Lifetime enhancement of a circulated cooling perovskite liquid quantum dots system for laser illuminations

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ABSTRACT Perovskite quantum dots (QDs) attracted a lot of attention recently due to their high light conversion efficiency, and high purity. However, perovskite materials are sensitive to heat. High temperature will cause serious quenching problem of the perovskite QDs. In order to solve the QDs thermal quenching problem without destroying their optical characters. A circulating liquid quantum dots converter (CQD-converter) was developed. A closed loop pump tube coated with Teflon was utilized to prevent perovskite QDs from the external environment. A peristaltic pump was utilized to drive the liquid QDs through a semiconductor cooling plate for dissipating the heat of the QDs solution. The lifetime of the perovskite QDs can be significantly improved under a 450nm laser excitation. The effects of temperature and flow rate on the optical properties of QDs were also investigated. Compared to the static liquid quantum dots(SQD-converter), which quenched after 7 min, the optical properties were maintained after 600 min for the CQD-converter.

INDEX TERMS Circulating liquid perovskite quantum dots, laser, semiconductor cooling plate.

I. INTRODUCTION

Perovskite QDs(QDs) are widely used in battery[1], display[2], medical[3, 4], and biological fields[5] because of their tunable emission wavelength, high purity of color, wide absorption spectrum, narrow fluorescence spectrum, high stability, high quantum yield, and excellent solution processing ability[6]. Perovskite QDs are expected to replace phosphors as the core material for next-generation optoelectronic devices[7]. As an up-conversion luminescent material, the high purity of the perovskite QDs requires a purer excitation source to excite (such as blue laser or UV laser). However, the applications of perovskite QDs still have some limitations. A fatal reason is the poor thermal stability of the perovskite QDs (agglomeration quenching, easy water-oxygen decomposition, etc.)[8]. Due to the extremely high energy density of the high power laser, the conventional packaging method makes it difficult for the perovskite QDs to resist high temperature damage. It is difficult to apply to laser illumination or display, which suppressed the characteristics of high color purity.

Therefore, many scholars have studied how to improve the reliability of perovskite QDs[9, 10]. A material modification is an effective method to improve perovskite QDs stability[10-12]. For example, a coating (SiO₂ coating, AlO₃ coating, etc.) [13-15] was formed on the QDs surface during the progress of the synthesis to improve stability in water, light, and heat. The composite of Mn²⁺ doped CsPbCl₃ perovskite embedded in zeolite-Y was successfully prepared by Shi Ye’s group[16]. In this way, synthetic QDs had much better resistance to elevated temperature and moisture. In addition, using porous adsorbent materials[14, 17, 18] (such as zeolite or porous silicon) to improve QDs stability is also effective. The above researches show optimizing QDs materials can indeed improve QDs efficiency and improve stability. However, those methods are difficult to avoid the loss of stokes, and the heat production problem is still serious. Hence, some scholars focus on the issue of heat dissipation[19-21]. Jehong Park, et al.[22] proposed placing a thermally graded layer (TGL) between the phosphor layer and the aluminum layer to efficiently transfer the heat generated by the phosphor layer to a high thermal conductivity aluminum. A QDs film with a spherical shell structure was proposed by Chen’s group to improve the optical
and thermal performance for WLEDs[23]. Tang’s group[24] studied the location of K2SiF6:Mn++ (KSF) phosphor and the green CsPbBr3 QDs on the optical and thermal properties of WLEDs. It could demonstrate that the phosphor layer under the QDs layer can enhance heat dissipation.

However, integrating QDs into the solid mixture of light-emitting diode devices, the conversion efficiency of QDs will decrease, which is called “the host matrix effect”[25]. Maintaining QDs in the liquid state is a way not only to effectively ensure conversion efficiency but also improve QDs stability. Using liquid QDs as luminescent materials and heat transfer materials would be an effective method[26-30]. The red luminescent perovskite QD solution was used as the color conversion layer and integrated with the original YAG:Ce-based light-emitting diode. The Ke Bi’s team[31] prepared a warm white LED device. As a color conversion layer, the liquid type QD not only maintained the initial quantum efficiency but also compensates for the short red emission and the relatively low color rendering index (CRI) of the visible light spectrum region of the phosphor. Li[25] proposed a new LED package that injected QDs into the LED device in a solid-liquid mixed state. Liquid QDs can not only improve the optical performance of the light-emitting device but also improve thermal stability. Whereas, for high-power laser illumination, due to the concentration of the laser beam and the concentration of energy, the single static liquid QDs cannot transfer heat rapidly, and still cause thermal quenching of the QDs.

