SPECIAL TOPIC — Physical research in liquid crystal

Random lasing from dye-doped negative liquid crystals using ZnO nanoparticles as tunable scatters*

Long-Wu Li(李龙武)[1], Zhen-Zhen Shang(尚真真)[2], and Luogen Deng(邓罗根)[2,†]

[1] School of Physics and Electronic Science, Guizhou Normal University, Guiyang 550001, China
[2] School of Physics, Beijing Institute of Technology, Beijing 100081, China

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This work demonstrates the realization of a lasing in scattering media, which contains dispersive solution of ZnO nanoparticles (NPs) and laser dye 4-dicyanomethylene-2-methyle-6-(p-dimethylaminostyryl)-4H-pyran(DCM) in negative liquid crystals (LCs) that was injected into a cell. The lasing intensity of the dye-doped negative LC laser can be tuned from low to high if the NPs concentration is increased. The tunability of the laser is attributable to the clusters-sensitive feature in effective refractive index of the negative LCs. Such a tunable negative liquid crystal laser can be used in the fabrication of new optical sources, optical communication, and liquid crystal laser displays.

Keywords: random laser, negative liquid crystal, laser threshold, ZnO nanoparticles

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1. Introduction

Random lasers aim to combine the flexibility of gain media with the technological advantage of optical scattering materials,[1–7] having the ultimate goal of electrical pumping. The optically pumped random lasing from the dye-doped nematic liquid crystal system was first realized by Strangi *et al.*[8–14] and the random lasing based on the dye-doped polymer dispersed liquid crystals was first studied by Wiersma's group.[15,16] A host-guest system for random lasing, which was composed of dye-doped polymer dispersed liquid crystal containing ZnO NPs, has been studied by Li *et al.*, in which laser dye 4-dicyanomethylene-2-methyle-6-(p-dimethylaminostyryl)-4H-pyran (DCM) was adopted as the active medium.[17] Since then, random lasing and amplified spontaneous emission in these combination materials have attracted increasing theoretical and experimental interest.[18] They have been observed in many compound mixtures,[19] such as semiconductor nano-powders,[2] polymer-dispersed liquid crytals,[20] polymer thin films,[21] liquid crystal films,[22] and suspensions of dielectric particles in laser dyes.[11] However, random lasing in the system for dye-doped negative liquid crystals has not been studied yet.

In this work, we embedded disorderly distributed ZnO NPs within the negative LC structure, forming the superior optical medium that can offer higher lasing efficiency. The system of negative LCs/DCM/ZnO NPs was optically pumped with nanosecond pulses. This system has many advantages. On the one hand, the host efficiently absorbs the pump light and non-radiatively transfers it via optical scattering process to the emitting DCM molecules with the efficiency up to 85%. On the other hand, multiple light scattering reduces bimolecular annihilation and lowers the laser threshold. In contrast with previous nematic liquid crystal (NLC) lasing[23,25] and cholesteric liquid crystal (CLC)[24,26,27] lasing, we employ negative LCs as host, resulting in a higher Q factor (up to 6050). Besides, our devices show an appreciable threshold behavior with the output intensity jumping by one order of magnitude. The emitted light radiates on the surface with an angle of a few degrees, whose intensity increases with pump energy. Transmission spectra of these devices show a set of modes at 605 nm, 600 nm, and 610 nm, of which only the mode at 605 nm sufficiently overlaps with the lasing of DCM molecules.

2. Sample preparation and experimental setup

Negative LCs ($n_e = 1.5778$, $n_o = 1.4833$, $\Delta n = 0.0945$, $\varepsilon_{\parallel} = 5.169$, $\varepsilon_{\perp} = 11.545$, $\Delta\varepsilon = -6.376$, colorless transparent liquid) of average molecular weight (Mw)154, were purchased from Beijing Jinxunyang Opt–Electronic Materials Technology Co., and DCM from Exciton Ltd, respectively and used as received. Three different solutions were prepared by dissolving 0.008 g DCM in 1.968 g negative LCs and adding ZnO NPs to dye-doped negative LCs, with a weight ratio of 0.08 g, 0.16 g, and 0.24 g, respectively. Figure 1 shows the SEM image of ZnO NPs. The random lasing samples consisting of materials of negative LCs, ZnO NPs, and DCM are prepared by hand stirring. Solutions were then injected into clean cells, to produce samples A, B, and C, corresponding to the weight of ZnO NPs mentioned above. The resulting sample thickness

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†Corresponding author. E-mail: luogen@bit.edu.cn

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was measured as approximately 10 μm, and emission was collected from the edge. Fabricated samples are optically pumped at 532 nm using laser pulses of 10 ns duration and 10 Hz repetition rate from a tunable YAG system. Figure 2 sketches part of the experimental set up for the random lasing measurements, showing how the pump beam is applied to the sample.

