GSJ: Volume 11, Issue 8, August 2023, Online: ISSN 2320-9186

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ULTRA-LOW SENSITIVE FBG HYDROGEN GAS SENSOR BASED ON LASER ABLATED FIBER MICRO-TRENCHES AND PT-WO_3

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KeyWords
Femtosecond laser, Fiber Bragg grating, Fiber optics sensor, Hydrogen sensor, Pt-WO_3,

ABSTRACT

The correlation between hydrogen concentration (0–0.5%) and peak wavelength shift of FBG optical fiber sensors were investigated and analyzed. In order to enhance its sensitivity, the fiber cladding was ablated into eight straight micro-cavities (19 µm in depth) using Femtosecond laser facility. This process was aimed at increasing the fiber cladding surface area covered by hydrogen sensitive transducer. Pt-WO_3 nano-lamellae were prepared by hydrothermal process at molar ratio of 1:5 respectively and deposited on the surface of fiber cladded micro-trenches forming ~2 µm uniform coating. The choice of Tungsten oxide (WO_3) as the hydrogen gas transducer was dictated by the following facts. First, it reacts exothermically in low hydrogen environment under Pt catalyst generating massive heat leading to FBG central wavelength shift. Secondly, the Pt-WO_3 nano-lamellae exhibits a morphological porosity in its micro-structure thus, enhancing hydrogen gas absorption and desorption. The proposed sensor has a quick hydrogen response and recovery time of 25 and 30 s respectively. Additionally, it exhibits a high sensitivity of 434.21 pm⁄H% within the range of 0%–0.4%.

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1.0 Introduction

Hydrogen gas is a clean energy source, and enjoys excellent properties such as high efficiency, non-pollution, sustainability, and abundance in availability thus; it plays a pivotal role in solving the energy crisis in the world [1]. Hydrogen has a wide application in engineering, petroleum and metallurgical industries among other fields [2]. However, hydrogen is also highly flammable and explosive gas due to its low minimum ignition energy and explosive limit (4%). Additionally, its high diffusion coefficient and combustion heat aggravates its potential danger in industries. Thus, strategy must be employed to mitigate the risks of explosion especially during hydrogen gas utilization, storage and transportation [3]. Recently, researchers are engaged in developing high-sensitive, high-precision, rapid, robust and real-time hydrogen sensors in order to realize fast detection of hydrogen leaking and accurate hydrogen concentration measurement (especially below 4%) [4]. Fiber Bragg grating sensor has superior characteristics compared to conventional electro-chemical sensor in remote and hostile environments, such as safety, high selectivity and sensitivity, high stability and miniature size.

Usually, Palladium (Pd) and Tungsten oxide (WO_3) are the most common types of hydrogen sensitive materials adopted for use in fiber hydrogen sensors. Palladium alloy thin films, offers a superior sensitivity compared to pure Pd. Pd-based film, however, is easy to form blisters, crack and ultimately peel off due to α-β phase transition and accumulation of lattice dislocations caused by its volume expansion during uptake and desorption of the gas [5]. Inclusion of composite films such as Pd-Ag, Pd-Mg and Pd-Ni reduces the extent of α-β phase transition, thus improving sensitivity [6]. On the other hand, the optical properties of WO_3 in visible region such as transmittance, reflective, refractive index and absorption gets modulated when exposed to hydrogen environment and therefore become versatile to external stimulus. In addition, when WO_3 is exposed to hydrogen gas, its color changes from greenish yellow to blue [7-8]. This gasochromic effect makes WO_3 possible candidate for hydrogen detection. Interestingly, WO_3 exist in various morphologies namely nanowires [9], nanorods [10], nanolamellae [11] and nano-sheets [12]. However, WO_3 nanolamellae has been reported to have highest hydrogen response sensitivity and can detect lower hydrogen concentration (0.02%) [10]. Recently, the Pt-load WO_3 is widely used as hydrogen sensitive material due to its simple fabrication and high hydrogen selectivity. Pt-WO_3 is highly sensitive to low hydrogen concentration due to its large surface to volume ratio. When Pt is utilized as the catalyst, WO_3 drastically react with hydrogen and continuously generate heat as the hydrogen concentration increases [13-14]. Once, Pt is sputtered on WO_3 film, it facilitates absorption and desorption of hydrogen by dissociating hydrogen molecule in to atoms and thus decreasing the reaction activation energy [15].

