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Hydrogel Improved the Response in the Titania/Graphene Oxide One-Dimensional Photonic Crystals

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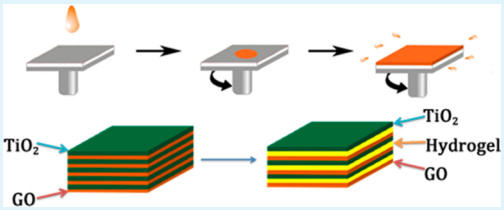
Supporting Information

ABSTRACT: Recently, one-dimensional photonic crystals (1DPCs) have attracted considerable interest because they exhibit a material-specific response profile to external stimuli. In our previous work, TiO_2/GO 1DPCs, the stopbands of which can be made to span the whole visible range, were fabricated by spin-coating technique. The prepared 1DPCs have a double response to both dimethyl sulfoxide and alkali solution. However, the response is slow, insensitive, and irreversible. To improve the responsiveness of the 1DPCs, poly(ethylene glycol) (PEG)-cross-linked poly((methyl vinyl ether)-*co*-maleic acid) (PMVE-*co*-MA) hydrogels were embedded in those crystals. The results demonstrated that modified 1DPCs with different stopbands could be obtained by controlling the speed of the spin-coating technique. The prepared 1DPCs have better responsiveness to external solution pH.



KEYWORDS: *1DPCs, hydrogel, TiO_2, GO, DMSO, pH*

1. INTRODUCTION

Photonic crystals, which can modulate light within a certain wavelength by photonic stopbands, are a new type of structural material whose dielectric refractive index changes in spatial periodic. The term photonic crystal was first introduced in 1987 by Eli Yablonovitch and Sajeev John.[1,2] Photonic crystals are composed of regularly repeating and periodic structures of high and low dielectric constant (refractive index) that affect the propagation of optical waves. When the change of dielectric constant is large enough and the change cycle corresponds to the wavelength of light, the dispersion relation of the light waves will appear as a banded structure; this is known as a photonic band structure. Whether or not photons propagate through this structure depends on their wavelength. Disallowed bands of wavelengths are called photonic band gaps, or photonic stopbands.[1,2,14,15] According to the variations of refractive indexes in space, photonic crystals can be classified as one-dimensional (1D), two-dimensional (2D), and three-dimensional (3D) photonic crystals. Their common characteristic is the presence of photonic stopbands.

Because of their variety of microstructures and optical properties, photonic crystals display potential applications in displays,[3] fiber,[4] color printing,[5] optical devices,[6−8] and photovoltaics.[9] Furthermore, if photonic crystals containing stimuli-responsive materials respond to external stimuli, such as light,[10] pH,[11] organic solvent,[12] temperature,[13] and so on, their optical properties can be tuned by changing external stimuli.[14,15] As a consequence of this characteristic, photonic crystals can be designed for chemical and biological sensing, for instance environmental monitoring,[16−19] medical examination,[20] biotechnology fields,[21−23] and so on when stimuli-responsive materials are embedded in them.

Bragg stacks and distributed Bragg mirrors are examples of 1D photonic crystals (1DPCs), which are composed of two or more alternating high- and low-refractive-index materials. The photonic stop bands of 1DPCs could be estimated from Bragg's Law;[24,25] according to it, the optical properties of 1DPCs can be tuned by changing incident angles, periods, and the refractive index.[26] Recently, 1DPCs have exhibited a material-specific response profile to external stimuli, and thus they have attracted great attention. Besides, compared with 2D photonic crystals and 3D photonic crystals, 1DPCs are the simplest photonic crystals. In theory, 1DPCs have a simple preparatory process and low cost. However, because the study of one-dimensional photonic crystals is mainly focused on the theoretical research, the preparatory approaches are unitary. Sputtering,[27,28] chemical vapor deposition,[29,30] evaporation,[31] holographic polymerization,[32] and sol−gel process[33] are alternative methods by which to prepare 1DPCs. But all these methods need either complex instruments or complicated preparatory processes. Besides the approaches mentioned above, novel methods for preparing highly sensitive, excellent optical properties, and reversibly tunable 1DPCs in a facile method are highly desired at present.[34−36] In recent years, with the development of bottom-up self-assembly strategies, a lot of functional 1DPCs have been prepared based on dip-, spray-, or spin-coating.[37−39] Spin-coating is a convenient and low-cost method by which one can easily adjust the period of 1DPCs by controlling the rotational speed, solution concentration, and the

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time of spin-coating. A lot of work was reported concerning the fabrication of functional 1DPCs based on spin-coating.[12,40−43]

In our previous work,[44] TiO_2/GO 1DPCs were fabricated by spin-coating technique. The results demonstrated that 1DPCs with different stopbands could be obtained from controlling spin-coating and incident angles. The prepared 1DPCs have a double response to both dimethyl sulfoxide (DMSO) and alkali solution. However, we found that the sensor had some shortcomings; the response of the 1DPCs was insensitive, irreversible, and slow.

