Stability Study of Colloidal Gold Nanoparticles

Thaung Hlaing Win[*], Yi Yi Myint[**]

Abstract

Nanostructures have been extremely attractive because of their unique properties and potential applications in nanoscience and nanotechnology. Colloidal gold nanoparticles (Au NP) were obtained by chemical reduction of hydrogen-tetrachloroaurate ($HAuCl_4$) in water with sodium citrate ($Na_3C_6H_5O_7.2H_2O$). Upon ageing, the extinction properties of colloidal Au NPs along with its pH values were examined by UV-vis spectrophotometry.

Key words: gold nanoparticles, chemical reduction method, plasmonics

Introduction

Metal nanostructures show unusual and interesting optical properties due to their ability to sustain surface plasmons, which are oscillating electrons that exist at the interface between real metal and dielectric [2]. Light concentration and local field enhancement provided by metal nanostructrues have led to tremendous applications such as sensing, optical waveguides, nano-antennas and non-linear optics. In organic solar cells, the metal nanoparticles (NPs) were introduced to improve light harvesting capacity in the device using a phenomenon called surface plasmonics.

Among the synthesis methods of metal nanoparticles, the chemical reduction method has been widely studied since it brings the advantages of yielding nanoparticles without aggregation, high yield and low preparation cost [4]. The chemical reduction method involves the reduction of metal precursor by a reducing agent in the presence of a suitable stabilizer, which is necessary in protecting the growth of metal particles through aggregation. The particle size and aggregation state of metal nanoparticles are affected by various parameters, such as initial metal precursor concentrations, reducing agent/ metal precursor molar ratios, and stabilizer concentrations. Adjusting the stabilizer concentration and selecting the proper stabilizer agents would result in the stability of colloidal nanoparticles.

Experiment

For the preparation of gold nanoparticles, hydrogen-tetrachloroaurate ($HAuCl_4$) and sodium citrate ($Na_3C_6H_5O_7.2H_2O$) were used, as a metal salt precursor and a reducing agent. 114 mg of $Na_3C_6H_5O_7.2H_2O$ was added to 10 ml of distilled water to create a 38.8 mM solution while 33.9 mg of $HAuCl_4$ was added to 100 ml of distilled water to create a 1 mM solution. Firstly, a solution of 100 ml 1mM hydrogen-tetrachloroaurate ($HAuCl_4$) in water is boiled in reflux conditions under vigorous stirring and secondly 10 ml of 38.8 mM aqueous sodium citrate is added all at once to the $HAuCl_4$ solution. The yellow color in the aqueous solution due to the presence of $HAuCl_4$, turns clear over dark blue leaving a deep reddish color within a few minutes indicating the formation of gold nanoparticles. This mixture is further stirred and boiled for fifteen minutes, and is then removed from the heat while stirring is continued till room temperature is reached. As-prepared colloidal gold nanoparticles solution was added to two 5 ml glass vials. Then 10 drops of 1M HCl and 1M NaOH was added to each vial and the mixtures were stirred. The changes in color of colloidal gold nanoparticles in each vial were monitored followed by optical characterization. The preparing steps of Au nanoparticles synthesis is shown in Fig. 1.

[*] Dr, Assistant Lecturer, Department of Physics, Yadanabon University
[**] Dr, Professor, Department of Physics, Yadanabon University

Stability of Au nanoparticle depends strongly on the pH of the working solutions, and its growth can be stopped by adding the small amount of minerals acids. The pH of a reaction mixture plays an important role in the preparation of colloidal nanoparticle solution. The pH of the solutions were measured by the pH meter (KEDIDA pH CT6021A).pH meter was calibrated with three buffer solutions with pH values of 4.003, 6.860 and 9.182.The pH meter has automatic temperature compensation and a resolution of $\pm$ 0.1pH.

