Determination of Gold Nanoparticle Sizes from Their Plasmon Resonance within the Optical Spectrum

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Abstract. Nanoparticles have exciting properties that can be tailored by altering their size, density and shape. Several essential properties of the nanoparticles have been investigated for various applications. One such property strongly affected by the nanoparticle size is localised surface plasmon resonance (LSPR). The resonance from metal nanoparticles has been used in dye-sensitised solar cells to improve their performance. In this work, the dependence of plasmonic properties on the nanoparticle sizes is shown. The gold nanoparticles were prepared using a reduction process where the hydrogen tetrachloroaurate acid was used as the base gold salt and reduced by sodium citrate composed at different molarity ranging from 0.015 to 0.035 mol/L. The method produces monodispersed nanoparticles whose sizes are sensitive to the concentration of chemicals used and the completeness of the reduction process. The process took approximately 18 minutes, and the colour changed from pale yellow to wine red. The absorbance of resulting gold nanoparticles was determined using a UV Vis spectrophotometer within 300 nm to 800 nm. The LSPR peaks were found to occur within 518 nm to 520 nm, and from a Gaussian fit, the FWHM ranged from 45.5 to 51.0 nm. The absorption peaks had a narrow range of 14 nm over sodium citrate's molarity content. A high molarity concentration of 0.035 mol/L produced a small particle with a diameter of 17 nm, while a low concentration of 0.015 mol/L produced a size of 26 nm. The interaction of electrons in the specific orbitals, sp- and d- of nanoparticles exhibited pronounced multiple resonances with a reduction of nanoparticle sizes.

Keywords: Localised surface plasmon resonance; Full width at half maximum; Gold nanoparticles (AuNP); Sodium citrate.

INTRODUCTION

The rising motivation in nanoparticle research is due to the famous quantum size, which makes them exhibit unique properties such as localised surface plasmon resonance (LSPR) from their bulk counterparts [1, 2]. These properties can be tailored by controlling the nanoparticle size, shape and concertation during synthesis [2]. One of the significant properties of the nanoparticle is their strong absorption of the optical spectrum [2, 3]. This has led to the widespread application of nanoparticles in the development of nano-devices for various applications such as physical, biomedical and biological [1, 4].

Several metal NP synthesis protocols have been developed. An approach to achieving a monodispersed metal NP is vital to attain a catalytic action with high accuracy [5]. The classical nucleation theory approach commonly uses the chemical reduction process with a low crystallisation potential reducing agent. To synthesise gold nanoparticles using a similar system, Au(III) was introduced in deionised water as hydrogen tetrachloroaurate [6]. Synthesis of AuNP with different sizes during a reduction process could be achieved in several ways. Reducing agent plays a critical role during chemical routines as it also serves as a capping agent and a pH mediator [7]. Variation in concentration levels of a given re-

ducing agent calculated by equation 1 gives rise to AuNPs of different sizes [6, 7].

$$C = \frac{m}{v} \times \frac{1}{MW}, \quad (1)$$

where *m* is the mass of solute, *v* is the volume of solution in litres and *mw* molar weight.

UV-Vis technique offers a reliable method of obtaining absorbance data from NPs useful in evaluating LSPR peak wavelength. Photons incident on a material can be transmitted, scattered or absorbed. The extent of photon absorption depends on the material's bandgap, and the absorbance scatter reveals whether LSPR peaks are within the material [8]. The LSPR peaks range determines whether the NPs were monodispersed or polydispersity. As the sizes of NPs decrease during the nucleation process, the LSPR undergoes a blue shift [8–10]. There is a strong relationship between LSPR peaks and FWHM value, revealing the lifetime of SPR from a nanoparticle [11]. The variation of LSPR wavelength and FWHM in a monodispersed can be used to determine the NP sizes as shown in Equation 2.

$$\lambda_{LSPR} = \lambda_0 + L_1 \exp(L_2 D), \quad (2)$$

where L_1 and L_2 are fit parameters and D is the nanoparticle size [11].

This variation has been used further to explain the NP size dependence on the pH of the reducing agent in a reduction process [12].

The LSPR peaks were obtained from absorbance spectra within the optical region of the spectrum. FWHM values for each height were obtained by fitting a Gaussian curve on each mount. These plasmonic properties were used in calculating the AuNP sizes for different molarities of the reducing agent.

