

Localized surface plasmon resonance nanochips with molecularly imprinted polymer coating for explosives sensing

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Abstract. Sensor elements based on localized surface plasmon resonance phenomenon in arrays of Au nanostructures on glass substrates (nanochips) with molecularly imprinted acrylamide copolymer coating have been proposed for explosives analogues sensing in liquid and vapor phase. Nanochips exhibited detection limits of 1 pM in aqueous solution and 0.1 ppm in gaseous state against 4-nitrophenol. Vapor phase sensing of 4-nitrotoluene, 1-nitronaphthalene and 5-nitroisoquinoline using the developed 4-nitrophenol-imprinted plasmonic nanochips demonstrated partially selective response with time to signal saturation starting from 2 minutes.

Keywords: localized surface plasmon resonance, gold nanostructures, nanochip, molecularly imprinted polymer, sensor, explosives.

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1. Introduction

Globally, there is a problem concerning the lack of suitable tools for sensitive and selective detection of explosives by police forces. A number of attempts were made to address this problem using various recognition elements and sensor principles [1]. Each of these methods has advantages, but overall they suffer from the fact that it is extremely difficult to combine sensor robustness, required for police operation, with high sensitivity necessary for detecting trace quantities of explosive material. Willner and co-workers [2] have reached the femtomolar level of sensitivity for detection of some very small molecules, like amino acids and chemical analogues of explosives. This result was obtained by exploitation of surface plasmon resonance (SPR) and localized surface plasmon resonance (LSPR) phenomena in a nanosystem, where a molecularly imprinted polymer matrix is saturated with small size gold nanoparticles, chemically linked in a network (LSPR nanoantenna) and placed onto the surface of thin gold film that generates plasmonic electron oscillations. Unfortunately, these important scientific investigations have not yet resulted in practical applications, mostly

because of the difficult immobilization procedure that cannot be easily combined with mass-manufacturing of explosives detectors. One of the possible ways to promote the LSPR nanoantenna concept for its practical implementation is to simplify the sensor fabrication and signal readout format, specifically by redeveloping the sensitive element preparation protocol and discarding the mechanical movement of the sensor components during the measurements.

This work is aimed at a new branch in chemical- and biosensing based on development and exploitation of arrays of noble metal nanoparticles deposited onto dielectric substrates, the so-called “plasmonic nanochips” [3]. This technique becomes more and more popular with increasing possibilities of nanopatterning, *i.e.*, preparation of structures with dimensions from several to hundreds of nanometers. These nanostructures generate LSPR in visible spectral range and serve as an attractive object for sensing of different types and sizes of molecules.

LSPR properties of gold and silver nanoparticles are well known [4-6]. The position of LSPR wavelength peak depends on various nanoparticle parameters, namely: material, size, shape and distance between

particles [7-9]. One of the most useful properties of LSPR is its sensitivity to environment changes [10, 11], which is a basis for LSPR sensing. Specifically, any interaction between nanoparticles and molecules in their vicinity leads to the unique LSPR wavelength peak shift, which can be used to develop sensitive elements for biosensors or detectors [4-7, 12-15].

The disadvantage of this sensing method is its non-selectivity, which can be improved using the technology of molecularly imprinted polymers (MIP) [16]. In recent decades, the attention of analytical scientists and engineers has been focused on the development of MIP-based artificial receptors [17-19]. These materials are very robust and can be exploited at extreme environmental and storage conditions. MIPs have a good binding affinity to relevant forensic and environmental targets, which is typically expressed in subnanomolar dissociation constants [20]. Integration of LSPR and MIP methods looks promising for obtaining stable and sensitive sensor elements with good selectivity [21-25].

In this paper, we have presented the results of developing technology for producing the LSPR-MIP nanochips aimed at detection of small organic molecules exemplified by explosive analogues. The peculiarities of fabrication of selective plasmonic nanochips that allow obtaining the stable operation parameters as well as protocols of chemical synthesis of selective polymer layer are discussed. The reached detection limits using this type of nanochips were in the picomolar and ppm ranges for aqueous and gaseous analytes, respectively.

