Tunable Chiroptical Response of Chiral Plasmonic Nanostructures Fabricated with Chiral Templates through Oblique Angle Deposition

Tong Fu, Yu Qu, Tiankun Wang, Gang Wang, Yongkai Wang, Hui Li, Juan Li, Li Wang, and Zhongyue Zhang

School of Physics and Information Technology, Shaanxi Normal University, Xi’an 710062, China

ABSTRACT: Chiral plasmonic nanostructures (CPNs) with a strong chiroptical response in visible and near-infrared regions were fabricated with homemade SiO₂ chiral templates through oblique angle deposition. The circular dichroism spectra of the CPNs showed that the chiroptical response was amplified with increased deposition thickness of silver. Simulation results demonstrated that only the magnetic dipole mode was excited when the deposition thickness was small. Magnetic and electric dipoles emerged and coupled to each other with increased silver deposition thickness. As a result, chiroptical enlargement occurred. This study provides a concise method of fabricating CPNs with a tunable chiroptical response.

1. INTRODUCTION

A structure is chiral when it cannot be overlapped with its mirror image. Chirality is a fundamental feature of living things and perhaps even a must for life. All amino acids are chiral except for glycine, and all of them exist in one possible handedness. Electromagnetic waves can also be chiral according to the photon spin, that is, left circularly polarized (LCP) and right circularly polarized (RCP) light. Circular dichroism (CD) is the difference in the absorption coefficient when a chiral structure interacts with a different chiral electromagnetic wave. Most naturally occurring chiroptical systems originate from the coupling between the electric and magnetic dipoles in the chiral medium; this coupling is usually weak. Many studies have shown that chiral plasmonic nanostructures (CPNs) lead to significant chiroptical effects and have resulted in several completely new concepts and applications in physics, such as negative refraction, broadband circular polarization, and biosensing.

The most straightforward image of chiral configuration is the helix, and a strict helix presents broadband chiroptical properties in the near-infrared (IR) region because of standing wave superposition. Utilizing individual nanoparticles or nanorods to replace the helix is an insightful and easy approach to achieve 3D chiral configurations. The chiral plasmonic mode has been explored by tuning the interdistance of particles. Another typical type of 3D CPNs is bilayer, twisted nanostructures, in which magnetic and electric resonances arise simultaneously; these structures present a remarkable chiroptical response. 2D CPNs cannot be superposed with their mirror images through in-plane rotations and translations. The chiroptical response of 2D CPNs is comparably weak because they only have the electric or magnetic oscillation mode. Switching of chiroptical modes usually necessitates the remake of CPNs or modification of their configuration. Oblique angle deposition (OAD) is regarded as an industrial technique to prepare CPNs due to its low cost and scalability. With the assistance of shadowing templates, diverse CPNs with chiroptical response located in visible and near-IR regions have been fabricated, yet the chiroptical mode of such CPNs is monotonous; therefore, the strength of chiroptical is hardly manipulated.

A chiral template-assisted method was proposed in the present study. CPNs were fabricated with homemade chiral templates on polystyrene (PS) nanosphere through OAD. The chiroptical mode and the strength of the chiroptical response of CPNs can be adjusted easily by changing the deposition thickness of silver (Ag) because of the use of chiral templates. By increasing the deposition thickness of Ag, the chiroptical mode switched from magnetic dipole mode to electric and magnetic dipole coupled mode. As a result, the strength of the chiroptical response increased correspondingly. CPNs can be achieved with a wide choice of materials because of the versatility and tunability of chiral templates. Moreover, the CPNs are applicable in diverse areas due to the concise fabrication process.

