Localized Surface Plasmon Resonance based Photonic Crystal Fiber for Cadmium Detection

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Abstract

In this work, fabrication of Localized Surface Plasmon Resonance based fiber optic sensing probe for cadmium detection in an aqueous solution is reported. Multimode fiber-photonic crystal fiber-multimode fiber structure coated with gold nanoparticles make up this probe. The proposed sensor's sensitivity is 1.564 nm/ppm. Furthermore, the sensor is small in size, immune to electromagnetic interference, making it ideal for a wide range of harsh environments and real-time measurement.

Key Words: Optical Fiber, Photonic Crystal Fiber, Sensors, Environmental Monitoring.

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Introduction

The growth of human societies was accompanied by a development in all areas of life, especially in the field of the industrial sector due to the urgent need for many industrial products, and this led to the need to pay attention to controlling levels of environmental pollution resulting from the use of many mineral elements in the industry, despite the various harmful effects on health Mankind (Ghaedi *et al.*, 2011) (Gupta, Jain and Kumar, 2006) (Kazemi, Shamsipur and Sharghi, 2009); As cadmium is one of the most important pollutants available in abundance in industrial products, such as the manufacture of electroplating, batteries and many chemical industries, (Fthenakis, 2004)and in some foodstuffs or living creatures that are a food source for many peoples such as shellfish and its kinds, mushrooms and herbs Marine and cocoa powder and others (Chuen, 2017) and it will move to the human body and concentrate in the nervous system, causing cancer. As a result, detecting and quantifying cadmium pollution is becoming more essential as environmental concerns and health safety become more relevant. Generally, atomic absorption spectroscopy (Jarzyńska and Falandysz, 2011) and electrochemical, as well as inductively coupled plasma mass spectrometry (Jarzyńska and Falandysz, 2011) have been employed to determine cadmium (Bakhtiarzadeh and Ab Ghani, 2008). Most of the techniques mentioned above have a high cost, difficult experimental work conditions, and the long time required to conduct measurements, so it was necessary to suggest alternative measurement methods that are easy and less expensive. This research relied on using optical fibers to detect cadmium in water. Fiber optic sensing probes technology has unique advantages such as high sensitivity, rapid reaction, small size, electromagnetic interference isolation, and easy production, which has overcome the disadvantages of the above-mentioned conventional methods (Vargas-Rodriguez *et al.*, 2015) (Zhou *et al.*, 2015).

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Optical absorption (Memon *et al.*, 2017), fiber modal interference (Zhao *et al.*, 2017), fiber grating (Sarkar *et al.*, 2015), plasmonic(Coelho *et al.*, 2015) and fluorescence (Tan, Zhang and Chen, 2011) detection methods are among the many technologies of fiber optic technologies which were suggested. Due to their small size, low cost, and flexibility, localized surface plasmon resonance (LSPR) sensors have piqued interest among various types of fiber optic sensing probes (Hu *et al.*, 2019). Light can be propagated from the core of the metal fiber to the metal, which is used for SPR excitement, using a number of schemes, such as side polishing (Jing *et al.*, 2019), fiber's etching (Coelho *et al.*, 2015), the use of tilted fiber Bragg grating (Caucheteur *et al.*, 2011)or long period fiber grating (Hu *et al.*, 2014), also utilizing distinctive fiber like photonic crystal fiber (PCF) (Rifat *et al.*, 2018).

PCF-based LSPR sensors stand out among these systems for a variety of reasons, including the ability to easily handle fiber optic dispersion by properly designing the sizes and locations of the air-holes in order to promote phase matching and coupling between the leaky core mode and SPP mode. Plasmonic PCF are particularly appealing because of their flexibility, which includes monomodal behavior, high nonlinearity, and highly controlled birefringence.

A fiber optic localized surface plasmon resonance (LSPR) cadmium sensor with a multimode fiber-photonic crystal fiber-multimode fiber (MMF-PCF-MMF) structure is described in this article. The metal substance used to stimulate LSPR is typically silver or gold. Silver, on the other hand, is simpler to rust than gold. As a result, gold is increasingly often utilized as a coating material. The (MMF- PCF-MMF) structure is coated with gold nanoparticles (Au-NPs) in this study, and the effect of the thickness of the (Au-NPs) on the cadmium sensing performance of the as-fabricated LSPR sensing structure is studied.