1DPCs made up of TiO_2 and GO possess good stability and excellent optical properties due to the large difference in refractive indexes. Their optical properties can be tuned by filling the interspace with gases or solvents. However, any changes in optical properties are small because the thickness of the layer, whether TiO_2 or GO, is difficult to change. Environmentally sensitive hydrogels, in contrast, have the ability to sense changes of humidity, pressure, temperature, and so on.[40,45−48] Hydrogels will show different degrees of swelling when acid, alkalis, or organic solvents are incorporated into the polymer network. So when hydrogels are embedded in 1DPCs, their optical-responsive properties can be improved greatly due to a large increase in the period of the 1DPCs: the shift of stopbands will be more obvious; the response speed will be faster; one can even prepare specific sensitive 1DPCs by using different hydrogels.[15,35,40,45,55] Yang and co-workers reported an organic/inorganic hybrid 1DPC that has a high water-vapor and organic solvent sensitivity with a response time of less than 3 min, made by using the spin-coating method.[40] Gong and co-workers prepared a novel anisotropic hydrogel 1DPC, which has a high compressive and tensile mechanical stimuli sensitivity, by a one-pot polymerization.[45] Therefore, to improve the response of the 1DPCs, the hydrogels were introduced.

In this paper, we report a facile method to prepare TiO_2/GO 1DPCs modified with poly(ethylene glycols)-cross-linked poly((methyl vinyl ether)-*co*-maleic acid) (PEG-cross-linked PMVE-*co*-MA) hydrogel. The 1DPCs were successfully prepared through alternating thin films of TiO_2 sol, hydrogel, and GO nanosheet by spin-coating, which is a convenient and low-cost method. We researched the changing optical properties of the 1DPCs, which can be displayed by the change of the stopband and the peak intensity through changing the period. Compared with previous hydrogel-free 1DPCs, the 1DPCs modified with hydrogel have better responsiveness. The response speed is faster. For all solutions tested, the detection was finished in 10 min. Furthermore, the pH-responsive behavior of 1DPCs modified with hydrogel is reversible and can be repeated about five times.

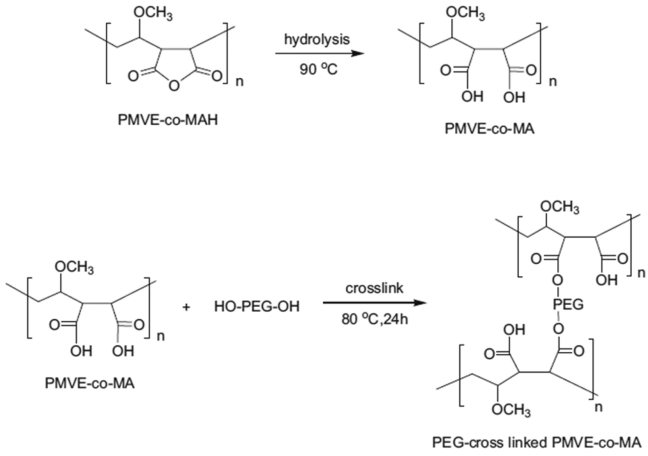
2. EXPERIMENTAL SECTION

2.1. Materials. GO was bought from Nanjing XFNano Materials Tech Co., Ltd. (Nanjing, China). Tetrabutyl titanate was obtained from Shanghai Ling Feng Chemical Reagent Co., Ltd. Poly((methyl vinyl ether)-*co*-maleic anhydride) (PMVE-*co*-MAH) (M_w = 1 080 000, M_n = 311 000, MDW = 3.47) was obtained from Sigma−Aldrich (Shanghai, China). Poly(ethylene glycols) (PEG_{20K}: M_w = 29 400, M_n = 22 000, MDW = 1.34), ethanol, glacial acetic acid, acetone, *N*,*N*-dimethylformamide (DMF), trichloromethane (TCME), tetrahydrofuran (THF), 1,4-dioxane, ethyl acetate, toluene, DMSO, sodium hydroxide, and hydrochloric acid were obtained from Sinopharm Chemical Reagent Shanghai Co., Ltd. All other reagents were used as received. The silicon wafers were soaked in the mixture of 98% H_2SO_4/30% H_2O_2 (volumetric ratio 3:1) for 24 h, then rinsed with deionized water several times, and finally were dried with N_2 stream.

