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Sensitive detection of 2,4,6-trinitrotoluene by tridimensional monitoring of molecularly imprinted polymer with optical fiber and five-branched gold nanostars

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ABSTRACT

A new approach for optical chemical sensor based on molecularly imprinted polymer (MIP) and localized surface plasmon resonance (LSPR) in plastic optical fibers (POFs), for the selective detection and analysis of 2,4,6-trinitrotoluene (TNT) in aqueous solution, has been developed. LSPR is excited in five-branched gold nanostars (GNS), suspended in an MIP specific for TNT (GNS-MIP), which assures the selectivity. This sensing layer has been deposited directly on two different POF platforms, i.e. tapered and not-tapered POF. Both sensors show better performance than a similar one previously proposed, in which the surface plasmon resonance (SPR) was excited in a thin gold layer at the surface of the POF in contact with the MIP layer (specific for TNT). In particular, in the sensor with a GNS-MIP sensing layer on the not-tapered POF the sensitivity was 8.5×10^4 nm/M, three times higher than in the gold layer sensor. In the sensor with GNS-MIP sensing layer on tapered POF the sensitivity increases further up to 8.3×10^5 nm/M, thirty times higher than in the gold layer sensor, because the penetration depth of the evanescent field increases and the number of the interaction sites of TNT, in the MIP involved in the generation of the signal, increases accordingly.

1. Introduction

Localized surface plasmon resonance (LSPR) is a very sensitive technique for determining small refractive index changes at the interface between a metal and a dielectric medium. Thus it can be a useful tool for surface and nanostructured-surface interaction analysis and marker-free sensing, in different areas of bio and chemical sensing, as reported in several recent review papers [1–4]. The signal, i.e. the change of refractive index at the metal-dielectric interface, is due to the adsorption/combination of the considered substance (i.e. the analyte) at the sensor surface. It is measured through the variation of the LSPR (in sensors employing metal nanoparticles) as well as of SPR (in sensors employing thin metal layers).

In the present investigation, LSPR is applied as the transduction method to obtain a device with characteristics suitable for on line and remote sensing. As a proof of principle, 2,4,6-trinitrotoluene (TNT), a nitroaromatic explosive with low molecular mass (mw = 227.14), has been considered. LSPR sensors based on bio or synthetical receptors are commonly regarded as suitable for the analysis of medium or large molecular weight analytes, however several approaches have been proposed for the detection of low molecular mass substances too, mainly based on interaction reactions with receptors of biological origin which give by-products inducing measurable refractive index changes at the surface of the optical device. A different approach is that based on molecularly imprinted polymers (MIPs), which are synthetical porous solids containing specific interaction sites that have been proved to change their refractive index when small molecules, as for example nicotine [5] and TNT [6], are adsorbed. MIPs are obtained by the molecular imprinting methods [7,8], and contain specific sites interacting with the molecule of interest according to a "lock and key" model. The high thermodynamic stability of the MIP-analyte adducts and their fast kinetics of formation make MIPs suitable receptors to be used in combination with SPR as transduction method. Additional favorable aspects for sensing in comparison to bioreceptors such as, for example, antibodies [9], include a better stability out of the native environment, a better reproducibility and

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a lower cost. Finally, MIPs, as other bioreceptors, are highly selective. In the case of the MIP for TNT here considered, the selectivity has been found to be very good, even against molecules of similar chemical structure [6].

The aim of the present investigation is to demonstrate that the LSPR phenomenon can be exploited instead of SPR in order to improve the sensitivity and the detection limits of an MIP sensor based on POF, considering as a proof of principle the detection of TNT.

A large number of sensors based on optical fibers have been proposed with various advantages, as for example sensors based on microstructured optical fibers [10–12], however in this work we use an SPR sensor based on a common plastic optical fibers (POF), simply worked out by eliminating the cladding. This platform has been shown to give a sufficiently high optical sensitivity for sensing purposes, about 2×10^3 nm/RIU [13]. This approach has some similarity with the slot shaped microstructured optical fiber previously proposed [14] which has a similar sensitivity while requiring a much more complex preparation than that here proposed. Sensors based on SPR in plastic optical fibers present several advantages over the most widely used silica fibers. POFs are especially advantageous due to their excellent flexibility, great numerical aperture, large diameter, easy and low cost manipulation and ability to withstand smaller bend radii than glass [5,6]. In SPR sensors, the use of an optical fiber, instead of the classical Kretschmann (prism) geometry or other set-ups as for example that of Spreeta sensor [15,16], is good for remote sensing and reduces the cost and the dimension of the device, with the possibility of implementation in sensor array and easy integration of the SPR sensing platform with optoelectronic devices, and for data processing as well. Moreover, the multiple reflections of light occurring in the optical fiber allow to excite the sample to a large extent, so the detection sensitivity to the analytes can be excellent. An SPR platform in POF is an optimal approach both for biosensing and for MIP sensing [5,6]. However, the SPR approach allows to monitor only the sites of MIP very near to the gold layer, in an almost two-dimensional way, due to the very low penetration depth of the light. In other words, the signal (i.e. the local refractive index change, resulting in SPR variations) is produced by the interaction with only a limited number of sites. It can be imagined that metal nanoparticles would allow a larger interface between the metal and the dielectric, and a larger connection with the interaction sites, if the contact with MIP takes place in a tridimensional way, as it occurs when the metal nanoparticles are dispersed in the bulk of the dielectric medium. Actually this approach, based on localized surface resonance has been demonstrated to be effective in the case of a sensor for dopamine [17], in which spherical gold nanoparticles were dispersed in a molecularly imprinted polymer deposited over a gold layer. Another example is a sensor for TNT [18] in which the use of spherical gold nanoparticles in an electrochemically polymerized MIP allowed impressively low detection limits to be reached.

