SYNTHESIS OF GOLD NANOPARTICLES USING CETYLTRIMETHYAMMONIUM 4-VINYLBENZOATE AS A REDUCING AND CAPPING AGENT

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ABSTRACT

Synthesis of gold nanoparticles (Au NPs) using cetyltrimethylammonium 4-vinyl benzoate (CTAVB) as a mild reducing and capping agent using a seedless method has been studied. In this present work, the effects of Au precursor and CTAVB concentration on the final product of Au NPs have been investigated. The particles were collected and characterized using an ultraviolet-visible spectrophotometer and a transmission electron microscope. The results show that the particle shape is dominated by triangular plate structure and its size is significantly affected by the concentration of Au precursor and CTAVB. The formation of triangular plate structure is ascribed due to a slow reduction rate of Au atoms which allows the seeds with structural defects, mainly stacking faults, stay longer in the solution and growth further into triangular plate structure.

Keywords: Gold Nanoparticles, Triangular Plate Structure, Mild Reducing Agent, Seedless Growth Method, Capping Agent

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INTRODUCTION

Over the past decades, research interest on gold nanoparticles (Au NPs) has received extensive attention because of their unique physical and chemical properties. These lead to the use of Au NPs for many potential applications, such as catalyst,^{1,2} sensors,³⁻⁵ surface-enhanced Raman scattering,⁶⁻⁸ drug delivery,^{9,10} and photothermal treatments.^{11,12} Because the sizes and shapes of Au NPs play an important role in determining their properties, tremendous research efforts have been developed to the synthesis of Au NPs with various sizes and shapes.

So far, the seed-mediated growth method is the most versatile approach for the fabrication of Au NPs with various sizes and shapes.¹³⁻¹⁷ This method is a two-step process, involving the seeds synthesis with a strong reducing agent and the addition of those seeds into the growth solution consisting of a mild reducing agent for their growth. To obtain high-quality of Au NPs with a given shape and size, experimental condition of the growth solutions should be tightly controlled, such as temperature, the nature and purity of the reactants, and particularly the seed condition. It has been reported that the activity of small seeds (3-5 nm) which generally produced by the reduction of Au precursors with sodium borohydride is considerably vary during aging and could cause an obvious change on the size and shape of the final product.¹⁸ This deliberate control over the conditions of the seed for the seed-mediated growth method has initiated many researchers to develop an easy and simple method for the synthesis of Au NPs. Currently, the synthesis of Au NPs with the two-step seed-mediated method has been simplified to a one-step synthesis.¹⁸⁻²² This approach is done to remove the preparation of seed, i.e. by adding a reducing agent directly into the growth solution. This reducing agent should be strong enough to produce the seeds, while still able to balance a further growth process to obtain the desired Au NPs with a certain size and shape. Recently, a seedless method of synthesizing Au NPs using cetyltrimethylammonium 4-vinyl

benzoate (CTAVB) which serves as a mild reducing as well as a capping agent has been reported by our group.¹⁹ Few different shapes and sizes of Au NPs had been produced by controlling the concentration of surfactant, Au precursor, and pH. While the ability of CTAVB molecules as a reducing agent in low pH ($\text{pH} < 3$) has been well elaborated in the previous study, its ability in neutral pH has not been explored. Thus, in this study, the synthesis and characterization of Au NPs using CTAVB molecules in neutral pH are presented by investigating the effect of Au precursor and reducing agent concentration to the final product of Au NPs. This provides new information and a more extensive understanding of this present method for synthesizing Au NPs. Such information is also useful for the possible fabrication of other metallic nanoparticles using this current method.

EXPERIMENTAL

Material

4-Vinylbenzoic acid (VBA, 97%), Cetyltrimethylammonium bromide (CTAB, $\geq 98\%$), gold (III) chloride hydrate ($\text{HAuCl}_4 \cdot x\text{H}_2\text{O}$, 99.99%), sodium hydroxide (NaOH , $\geq 98\%$) and an anion exchange resin (Dowex Monosphere 550A UPW) were purchased from Sigma Aldrich.

Synthesis of Cetyltrimethylammonium 4-Vinylbenzoate (CTAVB)

CTAVB was fabricated adopted from a previously reported method.^{23,24} In a brief, the counterions of CTAB, i.e. the bromide ions, were substituted with hydroxide ions using an anion exchange method to form cetyltrimethylammonium hydroxide (CTAOH). Then, the CTAOH was neutralized by adding an equimolar of VBA. The solution was stirred till it formed a homogeneous solution (CTAVB solution). After that, the CTAVB solution was dried using a freeze-drying method.

