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Graphene Oxide Based-Tapered Optical Fiber Sensor for Hydrogen Sensing Application †

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Abstract: Hydrogen (H_2) is the most common element on earth and is found mainly with oxygen in water and hydrocarbons. Hydrogen has applications in many industries. It is used in liquid to propel rockets, cryogenic research in superconducting studies, and oil refining. This paper aims to develop tapered optical fiber sensors coated with graphene oxide (GO) for H_2 sensing applications. The optical fiber was fabricated by tapering a standard optical fiber via a cost-effective and simple tapering technique. The author has a varied parameter from waist diameter to 20 μm with a fixed length of 10 mm and an up/down taper of 5 mm. Micro-nano characterization techniques such as FESEM, EDX, AFM, and XRD were utilized to obtain detailed structural properties of these nanostructures and fundamentally understand their functions concerning optical sensor performance. The responses of the developed sensor toward H_2 were measured through the change in absorbance within the concentrations of 0.125–2.00% in synthetic air. The developed sensor indicated high sensitivity toward the change in H_2 concentration at 100 °C. The observed response and recovery time for 2.00% H_2 were calculated as 2 min and 11 min, respectively. The developed optical fiber sensor achieved high selectivity and excellent stability toward H_2 gas upon exposure to other gases such as ammonia (NH_3) and methane (CH_4).

Keywords: hydrogen (H_2); graphene oxide (GO); tapered fiber; optical sensor

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1. Introduction

Hydrogen as a clean and sustainable energy and material source has aroused exponentially growing attention through the world [1]. However, naturally colorless and odorless hydrogen is extremely flammable and explosive, especially in the mixture with air (the lower explosive limit of hydrogen is 4%). Therefore, the detection of low concentrations of hydrogen in the gas mixtures is essential to mitigate the danger of explosion caused by leaks of hydrogen during its production, storage, transportation, and usage [2]. The modern hydrogen sensors must meet the following requirements: rapid response/recovery, high sensitivity, excellent selectivity, and low detection limits [2].

Over the past decades, various types of hydrogen gas sensors have been developed, including semiconductor [3], thermoelectric [4], or surface acoustic wave type [5]. Among them, the optical-fiber sensors provide a range of advantages, including simplicity, cost-

efficiency, high sensitivity, possibility of remote sensing, electric insulation, and simple integration with another devices [6]. Several structures of optical fiber hydrogen sensors have been proposed, such as Fabry−Perot interferometer [7] or fiber Bragg gratings [8] and show a large detection range but commonly, low sensitivity. An alternative approach consists of the utilization of the tapered fiber to increase the sensitivity toward the hydrogen, since in this case, the dimension of the taper can be controlled as well as the process is also simple and fast. The tapered optical fiber can be utilized by coating it with palladium nanostructured that is sensitive to H_2 gas.

Graphene oxide (GO) is a unique two-dimensional layer of carbon atoms covalently arranged in a honeycomb lattice with many functional groups that make its physical and chemical properties different from graphene [9]. The hydrophilic nature of GO allows it to be easily deposited on various substrates in thin film form using simple sedimentation methods such as drop coating and spray coating techniques [10]. GO is successfully used in many applications in electronics, conductive films, electrode materials, and compounds [11,12].

In this work, an optical fiber coated with graphene oxide was developed for hydrogen gas detection. The optimized H_2 sensor successfully detects H_2 gas at room temperature with excellent response, recovery, and repeatability.

2. Materials and Methods

2.1. Design and Fabrication of Optical Fiber Transducers

As a transport platform, the H_2 gas sensor was fabricated using multimode fiber (MMF) with cladding and core diameter to 125 μm and 62.5 μm, respectively. The multimode optical fiber core has a large diameter that allows a strong interaction of light with the sensor layer coated in the tapered region. Multimode optical fiber provides low attenuation loss and is flexible at high temperatures, making it attractive for use as a hydrogen sensor in harsh environments. The fabrication procedure is done by tapering multimode fibers using the Vytran Glass Processing System (VGPS). It has varied parameters from waist diameter to 20 μm with a fixed length of 10 mm and an up/down taper of 5 mm. It is reported in [13] that the size of the waist diameter of the tapered optical fiber will affect the sensitivity of the sensor. This is due to the depth with which the evanescent field penetrates the coated sensor layer. According to [14], this range of waist diameters yields a strong response to the gas sensor. Figure 1 shows an image of the fabricated tapered optical fiber, which shows the tapered region.

