Measurement of the Polarizability Tensor of Gold-Nanoparticle-Functionalized Tips

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The polarizability tensor of a gold-nanoparticle (GNP) functionalized tip is measured by applying two types of scattering measurements – rotating polarizer analyzer ellipsometry (RPAE) and rotating polarizer ellipsometry (RPE). A suitably small GNP, less than 100 nm in diameter, can be regarded as a good electric dipolar scatterer when the far-field scattered field is considered. In the dipole approximation, we demonstrate how the scattering function of a GNP - the polarizability tensor - is correctly read from each method. The pros and the cons of the two detection schemes are discussed, and their results are compared with experimental measurements.

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I. INTRODUCTION

The element size in current optical systems has come down to a nanometer scale. There have been many efforts to experimentally investigate the optical properties of a single nano-object excluding the possible inhomogeneities which are inherit in an ensemble state [1–3]. Since the optical property of a nano-object strongly depends on its geometry - size, shape, and orientation [4], direct experimental access to it is of primal importance in understanding the optical characteristics of each element, and beyond when designing a nano optical system consisting of many nano-objects.

One nano-object, the metal particle has been used in a wide range of applications owing to its good photostability. For example, the gold nanoparticle (GNP) is an excellent candidate for a tracking label in bio-sensing [5]. It can also serve as a nano-antenna to enhance the spontaneous emission rate of single molecules by using its plasmon resonance [6]. Moreover, a small GNP, less than 100 nm in diameter, is a good dipolar scatterer, and it could be used as a nano-sized polarizer to detect the local electric field polarization vectors [7,8]. In the reconstruction of the local polarization vectors from the detected far-field signal radiated by the GNP, it is crucial to correctly and efficiently measure the polarizability tensor of the GNP. In previous works [7,8], the

method to get the polarizability tensor was not fully discussed. Here, we theoretically present detailed principles and procedures for reading the polarizability tensor from two different scattering measurements – rotational polarizer analyzer ellipsometry (RPAE) and rotational polarizer ellipsometry (RPE). In addition, we show that the dipolar approximation is suitably valid when a GNP with the diameter less than 100 nm scatters light into the far-field by showing the experimental results obtained by applying RPAE. In the next section, we show that the two methods give a consistent result in the dipolar region. By comparing two methods, the pros and cons of each method are discussed. Finally, we show the experimental results validating the model and the data process.

II. EXPERIMENTS AND RESULTS

Tips functionalized with GNPs [9] are prepared as follows. Sharp glass fiber tips with a tip apex size of 100 ~ 200 nm are made by chemical etching (hydrofluoric acid, 48 %, 65 minutes) or by using a puller machine. Then the tips are chemically treated to generate a chemical layer sticky to the GNP. For the case of 3-aminopropyltriethoxysilane (APTES), the GNP is bonded to the glass fiber through an electrostatic force; on the other hand, 3-aminopropyltrimethoxysilane (APTMS) forms a layer that covalently bonds to the GNP [10]. This surface-treated tip is scanned onto a

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Fig. 1. (a) SEM picture of a GNP functionalized tip. (b) Projection of an arbitrary ellipsoid onto a plane makes an ellipse. In the same analogy, the geometrical shape of the polarizability tensor of an ellipsoidal GNP in a 2-dimensional plane can be regarded as an ellipse.

cover glass or a slide glass onto which the GNPs are spin-coated. When the tip moves across a GNP, the GNP eventually sticks to the tip, and the two moves together. A scanning electron microscope (SEM) image of a tip attached with a 100-nm-diameter GNP is shown in Fig. 1(a). The size variation of the GNPs in the colloid was less than 8 % (data sheet of BBInternational Inc.) and there was a small variation in shape also. Additional to these intrinsic morphological distributions, the attaching process can generate a deformation in the particle shape due to the applied forces between the tip and the sample surface. Therefore, the geometrical shape of the GNP, in general, can be assumed to be an arbitrarily-oriented ellipsoid. Experimental data in the later part of this report show that this assumption is quite well valid.

The polarizability tensor of the GNP is measured in a 2-dimensional plane ($x-z$ plane), as depicted in Figs. 1 – 4. The complete 3-dimensional polarizability tensor can be obtained by performing this 2-dimensional measurement in three orthogonal directions. The tip end is illuminated by using a 780-nm cw laser light, and the incident beam polarization is rotated using a half-wave plate. The polarization state of light scattered off the tip is analyzed by applying two ellipsometry techniques – RPAE and RPE. For a suitably small GNP, below 100 nm in diameter, the far-field scattering is dominated by the electric dipole radiation [11]. In that case, the polarizability tensor is described in a 2×2 matrix in a 2-dimensional plane. This is schematically demonstrated in Fig. 1(b). The projection of an arbitrarily-oriented ellipsoid onto a 2-dimensional plane makes an ellipse. By determining the projected ellipse in three orthogonal directions, one can reconstruct the original ellipsoid.

