

Optical Chemical Sensors for Industrial Applications

Keynote Paper

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Abstract— The market for accurate and inexpensive sensors of chemical compounds in gases and liquids is increasing at a steady pace and it is expected that in 2015 the global demands should reach a level of more than US\$ 17 billion. Industrial applications of optical chemical sensors include process and quality control, as well as environmental pollution measurements in different fields that include process industry, automotive, biomedical industry, power engineering, oil and gas industry and food industry. Optical sensing methods offer some distinctive advantage over other approaches, including the applicability in dangerous, flammable and explosive environments, high sensitivities, compact design and insensitivity to external interference. They can be used to recognize trace amounts of a wide range of different chemicals, are compatible with the existing control systems and can be used for multianalyte detection. This work first shortly reviews different schemes utilized for optical chemical sensing in gases and liquids. These include various planar and fiber-optic waveguide systems that utilize absorption, transmission or reflection spectroscopy, fluorescence measurements that may be applied to propagating or evanescent waves. Affinity sensing is considered, where the optical sensor surface or a special intermediate receptor layer binds the targeted analyte, which in turn causes physicochemical transformations that modulate the optical properties of the system. The most part of the presentation is dedicated to sensors utilizing surface plasmon polaritons in metal-dielectric nanocomposites. These devices offer label-free, real-time and multianalyte operation with sensitivities even reaching single molecule level. Different schemes are considered including the use of optical metamaterial structures for adsorption-based sensing. The advantages and disadvantages of these sensing schemes are considered.

Keywords—chemical sensors; adsorption; plasmonic sensing; nanophotonics; metamaterial sensors

I. INTRODUCTION

The continual development of industry and the increasing sophistication of the applied methods and protocols pose a general requirement for more complex sensing and control of different processes. The measurement results must be accurate, there should not be a lag between the appearance of a signal and its reading which calls for sensor speed and its online availability, the sensing devices must often be applied under

difficult conditions that include aggressive media, high or low temperatures, vibrations, electric or magnetic disturbances, etc. In addition to that, a sensor must not perturb the industrial process itself – for instance, electronic devices may ignite flammable or explosive media or cause electromagnetic interference.

All-optical sensors meet many of these conditions, since they do not convey electric signals at all and are thus neither sensitive to external interference, nor they cause any; they are often made of robust materials and are very fast. Because of that they are applicable in dangerous, flammable and explosive environments, high sensitivities, compact design. Their design may be very compact, especially if nanophotonic devices with evanescent waves are used. Their sensitivities are extremely high, ensuring even the detection of single molecules [1]. They can be used to recognize trace amounts of a wide range of different chemicals, are compatible with the existing control systems and can be used for multianalyte detection.

Obviously, the qualitative and quantitative assessment of chemical substances is not limited to process and quality control in processing industry and chemical plants. Chemical sensing finds intensive use in automotive, biomedical industry, power engineering, oil and gas industry and food industry, among other fields. For instance, a thermal power station will need to control its greenhouse gases emission, as well as the levels of different other pollutants. Generally, one will need to observe the levels of different industrial by-products in the environment and monitor the possible appearance of dangerous substance to prevent, avoid or mitigate chemical accidents.

It is expected that at the present pace the global sensor market will reach US\$ 154.4 billion in 2020 [2]. The second fastest growing segment in it are chemical and biological sensors, which should reach US\$ 32.8 billion in 2020, while in 2015 the global demands should exceed a level of US\$ 17 billion. The photonic sensors should reach a level of about US\$ 8 billion in 2015.

A large body of literature is dedicated to chemical sensors that base their operation on optical mechanisms. Numerous research articles are being published in this field (e.g. [1, 3-11]). A number of review paper has been published dedicated to

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optical chemical sensors [12-19], as well as a number of books [20-32]. These are written from different viewpoints and illuminate different facets of optical chemical – but also biological – sensor technologies and applications.

Contrary to the majority of the previous publications, this paper gives a broad overview of different optical sensors of chemical or biological analytes through an attempt to give a systematic "bigger" picture. The accent is given to nanophotonic affinity-based sensors. A possible classification of various methods and mechanisms is proposed. The goal of such a concept is to create a broad framework where not only all of the existing devices can fit, but it may also point out to novel structures and methods.

II. GENERAL CONSIDERATIONS

A chemical sensor can be described as an analytical device that converts the chemical information about a chemical substance (analyte) into a readable output signal, usually electric or optical one. The chemical information may range from the simple presence, over the concentration of the analyte to a total analysis of multiple analytes. The output signal may be readable by an instrument or directly by an observer, and is proportional to the concentration of the analyte. The sensor is self-contained, i.e. all its units are located within the same package.

Analyte itself is defined as a chemical substance present as a constituent in a complex sample and is of interest for an analytical procedure. It may denote chemical element, component or ion. From this point of view, a simple litmus paper strip may be defined as a non-reusable pH sensor with optical readout. Analyte may also be a biological substance, since the sensing mechanisms applied are identical in both cases, i.e. we assume there is no fundamental difference between a chemical and a biological sensor.

Some requirements posed to a chemical sensor include:

- Maximum sensitivity (defined as the ratio between the amount of the target analyte in a complex sample and the output signal.)
- Maximum selectivity (the ability of the device to discerns between different analytes, including the similar ones.)
- High signal-to-noise ratio (much larger value of the useful signal than that of the extrinsic and intrinsic noise).
- High dynamic range (large ratio of the highest to lowest measurable concentration)
- Fast response (response time being defined as the time between the onset of a concentration change at the sensor input and the moment the sensor measures a certain percent of the final value. Ideally it is a real-time operation).
- Maximum resolution (the smallest distinguishable concentration variation).

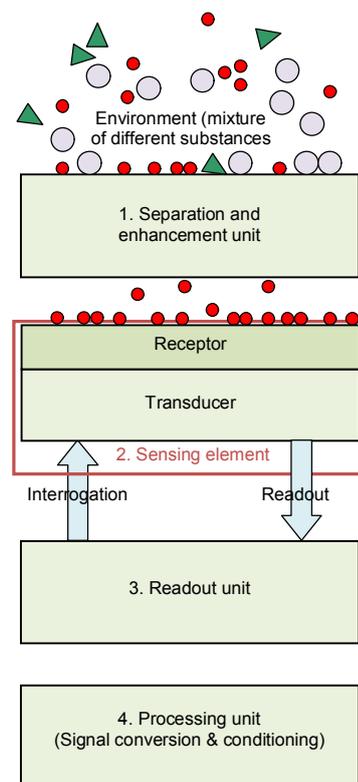


Figure 1. Layout of a general chemical sensor consisting of (1) separation and enhancement unit; (2) sensing element consisting of a receptor and a transducing element, (3) readout unit and (4) processing unit for signal conversion and conditioning. Red circles denote targeted analyte particles

- Compact dimensions.
- Simplicity (as simple design and use as possible; for instance, label-free operation).
- Reusability (no need to discard the sensor after use or to regenerate it).
- Possibility of parallel sensing of several analytes (multianalyte operation).
- Nondestructive operation.
- Possibility of online use.
- Minimal hysteresis (defined as the difference between the sensor readout with measurand increasing and decreasing)
- Minimum drift (signal variation with time for the same value of analyte concentration)
- Maximum operating life (defined either for continuous operation or for the number of repeated measurements)
- Low cost.

A general affinity-based chemical sensing system is schematically presented in Fig. 1. It consists of four main blocks, (1) the unit for separation and possibly reaction

enhancement, (2) the sensing element – the structure where the analyte concentration causes a proportional change of the optical properties of the material, for instance refractive index change, (3) readout unit, the part of the device where the signal is generated and (4) the processing unit, where signals are conditioned and communicated further.

