Liquid crystals, photonic crystals, metamaterials, and transformation optics

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Recent advances of modern optics have been made possible with the development of unique materials, most notably liquid crystals (LCs), photonic crystals (PCs), and metamaterials (MMs). LCs have already completed a revolution in the way we present information nowadays, enabling an entire industry of flat panel liquid crystal displays (LCDs). PCs (1) and MMs (2) are further behind in terms of broad commercialization, but the change they produce in our understanding of how matter can control light is no less revolutionary, fueling dreams that only recently were science fiction, such as subwavelength imaging and focusing, invisibility cloaking, black hole-like light trapping, and more. PCs and MMs are formed by building units of a size s intermediate between the molecular scale m = (1–3) nm and the optical wavelength λ and cannot be simply synthesized as small organic molecules that form LCs. Design, manufacturing, and control of properties of PCs and MMs at the scale $m < s \leq \lambda$ is the major challenge. There are a variety of ways by which the LCs can help in the development of PCs and MMs; one of the latest advances is presented in PNAS by Ravnik et al. (3).

A PC is a periodic structure that modulates the refractive index at the scale $s \approx \lambda$. The structure is designed to form "photonic bandgaps" (i.e., a range of wave vectors for which light cannot propagate) (1). To provide the full bandgap in all directions, the PC should be 3D, which represents a challenge. In addition, the PC often needs to have structural defects, such as points (to trap light) or dislocations (to guide light). One of the approaches is self-assembly of small particles, typically spheres, from water solutions into 3D colloidal crystals. In the MM, an elementary "metaatom" is an artificial combination of dielectric and metal elements, such as split-ring resonators or paired metal nanorods, of the typical size s = (10–100) nm (2). Because $s << \lambda$, the closely packed metaatoms still form a "material" that is continuous at the scale λ, and thus can be characterized by an effective refractive index n. Combining a noble metal with a large negative real part of the dielectric permittivity and a regular dielectric of positive permittivity, one can achieve practically any value of n, including $n < 0$ (2). The MMs are pro-
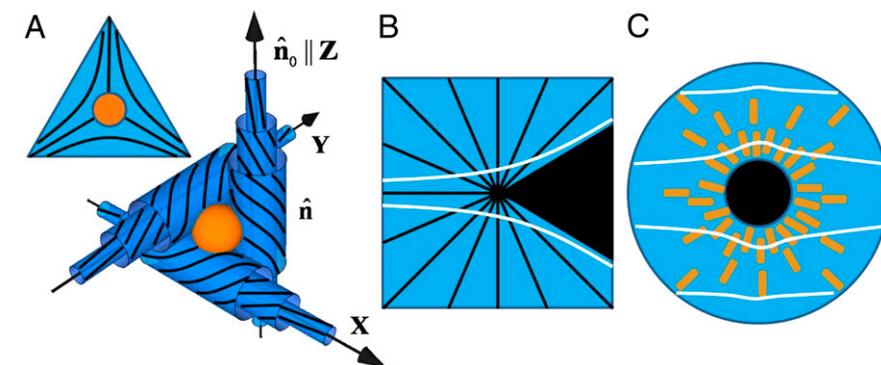

Fig. 1. (A) Blue phase formed by double-twisted cylinders, serving as a template for colloidal spheres trapped at the disclination cores (*Inset*). (B) Radial configuration of the director bends the extraordinary ray away from the disclination, leaving a segment unilluminated. (C) Optical cloak with radially oriented metal nanorods of variable concentration bends the polarized light around the central circle, in which one can hide objects from an external observer.

duced mostly by top-down techniques, such as electron beam lithography. Because s is submicron, a large MM is hard to manufacture. Another challenge is to make the MM reconfigurable/switchable. A still higher level of complexity is required to produce MMs and PCs for transformation optics applications, in which the density, shape, and arrangements of s-elements vary from point to point over the scales much larger than λ to produce a variable n (4).

In LCs, the small rod-like molecules are free to move around as in a regular fluid, but they remain locally parallel to each other, thus establishing an orientational order along a nonpolar axis $\hat{\mathbf{n}} = -\hat{\mathbf{n}}$ called the director. In the simplest case of the so-called "nematic" LC, there is no other type of long-range order and $\hat{\mathbf{n}}$ is the optic axis. Because of the anisotropy of dielectric permittivity at low and high (optical) frequencies, the nematic LCs are widely used as tunable component infiltrating PCs (5, 6) and MMs (7). The degree and direction of the orientational order of the nematic filler can be controlled by a variety of means (temperature, pressure, and electromagnetic fields), thus allowing one to tune the PC and MM hosts dynamically.

