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Red light emitting solid state hybrid quantum dot–near-UV GaN LED devices

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Abstract

We produced core–shell (CdSe)ZnSe quantum dots by direct colloidal chemical synthesis and the surface-passivation method—an overcoating of the core CdSe with a larger-bandgap material ZnSe. The (CdSe)ZnSe quantum dots(QDs) play the role of a colour conversion centre. We call these quantum dots nanophosphors. We fabricated red light emitting hybrid devices of (CdSe)ZnSe QDs and a near-UV GaN LED by combining red light emitting (CdSe)ZnSe quantum dots (as a colour conversion centre) with a near-UV(NUV) GaN LED chip (as an excitation source). A few good red phosphors have been known for UV excitation wavelengths, and red phosphors for UV excitation have been sought for a long time. Here we tested the possibility of using (CdSe)ZnSe QDs as red nanophosphors for UV excitation. The fabricated red light emitting hybrid device of (CdSe)ZnSe and a NUV GaN LED chip showed a good luminance. We demonstrated that the (CdSe)ZnSe quantum dots were promising red nanophosphors for NUV excitation and that a red LED made of QDs and a NUV excitation source was a highly efficient hybrid device.

1. Introduction

The development of full colour displays and solid state light emitting devices is one of the main challenges in the communication and information and illumination industries. Incandescent bulbs and halogen lamps have been widely used to light houses and offices but are energy inefficient. Depending on the country, lighting uses 16–22% of all the electricity produced worldwide. Increasing the efficiency of lighting devices by even a small amount will have a tremendous impact on savings in cost and energy use. The development of new energy-efficient, long-life devices generating white light is demanded by the lighting industry. This can be achieved by generating power-efficient and highly luminescent red, green, and blue (RGB) light emitting diodes (LEDs), laser diodes (LDs), or UV LEDs combined with a mix of phosphors optimized for RGB emission, in addition to the reduction of the cost per lumen.

Recently, full colour displays made of RGB LEDs or white light emitting diode (white LED) illumination systems, which are energy-efficient (with 1/10th power consumption of an ordinary light bulb), reliable and have long lifetime (~100000 h), have been given much attention for future use. Progress in group III–V GaN semiconductor technology has enabled the development of bright long-lived blue light emitting diodes [1] and blue laser diodes [2]. However, the achievement of full colour displays from InGaN-based LEDs is rather limited by difficult and unreliable control of [In] concentration and complex fabrication processes. Thus, using GaN-based highly efficient blue InGaN LEDs combined with phosphors [3, 4], (CdSe)ZnS quantum dot–polylaurylmethacrylate (PLMA) polymer composite nanophosphors [5] and π-conjugated polymer films [6], research groups have shown the possibilities of producing white light emitting or wavelength down-conversion LEDs.

The colour quality of a white light source is defined by the colour rendering index (CRI) [7] and the Commission Internationale de l’Eclairage (CIE) [8] chromaticity coordinates. CRI means how close the light source is to natural light. Nowadays the fluorescent lamps which are widely used to light houses and offices are relatively energy efficient have a CRI of about 75 and contain environmentally toxic Hg vapours as one of their constituents. New lighting sources with high energy efficiency, long life and high CRI are being demanded. For good colour rendering of various colours it is necessary to
develop white lighting sources that comprise RGB light emitters. Colour rendering is an essential figure of merit for a light source besides luminous efficiency. Inorganic InGaN-based UV LEDs are energy efficient and can be used as an excitation source for RGB emitters. Red phosphors are really needed in solid state lighting: highly efficient yellow phosphors are readily available but the development of efficient red phosphors still lags behind [9, 10]. In order to realize a light source with high CRI, most of all, red emitting phosphors with narrow emission around 610 nm are required. This challenge can be met by ‘nanophosphors’ called quantum dots (QDs). We propose semiconductor quantum dots produced via a wet chemical method as one of the possible solutions to the red phosphor problem. By combining an InGaN semiconductor diode for UV light emission with highly photoluminescent QDs we can realize new highly energy efficient solid state lighting devices with high CRI. Typical conventional phosphors—solid luminescent materials—are usually made from a suitable host material to which an activator is added. An appropriate excitation source is required to get the optimum emission from phosphors. There is a limited match between excitation sources and conventional phosphors. However, quantum dots have advantages over the other colour conversion materials such as conventional phosphors in that each colour of a QD has a broad absorption feature but a narrow emission profile. In addition, all QD colour can be simultaneously excited by a single excitation source but a narrow emission profile. In addition, all QDs allow one to control the emission properties with much greater precision. QDs are promising colour conversion nanophosphors for solid state lighting devices in this respect. Nanophosphors, optically excited by UV or blue light sources and fluorescing in the visible spectral range with a high PL efficiency and a narrow emission feature, can play a role as colour conversion centres in solid state lighting devices. In this paper, we report semiconductor QDs as new promising photoluminescent materials for incident wavelength conversion. By tuning the size of a semiconductor QD, we produce highly luminescent red QDs on a large scale via a direct colloidal synthesis. QDs can be photoluminescent for any incident light with energy larger than their band gap. We demonstrate a red emitting hybrid device consisting of red QDs as colour conversion centres and a near-UV (NUV) LED chip as an excitation source.