In this work, we proposed a circulating liquid quantum dots converter (CQD-converter) that avoids thermal quenching and improves the stability of laser-excited QDs illumination. The whole loop is filled with perovskite QDs solution. The entire circulation line uses a pump tube coated with Teflon to ensure that the circulation line is not affected by the environment. The pump tube is driven by a peristaltic pump that circulates the liquid QDs in the line. And the pump tube is cooled by the semiconductor cooling plate. The effects of cryogen temperature and peristaltic pump speed on the optical properties of perovskite QDs were investigated. The static liquid quantum dots converter (SQD-converter) were quenched after 7 min under high power laser. However, the optical properties were maintained at 600 min under liquid circulation. Our work may inspire the application of QDs for high power laser lighting or display.

II. Experimental

Perovskite QDs were synthesized based on the method by Yu Tong group[32]. 0.1100g lead(II) bromide (PbBr2, >98%), 0.0326g caesium carbonate (Cs2CO3, >99.9%), 10ml octadecylene (ODE, >90%), 2ml oleylamine (OLA, >80%) and 0.1ml oleic acid(OA, >90%) were mixed evenly in a 30ml reagent bottle (above-mentioned materials were purchased from Aladdin). The reaction was processed by ultrasonication at the power of 150W for 5min. The ultrasonication tip was immersed over 1/2 of the reaction mixture. In order to accelerate the crystallization rate of the reaction, the mixture was immersed into the ice water for 3 min to 5 min. After the reaction was completed, two centrifugations were carried out to remove the redundant oleic acid and oleylamine. The first centrifugation was to extract the precipitation of the reaction at a speed of 10000 r/min for 10 min. Then, the precipitation was dissolved in the unreacted precursor of hexane(C6H14, >97%, purchased from Richjoint). In the next step, the supernatant was extracted to preform a second centrifugation at a speed of 3000r/min for 5 min to obtain a smaller particle size perovskite QDs. The final yellow solution consisted of green-emitting perovskite QDs, which were dispersed in hexane.

![Fig.1](image1)

Fig.1 (a) The TEM image, (b) the size distribution histogram and (c) the PL emission and absorption spectrum of the perovskite QDs.

The regular square morphology of the QDs was characterized by transmission electron microscope(TEM) as shown in Fig.1(a). The histogram is shown in Fig.1(b) revealed that the QDs have an average particle size of 13.56nm with a normal distribution. Fig.1(c) shows the absorption and PL emission spectra from 400nm to 580nm. The insert image in Fig.1(c) is the liquid green-emitting perovskite QDs excited under a UV light. The peak wavelength of the PL emission spectrum is 514nm. The full width at half maximum (FWHM) of the PL emission spectrum is 18nm.

The experimental setups are illustrated in Fig.2 including two types of liquid QDs configuration and test equipment. As shown in Fig.2(a), the SQD-converter was a silica glass cuboid with a hollow rectangular transparent window (50 mm × 13 mm × 5 mm) and two connectors (14 mm × ∅ 4 mm). Each connector was connected to a syringe through a Teflon tube in order to prevent the air pressure increasing rapidly during the experiment. The silica glass cuboid was filled with liquid perovskite QDs. The CQD-converter is shown in Fig.2(b). It has the same silica glass cuboid, but the two connectors of the cuboid were connected to a peristaltic pump (Kamoer, LabUIP220v) and a semiconductor cooling plate (40mm×40mm×1mm) through a Teflon tube. The whole loop is finally fulfilled with liquid QDs. During the optical measurement, the silica glass cuboid was placed in an integrating sphere with a diameter of 1.2 m. The remaining equipment was connected to the outside of the integrating sphere to avoid optical power absorption. A laser source (LWBL-450nm-10W-F) was installed at the top of the integrating sphere through an optic fiber. When the peristaltic pump and laser were turned on, the liquid QDs began to circulate stably transferring the heat generated by converting...
the blue laser light to the cooling block. The optical parameters were collected through a spectroradiometer from Ocean Optics®. At the semiconductor cooling plate temperature of 5 °C and the peristaltic pump flow rate of 30 ml/min, the synthesized QDs solution was separately injected into two devices under a laser excitation of 0.5 A to measure their thermal stability.

