Polarization dependent Bragg diffraction and electro-optic switching of three-dimensional assemblies of nematic liquid crystal droplets

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We report the fabrication of three-dimensional lattices of bipolar nematic liquid crystal droplets. The electro-optic properties of these materials consist of transitions between opaque, Bragg diffracting, and transparent states. These occur continuously at moderate electric (E) fields through bipolar axis rotation of the nematic droplets. An E field applied normal to the hexagonally close packed planes results in a Bragg diffraction pattern that is polarization independent. Application of in-plane fields allows switching between diffracting and transmitting states that depends on the polarization of the incident light. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2187430]

Active control over both the direction and the intensity of light is an important goal of photonic devices. One class of electro-optic devices that can achieve this consists of periodic organizations of liquid crystal (LC) that modulate the direction and intensity of the incident light through the use of Bragg diffraction. Such photonic devices have potential utility for information display or beam steering applications. The requisite ordering of the LC regions is commonly achieved through the use of holographic polymer dispersed liquid crystals (HPDLCs); these are formed by selective phase separation and polymerization of a LC/polymer mixture in the presence of a periodic pattern formed by interfering high intensity coherent light beams. While this is a very flexible method of producing high fidelity holographic structures, the resultant devices require very high switching fields because of the intrinsic coupling between the LC and the polymer matrix.[1,2] An alternate method for producing these devices relies on the use of three-dimensionally ordered templates formed from colloidal crystals; the LC is infiltrated into the void space that remains when the interstices of the colloidal crystal are polymerized and the colloids removed.[3,4] These devices also suffer from a high switching field, as well as a complex fabrication, limiting their applicability. Thus, widespread use of this class of photonic device has been severely hampered, and demands simpler fabrication with more highly controlled switching that is achieved at lower applied fields.

In this letter, we report a strategy for the formation of photonic devices based on switching the Bragg diffraction from droplets of nematic LC that are self-assembled into three-dimensional ordered arrays. We use highly uniform nematic LC droplets to facilitate self-assembly of high fidelity structures and to achieve optical switching at low applied fields. We demonstrate two switching modalities with these photonic devices for normally incident light: application of a switching field in the direction of the incident light provides polarization independent switching from opaque to diffracting to transparent. Alternatively, application of an in-plane switching field provides polarization sensitive Bragg switching. These devices provide a flexible and simple-to-implement way of creating photonic devices based on Bragg diffraction.

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We prepare micrometer sized droplets of nematic LC, pentylcyanobiphenyl (5CB), in an aqueous polymer solution, as described in Ref. 5. We extrude LC through a narrow capillary into a co-flowing fluid. Droplets are formed when the drag force exerted on the growing droplet by the flowing continuous fluid exceeds the surface tension force that holds the droplet to the capillary tip; because snap-off occurs when the forces are precisely balanced, highly uniform droplets are produced, with a polydispersity in radius below 3% of the mean.[5] The droplets are stabilized against coalescence through the addition of 1 wt % polyvinyl alcohol (PVA); this also provides strong planar anchoring of the LC molecules at the surface.[6] The resultant droplets have a bipolar structure: the nematic director field, **n**, which signifies the average orientation of the LC molecules, is everywhere parallel to the droplet surface and is characterized by the presence of two point disclinations, called boojums, where the director field rotates through 2π around a singular point. An example of a single bipolar nematic droplet, of diameter $d=30\ \mu$m, viewed through crossed polarizers is shown in Fig. 1(a). The highly uniform size of these droplets allows us to self-assemble them into ordered colloidal crystals. This is accomplished through sedimentation into a hexagonal well with a typical cross sectional area of 5 mm^2, defined lithographically in a layer of photoresist on a glass slide coated with indium-tin-oxide (ITO). The droplets are initially disordered, as shown in Fig. 1(b), but the hexagonal symmetry facilitates self-assembly into hexagonally close-packed (HCP) layers that randomly stack as the sedimentation proceeds, as shown in Fig. 1(c). The resultant structure is random HCP (RHCP), similar to that formed by the crystallization of hard sphere colloids.[7] The depth of the well is typically 450 μm, so the resultant crystals have$\sim$15 layers. The continuous phase of water is evaporated and, as a result, the drops adopt the faceted polyhedral shape while remaining encapsulated by PVA walls [Fig. 1(d)]. This fabrication method avoids the usual polymerization induced phase separation employed in fabricating polymer dispersed liquid crystals (PDLCs) (Ref. 8) and HPDLCs, (Ref. 2) and prevents deformation of the drops in a direction within the HCP layers, as reported for two-dimensional LC droplet based structures.[9] To apply a normal electric field, the cell is sealed on top with a second ITO coated glass slide. To apply in-plane electric fields a preliminary patterning step is performed to remove the ITO from the

