

# Demonstration of Switching Plasmonic Chirality via Geometric Transformations for Biosensing Applications



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**Abstract** The ability to detect and differentiate between left and right-handed biopolymers has important biosensing applications. Although this can be done using circular dichroism (CD), the CD signal is usually weak. To amplify it, plasmonic nanostructures can be used. This paper presents a simulation study of the use of a planar array of cubic nanostructures, demonstrating the switching of chirality through performing geometric transformations. It has been found that when the cubes are rotated about their vertical axis and when the angles  $\varphi$  and  $\theta$  of incident light are varied, CD can be observed, and performing the opposite action results in the switching of CD. As the use of cubes as compared to other structures, such as the chiral gammadion structure in reported works, has the merit of being easier to fabricate, the methods described in this paper have much potential in being used to detect chiral biopolymers.

**Keywords** Circular dichroism · Plasmonic nanostructures · Switching of chirality · Simulation study

## 1 Introduction

The building blocks of life comprise amino acids, nucleic acids and sugars [1], all of which are chiral molecular units [2, 3], where the mirror image of the molecular unit does not superimpose with its original unit [3]. Biopolymers, which are macromolecules formed from these units, also exhibit chirality on molecular and supramolecular scales [4]. The ability to detect chiral biopolymers and distinguish between the left- and right-handed biopolymers is important as it has extensive biosensing applications in biomedical and pharmacological fields [5], such as the

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detection of amyloid diseases [4]. However, there is substantial difficulty in differentiating left- and right-handed biopolymers due to their similar physical and chemical properties [6].

One way to differentiate left- and right-handed biopolymers is by making use of their interaction with left- (LCP) and right- (RCP) handed circular polarized light [7]. Biopolymers with the same handedness as the incident circular light waves interact more strongly with the light, thus absorbing a greater fraction of the light, as opposed to biopolymers with opposite handedness as the incident circular light waves [8]. The differential absorption of LCP and RCP light is known as circular dichroism (CD) [7, 9]. Unfortunately, the CD signal is weak [5, 10], and therefore not very sensitive and does not provide a robust method for judging handedness in dilute solutions [5].

To amplify the CD signal, plasmonic nanostructures can be used as a light field enhancement method [11], where localized surface plasmon polaritons interact with the chiral molecules. The localized field allows for a longer time of interaction with the chiral molecules, thereby producing a stronger CD signal to be detected. The most common nanostructure used to amplify the CD signal is the gammadion cross, which is chiral [12]. Reported works have demonstrated experimentally that the sensitivity detection of chiral molecules improved by a factor of  $10^6$  using gammadion plasmonic structures [4]. In addition, numerous three-dimensional (3D) chiral nanostructures have also been proposed, such as metal helix structures [13–15] and layer-by-layer chiral plasmonic nanostructures [16]. Furthermore, it has been discovered that CD can be observed in not only intrinsic chiral structures, but also in achiral structures with an oblique incident light beam [17]. The use of planar arrays of achiral nanostructures, such as L-shaped nanostructures, has been explored as such nanostructures present an advantage in being easier to fabricate than the aforementioned 3D or planar chiral nanostructures [17].

This paper presents a simulation study of a planar array of achiral cubic plasmonic nanostructures for the detection of chiral molecules. Although naturally achiral by themselves, it is expected that cubes can exhibit chiral properties when geometric transformations, namely rotations, are applied to them or when light is incident on them at oblique angles. In addition, performing the opposite action should result in the switching of the CD spectrum. In this study, the cubes were rotated in the  $xy$ -plane and the resultant CD spectra are presented. In addition, the effect of oblique incidence on the nanostructures was also studied, by varying the angle(s) of light incident on the cubic nanostructure array. Compared to gammadion nanostructures and other chiral structures, the benefit of using cubic nanostructures lies in the comparative ease in fabrication, similar to the achiral L-shaped nanostructures.

