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Porous Polyvinylidene Fluoride Thin-Film Sensors from Colloidal Crystal Templates

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With the development of the materials science, biosensors tend to be thin, flexible, versatile, and are extensively employed in biotechnology, clinical diagnosis, biochips, etc. However, most existing biosensors are single-functionalized and destitute in contrivable microstructure, which result in some inherent limitations. In this work, a novel thin-film sensor that had dual response generated from one stimulus was designed based on the colloidal crystal templates and devisable circuit system. Benefiting from designed platinum coating, the thin-film appeared as a flexible strain sensor which presented corresponding resistance changes with the slight deformation of the thin-film. In addition, with the sacrificial template method, the porous thin-film derived from the colloidal crystal template was endowed with manageable porous structure and splendid structural color, and the resultant color could be various when the environment changed. These features laid the foundation for the construction of multifunctional thin-film biosensor and presented potential applicability for a variety of biological research and flexible sensing devices.

Keywords: Colloidal Crystal, Structural Color, Flexible Electronics, Biosensor, Inverse Opal.

1. INTRODUCTION

Biosensors, which consist of related bioactive materials and physical or chemical transducers that could convert biologically active signals into electrical signals, have been widely observed and intensively investigated in marine exploration, environmental protection, resource survey, medical diagnosis and bioengineering [1–11]. Over the last several years, researches have demonstrated various feasible applications of these biosensors in the field of clinical diagnostic examination, monitoring during treatment, fermentation industry, food industry, robots, etc. [12–16]. Polyvinylidene fluoride (PVDF) is a kind of unique piezoelectric characteristic which can transform the deformation to electric signal, and has been widely observed and intensively investigated as a popular example in flexible organic piezoelectric for sensors [17–22]. However, the current PVDF material always requires additional cumbersome poling process to achieve enough excellent piezoelectric characteristic. Therefore, there is still a strong demand for exploiting a low-hanging modification PVDF material to gain better electrical properties.

In this paper, we presented a kind of PVDF thin-film sensor engineered with proper circuit system. To obtain an electric sensor, the pure PVDF thin film was covered with a designed metal mask and sputtered with a stable metal coating. After a bending experiment, the optimized circuit system was achieved, which could appear to reversible and regular impedance changes with the weak deformation. However, this thin-film was similar to most existing biosensors extremely lacking the controllable microstructure of the material, which restricted its potentials in biological and biomimetic applications. In addition, the resultant film with single electric property was insufficient for the burgeoning sensor technology, while a multi-function sensor was undoubtedly anticipated.

Herein, we further developed a multi-functionalized PVDF thin-film sensor with designed circuit system and periodical pores for electrical response and optical feedback. Besides the strengths from the circuit system, the film was endowed with periodical pores derived from colloidal crystal templates. Colloidal crystals are three-dimensional ordered array structures formed by the self-assembling of monodisperse nanoparticles under gravity, electrostatic force or capillary force [16, 23–27]. Due to the periodic structure, colloidal crystals not only got widely explored in material processing, self-assembly and

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phase transition, but also gained particular relevance in photonic sensor [28–30]. When colloidal crystals film was replicated by PVDF, the resultant film could inherit the periodic arrangement and manage the light as well. This property endowed the PVDF thin-film with brilliant photonic properties and provided broad application prospects in physical sensor and optical detector. Therefore, it was demonstrated that the film manifested an accurately controlled nanostructure, and gained the excellent response to the real-time deformation with the optimized design of circuit and the photonic structure. As a result, the integrated sensor had dual sensitive components that could be monitored simultaneously for the more precise and comprehensive understanding of the object or environment. Therefore, the porous PVDF thin-film sensors are highly desirable in tissue engineering and flexible electronics.

2. MATERIALS AND METHODS

2.1. Materials and Characterization

Three kinds of SiO_2 nanoparticles with sizes of 240, 277 and 330 nm were purchased from Nanjing Nanorainbow Biotechnology Co. Polyvinylidene Fluoride (PVDF), was purchased from Sigma Aldrich (St. Louis, MO) *N*,*N*-dimethyl formamide (DMF), hydrofluoric acid (HF), ethanol were purchased from Aladdin, Shanghai. Deionized water with a resistivity of 18 $M\Omega \cdot cm$ was acquired from a Millipore Milli-Q system.

