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FEATURE ARTICLE

High effective sensors based on photonic crystals

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Photonic crystals have been extensively studied as high effective sensors for environmental monitoring and chemical and biological detections. This paper reviews recent achievements on photonic crystal sensors. Especially, the band gap responsiveness and the ability in amplifying spontaneous emission are demonstrated in the reported photonic crystal monitors/sensors. They are of great importance for optical monitors/sensors visualized by the naked eye and sensors based on fluorescence applications. The photonic crystal sensors are promising for low-cost and high effective sensors and detection methods, although challenges still exist in practical applications.

Keywords sensor, monitor, photonic crystal, photonic band gap, fluorescence

1 Introduction

Since Yablonovich and John theoretically showed the ability of three-dimensional (3D) periodic dielectric materials to possess a photonic band gap (PBG) in 1987 [1,2], PBG materials, namely photonic crystals (PCs), have become an important and popular research area [3]. PCs are composed of periodic dielectric or metallo-dielectric nanostructures, which essentially contain regularly repeating internal regions of high and low dielectric constants. Light travelling through PCs experiences a periodic variation of the refractive index and it is dependent on the wavelength of photons whether the light can propagate through such structures. The propagation of photons of certain wavelength/energy would not be allowed in PCs, just like there is a band of forbidden energy (the band gap) for electrons in a semiconductor. Disallowed bands of wavelengths are called PBGs [1,2]. These distinct optical phenomena make PCs facilitate two fundamentally optical principles: the localization of light and the controllable inhibition of spontaneous emission of atoms and molecules [4–8]. The new optical principles give rise to distinct optical phenomena, such as modification of spontaneous emission, omni-directional high-reflecting mirrors, and low-loss waveguide. These unique properties make PCs promising materials in many research areas that deal with visible, UV and near-infrared electromagnetic radiation as well as new sensor switching and wave-guiding materials in the future. In this report, we extremely focus on the applications of PCs in chemical and biological sensors. Among many kinds of PCs made from various approaches, including two-photon or X-ray lithography, layer-by-layer woodpile [9], and e-beam fabrication, colloidal crystals and inverse opals provide facile and low-cost strategies for 3D PCs with submicrometer periods [10–12]. Colloidal crystals are from silica or polymer colloids that self-assemble to close-packed arrays of spheres under ambient conditions, as shown in Figure 1(a). The structures of colloidal crystals are similar to natural gemstone opals, so that the colloidal crystals are also called artificial opals. They diffract visible and near-infrared light assigned to the submicrometer diameters of colloids. Although the colloidal crystals have not a full PBG but a pseudogap due to the inevitable crystal defects generated during the assembly process and the low reflective indices of the colloidal spheres, the period structure is good enough for certain types of quantum optical phenomena [8,13–15], as shown Figure 1(b). The colloidal crystals have shown their ability in prohibiting photon propagation in certain directions [16–19], improving optical switches [20,21], and optimizing the emission properties of active materials in the lattice structures [22]. Moreover, the simple close-packed segments can serve as units of integrated PCs for complex periodic architecture applications. They are important precursors for future studies in PBG materials with a full PBG.

