Sensors and Actuators B 254 (2018) 239–247

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Zinc oxide nanoparticle incorporated graphene oxide as sensing coating for interferometric optical microfiber for ammonia gas detection

Haiwei Fu*, Youhua Jiang, Jijun Ding, Jingle Zhang, Min Zhang, Yi Zhu, Huidong Li

Ministry of Education Key Laboratory on Photoelectric Oil-Gas Logging and Detecting, School of Science, Xi'an Shi you University, Xi'an, 710065, China

ARTICLE INFO

Article history:
Received 22 January 2017
Received in revised form 9 June 2017
Accepted 10 June 2017
Available online 15 June 2017

Keywords:
Optical microfiber
GO-ZnO composite
Interferometer
Ammonia sensing

ABSTRACT

A simple and reliable method by combination of sensing coating and interferometric optical microfiber to detect the concentration of ammonia is reported in this study. The sensor is fabricated by coating the tapered microfiber interferometer (MFI) with zinc oxide nanoparticle incorporated graphene oxide (GO-ZnO). GO-ZnO nanocomposites serving as an electron acceptor trap electrons after ammonia absorption and then change the surface refractive index of the optical microfiber in MFI. Subsequently, the MFI translates the tiny refractive index change into wavelength shift of the transmission spectra. As prepared sensor exhibits a good repeatability and high sensitivity to ammonia with different connections from 4 ppm to 140 ppm at room temperature. The gas sensor response to ammonia has been studied in different moisture level and show reliable operation in low humidity atmosphere. In addition, the gas sensor also displays an excellent selectivity to ammonia compared to several possible interfering volatile organic compounds. This may be attributed to the selective ammonia absorption at the GO-ZnO surface and the additional synergistic effects of GO-ZnO nanocomposites that are desirable and advantageous for gas sensing.

1. Introduction

There is a high demand for developing highly sensitive, selective, and simple yet reliable sensors for the detection of toxic and inflammable gases. Gas sensor have attracted considerable attention in recent years, due to their extensive application foreground in many fields such as environmental monitoring, industrial production and safety, medical diagnosis, and industrial wastes [1,2]. Ammonia as one of hazardous gases, humans can smell at a concentration of about 55 ppm when exposed to it for the first time [3]. The Occupational Safety and Health Administration (OSHA) requires that humans working in an environment where the ammonia concentration is above 25 ppm no more than 8 h and no more than 15 min when the concentration beyond 35 ppm. All these limits are close to or below the concentrations at which humans can potentially smell ammonia [4]. Indeed, ingesting excess ammonia can cause pulmonary edema or even death. However, ammonia has a wide range of applications in daily life, including purification, manufacturing of nitrogenous fertilizers and ammonium hydroxide, preparation of liquid nitrogen, etc. Moreover, as one of the major human metabolites, detection the content of ammonia in the breath or urine can provide an early diagnosis for related diseases [5]. Therefore, no matter from the consideration of industrial safety or from the health care, the sensitive detection of ammonia has a broad prospect of application and value.

Devices based on optical techniques, especially those that combine optical fiber structures and nanomaterials shows a bright prospect for development of chemical and gas sensors. Optical fiber sensing technology is suitable to application in harsh environments, which can provide unique opportunities in many conditions that are impossible for electronic sensors (e.g. strong electromagnetic fields, flammable and explosive gases). The crucial factor of optical fiber gas sensor is the sensitive material that changes its optical properties in the presence of the target gas molecules. The performance of optical fiber gas sensors, such as sensitivity, response/recovery times and selectivity, greatly depend on the properties of the coating material. Research in optical fiber gas sensors has focused on the development of functionalized materials [6]. For the past years, there are various kinds of nanomaterials and nano-composited materials, including metal oxide nanohybrid structures (nanoparticles, nanorods, nanowires and thin films [7–10]) and different carbon materials such as carbon nanotube (CNT), graphene and its derivatives (graphene oxide (GO), reduced graphene oxide (RGO)), etc. have been extensively explored as var-

* Corresponding author.
E-mail address: hwfu@xsyu.edu.cn (H. Fu).

http://dx.doi.org/10.1016/j.snb.2017.06.067
0925-4005/

Table 1
List of various gas sensing devices that combine optical fibers and sensitive materials.

No.	Material	Principle/method	Analyte	Performance	Reference
1	Pd film	Cladding modified micro-FBG	Hydroge Conc.0–5%	Response time 60 s	Yu et al. [18]
2	AgNP–GO composites	Cladding removed PMMA optical fiber	Ammonia 0–500 ppm	Sensitivity can be improved by decreased particle size of Ag	Kavinkumar et al. [19]
3	PAA-amino -CNTs	Cladding modified core-FBG	CO_2 1000 −4000 ppm	Response/recover time (3.07 min/2.95 min)	Shivananju et al. [20]
4	Graphene	All optical MZI based on GMHW	NH_3 40–240 ppm	Response time (0.5 s) Sensitivity – 6 pm/ppm	Yao et al. [21]
5	GO	Microfiber knot Resonator (GMKR)	NH_3, CO 0–300 ppm	Sensitivity for NH_3 and for CO are different	Yu et al. [22]
6	PDDA/TSPP	Long period grating (LPG) optical fiber	Ammonia 0–168 ppm	Highly sensitive (0.7 nm/ ppm) and selective	Wang et al. [23]
7	ZnO-PMMA	Coated on the tip of fiber to form a FPI	H_2S 1–5 ppm	Low response/recover time and high sensitivity	Kitture et al. [24]
8	RGO	Coated on the surface of etched FBGs	NO_2 0.5–3 ppm	Response time (40 min), the sensor can be improved to sub ppb level	Sridevi et al. [25]

