Photo-acoustic spectroscopy with widely tuneable laser enables circular dichroism mapping

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Abstract. Sensitive and reliable characterization of chirality in nanostructures and molecules is of great importance in multidisciplinary research combining physics, chemistry and nanotechnology, with potential applications in pharmaceutical and agrochemical industry. Chirality is connected to circular dichroism (CD) - the absorption difference when the chiral medium is excited with circular polarizations of opposite handedness. Hence, measuring chirality by direct absorption measurements is of great interest in nanophotonics and plasmonics community, where the nanostructured media can enhance chiro-optical effects. Here we present a recently constructed photo-acoustic spectroscopy (PAS) set-up, which offers many degrees of freedom in characterization. We use a laser which is widely tuneable in the near-infrared (680-1080 nm) and visible (340-540 nm) ranges. The laser output is modulated with a mechanical chopper, where its frequency defines the penetration depth of the thermal signal. The input polarization is controlled by a linear polarizer and a quarter-wave plate, and the laser can be focused before impinging on the sample in the tightly closed photo-acoustic cell. The cell is placed on translational and rotational stages, which allows for the spatial mapping and extrinsic chirality measurements. Finally, a sensitive microphone measures the pressure changes in the cell, enabling scattering-free measurement of absorption and CD.

1 Introduction

Chirality, the lack of mirror symmetry, is a common property of the living world at all scales. At the molecular level, being "left" or "right" defines the biological activity and toxicity of molecules. Chiral media differently absorb circular polarizations of opposite handedness, exhibiting circular dichroism (CD). Natural CD of chiral molecules is usually low and it lies in the ultra-violet range, but modern nanotechnology can provide novel nanostructured substrates to enhance chiro-optical interactions [1,2]. Moreover, development of scattering-free measurements of absorption are preferred in characterizing the real CD response (as opposed to the extinction dissymmetry factor g).

We previously used photo-acoustic spectroscopy (PAS) with a lamp source to measure scattering-free absorption in nanostructures supporting resonances in the visible and near-infrared range [3]. We then excited nanostructured asymmetric samples at oblique incidence to induce "extrinsic" chirality, measuring photo-acoustic response at single laser wavelength [4]. However, for the complete characterization of chiro-optical resonances and optimization of CD, one needs to investigate nanostructures' behaviour in a broad wavelength range [5,6]. Here, we enrich the PAS set-up with many new degrees of freedom: a widely tuneable laser and chopper, possibility of focusing, and translation and rotation stages. In this way, we overcome previous limitations such as low power and inability to precisely tune the polarization with a lamp source. Moreover, our set-up allows for dispersion (wavelength-incidence angle) mapping, as well as the spatial mapping.

2 Photo-acoustic spectroscopy set-up

PAS is a photo-thermal, scattering-free technique where the light beam, modulated in time, gets absorbed in a sample in a closed photo-acoustic cell; this periodic absorption creates pressure changes, which correspond to an acoustic signal caught by a microphone. The schematic of our PAS set-up is shown in Fig. 1. We use a laser which is widely tuneable in the infrared range: 680-1080 nm, and further extended in the visible (340-540 nm). We use it in a linear characterization mode, where we modulate it with a mechanical chopper at frequency f (here at 81 Hz, otherwise in the 27-1200 Hz range); f defines the penetration depth of the thermal signal, which shows great promise for the depth profiling of non-homogeneous materials, such as nanomaterials covered by chiral layers. The polarization state is defined by a linear polarizer followed by a quarter-wave plate, with optional lens for PAS characterization of small areas (not shown here). For

