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Plasmonic sensors in multi-analyte environment: Rate constants and transient analysis

Olga M. Jakšić[a,*], Danijela V. Randjelović[a], Zoran S. Jakšić[a], Željko D. Čupić[b], Ljiljana Z. Kolar-Anić[c]

[a] Centre of Microelectronic Technologies, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia
[b] Centre of Catalysis and Chemical Engineering, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoševa 12, 11000 Belgrade, Serbia
[c] Faculty of Physical Chemistry, University of Belgrade, Studentski trg 12-16, 11000 Belgrade, Serbia

ABSTRACT

This paper investigates multicomponent gas adsorption at the active surface of plasmonic chemical sensors and shows that there are situations where transients in a single sensor element can be used for simultaneous detection of different gases in multicomponent mixtures. A general master equation set is provided, describing multicomponent adsorption. Analytical expressions for sorption rates are derived and high-accuracy simplified models are proposed. Expressions for adsorption rate constants and rates and for number of binding sites are proposed. The derived analytical model takes into account the adsorbate molecule size, distribution of binding sites as determined by the crystallographic structure of the sensor surface and multi-site adsorption. The model allows for the calculation and optimization of deterministic behavior of the system. It is shown that trace amounts of target gas species can be made detectable by adding controlled amounts of known carrier gas. Besides being applicable in plasmonic sensor design and optimization, the obtained results may be of importance in situations where fast and low-cost detection of trace amounts of gases is needed, including natural gas leakage in residential heating, radon outgassing in dwellings, environmental protection, homeland defense and hazardous materials management, greenhouse footprint investigations, etc.

Keywords: Adsorption–desorption kinetics; Plasmonic sensor; Gas sensor; Multi-analyte surface plasmons polaritons; nanoplasmonics

1. Introduction

There is a need for simultaneous multi-analyte detection in various applications (gas chromatography, greenhouse gas footprint, etc.), but the available options are quite limited. Some of them are an early stage of investigation (Azcón et al., 2012; Basker and Zabe, 2012a, 2012b; Blecka et al., 2011; Lagrone et al., 2012; Macfie et al., 2012; Woudenberg et al., 2012) and some are constrained by the targeted number of analytes like in multi-channel sensor platforms for biosensing (Djurić et al., 2007; Homola et al., 2005; Yu and Li, 2009). Plasmonic sensors are especially promising as miniaturized optical devices fabricated by the use of nanostructures, nanoparticles and nano arrays (Stewart et al., 2008), having high sensitivities (2.5×10^{-8} for RI change, (Slavík and Homola, 2007)) and extremely fast read-out (according to Byard et al. (2012), about a nanosecond). There are nanoengineered sensor platforms capable for the detection of two (Wright et al., 2012) or more analytes (Homola et al., 2005) simultaneously, but it is not always the case that the nanostructured array of sensors gives improvements over the single sensor area (Joy et al., 2012).

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[*] Corresponding author. Tel.: +381 11 2628 587/64 5057 959; fax: +381 11 2182 995.
E-mail addresses: olga@nanosys.ihtm.bg.ac.rs (O.M. Jakšić), zcupic@nanosys.ihtm.bg.ac.rs (Ž.D. Čupić), lkolar@ffh.bg.ac.rs (Lj.Z. Kolar-Anić).

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There is also another approach: single sensor employment. It has been investigated by monitoring the free diffusion–physisorption of the analytes in multiple microfluidic channels (Ghafarinia et al., 2012). Also, the surface of a single plasmonic sensor can be functionalized so that multiple modes of operation co-exist and enable simultaneous detection of different analytes (MacKay and Lakhtakia, 2012; Swiontek et al., 2013), but the fabrication of such a special surface, chiral sculptured thin film (CSTF), a form of biomimetic nanoengineered meta materials, represents a significant technological challenge.

We address here the adsorption kinetics at the surface of a single-element plasmonic sensor and consider the possibility that the regular measurement with proper data analysis and interpretation might be sufficient for the multiple measurands identification.

Adsorption and desorption (ad) processes are crucial for the operation of micro and nano systems. They may be favorable like in adsorption-based bio and chemical sensors (Anker et al., 2008; Barnes et al., 2003; Eggins, 2002; Jaksic et al., 2009; Willets and Van Duyne, 2007), or they can be unfavorable, causing adsorption-induced mass fluctuations (Vig and Kim, 1999; Yong and Vig, 1989). Plasmonic sensors base their operation on the existence of a surface-bound electromagnetic wave at an interface between a medium with positive relative dielectric permittivity (air for instance) and another one with negative permittivity (good metals like gold or silver), coupled with collective oscillations of electron gas within the negative permittivity part. Alternative plasmonic materials (Boltasseva and Atwater, 2011) like e.g. transparent conductive oxides, intermetallic, graphene, etc. have also been studied, because they ensure lower absorption losses and wider choice of operating frequency ranges.

