

# A Universal Sensor for Mercury (Hg, Hg<sup>I</sup>, Hg<sup>II</sup>) Based on Silver Nanoparticle-Embedded Polymer Thin Film

**G. V. Ramesh and T. P. Radhakrishnan**

**School of Chemistry, University of Hyderabad**

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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  $\text{Hg}^{2+}$  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  $\text{Hg}^{2+}$  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<sub>3</sub> + 2.53 mL PVA  
0.75 mL water



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

# Results and Discussion

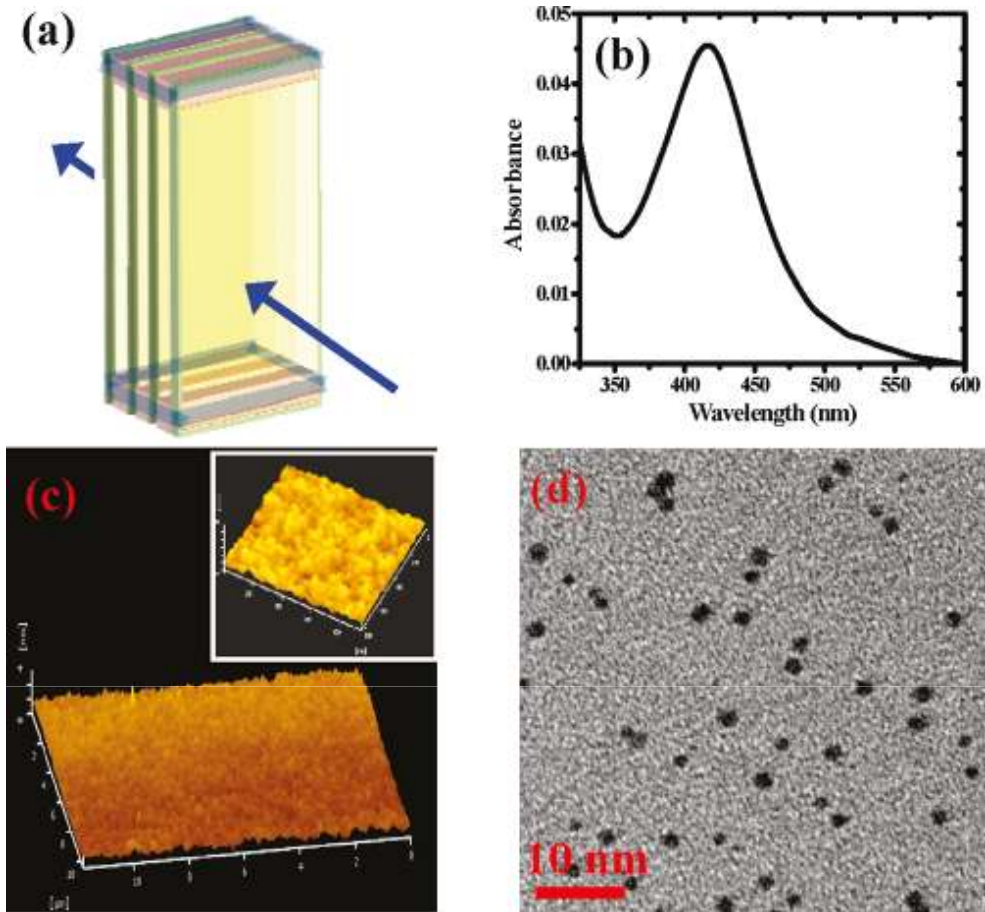


Figure 1. (a) Schematic diagram of the Ag-PVA thin film pack sensor; four film-coated glass plates ( $25 \times 6 \times 1.5 \text{ mm}^3$ ) packed with thin Teflon spacers at the two ends tied with Teflon tape form the sensor element; path of the light beam in the spectrometer is shown. (b) SPR spectrum, (c) AFM topography image ( $\sim 12 \mu\text{m} \times 10 \mu\text{m} \times 4 \text{ nm}$ ); inset ( $\sim 1 \mu\text{m} \times 1 \mu\text{m} \times 4 \text{ nm}$ ), and (d) TEM image (scale bar = 10 nm) of Ag-PVA thin film sensor.

