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# Nanoplasmonic Sensors

 Springer

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# Preface

Plasmonics is the science of light-matter coupling through surface plasmon polaritons (SPPs) or surface plasmons. Simply put, surface plasmons are optically excited collective oscillations of the free electrons at a metal surface. Formally, SPPs are the quanta of charge density collective oscillations that are tightly confined at the interface of materials with negative and positive permittivities. However, surface plasmons can be comfortably described in the classical electrodynamics without evoking quantum mechanics. They represent actual mechanical oscillations (with very small displacements though) of the electron gas under the influence of the electromagnetic field of the incoming light.

Nanoplasmonics explores surface plasmon modes confined in the nanosized, i.e., subwavelength metal structures—localized surface plasmons (LSP). Although light interaction with nanoscopic matter has been observed for centuries, like stained glass goblets manufactured in the Roman Empire or spectacular windows in medieval churches, and was theoretically described already by Michael Faraday and Gustav Mie more than a century ago, only recently our ability to fabricate and control the matter at a nanoscale brought to life what is known as nanoplasmonics. Over the past decade nanoplasmonics has developed into a burgeoning field, where exciting opportunities are opening for the increasing number of application areas, including photonics, biomedical imaging and sensing, (photo)catalysis, and molecular spectroscopy to name a few.

The key features that enable such development are subwavelength confinement, large cross-section for scattering and absorption of light, and most important for sensing applications, strongly enhanced electromagnetic fields in the direct proximity of the nanostructures. Through such field enhancement nanoplasmonic resonances sensitively depend on the minute variations of the surrounding dielectric medium. This fact essentially forms the basis for nanoplasmonic sensing—a merely refractive index sensing, but with the powerful extension that the probed volumes are in the nanoscale. Small enough so a presence of even single biological or chemical molecular species becomes detectable in various nanoplasmonic sensing schemes.

With the present book we attempt to overview the current status of nanoplasmonic sensing, with the relevant highlights of the past decade of its extensive development and looking in the nearest future for this science and technology area. In Chap. 1 we start with the general principles of biosensors, outline surface plasmon resonance basics and applications such as in drug discovery, food industry, medical diagnostics, review the advantages of localized surface plasmon resonances (LSPR) from the basic physics of SPPs, and describe the principles of sensing with LSPR—"bulk" and "thin/molecular layer" approaches. This chapter further gives hints on the comparison of the propagating vs. localized plasmons for bulk refractive index (RI) and molecular sensing, substrate effects, and the importance of electromagnetic fields confinement. It ends with highlighting the single-molecule detection with LSPR. Chapter 2 focuses on the unique characteristics of LSPR: short EM fields decay for study of protein conformational changes and gas sensors in combination with metal-organic frameworks; going from single-nanoparticle sensing to wide-field single-nanoparticles imaging and spectroscopy; coupling LSPR with molecular identification through surface enhanced Raman scattering (SERS) and laser desorption ionization mass spectroscopy (LDI-MS). It gives the historical retrospect on the development of RI LSPR sensing, and gives the recipes for improving the limits of detection, for example, by using resonant molecules (chromophores) or utilizing plasmonic nanoparticles as labels. Chapter 3 presents nanoplasmonics combined with the studies of artificial cell membranes: the design nanoplasmonic biosensor for particular life science application. Further, here nanoplasmonic sensing is combined with quartz crystal microbalance with dissipation (QCM-D) mass and viscosity sensing technique. Chapter 4 brings nanoplasmonic sensors inside the living cells and helps to map with nanoplasmonic sensing time-resolved intracellular biochemical distribution. With specially designed plasmonic nanostructures it is possible to utilize the antenna effect for light and convert far-field radiation into local heat, earning intracellular nanoplasmonic gene switches through photothermal DNA dehybridization and gene silencing on-demand. Nanoplasmonics here defines the properties of intracellular plasmon resonant energy transfer (PRET) biosensors. Addition of magnetic layer to plasmonic nanostructures moves nanoplasmonic sensing towards externally controllable sensors. Nanoplasmonic molecular rulers—DNA-conjugated Au nanoparticles—are also outlined in this chapter. Chapter 5 focuses on the single plasmonic nanoparticle biosensing that dramatically reduces detection limits and in general allows miniaturizing of the sensor and the fluidic system. In Chapter 6 array-based nanoplasmonic sensors that move towards the point-of-care applications are featured. This includes multianalyte detection (multiplexing), handling of complex analyte media, and performing kinetic analysis of the complex fluids, addressing nonspecific binding to the sensor surface. Chapter 7 highlights optical tweezers in combination with SERS. This allows for manipulation of nanoplasmonic particles sensors, sensing in confined (intracellular) volumes, and addressing sensing interactions in colloidal systems. Nanoplasmonic

