Reactive & Functional Polymers 71 (2011) 335–339

Contents lists available at ScienceDirect

Reactive & Functional Polymers

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

Enhanced sucrose sensing sensitivity of long period fiber grating by self-assembled polyelectrolyte multilayers

Qiushun Li [a,c], Xu-lin Zhang [b], Yong-Sen Yu [b], Ying Qian [b], Wen-Fei Dong [b,*], Yong Li [d], Jianguo Shi [c], Juntao Yan [a], Hongyan Wang [a,*]

[a] *College of Chemistry, Jilin University, Changchun 130012, China*
[b] *State Key Laboratory on Integrated Optoelectronics, College of Electronic Science and Engineering, Jilin University, Changchun 130012, China*
[c] *Key Biosensor Laboratory of Shandong Province, Biology Institute of Shandong Academy of Sciences, Jinan 250014, China*
[d] *College of Science, Guangdong Ocean University, Zhanjiang 524088, China*

ARTICLE INFO

Article history:
Available online 4 December 2010

Keywords:
Self-assembly
Polyelectrolyte multilayer
Long period fiber grating
Sucrose
Chemical sensor

ABSTRACT

The response laws of long period fiber grating (LPFG) coated with polyelectrolyte multilayers (PEMs) of poly(allylamine hydrochloride) (PAH)/poly(sodium-p-styrenesulfonate) (PSS) to a series of concentration of sucrose solutions were investigated. Experimental results showed that the central wavelengths of LPFG spectra move to short-wave as concentration of sucrose solution increase. Pure LPFGs show the optimal sensitivity to 55–60% of sucrose solutions. With increasing number of the layers, the most sensitive regions of LPFGs to sucrose solutions will shift from high concentration to low concentration by matching average refractive index of films and sucrose solutions with that of LPFG cladding. LPFGs assembled with 100 bilayers of PAH/PSS exhibited the optimal sensitivity to 20–25% of sucrose solutions. However, LPFGs coated with 115 bilayers were more sensitive to a lower concentration (<5%) of sucrose solution. Therefore, the sensitivity of LPFG to the small molecular weight analytes can be strongly improved by designing the refractive index and thickness of PEM overlay, as confirmed and interpreted by theoretical simulations.

Long period fiber gratings (LPFGs) are a class of fiber gratings with the period from several tens to hundreds of microns. As a transmissive and passive fiber optic device, they possess a number of attractive merits such as immunity electromagnetic interference, low insertion loss, low cost and easy production, high sensitivity and so on. Thus, LPFGs are extensively interested in fiber telecommunication and optical sensing technology field.

In recent years, in addition to being used as thermal and stress sensors [1], LPFGs are also employed as chemical sensors which can be used to determine the concentration of chemical substances by directly immerging in gas or liquid. Zhang and coworker developed a temperature compensation LPFG sensor to measure the concentration of many chemical components which including ethanol, 1-hexanol, methyl cyclohexane and hexadecane [2]. Chong et al. use LPFG to measure the solution concentration of sweet, salt and sugar, the experimental results showed that LPFG not only can distinguish different chemical solution according to the different refractive index, but also can monitor the change of the concentration of a particular chemical solution [3]. Falciai and coworkers use LPFGs measure the concentrations of sodium chloride, calcium chloride and ethylene glycol in aqueous solutions, which confirms that the measurement accuracy of LPFGs to three kinds of solution is similar to that of the Abbe Refractometer in low concentrations, and is greater than that of the Abbe Refractometer at high concentrations [4]. LPFGs are used by Allsop et al. in oil refining process to monitor the content of aromatic compounds such as benzene and xylene [5].

But only when the external environmental refractive index is close to that of the fiber cladding, LPFGs can represent a higher sensitivity [6]. If the environmental refractive indices are smaller or higher than that of fiber cladding, LPFGs would present a lower sensitivity [6–8]. In many cases, however, the refractive index of measured solution or gas does not approach that of fiber cladding, the further development and the practical application of LPFG are restricted severely.