2. Experimental

Present approach involved the development of plasmonic nanochips in the form of random arrays of Au nanostructures immobilized on the surface of glass slides, which are superior to colloidal Au nanoparticles in terms of aggregation due to their fixation on the solid substrate. Sensor Au nanochips (Fig. 1a) were fabricated using the glass slides (13×25 mm) as substrates. Before metal film deposition, substrates were cleaned in an ultrasonic bath with a surfactant, then treated in "piranha solution" (H₂SO₄-H₂O₂ mixture) for 30 min, triply rinsed with a copious amount of deionized water and finally dried using N₂ flow. Gold island film fabrication was carried out by thermal vacuum evaporation method at a pressure of 10⁻³ Pa with deposition speed of about 0.11 to 0.14 nm/s. The mass thickness of gold island film of 10-12 nm was chosen as the value that allows separate well-defined Au nanostructures to be obtained with an expressed LSPR peak (Fig. 1b) after thermal annealing (550 °C, 2 hours in air atmosphere) [26].

The MIP coating based on acrylamide copolymer was used to synthesize LSPR-MIP nanochips. For this purpose, the Au nanochip surface was firstly functionalized with a layer of 3-mercaptopropyl diethylcarbodi-thioate, which acts as a UV-sensitive initiator for the polymerization reaction. After that, the process of UV-induced photochemical polymerization of acrylamide monomers mixture (acrylamide, N,N'-methylenebis

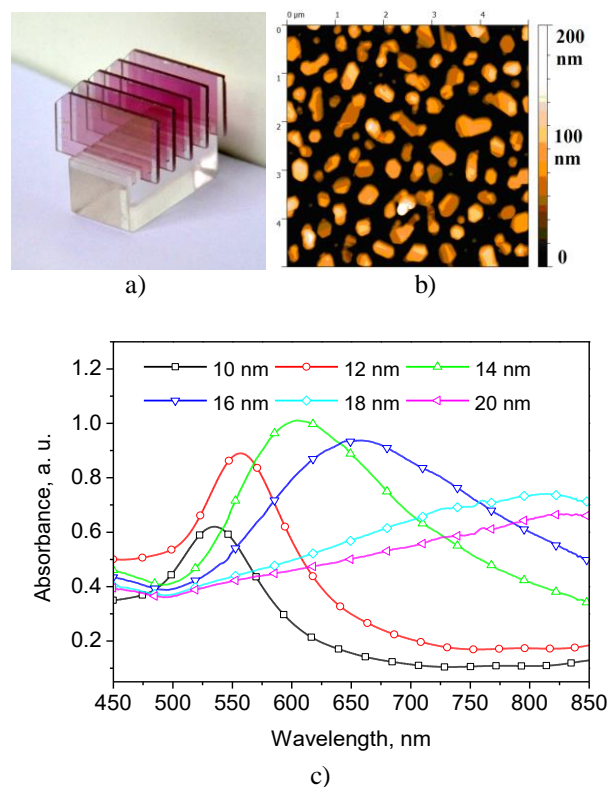


Fig. 1. (a) Photograph of Au nanochips. (b) TEM image of massive gold nanostructures on the surface of nanochip. (c) Light extinction spectra of Au nanochips fabricated from gold island films of different mass thickness.

(acrylamide) and N-(3-aminopropyl) methacrylamide hydrochloride) in the presence of the explosive analogue molecule 4-nitrophenol (4-NP) in an aqueous solution was performed. 4-NP was utilized as a model nitro-group containing template molecule, since its molecular structure resembles that of trinitrotoluene explosive. Finally, polymer-coated Au nanochip was washed in an aqueous solution of 4-(2-hydroxyethyl)piperazine-1-ethanesulfonic acid to remove explosives analogue template and then dried to yield an LSPR-MIP nanochip, which was further used for sensing.