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2. EXPERIMENTAL SECTION

The fabrication scheme is shown in Figure 1. Self-assembled PS nanosphere monolayers with a diameter of 380 nm were prepared on glass substrates through the air–water interface technique. Details of PS nanosphere monolayer preparation are presented in the Supporting Information, Section S1. Three steps of deposition are needed to fabricate the CDNs. Depositions of SiO$_2$ (two steps) onto the monolayer substrate were conducted through OAD to form the chiral templates. Both depositions adopted the same tilt angle of $\theta = 86^\circ$ with respect to the normal substrate (Figure 1a,b). The angle of substrate azimuthal orientation was defined as $\varphi$ and is shown in Figure 1a. For right-handed templates, the rotation of $\Delta \varphi$ was $\Delta \varphi = -90^\circ$ and that for left-handed templates was $\Delta \varphi = 90^\circ$ (Figure 1b). The deposition thicknesses were set as $T_1 = T_2 = 60$ nm for the first and second depositions. The last stage was the normal incident deposition of Ag on chiral templates to form the left-handed CPNs (L-CPNs, as shown in Figure 1c, where the deposition thickness was set as $T_3$). The set deposition thicknesses of $T_1$, $T_2$, and $T_3$ were monitored by a quartz crystal microbalance positioned at normal incidence to the vapor source in OAD (refer to Supporting Information, Section S1 for further details).

Figure 1. Schematics of the fabrication process (a) shadow growth of first SiO$_2$ layer; (b) shadow growth of second SiO$_2$ layer to form left-handed chiral templates (bottom is top view of left handed chiral template); and (c) normal deposition of Ag layer to form left handed CPNs (bottom shows L-CPNs viewed from different angle).

3. RESULTS AND DISCUSSION

The CPNs possessed a distinct morphology in the large-scale area; this is because they have different orientations on the microscale, details can be found in our previous study. Scanning electron microscopy (SEM) images with the typical morphology of L-CPNs are shown in Figure 2 at various deposition thicknesses. The SEM image with $T_3 = 10$ nm is shown in Figure 2a. On one hand, the Ag on the chiral templates of SiO$_2$ formed an L-shaped structure and separated with the Ag on the nanosphere (artificially colored light blue in the Figure insets). On the other hand, the Ag on the nanosphere was not a strict film but separated Ag islands (artificially colored light red in the Figure insets). Minimization of surface energy causes Ag atoms to condense onto the surface of the nanosphere; these atoms then present a tendency to form separated islands. Subsequent Ag vapor flux was filled in the gap of Ag islands with increasing $T_3$ and the L-shaped structure connected the Ag to the nanosphere (Figure 2b). The L-CPNs became a strict film when $T_3 = 20$ nm, and almost all of the Ag islands were connected to one another, as shown in Figure 2c. Figure 2d shows the transmission electron microscopy (TEM) image of a single L-CPN on nanosphere. The Ag film split in the outer edge of SiO$_2$ chiral templates because the growth direction of SiO$_2$ chiral templates is along the outward direction of nanosphere. This split is clearly identified from the TEM image. (Additional TEM images are provided in Figure S1.)

All CD spectra were measured with photon normal incidence with respect to the substrate, as illustrated in Figure 3a. The unpolarized absorption of the PS nanosphere, the SiO$_2$ chiral templates, and CPNs with $T_1 = T_2 = 60$ nm and $T_3 = 10$ nm are depicted in Figure 3b. All spectra showed an absorption peak at around $\lambda = 520$ nm (marked by dashed arrow and “PS” in Figure 3b), which signifies the first diffracted order of 2D close-packed monolayer arrays. The unpolarized absorption of CPNs showed no distinct handedness-dependent feature, as indicated in Figure 3b. A broad peak appeared at $\lambda = 620$ nm, and this peak corresponds to the localized surface plasmon resonance (LSPR) of the Ag film. The CPNs showed a distinct chiroptical response at around $\lambda = 550$ nm. The L-CPNs exhibited positive rotation in the visible range from 500–700 nm, which implies that the absorption of LCP light was stronger than that of RCP light. The maximum amplitude of $+0.434$ deg was reached at $\lambda = 560$ nm. The R-CPNs, as
expected, showed an opposite trend of rotation and reached the maximum amplitude of $-0.541$ deg at $\lambda = 565$ nm. The chiroptical response of CPNs did not result from the chiral templates nor from induced chiral current in the Ag film by chiral templates, as verified in Supporting Information Sections S3 and S4. Moreover, a series of experiments was conducted to demonstrate that the optical properties of linear dichroism and linear birefringence are negligible (see Supporting Information, Section S5). This is reasonable because hexagonal close-packed CPNs on the PS nanosphere are isotropic on the macroscale, even if they have different orientations on the microscale.