2.2. Synthesis and Preparation of 1DPCs. The titania sol was prepared according to ref 49. Briefly, 4 mL of tetrabutyl titanate and 2 mL of acetic acid were dissolved into 42 mL of ethanol, then dipping the above mixture into the above conical flask, and then stirring 5 h at room temperature. To get different thicknesses of the film, the titania sol was diluted with different volumes of ethanol before use. Besides, the concentration of the GO solution was 1 mg/mL.

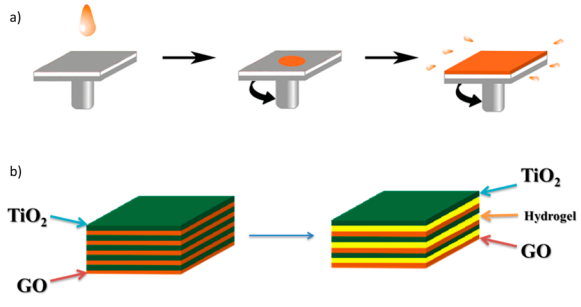
PMVE-*co*-MAH (0.7800 g) was added to 20 mL of deionized water in a 100 mL round-bottom flask and heated at 90 °C to hydrolyze for 2 h to obtain a clear solution of poly((methyl vinyl ether)-*co*-maleic acid) (PMVE-*co*-MA) with vigorous stirring. PEG_{20K} (0.3913 g) was added to the above PMVE-*co*-MA aqueous solution to obtain the uniform mixture of PEG and PMVE-*co*-MA (Scheme 1).[50]

Scheme 1. Crosslinking Reaction of PMVE-co-MA with PEG[50]



2.3. Fabrication of 1DPCs. The 1DPCs were fabricated by spin coating (Scheme 2a). The structure of 1DPCs was changed from simple TiO_2/GO to TiO_2/hydrogel/GO (Scheme 2b).

Scheme 2. (a) Schematic Representation of the Processes Used to Fabricate 1DPCs by Spin-Coating. (b) Structural Representation of Simple TiO_2/ GO 1DPC (left) and TiO_2/ Hydrogel/GO 1DPC (right)



Preparation of the TiO_2/GO 1DPCs: the 1DPCs were prepared totally according to our previous work.[44]

Preparation of the TiO_2/hydrogel/GO 1DPCs: the 1DPCs were fabricated by spin-coating method. The GO solution, the mixed solution, and the titania sol were spun alternately at 4800 rpm for 50 s in turn (these spin-coating parameters only are used for fabricating 1DPCs in Sections 3.3, 3.4, and 3.5). Different thicknesses of films were achieved by changing the concentration of the solutions, the time of spin-coating, and the spin-coating rate. Both of these solutions were spin-coated onto a silicon wafer. Every layer was baked at 60 °C for 10 min. The first layer was GO layer, and the last layer was titania layer in

all our experiments. Then the 1DPCs were baked at 80 °C for 24 h to induce the esterification reaction between PEG and PMVE-*co*-MA for the formation of gel (Scheme 1). The number of the total layers of the film materials was $3N$ (N is the number of TiO_2 layers).

2.4. Measurement of Reflective Spectra. Photographs of the 1DPCs were taken by a digital camera (Canon EOS 5D Mark II). The spectra of the 1DPCs at normal incidence were recorded by using a microscope (OLYMPUS BX51) equipped with a fiber optic spectrometer (Ocean Optics, QE65000) at an incidence angle of 0°.

2.5. Measurements of Scanning Electronic Microscopy (SEM). The morphology images of the photonic crystal film were taken with a Zeiss Ultra Plus field emission SEM operating at 5 kV (Zeiss, Oberkochen, Germany).

