PHYSICAL REVIEW E **78**, 020701(R) (2008)

Photochemical switching between colloidal photonic crystals at the nematic-air interface

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(Received 19 May 2008; published 22 August 2008)

A direct observation of the photochemical switching between colloidal crystals with different lattice constants in a liquid-crystal (LC) emulsion is reported. Glycerol droplets introduced in a nematic liquid crystal form two-dimensional hexagonal colloidal crystal at the nematic-air interface with a lattice constant depending on the surface tension σ_{LCA}. We dope an azobenzene derivative into the LC emulsion to modulate the colloidal structures by using *cis-trans* photoisomerization of the doped dye. The photoisomerization changes σ_{LCA} and the lattice constant of colloidal crystals with a relaxation time $T \sim 10$ s. A simple theoretical description, which qualitatively agrees with experimental results, has been proposed. Possible applications in infrared range photonic crystals are discussed. The number of different kinds of dyes N set the number of different possible photonic crystals as 2^N, which may be transformed one into another by corresponding $2N$ light beams inducing *cis-trans* photoisomerization of the doped dyes.

DOI: 10.1103/PhysRevE.78.020701 PACS number(s): 42.70.Df, 42.70.Gi, 61.30.Hn

Photonic crystals (PCs) are dielectric structures which consist of periodically modulated substances with different refractive indices. Electomagnetic waves inside them have structure of photonic bands with possible stop bands (band gaps) for definite frequencies [1]. Fundamentally optics of PCs has two distinctive unique features: (1) the localization and trapping of light [2] and (2) the complete inhibition of spontaneous emission over a broad frequency range [3–5]. Both three-dimensional (3D) and two-dimensional (2D) PCs have a lot of possible applications in telecommunications, especially in the range of visible and infrared frequencies. The most recent trends in this field are connected with active PCs which have tunable or switchable parts to change the optical properties of the PCs continuously and reversibly [6]. This gives rise to tunable optical waveguides, splitters, filters, and tunable field-sensitive polarizers [7]. The tuning or switching of PCs has been proposed or achieved by producing structural changes, by the incorporation of a ferromagnetic material, by varying the density of the plasma of free electrons in a semiconductor constituent, by taking advantage of optical nonlinearities caused by intense laser illumination, and by infilling the PC with a liquid crystal (LC) [6]. Utilization of liquid crystals to achieve tunable properties of PCs was first suggested in [8] where an inverse opal PC infiltrated with nematic LC was shown to have the complete electro-optical tunability of a 3D photonic band gap (PBG). Later, a 2D PC composed of square-lattice Si dielectric cylinders surrounded by LC was considered [7] as well as an inverted problem of band structure for a square lattice of LC cylinders in Si [6]. It was found that external electric field $\mathbf{E}$ which orientates LC may be efficient to tune PBG to center frequency ratios $\Delta w/w_0$. However, all these methods remain having a center frequency w_0 almost the same as they do not change the initial lattice constant of the PC. We propose a method to change it with the help of ultraviolet (UV) light and to switch between different colloidal PCs in LC.

LC emulsions have been given considerable attention during the last few years [9–18]. Elastic interactions between droplets immersed into LC lead to nontrivial behavior with the formation of a variety of ordered structures. So far, linear chains of small water droplets in an aligned liquid crystal in large nematic drops [19,21] and highly ordered arrays of oil droplet chains in a nematic host [9–12] have been observed. As well, a two-dimensional hexagonal lattice of glycerol droplets at the surface of a nematic cell with hybrid boundary conditions [13–15] has been obtained. In this paper, we prepared a LC emulsion containing a small amount of an azobenzene compound according to [14]. As a host liquid crystal; a room temperature nematic liquid crystal (4-cyano-4′-phentibiphenyl) doped with an amphiphilic azobenzene derivative [4-octyl-4′-(3-carboxypropyloxy) azobenzene], $\lambda_{max}=350$ nm, has been employed.

Uniformly dispersed glycerol droplets with the typical diameter of 3 μm appeared at the surface of the liquid crystal, see Fig. 1(a).

