



# Graphene oxide coated U-bent plastic optical fiber based chemical sensor for organic solvents

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## ABSTRACT

This study describes the development of a refractive index (RI) based fiber optic chemical sensor using a U-bent plastic optical fiber (BPOF) probe made of 0.5 mm polymethylmethacrylate (PMMA) core and optimum bend diameter of 1.4 mm coated with graphene oxide (GO) film. GO film on BPOF sensor surface significantly enhance the RI sensitivity of the sensor as well as its chemical resistance due to improved refractive index contrast and PMMA surface passivation by GO respectively. GO was chemisorbed to hexamethylenediamine (HMDA) functionalized BPOF probe surface by identifying the optimum GO concentration (100  $\mu\text{g/ml}$ ) and incubation time (24 h). An enhanced RI sensitivity of  $9.42 \pm 0.37$  ( $\Delta A_{845\text{nm}}/\Delta \text{RIU}$ ) was achieved using GO coating of thickness 3.3  $\mu\text{m}$ , which is 3.6 times higher than that of the bare BPOF probe. The RI sensitivities in presence of organic solvents including methanol, ethanol and isopropyl alcohol are found to be  $12.75 \pm 1.19$ ,  $9.97 \pm 0.66$  and  $13.93 \pm 0.92$  ( $\Delta A_{845\text{nm}}/\Delta \text{RIU}$ ) respectively. GO film over BPOF was stable even after incubation of the probes in the alcohols over 12 h. In addition, GO-BPOF probes were able to tolerate acetone environment for a prolonged duration of 30 min as opposed to 10 min in case of the bare probes due to improved chemical resistance. Hence, the GO-BPOF could potentially be utilized as a sensitive RI sensor not only for aqueous solutions but also for reactive organic solvents such as alcohols and acetone which are known to damage the PMMA surface.

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## 1. Introduction

Refractive index (RI) is a fundamental optical parameter that can be widely exploited for identification of chemical substances in numerous analytical applications including food processing and chemical industry. RI based chemical sensors are commonly employed for quantitative and qualitative assessment of chemical substances. Over the past few decades fiber optic refractive index (FORI) based chemical sensors are being extensively explored due to several advantages including small size, low power consumption, multiplexing capabilities and greater portability [1]. In addition, availability of low cost LEDs, laser diodes and photodetectors with ever-increasing range of wavelengths allows realization of affordable fiber optic chemical sensors [2]. Fiber optic sensors based on evanescent wave interaction with the medium are known to render very high sensitivity [3,4]. Evanescent wave based fiber optic sensor relies on the principle of attenuated total reflection, in which the change in the RI of the surrounding medium and/or presence of optically active substances within the vicinity of evanescent

field influences the intensity of light propagating through the fiber [5].

In recent years, plastic optical fibers (POF) have gained a great attention due to their ease in machinability, robustness, ease of optical coupling and handling [6]. High evanescent field strength and improved depth of penetration into the medium are crucial for achieving efficient interaction of light with the medium and thereby obtaining higher sensitivity. Various fiber geometries including straight de-cladded fibers [7], laterally polished [8], partially polished [9], D-shaped [10], cuvetted with inline sub millimeter hole [11], coiled POF [12], micro bent [13], bent with structural imperfections [14] and U-bent [5] have been investigated for this purpose. While tapered fiber probes give rise to superior evanescent wave interaction with the medium [15], bending the fiber offers probe robustness and ease in operation allowing dip type sensors.

Apart from adopting various modifications in fiber probe geometries, probes have been coated with plasmonically active noble metals (gold and silver), metal oxides and dielectric layers include agarose [16], PTCF fluorescent film [17], silicon nitride [18], Pd [19], Pd/WO<sub>3</sub> [20], Pd/Au [21], TiO<sub>2</sub>/SiO<sub>2</sub> [22], porphyrin doped TiO<sub>2</sub> [23] to obtain significantly higher (up to 10 fold improvement) RI sensitivity [24]. The properties of the coating together with the

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fiber probe geometry will determine the penetration depth of the evanescent field within the modified region [25]. An improved RI sensitivity has been achieved with the help of tin dioxide coating whose RI value is slightly lower than that of the fiber core, in comparison to metal thin films of optimum thickness [26]. The use of coatings with a RI value close to that of the fiber core results in a reduction of refractive index contrast that significantly increases the depth of penetration. This also results in decrement in the intensity of light passing through the fiber. The combined effect of increase refractive losses and depth of penetration of the evanescent field leads to higher sensitivity [17].

