The research of colorimetric sensor based on one-dimensional Fibonacci quasicrystal structure

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Abstract. Based on the principle of photonic crystal structure color, a one-dimensional Fibonacci quasi-crystal structure colorimetric sensor is designed and optimized. The optical model of quasi-crystal structure was constructed by iterative method with the number of iterations being 5. Quasicrystal structure consists of alternating arrangement of chitin and ethanol. A structure with higher color sensitivity was designed by changing the chitin filling ratio in the quasicrystal structure. Based on this structure, a high-sensitivity colorimetric sensor was designed by changing the amount of ethanol volatilization to monitor the change of reflectance spectrum.

1. Introduction

Since E. Yablonovitch and S. John proposed the concept of photonic crystals in 1987 [1], research on photonic crystals has become active, and scholars have done a lot of research on the bandgap properties of photonic crystals [2-3]. Photonic crystals are periodically arranged by dielectric materials of different refractive indices. Generally divided into one-dimensional photonic crystal, two-dimensional photonic crystal and three-dimensional photonic crystal. The existence of photonic band gaps in photonic crystals is the cause of structural coloration [4]. When visible light is irradiated on the photonic crystal, the forbidden band limits the light of a particular wavelength that cannot pass through and is then reflected. The reflected light will form a coherent diffraction on the surface of the crystal. Eventually this particular wavelength of light will be perceived by the human eye in a particular’s color. In fact, structure color are common in nature. Such as peacock feathers, butterfly wings, gem beetle shells and other insects, etc [5]. Changes in animal’s color represent a variety of functions such as display, warning, camouflage, and communication. Therefore, a large number of scholars have studied a series of color tunable photonic crystal materials with significant optical response under external stimuli [6]. The photonic crystal structure color has the advantages of high brightness, high saturation, and never fading, which the pigment does not have. At the same time, the photonic crystal structure color’s material has the advantages of wide material selection, simple structure, good stability and high practical value [7-9], so it is widely used in sensing, detection, anti-counterfeiting identification, printing and so on. The porous mixed metal oxide MMO-TiO2 one-dimensional photonic crystal structure can be fabricated into a colorimetric sensor to detect the pH of some volatile organic compounds or solutions [10].

On this basis, a one-dimensional Fibonacci quasicrystal structure was constructed by iterative method to prepare the colorimetric sensor. The number of iterations was 5 times. The design of the structure is inspired by the butterfly wing’s color, which is equivalent to filling the volatile medium ethanol into the butterfly wing structure. Monitor the change in reflectance spectrum by changing the
amount of ethanol volatilization, and finally observe the change in color to measure the change in temperature. In this paper, a structure with higher color sensitivity is designed by optimizing the filling ratio of the medium.

2. Theory

2.1 Photonic crystal structure color
One-dimensional photonic crystals, also known as Bragg stacks, are composed of two different refractive index media stacked in one direction. The color exhibited by photonic crystal materials is the result of light reflection and interference [11]. The wavelength of the reflected light obeys the Bragg-Snell rule [12-13], and its formula is as follows:

$$\lambda = 2D(n_{\text{eff}}^2 - \cos^2 \theta)^{1/2}$$  \hspace{1cm} (1)

Where \(\lambda\) is the wavelength of the reflected light; \(D\) is the distance of the diffraction plane, that is, the period of the filling medium; \(n_{\text{eff}}\) represents the relative refractive index of the medium in the photonic crystal structure; \(\theta\) is the angle of incidence when light is irradiated onto the structure. The colorimetric sensor is designed based on the principle that the change in relative refractive index causes a change in the reflection wavelength, which in turn causes a change in color.

2.2 Fibonacci quasicrystal sequence
After the publication of the quasi-crystal research report for the first time in 1984, it immediately attracted the interest of global scholars in the research of crystal. As a special photonic crystal, quasicrystal is a non-periodic structure, but it also has some optical properties of photonic crystals. The Fibonacci model is a relatively common quasicrystal structure. There are many methods for constructing Fibonacci sequences. The iterative method listed below is the simplest and most visual method, which is explained by the rabbit breeding problem. Suppose there are two rabbits A and B, A is a big rabbit, and B is a small rabbit. The big rabbit will have a bunny: A→AB; The bunny will grow into a big rabbit: B→A [14]. If the cycle continues, you get a sequence like ABAABABAABAAB…. This sequence is the Fibonacci quasicrystal sequence. The length of the sequence depends on the number of iterations.

2.3 Optical model
Quasicrystals, as a special photonic crystal structure, can also be designed by changing the relative refractive index of the colorimetric sensor. This paper constructs an optical model of a one-dimensional Fibonacci quasicrystal [15] structure, and the optical response is simulated by the Finite Time Domain Difference Method (FDTD). As shown in FIG. 1A, the quasicrystal structure is generated by iteratively iterating five times, and chitin and ethanol are alternately arranged from right to left. The design of the structure is inspired by the butterfly wing color, which is equivalent to filling the volatile medium ethanol into the butterfly wing structure. The plane wave is selected as the incident light source and incident from the left side, and the wavelength range is selected from 400 nm to 800 nm. The simulation area is set to 2D and add a reflectance spectrum monitor behind the light source. As shown in FIG. 1B, as the external temperature increases, the ethanol volatilizes in percentage (each layer is volatilized in equal proportions), and then causes a change in the relative refractive index of the structure. The thickness \(T\) of a single layer of chitin and ethanol in the structure is set to 180 nm. The media a, b, and c represent chitin, ethanol and air, respectively, and the refractive indices are 1.36, 1.56 and 1 respectively (the refractive index is only the real part).
3. Simulation result analysis

