Supporting Information

Coherent Random Lasing in Colloidal Quantum Qot Doped Polymer Dispersed Liquid Crystal with Low Threshold and High Stability

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Experimental Details

Chemicals

Cadmium oxide (CdO, 99.99%), Zinc acetate (Zn(AH)·2H2O, 99.9% powder), selenium (Se, 99.999%, powder), 1-octadecene (ODE, 90%), oleic acid(OA, 90%), oleylamine (OAm, 70%), 1-dodecanethiol (DDT, 98%), tributylphosphine (TBP, 98%) were purchased from Aldrich, aladdin and Alfa Aesar. Acrylic resin and photoinitiator were purchased from Sartomer. All reagents were used as received without further experimental purification.

Synthesis of ZnCdSeS/ZnS Red QDs

For a typical synthesis of red ZnCdSeS/ZnS alloyed QDs, 5.8 g of CdO, 30 g of 1-octadecene (ODE) and 21 g of oleic acid (OA) were placed in a 500 ml three neck flask under vigorous stirring and degassed at 160 ºC for 30 min. Then the reaction flask was heated to 300 ºC in 15 min under N_2, yielding a clear solution of $Cd(OA)_2$. After the temperature was elevated to 300 ºC, 3 ml of oleylamine (OAm) was dropped into the system at the rate of 1ml/min. subsequently, 3 mmol of Se in 1.5 ml TBP was quickly injected into the reaction system and maintained for 5 min, and 1 ml of 1-octanethiol(DDT) dispersed in 6 ml ODE was slowly purged into above mixture at the rate of 2 ml/min for the formation of CdSeS core with chemicals composition gradient. For the following ZnS shelling, 4.2 g of $Zn(AH)_2·2H_2O$ was introduced into the mixture at the temperature of 60 ºC and degassed for 30 min at 160 ºC to remove water. After then the temperature was raised to 315 ºC and 3 ml of OAm was dropped into the system at the rate of 1 ml/min. At the end, 1 ml of DDT dispersed in 6 ml ODE was dropwisely injected to the core growth solution and the shelling reaction was maintained at 315 ºC for 60 min for ZnS shell growth. The reaction was cooled to room temperature naturally and octane and ethanol was added, then the suspension was centrifuged and the supernatant was removed and the procedure was repeated for three times. The red ZnCdSeS/ZnS alloyed QDs were subsequently dispersed in toluene for further characterization and usage.

Preparation of red QDs resin

The resin was selected as acrylic resin as its ideal compatibility with red ZnCdSeS/ZnS QDs. The brief preparation of red QDs resin as follows: A certain amount of acrylic resin and 5 wt% of the photoinitiator 184 were added into a glass

flask at ambient conditions and stirred for 30 min, obtaining a clear solution, marked as sample A. Then as-prepared red ZnCdSeS/ZnS QDs powder was put into a 20 ml round flask and 10 g of sample A was introduced into it. The mixture was mechanically stirred for 4 hours at room temperature and protected from light and dispersed for further 30 mins under ultrasonic condition. Ultimately, a uniform and transparent red QDs resin colloid was obtained.

Measurement of random laser

The excitation laser was provided by a frequency doubled Nd:YAG pulse laser (wavelength: 532 nm, repetition rate: 10 Hz, pulse duration: 10 ns). A λ/2 waveplate for 532 nm light and a polarizer were placed in front of the excitation laser to control the pump energy per pulse incident on the samples. Each pulse was divided into two parts using a beam splitter, and the smaller portion was monitored with an energy meter The excitation beam was focused on the capillary tube using a cylindrical lens. The length and width of the pump stripe on the sample was fixed at 5 mm and 1 mm, respectively.

Characterizations

UV-vis absorption and PL spectra were measured by Shimadzu UV-1780 and HORIBA Fluoromax-4 fluorescence spectrometer, respectively, transmission electron microscopy (TEM) studies were performed using a JEOL JEM-2010 electron microscope operating at 200 kV. Micro-images of QD-PDLC structure were measured by OLYMPUS CX31P-OC-2 polarizing microscope. Fluorescence micrographs of QD-PDLC were measured by OLYMPUS IX-73 Fluorescence microscope. The pump laser energy were detected by GENTEC laser energy meter.

Figures and Tables

Figure S1. Typical acrylic resin structures.

Figure S2. Micro-structure of the QD-PDLC with QD concentrations of 2 wt%, 5 wt%, 7 wt%, and 10 wt% imaged with a polarizing optical microscope with (a)-(d) parallel and (e)-(h) fluorescence microscope.

