Plasmonic Enhanced Chiral Metamaterials

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ABSTRACT

Methods are presented for tuning and enhancing the optical activity of planar chiral polymer-based metamaterials. One approach involves patterning a chiral polymer into planar chiral shapes to achieve a superposition of molecular and geometric chirality. Such materials can be fabricated using femto-second pulsed laser-based patterning of chiral polymer media. This is demonstrated via the fabrication of a planar chiral metamaterial consisting of a two-dimensional array of chiral L-structures. Another approach involves the introduction of subwavelength metallic nano-inclusions into a chiral media to further enhance its optical activity via field enhancement at the plasmon resonant wavelength of the particles. Computational modeling is performed to demonstrate the viability of achieving enhanced optical activity using both of these approaches.

Keywords: Chiral materials, optical activity, plasmonics, metamaterials, negative index materials.

1. INTRODUCTION

Metamaterials are engineered materials with sub-wavelength constituent elements that are designed to produce bulk electromagnetic (EM) properties not found in nature. The interest in metamaterials has grown steadily since the seminal theoretical work by Pendry *et al*. [1] and subsequent experimental work by Shelby *et al*. [2]. Various interesting and exotic phenomena can be realized using metamaterials such as negative refractivity, sub-diffraction-limit imaging, slow light and cloaking. Applications of such materials span the EM spectrum with potential transformative impact in the fields of imaging (super-lens), data storage, optical switching and stealth technology, among others. Much of the research in this field has focused on the development of negative index materials (NIMs) as first proposed by Veselago [3]. Many early NIMs were designed to have simultaneous negative values of permittivity ε and permeability μ, which was achieved by exploiting EM resonance involving sub-wavelength metallic structures such as split-ring resonators or paired nanowires. To date, the majority of metamaterials for THz applications have been fabricated using "top-down" techniques such as electron-beam lithography or focused-ion beam milling. While these methods provide sufficient nanometer resolution for tailoring sub-wavelength constituent elements, they tend to be limited to the fabrication of 2D planar materials on rigid substrates at low throughput and with high-cost.

In this paper, we discuss a fundamentally different approach to metamaterials that involves the use of chiral polymers [4]. Chiral metamaterials offer an alternate route to NIMs as compared to the more conventional metallic-structure-based resonance approach. The chirality of a material can be characterized in terms of a chirality parameter κ. If κ is sufficiently large, a bulk negative index can be realized within the material. Specifically, in a chiral material, negative refraction will occur at one of the eigen (circular) polarization states of the incident field if κ is larger than the square root of the product of real parts of permittivity and permeability, i.e. when

$$\kappa > \sqrt{\varepsilon' \cdot \mu'} \tag{1}$$

where the refractive index is given by

$$n = \sqrt{\varepsilon' \cdot \mu'} - \kappa \tag{2}$$

and ε' and μ' are the relative values of the real parts of the permittivity and permeability, respectively. Our strategy is to use a laser to fabricate materials with enhanced multiscale chirality (sufficiently large κ) in order to obtain polymer-based NIMs without resorting to top-down fabrication. In the following, we report of the progress towards this end by describing the synthesis, and demonstrating the fabrication, of novel 2D planar media possessing multiscale chirality. We also present modeling results that demonstrate the viability of using subwavelength gold (plasmonic) nanoinclusions to enhance the optical activity (rotation of incident polarization) of such media.

2. MATERIALS AND METHODSS

Polymer-based chiral media has been fabricated using a formation of a photoresist-chiral polymer mixture consisting of SU-8 2025 from Microchem, and Chiral Poly (fluorene-alt-benzothiadiazole) (PFBT) in a mixture ratio of

35:1. The PFBT was synthesized using palladium-catalyzed Suzuki polycondensation as the final step, and purified with a Soxhlet extraction. We introduced chirality in PFBT of the fluorene-based monomer modified with (S)-3,7-dimethyloctyl substituents at the 9-positions as shown in

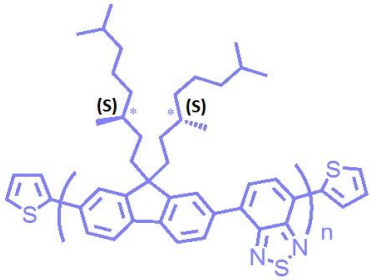


Figure 1. Chemical structure of PFBT polymer.