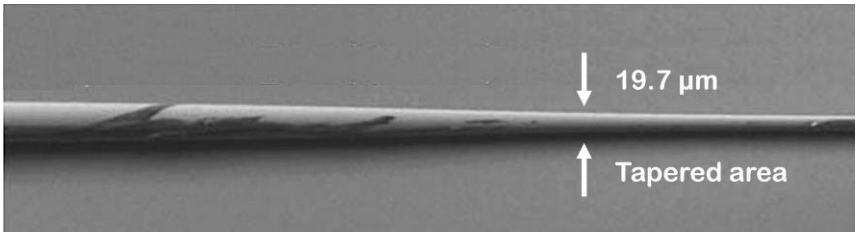

Figure 1. FESEM image of tapered multimode optical fiber (MMF).

2.2. Synthesis and Deposition of Graphene Oxide

Graphene oxide (GO) was obtained from modified graphite flakes using the modified hummers method [15]. In a typical procedure, 10 g of graphite powder was dispersed in concentrated sulfuric acid (H_2SO_4) with stirring below 20 °C. A strong oxidant agent, potassium permanganate ($KMnO_4$), was gradually added to the reaction vessel by stirring in an ice bath for two hours. The mixture was kept at room temperature and stirred for 96 h. Diluted sulfuric acid (5.0 wt%) and hydrogen peroxide were added to the reaction system. The mixture was then centrifuged and washed with HCl and deionized water until the filter was neutral, removed remaining impurities, and dried at room temperature.

Graphite oxide was obtained by drying the precipitate at room temperature. 200 mg of prepared graphite oxide powder was dispersed in 800 mL deionized water. The graphite oxide dispersion was treated with ultrasonic for about 2 h to exfoliate it in individual graphene oxide layers.

In this work, the GO solution was dropped (approx. 15 μL) on the base of the tapered optical fiber through a fine pipette and heated at 50 °C for 1 h to ensure complete evaporation of the aqueous medium.

The proposed H_2 sensor was installed in a customized chamber and connected one side to a tungsten halogen lamp (Ocean OpticsTM HL 2000, wavelength range from 360 to 2400 nm) via optical fiber cables as shown in Figure 2. On the other hand, the fabricated sensor was connected to a spectrophotometer (Ocean OpticsTM USB-4000, spectral range 200–1100 nm) which was used to measure the absorbance. The spectrophotometer is connected to the computer via a USB port. The optical response measured by the spectrophotometer was generated and analyzed in real-time with SpectraSuite (version 6.2).