III. Result and discussion

To investigate the effect of heat dissipation of the CQD-converter, the infrared data of two converter were compared. As shown in Fig.3, the average temperature of the CQD-converter is lower than the SQD-converter under 0.5A laser excitation. For the SQD-converter, in the first 200s, the temperature rapidly increases with time. After 200s, the temperature rise trend becomes slow. It may be caused by a portion of the heat removed by the volatilization of hexane in the perovskite QDs solution. Until 750s, the temperature rises to a maximum of 76°C. At this moment, the hexane is rapidly evaporated. Subsequently, the laser was turned off and the temperature of the excitation region is parabolically decreased. For the CQD-converter, When the laser was turned on, the temperature rises rapidly to 50 °C. Under the action of circulating medium and semiconductor cooling plate, the temperature is stable quickly. Due to the turbulent flow in the whole loop, the temperature fluctuates up and down within 50 °C, but the overall tends to be stable. Highest temperature IR images of two converter is shown in the insert photographs in Fig.2. From the IR images, it can be seen that in the region of the excited silica glass cuboid, the temperature of the SQD-converter is higher than the CQD-converter.

In order to verify the advantages of the CQD-converter on the lifetime, the spectrum after stimulated by a 450nm laser (at 500mA) were collected as shown in Fig.4. Both of the spectrum of the SQD-converter and (b) the CQD-converter decreases with time. However, the spectrum (480nm-550nm) of the excitation light of the SQD-converter decreases dramatically within 420s. The peak output value of the excitation light (513nm) of the SQD-converter reduces from 0.00413W/nm to 0.00087W/nm. the optical power of the green emission reduces from 0.102W to 0.026W (Fig.4(a) inset image). Compared with the SQD-converter, the excitation light of the CQD-converter decreases much slower. The peak output value of the excitation light (513nm) reduces from 0.032W/nm to 0.026W/nm. The optical power of the green emission reduces from 0.8041W to 0.6053W(Fig.4(c) inset image). For the SQD-converter, initially, as the temperature of the SQD-converter increases continuously, the spectrum of excitation light decreases rapidly from 0 to 120s. Between 120 to 360s, the peak value of excitation light drops slightly. It indicated that there was no obvious quenching phenomenon of the perovskite QDs during this period. After 360s, the reason for the reduction of the excitation light was mainly caused by the quenching of the QDs. For the CQD-converter, after 7200s cycling, the peak output value of the excitation light (513nm) rose from 0.032 W/nm to 0.045 W/nm, an increase of 28.9%. As the irradiation time increase, the QDs began to quench and the peak output value of the excitation light gradually decreases. After 10 hours of irradiation, the peak drops by19.5%.

From the above results and discussion, it would be easy to deduce that the CQD-converter have better stability in optical performance. Fig.5(a) shows a comparison of the radiation power of the SQD-converter and the CQD-converter. The change rule of radiation power is in accordance with the variation of the output spectrum. Due to the thermal effect, the radiation power of the SQD-converter goes down faster than...
the CQD-converter. For the SQD-converter, the radiant power drops from 0.218W to 0.133W within 420s (about 38.99%). Nevertheless, the CQD-converter only drops from 1.38W to 1.14W within 36000s (about 17.39%). As shown in Fig.5(b), The offset of the CIE (x, y) coordinate diagram of the SQD-converter is large. The excitation light began to turn blue after 120s, which corresponds to the decrease of radiation power. The CIE (x, y) coordinate diagram of the CQD-converter has a small bias range within 36000s.

