

## Hybrid Porous Silicon- Rhodamine B Derivative Nanostructures as Chemical Sensor for Hg(II) Detection.

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Sensing of heavy metals in aqueous solutions has been performed by developing porous silicon (PSi) hybrid materials. The Rhodamine organosilane derivative (Rh-UTES) was used as metal receptor through formation of luminescence chelates within the porous silicon microcavities (PSiMc). The attachment of organic derivative into PSiMc was confirmed by FTIR, specular reflectance and scanning electron microscopy (SEM). The complexing ability of Rh-UTES receptor to Hg<sup>+2</sup> detection was investigated by fluorescent spectroscopy and microscopy. We found that the fluorescent intensity of the PSiMc hybrid device is metal concentration dependent. Similar behavior was observed in liquid and solid phase. Metal-Ligand affinity was study by electrochemical techniques.

### Introduction

Mercury ion and its complexes are highly toxic, and arise from a variety of natural and human-generated sources. The need for analytical methods for the sensitive and selective determination of mercury ion is of great interest, especially in on site analyses for rapid screening applications (1-2). Fluorescence detection with metal ion-responsive chemosensors offers a promising approach for simple and rapid tracking of metal ions for biological, toxicological, and environmental monitoring (3). The Chemical-surface functionalization of ordered nanoscale structures can be used to produce materials that have the desired surface properties for sensing applications (4). The rhodamine and its derivatives are framework for constructing fluorescent chemosensors, these derivatives have been immobilized into different inorganic supports: gold nanoparticles, mesoporous silica and polymeric nanoparticles have been used to develop rhodamine hybrid devices that are able to detect mercury ions (5-8). In this context, our research group proposes a new method to develop a fluorescent chemical sensor for mercury detection Hg. The sensor is mainly based on the optical properties of porous silicon structures (PSiMc) (9) coupled with the fluorescent properties of Rh-UTES ligand derivative, which is covalently linked to PSiMc and acts as receptor of metal ions. The main advantage of the proposed method is the simplicity of the system and the fact that the hybrid sensor should

be easy to carry for field applications. The PSiMc has proved to be a suitable material with unique optical properties for the development of this kind of fluorescent sensor (9). Our previous approaches in this field have shown that the detection of fluorescent molecules is possible using the optical properties of specific PSi structure (mirror or microcavity) (10). Increased excitation and enhanced emission, both driven by the efficient reflection of light and resonance effects within the PSi microcavities, allowed the enhancement of the fluorescent response of the Rh-UTES derivative even at low molecular concentration (11-12). Hence, the variation of this method was used here to produce detection of low concentrations of heavy metals by forming metal complexes within the pores that turn-on the luminescence emission.

## Methods

### Synthesis of rhodamine fluorescent derivative (Rh-UTES).

Rhodamine fluorescent derivative (Rh-UTES) was obtained from the reaction of m-xylenediisocyanate, 3-aminopropyltriethoxysilane (APTES) and the previously synthesized Rh-amine derivative, in one step (13). Rh-UPTES was obtained as beige solid, and characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and FTIR techniques.

### Synthesis of porous silicon.

PSi samples were prepared by the wet electrochemical etching process using high doped, p-type (boron doped) silicon wafers (thickness 500-550  $\mu\text{m}$ , with a 0.001-0.005  $\Omega\text{-cm}$  resistivity, and with the crystallographic orientation of (1, 0, 0)). The PSiMc structures were fabricated alternating layers of high porosity, with configuration of  $(\text{HL})_{x5} \text{HH} (\text{LH})_{x5}$  (where H and L are the high and the low current density layers respectively) with a cavity centered at 750 nm. The first layer of the structure was etched at 75  $\text{mA}/\text{cm}^2$ . This current density produces the formation of large pores assuring a good penetration of the organic molecules and metal ions. For the second layer the current density was reduced to 30  $\text{mA}/\text{cm}^2$ . The PSiMc samples were thermally oxidized at 600  $^\circ\text{C}$  in  $\text{O}_2$  atmosphere to stabilize and protect them against natural aging (14). Infiltration of Rh-UTES into PSiMc was performed following one step method through silane chemistry. The nonspecific binding was eliminated by rinsing with appropriate solvents and dried with  $\text{N}_2$  after each step. Once obtained, the PSiMc/Rh-UTES sensors were exposed to aqueous solutions containing different metal ion  $\text{Hg}^{2+}$  concentration.

## Discussion

Rh-UTES derivative was successfully synthesized from a rhodamine base in a relatively good yield (3.21g, 80%). To evaluate the metal ion binding capability of this new compound, a colorimetric evaluation was performed in a liquid phase. It was observed that after the  $\text{Hg}^{2+}$  addition the colorless solution immediately become pink. It is interesting to notice that the color intensity of the solution is linearly dependent of the metal concentration.

The spectroscopic property of the Rh-UTES compound in solution toward metal ion complexation was studied (13). In the absence of specific guest cations, particularly in CH<sub>3</sub>CN (ACN) solution, the Rh-UTES exhibited a slight fluorescence emission corresponding to the rhodamine molecule in a spirolactam form. In the presence of Hg<sup>2+</sup> ions, Rh-UTES compound remarkably shows an enhancing fluorescence emission centered at 583 nm. The Rh-UTES compound in the presence of other metal ions did not induce any apparent fluorescent enhancement or color change, thus validating its high selectivity towards Hg<sup>2+</sup> (Figure 1).

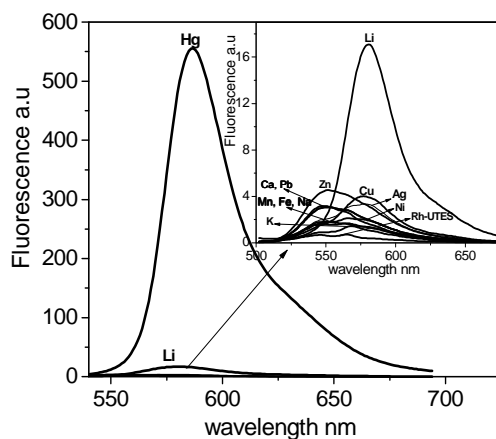


Figure 1. Fluorescence spectra of Rh-UTES (10  $\mu$ M in ACN) derivative upon addition of 100  $\mu$ M of various metal cations.  $\lambda_{\text{exc}} = 485$  nm.

In solid phase, photoluminescence (PL) measurements were used to characterize the performance of the fluorescent sensor. The infiltration of the organic molecules was confirmed by the increased fluorescence intensity of the PSiMc/Rh-UTES device. In addition, PSi hybrid devices have proved to be a good candidates for electrochemical studies (14). Therefore, in this work, the Hg<sup>2+</sup> detection, through voltammetric techniques as well as the limit detection will be also discussed.

Further details of these results will be given in a forthcoming publication (13).

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