Material and Methods

Operation Principle of Sensor Configuration

As light travels through the photonic crystal fiber core, some of this light penetrates the cladding and interacts with the metal coated over the exposed fiber core at an angle of θ. Surface plasmon resonance (SPR) occurs when the value of θ is the same as that of the resonance angle, resulting in the excitation of surface plasmons in the metallic material. These excited surface plasmons will generate a localized strong electromagnetic field which will scatter light, resulting in the formation of flour absorption bands at certain resonant wavelengths (Tu, Sun and Grattan, 2012). Differences in concentration of the surrounding environment will affect the wavelength at which flour absorption occurs resulting in a difference in the resonant wavelength of the absorption bands (Homola and Piliarik, 2006).

Synthesis of Gold Nanoparticles AuNPs / PVP

In a two-electrode electrochemical cell, gold nanoparticles are synthesized using the Electrolysis process as seen in the Figure 1.a. Two electrodes of 99% purity gold were made, one anode and the other as a cathode, and the two electrodes were immersed vertically face-to-face at a constant distance of 4 cm in distilled water. The electrodes (gold) are electrically connected to the electric voltage through the voltage regulator. When a voltage of 30 volts is applied to gold, the crystal structure of the metal is broken, and gold begins to vaporize, condensing into pure water to form colloidal particles. Thus, we got the gold solution and tested the size of the minutes in the simplest way, which is to pass the laser through the solution. The laser beam appeared as a straight line along its path through the colloidal solution of the gold nanoparticles, as shown in Figure 1.b, which indicates that the particles are of the nanoscale size. The prepared gold nanoparticle colloidal solution is taken and dissolved in it (0.1 g) of the polymer (PVP) at a temperature of (60-70 degrees Celsius). At that time, a polymer is obtained with nanoparticles in gold (Au-NPs/PVP). After that, the solution was cooled down to room temperature while being stirred continuously. The diameters of the NPs reported in this work are 15 and 30 nm, as shown in Figure 1.d using transmission electronic microscopy (TEM). The picture shows that the particles are roughly spherical. The prepared (Au-NPs/PVP) colloid was stored at room temperature as shown in Figure 1.c.

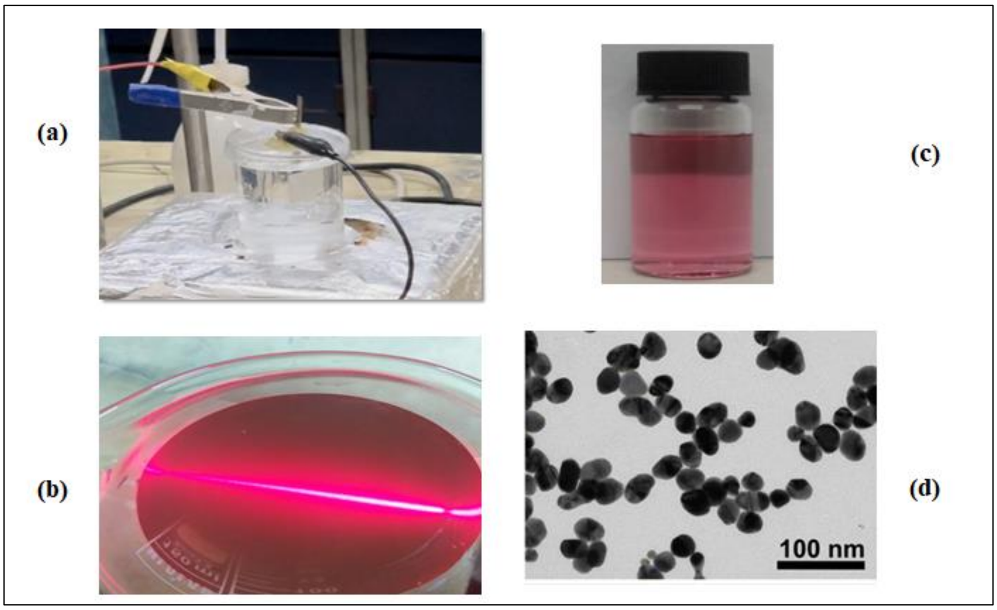

Figure 1. (a) photograph of Au nanoparticle synthesis in distilled water by two-electrode **electrochemical** cell. (b) Mechanism for testing the particle size of Au-nanoparticle. (c) Colloidal Solution. (d) TEM image of Au nanoparticle.