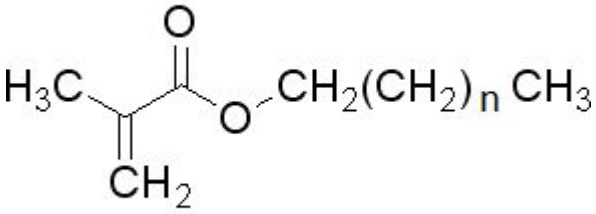
Figure S3. Micro-pictures of QD-PDLC with 30 wt%，40 wt%，60 wt%，70 wt% LC doping ratios under a polarizing optical microscope with parallel polarizers.

Figure S4. Output intensity (red line) and FWHM (black line) of the emission spectrum from capillary tube with different inner diameter as functions of laser pumping energy.

Figure S5. Plots of random laser intensities and thresholds measured under continuous excitation using 532 nm nanosecond laser pulses with pump influence of 100 μJ/cm^2 in air over 15 days (3 hours each day).

Table S1. QDs based random lasing properties reported in recent years.

(a)



(b)

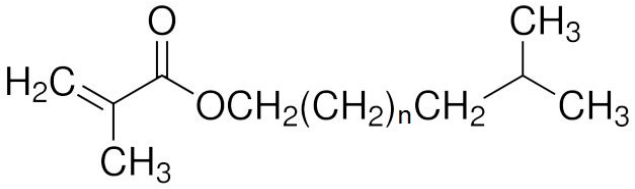


Figure S1. (a, b) typical acrylic resin structures.