Binqing Wu et.al., developed hydrogen sensor of PMF coated with Pt-loaded WO_3/SiO_2 powder. Although they found existence between hydrogen sensitivity and the length of the PMF coated with Pt-loaded WO_3/SiO_2 , the sensitivity achieved was low at 14.61 nm/% within the range of 0%–0.8% (vol%) [16]. Besides, FBG related sensors, Jin-xin Shao et. al., suggested hydrogen sensor based on interference theory by simply splicing a no core fiber between two single mode fibers. The composite film of Pd/WO_3 detected the variation of hydrogen concentration and achieved sensitivity of 1.26857 nm/% [17]. Xian et.al.,[18], suggested that the hydrogen sensitive layer Pt:WO_3, enjoys optimum performance in sensitivity, selectivity and stability when its molar ratio is 1:5. Fiber diameter reduction methods such as taper [19-21], corrosion [22] and femtosecond laser ablation [23-24] accompanied by applications of sensitive coatings improves sensitivity of FBG sensors.

In this paper, a highly sensitive hydrogen sensor for ultra-low hydrogen concentration based on fs laser fiber cladding machining combined with Pt-load WO_3 composite coating is proposed. Our work emphasizes on the hydrothermal synthesis of Pt-loaded WO_3 nano lamellae, fabrication and the testing of the hydrogen gas sensor.

2.0 Principle

Fiber Bragg grating (FBG) is a regular perturbation of the refractive index along the fiber length which is formed when an intense optical light is subjected to the fiber core. When FBG is subjected to mechanical stress, the Bragg wavelength will shift towards shorter wavelengths and when subjected to axial strain, Bragg wavelength shift to longer wavelengths.

$$\lambda_B = 2n_{eff}\Lambda \qquad (1)$$

Consider eight micro-grooves laser ablated, sensor probe head as shown in Fig. 1(i). In order to evaluate, the effect of laser processing on the optical fiber, we consider the total profile area of the fiber before and after laser processing and thin film application. The coated surface area of the micro-structured sensor probe is evidently greater than that of standard FBG. Where *h* and *w* represent depth and width of the microgroove respectively as shown in Fig. 1(ii).

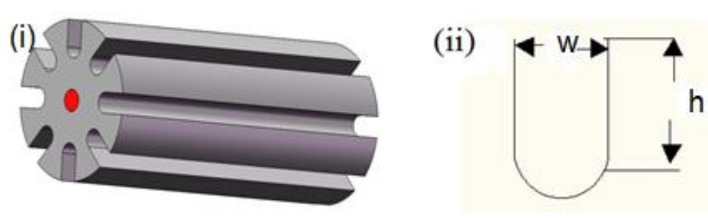

Fig.1: (i) Profile face diagram of the proposed sensor probe (ii) micro-groove dimensions side diagram.

3.0 Experimental details

3.1 Synthesis of WO_3 Nano lamellae

A solution of Na_2WO_4 (0.66 g) and $H_2C_2O_4$ (0.18 g) was dissolved in 40 ml of distilled water. Thereafter, HCl (3 mol/l) was added drop wise until precipitation. The mixture was transferred into a Teflon-lined stainless steel autoclave and was kept at 180°C for 12 h as suggested by [27]. The resulting product was washed several times and dried at 70°C.

3.2 Preparation of Pt-WO_3

The Acetylacetone platinum (Pt(acac)$_2$) and WO_3•$2H_2O$ powder was mixed together at the molar ratio of Pt:W=1:5 and fine ground. The molar ratio of Pt:W affects the performance of the hydrogen sensitive material. Subsequently, the mixture was centrifuged, dried and annealed in air annealed at 315 °C for 2 hours. Finally, the product (Pt-WO_3) mixed with deionized water was deposited on the surface of micro-structured FBG and standard FBG to form a 1-2 µm of coating.