Preparation of Heavy Metal solutions with Water

Heavy metals polluting the environment, such as cadmium (Cd) was used in this work. Tables (1) shows certain properties of cadmium (Ernst, 1996). Cadmium Solution was prepared with 1ppm concentration by dissolving a 1mg of cadmium nitrate ($Cd(NO_3)_2$) in 1L of distilled water and then stirred using magnetic stirrer until dissolved. This step was repeated to prepare 2ppm, 3ppm, and 4ppm cadmium solution concentration. Figure) shows pictures of heavy metal solutions(cadmium).

Table 1. Some characteristics of the cadmium metal

Atomic number	**48**
Atomic weight	**112.414**
Atomic radius(nm)	**0.151**
Crystal structure	**HCP**
Melting point(K)	**594.22**
Density (g/cm^3)	**8.65**
Electrical Resistivity (10^{-9} ohm. cm) at 300K	**72.7**
Thermal Conductivity (W/m. K) at 300K	**96.6**

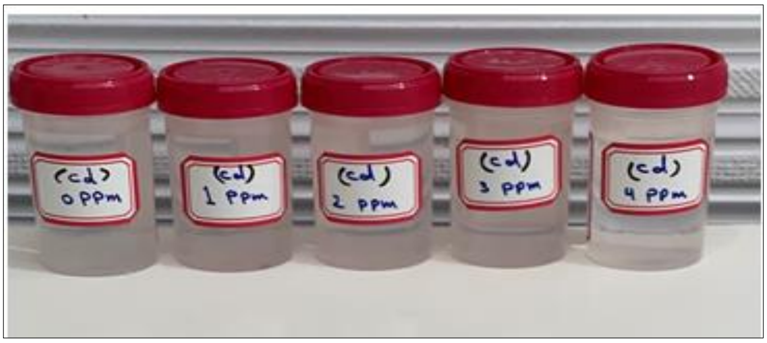

Figure 2. Photographic images of Cd heavy metal solutions with different concentrations in distilled water

Sensing Fabrication and Coating

The sensing probe mainly consists of a piece of a single mode photonic crystal fiber (PCF) spliced between two common multimode fibers MMFs (62.5mm core diameter and 125mm cladding diameter). The first step in this sensor fabrication is removing the coating of the PCF by optical fiber stripper (JIC - 375 Tri - Hole) (by Fujikura Corporation), and the Fiber Cleaver (CT-30) was used to cut the part (PCF) to the length required and by an angle of 90 ° to create to achieve a perfectly flat and smooth end face. Two MMFs and a PCF have been fusion-spliced via commercial fiber splicer (FITEL-S178) in the manual mode (Fujikura FSM-60S). The cladding of the sensing region was etched from 125 to 18 μm by a chemical etching process to boost the efficiency of the sensing probe

and make it more sensitive to heavy metals.
Finally, Au NPs colloid with a thickness (40 nm) has been coated on PCF's surface via the use of the immersion method. Also, the gold was selected since it is providing high sensitivity and good stability compared to other often utilized LSPR coating materials, like copper and silver. The summery of these steps are shown in Figure (3). Using the same these above steps, (PCF) sensing probe was fabricated but it was coated with 75 nm of the synthesized (Au NPs/PVP).

