A Universal Sensor for Mercury (Hg, Hg\textsuperscript{I}, Hg\textsuperscript{II}) Based on Silver Nanoparticle-Embedded Polymer Thin Film

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Introduction

- Mercury is highly toxic in all its oxidation states, 0, +1 and +2.
- Development of efficient sensors for mercury is of great interest due to its very low allowed level in food and drinking water (\(\sim 2\) ppb).
- Electrochemical, conductivity, color, and fluorescence based mercury sensors have been developed.
- Direct sensing of elemental mercury has mostly been carried out in the vapor state.
- Aggregation of nanoparticles induced by the interaction of ligands with Hg\(^{2+}\) is reported.
- Selectivity would be high as redox reactions do not occur with the majority of transition metal ions with silver nanoparticles.
• The higher sensitivity to oxidation and greater susceptibility to degradation during functionalization compared to Au, are some of the handicaps of Ag nanoparticles.
• In this paper silver oxidation is overcome by embedding into PVA matrix and as redox chemistry is expected with Hg$^{2+}$ special functionalization is not needed.
• Easy preparation, cheap, portability and easy handling make this Ag nanoparticles embedded PVA thin film important.
Experimental Section

1.5 mg AgNO$_3$ + 2.53 mL PVA + 0.75 mL water → Spin coating on glass plate

Spin coating on glass plate → Hot air oven 130 °C, 2 h → Ag nanoparticles

For TEM

Spin coating of few drops of a solution of 1 g polystyrene in 8 mL toluene
Figure 1. (a) Schematic diagram of the Ag-PVA thin film pack sensor; four film-coated glass plates (25 x 6 x 1.5 mm$^3$) packed with thin Teflon spacers at the two ends tied with Teflon tape form the sensor element; path of the light beam in the spectrometer is shown. (b) SPR spectrum, (c) AFM topography image ($\sim 12 \, \mu m \times 10 \, \mu m \times 4 \, nm$); inset ($\sim 1 \, \mu m \times 1 \, \mu m \times 4 \, nm$), and (d) TEM image (scale bar = 10 nm) of Ag-PVA thin film sensor.
Figure 2. Temporal variation of the SPR spectra of Ag-PVA thin film immersed in aqueous solutions with different concentrations of Hg$^{2+}$ (note the longer time interval for the case of pure water i.e., [Hg$^{2+}$] = 0 ppb); absorbance at $\lambda_{\text{max}}$ at zero time is normalized to 1.0 in each case.
Figure 3. Relative change in absorbance, $RA_t$ as a function of time for different concentrations of the analyte in aqueous medium (with trace PVA as stabilizer in the case of Hg), (a) $Hg^{2+}$, (c) $Hg_2^{2+}$ ($[Hg^+] = 1/2[Hg_2^{2+}]$), and (e) Hg. Variation of $RA_6$ with the analyte concentrations (10 ppb - 1 ppm): (b) $[Hg^{2+}]$, (d) $[Hg^+]$, and (f) $[Hg]$; the least-squares fit to a straight line is indicated in each case.
Figure 4. TEM images of Ag-PVA film immersed for 12 min in (a) pure water, (b) an aqueous solution of 1 ppm Hg$^{2+}$ ions and (c) an aqueous solution of 1 ppm Hg (with trace PVA); scale bar = 10 nm. (d) Temporal evolution of different nanostructures in the film immersed in the Hg$^{2+}$ solution, under the electron beam; two selected regions in a larger area image are shown for different time periods and with different magnifications in order to highlight the observations; top panel: 20-60 s, scale bar = 100 nm; bottom panel: 0-10 min, scale bar = 20 nm).
Figure 5. Comparison of the response of the Ag-PVA film sensor, $|\Delta \lambda_6| \cdot R A_6$ (see text for definition) to different analytes; the concentration level of the aqueous solutions are indicated in terms of the metal ion or the molecule in the case of $\text{HNO}_3$. 
Figure 6. Schematic representation of the swelling of the Ag-PVA film in aqueous medium and the sensitive changes in the SPR spectrum of the film induced by Hg$^{2+}$/Hg$_2$^{2+}/Hg$^{0}$ in the solution.
Conclusions

• Fast, sensitive and selective detection of mercury in all its oxidation states is demonstrated.
• The thin film matrix facilitates the observation of the characteristic blue shift of the SPR spectrum upon interaction with mercury, enhancing the selectivity of the detection.
• Low-cost, linear response over a wide range of concentrations, ease of deployment and the feasibility of both in situ and ex situ analysis are prominent features of the thin film sensor.
Thank you