Lasing of self-organized helical cholesteric liquid crystal micro-droplets based on emulsification

Pei-zhi Sun,[1] Zhen Liu,[1] Wei Wang,[1] Xiaoqian Wang,[1,4] Hui-min Zhang,[1] Yun-xing Lu,[1] Wei Hu,[3] Yanqing Lu,[3] Dong Shen,[1] and Zhi-gang Zheng[1,2,*]

[1]*Department of Physics, East China University of Science and Technology, No. 130, Meilong Road, Shanghai 200237, China*
[2]*Liquid Crystal Institute and Chemical Physics Interdisciplinary Program, Kent State University, Kent, Ohio 44242, USA*
[3]*National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures and College of Engineering and Applied Sciences, Nanjing University, Nanjing 210093, China*
[4]*xqwang@ecust.edu.cn*
[*]*zgzheng@ecust.edu.cn*

Abstract: Lasing of self-organized helical cholesteric liquid crystal (CLC) micro-droplets was achieved based on emulsification of CLC/Polymer/Water mixture. It was found that the concentrations of CLC and polyvinyl alcohol play an obvious role on the improvement of lasing performance as the ratio of their concentrations is in the range of 1:10~1:9. In addition, the size of CLC micro-droplet is dependent on aforementioned concentrations, and shows to be proportional to lasing energy threshold.

OCIS codes: (230.3720) Liquid-crystal devices; (160.3710) Materials; (140.0140) Lasers and laser optics.

References and links

1. I. P. Ilchishin, E. A. Tikhonov, V. G. Tishchenko, and M. T. Shpak, "Generation of a tunable radiation by impurity cholesteric liquid crystals," JETP Lett. **32**, 24–27 (1980).
2. V. I. Kopp, B. Fan, H. K. M. Vithana, and A. Z. Genack, "Low-threshold lasing at the edge of a photonic stop band in cholesteric liquid crystals," Opt. Lett. **23**(21), 1707–1709 (1998).
3. J. P. Dowling, M. Scalora, M. J. Bloemer, and C. M. Bowden, "The photonic band edge laser: A new approach to gain enhancement," J. Appl. Phys. **75**(4), 1896–1899 (1994).
4. J. Schmidtke and W. Stille, "Fluorescence of a dye-doped cholesteric liquid crystal film in the region of the stop band: theory and experiment," Eur. Phys. J. B **31**(2), 179–194 (2003).
5. Y. Huang, Y. Zhou, C. Doyle, and S.-T. Wu, "Tuning the photonic band gap in cholesteric liquid crystals by temperature-dependent dopant solubility," Opt. Express **14**(3), 1236–1242 (2006).
6. K. Funamoto, M. Ozaki, and K. Yoshino, "Discontimuous shift of lasing wavelength with temperature in cholesteric liquid crystal," Jpn. J. Appl. Phys. **42**(2), L1523–L1525 (2003).
7. J.-H. Lin, P.-Y. Chen, and J.-J. Wu, "Mode competition of two bandedge lasing from dye doped cholesteric liquid crystal laser," Opt. Express **22**(8), 9932–9941 (2014).
8. A. Chanishvili, G. Chilaya, G. Petriashvili, R. Barberi, R. Bartolino, G. Cipparrone, A. Mazzulla, and L. Oriol, "Phototunable lasing in dye-doped cholesteric liquid crystals," Appl. Phys. Lett. **83**(26), 5353–5355 (2003).
9. T.-H. Lin, Y.-J. Chen, C.-H. Wu, A. Y.-G. Fuh, J.-H. Liu, and P.-C. Yang, "Cholesteric liquid crystal laser with wide tuning capability," Appl. Phys. Lett. **86**(16), 161120 (2005).
10. A. Chanishvili, G. Chilaya, G. Petriashvili, R. Barberi, R. Bartolino, G. Cipparrone, A. Mazzulla, and L. Oriol, "Lasing in dye-doped cholesteric liquid crystals: two new tuning strategies," Adv. Mater. **16**(910), 791–795 (2004).
11. S. Furumi, S. Yokoyama, A. Otomo, and S. Mashiko, "Phototunable photonic bandgap in a chiral liquid crystal laser device," Appl. Phys. Lett. **84**(14), 2491–2493 (2004).
12. G. Chilaya, A. Chanishvili, G. Petriashvili, R. Barberi, R. Bartolino, G. Cipparrone, A. Mazzulla, and P. V. Shibaev, "Reversible tuning of lasing in cholesteric liquid crystals controlled by light-emitting diodes," Adv. Mater. **19**(4), 565–568 (2007).
13. L.-J. Chen, J.-D. Lin, and C.-R. Lee, "An optically stable and tunable quantum dot nanocrystal-embedded cholesteric liquid crystal composite laser," J. Mater. Chem. C Mater. Opt. Electron. Devices **2**(22), 4388–4394 (2014).
14. H. Yu, B. Tang, J. Li, and L. Li, "Electrically tunable lasers made from electro-optically active photonics band gap materials," Opt. Express **13**(18), 7243–7249 (2005).
15. J. Schmidtke, G. Junnemann, S. K. Baumann, and H. Kitzerow, "Electrical fine tuning of liquid crystal lasers,"