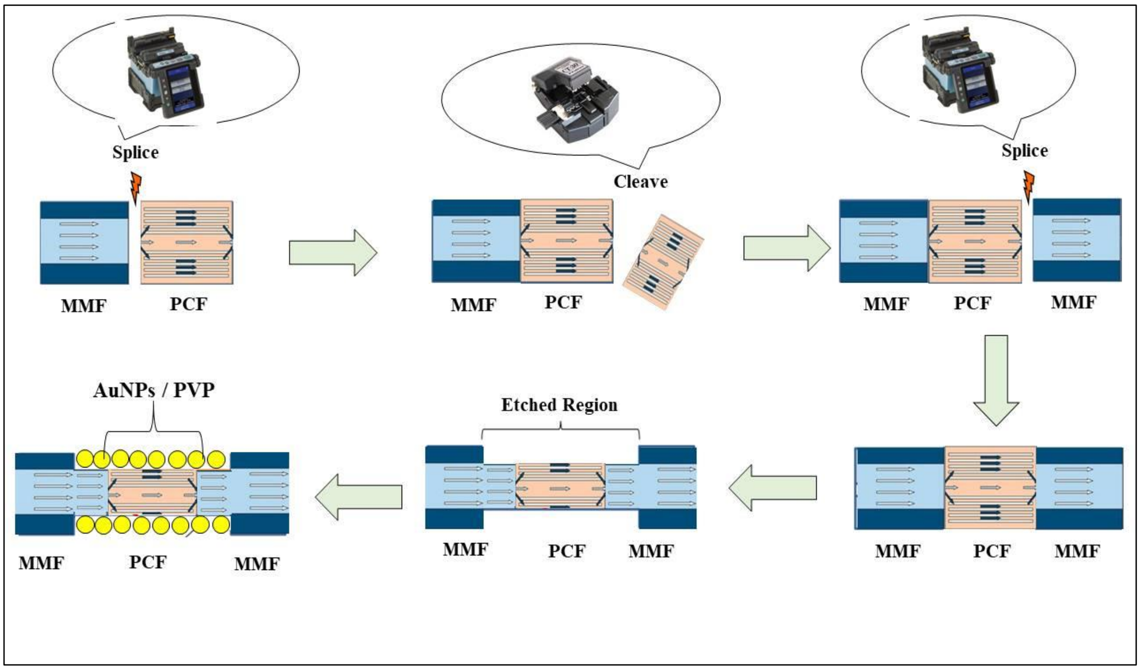

Figure 3. The fabrication process for photonic crystal fiber sensing probe

Experimental Set-up

The experimental set-up for evaluating the performance of (PCF) sensing probes fabricated in this work and which were illustrated in section (2.) are presented in Figure (4). As illustrated in Figure (4), one end of the MMF is connected to one end of a 2x1 fiber coupler and it is illuminated by light from a blue laser source (450nm and 50mW) connected to the other end of the coupler. In order to evaluate the (PCF) sensing probe performance, the sensor probeis installed in the plastic container and filled it by distilled water. The other end of the MMF is connected to the optical spectrum analyzer (OSA) with a precision of (0.065nm), which is provided by the Ocean Model (2000) company to monitor the difference in the transmission spectrum at the output. At the beginning of the work, the spectrum of distilled water was recorded to become the reference sample, after that the resulting transmission spectrum was continuously monitored with different concentrations of cadmium (Cd). Before each measurement, the (PCF) sensing probe is cleaned with distilled water to prevent residual mineral residues from remaining on the fibers. The spectral curves for each concentration are shown on the computer screen connected to the spectroscope according to a special analyzer program prepared by the analyzer manufacturer, which is a specially designed program provided by Ocean Optics for Real time spectrometer data acquisition. All spectra are subsequently processed with MATLAB (MathWorks) and mapped with Origin Pro 8 (Origin Lab).

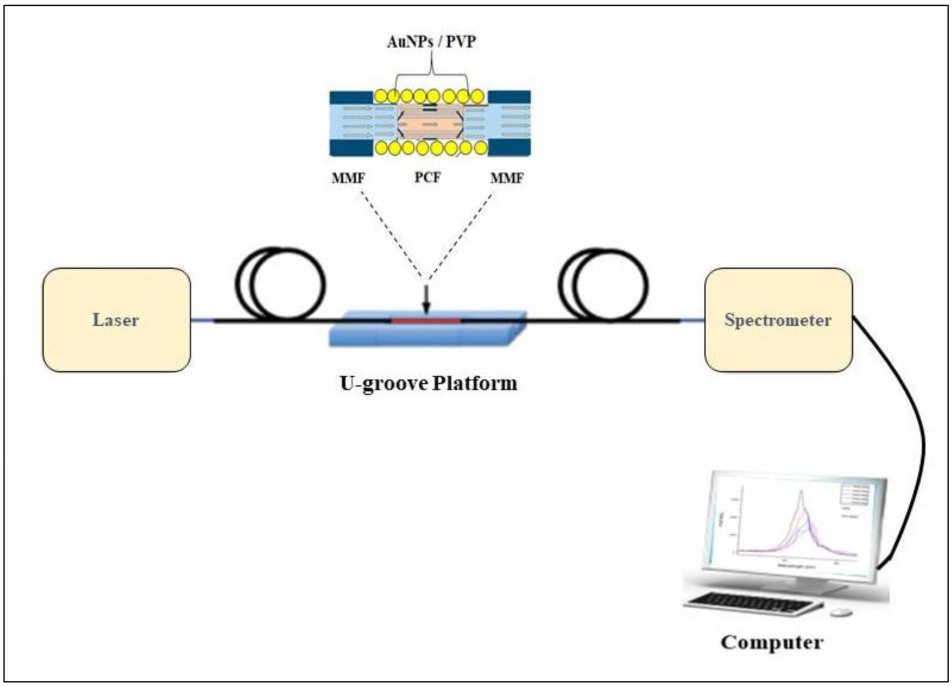

Figure 4. Schematic diagram of the (PCF)sensing probe

Result and Discussion

Characterization of (Au-NPs/PVP)