3.3 Laser machining of micro-cavities

In order to manufacture straight line micro-cavities, the laser power density at the fiber position were controlled between 18 to 20 mW by an optical attenuator and a diaphragm. The specimens were mounted on a high-precision three-axis computer and laser ablation process monitored by real-time CCD. The optical spectrum analyzer (OSA) in situ monitored the reflective spectrum of FBG fiber as shown in Fig. 2. In addition, a specifically designed rotating jig is used to hold and drive the optical fiber. All the samples were manufactured at 5 mm/min laser feed rate. The numbers of straight microgrooves were evenly distributed along cladding surface by fixing the angle of rotation of the gear fixture to 45^o in order to produce eight microgrooves. The micro-grooved section was dipped in HF solution to remove loose debris. The depth of the micro-cavities was about 19 µm.

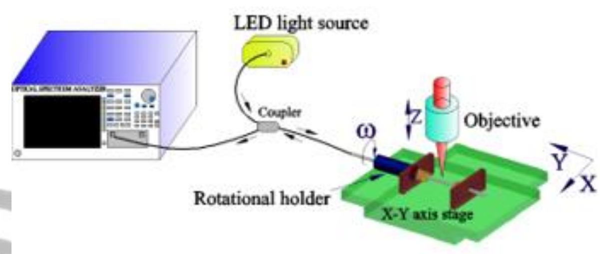

Fig. 2: The schematic of the experimental system.

3.4 Fabrication of sensor probe

The sensor device was fabricated by uniformly coating the as-synthesized Pt/WO_3 powder mixed with an appropriate amount of de-ionized water on the laser machined fiber surface as shown in figure 3. The FBG fiber was fixed on a glass substrate with a groove for easy application of Pt/WO_3 coating on the FBG section. The nano-lamellae formed a smooth and uniform coating of 1-2 µm.

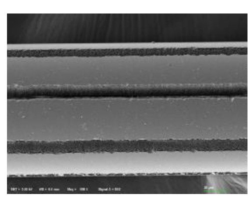

Fig.3: Laser induced micro-trenches on the SMF and coated with Pt/WO_3

3.5 Hydrogen sensing characterization.

The FBG hydrogen gas sensing characterization system, consisted of a tunable light source, a 3-dB optical fiber coupler, a sensing probe and a customized optical spectrum analyzer with a resolution of 1 pm. The sensing probe, FBG coated with Pt/WO_3, was placed in a sealed transparent chamber for the hydrogen sensing performance calibration. Hydrogen gas at various concentrations was controlled by a commercial electrochemical hydrogen meter (RBT-6000 -ZLG/A; Ruian Company, China). The gas was injected into the sealed chamber, and the shifted FBG wavelengths were recorded. The hydrogen sensing performance test was conducted at room temperature with air as the carrier gas and 80% relative humidity.

4.0 Results and discussions

In the presence of hydrogen gas, Pt-loaded WO_3 FBG hydrogen probe undergoes an exothermic reaction in hydrogen atmosphere

[25]. The chemical reaction can be expressed as follows,

$$WO_3 + \frac{1}{2}xH_2 \xrightarrow{Pt} H_xWO_3 \quad \text{...2}$$

$$H_xWO_3 + \frac{1}{4}xO_2 \xrightarrow{Pt} WO_3 + \frac{1}{2}xH_2O \quad \text{.................................3}$$

During exothermic reaction, hydrogen concentration in the chamber leads to temperature change in presence of oxygen gas. This phenomenon results from the gasochromic effect reaction observed only in the case of the noble metal-loaded WO_3 system. In the absence of hydrogen, H_xWO_3 undergoes oxidation to form WO_3 in air [26]. This effect ensures hydrogen sensor's repeatability.

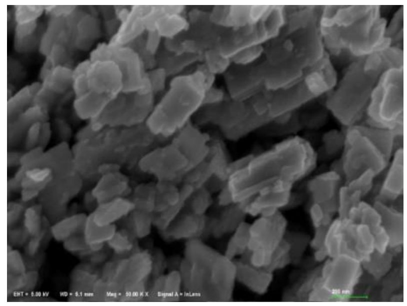

Fig.4: The morphological analysis of Pt-WO_3 nano-lamellae as investigated by the scanning electron microscopy.

