Planar chiral metamaterials for biosensing applications
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ABSTRACT

There has been a considerable effort recently in the development of planar chiral metamaterials. Owing to the lack of inversion symmetry, these materials have been shown to display interesting physical properties such as negative index of refraction and giant optical activity. However, the biosensing capabilities of these chiral metamaterials have not been fully explored. Ultrasensitive detection and structural characterization of proteins adsorbed on chiral plasmonic substrates was demonstrated recently using UV-visible circular dichroism (CD) spectroscopy. Second harmonic generation microscopy is an extremely sensitive nonlinear optical probe to investigate the chirality of biomaterials. In this study, we characterize the chiral response of chiral plasmonic metamaterials using second harmonic generation microscopy and CD spectroscopy. These planar chiral metamaterials, fabricated by electron-beam lithography, consist of right-handed and left-handed gold gammadions of length 400 nm and thickness 100 nm, deposited on a glass substrate and arranged in a square lattice with a periodicity of 800 nm.

Keywords: chiral plasmonic metamaterials, nanostructures, second harmonic generation, circular dichroism

1. INTRODUCTION

There is a growing interest in the development of plasmonic nanostructured surfaces or metamaterials for applications in biosensing [1]. The coupling of light to surface plasmons results in a strong enhancement of the local electromagnetic field, commonly referred to as “hotspots”. This significantly enhances the light-matter interaction at the surface of the plasmonic metamaterial leading to applications involving surface enhanced Raman scattering (SERS) [2] and surface enhanced coherent anti-Stokes Raman scattering (SECARS) [3]. Moreover, frequency of the surface plasmon resonances excited by the incident light are highly sensitive to the dielectric environment surrounding the metal. This property of the change in plasmon frequency as a function of the refractive index of the metal and the surrounding dielectric medium is used in surface plasmon resonance (SPR) based biosensors [1].

Planar chiral plasmonic metamaterials (CPMs) have been extensively studied in the past decade for their interesting optical properties such as negative index of refraction [4, 5] and giant optical activity [6, 7]. They consist of a two-dimensional array of periodically arranged, chiral structures. These structures are subwavelength in size and are typically made up of a metal-on-dielectric structure and written by electron-beam lithography or ion beam milling. The surface plasmon resonances excited in the chiral nanostructured grating give rise to these unique optical properties. In fact, in addition to the usual enhancements of electromagnetic field intensity at the surface of the plasmonic metamaterial, chiral electromagnetic fields are induced therein such that the optical chirality is much higher than that of circularly polarized light [8-10]. This increases the interaction of the incident light with chiral material adsorbed on the CPM leading to enhanced sensitivity of a chiroptical measurement. Based on this principle, ultrasensitive detection and structural characterization of proteins adsorbed on CPMs was recently demonstrated using UV-visible circular dichroism (CD) spectroscopy [11,12].

Second harmonic generation (SHG) is the second-order nonlinear optical response of a material in the presence of a strong electromagnetic field. In this process, light at twice the frequency of the incident optical field is generated due to the induced second-order nonlinear polarization [13].

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However, in the electric-dipole approximation, SHG is only allowed in materials that lack centrosymmetry and since surfaces and interfaces inherently satisfy this condition, they are ideally suited for characterization based on SHG [14, 15]. In addition to the breaking of symmetry at the surface, symmetry is also broken in chiral molecules due to the lack of inversion symmetry. This has led to polarization-dependent SHG spectroscopy becoming a very sensitive tool for characterizing two-dimensional chirality [16-18]. The two enantiomers of the chiral molecules can be distinguished based on this technique since the SHG signal from the chiral thin film has a different response when excited by left-handed circular polarized (LCP) and right-handed circular polarized (RCP) light at the fundamental frequency. In addition to spectroscopy, SHG microscopy has emerged as a viable in vivo imaging modality for label-free visualization of structural changes to tissue for early disease diagnosis [19].

SHG has been successfully applied for studying the microscopic and macroscopic second-order nonlinear response of CPM [20-26] of various shapes such as L-shaped [21], G-shaped [22], star-shaped [23] structures and twisted-cross gold nanodimers [24]. In this paper, we investigate the SHG response of CPMs with gammadion-shaped unit cell. We first describe the design of such a CPM including a summary of the main results of numerical simulations of the electric field distribution. We experimentally characterize the chiral response of the CPM in the presence of chiral molecules adsorbed on the surface by means of UV-visible CD spectroscopy. Our objective is to study the effect on the SHG intensity when chiral molecules are adhered to the surface and compare with CD measurements.