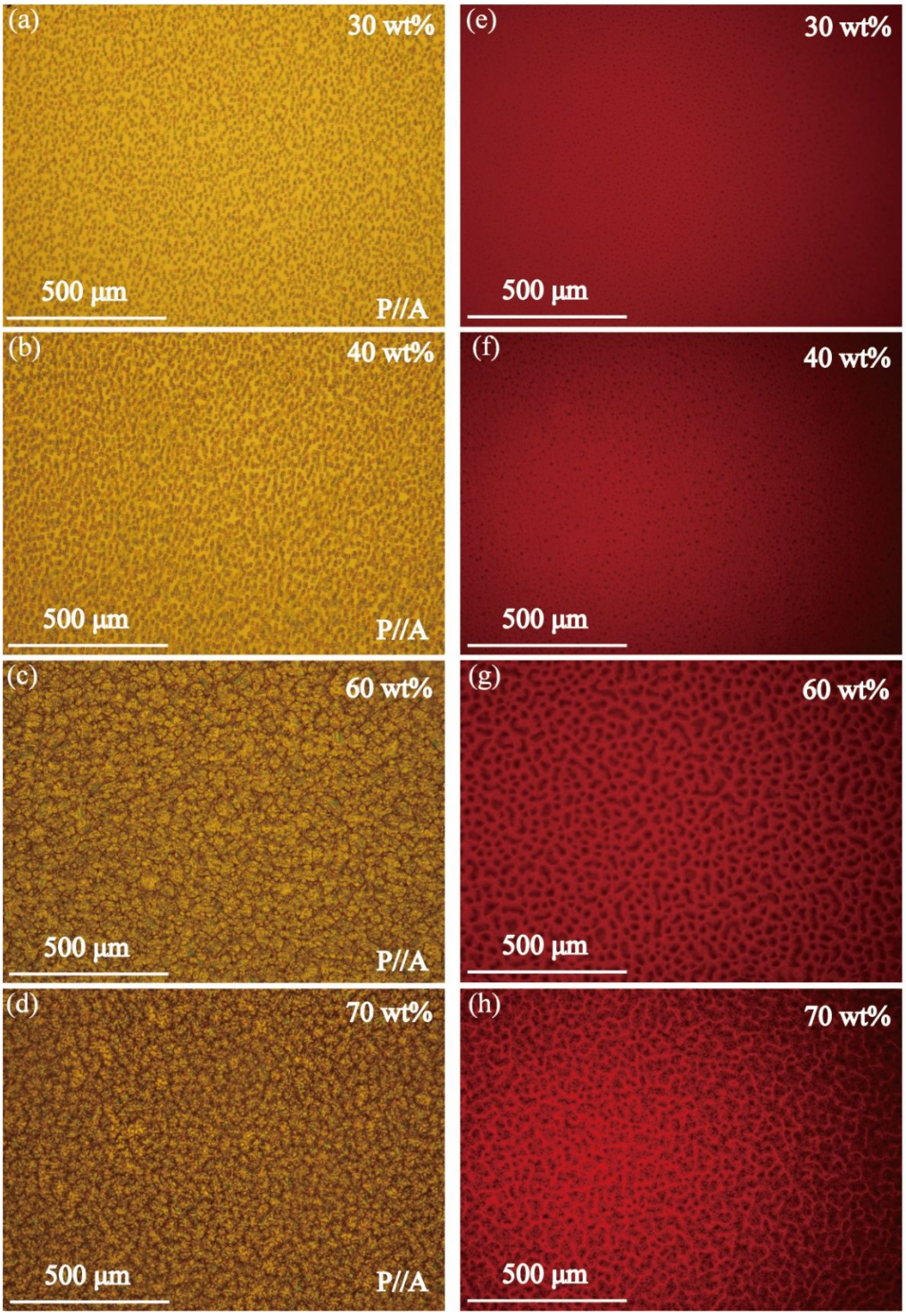


Figure S2. Micro-structure of the QD-PDLC with QD concentrations of 2 wt%, 5 wt%, 7 wt%, and 10 wt% imaged with a polarizing optical microscope with (a)-(d) parallel and (e)-(h) fluorescence microscope.

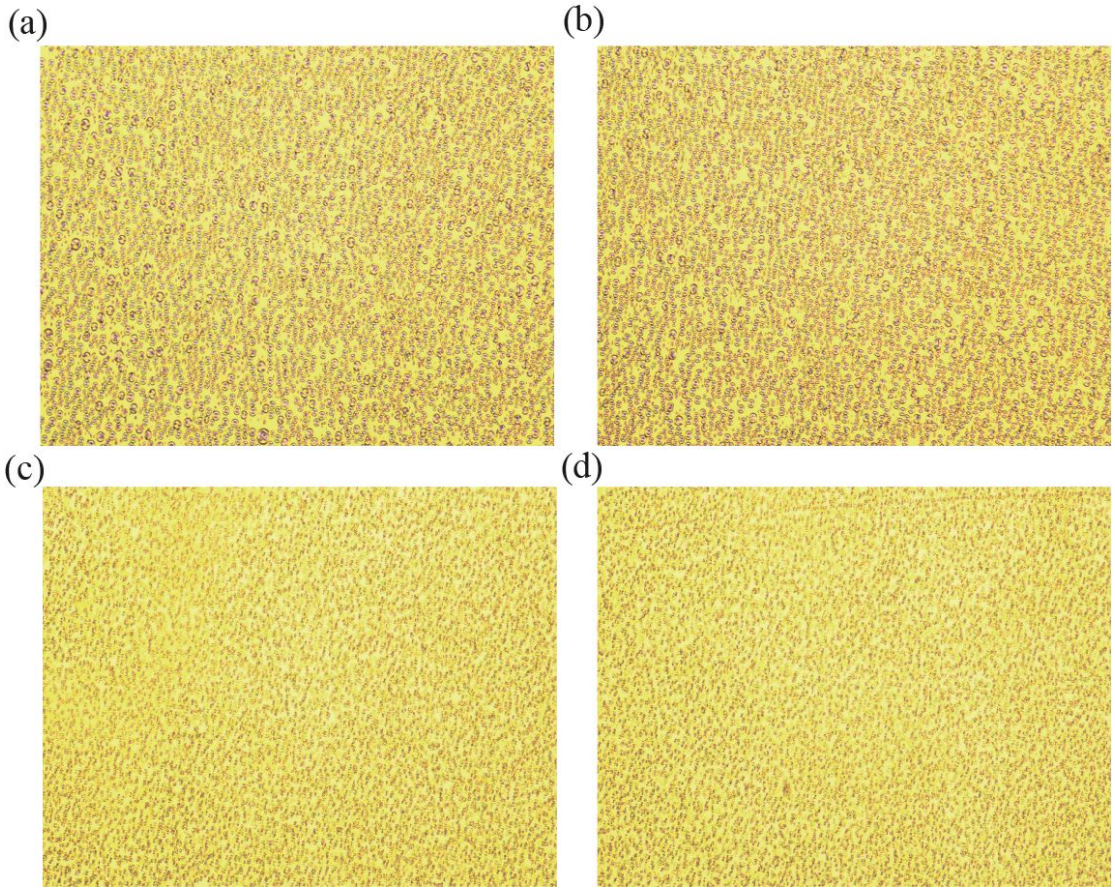


Figure S3. Micro-pictures of QD-PDLC with 30 wt%, 40 wt%, 60 wt%, 70 wt% LC doping ratios under a polarizing optical microscope with parallel polarizers.