sensing for applications in nanomaterials science and catalysis is the emphasis of Chapter 8. It details the concepts of direct and indirect nanoplasmonic sensing and features nanoplasmonic sensors for optical gas detection. Direct sensing encompasses the sensing modality when nanoplasmonic particles act as sensors and the studied entities; it is used in studies of oxidation and corrosion, metal hydrides formation, liquid–solid phase transition, chemical surface reactions, and surface charge transfer. With indirect sensing plasmon nanoparticles function as sensors of processes on or in adjacent (nano)materials. It is used for gas sensing at metal oxide composite films, in heterogeneous catalysis (CO and H<sub>2</sub> oxidation on Pt), optical calorimetry, hydrogen storage, and polymer phase transitions. In Chapter 9 plasmonic crystals—arrays of nanoholes or nanoposts, fabricated via soft nanoimprint lithography—are highlighted. They are used for the prime RI sensing: for example, probing polyethylene glycol concentrations in thin films, mechanical deformation of hydrogels resulting from pH changes, and allowing 2D chemical imaging of protein thin films. Interestingly, such quasi 3D plasmonic crystals can be characterized by the concepts used for crystalline matter in solid state physics—for example, they feature the “plasmonic” Brillouin zone. Chapter 10 evaluates the general performance of nanoplasmonic sensors. It gives the definition of noise, stability, detection limit, dynamic range, sensitivity vs. resolution, diffusion vs. reversible binding of analytes, and figure-of-merit (FOM) of nanoplasmonic sensors. The chapter further discusses the importance of surface chemistry, probe affinity and density. Strategies are given for performance maximization. In Chapter 11 you will find the discussion of the spatial and spectral plasmonic modes engineering for biochemical sensors in relation to “top-down” nanoplasmonics. One of the fine practical examples of such engineering are nanoplasmonic dimers, by the interparticle distance calibration adopted for the target analyte positioning. Result is the biosensing down to single-molecule detection limit. Chapter 12 comprehensively presents the integration of nanoplasmonic sensing elements with optical fiber technology, as the latter is very important transducer in analytical sciences to probe environments prohibitive for traditional spectroscopic probes. Such sensor scheme includes plasmonics inside or on the tip of the fibers for remote SPR and SERS measurements. The FOM—quotient between sensitivity and width of the resonance, a parameter that is equivalent both in wavelength and energy scales—is presented in Chapter 13. To maximize FOM it is shown on the example of gold nanoparticles that the existence of the optimized spectral region is needed, coinciding with the region where quotient of real to imaginary parts of the metal dielectric function reaches maximum. The importance of the supporting substrate and adhesion layer for the sensor is also discussed. Chapter 14 presents random evaporated gold island films—bottom-up nanoplasmonic sensors and transducers. It is in fact one of the earliest techniques for the preparation of LSPR systems and further use them for sensing. Details of the technique are given, the sensitivity of resulting transducer platform and biosensing case studies of immunoglobulin antibody–antigen recognition are outlined, with a

special focus on improving the stability of the sensing platform. Finally, Chapter 15 introduces the electrical detection of surface plasmons that is very relevant for the integrated biosensing. Evaluation of the sensitivity and FOM is given, and the metal-semiconductor-metal plasmons launch and detection are discussed in detail.

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