Reflectance response of tapered optical fiber coated with graphene oxide nanostructured thin film for aqueous ethanol sensing

Article *in* Optics Communications · November 2014

DOI: 10.1016/j.optcom.2014.06.035

9 authors, including:

Ahmad Ashrif A Bakar
National University of Malaysia

A. Z. Sadek
Deakin University

Hn Lim
Universiti Putra Malaysia

Huang Nay Ming
Xiamen University of Malaysia

Optics Communications 331 (2014) 320–324

Contents lists available at ScienceDirect

Optics Communications

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

Reflectance response of tapered optical fiber coated with graphene oxide nanostructured thin film for aqueous ethanol sensing

A.A. Shabaneh [a,b], S.H. Girei [a,b], P.T. Arasu [a,b], W.B.W.A. Rahman [c], A.A.A. Bakar [c], A.Z. Sadek [d], H.N. Lim [e], N.M. Huang [f], M.H. Yaacob [a,b,*]

[a] Wireless and Photonics Network Research Centre, Engineering and Technology Complex, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[b] Photonics Laboratory, Department of Computer & Communications Systems Engineering, Faculty of Engineering, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[c] Department of Electrical, Electronic and Systems Engineering, Faculty of Engineering and Built Environment, Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor, Malaysia
[d] Institute for Frontier Materials, Deakin University, Geelong, Victoria 3220 Australia
[e] Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, 43400 UPM Serdang, Selangor, Malaysia
[f] Low Dimensional Materials Research Centre, Physics Department, University of Malaya, 50603 Kuala Lumpur, Malaysia

ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form
27 May 2014
Accepted 22 June 2014
Available online 2 July 2014

Keywords:
Graphene oxide
Ethanol
Optical sensing
Reflectance
Optical fiber sensor
Dip-coating

ABSTRACT

In this work, optical sensing performance of tapered multimode fiber tip coated with graphene oxide (GO) nanostructured thin film towards aqueous ethanol with different concentrations is investigated. The tapering process of the optical fiber is done by a glass processing machine. The multimode optical fiber tip is dip-coated with GO and annealed at 70 °C to enhance the binding of the nanomaterials to the silica fiber. FESEM, Raman microscopy and XRD analyses are performed to micro-characterize the GO thin films. The morphology of the GO is observed to be in sheets forms. The reflectance response of the GO coated fiber tip is compared with the uncoated tip. The measurements are taken using a spectrophotometer in the optical wavelength range of 550–720 nm. The reflectance response of the GO coated fiber tip reduced proportionally, upon exposure to ethanol with concentration range of 5–80%. The dynamic response of the developed sensor showed strong reversibility and repeatability when it is exposed to ethanol with concentrations of 5%, 20% and 40% in distilled water. At room temperature, the sensor shows fast response and recovery as low as 19 and 25 s, respectively.

1. Introduction

Graphene oxide (GO) consists of carbon bonded with oxide functional groups [1]. GO are widely used for the improvement of electrochemical sensors [2]. It is an attractive material due to the ability of detecting different types of chemicals such as ethanol and benzene [3]. Excellent transparency, high surface-to-volume ratio and high thermal conductivity as compared to other semiconductors are some of the unique optical and physical properties of GO [4–7].

Electrical transducers for ethanol sensing have been widely explored. Weng et. al [8] and Bairiu et. al [9] developed amperometry ethanol sensors with sensitivity of 3.08 $\mu A\ \mu M^{-1}\ cm^{-2}$ with sputtered Ni/Pt/Ti as the sensing layer and 7.8 $mA\ mM^{-1}\ cm^{-2}$ on silicon nanowires with palladium–nickel electrode, respectively. Although electrical sensors are relatively low in cost and offer high sensitivity, optical fiber sensors are currently attracting considerable interest due to their exceptional characteristics such as immunity to electromagnetic interference, temperature and large bandwidth compared to electrical transducing platforms [10–12]. Optical fiber has also low attenuation of 3.5 dB/km compared to electronic transducers system that have very high loss and need to be compensated with amplifiers.

One of the most suitable optical transducing platforms for sensing applications is tapered optical fiber. Tapered optical fiber is found to be more sensitive as compared to the conventional fiber due to the manner of light propagation in its core. Larger fraction of the optical power propagates outside the tapered fiber core as compared to the normal fiber core and thus, allowing the interaction of the light with the sensing layer [13]. However, the integration of GO with tapered optical fiber as a chemical sensor is yet to be fully explored. It is anticipated that GO with its high surface-to-volume ratio when integrated with tapered fiber will lead to the enhancement in the device sensitivity [14].