Furthermore, PBG materials with full PBGs can be

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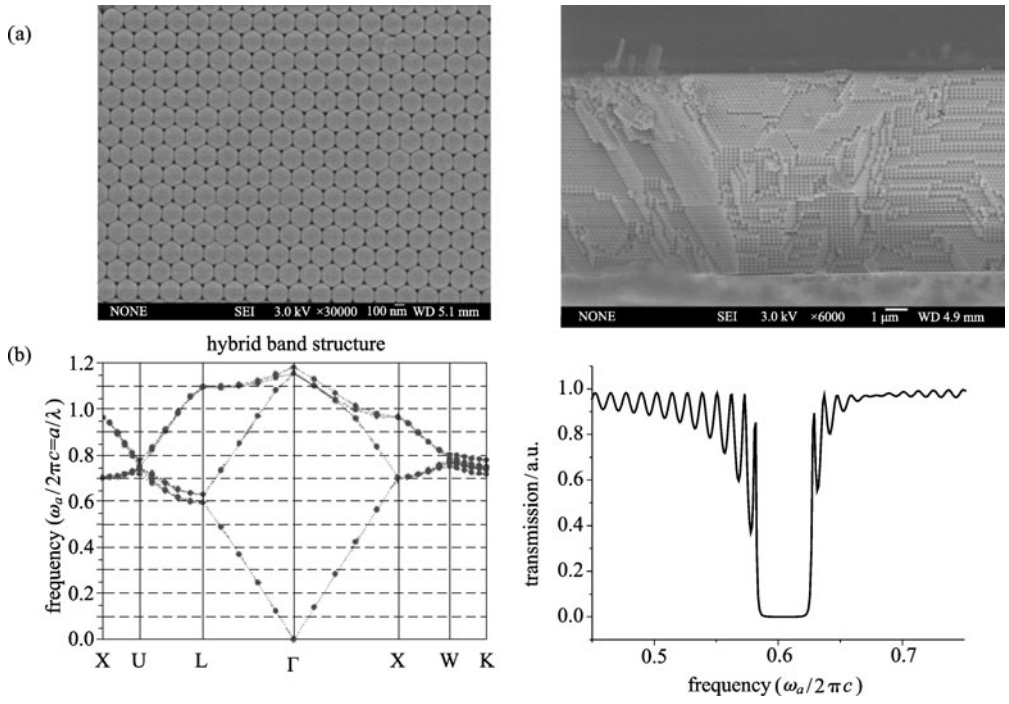

Figure 1 (a) Scanning electron microscopy (SEM) images of the typical top- and cross- views of the colloidal crystal. (b) Dispersion relation for the colloidal crystal.

achieved by replicating these structures with higher index materials [23]. Starting from a closed-packed array of latex or silica spheres as a template, three dimensionally ordered macro-porous (3DOM) structures, named inverse opals, have been created with various compositions. This strategy provides a facile method to fabricate artificial PBG materials with high indices and extremely expands the kinds of PBG materials into metal oxides [24,25], metal chalcogenides [26], pure metals, metal alloys [27–30], carbon [31] , sodium chloride, and polymers [10, 32–34].

Colloidal crystals or inverse opals both have periodical and repeated unit structures at wavelength scale. Light at frequencies within the band gaps cannot propagate through the PC materials, as shown in Figure 1(b). Their band gaps appear as minima in the transmission and give rise to Bragg peaks in the reflection, as shown in Figure 2, which is given by Eq. (1).

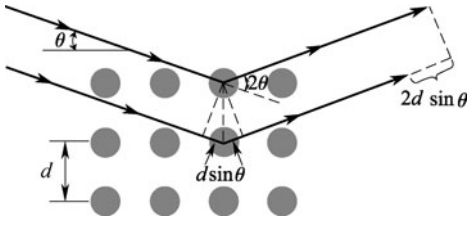

Figure 2 Schematic illustration of the light diffraction in the colloidal crystal.

$$\text{Bragg's law}: m\lambda = 2nd_{\text{hkl}}\sin\theta, \quad (1)$$

where m is the order of the diffraction, λ is the wavelength of the diffracted light (or the so-called stop band), n is the effective refractive index of the 3D array, d_{hkl} is the interplanar spacing along the [hkl] direction, and θ is the Bragg angle.

This equation indicates that the position of the stop band is directly proportional to the lattice constants and the effective refractive index of the dielectrics. It means that the optical properties of the colloidal crystals and inverse opals can be tuned by reasonable design of the structure units. Any variation in the lattice constants or the effective refractive index will result in changes in the diffraction peak. If the modulation amplitude of the dielectric constant could be quickly altered, these materials could be utilized for optical switches, sensors, and light shelters. Hence, colloidal crystals/ inverse opals can serve as an optical sensor that is capable of displaying and measuring environmental changes. In this regard, colloidal crystals/inverse opals represent a class of ideal candidates for fabricating optical sensors that can be used to monitor, to measure, and to display environmental variations in terms of color changes (which can even be easily visualized by the naked eye). The optical sensors fabricated using these approaches are potentially useful in a number of fields such as clinical diagnostics and environmental monitoring.

