

Fiber Optic Based Evanescent Wave Sensor for the Detection of Elemental Mercury Utilizing Gold Nanorods

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ABSTRACT

Mercury is a well-studied neurotoxin that is of particular concern to infants and pregnant mothers. Nearly half of the anthropogenic mercury that is released into the environment comes from the combustion of fossil fuels, mostly coal to provide electrical power [1]. Additionally recent regulations in the United States have renewed focus on the monitoring and emissions of mercury from these large stationary combustion sources [2]. Current methods for mercury detection either do not have sufficient sensitivity for ambient measurements near sources or are complicated and costly [3]. We developed a fiber optic based sensor for the detection of atmospheric elemental mercury that uses gold nanoparticles as the sensing medium. Previous work established that the localized surface plasmon resonance peak blue-shifts when exposed to mercury in an aqueous environment, with the addition of a reducing agent [3][4]. Fiber optic evanescent sensors have been used as chemical and biological sensors [5] [6]. Combining these two results has allowed us to develop a stable mercury sensor with a sensitivity in the micrograms per cubic meter range, comparable to commercial sensors, at a fraction of the cost.

Keywords: mercury, gold nanoparticles, environmental sensing, fiber optic evanescent wave sensor

1 INTRODUCTION

Mercury has been well established as a neurotoxin that has been linked to a variety of health effects. It is of particular concern to infants and pregnant mothers, due to the vulnerabilities of the developing nervous system. The majority of the anthropogenic mercury is released by coal combustion, which undergoes a complex, and still under study process, where it is transported through the environment. Much of the mercury ends up bioaccumulating in fish, a concern to human populations [1]. Recent regulations in the United States have renewed interest in monitoring and controlling mercury emission from power plants [2]. While highly variable, the concentration of mercury in the exhaust is typically around 1-20ug/m³ [7],

and atmospheric concentrations of mercury are typically lower, around 1ng/m³ [8]. Current methods for mercury detection either do not have sufficient sensitivity for ambient measurements near sources or are complicated and costly [3].

Mercury has a well-known and studied affinity for gold, readily forming an amalgam [9], and the high sensitivity of the longitudinal localized surface plasmon resonance, LSPR, of noble metal nanorods to changes in aspect ratio and dielectric constant [10], make gold nanorods a particularly well suited medium for sensing elemental mercury. Previous work has detected mercury with gold nanoparticles [3] [4], though in an aqueous environment, where there are concerns about stability of the particles and practicality of the method.

Stripped fiber optic evanescent wave sensors provided a convenient and versatile sensing platform, and have been used to detect a variety of chemical and biological substances [5][6]. The evanescent wave which extends from the fiber optic core has a penetration depth given by [11] :

$$D_p = \frac{\lambda}{2\pi n_1 (\sin^2 \theta - \sin^2 \theta_c)^{0.5}} \quad (1)$$

Where λ is the wavelength, n_1 is the refractive index of the fiber, θ is the angle between the interface and the ray path, and $\theta_c = \arcsin(n_2/n_1)$, with n_2 being the refractive index of the surrounding material. For the system investigated here, a silica fiber core surrounded by air, the evanescent wave will extend between 400nm and 100nm from the boundary of the fiber at the resonance peak of the gold nanorods, around 750nm. Thus the stripped fiber optic cable provides an excellent platform for coupling light from the fiber optic cable into the nanorods. Additionally, it provides a convenient means to both expose and measure absorption changes in the nanorods.

2 EXPERIMENTAL

600 μm inner diameter plastic clad silica fiber optic cables were purchased from ThorLabs. The cables were cut to approximately 25cm, and an approximately 5 cm section of cladding from the middle of the cables was removed by heating with small gas-oxygen torch followed by rinsing with deionized water and careful rubbing with tissue wipes. The gas-oxygen torch was also used to heat this decladded section of the fiber in order to bend it into U-shape.

After the cables were fabricated gold nanorods were attached to the bare portion of the fiber optic cable using a method derived from Frederix et al. [12]. Briefly, the cables were cleaned in a mild detergent and Millipore purified water. They were then further cleaned in 2M NaOH for 1 hour, and a further treatment in a 1:1:5 solution of H_2O_2 , $\text{NH}_3(\text{aq})$ and H_2O for 7min at 80 $^\circ$ -90 $^\circ$ C to provide a fresh oxide layer. The cable was then rinsed again in Millipore water and dried before being immersed in a 95:5 methanol, water solution with 2% (v/v) of 3-mercaptopropyl)methyltriethoxysilane. The sample was left overnight, then removed and rinsed in 1ml of methanol, before being annealed for 10min at 105 $^\circ$ C. At this point reference spectra were obtained before the nanorods were applied.