3. RESULTS AND DISCUSSIONS

3.1. Characterization of 1DPCs. Figure 1a shows the cross-sectional SEM image of a TiO_2/GO 1DPC ($2N$, N = 4, N is the number of TiO_2 layers), which was prepared totally according to our previous work.[44] One cannot see the obvious multilayered structure of the 1DPC in the SEM image. Figure 1b shows the cross-sectional SEM image of a TiO_2/hydrogel/GO 1DPC ($3N$, N = 4), from which one can see the obvious multilayered structure and that the 1DPC contains eight layers, rather than the theoretical 12 layers. When hydrogel is embedded in 1DPC between the TiO_2 layer and the GO layer, we can see the multilayered structure of 1DPC. We are speculating that this is because titania and GO cannot be distinguished by a secondary electron image.

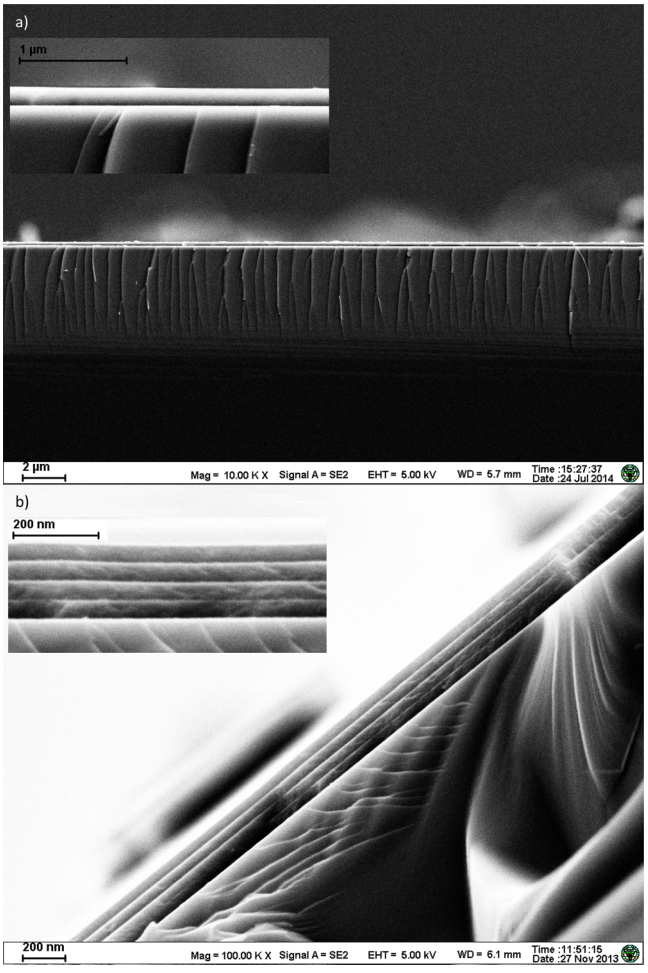


Figure 1. (a) Cross-sectional SEM images of a TiO_2/GO 1DPC ($2N$, N = 4), which was disembedded hydrogel; (inset) is a magnified image. (b) Cross-sectional SEM images of a TiO_2/hydrogel/GO 1DPC ($3N$, N = 4), which was embedded hydrogel; (inset) is a magnified image.

3.2. Optical Properties of TiO2/Hydrogel/GO 1DPCs. Figure 2 shows the reflective spectra of three TiO_2/hydrogel/GO 1DPCs, which were adjusted by controlling the rotational speed and the time of spin-coating. The speeds of spin-coating are 4500, 4000, and 3000 rpm, respectively. The photonic stopbands are at 487, 520, and 589 nm. As the photonic stopband falls into the visible region, the materials present obvious color. From the optical photographs in Figure 2, we can see that the TiO_2/hydrogel/GO 1DPC with the photonic stopband at 487 nm presents a blue color, at 520 nm presents a green color, and at 589 nm presents a yellow color. It can thus be seen that the stopbands of TiO_2/hydrogel/GO 1DPCs can be tuned to the full-color range.

