Fabrication and Circular Dichroism of Ladder-shaped Nanostructures by oblique angle deposition technique

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***Abstract*—This paper reports that a ladder-shaped chiral nanostructure formed on a glass substrate by oblique angle deposition technique, where hexagonal close-packed (HCP) etched microspheres were removed. The nanostructure exhibits Circular Dichroism (CD). Moreover, the CD of this structure in different local area presents anisotropy, which was investigated both experimentally and theoretically. This chiral nanostructure lay the groundwork for the applications in chiral optical devices.**

Keywords—oblique angle deposition; ladder-shaped nanostructures ; chirality

I. INTRODUCTION

More and more researches of plasmonic nanomaterials have focused on the chiral metamaterials recently. This is due to the advancement of chiral metamaterials open up a series of potential applications in negative refractive index media, superchiral field based biosensing, the actual detection of biological medicine and pharmacology. Chiral metamaterials are a type of structures that cannot be superposed with their mirror images [1]. Metallic chiral nanostructures interact with incident light to generate surface plasmon resonances. However, due to structural asymmetry, modes of localized surface plasmon resonance (LSPR) on structure are different. As a result, the metal chiral nanostructures exhibit strong circular dichroism (CD). Since CD is related to geometric shape and size of the structure, the CD of the metal chiral nanostructure can be regulated by adjusting the parameters of the structure. Circular dichroism spectroscopy is considered as a signal which represent the intensity of chirality by different absorbance for Left-handed and Right-handed circularly polarized light.

II. EXPERIMENTAL DETAILS

2.1. Materials

All deionized water was ultrapure (18.25 MΩ cm^{-1}) from a Lab superpure water system. The glass slides (15 × 15 mm^2) used as substrates were washed in hot piranhas solution at a 4:1 ratio of sulfuric acid and hydrogen peroxide for at least 30 minutes to create a hydrophilic surface. Commercially available 10 wt% polystyrene (PS) nanospheres with 500 nm diameter were purchased from Huge Biotechnology Co. Ltd. The silver(99.999%) for vapor deposition was purchased from Zhongnuo Materia Co. Ltd. Toluene, acetone, and 2-propanol were used as cleaner of PS nanospheres.

2.2. Preparation of Etched Colloidal Templates

Figure 1a shows a typical SEM image of a colloid monolayer with 500 nm diameter PS nanospheres fabricated using an air−water interface method [2]. In brief, 0.01 % PS nanosphere solution in a mixture of deionized water and absolute ethanol were dropped onto the surface of water in a 10 cm diameter glass culture dish containing about 24 ml of ultrapure water. After that, the monolayer nanospheres were lifted onto the glass substrate, and single-layered colloidal crystals were obtained when the slides became dry. Then, these microspheres were etched for 18 minutes by plasma cleaner (PDC-32G-2) to reduce their diameter. Fig. 1b-d show SEM images of etched nanospheres with the pressure of 400 millitorts under Ar plasma.

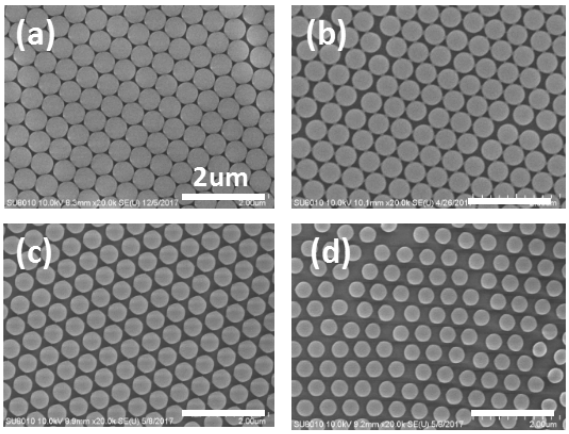

Fig. 1. (a) a SEM image of the colloid monolayer with 500 nm diameter. (b-d) SEM images of 500 nm-diameter nanospheres after plasma etching for time of (b) 12 min. (c) 15 min. and (d) 18 min.

