

Proceedings

# Highly Sensitive Hydrogen Sensor Based on Palladium-Coated Tapered Optical Fiber at Room Temperature †

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**Abstract:** This paper describes the application of a palladium (Pd)-coated tapered optical fiber in order to develop a hydrogen (H<sub>2</sub>) sensor. A transducing channel was fabricated with multimode optical fiber (MMF) with cladding and core diameters of 125 μm and 62.5 μm, respectively, in order to enhance the evanescent field of light propagation through the fiber. The multimode optical fiber was tapered from a cladding diameter of 125 μm to a waist diameter of 20 μm, waist-length of 10 mm, and down taper and up of 5 mm, and coated with Pd using the drop-casting technique. In order to establish the palladium's properties, various characterization techniques were applied, such as Field Emission Scanning Electron Microscopy (FESEM), Energy Dispersive X-ray (EDX), and X-ray Diffraction (XRD). The developed palladium sensor functioned reproducibly at a gas concentration of 0.125% to 1.00% H<sub>2</sub> at room temperature in the synthetic air. In this case, the response and recovery times were 50 and 200 s, respectively. Furthermore, this study demonstrated that the production of a dependable, effective, and reproducible H<sub>2</sub> sensor by applying a basic, cost-effective method is possible.

**Keywords:** tapered optical fiber; hydrogen (H<sub>2</sub>); palladium (Pd); drop-casting technique

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## 1. Introduction

Hydrogen (H<sub>2</sub>) has a high energy content, making it an ideal clean fuel with several application potentials in different industries [1]. The combustion of hydrogen in the air creates water, a common earth element; H<sub>2</sub> can hence be sourced from water, hydrocarbons, and biomass. H<sub>2</sub>, a clean source of energy, can be utilized to fulfil the ever-increasing demand for energy. However, hydrogen is flammable at concentrations >4 vol% in the air and can explode at a wider range of 15–59 vol% at standard pressure [2]. Therefore, effective H<sub>2</sub> monitoring systems must be developed to help identify leakages arising from the invisible, flammable, and odourless nature of the gas.

On the other hand, optical sensors rely on the use of optical fibers that offer interesting properties, such as lightweight, small size, resistance to electromagnetic interference, instability, and

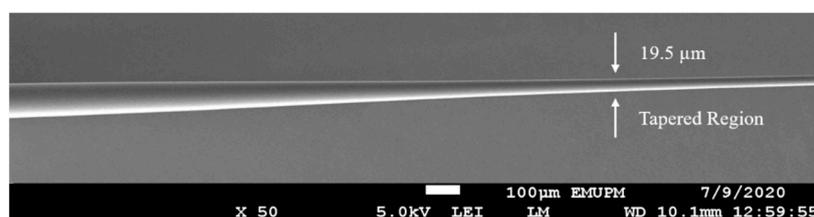
rigidity in harsh environments [3]. These interesting properties make optical fibers ideal candidates for sensing in a rugged environment [4]. Palladium (Pd) is currently receiving interest in many applications, such as H<sub>2</sub>, the hydrogenation process, and the detection of H<sub>2</sub>. The high sensitivity, good selectivity, and ability to operate at room temperature of Pd nanoparticles make it the ideal and noble metallic catalyst for H<sub>2</sub> sensing [5].

In recent years, several hydrogen optical sensors have been reported using palladium as an energy transformer. Most of them rely on fiber gratings (FBGs) [6] and plastic optical fibers [7]. Most fiber-optic sensors need some modification to the cladding to make it sensitive to its surroundings [8]. These modifications include chemical etching [9], side polishing [10], or shape-D [11]. In this research, dissolved tapered optical fiber-coated palladium is used to detect gaseous hydrogen.

## 2. Experiments

### 2.1. Fabrication of Tapered Optical Fiber

The H<sub>2</sub> gas sensor was fabricated using multimode optical fiber (MMF) with cladding and core diameters of 125  $\mu\text{m}$  and 62.5  $\mu\text{m}$ , respectively, as a transducing platform. Tapered MMF was used as the transducing platform. The tapering was done using the Vytran glass processing machine (Vytran GPX-3400). The machine works based on the heating and pulling process, using a graphite filament as a heater to achieve the desired geometry of the tapered profile. The MMF was tapered from a cladding diameter of 125  $\mu\text{m}$  to a waist diameter of 20  $\mu\text{m}$ , waist-length of 10 mm, and down taper and up of 5 mm. Figure 1 shows the image of the fabricated tapered optical fiber showing the down taper region. This tapered geometry, as per [12], offers a strong response between the gas-sensing layer and the evanescent field.