GO is a monolayer of two-dimensional carbon based material generally obtained by oxidation of graphite in presence of strong acid and oxidizing agent [27]. The RI of GO (<10 layers) was found to be 1.2–0.24i and anticipated to increase with number of GO layers [28]. Thus, low refractive index contrast (difference in refractive indices of fiber core and GO cladding layer) could be achieved by using multiple layers of GO which is known to increase the sensitivity of the sensor. In addition, the rich density of oxygen containing functional groups and large surface area (theoretical limitation:  $2630\text{ m}^2\text{ g}^{-1}$ ) facilitates the interaction of GO to a vast range of organic solvents. Due to the presence of carboxylic groups and hydroxyl groups it disperses well in water with a strong negative charge at the surface. The presence of negative charge and enriched functional groups:  $2630\text{ m}^2\text{ g}^{-1}$  facilitates the interaction of GO to a vast range of organic solvents. Due to the presence of carboxylic groups and hydroxyl groups it disperses well in water with a strong negative charge at the surface. The presence of negative charge and enriched functional groups:  $2630\text{ m}^2\text{ g}^{-1}$  facilitates the interaction of GO to a vast range of organic solvents. Due to the presence of carboxylic groups and hydroxyl groups it disperses well in water with a strong negative charge at the surface. The presence of negative charge and enriched functional groups results in ease of deposition to different substrates. Recently, graphene and GO based coatings have been used to improve the RI sensitivity [29,30]. It has been used to detect nitrogen dioxide, ethanol, humidity and heavy metals [31]. In addition, deposition of GO over a sensor surface is anticipated to enhance the density of functional groups including hydroxyl, epoxy, carbonyl and carboxylic groups [32] in comparison to limited availability of functional groups on PMMA surface of POF probe. The rich functional group density on GO readily makes it suitable for immobilization of biomolecules for biosensing applications [33].

In this article, we report a GO coated U-bent plastic optical fiber (GO-BPOF) probes with a significant enhancement in RI sensitivity and chemical resistance by taking the advantage of remarkable reduction in the refractive index contrast and improved interaction of organic solvents with GO respectively. Optimum conditions for GO chemisorption to the PMMA core surface of a BPOF probe including probe heat treatment, PMMA surface functionalization as well as the GO concentration and incubation times for effective surface coverage are investigated in detail. In addition to the ability of GO-BPOF probes as RI based chemical sensors for organic solvents including alcohols and acetone, the chemical stability of the GO layer on BPOF probe surface is thoroughly evaluated for the first time to the best of our knowledge.

## 2. Materials and methods

Super ESKA™ plastic optical fibers of  $500\text{ }\mu\text{m}$  (SK 20,  $n_{\text{core}}=1.49$  and  $n_{\text{cladding}}=1.41$ ) were procured from Mitsubishi Rayon Co., Ltd., Japan. All chemicals used including D-glucose, sodium chloride, potassium chloride, di-sodium hydrogen phosphate, potassium dihydrogen phosphate, graphite flakes, potassium permanganate, concentrated sulphuric acid, sodium

nitrate, hydrochloric acid, hydrogen peroxide, hexamethylenediamine (HMDA), sodium hydroxide, methanol (MeOH), ethanol (EtOH), propanol (Isopropyl alcohol-IPA) and acetone were of analytical grade. Deionized water (DI) obtained from Millipore was used for all experiments. Absorbance spectra from the fiber optic probes were recorded with the help halogen light source (HL 2000, Ocean Optics Inc., USA) and fiber optic spectrometer (USB 4000 XR1ES, Ocean Optics Inc., USA) by coupling the fiber ends with SMA connectors and bare fiber adapters (BFTU, Thorlabs Inc., USA). Microscopic images were taken using a research microscope (Model RXLr-4IT from Radical scientific Equipments, India).

### 2.1. U-bent POF (BPOF) probe fabrication and functionalization

The U-bent probes were prepared and amine functionalized as described elsewhere [5]. Briefly, the plastic optical fibers of  $500\text{ }\mu\text{m}$  diameter and of length  $25\text{ cm}$  were used in the experiments. The U-bent POF probes were made by inserting the fiber into a capillary of  $1.9\text{ mm}$  diameter and heating it at  $100\text{ }^\circ\text{C}$  for  $10\text{ min}$ . The U-bent portion was de-cladded by chemical etching using ethyl acetate. The U-bent region was cleaned with ethanol and washed with DI water. Then, the probes were incubated in  $1\text{ M}$  sulphuric acid to obtain hydrophilic surface through acid hydrolysis. Then, the  $\text{NH}_2$  groups were created on the sensor surface through amidation of carboxylic groups formed during the acid treatment with  $10\%$  v/v HMDA solution prepared in  $100\text{ mM}$  borate buffer for  $2\text{ h}$  at room temperature. The probes were then treated with  $1\text{ M}$  NaOH followed by thorough washing with DI water and stored in capillaries filled with  $\text{N}_2$  gas.

