High Sensitive Ammonia Gas Sensor Based on Graphene Coated Microfiber

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Abstract— We report a sensitive all-fiber ammonia gas sensor based on graphene coated microfiber. Through light deposition and interaction with the evanescent filed of the microfiber, the graphene can be effectively coated onto it. The absorbed ammonia gas molecules significantly influent the conductivity of the graphene, resulting in the increase of the refractive index, which makes the transmission optical power change with a sensitivity of 0.1352 dBm/100 ppm and high resolution of 0.74 ppm. The obtained results may have great potential applications in sensing fields with high sensitivity, fast response, easy fabrication and tunable ability.

1. INTRODUCTION

Ammonia is a kind of common poisonous gas in the atmosphere, mainly comes from the world of nature and artificiality. Being colorless and smelly, the ammonia gas may have irritation and corrosion effects to the human eyes and the upper respiratory tract mucous membrane. Therefore, ammonia gas sensor has been widely used in the fields of fire, agriculture, chemical industry, medicine, etc., including portable, pumping suction and fixed type, the detection principle of which mostly are electrochemical principle. However, miniaturized, high sensitivity and electrical magnetic immune ammonia gas sensors are badly in need of for severe environment.

In recent years there has been reported a variety of new methods for the detection of ammonia. Based on the Lambert-Beer's law, the traditional spectroscopy method is to detect the species and concentration according to the selective absorption to the spectra, which includes tunable diode laser absorption spectrum (TDLAS), non-dispersive infrared spectrum (NDIR) and Fourier transform infrared spectrum (FTIR) [1] etc.. Nevertheless, these methods need lots of additional circuit and measurement instrument with complex operations. D. Cheng [2] proposed to use the near-field technology to prepare the polyaniline nano-fiber sensor and obtained the sensitivity of 2.7% at 1×10^{-6}. In the meantime, the carbon nanotube sensor, prepared by using two-dimensional electrophoresis technology, has good linear response when the concentration is higher than 20×10^{-6}. Fazel Yavari [3] demonstrated a macro graphene foam-like three-dimensional network ammonia gas sensor comprised of few-layer graphene sheets with the sensitivity of 30% at 1000 ppm by detecting the electrical resistance. However, the sensor was susceptible to electromagnetic interference and the preparation process was complicated.

Micro/nano-fiber (MNF) [4] is a new type of optical waveguide with the diameter reaching to micron and nanometer level, featured with compact size, good flexibility, low loss, large evanescent field and ease of integration, which has a wide application in communication and sensor systems. Graphene [5] has monolayer thickness of 0.335 nm, which appears as single two-dimensional hexagonal lattice with high surface-to-volume ratio and excellent electronic-photonic properties. It has been used as transparent conductive film, lithium ion battery, super capacitor, organic photovoltaic cell, electron field emitter, catalyst and gas sensor. Combining the advantages of MNF and graphene, we propose a passive and high sensitive ammonia gas sensor based on graphene coated microfiber (GCMNF), which is of easy fabrication, miniaturization, low cost and high sensitivity.

2. WORKING PRINCIPLE

Graphene has large specific surface area to increase the contact area between sensor and ammonia gas molecules, thus improving the sensitivity. Due to being similar to the P-type semiconductor, when the molecules absorbed on the surface of graphene, its impurity band will emerge near the Fermi level and change the electronic properties of graphene [6]. If the absorbed gas appears pull-electrical-effects [7], the holes will increase, making the electrical conductivity increase. On the

contrary, if the absorbed gas appears giving-electrical-effects, the redundant holes will be consumed, making the electrical conductivity decrease. Here ammonia gas molecule is the latter one, which makes the decreasing of the graphene electrical conductivity.

According to Ref. [8], the electrical conductivity and refractive index of graphene have the relationship of

$$\varepsilon_{eff} = 1 + i\sigma_c/\omega\varepsilon_0 d \tag{1}$$

$$n = \sqrt{\varepsilon_{eff}} \tag{2}$$

Here σ_c is the electrical conductivity, d is the thickness of graphene, ε_{eff} is the effective permittivity, n is the refractive index of graphene. The real part of refractive index of graphene can be calculated as

$$n_{gr} = \left[\frac{-(\sigma_i - \omega\varepsilon_0 d) + \sqrt{(\sigma_i - \omega\varepsilon_0 d)^2 + \sigma_r^2}}{2\omega\varepsilon_0 d}\right]^{\frac{1}{2}} \tag{3}$$

The simulation result is showed in Fig. 1, where the refractive index of graphene increases along with the increasing of the imaginary part of the electrical conductivity. According to the optical waveguide theory, the larger the refractive index of graphene, the larger of the n_{eff} [9]. Then the evanescent field increases as well as the transmission optical power in the core decreases along with the increasing of the n_{eff}. Based on the above analyses, the sensing of ammonia gas concentration can be achieved by measuring the variation of the transmitted optical power.

