Heating Effects on Optical Properties of Metal Nano Particle

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Abstract. Localized Surface Plasmon (LSPR) occurs on the interface of Metal Nano Particle (MNP) when illuminated with electromagnetic wave, at a specific electromagnetic energy (wavelength). In this work, we model the gold nanoparticle (AuNP) composite by its atomic polarizability, that is related to the absorption, and its dependence on temperature. To compare the resulted LSPR frequency shift when the AuNP system is heated, we synthesized the MNP composite of polymer (oleylamine) capped gold nanoparticle (AuOA) and measured the optical properties which is related to the LSPR resonance frequency through the atomic polarizability of the composite. The temperature dependence effect is observed by depositing the AuOA onto a thin film after mixing with a polymer solvent (P3HT : PCBM) and heating it. It is found that a perceptible blueshift of the LSPR signal is observed which is contrary to the prediction from the model. This effect can be attributed to the thermal expansion of the thin films due to the heating process. After heating, the relative distance between two nanoparticles becomes larger, thus the weakening of surface plasmon interaction between the particles.

1. Introduction

In recent years, nanometer-sized particle structures (nanoparticles, NP) have been an excellent choice of optical materials incorporated in various devices for specific application. One type of NP that has a characteristic interaction with electromagnetic waves is metal nanoparticles (MNP). When a metal nanoparticle is illuminated by light waves, its free electrons oscillate in response to the oscillating electric field of the incoming light. This electronic oscillation then re-radiates light which at certain frequency it has an important feature which is concentrated on the border between the metal and the background dielectric material, this wave is known as the Localized Surface Plasmon (LSP) wave [1]. Light shining with a wavelength that is close to the surface plasmon resonance wavelength, will provide efficient conversion of optical energy to thermal energy through the Joule heating [2], leading to a field of study known as Thermoplasmonic [3].

Due to this thermal energy build up at Localized Surface Plasmon Resonance (LSPR) frequency, various applications have been proposed. Some notable applications are cancer treatment [4] and water purification [5] to name a few. The important factor for the various possible applications is the plasmonic temperature rise on and around the MNPs.

An indirect way to determine the temperature around the MNP is to examine the temperature induced shift of the LSP resonance. This work reports a preliminary study on theoretical analysis of gold nanoparticle (AuNP) composite (AuNP capped with oleylamine) and the measurement of its LSP resonance shift.
2. Gold Nano Particle Composite

We consider a gold NP ($\varepsilon_1(\omega)$) capped with dielectric material ($\varepsilon_2$), whose geometry is depicted in Fig. 1, immersed in a host medium ($\varepsilon_3$). With the dimension of the considered composite far less than visible light wavelength, the analysis can be performed using the quasi-static approach.

**Figure 1.** Geometry of AuNP composite.

Suppose the composite is illuminated by electromagnetic wave with electric field linearly polarized in z-direction, $E_0$ (see Fig. 1), then the electric field in the host medium ($\varepsilon_3$) can be obtained from the electrostatic potential solution of the Laplace equation as

$$E_3 = E_0 + E_{dip}$$

(1)

where

$$E_{dip} = \frac{p}{4\pi\varepsilon_0\varepsilon_3 r^3} \left(2\hat{r}\cos\theta + \hat{\theta}\sin\theta\right).$$

(2)

The dipole moment is given by

$$p = \varepsilon_0\varepsilon_3 \alpha E_0$$

(3)

with the atomic polarizability of the composite system is found to be [1]

$$\alpha = 4\pi R^2 \frac{\varepsilon_2 - \varepsilon_0}{\varepsilon_2 + \varepsilon_0 + 2\varepsilon_3} \frac{\varepsilon_1 - \varepsilon_2 (\varepsilon_3 + 2\varepsilon_2)}{\varepsilon_1 + 2\varepsilon_2 + 2\varepsilon_3 + 2\varepsilon_1 - \varepsilon_3} f$$

(4)

and $f = (R_1 / R_2)^3$ is the volume fraction of the gold inclusion.