In order to get deep insights concerning effect of hydrogen gas on the Pt/WO_3 film, field emission scanning electron microscope (FE-SEM, Zeiss Ultra plus, German) was employed to study surface morphology before and after hydrogen sensing tests as shown in figure 4. Pt-WO_3 nano-lamellae's porosity allows deep diffusion of hydrogen molecule towards the fiber surface, thus occurrence of bleaching process during hydrogen reaction. Laser assisted machined fiber cladding enhances the surface area coated with the film. As a result, exothermic reaction occurs due the interaction between hydrogen gas and Pt-WO_3 in the fiber trenches releasing high temperature that in turn leads to FBG wavelength shift.

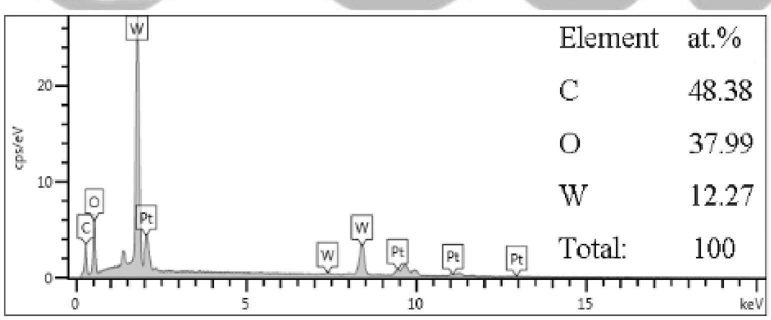

Fig.5: Elemental analysis of Pt/WO_3 nano-lamellae.

The figure 5 indicates the constituents' elemental composition Pt/WO_3 as analyzed using energy dispersive X-ray spectrometer (EDS) attached to the FE-SEM. The average atomic ratio of Pt:W is about 1:5 as worked out in terms of molar mass ratio between WO_3 powder and Pt(acac)$_2$ during synthesis process. Due to decomposition of Pt(acac)$_2$, there is high concentration of carbon in the Pt-WO_3 lamellae that suggest the presence of organic matter.

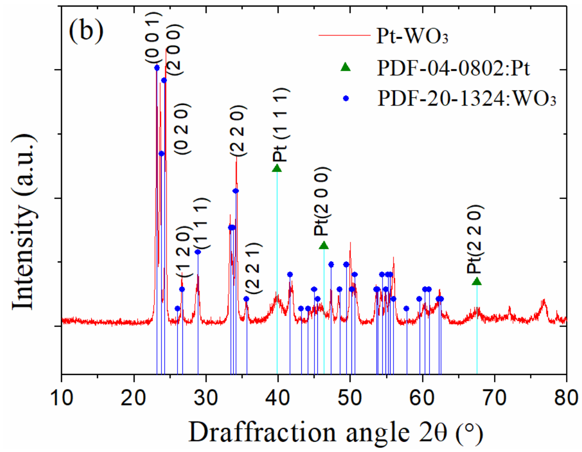

Fig. 6: presents the XRD patterns of Pt-WO_3 nano-lamellae after annealing at 315°C.

There were many intensive peaks observed at 2θ values of 23.04, 23.49, 24.10, 28.68, 33.98, 41.56, and 55.62 among others as shown in figure 6. Based on XRD analysis, WO3 nano-lamellae have monoclinic phase (PDF card No.20-1324), indicating that the crystal remained crystalline in nature before and after annealing. The Pt particles can be indexed to be face-centered cubic phase of Pt (PDF NO.04-0802), indicating that Pt(acac)2 dissociated due to high annealing temperature into elemental crystal Pt with varying atomic orientations.