One of the chemicals frequently utilized in the industries such as biomedical, chemical and food is ethanol [15–18]. Ethanol

* Corresponding author.
E-mail address: hanif@upm.edu.my (M.H. Yaacob).

http://dx.doi.org/10.1016/j.optcom.2014.06.035
0030-4018/

sensors are also widely deployed for health applications such as breath analyzer. However, most of the ethanol sensors are based on electrical domain. Only a few studies have been reported on ethanol sensing using optical domain [19].

The development of optical sensors coated with GO is still in their maturing stage. One of the advantages of these types of sensors is room temperature operation thus reduced power consumption and complex circuitry. Therefore, there are exciting opportunities in the investigation of the sensing properties of GO nanostructured thin film deposited onto tapered optical fiber tip. This paper presents performance analysis of ethanol sensor based on tapered multi-mode optical fiber (MMF) tip coated with GO via a dip-coating technique. The microcharacterization results of the GO thin film are investigated via field emission scanning electron microscopy (FESEM), Raman spectroscopy, and X-ray diffraction (XRD). The dynamic responses of the developed fiber sensor with and without GO towards different concentrations of ethanol (5–80%) are also reported.

2. Experimental

The synthesis of GO is done using the simplified Hummers' method [20] with ultrasonic agitation after chemical oxidation of graphite. The obtained GO solid is suspended in water with the concentration of 0.5 mg/ml. The GO solution is used to coat the nanostructured thin film onto optical substrates via the dip-coating technique. The dip-coating of GO onto tapered fiber tip and glass substrate is done using a PTL-MMB01 dip coater machine. The film is produced using dipping and withdrawal speed of 200 mm/min. Prior to the deposition, the substrates are annealed at 70 °C to enhance the binding of the nanomaterial to the tip [21]. The dip-coating process was repeated three times. After that, the samples are dried in the air for 1 h and then heated up in the oven for 10 min at 70 °C to improve the film adhesion [22]. The films were deposited onto fiber tip and quartz substrates for ethanol sensing investigation and micro-characterization, respectively. Table 1 summarizes the preparation parameters of the GO thin films.

A standard multi-mode silica fiber with core and cladding diameter of 62.5 μm and 125 μm respectively is used in this experiment. The fabrication of the tapered fiber is done with a glass processing workstation (Vytran GPX-3000, USA) shown in Fig. 1. Initially, the polymeric coating of the bare optical fiber for several centimeters is removed using a fiber stripper and then cleaned with alcohol. The optical fiber is then placed on the glass processing workstation with the area to be tapered is just above the filament. The two end of the fiber are fixed to the fiber holding block. This machine operates by pulling the two ends of the fiber while it is heated by the filament. The power of the filament heater was set to 38 W. The fiber holding block controls the pulling distance from both ends of the fiber. The dimensions of the fiber are configured according to the taper parameters as shown in Fig. 2. Tapered fibers with waist diameter of 50 μm, waist length of 10 mm and down/up taper length of 5 mm are fabricated. The tapered fiber is then cleaved at the middle to achieve a tapered tip of 5 mm length to be coated with the nanomaterials.

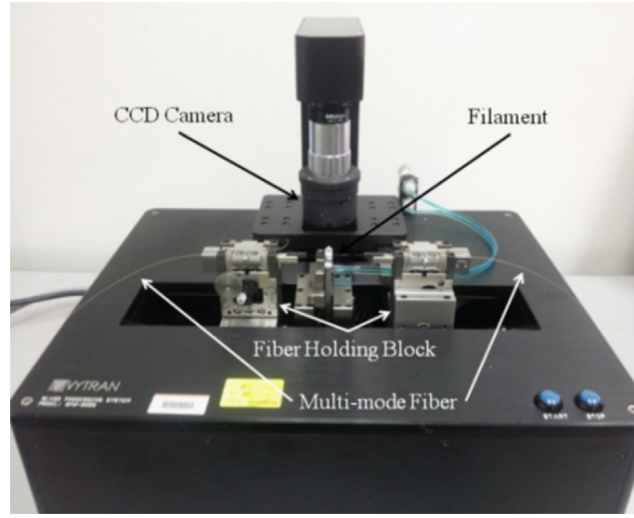

Fig. 1. Optical fiber tapering system.

