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Plasmonic structures for sensors

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Abstract. The article provides a brief overview of the use of surface plasmon resonance in optical sensors of various types. Such sensors are widely used in healthcare, security, food safety and environmental monitoring. The physical basis and design of plasmon-enhanced sensors, such as colorimetric sensors, sensors based on plasmon-enhanced fluorescence, and surface-enhanced Raman sensors, are considered.

Keywords: plasmons, sensors, resonance, field enhancement, Raman scattering

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Материалы конференции
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Плазмонные структуры для сенсоров

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Аннотация. В статье представлен краткий обзор использования поверхностного плазмонного резонанса в оптических сенсорах различных типов. Такие сенсоры широко используются в здравоохранении, системах безопасности и мониторинге окружающей среды. Рассмотрены физические основы и конструкция сенсоров с плазмонным усилением, таких как колориметрические сенсоры, сенсоры на основе плазмонно усиленной флуоресценции и сенсоры на основе поверхностно усиленного комбинационного рассеяния.

Ключевые слова: плазмоны, сенсоры, резонанс, усиление поля, рамановское рассеяние

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Introduction

Surface plasmon resonance (SPR) is a phenomenon caused by collective oscillations of conduction electrons in metallic nanostructures [1]. Both the intensity and position of the SPR are highly dependent on the size, shape, and composition of the nanostructures, as well as the dielectric properties of the environment [2–4]. The latter makes it possible to create optical sensors using plasmonic metal nanostructures.

There are two different forms of plasmon resonance: nanoparticle localized plasmon resonance (LSPR) and propagating surface plasmon polaritons (SPP) [5]. LSPR is observed if the dimensions of the metal nanostructure are smaller than the wavelength of the incident light. In this case, collective nonpropagating oscillations of surface electrons arise in a metallic nanostructure. The LSPR frequency ω_α along the α axis in an ellipsoidal nanoparticle is determined by the formula [6]

$$\omega_\alpha = \omega_p / \sqrt{1+\varepsilon_{diel}\left(1/L_\alpha - 1\right)} \tag{1}$$

where ω_p is Drude plasma frequency, ε_{diel} is dielectric constant of surrounding media, L_α is geometrical factor for a given axis (for a sphere L_α=1/3). As can be seen from (1), the resonant frequency depends on the refractive index of the environment, which is the basis for plasmonic sensors. Also known is the phenomenon of high concentration of the incident electromagnetic (EM) field around the nanostructure due to LSPR. A local EM field influences optical processes such as nonlinear optical effects, fluorescence, and Raman scattering.

In contrast to LSPR, SPPs are propagating electron oscillations on a metal/dielectric surface, in particular, on the surface of thin metal films. The wave vector SPP can be written as [6]

$$k_{SPP} = \frac{\omega}{c}\sqrt{\frac{\varepsilon_{Me}\cdot\varepsilon_{diel}}{\varepsilon_{Me}+\varepsilon_{diel}}} \tag{2}$$

where ε_{Me} is dielectric function of metal. Due to the mismatch between the momentum of the incident light and the propagating plasmon-polariton, the SPP cannot be excited by radiation in free space. To excite the SPP, momentum matching is required, for example, due to attenuated total internal reflection or a periodic structure. As can be seen from (2), the propagation of SPP depends on the refractive index of the environment, which is used when creating sensors.

SPP Based Plasmonic Sensors

Surface propagating SPPs or mixed mode SPP/LSPR can be used to detect changes in the refractive index of the environment. Since an additional pulse must be provided to excite the SPP, prism or grating circuits are used. The classic setup for SPP excitation is the Kretschmann configuration [7]. In this configuration, a metal film deposited on the prism (usually a noble metal, most often gold) almost completely reflects the incident radiation, except at a certain angle when the SPP is excited, called the SPR angle. This angle depends on the refractive index of the environment, which makes it possible to detect changes with a high degree of accuracy. For example, if molecules (an analyte) in an aqueous solution bind to ligands immobilized on a plasmonic metal film, the SPP band is redshifted due to the higher refractive index of the molecules [8, 9]. In this way, the concentration of analyte molecules in solution can be detected.

LSPR Based Plasmonic Sensors

Noble metal nanoparticles such as Au, Ag and Cu exhibit LSPR in the optical range and are widely used to create plasmonic sensors [10]. According to (1), the position of the LSPR depends on the shape of the nanoparticle and the dielectric environment: the wavelength of the LSPR peak shifts when the analyte binds to the functionalized surface of the nanoparticle, changing the local refractive index. Colorimetric plasmonic sensors based on the shift of the LSPR peak in colloidal solutions with nanoparticles are a simple and convenient method for detecting analytes in solution, since this technique provides direct visualization of the analyte concentration. For example, functionalized gold nanoparticles have been used for the colorimetric detection of heavy metals, small biological molecules, and biomacromolecules [11–13].

Plasmon-Enhanced Fluorescence (PEF) Sensors

The enhancement of the EM field near the surface of nanoparticles due to LSPR can be used for plasmon-enhanced fluorescence spectroscopy. Enhancement of the fluorescence of sensors based on LSPR is possible due to the enhancement of excitation and/or emission [14]. In both cases, stronger local electromagnetic fields will lead to higher enhancement. According to (1), the enhancement of the EM field near a sharp tip will be higher due to the geometric factor (the effect of a needle or lightning rod); thus, nanorods and prolate ellipsoids will have an increased PEF effect compared to nanospheres. The plasmonic fluorescence enhancement factor is usually in the range of 10–100, but can be higher in optimized plasmonic nanostructures, reaching even 10^3 [15]. Xie et al utilized a Ag nano-triangle array to enhance the fluorescence of near-infrared (NIR) dyes [16]. They obtained that the fluorescence of a low quantum-yield (4%) NIR dye can be enhanced by two orders of magnitude using the Ag triangle array pattern.

Surface-Enhanced Raman Scattering Sensors

Surface enhanced Raman scattering (SERS) is one of the most powerful and promising analytical methods for bio- and chemical analysis due to a number of advantages: (1) high selectivity of the method due to the unique spectral characteristics of analytes, (2) high sensitivity up to the detection of single molecules, (3) ease of operation, (4) the possibility of detecting multicomponent compounds with a single excitation laser due to narrow spectral bands [17–20]. Raman scattering itself is ineffective due to the small scattering cross section (10^{-28} ~ 10^{-30} cm^2/molecule). However, amplification of the local EM field in plasmonic nanostructures gives Raman signal amplification from 10^4 to 10^8 [21]. Maximization of the plasmonic electromagnetic field is crucial for the development of a sensitive SERS probe, so much effort has been devoted to the development of SERS substrates [22–24].

In our experiments, we use both self-organizing silver nanoisland films on the glass surface and dendritic structures as SERS substrates [25–28]. The advantages of dendritic structures are the high amplification of the local field compared to nanospheres, as well as stability and resistance to external influences. In our work, we obtained an enhancement of the Raman signal up to 10^6–10^7 on the basis of silver dendritic structures [27]. The formation of nanoislands by out-diffusion technique in combination with glass polarization and etching can be carried out in microchannels in glass, which is very promising for microfluidics [29, 30].

Conclusion

Structures exhibiting plasmon resonances can be easily adapted to various sensory applications through the choice of material and structure. This provides flexibility for the development of plasmon-enhanced sensors and opens up great opportunities for the use of such devices. In the future, plasmonics will be developed to enhance the sensor signal and to develop new detection devices based on fluorescence and SERS. At the same time, the efficiency of plasmon-enhanced sensors directly depends on the design of plasmonic structures and the development of new methods for their fabrication.

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