### 2.2. GO synthesis and characterization

GO was synthesized from graphite by modified Hummer's method [34]. In brief,  $2\text{ g}$  of graphite flakes and  $1\text{ g}$  of sodium nitrate (catalyst) were mixed together in  $50\text{ ml}$  of sulphuric acid ( $98\%$ ). The reaction mixture was stirred continuously for  $1\text{ h}$  at room temperature. Then,  $6\text{ g}$  of  $\text{KMnO}_4$  was added to the reaction mixture very slowly while maintaining the reaction temperature lower than  $15\text{ }^\circ\text{C}$  in order to prevent overheating and explosion. Soon after the addition of  $\text{KMnO}_4$ , the temperature was raised to  $35\text{ }^\circ\text{C}$  and stirred continuously for  $12\text{ h}$  during which a brownish gray paste was obtained. Then, the reaction mixture was diluted with DI water ( $10\text{ ml}$ ) as a result of which the solution turns brownish yellow. Then, the reaction temperature was raised to  $85\text{--}90\text{ }^\circ\text{C}$  and stirred for  $30\text{ min}$ . Subsequently,  $\text{H}_2\text{O}_2$  ( $50\text{ ml}$ ) was added to terminate the reaction. The synthesized GO was washed by rinsing with  $10\%$  HCl and DI water. DI water wash was continued until the pH of the solution becomes neutral followed by filtration and drying.

The GO powder obtained by the above method was dispersed in DI water using ultrasonication (stable over three weeks [35]). The dispersed GO solution was characterized with UV-vis absorption spectroscopy (Agilent technologies Cary 60 UV-vis) and Raman scattering spectroscopy (Horiba Jobin-Yvon Lab RAM HR Evolution). GO dispersed in water ( $10\text{ }\mu\text{g/ml}$ ) was characterized with UV-vis spectroscopy taking DI water as the reference. Raman scattering spectrum was obtained by drop casting the GO dispersion ( $100\text{ }\mu\text{g/ml}$ ) on a glass plate and recording the sample with  $532\text{ nm}$  laser.

### 2.3. GO deposition on BPOF probes

The bare and amine functionalized BPOF probes were coated with GO ( $100\text{ }\mu\text{g/ml}$ ) by dip coating technique following a pre and post heat treatment at  $50\text{ }^\circ\text{C}$  for  $10\text{ min}$ . The dip coating protocol for effective GO coating was optimized as follows: (i) influence of probe surface functionalization, (ii) post heat treatment for GO adhesion (iii) influence of GO solution concentration includes  $1\text{ }\mu\text{g/ml}$ ,

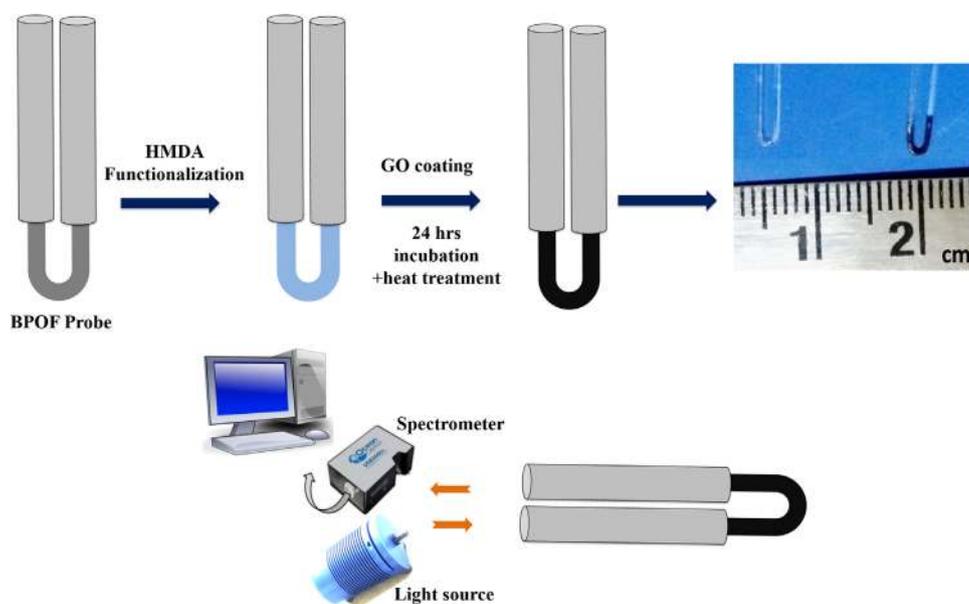


Fig. 1. Schematic representation of the optical setup and photographic image of bare BPOF (left) and GO-BPOF probe (right).

10  $\mu\text{g/ml}$ , 50  $\mu\text{g/ml}$  and 100  $\mu\text{g/ml}$  while maintaining the incubation time as 24 h and (iv) influence of incubation time such as 2, 4, 6, 12, 15, 18, 21 and 24 h with 100  $\mu\text{g/ml}$  of GO solution. After which, the dip-coating parameters were deduced with the help of Raman scattering spectrum and RI sensitivity values obtained from each probe. Subsequently, GO-BPOF probes were dipped in the organic solvents over a duration of 24 h and evaluated with Raman scattering spectroscopy.