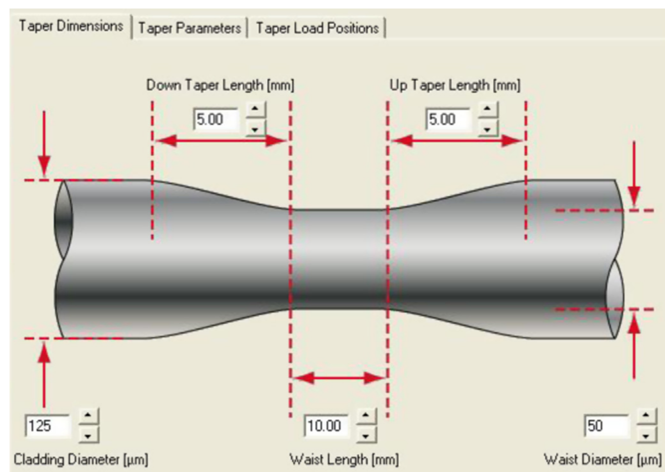

Fig. 2. Tapered fiber parameters.

The ethanol sensing setup consists of a tungsten halogen light source (HL-2000, Ocean Optics, USA) with wavelength emission ranging from 360 to 2500 nm and a spectrophotometer (USB4000-VIS-NIR, Ocean Optics, USA) with spectral response from 200–1100 nm as shown in Fig. 3. The tapered optical multi-mode fiber tip coated with GO thin film is connected to 1 × 2 coupler (50:50 coupling ratio). The coupler was connected to the light source and the spectrophotometer using optical cables. Reflectance measurement is performed by transmitting the optical signal into the standard optical fiber. The reflected signal from the fiber tip is collected by the spectrophotometer. Subsequently, the response from the developed sensor was processed by the computer via SpectraSuite software.

Table 1
Preparation parameters of GO thin film.

Preparation parameters	
Annealing temperature (°C)	70
Dip coater reaction time (m)	18
GO concentration (mg/ml)	0.5
Type of substrate	Multimode fiber (MMF) & quartz
MMF tip diameter (μm)	50
Surface area of the tapered fiber tip (m^2)	7.869×10^{-7}

3. Results and discussion

3.1. Tapered optical fiber properties

Fig. 4 shows the image of the tapered optical fiber taken by the glass processing system CCD camera. The waist diameter of the fiber decreases linearly from 125 μm to 50 μm. The inset shows

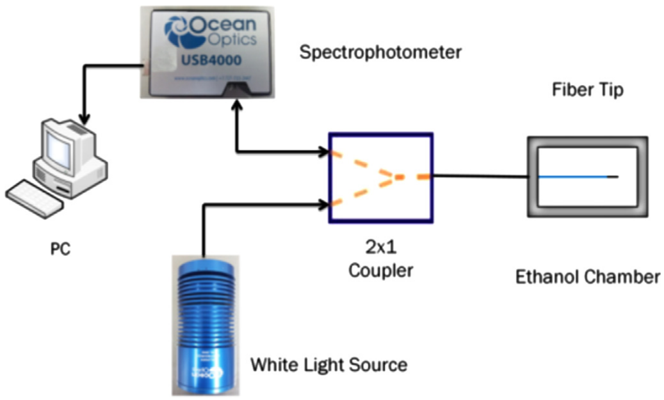

Fig. 3. Schematic diagram of experimental setup.

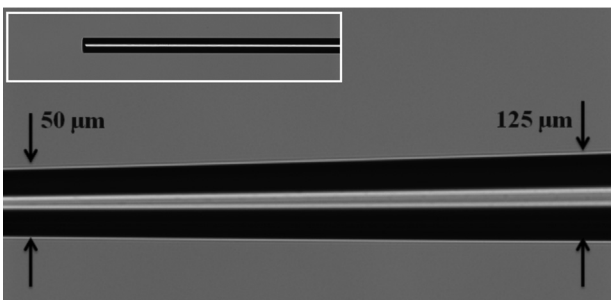

Fig. 4. The image of the fabricated tapered optical fiber. The inset shows the tip of the tapered optical fiber.

the tip of the tapered multi-mode optical fiber. The tip is cleaved precisely in the middle of the tapered region to give a dimension of 50 μm tip. To ensure propagation power loss is kept as low as possible, and to avoid coupling between the fundamental mode and higher order modes, the taper's local length scale is kept much larger than the coupling length between these two modes [23]. The loss of the tapered fiber in this experiment is measured to be 1.1 dB.