The absorption spectrum for (Au-NPs/PVP) solution is measured using (T60 UV-VIS-Near IR) spectrophotometer, over the wavelength range from 200 nm to 1100 nm. The UV-VIS spectrum of the (Au-NPs/PVP) shows a LSPR peak at a wavelength of 525 nm, as illustrated in Figure (5). Absorption is ascribed to the characteristic Localized Surface Plasmon Resonance (LSPR) absorption of prepared gold nanoparticles (Au-NPs/PVP). The presence of only one LSPR peak in the entire spectrum confirms the (Au-NPs/PVP) to be symmetric.

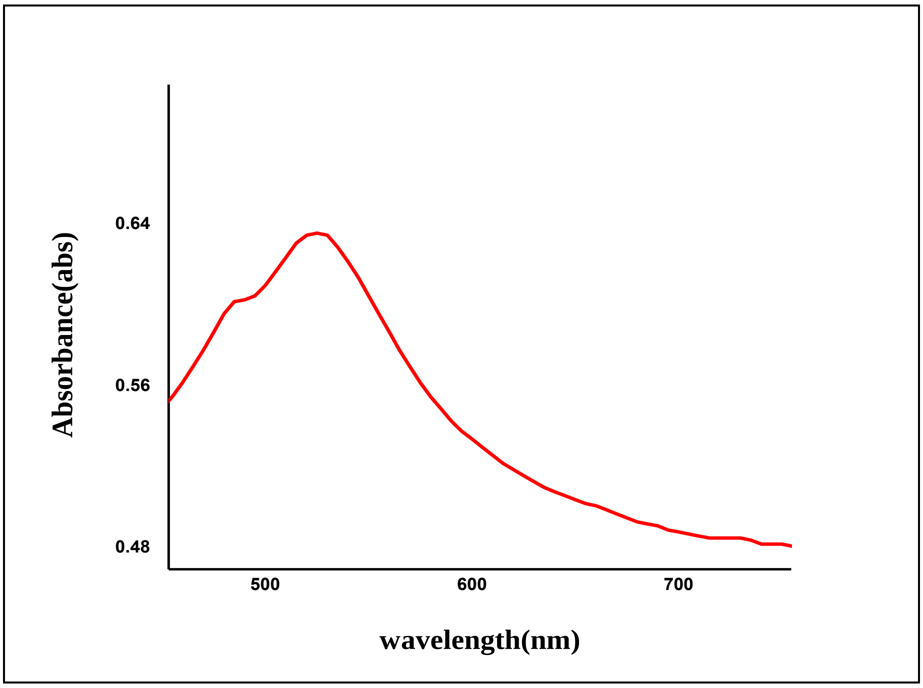

Figure 0. UV-VIS spectrum of the (Au-NPs/PVP)

Heavy Metal ion Detection Ability of Au NP-coated Fiber

A fiber optic sensing probe was prepared for the detection of heavy metal ions, as stated in section (2). The features of these cadmium ion detecting probes will be discussed.

- *Characterization for Cadmium ions*

For the characterization of cadmium ions fiber optic sensing probes, LSPR curves were recorded for cadmium ions concentrations in distilled water varying from (0-4) ppm at room temperature. Figure (6) shows the LSPR spectra for (PCF) sensing probe coated with Au NPs colloid with thickness (40 nm). The LSPR spectra indicate a redshift in the LSPR spectrum or resonance wavelength with rising cadmium (Cd) solution concentration, which is the consequence of increasing the dielectric constant of Au NPs colloid as cadmium (Cd) solution concentration rises (Jorgenson and Yee, 1993) (Singh, Mishra and Gupta, 2013).

As previously stated, all of the solutions produced had the same refractive index within the refractometer's precision, thus the red shift in the LSPR spectra is due to an increase in the concentration rather than a change in the solution's refractive index.

As the concentration of ions rises, heavy metal (cadmium) ions bind on the sensing probe surface (Au NPs colloid), causing a change in the dielectric characteristics of the (Au NPs colloid) and therefore a shift in the resonance wavelength. Higher concentrations of heavy metal ions attach to the surface of the (Au NPs colloid), causing a significant shift in the spectrum's resonance wavelength.

