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ARTICLE

Graphene Oxide Hydrogel Improved Sensitivity In one-dimensional photonic crystals for detection of beta-glucan

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Hydrogels are environmental sensitive and they were introduced to 1DPhCs to improve the sensitivity in our previous research. In this paper, a new method was developed for quantitative determination of beta-glucan in oat by introducing Graphene oxide (GO) hydrogels in one-dimensional photonic crystals (1DPhCs) with a polyaniline (PANI) defect layer. GO hydrogels were synthesized via one-step hydrothermal method, characterized with scanning electronic microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and then they were employed as a component to fabricate 1DPhCs using spin-coating method. Synthesized 1DPhCs were combined with Congo red dye and in use for the quantification of beta-glucan. Reflection spectra demonstrated that a linear relationship existed between the photonic band gap and the beta-glucan concentration within 1 mg/mL–10 mg/mL. The detection limit for beta-glucan is 0.18 mg/m L with a sensitivity of 7.53nm•mL/mg.

Introduction

Photonic crystals are periodic layered structures that can modulate light within a certain wavelength through a photonic bandgap. 1DPhCs are the simplest photonic crystal structure. Defective photonic crystals can be obtained by breaking the periodicity of the photonic crystal structure. This process is conducted by changing the physical parameters, such as changing the thickness of one of the layers, adding another medium to the structure or removing a layer from the photonic crystals.¹⁻⁵ Defective photonic crystals can be used to design chemical and biological sensing, such as environmental monitoring⁶⁻⁹, medical examination¹⁰ and biotechnology fields¹¹⁻¹³, and tunable transmission filters that can be particularly used in photonic applications.¹⁴

Environmentally sensitive hydrogels that are sensitive to humidity, pH, temperature, pressure and so on have been introduced to 1DPhCs.¹⁶⁻²² To a certain extent, the optical responsive properties of 1DPhCs can be improved when hydrogels are embedded in 1DPhCs.¹⁵ Yao and co-workers introduced poly (ethylene glycol) (PEG)-cross-linked poly (methyl vinyl ether-co-maleic acid) (PMVE-co-MA) hydrogels to 1DPhCs to improve the response. The results revealed that 1DPhCs modified with hydrogel had better responsiveness and the response speed was faster.¹⁵ Graphene oxide (GO) hydrogel has a well-defined three-dimensional porous network and excellent mechanical and electrical properties that make it attractive in a wide variety of applications, such as high-performance nanocomposites and supercapacitors.²³ In this

study, we prepared the GO hydrogel using the method of Yuxi Xu et al.²³ The synthesised hydrogel was used as building block to fabricate 1DPhCs. To obtain proof of concept, we examined the response of the obtained 1DPhCs to oat beta-glucan solutions.

Oat is known for its excellent functional and nutritional properties that include essential fatty acids, vitamins, sterols, antioxidants, and soluble fibre, especially beta-glucan.²⁴ Beta-glucans in oats are linear polysaccharides composed of glucose units joined by glycosidic bonds β -1, 3 and β -1, 4.²⁵ Oat beta-glucan is effective in lowering cholesterol and the glycemic index. Currently, many methods are used to quantify beta-glucan based on two different principles, enzymatic degradation of the beta-glucan polymer³⁴ and specific binding of dye to the beta-glucan, such as calcofluor²⁵ and aniline blue dye.²⁶ The specific binding of the dye Congo red to beta-glucan is also in the column. In this study, we combined the dye Congo red with a one-dimensional photonic crystal having a PANI defect to quantify beta-glucan. PANI is a typical conducting polymer that has opened up a new promising field in material science and engineering.²⁷ Conducting polymer has unique electronic and optical properties, and it can be applied in advanced devices such as sensors, batteries and electro-optic devices.²⁸⁻³⁰ We intended to use the structural features of PANI and the GO hydrogel to detect beta-glucan in this study. The spectral changes and responses of the TiO₂/GO hydrogel 1DPhCs with a PANI defect to beta-glucan were compared with those of TiO₂/GO 1DPhCs with a PANI defect.