Synthesis of Au NPs with Various Concentration of Au Precursor

Briefly, 25 mL of distilled water was added into 81 mg CTAVB and stirred till it formed a homogeneous solution. Then, a certain amount of 7.0 mM of gold precursors was added to the CTAVB solution to produce a various concentration of Au precursor of 0.1, 0.2, 0.3, 0.4, and 0.5 mM. The mixture was stirred for 10 minutes followed by storage at 30°C for various reaction times in a water bath. The Au NPs formed at a certain reaction time were collected by taking 2.0 mL of the solution followed by centrifugation for two times.

Synthesis of Au NPs with Various Concentration of Au Precursor

A certain amount of CTAVB was dissolved in 25 mL of distilled water to give a concentration of CTAVB 5, 7.5, 10, and 15 mM. Then, 714 μL of 7.0 mM HAuCl_4 was added into the various concentration of CTAVB solution giving a final concentration of 0.2 mM HAuCl_4 . The mixture was stirred for 10 minutes followed by storage at 30°C for various reaction times in a water bath. After the reaction was completed, the samples were collected by taking 2.0 mL of the solution followed by centrifugation for two times.

Synthesis of Au NPs with Various Concentration of Au Precursor

For CTAVB molecules, the powder was characterized using Fourier-transform infrared spectrometer (FTIR, Shimadzu FTIR, IR-prestige 21) and X-ray photoelectron spectrometer (XPS, Thermo VG Scientific K-alpha XPS with Al $\text{K}\alpha$ X-ray source). For Au NPs, the product obtained at a certain reaction time was characterized using an ultraviolet-visible (UV-vis) spectrophotometer (PerkinElmer Lambda 650) and a transmission electron microscope (TEM, Tecnai F30, 300 kV). The UV-vis measurements were conducted by taking 0.5 mL of the sample at each reaction time, while those for TEM, 2.0 mL samples were collected, followed by centrifugation two times for 10 minutes at 10,000 rpm to remove an excess amount of surfactant. After that, the sample was dropped on the TEM Grid and then evaporated at room temperature.

RESULTS AND DISCUSSION

Synthesis of Cetyltrimethylammonium 4-Vinylbenzoate (CTAVB)

The synthesis of cetyltrimethylammonium 4-vinylbenzoate (CTAVB) was performed by substituting the bromide counter ions of cetyltrimethylammonium bromide (CTAB) with hydroxide ions (OH^-) through

the anion exchange method, resulting in the formation of cetyltrimethylammonium hydroxide (CTAOH). The CTAOH was further neutralized by adding an equimolar of 4-vinylbenzoic acid (VBA) to form CTAVB by following the reaction in Scheme-1:

Scheme-1: The Reaction between CTAOH and VBA Forming CTAVB

The as-synthesized CTAVB was dried using the freeze-drying method and further characterized using FTIR and XPS. Fig.-1 shows the FTIR spectrum for CTAB and CTAVB molecules. The characteristic spectrum of both molecules are almost identical, except the appearance of few new peaks originated from vinylbenzoate (VB⁻) counter ions. The FTIR spectrum of CTAB shows two intense peaks at 2918.4 cm⁻¹ and 2849.5 cm⁻¹ which correspond to -C-H stretching and anti-stretching vibration in the -CH₂ group, respectively. The other two intense peaks appeared at 1463.1 cm⁻¹ and 1472.2 cm⁻¹ are assigned as the scissoring mode of -CH₂. The shoulder bands with weak intensity at 2950.3 cm⁻¹ and 2959.9 cm⁻¹ are associated with N-CH₃ symmetric vibration, while few peaks appeared from 3009 cm⁻¹ to 3030 cm⁻¹ correspond to asymmetric vibration of N-CH₃. The scissoring mode for N-CH₃ and vibration of C-N are observed at 1396.5 cm⁻¹ and 912.4 cm⁻¹. Those values are in accordance with the previous results²⁵. The most distinctive peaks for CTAVB molecule appear at 1585.6 cm⁻¹ and 1542.2 cm⁻¹ which might be attributed from asymmetric and symmetric -CO₂ stretching of a carboxylate group originated from VB⁻ counter ion in CTAVB molecule. It should be noted for pure VBA molecules, only C=O (at 1730-1700 cm⁻¹) and C-O (at 1320-1210 cm⁻¹) stretch are observed²⁶. Thus, the results suggest that the VBA molecule interacts with the ammonium head group of CTA⁺ through electrostatic interaction. A broad peak appeared at the region of 3000-3700 cm⁻¹ for both samples are associated with the O-H stretching vibration which could be attributed from the moisture adsorbed during the analysis.