#260004 Received 25 Feb 2016; revised 16 Mar 2016; accepted 16 Mar 2016; published 18 Mar 2016

Appl. Phys. Lett. **15**(12), 974–977 (2013).
16. H. Finkelmann, S. T. Kim, A. Munoz, P. Palffy-Muhoray, and B. Taheri, "Tunable mirrorless lasing in cholesteric liquid crystalline elastomers," Adv. Mater. **13**(14), 1069–1072 (2001).
17. B.-W. Liu, Z.-G. Zheng, X.-C. Chen, and D. Shen, "Low-voltage-modulated laser based on dye-doped polymer stabilized cholesteric liquid crystal," Opt. Mater. Express **3**(4), 519–526 (2013).
18. L. Saadaoui, G. Petriashvili, M. P. De Santo, R. Hamdi, T. Othman, and R. Barberi, "Electrically controllable multicolor cholesteric laser," Opt. Express **23**(17), 22922–22927 (2015).
19. C.-T. Wang and T.-H. Lin, "Polarization-tunable chiral nematic liquid crystal lasing," J. Appl. Phys. **107**(12), 123102 (2010).
20. M. Humar and I. Muševič, "3D microlasers from self-assembled cholesteric liquid-crystal microdroplets," Opt. Express **18**(26), 26995–27003 (2010).
21. D. J. Gardiner, S. M. Morris, P. J. W. Hands, C. Mowatt, R. Rutledge, T. D. Wilkinson, and H. J. Coles, "Paintable band-edge liquid crystal lasers," Opt. Express **19**(3), 2432–2439 (2011).
22. P. J. W. Hands, D. J. Gardiner, S. M. Morris, C. Mowatt, T. D. Wilkinson, and H. J. Coles, "Band-edge and random lasing in paintable liquid crystal emulsions," Appl. Phys. Lett. **98**(14), 141102 (2011).
23. D. J. Gardiner, W.-K. Hsiao, S. M. Morris, P. J. W. Hands, T. D. Wilkinson, I. M. Hutchings, and H. J. Coles, "Printed photonic arrays from self-organized chiral nematic liquid crystals," Soft Matter **8**(39), 9977–9980 (2012).
24. Z.-G. Zheng, B.-W. Liu, L. Zhou, W. Wang, W. Hu, and D. Shen, "Wide tunable lasing in photoresponsive chiral liquid crystal emulsion," J. Mater. Chem. C **3**(11), 2462–2470 (2015).

1. Introduction

Cholesteric liquid crystal (CLC) is a typical self-organized photonic superstructure which possesses many unique and interesting properties with potential applications. By virtue of its one-dimensional periodic structure, and embedded some amount of laser dyes, the CLC laser was achieved with an external pumping [1]. Such kind of lasing system has attracted tremendous attention due to the competitive advantages including simple fabrication, lower threshold and wide tuning range over the conventional lasers. The mechanism of CLC lasing can be explained by the photonic crystal model, *i.e.*, the photon density of state (DOS) is suppressed in a certain energy gap called photonic band gap (PBG) but enhanced at the band edges where the group velocity of the photons approaches zero [2,3]. Lasing generally occurs at the band edges owing to the maximum DOS. Schmidtke *et al*. experimentally verified that the lasing usually generates at the long-wavelength edge of the CLC band gap [4]. Accordingly, the approach of utilizing external stimuli such as temperature [5–7], light [8–13], electric field [14,15], and mechanical stress [16] to change the periodic structure (*i.e.*, helical pitch) of CLC and consequently tune the lasing wavelength has been extensively adopted in series of previous works. In addition, both of the emission intensity and polarization can be electrically controlled [17–19]. An omnidirectional lasing of CLC droplets based on the mixture of CLC and glycerol was reported [20].