To show how the deposition thickness of Ag influences the CD signal, the CD spectra with increasing $T_3$ are presented in Figure 4b. With $T_3$ increasing from 10 to 15 nm, the magnitude of the CD peak significantly increased from $+0.434$ deg and $-0.541$ deg to $+0.814$ deg and $-0.839$ deg for L-CPNs and R-CPNs, respectively. Furthermore, the CD peak red-shifted to a wavelength of around $\lambda = 610$ nm. The same trend was displayed when $T_3$ was further increased, and the position of the CD peak reached its peak at $\lambda = 625$ when $T_3 = 20$ nm. The CD peak remained at $\lambda = 625$ nm when $T_3 = 25$ nm (Figure S6). Dissymmetry factor $g$ is a parameter to evaluate the chirality of a chiral structure and is a dimensionless quantity factor. The $g$ factor is defined as $g = \Delta A/A$, where $\Delta A = CD (\text{deg})/33$ is the differential absorption between LCP and RCP light and $A$ is the unpolarized absorption. For the CPNs, the $g$ factor was also calculated, as shown in Figure 4c. The magnitude of the $g$ factor is higher than 0.03 around the peak and is comparable to those in recent studies.23

Quantitative analysis of CD spectra with increasing $T_3$ is shown in Figure 5. The position of the CD peak red-shifted with increasing $T_3$ and reached its peak when $T_3 = 25$ nm, as...
shown in Figure 5a. However, the value of the CD peak displayed trends different from that of position. Figure 5b clearly shows that the values of the CD peaks increased with increasing $T_3$, even when $T_3 = 25$ nm. Enlargement and red-shifting of the LSPR mode of Ag occurred with increasing $T_3$, as marked by solid arrow in Figure 5c. These phenomena are related to the enlargement and red-shifting of the chiroptical response. Moreover, given the use of chiral templates, the plasmonic material required only normal incident evaporation. The effect of the surface diffusion of the incident material can be eliminated, so a wide choice of materials can be used to fabricate CPNs (Supporting Information, Section S8).

Three models were simulated with the finite element method (FEM) to interpret the experimental results (see Supporting Information, Section S8 for further details). The simulated geometric models are based on SEM and TEM images, which are shown in Figure 6a. The thickness of the chiral templates of the SiO$_2$ layer was estimated to be 30 nm (see Supporting Information Section S3). CPNs were assumed as L-shaped structures on L-shaped SiO$_2$ when $T_3 = 10$ nm, and the influence of the Ag island on the nanosphere was ignored (Figure 6a). The size distribution of Ag islands is shown in Supporting Information Section S8 along with the absorption spectrum of the Ag islands with average size. The absorption peak is located at $\lambda = 485$ nm. Therefore, the Ag islands did not contribute to the chiroptical response. The thickness of the L-shaped structure was $t_1 = 10$ nm. As $T_3$ approached 15 nm, the influence of the Ag film on the nanoparticle was considered and...
simplified as a disk that connects to the L-shaped structure on the inner side but splits on the outer side of the L-shaped structure. The thickness and radius of the disk were \( t_1 = 10 \text{ nm} \) and \( r = 150 \text{ nm} \), respectively. When \( T_3 = 20 \text{ nm} \), the parameters were set as \( t_1 = t_2 = 12 \text{ nm} \) and \( r = 180 \text{ nm} \). The CD spectra were defined similarly as the experimental one (\( \Delta A = A_{\text{LCP}} - A_{\text{RCP}} \)) in the simulation. The L-shaped structure showed a CD peak with a maximum of \( \Delta A = 0.059 \) at \( \lambda = 570 \text{ nm} \), which means that \( A_{\text{LCP}} \) is larger than \( A_{\text{RCP}} \) (Figure 6b). When the L-shaped structure was connected to the disk with \( r = 150 \text{ nm} \), the CD peak remarkably increased to \( \Delta A = 0.122 \), and the position of the CD peak red-shifted to \( \lambda = 577 \text{ nm} \). When \( r = 180 \text{ nm} \) together with \( t_1 = t_2 = 12 \text{ nm} \), the CD signal enlarged to \( \Delta A = 0.163 \), namely, 2.8 times that of the L-shaped structure with thickness \( t_1 = 10 \text{ nm} \), and red-shifting occurred from \( \lambda = 570 \) to 585 nm. The simulation results presented similar trends of enlargement and red-shifting as the experimental results.