#### 2.4. Experimental setup

Bare or GO-BPOF probes were coupled to a halogen light source and a fiber optic spectrometer at either of its ends by using SMA connectors and bare fiber adapters for RI sensing (Fig. 1). The sensing region of the bare or GO-BPOF probes was dipped in glucose solutions of subsequently higher concentrations from 0% (w/v) to 10% (w/v). The corresponding absorbance response at 845 nm was recorded with integration time as 5 or 100 ms and averaging as 100. RI sensitivity of the sensor was calculated as ratio of change in absorbance at 845 nm to the difference in RI between reference and highest RI measured. The same experimental set up and recording parameters were employed for chemical sensing, where the probes were subjected to organic solvents including methanol (MeOH, 50% v/v), ethanol (EtOH, 50% v/v and 100% v/v) and isopropyl alcohol (IPA, 50% v/v and 100% v/v). All the experiments were carried out in triplicates.

### 3. Results and discussion

#### 3.1. Characterization of GO

Raman scattering and UV–vis absorption spectroscopic characterization of as prepared GO solution was carried out in order to confirm the synthesis of GO. Optical absorbance spectrum of the GO solution with peak absorbance at 232 nm and shoulder peak at 300 nm due to  $\pi$ - $\pi^*$  transition of the carbon atoms C=C bonds and  $n$ - $\pi^*$  transitions of C=O bonds respectively (Fig.S1A) is in good agreement with the reported literature [28].

The Raman scattering spectrum of the GO was obtained by drop casting 10  $\mu\text{l}$  of GO dispersion (100  $\mu\text{g/ml}$ ) on a glass slide is depicted in Fig. S1B. The spectral features including (i) the D band

at  $\sim 1348\text{ cm}^{-1}$  due to the disorder in the graphene sheet as a result of presence of hydroxyl and epoxide groups on the basal plane and local defects, (ii) the G band at  $\sim 1592\text{ cm}^{-1}$  that corresponds to the first order scattering of E2g mode as a result of the bond stretching of  $\text{sp}^2$  carbon pairs in both rings and chains [36] and (iii) the 2D band around  $\sim 2685\text{ cm}^{-1}$  which is the second order D band that involves two phonons with opposite momentum confirm the characteristics of GO [30].

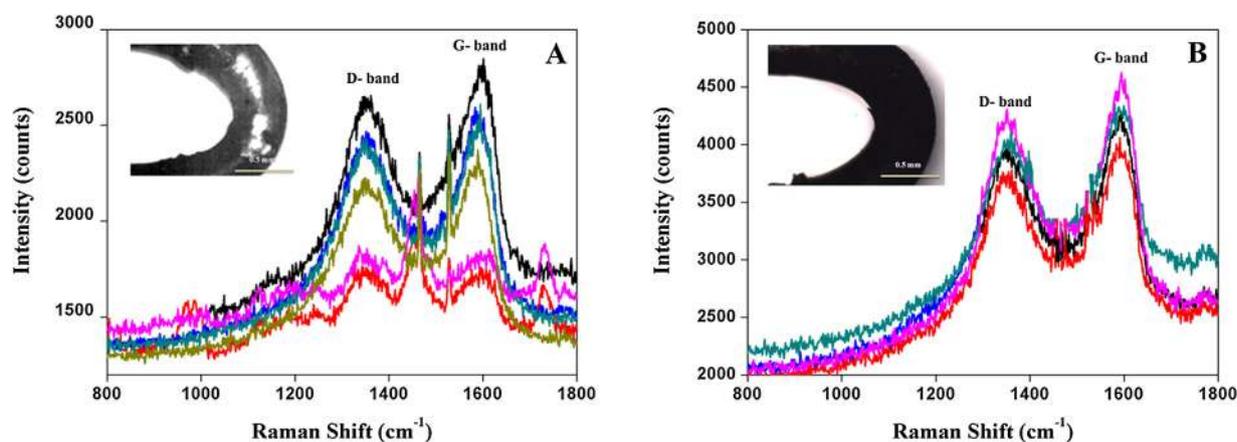
#### 3.2. Optimization of GO chemisorption on BPOF probes