Results and discussion

Characterisation of Materials

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Figure 1(a) presents the photograph of the GO solution and the GO hydrogel. The difference between the GO hydrogel and the GO solution is clear from figure. The microstructures of the GO solution (Figure 1(c), 1(e)) and the GO hydrogel (Figure 1(b), 1(d)) were imaged by SEM using freeze-dried samples. As shown in Figure 1, the GO hydrogel has a larger sheet size than the GO solution. The larger sheet size of the GO hydrogel resulted in higher activity, which was revealed by the enhanced electron transfer rate in the reaction, and the surface chemistry served as another factor.³³

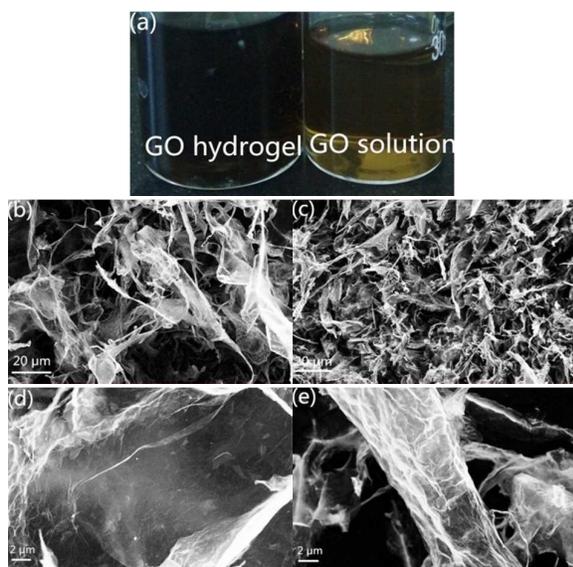


Figure 1 (a) photograph of the GO solution and the GO hydrogel; (b), (d) SEM images of the GO hydrogel; (c), (e) SEM images of the GO.

Figure 2 shows the FTIR of the GO solution and the GO hydrogel. For the GO solution, the peak at 3411.5 cm^{-1} was attributed to the O–H stretching vibrations of water molecules and structural OH groups. The adsorption peak at 1725.2 cm^{-1} was attributed to the C=O stretching vibration from carbonyl and carboxyl groups. The obvious peak at 1623.8 cm^{-1} was assigned to the C=C stretching vibration. The peak at 1384.7 cm^{-1} was attributed to O–H bending vibration of the structural OH groups. The adsorption peaks at 1220.7 cm^{-1} and 1047.2 cm^{-1} were attributed to the C–O stretching vibrations. For the GO hydrogel, the O–H peak of the water molecules was shifted to 3428.9 cm^{-1} . A new adsorption peak assigned to the O–H stretching vibration of the structural OH groups appeared at 3153.1 cm^{-1} . C=O peak with a stronger intensity was shifted to 1723.2 cm^{-1} . Two C–O peaks in the GO solution changed into one C–O peak at 1128.2 cm^{-1} .

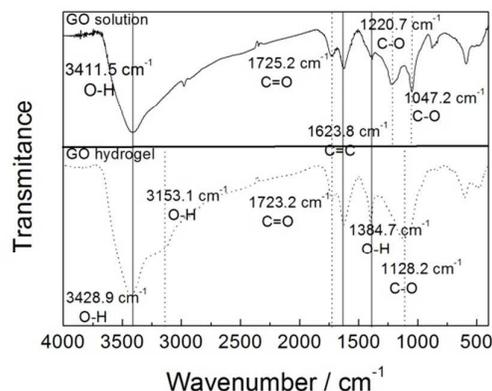


Figure 2 FTIR of the GO solution (—) and the GO hydrogel (----)

