Fabrication of disordered porous structures by solvent-assisted reorganisation of liquid crystal materials

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ABSTRACT

Shaping of self-assembled soft materials is of interest for material science and nanotechnology applications because it can provide a flexible and easy method to obtain a single domain in a large area, which is used in opto-electronic and patterning applications. Here, we fabricated disordered porous structures of liquid crystals (LCs) by using a solvent-assisted treatment. Initially, the LC-based layered structures had either toric focal conic domains (TFCDs) or planar aligned samples. After treatment, disordered porous structures with randomly oriented layers were obtained although both initial and final states exhibited short-range ordering of the LC molecules. This behaviour was precisely analysed by polarised optical microscopy (POM), field-emission scanning electron microscopy (FESEM) and grazing incidence X-ray diffraction (GIXD) methods. Our resultant platform showed that disordered porous structures formed by LC materials can be used for tuneable and reversible multiple scattering applications.

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Introduction

Soft materials have been widely used for light guiding in displays, micro-lens arrays and vortex lenses. For these applications, shaping of soft materials is very important. Among the various kinds of soft materials, the supramolecular liquid crystal (LC) phase is the fastest and easiest tool for producing micro- and nano-structures. For example, micro-scale dimple structures, such as toric focal conic domains (TFCDs), in large areas can be spontaneously generated in the antagonistic boundary conditions of molecule-philic and -phobic substrates. These simple structures have shown good feasibility in lithography applications and in light-guiding experiments, as reported in previous works.

In general, long-range ordered structures are of interest for practical application; however, disordered micro- or nanometre-scale structures may also be of practical interest. A typical example is multiple scattering media for nanophotonics applications, which can be achieved by spraying and dispersing nanoparticles, as well as the soft matter-assisted bottom-up approaches. However, these methods do not allow simple and fine control of the transmittance and reflectance properties of the resultant multiple scattering media.

In this study, three-dimensionally (3D) disordered porous structures were fabricated based on 2D smectic LC-layered structures using a solvent-assisted treatment. The smectic layers in TFCDs or planar aligned samples were changed from ordered to disordered structures to yield the characteristics of a multiple scattering medium in the full visible range, as a function of the repeat time of the process and the co-solvent ratio. These sequential changes were directly
observed using polarised optical microscopy (POM), field-emission scanning electron microscopy (FESEM) and grazing incidence X-ray diffraction (GIXD) methods for determining the molecular ordering and orientation. The resultant disordered nano- and micro-structures based on LCs suggest a new type of multiple scattering medium with reversible and adjustable characteristics for many purposes.

**Results and discussion**

To achieve our goal described above, a rod-like semi-fluorinated LC molecule, Y002, was prepared. This material exhibits smectic A (SmA), smectic E (SmE) and crystal phases upon cooling from the isotropic state (Figure 1(a)).[14–16] The powder sample of Y002 was dropped onto the polyethylenimine (PEI)-coated Si wafer at isotropic temperature (~ 200 ℃) and was cooled to obtain TFCDs with dimple structures in the SmA (~ 180 ℃) phase (Figure 1(b) and 1(c)). Then, the sample was cooled to crystal phase and covered by a glass plate without spacers, to induce a solvent to partially dissolve Y002 by capillary action (Figure 1(d)). The selection of solvent is very important to obtain the desired porous structures, because the degree of swelling and dissolving of solvent on the LC film is the key in this process. For this, we tested 10 kinds of solvent that can be classified into three categories: non-polar, polar aprotic and polar protic (Figure 2). Based on these preliminary tests, non-polar and polar aprotic solvents showed better properties for our purposes as opposed to polar protic solvents. Isopropyl alcohol (IPA), one of the polar protic solvents, was finally selected, showing appropriate ability to mobilise LC, and thus self-assembled layer structures were not totally destroyed – indeed there was negligible mass loss. A solvent annealing step was then conducted, which was characterised by solvent concentration and annealing time. In this step, we fixed solvent concentration and annealing time (~2 min) to maintain the same condition for various experiments. After 2 min, the cover glass was removed and the sample was maintained for a few minutes until the solvent had completely evaporated. Finally, a disordered medium was obtained over a large area by repeating the last procedure, spanning several square millimetres (Figure 1(e)).