##### 3.2.1. Influence of BPOF probe surface functionalization

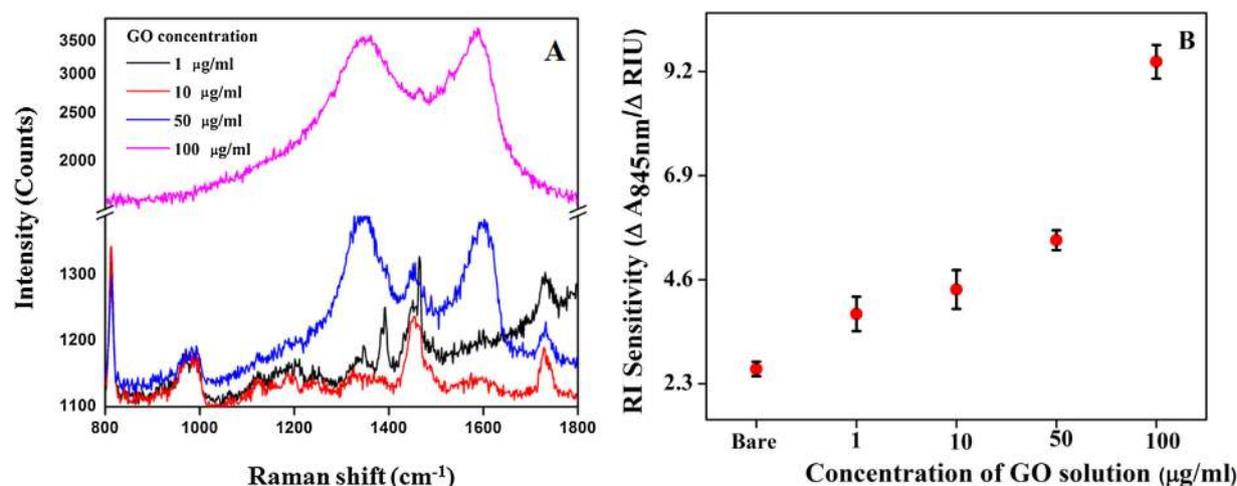
Bare as well as HMDA functionalized BPOF probes were dipped in 100  $\mu\text{g}$  GO dispersed in 1 ml of DI water over a duration of 24 h to obtain GO-coated BPOF (GO-BPOF) probes. Microscopic images (Fig. S2) reveal an improved binding of GO to HMDA treated probe resulting from the interaction between the amine groups on the probe surface and several functional groups including epoxy, phenolic-OH and carboxyl on GO. The epoxy groups at the basal plane of the GO found to undergo nucleophilic substitution reaction and the carboxylic groups at the edges results in amidation reactions with the  $\text{NH}_2$  groups. In addition, the presence of hydroxide and carboxylic acids sites also results in hydrogen bonding and electrostatic attraction [37].

##### 3.2.2. Post heat treatment for GO adhesion

GO-BPOF probes were thoroughly washed with DI water to test the adhesion of GO film on the BPOF probe surface. Naked eye observations show removal of GO over a large section of the bare probe upon washing with DI water leading to discontinuous patches on probe surface. A similar effect, however at a less pronounced level was observed for HMDA treated probes resulting in a non-uniform GO coating (Fig. S2). In order to improve the adhesion of GO to BPOF probe surface, the fiber probes were subjected to heat treatment at 50  $^\circ\text{C}$  for 10 min before washing with DI water. A significant improvement in the GO adhesion to the POF surface was observed after DI wash. Raman scattering spectra of GO coated bare and HMDA probes were obtained after heat treatment to verify the GO coverage over the fiber probe surface (Fig. 2).



**Fig. 2.** Raman scattering spectra obtained from (A) bare and (B) HMDA functionalized BPOF probes coated with GO. The BPOF probes were heat treated after GO coating to improve GO adhesion. Raman scattering spectra were recorded at different points over a given sensor surface.



**Fig. 3.** (A) Raman scattering spectrum of BPOFs coated using different concentrations of GO solutions (1 µg/ml, 10 µg/ml, 50 µg/ml and 100 µg/ml) and incubation of 24 h followed by post heat treatment at 50 °C for 10 min. (B) RI sensitivity ( $\Delta A_{845\text{nm}}/\Delta \text{RIU}$ ) of BPOF probes without and with GO coating using varying concentration of aqueous GO solution.

The visual observations of non-uniform and limited surface coverage of GO on the bare probes are in agreement with the significant variations in intensities of D and G bands in Raman scattering spectra is shown in Fig. 2(A). The HMDA functionalized probe shows improved surface coverage of GO forming a uniform, thick black layer of thickness 3.3 µm (obtained from optical profilometry measurement, Fig. S3), over the sensor surface with homogenous intensities of D and G band as shown in Fig. 2(B). The results on bare and amine functionalized POF probes confirm that chemisorption of GO to POF is a necessary step to obtain stable GO binding with complete surface coverage.

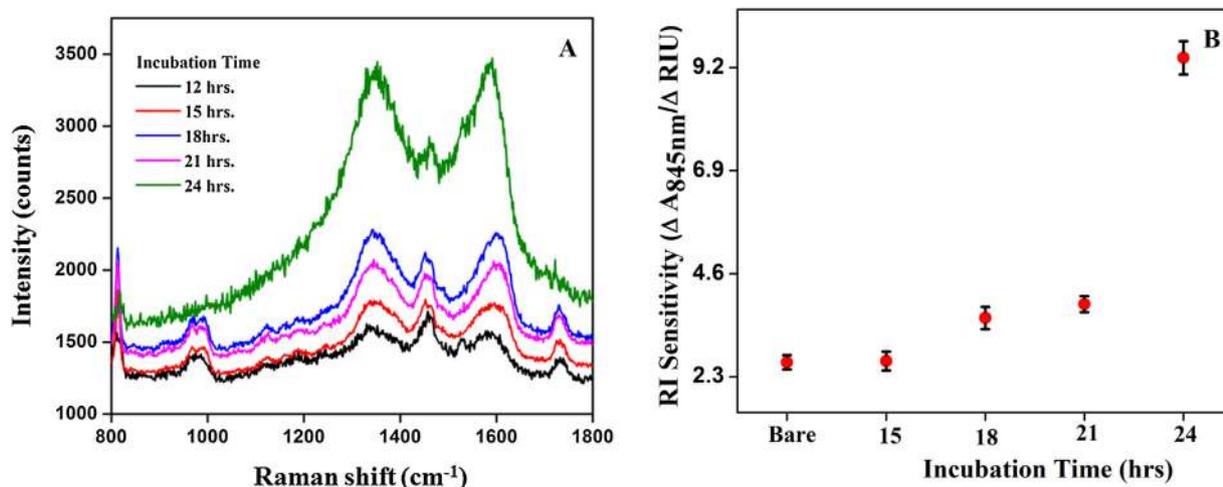
### 3.2.3. Influence of GO solution concentration

