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

Mohammed Majeed Alkhabet [1], Saad Girei [1,2], Suriati Paiman [3], Norhana Arsad [4], Mohd Adzir Mahdi [1] and Mohd Hanif Yaacob [1,*]

[1] Wireless and Photonics Network Research Center, Faculty of Engineering, University Putra Malaysia, UPM Serdang 43000, Selangor, Malaysia
[2] Department of Computer Engineering, Federal Polytechnic Mubi, Adamawa State, Nigeria
[3] Department of Physical, Faculty of Science, University Putra Malaysia, Serdang 43000, Selangor
[4] Department of Electrical, Electronic and System Engineering, Faculty of Engineering and Built Environment, University Kebangsaan Malaysia, UKM Bangi 43600, Selangor, Malaysia
* Correspondence: hanif@upm.edu.my; Tel.: +60-16-328-9044
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Abstract: This paper describes the application of a palladium (Pd)-coated tapered optical fiber in order to develop hydrogen (H_2) sensor. A transducing channel was fabricated with multimode optical fiber (MMF) with cladding and core diameters of 125 μm and 62.5 μm, respectively, 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 FESEM, EDX, and XRD. The developed palladium sensor functioned reproducibly at a gas concentration of 0.125% to 1.00% H_2 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_2 sensor by applying a basic, cost-effective method is possible.

Keywords: tapered optical fiber; hydrogen (H_2); palladium (Pd); drop-casting technique

1. Introduction

Hydrogen (H_2) has 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_2 can hence be sourced from water, hydrocarbons, and biomass. H_2, 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_2 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_2, the hydrogenation process, and the detection of H_2. The high sensitivity,

good selectivity, and ability to operate at room temperature of Pd nanoparticles make it the ideal and noble metallic catalyst for the H_2 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 [7,8]. Most fiber-optic sensors need some modification to the cladding to make it sensitive to its surroundings [9]. These modifications include chemical etching [10], side polishing [11], or shape-D [12].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_2 gas sensor was fabricated using Multimode Optical fiber (MMF) with cladding and core diameters of 125 μm and 62.5 μm, 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 μm to a waist diameter of 20 μm, 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 [13], offers a strong response between the gas-sensing layer and the evanescent field.

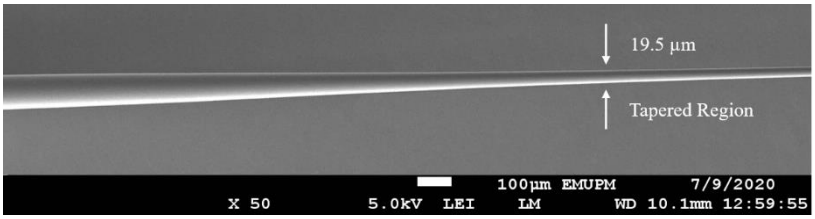

Figure 1. SEM micrograph of the transition region of the prepared tapered MMF.

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 ($PdCl_2$), 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 (approx. 10 μL) was dropped into the base of the tapered optical fiber through a micropipette and heated at 80 °C for 15 min in the oven to ensure complete evaporation of the aqueous medium [14].

The experimental setup of the gas optical sensing system consists of a light source (Tungsten Halogen, HL-2000, Ocean Optics USA) with coverage wavelength of 360 to 2500 nm, a spectrophotometer (USB 4000, Ocean Optics 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 4 illustrates the experimental setup of the H_2 sensor.

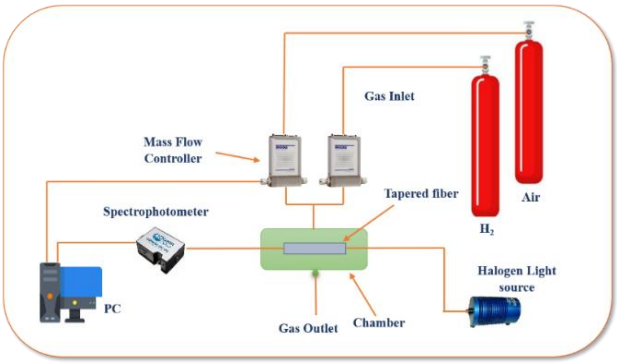

Figure 2. Illustrates the experimental setup of the H_2 sensor.