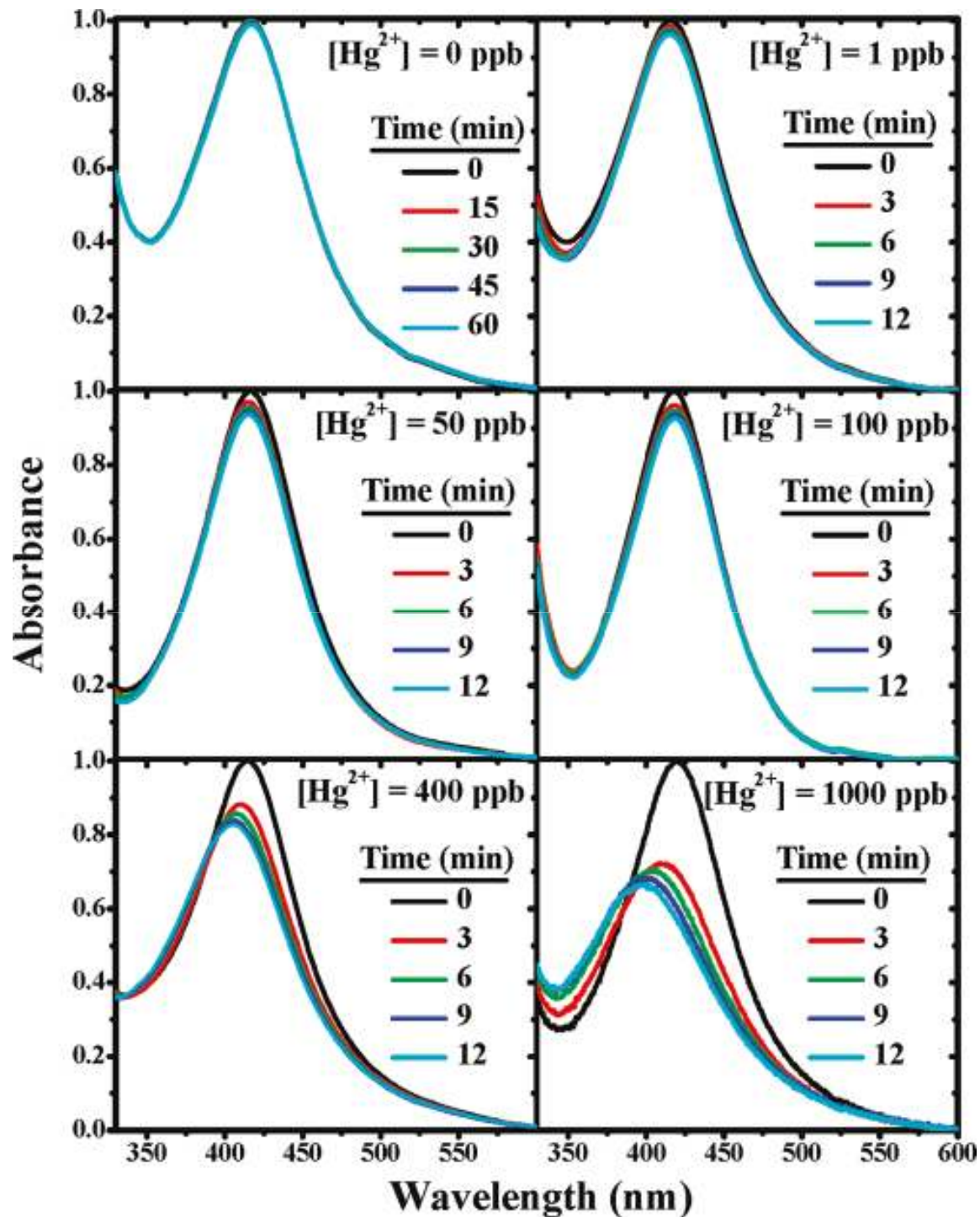


Figure 2. Temporal variation of the SPR spectra of Ag-PVA thin film immersed in aqueous solutions with different concentrations of  $\text{Hg}^{2+}$  (note the longer time interval for the case of pure water i.e.,  $[\text{Hg}^{2+}] = 0$  ppb); absorbance at  $\lambda_{\text{max}}$  at zero time is normalized to 1.0 in each case.