From the standard Poynting vector calculation, the absorption cross-section of a single AuNP composite can be shown to be given in terms of the atomic polarizability as

$$\sigma_{abs} = k \text{Im}(\alpha),$$

(5)

$k$ is the wave number. However, the measured quantity in an experiment, is the absorbance $A$, which is the logarithm of the reciprocal of transmittance. Using the Beer-Lambert law, the absorbance can in turn be calculated from the atomic polarizability as

$$A = \sigma_{abs} n L = k \text{Im}(\alpha) n L,$$

(6)

where $n$ is the scatterer density and $L$ is the absorption path length.
As a cursory example, we take an AuNP of radius $R_1 = 10 \text{ nm}$ with permittivity $\varepsilon_1$ taken from Johnson and Christy [6], capped with a dielectric of thickness $\Delta t = R_2 - R_1 = 1 \text{ nm}$ of permittivity $\varepsilon_2 = 2.25$ immersed in water ($\varepsilon_3 = 1.77$). The normalized absorbances of the bare AuNP and the capped AuNP are depicted in Fig. 2. As can be seen from this example, there is clear localized surface plasmon resonance (LSPR) around the wavelength $\lambda \sim 500 \text{ nm}$.

![Figure 2. Normalized Absorbance of bare AuNP and capped AuNP.](image)

Further, it is readily noticeable that with a very thin dielectric capping, the position of LSPR shows negligible shift. As the aim of this work is to study the temperature dependence of the LSP resonance, the negligible LSPR shift due to the dielectric capping of AuNP supports the use of this capped AuNP composite for the measurement of LSP resonance shift.

3. Temperature Dependence of the Physical Parameters

Our interest is to see the effect of temperature change on the LSP resonance. In order to model this temperature dependence, we use the Drude model phenomenologically corrected with an interband transition to describe the permittivity for the metal as [7]

$$\varepsilon_{Au}(\omega, T) = \varepsilon_B - \frac{\omega_p^2(T)}{\omega^2 + i\omega\gamma(T)} + \frac{\Gamma}{1 + \exp[-(\omega - \omega_c)/\Delta]}.$$  (7)

The first two terms are the standard Drude model with $\omega$ is the incident wave frequency, $\varepsilon_B = 9.84 \text{ eV}$ is the bulk contribution, $\omega_p(T)$ is the temperature dependent plasma frequency and $\gamma = 0.072 \text{ eV}$ is the bulk damping constant. The last term in Eq. (7) above is inserted to take into account the frequency-dependent contribution of the interband transition with $\omega_c = 2.4 \text{ eV}$ is the interband transition frequency and two fitting parameters ($\Gamma$ and $\Delta$), which for gold have the values $\Gamma = 5.6$ and $\Delta = 0.17 \text{ eV}$. The temperature dependence of $\omega_p(T)$ is due to the expansion of volume in the definition of this frequency [8]

$$\omega_p(T) = \frac{\omega_{p,0}}{\sqrt{1 + \beta(T - T_0)}}.$$  (8)

with the plasma frequency at the room temperature $T_0 = 20^\circ \text{C}$, $\omega_{p,0} = 9.01 \text{ eV}$ and the volume thermal expansion coefficient of gold, $\beta = 4.17 \times 10^{-5} \text{ K}^{-1}$ [9].

We use the Drude model corrected with interband transition above for permittivity of gold $\varepsilon_1$ in Eq. (4). Taking the other data to be the following: the oleylamine capping typically has a permittivity of $\varepsilon_2 = 2.13$ and the background medium of permittivity $\varepsilon_3 = 3.61$ [10] and the gold core radius $R_1 = 20 \text{ nm}$ and outer-radius of the polymer capping $R_2 = 25 \text{ nm}$ we can calculate the absorbance spectrum at $T = 20^\circ \text{C}$ and $T = 150^\circ \text{C}$, the results is given in Fig. 3 below.
Figure 3. Simulation of the absorbance spectra of AuNP capped with Oleylamine polymer at room temperature of 20°C (solid blue curve) and at 150°C (dashed red curve). A slight redshift is observed on the LSP resonance peak due to a change of frequency (inset).