Recently, a novel CLC micro-droplet laser based on emulsion consisting of aqueous solution of the polymer, polyvinyl alcohol (PVA), and the CLC doped with a small amount of laser dye was demonstrated [21–23]. Distinct from the conventional CLC laser which should be confined in a planar aligned liquid crystal (LC) cell, such CLC micro-droplet laser can be formed just by covering the emulsion on a single substrate without any surface alignment, thereby significantly simplifying the preparation process and enabling the realization of film laser by coating the material on a flexible substrate. The drying of wet emulsion under room temperature leads to a shrinkage of the material on thickness, thereby forcing the random distributed helical axes of CLC droplets to transform into a uniform alignment perpendicular to substrate. Excited with a certain pumping light, the laser is emitted along the normal direction of substrate. In the very recent, a broad wavelength-tuning of such micro-droplet laser stimulated by light was realized through the doping of photosensitive azobenzene based chiral molecular switch [24].

Generally, the performances of such CLC micro-droplet laser are closely related with the arrangement of LC molecules in the droplet; while the arrangement is mainly influenced by the size of CLC droplets and the density of polymer network if the anchoring and pumping conditions are invariable. In other words, there must exist an optimized condition for the

#260004 Received 25 Feb 2016; revised 16 Mar 2016; accepted 16 Mar 2016; published 18 Mar 2016

content of the components—PVA and CLC, which plays an essential role in the characteristic of the dried laser film and further in the performance of laser emission. However, the relevant works aiming at such aspect are rarely and lack of systematic study at present. In this paper, the concentrations of PVA and CLC were varied, in order to explore their influences on the characteristic of laser film as well as the performance of laser emission. Furthermore, the size and the distribution of CLC micro-droplets, and their lasing energy thresholds (LETs) were investigated.

2. Materials and experiments

CLC was composed by a commercial nematic liquid crystal SLC1717 (from SliChem, China) and a certain amount of chiral dopant, R811 (from Merck). A small amount of laser dye (~0.5 wt%), 4-dicyanomethylene-2-methyl-(6-4-dimethylaminostryl)-4H-pyan (DCM, from Aldrich), was doped into CLC as the gain medium. The weight ratio of R811 was 26.3% for the consideration of the matching between the PBG of CLC and the emission band of DCM. Such laser dye-doped CLC was mixed with the aqueous solution of polyvinyl alcohol (PVA, provided by ACROS ORGANICS, molecular weight: 16000) in further to form the CLC emulsion. The emulsion was uniformly coated on a glass substrate using the doctor blade; the thickness was controlled by two 80-μm-thick Kapton strips as illustrated in Fig. 1(a). The samples were reserved in a dark ambient at room temperature until the water was evaporated. Consequently, the thickness of dried film shrank, forming many dispersed oblate LC droplets.

A linearly polarized second-harmonic switched neodymium-doped yttrium aluminium garnet (Nd:YAG) pulsed laser (λ = 532 nm; pulse width: 8 ns; Beamtech Co. Ltd. Canada) was used as the pumping source to excite the laser dye in the samples; and a quarter wave plate was set to convert the pump laser to the left-handed circular polarization, *i.e.*, opposite to the handedness of CLC. The emitted laser was detected and tested by a fiber connected USB spectrometer (Avaspec-2048 from Avantes, resolution: 1.60 nm).