ious chemical and gas sensing applications [11–13]. In particular, graphene materials are considered as an excellent kind of sensor materials due to its larger specific area can maximizes the interaction between the adsorbates, and unique electrical properties such as high mobility and low electrical noise [14]. As a research hotspot in recent years, combining graphene with metal oxides are extensively investigated to improve gas sensing performance. The hybrid nanostructures not only display the individual properties of the nanoparticles and of graphene, but also show additional synergistic effects that are desirable and advantageous for gas sensing, particularly in achieving good gas response at room temperature, high sensitivity and selectivity to targeted gas molecules [15,16]. Optical gas sensing devices, especially based on optical fibers and nanomaterials provide a platform that offers several advantages over other sensing technologies [17]. Several results of the optical fiber gas sensing devices based on different materials are summarized in Table 1. However, most of these reports have their respective limitations, such as bad selectivity, sluggish response, incomplete recovery, or low sensitivity. Therefore, developing a simple and reliable, high sensitivity and selectivity gas sensor is the research hotspot for optical fiber gas sensing technology.

To date, among these various types of optical fiber gas sensors, tapered microfiber sensor are attractive, given the additional advantages of high sensitivity and miniature size. A tapered microfiber is fabricated by simultaneously heating and stretching a short section of optical fiber into micron scale in diameter. The tapered waist region exposes the evanescent field beyond the surface and thus interact with surrounding medium. With coating functionalized material onto the sensing region, any slight changes of the environment compositions can be detected due to the any change in optical characteristics of the sensitive coating, which will lead to changes in the transmission spectrum of tapered microfiber. Therefore, the tapered microfiber sensor shows a bright prospect for a variety of sensing applications.

In this work, we demonstrate a simple and reliable way of fabricating the GO-ZnO coated MFI for ammonia gas sensing. The MFI is achieved by tapering a section of multi-core fiber (MCF) down to micron scale in diameter. The surface evanescent field of the microfiber can be significantly enhanced by the GO-ZnO coating, which is shown to be sensitive to the changes in the optical properties of the coating. Then a high sensitive and selective ammonia gas sensor have been realized by monitoring the wavelength shift of the transmission spectrum which occur due to the significant changes in effective refractive index caused by the adsorption of ammonia molecules on GO-ZnO coating.

2. Experimental

2.1. Evanescent wave in MFI

The procedure of the fabrication MFI are reported in our previous work [26], but the difference is that we are using multi-core fiber (MCF) in this work. Briefly, a section of MCF is tapered down to micron scale in diameter by using a flame-heated fiber tapering machine. The used MCF is produced by Futong Group, whose sectional view is showed in Fig. 1(c), the MCF has a central core and other six side cores that are arranged in a quasi-hexagonal array. All the seven cores have the same diameter of 10.31 μm, the core-to-core pitch (Λ) is designed with 38.78 μm. There are two main reasons and advantages to use such multi-core fiber: i) The special core distribution of the used MCF make it easier to induce the intermodal coupling and produce interference. The oscillation transmission spectrum of the middle-tapered MCF interferometer have extremely high extinction ratio and low insertion loss. ii) MCF presents a circular symmetric structure making it a polarization-independent fiber device.

The hydrogen flame heated the MCF once accompanied by slowly stretching the optical fiber with two translation stages. The profile parameters are mainly determined by the moving speed of the stages. A tapered microfiber with a uniform region of 12.5 μm in diameter is fabricated to use in gas detection. The intermodal coupling among multiple core modes in the MCF are strongly determined by the evanescent field and the pitch size Λ, the strong evanescent field and the small pitch size can be obtained by controlling the waist diameter of the MCF. In the process of adiabatically tapering, when the waist diameter of the MCF decrease, the core diameter and the pitch size Λ simultaneously diminished. The ratio between the core diameter and the pitch size is not changed both before and after tapering. When the light enters the center core of the middle-tapered MCF interferometer, the intermodal coupling occurs predominately between the center core mode and side core modes [27]. Herein, we assume that the difference in effective refractive indices is Δn, and then the phase difference between the two modes can be described as:

$$\delta\phi = 2\pi\Delta nL/\lambda \quad (1)$$

Where, λ is central wavelength of the optical source, and L is the effective physical length of the interferometer. The difference in effective indices between center core mode and side core mode are sensitive to external environment refractive index. The relationship between the wavelength shift and external RI (n_{ext}) can be expressed by formula (2), which obtained by taking a small varia-