

# 3D Chiral Metamaterials for Biosensing - INVITED

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**Abstract.** In this contribution we will discuss the experimental application of 3D chiral metamaterials as high sensitivity biosensors, exploiting circular dichroism in transmission. 3D metamaterials with chiral features can be realized by highly accurate and highly localized bottom-up nanofabrication approach. Large chiroptical effects can be engineered, originating from the single element optical resonances, but collective interactions in arrayed configurations can play a significant role, further enhancing these effects. Capability of biomarker detection in the femtomolar range is demonstrated even in complex biofluid matrix.

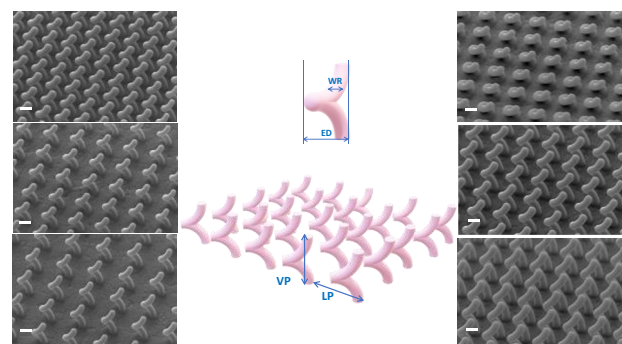
## 1 Introduction

Artificial plasmonic nanostructures with complex and tunable geometries can enable new optical properties for biosensing applications. Plasmonic nanostructures confine light at nanometer dimension, also offering miniaturization possibilities and integrability in microfluidic systems[1]. The plasmonic biosensing basic principle is to detect the shift of plasmonic resonances induced by changes in the surrounding environment. Chiral nanostructures add to plasmonic effects, a different response when interacting with circularly polarized light of different handedness, being good candidates for the detection of low concentration analytes, even in complex biofluids [2]. However, the fabrication of 3D chiral nanostructures is challenging, because of the complexity of the shapes to realize. Focused ion/electron beam technology demonstrated high geometrical accuracy at the nanometer scale in the fabrication of complex chiral elements [3]. Here, we will show our activities on the engineering of chiral objects at the nanoscale, obtained by focused ion beam technique. We studied new strategies for shaping metal-dielectric core-shell systems and we also investigated the diffractive coupling regime among multiple elements ordered in periodic arrays, along the in-plane and out-of-plane directions, to totally control the overall optical response with the 3D lattice parameters. The engineering of these features allowed to achieve high refractive index sensitivity and high specificity even in complex body biofluids.

## 2 Results and discussion

We developed a nanofabrication procedure to realize helix-based, fully 3D, metallic nanostructures with a controlled periodicity both in-plane and out-of-plane. The approach employs focused ion/electron beam processing in deposition mode, where various precursors can be used

[3]. In this way, a fine understanding of chiral light-matter interaction at the nanoscale can be pursued, and chiroptical properties can be widely tailored by tuning materials and architecture (Figure 1). Moreover, the flexibility of the technology allows to study fundamental diffractive aspects, leading to the concept of chiral metacrystal [4,5], where different chiral dipolar modes can be excited along the helix arms. These in turn generate far field optical resonances with a specific radiation pattern suggesting that a combination of efficient dipole excitation and diffractive coupling matching controls the collective oscillations among the neighbour helices.

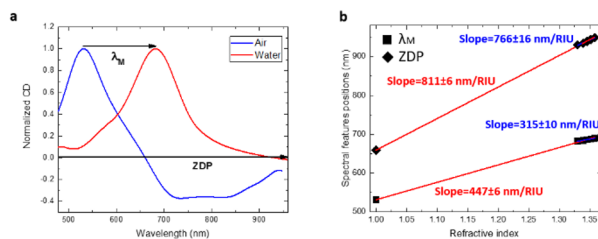


**Fig. 1.** The unit cell of the chiral metamaterials consists of a metallic helix identified by the external diameter ( $ED = 300$  nm), the wire diameter ( $WD = 100$  nm) and the vertical pitch ( $VP$ ). In array configuration, the lattice period ( $LP$ ) determines the mutual helix interaction. Scanning electron microscopy images show views of arrays with different  $LP$  and  $VP$  parameters. Scale bar corresponds to 100 nm.

In view of biosensing application, suitable functionalization protocols are needed for the proposed metamaterial, consisting of a conformal coverage with a polymeric shell [5]. The resulting core-shell architecture modifies the chiral metamaterial near- and far-field optical response and shows a circular dichroism (CD) spectrum in transmission which is highly sensitive to

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changes in the external medium optical properties. In particular, the bisignated shape of CD spectrum offers two spectral features available for biodetection tracking: the maximum dichroism point ( $\lambda_M$ ) and the zero-dichroism point (ZDP), with different sensitivities to refractive index changes (Figure 2). Application of the proposed compact chiral metamaterial for the detection of biomarkers clinically relevant for neurodegenerative diseases (TAR DNA-binding protein 43), in spiked solution and in human serum, will be also discussed.



**Fig. 2.** CD spectra of the measured core-shell nano-helices arrays in air ( $n = 1$ , blue line) and water ( $n = 1.333$ , red line). b) Trend of the spectral position of  $\lambda_M$  (Black square) and ZDP (black rhombs) measured in air and for glycerol-water solutions at different concentration corresponding to different RI variations from  $n=1.333$  (100% water, 0% glycerol), to  $n=1.346$  (80% water, 20% glycerol). The lines correspond to their respective calculated linear fitting. The linear fitting turns out an index sensitivity of 315 nm/RIU for  $\lambda_M$  and 766 nm/RIU for ZDP. The sensitivity obtained from the linear fitting in the RI range from  $n=1$  to  $n=1.346$  (red line) is instead 447nm/RIU and 811 nm/RIU.

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