The only parts that each sensor must have are the sensing element and the readout unit, while separation/enhancement unit and processing unit are optional. Also, two or more presented blocks may be integrated into a single unit, so that Fig. 1 represents a functional, rather than a structural division of the device.

According to IUPAC, the sensing element itself consists of a receptor that transforms chemical information into energy measurable by transducer and a transducing unit that converts this energy carrying chemical information into a useful analytical signal [33]. Different operating mechanisms of transduction can be met in chemical sensors, including optical, electrochemical, chemical, mass sensitive (piezoelectric and surface acoustic), magnetic, thermometric [33]. Other mechanisms may include different types of radiation like ionizing (X-ray, beta, gamma), microwave, terahertz, etc. In our case the transducing mechanism must include optical processes.

Further we consider the sensing process itself. The liquid or gaseous environment around the sensor represents a complex mixture of different substances that includes one or more analytes to be detected and quantified. In Fig. 1 these substances are represented by different symbols (triangles, small or larger circles).

In order to improve sensor selectivity, i.e. to avoid false positives, we are interested to separate the target analyte from the mixture of other substances even before it triggers the sensor response. This may be done by different schemes for analyte separation, that include the use of receptors (ligands), the application of filtering structures, etc. The same structure may be utilized to enhance the reaction, thus amplifying the sensor signal. Upon that analyte arrives to the active surface of the sensing element.

In this text we limit ourselves to all-optical sensors of chemical substances. This means that some optical property of the material of the sensing element is modified by the presence of analyte. Such sensors are sometimes denoted as optodes or optrodes. Lübbers and Opitz utilized the term optode in 1975 [34], while the term optrode was first utilized in 1984 [35] to denote a chemically functionalized fiber tip.

The change of the chosen optical property modulated by the presence of analyte is further read out by a propagating or evanescent electromagnetic wave with a frequency in the optical range. This readout may be passive (there is no external interrogating beam, the structure itself emits the output signal) or active (an interrogating optical beam impinges on the sensing element, the presence of analyte changes its properties, and the modulated beam is further used as the output signal).

The processing unit may include light source for interrogating beam (e.g. LED diode or laser), photodetector for

the conversion of the optical output signal to electric signal, amplifiers, multiplexers/demultiplexers, etc.

III. SENSOR EXPOSURE MODES

Chemical sensors generally may function in four possible modes of exposure to the analyte:

- Remote mode
- Immersion
- Adsorption
- Absorption

Remote mode is used when the sensor is removed far from the analyte-containing medium and the sensor has either to act actively and use electromagnetic beam to probe the medium at a distance or act passive and detect the emissions from the tested medium. An example of the remote mode of operation would be spectral measurement, used even to assess the chemical properties of deep space objects. This mode of operation that generally belongs to remote sensing is sometimes excluded from the definitions of the chemical sensor because of the lack of physical contact with analyte.

Immersion is the situation when the sensor is wholly or partially surrounded by the medium, but no further binding processes occur at its surface or within its bulk. This would be the case when a sensing probe is dipped into fluid and the optical properties of fluid are directly measured. Alternatively, the measured fluid may fill a large cavity within the sensing probe. In both cases the bulk properties of the measured fluid are those that trigger the sensor response.

Adsorption is a process in which an atom or molecule of a liquid or gaseous substance is bound to a solid surface. The adsorbed layer may be extremely thin, even monatomic or monomolecular, and it may not cover the whole surface, and still be sufficient to trigger a response of the chemical sensor. The bound substance is called adsorbate, and the solid surface to which the adsorbate adheres is called adsorbent. Adsorption occurs due to the presence of surface forces. The result of adsorption is an increase of the concentration of adsorbate at the adsorbent surface. A typical example of adsorption is condensation at the surface. Adsorbate may be physisorbed (bound by van der Waals forces or by electrostatic forces) or chemisorbed (bound by covalent bonding). The process opposite to adsorption is desorption – the removal of adsorbate particles from the adsorbent.

If the binding of substance occurs within the volume of a solid object, the effect is called absorption, the substance dissolved within the volume is the absorbate and the volume permeated by the absorbate is the absorbent. Absorption is not a consequence of surface forces. A typical example of absorption is incorporation of hydrogen atoms within palladium crystal lattice.

If the binding of particles from liquid or gas occurs within pores, like in nanoporous materials, the process will occur within the volume of the object and still it will be denoted as adsorption, because binding is a consequence of surface forces.

An example of such volume adsorption is binding of gases in zeolites or in activated carbon.

Adsorption and absorption both belong to the group of processes called sorption. Chemical sensors generally may use any or both of the two sorption mechanisms for their function. In the case of optical devices, the increased concentration of the analyte (sorbate) changes the optical properties of sorbent material. These changes are detected by the readout beam.

The adsorption kinetics is usually described by isotherms that define the amount of the adsorbed substance at a constant temperature. For gas adsorption one typically uses the simple Langmuir isotherm that assumes a monolayer adsorption. If multilayers are formed by the adsorption of particles onto already adsorbed particles, one utilizes Brunauer-Emmett-Teller (BET) isotherm. An illustration can be seen in Fig. 3. There are other isotherms that are used to analyze adsorption at the surface of chemical sensors [34, 35], but we will not consider them in this text.

More than one process may occur concurrently within the same structure. For instance, an analyte may adsorb to the surface of a structure and at the same time diffuse and permeate its bulk.

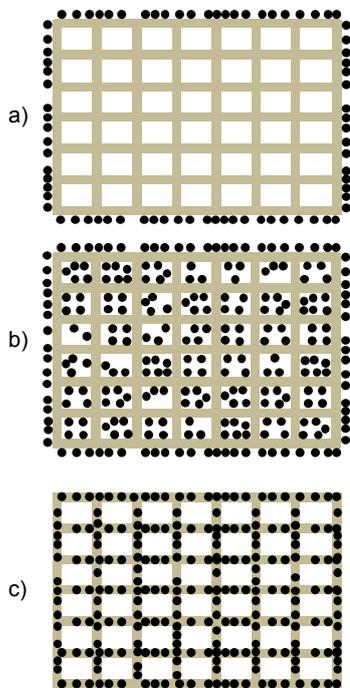


Figure 2. Sensor exposure modes: a) surface adsorption; b) bulk adsorption in nanopores; c) absorption (permeation/dissolution). In all three cases the active part of the sensor is a porous ordered structure.

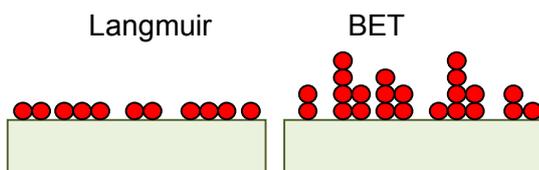


Figure 3. Examples of Langmuir (left) and BET (right) adsorption.

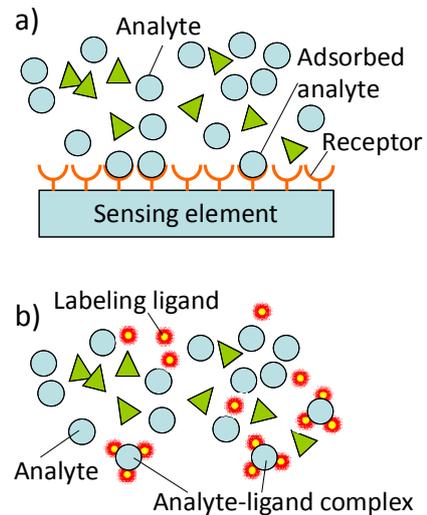


Figure 4. Two mechanisms of operation of affinity-based sensors. a) receptor layer at the sensor surface binds targeted analyte and discards undesired similar species; b) ligand (e.g. fluorescent molecule) labels the analyte particles.