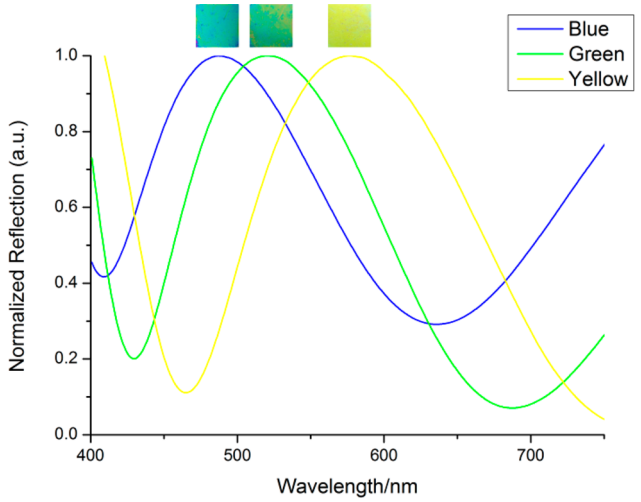


Figure 2. Reflective spectra of three 1DPCs modified by hydrogel with different periods. (inset) Corresponding photographs.

3.3. Detection of Water Based on TiO_2/hydrogel/GO 1DPCs. To prove the concept, we compared the sensitivity of TiO_2/hydrogel/GO 1DPCs to TiO_2/GO 1DPCs. We soaked these two 1DPCs in the DI water. This is shown in Figure 3. From Figure 3, we can see that the photonic stopband of the hydrogel-free 1DPC did not shift, whereas the photonic stopband of 1DPC modified with hydrogel changed from 476 to 487 nm, which is a red shift. It is believed that the 1DPCs modified by hydrogel are more sensitive than the hydrogel-free 1DPCs.

3.4. Detection of Organic Solvents Based on TiO_2/Hydrogel/GO 1DPCs. In our previous work, when TiO_2/GO 1DPCs were immerged in most of the solvents used in the laboratory, such as ethanol, acetone, DMF, TCME, THF, 1,4-dioxane,ethyl acetate, and toluene, the colors did not change, and the photonic stopbands did not shift, even during the very long reaction time of 24 h. Meanwhile, TiO_2/GO 1DPCs only responded to DMSO in experiments.[44] To improve the responsiveness of TiO_2/GO 1DPCs, PEG-cross-linked PMVE-*co*-MA hydrogels were embedded in those crystals. Theoretically, the sensitivity of hydrogel to organic solvents is more than that to both GO and TiO_2 because the hydrogels will swell upon exposure to organic solvents. This process will increase the thickness of the hydrogel layer and then result in

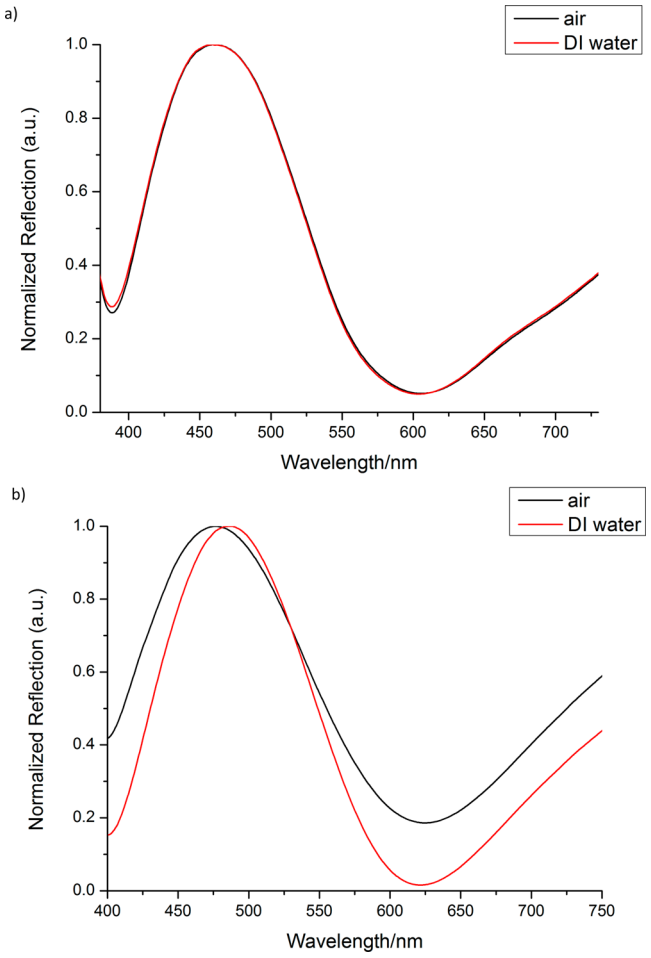


Figure 3. Reflective spectra of 1DPCs immersged in DI water for 10 min. (a) TiO_2/GO 1DPC. The total number of layers ($2N$) is eight. (b) TiO_2/hydrogel/GO 1DPC. The total number of layers ($3N$) is 12.

an increase of the period of the 1DPCs and a changing of their optical properties. TiO_2/hydrogel/GO 1DPCs were supposed to have a response to a greater variety of organic solvents.