From now on, we describe how the polarizability tensor values are correctly read by using the two scattering measurements. In RPAE, the incident laser light is loosely focused at the tip's end by using a lens of 10 cm in focal length while rotating the incident polarization by using a half-wave plate. The polarization of the scattered light is analyzed by rotating a linear polarizer

Fig. 2. (a) Schematic of RPAE. A 780 nm plane wave is focused at the tip end part by using a lens of 10 cm in focal length, while using a half-wave plate to rotate the incident polarization. The polarization of the scattered light is analyzed by rotating a linear polarizer (analyzer) in front of the APD. (b) Three black-colored polar plots show the square root of the scattered light intensities as a function of the analyzer angle for incident polarizations of 0 (black solid), 45 (black dashed), and 90 (black dotted) degrees from the x -axis. The red ellipse is constructed by connecting the maxima of the polar plot of every incident polarization.

Fig. 3. (a) Experimental schematic of RPE. Same configuration compared to RPAE, except that no analyzer is in the detection part. The APD measures the total intensity of scattered light. (b) The outer black polar plot shows the square root of the scattered light intensity as a function of the incident polarization. The inner red ellipse is determined by choosing the maxima and the minima of the polar plot (black curve) as the semi-major and the semi-minor axes of an ellipse (red).

(analyzer) in front of an avalanche photo diode (APD, C-4777-01, Hamamatsu) in the direction of incidence. The experimental schematic is shown in Fig. 2(a). Here, we assume a simple case of a polarizability tensor (α) which is symmetric in the laboratory frame with null values of off-diagonal terms, $\tilde{\alpha} = \begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix}$. A general case of

Fig. 4. (a) Two peanut-shaped polar plots are measured by applying RPAE. The incident polarization angle values are 0 (black open circles) and 90 (red filled circles) degrees. The blue curve is measured by applying RPE. (b) Another measurement applying RPE. The solid curve shows the measured data, and the inner dashed ellipse is made by choosing the maxima and the minima of the polar plot as the semi-major and the semi-minor axes. (c) The red ellipse is the same as the dashed one in (b), and the outer black curve shows the re-calculated polar plot from the ellipse parameters.

an arbitrarily-oriented ellipse with non-zero off-diagonal terms will be discussed later.

Figure 2(b) shows polar plots of the square root of the scattered light intensity as a function of the analyzer angle. Polar plots are shown for incident polarizations of 0 (black solid), 45 (black dashed), and 90 (black dotted) degrees from the x-axis of the laboratory frame. Note that, for the case of 45 degrees, the long axis of the dashed polar plot - the polarization direction of the scattered light - deviates from the incident polarization direction ($b > a$). The incident and the scattered lights are related through the following relations [12]:

$$\vec{p} = \vec{\alpha} \vec{E}_{inc}, \quad (1)$$

$$\vec{E}_{dipole} = \frac{1}{4\pi\epsilon_0} \left\{ k^2 (\vec{n} \times \vec{p}) \times \vec{n} \frac{e^{ikr}}{r} \right\}, \quad (2)$$

where $\vec{p}$, $\vec{E}_{inc}$, and $\vec{E}_{dipole}$ are the dipole moment induced at the GNP, the incident electric field, and the far-field radiated electric field due to the induced dipole moment $\vec{p}$, respectively. Here, $\vec{n}$ is the detection position vector and is taken to be $-\hat{y}$ in the configuration of Fig. 2. The maxima of the polar plot of every incident polarization (red dots) make an ellipse with a semi-major axis of b and a semi-minor axis of a ($b > a$). From this, the original tensor value can be extracted.