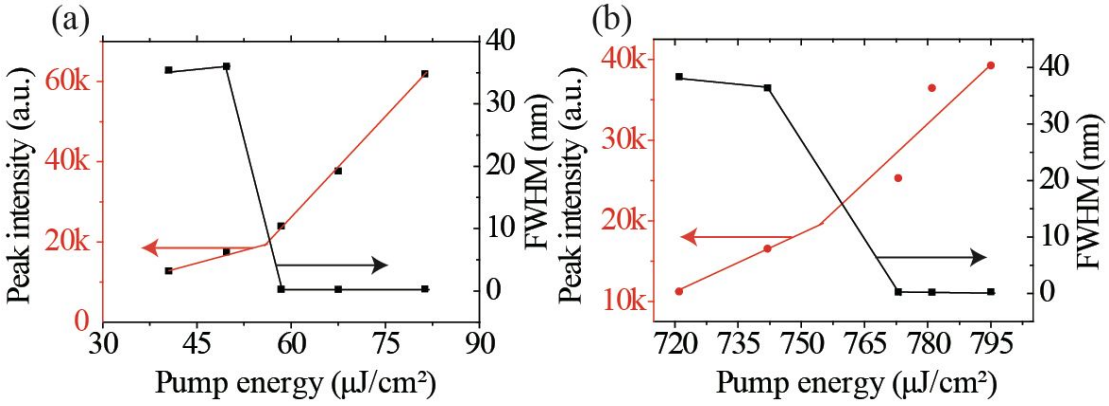


Figure S4. Output intensity (red line) and FWHM (black line) of the emission spectrum from capillary tube with different inner diameter as functions of laser pumping energy.

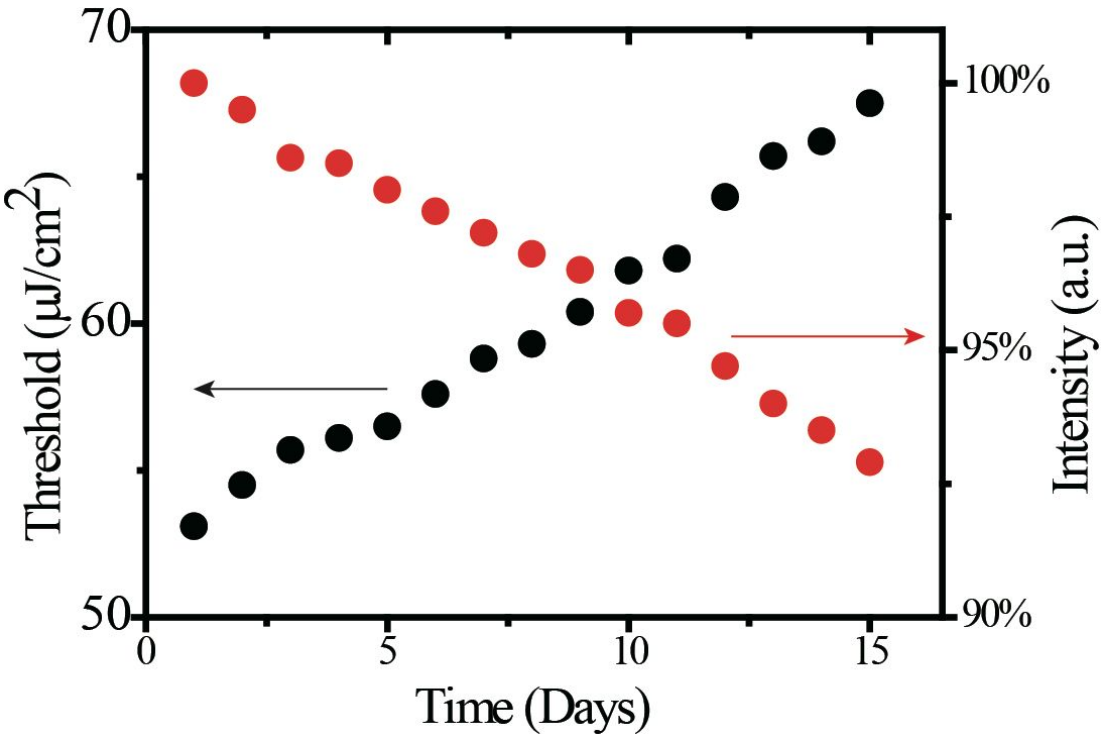


Figure S5. Plots of random laser intensities and thresholds measured under continuous excitation using 532 nm nanosecond laser pulses with pump influence of 60 μJ/cm^2 in air over 15 days (3 hours each day).