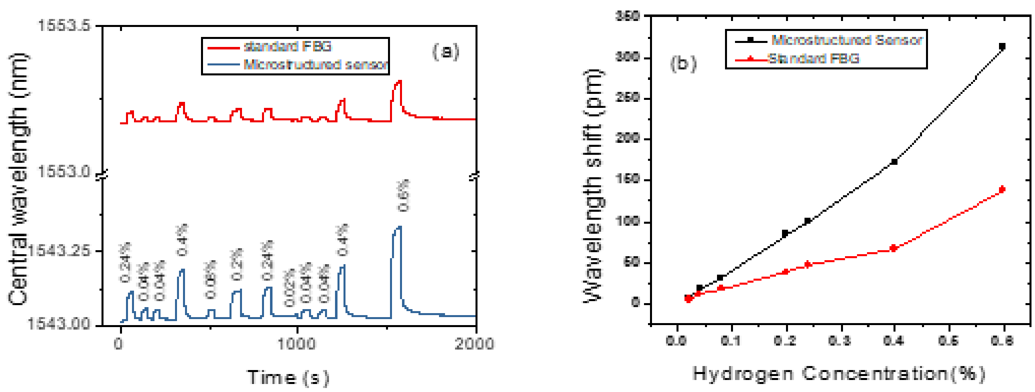

Fig. 7 (a) and (b) Comparison of standard and microstructured Pt-WO_3 coated hydrogen probes at different hydrogen concentrations (0.02-0.6%)

At an ambient room temperature, the micro-structured sensor probe shows minimum detection of 0.02% H in air. The standard FBG coated with the hydrogen sensitive material at the same concentration seldomly detects. At 0.6%H, micro-structured sensor and standard FBG probes records 10 and 25 pm respectively. Hydrogen gas sensitivity (0.02-0.4%) for micro-structured and standard FBG is 434.21 pm/ H% and 160.53 pm/H% respectively as shown in figure 7(a) and (b).

The sensitivity difference can firstly be attributed to the increased surface area of the micro-structured sensor probe coated with Pt-WO_3. The exothermic reaction depends on hydrogen gas present plus fiber surface area coated. The heat generated is more on sensor micro-structured than standard FBG, thus wavelength shift difference. Secondly, the laser machined micro-trenches operated on the fiber cladding at 20 mW are about 19µm in depth. Thus, the micro-trenches habouring the sensitive WO_3 particles are likely to generate massive heat in the interior of fiber cladding in hydrogen ambient environment. The eight micro-trenches being parallel and proximal to the core, when covered with porous Pt-WO_3 nano-lemmae reacts exothermically with hydrogen gas offers massive heat to the FBG leading to wavelength shift.

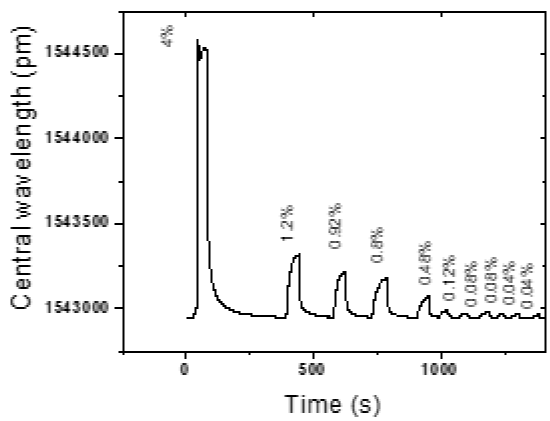

Fig. 8: Response curve of hydrogen gas probe at different hydrogen concentration (0.04-4%).

The Fig.8 above illustrates the dynamic performance of the Pt/WO_3 nano-lemmalae when exposed to H_2 with different concentrations from 0.04-4%. The sensor probe detection shows repeatability towards H_2 even at low concentrations, with typical response and recovery time 25 and 30 s respectively.

The solid and dot line in Fig. 9 (a) represented a linear fit of the data with a good linear regression. The slope represented the hydrogen sensor sensitivity of 170 pm/%H for the laser ablated sensor probe. Sensor response to various H_2 concentrations (0.04-1.4%) is shown in Fig.9 (b). It was evident that wavelength shift increased proportionately with volume of H_2 present in the gas chamber. This is due to the amount of heat transmitted to the FGB within the fiber core due to exothermic reaction between WO_3 and H_2 under Pt catalyst occurring on the silica cladding. Upon discharging gas out of the chamber, the wavelength shift abruptly reduced. During this period, there is limited hydrogen gas in the chamber and H_xWO_3 undergoes oxidation to form WO_3 in air.