Then, the LC emulsion was irradiated at 30 °C with ultraviolet (UV, $\lambda=365$ nm, 50 mW/cm^2) light that preferentially induces the *trans*-to-*cis* isomerization of the dye. We could observe condensation of the droplets in the irradiated area as shown in Fig. 1(b). The photochemical condensation was completed at about 300 s. During this process, an interdroplet distance (lattice constant) was reduced from $l_{trans}=6.1$ μm to $l_{cis}=3.7$ μm. Irradiation of spatially-modulated light by using photomasks enables one to fabricate patterned colloidal crystals [15], consisting of different concentrations of droplets (Fig. 2).

These patterns could be fabricated within a few minutes at room temperature. When the irradiation of the light was terminated, the structure relaxed to the initial state. Typical relaxation time of the diffusion is of the order of hours and is presumably associated with the thermal *cis*-to-*trans* isomerization.

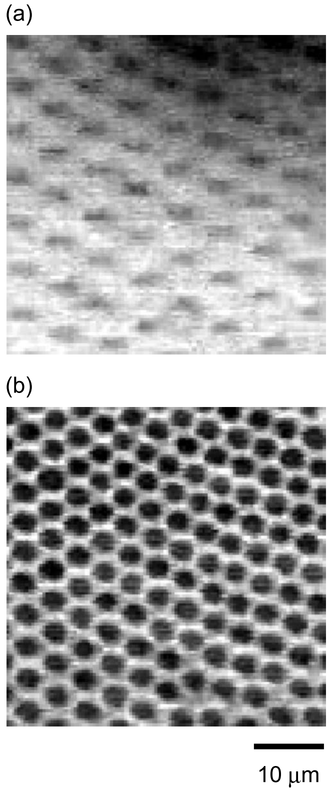

FIG. 1. Photochemical condensation of glycerol droplets in the LC emulsion (a) before and (b) after photoirradiation. A diameter of droplets is approximately 3 μm. Irradiation of ultraviolet ($\lambda=365$ nm, 50 mW/cm^2) light was performed at 30 °C where the LC exhibits a nematic phase.

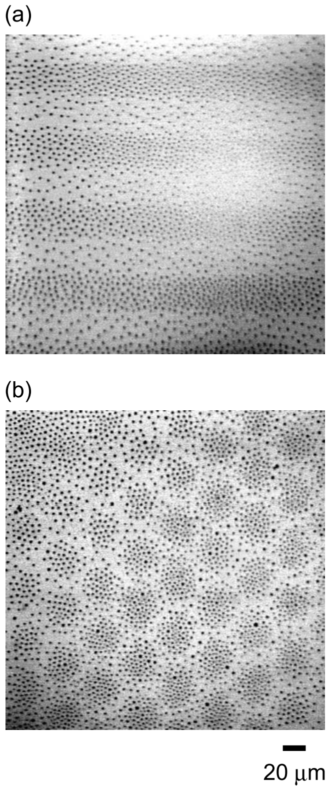

FIG. 2. Photochemical fabrication of patterned colloidal crystals: (a) linear grating and (b) hexagonal structure. Photoirradiation was performed at 30 °C.

Irradiation of the close-packed crystal with visible ($\lambda=435$ nm) light causes rapid *cis*-to-*trans* isomerization. This process induces nearly instant pulling of droplets out of the irradiated region. The alternation of both processes opens the way to modulate the lattice constants by irradiation with UV (50 mW/cm^2) or visible (100 mW/cm^2) light as shown in Fig. 3.