3.2. GO film properties

The morphology of the GO nanostructured thin film is observed by field emission scanning electron microscopy (FESEM). FESEM image is obtained using FEI Nova Nano SEM 400 operated at a 20.0 kV source. Fig. 5 shows the FESEM image of the GO films. It reveals that the GO thin films are nanosheets. Its translucency is obvious as creases on the edges and small pieces of graphene oxide could be observed on the other side of the sheet. Moreover, the folding of the GO sheets contributes to a darker intensity on the sheet [24]. This implies that the graphene oxide is single to a few layers thick. Furthermore, the GO sheets adhered well to the substrate, promoting reflectance on the GO thin film. The thickness of the nanostructured GO thin film is estimated to be approximately 20–30 μm, due to the overlapping of the nanosheets. This FESEM is performed to verify the uniformity of the coating of GO films on the substrates.

Fig. 6 shows the Raman spectrum of the GO thin film. The measurements are carried out by Raman spectrometer (Renishaw inVia) using laser source with $\lambda = 514$ nm. The spectrum reveals the four characteristic D, G, 2D and S3 peaks of GO. The D peak at about 1350 cm^{-1} generates from the breathing modes of six-membered rings that are activated via structural imperfections caused by the attachment of hydroxyl and epoxide groups on the carbon basal plane. The G peak at 1600 cm^{-1} duly corresponds to the first-order scattering of the E_{2g} phonon mode at the Brillouin zone center. The 2D peak at 2690 cm^{-1} is the second order of the D peak and the S3 peak at 2930 cm^{-1} is due to the imperfect activated grouping of phonons [4,5,25].

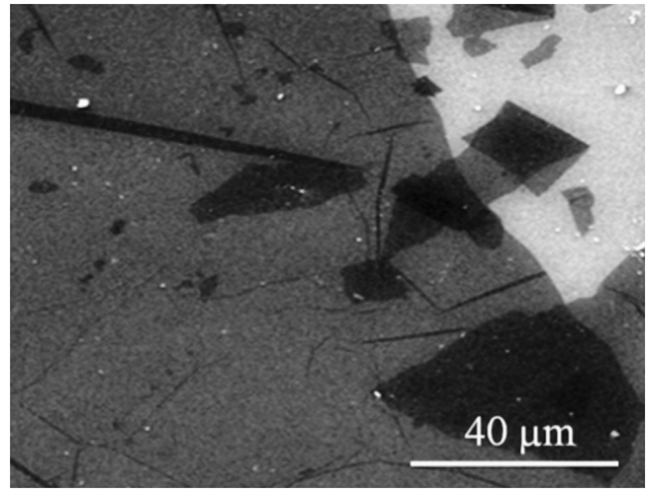

Fig. 5. FESEM image of graphene oxide sheets on glass substrate.

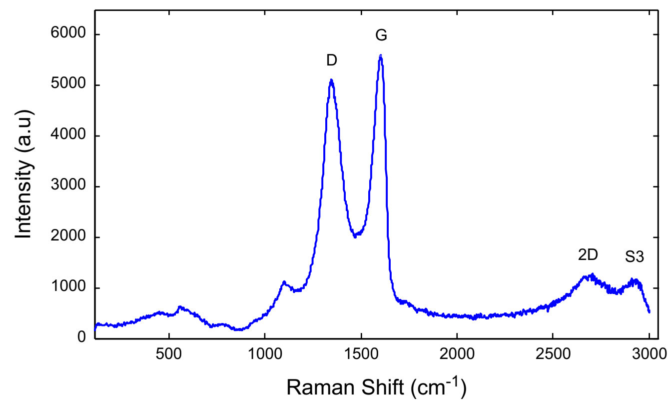

Fig. 6. Raman spectra of GO thin film on glass substrate excited with a 514 nm laser.