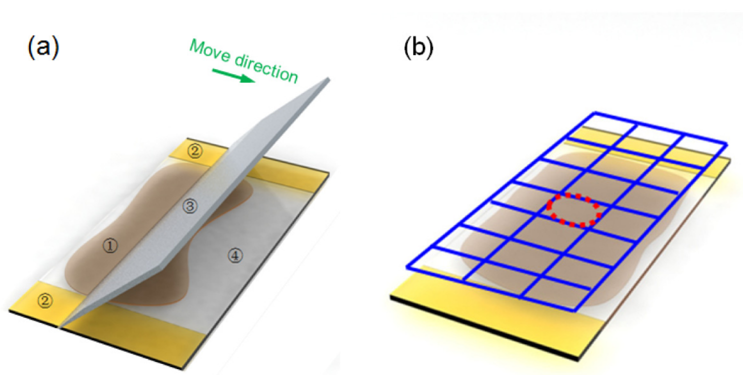

Fig. 1. Schematics of (a) the preparation of CLC micro-droplet laser (①:emulsion ②:Kapton strip ③:doctor blade ④:glass substrate); (b) numerical statistic of effective CLC micro-droplets (the whole sample was divided into twenty-one square regions as depicted by blue solid cross-lines; number of effective droplets in every square region as enclosed by red dashed circle was counted one by one and summed up).

Several samples with different concentrations of CLC and PVA were prepared. The concentration of the CLC—*x*—varied from 1wt% to 5wt%, specifically 1wt%, 2wt%, 2.3wt%, 2.5wt%, 3wt%, 4wt% and 5wt%; likewise, concentration of PVA—*y*—varied from 10wt% to 24wt% with the interval of 2wt% (the mixture would go beyond saturation if the ratio of PVA exceeds 24wt%). The remaining part was water. To evaluate the characteristic of laser emission of the samples, a parameter—*F*—was defined, representing the number of effective CLC micro-droplets (herein, effective droplet was defined as a droplet possesses the well-defined helical structure and can be excited to emit the typical laser). The larger of *F*, the

#260004 Received 25 Feb 2016; revised 16 Mar 2016; accepted 16 Mar 2016; published 18 Mar 2016

better lasing performance of the sample. For facilitating numerical statistic of such micro-droplets, herein, as depicted in Fig. 1(b), the entire sample was uniformly divided into twenty-one regions. The number of effective CLC micro-droplets in every region were counted and summed up to obtain the value of *F*. Similar experiment was carried out for three times and the average value of *F* was calculated. Consequently, the optimized weight ratios of the components in the mixture were determined.

3. Results and discussions

The typical texture of an effective CLC micro-droplet (inset of Fig. 2(a)) and its corresponding lasing spectrum are shown in Fig. 2(a). A uniform yellow-and-green reflection color was observed due to a well-defined helical structure of CLC with the helical axis perpendicular to the substrate; the defect rings were caused by the molecular anchoring from the curve surface of CLC micro-droplet. The spectrum clearly shows a single-mode laser emission with a peak at 607 nm which corresponds to the long-wavelength edge of the PBG of CLC micro-droplet. The band-width is about 1.5-1.7 nm, however the accurate band-width may be smaller than the tested value due to the resolution limitation of the spectrometer. The relationship between the pump energy and emission energy shown in Fig. 2(b) indicates an abrupt linear rising of emission energy as the pump energy increases to a turning point which is generally defined as the LET.

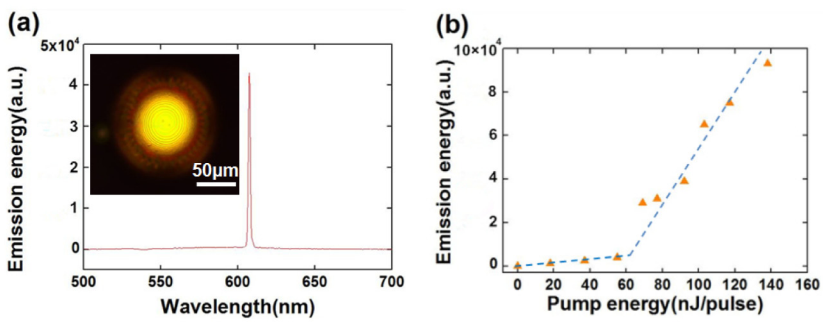

Fig. 2. (a) Emission spectrum of a CLC micro-droplet and the corresponding optical texture (the inset) and (b) the pump energy dependent lasing emission energy of such micro-droplet. Concentrations of CLC and PVA are 2.0 wt% and 18.0 wt%, respectively. Diameter of the focused pumping light is manipulated to approximately equal to the diameter of the micro-droplet, which is ~120 μm, and the reputation rate of pumping light is 1 Hz.