Fig.-1: FTIR Spectra of CTAB and CTAVB

To check whether the bromide counter ions of CTAB have been replaced by VB⁻, the XPS measurement was conducted. The measurement was done for three different batches of CTAVB. Fig.-2 represents the survey spectrum of CTAB and CTAVB molecule, while the inset shows high magnification spectra for bromide (3s, 3p, and 3d) before and after anion exchange. The black line shows a survey spectrum of CTAB molecule consisting of its characteristic peaks, i.e. Br (3d) at 96 eV, Br (3p) at 179 and 185 eV, Br (3s) at 252 eV, C (1s) at 283 eV, and N(1s) at 400 eV which are consistent with the reported values²⁷.

For the CTAVB molecule, a new peak is shown at 530 eV which corresponds to O (1s) belong to VB⁻ counter ions. The peaks of bromide ions were disappeared after they have been replaced with VB⁻ as it was shown at a high magnification XPS spectrum (Fig.-2 inset). This indicates that the CTAVB has been well prepared for further use in the synthesis of Au NPs.

Synthesis of Au NPs with Various Concentrations of Au Precursor

Figure-3 (a-e) shows the TEM images of Au NPs for various concentrations of Au precursor. The TEM images clearly show the formation of Au NPs which are dominated by triangular plate structure and its size becomes bigger as the concentration of Au precursor increases. The corresponding normalized UV-vis spectra are shown in Fig.-4a. It can be seen that the localized surface Plasmon resonance (LSPR) peaks position become red-shifted as the concentration of Au precursors increases indicating the formation of bigger particles. The UV-vis spectra show a unimodal peak when the concentration of Au precursors was at 0.1 and 0.3 mM, suggesting fairly monodisperse particles were formed. However, when the concentration of the Au precursor was at 0.3 mM, slightly polydispersed particles started to form. When the concentration of the Au precursor was further increased to 0.4 mM, the UV-vis spectrum with a weak shoulder above 600 nm was shown.

Fig.- 2: XPS Spectra of CTAB and CTAVB Synthesized for Three Different Batches. The inset shows the High Magnification Spectra for Bromide Ions for Clarity

An obvious broad peak at a wavelength longer than 600 nm peak was observed when the concentration of Au precursor was at 0.5 mM. These indicate the formation of more polydispersed particles. The formation of a polydispersed particle at the concentration of Au precursor ≥ 0.3 mM might be originated from additional nucleation. By the assumption that the reducing agent is sufficient to reduce all the precursor in the solution and the concentration of atoms still above the level of minimum supersaturation, the additional nucleation might occur as predicted by LaMer and co-workers.^{28,29} The different time of nucleation will produce particles with different sizes as the final products, meaning an increase in polydispersity. The expected results in term of particle polydispersity from the UV-vis spectrum for each sample are in accordance with the corresponding calculated particle size obtained from TEM measurement (Fig.-4b). Here the size of Au NPs was measured and presented as a triangular plate structure which is a more dominant shape in this present method. Based on these experimental results, the optimum Au precursor concentration to obtain monodisperse Au NPs was ≤ 0.2 mM.

It has been experimentally observed that the seed crystallinity is mainly determined by the reduction rate. When the reduction rate of the atom is very fast, most seeds will form a single-crystalline structure because of their rapid size increment. As the reduction rate is slowed down, the seeds with defects, such as single and multiple twinned structure could appear and grow into right bipyramid and decahedron, respectively. The plate with stacking faults might appear when the reduction rate is significantly slowed

down and grow further into hexagonal and triangular plate structure²⁹. In our present method, when the concentration of the Au precursor was 0.1 mM, the formation of the particles began at approximately 6 h, and the particle growth was completed within 24 h. The time required to complete the reaction increased as the concentration of Au

