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ZIF-8-based surface plasmon resonance sensors for chemical vapor optical detection with LEDs

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Summary:

The use of sorption coatings to functionalize samples is a frequent strategy to enhance the sensitivity and selectivity of some gas sensors. In this regard, metal-organic frameworks have recently attracted attention because their nanometre-sized pores allow the molecular adsorption of gases into their structure, which modulates the refractive index of this material depending on the amount of adsorbed gas molecules. This research explores their use in surface plasmon resonance sensors for volatile organic compound optical detection and the further miniaturization of the sensing device to achieve smaller and portable gas sensors.

Keywords: Gas sensor, surface plasmon resonance, optical detection, metal-organic frameworks, volatile organic compounds

Headlines

Surface plasmons generated between a metal film and its surroundings are extremely sensitive to the composition of the neighboring and can be used in gas sensing applications.

Metal organic frameworks can increase the sensitivity of gas sensors by several orders of magnitude.

Background, Motivation an Objective

Volatile organic compounds (VOCs) have been linked to several health issues and other environmental problems such as global warming by infrared absorption or formation of ground-level ozone [1]. Therefore, the analysis of VOCs is key to monitor air quality and prevent severe health problems that occur due to their long-term inhalation and exposure.

Gas chromatography coupled with mass spectroscopy (GC-MS) is currently the established method for VOCs analysis. However, GC-MS is expensive, bulky, and must be done off-site. Even though there are more practical methods, also sensitive to VOCs, they present cross-sensitivity to many gases, making it difficult to distinguish between gas species and affecting its response.

In this sense, a pathway to increase the response of gas sensors relies on the functionalization of their surface with porous solids in order to increment the concentration of gas molecules at the surface and even tailor selectivity by chemical affinity or pore size [2]. On this matter, metal-organic frameworks (MOFs) are porous materials with a refractive index (RI) that is modified depending on the amount of adsorbed gas molecules in its structure. Therefore, tracking the variation of the MOF when exposed to different gaseous atmospheres via RI sensing mechanisms such as Fabry-Pérot interferometry or surface plasmon resonance (SPR) [3] can lead to a new generation of gas sensors.

Our goal is to monitor different VOC concentrations with MOF-coated SPR sensors by tracking the red-shift of the surface plasmon resonance wavelength under the different atmospheres. In parallel, we are also working on the miniaturization of our monitoring system to obtain portable, cost-efficient and smaller gas sensors.

Methodology

The ZIF-8 film (Fig. 1a), which is the MOF that has been used, is grown via the layer-by-layer deposition method reported by Hupp *et. al.* [4]

on top of SPR substrates containing gratings with periods of Λ=400 nm and Λ=500 nm. Gas sensing measurements are then conducted via spectral interrogation on the fabricated samples at room temperature, which are placed in a holder inside a home-built aluminum chamber with a quartz window and connected to two mass flow controllers (MFC) that command the gas flux entering the gas chamber.

In addition to the previously presented results in Eurosensors 2023 [5] and considering the miniaturization of the current optical set-up, measurements are now being conducted by illuminating the sample with LEDs instead of white light. With this aim, the LED needs to be adjusted to the period of the diffraction gratings and the thickness of the deposited ZIF-8 film, both responsible for the resulting SPR wavelength, to obtain the maximum sensitivity of our sensors (Fig. 1b).

To further miniaturize our device, we have also substituted the spectrometer for a photodiode (PD) and gas measurements are currently being tested.

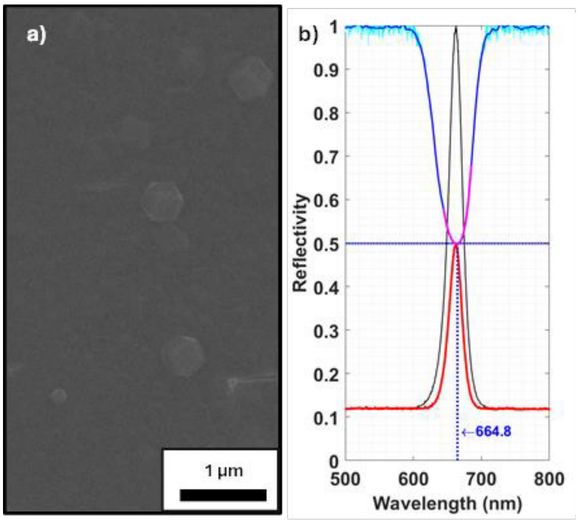

Fig. 1. (a) SEM image of a ZIF-8 layer (b) spectrum of a 660nm-LED (black curve) adjusted to the Λ=400 nm SPR dip (blue curve). The red curve represents the simulated response that would be acquired with a PD.

Results

We will present the gas sensing results of the fabricated samples when exposed to different concentrations of VOCs using LEDs as illumination source, as well as the simulated response with a PD. As an example, Fig. 2a shows the simulated reflectivity that would be acquired with a PD, while Fig. 2b shows a preliminary result of the response of the sensor to synthetic air (SA) and saturated ethanol (EtOH) pulses.

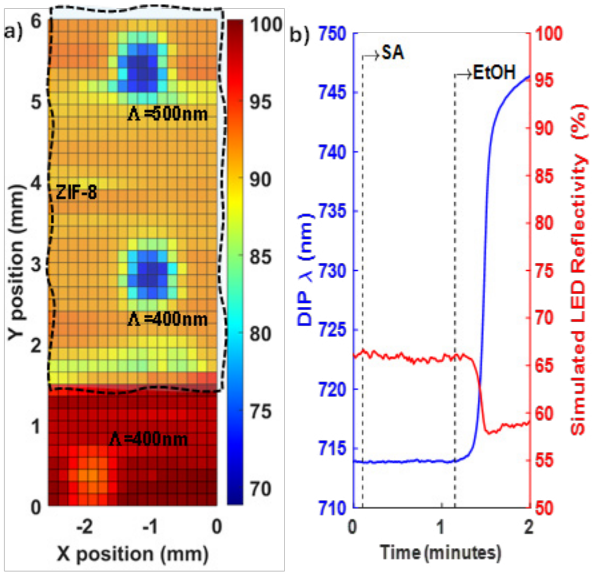

Fig. 2. (a) Simulated reflectivity acquired by a PD using a 660nm-LED to scan the chip (b) red-shift of the Λ=400 nm SPR dip under SA and saturated EtOH atmospheres (blue curve) when illuminating with a 680nm-LED and simulated PD response (red curve).

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