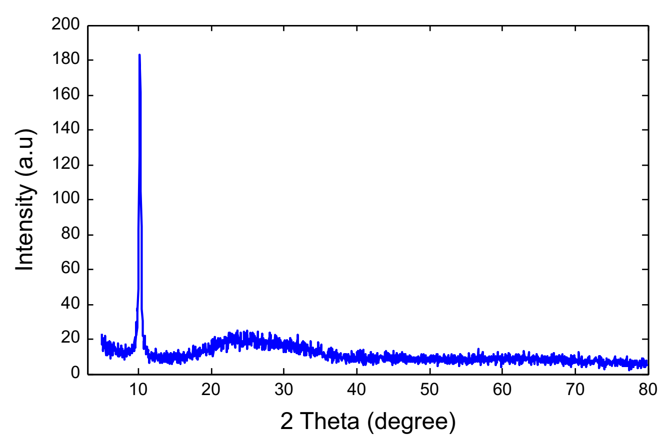

Fig. 7. XRD of GO thin films.

XRD analysis of the dip-coated GO thin film is shown in Fig. 7. The diffraction peak of GO is at 10.24° with 001 reflection which corresponds to the layer-to-layer distance of 8.63 Å. The interlayer distance for GO is significantly larger than pristine graphite (3.36 Å) due to the intercalating oxide functional groups [26]. These microcharacterization results are significant to verify the morphology of the GO nanostructured thin films.

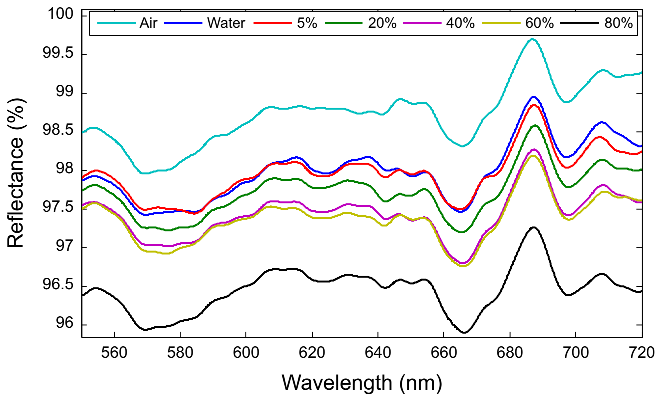

Fig. 8. Reflectance spectra (550–720 nm) of tapered fiber tip sensor towards different ethanol concentrations.

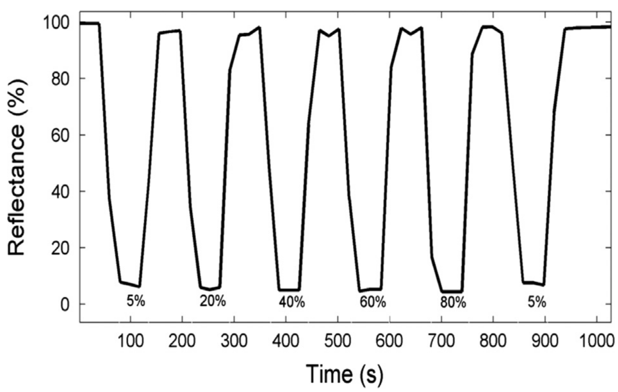

Fig. 9. Dynamic response of uncoated and tapered fiber tip sensor towards different concentrations of ethanol, integrated over wavelength range of 500–800 nm.

3.3. Reflectance spectra response

Fig. 8 shows the reflection spectra response of tapered multi-mode fiber tip coated with GO exposed to air and different concentrations of ethanol at room temperature. It has been observed that the reflectance spectrum of the GO coated fiber tip decreases when exposed to different concentrations of ethanol for a wavelength range of 550 nm–720 nm as shown in Fig. 8. In a tapered fiber, a higher fraction of evanescent wave field passes inside the cladding, which is sensitive to the physical environment of their surroundings. The interaction between the GO on the tapered fiber tip and different concentrations of ethanol molecules transforms the optical characteristic of the GO films, resulting in the proportional response of the developed sensors towards ethanol. Fig. 8 also shows a significant depth of spectrum at wavelength 660–680 nm. It is expected that the reflection depth around this range is due to over-tone and combination tone of O–H stretched reflection centered around 665 nm with reflectance of 95% [27]. The peak around 685 nm is also expected due to the induced reflection of water [28]. It can be surmised that the hydrogen bonding of the functionalized groups on GO with reflected molecules is responsible for this response [16].