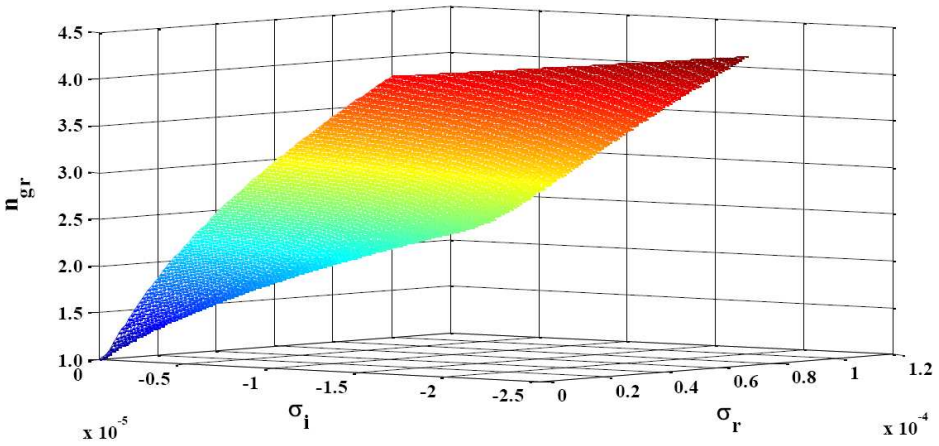

Figure 1: The real part of refractive index of graphene changes with the real and imagine parts of conductivity.

3. SYSTEM CONFIGURATION

The microfiber is bilaterally stretched from a standard single-mode-fiber (SMF) by using the flame-heating and taper-drawing technology. The microscope image of microfiber with the waist diameter of about 5 µm and the length of 10 mm is shown in Fig. 2(a). The graphene dispersion is confected by mixing 2 mg reduction of oxide graphene powder into 20 ml anhydrous ethanol with concentration of 0.1 mg/ml, and then the solution is dispersed by 80 w–59 kHz ultrasonic cleaner for 60 mins to make the graphene disperses in the ethanol uniformly, as depicted in Fig. 2(b). Then fix the two ends of the microfiber onto the three-dimensional alignment stages, and adjust the stage to make the whole microfiber dangling in the V groove. The whole deposition structure is shown in Fig. 2(c).

When 13 dBm of radiation from a broadband optical source is propagating in the microfiber, we drip several drops of graphene dispersion into the V groove, making the microfiber immersed in it. Based on the [10], the light injection from air into the dispersion thermally causes swirl and convection at the boundary, which helps to carry the graphene particles closer to the microfiber. Then, the optical tweezer effect can trap micro/nano-sized objects by the optical intensity diversion in the solution. The microfiber has large evanescent field, which causes the optical intensity diversion. The Lorentz force is applied onto the objects in the electromagnetic field and is stronger toward the higher optical intensity direction, thus tend to trap the graphene particles onto the microfiber.

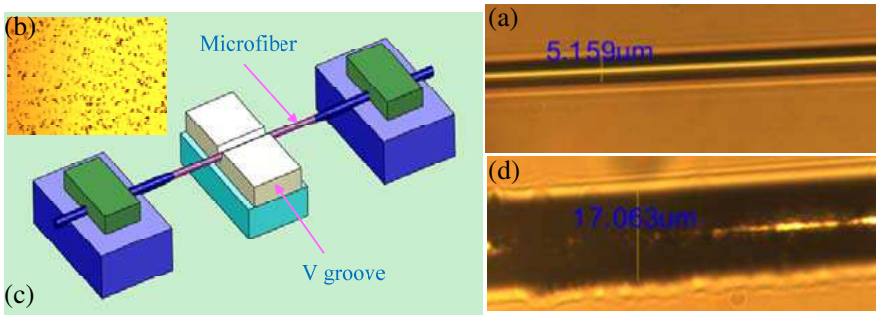

Figure 2: (a) Microscope image of bare microfiber, (b) microscope image of the graphene dispersion, (c) diagram of the deposition device, (d) microscope image of the graphene coated microfiber.