But in fact, as with TiO_2/GO 1DPCs, when TiO_2/hydrogel/GO 1DPCs were immerged in different organic solvents, we found that these organic solvents could not be detected in this system (as shown in Figure S1 in the Supporting Information), except for DMSO. When the TiO_2/hydrogel/GO 1DPC was immerged into DMSO the photonic stopband was 487 nm. The color-changing behavior can be obviously discerned by the naked eye, with the color changing from blue to green (Figure 4a). Figure 4b gives the reflective spectra of the 1DPC in DMSO with different soaking times. One can see that when soaking times are 1, 3, and 5 min, the photonic stopbands are 504, 516, and 541 nm, respectively. An increase of the bandwidth can be observed with an increase in the response time. Meanwhile, 1DPCs modified by hydrogel have a similar effect to that of the hydrogel-free 1DPCs. It also only has a response to DMSO, and the shift direction of the position of the photonic stopband is the same.

There are two possible reasons that TiO_2/hydrogel/GO 1DPCs also only responds to DMSO. First, as stated previously, the shift of the photonic stopbands in the organic solvent depends on the interaction between solvent and hydrogel. The interaction between solvent and hydrogel depends on the solubility parameter (δ) of organic solvents.

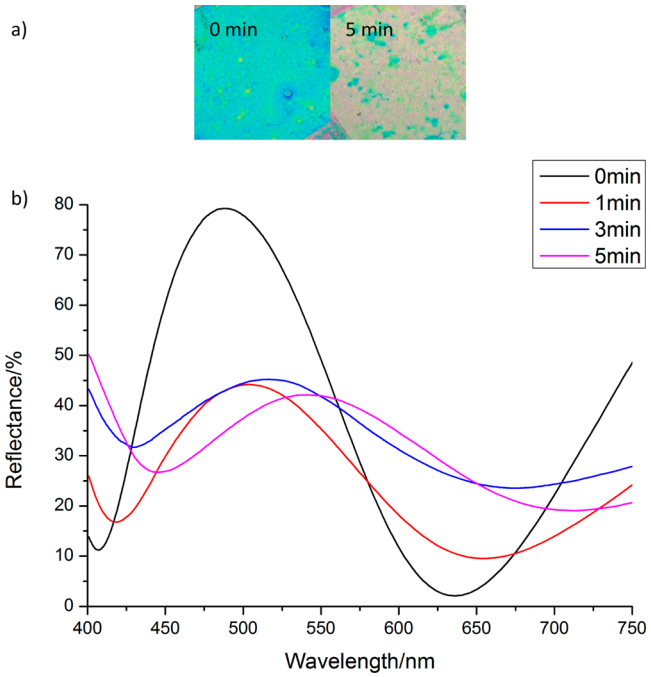


Figure 4. (a) Photographs of a 1DPC that was immerged into DMSO for different response time. (inset) Photograph at (left) 0 and (right) 5 min. (b) Optical properties of a 1DPC with response time. The total number of layers ($3N$) is 12.

δ is composed of dispersion cohesion (δ_D), polar cohesion (δ_P), and hydrogen-bonding cohesion (δ_H).[51] Among them, δ_D and δ_P play a major role, while δ_H plays an auxiliary role. The definition of δ_{DP} is the value of polynomial $(\delta_D^2 + \delta_P^2)^{1/2}$. The swelling degree of the hydrogel should increase with δ_{DP}.[16] Table 1 enumerates the solubility parameters of the different organic solvents, which are used in above experiments. From the table, we can see that the δ_{DP} of DMSO is the biggest in all of these organic solvents. Thus, we suspect that there is a critical value between the δ_{DP} of DMF and the δ_{DP} of DMSO; when the δ_{DP} is less than the critical value, the solvent elicits no response from the hydrogel layer.