The output pulse energy and polarization are controlled with a $\lambda/2$ wave plate (WP) followed by a neutral laser beam splitter (NBS). One pump beam is directed to a lens of $f = 10$ cm to enlarge the beam spot on the cylindrical lens with $f = 15$ cm to be converted to a narrow stripe. Spontaneous emission or lasing is amplified along the pump stripe to the sample laterals and edges. A multimode fiber probe is obliquely placed at laterals or edges of the sample to collect the emission. An optical spectrometer with 0.1-nm spectral resolution is used to record and display the spectrum. Figure 3 shows the formation of random lasing through multiple light scattering in the sample cell.

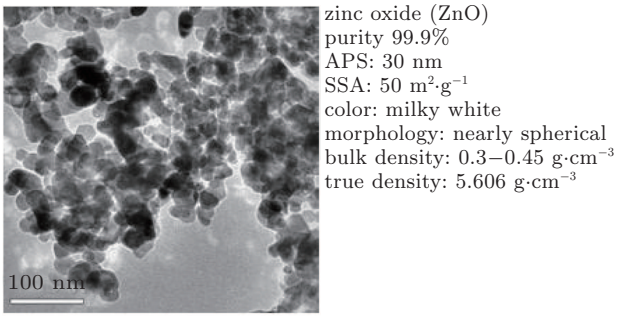


Fig. 1. SEM image of ZnO nanoparticles.

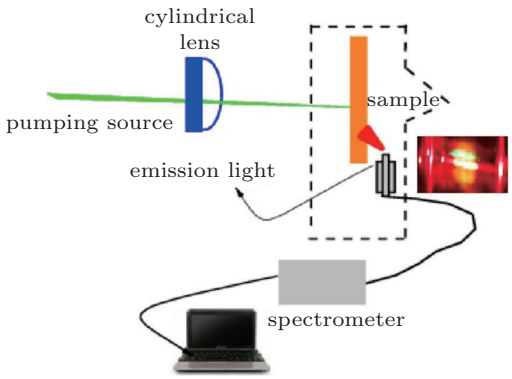


Fig. 2. (color online) Experimental setup for the measurement of random lasing.

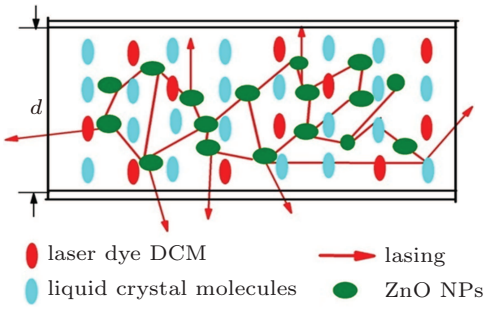


Fig. 3. (color online) Schematic diagram for the formation of random lasing through recurrent light scattering in the sample cell.

3. Results and discussion

Four samples with negative LC concentration 80 wt%, dye concentration 0.5 wt% and different ZnO NP concentrations (8 wt%, 16 wt%, 24 wt%, and 0 wt%) were tested. We find that the sample without ZnO NPs displays only amplified spontaneous emission, while other three samples produce random lasing. Figure 4 plots emission spectra for the sample without ZnO NPs at several pump energies, where the emission narrows into a single lasing peak as the pump energy passes the lasing threshold.