2. Experiment

2.1. Synthesis of (CdSe)ZnSe QDs

The synthesis of (CdSe)ZnSe QDs was done via fast nucleation followed by slow growth [11, 12]. Zinc oleate complex, Zn(OA)2, as the Zn precursor and Cd oleate complex, Cd(OA)2, as the Cd precursor were prepared by reacting CdO and zinc acetate complex, Zn(OAc)2, with oleic acid. In a typical synthesis, 0.4 mmol of CdO and 4 mmol of Zn(OAc)2 were mixed with 17.6 mmol of oleic acid. After heating the resulting solution at 120°C for 30 min, Cd(OA)2 and Zn(OA)2 were obtained. A Se shot was dissolved directly in tri-n-octylphosphine (TOP) to produce a solution of TOPSe. An excess of TOPSe was loaded into a syringe and its contents rapidly injected into a vigorously stirred reaction flask in

a single injection through a rubber septum. The resulting reaction mixture of Cd(OA)2 and TOPSe was heated to 300°C under 1 atm of N2 and maintained at that temperature for 10–15 min and then Zn(OA)2 were added. (CdSe)ZnSe, (core) shell QDs were formed in the reaction mixture. The QDs were purified with chloroform or acetone. The pure QDs were dispersed in a nonpolar solvent such as hexane and kept for other uses. The typical absorption and emission spectra of red emitting (CdSe)ZnSe QDs are shown in figure 1.

2.2. Fabrication of hybrid devices made of red (CdSe)ZnSe QDs and NUV LEDs

We produced optimal red emitting quantum dots for 405 nm NUV LEDs by tuning the size of II–VI semiconductor nanocrystallites via fast nucleation followed by slow growth. Briefly, a NUV LED chip with an area of 350 μm × 350 μm, which is an excitation source and part of a QD–NUV hybrid, has the following specifications. The electrode is made of Ni/Au and has a luminous intensity in the range of 8–10 mcd at the forward voltage Vf in the range of 3.3–4.0 V. The 405 nm radiation from the NUV LED excites QDs. QDs, or ‘nanophosphors’ down-convert the NUV radiation into the red emission.

Using the core–shell (CdSe)ZnSe QDs shown in figure 1, we fabricated a hybrid QD–NUV LED device. The QDs had a photoluminescence at 613 nm with a full width at half maximum (FWHM) of 32 nm. The quantum yield of the QDs dispersed in hexane solvent was measured at room temperature to be 60%. The structure of the hybrid device consisting of the NUV LED and red emitting QDs is shown in figure 2. A wire bonded bare NUV LED chip marked as a dotted circle in figure 2 was coated with red QDs dissolved in hexane. The hexane solvent was dried off. Transparent epoxy materials were put over the red QD–NUV LED chip to hardened and form a dome shape. The home-made hybrid device of a red QD–NUV LED was produced as shown in figure 3. Optical measurements were done at room temperature on a CAS-140B compact array spectrometer. The electroluminescence spectra of the hybrid device are shown in figure 4.

Figure 1. Absorption and photoluminescence spectra of red emitting (CdSe)ZnSe (core)shell QDs. Solid line for absorption and dotted line for emission.
3. Results and discussion

Generally, conventional phosphors require a matching excitation light source. In contrast, semiconductor QDs have a broad absorption feature and can be excited by any light sources radiating photons of a larger energy than the exciton energy of the QDs. Red emitting phosphors have been sought in the field of luminescent materials research for a long time [9]. Semiconductor QDs smaller than the bulk Bohr exciton radius can exhibit the quantum confinement effect and luminesce with the emission of various wavelengths depending on their size and shape [13]. A semiconductor QD is a really good candidate for a red luminescent material.

We fabricated a red light emitting QD–NUV hybrid LED as a prototype to develop energy efficient, colour-tunable, intensity-controllable, reliable and long-lived solid state lighting LED devices. GaN-based NUV light emitting diodes are the excitation source for the red emitting QDs and the QDs down-convert NUV light into emitted red light. The CIE colour chromaticity diagram on which the position of the red emission is marked as an X is given in figure 3. The red emission is located at $x = 0.6854$ and $y = 0.2722$. As shown by the CIE colour chromaticity diagram we obtain really good red light using the QDs and a NUV LED chip. A photo of the home-made red emitting device made of red QDs and NUV LEDs is also shown in figure 3. A large part of the NUV emission from the LED is converted into red light when it passes through the red semiconductor QDs, or ‘red nanophosphors’.