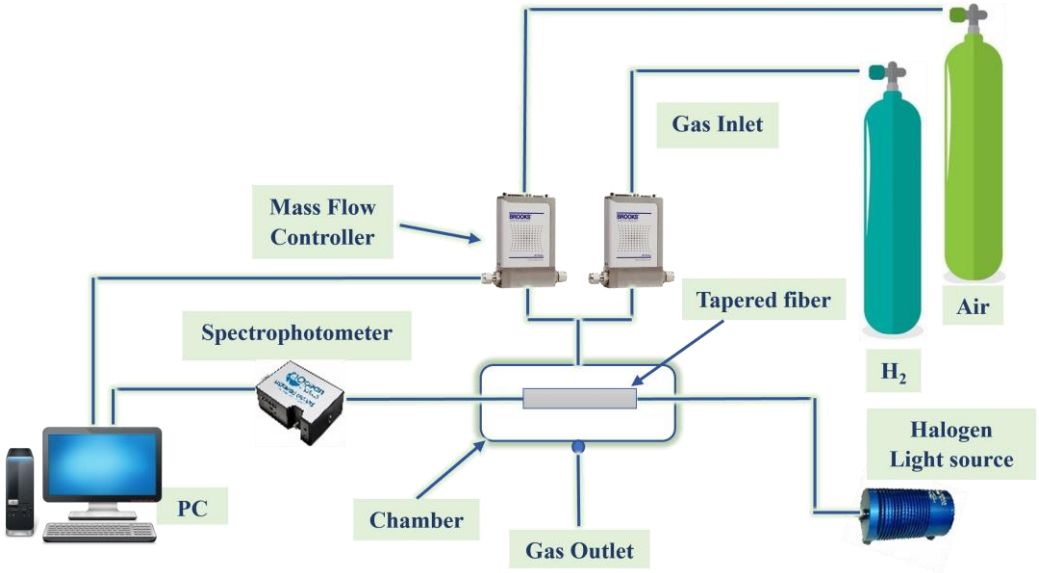

Figure 2. The experimental installation of the H_2 sensor.

The absorbance spectrum was taken from the proposed probes using a spectrophotometer, with air as a reference, and stored. Diluted H_2 was purified with different concentrations and 100% synthetic air alternately in the room, while SpectraSuite was processed and showed absorbance versus wavelength. The H_2 gas concentrations were varied from 0.125% to 2.00% to study the sensor sensitivity and its ability to quantify the concentrations. The dynamic responses (change in absorbance over time) of the sensor have been observed through changes in absorbance.

3. Results

3.1. Micro-Characterizations of Pd NPs

The author performed the FESEM characterization of the samples to analyze the GO morphological characteristics as shown in Figure 3. The images showed successful deposition of the GO on the surface of the tapered fiber in Figure 3b. The surface of the coated GO was relatively smooth with a wrinkled structure which can be linked to the edges of the GO sheets [16]. The wrinkles are important for GO surfaces because they provide a high surface area for strong sensing performance, as shown in Figure 3a. In addition, from the image is clear that the GO distribution is the same uniform as presented in [17,18].

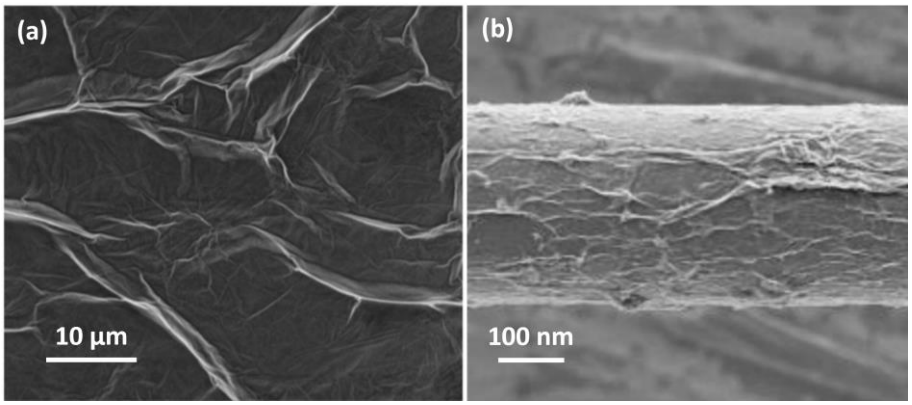

Figure 3. FESEM micrographs of tapered MMF coated with graphene oxide (GO).

The elemental composition of the GO was measured by EDX performed in FESEM. The EDX results confirm that the present elements of GO are C, O, and Si, as shown in Figure 4a. The silica fibers used the silicon peak (Si) as a substrate. On other hand, the crystalline structure of the GO was studied by XRD pattern analysis. The GO compound has a sharp intensity peak of 2θ at a value of 10.11°, corresponding to the (001) plane, as shown in Figure 4b. The reason for the presence of oxygen-containing groups, such as hydroxyl, epoxy, and carboxylate, could be the greater spacing of GO [19].

