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Optical bio-sensing devices based on etched fiber Bragg gratings coated with carbon nanotubes and graphene oxide along with a specific dendrimer

Sridevi S[a], K.S. Vasu[b], N. Jayaraman[c], S. Asokan[a,d], A.K. Sood[b,*]

[a] Department of Instrumentation and Applied Physics, Indian Institute of Science, Bangalore 560012, India
[b] Department of Physics, Indian Institute of Science, Bangalore 560012, India
[c] Department of Organic Chemistry, Indian Institute of Science, Bangalore 560012, India
[d] Robert Bosch Centre for Cyber Physical Systems, Indian Institute of Science, Bangalore 560012, India

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ABSTRACT

We demonstrate that etched fiber Bragg gratings (eFBGs) coated with single walled carbon nanotubes (SWNTs) and graphene oxide (GO) are highly sensitive and accurate biochemical sensors. Here, for detecting protein concanavalin A (Con A), mannose-functionalized poly(propyl ether imine) (PETIM) dendrimers (DMs) have been attached to the SWNTs (or GO) coated on the surface modified eFBG. The dendrimers act as multivalent ligands, having specificity to detect lectin Con A. The specificity of the sensor is shown by a much weaker response (factor of ~2500 for the SWNT and ~2000 for the GO coated eFBG) to detect non specific lectin peanut agglutinin. DM molecules functionalized GO coated eFBG sensors showed excellent specificity to Con A even in the presence of excess amount of an interfering protein bovine serum albumin. The shift in the Bragg wavelength ($\Delta\lambda_B$) with respect to the λ_B values of SWNT (or GO)-DM coated eFBG for various concentrations of lectin follows Langmuir type adsorption isotherm, giving an affinity constant of $\sim 4 \times 10^7\ M^{-1}$ for SWNTs coated eFBG and $\sim 3 \times 10^8\ M^{-1}$ for the GO coated eFBG.

1. Introduction

Fiber Bragg grating (FBG) [1,2], a periodic variation in the refractive index of the fiber core, is an optical sensing device that has emerged as mechanical [3,4], thermal [5,6], chemical and bio-sensors [7,8]. When a broad band light propagates through the FBG, a particular wavelength known as Bragg wavelength (λ_B) is reflected back based on the resonance condition given by $\lambda_B = 2n_{eff}\Lambda$, where Λ is the grating pitch and n_{eff} is the effective refractive index depending on the refractive indices of core (n_{core}) and cladding (n_{clad}) [2,8]. Any external perturbation such as strain, temperature, etc., which causes a shift in the Bragg wavelength of a FBG due to change in n_{eff}, can be easily measured by accurately measuring this shift. One of the important aspects in sensing using a FBG is discrimination of the temperature and strain effects, which can be achieved by different methodologies such as dual wavelength FBGs [9], Fabry Perot filter within a single FBG [10].

FBGs are generally less sensitive to the variations in the refractive index of the surrounding medium as the fiber core is well covered by the cladding layer. This limits the application of FBGs in chemical and bio-sensing. Therefore, Long Period Gratings (LPGs) [11,12] and etched FBGs (eFBGs) [13,14] have been utilized for chemical and bio-sensing applications. The light coupling between the cladding and the core makes LPGs sensitive to the surrounding medium, whereas in etched FBGs, the core is directly exposed to the surrounding medium. In the past, DNA hybridization and monolayer detection of biological reagents have been demonstrated using the eFBGs [15]. Recently, the covalent attachment of carbohydrates to the eFBGs has been used to study carbohydrate–protein interactions [16,17].

Single walled carbon nanotubes (SWNTs) and graphene based field effect transistors (FETs) have been used in many biological and chemical sensing application [18–20]. SWNTs and SWNT based nano-composites deposited on optical fibers using Langmuir Blodgett method have been employed as opto-chemical sensors to detect volatile organic compounds such as xylene and toluene by measuring the changes in reflectivity [21]. Recently, CO_2 gas sensing experiments were carried out by using the PAA-amino CNT complex coated eFBG [22]. Also, the area selective deposition of carbon nanotubes around and at the end of the fibers [23]

* Corresponding author. Tel.: +91 8022932271; fax: +91 8023608686.
E-mail addresses: sasokan@isu.iisc.ernet.in, sundarrajan.asokan@gmail.com (A.K. Sood).