2.3. Material Characterization

The films' morphology was observed using FEESEM (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. Pd NPs are clearly formed and separated.

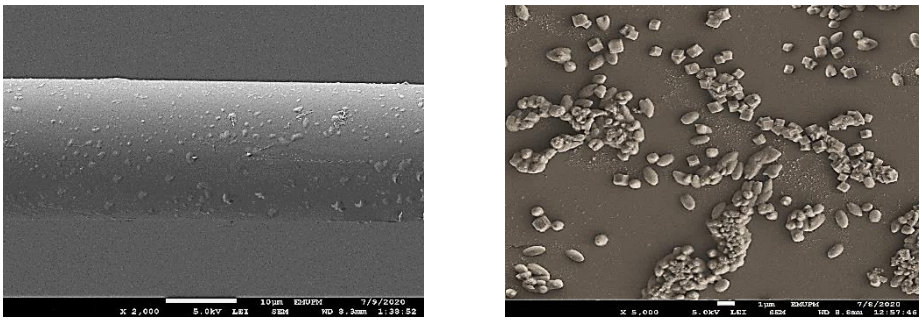

Figure 3. The FESEM micrograph of Pd NPs.

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 XRD patterns of the Pd-coated sensor recorded in range 2θ, from 30° to 90°. There are five distinct reflections in the reflection at 40.02° (111), 46.49° (200), 68.05° (220), 82.74° (311) and 86.27° (222). These characteristic reflections can be categorized into a face-centric cubic structure (fcc) of Pd. The stronger reflection (111) compared to the other four may indicate the preferred growth direction of the nanocrystals [15].

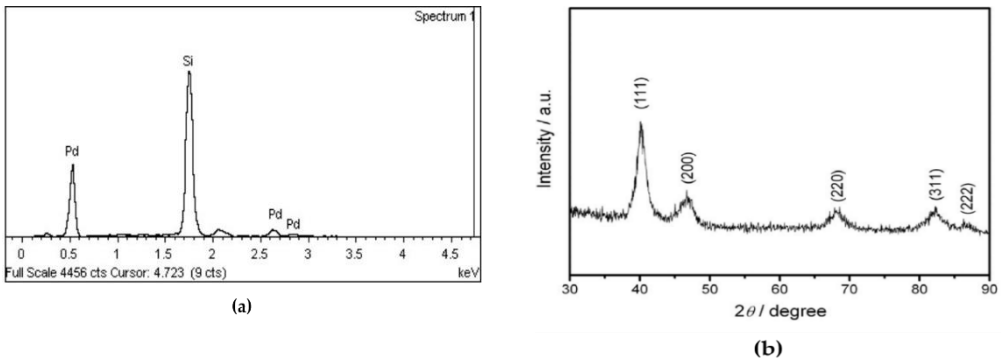

Figure 4. (**a**) EDX measurement of Pd NPs, and (**b**) XRD pattern of Pd NPs.

3. Results and Discussion

Figure 5 depicts the absorption spectra of the sensor coated with Pd to synthetic air and 1.00% H_2 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_2 concentrations in air, at room temperature. The response time and recovery time of the Pd costed sensor was 50 s and 200 s, respectively. Changes in absorption at 0.125% H_2 are about 24% and 52% higher at 1.00% H_2. The Pd coated sensor showed stronger absorbance and recovery of H_2 at higher absorption changes as compared to the works of [8,16]. Sensor repeatability was confirmed by exposure of the sensor to 3 cycles of 1.00% H_2, as shown in Figure 5c. Overall, the Pd coated sensor showed a high level of absorption and good repeatability of H_2.