The optical absorption and transmission of gold nanoparticles solution were measured by ultraviolet-visible (UV-vis) spectrophotomery (UV-1600). The wavelength range of 200-700 nm was scanned with step interval of 10 nm. A baseline measurement was made with distilled water as a reference solution.
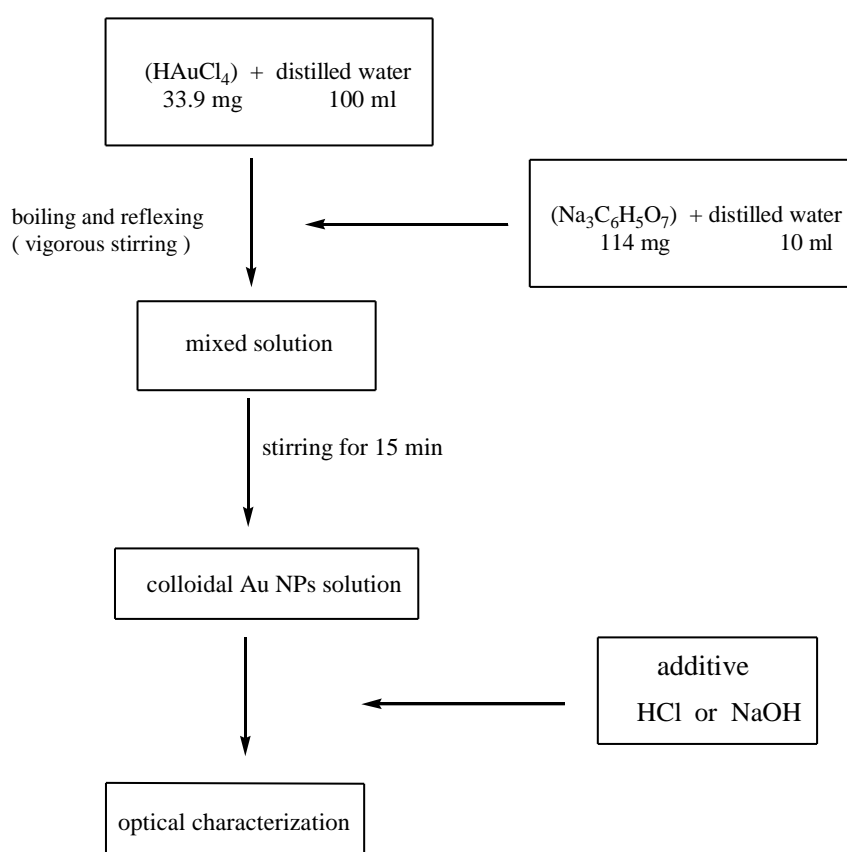
$(HAuCl_4)$ + distilled water
33.9 mg   100 ml

boiling and reflexing
(vigorous stirring)

$(Na_3C_6H_5O_7)$ + distilled water
114 mg   10 ml

mixed solution

stirring for 15 min

colloidal Au NPs solution

additive
HCl or NaOH

optical characterization

Figure 1. Preparation steps for colloidal gold nanoparticles

Results and Discussion
Effect of additive on extinction properties of colloidal Au NPs
Fig. 2 shows the extinction spectra of colloidal Au NPs solutions [pristine Au NPs and Au NPs with additives (NaOH and HCl) corresponding to pH values of 6.9, 8.7and 2.1 respectively]. The extinction spectrum of pristine Au NPs solution peaks at $\lambda_{max} = 520$ nm attributing to the s-p (conduction band) transitions of electrons. Upon adding HCl and NaOH, the color of the solution changed from deep reddish to light reddish color and no color changed respectively. The absorption band of AuNPs solution with HCl additive (pH 2.1) is blue-shifted while that with NaOH additive (pH 8.7) is red-shifted.
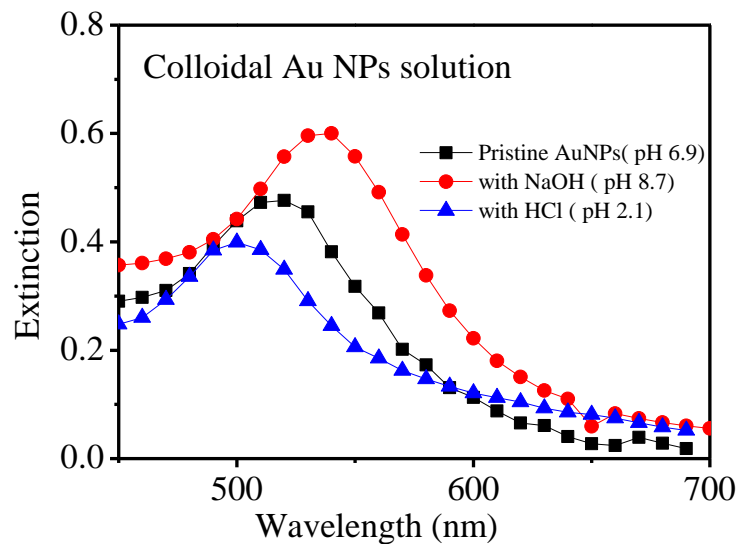
Figure 2. The extinction spectra of colloidal Au NPs solutions [Pristine Au NPs versus Au NPs with additives (HCl and NaOH)].

Ageing Effect on extinction properties of colloidal Au NPs

Fig. 3(a) shows the extinction spectra of pristine colloidal Au NPs solutions (as-prepared and aged for 5, 10 days). Upon ageing for 5 days, the extinction peak positions of Au NPs remained unchanged at 520 nm but the extinction intensity significantly increased. Increased intensity can be attributed to surface higher electron concentrations of colloidal gold nanoparticles induced by pH modulation. Upon ageing for 10 days, the extinction intensity significantly decreased.

