Magnetochiroptical Metasurfaces for Chiral Biosensing Down to the Few-Molecule Level

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***Abstract*—In this study we describe a metasurface with square two-dimensional nanocavities designed for enhanced chiral molecule sensing. Employing magneto-optical hyperbolic metamaterials, the structure achieves high sensitivity, enabling label-free biosensing at the few-molecule level. The results demonstrate significant potential for pharmaceutical and biosensing applications.**

***Keywords*—Few-molecules sensing, hyperbolic metamaterials, magnetochiroptical, magnetic circular dichroism, metasurfaces.**

I. Introduction

Chiroptical biosensing employs chiral optical fields to probe chiral and/or achiral analytes by detecting changes in the properties of chiral light. Conventional measurements involve monitoring alterations in the absorption levels of left-handed circularly polarized (LCP) and right-handed circularly polarized (RCP) light after their interaction with chiral samples [1]. This technique, known as circular dichroism (CD) spectroscopy, relies on the differential absorption of LCP and RCP light [2]. Though CD spectroscopy is effective for large volume samples, high concentrations, or large molecules, it is unsuitable for small molecules, low concentrations, or small volumes due to the significant disparities between the wavelength of light and the molecules sizes. There is therefore a need to devise mechanisms enabling detection at the few-molecule level. One promising approach to achieve this goal is by exploiting strongly enhanced and localized chiral optical near-fields associated with nanophotonic dielectric or plasmonic nanostructures, which may possess intrinsic [1], [3] or extrinsic [4], [5] chirality. However, these approaches are still limited by the passive nature of their physical principles.

In this work we employ a magnetochiroptical metasurface [6], [7], comprising a square two-dimensional array of rectangular nanocavities, to improve refractometric sensing of both chiral and achiral analytes. Our design involves engineering the nanocavities on thin heterogeneous bilayers of metallic and magneto-optical (MO) dielectric materials, tailored to operate at a wavelength of $\lambda = 800$ nm. With this setup two fundamental physical mechanisms are combined. Firstly, the nanocavities serve as diffractive gratings, facilitating the excitation of plasmonic modes within the multilayer structure. Secondly, the metal/dielectric multilayer acts as an effective hyperbolic metamaterial (HMM), with wavelength ranges where $\varepsilon_\perp \varepsilon_\parallel < 0$. This characteristic enables the excitation of bulk plasmon polariton (BPP) resonances, thus confining the resonantly enhanced optical fields within the structure, and consequently, within the nanocavity regions [8], [9]. By operating on this principle, our approach yields a remarkable enhancement in sensitivity compared to prior methodologies. Significantly, we achieved a sensitivity on the order of $S = 300$ nm/RIU, a value that distinguishes itself as highly competitive with state-of-the-art systems.

This work has been partially funded by the project XGM-AFCCT-2024-3-1-1 supported by xGMobile–EMBRAPII–Inatel Competence Center on 5G and 6G Networks, with financial resources from the PPI IoT/Manufatura 4.0 from MCTI grant number 052/2023, signed with EMBRAPII. We also acknowledge financial support from the Brazilian agency National Council for Scientific and Technological Development-CNPq (403612/2020-9, 403827/2021-3, 314671/2021-8), FAPESP (2023/08999-9, 2018/22214-6), FAPEMIG (APQ-04523-23), and RNP, with resources from MCTIC, Grant No.01245.020548/2021-07, under the Brazil 6G project of the Radiocommunication Reference Center (Centro de Referência em Radiocomunicações - CRR) of the National Institute of Telecommunications (Instituto Nacional de Telecomunicações - Inatel), Brazil.

II. Methodology

Fig. 1(a) depicts the proposed nanostructure, consisting of alternating slabs of silver (Ag) and cerium-substituted yttrium iron garnet (Ce:YIG), with a periodic array of cavities along the xy-plane. The cavities are assumed to extend up to the silica (SiO_2) substrate surface. Both the medium inside the nanocavities and the superstrate medium are considered aqueous. The different geometrical parameters are illustrated in the inset of Fig. 1(a), with the pink beam representing perpendicular incidence of CP waves, while the green arrow denotes the magnetization (**M**) direction along the $\pm z$-axis. To quantify the magnetically induced chirality within the proposed achiral nanostructure, we utilize magnetic circular dichroism (MCD), defined as MCD $(^\circ) = \tan^{-1}\left(\frac{R_{\mathrm{RCP}}-R_{\mathrm{LCP}}}{R_{\mathrm{RCP}}+R_{\mathrm{LCP}}}\right)$, where R_{RCP} and R_{LCP} are reflectances for RCP and LCP wavefronts, respectively. In our calculations, we maintained the superstrate refractive index at $n_{\mathrm{s}} = 1.33$. The refractive indices within the cavities range from $n_{\mathrm{a}} = 1.33$ to $n_{\mathrm{a}} = 1.38$, indicating the presence of the analyte confined within these regions. Under these conditions, we optimized the geometrical parameters to achieve maximum MCD response around $\lambda = 791$ nm. Permitivity values were taken from experimental reports for Ag [10], SiO_2 [11] and Ce:YIG [12] materials. Notably, Ce:YIG exhibits magnetic anisotropy, manifesting non-zero