![Fig.4. (a) The output spectrum variation of the SQD-converter. The inset image is the optical power of the green emission. (b) Green peak spectrum of the SQD-converter (zoomed in). (c) The output spectrum variation of the CQD-converter. The inset image is the optical power of the green emission. (d) Green peak spectrum of the CQD-converter (zoomed in).](image)

The influence of the semiconductor cooling plate on CQD-converter is discussed by changing the temperature of the semiconductor cooling plate. A 450nm laser (500mA) and a 30ml/min flow velocity of the peristaltic pump were used to this experiment. The temperature of the semiconductor cooling plate was controlled via PID method. The thermocouple collected the actual temperature on the semiconductor cooling plate. We can observe the collected temperature through the display window.

![Fig.5 (a) The total radiation power variation and (b) the CIE (x, y) coordinate diagram of the SQD-converter and the CQD-converter](image)

At first, the temperature of the semiconductor cooling plate was set to 20°C. Subsequently, the temperature decreased by 5°C. The output spectrum variation of the CQD-converter is shown in Fig.6(a). When the temperature drops from 20°C to 0°C, the output spectrum has an upward trend, but there is no obvious redshift. The peak output value of the excitation light increases from 0.019W/nm to 0.027W/nm. The grown rate is 29.63%. The optical power of the green emission rises from 0.529W to 0.712W (about 25.70%). This may be due to the semiconductor cooling plate temperature drop, more heat produced by laser driving the CQD-converter is dissipated. As the temperature decreases, the peak output value of the excitation light rises slowly. The heat generated by the laser drive the CQD-converter was quantitative over a long period
of time. Fig.6(b) shows the trend of total radiation power and the luminous flux variation with the temperature of the semiconductor cooling plate decrease. The variation of the total radiation power is similar to the variation of luminous flux variation. As the temperature of the semiconductor cooling plate gradually decreased, both of them show a steadily upward trend. Meanwhile, the rising slope gradually flattens. The CIE (x, y) coordinate diagram of the variable temperature CQD-converter is shown in Fig.6(c). When the temperature drops from 20 °C to 0 °C, the CIE (x, y) coordinate are significantly offset. CIE color coordinates moves the blue side from (0.141,0.321) at 20 °C to the green side (0.134,0.378) at 0 °C. It indicates that Optical performance variation with temperature change can be used in fields such as temperature sensors.

Apart from studying the temperature change, we also explored the influence of the flow velocity of the peristaltic pump to the CQD-converter. Set the temperature of the semiconductor cooling plate to 5°C. The laser is driven by a current of 500mA. The initial flow velocity was 30ml/min. Subsequently, the peristaltic pump flow velocity was increased in increments of 20ml/min.

The output spectrum variation with different flow velocities of the CQD-converter is shown in Fig.7(a). As the flow velocity changes from 30ml/min to 170ml/min, the output spectrum shows an upward trend. For the excitation light(480nm-550nm), when the flow velocity rises from 30ml/min to 170ml/min, the peak value increases from 0.013W/nm to 0.032W/nm, increased by 59.38%, the optical power of the green light emission increases from 0.339W to 0.773W, increased by 56.14%. Table 1 shows the optical power of the green light emission and increment for each 20ml/min flow velocity increments. When the flow velocity of the peristaltic pump rise from 30ml/min to 50ml/min, the increment of the optical power of the green light emission is approximately 26.59%. However, the increment is only 15.02% in the next increase of the flow velocity. One of the reasons for the large increase in the start is that the per unit time of laser irradiates the excitation area was reduced, and the amount of heat generated was reduced. Another reason for the phenomenon was the perovskite QDs deposition increased the liquid concentration. However, the increase in QDs concentration is a trace amount. As the flow velocity increased, the deposition of QDs decreases. The main reason for the increase in the output spectrum is due to the increase in flow velocity. The CQD-converter heat dissipation performance is improved.