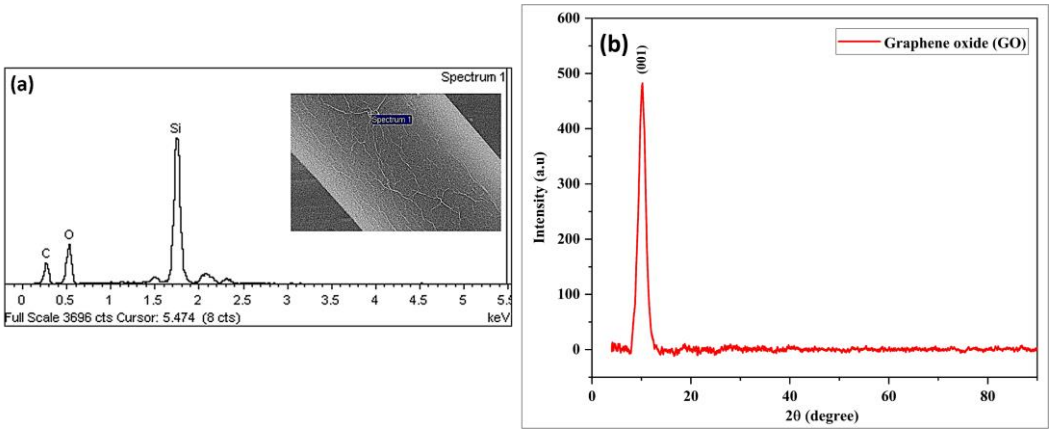

Figure 4. (**a**) EDX measurement of GO and (**b**) XRD pattern for both samples GO thin film.

Atomic force microscopy (AFM) is used to verify the surface roughness and thickness of GO. A 10 µm × 10 µm scan was assigned to the boundary area for AFM analysis. As shown in Figure 5, the average surface roughness of the GO was 26 nm. A rough sensing layer is important because it provides easy diffusion of gas molecules into or out of the layer. Consequently, the sensing performance parameters of the gas sensors, such as response time and sensitivity, can be significantly improved [20]. The thicknesses of the GO thin films were measured. A portion of the substrate was covered with aluminum tape to differentiate between coated and uncoated sites during the coating process. The thickness of the GO coatings was measured as 610 nm.

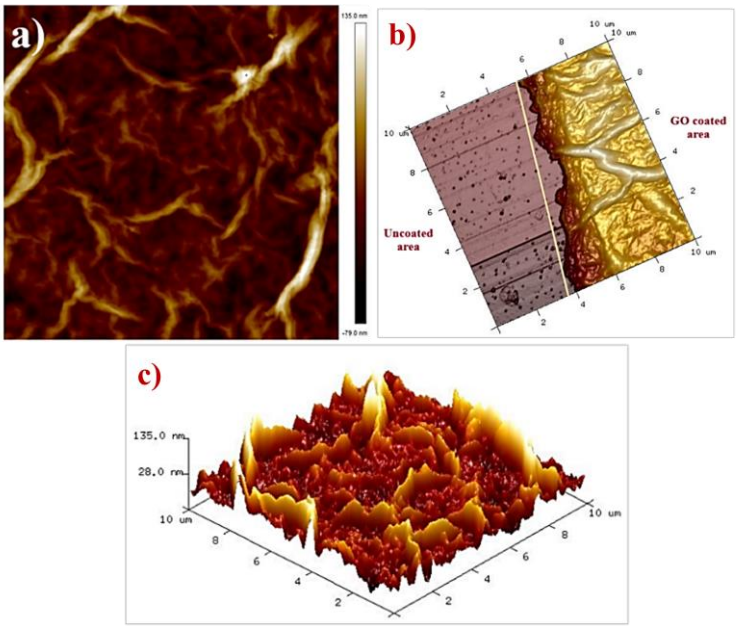

Figure 5. (**a**) 2D topography of AFM images of GO, (**b**) 3D AFM images of GO and (**c**) 3D AFM topography images of the boundary region between the uncoated and coated fibers of GO.

