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Characterization of Hybrid Composites of Nano YAG:Ce-CdSe/ZnS Quantum Dots and Conjugate Polymer Used for Solid State Lighting

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ABSTRACT

White light was obtained by mixing blue light from emission of Indium Gallium Nitride (InGaN) chip and green-yellow-red light form the fluorescence of nano-$Y_3Al_5O_{12}$:Ce (YAG:Ce), CdSe/ZnS quantum dots (QDs) and Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) polymer hybrid composite. The hybrid composite was coated on InGaN chip by way similar to slurry method. To achieve an efficient white light emitting diode (WLED) it is necessary to obtain a hybrid composite as homogeneous as possible and with excellent thickness uniformity. The used QDs have core-shell structure with thirteen ZnS monolayer. The properties of YAG:Ce, CdSe/ZnS QDs and MEH-PPV polymer hybrid composite prepared by slurry method were examined using photoluminescence. In this paper, the WLED fabricated by coating the hybrid composite was examined by PMS-50(PLUS) UV-VIS-near IR Spectrophotocolorimeter. The chromaticity of WLED depends on the thickness of the hybrid composite layer. The thickness of this layer could be easily controlled by slurry method. The luminous efficiency of WLED was 20.8 (lm/W) with a colour rendering index (CRI) of 75.8 at 200 mA. The WLED exhibited white light with a CIE coordinates of (0.30, 0.35).

Keywords: *Solid state lighting, hybrid composite, quantum dots, white light-emitting diodes*

1. INTRODUCTION

Since energy consuption in lighting now is increasing day-by-day, replacing high-power, but low luminescence electrical lamps by energy-efficient light sources plays an important role in the environment sustainability. Solid-state lighting (SSL) is an attractive replacement for current lighting technologies because of low power consumption and no-pollution with Hg gas (in the fluorescent lamp). There are basically three approaches for generating white light using lighting emitting diodes (LEDs) as the source for SSL [1-4]. The first way is using the red, green and blue LEDs (RGB-LEDs) to make white light with CRI greater than 80 [5]. However, for this device, a complicated integrated circuit (IC) control system is needed to balance between the different colours (red, green, and blue). The second one is using the UV-LED chip to excite phosphor layer emitting at three colours: red, green and blue. The combination of these three colours will make the white light. The commercialized White LED (WLED) is a UV LED chip plus phosphor. The phosphors convert some of the UV LED light to red, green, and blue light, creating a mixture of three colours that gives the appearance of white light. However, it is difficult to obtain the uniform colour combination between three red, green, and blue light colours. The third one is using blue LED chip InGaN to excite the yellow phosphor such as Y3Al5O12:Ce (YAG) phosphor; blue and yellow light can also produce white light. This is a very easy method to fabricate WLED, but the colour rendering index (CRI) is not high.

The three methods mentioned above are now used widely. However, is difficult to create white light with a continuum spectrum band close to the solar spectrum. In addition, it is not easy to control colour correlated temperature and the colour rendering index (CRI) of LEDs. In this work, the blue InGaN chip was used to excite YAG powder, CdSe/ZnS quantum dots (QDs) and Poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) polymer hybrid composite. The MEH-PPV has a well known absorption peak at 445 nm and two emission peaks around 590 nm and 640 nm [6]. With their excellent photo-electronic properties, the quantum dots, and especially the II-VI family semiconductor quantum dots, are now widely used in photo- and electro-luminescence device such as inorganic and organic light emitting diodes. YAG:Ce used in this report was a powder with an average size of 300 nm.

Quantum dots have many applications in optoelectronic device such as LEDs because of their superior properties resulting from the three-dimensional confinement effect of the charge carrier. QDs have high emission efficiency and size-tuned photoluminescence (PL) [7-8]. The YAG:Ce, CdSe/ZnS-QDs and MEH-PPV emit, respectively, green (from 500 to 620 nm), green- yellow light (form 545 to 610 nm) and yellow-red (590 nm and 640 nm). A part of the blue light converted into green and yellow-red lights. Thus, blue, green and yellow-red lights can be combined to produce white light. The mixture blue light from emission of indium gallium nitride (InGaN) chip and the green, yellow and red light from the fluorescence of YAG:Ce, CdSe/ZnS-QDs and MEH-PPV, respectively were exploited to achieve a continuous spectrum band through from the blue light to red one.

The colour rendering index (CRI) of YAG:Ce phosphor-based white light-emitting diodes (LEDs) is expected to be poor, due to the lack of red spectral component. To compensate for this, CdSe/ZnS QDs and MEH-PPV polymer were blended into YAG:Ce nanophosphors. In this paper, the results obtained on WLEDs made by combining blue InGaN chips with YAG:Ce, colloidal core/shell CdSe/ZnS quantum dots (QDs) and MEH-PPV polymer hybrid composite, are presented.