Below, a theoretical description for the dynamics of such photochemical switching between crystal structures in the liquid crystal emulsions is suggested. As a result of using fluorescence confocal polarizing microscopy (FCPM) [14] glycerol particles are found to be located at the surface of the nematic liquid crystal. In our case there are four contributions [16] in the energy of spherical droplets of radius R_0 which is positioned on the depth h from the surface of the LC in the isotropic phase, namely, the energy of the glycerol-air interface $U_{GA}=\sigma_{GA}2\pi R_0^2(1-\frac{h}{R_0})$, the energy of the glycerol-LC interface $U_{GLC}=\sigma_{GLC}2\pi R_0^2(1-\frac{h}{R_0})$, the energy of the LC-air interface $U_{LCA}=-\sigma_{LCA}\pi R_0^2(1-\frac{h^2}{R_0^2})$, and an additional part which describes the change of gravitation energy $U_g=-\Delta mg(R_0-h)$. The minimum of the total surface energy $U_{is}=U_{GA}+U_{GLC}+U_{LCA}+U_g$ brings the equilibrium depth of the particle $\frac{h}{R_0}=\frac{\sigma_{GA}-\sigma_{GLC}}{\sigma_{LCA}}-\frac{\Delta mg}{\sigma_{LCA}R_0}$. The gravitational energy is much less than the surface energy for particles of micron size: $\rho\frac{4\pi}{3}R_0^3g\sim10^{-14}N$ with the difference of densities $\Delta\rho=\rho_G-\rho_{LC}\approx260$ kg/m^3 is smaller than the surface energy $\sigma_{LCA}R_0\sim10^{-8}N$. Neglecting gravitation energy and using experimental values [15,20] for the surface tension $\sigma_{LCA}=3.9\times10^{-2}$ J/m^2 and $\sigma_{GLC}=1.9\times10^{-2}$ J/m^2, $\sigma_{GA}=5.5\times10^{-2}$ J/m^2, the equilibrium depth $h=0,89R_{0.}$ was obtained, which is in rather good agreement with the experimental results of [14]. This means that some part of the glycerol droplet is not completely immersed into the liquid crystal.

After cooling of the sample (Petri dish with a layer of the glycerol on the bottom and the nematic layer placed over the glycerol) from the temperature of 50 °C at which the liquid crystal is in the isotropic phase to temperature ($T_{is\text{-}nem}=35$ °C), the glycerol droplets appear. When the temperature is decreased below the $T_{is\text{-}nem}$ and the liquid crystal turns into a nematic phase, additional anchoring appears on the surface of the glycerol droplets. The anchoring energy gives rise to the additional buoyancy vertical elastic force which acts on the particle. To estimate the order of magnitude for this force the result [14] is used. This force can be expressed as

$$f_{el}=\frac{\partial}{\partial z}W_{anch}(z)\sim\frac{\partial}{\partial z}\oint_{\Omega(z)}W(\mathbf{n}\nu)^2ds, \qquad (1)$$

where $W_{anch}(z)$ is the anchoring energy of the particle and $\Omega(z)$ is part of the droplet surface within the liquid crystal. The order of the force is $f_{el}\sim4\pi WR\sim10^{-10}N$ for anchoring energy $W=10^{-5}$ J/m^2. This force is much greater than the standard Δmg buoyancy force. This expelling force deviates the air-nematic interface from a flat horizontal plane and induces the capillary attraction between particles. Then, the

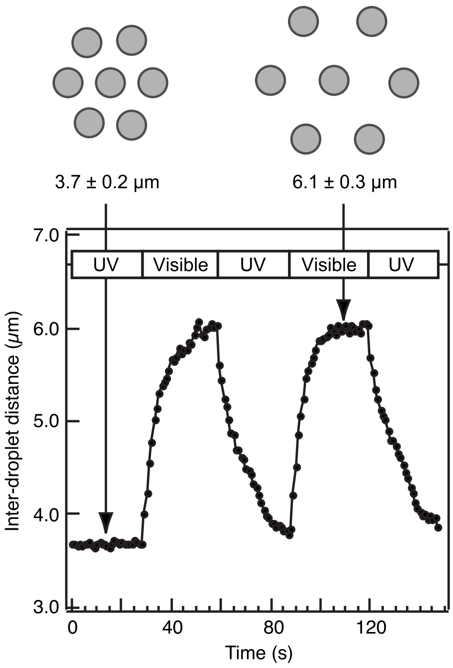

FIG. 3. Photonic manipulation of the lattice constants under the illumination of UV (λ=365 nm, 50 mW/cm^2) or visible (λ=435 nm, 100 mW/cm^2) light at 30 °C.