The thickness $T$ of a single layer of chitin and ethanol in the structure is set to 180 nm. However, the structure of different media fill ratios will have different optical response results, which are mainly reflected in the reflection spectrum curve and the chromaticity diagram. This paper simulates the structure of several different chitin filling ratios. To analyze the effect of media fill on color’s sensitivity of quasicrystal structures. In the process of ethanol from 0% volatilization to 100% volatilization, the quasi-crystal structure under several different filling ratios exhibits a blue shift of the reflection spectrum curve and the peak value also increases. The reason is that the refractive index of ethanol is larger than that of air. As the temperature increases, the ethanol in the structure volatilizes into air, which causes the relative refractive index of the structure to change. It is observed that with the increase of the chitin filling ratio, the overall reflection spectrum curve shows a right shifting trend during the evaporation of ethanol. When the chitin filling ratio is 0.5, a new peak appears at 400 nm. When the filling ratio is increased to 0.6, a relatively complete peak appears, and the two peaks interfere with each other to form a mixed color. In contrast, the color’s change of a single peak is more obvious. The wavelength of the reflected light depends on the change of the relative refractive index. The more obvious the relative refractive index changes during the evaporation of ethanol, the higher the color’s sensitivity of the structure. Moreover, if the chitin filling ratio is too large, the actual production difficulty will increase. Therefore, when the actual production of the sensor, a smaller chitin filling should be selected.

![Image of optical model and reflection spectrum curves](image)

**Fig. 2** The reflection spectrum of several different chitin filling ratio structures
(A–F represent the chitin filling ratio of 0.1–0.6)
The relative wavelength is the ratio of the full width of the half-maximum of the spectrum to the center wavelength, and the fitted curve reflects the change of the reflectance spectrum curve with the increase of the proportion of ethanol volatilization. The greater the slope of the curve, the more obvious the change in the structure’s color, the higher the sensitivity. But also consider whether the linear correlation coefficient is close to 1. As shown in Fig. 3, the fitting curve of the relative wavelength with the evaporation ratio of ethanol is given. The four curves are chitin filling ratio 0.1–0.4. It is observed that when the filling ratio is 0.2, the slope value of the curve at this time is at most 0.0028, but its correlation coefficient is \( R=0.91929 \). When the filling ratio is 0.3, the slope of the curve is 0.00198, and the correlation coefficient is \( R=0.96948 \). The slope is very close to a structure with a filling ratio of 0.2 and the correlation coefficient is closest to 1. This indicates that the relative wavelength has the highest linear correlation with the ethanol volatilization ratio, and the fitting effect is the best.

![Fig. 3Fitting curve of relative wavelength with ethanol volatilization ratio under different filling ratios.](image)

The chromaticity diagram can show the color change of the reflected light during the evaporation of ethanol, and each reflection spectrum curve corresponds to a chromaticity coordinate. As shown in Fig. 4, although several structures exhibit color’s changes as the amount of ethanol volatilization increases, there are differences in sensitivity. It is observed that when the chitin filling ratio is 0.3, the color change of the reflected light is most significant as the ethanol is continuously volatilized, showing a relatively regular gradual process and conforming to the blue shift of the reflection spectrum. Consistent with the above analysis, it satisfies both the slope of the fitted curve and the high linear fit. At this time, the sensor structure has a higher sensitivity. The chromaticity coordinates of a-f are CIE: (0.437, 0.434), CIE: (0.402, 0.448), CIE: (0.388, 0.468), CIE: (0.367, 0.468), CIE: (0.343, 0.444), CIE: (0.315, 0.402). Therefore, in the case where the quasi-period of the quasicrystal structure is determined to be 180 nm, the structure with a chitin filling ratio of 0.3 has the highest sensitivity and the most obvious color change, and is more suitable for the production of a colorimetric sensor.
Figure 4 Chromaticity diagram of four different chitin filling ratio structures (A-D is the filling ratio of 0.1-0.4, a-f is the color change when the ethanol volatilizes from 0% to 100%)

4. Conclusions

In this paper, a one-dimensional Fibonacci quasi-crystal structure colorimetric sensor is designed based on the photonic crystal structure color, and the change of external temperature is monitored by observing the change of color. The filling medium gradually evaporates as the temperature increases, and the relative refractive index of the structure changes, eventually resulting in a difference in the color of the reflected light. When the thickness T of a single layer of chitin and ethanol in the structure to be 180 nm, changing the chitin filling ratio will have a large effect on the sensing characteristics of the structure. Through comparative analysis, it is found that when the chitin filling ratio is 0.3, the color change of the structure is the most significant, and the color sensitivity is the highest, which is most suitable for the production of colorimetric sensors. The sensor has the advantages of miniaturization, low cost, easy portability and convenient use. Higher color sensitivity than equivalent conditional periodic photonic crystal structures. If the volatile medium ethanol is replaced by a porous structure that differs greatly from the refractive index of chitin, it can be used to detect the pH of a volatile gas or liquid. This can be used as a new research idea. All above results can provide reference for the production of colorimetric sensors.

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