POM images were acquired during repeating of the process for demonstrating the initial (TFCDs: T), intermediate (I) and final (disordered medium: D) states (Figure 3(a)–(c)). Here TFCDs refer to the layer structures of sample Y002 in SmA phase, which can be maintained even after cooling down to the Cr phase. [1,2,9,12,14,15,17,18,29] Hexagonally arrayed TFCDs in the initial state exhibit typical Maltese cross patterns owing to the radially arranged molecules on the bottom substrate (Figure 3(a)).[17] When the TFCD film was

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**Figure 1.** (colour online) The material and its phase transition temperature. Schematic showing the experimental procedures. (a) Chemical structure and thermal phase transition of the LC material, Y002; (b) 1 wt% of PEI solution is spin-coated on the Si wafer; (c) a TFCD film is prepared on this substrate; (d) the TFCD film is covered by a glass and 4 μL of IPA is injected using capillary force at 45 ℃; (e) after ~2 minutes, the coverglass is removed at 25 ℃ and the procedure is repeated to obtain the fully grown disordered structures.
exposed to the solvent, the solvent molecules dissolved the exposed LC molecules, leading to a state of chemical non-equilibrium. Under this procedure the disordered structure was generated, resulting from rapid solvent evaporation. The intermediate state exhibited blurred birefringence in the corresponding POM image, indicating that some LC molecules were dissolved and demonstrating a partially disordered structure. Figure 2. (colour online) Dissolving tests used to select the appropriate solvent for the experiment. Top-view SEM images show how the morphology changes according to solvents. Hexane, toluene and chloroform can be classified as non-polar solvents, while DCM, acetone and DMF can be considered as polar aprotic solvents. Other solvents are polar protic solvents. Based on these results, the TFCD film of Y002 molecule could be dissolved in either non-polar or polar aprotic solvents rather than polar protic solvents, and this is why IPA was chosen for our system.
molecular arrangement (Figure 3(b)). A very dark image was observed in the final state, but this does not imply that the sample disappeared after the process. Rather, the disordered LC molecules diffused visible light (Figure 3(c)), which was confirmed by measuring the sample weight (Table 1). This measurement will be discussed in detail later.

Table 1. This table shows the mass loss of samples. For each sample, the mass was measured before and after the process. The average mass loss was about 0.15 mg, which was negligible considering the total mass (~145 mg), supporting the notion that disordered porous structures were formed by reorganisation of LC molecules.

|       | TFCD film on wafer | Disordered porous film on wafer |
|-------|--------------------|---------------------------------|
| Sample 1 | 145.55 mg          | 145.4 mg                        |
| Sample 2 | 145.6 mg           | 145.4 mg                        |
| Sample 3 | 145.9 mg           | 145.8 mg                        |

Transmittance and reflectance characteristics of the sample in the different states were also measured quantitatively (Figures 3(d) and 4). The transmittance of the TFCDs was ~85% in the full visible range, implying that most of the visible light propagates through the LC film owing to the perpendicularly oriented LC molecules in the TFCD layers, although tangentially aligned LC molecules near the dimple sites scatter the light to some extent.[1] After repeating the process 10 times, transmittance was significantly decreased to less than 10% in the final state, regardless of the visible-light wavelength. This trend was confirmed by analysing the reflectance, which was increased through the process, although there was some loss in reflected light due to strong scattering near the sample surface (Figure 4). The serial images of the LC film (with ‘KAIST’ marks in the background) demonstrate how the film transits from transparency to opacity (Figure 3(d)).
To demonstrate the adjustable transmittance obtained in our system, we used water with IPA as a co-solvent, and varied the volume ratio for changing the relative transmittance of the planar aligned LC sample (Figure 5). Based on the solvent test, Y002 is not dissolved in water while IPA is miscible with water (Figure 2). Therefore, we used co-solvent with water to show how the degree of deformation depends on the IPA/water volume ratio. After twice repeating the solvent-assisted process (Figure 1(d)), the optical properties were measured for different conditions. The transmittance of the IPA:water (0:5) volume ratio sample was approximately 90%, implying that most of the visible light propagated through the LC film because there was no deformation in the planar aligned sample.