IV. AFFINITY SENSORS

In our further consideration we analyze adsorption-based sensors. The medium around a chemical sensor typically contains several competing species that may simultaneously adsorb on the same substrate. It may happen that two or more of these adsorbates cause the same modulation of sensor parameters and thus an identical output. This makes a great problem with sensor sensitivity. A way to avoid it is to utilize affinity sensors, i.e. the devices that specifically bind to a target analyte.

The term "affinity sensor" was used by Schultz et al in 1970ties [36, 37] to describe a glucose sensing device. In affinity sensors one utilizes material that preferentially binds the targeted analyte. This material is denoted as receptor and can be deposited to the active surface of the sensor to promote target-specific binding. This material is sometimes also denoted as ligand. An illustration of this case can be seen in Fig. 4a.

One also utilizes the term ligand to denote signal-triggering substance (for instance, fluorescent labeling molecule) that binds to the target analyte in order to ensure its detection, Fig. 4b. Thus affinity sensor may be a device utilizing a layer of target-analyte binding receptor material deposited onto its surface, but also a device utilizing ligand molecules for labeling.

V. A POSSIBLE SYSTEMATIZATION

In the further text we introduce a classification of optical sensors of chemical (or possibly biological) analytes. To this purpose we observe the main properties of interest. We can consider *what* parameter is read out (sensor output), *how* is it modulated, i.e. which optical phenomenon is utilized to generate the output signal and *where* it all occurs, i.e. what type of structure is utilized as the active part of the sensor. These

what, how and where are interdependent and define the behavior of the sensor.

A. *What is modulated (macroscopic readout)*

The external world can only see changes of the macroscopic properties of a chemical sensor caused by the presence of an analyte. These may be any electric, thermal, electric, chemical, etc. properties observable by our instruments. One could imagine devices that change temperature due to some kind of interaction between the active part and the analyte, modulate electric potential, change optical transmission, even, in some more exotic situations, change shape (like in bimaterial devices). The sensor may be called optical as long as the basic interaction that causes modulation is optical.

In a strict sense we can assume that the macroscopic output is also optical. This is the simplest situation, and one can always assume that a device converting optical interaction to non-optical signal basically consists of two or more units, one generating optical output, the other converting the optical output to non-optical. Thus for the sake of simplicity, in this text we consider only the optical output.

Two most obvious optical parameters to modulate are the scattering parameters of the sensor – its optical transmittance T and optical reflectance R . These are connected with the optical absorbance as $A = 1 - T - R$. Of course, the interaction can also cause optical emission or modify the already existing emission. One can also utilize devices that change the polarization of the utilized optical waves (chirality or handedness of the light). Thus the following macroscopic optical outputs can be utilized for sensor readout:

1. Reflection
2. Transmission
3. Absorption
4. Emission
5. Polarization
6. Phase change

One should mention that the use of the above may not be obvious at a first glance. For instance, in conventional surface plasmon polariton-based devices one varies the measurement spatial angle in order to obtain the sensor. Yet, the underlying principle of signal readout is the determination of reflectance minimum related with plasmon resonance.

The following parameters may be varied when observing the quoted outputs:

1. Intensity (amplitude)
2. Wavelength (spectral dependence)
3. Temporal dependence
4. Spatial distribution.

Different outputs and varying parameters can be combined when obtaining the macroscopic output from the sensor. For instance, when measuring reflection, one can observe its

intensity at a given moment and for a given wavelength, or alternatively observe its distribution across wavelengths (reflection spectroscopy), temporal dependence (changes of reflection coefficient over time), spatial dependence (reflection may vary across the analyzed surface). This does not relate with the intrinsic transduction mechanism used to obtain a particular change. Different mechanisms that can be used to modulate macroscopic output are given in the next subsection.

B. *How is it modulated (optical transduction phenomena)*

The optical phenomena that are being modulated are the heart of an optical chemical sensor. They are the transduction mechanisms itself that define the sensor behavior. These mechanisms further modulate transmission, reflection, absorption or emission of optical radiation.

The IUPAC definition of the main modes of transduction of optical sensors include absorbance, reflectance, fluorescence, refractive index, optothermal effect and light scattering [33]. However, such a definition simultaneously uses several criteria instead of a single one, since for instance absorbance modulation actually represents a consequence of refractive index change (being proportional to the imaginary part of the complex refractive index that describes losses), reflectance changes are the consequence of the changes of the real part of the refractive index, etc. On the other hand, it does not take into account some other phenomena, like e.g. photoacoustic, electrochromic, etc. In this text we opted to utilize instead different microscopic mechanisms that modulate the properties listed as macroscopic outputs in subsection A. Some of them include:

1) *Wave superposition*

- Interferometry
- Optical resonators
- Diffractive methods

2) *Evanescent wave mechanisms*

- Total internal reflection
- Surface plasmon polaritons
- Extraordinary optical transmission
- Surface enhanced Raman scattering (SERS)
- Surface enhanced infrared absorption (SEIRA)
- Dyakonov waves

3) *Photoluminescence phenomena*

- Fluorescence
- Fosforescence

4) *Polarimetry/ellipsometry*

- Optical rotation (optical activity)
- Optical rotatory dispersion
- Circular dichroism

5) Scattering

- Rayleigh scattering
- Mie scattering
- Tyndall scattering
- Brillouin scattering
- Raman scattering
- Fano resonance

6) Nonlinear optical phenomena

- Harmonic generation by frequency mixing (second, third, high harmonic generation)
- Optical rectification
- Optical parametric generation, amplification, oscillation
- Spontaneous parametric down conversion
- Light-plasma interaction
- Stimulated Brillouin scattering
- Cross-polarized wave generation
- Optical soliton interactions
- Kerr effect
- Four-wave mixing

7) Quantum optical phenomena

- Upconversion
- Electromagnetically induced transparency
- optically active quantum structures (e.g. quantum dots)

8) Photothermal effects

9) Photoacoustic and acousto-optic effects

10) Photoelasticity

11) Electro-optical mechanisms

- Electroabsorption
- Stark effect
- Franz-Keldysh effect
- Electrochromic effect
- Pockels effect
- Electron-refractive effect
- Electro-gyration

12) Transformation optics

- Superabsorption and "optical black holes"
- Superlensing

- Hyperlensing
- Sensor cloaking

Many of the above described sensing schemes reduce to refractometric ones since they are based on modification of the complex refractive index. Also, two or more may be combined in the same sensor.

C. Where is it modulated (device structures)

We assume that an optical chemical sensor is basically an optical waveguide in a most general sense, i.e. a structure that supports electromagnetic (EM) waves. These waves may be propagating or localized, sinusoidal or exponentially decaying (evanescent); they may be transmitted, reflected, absorbed or emitted. The structure itself may have an arbitrary geometry and its electromagnetic properties can be described by a given spatial distribution of its complex refractive index

$$n(\omega, \vec{r}) = n_{\text{Re}}(\omega, \vec{r}) + i \cdot n_{\text{Im}}(\omega, \vec{r}) \quad (1)$$

where ω is the angular frequency, r is the spatial position vector, "Re" stands for real and "Im" for imaginary part of the refractive index. Thus in a general case n is frequency dispersive, inhomogeneous (spatially varying), anisotropic (with properties in a given point varying in dependence on the EM wave direction) and lossy.

The complex refractive index is the basic material property in optical systems generally. In

A division of waveguiding structures for optical sensors can be done based on the dimensions of their characteristic features compared to the operating wavelength λ :

1) *Superwavelength* (characteristic dimensions much larger than λ),

- Spectroscopic cells

2) *Mesoscopic* (characteristic dimensions comparable with λ),

- Planar waveguides
- Fiber optics
- Photonic crystals

3) *Subwavelength* (characteristic dimensions much smaller than λ)

- Surface plasmon polariton devices
- Nanoplasmonics
- Metamaterials

In the further text we will shortly describe the properties of some mesoscopic and subwavelength structures. Our stress will be on the subwavelength structures for chemical/biological sensors.