2 PCs optical sensors based on the lattice constants changes

As the lattice is one of the crucial factors for the position of the band gap, some PC sensors based on the concept of stimulus response changes of the lattice constants have been reported as shown in Figure 3. Optical sensors have been fabricated by combining the responsiveness of polymer gels (or other kinds of functional materials) to environmental stimuli with the diffractive property of 3D colloidal arrays [35–55]. Control of the spatial structure was realized by taking advantage of the volume phase transition of hydrogels, where the photonic band structures were tuned by controlling the temperature, the pH, and the ionic state [35–40].

A number of such kind of smart sensors have been demonstrated through the work of Asher et al. [38,43,44]. In their work, the PC material, named a polymerized crystalline colloidal array, consisted of a hydrogel and a crystalline colloidal array (CCA) [35,45]. The highly charged colloidal spheres were embedded in hydrogel materials and were assembled into 3D colloidal crystals. Embedding the crystalline array in a polymer matrix helps to retain its ordered structure when exposed to varying environments. As known, hydrogels can smartly respond to the chemical and physical environments, such as pH, temperature, ions, stresses, and bioactive factors. When the hydrogels swell/shrink as a response to the external stimulus, the space of the CCA is changed. This will result in changes of the diffraction wavelength and appears in terms of material color change. The corresponding explanation is given by the scheme shown in Figure 3(a). Diffractive devices sensitive to temperature changes have been fabricated from CCA embedded in poly (Nisopropylacrylamide) (PNIPAM) [45] and from the colloidal spheres of PNIPAM [40]. When the reversible shrinkage of this material had a moderate change with temperature, the volume change of PNIPAM hydrogel took place and resulted in a change of the lattice spacing and the modification in the intensity and position of the Bragg diffraction peak [36–38]. Colloidal crystals responsive to Pb^{2+}, Ba^{2+}, and K^{+} have also been fabricated from hydrogels by incorporating crown-ether groups into the gel matrix [35,46]. The hydrogels change volume in response to the number of charged groups covalently attached to the gel. When these cations are selectively trapped by the crown ethers, the counterions are drawn in and the Donnan osmotic pressure of the hydrogel is increased. As a result, the matrix swells and the lattice spacing is changed, and hence changes the wavelength of the diffracted light. Asher et al. reported a ~150 nm red shift responding to the concentration of Pb^{2+} varying from 0.1 $\mu mol \cdot L^{-1}$ to 10 $mmol \cdot L^{-1}$. Additionally, they also demonstrated an enzymatic-based glucose sensor with reversible swelling in artificial tear fluid solution according to the gel swelling with the conversion of glucose to gluconic acid by the enzyme [43,44]. Structural changes of these types in the order of micrometer dimensions were also achieved by using nanogels, which resulted in volume switching in nanoseconds and had more potential for practical applications [47]. In our