The electric properties of the material were measured by using a digital storage oscilloscope and a semiconductor characterization system (Keithley 4200). The platinum coating was sputtered by Vacuum Sputter Apparatus (Q150TS, Quorum, UK). The impedance response was measured with a digital multimeter (Agilent 34410A). The microscopy images of silica colloidal crystal templates, cured PVDF films containing nanoparticles and porous PVDF films were measured separately by an optical microscope (BX51, Olympus) equipped with a charge-coupled device camera (Media Cybernetics Evolution MP5.0) and the reflection spectra of the above samples were collected by a microscope equipped with a fiber optic spectrometer (USB2000-FLG, Ocean Optics). Scanning electron microscope (SEM) images of samples were taken by a scanning electron microscope (S-3000N, Hitachi).

2.2. Fabrication and Measurement for Designed Metal Coating

In this work, the DMF solution with 0.1 g/mL PVDF was dropwise dripped on the glass slide. By heating for half an hour, the pure PVDF thin film was obtained after the completely volatilizing of the DMF solvent. Then, to obtain optimized circuit design, the pure PVDF films were covered with varisized metal masks and sputtered for 20 minutes. Then, the films with designed platinum circuit were employed in repetitive bending experiments. During the bending process, a digital multimeter was connected to both sides of the circuit to measure the real-time impedance.

2.3. Preparation of Porous PVDF Thin Film Sensors

These porous PVDF thin film sensor was manufactured by a sacrificial template method. Firstly, the SiO_2 nanoparticle solution (1%, w/v) with different particle diameters were separately assembled on glass slides by using a vertical deposition method. Due to the surface tension, a meniscus was formed on the surface of the glass substrate. As the solution at the liquid level evaporated, the interaction between the silica particles drove the surrounding colloidal particles into the boundary zone, and the capillary force induced the particles in the substrate-air-solvent interface arranged into a dense colloidal crystal structure. Because the preparative technique of the colloidal crystal templates was very experienced, more than 95% of the templates presented perfect structure. Then, the template was calcined at 500 °C for 4 hours to enhance the mechanical strength.

The DMF solution with a concentration of 0.1 g/mL PVDF was dropwise dripped on the templates and infiltrated into the voids of the silica nanoparticle, and then the composite film was heated at 60 °C for half an hour to volatilize the DMF solvent and solidify the PVDF film. After etching (4 wt% hydrofluoric acid) the silica nanoparticles of the composite film and washing with deionized water for three times, the PVDF thin film with ordered nanopores was accomplished.

3. RESULTS AND DISCUSSION

In a typical experiment, the pure PVDF thin films were prepared with dripping the PVDF/DMF solution on the glass slides. With a laboratory heating plate, the DMF solvent evaporated within an hour (Fig. 1(A)). To characterize the electrical properties of the pure PVDF material, impedance characteristic was represented with semiconductor test system. With a certain voltage, the resistance values and the real-time current of the PVDF films were monitored, meanwhile an ohmic resistor was chosen as the control group (Fig. 1(B)). Contrasting to the regular current of the control group, the pure PVDF film showed the extremely high impedance which close to interrupted circuit (Figs. 1(C, D)). As for their piezoelectric property, the pure PVDF films without any additional treatment were explored by applying a certain regular force on them. As shown in Figure 2, the PVDF film only generated extremely feeble, instantaneous and irregular voltage with the force. To solve this problem, in current studies, many strategies were adopted to modulate crystalline regions, thus to acquire a preeminent piezoelectric response, such as applying an effective electric field at a specific temperature using polar solvents or incorporating small amounts of other polymers. However, these methods were limited by the cumbersome modification and polarization process. Therefore, the PVDF film still needed further

