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Extrinsic chirality in metasurfaces: traditional and unconventional experiments - INVITED

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Abstract. Plasmonic nanostructures with achiral, but asymmetric shapes can exhibit chiro-optical phenomena at the nanoscale, given that the nanostructure-light interaction symmetry is broken. Such behaviour is defined as extrinsic chirality, and it is induced by properly arranging the experimental set-up. We show measurement techniques for extrinsic chirality in low-cost, asymmetric samples with nanostructures organized in metasurfaces. We employ widely tuneable chiro-optical characterization of transmission and reflection, as well as the circular polarization degree of the transmitted signal; near-infrared range (680-1080nm) and oblique incidence allow for the detection of resonant features in extrinsic chirality. Other, unconventional experiments use photo-thermal consequences of chirality governed absorption in metasurfaces. Photo-acoustic spectroscopy directly gives circular dichroism as a differential absorption of the left and right circular polarizations exciting the sample. Photo-deflection spectroscopy gives additional information of diffraction phenomena governed by the extrinsic chirality. We showed that these techniques can monitor the extrinsic chiral behaviour of the hybrid plasmonic metamaterials. Moreover, they can be used in combination with fluorescence-detected circular dichroism to measure the emission properties of fluorescent materials.

1 Introduction

Metasurfaces, specially engineered periodically arranged nanostructures, can enhance electromagnetic fields in their vicinity, and tailor their properties in the far-field; this offers applications from sensing, over flat optics, to optical quantum information. Introducing chiral geometric shapes at the nanoscale opens additional degrees of freedom, such as diverse interaction with left and right circular polarizations (LCP and RCP, respectively). This difference in absorption is defined as circular dichroism (CD) and it is attractive for applications in chiral sensing when metasurfaces are coupled with chiral molecules. CD of natural chiral molecules is ultralow and difficult to measure, so the metasurfaces can be designed to boost CD signals [1].

Chiro-optical effects in metasurfaces can be induced even if the material is not intrinsically chiral. In metasurfaces with asymmetric shells, a proper experimental orientation of the sample with respect to the incoming field can be used to obtain CD [2]. This induced effect is called extrinsic chirality (and, sometimes, "fake" chirality), and it happens when the average asymmetry vector, light wave-vector and the sample's surface normal do not lie in the same plane. Achiral, but asymmetric samples have simpler geometry for fabrication, and were shown to give chiro-optical effects in both near- [3] and far-fields [4,5]. In the following, we present experimental methods used for extrinsic chirality measurements in metasurfaces, as well as additional possibility of our set-up to measure fluorescence-detected circular dichroism.

2 Experimental set-ups

The schematic of the conventional way to measure extrinsic chirality is shown in Fig. 1(a). A near-infrared laser (Chameleon Ultra II by Coherent Inc.) allows for the characterization from 680 nm to 1080 nm range; we use it in the linear mode, by modulating it with a mechanical chopper. This wave impinges on a linear polarizer (LP) and a rotating quarter wave plate (QWP), which define the polarization state of the incident beam; here we focus on linear horizontal, LCP and RCP excitations. The sample can be rotated in the xz plane to allow for the oblique incidence; it can also be in-plane rotated to ensure the position for a non-planar triad of vectors. Asymmetric low-cost metasurfaces are usually obtained by depositing a thin plasmonic layer on nanostructured dielectric substrate under oblique incidence [2,4-8]. For extrinsic chirality, the optimal position of the non-planar triad of vectors is when the average asymmetry normal (metal deposition direction) aligns with the y-direction in Fig. 1(a). To measure the CD in extinction, we record the total transmitted intensity caught by a Si photo-diode (PD). For metasurfaces on non-transparent substrates, PD is put on the reflection pathway [5]. Moreover, this set-up allows for the full characterization of Stokes parameters and their dependence on the excitation wave-vector and polarization. This is done by adding a QWP-LP pair

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before the PD, in order to resolve the transmitted circular polarization degree.

In Fig. 1(b) we modify the set-up to measure the CD behaviour of the samples which emit light. The femtosecond laser is here used in non-linear mode, and the blue excitation is obtained from the red fundamental beam by means of a second harmonic generation (SHG). This blue beam is now circularly polarized and, after a pair of short pass filters, it excites the sample. The sample fluorescence intensity depends on the differential absorption between LCP and RCP at the excitation wavelength; this signal is measured by a spectrometer in the broad blue to red visible range. We applied this set-up to characterize intrinsically chiral molecules [9]. Applying it to the metasurfaces covered by emitting material is the subject of future work.