Characteristic and performances of lasing connect closely to the contents of CLC and PVA as reflected in Table 1. It is obvious that the number of effective CLC micro-droplets—*F*— decreases almost monotonically with the increasing of the weight ratio of CLC when the concentration of PVA—*y*—is constant; while there exists a maximum of this number as the content of CLC is invariable. In addition, it is noteworthy that the effective CLC micro-droplets are significantly less in the cases of higher CLC-content (x≥2.5 wt%) and lower PVA-content (y≤16.0 wt%). Because of the phase separation between CLC and PVA and the emulsification, the above two cases usually lead to a large size of CLC droplets as shown in Figs. 3(a) and 3(b), as well as the aggregation of these droplets, which disturbs the well-defined helical arrangement of LC molecules in the droplets and generates lots of defects as presented in Fig. 3(c), consequently influencing the laser emission. However, it is not implied that a better lasing performance can be achieved at the situations of much lower concentration of CLC and higher concentration of PVA. Table 1 shows that the number of effective CLC micro-droplets is only 10 as the concentrations of CLC and PVA are 1.0 wt% and 24.0 wt%, respectively. This reason may lie in the size-decreasing of CLC micro-droplets and stronger anchoring of the polymer—PVA, which cause the light scattering and the distortion of the helical structure of CLC micro-droplets, resulting in the disappearance of laser emission, but

#260004 Received 25 Feb 2016; revised 16 Mar 2016; accepted 16 Mar 2016; published 18 Mar 2016

replaced by the occurrence of wide band-width, low intensity fluorescent emission. As the size of CLC micro-droplets is smaller than 30 μm, the probability of lasing is significantly decreased. Table 1 indicates that the number of effective CLC micro-droplets—*F*—reaches the maximum, 20, in the case that the contents of CLC (*x*) and PVA (*y*) are 2.0 wt% and 18.0 wt%, respectively; or 2.3 wt% and 22.0 wt%, respectively, *i.e.*, the optimized concentration ratio of CLC and PVA—*x*/*y*—should be in the range of 1:10~1:9. By combining the results of Table 1, Fig. 3(a) and Fig. 3(b), it can be deduced that a more favorable average diameter of CLC micro-droplet for a better lasing performance should be in the range of 60-70 μm.

Table 1. The values of *F* at concentrations *x* and *y*

x(wt %) \ y(wt%)	10.0	12.0	14.0	16.0	18.0	20.0	22.0	24.0
1.0	7	9	10	12	14	12	11	10
2.0	7	9	7	11	20	15	20	18
2.3	4	3	5	5	13	17	20	19
2.5	2	3	7	7	6	7	7	9
3.0	2	2	7	7	7	6	5	5
4.0	1	2	4	4	6	8	8	8
5.0	0	1	3	3	3	2	3	6

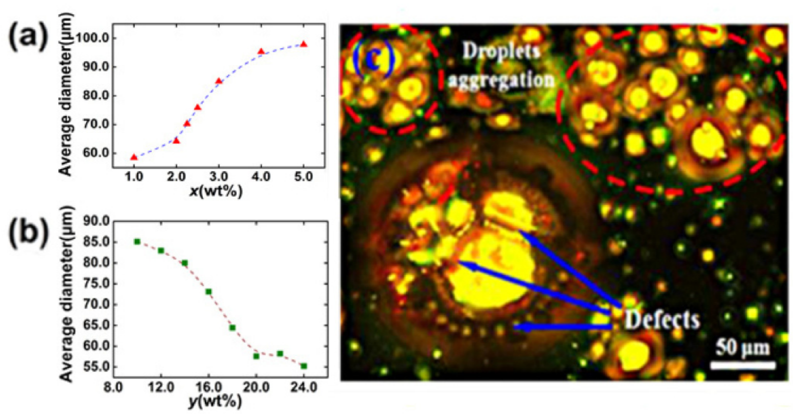

Fig. 3. Average diameter of CLC micro-droplets changes with the increasing of (a) CLC concentration when PVA concentration is 18.0 wt%; and (b) PVA concentration when CLC concentration is 2.0 wt%. (c) Texture micrograph of CLC droplets in the case of $x = 4.0$ wt% and $y = 14.0$ wt%.

