Optical alignment of achiral nanoparticles via the use of induced chiral force

M. C. Toh¹ · W. K. Phua¹ · E. H. Khoo¹

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Abstract

A chiral force was found to be induced upon rotation of planar nanoparticles under irradiation of linearly polarized light. The chiral force arises due to differing absorptions of left and right circularly polarized light, correlating with the circular dichroism (CD) of rotated nanoparticle. Charge distribution profiles, which arises from the excited localized surface plasmon polaritons induced by the light, can be used to predict the CD. This offers a simple method of using charge distributions to predict the dynamics of nanoparticles for optical alignment and orientation in the fabrication of various optical devices.

Keywords Chiral · Circular dichroism · Planar · Plasmonics

1 Introduction

Noble metal nanostructures have been of much interest due to their plasmonic behavior. Light being an electromagnetic wave, interacts with the metallic nanoparticle, resulting in resonance in the oscillation of electrons on the nanoparticle called surface plasmon polaritons (SPP). This results in many applications of such plasmonic nanostructures, such as in photovoltaics [1], optical antennas [2], metamaterials [3], surface-enhanced Raman spectroscopy [4] and biosensing [5].

The plasmonic behavior is highly sensitive to the orientation of the nanoparticle with respect to the polarization of the light source [6, 7], thus making controlled orientation and alignment of nanoparticles highly desirable. There are various methods of aligning such nanoparticles, which mainly require secondary structures [8–10].

As an alternative to using such secondary structures, light being used to drive the plasmonic oscillations can

also be utilized to rotate the nanoparticles. Similar to how dipoles experience torque in an electric field, plasmonic nanoparticles experience torque under electromagnetic radiation.

Instead of analyzing the torque directly using numerical calculations, we offer a simpler alternative by looking at the charge distribution profiles, which can be analyzed to predict the CD signature formed [11–16]. The chirality [17–19] can then be used to predict the torque. Due to differing absorptions of left and right circularly polarized light, as indicated by the CD signature, it is expected that a restoring force should act in order to bring the object back to a stage of zero CD. This creates specific orientations in which the nanoparticle would align to.

We also investigate this effect with different background refractive indexes to open up more applications. Cubic nanoparticles will be investigated in this study, due to their simple structure and usefulness in modelling more complex structures [12].

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✉ E. H. Khoo, khooeh@ihpc.a-star.edu.sg; W. K. Phua, phuawk@ihpc.a-star.edu.sg | ¹Institute of High Performance Computing Astar, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632, Singapore.

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2 Methods and simulation setup

The finite-difference time-domain (FDTD) method was used for the simulations. The FDTD method is commonly used to solve electromagnetic boundary value problems. Essentially, it discretizes space and time and approximates the derivatives of the field components using finite differences. The fields are then calculated for every time step using Maxwell's curl equations. The FDTD method works with both steady-state and transient sources. Although steady-state sources are the object of interest, transient sources offer an efficient way to obtain the frequency domain data for steady-state sources, which can be easily obtained through a Fourier transform.

A gold cubic nanoparticle of side length 200 nm was simulated in air, irradiated in the negative z direction with linearly polarized light in the y direction as shown in Fig. 1. The nanoparticle was rotated anticlockwise at an increment of 15° . Perfectly matched layers were set at all sides of the simulation region. A single nanoparticle system is investigated as its behavior is identical to that of an array of nanoparticles with sufficiently large period. Simulation mesh size was set to 2 nm in all three directions to ensure convergence and thus accuracy of data. Gold permittivity values were taken from data by Johnson and Christy [20].

To determine the torque induced on the nanoparticle under linearly polarized light, the volumetric technique was used, where the Lorentz force shown in Eq. 1 is calculated at every point of the mesh [21, 22].

$$\mathbf{F} = q\mathbf{E} + q\mathbf{v} \times \mathbf{B} \quad (1)$$

We define circularly polarized light from the point of view of the source. Charge density and time averaged force distribution profile data are collected from the frequency domain data. Absorbance was calculated using

transmittance (T) and reflectance (R), which are calculated values based on fraction of intensity of the original light source. Absorbance of 0.5 mean that 50% of the source power is absorbed.

$$A = 1 - T - R \quad (2)$$

3 Results and discussion

In order to determine the charge distribution, we first need to determine the SPP resonance wavelength of the nanoparticle.

From Fig. 2, we observe that there is a redshift in absorbance resonance wavelength for the 45° rotated nanoparticle compared to the 0° rotated nanoparticle. This is due to an increased charge separation as the surface plasmons are able to oscillate along a larger length, resulting in a lower restoring force. As a result, there is a lower frequency of electron oscillations and thus a higher resonance wavelength.