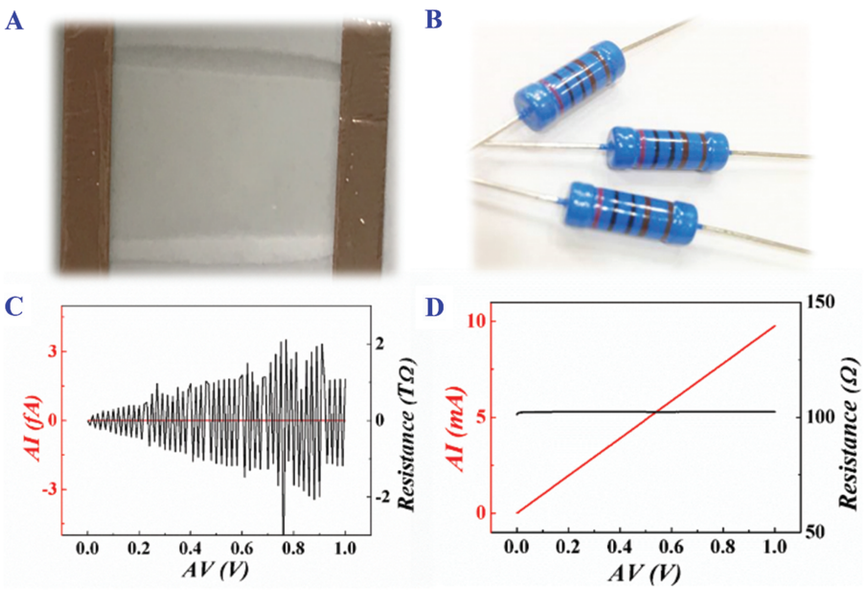

Figure 1. The impedance characteristic of the pure PVDF thin films. (A) The optical image of the pure PVDF film. (B) The optical image of the ohmic resistor. (C) The impedance characteristic of the pure PVDF film. (D) The impedance characteristic of the ohmic resistor.

modification to gain better electrical properties for intelligent sensing.

To gain an effective electrical response, the immobilized metal lamina was taken into consideration due to its repeatable lossless stretching and bending ability [31–34]. Thus, to gain desired shape, a stable metal coating was controllably sprayed on the PVDF thin film that was already covered by a metal mask (Fig. 3). Due to the chemical stability and high electrical conductivity, platinum was selected as the metal coating to explore an optimized

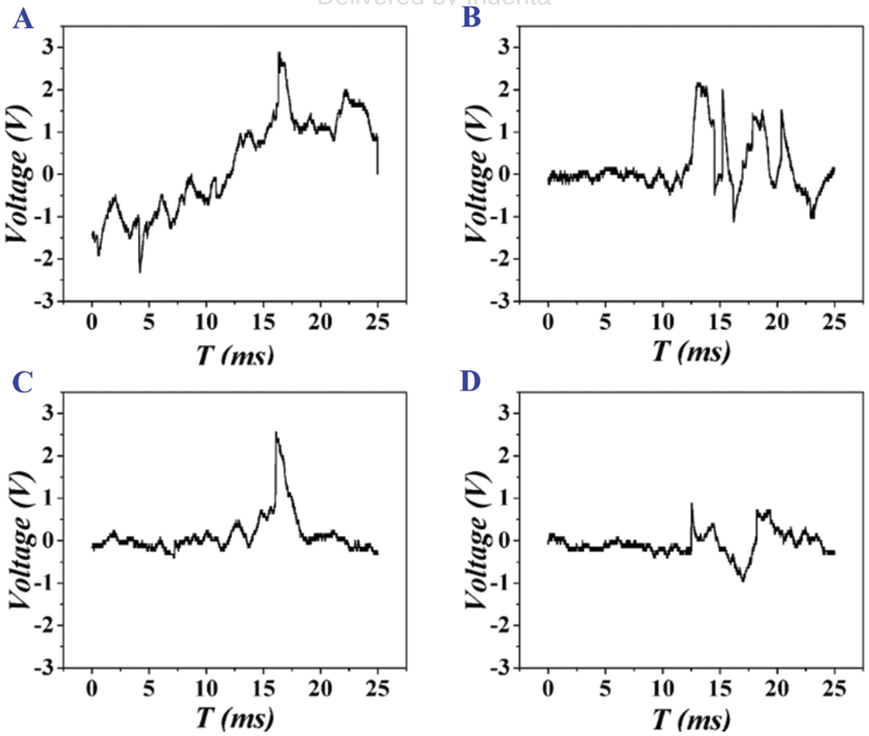

Figure 2. The piezoelectric characteristic of the PVDF films without any poling treatment. (A–D) The piezoelectric characteristic of the PVDF films without any poling treatment.