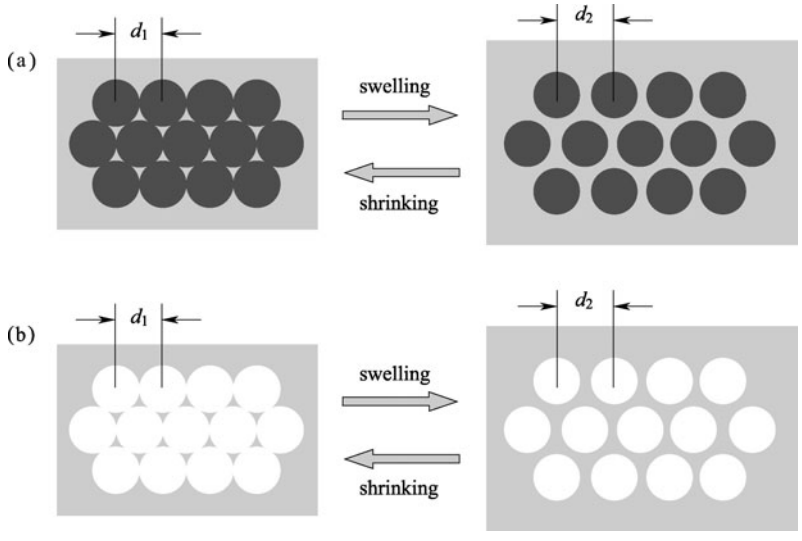

Figure 3 Schematic illustration of (a) colloidal crystals fixed by gel network and (b) the 3DOM material from contractile materials. The gel swelling mainly results from an increased osmotic pressure within the gel due to a Donnen potential arising from the counterion movement to the crown ether bound cations [35] or different amounts of solution absorption [41] , as well as the gel different volume according the situation [42,53–55].

work, a colorful humidity sensitive PC hydrogel was demonstrated. These materials showed advantage of a large tuning range over the entire visible spectrum as well as being completely reversible [41]. Additionally, Braun et al. synthesized sensitive pH sensors of tunable inverse opal hydrogels with a tunably pH sensitivity of potentially 0.01 pH unit [39], as shown in Figure 3(b). Mechanically tunable PCs, possibly acting as electric/thermal/pressure sensors, have been fabricated using elastic polymers and the band can be controlled by an external mechanical force [48,49]. Ozin et al. demonstrated a new silica-based PC material for the fingerprint application [49]. They created an inverse opal from an elastic compound using a close-packed array of SiO_2 spheres as a template. In response to the applied pressure, the resultant inverse opal displayed a blue shift in its photonic band gap and took a color-based response, which is assigned to the spacing changes of the pores, as shown in Figure 3(b). The effect is reversible, and the films can be subjected to thousands of stress cycles without significantly impairing their optical quality [49]. In addition, the control of the photonic band structure has also been realized by utilizing the phase transition of colloidal crystals in solution/electric field. They can act as light-switches, print papers, or biogenetic sensors [50–52].

For rapid and handy stimulant detection with high sensitivity and specificity, Li et al. reported a general protocol for the synthesis of imprinted photonic-hydrogel films with inverse opal structure combining colloidal-crystal and molecular-imprinting techniques [53–55]. These imprinted photonic-hydrogel films were highly specific to analytes, even if in a competitive environment assigned to molecular imprinting. At the same time, the bicontinuous, hierarchical inverse opal structure enabled these polymers to reveal a label-free molecular recognition rapidly and sensitively [53–55].

Moreover, large shifts in the optical stop band have been demonstrated by controlling the lattice constants during self-assembling process of the colloidal sphere arrays through an external magnetic field, which can act as displays [56,57]. Yin et al. have succeeded in controlling the color of very small iron oxide particles suspended in water, simply by applying an external magnetic field to the solution [58–61]. In order to have these nanoparticles self-assembled into three-dimensionally ordered colloidal crystals in a magnetic field, the crucial factor is to design the structure of iron oxide nanoparticles through chemical synthesis. Their discovery has potential to greatly improve the quality and size of electronic display screens and to enable the manufacture of products such as erasable and rewritable electronic paper and ink that can change color electromagnetically.