Amine functionalized BPOF probes were dipped in GO solution of varying concentrations including 1, 10, 50 and 100 µg/ml for 24 h. The surface coverage and uniformity of the coatings were evaluated with Raman scattering spectroscopy (Fig. S4). The Raman scattering spectra collected randomly from different points on the probes treated with 1, 10 and 50 µg/ml GO showed varying scattering intensities at characteristic D and G bands, while the probes dipped in 100 µg/ml of GO showed a significant increase in the scattering intensity all throughout the fiber and complete absence of PMMA peaks, suggesting a saturated surface coverage over the U-bent region with 100 µg/ml of GO (Fig. 3A). Subsequently, absorbance

response from the GO-BPOF probes obtained from each of the above four GO concentrations was recorded while subjecting them to glucose solutions of increasing RI value (Fig. S5). The RI sensitivity values of the GO-BPOF probes for each GO concentration calculated as change in absorbance at 845 nm for a maximum change in the RI (with reference to water) are plotted in Fig. 3B. GO-coated fiber probes showed only a marginal increment in the RI sensitivity for GO concentrations upto 50 µg/ml, while a significant increase of at least 2-fold in the case of 100 µg/ml. The enhancement in RI sensitivity of GO-BPOF is attributed to the reduced refractive index contrast and subsequent improvement in evanescent wave interaction. All the subsequent studies were carried out with GO solution of 100 µg/ml concentration.

### 3.2.4. Influence of incubation time

The incubation time necessary for the formation of continuous GO film on the probe surface to obtain high RI sensitivity was determined by subjecting BPOF probes to varying incubation times. The influence of incubation time was investigated by dipping the probes in 100 µg/ml GO solution for 2, 4, 6, 12, 15, 18, 21 and 24 h. Raman scattering spectra obtained randomly from different regions of each of the GO coated probes incubated for 2, 4, 6 and 12 h showed a considerable variation in the spectral characteristics indicating an inconsistent GO coverage over the probe surface (Fig. S6). The



**Fig. 4.** (A) Raman scattering spectrum of BPOFs coated with GO solutions of concentration 100  $\mu\text{g/ml}$  at varying incubation time includes 2, 4, 6, 12, 15, 18, 21 and 24 h followed by post heat treatment at 50 °C for 10 min. (B) RI sensitivity ( $\Delta A_{845\text{nm}}/\Delta \text{RIU}$ ) of bare and GO-BPOF probes using varying incubation time.

probes incubated for 15, 18 and 21 h show uniform Raman scattering intensities revealing an improvement in surface coverage of GO with time (Fig. 4A). Interestingly, the probes incubated for 24 h were distinct from that of 15, 18 and 21 h not only with respect to the Raman scattering spectra but also in terms of visual appearance as a prominently thick black film over the surface. In addition, the RI sensitivity obtained from these probes was significantly higher than that of lower incubation times. The RI sensitivity (Fig. 4B) of 15, 18, 21 and 24 h GO-BPOF probes were as follows  $2.65 \pm 0.21$  ( $n=3$ ),  $3.61 \pm 0.25$  ( $n=3$ ),  $3.92 \pm 0.18$  ( $n=3$ ) and  $9.42 \pm 0.37$  ( $n=3$ ) respectively. For all the subsequent studies, the GO-BPOF probes were prepared by incubating probes in 100  $\mu\text{g/ml}$  GO solution for 24 h.

### 3.3. Chemical sensing

Bare and GO-BPOF probes were subjected to organic solvents such as methanol (MeOH, 50% v/v), ethanol (EtOH, 50% v/v and 100% v/v) and isopropyl alcohol (IPA, 50% v/v and 100% v/v) and their corresponding absorbance response at 845 nm was monitored real-time (Fig. S7). MeOH (100%) was not taken into consideration, as its RI value is lower than that of water, which is taken as reference and thus leads to negative absorbance. RI values of each organic solvent were obtained from elsewhere [37]. The temporal response and absorbance response at 845 nm from the bare and GO-BPOF probes are as shown in Fig. 5A and B respectively. The absorbance response of the probes was found to increase with an increase in the volume fraction of the organic solvents. The result demonstrates the ability of the GO-BPOF probes in sensing organic solvents of varying concentrations.

