The Comparative Aging Study for Different Co-precipitation Methods of Quantum Dots in NaCl Solids

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Abstract: A comparative study about colloidal quantum dot and NaCl co-precipitation methods was set up. After the 300-hour aging tests, the samples made by saturated-salt method is better in terms of degradation and spectral characteristics.
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1. Introduction

Colloidal quantum dots (CQDs) are nanometer-scale particles made of semiconductor and their highly efficient light-emitting capabilities have been regarded as the possible candidate for the next generation of solid-state lighting [1]. Narrow linewidth, large color-gamut coverage and size-dependent emission wavelength place them in a good position to compete with other materials such as YAG nanophosphor. However, CQDs are easily degraded by environmental influences such as temperature, oxygen, humidity, etc. Previously, we demonstrated the hybrid CQD LED with long lifetime when CQDs were sealed in ionic crystals [2,3].

In this work, we will compare three different methods of CQDs recrystallization with ionic crystals and their effects towards lifetime of the hybrid LEDs. Different baking-temperatures and different light excitation intensities were used as the control variables in the experiments. Measurements from CQDs light emission will be shown for the comparison.

2. Fabrication and experiment

In this work, we used water-soluble 610nm CdTe colloidal quantum dots capped with carboxylic acid. The CdTe QDs in powder form are purchased from Sigma-Aldrich®. Three different methods were applied to seal the CQDs: traditional (or saturated-salt), methanol-assisted, ethanol-assisted methods [4,5]. For traditional method, the salt solutions were prepared with 6.88g of NaCl in 20ml deionized water on hot plate at 30°C. The CQD powders were then added into water and pour into saturated NaCl solution slowly. After 20 hours, the CQDs were sealed inside the NaCl crystals and they can be dried for later use. For methanol- and ethanol-assisted method, the CQD powders were first dissolved in the DI water with saturated NaCl concentration. For the methanol-assisted method, the syringe loaded with this CQD+NaCl solution was used to inject them into the methanol. For the ethanol-assisted method, the ethanol solvent will be poured directly into the CQD+NaCl solution. The re-crystallization process of the CQD in NaCl took about 15 hours in methanol method and a few minutes in the ethanol method, respectively.

At the end of all three method, the CQD embedded NaCl crystals need to be filtered and dried before using in the experiments. Fig. 1 shows the powders under the UV light. After the CQDs were properly manufactured, they were grinded into finer grains and mixed with PDMS by the similar method we described previously [2,3]. We study two different factors for their influences towards the lifetime and performances of the CQDs under different percipitation methods: temperature and light excitation intensity. In the temperature-aging test, samples are placed on one 60 °C and one 120 °C hotplates, respectively. In the light excitation intensity test, the samples were lifted above a blue LED, as shown I n Fig. 2, to avoid extra heating from the LED. The injection currents of the LED are set to be 20mA and 200mA for low and high excitation intensities. The corresponding photonic power intensities are 62mW/cm2 and 568mW/cm2, respectively. The characteristics of the samples were regularly measured in the Acton SP2150 PL system. Fig. 3 shows the PL spectra of the samples by the three synthesis methods.

Fig. 1. The CQD+NaCl for three synthesis methods under UV light.

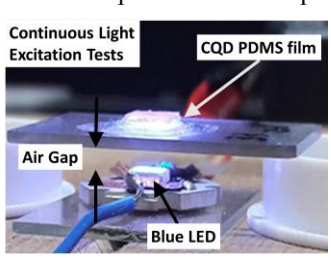

Fig. 2. The continuous light excitation experiment setup.

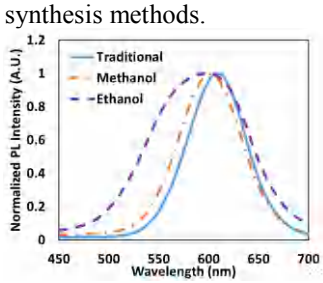

Fig. 3. The PL spectra for three different co-precipitation methods.