energy of elastic-capillary interaction between two particles caused by the expelling force f_{el} can be written in the form [14]

$$U_{elc} = \frac{f_{el}^2}{2\pi\sigma_{LCA}} \ln\left(\frac{r}{\Lambda}\right), \tag{2}$$

where $\Lambda = \sqrt{\sigma_{LCA/g\rho_{LC}}} \sim 2$ mm is the capillary length. In order to understand the behavior of particles introduced in the LC, it is also necessary to take into account their interactions through bulk deformation of the director elastic field. As it has been shown [21–23], a foreign particle introduced into the liquid crystal causes a distortion that ranges much longer than the size of the particle and thus provides a way for them to effectively interact elastically with each other. In the paper [23], it has been shown that the type of the far-field bulk interaction between particles immersed into a nematic host is determined by the local symmetry around the particle. If the director field around the particle is not symmetrical in one plane, an elastic dipole moment perpendicular to this plane arises and yields dipole-dipole interaction. Effective elastic dipole moment $\mathbf{p} = (0, 0, \alpha_z R^2)$, which is perpendicular to the interface [14,21], brings dipole repulsion between particles,

$$U_{elb} = K\frac{\alpha_z^2 R^4}{r^3}, \tag{3}$$

where K is the Frank elastic constant in the one constant approximation and α_z is a constant which takes into account that the droplets are not completely immersed into the LC. The sum of both elastic-capillary attractive and bulk repulsive parts $U = U_{elc} + U_{elb}$ has a minimum at

$$l_{eq} = \gamma\left(\frac{\sigma_{LCA} K}{W^2} R^2\right)^{1/3}, \tag{4}$$

where γ is a constant and l_{eq} is the lattice constant of the colloidal photonic crystal. The photoirradiation induces the isomerization *trans* to *cis* of the dye molecules and changes the anchoring W on the surface of droplets, surface tension σ_{LCA}, and elastic constant K. Corresponding values δW, $\delta K \propto c_{cis} S^2$, where c_{cis} is the concentration of *cis* isomers and S is the scalar order parameter [24], while $\delta\sigma_{LCA} \propto c_{cis} \gg \delta W$. So the contribution of the isotropic surface tension $\delta\sigma_{LCA}$ is the dominant. The polarity of *cis*-isomers is much greater than that of the *trans*-isomers, which results in a decrease of the surface tension by irradiation with UV light [25,26]. If we dissolve more than one kind of dye (N different kinds of dyes) it will set the total surface tension of the LC air as $\sigma_{LCA,J} = \Sigma_i \sigma_i^\mu c_i^\mu$, where $\mu = (trans, cis)$, i enumerates different dyes, and σ_i^μ, c_i^μ are the corresponding surface tensions and concentrations of dyes in different states. It is obvious that the total number of different combinations for $\sigma_{LCA,J}$ is 2^N, everyone of them set to the following lattice constant $l_{eq,J} \propto \sigma_{LCA,J}^{1/3}$. With the help of $2N$ light beams it is possible to switch between 2^N different colloidal photonic crystals.

The dynamics of the light-induced switching can be qualitatively described in the following way: as the time of *cis* to *trans* isomerization is very fast, this process may be considered as immediate, so that after it every particle moves in the collective effective potential U_{eff} with new σ_{LCA}. It can be presented as $U_{eff} = U(d_0) + \frac{1}{2}\frac{\partial^2 U}{\partial r^2}\big|_{r=d_0}(r-d_0)^2 = U(d_0) + \frac{1}{2}k$ $(r-d_0)^2$ where $d_0 = l_{cis} = 3.7$ μm is a lattice constant in the *cis* state and $d_0 = l_{trans} = 6.1$ μm is the lattice constant in the *trans* state. The effective force $F_{eff} = -\frac{\partial U_{eff}}{\partial r}$ is balanced with the force of the viscous Stocks drag for the sphere with effective viscosity μ_{eff}. The dynamical equation in this case can be written in the following form:

$$6\pi\mu_{eff} R_0 \frac{d\Delta r}{dt} = -k\Delta r, \tag{5}$$

where $\Delta r = r - d_0$ and $k = \frac{\partial^2 U}{\partial r^2}\big|_{r=l_{cis/trans}}$. The solution of this equation is

$$\Delta r = \Delta r_0 \exp(-\gamma t), \tag{6}$$

where $\Delta r_0 = l_{trans} - l_{cis}$. The time of the dynamical switching between crystals can be estimated as