2. EXPERIMENTAL

The CdSe/ZnS QDs are synthesized in the presence of organic compounds as trioctylphosphine oxide (TOPO), trioctylphosphine (TOP) and hexadecylamine (HDA). The QDs obtained having multi-shell structure with the size 4.9 nm and 4.5 in diameter of core. The pure MEH-PPV Powder and CdSe/ZnS QDs was prepared by dissolving in toluene solvent with a ratio of 1 mg of MEH-PPV powder and 1 ml CdSe/ZnS in 2 ml toluene. The YAG:Ce powder and the MEH-PPV and CdSe/ZnS QDs solution were mixed in one together with transparent epoxy. Then this composite was coated on the glass substrate and blue LED chip for investigation of absorption, photoluminescent, and electroluminescence properties. The absorption and luminescence properties of films were recorded on UV/VIS/NIR Spectrophotometer V570-Jasco and high resolution spectrometer Model Microspec-235b, respectively. The electroluminescence properties were measured by using integrating sphere equipped with a calibrated spectrophotometer.

The blue InGaN LED chip used in this research has the peak wavelength at 460 nm. 1W power blue LED has been used in the study, with the die size around 1100 µm x 1100 µm. The die was then bonded on the heat sink using Indium. The quality of thermal resistance between the LED die and the substrate determined the working temperature of the LED chip. The gold wires were bonded on electrode pads by using digital thermo sonic multipurpose wire bonder model 626. Four gold wires (diameter of 20 µm) are used for power LED in order to increase the heat dissipation. The CdSe/ZnS QDs and MEH-PPV polymer hybrid composite were dropped onto the surface area between the top of the LED chip to convert a part of blue light into green and yellow-red lights [9]. The luminous flux and photoluminescence of the white LED was measured by using PMS-50(PLUS) UV-VIS-near IR Spectrophotocolorimeter with integrating sphere equipped, a calibrated spectrophotometer, and high resolution spectrometer.

3. RESULTS AND DISCUSSION

Before coating YAG:Ce, CdSe/ZnS-QDs and MEH-PPV polymer hybrid composite on blue LED chip, the absorption and photoluminescent (PL) properties have been carefully analyzed. Fig. 1 shows the absorption and photoluminescence spectra using an exciting electromagnetic radiation at 442 nm for CdSe/ZnS. From Fig. 1 one can see that the CdSe/ZnS film has an absorption peak a 545 nm and two emission peaks at around 520 nm and 570 nm. CdSe QDs have one emission peak depending on size [10]. However, from Fig.1 we see that CdSe/ZnS has one more emission peak at 520 nm, which results from shell of QDs. The CdSe/ZnS QDs used in this paper has a core-shell structure QDs with thirteen ZnS monolayer. It is appropriate for application in solid state lighting.

The absorption and photoluminescent spectrum of MEH-PPV films are showed in the Fig. 2. From Fig. 2 is noticed that the MEH-PPV film has an absorption peak a 480 nm and two emission peaks at around 590 nm and 640 nm. From absorption of CdSe/ZnS QDs and MEH-PPV polymer is concluded that the InGaN blue LED chip with 460 nm emissions can be used to excite the luminescence of CdSe/ZnS QDs and MEH-PPV polymer hybrid composite.

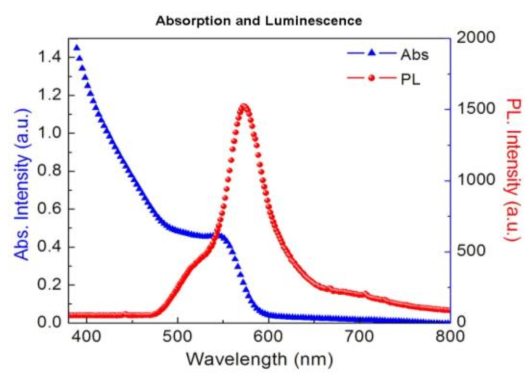

Figure 1 Absorption and Photoluminescence spectra of CdSe/ZnS QDs

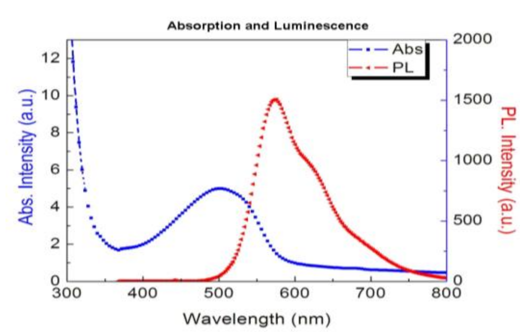

Figure 2 Absorption and Photoluminescence spectra of a MEH-PPV film

Figure 3 depicts photoluminescent spectrum of CdSe/ZnS and MEH-PPV. The outcome of the superposition of the emission peak at 520 nm of CdSe/ZnS with the emission spectrum of CdSe/ZnS and MEH-PPV is an overall spectrum spreaded from 500 to 700 nm. This expansion the spectrum shows the potential application of CdSe/ZnS QDs and MEH-PPV polymer hybrid composite for WLED.