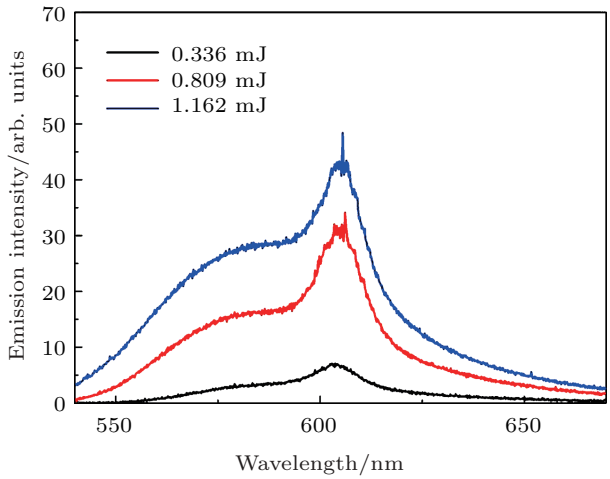


Fig. 4. (color online) The dependence of emission spectra on pump energy for the dye-doped negative LC system (without ZnO NPs).

Figures 5(a), 6(a), and 7(a) show the emission spectra of the 8 wt% sample (pump energy of 1.7 mJ), the 16 wt% sample (pump energy of 0.71 mJ), and the 24 wt% sample (pump energy of 0.091 mJ). It is noted that the 24 wt% sample is pumped at a linear level (pump energy is a nearly linearly increasing function). From Figs. 5(a), 6(a), and 7(a), we find that at high pump energies, the random emission from the 8 wt% sample is much broader, while the lasing from the 16 wt% and 24 wt% samples is characteristics of lasing. From the spectral shapes of the 16 wt% and 24 wt% emission and their peak locations of 600 nm and 604 nm, we conclude that the emission corresponds to a combination of random lasing and fluorescence, as dye-doped nematic liquid crystal lasing wavelength is known to be ≈ 605 nm.[9] Since we are primarily concerned with random lasing in negative LCs containing ZnO NPs, this study will focus only on the samples with ZnO NP concentrations of 8 wt%, 16 wt%, or 24 wt%. We characterize the random lasing properties of the 8 wt%, 16 wt%, and 24 wt% samples by considering three random lasing features: peak intensity, peak wavelength, and random lasing threshold. Figure 5(b) shows the peak intensity and pump energy for the 8 wt% sample, while figures 6(b) and 7(b) show the same quantities for the 16 wt% and 24 wt% samples, respectively.

From Figs. 5(a) and 5(b), we can see that the transition to random lasing for the 8 wt% sample is slow, with the linewidth narrowing from 20 nm to 0.2 nm. While the transition for the 8 wt% sample is found to be gradual, the transition to random lasing for the 16 wt% and 24 wt% samples is abrupt. From Figs. 6(a), 6(b), 7(a), and 7(b), we observe that the linewidth changes from 5 nm to 0.1 nm and the the slope of intensity quickly increases. This quicker transition into lasing suggests that there is less competition between amplified spontaneous emission and lasing in the 16 wt% and 24 wt% samples, than in the 8 wt%. These results clearly indicate that, in the transparent state, the negative LC molecules and the dye molecules are vertically aligned on each substrate: this allows most of the arbitrarily polarized light to pass through the negative LC cell. ZnO NPs are used as scatters and DCM dyes are employed to absorb the incident light. When the absorption axes of the dye molecules and the polarization of the incident light are aligned, dye molecules strongly absorb the incident light. The incident light is simultaneously scattered by NPs and absorbed by molecules while in this state, as can be seen in the random lasing images shown in Fig. 3. In summary, negative LCs have higher transmittance in the transparent state, i.e., lasing at low pump intensity does not disturb the initial alignment of negative LCs, so we can obtain a high lasing efficiency.