## 2 METHODS

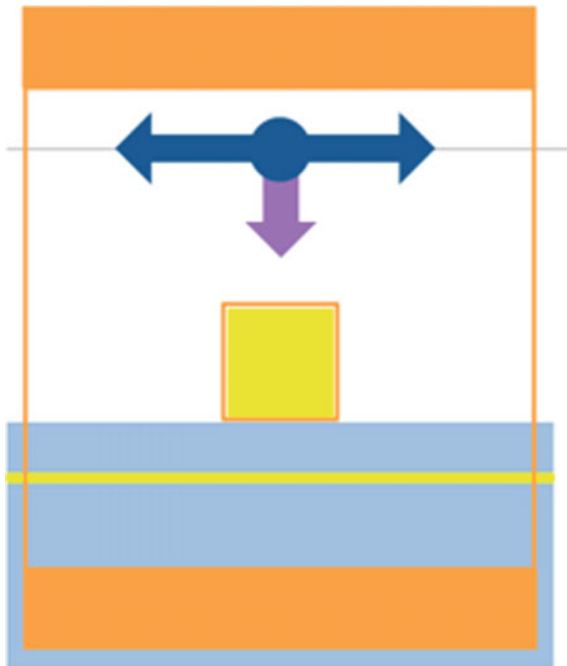
The simulations were designed and run using Lumerical's Nanophotonic finite-domain time-difference (FDTD) Simulation Software. The FDTD method is a grid-based numerical modeling technique that approximates the derivatives in the

Maxwell curl equations by finite differences. Material properties are defined at various spatial coordinates and fields are then calculated for small successive time steps where the step size is small compared to the inverse of the frequency of the source [18].

The design of the simulation is as shown in Fig. 1. A gold cubic nanostructure of sides 200 nm was positioned atop a larger borosilicate glass substrate of reflective index 1.517. Water is chosen to be the background medium and the background index is set to 1.333. A fine mesh with cell division of 20 nm in the x-, y- and z-directions was placed around the cube. The simulation region was set to 800 nm in the x- and y-directions to create an array in the xy-plane with a periodicity of 800 nm. A perfectly matched layer (PML) was set in the z-direction to impose absorbing boundary conditions to prevent reflections of energy back into the structure that was being simulated. A monitor was placed 100 nm beneath the cubic nanostructure to measure the intensity of the electric field of transmitted light. Two light sources of plane waves were used to create circularly polarized light, where one of the light source has its polarization angle set to  $0^\circ$  and another to  $90^\circ$ . The phase angles of light sources also differ by  $90^\circ$ .

To obtain the CD spectrum, two simulations were run, one with LCP light and one with RCP light, where the phase angle of the second light source was  $-90^\circ$  and  $+90^\circ$  respectively. It should be noted that although CD by conventional definition is the difference in the absorption of LCP and RCP light, Lumerical's FDTD solutions provide only the data on transmittance and not absorbance.

**Fig. 1** Design of simulation of cubic nanostructures (not drawn to scale)



However, given that  $I = T + R + A + S$ , where  $I$  is the total intensity of incident light and  $T$ ,  $R$ ,  $A$  and  $S$  are the transmitted, reflected, absorbed and scattered light respectively, and since reflected LCP and RCP light are approximately equal and scattered light is negligible, CD can be approximated to be the difference in transmitted RCP and LCP light when the incident light is of equal intensity. Therefore, in this paper, CD is defined by

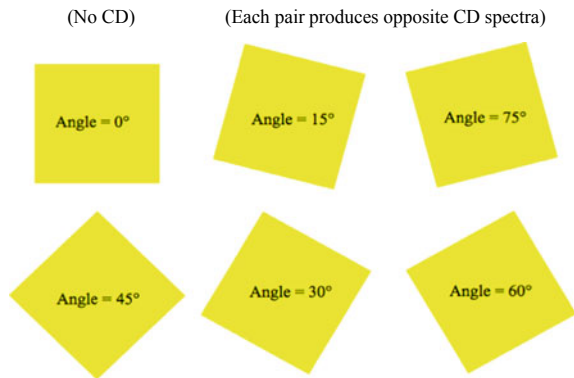
$$CD = T_R - T_L. \quad (1)$$

The array of cubic nanostructures to be simulated as illustrated in Fig. 1 would not produce CD signals as it is achiral. To produce CD signals, geometric transformations were performed to break the symmetry. This was attempted in two ways:

First, the cube was rotated clockwise about its vertical axis in the  $xy$ -plane from  $0^\circ$  to  $75^\circ$  at regular intervals as shown in Fig. 2. Incident light was normal to the top surface of the cube. It was expected that deviation from the  $45^\circ$  mark by the same amount in opposite directions, i.e. the cube being rotated  $15^\circ$  and the cube being rotated  $75^\circ$ , as well as  $30^\circ$  and  $60^\circ$ , would produce opposite CD spectra due to their being mirror images. No CD signal was expected to be observed when the cube is rotated  $45^\circ$  because, similar to that for  $0^\circ$ , the cube would be symmetrical and therefore achiral.

Second, the angles at which light is incident on the cubic nanostructure array were varied while keeping the angle of rotation of cube to  $0^\circ$ . The angles  $\varphi$  and  $\theta$  (as illustrated in Fig. 3) were varied first separately and then together. In the first trial, angle  $\varphi$  was varied from  $-75^\circ$  to  $75^\circ$  while angle  $\theta$  was kept to  $0^\circ$ . In the second trial, angle  $\theta$  was varied from  $-75^\circ$  to  $75^\circ$  while angle  $\varphi$  was kept to  $0^\circ$ . In the third trial, both angles  $\varphi$  and  $\theta$  were varied from  $-75^\circ$  to  $75^\circ$  where  $\varphi = \theta$ . In all three cases, it was predicted that deviation from the  $0^\circ$  mark by the same amount in opposite directions, e.g. angle(s)  $\varphi$  and/or  $\theta$  of incident light being  $15^\circ$  and that being  $-15^\circ$ , would produce opposite CD spectra.

**Fig. 2** Top view of the cube being rotated  $0^\circ$ ,  $15^\circ$ ,  $30^\circ$ ,  $45^\circ$ ,  $60^\circ$  and  $75^\circ$



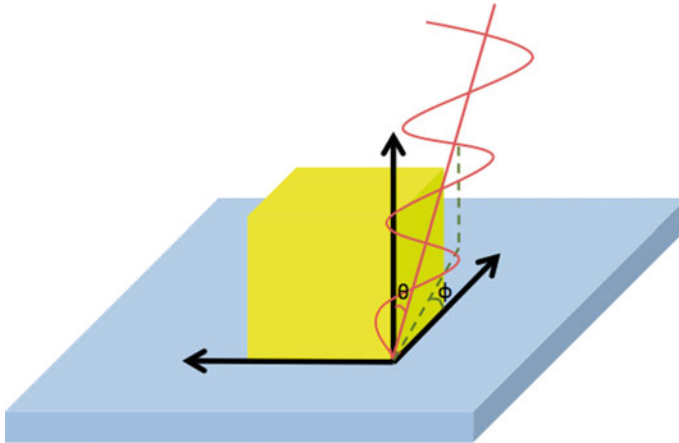


Fig. 3 Schematic diagram showing oblique incidence of light on the cube

### 3 Results and Discussion

The attempt to produce CD by rotation of the cubic nanostructures was successful and the CD spectra obtained is as shown in Fig. 3. As predicted, the CD spectra of the cube rotated 75° and 60° are the negative of the CD spectra of the cube rotated 15° and 30° respectively, where the CD at every wavelength for 15° and 75°, as well as 30° and 60°, has equal magnitude but opposite signs. The flipping of the sign of CD indicates a switching behaviour resulting from a change in the handedness of the nanostructure. Also, no CD signal is produced at 0° and 45°, which confirms the hypothesis. It is noted that of the three modes, the first provides the most significant switching effect (Fig. 4).