3 PCs optical sensors based on refractive indices changes

For ordered structures, their optical diffractions follow Bragg's law (Eq. (1)). In the case of colloidal crystals and 3DOM, the mean refractive index is determined using the volume average of the dielectric constants of different compositions in their refractive index

$$n_{\text{eff}}^2 = \sum\nolimits_i n_i^2 V_i, \tag{2}$$

where n and V are the refractive index and volume fraction of each component phase, respectively. The changes in their components will lead to changes in the optical diffraction and the shifts in the Bragg diffraction wavelength, as shown in Figure 4. By exploiting the property, these PBG materials can be used to construct chemical and biological sensors for detecting the surrounding medium [62]. Our group prepared oil-sensing materials from a superoleophilic phenolic resin PC, which show a high sensitivity and selectivity for different petroleum oils. An inverse opal with both superoleophilic and superhydrophobic properties is fabricated using a phenolic resin as precursor and colloidal crystals as templates. The stop band of the inverse opal can shift reversibly upon sorption of oils, whereby the peak position is a linear function of the refractive index of the adsorbed oil, e.g., a variation in the refractive index of 0.02 will result in a stop band shift of 26 nm [63]. Moreover, a colorful oil-sensitive carbon inverse opal was fabricated and the color shift upon absorption of the oil was reversible, and was easily visible to the naked eyes

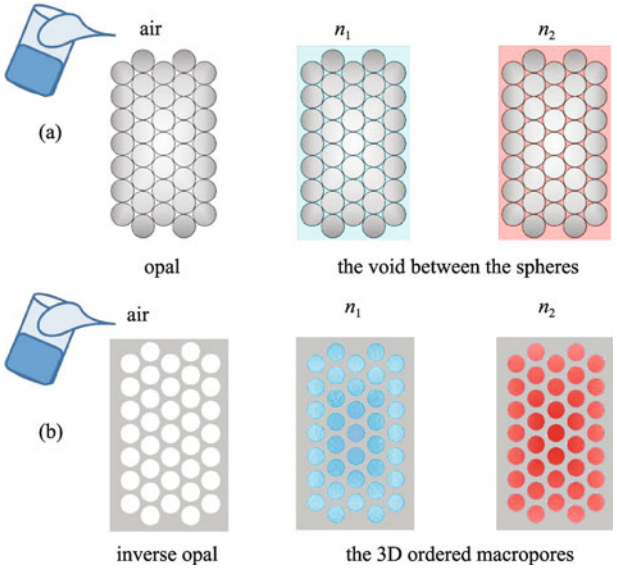

Figure 4 Schematic illustration of the opal/inverse opal films which are sensitive to different solutions. The opal/inverse opal film is infiltrated with the functional materials which assume different states according to the external situation.

[64]. As-prepared inverse opals showed excellent oil-sensing stability in cyclic sorption experiments, and suggested a promising and economical alternative to traditional oil-sensing materials.

Furthermore, various sensing materials have already been prepared by introducing functional materials into PCs, which can directly respond to external stimuli via optical signals, as shown in Figure 5. One strategy is to fabricate responsive PCs, comprised of liquid crystals (LCs) and inverse opal films, by infiltrating LCs into the voids in the PC structures [65–68]. Sato et al. have acquired a number of responsive PCs [66,69–71]. The refractive indices of the LCs varied with orientation, phase and temperature. When the LCs were in the nematic phase, the film was opaque because the light was scattered due to the nonuniform anisotropic refractive indices in the voids. On the other hand, when the LCs were converted to the isotropic phase, the film consisted of periodic refractive indices of LCs and an inverse opal frame work, and a stop band was observed in the spectrum. Therefore, environmental changes could lead to spectral shifts in the Bragg diffraction wavelength of these responsive PCs, which can play a role in sensors. In particular, the optical properties were drastically changed by thermal- or photo-induced isothermal phase transitions of the LCs, leading to thermally/photo-induced tunable structural color materials [72]. Another strategy based on a similar mechanism used dyes as a medium for changing the refractive indices [69,73].

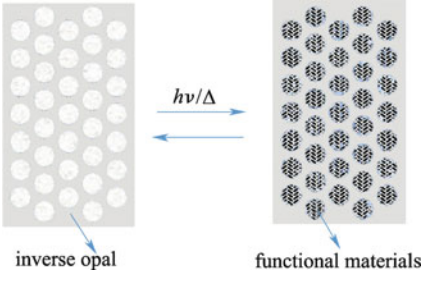

Figure 5 Schematic illustration of a functional inverse opal film responding to external stimuli. The inverse opal film is infiltrated with the functional materials which have different states according to the external situations. Therefore, the optical of the inverse opal can respond to the external stimuli.