3. Results and discussion

Kinetic measurements of analyte detection in aqueous phase by using the fabricated LSPR-MIP nanochips were carried out with a home-made two-channel photometer with a photodiode-based principle for registration of transmitted light. Aqueous analyte solutions were pumped through the measuring flow cuvette containing LSPR-MIP nanochip by means of a peristaltic pump. The reference channel of the photometer operated with a flow of deionized water. Kinetic dependences of absorbance during the inlet of analyte solutions of various concentrations into the operation channel of the photometer were recorded. 4-NP-imprinted LSPR-MIP nanochip exhibited a monotonous decrease in absorbance

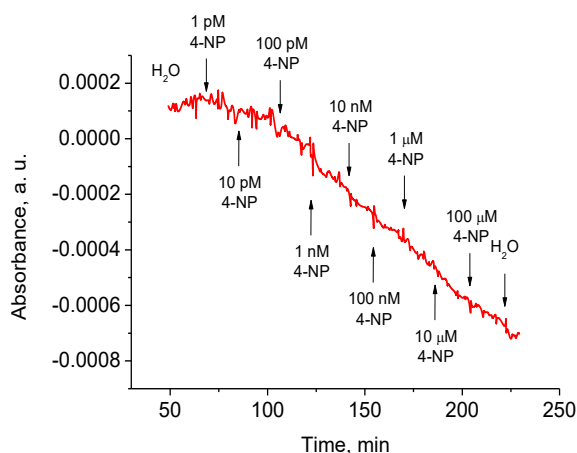


Fig. 2. Kinetic dependences of absorbance of 4-NP-imprinted LSPR-MIP nanochip during its interaction with various concentrations of 4-NP in the aqueous phase.

in the 4-NP concentration range of 1 pM...100 μM (Fig. 2), which may be attributed to the accompanying swelling of the MIP during interaction with the analyte in the aqueous phase.

Kinetic measurements of LSPR response upon detection of different types of explosive analogues in the vapor phase by using the fabricated Au nanochips with 4-NP-imprinted and non-imprinted acrylamide copolymer coatings were carried out. Single-channel LSPR sensor NanoPlasmon-003 with a compact spectrometer based on a diffraction grating was used for measurements. The experiments were performed in light transmission mode at the stabilized temperature of about 40 °C in spectrophotometric cuvettes with small amounts (~2 mg) of each explosive analogue in the powder form.

The results of this study indicate that the prepared nanochip reacts on the presence of explosives analogues vapors, and kinetic curves exhibit typical Langmuir shape with saturation. The influence of 4-NP vapor on the 4-NP imprinted chip, in comparison with that of non-imprinted chip, is shown in Fig. 3. It can be seen that the final LSPR peak wavelength shift observed with the imprinted chip is twice the shift observed with the non-imprinted one, which demonstrates the efficiency of the MIP for sensing the analyte molecules.

Moreover, these chips exhibit sensitivity to a number of explosives analogues with molecular structure similar to the template molecule, as shown in Fig. 4. The LSPR peak shifts over time upon nanochip exposure to gaseous analytes 4-NP, 4-nitrotoluene (4-NT), 1-nitronaphthalene (1-NN) and 5-nitroisoquinoline (5-NI) with the concentrations 0.1 to 20 ppm were detectable and reproducible. However, the value of LSPR response of 4-NP-imprinted sensitive layers on other explosive analogues is, as expected, obviously lower. This implies that the developed LSPR-MIP nanochips exhibit some degree of selectivity. It should be noted that the response

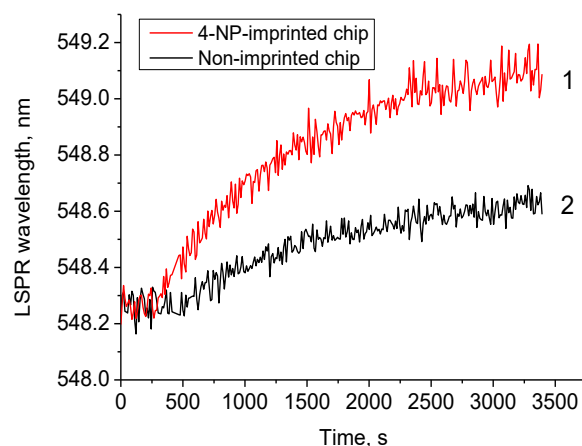


Fig. 3. Kinetic dependence of the LSPR peak shift for 4-NP-imprinted (1) and non-imprinted (2) LSPR nanochips in the presence of 4-NP vapor. 4-NP vapor was added at 300 s.

time up to saturation level differs from 2 min for 4-NT up to 33 min for 5-NI. The quick response for 4-NT shows a promising possibility of LSPR-MIP nanochips for the detection of vapors of organic molecules with extra-low molecular weight.