In order to improve the sensitivity of LPFG biosensor, numerous surface engineering approaches, i.e. Langmuir–Blodgett (LB) films and layer-by-layer (LBL) films had been utilized to modify the surface of optical fibers [9–16]. For instance, James et al. [10–12] coated nano-membrane of higher refractive index than fiber cladding on the LPFG surface using LB technology, the experiments showed that the amplitude of central wavelength shift of attenuation band increases. However LB technique requires rather expensive instruments and it is not applicable for many kinds of

---

* Corresponding authors.
E-mail addresses: dongwf@jlu.edu.cn (W.-F. Dong), wang_hy@jlu.edu.cn (H. Wang).

1381-5148/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.reactfunctpolym.2010.11.012

non-amphiphilic materials. Therefore, LBL technique, which is based on a continuous assembly between positively and negatively charged materials, offering an easy and inexpensive process for multilayer formation had been developed quickly [13–16]. For example, Ignacio Del Villar and coworkers who deposited polyelectrolyte films of higher refractive index than the cladding on the surface of LPFGs using LBL self-assembly technology, proved that when the films are thick enough, cladding mode will be guided by overlayers, inducing the movement of central wavelength of spectral attenuation band [17]. Wang et al. dipped LPFG in polyelectrolyte poly(allylamine hydrochloride) (PAH) and poly{1-[4-(3-carboxy-4-hydroxyphenylazo)-benzensulfonamido]-1,2-ethanediyl,sodium salt} (PCBS) at different pH to regulate the film thickness and refractive index, finding that the higher the refractive index of coating layer or the greater film thickness, the larger the central wavelength of attenuation bands in the transmission spectrum shift [18]. Although these novel polyelectrolyte multilayer (PEM) coated LPFGs can be facilely utilized to detect the biomaterials, i.e. protein, DNA, enzyme, etc., it will still be a big challenge for us to achieve a high sensitivity of LPFG to those analytes ***with low molecular weight***.

In this letter, PEMs of PAH/poly(sodium-p-styrenesulfonate) (PSS) were deposited on the surface of LPFGs and their response laws to a series of concentrations of sucrose solution were investigated. The main point was to understand the effect of refractive index and thickness of PEM overlay on sensing sensitivity of LPFGs.

Prior to measuring the spectra of PEM coated LPFGs, let us discuss the overlay effect at first. As well-known, the working mechanism of LPFGs is that lights are coupled from the propagating guided mode to co-propagating cladding modes. The coupled mode equations are as follows [19]:

$$\begin{aligned} &\frac{dA^{co}}{dz} = i\kappa^{co-co}_{01-01}A^{co} + i\sum_{v}\frac{m}{2}\kappa^{cl-co}_{1v-01}A^{cl}_{v}\exp\left(-i2\delta^{cl-co}_{1v-01}z\right) \\ &\sum_{v}\left[\frac{dA^{cl}_{v}}{dz} = +i\frac{m}{2}\kappa^{cl-co}_{1v-01}A^{co}\exp\left(+i2\delta^{cl-co}_{1v-01}z\right)\right] \end{aligned} \tag{1}$$

Here, we mainly focus on the change of the resonance wavelength in order to find out the mechanism of LPFG's sensitivity to the ambient refractivity. The resonance wavelength can be approximately calculated by:

$$\delta^{cl-co}_{1v-01} + \kappa^{co-co}_{01-01}/2 = 0 \tag{2}$$

where δ^{cl-co}_{1v-01} is defined as:

$$\delta^{cl-co}_{1v-01} = \frac{1}{2}\left(\beta^{co}_{01} - \beta^{cl}_{1v} - \frac{2\pi}{\Lambda}\right) \tag{3}$$

β^{co}_{01} is the propagation of the core mode and β^{cl}_{1v} is the vth order cladding mode, Λ is the period of the grating. κ^{co-co}_{01-01} is the core-mode-core-mode coupling constant which can be calculated by:

$$\kappa^{co-co}_{01-01} = \frac{\omega\varepsilon_0 n_1^2\sigma(z)}{2}\int_0^{2\pi}d\phi\int_0^{a_1}\mathrm{rdr}\left(|E^{co}_r|^2 + |E^{co}_\phi|^2\right) \tag{4}$$