3. Results and Discussion

After the samples from three different methods are finished, they can be tested under various conditions. For thermal experiment, Fig. 4 shows the relationship between intensity and aging time for thermal experiment. Traditional salt synthesis and methanol-assisted synthesis methods maintain 64.2% and 73.9% after 300 hours at 60 ºC. The intensity of ethanol-assisted synthesis methods dropped to 18.7% at the same condition. If we set 50% of degradation as the failure criterion, their lifetimes are 590 hours (traditional) and 1976 hours (methanol), while the ethanol sample failed after 8 hours. As for high temperature bake (120 ºC), all three samples dropped dramatically in less than 5 hours into the experiments. After that, a more stable intensity trend can be expected.

For light excitation aging tests, we placed three samples on the blue LED at 20mA and 200mA, and we can see that the traditional synthesis method maintains 91.4% and 84.8% after 300 hours for 20mA and 200mA, respectively. Methanol synthesis method maintains 79.3% and 69.2% after 300 hours. Ethanol synthesis method degraded faster than the other two, and the intensity dropped to 19.2% and 14.9% after 300 hours at 20mA and 200mA as shown in Fig. 5. Highly stable light emission can be expected from both the traditional and methanol assisted methods. By using the same 50% criterion, more than 4000 hours of lifetime (4021 hours for the traditional method and 4290 hours for the methanol assisted method) can be expected from both methods at 20mA of test condition, while the ethanol method failed within 3 hours. Fig. 6 shows peak shift and FWHM of three different synthesis methods for thermal and light experiment. The strong blue shift can be obvious in ethanol-assisted synthesis method and we believe that it is attributed to irreversible photo-oxidation of QDs which results from incompletely cover of the QD for ethanol-assisted method [4]. Besides, we can see that FWHM shift change very little (no increase or even decrease) for thermal experiment no matter at 60 ºC or 120 ºC for traditional synthesis methods.

From these aging tests, several things could be found out: A. the high-temperature condition is more detrimental towards CQDs than the light excitation. This difference can be seen especially in the medium level of heat. B. The traditional method to embed CQD in NaCl is still the best way to prevent from the outside erosion. It took much longer (20hours vs. 15hours, vs. a few minutes) to recrystallize for the traditional method, but the sealing could be more complete in the traditional way. C. Between methanol and ethanol assisted method, the methanol assisted method is better in terms of FWHM widening or intensity degradation. Possible cause could also be the better sealing of the CQDs to the NaCl crystal.

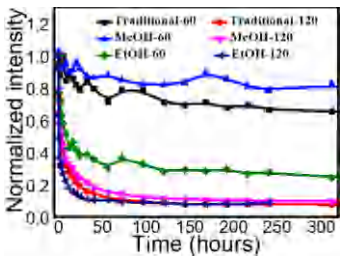

Fig. 4. The normalizes intensity of three different synthesis methods under high (120ºC) and Low (60ºC) temperatures.

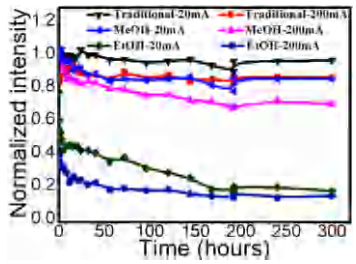

Fig. 5. The normalizes intensity of three different synthesis methods at high (200mA) and Low (20mA) currents.

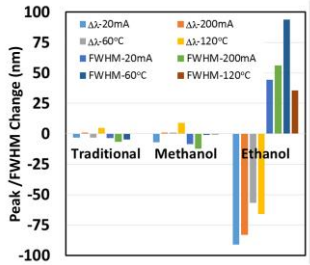

Fig. 6. The comparison of $\Delta\lambda_{peak}$ and FWHM among the three different methods.

4. Conclusion

In conclusion, three methods of embedding CQDs into NaCl were compared for the longevity of CQD light emission under independent high temperature and strong light aging process. From the measured results, we find out that the temperature factor have a more pronounced impact on CQDs than the light excitation does. Among three methods, the traditional method is preferred and preserve the light emission characteristics much better than the other two. This study can clarify the major issue when the CQDs are integrated into the next generation of solid state light source and should be useful for the process integration in the future.

5. Reference

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