Next, RPE is applied in measuring the same polarizability tensor, $\vec{\alpha} = \begin{pmatrix} a & 0 \\ 0 & b \end{pmatrix}$. Here, the incident beam polarization is also varied, but there is no analyzer in front of the APD as shown in Fig. 3(a). The outer black curve shows a polar plot of the square root of the scattered light intensity as a function of the incident polarization. When the incident beam polarization is θ , the polarization angle φ of the scattered light is given as

$$\varphi = \tan^{-1} \left(\frac{b}{a} \tan \theta \right), \quad (3)$$

and the square root of the intensity is calculated as

$$r_1 = r_2 = \left(\frac{a^2 + b^2 \tan^2 \theta}{1 + \tan^2 \theta} \right)^{-\frac{1}{2}}. \quad (4)$$

The inner ellipse and the outer polar plot do not encounter each other, except at the maxima and the minima of the black curve, which correspond to the major and the minor axes of the inner ellipse. By taking the four minima and maxima points of the outer polar plot, the inner ellipse - the polarizability tensor - can be determined. This RPE takes less measurement time compared to the RPAE, but it is less accurate because it has a fewer number of data points [13]. In addition, to apply RPE, prior knowledge on whether the scatterer is a good dipolar scatterer is needed; otherwise, the measured data can be misleading.

In previous sections, we assumed a polarizability tensor for a simplified case - symmetric to the x and the z axes. However, in a general case, the off-diagonal elements have non-zero values, which implies that the major axis of the ellipse deviates from the laboratory axes. With a defined as the length ratio between the major and the minor principal axes and ζ as the angle between the major axis of the scatterer and the x-axis in the laboratory frame, the polarizability tensor can be written as,

$$\begin{aligned} \vec{\alpha} &= \begin{pmatrix} \cos \zeta & -\sin \zeta \\ \sin \zeta & \cos \zeta \end{pmatrix} \begin{pmatrix} a & 0 \\ 0 & 1 \end{pmatrix} \begin{pmatrix} \cos \zeta & \sin \zeta \\ -\sin \zeta & \cos \zeta \end{pmatrix} \\ &= \begin{pmatrix} a \cos^2 \zeta + \sin^2 \zeta & (a-1) \sin \zeta \cos \zeta \\ (a-1) \sin \zeta \cos \zeta & a \sin^2 \zeta + \cos^2 \zeta \end{pmatrix}. \end{aligned} \quad (5)$$

Figure 4 shows experimentally measured data for two GNP-attached tips by applying RPAE and RPE. Two peanut shaped polar plots in Fig. 4(a) show the square root of the scattered light intensity for incident polarizations parallel to the x-axis (black open circles) and the z-axis (red filled circles) of the laboratory frame. The dipolar radiation pattern of the polar plots shows that the attached GNP is a good dipolar scatterer. The outer blue curve is measured by applying RPE. It shows the polar plot of the square root of the scattered light intensity as a function of the incident polarization. From these measurements, the values of a and ζ are determined as 1.05 and 80 degrees, respectively, and the resultant polarizability tensor in the x-z plane is given as $\vec{\alpha}_1 = \begin{pmatrix} 1 & 8 \times 10^{-3} \\ 8 \times 10^{-3} & 1.04 \end{pmatrix}$. In this case, the GNP shape is quite circular and the off diagonal terms are negligible compared to the diagonal terms. Note that with a small ellipticity ($a \approx b$ in Fig. 3), the polar plot obtained by applying RPE directly gives the ellipse of the polarizability tensor from Eqs. (3) and (4). The maxima of the two polar plots obtained by applying RPAE clearly touch the polar plot obtained by using RPE, demonstrating that the two methods give consistent results. Figure 4(b) shows the result obtained by applying RPE to a different GNP. Here, the a and the ζ values are 1.62 and 33

degrees, and the resulting polarizability tensor is given as $\vec{\alpha}_2 = \begin{pmatrix} 1.208 & 0.257 \\ 0.257 & 1 \end{pmatrix}$. In this case, the scattering function of the GNP (inner dashed line of Fig. 4(b)) is quite elliptical, and the major axis is rotated from the laboratory frame. To check the quality of the measured data, we fitted the polar plot with the determined $\vec{\alpha}$ (black curve in Fig. 4(c)). The similar shapes of the polar plots in Figs. 4(b) and (c) validate the model and the measurement.

III. CONCLUSIONS

In this work, we demonstrate how the optical response of a GNP attached tip, the polarizability tensor, can be measured by applying two different scattering measurements – RPAE and RPE. RPAE takes more time in determining the tensor values, but generally gives more accurate results compared to RPE. Also it gives information on the dipole nature of the tip. In comparison, RPE takes less measuring time, but this method needs prior knowledge whether the tip is a good dipolar scatterer. For our cases, the diameter of the GNP attached to the tip is less than 100 nm in diameter, and the electric dipole radiation was dominant in the far-field scattering process, allowing both measurements to give consistent results with each other. The measured data were clearly well reconstructed by using a simple calculation validating our analysis methods.

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