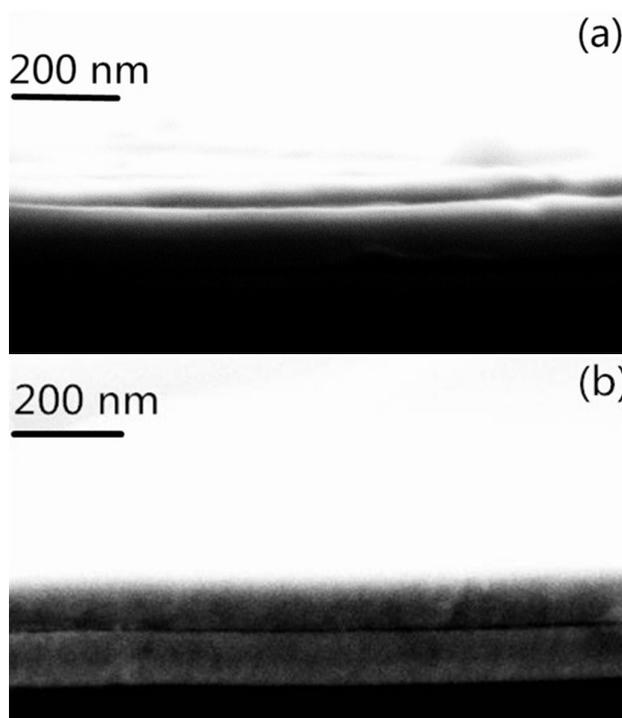


Figure 3 (a) SEM image of a TiO_2/GO 1DPHC with a PANI defect; (b) SEM image of a TiO_2/GO hydrogel 1DPHC with a PANI defect

The cross-sectional SEM images of the TiO_2/GO 1DPHC with a PANI defect and the TiO_2/GO hydrogel 1DPHC with a PANI defect were almost identical (Figure 3). Figure 3 shows that the cross-sectional SEM images of the TiO_2/GO 1DPHC with a PANI defect and the TiO_2/GO hydrogel 1DPHC with a PANI defect are almost identical. 1DPHCs was divided into two parts by the PANI defect. The edge between the different layers could not be observed because no obvious border was found between the GO layer and the TiO_2 layer under the irradiation of the electron beam.¹⁵

Detection of beta-glucan using 1DPHCs

Detection principle. Figure 4 illustrates the fabrication of 1DPhCs diagrammatically, in which the thicknesses of TiO₂, GO/GO hydrogel and PANI are denoted by d_T , d_G , and d_P , respectively. The total transfer matrix can be expressed as Equation (1)¹⁴:

$$M = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix} = (M_T M_G)^2 M_P (M_T M_G)^2 \quad (1)$$

where the transfer matrix M_i is influenced by θ , d_i and n_i ($i=T, G, P$). Once the matrix elements in Equation (1) are known, transmittance and reflectivity can be calculated using Equations (2, 3 and 4):

$$T = |t|^2 = \frac{4p}{(M_{11} + M_{12}p) + M_{21} + M_{22}p} \quad (2)$$

$$p = \cos\theta \quad (3)$$

$$R = 1 - T \quad (4)$$

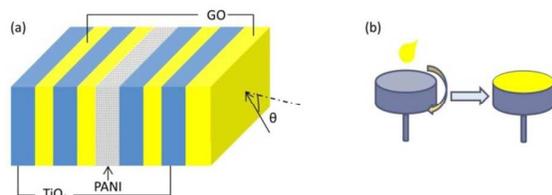


Figure 4 (a) The structure of one-dimensional photonic crystal with a PANI defect the incident angle is θ ; (b) Schematic representation of the processes used to fabricate 1DPhCs by spin-coating.