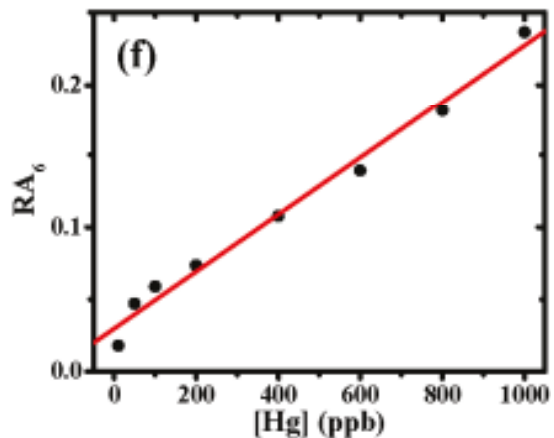
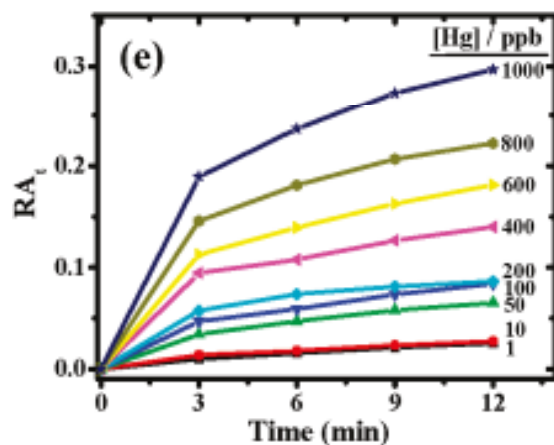
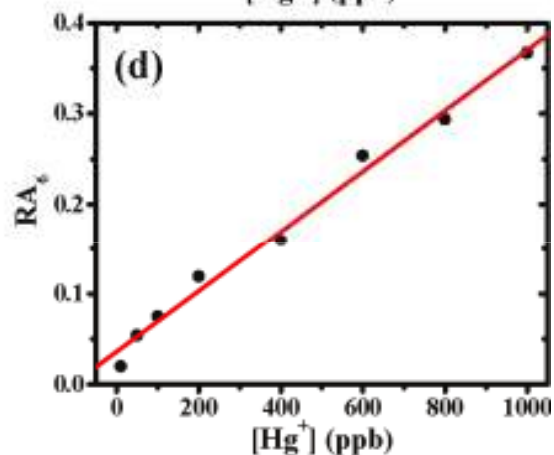
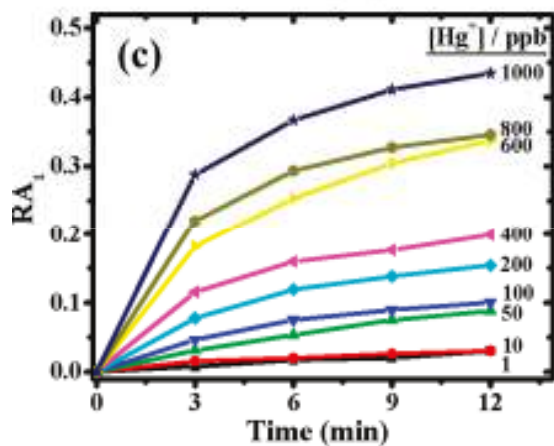
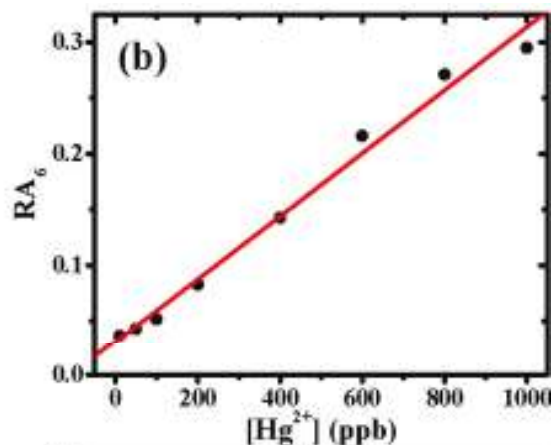
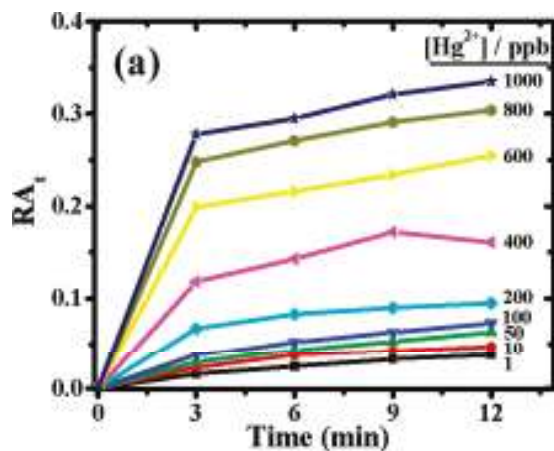