To determine the chiroptical mechanism of CPNs with different thicknesses, Figure 7 shows the calculation absorption spectra for LCP and RCP light excitation as well as the \( \Delta A \) spectra. Figure 7c,d shows the near-field charge distributions of the L-shaped structure at \( \lambda = 570 \text{ nm} \) for both excitation polarization. The equivalent current is marked with black dashed arrows. It can be clearly observed that the near-field charge is mainly distributed on the surface of the CPNs. Only the magnetic dipole mode was excited for the L-shaped structure under the excitation of LCP and RCP light. Under LCP light excitation, the magnetic dipole was around the entire L-shaped structure (Figure 7c). However, under RCP light excitation, the magnetic dipole mainly resided in one arm of the L-shaped structure (Figure 7d). The chiroptical mode was distinctly altered from that of the L-shaped structure when the L-shaped structure was connected to the disk. The equivalent current in the L-shaped structure coupled to that in the disk and formed a magnetic dipole moment, and an electric dipole appeared on the other side of the disk (Figure 7g,h). Equivalent magnetic and electric dipole moments are marked by black solid arrows and translated to the bottom part of Figure 7g,h. The angle between the electric and magnetic dipole moments is <90° for both LCP and RCP excitations (Figure 7g,h).

The enlargement and red-shifting of the chiroptical response when \( T_3 \) increased can be attributed to two facts. First, only magnetic dipole can be excited when \( T_3 \) is small, and the CD response is weak. Both magnetic and electric dipoles are excited when \( T_3 \) is increased; they couple to each other and result in the enlargement of the CD response. Second, the L-shaped structure connects with the Ag film on the nanosphere, the dimension of which increases with increasing \( T_3 \). Thus the electric resonance length of the electric dipole moment increases and causes the red shift. The simulation enlargement is larger than that of the experimental one because of the cancellation effect caused by the random orientation of the PS array in the experiment. The limitation of the red shift in the spectra is due to the CPNs reaching the dimension limitation, which is the dimension of the nanosphere. Moreover, the red shift in the simulation results is weaker than that in the experimental one because the electric resonance length in the experiment is on the curved Ag shell, which is larger than the disk in the simulation.

4. CONCLUSIONS

Large-scale CPNs were fabricated with homemade chiral templates. Both experimental and simulation results showed a tunable chiroptical response in the visible to near-IR regions. The simulation results revealed that the use of chiral templates caused the CPNs to possess a tunable chiroptical mode by tuning the deposition thickness of Ag. Only the magnetic dipole was excited when deposition thickness of Ag was small. Increasing the deposition thickness resulted in both electric and magnetic dipoles being excited and coupling to each other, thus causing the CD response to become stronger. This result provides a concise method to fabricate CPNs with a tunable chiroptical response mode. Moreover, CPNs can be fabricated with a wide choice of materials because of the versatility of chiral templates. The chiral electric field is mainly on the surface of CPNs, which could be used in the application of sensors to amplify the CD signal of chiral molecules. The versatility of chiral templates and the tunable chiroptical mode make the application of CPNs in diverse areas very promising.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b10833.

**Experimental and simulation details, TEM and SEM images, and additional CD spectra.** (PDF)

### AUTHOR INFORMATION

**Corresponding Author**

*E-mail: zyzhang@smnu.edu.cn. Tel: 86-029-81530764.

**ORCID**

Zhongyue Zhang: 0000-0002-2843-429X

**Notes**

The authors declare no competing financial interest.

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