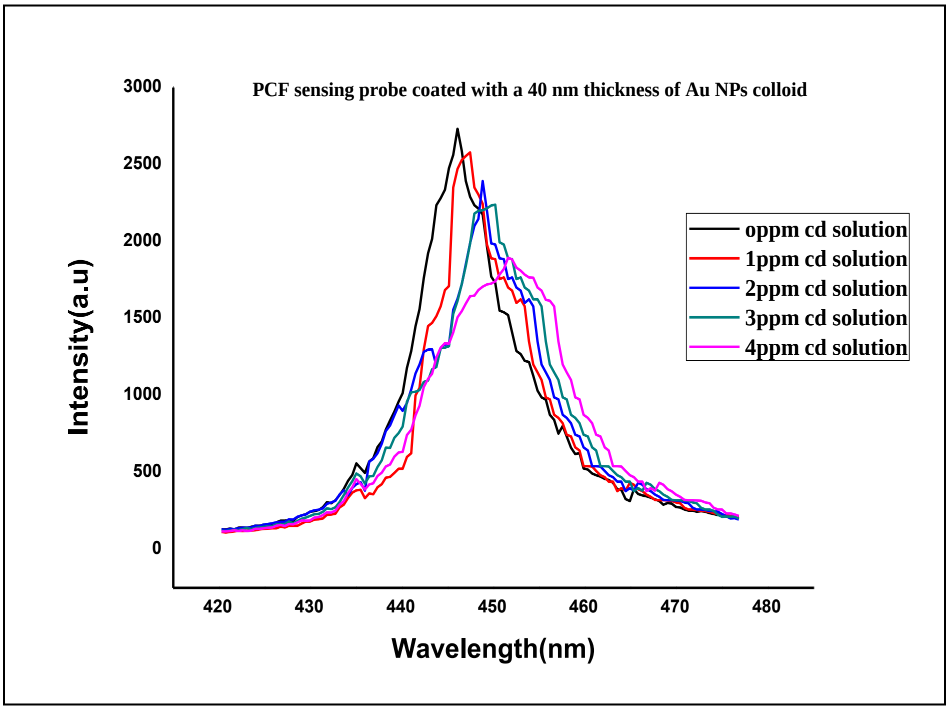

Figure 6. Response of photonic crystal fiber coated with Au NPs colloid (40 nm) in different concentrations of cadmium solution

The LSPR spectra for the detecting sensor (PCF) were collected in order to examine the function of increasing the thickness of the (Au NPs) colloid (75 nm). Figure (7) shows the LSPR spectra for this probe for various concentrations of (cadmium) ions (between 0 ppm and 4 ppm). Because of the binding of (cadmium) ions on the sensing probe surface (Au NPs colloid), the LSPR curves move toward higher wavelengths, similar to Figure (6), although the shift in SPR spectra is larger than that of Figure (7). This suggests that the thickness of the (Au NPs colloid) is essential in the binding of heavy metal ions, resulting in a red shift in LSPR curves. This implies that thickness of the (Au NPs colloid) plays an important role in the binding of heavy metal ions i.e. red shift in LSPR curves. Therefore, the (PCF) sensing probe coated with Au NPs colloid with diameter (75 nm) shows large shift in LSPR spectra. This is in agreement with the earlier reported results(Rai *et al.*, no date).