Fig. 1 and described in [5]. The photoresist-chiral polymer mixture is stirred for 24 hours, and then spin coated at 1000 rpm on a glass substrate. After spin coating, the sample is baked for 30min at 95C to evaporate the solvent before performing lithograph patterning. The circular dichroism (CD) (differential absorption of left and right circularly polarized light) and absorption spectra of both the pure PFBT polymer and SU-8/PFBT blend are shown in Fig. 2. Note that the SU-8/PFBT exhibits a 68-fold increase in optical activity at λ = 500 nm. The reason for the enhanced optical activity is presently not fully understood and is the subject of continued investigation by our group. The

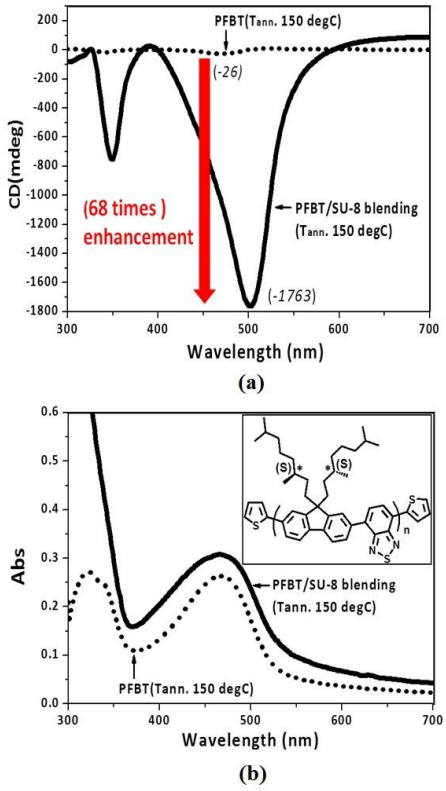


Figure 2. CD (a) and UV-vis absorption (b) spectra of: (dots) annealed pure PFBT film; (Solid) PFBT/SU-8 blending, 1/30 mass ratio film spin-coated from 20% solid content solution; after prebaking and annealing.

chirality parameters for the PFBT polymer and the SU-8/PFBT are on the order of $\kappa \sim 10^{-5}$ and 2×10^{-3}, respectively.

In order to obtain multiscale chirality, the chiral SU-8/PFBT film can be patterned into a planar array of L-structures using two-photon photolithography (TPL). We use a near IR (800nm) writing wavelength and a schematic of the writing set up is shown in Fig. 3a. In this system, a piezo-stage moves the sample relative to a fixed laser beam and a desired pattern is produced within the sample by controlling the motion of the stage while exposing the sample. Once the sample is patterned, it is developed with Propylene Glycol Methyl Ether Acetate for 3 hours, which removes the unexposed material leaving only the patterned media. We have recently reported the use of this method for writing novel sub-wavelength polymer-based planar plasmonic metamaterials, which were prepared using SU-8 with a high gold precursor (metallic salt) loading [6, 7]. Specifically, we used a femtosecond-pulsed laser to induce two-photon initiated in situ reduction of the metal salt and simultaneous polymerization of the SU8. Gold nanoparticles are formed during the writing process, which renders a plasmonic functionality in the written structures. Fig. 3b shows examples of different written structures, which demonstrate the versatility of the writing process [6, 7]. The present effort on patterning chiral SU-8/PFBT film is an extension of this prior work on plasmonic structures.

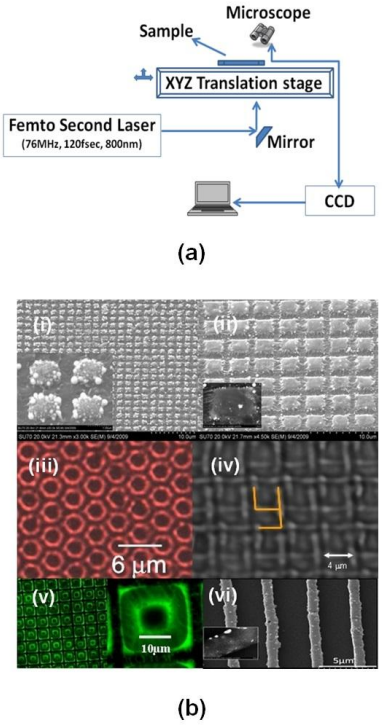


Figure 3. Laser-based TPL fabrication of metamaterials: (a) schematic of the TPL laser writing system, (b) SEM images of fabricated polymer-based plasmonic structures (i) cauliflowers, (ii) blocks; Confocal microscope image of (iii) hexagonal ring structures; (iv) planar chiral Y structures with highlighted geometry; (v) donuts; and SEM image of (vi) grating structure.