Based on these equations, the relations between the effective refractive index of different cladding modes with the overlay thickness can be simulated and the results are shown in Fig. 1a. It can be observed that as the overlay thickness increases, the effective refractive index of cladding modes increases slightly until a critical point is reached. It is very interesting because at this point the effective refractive index which can cause a larger shift of the resonance wavelength increases greater. The reason is that at this point the average refractive index of the overlay and ambient medium is the nearest to that of grating cladding, so the sensitivity to any change (overlay thickness, overlay refractive index, ambient refractive index, etc.) is largely increased [10]. Therefore, PEM overlay and its thickness are the very important factors for controlling sensitivity of LPFGs.

Then, we will focus on the effect of the overlay thickness on sensing sensitivity to ambient refractive index. Our simulation parameters are: fiber core refractive index: 1.4681, cladding refractive index: 1.4628, overlay refractive index: 1.55, core radius: 4.15 μm, cladding radius: 57 μm, period of fiber grating: 460 μm. We calculate the resonance wavelength sensitivity to the ambient refractive index for different overlay thickness and the results are shown in Fig. 1b. From our simulation result, we can draw two conclusions: (1) LPFGs with overlay have higher sensitivity to the ambient refractive index change than pure LPFGs. (2) As overlay thickness increases, the most sensitivity region to the ambient refractive index move from higher ambient refractive index to the lower one. Therefore, by controlling the ambient refractive index or overlay thickness of LPFGs, the most sensitive region of sucrose solution can be easily optimized.

In order to prove our simulations, PEM coated LPEGs will be developed by well-known layer-by-layer self-assembly techniques. Herein, LPFGs were firstly fixed straightly on the Teflon shelves, and then were treated using chemical reagents to make the surface generate negative charges. Subsequently, LPFGs were repeatedly immersed in 1 mg/L of PAH (containing 0.5 M of NaCl) and 1 mg/L of PSS (containing 0.5 M of NaCl) to obtain multilayer films. The PEM film thickness at different number of bilayers was measured by using I-Elli2000 ellipsometer. Fig. 2a showed the relationship between number of bilayers and film thickness. Obviously, the film thickness is gradually increasing with the increasing number of layers. There is approximately a partially linear relationship between number of layers and film thickness.

The optical responses of LPFGs to PEM overlays were measured by Ando AQ-6315A spectrometer with 0.05 nm of resolution at 15 (±0.1) °C. Fig. 2b shows the change of the central wavelengths of the attenuation bands in the transmission spectrum of LPFG in water with different number of bilayers. It is clearly observed that the central wavelengths gradually move to short-wavelength when the number of layers increases. The reasons of blue-shifts of the central wavelength of the attenuation bands can be explained by the relations between central wavelengths of attenuation band of LPFG spectra and effective refractive index of LPFG cladding [20]:

$$\lambda_i = \left[n_{\mathrm{core}} - n^{(i)}_{\mathrm{cladding}}\right]\Lambda \quad i = 1,2,3,4,\ldots \tag{5}$$

As discussed before, the increasing of overlay thickness will result in an increase of n_{cladding} while n_{core} almost stay the same. Thus from the formula (5), the central wavelengths of attenuation band will display a blue shift.

On the other hand, as shown in Fig. 2b, the magnitude of the central wavelength of attenuation band gradually increases at the beginning until reaching a maximum value, and then decreases with the increase of number of layers. The reason is because the refractive index of overlay is close to the vicinity of the index of fiber with increasing assembled layers [21], which can induce the magnitude of the wavelength shift of attenuation band to become stronger. However, when the film is thick enough, the refractive index of films will be higher than that of grating cladding. Thus the magnitude of the wavelength shift becomes weaker.

In the following experiments, we will study the responses of PEM coated LPFGs to sucrose solutions by controlling their thickness. As shown in Fig. 3a, c and e, for both pure and PEM coated LPFGs, their central wavelengths of attenuation bands are all shifting gradually to short-wavelength with increasing concentration of sucrose in aqueous solution. By increasing the concentrations of sucrose, the refractive index of sucrose solution is gradually close to that of grating cladding, which can cause blue-shift spectra. In