2. DESIGN OF CHIRAL PLASMONIC METAMATERIALS

The unit cell of our CPM consists of a right-handed (RH) gold gammadion as shown in Fig. 1a with arm length of 400 nm, width 80 nm and period of 800 nm arranged in a square lattice. The structure comprises of a 100 nm thick gold layer, on top of a 5 nm adhesion layer deposited on the borosilicate glass substrate (Fig. 1b). We performed numerical simulations of electromagnetic fields in the vicinity of the RH-CPM covered by water, using a commercial finite-difference time domain (FDTD) package (Lumerical version 8) with a mesh size of 4.0 nm. Permittivity values for gold and glass were taken from Ref. 27, while the permittivity of water was taken as 1.33.

The simulated transmission, reflection and absorbance spectra are shown in Fig. 2 for RCP and LCP light incident on the RH-CPM. The three prominent peaks (dips) in transmission (reflection) spectrum are attributed to the excitation of three different plasmon resonances at ~ 550 nm, 650 nm and 800 nm in the CPM. It can be seen that there is a larger difference between the intensity of RCP and LCP light transmitted or reflected at 800 nm. This gives rise to a large CD signal at 800 nm as described in Section 3.1 below. The higher values of the simulated absorbance seen for lower wavelengths in Fig. 2b, is consistent with the higher absorbance for metals in the visible wavelength region. There are two keys points to be noted in Fig. 2b: (i) The higher absorbance at ~600 nm than at ~800 nm implies that a larger electric field intensity exists at the surface of the gold at 600 nm and (ii) The absorbance is higher when RCP light as compared to the LCP light is incident on the RH-CPM. Fig. 3 illustrates the FDTD simulation of the distribution of the electromagnetic field at the center of the RH-CPM for the plasmon resonance at 800 nm. It is evident that the electric field density is much stronger when RCP light is incident on the RH-CPM (Fig. 3b). This is consistent with the higher absorbance for RCP light at 800 nm as seen in Fig. 2b.

![Figure 1. Top view (a) and side view (b) of the unit cell of the RH-CPM covered with water.](http://proceedings.spiedigitallibrary.org/ on 03/05/2015 Terms of Use: http://spiedl.org/terms)
3. CHARACTERIZATION OF CHIRAL PLASMONIC METAMATERIALS

The CPM used for the experiments were fabricated by the group of Dr. Nikolaj Gadegaard at the University of Glasgow. The structure consists of right-handed gold gammadia with same dimensions as in Section 2, and arranged in a squared lattice geometry with a period of 800 nm. The fabrication is achieved on a glass substrate using electron-beam lithography and subsequent gold deposition (100 nm) and lift-off.

3.1 Circular Dichroism spectroscopy

UV - Vis CD spectroscopy is a well-established linear optical technique for characterizing chiral samples and involves the measurement of the differential absorbance of left and right circularly polarized light incident on a chiral material. A commercial CD spectropolarimeter (Jasco - J810) was used to probe the optical properties of the RH-CPM in the presence of water and various chiral biomolecules. The sample consisting of a 1x1 cm$^2$ glass chip was placed in a custom-made holder and inserted inside a quartz cuvette with a path length of 1 cm, such that $\sim 4 \times 10^7$ gammadia were in the optical beam path. In all the CD measurements, a blank sample was first taken with the gammadia in the presence of water, and then followed by the gammadia in the presence of chiral samples. Fig 4 shows the experimental data obtained...
on a RH-CPM in the presence of water, left handed (L-) Tryptophan and right handed (D-) Arabinose. It can be seen that there is a difference in the wavelength shift when the water is replaced by (L-) Tryptophan as opposed to D-Arabinose and is consistent with earlier results [11]. It is also evident that there is a good match between the experimental and simulation results of the CD spectrum of the RH-CPM. The CD spectrum is calculated by taking the difference in the transmitted RCP and LCP electric field intensity from the FDTD simulations and dividing by the total transmitted field intensity.

Figure 4. CD spectrum (experimental data) of RH-CPM in the presence of water (black), L-Tryptophan (blue) and D-Arabinose (red). The modeled CD spectrum of RH-CPM in the presence of water is shown by the dashed line.