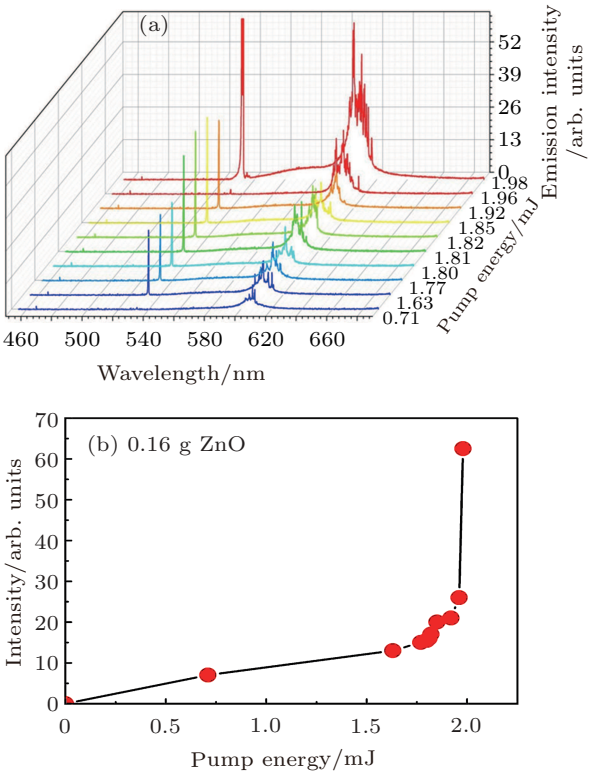


Fig. 6. (color online) (a) Evolution of the emission spectra of dye-doped negative LC solution inside the cell with (0.16 g) ZnO NPs as pump energy increases from 0.71 mJ to 1.98 mJ. (b) Output intensity of the random laser as a function of the incident pump pulse energy obtained from panel (a), where the lasing threshold is 0.71 mJ.

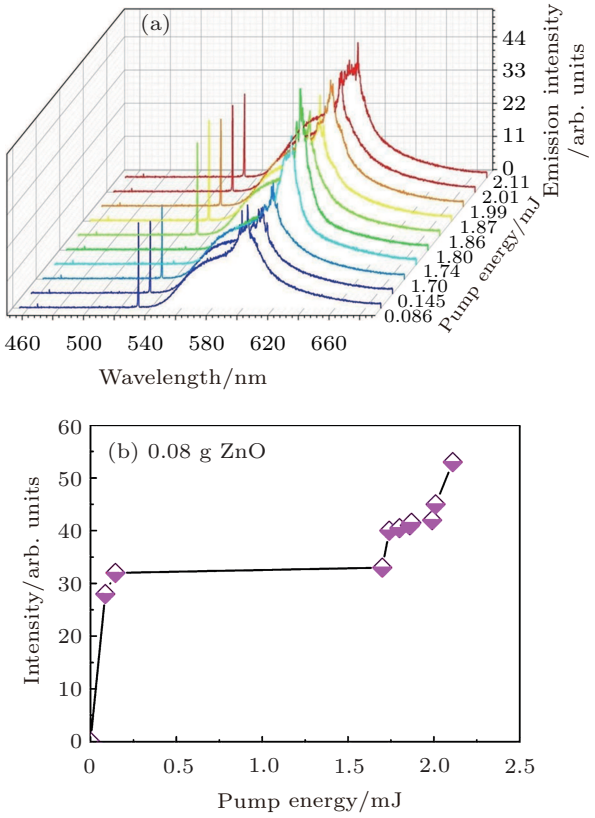


Fig. 5. (color online) (a) Evolution of the emission spectra of dye-doped negative LC solution inside the cell with (0.08 g) ZnO NPs as the pump energy increases from 0.086 mJ to 2.11 mJ. (b) Peak intensity of emission spikes as a function of pump pulse energy obtained from panel (a).