3.2. H_2 Sensing Performance of GO and Pd/GO Based Optical Sensor

The tapered Hydrogen optical fiber sensor coated with GO was tested towards various H_2 concentrations ranging from 0.125% to 2.00% in synthetic air at 100 °C. Figure 6a illustrates the absorbance spectra of the developed tapered optical fiber sensor toward different H_2 concentrations. A distinctive absorbance change can be observed over the wavelength range of 550 nm to 850 nm. This wavelength is selected as the absorbance spectrum demonstrates the largest response toward H_2 within this range based on experiments. The absorbance magnitude proportionally increased when H_2 concentration increased. Between 550 to 850 nm, the absorption changes were associated with the GO coated sensor. However, the absorption changes were relatively high in the GO, which may be attributed to the presence of OH in GO [21].

As a result, the GO-based sensor was not suitable as an active sensing layer for optical gas sensing applications as shown in Figure 6b. At a gas level of 0.125% H_2, the gas absorption in the GO layer showed a change in absorbance of 5%. At a concentration 2.00% higher, the absorbance increased to 35%. The observed response and recovery time for 2.00% H_2 were calculated as 2 min and 11 min, respectively.

The proposed sensors were subjected to 3 cycles of H_2 with 2.00% concentration to observe the repeatability of the sensors, as shown in Figure 6c. It was observed that the sensors achieved similar sensitivity, response, and recovery time. This exhibits excellent sensor repeatability, which is important for accurate H_2 detection. Overall, the repeatability of the dynamic response of fabricated GO based sensor showed a high level of absorbance and good repeatability at 2.00% H_2.

Figure 6d presents the plots of the cumulative absorbance change as a function of the H_2 concentration of the GO sensing layers in the wavelength range of 550–850 nm. Depending on the figure, the decrease in absorbance is proportional to the increase in H_2 concentration. The sensitivities of the tapered optical fiber sensor-based GO were 19.03./vol%, with an excellent linear slope of approximately 90%.