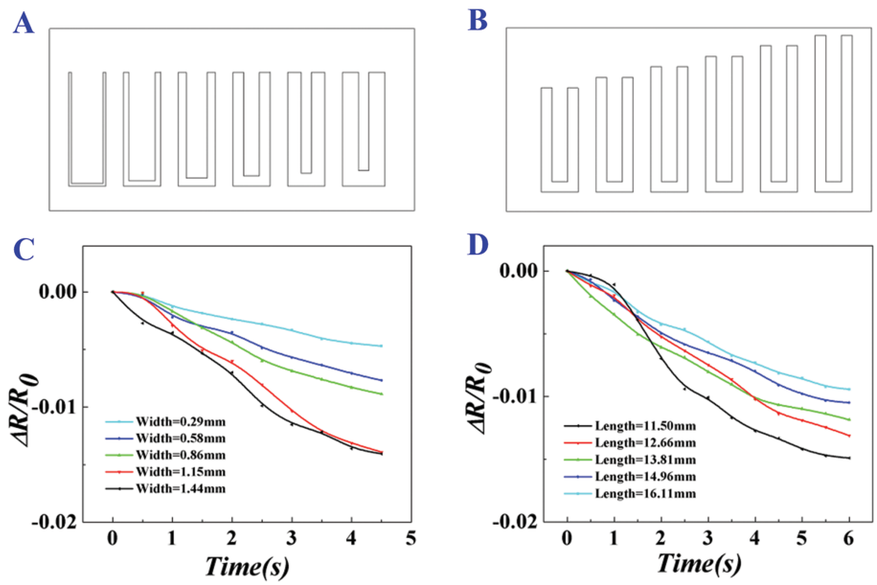

Figure 3. The electronic sensing of the platinum coating. (A, B) The schematic diagram of the metal mask with different widths (A) and lengths (B). (C, D) The impedance response of the PVDF films with different widths' (C) and lengths' (D) platinum coating during the bending process.

electrical response. Mask patterns with different lengths and widths were employed, and PVDF films with different forms of metal coating were obtained after a 20-minute metal sputtering (Figs. 3(A, B)). Then, the electric properties of the PVDF films with different circuit paths were investigated in bending experiments. By utilizing a digital multimeter which was contacted with the fixed bottom of paths, the circuit paths were given a real-time impedance monitoring during the PVDF film bending process. As the bending degree increased, the resistance between the paths showed a synchronous decrease. In particular, the shortest and widest circuit paths exhibited the most outstanding response (Figs. 3(C, D)). Consequently, the metal coating with the minimum resistance was regarded as the most sensitive inductor for electronic sensing. This indicated that the sputtered PVDF film had potential in the achievement of a variety of intelligent electric sensors.

To obtain a steerable microstructure, the PVDF thin-film was processed with colloidal crystal templates (Fig. 4(A)). By vertical deposition method, the silica nanoparticles could slowly self-assemble to form a dense colloidal crystal template, and presented an ideal hexagonal close packing (Fig. 4(B)). After infusing the PVDF/DMF solution in the template and volatilizing the DMF solvent, the silica nanoparticles still maintained an orderly arrangement and were completely wrapped in the cured PVDF film

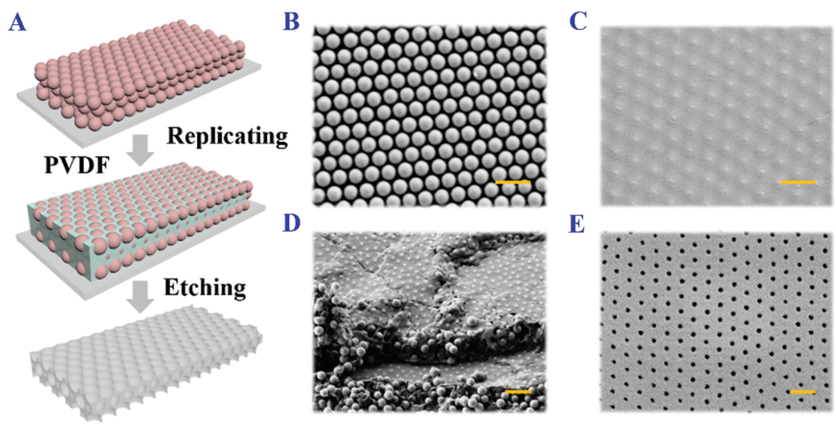

Figure 4. The generation process of the replicated porous PVDF film. (A) Schematic diagram of the generation process of the replicated porous PVDF film. (B) The SEM image of colloidal crystal template. (C) The SEM image of colloidal crystal template covered with PVDF film. (D) The SEM image of the cross section of colloidal crystal template covered with PVDF film. (E) The SEM image of replicated porous PVDF film. Scale bars were 1 um.

(Figs. 4(C, D)). Finally, by etching the silica nanoparticles with HF, a free-standing PVDF film sensor was acquired with mainly hexagonal symmetry nanopores (Fig. 4(E)).