A 2D array of planar L-structures fabricated using this method is shown in Fig. 4. Note that while the L geometry is not chiral in a 3D sense, it is considered chiral in a 2D planar sense because it cannot be mapped onto its mirror image using a sequence of rotations or translations confined to the plane, i.e. it needs to be lifted out of the plane and

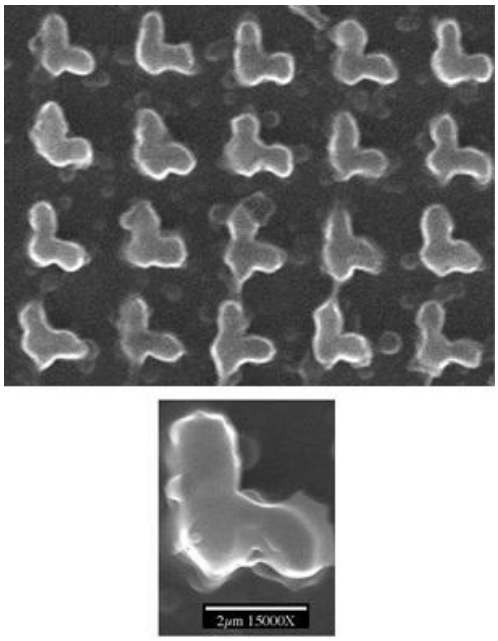


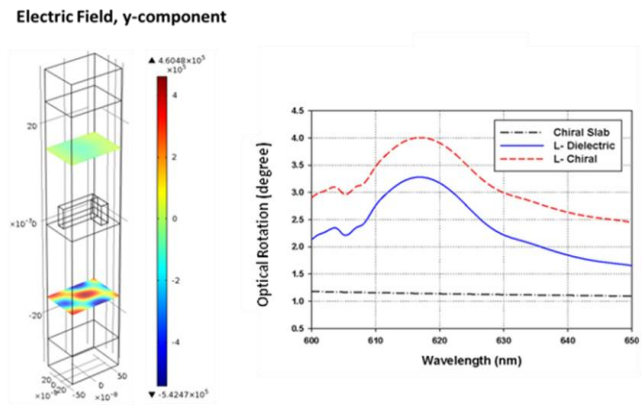
Figure 4. SEM of fabricated chiral polymer-based chiral L-structures.

rotated to achieve this. However, in addition to the planar geometric chirality, the L-structures possess intrinsic chirality due to the constituent SU-8/PFBT. Thus, the material shown in Fig. 4 represents a 2D planar metamaterial with multiscale chirality.

3. MULTISCALE AND PLASMONIC ENHANCED CHIRALITY

In this section we use computational electrodynamics to demonstrate that the optical activity of a media can be enhanced by engineering multiscale chirality into a media or by using subwavelength plasmonic inclusions. We use the finite element-based (FE) COMSOL multiphysics RF solver (www.comcol.com) to compute optical rotation for such media.

Consider the array of L-structures shown in Fig. 4. The computational domain for a unit cell of this array is shown in Fig. 5a. In this model, the structure resides on a glass substrate, which has a refractive index of 1.4. The base of the computational domain is 1050 nm by 750 nm, and its height is 2 microns along the z-axis. The dimensions of the L-shape are as follows: 750 nm in length, 450 nm at the base, the width of both branches is 150 nm and the thickness is 400 nm. Note that while these dimensions are slightly smaller than the fabricated structures shown in Fig. 4, the analysis presented here is scalable as long as the molecular chirality can be tuned to overlap the structural chirality. The isotropic refractive index of the L-structure is taken to be 1.6, which is essentially that of SU8. Scattering (low reflection) boundary conditions with Perfectly Matching Layers (PML) are applied at the top and bottom of the solution space as described in references [8, 9]. Double periodic boundaries are imposed on the side boundaries to account for the fact that this structure is one element of a 2D array, i.e. the periodic conditions account for the presence of the other elements, even though they do not appear in the model. The incident field is generated by a time-harmonic surface current source positioned in the x-y plane immediately beneath the upper PML]. The magnitude of the surface current is chosen to provide an x-polarized plane wave with a field magnitude of $E_x = 2x10^6$ V/m in free space, i.e. absent the structure and E_y=0 V/m, i.e. the incident field x polarized [8, 9].



(a) **(b)**

Figure 5. Photonic analysis of multiscale chirality for L-structure chiral media with κ=0.01 (a) computational domain showing E_y enhancement. (b) Optical rotation vs. λ for a 400nm thick chiral slab (black dotted line), Dielectric L-structure (solid blue) and chiral L-structure (hashed red line).