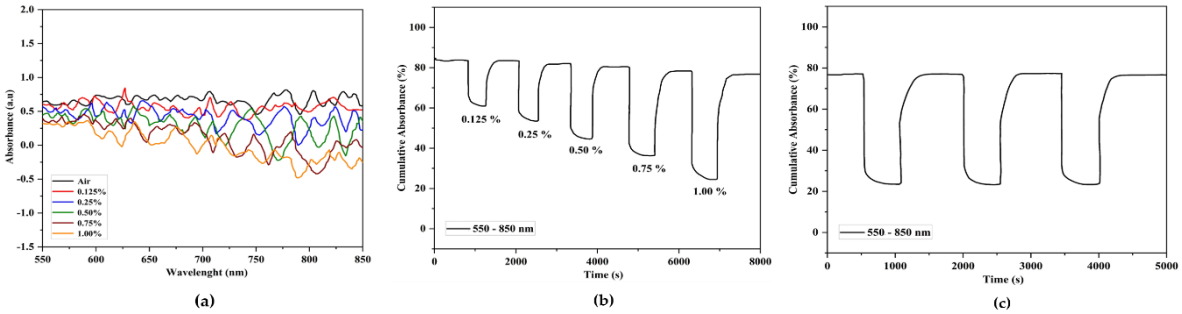

Figure 5. (**a**) Absorbance versus optical wavelength, (**b**) Dynamic absorbance curves, and (**c**) repeatability of Pd coated sensor.

Absorbance versus H_2 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_3 and CH_4 gas at 1.00% concentration, as shown in Figure 6b. The Pd coated sensor showed a remarkably high H_2 absorbance response with a weak response for other gases. According to [17], CH_4 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_3, probably because of Pd since it is more suitable for dissociating the H_2 gas [18].

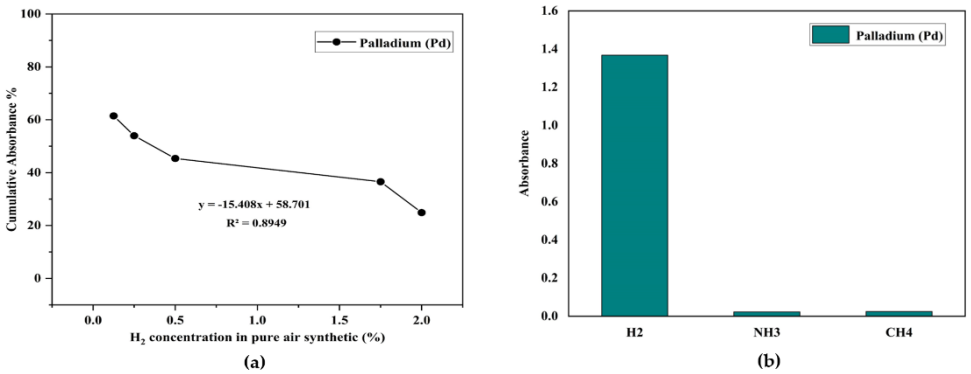

Figure 6. (**a**) Absorbance changes at different H_2 concentrations for Pd coated sensors, (**b**) The selectivity of Pd coated sensor.

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_2 gas molecules, resulting in it changing into PdHx (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.

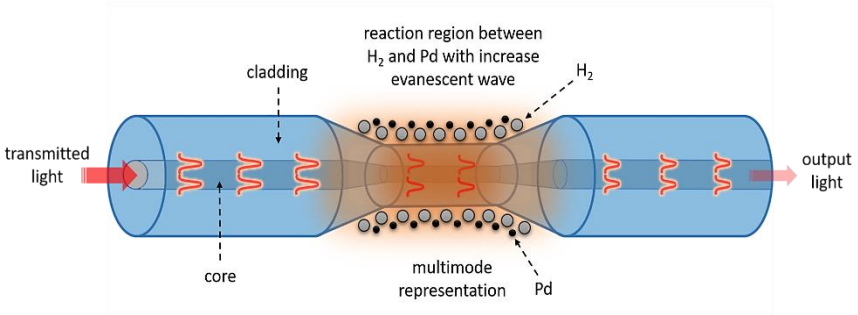

Figure 7. Hydrogen-Palladium sensing mechanism.

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_2 gas. These evaluations indicated that the Pd-coated sensor exhibited a 52% change in the absorbance response when exposed to 1.00% H_2 in synthetic air. The outcome of the study suggests that it is possible to develop an efficient, reliable, and reproducible H_2 sensor by using a cost-effective and straightforward approach under real atmospheric conditions.

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