Fig. 3(b) shows the extinction spectra of Au NPs colloids with NaOH (as-prepared and aged for 5 and 10 days). It was found that the NaOH-added Au NPs colloids further change its pH value upon ageing (5 and 10 days). In addition, this is no color change. The extinction peak of as-prepared NaOH-added Au NPs is decreased after 5 and 10 days .This ageing study indicates that the stability of NaOH-added Au NPs colloids starts deteriorated beyond 10 days-ageing.

Fig. 3(c) shows the extinction spectra of Au NPs colloids with HCl (as prepared and aged) for 5 and 10 days. It was found that the HCl-added Au NPs colloid not further change its pH value upon ageing (for 5 and 10 days). The stability of these NPs colloids was even worse since the surface plasmon peak of Au NPs was totally disappeared after 5 day.
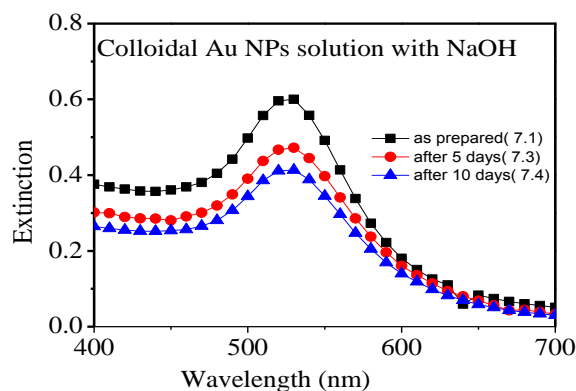
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Figure 3(a). The extinction spectra of pristine colloidal Au NPs solution (as-prepared and aged for 5 and 10 days).
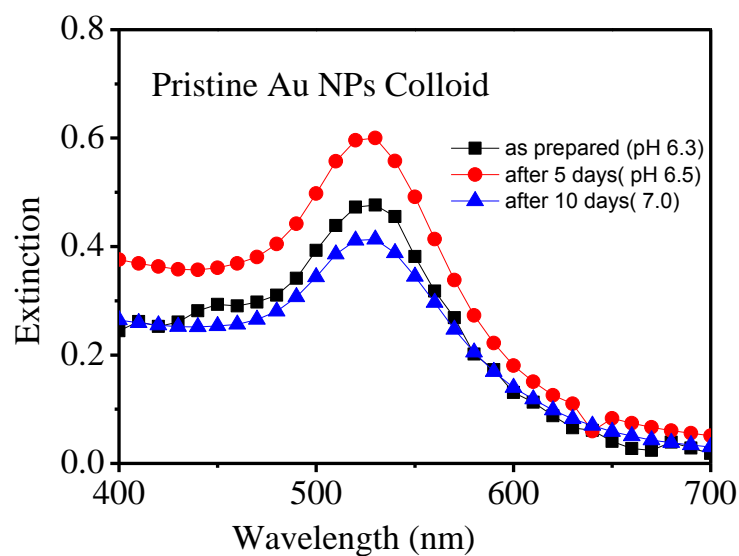
Figure 3(b). The extinction spectra of colloidal Au NPs solution with NaOH (as-prepared and aged for 5 and 10 days).
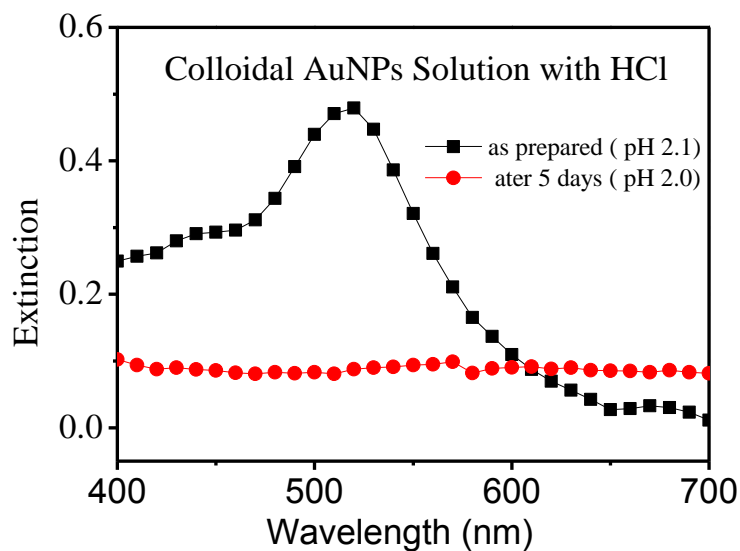

Figure 3(c). The extinction spectra of colloidal Au NPs solution with HCl (as-prepared and aged for 5 days)

Conclusion

Extinction peak of Au NP colloid is red-shifted in basic environment and blue-shifted in acidic environment suggesting the NP size modulation. For pristine Au NPs, extinction peak intensity is maximized after 5 days attributing to higher concentration of surface electrons in AuNP colloids. With additives (NaOH or HCl), extinction peaks of Au NP colloids degraded even after 5 days indicating the poor stability of colloids.

Acknowledgements

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