The intrinsic chirality of the L-structure is introduced via the bulk chirality parameter, κ, which is related to macroscopic optical rotation of the medium.

To demonstrate multiscale chiral enhancement we start with a base case by calculating the rotation of an un-patterned slab of chiral material. This slab (not shown) spans the entire cross-section of the computational domain and has a thickness of 400 nm, the same as that of the L-structure. The chirality parameter for the slab is set to κ = 0.01, which is consistent with the fabricated material characterized in Fig. 2. The optical rotation due to the slab is shown as the dotted black line in Fig. 5b. This plot has a slight downward slope because the rotation is proportional to the thickness of the slab divided by the wavelength and therefore decreases with increasing wavelength. Next, we compute the optical rotation due to a purely dielectric L-structure. This is plotted as the solid blue line in Fig. 5b. Note that this plot exhibits a maximum rotation of

approximately 3.25° at approximately 617 nm. We repeat this analysis, but this time we use a chiral material for the L-structure with κ =0.01, instead of a non-chiral dielectric. Thus, this structure possesses multiscale chirality owing to its geometric shape and its inherent molecular chirality. The optical rotation of this structure is plotted as the hashed red line in Fig. 5b. Note that there is an enhancement of optical rotation as compared to the dielectric L-structure due to the combined geometric and intrinsic chirality, i.e. multiscale chirality.

Lastly, we demonstrate that the optical rotation of a chiral media can be enhanced using plasmonic (e.g. gold) nanoparticle inclusions. It is well known that localized surface plasmon resonance (LSPR) in such particles is accompanied by high localized field enhancement due to coherent oscillations of the conduction band electrons. If a gold nanoparticle is embedded within a chiral media, then at plasmon resonance the field enhancement in the vicinity of the particle will enhance the chiral response of the local media, thereby enhancing the optical rotation. In Fig. 6a, we show a computational model of a gold nanorod embedded in a slab of chiral media. The media is illuminated with strictly x-polarized light (along the length of the nanorod) as described above. Optical rotation is evident via the presence of E_y as shown in Fig. 6a.

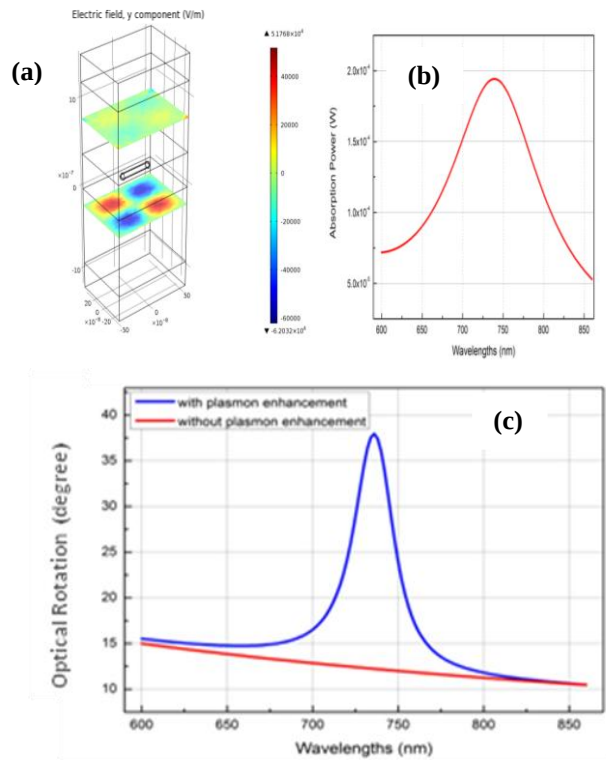


Figure 6. Photonic analysis of a gold nanorod in a chiral media with κ = 0.25: (a) computational domain and E_y field, (b) absorbed power vs. λ for the nanorod , (c) optical rotation vs. λ for the chiral slab (solid red line) and with the nanorod (solid blue line).

Fig. 6b shows the plasmonic resonance absorption of the nanorod. The interactions between the particle localized field and the chiral molecules give rise to optical rotation enhancement in the vicinity of plasmon resonance (Fig.6c). Hence, plasmon enhancement of optical rotation can be achieved by embedding metallic particles in chiral media.

4. CONCLUSIONS

We have demonstrated that the viability of achieving enhance optical rotation in a planar media by leveraging multiscale chirality intrinsic chirality effect by introducing multiscale chirality: fabricating chiral media into chiral structure. Moreover, we demonstrated for the first time that chirality enhancement can be achieved with plasmonic particles due to their localized field interactions with the chiral molecules.

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