Table 1. Solubility Parameters and Molar Volume of the Different Organic Solvents[51]

solvents	δ_D	δ_P	δ_H	δ_{DP}	molar volume
ethyl acetate	15.8	5.3	7.2	16.7	98.5
THF	16.8	5.7	8.0	17.7	81.7
toluene	18.0	1.4	2.0	18.1	106.8
TCME	17.8	3.1	5.7	18.1	80.7
ethanol	15.8	8.8	19.4	18.1	58.5
acetone	15.5	10.4	7.0	18.7	74.0
1,4-dioxane	19.0	1.8	7.4	19.1	85.7
DMF	17.4	13.7	11.3	22.1	77.0
DMSO	18.4	16.4	10.2	24.6	71.3

Second, the sizes of both the solvent and solute molecules are important for permeation, diffusion, and chemical resistance phenomena. Smaller molecules tend to be more readily soluble than larger ones. The Hildebrand solubility parameter theory also points to smaller molar volume solvents as being better than those with larger molar volume, even though they may have identical solubility parameters.[52,53] From Table 1, we can

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see that after ethanol, the molar volume of DMSO is the second-smallest and thus that DMSO has excellent permeation and diffusion. However, although the molar volume of ethanol is 58.5, it cannot cause a response to 1DPCs because of the too-small value of its δ_{DP}.

3.5. Detection of pH Based on TiO_2/Hydrogel/GO 1DPCs. When 1DPCs modified by hydrogel were immerged in acid solution, neutral solution, and weak alkaline solution, the colors did not change (Figure 5a), and the photonic stopbands

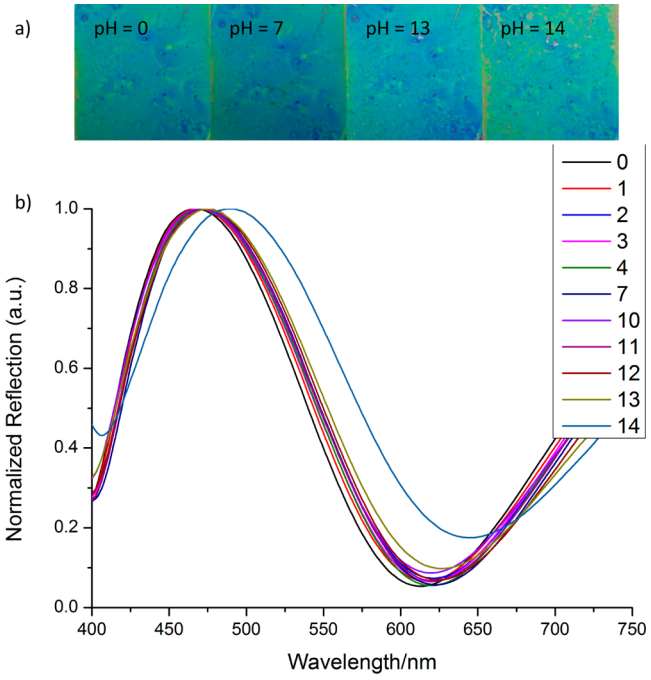

Figure 5. (a) Photographs of a 1DPC which was immerged into different pH solution after 10 min. (inset) Photograph, from left to right, is followed by 0, 7, 13 and 14 min. (b) Optical properties of a 1DPC that was immerged into different pH solution after 10 min. The total number of layers ($3N$) is 12.

did not shift (Figure 5b). This color-changing behavior can be obviously discerned by the naked eye with the color changing to blue-green (Figure 5a). The color shifted toward the red end of the spectrum when the 1DPCs were immerged in alkali solutions, especially in solutions with a pH of 14 (Figure 5b). Figure 5b shows the different photonic stopbands in different soaking times. When the soaking times are 0, 1, 3, 5, and 10 min, the photonic stopbands are 468, 476, 483, 485, and 490 nm, respectively. The system reaches a balance and remains unvaried after the response time increases to 10 min. The color of the film changed from blue to blue-green (Figure 6a).