Table S1. QDs based random lasing properties reported in recent years.

Active Material	Structure	Threshold	Pump Pulse Length	Ref.
ZnCdSeS/ZnS QDs **(Our work)**	QDs doped polymer dispersed liquid crystal	50 μJ/cm^2	10 ns	--
Carbon dots	Carbon Dots/Au–Ag Nanowire Composites	48 μJ/cm^2	5 ns	1
Carbon Dots	Carbon dots deposited on the GaN nanorods film	3.89 mJ/cm^2	3-5 ns	2
CdSe/ZnS QDs	QDs deposited on Ag nanoparticles film	2.2 mJ/cm^2	5 ns	3
CdSe/CdS QDs	QDs thin film	2.5 mJ/cm^2	1.3 ns	4
ZnO QDs	ZnO film	72.1 μJ	3-5 ns	5
CdSe/ZnS QDs	QDs doped disordered polymer	7 mJ/cm^2	10 ns	6
Perovskite QDs	QDs deposited on wrinkled reduced graphene oxide	10 μJ/cm^2	55 ps	7
Perovskite QDs	QDs embedded glass	200 μJ/cm^2	50 fs	8
Perovskite QDs	QDs/SiO_2 composite film	40 μJ/cm^2 .	100 fs	9
Perovskite QDs	$CsPbBr_3$ QDs film	970 μJ/cm^2	100 fs	10

Reference

[1] Yuan, F,; Xi, Z.; Shi, X. Ultrastable and Low-Threshold Random Lasing from Narrow-Bandwidth-Emission Triangular Carbon Quantum Dots. *Adv. Opt. Mater* **2018**, *7*.6.

[2] Liao,; W. C.; Liao.; Y. M.; Su,; C. T. Plasmonic Carbon Dots Decorated Nanostructured Semiconductors for Efficient and Tunable Random Laser Action. *ACS Appl. Nano. Mater* **2018**, *1*. 152-159.

[3] Yao, Y. C.; Yang, Z. P.; Hwang, J. M.; Su, H. C.; Haung, J. Y.; Lin, T. N.; Shen, J. L.; Lee, M. H.; Tsai, M. T.; Lee, Y. J. Coherent and Polarized Random Laser Emissions from Colloidal CdSe/ZnS Quantum Dots Plasmonically Coupled to Ellipsoidal Ag Nanoparticles. *Adv. Opt. Mater.* **2016**, *5*, 1600746.

[4] Gollner, C.; Ziegler, J.; Protesescu, L.; Dirin, D. N.; Lechner, R. T.; Fritz-Popovski, G.; Sytnyk, M.; Yakunin, S.; Rotter, S.; Yousefi Amin, A. A.; Vidal, C.; Hrelescu, C.; Klar, T. A.; Kovalenko, M. V.; Heiss, W. Random Lasing with Systematic Threshold Behavior in Films of CdSe/CdS Core/Thick-Shell Colloidal Quantum Dots. *ACS Nano* **2015**, *9*, 9792-9801.

[5] Sun, T. M.; Wang, C. S.; Liao, C. S. Stretchable Random Lasers with Tunable Coherent Loops. *ACS Nano* **2015**, *9*.12436-12441.

[6] Cao, M.; Zhang, Y.; Song, X. Random lasing in a colloidal quantum dot-doped disordered polymer. *Opt. Express* **2016**, *24*.9325-9331.

[7] Hu,; H. W.; Haider,; G.; Liao,; Y. M. Wrinkled 2D Materials: A Versatile Platform for Low-Threshold Stretchable Random Lasers. *Adv. Mater* **2017**,*29*.1703549.

[8] Yuan, S.; Chen, D.; Li, X. In Situ Crystallization Synthesis of CsPbBr3 Perovskite Quantum Dots Embedded Glasses with Improved Stability for Solid-State-Lighting and Random Upconverted Lasing. *Appl. Mater & Inter* **2018**,*10*.18918-18926.

[9] Li, X.; Wang, Y.; Sun, H. Amino-Mediated Anchoring Perovskite Quantum Dots for Stable and Low-Threshold Random Lasing. *Adv. Mater* **2017**,*29*.1701185.

[10] Tang, X.; Hu, Z.; Chen, W. Room Temperature Single-Photon Emission and Lasing for All-Inorganic Colloidal Perovskite Quantum Dots. *Nano Energy* **2016**, *28*.462-468.