In addition to the simple nematic structure, the rich world of LCs offers phases with spatial modulation of density and molecular orientation, periodic in one (smectics and cholesterics), two (columnar phases), or three (blue and cubic phases) dimensions. The period is often in the

range of 10 nm to 1 μm relevant to PCs and MMs. In particular, the LC blue phases with a period $p \sim 10^2$ nm represent a self-assembled 3D photonic bandgap material by themselves (8, 9).

The blue phases are formed by chiral molecules. Chirality forces the neighboring LC molecules to be slightly twisted with respect to each other. Let $\hat{\mathbf{n}}_0$ be a local director (Fig. 1A). Moving away from $\hat{\mathbf{n}}_0$ along any radial direction perpendicular to $\hat{\mathbf{n}}_0$, one observes a helicoidal twist of chiral molecules. Because the twist persists along two coordinate axes perpendicular to $\hat{\mathbf{n}}_0$, it is called a "double twist." As the distance from the axis $\hat{\mathbf{n}}_0$ increases, the double twist gradually becomes a unidirectional twist, which is not as efficient as the double twist in packing the chiral LC molecules. To avoid the unidirectional twist, the structure breaks down into many double-twisted cylinders of a finite diameter $\sim p$, forming a frustrated phase. Because the chiral forces are relatively weak compared with the forces responsible for parallel orientation of the LC molecules, one finds $p >> m$, a fortunate property to combine with PCs and MMs. To tile space continuously with the double-twisted elements, the blue phase develops a network of linear defects and disclinations. The disclinations are

defects of orientational order, around which $\hat{\mathbf{n}}$ realigns by π (Fig. 1*A*, *Inset*). At the core of disclinations, the director gradients are so strong that the material is partially melted. Ravnik et al. (3) present extensive computer modeling to demonstrate that the blue phases serve as an excellent 3D template for colloidal spheres. The particles reside in the structural traps created by the disclinations lattice and produce colloidal crystals bound by forces one to two orders of magnitude stronger than those formed from water dispersions. The reason is the elastic nature of the LC: A sphere of radius $R \approx 100$ nm that replaces a distorted region reduces the elastic energy of the LC by approximately $KR \sim k_B T(R/m) \sim 10^2 k_B T$, where $K \sim k_B T/m$ is the typical LC elastic constant.

The approach proposed by Ravnik et al. (3) to simulate the complex colloidal-LC composites opens the door for studies of the templating ability of many other LC structures, such as recently discovered LC phases of "bent-core" molecules (e.g., ref. 10). In addition to the disclination, other defects, such as focal conic domains in smectic LCs (11) or even the LC-air interface (12), can trap colloids and produce periodic arrays. Particles other than spheres, such as metallic wires (13) and more complex shapes (14), would be of interest to explore. Once created, the LC structure can be polymerized, thus fixing the desired pattern of materials' properties.

In addition to serving in LCDs and as tunable fillers and templates for PCs and MMs, LCs have a potential in transformation optics. Transformation optics uses the equivalence of coordinate transformation and renormalization of permittivity and permeability to design a medium with gradiently distributed properties that could send light through curved predetermined trajectories. The LCs provide a natural fit for the concept of transformation optics, as their tensor properties can be easily tailored to vary in space and time. In 1919, Grandjean considered light propagation around the LC disclination with a radial $\hat{\mathbf{n}}$ (15, 16).

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The rays were shown to bend away from the disclination core and leave a segment of an opening angle $2\pi(1 - n_o/n_e)$ unilluminated, where n_o and n_e are the ordinary and extraordinary refractive indices, respectively (Fig. 1*B*). The structure is reminiscent of the invisibility cloak proposed by Shalaev's group (17), in which an isotropic dielectric cylindrical shell is pierced with metal nanorods (Fig. 1*C*). The concentration of nanorods is high at the inner surface of the shell and low at the outer boundary, so that the refractive index n_e changes from 0 to 1 between the two surfaces. The rays now bend around the inner surface, never entering the interior space, which means that an object placed there would be invisible to an external observer. The very possibility of LC orientational order in dispersions of metal nanorods has already been demonstrated (e.g., ref. 18), including the case of spatially varying the concentration of radially aligned metal nanorods (19). By creating, for example, a nematic LC with aligned metal elements, one can control not only the direction of optic axis but the absolute value and the sign of the refractive indices, determined by the filling fraction of the metal. The problem of absorption losses can be addressed by adding gain materials, such as fluorescent dyes, that are easy to dissolve in an LC. Recent works with solid crystals demonstrate that even standard birefringence is sufficient to produce spectacular effects, such as optical cloaking of a macroscopic object (20, 21). The advantage of LCs is that their optical anisotropy is supplemented with the flexibility to design practically any configuration of the optic axis and then change it, for example, with the electric field, as in LCDs. A problem of light scattering at director fluctuations in LCs can be mitigated by using smectic rather than nematic LCs and by limiting the spatial extent of the LC elements. There is no doubt that future research will produce unique hybrid materials for optical applications with LC elements.

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