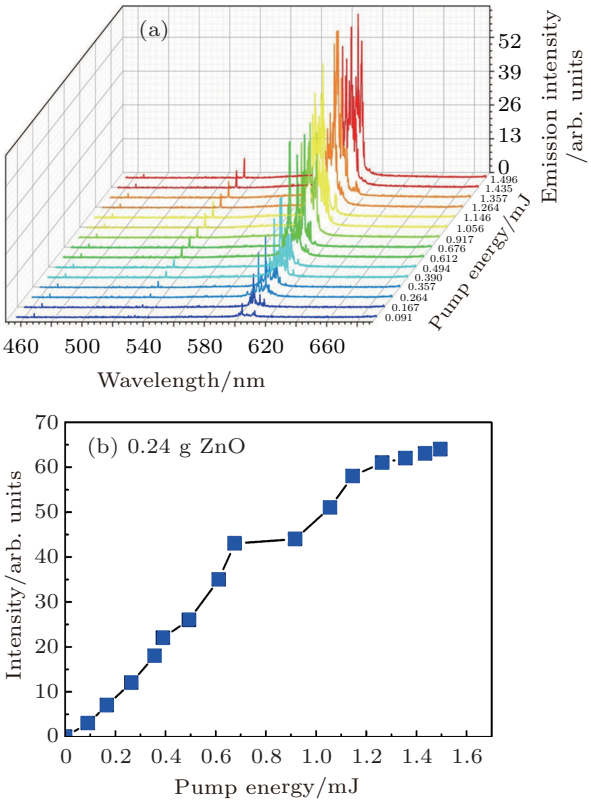


Fig. 7. (color online) (a) The emission lasing spectra of dye-doped negative LCs solution with (0.24 g) ZnO NPs when pumped at different energies. (b) Lasing emission peak intensity versus pumping energy obtained from panel (a).

We can also clearly understand that the lasing intensity of dye-doped negative LCs has been enhanced in presence of ZnO NPs and such an enhancement strongly depends on concentrations of NPs. The lasing intensity of the dye-doped negative LCs with ZnO NP material has been enhanced due to constructive combination emissions from ZnO NPs and LCs. Because they have the same wavelength span in their emission bands and light scattering phase at room temperature, hence, incident photons get elastically scattered to excite more dye molecules and give enhanced photon counts. Cao *et al.* have reported earlier that the random lasing of dye-doped ZnO NPs can be enhanced using light scattering property of the ZnO.[2]

The emission intensity in dye-doped negative LCs with ZnO NPs increases with the concentration of ZnO NPs. It is owing to the increase of scattering area with concentration of ZnO NP materials. In our previous study,[17] we have utilized this fact to enhance the lasing intensity in DDCLCs doped with Ag NPs. It is also worth to notice from Figs. 5(a), 6(a), and 7(a) that not only the lasing intensity of dye-doped negative liquid crystal is enhanced in the existing of ZnO NPs, but also the emission peak is shifted towards the longer wavelength. The redshift in emission bands is ascribed to the change in effective refractive index of the negative liquid crystal due to the presence of ZnO NPs. The local orientation of the LC molecules in close proximity to the nanostructures appears to give rise to a shift in the emission band. In the case of imperfect planar nematic, dielectric fluctuation contributes more to the polarization of the scattered light, while the ZnO NPs contribute more to the scattered light. Therefore, it should be noted that the photon transport is governed by the disorder even in the liquid crystal phases and that the less dipolar liquid crystal molecule favors high mobility in a liquid crystal phase. From photon transport point of view, the aromatic core in the liquid crystal molecule provides a hopping site for photons and the self-organization of liquid crystal molecules makes a closely packed molecular aggregate favorable for fast photon transport. Thus, the NPs have finite dipole moments that should interact with the dipole moments of LC molecules. Due to dipole–dipole interaction between the NPs and negative liquid crystal molecules, the contribution of dipole moment along the LC molecule direction increases. This increases the value of spontaneous polarization in the ZnO embedded LCs, which is a measure of random lasing. A strong local electric field is produced due to the large dipole moment of the ZnO materials. It induces a dipole moment to the neighbor negative molecules and reinforces the polarization realignment under electric fields. Energy transfer between LC molecules and ZnO structures increases the dye molecular interaction.