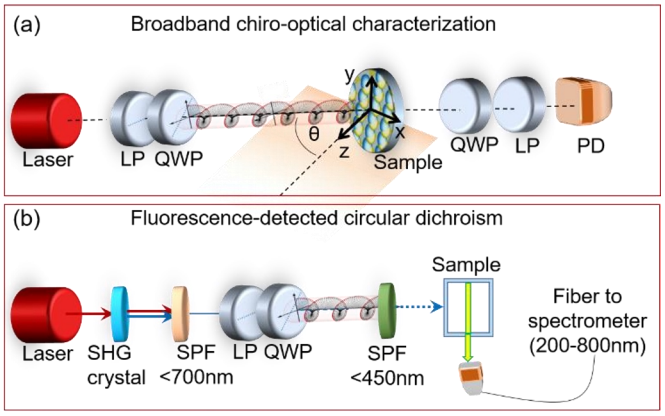

Fig. 1. (a) Experimental set-up: the near-infrared light is directed through a linear polarizer (LP) and a quarter wave-plate (QWP), and impinges on the sample at angle of incidence θ. The sample is oriented such that the incident wave-vector, the average asymmetry vector, and a surface normal form a non-planar triad of vectors. Additional QWP-LP pair is put on the transmitted pathway to resolve the Stokes parameters. A Si photo-diode (PD) detects the transmitted field intensity. The same pair of components can be put on the pathway of the reflected field. **(b)** Fluorescence-detected circular dichroism can be measured in a similar set-up for emitting chiral samples.

Measuring chiro-optical properties in the absorption without the influence of scattering is enabled by photothermal technique called photo-acoustic spectroscopy, Fig. 2(a). Here, the extrinsic chirality is measured in a sample closed in a photo-acoustic cell; the impinging light beam is modulated in time, leading to pressure changes in the cell. These pressure changes correspond to a photo-acoustic signal caught by a microphone. Therefore, the direct, absorption CD signal is obtained at oblique incidence for asymmetric metasurfaces [6]. Photothermal effects can also be used as an alternative to diffraction spectroscopy when one is interested in the extrinsic chirality of metasurfaces in their range of diffraction. We use photo-deflection technique to study intensity of the diffracted orders by asymmetric metasurfaces excited by LCP or RCP polarized Ar laser, Fig. 2(b). Extrinsic chirality leads to the different intensities of diffracted orders, which are reflected from the underlying mirror, and reabsorbed on the substrate [10]. There, local heat sources deflect a He-Ne probe beam due to the Mirage effect. The measured deflection characterizes the chiro-optical effects of the metasurface interaction with the pump beam.

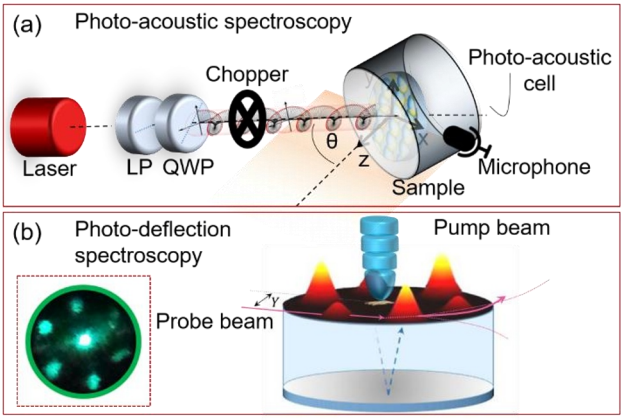

Fig. 2. (a) Photo-acoustic spectroscopy allows for the scattering-independent absorption measurement, hence the direct characterization of CD. **(b)** Photo-deflection spectroscopy allows for the characterization of extrinsic chirality in the diffraction range of asymmetric metasurfaces; inset: photo of the different intensities of the diffracted orders.

3 Conclusions

In conclusion, we investigate extrinsic chirality in asymmetric metasurfaces with different experimental methods. The conventional approach uses a widely tuneable laser and polarizing components to control and resolve the input and the output polarizations, respectively. The sample is rotated to obtain non-planar triad of vectors. Unconventional approaches use photothermal phenomena for the characterization of total absorption and diffraction in metasurfaces. We believe that these methods can be combined to fully characterize asymmetric metasurfaces for chiral molecule sensing or for chiral emission and manipulation.

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