2.3. Fabrication Ladder-Shaped Chiral Nanostructure

These templates were loaded into a E-beam evaporator (DE500) at a polar angle $\theta = 40°$ with respect to the substrate normal. After 20 nm Ag deposition in the original orientation of the domain with respect to the vapor incident plane, the substrate was azimuthally rotated by $\Delta\varphi = 120°$, and then another Ag layer of 20 nm was deposited. The thicknesses of three-step depositions were set as T_1, T_2 and T_3 in the vacuum deposition system. This process was repeated until a total film thickness of $D_1 = 100$ nm, $D_2 = 200$ nm and $D_3 = 300$ nm were achieved. After the deposition, the substrates were allowed to cool in the vacuum. Once removed from the chamber, the colloid template was detached from the substrate using scotch tape. In the end, the substrates were rinsed in toluene, acetone, and 2-propanol successively to remove PS residual [3].

2.4. Characterization

The scanning electron microscopy (SEM) images were taken from with a primary electron energy of 5 kV, and the samples were sputtered with a layer of Pt (about 2 nm thickness) prior to imaging to improve the conductivity [4]. The Atomic Force Microscope (AFM) images were taken with a Free Vibration Amplitude 500 MV. The custom optical system consists of a quarter waveplate, a linear polarizer and lenses with different focal lengths, etc.

III. Results and Discussion

3.1. Morphology

The following two figures are obtained by scanning two locations on the same sample. The microsphere template is arranged in a hexagonal close-packed pattern, and its structure after shadow deposition is also presented according to the pattern of the template. As shown in Fig. 2, three rotating arms is created and lengths of arms are different in the two figures. The silver deposited in three different directions is not uniformly distributed. The deposited silver film is thicker in the bright area than the blurred area.

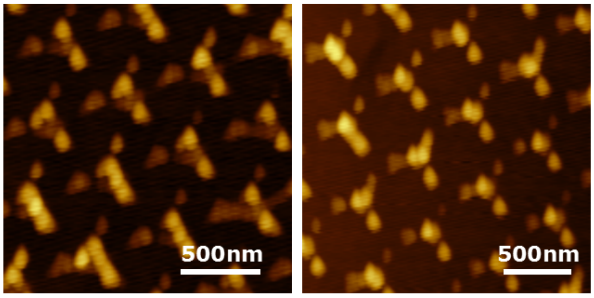

Fig. 2. AFM images of Ag stair-step nanostructures in different domains with $\varphi_0 = 15°$ and 25°.

3.2. Chiroptical Properties

We made three sets of different samples of the ladder and specific parameters are displayed in the table 1. Here, the thickness differences between adjacent two steps are 0 nm, 50 nm, 100 nm in three groups of samples, respectively. ΔT is used to characterize the CD response of the ladder-shaped nanostructure [5]. ΔT is calculated by

$$\Delta T = T(RCP) - T(LCP) \quad (1)$$

T(RCP) and T(LCP), were measured by the custom optical system with circularly polarized incident light at normal incidence.

TABLE I. THICKNESS PARAMETERS OF STRUCTURE

	D_1 (nm)	D_2 (nm)	D_3 (nm)
sample 1	100	100	100
sample 2	100	150	200
sample 3	100	200	300

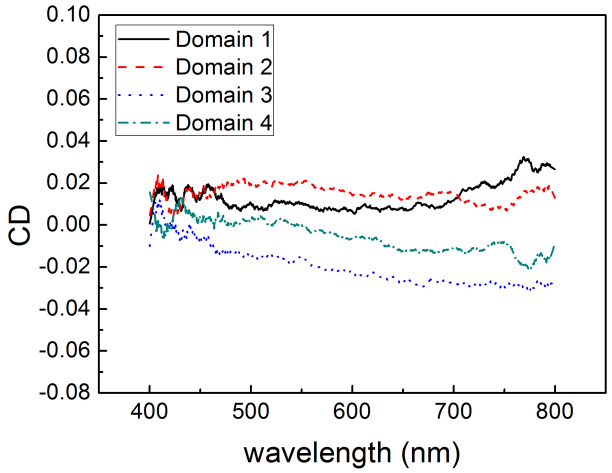

Fig. 3. Measured circular dichroism of different positions on the sample 1.