As the IPA relative volume increased, the film transmittance decreased, with the 5:0 sample exhibiting the relative transmittance of ~20%. The resultant transmittance variations depending on co-solvent ratio enable fabrication of multiple scattering media with adjustable transmittance, which is a useful feature for optical applications.

Indeed, contrary to previously reported methods, [21–28] our LC-based multiple scattering system is reversible and can be converted to an opaque medium by chemical treatment, while heating and cooling can be used to reversibly change the film transparency (Figure 6 and video S1–S3 in the Supplemental Material). During this process, the opaque disordered structure develops into one with a Maltese cross pattern via the isotropic state, implying the reusability of our multiple scattering platform.

To observe the deformed structures on the nanometre and micron scales, we performed SEM experiments (Figure 7). In the initial state the dimple structures were clearly observed, capturing the line defects of the TFCDs, and a cross-sectional view revealed tangentially aligned smectic layers (Figure 7(a)). In the intermediate state the solvent, IPA, was smeared on the LC film through the bottom and top glass substrates by capillary action, which was directly observed by examining the cross-sectional view in which disordered porous structures were clearly visible on the top and bottom sides (Figure 7(b)). This confirms that the smectic layer orientation of the LC materials is negligible because the homeotropically aligned LC molecules at the LC/air interface on the film top and the planar aligned LC molecules on the bottom substrate demonstrate almost the same rate of porous structure emergence, although the top part...
exhibits a somewhat higher rate owing to its geometrical organisation of dimple structures. In Figure 7(c), the top-view image reveals fully grown disordered porous structures throughout the sample, while the corresponding cross-sectional view shows that the top and bottom disordered parts are connected and form completely disordered porous structures. Basically a large LC droplet sample was used; thus, the sample thickness varied owing to the surface tension of the LC molecules, inducing the size variation of the TFCDs in the initial state, as reported previously.[18] However, the morphology in the final state is not dependent on sample thickness because randomly oriented LC-layered structures have identical 3D disordered shapes.

At this point the question of mass preservation can be asked because the solvent, IPA, can in principle wash out the LC sample during the process. To investigate this issue, the mass was measured before and after the process, and the calculated mass difference was found negligible, as shown in Table 1, in which the average mass loss is listed as 0.15 mg for the ~145 mg sample, supporting the idea that the disordered porous structures formed as a result of reorganisation during solvent evaporation. To test this hypothesis, we compared the cross-sectional views of the sample before and after the process (Figure 8), and verified that the LC film thickness increased owing to the partial dissolution and reorganisation of the LC molecules in the final state. The quantitative analysis of the LC film expansion was performed by measuring the difference in thickness between the initial and final states, which amounted to ~36.1%. We also calculated the physical porosity of the film by calculating \( V_v \) and \( V_T \), which are the void and total volume, respectively.[29–31] The resultant physical porosity, defined as \( V_v/V_T \), was ~0.265, comparable to previously reported values.[29–31]

The nanometre-scale ordering and orientation of the smectic layered structures under different conditions were directly examined in GIXD experiments with a synchrotron radiation source at the 9A beam-line of the Pohang accelerator laboratory (PAL) (Figure 9). The experimental set-up is described in Figure 9(a). The layer structure in our sample is not a simple single layer but a relatively complex one that has bi-layered and modulated characteristics.[32] Considering this layering structure, the GIXD patterns showed complex peaks both on- and off-meridian (Figure 9(b)). Two diffraction spots at a small-angle region appeared symmetrically (off-meridional line) with respect to the diffraction corresponding to the modulated layer structure. Diffraction peaks can be interpreted as \((0l)\) \((l = \text{even numbers})\) and \((1l)\) \((l = \text{odd numbers})\) by the selection rule.[32] Corresponding wide-angle peaks observed at \( \chi \) ranged approximately 0° and 180°.
Figure 7. (colour online) Top and cross-sectional SEM images acquired during the process. (a) TFCDs with dimple structure shown in the top-view image. Inset shows a perspective model view of a dimple structure; cross-sectional view shows tangentially aligned smectic layers. (b) Smectic layers are deformed, but radially ordered layers are still seen (yellow arrow). Cross-sectional view image, showing disordered porous structures generated from top and bottom parts. (c) Disordered porous structures are fully grown in the final state. All scale bars in main plots are 15 μm. Insets in (b) and (c) are magnified SEM images that clearly show pores, and the scale bars in all insets are 5 μm.