Nanorods were Nsol brand polymer stabilized nanorods from Nanopartz, with a diameter of 25nm and an axial length of 86nm. The concentrated nanorods were diluted 1:90 with ethanol, this ratio providing a good balance between aggregation of the nanoparticles and sufficient coverage to provide a strong absorbance response. 400 μl of the diluted nanorod solution was applied to the bare, salinized, fiber optic section drop wise from a pipette, set overnight, and then rinsed with 1ml of Millipore water to remove excess particles. A schematic of the final device is given in figure 1:

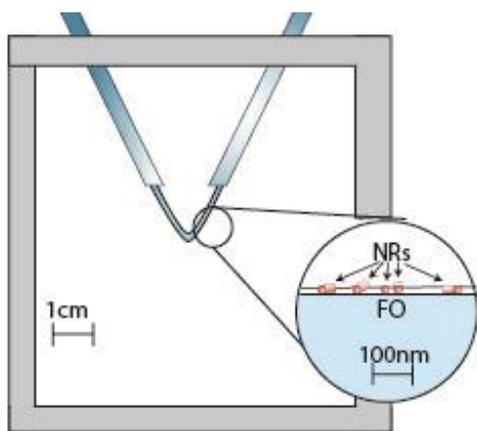


Figure 1: Schematic of sensor. The box around the sensor represents the HDPE container used to protect the delicate fiber optic.

Exposing the functionalized fiber optic cable to a known and controlled amount of mercury vapor is key to validating its response as a sensor. To achieve this, the sensor was installed into an enclosed flow system, which made use of a Vici brand Permeation Tube. This permeation tube contains a saturated two-phase mixture of mercury liquid and vapor inside a membrane permeable to the vapor phase. The entire exposure apparatus is shown in figure 2.

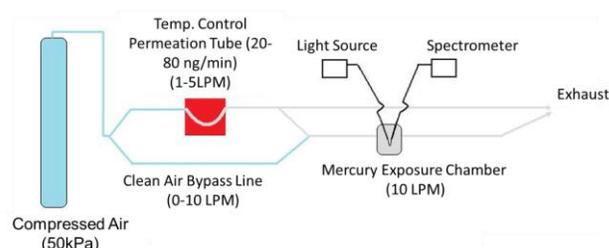


Figure 2: Schematic of exposure set up

3 RESULTS

Upon exposure to mercury vapor the Longitudinal Localized Surface Plasmon Resonance Peak, LSPR, of the sensor showed a measurable blue shift, as shown in figure 3.

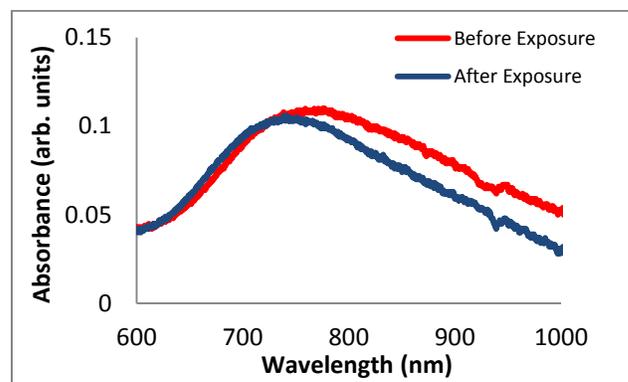


Figure 3: Blue shift of gold nanorods on a fiber optic sensor after exposure to 15 $\mu\text{g}/\text{m}^3$ of Hg for 90min.

Since the shift in the LSPR peak is proportional to the mass of the mercury adsorbed onto the nanorod surface, and before saturation, the rate of mercury adsorbed is limited by diffusion to the surface, it is then possible to relate the rate of peak shift to the concentration of mercury in the air. This provides a mechanism for calibrating the sensors. Sensors were exposed to a range of concentrations, and a generally monotonic trend with increased shift rate and increased concentration was found, shown in figure 4.

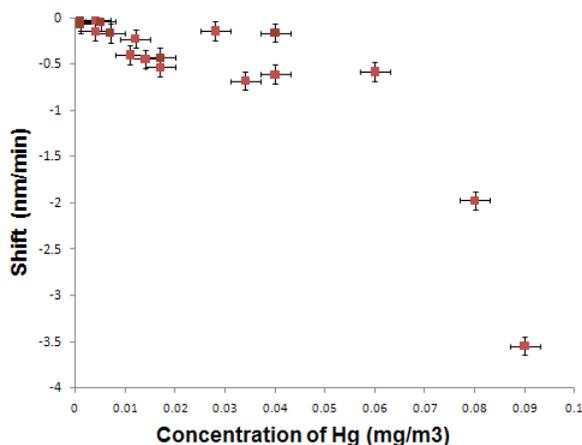


Figure 4: Shift rate of the LSPR peak of the fiber optic sensor versus concentration of mercury in the air stream.

4 CONCLUSION

We have demonstrated a highly sensitive mercury vapor sensor, that is straightforward to operate and easy and inexpensive to fabricate. There is still further work needed in refining the calibration of the sensor, and the consistency of response, though the sensitivity of this system along with its easy of manufacture and operation suggests that it could prove valuable in the detection of mercury in the environment.

Acknowledgements

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