The Sensitivity of Surface Plasmon Resonance Damping for Colloidal Silver Nanoparticles

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Abstract. The impact of environmental conditions (ionic strength and type of electrolytes) on the damping of surface plasmon resonance spectra of silver nanoparticles (AgNPs) colloids suspensions were investigated. This study is structured for analyzing the interaction of three different sized (20, 50, and 80 nm) silver nanoparticles, which electrostatically stabilized (sodium citrate) with non-adsorbent media (e.g. NaCl and NaOH). The absorption spectra were observed using a UV- visible / NIR spectrophotometer in the range of 300 – 1000 nm. Taking advantage of the sensitivity of surface plasmon resonance (SPR) on the refractive index of the surrounding medium on the silver nanoparticles, the role of ionic media’s refractive index in changing the sensitivity of SPR on damping and plasmon resonance shift were investigated experimentally and compared with theory results thoroughly. The results of experiment revealed that the absorption spectra are blue shifted, due to the increase in perturbation of conduction electron density of AgNPs when the electron density of surrounding media increases and electrons transfer from Cl⁻ or OH⁻ ions to the NPs. The results of sensitivity of SPR damping corroborate the assumption that the damping of resonance strongly depend on type and concentration of ionic surrounding media (chemical interface damping). It is demonstrated that the sensitivity of SPR damping is depended on primary particle size.

1. Introduction

Silver colloids suspension exhibit a diversity of research interest for many decades as a result of their intriguing electronic and optical properties. The optical properties of silver nanoparticles (AgNPs) are strongly dependent on the particle size, shape, coating, and local dielectric of surrounding media [1-5]. The excitation of surface plasmon resonance (SPR) of AgNPs that is due to the coupling of incident wavelength to the collective oscillation mode of the conduction electrons and contribution of interband transition from the 4d to the 5sp band in the AgNPs are responsible for the generally observed increase in the optical absorption spectra [6]. The change in the absorption spectra is a function of varying the chemical and physical properties of the environment of AgNPs colloidal surface. Studies in the literature report, the analysis of the surrounding medium refractive index effect on SPR response of metal NPs [4, 5]. According to linear correlation between refractive index and concentration in non-absorbing media [7], the results are presented as a function of concentration.

Despite the concern regarding the environmental impacts of the AgNPs, there was lack of information available with regards to the effect of non-adsorbent ionic media (e.g. NaCl and NaOH)
concentration sensitivity on coupling plasmon resonance by considering the NPs size effect. Therefore, the main objective of this study was to investigate SPR sensitivity (S_exp) of AgNPs suspensions on to the concentration of non-adsorbent ionic media. The numerical differentiation was utilized to explain the sensitivity of damping (nm\(^{-1}\)) of absorption efficiency for SPR on the basis of the medium refractive index and salt concentration of different sized AgNPs. The sensitivity of absorption of plasmon resonance from Mie theory was compared to experimental sensitivity.

2. Experimental Details
Spherical AgNPs (brand Cytodiagnostic) with three different size (e.g. 20, 50, and 80 nm) were investigated. All AgNPs were purchased from Sciencewerke Co. (Singapore) were supplied in 2mM citrate. Non-functionalized standard AgNPs were used. Size distribution and morphology of AgNPs suspension are analyzed using “Phillips CM12 with Docu Version 3.2 image analysis” transmission electron microscopy (TEM) and Dynamic Light Scattering (DLS) to verify the samples size. The hydrodynamic diameter (HDD) was measured using a zetasizer nonseries Malvern instrument with 633 nm laser source. Zeta potential of aqueous AgNPs were measured using the Smoluchwaski’s approximation with the same instrument. The aqueous AgNPs colloidal absorption spectra were measured in the wavelength range of 300 – 1000 nm. The presence of the surface plasmon resonance (SPR) peak verified using a UV-visible / NIR spectrophotometer (Shimadzu UV/VIS/NIR UV3600). The HDD and SPR peak of AgNPs were examined as a function of salt solution concentration (0.01, 0.03, 0.04, 0.1 and 1 M) of suspended media. Sodium chloride (NaCl) and sodium hydroxide (NaOH) which are ionic compounds with a molar mass of 58.44 g/mol and 40 g/mol respectively (brand Sigma-Aldrich) were used as a function of salt solution concentration. Surface charge properties of three different AgNPs size were examined under same conditions. The AgNPs were analysed following the steps, (1) preparation of salt concentration (e.g. 0.01 M NaCl), (2) 30% volume fraction AgNPs suspensions were dispersed in 3 mL cuvette, (3) instantly, samples of AgNPs suspended in salt were analysed for SPR peak then particle size and zeta potential. The TEM image and size distribution of 20, 50 and 80 nm primary AgNPs are shown in Figure 1. Table 1, summarises the primary particles hydrodynamic size (d. nm), zeta potential (ζ. mV), FWHM (full width at half maximum) and the area of absorption spectra.