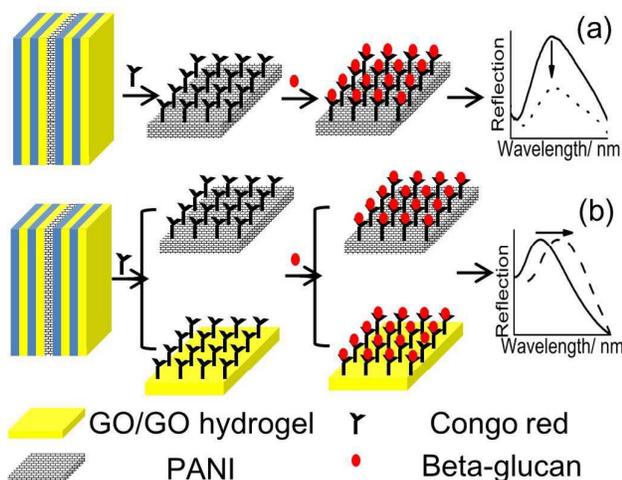


Figure 5 (a) Schematic diagram of the detection of beta-glucan by TiO₂/GO 1DPhCs with a PANI defect: The change of the defect layer led to difference in reflection spectra; (b) Schematic diagram of the detection of beta-glucan by TiO₂/GO hydrogel 1DPhCs with a PANI defect: Not only the change of the defect layer, but also the change of the GO hydrogel layer led to difference in reflection spectra.

The position of the Bragg peak of 1DPhC can be calculated using the following formula³¹:

$$m\lambda_{\text{Bragg}} = 2D \sqrt{n_{\text{eff}}^2 - \sin^2 \theta} \quad (5)$$

where n_i ($i=T, G, P$) is the refractive index of TiO₂, GO/GO hydrogel and PANI, t is the transmission coefficient, T is the transmittance, R is the reflectivity, m is the diffraction order, D is the period, λ_{Bragg} is the position of Bragg peak, θ is the incident angle and n_{eff} is the effective refractive index. In the detection of beta-glucan using TiO₂/GO 1DPhCs with a PANI defect, the difference in reflection spectra was caused by the defect layer whose refractive index was changed in the process of detecting. According to Equation (1-4), this difference was detected by obvious change in reflection intensity and negligible change in photonic bandgap³⁵ when θ , d_i ($i=T, G, P$), n_T , and n_G are constants (Figure 5(a)). In the detection of beta-glucan using the TiO₂/GO hydrogel 1DPhCs with a PANI defect, the difference in reflection spectra was caused by the change of the GO hydrogel layer. On the basis of Equation (5), the change of the GO hydrogel layer led to the change in photonic bandgap (Figure 5(b)).

Detection of beta-glucan. The sensitivity of TiO₂/GO 1DPhC with a PANI defect was evaluated from the changes in the reflection intensity. Figure 6 shows the reflection spectra of the TiO₂/GO 1DPhCs with a PANI defect mixed with different concentrations of beta-glucan solutions. When 1DPhC was soaked in beta-glucan solutions at different concentrations, a decrement in the reflection intensity related to the beta-glucan concentration was observed. The defect layer decreased the reflection intensity by 19.3%.

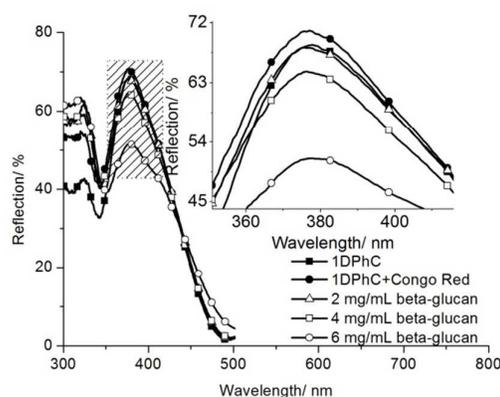


Figure 6 Reflection spectra of TiO₂/GO 1DPhCs with a PANI defect mixed with different concentration of beta-glucan solutions.

Figure 7 shows the reflection spectra of the TiO₂/GO hydrogel 1DPhCs with a PANI defect mixed with different concentrations of beta-glucan solutions. In the evaluation of the sensitivity of the TiO₂/GO hydrogel 1DPhCs with a PANI defect using similar operation conditions, the photonic bandgap had a red shift of 47.6 nm which was caused by the change of the GO hydrogel layer. Abbe refractometer was used to measure refractive index. The result showed that $n_G=1.328$, $n_C=1.332$, and $n_B=1.340$ (n_G = refractive index of the GO hydrogel, n_C = refractive index of Congo red, and n_B = refractive