To investigate the effect of the colloidal crystal templates, silica nanoparticles with various diameters were chosen for the fabrication of the thin-film sensor (Fig. 5). After a period of self-assembly, silica nanoparticles were gradually deposited to colloidal crystal templates and possessed the capability to modulate photons, presenting brilliant structural colors and reflection spectra. Particularly, the main characteristic reflection peaks of the templates with specific structural color can be calculated by the Bragg Snell equation:

$$\lambda = 1.633D(n^2_{\text{average}} - \cos^2\theta)^{1/2} \quad (1)$$

where D is the center-to-center distance between two neighboring nanoparticles, n_{average} refers to the average refractive index of the template, and θ is the Bragg glancing angle of incidence of the light falling on the template. Therefore, templates with a variety of structural colors and reflection spectra could be prepared by changing the diameters of the silica nanoparticles. After replicating the construction of various templates, the porous PVDF film could possess controllable microstructure derived from silica nanoparticles, and inherit the photonic band gap (PBG). Obviously, apart from regulable micro-scale construction, the porous PVDF film manifested modulable macroscopic vivid optical properties. In addition, because of the discrepant refractive index, the templates filled with PVDF component demonstrated larger reflection wavelength values in comparison to the original templates, while in the meantime, the porous PVDF films showed blue shifts in reflection spectra. On the basis, a type-combined transducer based on such porous film could be achieved with the integration of electronic sensing and optical sensing for a comprehensive signal response.

With the development of integration technology and ultra-micro fabrication technique, sensors are gradually achieving to the stage of multi-function, high performance and miniaturization [35–39]. To implement this integration, a multifunctional biosensor was proposed by

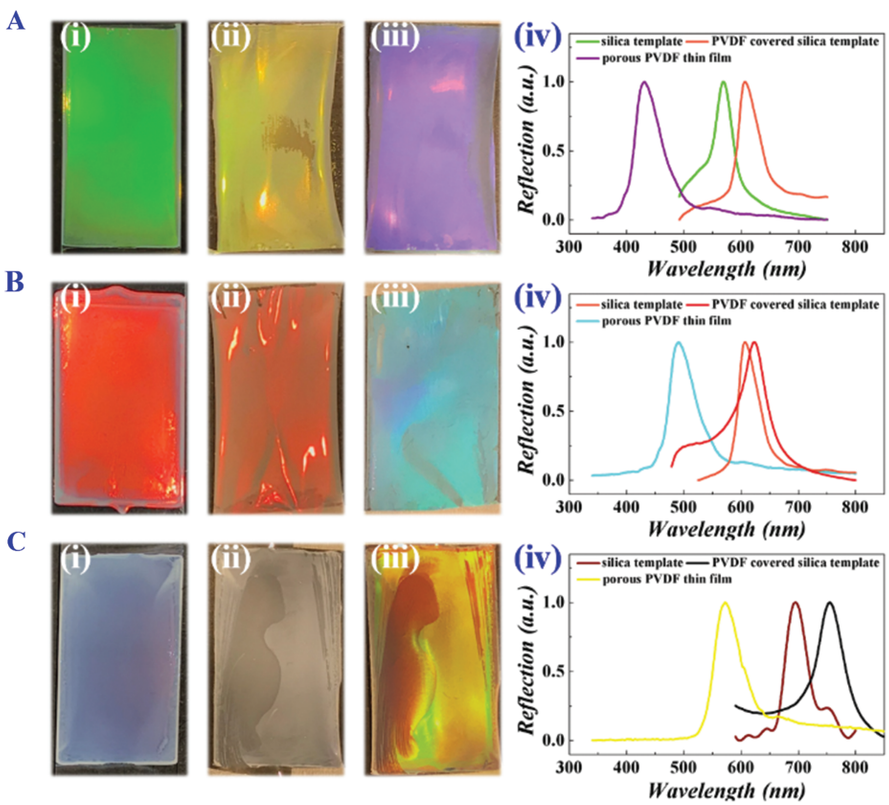

Figure 5. Images and reflection spectra of films derived from three kinds of colloidal crystal templates. (A) The films were self-assembled by 240 nm silica nanoparticles. (i) The optical image of colloidal crystal template. (ii) The optical image of colloidal crystal template covered with PVDF film. (iii) The optical image of replicated porous PVDF film. (iv) The reflection spectra of the three films. (B) The films were self-assembled by 277 nm silica nanoparticles. (i) The optical image of colloidal crystal template. (ii) The optical image of colloidal crystal template covered with PVDF film. (iii) The optical image of replicated porous PVDF film. (iv) The reflection spectra of the three films. (C) The films were self-assembled by 330 nm silica nanoparticles. (i) The optical image of colloidal crystal template. (ii) The optical image of colloidal crystal template covered with PVDF film. (iii) The optical image of replicated porous PVDF film. (iv) The reflection spectra of the three films.