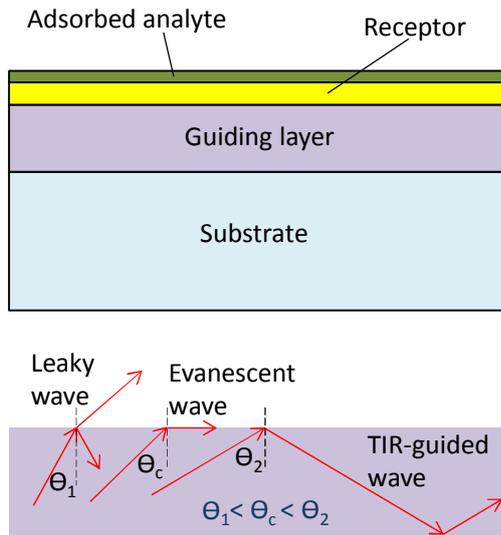


Figure 5. Generic structure of a chemical sensor based on optical waveguide (top) and the scheme of optical wave propagation in the guiding layer (bottom).

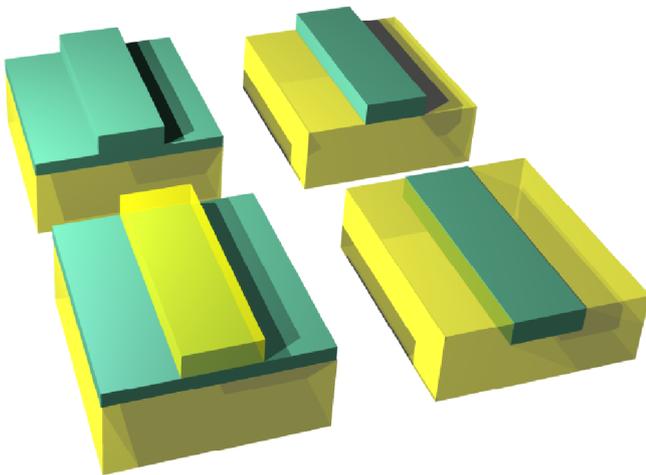


Figure 6. Some types of rectangular channel waveguides. Top left: ridge waveguide; top right: rib waveguide; bottom left: strip-loaded waveguide; bottom right: embedded waveguide. Waveguiding layer is denoted by darker color.

VI. PLANAR WAVEGUIDES

Many chemical and biological sensors base their operation on all-dielectric optical waveguides that utilize total internal reflection (TIR) for the wave propagation. In order to ensure waveguiding, the dimensions of such an optical guide along at least one axis should be comparable to the operating wavelength. A generic structure of a chemical sensor based on planar optical waveguide is shown in Fig. 5.

The bottom part of figure 5 illustrates how TIR supports a propagating wave within the waveguide. If the refractive index within the guide is larger than that of its environment, the propagation of a light beam within it will depend on its angle of incidence on the boundary between the guide and the

ambient. If this angle is small enough, a part of the beam will reflect from the boundary, and a part will refract. When increasing the angle, the output beam will refract at an increasingly larger angle. For the incidence under the critical angle θ_c no light will leave the guide, and no light will be reflected too. All of it will instead propagate as an evanescent wave strictly along the boundary. For even larger angles of incidence the beam will be fully reflected from the boundary, it will travel to the boundary at the opposite side of the guide, bounce from it, and thus propagate through the guide after repeated reflections from its boundaries – this is the TIR effect.

If analyte is adsorbed at a boundary, usually via a receptor layer that specifically binds it, it will modify the local value of the refractive index. Thus the propagation constant of the guided mode will be changed and the ensuing change in propagation will be detected by some of the previously quoted external means. Thus the waveguide-based sensors are typical refractometric sensors. However, any of the previously listed transducing mechanism could be in principle used for their operation. Also, besides the described affinity method, some other mechanism could be used as well, for instance bulk absorption that causes physical swelling and the resulting change of the waveguide dimensions.

Fig. 6 illustrates some typical planar waveguide structures utilized in chemical sensing. These are rectangular waveguides denoted as channel waveguides. Top left picture represents a ridge waveguide; top right is a rib waveguide. Bottom left is a strip-loaded waveguide where a lower index material is deposited over a strip waveguide. Finally, bottom right picture represents an embedded waveguide. Besides these geometries, different other refractive index profiles and geometries can be also used.

VII. OPTICAL FIBERS

An optical fiber may be regarded as a special case of general optical waveguide where full cylindrical symmetry exists and where the length of the structure is much larger than its radial dimensions. Optical fibers are widely used in optical communications [38], but one of their important applications is in fiber optical sensing [31]. They are used for sensing of a wide range of physical quantities, and one of their applications is chemical and biological sensing.

In conventional optical fibers the propagation is again based on the principle of total internal reflection, the same as in planar waveguides. A typical optical fiber consists of a core with a higher refractive index and a cladding with a lower refractive index. If the refractive index abruptly changes between the core and the cladding, such structure is denoted as step-index fiber. If there is a gradient of refractive index, it is denoted as graded index structure. Fig. 7 shows some typical situations. The case (a) represents a multimode fiber with step index profile. The core has a larger refractive index and thus a TIR-guided propagation is enabled, the same as in the case of planar guides. The case (b) represents a single-mode fiber (smaller diameter core), (c) is a fiber with a gradient of refractive index and (d) is the situation with multiple steps.

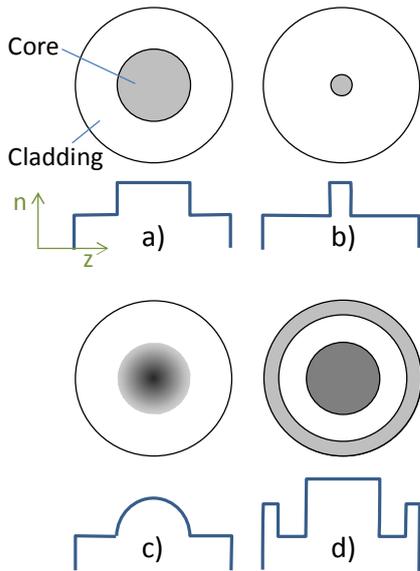


Figure 7. Some profiles of optical fibers: cross section and refractive index values. Darker shading corresponds to higher refractive indices. a) multimode fiber with step profile; b) single-mode fiber, step profile; c) graded index fiber; multiple-step fiber.

The usual way to utilize an optical fiber is to remove a part of cladding and let the evanescent field at the core boundary interact directly with the analyte. Another way is to utilize inverted profile fibers, for instance inverted graded index (IGI), where larger value of index are near the fiber surface [39].

As far as the readout is concerned, the most often used mechanisms are absorbance (as defined by Beer-Lambert-Bouguer extinction law), fluorescence measurement, diffraction on grating inscribed directly in the fiber and surface plasmon polaritons (to be described in more detail further in this text). Various phenomena can be utilized here, as defined in the description of transduction mechanisms.

One can use one fiber for illumination and another for detection, or alternatively the same fiber is used for both (Fig. 8).