The stronger fluorescence emission can be significantly amplified in their diffusive routes through a multiple scattering mechanism of the randomly distributed ZnO NPs so as to generate anisotropic random lasing shown in Figs. 5(a), 6(a), and 7(a). To explain the controllability of ZnO NPs in random lasing, we further measured the emission spectra of the 8 wt%, 16 wt%, and 24 wt% ZnO NPs added dye-doped negative liquid crystal and ZnO NP-free dye-doped negative liquid crystal cell. Measured emission spectra are shown in Figs. 4, 5(a), 6(a), and 7(a), respectively. Apparently, the emission spectra of dye-doped negative liquid crystal containing ZnO NP cells increase when the concentration of ZnO NPs increases from 8 wt% to 24 wt%. This is owing to that the direction of transition dipole moments of the dye molecules may follow the direction of the LC director fluctuation. This occurrence causes the absorption of the dye molecules and thus the spontaneously emitted fluorescence increases with the increase of the pump energy after the addition of the ZnO NPs. This phenomenon leads to the increase of the intensity of the scattering fluorescence light via the multi-scattering of ZnO NPs and thus the enhancement of the obtained random lasing strength. The contrast between the refractive indices of negative LCs and ZnO NPs experienced by the Z component of fluorescence light propagating along y direction in the XY plane increases from $|n_{\rm e}-n_{\rm NPs}|=|1.5778-2.37|$ to $|n_{\rm o}-n_{\rm NPs}|=|1.4833-2.37|$. This variation decreases the diffusion constant and increases the scattering strength, and thus increases the random lasing intensity for the Z component. On the other hand, the refractive indices experienced by X component of the scattering fluorescence will increase from $n_{\rm o}$ to $n_{\rm e}$ with increasing ZnO NP concentration from 8 wt% to 24 wt%. Therefore, the contrast between the refractive indices of negative liquid crystals and substrates for the Y component increases from $|n_{\rm o}-n_{\rm g}|=|1.4833-1.53|$ to $|n_{\rm e}-n_{\rm g}|=|1.5778-1.53|$ when increasing ZnO NPs from 8 wt% to 24 wt%, where $n_{\rm g}=1.53$ (refractive indices of substrates). This result indicates that the confinement strength for the X (Y) component in the negative LC layer will increase with the increase of ZnO NPs from 8 wt% to 24 wt%. The above mentioned findings suggest that both the index contrasts between the negative liquid crystals and ZnO NPs and between the negative liquid crystals and the substrates are crucial in determining random lasing. The contribution levels of the elements influence the tunableness of random lasers, including the strength of the scattering due to the index contrast between negative LCs and ZnO NPs, the strength of spontaneous emission due to the orientation of dye molecules and the strength of confinement due to the index contrast between negative liquid crystals and substrates.

To interpret the experimental observation better, we take into account the fact that $n_{\rm th}$ (threshold population inversion) is in inverse proportion to the stimulated emission cross section

σ_{em}^{dye}, which can be described by the following equation:[28]

$$n_{th} \approx n_{th}^{0} \approx -\frac{\ln R}{\ell \sigma_{em}^{dye}}, \quad (1)$$

where ℓ is the dimension of active laser medium in cells, and R is the effective reflection coefficient, representing the residual optical feedback caused by the negative LC cells. This means that we have $n_{th,590} > n_{th,605}$ by considering $\sigma_{em,605}^{dye} > \sigma_{em,590}^{dye}$. The lasing mode near the wavelength of 605 nm that matches with the spontaneous emission peak of DCM molecules containing ZnO nanoparticles must first reach the condition of threshold population inversion. Equation (1) for threshold population inversion can be changed into

$$n_{th} = -\frac{\ln R}{\ell \sigma_{em}^{dye}(1+cf)}, \quad (2)$$

where f is the volume fraction of negative LCs (the negative LCs in the active medium is a variable) and c is the phenomenological constant. It is obvious that there is a decreasing function of lasing wavelength in the emission frequency band. We can infer that the redshift effect observed here is due to the fact that the velocity of threshold population inversion of dye molecules increases as adding NPs, so long wavelengths are more amplified than short wavelengths. Obviously, such a shift provides much wavelength tunability, and it is possible that the ability of control emission wavelength can be extended by varying the ratio of doped LCs. Hence, we believe that the coherent feedback is caused by light scattering from the negative LCs combined with the ZnO NPs.

4. Conclusion

In conclusion, we investigated the negative LCs-induced random lasing changes in the sample containing ZnO NPs of wavelength-scale for the first time. Experimental results indicate that frequency shifts, Q factor changes, and threshold behaviors are induced by negative LCs. However, when ZnO nanoparticles are added, the random lasing is attributable to the enhancement of the fluorescence emission via the multi-scattering of NPs in the diffusion rout of the NPDDLC, and the threshold gradually reduces with the increase of the concentration of ZnO NPs. The plots of both frequencies and Q factors of modes versus pump energy are almost linearly (as shown in Fig. 7(b)). Hence, it exhibits a lower sensitivity compared with the results in the cholesteric liquid crystals.[24] We believe that the structural disorder introduced in negative LCs has an impact on the lasing of samples. This disorder may create more actives and reduce the sensitivity to negative LCs. Moreover, these results will give guiding significance for the manufacture of photonic devices based on random lasing.

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