Magneto-optical modulation for improved surface plasmon resonance sensors

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Metallic magnetoplasmonic nanostructures are used for the transducer layers in novel probes to achieve enhanced sensitivity.

Interactions between analyte molecules (in a liquid or gas phase) and sensitive layers of solid-state chemical sensors can provide a considerable amount of information, e.g., for environmental control, life science, or food safety purposes. Such sensors are composed of two main elements: the sensing layer and the transducer. The former is the part that interacts directly with the analyte (i.e., where the vapor molecules or biological analytes are physically or chemically adsorbed), and the transducer is necessary for converting these processes into a detectable electric signal.

Surface plasmon polaritons (SPPs) are transverse electromagnetic waves bound to a metal–insulator interface (typically in thin metal films). SPPs are excited—with the use of gratings or prism couplers—when collective oscillations of conduction electrons create regions of enhanced electromagnetic fields in direct proximity to a metal sensor. These regions are highly sensitive to the local changes in refractive index that occur at the surface of the thin metal film. This sensitivity, in turn, provides a capability for a label-free form of analytical detection. For this reason, surface plasmon resonance (SPR) phenomena\(^1\) are commonly used to measure the binding of biomolecules to gold surfaces, and for monitoring interactions between a sensing layer deposited on a metal transducer interface and gas/liquid molecule analytes.\(^1\)\(^,\)\(^2\) Current SPR technology, however, is associated with the low detection limits of amplitude-sensitive schemes. The sensitivity is therefore insufficient for label-free detection of low concentrations of low-molecular-weight analytes (e.g., drugs, vitamins, or antigens).\(^1\)

To overcome this problem, a number of different SPR modulation configurations have been proposed. For instance, an external modulation is often applied (e.g., in mechanical or phase-modulated SPR sensors) to improve the signal-to-noise ratio of the sensing measurements and to thus increase their limit of detection.\(^3\)\(^,\)\(^4\) As an alternative, a magneto-plasmonic (MP) modulation has been proposed. This modulation arises from the simultaneous excitation of magneto-optic (MO) effects and SPR in structures that have plasmonic and MO activity.\(^5\)\(^,\)\(^6\) On this basis, a new type of transducer—a magneto-optic-SPR (MO-SPR) active transducer (see Figure 1)—has been

Figure 1. (a) Photograph illustrating the composition of magneto-plasmonic multilayers (composed of noble and ferromagnetic metals). (b) Upon surface plasmon resonance (SPR) excitation, an enhancement in the transverse magneto-optic (MO) Kerr (TMOKE) signal, $\Delta R$, is recorded (c). $k_{sp}$: Plasmon wave vector. The direction of the applied magnetic field (B), with respect to the incident plane is indicated by the black arrow. $\theta_{SPR}$: Incidence angle of the light that causes SPR excitation. (c) The enhanced TMOKE signal makes it possible to sensitively probe refractive index changes at the metal/dielectric interface of MO-SPR transducers. (d) Illustration of the different stages of the sensing process. a.u.: Arbitrary units.

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proposed and suitable materials are required for the layers in these devices. For example, MP multilayers—composed of noble and ferromagnetic metals (gold or silver, and cobalt or iron)—are used because they combine the large MO activity of ferromagnetic materials and the exceptional plasmonic properties of noble metals. When SPR is achieved in MO-SPR transducers, large enhancements of transverse MO Kerr effects—see Figure 1(c)—are produced. These effects depend strongly on the excitation conditions of the SPP and, therefore, on the refractive index of the dielectric material in contact with the metal layer. This is the basis of the sensing principle for novel MO-SPR devices.

As part of our work on optical chemosensors, we have become fascinated by this novel research field. It has been our aim to realize and characterize these new kinds of active transducers. In particular, we are focused on studying the nanoscale properties of the transducer nanostructures and their influence on the sensing performance of the devices in which they are used. We conduct this work by using both theoretical and experimental methods. We are able to optimize the response of the sensors by properly combining the structural, morphological, chemical, magnetic, and optical properties of all the layers.

