution after 1 min of discharge. Size distribution of 570 AuNPs with average diameter of 123.8 ± 35.6 nm. The absorption peaks of aluminum and copper were emitted from the TEM specimen holder and TEM grid.
atoms formed sufficiently to grow into nanoscale with the average size of 5.7 nm. On the other hand, these reductions occurring at low pH, in which high reduction potential as discussed above, lead to the fast rate of nucleation, and forming dendritic structures. Finally, the coral-shaped particles are formed from a combination of these dendritic structures. This behavior in coral-shaped formation has been reported in numerous studies [19, 26].

In the case of solutions at high pH level (pH > 9), it can be considered that there is an absence of H\(^+\) ions in bulk liquid because of its too low concentration (<10\(^{-8}\) mol l\(^{-1}\)). The species e\(_{aq}\), H\(_2\)O\(_2\) only react with AuCl\(_4^-\) ions to form Au\(^0\). Consequently, the number of Au atoms significantly increases, resulting in the size of AuNPs becomes larger. However, in the case of the higher pH value, the transformation of [AuCl\(_4^-\)]\(^-\) form to [Au(OH)\(_4^-\)]\(^-\) ions is more complete. At the high pH, the low reduction potential, the rate of nucleation becomes slower. In addition, at the high pH, a sufficient OH\(^-\) covering around AuNPs creates an energy barrier, counteracting the Van der Waals’s force between particles, to prevent the aggregation to a further large size [27, 28]. These effects result in a decrease in the size of AuNPs synthesized in solutions at high pH. Note that the existence of H\(_2\)O\(_2\) at high pH aggregates single AuNPs into a large cluster as shown in figure 7(d).

In the case of pH 8 and pH 9, these solutions quickly become acid after 1 min of AC glow discharge. It leads to the change in the form of [AuCl\(_4^-\)]\(^-\) closely to AuCl\(_4^-\) after 1 min of discharge as discussed above. Thus, the size/shape of AuNPs formed during the time from 1 to 10 min of discharge is similar to the size/shape, small

Table 1. Important reactions induced by e\(_{aq}\), H, OH, H\(_2\)O\(_2\) radicals and their reduction potential values.

| No | Reaction | E\(_o\) (V) | References |
|----|----------|------------|------------|
| N1 | AuCl\(_4^-\) + 3e\(_{aq}\) → Au\(^0\) + 4Cl\(^-\) | 1.00 | [24] |
| N2 | 2AuCl\(_4^-\) + 3H\(_2\)O\(_2\) → 2Au\(^0\) + 3O\(_2\) + 6H\(^+\) + 8Cl\(^-\) | 0.31 | [24] |
| N3 | 2H\(^+\) + 2e\(_{aq}\) → H\(_2\) | 0 | [23] |
| N4 | H\(_2\)O\(_2\) + 2H\(^+\) + 2e\(_{aq}\) → 2H\(_2\)O | 1.76 | [24] |
| N5 | H\(_2\)O + e\(_{aq}\) → H + OH\(^-\) | −2.93 | [23] |
| N6 | AuCl\(_4^-\) + 3H → Au\(^0\) + 3HCl + Cl\(^-\) | — | [21] |
| N7 | Au(OH)\(_3^-\) + 3H → Au\(^0\) + 3H\(_2\)O + OH\(^-\) | — | [21] |
| N8 | AuCl\(_4^-\) + \(\frac{3}{2}\)H\(_2\)O\(_2\) + Au\(_{aq}\) → Au\(_{aq+1}\) + \(\frac{3}{2}\)O\(_2\) + 3HCl + Cl\(^-\) | — | [25] |

Figure 10. The change in the size and shape of AuNPs in the solution at pH 9 during AC glow discharge. The number in the left-top shows the time of the discharge. All scale bars are 100 nm.
spherical and coral-shaped, of AuNPs synthesized in acid solutions (pH4–pH6). Figure 10 shows the change in the size/shape of AuNPs during the discharge synthesized in the solution pH 9. The particles synthesized within 2 min of discharge are urchin-like with a size of approximately 100 nm. As continuing the discharge, the small spherical and branched AuNPs were formed after 4–6 min of discharge. And after 10 min of discharge, the shape of synthesized AuNPs is spherical and dendritic structures. Note that there has also the process fine-tuning in the shape of AuNPs synthesized earlier. This results in the abnormal change in the absorbance for these solutions (figure 8), of which the absorbance reached a maximum value after a few minutes (3–4 min) from the start of the discharge before decreasing back.

5. Conclusion

In summary, we experimentally investigated the effect of pH in HAuCl₄ solution on the size/shape of AuNPs synthesized by AC glow discharge on liquid. Our findings show that there are three distinct groups in the size/shape of AuNPs due to varying pH in the precursor solution. At pH ≤ 8, small spherical AuNPs with a size of 5.7 nm and coral-shaped clusters with a size up to 100 nm were formed after 10 min of AC glow discharge. In the case of pH 9, spherical AuNPs with the size of 120 nm and coral-shaped clusters with the size up to 100 nm were formed after 10 min of discharge. At a higher pH level, AuNPs with the size of 100 nm (at pH 10) to 30.6 nm (at pH 13) were generated after 10 min of discharge. When pH increases from 10 to 13, there has a decrease in the size of AuNPs.

Acknowledgments

The authors would like to thank Mr Katsuki Watanabe (Department of Materials Science and Technology, Nagaoka University of Technology) for assistance and valuable discussions with DLS operations.

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