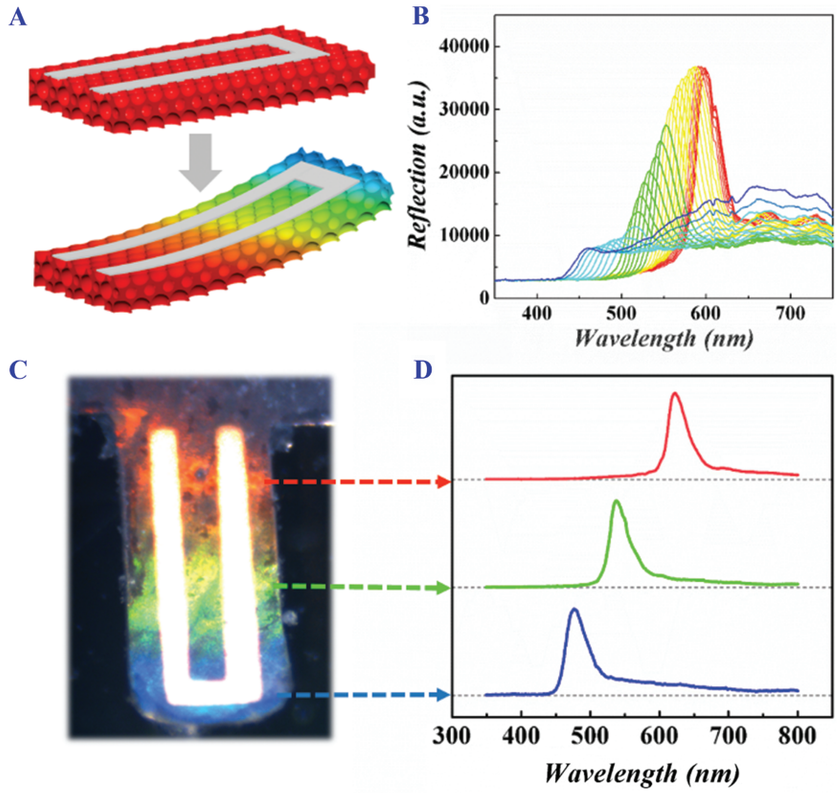

Figure 6. The construction of the multifunctional biosensor. (A) The schematic diagram of the porous PVDF film with designed circuit. (B) The optical dynamic response of the porous PVDF thin film: The reflection spectra from red to blue when the incident angle increasing from 0° to 60°. (C) The optical image of the bending PVDF film. (D) The reflection spectra of the bending PVDF film.

bringing colloidal crystal into the circuit-designed PVDF film (Fig. 6). The porous PVDF thin films, prepared by replicating colloidal crystal templates, were equipped with calculated metal circuit (Fig. 6(A)). The results showed that the microstructure of the porous films had few influence on the electrical response of the circuit. It was worth mentioning that the porous PVDF thin films were endowed with additional optical dynamic response owing to the periodic voids (Fig. 6(B)). For a fixed porous film, it was proved that the reflective spectrum of the structural color shifted to blue gradually along with the incident angle increasing. This change also could be observed by naked eyes. In addition, each bending film held a gradient of rainbow color, which provided respective bending degrees in different correspondent positions (Figs. 6(C, D)). Therefore, the real-time deformation such as bending degree could be exhibited numerically by variational impedance and wavelength. Hence, the PVDF film we prepared have huge potential in many applications to transform the mechanical signals to visual signals, such as biomechanics and tissue engineering.

4. CONCLUSIONS

In summary, we have developed an engineered PVDF thin-film sensor for dual photoelectric response. This sensor system was based on moldable and compliant PVDF films with the integration of devisable circuit system and ordered porous microstructure. By sputtering metal coating, the PVDF thin film with the optimal circuit system presented efficient functionality of electrical response to small deformation. In addition, the porous microstructure derived from sacrificial template method, could be manipulated with various templates, showing gorgeous structural color. Particularly, the splendid structural color could hold apparent angular dependence, leading to an ingenious color adaptability for real-time deformation such as bending. With the combination of the two functions, this sensor system could be highly responsive and offer comprehensive output for external stimuli. Thus, it could be envisioned that this PVDF thin film sensor system will find important applications in biomechanics and tissue engineering.

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