| AgNPs | DLS\(^{\ast}\) (d. nm) | DLS\(^{\ast}\) (ζ. mV) | FWHM (nm) | Area (100%) |
|-------|------------------------|------------------------|-----------|-------------|
| 20 nm | 23.13                  | -35.3                  | 63.46     | 56.76       |
| 50 nm | 54.13                  | -55.6                  | 66.71     | 66.45       |
| 80 nm | 83.82                  | -59.9                  | 181       | 159.3       |

\(^{\ast}\)DLS (Dynamic Light Scattering)
3. Result and Discussion

The calculated absorption spectra of Mie theory for the size of NPs varied from 10 to 90 nm. Figure 2(a), shows the particle size dependence of the maximum value of plasmon resonance absorption efficiency as a function of salt concentration. Mie theory results showed the absorption was increased by increasing the particle size of 30 nm. In the case of AgNPs more than 30 nm the absorption started to damp, due to the particles larger than 30 nm scattered light more than absorption. Therefore, AgNPs are more suitable due to its higher scattering contribution to absorption as compared to gold nanoparticles with the same size [8]. However, the redshift of SPR was significant for the particles size as a function of surrounding media concentration from the Mie simulation (Figure 2(b)). This is due to the changes of refractive index of non-adsorbents surrounding media (e.g. NaCl).

Figure 1: Size distribution histogram of (a) 20 nm, (b) 50 nm and (c) 80 nm AgNPs. TEM image indicates the physical structure of AgNPs used in this work.

Figure 2: Mie scattering theory calculated in different surrounding medium concentrations. (a) particle size vs. maximum value of absorption. (b) particle size vs. surface plasmon resonance.
The Mie theory calculated the damping sensitivity (\text{nm}^{-1}) of absorption efficiency (Q_{Abs}) as a function of AgNPs size to explore the sensitivity of SPR to the surrounding medium refractive index change as shown in Figure 3. The sensitivity increased with AgNPs size and reached the maximum of the plateau for a diameter of 20 nm. Based on the results of Mie calculation for the sensitivity of damping in 0.04 M concentration (refractive index = 1.3334) of media (Figure 3), one may conclude that the particle size of AgNPs colloidal is the important factor to enhancement and damping of plasmon resonance spectra.

![Figure 3: The change of Mie scattering theory sensitivity of damping (\text{nm}^{-1}) vs. particle size (nm).](image)

The anionic component of the surrounding ionic medium had a significant impact on the stability of AgNPs colloidal suspension. Aggregation was induced by adding the small amount of an ionic solution (e.g. NaCl and NaOH) stronger than threshold concentration which depended on the type of ionic media. The anionic component of the surrounding media electrolyte (Cl\(^-\) vs OH\(^-\)) had a considerable impact on the measured zeta potential (surface charge) and the aggregation of the electrostatically stabilised AgNPs as presented in Table 2, for different sizes of NPs. The use of OH\(^-\) rather than Cl\(^-\), as a surrounding medium of AgNPs resulted in higher measured zeta potential (mV) over the concentration range (0.01- 1 M) for three sizes of AgNPs. The increase in the measured values of zeta potential for citrate AgNPs suspended in NaOH was most likely the results of increasing OH\(^-\) concentration. Ag atoms at the surface structure of the NPs were unsaturated to the OH\(^-\) and H\(_2\)O molecule (nucleophilic), which can donate a pair of electrons. Therefore, increasing the OH\(^-\) concentration allowed the OH\(^-\) to effectively compete for the empty sites on the surface of AgNPs which produced a negative surface charge [9, 10]. However, adding the NaOH rather than NaCl resulted in a larger degree of aggregation at citrate AgNPs (Table 2). This indicated that how a minor change in the surrounding media charge could cause a significant change in the aggregated particle size and surface charge density. In general, AgNPs exhibiting high surface charge densities and surface plasmon resonance are extremely sensitive to electron charge density. The results of the experiment (Table 2) revealed that the absorption spectra were blue shifted (50 nm and 80 nm AgNPs suspensions), due to the increase in perturbation of conduction electron density of AgNPs when the electron density of surrounding media increased and electrons transfer from Cl\(^-\) or OH\(^-\) ions to the NPs [10].
Table 2: Effect of types of electrolyte on the hydrodynamic diameter (HDD) and SPR of AgNPs. (a) 20 nm, (b) 50 nm, and (c) 80 nm silver suspended in sodium citrate.