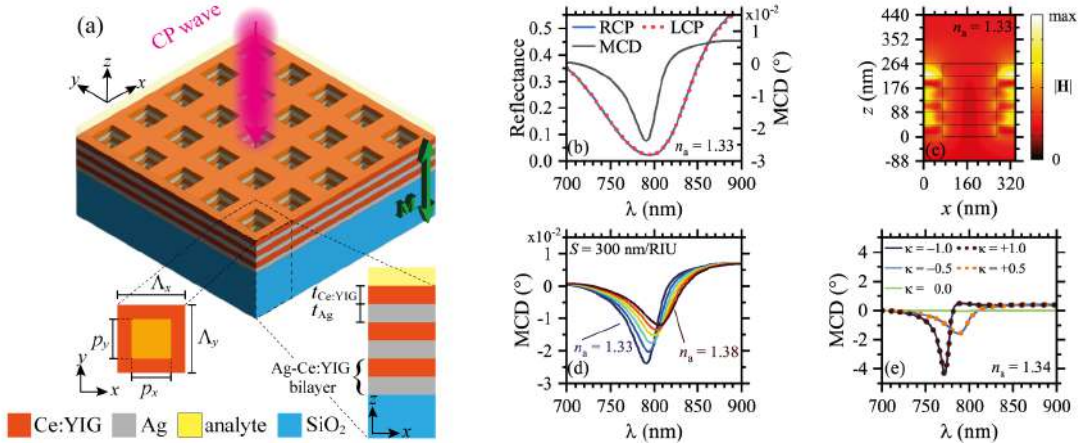

Fig. 1. (a) Schematic of the MO-HMM metasurface comprising a squared array of nanocavities in alternated Ag-Ce:YIG bilayers. (b) Reflectances for RCP (blue-solid) and LCP (red-dotted) and the respective MCD (black). (c) Normalized H-field profile of coupled BPP mode at the resonance wavelength $\lambda = 791$ nm for $n_{\mathrm{a}} = 1.33$. (d) Sensitivity for the analyte confined to the nanocavity regions, with refractive indices within the cavities range from $n_{\mathrm{a}} = 1.33$ to $n_{\mathrm{a}} = 1.38$. (e) MCD spectra for chiral analytes with $n_{\mathrm{a}} = 1.34$ and different chiralities.

off-diagonal components ($\varepsilon_{\mathrm{off}}$) in the permittivity tensor [12]. Simulations were performed using the finite element method (FEM), via COMSOL Multiphysics, for normally incident light and geometric parameters $\Lambda_x = \Lambda_y = 338$ nm, $p_x = p_y = 195$ nm and $t_{\mathrm{Ag}} = t_{\mathrm{Ce:YIG}} = 44$ nm.

III. Results

Reflectances in Fig. 1(b) are for right circularly polarized (RCP) (blue-solid line) and left circularly polarized (LCP) waves (red-dotted line), along with the corresponding MCD, denoted by the black-solid line. These measurements are depicted for an achiral analyte with $n_{\mathrm{a}} = 1.33$. The discrepancies between R_{RCP} and R_{LCP} arise from the magnetochiroptical effect induced by $\mathbf{M}$ along the $+z$-axis, resulting in MCD $\neq 0$. The reflectance resonance dips are related with the BPP modes (see Fig. 1(c)). Fig. 1(d) illustrates the refractometric sensing, considering achiral molecules for the analyte region varying from $n_{\mathrm{a}} = 1.33$ to $n_{\mathrm{a}} = 1.38$. The sensitivity was calculated as $S = 300$ nm/RIU for a small volume or concentrations in HMM platforms, which is competitive with recent literature [3], [4], [9]. The concept presented in this study holds promise for chiral molecule sensing, as illustrated in Fig. 1(e). Here, we consider the analyte region as an effective medium with $n_{\mathrm{a}} = 1.34$, akin to a glucose concentration of 5% in water. Utilizing constitutive equations in the Boys–Post form at the nanocavities, we conducted calculations for hypothetical chirality factors $\kappa = 0, \pm 0.5, \pm 1$. These results demonstrate the viability of our approach for sensing both achiral and chiral analytes.

IV. Conclusions

We have described a sensing strategy for both achiral and chiral analytes employing MO-HMM nanostructures. In our approach MCD spectra induced by the Faraday effect are exploited. The compactness of our nanostructure design is facilitated by nanocavities, enabling the excitation of BPP modes without the necessity of bulky prism couplers. The findings presented here offer promising prospects for pushing the boundaries of sensing down to the few-molecule level.

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