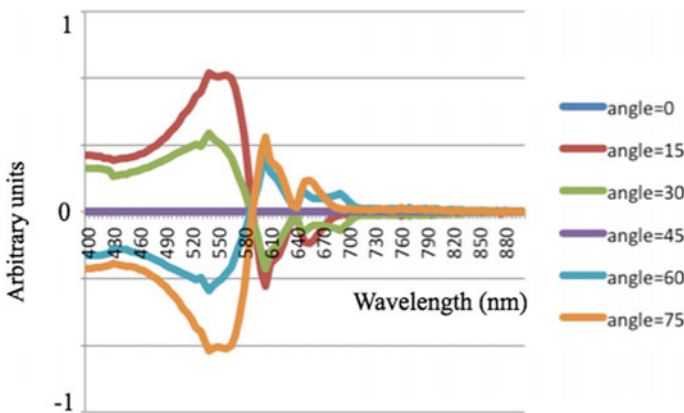
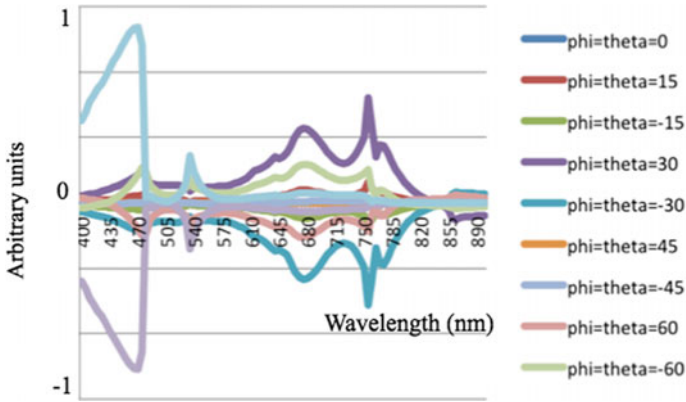


Fig. 4 CD spectra of cubic nanostructure array when cubes were rotated from 0° to 75°



**Fig. 5** CD spectra of cubic nanostructure array when both angles  $\varphi$  and  $\theta$  were varied from  $-75^\circ$  to  $75^\circ$

On the other hand, varying angles  $\varphi$  and  $\theta$  of incident light separately was unsuccessful at producing any discernible CD spectra, as the transmittance of RCP light was equal to that of LCP light for every setup. As existing literature indicates that CD could be observed when angles  $\varphi$  and  $\theta$  are varied separately for other structures such as the L-shaped nanostructures [17], it is likely that the lack of CD here can be attributed to the nature of the cube and more research can be done in this area.

However, CD was once again observed when both angles  $\varphi$  and  $\theta$  of incident light were varied at the same time. The CD spectra obtained is as shown in Fig. 5. As can be seen from the superimposed graphs, apart from  $45^\circ$  and  $-45^\circ$  where no CD was observed, the CD spectra of light incident at negative angles ( $\varphi = \theta = -15^\circ, -30^\circ, -60^\circ, -75^\circ$ ) are a vertical reflection of those at positive angles ( $\varphi = \theta = 15^\circ, 30^\circ, 60^\circ, 75^\circ$ ), thus successfully demonstrating the switching of chirality. Among the resonant modes observed, it is noted that the first mode provides the most significant switching effect for  $\varphi = \theta = 75^\circ$  and  $\varphi = \theta = -75^\circ$ .

## 4 Conclusion

It has been demonstrated that an array of achiral cubic plasmonic nanostructure is capable of producing the effect of switching of CD when geometric transformations namely rotation of the cube and variation of angles  $\varphi$  and  $\theta$  of incident light are performed. There is therefore much potential in using these methods to distinguish between left- and right-handed biopolymers, especially due to their relative ease in fabrication as compared to gammadion structures and other chiral nanostructures in reported works. For future research, the fabrication of planar cubic nanostructure

array with the aforementioned methods to produce CD can be carried out to experimentally verify the findings presented in this paper. In addition, the design of other simple nanostructures to amplify CD signals can be studied as well.

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