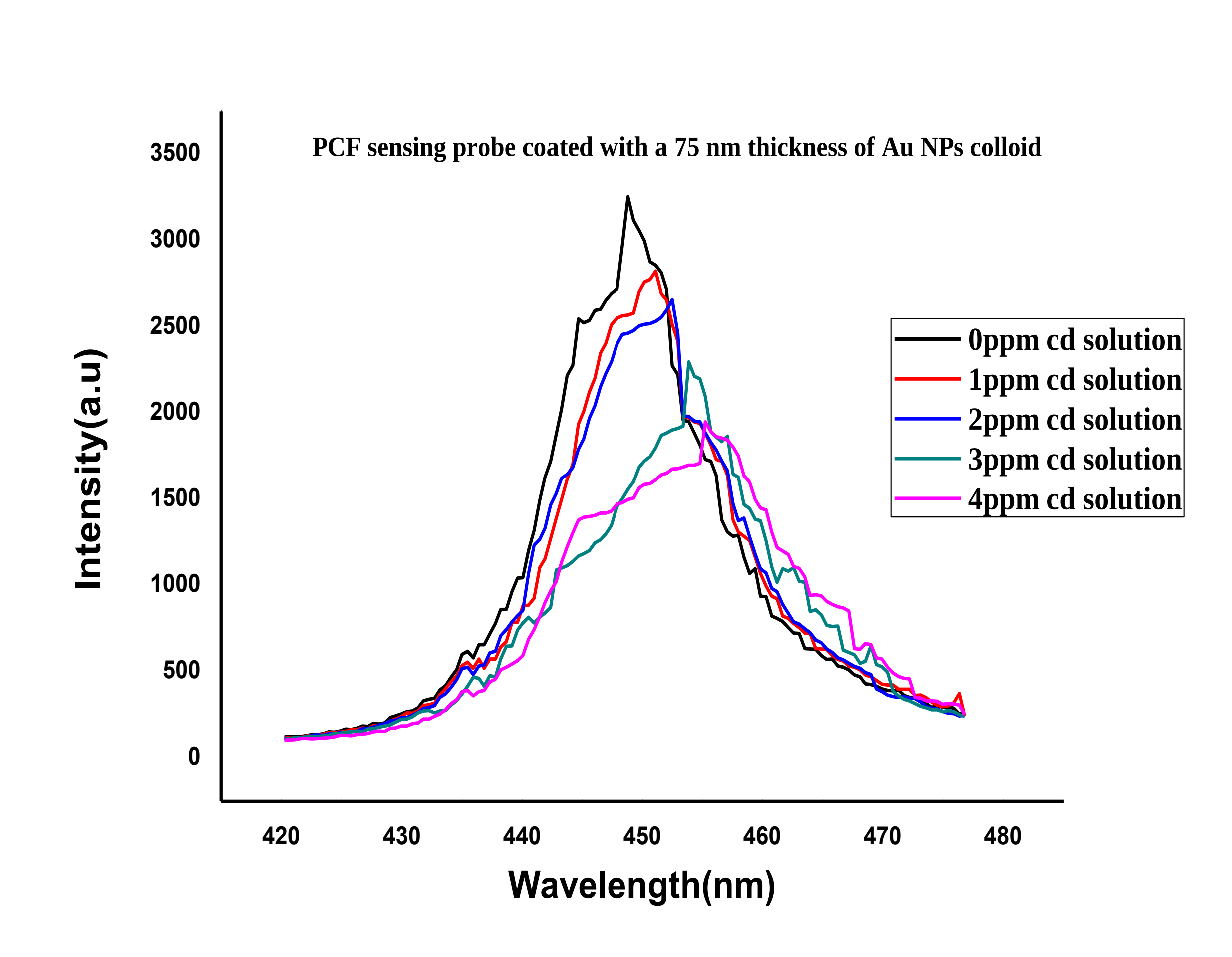

Figure 7. Response of photonic crystal fiber coated with Au NPs colloid (75 nm) in different concentrations of cadmium solution

The LSPR curves widen as the concentration of (Cd) ions rises, as can be seen in Figures (6) and (7). The increase in the number of reflections in the sensing area or the rise in the refractive index of the sensing medium causes the widening of LSPR curves. Because the same probe was used for all of the LSPR curves, the number of reflections in the sensing area is fixed in this instance. As a result, the sole explanation for the widening of the LSPR curves is a rise in the sensing layer's refractive index owing to an increase in the concentration of (Cd) ions. In other words, when the concentration of (Cd) ions rises, so does their interaction with the Au NPs colloid, which raises the Au NPs colloid's refractive index.

- *Resonance Wavelengths*

The resonance wavelength is the wavelength at which the LSPR curve reaches its greatest intensity. Figures (6) and (7), which correspond to each concentration of cadmium ion and their LSPR spectra, were used to determine these wavelengths. Furthermore, the shift in resonance wavelength for each concentration was determined by using the resonance wavelength for zero ion concentration as a reference for each kind of probe. Figure 1 shows how the shift in resonance wavelength varies with cadmium and zinc ion concentrations (8). The experimental data points for probes are solid squares and solid circles, whereas the best fit to data points is continuous lines.

