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Fluctuations in transient response of adsorption-based plasmonic sensors

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ABSTRACT

The basic parameters of a sensor element defining its ultimate performance are sensitivity and intrinsic noise. In plasmonic gas sensors both are determined by refractive index changes due to adsorption and desorption (a–d) of target analyte particles to the sensor active area. In this paper we present a general model that can be simultaneously used to determine sensitivity and intrinsic noise of a plasmonic sensor both during transients and in steady-state and is valid for multi-analyte environments. The model utilizes the conventional probabilistic approach. It is derived without any assumptions about the stochastic nature of the fundamental (a–d) process. It reveals how all stochastic properties of the processes with (pseudo) first order kinetics with the initial number of particles equal to zero can be fully determined from the deterministic solution, without any previous stochastic analysis. Based on the proposed model it is possible to establish the optimum moment for readout when fluctuations are minimal. Transients last longer and fluctuations are lower at lower temperatures. The insight into the transient dynamics opens the possibility to use a single element sensor for multiple analyte sensing. Another result is that a–d noise is higher for smaller adsorption areas, which may be important for micro and nanosystems generally, since each of them has to be kept immersed in some kind of environment and thus be subject to contamination by adsorption that can significantly influence their behavior. Besides being applicable for plasmonic sensors of trace amounts of gases and other nanoplasmonic devices used in sensing, the model is applicable for other adsorption-based sensors, as well as for the investigations of stochastic phenomena in micro and nanostructures.

1. Introduction

Among chemical sensors that can be applied both in vitro and in vivo, plasmonic sensors are among the most important ones [1,2]. They ensure direct and label-free, real-time, all-optical detection of analytes with extreme sensitivities. Plasmonic sensors base their operation on the existence of a surface-bound electromagnetic wave coupled with collective oscillations of electron gas. This wave is denoted as surface plasmon polariton (SPP). The adsorption of analyte particles at the interface causes a change of the dielectric permittivity in the location of field maximum, thus modifying the SPP propagation conditions that can be externally detected. There are two main classes of such sensors. One of them is based on propagating SPPs, and the other on localized plasmons-polaritons (nanoparticle-based sensors) [3]. In nanoplasmonic devices the sensor parameters, such as their frequency dispersion are tailored by their structure and composition, notable examples being arrays of nanoapertures or nanorods/nanowires.

Regardless of the nanostructures comprising a plasmonic sensor, the principle of operation is basically the same: analyte atoms or molecules arrive at an interface between a material with positive and with negative relative dielectric permittivity. Such interface supports propagation of surface plasmon polaritons. Usually the positive permittivity part is the dielectric medium around the sensor (gas or liquid). The negative permittivity part is most often metal (typically silver or gold), although other materials with Drude or Lorentz-type frequency dispersion may be used, for instance transparent conductive oxides [4]. Such materials reach negative values of permittivity near the surface plasmon resonance frequency.

The permittivity of the analyte particles at the interface changes the propagating conditions for SPP waves. This can be externally detected by coupling an interrogating light beam with

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the evanescent SPP modes. In the simplest case of a conventional planar surface plasmon resonance sensor the structure used for such coupling is a prism in Kretschmann or Otto configuration. Other structures can be used, like for instance diffraction gratings, end-fire couplers using optical fibers, etc., and nanoplasmonic/metamaterial sensors often ensure coupling by their very design (for instance transmission configuration in extraordinary optical transmission arrays) [5]. In this manner a plasmonic sensor is basically a detector of refractive index changes. Its selectivity can be enhanced by functionalization of the sensor surface for target-specific binding or by modifying the nanostructure of the sensor itself.

In adsorption-based plasmonic sensors the influence of adsorption–desorption processes is simultaneously crucial in defining their operating principle and in limiting their ultimate performance through stochastic fluctuations of the number of adsorbed particles [6–9]. A good knowledge of a–d processes is thus crucial for the assessment of the device function, both from the point of view of the achievable sensitivity and selectivity and regarding the ultimate performance.

Noise sources in plasmonics are numerous and insufficiently explored. While external noise sources (originating in the light source used for illumination of the sensor active area, the photodetector collecting the useful signal, circuitry for readout and data processing) [10] might be influenced by appropriate sensor design or readout procedure, intrinsic ones are fundamental, unavoidable, and a part of the very nature of the sensing mechanism itself [8,11,12]. Since the field of nanoplasmonics is relatively new, scientific efforts are mainly directed to fabrication [13–15] or applications [16,17] and literature referring to intrinsic noise in plasmonic sensors is very scarce. It is of obvious interest to investigate intrinsic noise phenomena and the pertinent mechanisms in plasmonic sensor structures.