| Molarity of media | NaCl | NaOH |
|-------------------|------|------|
|                   | DLS b | Zeta potential | SPR peak | DLS b | Zeta potential | SPR peak |
|                   | [nm]  | [mV]   | [nm]   | [nm]  | [mV]   | [nm]   |
| 0.01              | 119.9 | 0.55   | 39     | -24.2 | 401    | 36.01  | 0.57   | 40     |
| 0.03              | 80.81 | 0.25   | 38     | -9.8  | 401    | 28.32  | 0.76   | 42     |
| 0.04              | 55.06 | 0.14   | 38     | -24   | 402    | 34.78  | 0.51   | 44     |
| 0.1               | 311.6 | 0.43   | 104    | -29.3 | 391    | 384.6  | 0.28   | 82     |
| 1                 | 164   | 0.31   | 127    | -20.7 | 412    | 382.1  | 0.25   | 281    |
|                   |       |        |        |       |        |        |        |        |
|                   |       |        |        |       |        |        |        |        |
|                   |       |        |        |       |        |        |        |        |

(a) 20 nm silver suspended in sodium citrate

| Molarity of media | NaCl | NaOH |
|-------------------|------|------|
|                   | DLS b | Zeta potential | SPR peak | DLS b | Zeta potential | SPR peak |
|                   | [nm]  | [mV]   | [nm]   | [nm]  | [mV]   | [nm]   |
| 0.01              | 84.74 | 0.40   | 39     | -24   | 410    | 84.94  | 0.26   | 41     |
| 0.03              | 76.25 | 0.15   | 36     | -18.1 | 410    | 95.79  | 0.20   | 40     |
| 0.04              | 108.6 | 0.22   | 33     | -30.6 | 408    | 99.62  | 0.26   | 42     |
| 0.1               | 169.3 | 0.23   | 92     | -25.2 | 399    | 220.4  | 0.26   | 71     |
| 1                 | 183.6 | 0.26   | 77     | -10.2 | 405    | 277.3  | 0.29   | 101    |
|                   |       |        |        |       |        |        |        |        |
|                   |       |        |        |       |        |        |        |        |
|                   |       |        |        |       |        |        |        |        |

(b) 50 nm silver suspended in sodium citrate

| Molarity of media | NaCl | NaOH |
|-------------------|------|------|
|                   | DLS b | Zeta potential | SPR peak | DLS b | Zeta potential | SPR peak |
|                   | [nm]  | [mV]   | [nm]   | [nm]  | [mV]   | [nm]   |
| 0.01              | 110.2 | 0.22   | 153    | -34   | 472    | 84.06  | 0.17   | 153    |
| 0.03              | 163.8 | 0.28   | 196    | -28.9 | 463    | 211.4  | 0.39   | 204    |
| 0.04              | 189.2 | 0.29   | 315    | -20.8 | 448    | 217.9  | 0.26   | 227    |
| 0.1               | 236.2 | 0.26   | 206    | -20.4 | 455    | 237.9  | 0.28   | 238    |
| 1                 | 328.7 | 0.32   | 194    | -21.2 | 486    | 305.0  | 0.26   | 249    |
|                   |       |        |        |       |        |        |        |        |
|                   |       |        |        |       |        |        |        |        |
|                   |       |        |        |       |        |        |        |        |

(c) 80 nm silver suspended in sodium citrate

| Molarity of media | NaCl | NaOH |
|-------------------|------|------|
|                   | DLS b | Zeta potential | SPR peak | DLS b | Zeta potential | SPR peak |
|                   | [nm]  | [mV]   | [nm]   | [nm]  | [mV]   | [nm]   |

Depending on the results of sensitivity of SPR damping for NaCl (Figure 4), one may conclude that the surrounding media of citrate AgNPs colloidal was the important factor to the enhancement and damping of plasmon resonance spectra. This means that the type and concentration of surrounding media can affect the sensitivity of damping of plasmon resonance, which strongly depends on primary citrate AgNPs size (Figure 3).