However, there is an unexpectedly larger redshift for the 15° , 30° , 60° and 75° rotated nanoparticle, compared to that of both 0° and 45° rotated nanoparticle. Interestingly, for these angles of rotation, there are other modes of plasmon resonance present alongside the main dipole resonance. This results in a decreased restoring force due to interactions between the main dipole and the additional modes. As a result, there is a lower frequency of electron oscillations and thus a higher resonance wavelength. This is further explained in Figure S1 of the Supplementary Information.

The resonance wavelength of 600 nm was used to obtain the charge distribution profiles. Charge distribution

Fig. 1 Simulation setup of a cubic gold nanoparticle under irradiation of linearly polarized light in air

Fig. 2 Graph of absorbance of cubic nanoparticle against wavelength (nm), rotated anticlockwise at increments of 15°

Table 1 Charge distribution of cubic nanoparticle rotated anticlockwise at increments of 15° irradiated by 600 nm linearly polarized plane wave light source, obtained at xy plane cutting through the center of the nanoparticle.

The plus and minus symbols show the positions of the induced positive and negative charges while the green arrow shows the direction of the polarization vector.

Fig. 3 Graph of CD of rotated cubic nanoparticle against wavelength (nm), rotated anticlockwise at increments of 15°

profiles are essential to predict the torque acting on the nanoparticle as the torque arises due to the separation of charges and the individual forces acting on the charges. The charge distributions are used to predict the circular dichroism, which would then in turn relate to the induced torque.

The charge distribution profiles were normalized and are displayed in Table 1.

From the charge distribution profiles, we can observe skewness in the polarization vector, where the direction do not all point in the y-direction (in the case of the nanoparticle rotated at 15°, 30°, 60°, 75°), despite being irradiated with y-polarized light. Since linearly polarized light is the superposition of right and left circularly polarized light, the skewed polarization vectors suggest an unequal absorption of right and left circularly polarized light, also known as circular dichroism (CD). CD is defined as the difference in absorption of circularly polarized light,

$$CD = A_l - A_r \quad (3)$$

where A_l and A_r are the respective absorbances of left and right circularly polarized light.

The CD spectra for the cubic nanoparticle rotated at different angles are shown in Fig. 3 using the extinction and scattering spectrum. Peak CD is observed at the wavelength of 620 nm, slightly redshifted from that of the resonance wavelength of 600 nm. This is further explained in S2 of the Supplementary Information.

At resonance wavelength, the cubic nanoparticle exhibits negative CD for angles of 15° and 30° and positive CD for 60° and 75°. In fact, the CD for 15° and 75° are opposite signs of one another, similar to that with 30°

and 60°. We observe that there is a correlation between the skewness in charge distribution and the CD spectra. When the polarization vector (defined to be pointing from region of negative charge to positive charge) is skewed clockwise from the vertical (if pointing up, then right; if pointing down, then left), CD is negative and vice versa. When the polarization vector is centered, CD is zero.

Instead of obtaining the charge distribution from FDTD simulations, the charge distribution can be simply obtained via the superposition of the charge distributions of both LCP and RCP, which can be predicted from the dipole moment [11–13]. Next, we calculate the torque acting on the nanoparticle using Eq. 4, where τ is torque, $\mathbf{r}$ is the displacement vector and $\mathbf{F}$ is the Lorentz force calculated with the volumetric technique. A Riemann sum was used instead of the integral due to discretization used in FDTD methods.

$$\tau = \int \mathbf{r} \times d\mathbf{F} \quad (4)$$

Table 2 displays the torque induced for different angles of rotation. Torque in Table 2 is normalized against a combination of mesh volume and source power.

Interestingly, the torque and CD demonstrates a relationship, where a nanoparticle with positive CD experiences positive torque, negative CD experiences negative torque and no CD experiences no torque (essentially zero compared to other torques, which are orders of magnitude greater).

Positive torque indicates anticlockwise rotation while negative torque indicates clockwise rotation. A positive CD, where LCP light absorption is dominant indicates positive torque, while vice versa. Thus, dominant absorption of circularly polarized light results in rotation of nanoparticle in the same direction as the rotation of electric field vector by a continuous wave light source.

As circularly polarized light irradiates the gold nanoparticle, it induces plasmonic oscillations, and the induced charge causes a dipole moment in the same direction as the electric field vector. As the electric field rotates, the induced charges then experience an electric force due to the rotating electric field, and thus causes the nanoparticle to rotate in the same direction as rotation of that of the electric field. Thus, from the parity of the CD, the parity of the torque due to dominant absorption of either LCP or RCP can be predicted.