PCs have been suggested as a new type of spectrum-encoding carrier, whose code is the characteristic reflection peak originated from the stop-band [74,75]. As the peak position is based on their periodical structure, the code is very stable, and the fluorescent background is low. These properties render PCs suitable for highly sensitive detection. Gu et al. have demonstrated some kind of PC beads as new label-free immunosensors [76–79]. The average refractive index is determined from the volume average of the dielectric constants of different compositions,

$$n_{\mathrm{eff}} = \sqrt{n_{\mathrm{silica}}^2 V_{\mathrm{silica}} + n_{\mathrm{protein}}^2 V_{\mathrm{protein}} + n_{\mathrm{water}}^2 V_{\mathrm{water}}} \quad (3)$$

where n_{silica}, n_{protein}, and n_{water} are the refractive indices of silica, protein and water, respectively. Fixed at their typical bulk values, $n_{\mathrm{silica}} = 1.47$, $n_{\mathrm{protein}} = 1.42$, and $n_{\mathrm{water}} = 1.33$. V_{silica}, V_{protein}, and V_{water} are the volume fractions of polystyrene, protein and water, respectively. Both of the probe immobilization and antigen binding would result in a change in the average refractive index of the beads. This change could be detected as a corresponding shift in the diffraction-peak position. The shift in the diffraction-peak position with protein binding can be used in quantitatively estimating the amount of bound antigen.

Above all, the stop bands of the PC, which was fabricated from functional materials or filled up with functional materials, can be tuned by environmental stimuli. Therefore, the PCs can play a role as optical sensors.

4 PCs-assisted high effective fluorescence sensors

Fluorescence has long been recognized as an important tool for probing biological structure and function. The development of optically active structures that can enhance fluorescent intensity has gained much attention as a means of detecting fluorescent-tagged analytes at low concentrations for applications in DNA expression analysis and protein diagnostic assays. PCs can act as proposal cavities for the light photons and the PC resonators can exhibit high Q-factors due to their minimal losses. Therefore, the strong interest in PBG materials has been attractive due to the PC optical devices, which can confine and control the propagation of light. Furthermore, as demonstrated above, the PCs can act as a new type of spectrum-encoding carrier. Therefore, the PCs can provide a proposal carrier for the detection system based on the fluorescence detection.

Cunningham et al. used PC surfaces as a means of enhancing the detection sensitivity and resolution for assays that use a fluorescent tag to quantify the concentration of an analyte protein molecule [81]. The PCs used in their works are nanostructures composed of a periodically modulated low refractive index plastic/SiO_2 surface structure that is coated with a high refractive index dielectric [81,82].

Among such resonant structures of one-dimensional and two-dimensional PC slabs, the guided-mode resonance filter occurs in the periodic dielectric nanostructures [83]. The near-fields at an absorption wavelength of a fluorescent species can

be greatly enhanced. When this effect is combined with the coherent scattering phenomenon from the PCs, the PCs-enhanced fluorescence can be obtained at the same time [84]. These two effects were combined to enhance the fluorescence from semiconductor quantum dots and to achieve an overall enhancement of 108 [85].

Using the colloidal crystal, i.e., the low-cost PC, our group developed an optical DNA detection system where the read-out can be enhanced using a PC [86], as shown in Figure 6. The system could achieve an ultrasensitivity as low as 13.5 femtomolar and a selectivity of single base pair mismatch-discrimination. The detection is based on fluorescence resonance energy transfer (FRET), which has widely been used in biosensor systems [87]. However, energy loss through wave guiding and diffusion always hampers the process. We infiltrated the sensory system solution into a colloidal crystal with a stop band at the frequency of the energy transfer. Due to the dielectric cavity effect and the local resonance mode of the PC, light in the same wavelength range cannot scatter out of the PC. Thus, the FRET efficiency and the optical signal are both drastically enhanced. The low-cost PC enhances the transfer and improves the detection sensitivity from picomolar to femtomolar scale. The approach is also applicable to other biosensors.