When the flow velocity continues to increase to 110ml/min, the increment of the optical power of the green light emission also continues to decrease. For example, the flow velocity increases from 70ml/min to 90ml/min corresponding the increment decreased by 9.99%. For the flow velocity changed from 90ml/min to 110ml/min, the increment of the output power of the excitation light is about 6.05%. Continued to increase the flow rate of the peristaltic pump, there is a different trend from the previous. The increment of the output power begins to increase slightly. For the flow velocity changes from 110ml/min to 130ml/min, the increment of the output power increased by 6.64%. As for the flow velocity increases from 130ml/min to 150ml/min, the increment is about 7.06%. However, the increment of output power begins to decrease after a short rise. At 170ml/min, the increment is about 4.29%. The short rise may be caused by turbulence of QDs solution. Because of the working mode of the peristaltic pump which pumping of fluid by alternately

![Fig6](image_url)

**Fig.6.** The output spectrum variation of the CQD-converter versus the temperature of the semiconductor cooling plate. The inset image is the optical power of the green emission. (b) The total radiation power and the luminous flux variation of the CQD-converter. (c) the CIE (x, y) coordinate diagram of the CQD-converter versus the temperature of the semiconductor cooling plate.

![Fig7](image_url)

**Fig7.** The output spectrum variation of the CQD-converter versus the flow velocity of the peristaltic pump. (b) The total radiation power and the luminous flux variation of the CQD-converter. (c) the CIE (x, y) coordinate diagram of the CQD-converter versus the flow velocity of the peristaltic pump.
squeezing and releasing the pump tube, the turbulence phenomena increased with the increased of the flow velocity.

The turbulence phenomena would create many small bubbles. It may lead to instability of the CQD-converter.

<table>
<thead>
<tr>
<th>Flow velocity (ml/min)</th>
<th>Optical power (W)</th>
<th>Increment (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.339</td>
<td>0</td>
</tr>
<tr>
<td>50</td>
<td>0.461</td>
<td>26.59</td>
</tr>
<tr>
<td>70</td>
<td>0.542</td>
<td>15.03</td>
</tr>
<tr>
<td>90</td>
<td>0.603</td>
<td>9.99</td>
</tr>
<tr>
<td>110</td>
<td>0.642</td>
<td>6.05</td>
</tr>
<tr>
<td>130</td>
<td>0.687</td>
<td>6.64</td>
</tr>
<tr>
<td>150</td>
<td>0.739</td>
<td>7.06</td>
</tr>
<tr>
<td>170</td>
<td>0.773</td>
<td>4.29</td>
</tr>
</tbody>
</table>

The output spectrum of the green light emission and increment for each 20ml/min flow velocity increments.

Fig. 7(b) shows the trend of total radiation power and the luminous flux variation with the flow velocity of the peristaltic pump increased. From the image, it can be seen that the radiation power and the luminous flux increases with the flow velocity. This is in line with the trend of output spectrum changes. Furthermore, the slope variation of total radiation power and luminous flux is in according to the increment of drive current. (b) The total radiation power and the luminous flux variation of the CQD-converter. According to the above results, it can be deduced that both of reducing the temperature of the semiconductor cooling plate and increasing the flow velocity of the peristaltic pump can improve the conversion effect of the CQD-converter. The temperature of the semiconductor cooling plate varies from 20 °C to 0 °C, the total radiation power increases 20.68%. While, when the flow velocity increases from 30ml/min to 170ml/min, the total radiation power growth rate can reach 54.09%. Hence, changing the flow velocity is more effective than changing the temperature.

In order to illustrate the color stability of the CQD-converter, the output spectrum of the CQD-converter under various operation currents are shown in Fig.8(a). The experiment was tested by setting the temperature of the semiconductor at 5 °C and driven by a peristaltic pump at 30 ml/min.