Fig.- 3: TEM Images of Au NPs Synthesized at Various Concentrations of Au Precursor (a) 0.1 mM, (b) 0.2 mM, (c) 0.3 mM, (d) 0.4 mM, (e) 0.5 mM. and (f) High Magnification Image for Au NPs taken at Au Precursor 0.3 mM. Scale Bars: 50 nm (a-e), and 10 nm (f)

precursor increased because there were more precursors that should be reduced to form nuclei or to be consumed by the existing seeds (Fig.-S1). However, the reaction time to complete the reaction becomes saturated when the concentration of the Au precursor was at 0.5 mM. This saturation might be attributed to the insufficient amount of reducing agent (VB^-) to reduce all the Au precursors presence in the solution, making an incomplete reduction of Au ions to Au atoms. The time scale required for the reaction in this method is much slower compared to that of the reduction of Au ions to form Au atoms by sodium borohydride which typically takes around 2 minutes.^{13,14,16} Considering the time required for the reaction, the formation of defected seeds is expected. It should be noted here that the expected results obtained in this present work are in the absence of other additives or etchant which could alter the population of the seeds at early stage and morphology of the particle as the final product. The high magnification TEM image of the triangular plate and decahedral Au NPs is shown in Fig.-3f.

Synthesis of Au NPs with Various Concentration of CTAVB

The role of CTAVB which works as a capping and reducing agent has been investigated in our previous report.¹⁹ CTAVB contains a hydrophobic tail with an ammonium head group (CTA^+) and 4-vinylbenzoate (VB^-) as its counter ion. The results show that in the absence of CTA^+ , aggregated Au NPs were produced in which it confirmed the role of VB^- as a reducing agent. Meanwhile, with the presence of CTA^+ , isolated Au NPs were formed, suggesting the role of CTA^+ as a capping agent preventing the particles from aggregation. Thus, in this study, the work is focused on the effect of CTAVB concentration on the final morphology and size of the Au NPs.

To understand those effects, Au NPs was synthesized at a few different concentrations of CTAVB i.e. 5, 7.5, 10, and 15 mM, while maintaining the concentration of Au precursor at 0.2 mM. The concentration of Au precursor was chosen because it is at the range of optimum condition to obtain monodisperse particles as it was previously shown by UV-vis and TEM measurements. The TEM images show that the shape of the particles obtained at three different concentrations of CTAVB maintains their triangular plate structure (Fig.-5). However, the particle size becomes smaller as the concentration of CTAVB increases.

It is also found that the particles size synthesized at 5 mM of CTAVB concentration was rather polydispersed. The critical micellar concentration (CMC) of CTAVB at room temperature is 0.16 mM which is lower than that of CTAB (1 mM). This is due to the presence of large organic counterions (VB⁻). CTAVB solution forms entangled micelle at its CMC.

Fig.- 4. (a) Normalized UV-vis Spectra of Au NPs Synthesized at Various Concentrations of Au Precursor and (b) Their Corresponding Particle Sizes.

Above the CMC, CTAVB solution is more viscous and becoming gel-like at the concentration of approximately 23 mM²³. In this present work, the viscosity of CTAVB at the range of concentration used to synthesize Au NPs was investigated. The result shows that the viscosity of CTAVB linearly increased as the concentration of CTAVB was increased from 5 to 10 mM. However, a significant increment in viscosity was observed when the CTAVB concentration was at 15 mM (Fig.-S2). This significant increment could be attributed to the morphological change of the micelle as it is closed to its gel-like concentration. The increase in viscosity could retard the movement of Au atoms in the solution, resulting in a slow diffusion rate of Au atoms onto the surface of Au seeds. Because of this slow diffusion rate, the Au atoms could be localized and more seeds were created in the solution. In this case, most of the generated atoms were consumed to produced many nuclei, consequently, the final particle size of the particles would be smaller. Considering the monodispersity of the particles size and the viscosity of CTAVB solution, the optimum concentration for CTAVB to synthesize Au NPs in this present method was 7.5 mM.

Fig.- 5: TEM Images of Au NPs Synthesized at Different Concentration of CTAVB (a) 5 mM, (b) 7.5 mM, (c) 10 mM, and (d) 15 mM. Scale Bars: 50 nm

CONCLUSION

A seedless method for synthesizing Au NPs using CTAVB which serves as a capping and mild reducing agent has been developed in this study. The effects of Au precursor and CTAVB concentrations have been investigated on the morphology and size of the final product. The results show that the triangular plates structure dominated the morphology of Au NPs and their sizes were significantly affected by the concentration of both Au precursor and CTAVB. Slow reduction of VB^+ is considered to be the key to the formation of structural defects, mainly stacking faults, which further growth into triangular plates. Using this current method, it is possible to obtain a monodispersed triangular plate structure with controllable sizes by tuning a proper experimental condition, such as the addition of etchant, additive, and temperature. The approach reported here may also provide a new route for fabricating other metal nanoparticles with various shapes and sizes.

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