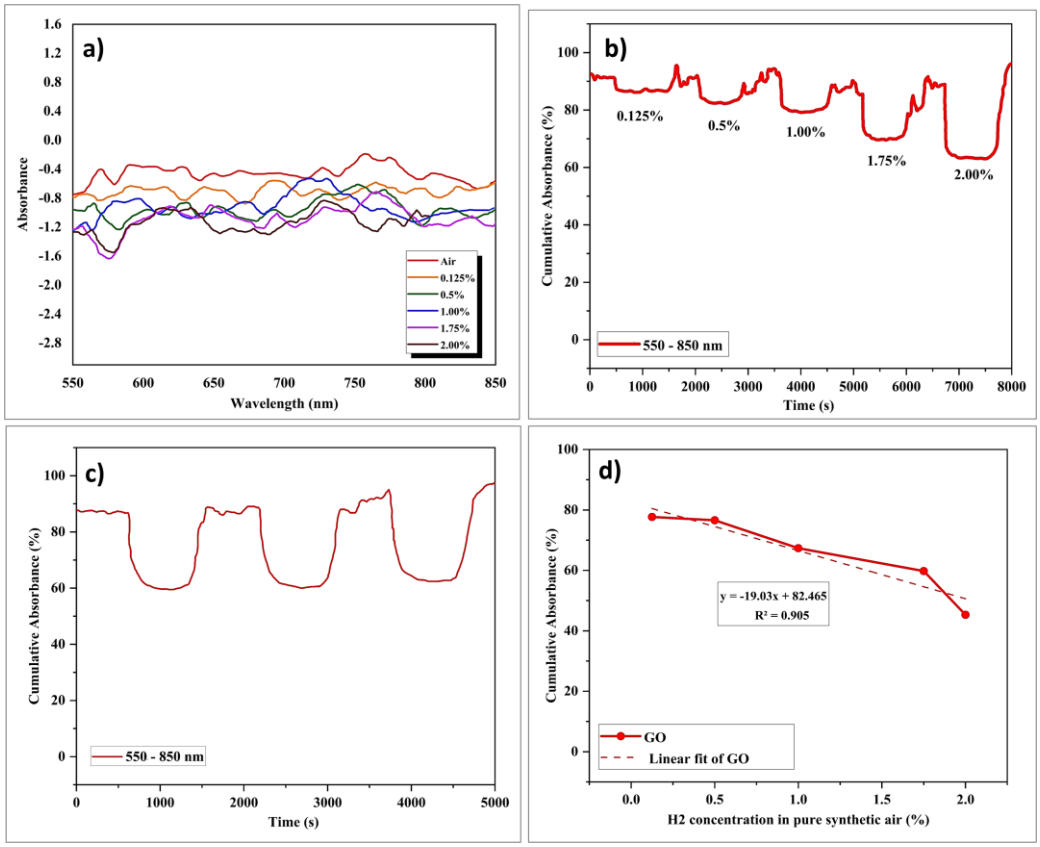

Figure 6. (**a**) GO Absorbance versus optical wavelength, (**b**) Dynamic absorbance curves of sensors coated with GO (**c**) The repeatability of the developed sensor and (**d**) Absorbance changes at different H_2 concentrations for coated GO.

A selectivity test was also performed for sensors coated with GO and Pd/GO nanocomposites towards ammonia (NH_3) and methane (CH_4). Figure 5.14 shows the selectivity measurement and comparison of H_2, NH_3, and CH_4 for a concentration of 2.00% at the same operating temperature of 100 °C. The GO based sensor has a lower H_2 absorbance response as compared to NH_3 and CH_4 as shown in Figure 7a. The stability of the GO based sensors for 14 days was also measured towards an H_2 gas concentration of 2.00% in synthetic air at 100 °C, as shown in Figure 7b. The sensor was stored in a closed container at 20 °C in a dry cabinet to avoid contamination of the sensor surface. After two weeks, the gas response was slightly reduced by 5%. This result indicates that the prepared gas sensors and present excellent stability.

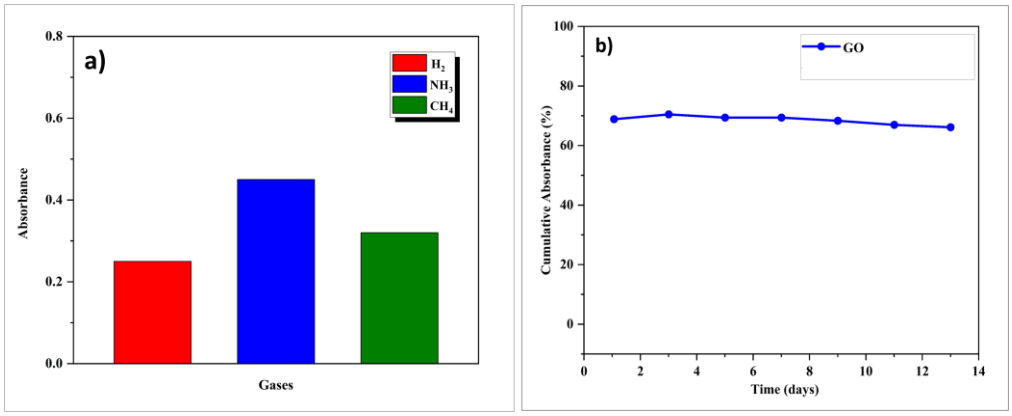

Figure 7. (**a**) Comparison bar graph of the selectivity of optical fibers coated with GO based sensor and (**b**) Stability of the GO based sensor.

4. Conclusions

This study shows that developing a tapered optical fiber sensor based on graphene oxide (GO) using a drop-casting technique is possible. Various concentrations of H_2 gas were used to evaluate the developed sensor performance at 100 °C. These evaluations indicated that the GO-coated based sensor exhibits 35% changes in the absorbance response when exposed to 2.00% H_2 in synthetic air. Response and recovery time were 2 min and 11 min, respectively. The sensing performance suggests that the tapered optical fiber coated with GO shows superior H_2 sensing at low temperatures compared to the other transducing platforms. The selectivity of the sensor can improve by coating thin layer of palladium (Pd) on the sensing device.

Author Contributions: Conceptualization, M.M.A.; methodology, M.M.A. and S.H.G.; validation, M.H.Y., A.L.K. and S.A.M.; writing—original draft preparation M.M.A.; writing—review and editing, S.H.G. and M.H.Y. 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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