From the Fig.8(a), it can be seen that obvious spectral saturation with increasing the operating current from 500mA to 1500mA. The output spectrum intensity increases gradually against the increasing drive currents with no apparent spectral peak shift. Owing to the CQD-converter absorbing more blue light energy, the peak output value of the excitation light is rising continuously. As shown in Fig.8(b), the total radiation power of the CQD-converter reaches 1131.74mW at 500mA. As the current increases, the total radiation power can reach 1879.7mW at 1500mA. Both of the total radiation power and the luminous flux shows an upward trend. We also tried to increase the drive current of the laser. However, when the drive current was increased to 1700 mA, large bubbles will be generated in the glass tube area. This may be because the laser drive current is increased, the flow rate is slow, and the temperature of the excitation region of the glass tube rises instantaneously. Whether the output spectrum image or the total radiation power graphics didn’t occur saturation. But it can be deduced that the total radiation power curve and the luminous flux curve have extreme values from the Fig.5(b). Fit the data using an exponential function based on the curve trend (the green line is fitted curve of the total radiation power, the blue one is the luminous flux). The exponential function of the total radiation power and the luminous flux is as the following equation.

\[ Y_1 = 2058.732 \times \left(1 - e^{-0.00154X}\right) \quad R_1 = 0.9889 \]  
\[ Y_2 = 657.598 \times \left(1 - e^{-0.00139X}\right) \quad R_2 = 0.9824 \]  

The fitting function is convergent. It can be calculated that the maximum value of the total radiation power is 2058.7mW. For the luminous flux, the maximum value can reach 657.6mW. Fig.8 (c) depicts the offset of the CIE (x, y) coordinates for different drive currents. It can be noted that the shift of the CIE (x, y) coordinates is slightly. The maximum offset of x is only 0.02 (varies from 0.139 to 0.137). As for the offset of the Y coordinate, it varies from 0.319 to 0.339(maximum offset is 0.01). It can be concluded that the CQD-converter have good color stability.
It can be seen from the above research that the temperature of the semiconductor cooling plate is adjusted to 0 °C, and the flow velocity of the peristaltic pump is increased to 170 ml/min, which can achieve the best optical performance under ideal conditions. In order to explore the optical performance of the CQD-converter under extreme conditions, the optical performance was tested at a temperature of 0 °C and a flow velocity of 170 ml/min. We varied the input current from 0 A to 2.3 A with an interval of 0.2 A and increased current to 2.7 A at 0.1 A intervals starting from 2.3 A to calculate the total radiation power. The result is as shown in Fig.9. Starting at 500mA current, the total radiation power increased approximately linearly with the drive current until the limiting current is 2100mA. Continued to increase the current, the total radiation power gradually became saturated. The highest total radiation power that can be obtained is 2208.27mW at 2500mA. When the drive current adjusted to 2600mA, the total radiation power drops to 2168.78mW. It can be concluded that the limit current that the CQD-converter can withstand under extreme conditions was 2.5A. The laser is a constant voltage laser, laser power increased linearly with current increased.

**IV. CONCLUSION**

In this work, we used a CQD-converter to dissipate the heat generated from the liquid perovskite QDs excited by a 450nm laser. The thermal and optical properties of static condition and circulating condition liquid QDs under laser excitation were tested and analyzed. For the SQD-converter, the temperature rose rapidly under the excitation of laser (at 500mA). At about 76 °C, hexane in the solution evaporates rapidly. The liquid perovskite QDs underwent thermal quenching after 420 s laser excitation. From the optical performance, the radiance power decreases by 38.99%. The CIE color coordinates move the green side from (0.1609,0.2772) at 20oC to the blue side (0.1713,0.1157). However, the CQD-converter exhibit significant heat dissipation characteristics. Under the action of the circulating medium and the semiconductor cooling plate, the temperature of the CQD-converter is stable and fluctuates around 50°C. Compared with the SQD-converter decrease of 38.99% in 420s, the radiance power decreased by 17.6% after 3600s. The offset of the CIE color coordinates is small. Meanwhile, the effects of the flow velocity of peristaltic pump, semiconductor cooling plate temperature and laser power on the optical properties of perovskite QDs were investigated. The radiant power increases as the temperature of the cooling plate decreases and the flow velocity increases. The highest laser drive current can reach 2100A (at about 8.49W) at 0 °C, 170ml/min flow velocity. Although the excitation light is still blue-green, high-power white lighting can be achieved after the red QDs are incorporated. The CQD-converter proposed in this paper has a certain enlightening effect on improving the thermal/optical performance of laser QDs illumination.

**REFERENCES**


Improved Stability for Solid-State Lighting and Random Upconverted Lasing,”