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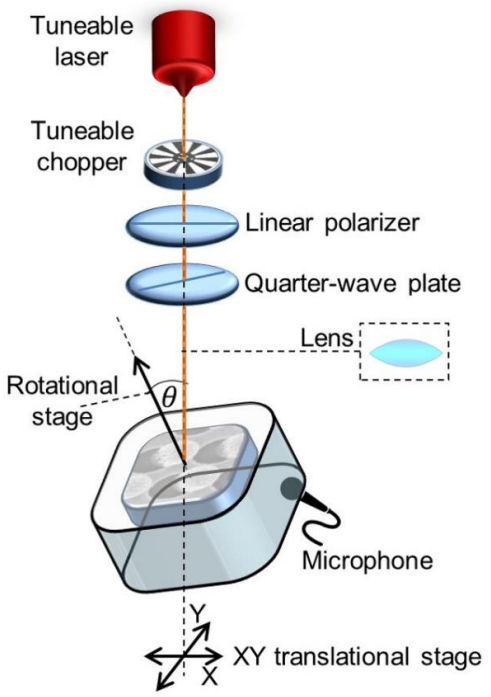

Fig. 1. Photo-acoustic spectroscopy with widely tuneable laser and chopper, coupled with translational and rotational stages.

materials which are not intrinsically chiral, we can induce it by rotating the photo-acoustic cell for angle θ with the ±40° limit. Furthermore, for materials that do not possess in-plane homogeneity, we can scan it by the XY translation stage in two dimensions with the step of 10 μm.

3 Mapping results

Here we test the PAS set-up on a well-known metasurface geometry [4,6]: large area of glass is covered by a low-cost Ag-based metasurface, here defined as Ag80. The metasurface is based on nanospheres self-assembled with 522 nm pitch, and covered by 80 nm of Ag under oblique deposition. Such deposition creates asymmetric Ag semishells, which further become chiral under excitation at oblique incidence (i.e. extrinsic chirality). We measure PAS absorption signal for left and right circularly polarized excitation (LCP and RCP, respectively), in the wavelength range of 680-1080 nm, and the incidence angle range of ±40°. CD is defined as:

$$CD[\%] = 100\frac{A_{LCP} - A_{RCP}}{A_{LCP} + A_{RCP}}.$$

Fig. 2 proves the expected extrinsic chiral behaviour in the near-infrared range, in agreement with extinction characterization of similar samples [5,7].

We further perform spatial mapping at two wavelengths giving the opposite CD for θ=-40°, i.e. 740 nm and 890 nm, Fig. 3. With metasurface in the center, upper left and bottom right corners of the sample show lower absorption and CD, which inverts for the two wavelengths. Each characterization can be redone with optimized precision.

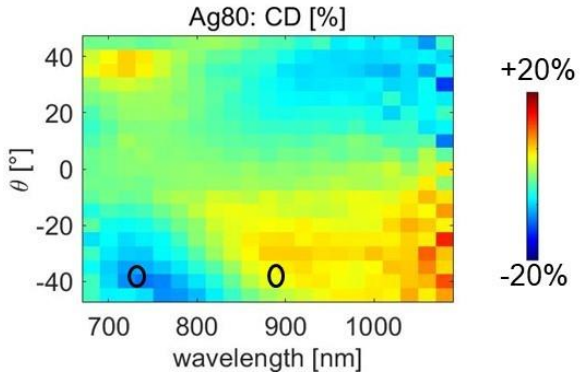

Fig. 2. CD wavelength-incidence angle map of Sample Ag80. Black circles represent wavelength points for spatial mapping.

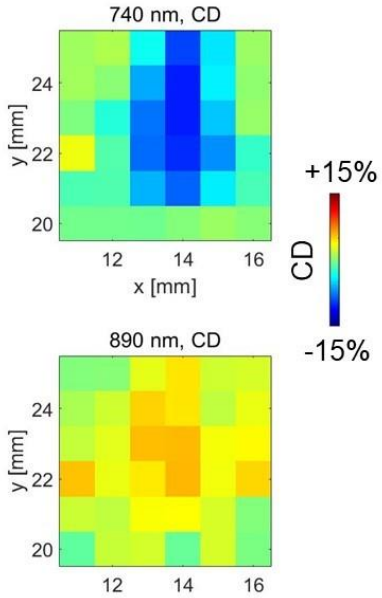

Fig. 3. CD 2D spatial map of Sample Ag80, excited at θ=-40° with wavelengths giving opposite CD: 740 nm and 890 nm.

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