Interestingly, the absorbance response of the probes dipped in different organic solvents is found to be higher than that from glucose solutions of the equivalent refractive index value. For example, the RI values of 50% v/v MeOH and 5% w/v glucose are around 1.3422 and 1.3402 respectively [38]. However, the RI sensitivities obtained from the GO-BPOF probes correspond to  $12.75 \pm 1.19$  and  $8.33 \pm 0.28$   $\Delta A_{845\text{nm}}/\text{RIU}$  respectively. Similarly, the probe response for 100% v/v EtOH and 100% v/v IPA gave rise to RI sensitivities of  $9.97 \pm 0.66$  and  $13.93 \pm 0.92$  respectively. We attribute the reason for increase in RI sensitivity of the probes in presence of organic solvents such as alcohols to their ability to effectively intercalate the GO layers and thus increasing the RI of the GO layer. The increase in RI of the GO layer around the fiber core reduces the RI contrast and thus leads to improved absorbance response

[39]. It may be noted that the sensitivity of the probe for 50% v/v MeOH is higher than that of EtOH and close to that of IPA despite the fact that the RI value of MeOH is much lower than the other two. This may be attributed to intercalation of GO by MeOH especially in MeOH/water mixtures as reported by You et al. [40].

#### 3.3.1. Chemical stability of the GO film

The GO-BPOF probes were incubated in organic solvents including methanol, ethanol and isopropyl alcohol over a duration of 12 h in order to evaluate the chemical stability of the GO film. The chemical stability of the GO film was evaluated from its ability to remain adhered to the sensor surface while dipped in organic solvents. The intensity of light passing through the probes was monitored real-time (Fig. S8) to identify any desorption of GO from the probe, which may result in a change in the spectral response from the probe. No considerable change in RI sensitivity was observed even after 12 h of incubation in organic solvents, indicating chemical stability of GO film adhered to the BPOF probe surface (Fig. S9). In addition, observations by naked-eye as well as microscopic images (Fig. S10) reveal an intact GO layer over the fiber probe surface. Raman scattering spectra (Fig. S11) obtained from several locations on the surface of these probes also consistently show only scattering intensity of D and G bands confirming a uniform GO film over the BPOF probe surface (without any PMMA characteristic spectral features that may point to desorption of a part of GO film).

#### 3.4. Chemical resistance of GO-BPOF probes

The bare and GO-BPOF probes were evaluated for their ability to withstand a highly reactive reagent, acetone, known to degrade the PMMA. Bare BPOF probes were able to withstand acetone environment for about 10 min while the GO-BPOF could sustain up to 30 min. This is evident from the absorbance response of the probes monitored in real time as shown in Fig. 6A, where an abrupt drop in the intensity of light passing through the fiber probe due to fiber breakage could be observed. Interestingly, the GO-BPOF probes were found to consistently break over the straight portion of the U-bent probe, more specifically at the interface between the cladding and GO coating. No visible damage to the GO coating or the fiber was observed over the other portions of a probe (Fig. 6B). The fiber breakage is attributed to the etching of PMMA core by acetone that permeates through the GO which is sufficiently thin and porous enough at the interface of the GO coating and the cladding. In case of bare BPOF probes, fiber breakage at a single point rather than uni-