MATERIALS AND METHODS

The glassware was cleaned by soaking them in a boiling solution of weak sodium carbonate for 10 minutes to remove grease or fat. Then they were rinsed with acetone, followed by deionised water. They were dried in the oven heated at 110oC for 6 hrs. Hydrogen tetrachroloaurate (III) trihydrate ($HAuCl_4$-$3H_2O$, 99.9%), sodium citrate ($Na_3C_6H_5O_7$, 99.0%), citric acid and hydrochloric acid were sourced from sigma Aldrich and of analytical grade.

AuNPs used in this study were synthesised using the Turkervich method [6]. Gold salt, 0.1wt% hydrogen tetrachloroaurate was used as the base of AuNPs. It was dissolved in deionised water, and the solution was topped to 50 ml. It was heated to boiling under vigorous magnetic stirring. A reduction bumper, Na3Ctr, was introduced to the resolution, and heating continued for 23 minutes until no further colour change was noted. The answer was cooled to room temperature under magnetic stirring. The process was repeated for different pH values of Na_3Ctr.

The absorbance data of the colloidal AuNPs was determined using a UV Vis spectrophotometer, and OriginPro software was used to plot the absorbance spectra. A Gaussian curve was fitted in each absorption peak to obtain the corresponding plasmon wavelength used to determine AuNP sizes, as in Equation 2.

RESULTS AND DISCUSSION

Figure 1 shows a linear fit for reducing the buffer's molarity and corresponding pH values. The rate of change was uniform at 100 l/mMol.

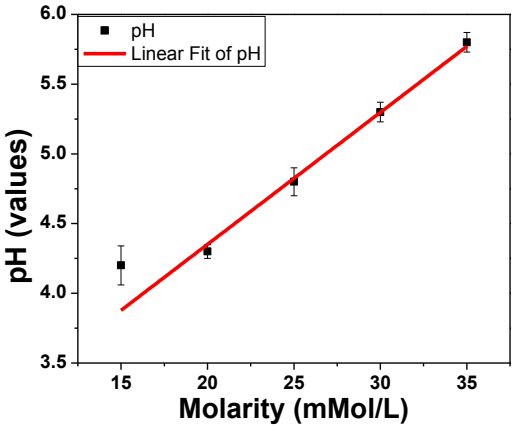

Figure 1 – Plot of pH versus molarity of sodium citrate

Thus, the reducing agent had high reduction potential with low crystallisation within the considered concentrations, and no solubility limits were reached. This made it an effective reducing agent and an excellent capping agent during the chemical process [13]. The spike in pH value at low molarity is due to the precipitation of Na_3Ctr. The

variation of pH in a reducing agent during the chemical process plays a crucial role in controlling the morphology and sizes of NPs [13, 14]

The AuNPs nucleation phases were presented by colour change during the reduction process within 18 minutes. Adding Na3Ctr to the $HAuCl_4$-$3H_2O$ while heating under vigorous magnetic stirring shows the reduction of Au(III) into colourless Au(0). The dark violet colour attained within 13 min was due to the formation of Au nanowires as an intermediate step during the nucleation process. This is consistence with Au nanowires absorbing most of the optical spectrum, giving the solution a dark violet colour [15].

Continued heating made the solution supersaturated, which led to the formation of spherical AuNPs. A blue shift in wavelength occurs with the AuNPs absorbing light in the blue–green regions giving the solution a wine-red colour.

Absorbance data from UV Vis confirmed the presence of AuNPs. Figure 3 shows absorbance spectra for colloidal AuNPs synthesised at different molarities of $Na_3C_6H_5O_7$. The LSPR peaks ranged from 518.2 nm to 521.0 nm as the molarity of the reducing agent was increased from 15 mM to 35 mM. The peaks exhibited a narrow shift of approximately 7.3 nm, indicating that NPs were monodispersed [16]. The presence of NPs was further tested using a laser beam, and Tyndall scattering was exhibited with all the samples obtained from varied molarity of reducing agent. For NPs with a diameter below 30 nm, the position of the LSPR peak is affected by interband transitions and electron density on the surface of the NP [17, 18].