Figure 2. (a) Schematic illustration of the experimental setup for an MO-SPR operating in a controlled atmosphere. In this configuration, organic macrocycle thin films—such as ethane-bridged zinc porphyrin dimers (b) or cobalt bis-porphyrin derivative-based thin films (c)—are used as sensing layers. Zn: Zinc. N: Nitrogen.

Figure 3. (a) Illustration of the different geometries of nanostructures—composed of bare-metallic and ferromagnetic materials—being investigated for use in TMOKE measurements. (b) A hybrid metallic-magnetic material in a core-shell configuration. (c) Schematic representation of localized SPR modulation that is induced from the application of an oscillating external magnetic field. $\Delta \lambda$: Change in wavelength. (d) Different optical and morphological characterization tools are used to support the design and theoretical investigation of MP nanostructures. For example, finite element modeling was used to obtain the mesh and electric field distribution (shown in the inset) of the nano-disk surface of a typical MP nanostructure in a resonance condition.

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that compose the MP transducers. In addition, we find that it is important to optimize the relative position of the interlayers, with respect to the specific dielectric used.15

On the basis of these basic concepts, we have demonstrated the possibility of using the enhanced MO signal of metal/ferromagnetic material trilayers for investigations of biomolecular interactions in a liquid phase.16 As a proof-of-concept, we functionalized a transducer surface with thiol chemistry to realize specific antibody (i.e., bovine serum albumin antibody) anchoring. We then used our sensors to record the binding between immobilized molecules and their complementary target molecules. Our results indicated that a better sensitivity and a lower limit of detection were achieved with our MO-SPR biosensor than with traditional SPR sensors.16 We have also used a similar approach to improve the gas sensing performance of traditional SPR sensors.17–19 In these studies, we used a thin nanostructured titanium oxide sensing layer or organic porphyrin macrocycles (see Figure 2). Our results indicated that the new magnetoplasmonic transducers (when used in a resonance condition) have a better sensitivity than plasmonic transducers that are used in classical SPR sensor techniques.10,16–19

In our more recent work we have been focusing on studying magnetoplasmonic effects in nanostructures that support localized surface plasmons. These nanostructures are composed of bare-metallic and hybrid-metallic magnetic materials distributed on planar substrates. Such structures exhibit interesting novel properties that arise from the modulation of the optical response to an external low-intensity magnetic field. We can thus use the unique properties of these nanostructures to control and manipulate light at the nanoscale. In addition, the planar distribution of the nanostructures makes them an effective choice for chip-based chemical sensors. We are currently investigating a variety of geometries for the bare-metallic and bare-ferromagnetic and hybrid-metallic magnetic materials (see Figure 3). Our results so far indicate that plasmonic effects can be used to effectively enhance the MO properties. Furthermore, our theoretical modeling is in good agreement with our experimental findings (see Figure 3).

In summary, in our recent research, we have demonstrated that novel magnetoplasmonic transducers can be used to provide sensitive detection capabilities in SPR-based sensors. In particular, we have used theoretical and experimental approaches to show that novel transducer probes can be realized through enhanced MO activity, arising from SPR excitation, in metallic and hybrid-metallic magnetic nanostructures. This phenomenon is applicable to extended thin films and a broad class of nanoparticles that are characterized by marked structural and compositional differences. We have also outlined our ongoing investigations into the influence of the geometry of our metallic and hybrid materials on the enhancement of MO activity. The ability to simultaneously exploit enhanced plasmonic and MO properties for high-performance sensing devices in this manner is paving the way for a wide variety of applications that span many disciplines (e.g., nanomedicine, telecommunications, and immunosensing).

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Roberto Rella is a physicist and has been a senior researcher at IMM since 2001. His research is connected with the optimization of device prototypes for optoelectronic sensing and biosensing applications.

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References

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