Plasmonic sensor based on gold nanodisk structures for toxic organic molecule detection

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Surface plasmons (SPs) are collective excitations of the free electrons at the interface between a metallic structure and a dielectric. This phenomenon can be optically observed in thin metals, in metal nanostructures and nanoparticles (NPs). Optical excitations remain localized in space in case of nanostructures [1–2]. Their unique properties enable a wide range of practical applications, having been in the past decade one of the most preferred sensing platforms for gas detection and biosensing [3] with high sensitivity and low cost. It is well-known that surface plasmon resonance (SPR) strongly depends on the refractive index of the surrounding medium (substrate, solvent, and adsorbates) of the surface/nanostructure [4]. Adsorption of molecules on the metal surface can lead to measurable spectral changes in both the wavelength and intensity of the SPR [2,5,6]. This high sensitivity allows SPR sensors to become a powerful analytical platform. In this work, we report experimental sensing results of a functionalized sensor based on plasmonic gold nanodisks, showing the capability to detect toxic organic molecules.

We designed plasmonic gold nanodisks arranged in a rectangular array on a silicon substrate [Fig. 1(a,b)] exhibiting a Mie resonance [Fig. 1(c)] around telecommunication wavelengths. Numerical CST Microwave Studio time domain simulations were performed. Simulated values are d = 200 nm, h = 20 nm and a = 400 nm. Silicon is modeled as $n_2 = 3.45$ and gold is modeled using Drude model with plasma frequency $\omega_p = 1.36\times10^{16}$ and collision frequency $\gamma = 1\times10^{14}\ s^{-1}$. Simulations predict a sensitivity to variations in the surrounding index (n_1) of 40 nm/r.i.u. The gold nanostructure was fabricated on a silicon substrate by standard electron-beam lithography with a single PMMA (poly-methyl-methacrylate) layer followed by a lift-off process. Final thickness of the gold film is 20 nm and 5 nm layer of chromium is deposited before the gold to improve gold adhesion. Figure 1(d) shows an electron scanning microscope (SEM) image of the fabricated structure and the measured dimensions. The total sample area was 100 × 100 µm. Infrared (IR) transmission spectra for the fabricated structure were performed using a Bruker^{TM} Fourier Transform IR spectrometer. The initial measurement after fabrication is shown in Figure 2. A resonance is observed around 1.1 µm, blueshifted with respect to simulations.

After the characterization of the plasmonic resonance spectrum and cleaning of the gold surface, we proceed chemical functionalization, performed by immersion of the gold surface in a 0,01M solution of 11-mercapto-undecanoic acid (MUA) in absolute ethanol for 3 hours. The deposition process is carried out at room temperature. In order to remove the excess reactants the sample is rinsed in absolute ethanol and deionized water and dried under a flow of dry air. The MUA monolayer is to be expected 1.7 nm thick with their thiol headgroup chemisorbed on the gold surface. The molecular axis is slightly tilted with respect to the gold surface normal [6].

For the sensing experiments we used first cadaverine (1,5-pentanediamine). The experiment was performed by immersion of the functionalized chip in 0,1 M aqueous solution of cadaverine for 10 seconds. Figure 2.A. shows the resulting transmission spectra after several binding events on the functionalized chip. The blue spectrum presents the resonance of the air-bare metal interface at 1.117 µm. The red spectrum, obtained after the metallic surface was modified with a monolayer of MUA, shows that the minimum in the transmission shifted to 1.133 µm. An additional shift to 1.186 um, corresponding to green spectrum, was observed after the binding of cadaverine molecules to the MUA active sites. Removal of the self-assembled monolayer (SAM) from the Au surfaces is of key importance for the recycling of the sensor in order to re-obtain a clean surface. Therefore, the gold surface was cleaned with Piranha solution (1:3 mixture of 30% H_2O_2-concentred H_2SO_4) for 1 min, copious amount of deionized water and absolute ethanol [5]. The resonance frequency obtained from the clean surface returned nearly to the original position. Anyway, several cleaning treatments should lead to a decrease in sensing area caused by erosion of gold, which could change slightly the plasmon resonance peak of the gold nanostructure.

