Review



Materials Science

Visualized optical sensors based on two/three-dimensional photonic crystals for biochemicals

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Abstract Responsive photonic crystals (RPCs) constructed by periodic two/three-dimensional (2D/3D) photonic crystals (PCs) and responsive-material hosts, are important visualized optical sensors. Their optical diffraction color can be tuned reversibly by external stimuli, such as pH, metal ions, biomolecules, vapors and solvents, hence leading to wide applications as visualized sensors. This review introduces the recent progress of RPCs based on 2D/3D PCs for visual detection of chemical and biological analytes, including the preparation of 2D PCs, 3D PCs films, 3D PCs microbeads and their applications as visualized sensors. The different cases of detecting various chemical and biological analytes by naked eyes are presented. Emphasis is given to the description of their respective sensing mechanisms with the different systems for chemical and biological analytes. Compared with 3D RPCs sensors, 2D RPCs sensors have shorter response time, better stabilization and higher production efficiency, however, the diffraction intensity of 2D RPCs based on monolayered 2D polystyrene (PS) microsphere array are weak. 2D RPCs sensors based on 2D Au nanosphere can significantly improve the diffraction intensity compared with traditional 2D RPCs sensors based on monolayered PS microsphere array. The much higher scattering cross section of Au nanosphere leads to 2D Au nanosphere array with ultrahigh optical diffraction intensity, which are

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highly helpful for their practical application as visual sensors and further quantitative detection by monitoring the diffraction peak position and intensity.

Keywords Optical sensor · Photonic crystal · Biochemicals

1 Introduction

Biological and chemical species are widely used in pharmacy, industry, agriculture etc. The extensive applications of these species would produce some residual agents in the environment, resulting in the pollutions in water and air to further threaten the human health. Therefore, it is important to realize sensitive and selective detection of these agents before their concentrations reach dangerous levels. The current detection of these agents mainly relies on sophisticated analytical techniques, such as Raman spectrum, high-performance liquid chromatography, gas chromatography [1, 2]. However, these techniques need expensive equipments and well-trained operators, that have disadvantages of high cost and complexity. Therefore, there is a strong demand to develop alternative methods with low cost and simple operation to detect chemical and biological species. Visual detections are popular and attractive since they can directly display the concentration of dangerous molecules in a short time and realize the detection without expensive equipments. Responsive photonic crystals (RPCs) are good candidates for visual sensors because they can display environmental stimuli by color changes [3–13].

RPCs have generally been created from PCs and responsive-material host. Their optical properties can be tuned by external stimuli. The PCs have photonic band gap

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(PBG) due to the periodic alignment of materials with different dielectric constants. The periodic structure will cause that the light with certain wavelengths or frequencies located in the PBG is prohibited from propagating through the periodic alignment, so resulting in the structure color [14–27]. PCs could be constructed by monodispersed units, i.e. monodispersed microspheres [28-34], micro fibers [35], nanopillars [36], nanowires [37], cellulose nanocrystals [38–40], chitosan nanofibrils [41]. In this review, we mainly introduce the PCs constructed by monodispersed microspheres and optical sensors based them. These microspheres are commonly made of silica (SiO₂), polystyrene (PS), poly(methyl methacrylate) (PMMA) or hydrogel, because the microsphere size of these materials could be readily controlled to prepare the monodispersed units from tens of nanometers to several microns [28–34]. In the past years, 3D PCs [28–30, 42] and 2D PCs [1–3, 5] have been widely investigated to prepare RPCs.

According to the different requirements, responsive materials have been designed to respond to various external stimuli, such as humidity [6], temperature [21-25], organic solvent [14], pH [8–10], ionic strength [11], mechanical force [12], metal ions [26], chemical and biological species [42–51], light and magnetism [52], vapors [53, 54]. In principle, a stimulus can induce a change in the refractive indices of the two periodic materials, or a change in the lattice constant of the PCs, which can tune the structure color of PCs [15]. Therefore, the analytes could be detected by such color changes [55, 56]. The preparations of novel PCs and responsive-materials have been developed in the past two decades, making the RPCs have many potential practical applications. Additionally, the RPCs have been successfully used in the fields of color displays [57–61], sensors [5, 15, 18, 19, 62, 63], encoded particles [42, 64-67], and so on [68-71].

This review will focus on recent developments of RPCs based on 2D/3D colloidal crystals, whose optical properties can be tuned by response to external stimuli. The objectives of this review are as follows: (1) briefly summarize the fabrication of 3D and 2D PCs by self-assembly of monodispersed microspheres; (2) introduce general strategies for creating RPCs; (3) give an overview of the various visualized sensors based on RPCs, and then emphasize the progresses in this field.

2 Reflection in PCs

The light reflection of certain wavelength from the PCs can be generally explained by the optical diffraction phenomenon like X-ray diffraction (Fig. 1). X-ray diffraction theory supposes periodically arranged atoms placed in a vacuum. A PC array consists of dielectric

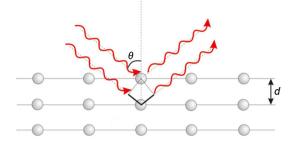


Fig. 1 (Color online) Schematic illustration of light reflection from PCs by using the similar explanation of X-ray diffraction. Reprinted with permission from ref. [5], Copyright © 2014 Wiley

microspheres within a dielectric medium such as air or solvent. Combining Braggs law with Snells law of refraction leads to Eq. (1), where λ is the wavelength of the reflected light, $n_{\rm eff}$ is the average refractive index of the photonic materials, *d* is the distance of plane spacing, and θ is the angle of incident light. Based on Eq. (1), there are several methods for tuning structural color, such as changing the *d*, $n_{\rm eff}$, and θ [5, 16, 46].

$$m\lambda = 2d \left(n_{\rm eff}^2 - \sin^2\theta\right)^{1/2}.$$
 (1)

3 Preparation of PCs

3.1 Preparation of 3D PCs films

Self-assembly is a well-known method to organize monodispersed microspheres into PCs films, such as lift-up [72], bladecoating [73], gravitational deposition [74, 75], vertical deposition [6, 9, 14]. Among various self-assembling methods, the vertical deposition-evaporation is a facile, inexpensive route to prepare close-packed PCs films with high quality. However, it has some disadvantages, such as more defects in PCs films, a long preparation time, low throughput, and difficulty in creating complex structures [52]. Non-close-packed (NCP) structure has been prepared via an electrostatic self-assembly in aqueous solution containing polymerizable monomers and monodispersed microspheres, followed by polymerization [11, 26, 47]. The repulsive electrostatic interactions keep the microspheres away from each other, and the monomers then have been polymerized around the NCP 3D PCs. The preparation time of this method is short, but it has very strict requirements for experimental conditions, for example, the polymerizable monomers should be non-ionic to avoid disrupting the charge stabilized PCs [1].

3.2 Preparation of 3D PCs microbeads

In order to improve throughput and further construction of complex PCs structures, 3D PCs microbeads have been prepared by microfluidic techniques [42, 52]. Unlike planar

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