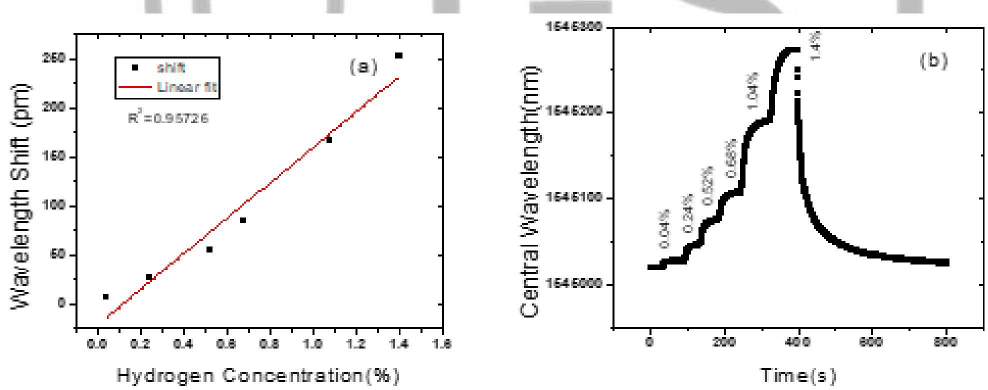

Fig.9(a): Hydrogen sensor probe sensitivity (b) Sensor response to various H_2 concentrations (0.04-1.4%)

Conclusions

In summary, Pt/WO_3 nano-lamellae, hydrogen sensitive material have been successfully synthesized and uniformly deposited on the surface of laser ablated micro-cavities making ~2 µm thick layer. When Pt-WO_3 is exposed to hydrogen ambient environment, the sensors' fiber probe temperature increases exothermically resulting in the FBG wavelength shift. Sensor has a quick response to hydrogen and exhibits a high sensitivity of 434.21 pm/H% within the range of 0%–0.4%. Micro-structured sensor probe is 2.7 times more sensitive than standard FBG sensor.

References

[1]. S.E. Hosseini, M.A. Wahid. Hydrogen production from renewable and sustainable energy resources: promising green energy carrier for clean development. Renew. Sustain. Energy Rev. **57**, 850–866 (2016).
[2]. P. Caumon, M.L.B. Zulueta, J. Louyrette, S. Albou, C. Bourasseau, C. Mansilla,: Flexible hydrogen production implementation in the French power system: expected impacts at the French and European levels. Energy. **81**, 556–562 (2015).
[3]. D.A.Crowl, Y.D. Jo: The hazards and risks of hydrogen. J. Loss Prev. Process Ind. **20** (2), 158–164 (2007).
[4]. W.J. Buttner, M.B. Post, R. Burgess, C. Rivkin: An overview of hydrogen safety sensors and requirements. Int. J. Hydrog. Energy. **36** (3), 2462–2470 (2011).
[5]. J. Dai, M. Yang, Y. Chen, K. Cao, H. Liao, P. Zhang: Side-polished fiber Bragg grating hydrogen sensor with WO_3-Pd composite film as sensing materials. Opt. Express. **7**, 6141–6148 (2011).
[6]. H. Zheng, J. Ou, M. Strano: Nanostructured tungsten oxide – properties: synthesis, and applications, Adv. Funct. Mater. **21** (12), 2175–2196 (2011).
[7]. Y.A. Lee, S. S. Kalanur, G. Shim, J. Park, H. Seo: Highly sensitive gasochromic H_2 sensing by nano-columnar WO_3-Pd films with surface moisture. Sens. Actuators B Chem. 238 111–119 (2017).
[8]. Z. Li, M. Yang, J. Dai, G. Wang, C. Huang, J. Tang, W. Hu, H. Song, Huang.: Optical fiber hydrogen sensor based on evaporated Pt/WO_3 film. Sens. Actuators B Chem. 206 564–569 (2015).

[9]. J. Kukkola, M. Mohl, A. Leino, J. Maklin, N. Halonen, A. Shchukarev, , Z. Konya, H. Jantunen, K. Kordas: Room temperature hydrogen sensors based on metal decorated WO_3 nanowires. Sens. Actuators B, Chem.186, 90–95 (2013).
[10]. A. Boudiba, C. Zhang, P. Umek, C. Bittencourt, R. Snyders, M. G. Olivier, M. Debliquy: Sensitive and rapid hydrogen sensors based on Pd–WO_3 thick films with different morphologies. Inter. J. Hydrogen Energy. **38** (5) 2565–2577 (2013).
[11]. R. J. Bose, N. Illyaskutty, K. S. Tan, R.S. Rawat, V. P. M. Pillai: Hydrogen sensors based on Pt-loaded WO_3 sensing layers. Europhys. Lett. **114** (6), 66002 (2016).
[12]. M.B. Rahmani, M.H. Yaacob, Y.M. Sabri. Hydrogen sensors based on 2D WO_3 nanosheets prepared by anodization.: Sens. Actuators B Chem. **251**, 57–64 (2017).