Figure 7 illustrates five cycles of the swelling−deswelling with little change in the stopband. The pH was 7 and 14, respectively. In our experiment, we found that this pH-responsive behavior could only be repeated five times. It is suspected that alkaline solution could dissolve TiO_2.[54,55] The TiO_2, which is prepared by sol−gel method, is amorphous. Compared with rutile titanium dioxide, anatase titanium dioxide, and titania nanoparticles, amorphous titanium dioxide reacts with strong alkalis relatively easily. When the repeat times increase, the structure of the 1DPCs may be destroyed. It may be possible to solve this problem by calcining amorphous titanium dioxide at high temperatures before use or by using

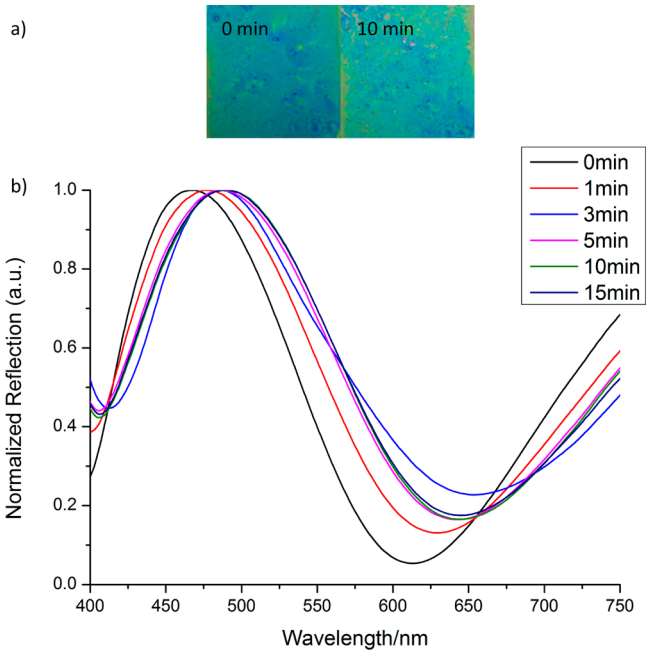

Figure 6. (a) Photographs of a 1DPC that was immerged into solution whose pH is 14 for different response time. In the photo from left to right is followed by 0 and 10 min. (b) Optical properties of a 1DPC with response time. The total number of layers ($3N$) is 12.

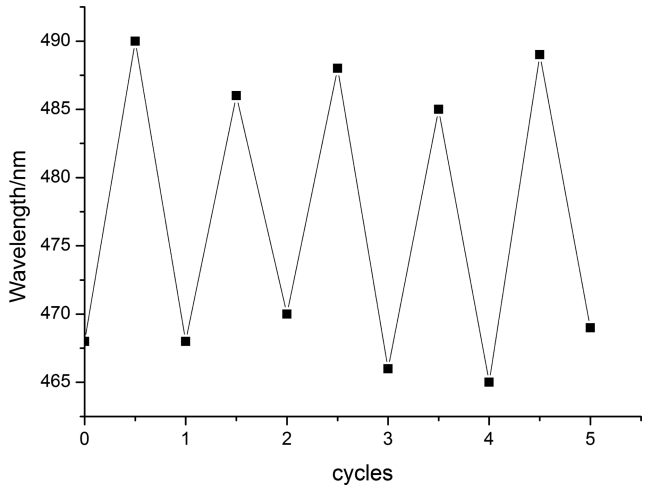

Figure 7. Swelling−deswelling cycles of the 1DPC that was immerged into solution whose pH is 14. The total number of layers ($3N$) is 12.

titania nanoparticle solution to replace TiO_2 sol. The crystal form of TiO_2 will convert to rutile and anatase, which are more stable, after it is calcined.

Compared with TiO_2/GO 1DPCs, TiO_2/hydrogel/GO 1DPCs show better responsiveness. The response of TiO_2/hydrogel/GO 1DPCs is quick; it only takes 10 min, as opposed to the 60 min taken with TiO_2/GO 1DPCs. Moreover, the color and photonic stopband change of the 1DPCs due to alkaline solutions is reversible. However, when we use TiO_2/GO 1DPCs, the change is irreversible.

4. CONCLUSION

In conclusion, the different colors of the TiO_2/hydrogel/GO 1DPCs are prepared by spin-coating technique. The optical properties of 1DPCs can be tuned by period. The SEM images

show the obvious multilayered structure of the TiO_2/hydrogel/GO 1DPCs. Our results show that the sensitivity of the sensor is improved by using TiO_2/hydrogel/GO 1DPCs. The response process is faster, more obvious, and repeatable. Considering the visible sensitivity, simplicity, and the low-cost fabrication approach, the TiO_2/hydrogel/GO 1DPCs would be promising in the future as economical and colorful sensors in the chemical and biological fields.

■ ASSOCIATED CONTENT

Supporting Information

Photographs of a TiO_2/hydrogel/GO 1DPC in different organic solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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