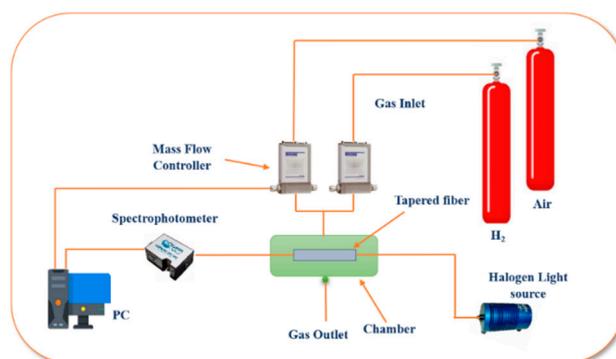


**Figure 1.** Scanning Electron Microscopy (SEM) micrograph of the transition region of the prepared tapered multimode optical fiber (MMF).

### 2.2. Palladium Functionalization of the Tapered Optical Fiber

The Pd sensor was fabricated following a simple one-step process. First, 0.1 mL of hydrochloride acid was mixed with 0.9 mL of palladium chloride (PdCl<sub>2</sub>), followed by the addition of 10 mL of deionized water. The solution was placed in an ultrasonic bath and left for 15 min to homogenize. The coating of the tapered optical fiber was done using the drop-casting technique. A drop of the mixture (approximately 10  $\mu\text{L}$ ) was dropped into the base of the tapered optical fiber through a micropipette and heated at 80  $^{\circ}\text{C}$  for 15 min in the oven to ensure complete evaporation of the aqueous medium [13].

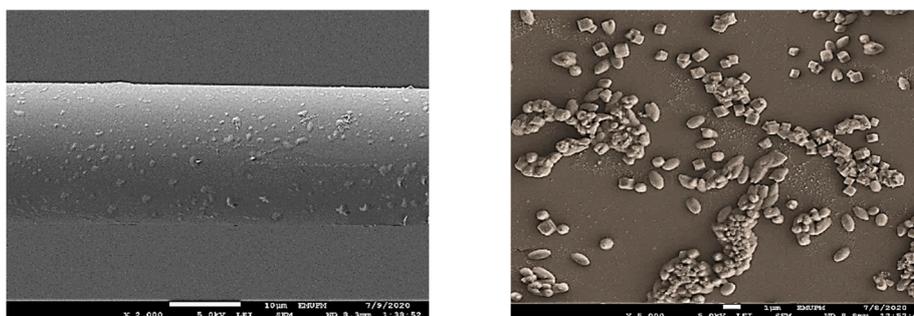
The experimental setup of the gas optical sensing system consists of a light source (Tungsten Halogen, HL-2000, Ocean Optics, Dunedin, FL, USA) with coverage wavelength of 360 to 2500 nm, a spectrophotometer (USB 4000, Ocean Optics, Dunedin, FL, USA) with a detection range of 200–1100 for monitoring the optical absorption spectrum, and a dedicated gas chamber. The Pd-coated sensor was placed in a closed gas unit and purged with the centrifuge from a computer-regulated mass flow controller at a gas flow rate of 200 sccm. Figure 2 illustrates the experimental setup of the H<sub>2</sub> sensor.



**Figure 2.** The experimental setup of the H<sub>2</sub> sensor.

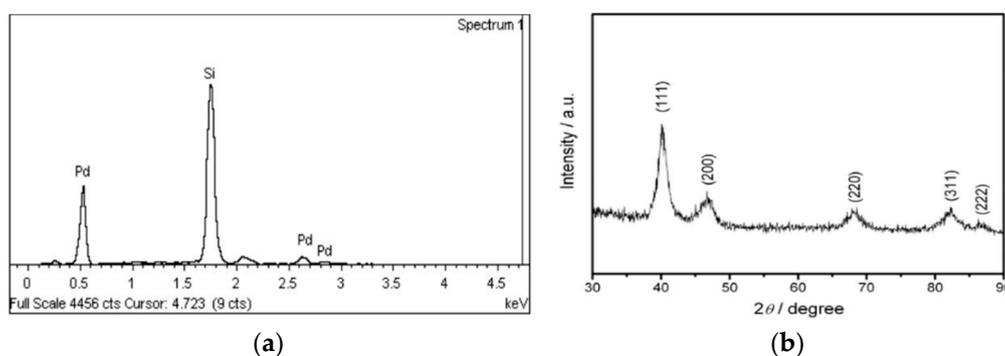
### 2.3. Material Characterization

The films' morphology was observed using FESEM (JSM-7600F), while their elemental composition was determined through an EDX analysis. Material identification, crystallinity, and phase transition of Pd were observed by an XRD analysis (APD 2000). Figure 3 illustrates the FESEM images of the Pd nanoparticles (NPs). Pd NPs are clearly formed and separated.