The obtained results show that the developed LSPR-MIP nanochips need further optimization in the aspects of selectivity, response time and sensitivity to be used in real sensors, which will be the object of future research. Firstly, optimization is necessary for parameters of arrays of gold nanostructures in Au nanochips, *i.e.*, geometry of gold nanoparticles and distance between them, which will improve the sensitivity. Secondly, improvement of molecular imprinting procedure to produce more binding sites, and tune the thickness of the MIP is required, which will improve the response time and increase the selectivity.

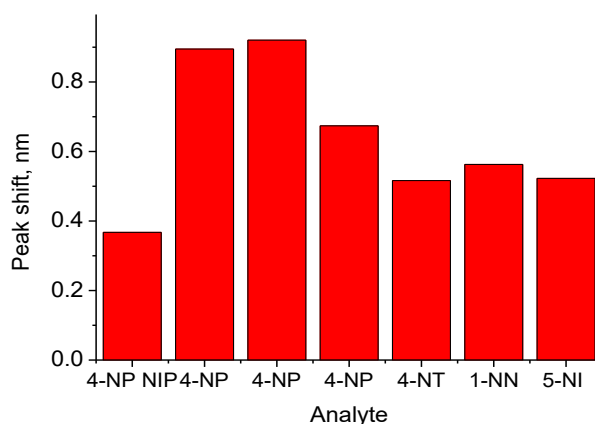


Fig. 4. Histogram of the LSPR response upon non-imprinted and 4-NP-imprinted LSPR-MIP nanochips exposure to different types of explosives analogue vapor.

4. Conclusion

LSPR-MIP nanochips in the form of arrays of plasmonic Au nanostructures on glass substrates with MIP coating based on acrylamide copolymer have been developed and demonstrated for explosives analogues sensing. Detection limits for such type of nanochips were shown to be in the picomolar and ppm ranges for aqueous and gaseous analytes, respectively. LSPR-MIP nanochips also exhibit promising parameters in terms of selectivity and response time, so we believe that optimization of their fabrication protocol will allow their application for field-operating explosives sensors.

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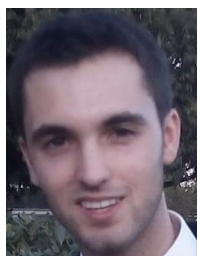


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Наночипи на локалізованому поверхневому плазмонному резонансі з молекулярно-імпринтованим полімерним покриттям для детектування вибухівки

В.І. Чегель, А.М. Лопатинський, В.К. Литвин, П.В. Демидов, J.P. Martínez-Pastor, R. Abargues, E.A. Gadea, С.А. Пілецький

Анотація. Сенсорні елементи, що базуються на локалізованому поверхневому плазмонному резонансі в масивах золотих наноструктур на скляних підкладках (наночипах) з молекулярно-імпринтованим покриттям на основі акриламідного кополімеру, були запропоновані для детектування аналогів вибухівки в рідкій та газовій фазі. Наночипи проявляють межі виявлення на рівні 1 пМ у водному розчині та 0,1 ppm у газоподібному стані для 4-нітрофенолу. Тестування чутливості з використанням виготовленого 4-нітрофенол-імпринтованого плазмонного наночипа до 4-нітротолуолу, 1-нітронафталіну та 5-нітроізохіноліну у газовій фазі демонструє частково селективний відгук із часом насичення сигналу від 2 хвилин.

Ключові слова: локалізований поверхневий плазмонний резонанс, наноструктури золота, наночип, молекулярно-імпринтований полімер, сенсор, вибухівка.