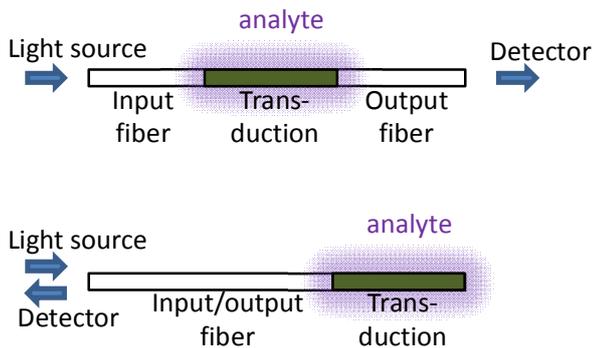


Figure 8. Readout schemes for chemical fiber optic sensors. Top: separate input and output (two-fiber scheme); bottom: single fiber scheme for simultaneous input and output.

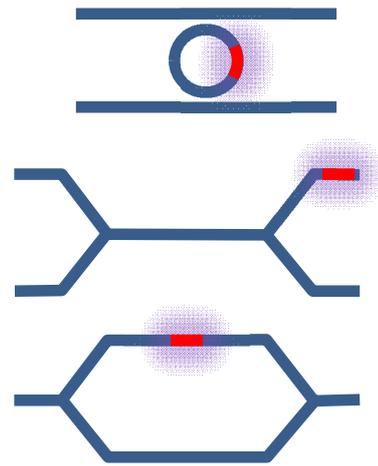


Figure 9. Top: Fiber ring resonator for chemical sensing; middle: fiber-based Mach-Zehnder interferometer as sensor; bottom: Michelson interferometer for chemical sensing.

One can fabricate resonators from fibers by performing coupling between a straight fiber section and a fiber ring, or between two fibers divided by a ring, as illustrated in Fig. 9 top. This ensures the appearance of sharp peaks in spectral characteristics, while the index change introduced by analyte results in a shift of the center frequency of the resonator.

Another possibility is to fabricate different interferometers using two branches of fibers, one of which is then exposed to analyte. Examples of such fiber structures for chemical sensing are Mach-Zehnder and Michelson interferometers (Fig. 9 middle and bottom).

VIII. PHOTONIC CRYSTALS

Photonic crystals are artificial structures with periodically changing refractive index in 1D, 2D or 3D, where the contrast between the low and high values of refractive index is sufficient to ensure the existence of the wavelength range in which no electromagnetic waves can propagate through the structure. The range of forbidden wavelengths is the photonic bandgap (PBG) and in that range a photonic crystal behaves as a near-perfect mirror. It could be said that photonic crystals represent a generalization of Bragg interference mirrors and also of Bragg gratings. Light in photonic crystals behaves similarly to charge carriers in semiconductors – besides the appearance of a bandgap, energy bands exist that correspond to the valence and the conductive band, it is possible to introduce defect and surface modes, etc.

The behavior of a photonic crystal is defined by the dimension of their unit cell and by the value of the refractive index (or dielectric permittivity) of each of its constituent parts.

The features of a unit cell of a photonic crystal are comparable to the wavelength and their behavior is based on the diffraction effects. In order to ensure the appearance of a full photonic bandgap, a photonic crystal structure must have a sufficiently large contrast of refractive index between its "high" and "low" parts.

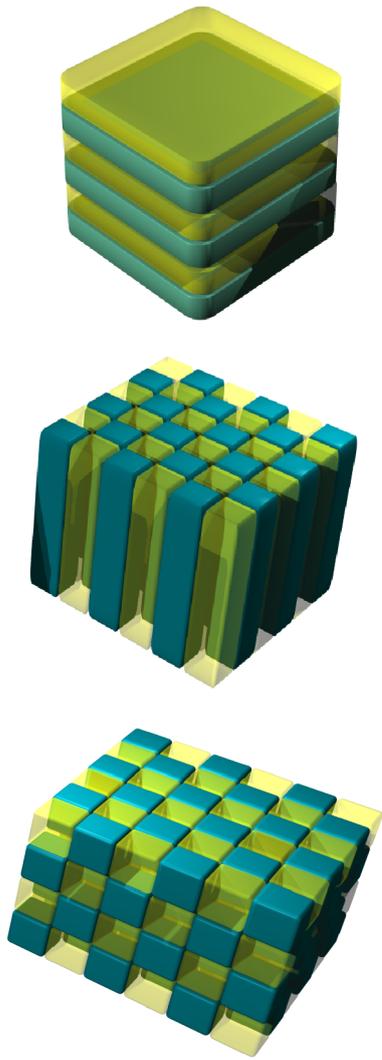


Figure 10. 1D, 2D and 3D Cartesian geometries (from top to bottom) for PBG-based chemical sensors

Photonic crystals were introduced in 1987 [40]. Until now they found a plethora of applications [41-43], among which an important place belongs to their use for chemical and biological sensing [19].

Structurally, there are three types of photonic crystals for chemical sensors, Fig. 10: high-contrast Bragg layers, basically functioning as interference-based dielectric mirrors (1D structures); planar waveguides or resonators utilizing 2D geometry and full 3D crystal.

The properties of photonic crystals can be tuned by the presence of analyte by two mechanisms:

- a) changing refractive index due to the presence of analyte (for instance by adsorption or absorption) and
- b) changing the unit cell dimensions, the simplest case being the shrinkage or swelling of the structure due to the presence of analyte, for instance by utilizing hydrogel that interacts with the targeted substance.

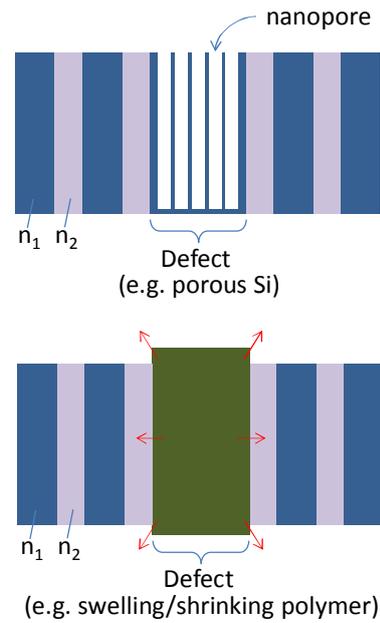


Figure 11. Use of 1D photonic crystals as chemical sensors. Top: absorption of analyte by porous defect (refractive index change); bottom: absorption of analyte in polymer that causes swelling (photonic crystal dimensions change)

The two basic methods of sensing of chemical substances are illustrated in Fig. 11 for the case of 1D photonic crystal. A layer with different thickness and/or refractive index is introduced in the structure. Depending on its properties, it functions as an acceptor or donor defect, as per equivalence with semiconductors. In the transmission spectrum it shows as a sharp peak (a dip in reflection). In the case shown in top the defect is made of a porous material with subwavelength holes, for instance nanoporous silicon. Upon exposure to chemicals, analyte fills the pores and modifies the effective value of refractive index. Instead of the scheme shown in Fig. 11, one can alternatively use structures where each layer is porous, but with different densities in different parts (higher hole-to-solid ratio means a lower effective refractive index).

The scheme shown in bottom illustrates the possibility to change the dimensions of the photonic crystal. To this purpose, a polymer layer is introduced as a defect. The exposure to analyte initiates specific binding between the polymer part and the analyte and the result is swelling or shrinking of the defect, which causes a shift of the defect peak. Again, as in the previous case, one can utilize the variable volume material not only for the defect, but for the whole photonic crystal or only for its high or low refractive index parts. In this case the whole photonic crystal is infused with analyte and the resulting thickness change modifies the spectral characteristics.

Obviously, the same kind of tunability is applicable in the case of 2D and 3D photonic crystals as well.