When dripping the graphene dispersion, the transmission loss increases first and then decreases gradually during the evaporation of ethanol. The optical power is collected by the optical power meter during the deposition process to measure the loss. Five minutes later, turn off the light source and wait for the ethanol to evaporate. When the power remains unchanged, it means that the ethanol is evaporated completely and the microfiber is well coated by graphene. Before and after the deposition, we both use alcohol and de-ionized water to clean the microfiber for 2 mins alternately to get rid of the dust and non-uniformly deposited graphene.

The graphene coated microfiber is clearly seen through the microscopy, as showing in Fig. 2(d). The thickness of the GCMNF is about 17.063 μm. It's a little thicker, maybe because of the high optical power leading to excess deposition, which may reduce the sensitivity of the GCMNF.

4. EXPERIMENT AND DISCUSSION

To evaluate the performance of the GCMNF for ammonia gas detection, we measured the transmission intensity of the GCMNF with ammonia gas concentration ranging from 0 to 500 ppm as shown in Fig. 3. The GCMNF was fixed into the gas chamber with the volume of about 1300 ml. The broadband light source was injected into the GCMNF and collected by the optical power meter. The catheter of the outlet was inserted into the beaker with water inside, in case of the ammonia leaking to the environment. 500 ppm of ammonia and nitrogen mixed gas as well as the pure nitrogen gas acted as the gas generators.

At first, we tested the stability of the broadband light source. The deviation of the output power of the light source was less than 0.001 dB in 20 mins, indicating that the light source was stable. Under the nitrogen atmosphere, enough NH_3 was injected into the chamber uniformly, which lasted for 200 s. To measure the reversibility of the system, inject N_2 instead of NH_3 and last for another 300 s. The pressure reducing valve was used to control the gas velocity and the power was detected every 30 s. We repeated the measurements for concentration rising and falling process and recorded the results to validate the repeatability of the gas sensor.

The experimental results are showing in Fig. 4. During the concentration of NH_3 increasing from 0 to 500 ppm, the translation power decreases from −6.82 to −7.84 dBm the first time and −6.72 to −7.38 dBm the second time, respectively. Through the linear fitting, we obtain the sensitivity of 0.1352 dB/100 ppm. Since the resolution of the commercial optical power meter can be as high as

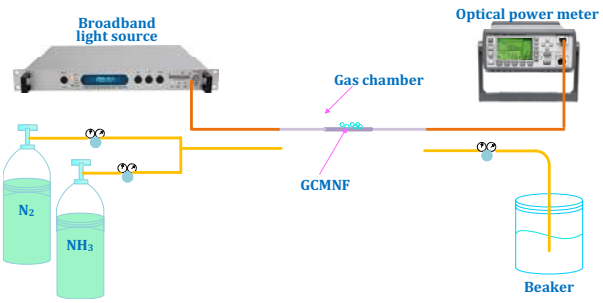

Figure 3: Schematic diagram of the ammonia gas sensor system.

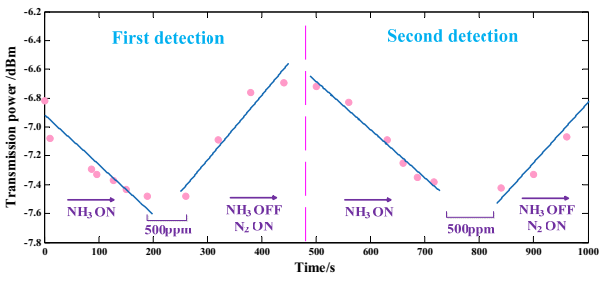

Figure 4: Transmission power changes with time.

0.001 dBm, the ammonia concentration resolution can reach to 0.74 ppm. When the concentration of NH_3 decreases from 500 to 0 ppm, the power is higher than the initial value, which may be result from the instability of the MNF.

The experiment errors mostly come from the following aspects, the air doesn't discharge completely and the NH_3 is discharged too quickly without full effect with the graphene. In addition, the MNF is unstable under the air impact, which also influences the transmission power.

It should be noted that the sensitivity can be improved by fabricating more uniform microfiber with small optical loss and appropriately adjusting the contact length between the graphene and MNF.

5. CONCLUSION

In conclusion, a sensitive all-fiber ammonia gas sensor based on the graphene coated microfiber is proposed and demonstrated. The absorption of the ammonia gas molecules have a strong influence on the refractive index of graphene, resulting in the transmission power change in microfiber with the sensitivity of 0.1352 dBm/100 ppm and high resolution of 0.74 ppm. In addition, the sensitivity is tunable by adjusting the coating thickness of graphene. Such a graphene coated microfiber with high sensitivity, fast response, easy fabrication, low cost and tunable ability would have great potential applications in environmental monitoring fields.

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