5 Conclusions and perspectives

In summary, a new class of tunable PCs for optical sensors has been described. These PCs hold great promise for design of affinity matrices that are capable of detecting environmental changes through simple monitoring the band gap peak position, using standard spectrophotometric techniques, or directly by the naked eyes. The key of optical sensors is to combine the functional materials and the ordered period structures. The periodic variety of the refractive index gives rise to unique brilliant colors, which can be tuned according to the environment deriving from the smart response of functional material to external stimuli. Therefore, they can be used as self-reporting sensors to measure various environmental changes such as pH, analytes, metal ions, humidity, and physical deformation. Moreover, they can play a role in a new type of label-free spectrum-encoding carrier. Simultaneously, they can remarkably enhance the detection based on fluorescence technique due to their capability of confining and controlling the propagation of light with minimal losses. This approach can greatly expand the PC application fields in chemical and biological sensors for highly specific and highly sensitive recognition. However, there are still a lot of challenges in practical applications. For example, for artificial opal and inverse opal structures, there are always some crystal defects and cracks that make the PC optical properties inequable and may result in detection error. The pseudogap can only inhibit the spontaneous emission in a certain direction. The PC with a full PBG and high ordered structure over a large area is our long-term goal. Above all, we believe that PCs will throw a new light on the study of novel optical sensors and high efficacious detection methods with the development of science and technology as well as the unremitting efforts to explore the unknown and increase knowledge of the PBG materials.

Yanlin SONG received his Ph.D. degree from the Department of Chemistry at Peking University in 1996. Between 1996 and 1998, he conducted research as a post-doctoral fellow in the Department of Chemistry at Tsinghua University. Working at Institute of Chemistry, Chinese Academy of Sciences (ICCAS) since 1998, he is now a Research Professor and Director of Laboratory of New Materials at ICCAS. His research interests include organic high-density data storage materials,

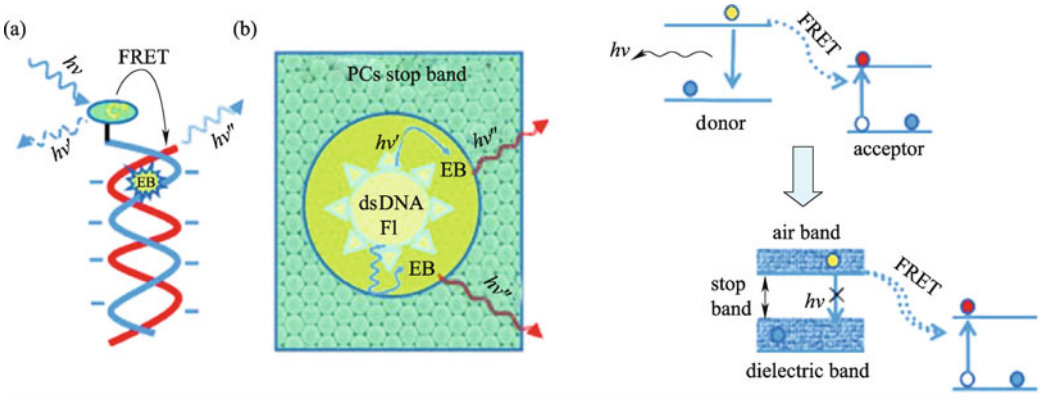

Figure 6 (a) Schematic illustration of DNA sequence detection based on a FRET mechanism. (b) Effect of the PC on FRET. [86]

manufacturing and applications of polymers photonic crystals, and nano-printing materials and technology. He has published more than 120 academic papers in scientific journals, and has been granted more than 30 patents. He was awarded the Second Prize of National Natural Science Award in 2005 and 2008 and the National Science Fund for Distinguished Young Scholars in 2006.

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