The established wave is denoted as the surface plasmon polariton (SPP). The adsorption of analyte particles at the interface causes the change of the dielectric permittivity in the location of field maximum that can be externally detected. There are two main classes of such sensors. One of them bases its principle of operation on propagating SPP (conventional surface plasmon resonance sensors), and the other on localized plasmons–polaritons (nanoparticle-based sensors) (Abdulhalim et al., 2008). All plasmonic sensors ensure direct and label-free, real-time, all-optical detection of analytes with extreme sensitivities.

In addition to engaging the propagating and localized plasmon polaritons on the surface there is another degree of freedom in sensor design and it is ensured by nanostructuring plasmonic sensors, thus obtaining 1D, 2D or 3D subwavelength plasmonic crystals. Examples include nanoaperture or nanowire arrays and generally electromagnetic/optical metal-dielectric periodic metamaterials (Bingham et al., 2008; Kabashin et al., 2009).

In all of these cases even miniscule alterations of the surface refractive index greatly influence the device performance and it is of utmost importance to ensure maximum control and enable tailoring of adsorption–desorption processes with a goal to maximize sensor sensitivity and selectivity and at the same time to minimize intrinsic noise caused by adsorption–desorption fluctuations (Jaksic et al., 2009). Thus, there is an obvious interest to establish a connection between the fundamental parameters of the ad process with the particular data that can be measured, calculated or estimated with the satisfactory precision for a specific application. Adsorption–desorption kinetics for different combinations of adsorbate molecules and adsorbent surfaces has been studied in various applications. Till now, rich scientific heritage of gathered data exists in physico-chemical databases available in bookshelves searchable online, for instance Landolt–Börnstein series (http://www.springermaterials.com/docs/index.html) or Pubchem Substance and Compound online database (http://pubchem.ncbi.nlm.nih.gov/). But still, there are situations where literature data are unavailable and experimental gathering of new data is unacceptable for budget or safety reasons (toxic or hazardous materials), so the determination of adsorption kinetics of different agents on such materials remains a non-trivial problem. Most of the available literature dedicated to plasmonic sensors skips this and goes directly for particular engineering solutions, while at the same time handling only a few materials (typically gold and silver for the plasmonic part) and defining specific methods and protocols for particular situations (De Mol and Fischer, 2010; Schasfoort and Tudos, 2008). This solves concrete engineering problems in a very satisfactory manner but at the same time hinders the possibility to optimize and enhance novel nanostructured sensors and impedes the introduction of new materials.

In this paper we derive a general analytical master equation set enabling modeling of multicomponent monolayer gas adsorption–desorption at different plasmonic sensor surfaces in various situations. We establish a connection between adsorption kinetics and material properties like the parameters of adsorbate gases including their atomic/molecular size as well as the crystallographic structure of the sensor surface. We present an estimation procedure to determine the number of adsorbed molecules for different material combinations in the case of multi-site adsorption. Finally we give some illustrative examples and their discussion.

2. Theory and calculations

We consider a situation schematically shown in Fig. 1 where the active solid sensor area A has a given surface density of binding sites n_s and is immersed in a finite container of a volume V, filled with a mixture of different gases, each at its partial pressure p_i and with its given molecular properties like molecular size, shape, orientation and mass. An adsorption site or binding site is defined as a location at the adsorbent surface where the adsorbate can make a single bond; multi-site adsorption may occur if an adsorbate molecule is larger than a single binding site (Do, 1998). Our interest is to determine kinetics of simultaneous multicomponent monolayer adsorption of all of the different species present in the mixture. We assume that in the starting moment the adsorbent surface of the sensor is completely free, i.e. that its surface coverage by gas adsorbate molecules is zero.

Our initial assumptions are as follows: We consider a monolayer gas–solid surface adsorption–desorption process with one or more ideal gas species. All particles of the same gas species are interchangeable. Adsorbate particles do not collide or interact with each other (there is no dissociative adsorption). The surface is homogeneous (the active binding sites are equal) so that the average residential time of adsorbed particles is the same for all particles of the same gas species.

2.1. *Single site adsorption*

Although multi-site adsorption will be considered later in this text, it is more convenient to start from a situation when a