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Dual Photonic-Bandgap Optical Films towards Generation of Photonic Crystal-Derived 2-Dimensional Chemical Codes

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A chemical-oriented 2-Dimensional (2D) optical code was first time constructed by integrating bi-layer or bistriate-structure responsive photonic crystals (RPCs), which not only represents high information capacity in encoding processes, but offers a facile route towards high performance sensors along with both accurate analysis and anti-jamming performances.

Today, two-dimensional (2D) barcodes are extensively exploited as quick response codes for industrial uses, especially in e-business field. Inspired by the commercial 2D barcodes, we expect to design a chemical-oriented 2D optical code by integrating bilayer or bistriate-structure responsive photonic crystals (RPCs), which would offer chemicals with their own characteristic codes for the first time.

Up to now, RPCs with easy-to-read and self-reporting traits have aroused great interests due to their unique light manipulation and inhibition capabilities in areas ranging from displays, inks and paints, to various chemical/biological sensors. Because different molecules normally lead to diverse optical signals namely the photonic bandgaps (PBGs), the recognition of specific molecules can thus be realized. Typically, diverse 3-dimensional macroporous films with inverse opal structures were developed to distinguish various solvents based on the corresponding value of average refractive index (RI). To further increase the selectivity and sensitivity of RPCs, specific functional hydrogels had been introduced to detect target analytes. Moreover, a series of reliable RPC-based sensors were also put into practice via improving their chemical resistivity and physical rigidity. Despite great advance has been attained, most of previous approaches mainly focused on single signal monitor, leading to low information densities and difficulties in sensing under interference environment.

Herein, we first time demonstrate a 2D optical code containing bilayer or bistriate-structure RPCs towards chemical encoding and
instance, A

the bottom layer of the resulting 2D optical code film can be
via a template method (Fig. S1). As the reflex peak originating from
the top layer is sufficiently thin (Fig. S2), diverse optical devices were successfully established toward organic

solvent recognition, real-time glucose detection, and anti-

interference thermal sensing (Scheme 1c). Furthermore, we also
designed a kind of PS lattice bearing with hard-core/soft-shell
structures, allowing them to be easily coated on flexible substrates
including papers and plastics, and then producing a series of robust
flexible 2D optical codes with tunable PBG signals, which would
undoubtedly facilitate the resulting 2D optical codes to commercial
uses (Scheme 1d).

Herein, the bilayer-structure 2D optical codes were constructed
via a template method (Fig. S1). As the reflex peak originating from
the bottom layer of the resulting 2D optical code film can be
detected when the top layer is sufficiently thin (Fig. S2), diverse
optical code series with different dual PBG signals can thus be
achieved by tuning the colloidal template sizes (Fig. 1a). The typical
spectra codes are listed in Fig. 1b, where the peak of the spectra
code strings is denoted by alphabets, such as A, B and C, while the
followed number indicates the specific wavelength of PBG. For
instance, A_{410}+A_{410}+C_{510}+C_{510} indicate the optical code series with PBGs at ca. 410, 510, and 670 nm, derived from the colloidal templates with diameter of 266, 315, and 420 nm, respectively (Fig. S3). When the top and bottom sides of the bilayer-structure RPCs are the same, such as A_{410}+A_{410}+B_{510}+B_{510} and C_{670}+C_{670} only single reflex peak could be noticed (Fig. 1b). However, when the two layers are constructed from different colloidal templates, two distinctive reflex peaks are realized, which enables to translate more spectra code information into the 2D optical codes compared to the conventional single reflex RPC materials.

Using the bilayer-structure RPCs as the 2D optical code, for the
first time, we offered various organic solvents with their own characteristic spectra codes. Fig. 1c shows the specific spectra of the A_{410}+A_{410}+C_{510}+C_{510} typed code sequentially infused with the diverse solvents with increasing RI (Table S1). The shift wavelength (Δλ) and the maximum intensity of the reflex peak in the presence of different solvents change along with the increase of solvent RI (n_{solvent}) (Fig. S4). In particular, a linear correlation between Δλ and n_{solvent} is noted (Fig. 1d), which is in good agreement with the derived formula (See Supporting Information):

\[ Δλ = λ - λ_o = (2d / m)(1 - Φ) n_{silica} + (2d / m)n_{silica} - λ_o \]

where λ and λ_o denote the sensing and control reflex peak positions, respectively, d is the spacing between close-packed planes of voids, m is the order of Bragg diffraction, Φ is the solid fraction of the inverse RPC, and n_{silica} is the RI of the silica wall. Also, these 2D RPC codes show distinctive color changes during the encoding processes, varying from blue (the blank sample, C-1) to blue-green (methanol, C-2), green (ethanol, C-3), yellowish-green (hexane, C-4), yellow (tetrahydrofuran, C-5), bright blue(chloroform, C-6), and orange (carbon disulfide, C-7). This feature shows the possibility for encoding various chemical solvents with the dual-PBG optical code, and even judging by visual observation. Additionally, the cyclical encoding and decoding processes reveal that the optical codes of the homologous position almost remain consistent for more than nine cycles, demonstrating their reliability in durative practical use (Fig. 1e).