Certain shapes such as cubic nanoparticles have an equilibrium position in which they will be aligned in a specific orientation under irradiation of linearly polarized

Table 2 Torques on square nanoparticle under irradiation by 600 nm linearly polarized plane wave light source, rotated anticlockwise at increments of 15°

Angle of rotation (°)	τ (Normalized unit)
0	-2.49×10^{-3}
15	-11.63
30	-12.67
45	-3.00×10^{-3}
60	12.67
75	11.63

Table 3 Torques on square nanoparticle in plastic under irradiation by 610 nm linearly polarized plane wave light source, rotated anticlockwise at increments of 15°

Angle of rotation (°)	τ (Normalized unit)
0	1.91×10^{-3}
15	-148.38
30	-189.82
45	-1.94×10^{-4}
60	189.83
75	148.38

Fig. 4 Determining equilibrium position by analyzing the two different cases of CD using charge density **Fig. 5** Graph of absorbance of cubic nanoparticle against wavelength (nm), rotated anticlockwise at increments of 15° in plastic

light. Figure 4 depicts the process to determine these equilibrium positions, by looking at the different cases of negative and positive CD and seeing if they share a specific resultant orientation which have no induced torque.

We then investigated the effect of changing the background from air to a plastic (Refractive index of 1.49), on the optical torque induced.

From Fig. 5, the general trend for absorbance with a plastic background is similar to that of an air background. There is a redshift in resonance wavelength for the 45° rotated nanoparticle compared to the 0° rotated

Fig. 6 Graph of CD of rotated cubic nanoparticle in plastic against wavelength (nm), rotated anticlockwise at increments of 15°

nanoparticle, along with a further redshift in resonance wavelength for 15°, 30°, 60° and 75° rotated nanoparticle, due to the additional modes of resonance.

However, there is also an additional redshift to all resonance wavelengths, as a result of increase in background index (from 1 of air to 1.49 of plastic). This is due to the polarizability of the plastic surrounding, resulting in attenuation of the surface charge induced by plasmonic oscillations. As a result, there is a decrease in the restoring force and thus a slight redshift in the resonance wavelength. Specifically for the 15°, 30°, 60° and 75° rotated nanoparticle (the orientations where optical torque is induced), the resonance wavelength is redshifted from 600 to 610 nm.

Table 3 displays the torque induced for different angles of rotation in plastic. Interestingly, there is a large increase (Of about an order of magnitude) in torque induced on the nanoparticle when the background is changed from air to plastic. This increase in torque can be attributed to the change in CD spectra and charge distribution.

Table 4 Charge distribution of cubic nanoparticle in plastic, rotated anticlockwise at increments of 15° irradiated by 610 nm linearly polarized plane wave light source, obtained at xy plane cutting through the center of the nanoparticle

The plus and minus symbols show the positions of the induced positive and negative charges while the green arrow shows the direction of the polarization vector

Fig. 7 $|E|$ distribution of cubic nanoparticle in air and plastic, normalized against source amplitude

From Fig. 6, we can observe that there is an increase in CD. As CD increases, the increased disproportionate absorption of circularly polarized light results in a greater magnitude of torque induced. The charge distribution profiles are displayed in Table 4.

We observe that the charge distributions remain relatively similar (see S3 of Supplementary Information) despite the change in refractive index. The relationship between torque, CD and charge distribution remains consistent. A charge distribution with a polarization vector skewed to the right corresponds to negative CD and negative torque, and vice versa.

However, due to an increase in background refractive index, there is an increase in surface charge localization, as indicated by the charge distribution profiles. From Fig. 7, we can see that there is a much higher electric field and thus much higher charge localization for the gold nanoparticle in plastic (b) compared to in air (a). As a result, there is a larger induced torque acting on the nanoparticle.

4 Conclusion

There exists a correlation between circular dichroism, charge distributions and induced torque of a nanoparticle when irradiated with linearly polarized light. These charge distribution profiles arise from excited localized surface plasmon polaritons induced by the electromagnetic fields of the irradiated light. Such charge distribution profiles result in induced torque acting on the nanoparticle due to the Lorentz forces on the individual charges. By analyzing the charge distributions, the circular dichroism of the nanoparticle can be predicted based on the skewness of the polarization vector, which can then be used to predict the induced torque. By analyzing the induced torque, specific equilibrium positions can be found for certain shapes of nanoparticles (such as 0° orientation for cubic nanoparticle) such that all of them will be aligned in a specific orientation under irradiation of linearly polarized light,

depending on the polarization direction. Increasing surrounding refractive index seems to be an effective tool in controlling the nanoparticle dynamics, with the equilibrium positions unchanged and yet the torque induced increases tremendously. However, there are shifts in resonance wavelengths which need to be taken into account.

Compliance with ethical standards

Conflict of interest M. C. Toh, W. K. Phua and E. H. Khoo declare that they have no conflict of interest.

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