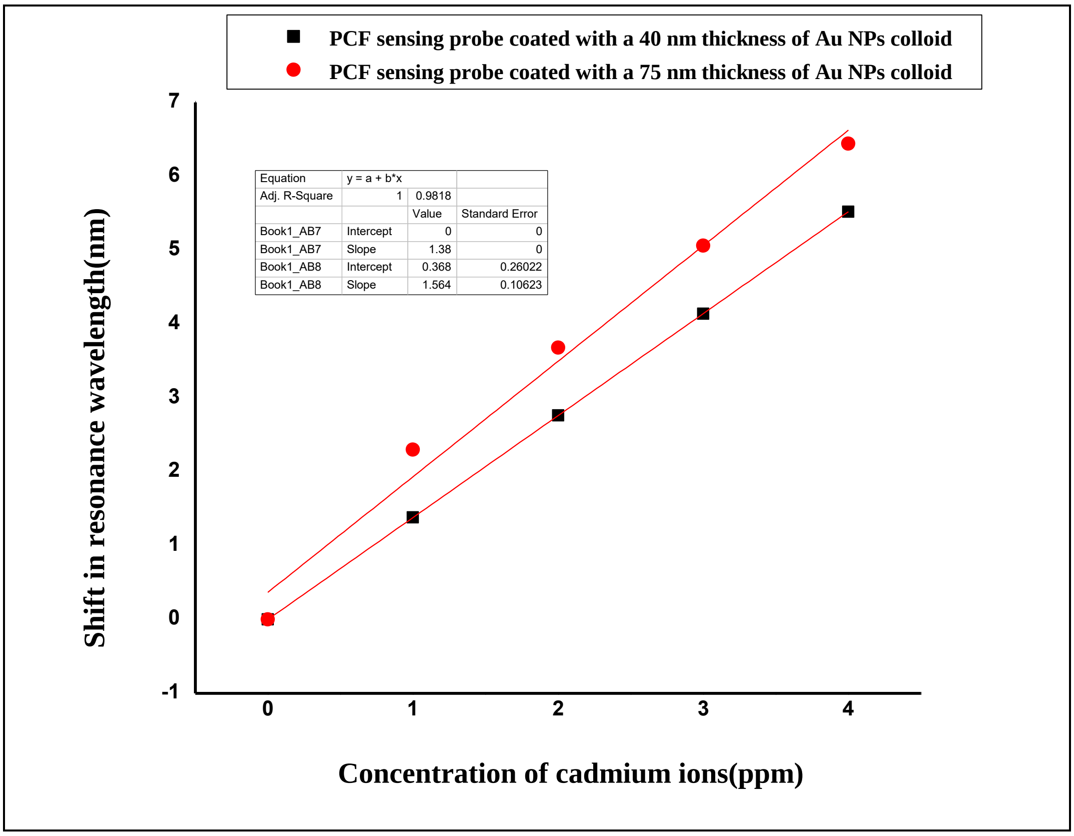

Figure 8. Shift in LSPR wavelength in different concentration of cadmium ion

Figure (8) shows that as the concentration of metal ions in the solution rises, so does the change in resonance wavelength. Furthermore, the change in resonance wavelength for a given concentration of metal ions is greatest for PCF sensing probe coated with Au NPs colloid with diameter (75 nm) for the tested heavy metal ions. This indicates that the Au NPs colloid, on its own merits, plays a significant part in the increase in the shift in the resonance wavelength.

Furthermore, the LSPR curves for probes coated with Au NPs colloid with diameter (75 nm) are more wide and shifted than those for probes coated with Au NPs colloid with diameter (50 nm) (40 nm). This is because to the high index of coated, which causes the SPR curves to widen and the shift in resonance wavelength to increase (Kim et al. 1999).

- *Characteristic Properties of the Sensor*

The sensor's sensitivity is measured in terms of the change in resonance wavelength per unit change in sample concentration or refractive index. The cadmium ion sensitivity of sensor probe coated with 40 nm Au NPs colloid was estimated from the slope of the linear fitting of LSPR red shift, yielding 1.38 nm/ppm, whereas the sensitivity of sensor probe coated with 75 nm Au NPs colloid yields 1.564 nm/ppm.

Conclusion

A highly sensitive heavy metals sensor based on a sensor probe and a Au NPs colloid acting as a cladding layer has been successfully developed in this contribution. An experimental cadmium sensing contrast was performed using an etched sensor probe coated with 40 nm of the Au NPs colloid and an optical fiber structure with the same structure but 75 nm of the Au NPs colloid coating. The coated PCF coated with 75 nm of the Au NPs colloid showed much higher sensitivity, according to the findings.

Declaration of Competing Interest

The authors declare that there are no conflicts of interest.

Acknowledgements

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