The result on Fig. 3 shows that mixture of YAG:Ce, CdSe/ZnS and MEH-PPV polymer can extend the luminescent spectrum on both shortwave and long wave. This behaviour is due to the contribution of YAG:Ce and QDs, which extend on shortwave (about 500 nm) and of MEH-PPV polymer and QDs, which extend on the long wave (about 700 nm). This is the advantage of YAG:Ce, CdSe/ZnS and MEH-PPV hybrid composite. Therefore, the possibility using the hybrid composite to fabricate WLED instead of using YAG has been demonstrated (see Fig. 4).

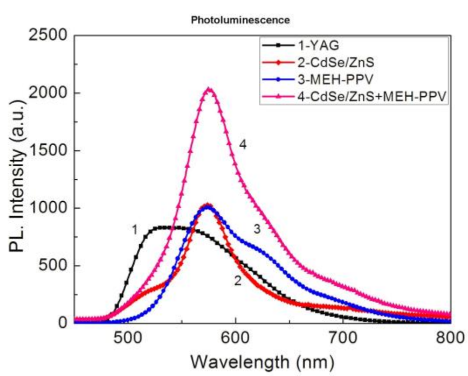

Figure 3 Photoluminescenc of YAG:Ce (1), CdSe/ZnS (2), MEH-PPV (3) and composite (4)

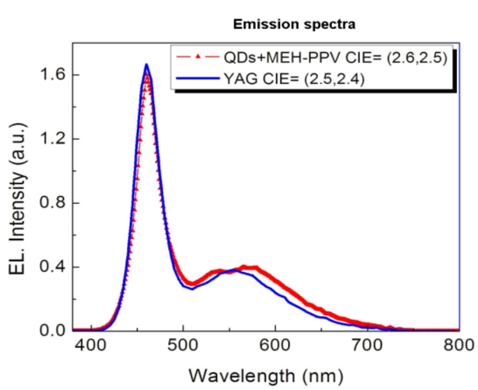

Figure 4 Emission spectra of a convetional (blue curve) and a composite (red curve) WLEDs

Figure 4 shows the electroluminescence spectra of a white LED made from coating the YAG:Ce inorganic powder, CdSe/ZnS QDs and MEH-PPV polymer hybrid composite and YAG on InGaN LED chip, at power supply is 3 V and 200 mA. From Fig. 4 one can expect that the mixed light emitted from three components as blue LED chip, YAG:Ce, CdSe/ZnS QDs and MEH-PPV polymer combine into a white light with a high CRI and high-efficiency lighting.

Figure 5 shows the other electroluminescence spectra of a white LED made from coating the YAG:Ce, CdSe/ZnS QDs and MEH-PPV polymer hybrid composite on blue LED chip with a suitable weight ratio of 1:2, at a power supply with 3 V and 200 mA. The luminous flux of the WLED was measured by using integrating sphere equipped with a calibrated spectrophotometer. Under 3 V applied voltage and 200 mA forward current, for YAG:Ce, CdSe/ZnS QDs and MEH-PPV polymer hybrid composite film (about 200 mm) coated on the blue LED chip. The results of the measured colour coordinate is shown in Fig. 6, at x=0.3078 and y=0.3532. Notice that the white light region is shown inside the ellipse with the centre at x=0.33 and y=0.33. Our WLED has colour rendering index Ra=75.8, luminescent power 41.40 mW and luminous efficiency 20.8 lm.

Due to the conjugate polymer + QDs composite the wavelength range was much expanded to the red edge. Thus, using these WLED for lighting one can diminish energy consumption and expect to the safety for human eyes (for children in particular).

Recently, we reported [11] that the MEH-PPV+TiO_2 composites. which were annealed in air, were not very stable and the blue light illumination was easily damaged. The luminescent intensity of polymer MEH-PPV decreased rapidly, after 30 minutes the PL intensity decreased by 12% [11]. In this work we used the MEH-PPV polymer blending into YAG:Ce, and CdSe/ZnS-QDs coating on the blue LED chip. It was observed that luminous intensity of the WLED coated by these composites was maintained unchanged for a long time. For this hybrid composite, the luminescent quenching and colour bleaching did not occur.