In order to demonstrate the gas detection capability of the optical sensor, we used another toxic organic molecule like methanediamine. In this case, the experiment was performed by exposing the functionalized chip to methanediamine vapour at 25ºC for 10 s. Results from the spectral measurements are shown in Figure 2.B. Here, a relevant resonance signal shift is observed when gas molecules are adsorbed on the MUA layer. The blue spectrum corresponding to the bare gold structure presents a resonance at 1.179 µm. For the functionalized surface with MUA, the red spectrum shows a peak to 1.192 µm and, after exposing to methanediamine vapour, the resonance shifted to 1.212 µm.

We have demonstrated experimentally the use of plasmonic gold nanodisks for the detection of toxic organic molecules in both gas and in aqueous solution. It was found that the peak shift for the gas sensor is 0.011 µm and for the detection of diamine in water 0.053 µm. From these values, one can conclude that the gold nanodisk structure for sensing presents increased sensitivity with regard to other configurations like nanoholes, whose resonance shift is 0.009 µm [6]. **Acknowledgment**. Financial support by the Spanish MICINN under Contracts No. TEC2008-06871-C02-02 and CSD2008-00066 (Consolider EMET) is gratefully acknowledged.

References

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Figures

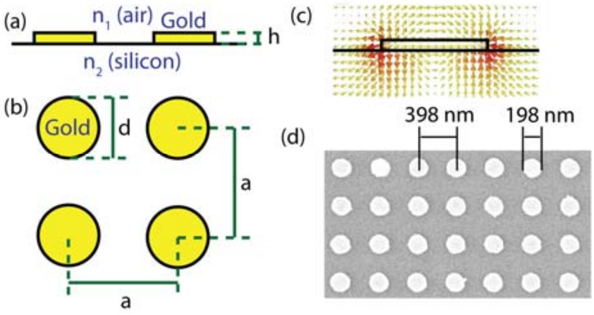

Figure 1: (a) Side view and (b) top view schematic of the designed gold nanodisks. (c) Electric field at Mie resonance. (d) Scanning electron microscope (SEM) photograph of the fabricated structure.

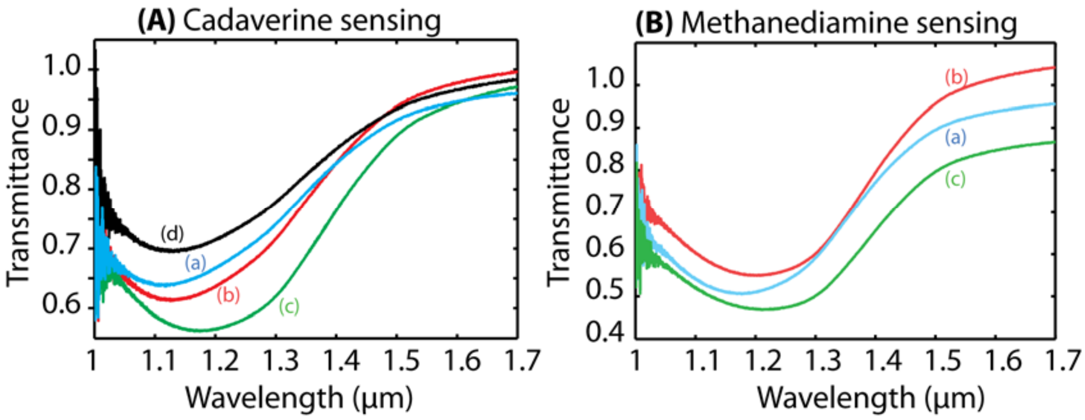

Fig. 2.A: Sensing of cadaverine in aqueous solution by chip immersion. (a) Measured transmittance spectra for the bare gold surface sample; (b) functionalized surface with MUA monolayer; (c) cadaverine detection (d) and regeneration of the resonance by cleaning of the gold surface. Fig. 2.B: Gas detection of Methanediamine. (a) Transmission spectra for the bare gold surface sample; (b) functionalized surface with MUA monolayer; (c) Resonance shift due to the adsorption of methadiamine molecules on the MUA layer.