**Figure 3.** The FESEM micrograph of Pd nanoparticles (NPs).

The EDX pattern of Pd shown in Figure 4a revealed that the important elements in Pd films are Pd and O, as evidenced by their respective peaks. Figure 4b reveals the XRD patterns of the Pd-coated sensor recorded in range  $2\theta$ , from  $30^\circ$  to  $90^\circ$ . There are five distinct reflections in the reflection at  $40.02^\circ$  (111),  $46.49^\circ$  (200),  $68.05^\circ$  (220),  $82.74^\circ$  (311), and  $86.27^\circ$  (222). These characteristic reflections can be categorized into a face-centered cubic structure (fcc) of Pd. The stronger reflection (111) compared with the other four may indicate the preferred growth direction of the nanocrystals [14].

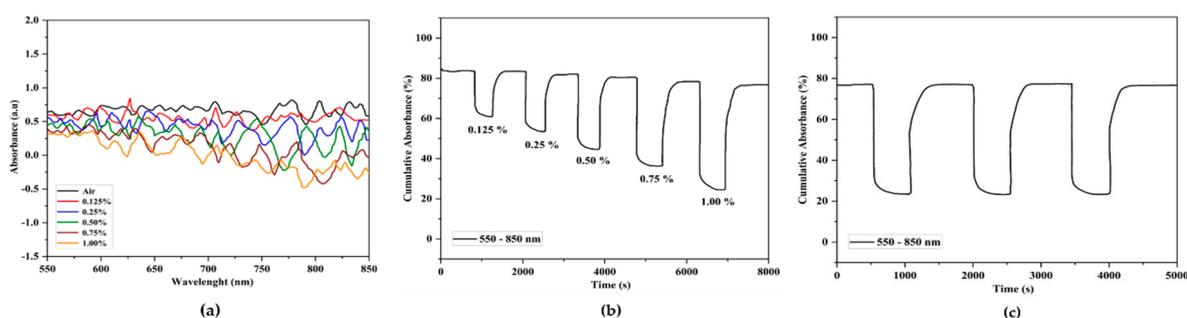


**Figure 4.** (a) EDX measurement of Pd NPs and (b) XRD pattern of Pd NPs.

## 3. Results and Discussion

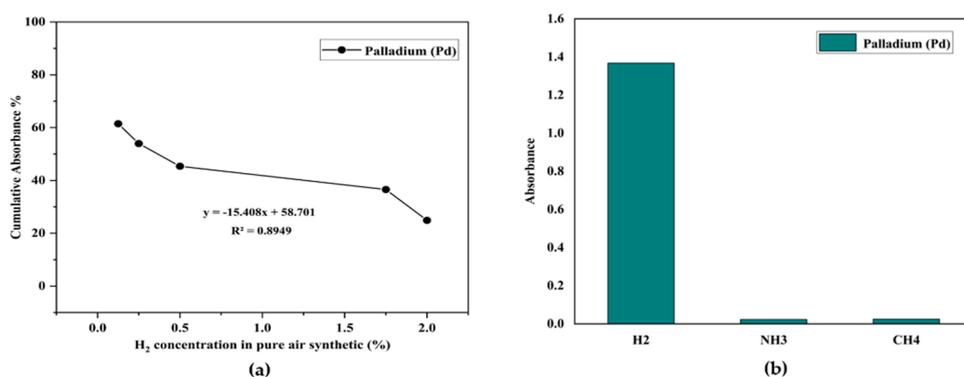
Figure 5 depicts the absorption spectra of the sensor coated with Pd to synthetic air and 1.00% H<sub>2</sub> at room temperature. The Pd sensor demonstrated notable changes in absorbance, especially in the wavelength range of 550–850 nm, as shown in Figure 5a. The overall sensor performance of the