Figure 8. (colour online) Cross-sectional SEM images of the samples before and after the process. Quantitative analysis of the LC film expansion was determined by measuring the difference in thickness between the initial and final states. Relative thickness increase is ~36%. All scale bars are 20 μm.
(Figure 9(b)), indicating that most of the layer structures in the TFCDs are planar and tangentially aligned, as previously reported.\cite{17} During the process, the meridional and off-meridional peaks in the small-angle region became weaker and merged (Figure 9(b)–(d)). The same trend was observed for the wide-angle region, in which sharp peaks at horizontal lines changed into circularly distributed weak peaks during the process (Figure 9(b)–(d)). These 2D diffraction patterns indicated that the initial ordered structure of TFCD film was transformed to a disordered structure. Figure 9(e) and (f) shows 1D in-plane and out-of-plane GIXD profiles. In the final state, strong (002), (103) and (105) peaks were observed in both $q_r$ and $q_z$ profiles, implying that the smectic layers of Y002 were randomly oriented. At this point, it can be determined that layer structures maintained their form and so three peaks still remained. In Figure 9(e), a strong peak at $q = 1.57 \text{ Å}^{-1}$ corresponding to ~0.40 nm was observed, which is typically found in the face-to-face stacking of aromatic groups of the molecules. In the $q_z$ profile, the diffraction peak at $q = 1.57 \text{ Å}^{-1}$ was strong in the initial state (marked ‘*’ in Figure 9(e)) and this peak was becoming weaker as the process proceeded. This indicated that molecules were randomly oriented in the final state. Also, these resultant peak intensities in azimuthally plotted 1D graphs confirmed that the aromatic stacking diffraction peak became weaker and had no angle dependence in the final state, implying that LC molecules were randomly oriented in the disordered porous structure (Figure 9(g)).

**Conclusions**

We fabricated LC-based disordered porous structures using a solvent-assisted treatment, obtaining a new type of reversible multiple scattering medium. Tangentially or planar aligned LC-layered structures...
were transformed into disordered porous structures during the process, resulting in the appearance of nanometre- and micron-scale long-range disordered structures with randomly oriented LC molecules. We believe that the obtained structure is a promising tuneable and reversible multiple scattering medium that will be used in optics and photonics applications.

**Experimental**

**Materials and methods**

The Si wafer was spin-coated with 1 wt% of polyethyleneimine (PEI) (used as purchased from Sigma–Aldrich) solution to induce planar alignment of the LC molecules. Then, the Y002 powder was loaded onto the Si wafer, heated above the isotropic temperature (−200 °C) and the sample was cooled to generate TCFDs in smectic A phase. The sample was cooled down to Cr phase and covered by a glass substrate and 4 μL of isopropyl alcohol (IPA) (Sigma–Aldrich) was injected by capillary action at 45 °C for ~2 minutes. After ~2 minutes, the cover glass was removed at 25 °C to evaporate the residual solvent. The processes of both injection and evaporation were repeated to obtain porous structures with progressively increasing disorder up to 10 times.

**Characterisation**

All of the experiments involving heat treatment were conducted on a heating stage, using a temperature controller (LTS420 and TMS94, LINKAM). The polarised optical images were observed by POM (LV100POL, Nikon). Transmittance and reflectance data (Figures 3(d) and 4) were collected from one sample at different states during the process, using a customised optical microscope equipped with a USB-2000+ spectrometer (Ocean Optics). Morphologies in the different states were directly observed using a field-emission scanning electron microscope (FE-SEM; S-4800, HITACHI) after a 2 nm-thick platinum coating. All GIXD experiments were performed at PLS-II 9A U-SAXS beamline of PAL in Korea. The energy of the X-ray beam was 11.06 keV and the sample-to-detector distance (SDD) was 225 mm. The incidence angle of the X-ray beam was 0.1°.

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**Disclosure statement**

No potential conflict of interest was reported by the authors.

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