[13]. B. Xu, C.L. Zhao, F. Yang, H. Gong, D.N. Wang, J. Dai, M. Yang: Sagnac interferometer hydrogen sensor based on panda fiber with Pt-loaded WO_3/SiO_2 coating. Opt. Lett. **7**, 1594–1597 (2016).
[14]. D. Jai, M. Yang, Z. Yang, Z. Li, Y. Wang, G. Wang, Y. Zhang, Z. Zhuang: Performance of fiber Bragg grating hydrogen sensor coated with Pt-loaded WO_3 coating. Sens. Actuators B Chem. **190**, 657–663 (2014).
[15]. Y. Zhang, H. Peng, X. Qian, Y. Zhang, and Y. Zhao: Recent advancements in optical fiber hydrogen sensors. Sens. Actuators B Chem. **244,** 393–416 (2017).
[16]. W. Binqing, Z. Chunliu, X. Ben, L. Yina: Optical fiber hydrogen sensor with single Sagnac interferometer loop based on vernier effect. Sensors and Actuators B 255 3011–3016 (2018).
[17]. X. Jin, G. Wen, S. Xi, Z. Ya: A New Hydrogen Sensor Based on SNS Fiber Interferometer with Pd/WO_3 Coating**.** Sensors 17, 2144 (2017).
[18]. Z. Xian, D. Yutang, J. M. Karanja, L. Fufei, Y. Minghong: Microstructured FBG hydrogen sensor based on Pt-loaded WO_3. Optics Express 25 (8)8777-8786 (2017).
[19]. S. Silva, L. Coelho, J. M. Almeida, O. Frazao, J. L. Santos, F. X. Malcata, M. Becker, M. Rothhardt, and H. Bartelt:H_2 sensing based on a Pd-coated tapered-FBG fabricated by DUV femtosecond laser technique. IEEE Photonics Technol. Lett. **25**(4), 401–403 (2013).
[20]. M. Noor, A. Talah, A. Rosli, P. Thirunavakkarasu, N. Tamcheck: Increased sensitivity of Au-Pd nanolayer on tapered optical fiber sensor for detecting aqueous Ethanol. Journal of the European Optical Society-Rapid Publications 13, (28) 1-8 (2017).
[21]. P. Minkovich, B. Sotsky: Tapered photonic crystal fibers coated with ultra-thin films for highly sensitive bio-chemical sensing. Journal of the European Optical Society-Rapid Publications 15, (7) 1-6 (2019).

[22]. J. Dai, M. Yang, Z. Yang, Z. Li, Y. Wang, G. Wang, Y. Zhang, and Z. Zhuang: Enhanced sensitivity of fiber Bragg grating hydrogen sensor using flexible substrate. Sens. Actuators B Chem. **196** (196), 604–609 (2014).
[23]. Z. Xian, Y. Dai, M. Zou, J. M. Karanja, and M. Yang: FBG hydrogen sensor based on spiral microstructure ablated by femto-second laser," Sens. Actuators B Chem. **236**, 392–398 (2016).
[24]. R. Mazur, E. Mazur: Femtosecond laser micromachining in transparent materials. Nat. Photonics. **2,** 219–225 (2008).
[25]. J. Dai, L. Zhu, G. Wang, F. Xiang, Y. Qin, M. Wang, M. Yang: Optical Fiber Grating Hydrogen Sensors: A Review. Sensors. **17**, 577 (2017).
[26]. S. Masuzawa, S. Okazaki, Y. Maru, T. Mizutani: Catalyst-type-an optical fiber sensor for hydrogen leakage based on fiber Bragg gratings. Sens. Actuators B Chem. **217**, 151–157 (2015).
[27]. W. Zeng, Y. Li, B. Miao, K. Pan: Hydrothermal synthesis and gas sensing properties of $WO_3 \cdot H_2O$ with different morphologies. *Physica E*. **56,** 183–188 (2014)