Adsorption–desorption induced fluctuations are the main source of intrinsic noise for plasmonic sensors as well as for various other nano and microstructures. They become increasingly important as the characteristic dimensions of the systems become smaller. Some related work has been done concerning adsorption–desorption fluctuations-induced noise in microresonator-based sensors [18–22]. Research has also been done concerning adsorption–desorption fluctuations-induced noise in (nano) plasmonic sensors [8,23].

However, the prior investigations were focused mostly on the equilibrium dynamics of adsorption–desorption processes and derivations based on the Langevin method utilizing the properties of the Poisson distribution applicable to the impinging molecules. A stochastic approach, on the other hand, is far less limiting – it does not require additional assumptions and is more informative and complete. More precisely, it gives an insight into the stochastic nature and the behavior of the system during its whole time evolution, both before and after the dynamic equilibrium (the steady state) has been reached.

In this contribution we use the stochastic analysis to determine time evolution of a–d processes in a plasmonic sensor. The stochastic approach is used for the analysis of multicomponent monolayer gas adsorption–desorption processes at the surface of nano-plasmonic sensors in realistic situations when the overall number of molecules in the system consisting of gaseous and adsorbed phase greatly exceeds the number of binding sites for each gas species. Stochastic analysis is performed using a pseudo-first order kinetic model in order to relate the fundamental phenomena with the ultimate performance of the sensors (adsorption kinetics with transient response, equilibrium behavior with steady-state response, fluctuations with intrinsic noise).

With this aim, we derived equations for the time evolution of the number of adsorbed molecules, a probability generating function for the number of adsorbed molecules, the time evolution of the mean value, variance and relative fluctuations of the number of adsorbed molecules. The results have been given as a function of time from the beginning of the process until equilibrium is reached and afterwards in case of single and multi-component situations.

2. Calculation method and models

The basic part of an adsorption-based plasmonic sensor of chemical or biological analytes is an adsorbent surface designed to support localized or propagating surface plasmons polaritons. Such an active surface must comprise binding sites available for adsorption, i.e. locations to which specific molecules or atoms can form an adsorption bond. Monolayer adsorption is considered, assuming that all binding sites are initially free and that the overall number of gas particles in the system remains constant during the measurement time. The latter assumption is valid for all situations where the number of gaseous particles that may approach the surface is always much larger than the number of the available binding sites at the surface. We assume that an adsorbate molecule occupies a single adsorption site only, as well as that they do not interact with each other and the adsorbed molecules do not dissociate.

2.1. Single-component adsorption

According to this model, one of the gaseous particles, denoted by A_g, arrives to the adsorbent surface to remain bound to a free site A_f, thus forming an adsorbed particle A_a. After some residential time desorption takes place and adsorption place becomes free again. This is described by the following quasi-chemical reaction with an adsorption rate constant k_a and a desorption rate constant k_d

$$A_g + A_f \underset{k_d}{\overset{k_a}{\rightleftarrows}} A_a \tag{1}$$

If treated as deterministic, this process can be mathematically represented with the following rate equation that relates the number of surrounding particles N_g, the number of adsorbed particles N_a and the number of free adsorption sites N_f

$$\frac{dN_a}{dt} = k_a N_g N_f - k_d N_a \tag{2}$$

Let us denote the number of gas particles initially present in the system by N_0, the total number of binding sites available for adsorption by M, the number of free binding sites by N_f, the number of adsorbed particles by N_a and the number of surrounding (gaseous) particles by N_g such that $N_0 = N_g + N_a$. In realistic and often met situations when the equilibrium constant (the ratio of the adsorption rate constant and the desorption rate constant) is small or the maximal number of the adsorbed particles on the observed surface is greatly outnumbered by the overall number of the particles in the system ($N_0 \gg N_a$) this process exhibits a pseudo-first order kinetics [24]. Hence, in that case the deterministic rate Eq. (2) is

$$\begin{aligned}\frac{dN_a}{dt} &= k_a(N_0 - N_a)(M - N_a) - k_d N_a \approx k_a N_0 (M - N_a) - k_d N_a \\ &= k_l (M - N_a) - k_d N_a \end{aligned} \tag{3}$$

The constant k_l equals the product of k_a and N_o. However, the true nature of the process is stochastic. Further we perform the stochastic analysis of the number of adsorbed particles to obtain the time evolutions of the mean value of that number, its moments, its standard deviations and its relative fluctuations. To this purpose we apply the conventional procedure of stochastic analysis [25–27].