In the present investigation, a particular kind of metal nanoparticles are used, i.e. five-branched gold nanostars (GNS) [19] instead of a gold thin film [20] or of classical spherical gold nanoparticles [17,18]. Their shape and dimension (about 80 nm) is shown in Fig. 1 (transmission electron microscopy image). The reason is that additional benefits are expected from the use of metal nanoparticles of this particular shape, besides the number and very thin dimensions of the branches, that increase the surface/mass ratio and the contact area with receptor holes in the MIP. In particular, they present multiple resonances [19] which are tunable and enter the near infrared range (maximum absorption in the 650–1600 nm range). This characteristics may both add flexibility to the sensor's design and increase its sensitivity. Finally, an interesting property of the POF platform is the easy preparation of tapered fibers, i.e. fiber with a zone of smaller diameter. Their implementation in SPR sensors has been demonstrated to considerably improve the sensor sensitivity in the case of SPR transduction [5,21], but as far as we know, it has never been applied to LSPR, even if in principle they should improve the sensitivity because they allow to interrogate a larger number of sites as the presence of metal nanoparticles as a discontinuous layer, does not prevent the penetration of the electric field further inside the surrounding matrix.

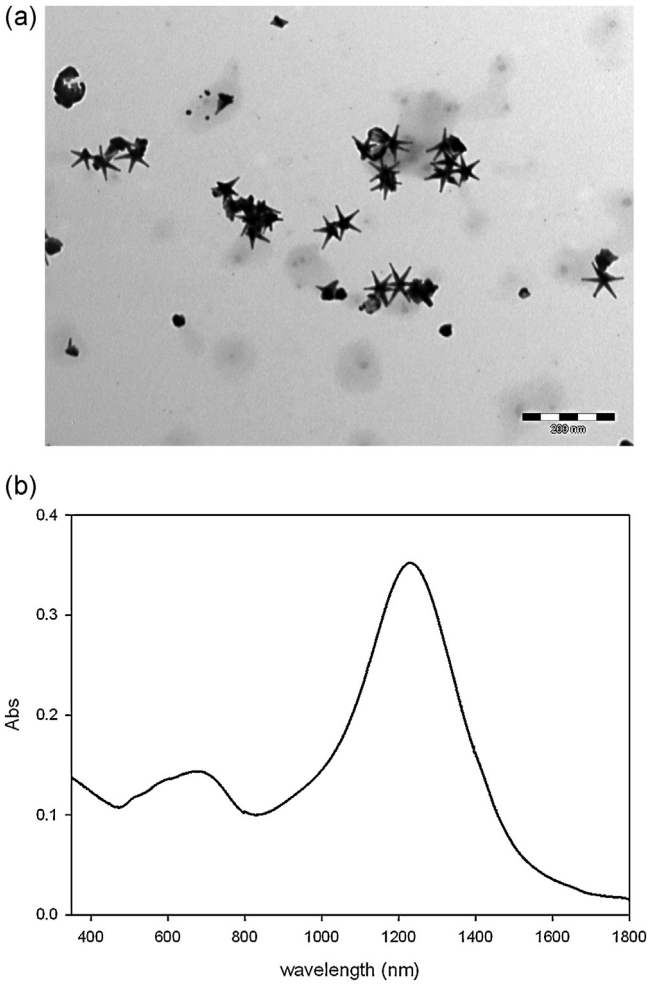

Fig. 1. (a) TEM image of the five-branched GNS used in this work (acquired on a Jeol JEM-1200 EX II 140 instrument). (b) UV–vis–nIR absorption spectrum of the five-branched GNS used in this work (sample is diluted 1:10 with bidistilled water and the spectrum is registered on a Cary6000i UV–vis–nIR spectrophotometer equipped with a 1 mm glass cuvette).

2. Materials and methods

2.1. Sensing layer

2.1.1. Preparation of five-branched gold nanostars

Gold nanostars were prepared according to a seed growth procedure previously published by some of us [19]. Briefly, a seed solution was prepared as follows. In a 20 mL vial, $HAuCl_4$ (5 mL, 5×10^{-4} M in water) was added to an aqueous solution of TritonX-100 (5 mL, 0.2 M). The mixture was gently hand-shaken and a pale yellow color was obtained. Then, a previously ice-cooled solution of $NaBH_4$ (0.6 mL, 0.01 M in water) was added. The mixture was gently hand-shaken and a reddish-orange color appears. The growth solution (10 mL) was prepared as follows. In a 20 mL vial, $AgNO_3$ (180 μL, 0.004 M in water) and $HAuCl_4$ (5 mL, 0.001 M in water) were added in this order to an aqueous solution of TritonX-100