3.4. Ethanol sensing performance

The presence of ethanol is detected by both tapered fiber tips with and without GO thin films as shown in Figs. 9 and 10. The tests were performed at room temperature. Fig. 9 shows the dynamic response of blank tapered fiber tip exposed towards different concentrations of ethanol. The measurement is taken by integrating the spectrum over a

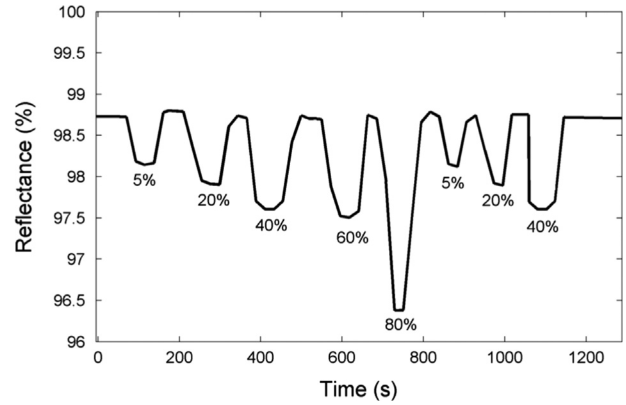

Fig. 10. Dynamic response of tapered fiber tip sensor coated with GO towards different concentrations of ethanol, integrated over wavelength range of 500–800 nm.

Table 2
Sensitivity of GO coated sensor tip towards ethanol concentrations.

Ethanol concentration (%)	Reflectance (%)	ΔC	ΔR	S ($\Delta R/\Delta C$)
5	98.2	–	–	–
20	97.9	15	0.3	0.02
40	97.55	20	0.35	0.0175
80	96.45	40	1.1	0.0275

wavelength range of 500 nm–800 nm. It indicates high sensitivity of the tapered fiber tip towards ethanol. However, the response from the blank fiber tip did not distinguish the different ethanol concentrations. The responses are expected solely due to the change of the ethanol refractive index.

On the other hand, the dynamic response is proportional to the different concentrations of ethanol solutions exposed to the tapered multi-mode fiber tip coated with GO nanostructured thin film as shown in Fig. 10. The response from the GO coated fiber tip changes according to the ethanol concentrations in the forward order. This is expected to be due to the change of refractive index as well as chemisorption of ethanol onto GO layer. A significant decrease in the reflectance is observed with respect to the response time. However, the reflectance response is descending with the increase in the concentrations of ethanol. The dynamic reflectance response decreased by 2.5% when the sensor was exposed to 80% of ethanol. The sensor recovered fully and returned to its initial base line upon exposure to air. In general, the response time for the GO coated fiber tip is less than 19 s, while the recovery time is less than 25 s. The response and recovery of the developed sensor are fast and stable. Furthermore, the sensor shows high sensitivity and repeatability. The repeatable behavior of the sensor with consistent reflectance response is confirmed after exposing the sensor with another cycle of 5%, 20% and 40% ethanol concentrations (Fig. 10). It can be observed that the GO sensor shows higher sensitivity (defined as the slope of the curve given by $S=R/C$, where S is the sensitivity, R is the sensor response, and C is the analyte concentration in %) than the uncoated sensor.

Table 2 summarizes the sensitivity of the GO coated sensor tip towards ethanol concentrations. The sensitivity of the sensor remains stable for all concentrations of ethanol. The result reveals a promising performance of GO coated optical fiber tip as a highly sensitive ethanol sensor.

4. Conclusion

This work presents the optical sensing performance of a tapered optical fiber sensor coated with GO nanostructured thin films towards aqueous ethanol. The main interest of the investigation is to identify the effect of combining tapered optical fiber which is a highly sensitive optical transducer with GO as one of the nanomaterials with the highest surface area. The sensing performance of the GO coated onto tapered fiber was compared with the performance of the uncoated and tapered fiber at room temperature. Both fiber sensors were sensitive towards ethanol by changing their reflectance responses upon exposure to different ethanol concentrations. The magnitude of response for the uncoated and tapered fiber is similar for all ethanol concentrations. This indicates that the sensitivity of the tapered fiber alone depends on the ethanol refractive index. However, the reflectance responses of the tapered fiber tip coated with GO films change proportionally with the different ethanol concentrations. This response is expected due to the chemisorption of the ethanol into the GO films changing the film refractive index. As a result, the evanescent field of the reflected light changes proportionally with the ethanol concentrations. The reflectance spectrum of the developed sensor decreases when exposed to different concentrations of ethanol for a wavelength range of 550 nm to 720 nm. Ethanol of 5% concentrations was successfully detected by the sensor with fast response and recovery (<25 s) at room temperature. Further enhancement that can be explored to improve the tapered fiber sensing performance is by varying the taper dimension as well as optimizing the operating temperature and the thickness of the GO films. In general, the high sensitivity of the tapered fiber sensor coated with GO thin films towards ethanol indicate their potential for applications in food analysis, wine identifications and breath analyzers.