Figure 3. Relative change in absorbance,  $RA_t$  as a function of time for different concentrations of the analyte in aqueous medium (with trace PVA as stabilizer in the case of Hg), (a)  $Hg^{2+}$ , (c)  $Hg_2^{2+}$  ( $[Hg^+] = 1/2[Hg_2^{2+}]$ ), and (e) Hg. Variation of  $RA_6$  with the analyte 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.

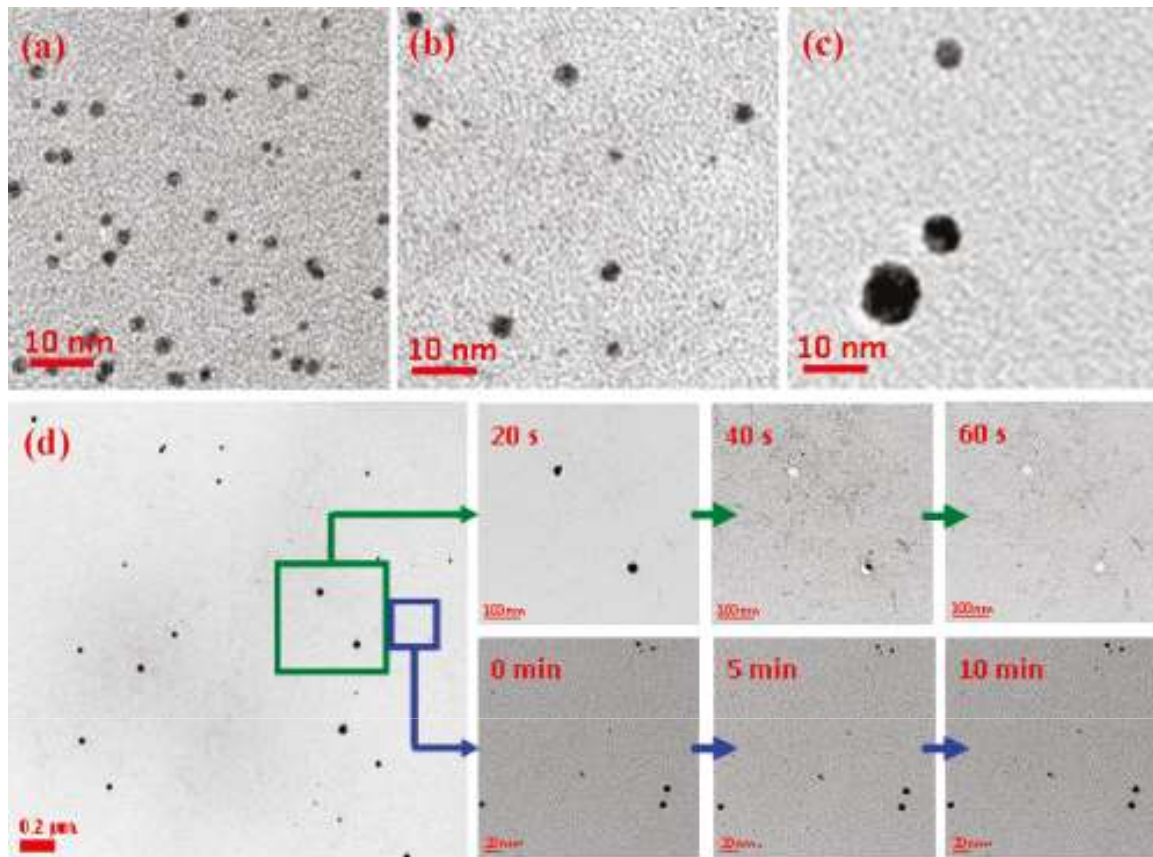


Figure 4. TEM images of Ag-PVA film immersed for 12 min in (a) pure water, (b) an aqueous solution of 1 ppm  $\text{Hg}^{2+}$  ions and (c) an aqueous solution of 1 ppm Hg (with trace PVA); scale bar = 10 nm. (d) Temporal evolution of different nanostructures in the film immersed in the  $\text{Hg}^{2+}$  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).