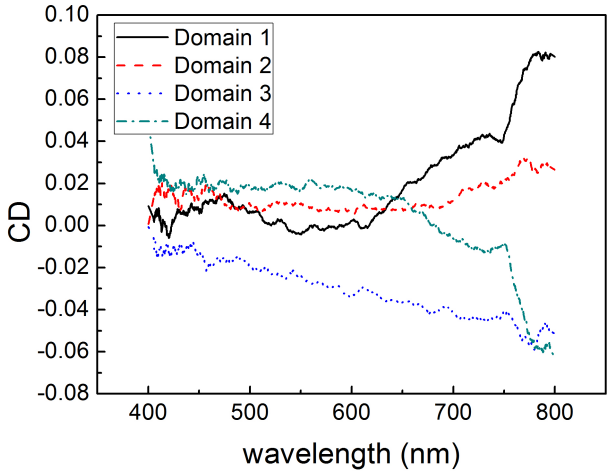

Fig. 4. Measured circular dichroism of different positions on the sample 2.

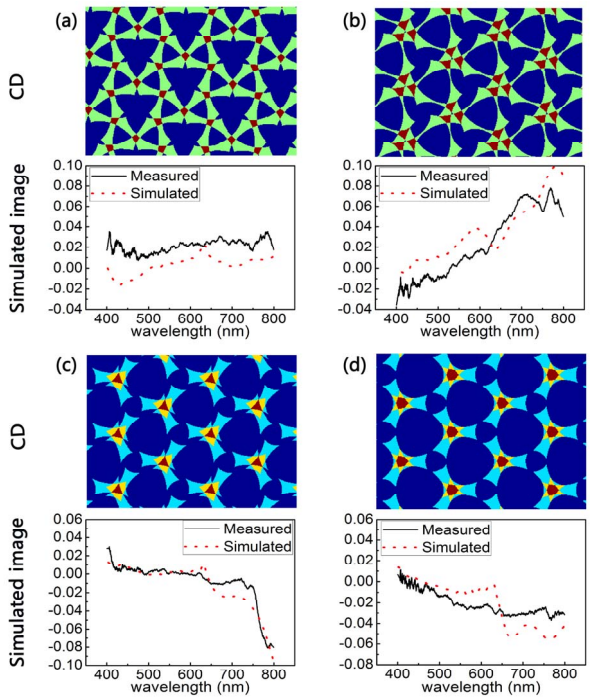

Fig. 5. (a−d) Simulated morphologies and circular dichroism spectrums of Ag stair-step nanostructures in differently orientated domains with φ_0 = 0°, 15°, 25°, 30°.

Figures 3 and 4 show the measured CD responses of four positions on the sample 1 and sample 2, respectively. These figures reveal that with the change of the thickness of Ag deposited thrice, the circular dichroism spectrum of the structure also changes distinctly. Overall, the local CD signals of Sample 2 is stronger than Sample 1 . This result is due to the fact that the asymmetry of the sample 1 is minimal. It is found that three-dimensional stair-step nanostructures exhibits good circular dichroism compared with planar structures.

As shown in Fig 5, we show the morphology simulation of ladder shaped nanostructure in individual domains which can be estimated by a program called Bead. This software can guide multi-angle deposition by adjusting shadowing effect of adjacent nanospheres. In addition, geometric models of the ladder shaped nanostructure in FDTD simulations were created based on the top-view simulated images. For different domains, all the resonances in the measured CD spectra are well reproduced in the simulated spectra at almost the same wavelength positions. However, there are still some small differences between the measured and simulated spectra. The shape of this shadowed region is a periodic function of φ [6]. The different localizations are due to monolayer orientations in the initial deposition. We define it as φ_0. As φ_0 increases from 0° to 30° , the arms of ladder shaped structures gradually become shorter and disjunct.

IV. Conclusions

In conclusion, we provide a simple method that metallic chiral nanostructures are fabricated on hexagonal close-packed (HCP) plasma-etched microspheres through multiple glancing angle depositions.

Furthermore, optical chirality of the ladder shaped nanostructure has been clearly revealed in individual domains. It was demonstrated experimentally that Ag nanostructures in different local areas present anisotropy, which closely connected with geometric shapes depend on the monolayer orientations. FDTD simulations confirm the CD responses in different domains. This large-area chiral metamaterials show promise to become high sensitivity detection CD substrate.

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