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has been used in mode-locking and bio-applications by monitoring the reflectivity measurements. Surface adsorption on eFBG sensors was analyzed using electrostatic layer by layer assembly of polyelectrolyte molecules to estimate the detection limit [24].

In this paper, we demonstrate that coating of functionalized SWNTs and graphene oxide (GO) on eFBG makes it a very sensitive device for biological and chemical sensing applications due to the change in refractive index of the GO or SWNT coating (which acts as a cladding layer) is more than that of silica. Here, the cladding layer of the FBG is etched using hydrofluoric acid [25] and the eFBG is treated with NaOH to modify the surface for the coating of SWNTs and GO. As a specific demonstration of the methodology, the carbohydrate–protein interaction has been probed using the mannose functionalized poly(propyl ether imine) (PETIM) dendrimers (DMs) as multivalent carbohydrate source. The dendrimers are macromolecules widely used to monitor many biologically relevant ligand–receptor interactions. Recently, we have shown that specific and non-specific carbohydrate–protein interactions can be studied by observing the changes in the electrical conductivity of the DM decorated SWNT FET device [19]. In the present work, we establish that the carbohydrate–protein interaction can be probed more sensitively by measuring the shift in the Bragg wavelength of the eFBGs coated with DM functionalized SWNTs (or GO).

2. Experimental

FBGs are inscribed in high numerical aperture single mode photosensitive silicate fibers of total diameter 125 μm doped with germania (M/s Nufern) with the core diameter of 9 μm. KrF excimer UV laser of wavelength 248 nm, pulse energy 6 mJ and repetition rate of 200 Hz is used to inscribe the grating using a phase mask of 1069 nm pitch (M/s Stocker Yale Inc.). After the inscription of a uniform grating in a photosensitive fiber, the Bragg wavelength reflected from the FBG is monitored by using an FBG interrogator (Micron Optics, SM130) with a wavelength repeatability of 1 picometer (pm). The Bragg wavelength values of the FBGs used for SWNT and graphene oxide coating experiments are 1539.9524 (±0.00144) nm and 1547.3773 (±0.00247) nm respectively. The numbers in the bracket denote the value of the variance estimated for the time series of the measured Bragg wavelength. To enhance the sensitivity of the FBG, the cladding layer is removed by an etching process. The etching is carried out by dipping the grating region (~3 mm) of the FBG in a 200 μL of 40% HF solution placed in a teflon block for ~2 h. This process reduces the thickness of the clad material from about 58 μm to about 0.5 μm; this procedure blue-shifts the Bragg wavelength by 1 nm. After etching, the Bragg wavelength values are 1538.9507 (±0.00151) nm for SWNT and 1546.3760 (±0.00277) nm for graphene oxide.

The etched FBG is treated with 0.2 N of NaOH solution at 40 °C for 3.5 h and subsequently kept in the NaOH solution for 30 min at room temperature. The treated FBG is rinsed with deionized water for 10 min. The NaOH treatment of etched FBG surface makes it hydrophilic by creating a few –OH groups on the etched portion of the FBG. The acid treated SWNTs and as prepared graphene oxide have functional groups such as –COOH, –OH, –O– on their surfaces. These functional groups lead to the formation of hydrogen bonding between the –OH groups presented on the NaOH treated etched FBG and the nanomaterials. In our experiments, after coating the nanomaterials on the etched FBG surface, we wash them for 3 times in deionized water to remove physically adsorbed SWNT or graphene oxide. The SEM image of graphene oxide coated etched FBG sensor shown in Fig. 1b is after washing it for 3 times, which confirms that the fiber coated with SWNT and GO is stable against repeated washing with water.