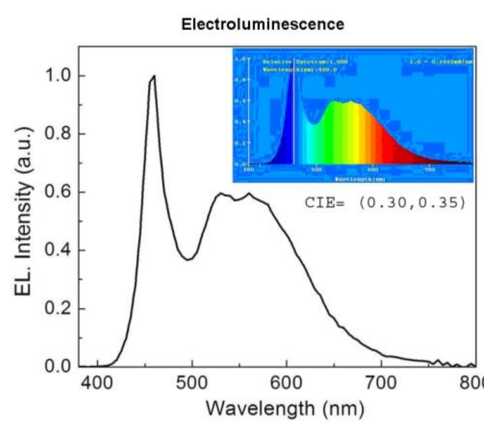

Figure 5 Electroluminescent spectra of a WLED made from the composite of YAG+QDs+MEHPPV

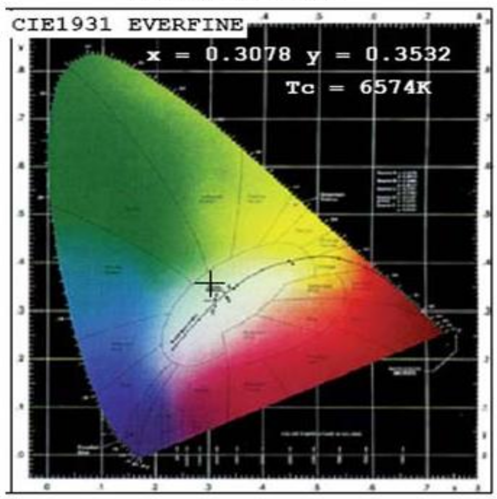

Figure 6 The CIE of a WLED made from composite film

Figure 7 shows the flux serve of the WLED that was working on 8 hour running by a day with applied power of ca. 400 mW (namely a voltage of 2 V and a current of 200 mA). During the first 30 days (one monthe) the flux was a little decreased, the it maintained almost constant value at ca 860 lm for over 100 days. The reason why the performance of these WLED was much enhanced is still not revealed. However, from the fact that the presence of CdSe/ZnS QDs instead of TiO_2 resulted in the enhancement of the lasting of WLED, one can attribute to the enhancement to the lack of oxygen atoms in CdSe/ZnS-QDs. This is in agreement with the observation that at a high temperature of about 80^{o}C, when the WLED is lighting, oxygen is the main factor that can damage C-H bonds in MEH-PPV, making the last be less sustainable under blue radiation [11].

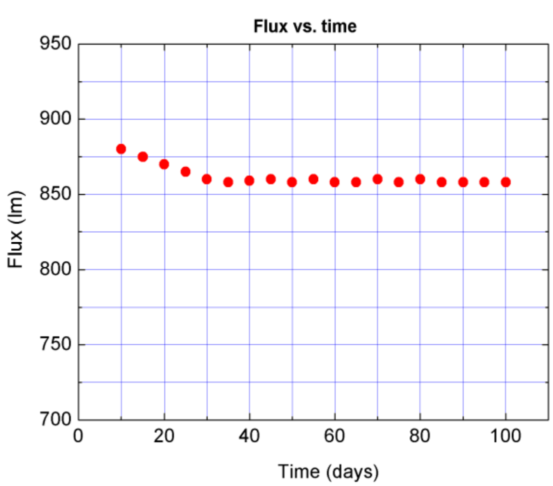

Figure 7 Time dependence of the flux of a composite WLED

4. CONCLUSION

The research described aimed to a WLED with broad spectrum band. Preliminary data such as the absorption and photoluminescent spectral properties of YAG, CdSe/ZnS core-shell QDs and MEH-PPV polymer have been reported. A novel WLEDs, composed of YAG:Ce, CdSe/ZnSe and MEH-PPV polymer and InGaN chip, are produced. We have investigated the colour bleaching and luminescent quenching effect of CdSe/ZnS QDs and MEH-PPV polymer hybrid composite under blue light illumination. The results suggest the application of the YAG:Ce, CdSe/ZnS core-shell QDs and MEH-PPV polymer hybrid composite as components for high-efficiency lighting. The YAG:Ce, CdSe/ZnSe and MEH-PPV hybrid composite can make WLED that have broad spectrum band from blue light to red. Especially, the green band to red one is suitable for human eye. The electroluminescent of WLEDs was also characterized. The WLEDs fabricated by coating the hybrid composite on the top of blue LED chip provide white light with a CIE-1931 coordinate of (0.30,0.35) and colour rendering index of 75.8. From this, one can suggest that using such WLEDs for lighting is a valuable contribution to the energy sustainability.

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