Acknowledgments

The authors would like to acknowledge Universiti Putra Malaysia for the project fund under Research University Grant Scheme (RUGS) No. 05-02-12-1882RU.

References

[1] K.P. Loh, Q. Bao, G. Eda, M. Chhowalla, Nat. Chem. 2 (2010) 1015.
[2] Y. Shao, J. Wang, H. Wu, J. Liu, I.A. Aksay, Y. Lin, Electroanalysis 22 (2010) 1027.
[3] Y. Liu, X. Dong, P. Chen, Chem. Soc. Rev. 41 (2012) 2283.
[4] S. Eigler, C. Dotzer, A. Hirsch, Carbon 50 (2012) 3666.
[5] X. Li, M. Liu, Z. Yan, Q. Wang, Y. Wang, Y. Wang, and X. Yu, in: Proceedings of the Photonics Global Conference (PGC) IEEE, p. 1 2012.
[6] J.A. Kim, T. Hwang, S.R. Dugasani, R. Amin, A. Kulkarni, S.H. Park, T. Kim, Sensors and Actuators B 187 (2013) 426.
[7] Q. Bao, K.P. Loh, ACS Nano 6 (2012) 3677.
[8] Y. Weng, J.F. Rick, T. Chou, Biosens. Bioelectron. 20 (2004) 41.
[9] B. Tao, J. Zhang, S. Hui, L. Wan, Sensors and Actuators B 142 (2009) 298.
[10] O.C. Compton, S.T. Nguyen, Small 6 (2010) 711.
[11] H. Rahman, S. Harun, M. Yasin, S. Phang, S. Damanhuri, H. Arof, H. Ahmad, Sensors and Actuators A 171 (2011) 219.
[12] Y. Tian, W. Wang, N. Wu, X. Zou, X. Wang, Sensors 11 (2011) 3780.
[13] S. Guo, S. Albin, Opt. Express 11 (2003) 215.
[14] K.Q. Kieu, M. Mansuripur, Photon. Technol. Lett., IEEE 18 (2006) 2239.
[15] Z.C. Luo, W.J. Cao, A.P. Luo, W.C. Xu, Appl. Phys. Express 5 (2012) 5103.
[16] C.S. Yeh, Int. J. Sci. Eng. 2 (2012) 1.
[17] R.J. Wu, Y.C. Huang, M.R. Yu, T.H. Lin, S.L. Hung, Sensors and Actuators B 134 (2008) 213.
[18] M. Parmar, R. Bhatia, V. Prasad, K. Rajanna, Sensors and Actuators B 158 (2011) 229.
[19] H. Teymourian, A. Salimi, R. Hallaj, Talanta 90 (2012) 91–98.
[20] M. Faisal, S.B. Khan, M.M. Rahman, A. Jamal, A. Umar, Mater. Lett. 65 (2011) 1400.
[21] H.N. Ming, Int. J. Nanomedicine 6 (2011) 1817.
[22] D. Yang, A. Velamakanni, G. Bozoklu, S. Park, M. Stoller, R.D. Piner, S. Stankovich, I. Jung, D.A. Field, C.A. Ventrice Jr., Carbon 47 (2009) 145.
[23] M. Zibaii, H. Latifi, M. Karami, M. Gholami, S. Hosseini, M. Ghezelayagh, Meas. Sci. Technol. 21 (2010) 105801.
[24] B. Renganathan, D. Sastikumar, G. Gobi, N. Rajeswari Yogamalar, A. Chandra Bose, Opt. Laser Technol. 43 (2011) 1398.
[25] H.N. Lim, N.M. Huang, C.H. Chia, I. Harrison, Inorganic nanostructures decorated graphene, in: Dr. Sukarno Ferreira (Ed.), Advanced Topics in Crystal Growth, InTech Publication: Rijeka, Rijeka, Croatia, 2013.
[26] M. Shanmugam, T. Bansal, C.A. Durcan, B. Yu, Electron Device Lett., IEEE 33 (2012) 1165.
[27] R.A. Litjens, T.I. Quickenden, C.G. Freeman, Appl. Opt. 38 (1999) 1216.
[28] V.S. Langford, A.J. McKinley, T.I. Quickenden, J. Phys. Chem. A 105 (2001) 8916.