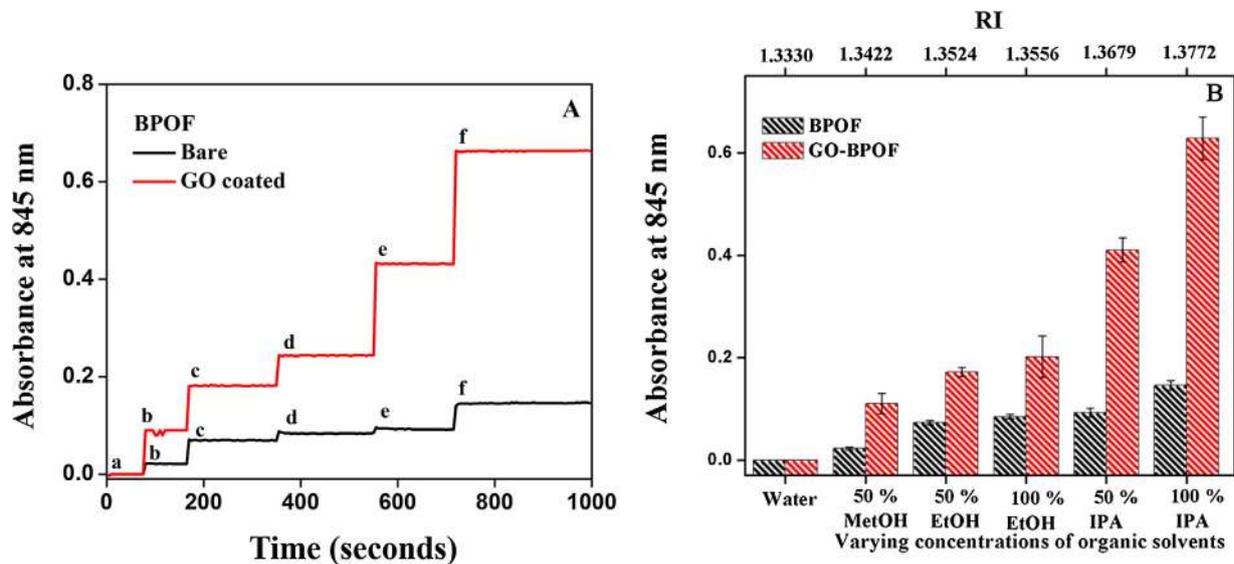


Fig. 5. (A) Temporal response and (B) Absorbance response at 845 nm wavelength obtained from bare and GO-BPOF subjected to organic solvents of varying concentrations including (a) Reference water, (b) 50% v/v MeOH, (c) 50% v/v EtOH, (d) 100% v/v EtOH, (e) 50% v/v IPA and (f) 100% v/v IPA.

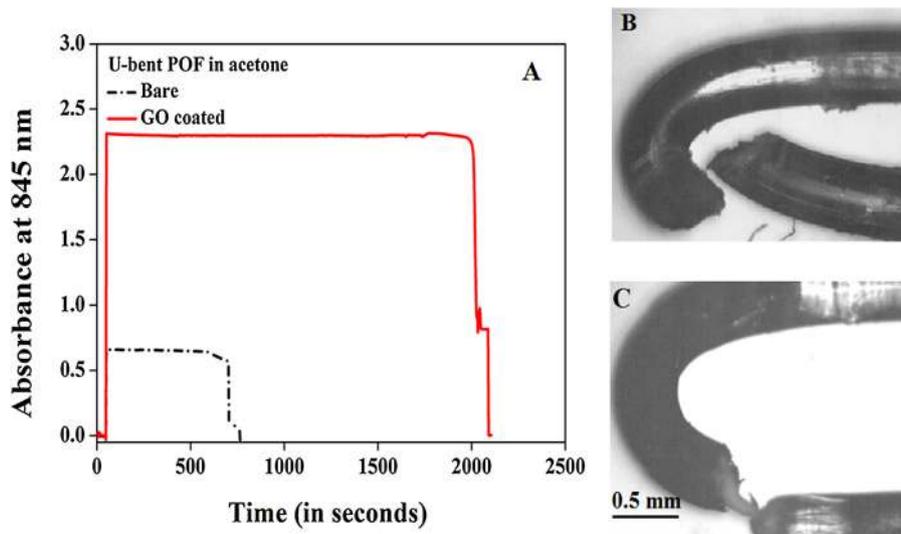


Fig. 6. Real time monitoring of optical absorbance response from bare and GO-BPOF probes dipped in acetone (at  $t \sim 50$  s). An abrupt drop in light intensity through the BPOF probes was observed indicating sudden fiber probe breakage. (B), (C) Microscopic image bare and GO-BPOF probes after dipping in acetone respectively.

form etching of the entire fiber was observed. However, the fiber breakage point for bare BPOF probe was random over the entire decladded region including the bend portions. (Further studies may be necessary to understand the phenomenon of PMMA etching by acetone and single-point breakage, which is outside the scope of the present study). These results demonstrate that the GO coating significantly enhances the chemical resistance of POFs and suitability of GO-BPOF probes for not only alcohols but also relatively harsh chemical environment, suggesting that they can be a potential alternative to brittle and expensive silica fibers.

#### 4. Conclusion

An evanescent wave based RI sensor is demonstrated using GO-BPOF probe with improved RI sensitivity and chemical resistance. A method to coat GO over BPOF probes is established by optimizing the deposition conditions. GO chemisorption on an amine functionalized BPOF probe by incubating in 100  $\mu\text{g/ml}$  GO solution for 24 h followed by post heat treatment at 50  $^{\circ}\text{C}$  for 10 min was found to

be optimum to obtain GO films with uniform surface coverage and improved adhesion. A 3.6 fold enhancement in the RI sensitivity was obtained due to the presence of GO layer on BPOF probes. A further enhancement in the absorbance response was observed from GO-BPOF probes in presence of organic solvents due to their effective interaction with GO film. The RI sensitivities ( $\Delta A_{845\text{nm}}/\Delta \text{RIU}$ ) obtained from the GO-BPOF probes correspond to  $12.75 \pm 1.19$ ,  $9.97 \pm 0.66$  and  $13.93 \pm 0.92$  with 50% v/v MeOH, 100% v/v EtOH and 100% v/v IPA respectively. The GO layer coated on to BPOF probes was stable in harsh organic chemical environments including ethanol, methanol and isopropyl alcohol. In addition, GO-BPOF probes were able to withstand acetone environment for prolonged duration of 30 min as opposed to only 10 min without GO coating, demonstrating improvement in chemical resistance of the plastic optical fibers. These results demonstrate the advantages of the GO-BPOF probes for sensing organic solvents and highly promising for potential application in industries such as pharmaceuticals, chemicals, fragrance, food and beverages.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.snb.2018.02.059>.

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