$$T = \frac{1}{\gamma} = \frac{6\pi\mu_{eff} R_0}{k}. \tag{7}$$

Substituting the experimental values $\sigma_{LCA} \sim 10^{-2}$ J/m^2, $\mu_{eff} = 0.1$ P, $R_0 = 3 \times 10^{-6}$ m, and $f_{el} \sim 10$ K [14] into Eq. (7), the average relaxation time of the photoinduced transformation between two colloidal photonic crystals is about $T = \frac{1}{\gamma} \sim 10$ s, which is in good agreement with the experiment. As a result we propose light-induced switching between colloidal photonic crystals with different lattice constants at the nematic-air interface. The number of different kinds of dyes N sets the number of possible different photonic crystals as 2^N, which may be transformed one into another by corresponding $2N$ light beams inducing *cis-trans* photoisomerization of the doped dyes. This light-induced switching may provide routes of fabrication and manipulation in photonic crystals.

[1] J. Joannopoulos, R. D. Meade, and J. Winn, *Photonic Crystals* (Princeton University, Princeton, NJ, 1995).
[2] S. John, Phys. Rev. Lett. **58**, 2486 (1987).
[3] E. Yablonovitch, Phys. Rev. Lett. **58**, 2059 (1987).
[4] V. P. Bykov, Sov. J. Quantum Electron. **4**, 861 (1975).
[5] S. John and K. Busch, J. Lightwave Technol. **17**, 1931 (1999).
[6] P. Halevi, J. A. Reyes-Avendano, and J. A. Reyes-Cervantes, Phys. Rev. E **73**, 040701(R) (2006).
[7] C.-Y. Liu and L.-W. Chen, Phys. Rev. B **72**, 045133 (2005).
[8] K. Busch and S. John, Phys. Rev. Lett. **83**, 967 (1999).
[9] P. Poulin, H. Stark, T. C. Lubensky, and D. A. Weitz, Science **275**, 1770 (1997).
[10] Y. Ch. Loudet, P. Barois, and P. Poulin, Nature (London) **407**, 611 (2000).
[11] P. Poulin and D. A. Weitz, Phys. Rev. E **57**, 626 (1998).
[12] P. Poulin, N. Francès, and O. Mondain-Monval, Phys. Rev. E **59**, 4384 (1999).
[13] V. G. Nazarenko, A. B. Nych, and B. I. Lev, Phys. Rev. Lett. **87**, 075504 (2001).
[14] I. Smalyukh, S. Chernyshuk, B. Lev, V. G. Nazarenko, A. Nych, U. Ognysta, and O. D. Lavrentovich, Phys. Rev. Lett. **93**, 117801 (2004).
[15] T. Yamamoto, J. Yamamoto, B. I. Lev, and H. Yokoyama, Appl. Phys. Lett. **81**, 2187 (2002).
[16] P. Pieranski, Phys. Rev. Lett. **45**, 569 (1980).
[17] P. Cluzeau, G. Joly, H. T. Nguyen, and V. K. Dolganov, JETP Lett. **75**, 482 (2002).
[18] P. Cluzeau, G. Joly, H. T. Nguyen, and V. K. Dolganov, JETP Lett. **76**, 351 (2002).
[19] W. B. Russel, D. H. Soville, and W. R. Schowalter, *Colloidal Dispersions* (Cambridge University Press, Cambridge, 1991).
[20] S. Ramaswamy, R. Nityananda, V. A. Raghunathan, and J. Prost, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **288**, 175 (1996).
[21] T. C. Lubensky, D. Pettey, N. Currier, and H. Stark, Phys. Rev. E **57**, 610 (1998).
[22] B. I. Lev and P. M. Tomchuk, Phys. Rev. E **59**, 591 (1999).
[23] B. I. Lev, S. B. Chernyshuk, P. M. Tomchuk, and H. Yokoyama, Phys. Rev. E **65**, 021709 (2002).
[24] B. I. Lev and S. B. Chernyshuk, JETP **116**, 1 (1999).
[25] K. Seki and M. Tachiya, J. Phys.: Condens. Matter **17**, S4229 (2005).
[26] K. Ichimura, S.-K. Oh, and M. Nakagawa, Science **288**, 1624 (2000).