index of beta-glucan). Figure S1 showed SEM images of TiO₂/GO hydrogel 1DPHC with a PANI defect before/after detecting beta-glucan. As shown in Figure S1, the thickness of TiO₂/GO hydrogel 1DPHC with a PANI defect changed from 177 nm to 184 nm. The result demonstrated that the refractive index and thickness of TiO₂/GO hydrogel 1DPHC with a PANI defect was altered when detecting beta-glucan and these changes gave rise to the shift of photonic bandgap. The position of the bandgap was related to the beta-glucan concentrations (Figure 8). The linear range was 1 mg/mL–10 mg/mL with the equation of $y = 437.6242 + 7.53414x$ (y = the position of bandgap, x = beta-glucan concentrations, $R^2 = 0.973$). The detection limit of the beta-glucan was estimated to be 0.18 mg/mL ($0.46 \times 3 / 7.53 = 0.18$).

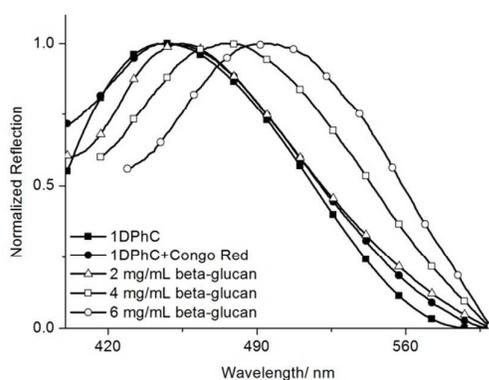


Figure 7 Reflection spectra of TiO₂/GO hydrogel 1DPHCs with a PANI defect mixed with different concentration of beta-glucan solutions.

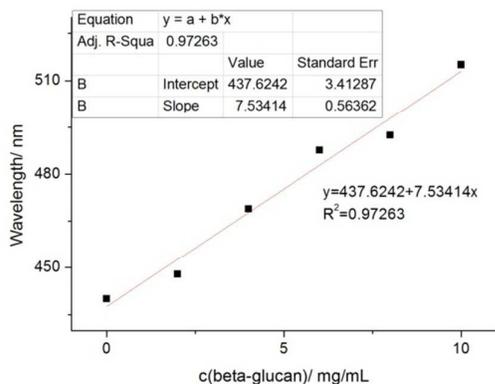


Figure 8 The position of the bandgap plotted against beta-glucan concentrations.

The sensitivity of the TiO₂/GO 1DPHCs with a PANI defect was compared with that of the TiO₂/GO hydrogel 1DPHCs with a PANI defect. The reflection spectra changes using TiO₂/GO 1DPHCs were observed from 2 mg/mL of the beta-glucan

solution, but the decrease did not have a regular pattern. Using TiO₂/GO hydrogel 1DPHCs, a linear relationship was found between the position of the bandgap and that of the beta-glucan concentrations.

In order to show the selectivity of TiO₂/GO hydrogel 1DPHC with a PANI defect toward beta-glucan, we measured the response of TiO₂/GO hydrogel 1DPHC with a PANI defect to different carbohydrates. Figure 9 shows the response to 6 mg/mL carbohydrate (glucose, starch, sucrose, maltose, mixture solution, and beta-glucan). As shown in figure 9, when soaked in first four carbohydrates, the photonic bandgap of 1DPHCs show little changes. In addition, the photonic bandgap of 1DPHC shifts 43 nm when soaked in mixture solution and 45 nm in beta-glucan, respectively. Two responses are similar which indicate the presence of other carbohydrates do not affect the response of TiO₂/GO hydrogel 1DPHC with a PANI defect to beta-glucan.

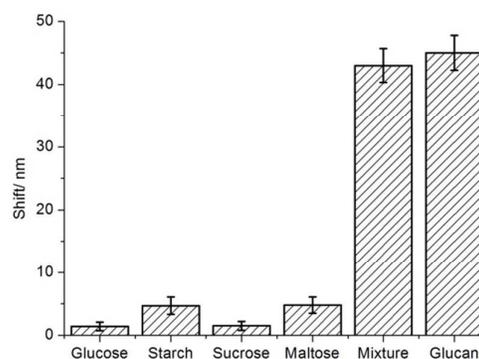


Figure 9 The response of TiO₂/GO hydrogel 1DPHC with a PANI defect to different carbohydrates.