A special kind of PBG structures often used for chemical sensing are the photonic crystal fibers [44-46], also called the microstructured optical fibers. These are a special kind of 2D photonic crystals that are produced in the form of fibers. A high refractive index contrast in these structures is obtained by

introducing hollow (air filled) channels within the fiber, or using some other type of microstructuring to ensure the contrast. There are several basic types of photonic crystal fibers, as shown in Fig. 12. The first type are the so-called holey fibers, structures with a hollow core and hollow channels around it (top left). The core may also be solid (top right). There are combination of hollow channels with conventional step index optical fibers (bottom left) where the channels ensure better index contrast and thus better guiding. Finally, there is a Bragg-type fiber (bottom right) which basically represents a cylindrical version of 1D photonic crystal and where concentric layer with alternating low and high refractive index are used to confine light.

Of the listed structures, those with hollow core are the most convenient for sensing, since the core can be filled with analyte, the interrogating light is simultaneously confined within the same space and the optical paths can be very long. However, structures with solid core were also proposed for chemical sensing [42].

IX. SURFACE PLASMON POLARITON DEVICES

Surface plasmons polaritons (SPP) may be defined as oscillations of free charge carriers in conductive material near an interface with dielectric which are coupled with electromagnetic radiation propagating across the interface. The relative dielectric permittivity ϵ in the conductive part is negative in the range of interest, and positive in the dielectric part. Typically the conductive material is metal (usually gold or silver). Other alternative materials can be sometimes used, for instance transparent conductive oxides (indium tin oxide, doped zinc oxide, tin oxide, etc.), semiconductor materials, intermetallics, graphene, etc. These conductors are all denoted as plasmonic materials [47-49].

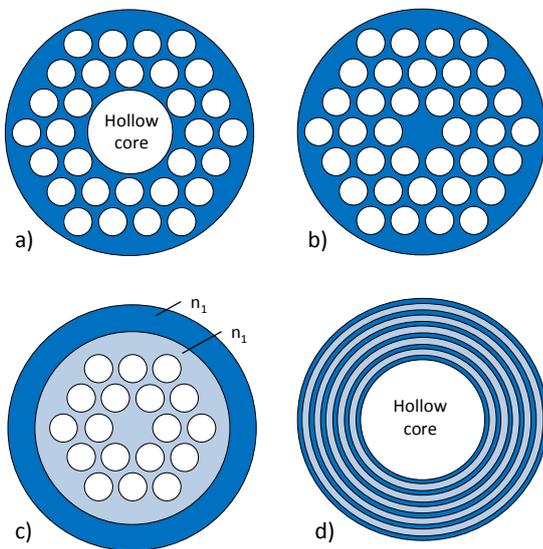


Figure 12. Different types of photonic crystal fibers for chemical sensors. a) hollow core fiber (holey fiber); b) solid-core fiber; c) mixed-type (hole-assisted fiber); d) Bragg fiber ("OmniGuide")

The electromagnetic wave in SPP is confined to the interface and evanescent (exponentially decaying) in the perpendicular direction. In chemical sensors one also encounters the spatially confined SPP that exist on a conductive nanoparticle (localized surface plasmons polaritons, LSPP). The science dedicated to the research and application of SPP phenomena and devices is called plasmonics [50-53].

In the simplest case, SPPs at the interface between two semi-infinite media with opposite signs of dielectric permittivity are not plane electromagnetic waves. Their energy is concentrated in the narrow region near the boundary plane. SPPs are TM (transverse-magnetic) polarized, and because of that they are called *polaritons*. In other words, magnetic field and wavevector of the SPP lay in the plane of interface, while electric field of the wave is both perpendicular and parallel to the wavevector components. TE polarized component of electromagnetic field cannot form a surface wave at a simple metal-dielectric interface.

A SPP wave has its largest value in the interface between the ϵ -positive and ϵ -negative part and decays exponentially in the both normal directions. If an analyte adsorbs to the sensor surface in an ultrathin layer, this will mean that the regions where the SPP is concentrated and the region where the analyte is present will overlap. Thus an SPP-based sensor will be able to "see" even minute amounts of analyte. Actually the conventional SPP sensors have long been able to distinguish even a few percent change of the composition of a monatomic or monomolecular layer [54].

The wavevector of a SPP is much larger than that of a propagating optical beam in the free space for the same frequency. Thus it is necessary to match the wavevector between the two. The most often used approach for the conventional SPP chemical sensors is the Kretschmann method [55]. An illustration of this method is shown in Fig. 5, with a dielectric hemicylinder presented (often a prism is used instead), with a goal to show that the interrogating beam is incident perpendicularly to the dielectric surface. The interrogating beam arrives to the metalized flat surface at exactly the critical angle and thus the created evanescent wave is matched to the SPP.

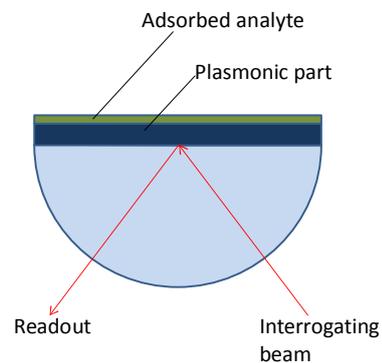


Figure 13. Kretschmann configuration for SPP sensor readout

At the surface plasmon resonance there will be a strong dip in the reflection spectrum that corresponds to a given angle of incidence and output. When an ultrathin layer of analyte adsorbs to the surface, its refractive index changes the propagating conditions of the evanescent SPP waves and thus the angle is changed. The angular shift is detected in the readout signal, and its amount is determined by the refractive index of analyte. Thus a SPP sensor is actually a refractometric sensor, basing its operation on the refractive index change within the near-surface layer with a subwavelength thickness.

The resonant nature of the SPPs actually represents an advantage for sensing purposes, since it causes steep gradients in their frequency dispersion, which results in large changes of scattering parameters for very small changes of the surface refractive index. Absorption losses in SPP structures are very large due to collisions of free carriers in the ϵ -negative material, which leads to shorter propagation paths, but this is not an issue for chemical sensing purposes.

The relative dielectric permittivity ϵ of plasmonic materials is negative below plasma frequency, and its dispersion is well-described by the electron resonance model of Drude [56], also denoted as Drude-Sommerfeld model

$$\epsilon = \epsilon_{\infty} - \frac{\omega_p^2}{\omega(\omega + i\Gamma)}, \quad (5)$$

where ω_p is the plasma frequency, Γ is the damping factor (i.e. the imaginary part of the complex dielectric permittivity), and ϵ_{∞} is the asymptotic dielectric permittivity. The plasma frequency is

$$\omega_p^2 = \frac{n_e e^2}{m^* \epsilon_0}, \quad (6)$$

where n_e is the free electron concentration in epsilon-negative part, e is the free electron charge ($1.6 \cdot 10^{-19}$ C), ϵ_0 is the vacuum permittivity ($8.854 \cdot 10^{-12}$ F/m), and m^* is the electron effective mass.

The damping factor is

$$\Gamma = \frac{e}{\mu m^*} \quad (7)$$

where μ is the mobility of free electrons.

In the case of interband transitions between the valence and the conduction bands, dielectric permittivity is given by Lorentz model [57]

$$\epsilon = \epsilon_{\infty} + \frac{\omega_p^2}{(\omega_0^2 - \omega^2) - i\Gamma' \omega}, \quad (8)$$

where ω_0 is the resonant frequency of the electron oscillator, while the apostrophe denotes values related with the concentration of bound electrons that participate in the interband transitions.

The propagation constant of a TM polarized wave at the metal (m)-dielectric (d) interface is given as

$$\beta = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_d}{\epsilon_m + \epsilon_d}}, \quad (8)$$

Thus a change of the dielectric permittivity (and therefore the refractive index) of the dielectric part at the interface will modify the propagation constant, thus changing the propagation of the SPP. This is the basis of the use of SPP structures for sensing.

The applicability of SPP resonance for chemical sensing enhancement has been recognized very early [15], and indeed some of the first proposed applications of the SPP were in refractometric sensing in thin layers at the ultrathin boundary layer between metal and dielectric. Currently this is probably the most often used optical method for chemical sensing [4, 53, 58-60].