The SWNTs used are of average diameter ~0.8 nm, with chirality (6, 5), purchased from M/s SouthWest NanoTechnologies and sonicated in 3:1 conc. H_2SO_4/conc. HNO_3 for 3 h at 40 °C [26]. The mixture is centrifuged and the residue is washed with water several times and dried at 100 °C. For the experiments, 0.25 mg of acid treated SWNTs have been dispersed in 1 mL of water. GO suspensions (0.25 mg/mL) have been prepared as described in [27,28]. The surface roughness and hydrophilicity of the etched FBG leads to the attachment of the acid treated SWNTs and λ_B is found to increase by ~12 pm after the attachment of SWNTs (with respect to the λ_B after NaOH treatment). This increase in the λ_B is due to the increase in the effective refractive index due to the SWNTs coating.

Mannose attached fourth generation PETIM dendrimer cluster glycoside, having ~30 mannose residues at the periphery of the dendrimer was utilized in the present study [19]. Aqueous solutions in water were prepared as mentioned in [19] with a concentration of 0.5 mM. The SWNTs coated eFBG is dipped in 0.5 mM DM solution to create carbohydrate (mannose) sites. As the SWNTs are p-type, DM molecules form SWNT-DM complexes, through charge transfer interactions [19]. The formation of SWNT-DM complexes result in the decrease of $\lambda_B \sim 10$ pm with respect to the λ_B of eFBG coated with SWNTs. The Bragg wavelength (λ_B^0) of the eFBG, after the formation of the SWNT-DM complex is 1539.09 nm. Same procedure is followed to coat GO on the eFBG surface and to form the GO-DM complex on the eFBG.

The solution of lectins concanavalin A (Con A) specific to mannose and non-specific peanut agglutinin (PNA), prepared in water (pH ~ 6.6) in the concentration range of 100 pM to 5 μM, are used in the experiments. The Bragg wavelength values have been monitored after treating the SWNT-DM (or GO-DM) coated eFBG at different concentrations of aqueous solutions of lectin Con A ranging from 1 nM to 5 μM. With the increase of Con A concentration, the difference $\Delta\lambda_B$ ($\lambda_B - \lambda_B^0$), has been found to increase.

3. Results and discussion

Fig. 1a summarizes the flow chart of coating of the GO and SWNT on etched FBGs, followed by the carbohydrate and specific protein interactions. Fig. 1b shows a scanning electron microscopic image of GO coated eFBG (captured using ULTRA 55, Field Emission Scanning Electron Microscope (M/s Karl Zeiss)). GO coated eFBG shown in Fig. 1b was made by dipping the NaOH treated eFBG in 200 μL of GO aqueous suspension for 20 min followed by washing with deionized water. From the SEM image we observed that the two dimensional GO sheets coated on the surface of etched FBG.

Fig. 2a shows the ratio $\Delta\lambda_B/\lambda_B^0$ as a function of concentration of the lectins Con A and PNA. The shift in λ_B is very significant; even for 1 nM of Con A, the shift $\Delta\lambda_B \sim 2$ pm and after the addition of 5 μM Con A, it increases to ~75 pm. A similar procedure has been carried out with the non-specific lectin, PNA. It is observed that the $\Delta\lambda_B$ value after 5 μM PNA treatment is only ~5 pm. The $\Delta\lambda_B$ for 5 μM of PNA treatment is less than the $\Delta\lambda_B$ for 2 nM of Con A treatment, showing the high specificity (by a factor of ~2500) of the sensor for the mannose–Con A interactions. Fig. 2a also shows the variation of $\Delta\lambda_B/\lambda_B^0$ as a function of concentration of the Con A without coating of SWNTs, which indicates that the eFBG coated only with DM is less sensitive when compared to the SWNT-DM coated eFBG.

Experiments have also been performed by coating the GO onto the eFBG. Fig. 2b shows the change in $\Delta\lambda_B/\lambda_B^0$ as a function of lectin concentration for the GO coated eFBG. The Bragg wavelength of the eFBG coated with the GO-DM complex is $\lambda_B^0 = 1546.55$ nm. The change in λ_B after addition of 1 μM Con A is found to be $\Delta\lambda_B \sim 150$ pm as compared to a $\Delta\lambda_B$ of ~20 pm for 1 μM PNA. The $\Delta\lambda_B$ value for 1 μM PNA detection is same as the $\Delta\lambda_B$ value for 500 pM of Con A (i.e., sensitive to detect Con A by a factor of