Experimental

Materials

GO was purchased from Nanjing XFNano Materials Tech Co., Ltd., (Nanjing, China). Tetrabutyl titanate was obtained from Shanghai Ling Feng Chemical Reagent Co., Ltd. Ethanol, glacial acetic acid, glucose, starch, sucrose, maltose and acetone were bought from Sinopharm Chemical Reagent Shanghai Co. Ltd. Beta-glucan was obtained from Nantong Zhenhua Biological Engineering Co., Ltd. Congo Red was bought from Shanghai SSS Reagent Co., Ltd. Protonated PANI was purchased from Shijiazhuang Jian Yada New Material Technology Co., Ltd. All other reagents were used without further purification. The silicon wafers were soaked in the mixture of 98% H₂SO₄/30% H₂O₂ (volumetric ratio 3:1) for 24 h, rinsed with deionised water, and dried with N₂ stream.

Synthesis

The titania sol was prepared according to the method described by reference 32. About 4 g tetrabutyl titanate was added to 16 mL ethanol, and 4 mL acetic acid was added dropwise. The reaction mixture was stirred for 5 h at room temperature until the appearance of a pale yellow transparent colour due to the TiO₂ solution. The solution was kept for further use and diluted twofold with ethanol before use. The concentration of the GO aqueous solution was 0.5 mg/mL. The preparation of the GO hydrogel was adopted from the procedure of Yuxi Xu et al.²³ A 20 mL portion of the 0.5 mg/mL homogeneous GO aqueous dispersion was sealed in a 25 mL Teflon-lined autoclave at 90 °C for 17 h. The autoclave was allowed to cool to room temperature, and then the GO hydrogel was prepared. The prepared GO hydrogel was characterised by SEM and FTIR and used for the fabrication of 1DPhCs.

Fabrication of 1DPhCs

Preparation of the TiO₂/GO 1DPhCs with a PANI defect: 1DPhCs were fabricated by spin coating at a speed of 6000 rpm for 50 s (Figure 4 (b)). PANI defect was introduced to 1DPhCs by embedding the PANI layer by sandwiching it between two identical multilayers, as shown in Figure 7(a). Each multilayer was composed of two layers of TiO₂ and two layers of GO deposited alternately on a silicon wafer.

Preparation of the TiO₂/GO hydrogel 1DPhCs with a PANI defect: The abovementioned procedure was also used for the preparation of TiO₂/GO hydrogel 1DPhCs with a PANI defect. The GO hydrogel was used instead of the GO solution.

Detection of beta-glucan using 1DPhCs

To evaluate the optical characteristics of 1DPhC with a PANI defect, reflection spectra were recorded from 300 nm to 1000 nm using a fibre optic spectrometer (Ocean Optics, QE65000). White light emerging from the optical fibre bundle, which was fixed at a certain detection area, was incident to the 1DPhC surface from the vertical direction. The reflected light was coupled to the detection fibre probe of the optical fibre bundle and analysed using Ocean Optics operating software.

To detect beta-glucan, 1DPhC was first soaked in Congo red for 30 min and then soaked in different concentrations of beta-glucan solutions for another 30 min. After the reaction, excess beta-glucan was removed by water. Consequently, changes in the reflection spectra with beta-glucan concentration were monitored. Evaluation of the results revealed that changes in the reflection spectra were directly related to the concentration of beta-glucan in the solution.

Conclusions

We successfully prepared and used GO hydrogels as building blocks in the fabrication of 1DPhCs. The TiO₂/GO hydrogel

1DPhCs with a PANI defect was used to quantify beta-glucan with a detection limit of 0.18 mg/mL. The sensitivity of this method was 7.53 nm·mL/mg. About 86% of oat cultivars in China contain 3%–5% beta-glucan. The results indicate that 1DPhC combined with Congo red can be used for the quantitative detection of beta-glucan concentrations in oats.

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