From the simulation above, it is seen that there is a slight redshift of the LSPR frequency, for a change of temperature of $\Delta T = 130°C$, from the calculation we found a redshift of $\Delta \lambda_{SPR} \approx 2\, \text{nm}$. This is as predicted from quasi-static approximation as well as Mie theory, i.e. larger MNP, the size of the MNP increases due to thermal expansion, leads to a redshift in LSPR frequency [11].

4. Experiment

Synthesis of gold nanoparticles capped by oleylamine (AuOA) was carried out in toluene environment. Tetrachloroauric acid (HAuCl$_4$) (61.7 mg) was dissolved in toluene (1 mL) and oleylamine (1.2 mL), and the mixture was boiled under reflux and stirring. This mixture was then injected into a mixture of oleylamine (2.9 mL) and toluene 49 mL which was firstly heated to 100°C. The dispersion solution of AuOA exhibited homogenous red wine color. The resulted AuNPs core-shell system, with the shell permittivity $\varepsilon_2 = 2.13$, are then mixed with P3HT:PCBM and deposited into a thin film with spin coating method. The thin film system are then heated up to a desired temperatures. Characterization of the thin film system was conducted by Scanning Electron Microscope (SEM) whereas the effect of thermal heating was measured by means of UV-Vis spectrometer.

5. Results and Discussions

Figure 4. SEM image of P3HT:PCBM (a) without addition of AuOA, (b) with addition of AuOA,

The SEM image of P3HT : PCBM thin film in Fig. 4(a) above shows nonhomogeneous polymer layer. This is due to an amount of solvent left after spin coating process. Furthermore, the 10 minutes
heating process at 135°C creates a number of holes on some spots. However, for thin film with AuOA, no bubble spot is observed since the addition of the two solvent assists the evaporation process.

*Figure 5.* Normalized Absorbance spectra obtained from thin film of 200 μL P3HT:PCBM mixed with (a) 25 μL; (b) 50 μL; and (c) 75 μL AuOA. Blue lines and red lines are, respectively, correspond to measurement at room temperature (RT) and after the thin films are heated at 150°C for 2 hours.

We then measure the effect of temperature change on the absorbance spectra of the thin films. The effect of AuOA concentration is observed by preparing thin films with different AuOA volume. For all samples, it is observed that the absorbance spectra undergo blue shift upon heating at 150°C. It is also important to note that the blueshift are more apparent for thin films with higher AuOA concentration. This effect can be attributed to the thermal expansion of the thin films due to the heating process. After heating, the relative distance between two nanoparticles becomes larger, thus the weakening of surface plasmon interaction between the particles which is known to result in blueshift of resonance spectra.

6. Conclusion

To measure the change of LSPR frequency due to heating, we have modelled the temperature dependence of atomic polarizability of a composite MNP through the temperature dependence of the permittivity of the metal (in the present work it is gold). From the model, as it was predicted, when the temperature of background medium increases due to heating, the LSPR frequency redshifted. To measure this LSPR frequency shift from experiment, we have synthesized gold nanoparticles capped by oleylamine (AuOA). A temperature dependence effect can be observed by depositing the nanoparticle onto a thin film after mixing with a polymer solvent (P3HT : PCBM). The resulted thin film can be considered to have good quality as can be seen from the corresponding SEM image. Upon the heating process at 150°C all the absorbance spectra of the thin films are blueshifted contrary to the prediction of the model. Further, a more pronounced shift is observed from sample with higher AuOA concentration. This blueshift might be related to the thermal expansion of the background material (not considered in the modelling) which results in the weakening of plasmon coupling. Further, more comprehensive modelling needed to be made and more precise measurement of better (purity) of the synthesized MNP should be performed in order to verify the prediction of the model and experimental measurement.

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