3.2 Second Harmonic Generation (SHG) Microscopy

The schematic of the experimental SHG microscopy setup is shown in Fig. 5. The light source is a femtosecond Ti:sapphire laser (Tsunami, Spectra-Physics) producing ~100 fs pulses at a repetition rate of 80 MHz and with tunability between 720 nm - 1000 nm. The diameter of the laser beam at 800 nm is increased using a pair of plano-convex lenses and the light is guided into a home-built microscope. The sample is placed on a three-axis automated stage (Max341, Thorlabs) that is computer controlled via Labview and can be scanned with a minimum step size of 60nm to generate an image. An oil immersion objective (60x, 1.35NA, Olympus,) focuses the light into a spot size of ~400 nm at the sample. The SHG light generated at the sample is collected in the backward direction by the same objective and is split off from the incident pump light by means of a dichroic mirror (Chroma Technology) that reflects light less than 700 nm. This light is filtered by a 700 nm short pass filter (Chroma Technology) to remove any residual excitation light while a band pass filter centered at 400 nm with a 40 nm bandwidth is used to separate the SHG signal. This light is coupled into a multimode fiber with a core diameter of 1mm and detected by a photomultiplier tube (H10721-20, Hamamatsu). The power of the pump beam is controlled by means of a half wave plate and a polarization beam splitter and is ~ 7.5 mW at the sample. A quarter wave plate inserted just before the objective enables excitation of the sample with left- or right-handed circularly polarized light.
The alignment of the SHG microscope was optimized by maximizing the SHG signal at 400nm generated in a nonlinear KDP (Potassium Dihydrogen Phosphate) crystal. The KDP sample was then replaced by a sample of RH-CPM immersed in water and sandwiched between two thin coverslips, such that it faced down towards the beam as illustrated in the inset in Fig. 6a. As the sample height “z” is scanned through the beam focus, two SHG peaks are prominent in the z-scan as seen in Fig. 6a and 6b. The peak at 2.48mm was confirmed to be the SHG signal from a single gold gammadion in the x-y location of the focused light spot while the more intense SHG peak at 2.65 mm is from the glass-oil interface. It is interesting to note that the SHG generated from the RH-gammadion by RCP light is twice as strong compared to the SHG generated by LCP light. The SHG image of the RH-CPM obtained by scanning the stage when z = 2.48mm is shown in Fig. 6c and Fig. 6d for incident RCP and LCP light, respectively. A periodic intensity distribution corresponding to the SHG signal from the periodically spaced nanostructures in the CPM lattice can be clearly seen in Figs. 6c and d. The pixel resolution in these images is 200nm and the false color scale indicates the voltage measured at the PMT. Note that the background signal has been subtracted from the SHG images. Similar to the results shown in Fig. 6a and 6b, the SHG intensity maps of Fig. 6c and 6d indicate that there is ~30% stronger SHG signal when the RH-CPM is excited by RCP light. This is consistent with the results of the simulation described earlier in Section 2.
4. SUMMARY

Tang and Cohen [8] introduced the concept of optical chirality to describe the degree to which the electric and magnetic field vectors wrap around a helical axis at each point in space. By means of precisely sculpted standing waves, they demonstrated the existence of superchiral light [9] with increased optical chirality as compared to circularly polarized light. An alternate route to achieving superchiral light is by means of using CPM [10, 12]. Chiral electromagnetic fields are induced around the chiral nanostructures such that the optical chirality is much higher than that of circularly polarized light [8-12] at the surface. This increases the interaction of the incident light with chiral liquid molecules adsorbed on the CPM leading to enhanced sensitivity of the CD measurement. As reported here, we have established capabilities in the design and simulations involving CPM. The chiral response of samples of RH-CPM in the presence of chiral liquids was characterized using UV-Vis CD spectroscopy.

The origin of SHG in CPMs is primarily associated with the surface local field enhancement (hot spots) at the fundamental frequency due to the surface plasmon resonance and the electromagnetic coupling between nanostructures. We have characterized the SHG response of RH-CPM in the presence of water, by means of SHG microscopy. We observed a significant increase in the SHG signal when RH-CPM is excited by RCP light. This is consistent with the
increased distribution of “hot spots” observed in the FDTD simulations when RCP light is incident on the RH-CPM. On-going work includes investigating the SHG response of the RH-CPM in the presence of chiral liquid molecules adsorbed at the gold surface.

The optical response of the CPM can be tuned by designing not only the shape and size of the individual unit cell in the CPM [25], but also by the ordering of the metamolecules in the CPM [26]. Future work will explore the possibility of optimizing design parameters of the CPM in order to achieve a uniform distribution of the enhanced electric field and optical chirality.

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