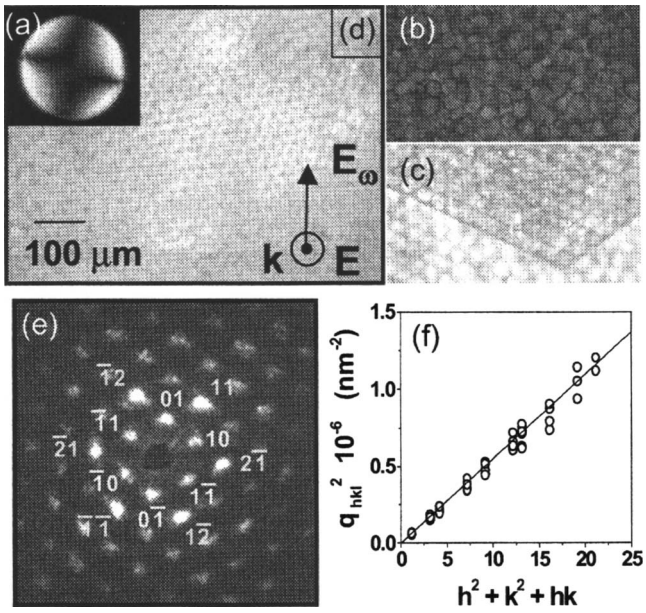

FIG. 1. (a) Photomicrograph of a bipolar nematic drop between crossed polarizers. (b),(c) Bright field images of emulsion droplets after adding them inside the well and after sedimentation of the first layer. In (c), some of the well edges can be identified. The typical final state after water evaporation is shown in (d). The **E** field is perpendicular to the hexagonal close packed planes and parallel to the incident light, which has a wave vector $\boldsymbol{k}$ and polarization direction $\boldsymbol{E}_\omega$. (e) Bragg diffraction pattern at $E=0.32$ V/μm. (f) Linear dependence of q_{hkl}^2 with (h^2+k^2+hk) indicating the hexagonal symmetry of the reciprocal lattice. From the slope $a=(31.0\pm1.5)$ μm.

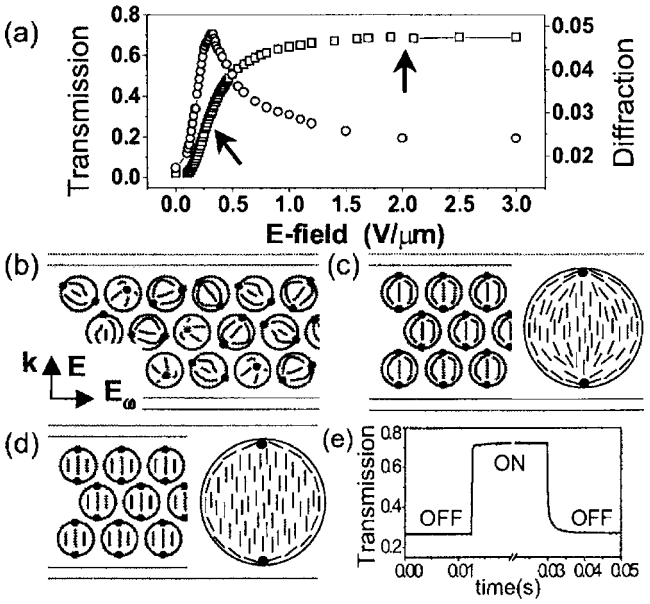

FIG. 2. (a) Transmitted (□) and first order diffraction peak (○) intensities of the three-dimensional crystal as a function of electric field. Arrows indicate the E fields for switching between Bragg diffraction and transparent states. Schematics of the switching mechanism: (b) $E=0$, the polar axis of every drop is randomly oriented and the structure is opaque; (c) $E=0.32$ V/μm, the polar axis of every drop is aligned with E and the system Bragg diffracts; (d) $E>2.0$ V/μm, index matching between the drops and the matrix renders the structure transparent. In (b) and (c) a cross section of the bipolar drop illustrates the microscopic states. (e) Response and relaxation dynamics of the transmitted beam for switching between $E_{\text{off}}=0.32$ V/μm and $E_{\text{on}}=2.0$ V/μm.

bottom of the well and to form in-plane electrodes outside it; in this case the top ITO is also omitted. Switching is accomplished by applying an ac voltage at 1 kHz across the electrodes.