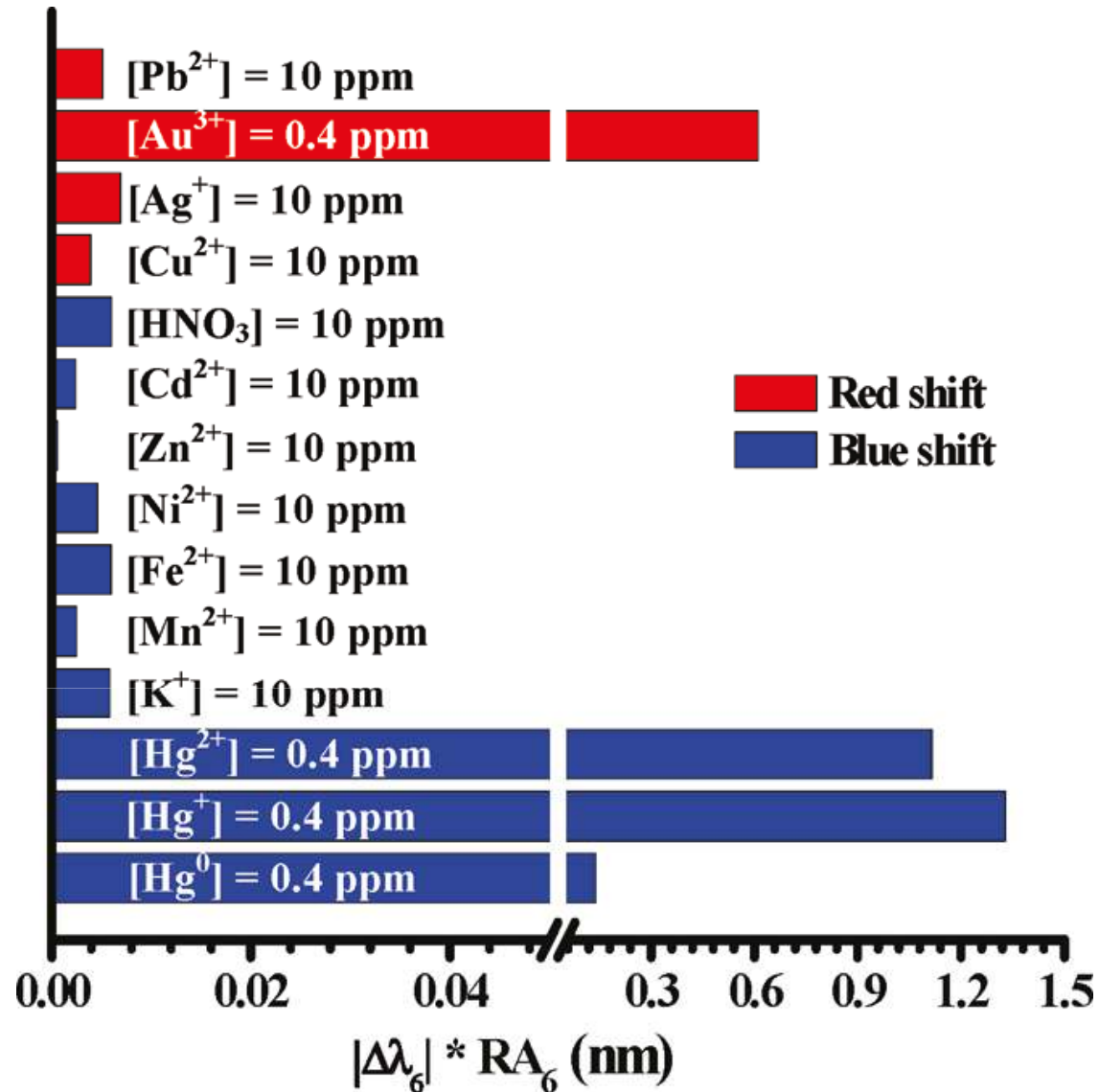


Figure 5. Comparison of the response of the Ag-PVA film sensor,  $|\Delta\lambda_6| * RA_6$  (see text for definition) to different analytes; the concentration level of the aqueous solutions are indicated in terms of the metal ion or the molecule in the case of  $HNO_3$ .