LET of every CLC micro-droplet in the dried film (2.3 wt% CLC; 18.0 wt% PVA) was tested at the room temperature, and furthermore, the relationship between LET and the square of diameter of droplet is shown in Fig. 4. LET increases with the enlarging of micro-droplet. As the square of diameter of CLC droplet is smaller than ~4393 μm^2, LET linearly and gently increases from ~4.6 nJ to ~17.0 nJ; while an abrupt linear rising of LET appears as the diameter exceeds 4393 μm^2. When the composition of material, the arrangement of LC molecules, the exciting conditions and the ambient temperature are identical, the density of LET is independent on the diameter of CLC micro-droplet. With respect to a certain droplet, if the density of LET is defined as *E* and the surface area that receiving excitation as *S*, thus its LET should be $LET = E \times S$; as aforementioned, *E* is a constant, therefore *LET* is proportional to *S*, *i.e.*, the size of droplet. When the size of droplet is too large to maintain the original helical arrangement of LC molecules, the structure of CLC is distorted, forming

#260004 Received 25 Feb 2016; revised 16 Mar 2016; accepted 16 Mar 2016; published 18 Mar 2016

arrangement defects, resulting in the increasing of the density of LET which leads to the abrupt rising of LET value starting from 4393 μm^2 as shown in Fig. 4, however the linear relationship is still presented. Such linear relationships in both cases of large droplet size and small droplet size confirm the independence of the density of LET on the droplet size. The slope of line is proportional to the density of LET. It is noteworthy herein that the pumping light is focused to a smaller diameter which is comparable to the diameter of micro-droplet, and therefore the tested value of LET is significantly smaller than the previous reported one. Besides, the well helical arrangement of CLC and the thicker film (*i.e.*, long gain-length) are another two possible reasons for the lower LET.

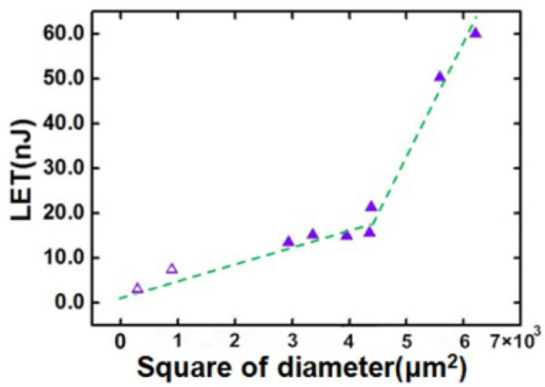

Fig. 4. Relationship between LET and the square of diameter of CLC micro-droplet. Hollow triangles indicate that the probability of the lasing of smaller droplet is lower than that of larger ones.

4. Conclusions

In conclusion, lasing of self-organized helical CLC micro-droplets was achieved based on the emulsification of CLC/Polymer/Water mixture. Such material is independent on the confinement of LC cell, and very easy to be achieved just by coating the material on one substrate without any alignment treatment, so it is promising in the future micro-photonic and display applications. The characteristic of the material and lasing performance are closely dependent on the component of materials. Herein, the influences of the concentrations of CLC and PVA on the performance of laser emission were investigated. The results indicate that the concentrations of CLC and PVA play an important role on the size of CLC micro-droplets, the distribution and number of effective CLC droplets, and the lasing energy threshold of the sample. Either lower or higher concentrations of CLC and PVA are not favorable to a better laser emission, therefore, a proper optimization of their concentrations is necessary for improving the lasing performance. Furthermore, the experiment shows a linear relationship between LET and the square of the diameter of CLC micro-droplet. This work might have profound significance on practical application of such laser material and facilitate mass production of the devices based on the material.

Acknowledgment

This work is sponsored by the National Science Foundation of China (No. 61435008, No. 61575063), the Chen-guang Talent Foundation of Shanghai Education and Development Committee (No. 12CG32), the Foundation of Laboratory of Solid State Microstructures, Nanjing University (No. M27005), and the Innovative Experiment Project for College Students, Shanghai (No. S15075).

#260004 Received 25 Feb 2016; revised 16 Mar 2016; accepted 16 Mar 2016; published 18 Mar 2016