The dual PBG traits also endow the 2D optical code with advantages for real-time monitoring applications. As the left part of Fig. 1f shows, an in-situ glucose monitoring system, with synchronous optical signals from the control (bottom) and sensing (top) layers of the 2D optical code, is set up. The concentration changes of the glucose can thus be directly recognized based on the wavelength intervals (Fig. S5). More attractively, when the control layer of the 2D optical code is immersed by the standard glucose sample, the concentration deviation of the sensing glucose solution from standard state can thus be distinguished (the right part of Fig. 1f). In order to take an example, a series mass concentration, 5%, 35%, and 50% of glucose samples and a standard control sample with the glucose mass concentration of 35% were utilized for concretely implementing our scheme (Fig. 1g and Table S2). It can be seen that, when the concentration of the sensing glucose sample approaches to that of the standard sample, the 2D RPC code displays overlapped optical signals due to similar RI values (Case 1). However, when the concentration of the sensing sample has a considerable departure from the standard state, the peak separation behaviour happens (Case 2 and Case 3). Through analysis of their relative positions, we can facilely conclude the variation tendency, which eliminates the need for original state recording and greatly simplifies the analysis and judgement processes comparing to conventional single reflex RPCs. Although, when the sensing and standard samples have close concentration values, the broad sensing and control peaks tends to be merged, thus leading to the difficulty in telling the exact extent of concentration deviation, this feature is still applicable in a wide variety of situations. For example, the optimal conditions normally span a broad range in strains breeding, and regulation is necessary only when the situation get seriously far out of the standard state.
considering that the temperature range is suitable for living beings, and it may find potential applications in biological areas.

In addition, the construction of flexible 2D optical codes on various substrates (e.g., paper, flexible plastic film) was also conducted, which would undoubtedly facilitate their practical uses. As shown in Fig. 3a, to enhance the adhesion between the 2D optical code and flexible substrates including papers and plastics, monodispersed lattices with hard-core/soft-shell structures were first prepared by grafting the polystyrene (PS) seed microspheres with acrylic resins (Fig. S7). Fig. 3b shows the optical image of the as-obtained lattice film without obvious cracks, implying the improved connectivity between the resin-grafted lattices. The corresponding infrared image of core/shell latices is presented in Fig. 3c. Compared to the infrared image of PS spheres (Fig. 3d), an obviously improved intensity at 1,732 cm\(^{-1}\) was noted, indicating the existence of soft resin fragments (Fig. S8). Also, a decreased thermal stability was found after the grafted polymerization, which further confirmed the successful incorporation of soft acrylic resins (Fig. S9). These monodispersed lattices with hard-core/soft-shell
structures can be facilely assembled onto various substrates such as polyethylene terephthalate (PET) and paper within 5 min via hand print (Video S1), allowing large scale preparation of the flexible 2D optical codes (Fig. 3e). Besides, these 2D optical code films still kept highly ordered structures (Fig. S10) and presented bright structural colours. By tuning the colloid size, a series of optical code films with different structural colours ranging from red, green to blue were obtained (Fig. 3f). Also, these films showed superior stability under rinse of water (Fig. 3h and Video S2), and could be bent like folded screens (Fig. 3i and Video S3). Moreover, in virtue of the transparency of the RPC layer (Fig. S11), dual PBG signals could also be achieved (Fig. 3g) on various flexible substrates for the development of diverse encoded spectrum series (Fig. 3j). These traits would greatly extend the 2D optical codes to large-scale practical applications in areas containing coatings, bio-encoding, and displays.

In summary, we demonstrate an operable strategy for the construction of chemical-oriented 2D optical code containing bilayer or bistratate-structure RPCs, which extend photonic crystals to be a candidate of 2D code materials for chemical recognition for the first time. These 2D RPC codes successfully integrate dual reflex peak signals into a single material, and thus they not only represent more information capacity in encoding process, but offer a facile route towards high precise and anti-jamming detection. Perhaps more interestingly, we have taken the example for creating a series of robust flexible film materials with 2D optical codes on a large scale by using as-prepared hard-core/soft-shell lattices. More practical applications of 2D RPC code materials, such as chemical sensing, anti-counterfeiting and flexible displays, will continue.

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Notes and references