X. OPTICAL METAMATERIAL SENSORS

The possibility to structure material at nanometer level has brought to a new paradigm, the electromagnetic metamaterials [61-67]. These can be defined as artificial structures with subwavelength features and with effective optical properties that exceed those of natural media. Theoretically envisioned in 1967 [68], practically described in 1999 [69] and experimentally proven in 2001 [70], metamaterials showed themselves applicable in a vast number of areas. The first described metamaterials were those with negative refractive index [69], but subsequently the term has spread to other structures with unusual values of refractive index, for instance zero refractive index. Metamaterials for the optical range were described in [71, 72], and those utilizing surface plasmons polaritons in [61].

Since one is able to tailor a metamaterial structure almost at will, this means that its dispersion relation could be fully tailored. It is thus possible to design modes with superluminal group velocities ("fast light"), near-zero ("slow light") and, as mentioned above, negative ("left-handed light," propagating in the direction opposite to that of the phase velocity) [73].

The possibility to design a frequency dispersion at will ensures tailoring of spatially strongly localized near-field modes (due to shortening of the wavelength for a given frequency), thus obtaining a very high density of states compared to the free space. The same energy that a propagating wave would carry and at the same frequency is here compacted into a much smaller space, thus ensuring much higher wave densities and much shorter wavelengths for that frequency. This ensures highly enhanced interaction of optical radiation with the surrounding material. This kind of engineering of optical interaction with matter ensures its maximization in the active area of a sensor, with a consequence

that its response is not only vastly increased, but also localized to a specific nano-volume. Thus a chemical sensor based on optical metamaterials will offer a significantly improved sensitivity. At the same time, a plethora of novel modes of operation will exist. Contrary to e.g. SPP sensors, no special readout schemes like Kretschmann prisms are necessary and the sensor designer freedom is much larger.

Among the first descriptions of metamaterial chemical sensors are [74, 75]. There are many different schemes for this kind of devices [7, 13, 76-78]. Among the most convenient ones are the so-called metasurfaces, i.e. planar metamaterials that are compatible with the conventional planar technologies [13, 79, 80].

Probably the best known negative index metamaterial for the optical range is the fishnet, [81-84] the structure that consists of a metal-dielectric-metal sandwich perforated by an array of nanoholes, Fig. 14. The use of fishnet metamaterials for chemical sensing was described in [85, 86].

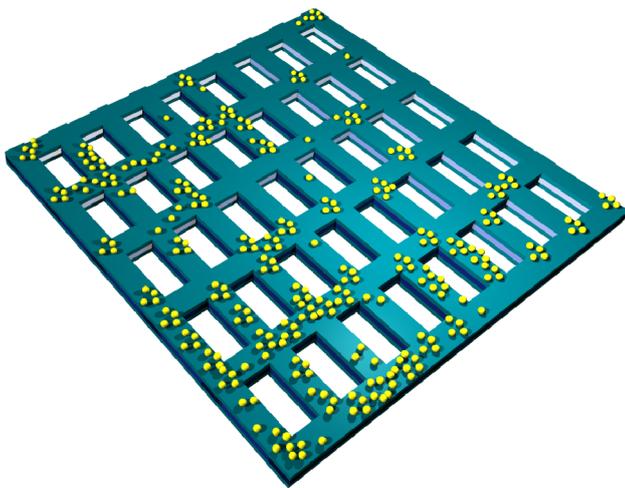


Figure 14. Fishnet metamaterial with rectangular holes. Spheres denote analyte atoms or molecules.

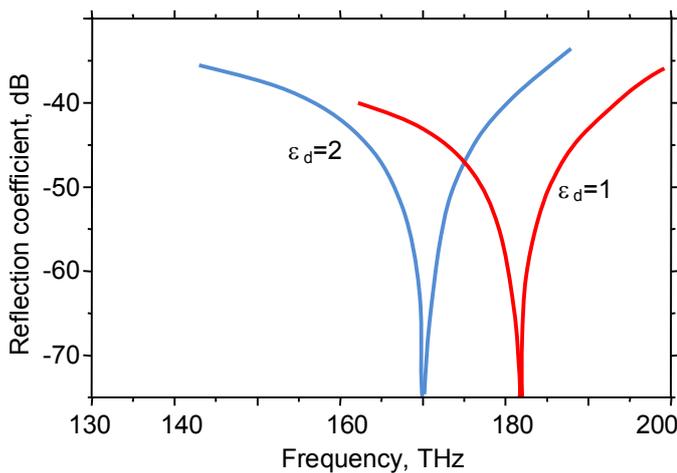


Figure 15. Spectral response of a fishnet metamaterial. Aperture size 320 nm x 280 nm, metal thickness 20 nm, dielectric thickness 200 nm, TM polarized in-plane response observed.

The whole structure is dipped into analyte-containing fluid, i.e. the absorption scheme is used to obtain the response shown in Fig. 15. This causes the shift of the dip in spectral reflection. This is a setup obtained by applying microfluidics where analyte flows through nanoapertures, as described in [87] for extraordinary optical transmission case. Thinner fishnets and smaller apertures are more strongly modified by analyte presence.

Due to their wider range of available values of refractive index, metamaterial structures ensure much better control over electromagnetic fields. Thus a whole new field of electromagnetic optics emerged, the transformation optics [88-92]. This ensured different applications, like hyperlenses for conversion between near-field and propagating far-field modes, cloaking devices, superconcentrators and superabsorbers [93-98]. All of these structures can be utilized in chemical or biological sensing [99], ensuring a large number of novel modes of operation of these devices.

XI. NANOPLASMONIC STRUCTURES

Nanoplasmonic structures [25, 100-102] are nanocomposites consisting of metals and dielectrics – or, in a more general case, of materials with positive and with negative relative dielectric permittivity). They represent a generalization of surface plasmon polariton structures – instead of having a simple flat boundary between semi-infinite metal and semi-infinite dielectric, the boundary here may have virtually any shape. A plethora of different field modes is possible in such structures. They ensure full control over both frequency dispersion and spatial dispersion, resulting in very high field enhancements and unprecedented resolutions. The behaviour of these structures is covered by the emerging science of plasmonics [50, 52]. Probably the best contemporary sensors of chemical and biological analyte belong to the class of nanoplasmonic devices [4, 12, 17, 25, 103].

Nanoplasmonic structures can be one-dimensional – planar superlattices with alternating metal and dielectric layers, 2D – metallic nanowires, nanorods, etc. embedded in dielectric, like nanometer-sized analogue of artificial dielectrics [104], or 3D – arrays of metallic nanoparticles embedded in dielectric). If the structure of nanoplasmonic composites is ordered and periodic, they are called plasmonic crystals [105]. Nanoplasmonic structures can be also quasiperiodic (plasmonic quasicrystals) [106], aperiodic [107] or even random [108].

The basic building block of a nanoplasmonic structure, i.e. the artificial "atom" of such a plasmonic metamaterial, can have any form. This is in contrast to the natural materials, where there is no choice regarding the shape of the building blocks. The shapes of this metallic "atom" within the dielectric host may vary from simple sphere to very complex form from regular to irregular [77].

A fact of large importance for sensing is the possibility to produce additional field localizations by changing the shape of the plasmonic inclusions and their geometry. Similar to the edge phenomena in macroscopic world, the plasmonic inclusions with sharp corners will localize electromagnetic fields, the amount of localization being larger for sharper corners. Also, plasmonic nanoparticles with small interparticle

distance (compared to the skin depth in metal) will cause strong coupling of surface plasmons polaritons between these particles, creating large field localizations in the space between them. This will cause high nonlocal effects and extreme localizations of electromagnetic field. A plethora of new modes and novel effects of interest for chemical sensing appears in such structures [105, 109].