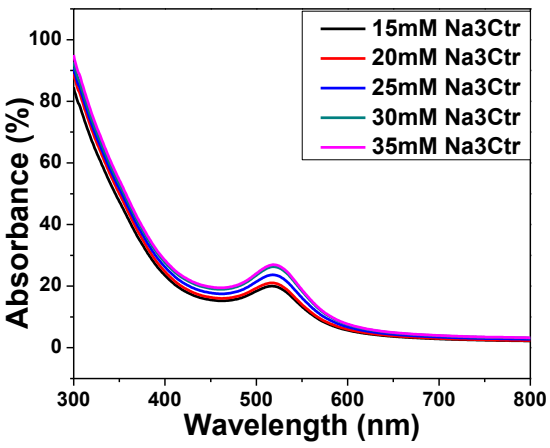

Figure 3 – Absorbance versus wavelength at selected molarities of Na3Ctr

For AuNPs, the interband transitions between the sp- and d- band with a sustained resonance of approximately 2.37eV, corresponding to a wavelength range of 520 nm, was noted.

To determine the FWHM values, a Gaussian curve was fitted in each of the absorption peaks. Figure 4 shows a Gaussian fit on 35 mM Na_3Ctr spectra, giving an FWHM value of 45.5 nm. The process was repeated for other molarities, and the values of FWHM obtained were recorded in Table 1. The values ranged from 45.51 nm to 51.04 nm, which were very low compared to the wavelength of the incident photons. Typical values of FWHM value give high integrity features to the AuNPs hence a better signal-to-noise ratio.

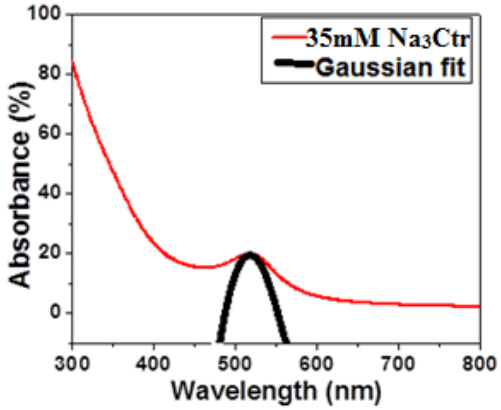

Figure 4 – Gaussian fit on a curve plot of absorbance versus wavelength on selected spectra

The lifetime of any SPR depends on the width of the absorption peak. The smallest width corresponded to a rise from 35 mM Na_3Ctr, representing NPs having the smallest size. The FWHM and the LSPR peaks depend on aggregation within the NPs colloidal with FWHM used to determine the dispersity of NPs

Table 1 – Variation of LSPR peak with FWHM

Molarity (mMol/l)	LSPR peak (nm)	FWHM (nm)
15	521.0	51.04
20	520.0	48.01
25	519.0	45.60
30	518.5	45.54
35	518.2	45.51

AuNP sizes were determined from their absorbance data within the optical spectrum. The measures were found to decrease with an increase in the molarity of the reducing agent, as

shown in Figure 5. The Boltzmann fit within the range of nanoparticle sizes had a coefficient of 0.20788. The rate of change of nanoparticle sizes at low and high molarities was low, whereby the sizes decreased from 26 to 17 nm as obtained from Equation 2, while the molarity increased from 15 to 35 mM. The dimensions of AuNP received due to different molarities were below 30nm, consistent with AuNP obtained from the variation of volume of the reduction agent [19]. The decrease in size is attributed to a complete reduction process, LSPR dipole coupling effect and electron interchange at NP orbits.

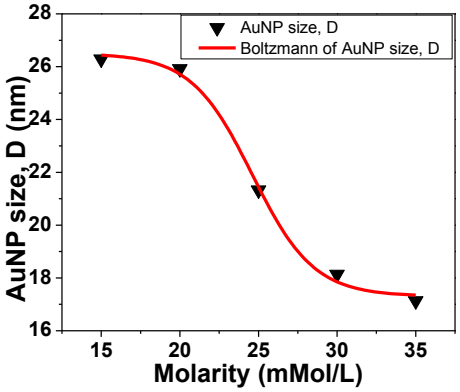

Figure 5 – Variation of AuNP sizes with the molarity of reducing agent

CONCLUSIONS

The pH values of sodium citrate used as a reducing agent increased linearly with molarity. No solubility limits were attained. A colour change consistent with gold nanoparticles absorption during nucleation was witnessed during the reduction process. Absorption peaks for AuNPs occurred at approximately 520 nm, with a narrow shift in LSPR wavelength for various concentrations being observed. The values of FWHM for all samples were relatively small, ranging from 45.51 to 51.04 nm, a clear indicator for quality AuNPs to foster a sustained Plasmon lifetime, making them suitable for application in photonics.

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