The calculated and empirical results of the plasmon resonance sensitivity (S) are shown in Figure 4. The calculated results indicated the magnitude of S_Mie in the case of 20 nm was higher than larger particles (50 and 80 nm) (Figure 3). The S_Mie was in good agreement with the calculated maximum absorption which is varied with particle size. The magnitude of absorption for citrate AgNPs 20 nm was higher than citrate AgNPs of 50 and 80 nm (Figure 2(a)). Figure 4, shows that the experimental SPR sensitivity (S_exp) of citrate AgNPs suspended in NaCl solution depended on particle size. Therefore, the value of S_exp for citrate AgNPs 20 nm and 50 nm was almost the same, whereas in the case of 80 nm shows lower value. The main difference between S_exp of these three -citrate AgNPs was from the low concentration of salt until threshold concentration where the aggregation of AgNPs started.
Figure 4: Calculated and empirical sensitivity of SPR damping for three different AgNPs size (20, 50 and 80 nm).

For confirmation and better understanding of S the additional experiments (using the same 20, 50 and 80 nm AgNPs colloidal) with different ionic media were performed. In this work, NaOH (sodium hydroxide) was deliberately chosen as the new aqueous solution medium. The AgNPs colloidal was suspended in different concentrations of NaOH solutions. For the clarity of purpose, the applied concentrations were the same value of previous experiment for NaCl. Compared trend of S_exp for AgNPs colloidal in NaOH and NaCl solutions are shown in Figure 5. The comparison between S_exp of the two media showed an insignificant difference at low concentration (0.01-0.03 M) for 20 and 80 nm AgNPs. However, the most significant variation in S_exp was observed for 50 nm AgNPs on the low concentration (0.01-0.03 M) of media (Figure 5).

In Figure 6, the S_exp of absorption spectrum of AgNPs in electrolyte matrix solutions (0.04 M) before NPs starting to aggregate is shown. The two ionic compounds (Cl- and OH-) were compared and showed that these two compounds very insignificantly different in value of sensitivity. However, in the case of 50 nm AgNPs the Cl- showed higher sensitivity. The reason for this might be due to AgNPs being suspended in NaCl aggregated faster than NaOH (Table 2).
Figure 5: The left hand side shows comparison between NaCl and NaOH solutions for SPR sensitivity of damping for AgNPs and the right hand side shows the zoom at low concentration. (a) 20 nm, (b) 50 nm, and (c) 80 nm.

Figure 6: Comparison between sensitivity of damping ($S_{\text{exp}} \text{ (nm}^{-1})$) for NaCl and NaOH (0.04 M) vs particle size (nm).

The finding of this study indicated that the SPR was very sensitive to the changes in the concentration and type of local surrounding medium of AgNPs in the presence of almost similar refractive index which
changed gradually from 1.333 to 1.34 for different concentrations (0.01, 0.02, 0.03, 0.04, 0.1, 0.152, and 1 M) of monovalent electrolyte matrix solutions. When the AgNPs were suspended in the media, which is contained the Cl⁻ ions, the absorption spectra damp more than other for 20 and 80 nm AgNPs. Consistent with the results in Figure 6, the plasmon resonance is a function of concentration and type of ions contained in solution despite the dependence on refractive index of surrounding media and interparticle distance results from aggregation of AgNPs. Furthermore, the S strongly depended on primary particle size of NPs.

4. Conclusion
In conclusion, experiments demonstrated that the values of maximum absorption spectra for the AgNPs suspension based were sensitive to the concentration and type of surrounding medium. The OH⁻ was less effective than Cl⁻ ions, especially in the case of particles 20 and 80 nm. Overall, the calculated and observed sensitivity of damping was attributed to the size decency of AgNPs.

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