One of the typical situations is encountered if randomly distributed plasmonic nanoparticles are utilized. They may be placed on a surface (Fig. 16) or mixed with a fluid that contains analyte.

The field intensity around the nanoparticles is high due to the establishment of localized surface plasmons polaritons (LSP) [110-113]. When analyte is present, its refractive index will change the electromagnetic conditions and the result will be for instance color shift. Fluorescence schemes can be also used in this case.

Another simple structure used for sensing are plasmonic nanomembranes [6, 114-117]. These are freestanding structures with thickness below 100 nm and extremely high aspect ratios, making their lateral dimensions reach millimeter, even centimeter range. When a surface plasmon polariton travels along one side of such a structure, it couples electromagnetically with the SPP on the other side. The result is the establishment of a long range surface plasmon polariton, which decays more slowly away from the surface and propagates at much larger distances than the usual SPP. This means that its "information distance" from the surface at which it can sense analytes is much larger than in conventional SPP structures. Because of that it is able to detect much larger analytes, including macromolecules and even different living cells.

A nanoplasmonic structure of a large importance for chemical sensing are extraordinary transmission arrays. If one opens nanoholes with dimensions much smaller than the operating wavelength in an optically opaque metal layer, according to the classical Bethe theory no light should be transmitted through the nanoholes because of the polarization of light. However, in 1998 Ebbesen experimentally proved that a near 100% transmission can be obtained through such aperture array and denoted the effect extraordinary optical transmission (EOT) [118]. It was proven later that the effect is a consequence of the establishment of surface plasmons polaritons at the front and the back surface and the coupling of the SPP between these surfaces.

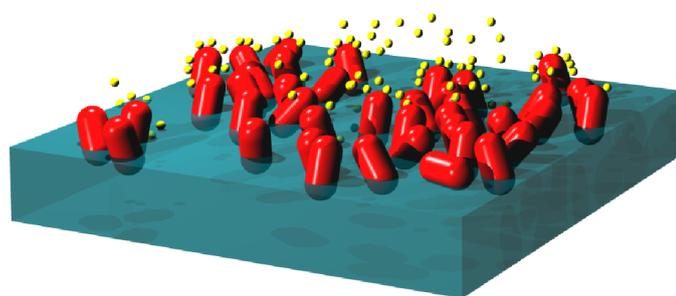


Figure 16. Nanoparticles placed on a substrate (capsule shapes) surrounded by analyte (small spheres).

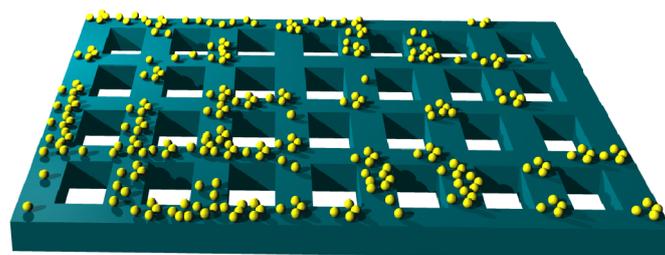


Figure 17. Extraordinary optical transmission structure.

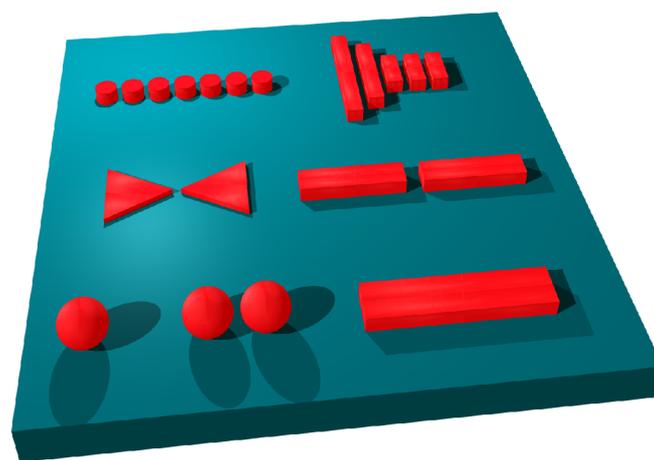


Figure 18. Various types of nanoantennas. Top left: linear nanoparticle array; top right: Udo-Yagi nanoantenna; middle left: bow tie antenna; middle right: two-wire nanoantenna. Bottom left: nanosphere, the simplest nanoantenna; bottom middle: nanodimer, two coupled spherical nanoantennas; bottom right: nanorod (single wire antenna).

The field intensity within the nanoapertures becomes several orders of magnitude larger than that impinging at the surface. Thus such structures ensure strong enhancement of nonlinear effects which is beneficial for selectivity of chemical sensing since different effects will occur in different analytes. At the same time, field concentration ensures high sensitivity chemical sensing at low analyte concentrations. Fig. 17 shows an EOT array.

Similarly to fishnet metamaterials, EOT structures are very convenient for microfluidic chemical sensing schemes, where fluid that contains analyte is pumped through nanoapertures [87].

Probably the most sensitive nanoplasmonic sensors are those based on nanoantennas [3, 119-122]. Nanoantenna or optical antenna is a plasmonic device that converts propagating waves into evanescent ones and back with a high efficiency. Field localization depends on the nanoantenna design and can be made deeply subwavelength. Thus interaction with photodetector active region can be vastly enhanced.

Nanoantennas are isolated structures, i.e. they function without a connection to any circuitry. Thus a simple spherical nanoparticle can be basically regarded as a dipole nanoantenna,

Fig. 18 bottom left. Other nanoantenna types met in literature include nanodimer, consisting of two nanosphere at a small (subwavelength) distance so that they are electromagnetically coupled. The distance between the two spheres in a nanodimer is denoted as feed gap and electromagnetic field localizations in it can be extremely strong. Other types are nanorod antennas (bottom right), bow tie antennas (middle left) that combine very small feed gap with the effect of sharp edges and thus ensures very high field localizations. Besides that it furnishes a broader bandwidth of optical frequencies. Two nanorods coupled together make a two-wire antenna (middle right). An array of nanodisks makes a complex linear nanoparticle array antenna. Stacking nanorods can make an equivalent of the classical Udo-Yagi antenna (top right). A vast number of different other nanoantennas has been reported until now.

In 2012 a golden nanorod antenna has been used to ensure sensing of single non-absorbing molecules [1]. The same type of nanoantenna was utilized for in-situ, real time interactions with biomolecules in infrared spectrum (the previously quoted SEIRA method) [3]. Different types of plasmonic antennas are being considered for various applications in chemical and biological sensing.

XII. CONCLUSION

A review of different optical sensing schemes for the determination of chemical, biochemical or biological properties has been given. From the point of view of industrial measurements one of the most convenient families of sensors are those utilizing optical effects, because of their inherent insensitivity to electromagnetic interference, robustness under difficult operating conditions (vibrations, temperature stress, corrosive or aggressive media, etc.) and built-in fire protection and Ex-proofing since typically no electric signals are present. We proposed a new classification that is more general than that given by IUPAC and thus points out to some possible novel measurement mechanisms. Our accent is given to the more recently proposed subwavelength structures that utilize near field effects, including those based on optical metamaterials and plasmonics. Such structure ensure an increased degree of design freedom and introduce a number of new modes of operation. Combined with possible wireless transfer of sensor signal and thus an increased density of measurement locations and even larger robustness against difficult measurement conditions, this ensures a bright future for optical chemical sensor applications in industry. Obviously, the described sensors can be utilized in other areas as well, including but not limited to homeland defense (detection of toxins, explosives, etc), biomedical applications and environmental protection.

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