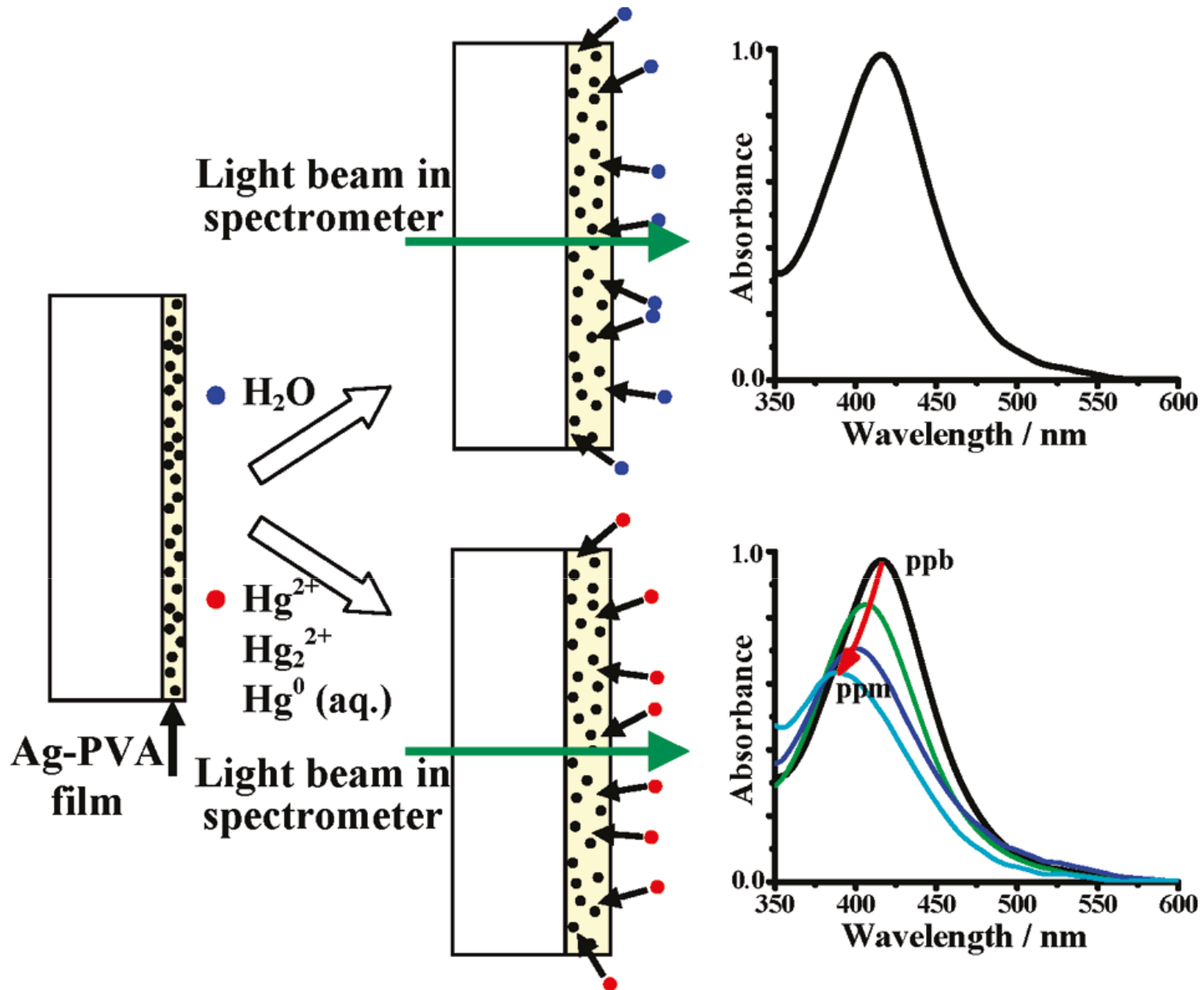


Figure 6. Schematic representation of the swelling of the Ag-PVA film in aqueous medium and the sensitive changes in the SPR spectrum of the film induced by Hg<sup>2+</sup>/Hg<sub>2</sub><sup>2+</sup>/Hg<sup>0</sup> in the solution.

# 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**