Pd coated sensor was monitored in terms of cumulative absorption, which is the product of a combination of response curves over a particular wavelength range. Figure 5b displays the dynamic response of the Pd coated sensors of about 0.125% to 1.00% H<sub>2</sub> concentrations in air, at room temperature. The response time and recovery time of the Pd costed sensor were 50 s and 200 s, respectively. Changes in absorption at 0.125% H<sub>2</sub> are about 24% and 52% higher at 1.00% H<sub>2</sub>. The Pd-coated sensor showed stronger absorbance and recovery of H<sub>2</sub> at higher absorption changes as compared with the works of [15,16]. Sensor repeatability was confirmed by exposure of the sensor to three cycles of 1.00% H<sub>2</sub>, as shown in Figure 5c. Overall, the Pd-coated sensor showed a high level of absorption and good repeatability of H<sub>2</sub>.



**Figure 5.** (a) Absorbance versus optical wavelength, (b) dynamic absorbance curves, and (c) repeatability of Pd-coated sensor.

Absorbance versus H<sub>2</sub> concentration for Pd-coated sensors is shown in Figure 6a. The sensitivity obtained from Pd-coated sensors was 15.40 vol%, with a slope of linearity of 89%. A test for selectivity was also done for the Pd-coated sensor on tapered optical fiber toward NH<sub>3</sub> and CH<sub>4</sub> gas at 1.00% concentration, as shown in Figure 6b. The Pd-coated sensor showed a remarkably high H<sub>2</sub> absorbance response with a weak response for other gases. According to [17], CH<sub>4</sub> gas is a stable gas that requires very high energy to dissociate H from C; hence, a high operating temperature is needed to enhance sensitivity toward this gas. The sensor is less sensitive toward NH<sub>3</sub>, probably because of Pd, as it is more suitable for dissociating the H<sub>2</sub> gas [18].



**Figure 6.** (a) Absorbance changes at different H<sub>2</sub> concentrations for Pd-coated sensors and (b) the selectivity of the Pd-coated sensor.

#### 4. The Sensing Mechanism for Tapered Pd NPs Coated Optical Fibers

The Pd-coated fiber sensor’s optical response occurs because of the reaction of palladium to hydrogen gas, as shown in Figure 7. Pd absorbs H<sub>2</sub> gas molecules, resulting in it changing into PdH<sub>x</sub> (where a small percentage expands the Pd particle size), and its functions are lesser than pure Pd. Following this, the hydrogen molecule splits into single hydrogen atoms at a dissociation rate, which is highly efficient. Subsequently, the Pd layer increases in thickness and size while absorbing hydrogen,

thereby also changing the layer's optical properties. The real and imaginary parts alter the permittivity of the Pd layer to result in a corresponding change of boundary conditions on the sensor surface.

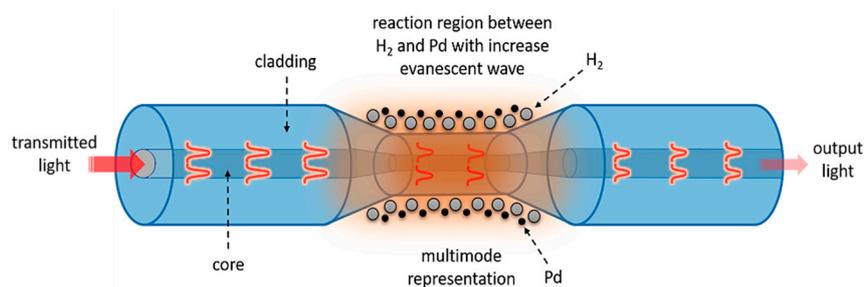


Figure 7. Hydrogen-palladium sensing mechanism.

## 5. Conclusions

This study demonstrated that optical fiber sensors could be developed from Pd NPs by employing a drop-casting technique. The performance of the developed sensor was evaluated in terms of its response at room temperature using different concentrations of H<sub>2</sub> gas. These evaluations indicated that the Pd-coated sensor exhibited a 52% change in the absorbance response when exposed to 1.00% H<sub>2</sub> in synthetic air. The outcome of the study suggests that it is possible to develop an efficient, reliable, and reproducible H<sub>2</sub> sensor using a cost-effective and straightforward approach under real atmospheric conditions.

**Author Contributions:** Conceptualization, M.M.A., S.H.G., and M.H.Y.; methodology, M.M.A. and M.H.Y.; writing—original draft preparation, M.M.A.; review and editing, M.H.Y., S.H.G., M.A.M., S.P., and N.A. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** The authors declare no conflict of interest.

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