Polarization-resolved surface-enhanced sensing of single-stranded DNA with Bloch surface waves

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Abstract. We describe a novel one-dimensional photonic crystal design allowing for the concurrent excitation of transverse-electric and transverse-magnetic Bloch surface waves, thus paving the way for polarization-resolved sensing experiments. We discuss its application for the surface-enhanced sensing of oriented DNA molecules through nanoscale birefringence measurements.

1 Introduction

One-dimensional photonic crystal multilayers are well-established and fully consolidated tools in the palette of nanophotonic design, yet they still offer exciting and unexplored possibilities with novel ways to control the local density of optical states in the energy-momentum space. Of particular interest for surface-enhanced sensing applications is the possibility to excite Bloch surface waves at the top layer of a truncated photonic crystal multilayer, which are solutions of the Maxwell equations that propagate along the surface but are exponentially confined along the perpendicular direction. The associated strong field confinement and enhancement at the surface makes them particularly suitable for molecular sensing and spectroscopy, both on-resonance (surface-enhanced absorption) and off-resonance (refractometric sensing) with the electronic or vibrational transitions of the investigated molecules [1-4].
In this framework, an appealing possibility is provided by the perspective of exploiting Bloch surface waves for polarization-resolved experiments, in which e.g. two perpendicular polarization axes are used to assess the orientation of molecules within a thin layer or electromagnetic fields carrying an enhanced optical chirality are exploited for the sensing of chiral molecules. To achieve this, it is mandatory to be able to concurrently excite the two eigenmodes of the system, namely a transverse-electric (TE) and a transverse-magnetic (TM) mode, to coherently superimpose them and engineer the polarization state of the resulting surface wave. This possibility is generally hindered by the fact that TE and TM modes possess different dispersion relations and therefore cannot be excited with the same photon energy and angle of incidence. In a series of recent works, we have discussed how to engineer the top layer of the truncated photonic crystal multilayer to tune the local refractive index and superimpose the TE and TM dispersion relations over a broad spectral range. By means of analytical and numerical analysis, we highlighted the superior performance that the combination of the two modes guarantees in chiral sensing [5,6] and in the optical sorting of chiral molecules [7]. While the experimental validation of those concepts is still ongoing, in this contribution we focus on a recent experiment in which we sensed the refractometric response of a molecular layer with both the TE and TM modes in order to assess the anisotropy (birefringence) that is a signature of the molecular orientation.

2 Materials and methods

The platform employed for the sensing experiments consists of a photonic crystal multilayer grown by reactive magnetron sputtering and made by 2 periods of alternating compact layers of SiO_2 (low refractive index) and Ta_2O_5 (high refractive index) with different thickness, terminated with an additional low-index layer incorporating a high refractive index inclusion, which was already experimentally demonstrated to sustain two partially-superimposed TE and TM surface modes [8,9].
In this work, we use such sensing platform to monitor the growth of single-stranded DNA chains on the sample surface by rolling circle amplification (RCA), an enzymatic reaction mediated by polymerase [10-12]. For the chosen grafting density these chains take a brush conformation, in which they are preferentially stretched away from the surface and oriented along the normal to

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the surface and thus display birefringence in their optical response.
In the experiments, we couple a collimated incoherent polychromatic LED source to the photonic crystal multilayer via a LASF9 right-angle coupling prism, which is optically matched using immersion oil. After fixing the angle of incidence, we monitor the spectral shift of the TE and TM modes during the amplification process.

3 Results and discussion

The main results of the experiment are summarized in Figure 1, which is obtained after conversion of the experimental spectral shift into an effective refractive index change, as performed by a combination of calibration experiments and simulations. In particular, for such a calibration, both the finite thickness of the molecular layer and the frequency dependence of the sensitivity are taken into account.

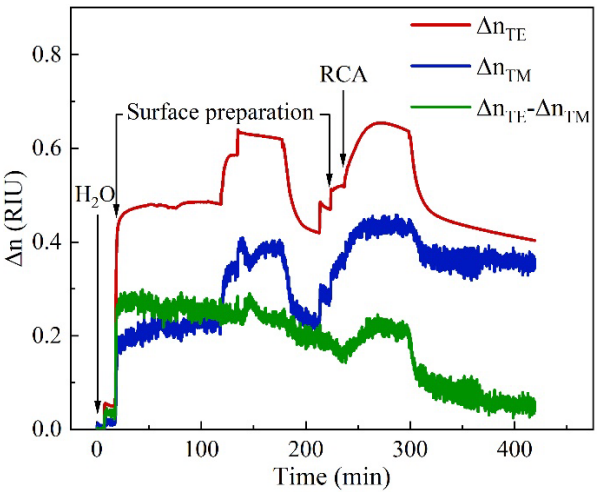

Fig. 1. Experimental results, demonstrating the detected change in the refractive index of the molecular layer after calibration. The red and blue curves are obtained from the experimental spectral shifts of the TE and TM modes, respectively, during the development of the protocol. The green curve is the difference between the blue and red ones, to highlight any specific birefringent contribution.

The red and blue lines represent the refractive index of the molecular film perceived by the TE and TM modes, respectively, while the green line represents their difference. If we disregard an instrumental linear background with a negative slope that characterizes the whole green curve, the main discontinuity that develops around 250 minutes after the start of the protocol is associated with (and compatible with) the birefringence of the single-stranded DNA brushes oriented perpendicular to the photonic crystal surface that develop during the RCA.

In conclusion, by monitoring the spectral shift of both the TE and TM surface modes in a photonic crystal multilayer, we were able to assess the molecular orientation exploiting the surface enhancement provided by Bloch surface waves. In perspective, the possibility provided by our design to excite the two modes concurrently allows performing this measurement as a single-wavelength reflectivity experiment, exploiting a coherent laser source. Moreover, the full control of the polarization state of the Bloch surface waves paves the way towards surface-enhanced circular dichroism.

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