We measure the optical properties of the device using a He-Ne laser incident normal to the film with a wavelength $\lambda=632.8$ nm in vacuum. In the absence of an applied field, the sample is opaque and no light is transmitted. On application of an E field parallel to the incident beam, the sample exhibits pronounced Bragg diffraction, as shown in Fig. 1(e), which is an image of the transmitted light projected on a screen and captured with a charge-coupled device (CCD) camera. The high degree of order in the sample is apparent by the 59 distinct peaks visible. The peaks in the Bragg diffraction pattern can be indexed to those expected for a light incident normal to the surface of a RHCP structure. Because the structure possesses two-dimensional order in three dimensions, the Bragg peaks in the reciprocal lattice are in fact Bragg rods. As a result, incident light of any wavelength satisfies the Bragg criterion and exhibits a sixfold symmetric diffraction pattern. We index the peaks using Miller indices (h,k); the z component of the scattering vector l equals 0, since for the light wavelength of our laser, the radius of the Ewald sphere $R=2\pi/\lambda\sim15$ μm^{-1} is about 100 times larger than the characteristic distances of the reciprocal lattice $2\pi/d\sim0.21$ μm^{-1}. The $(0,1)$ family of rods has lower intensity than the $(1,1)$ family; this occurs because the intensity distribution along these rods depends on the stacking order: the sum over the average phase factors modulates the layer form factor, decreasing the diffracted intensity. The Bragg condition for RHCP occurs for $q^2=16\pi^2/(3a^2)(h^2+k^2+hk)$, with $l=0$. A plot of q^2 vs (h^2+k^2+hk) results in a straight line that extends through the origin, as shown in Fig. 1(f). From the measured slope, we determine $a=(31.0\pm1.5)$ μm, in good agreement with the size of the droplets as determined by optical microscopy.

The transmitted intensity of the undiffracted beam and a single Bragg diffraction spot are plotted as a function of the applied field in Fig. 2(a). The intensity of a Bragg spot rises rapidly as the field is increased, reaching a maximum at $E=0.32$ V/μm. As E is increased further, the diffracted intensity decreases. Simultaneously the intensity of the directly transmitted beam increases, saturating at a maximum for fields above roughly 2.0 V/μm.

This electro-optic behavior is richer than the usual opaque-transparent and diffracting-transparent switching of PDLCs (Ref. 8) and HPDLCs.[2] Its origin is schematically depicted in Figs. 2(b)–2(d). In the absence of a field, there is no preferred orientation for the bipolar axis of the droplets; instead they are randomly oriented as depicted in Fig. 2(b), strongly scattering the incident light and making the film opaque. Application of a field in the direction of the incident light aligns the bipolar axes of all the drops parallel to the applied field. This decreases the difference between the effective index of refraction of the interior of the drops and that of the polymer matrix; moreover, all drops now have the same effective index of refraction. This results in the strong Bragg scattering. Since only rotation of the bipolar axes of the drops is needed, switching is achieved at a low applied field. As E is increased further, the field induced alignment of the LC increases causing an almost complete alignment of the director field with the applied field, as depicted in Fig. 2(d). This eliminates any remaining index of refraction difference between the droplets and the surrounding matrix, reducing the scattering and eliminating the Bragg peaks while

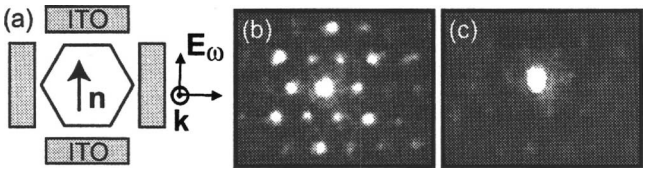

FIG. 3. (a) Geometry of the in-plane *E*-field experiment. Light is incident perpendicular to the hexagonal close-packed planes. The in-plane *E* field aligns the director field **n**. The light polarized parallel to **n** is diffracted (b) while that polarized perpendicular to **n** is transmitted (c).

increasing the transmitted intensity. This switching modality is independent of the polarization of the incident light.

The switching times between each of the three optic states differ significantly. Switching between the Bragg diffracting state and the transmitting state requires very short times. The on time is driven by the electric field and equals $\tau=0.5$ ms for switching between 0.32 and 2.0 V/μm [Fig. 2(e)]. The off time is driven by the restoring force provided by the anchoring energy. Since only a small rotation of some of the LC molecules is required, this time is only $\tau=2.1$ ms; it is lower than the times typically reported for PDLCs (Ref. 8) despite the fact that our drop size is at least an order of magnitude larger. By contrast, the off time for switching between transparent and opaque states is extremely long, $\tau_{\text{off}} \sim 3$ s, because there is very little elastic restoring forces to bring the bipolar axis back to its initial configuration.

A second switching modality uses the in-plane *E* field to align the director field of all of the droplets in a single direction normal to that of the incident light, as depicted schematically in Fig. 3(a). The result is a pronounced Bragg diffraction pattern for light polarized parallel to the director field and transmission for light polarized perpendicular to it, as shown by the CCD camera images in Figs. 3(b) and 3(c). Switching between the diffracting and transparent states is achieved by rotating the polarization direction of the incident light. Alternatively, the *E*-field direction could be switched with a second pair of electrodes; this would switch the structure in very short times. This geometry also possesses the completely off opaque state in the absence of any applied field.

The utility of photonic switches described here arises from the simplicity of their assembly. The use of highly monodisperse LC emulsion drops facilitates self-assembly of ordered arrays, making Bragg switching easily achievable. This self-assembly could be further improved by using templated surfaces to produce more precise ordering leading to crystalline three-dimensional structures. Such devices will have far more sensitivity to incident wave vectors in order to match the Bragg diffraction criterion. However, the diffraction pattern will be a series of points, rather than rods in reciprocal space. As a result, the diffraction efficiency will be even higher, leading to even greater photonic control.

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