We measured the optical characteristics of the hybrid device. It emits lights of 405 nm from a NUV LED chip and 639 nm down-converted through the red QDs as shown in figure 4. The dielectric mismatch is the dielectric constant discontinuity at the QD boundary. The dielectric mismatch at the QD boundary affects the exciton binding energy through the Coulomb energy [17]. Here the PL peak at 613 nm was obtained with QDs dispersed in hexane solvent, i.e. the QD–hexane boundary, and the PL peak at 639 nm was seen with

![Figure 2](image2.png)

**Figure 2.** The red emitting device structure made of red (CdSe)ZnSe QDs as a colour conversion centre and a NUV LED chip as an excitation source.

![Figure 3](image3.png)

**Figure 3.** The CIE colour chromaticity diagram showing the position of the red emission from the hybrid QD–NUV LED device. It is marked with an X. Coordinates are $(x = 0.6854, y = 0.2722)$. The photo image of a home-made red emitting hybrid device consisting of QDs and a NUV LED is given on the right.

![Figure 4](image4.png)

**Figure 4.** Electroluminescence spectrum of the hybrid device made of red (CdSe)ZnSe QDs as a colour conversion centre and a NUV LED chip as an excitation source.
QDs embedded in epoxy matrix in the hybrid device, i.e. the QD–epoxy boundary. The surrounding medium affected the exciton binding energy of the QDs differently to some extent. From the plot of intensity versus wavelength shown in figure 4 we estimated the peak areas at 405 and 639 nm measured on a fully sealed CAS-140B compact array spectrometer. From the intensity ratio of the two peaks, we found that 81% of the total emission of the LED was red. The total luminescent intensity of the hybrid device of a QD–NUV LED was measured to be 5.4 mcd. We put photochemically and thermally stable semiconductor QD materials into the role of colour emission centres on the NUV chip. Luminescent QDs (nanocrystals or artificial atoms) are zero-dimensional materials and their density of states are like those of atoms and so light emission from these ‘artificial atoms’ is quite strong. These QDs are never photobleaching and are expected to be promising candidates as phosphors. In particular, red phosphors for UV excitation have been sought for a long time. Here we tested the possibility of (CdSe)ZnSe QDs as red nanophosphors for UV excitation. The benefits of using UV LEDs as an excitation source are that they are rugged and durable, allow dynamic control of intensity and colour, are of small size, are energy efficient and have a high CRI when combined with RGB phosphors. By controlling the size of the dots, full colour emission is achieved due to a well-known quantum confinement effect [13–16]. That is, size-controlled (CdSe)ZnSe QDs generate luminescence spanning the visible spectrum from 470 to 650 nm. In addition, QDs have a broad absorption feature but a narrow emission profile—all colours of QDs can be simultaneously excited by a single excitation source and fluoresce very pure colours. So QDs combined with a short wavelength excitation source such as a UV LED can realize an intensity-controllable solid state light source with a high CRI. We have also been working on white light LEDs with a high CRI, consisting of RGB QDs and a UV LED, as new solid state lighting devices for the future. We show here that photochemically and thermally stable semiconductor QD materials are promising nanophosphors in the visible spectral range. We demonstrate highly luminescent red light emitting hybrid devices by combining a NUV LED chip with red photoluminescent (CdSe)ZnSe QDs which are urgently needed as colour conversion materials for solid state lighting. Further work on the application of RGB QDs for a UV LED chip for brand new solid state white light emitting diodes is in progress.

4. Conclusion

We produced core–shell (CdSe)ZnSe QDs by solution-based direct colloidal chemical synthesis and the surface-passivation method—an overcoating of the core CdSe with a larger bandgap material ZnSe. The (CdSe)ZnSe QDs played the role of colour conversion centres. In this respect, we call the QDs nanophosphors. We fabricated red light emitting hybrid devices of (CdSe)ZnSe QDs and a NUV GaN LED by combining red light emitting (CdSe)ZnSe QDs with a NUV GaN LED as an excitation source. A few good red phosphors have been known for UV excitation wavelengths, and red phosphors for UV excitation have been sought for a long time. Here we tested the possibility of using (CdSe)ZnSe QDs as red nanophosphors for UV excitation. The emission spectrum of (CdSe)ZnSe obtained by the excitation of a NUV LED chip with a peak wavelength of 405 nm show red fluorescence with a high conversion efficiency. The (CdSe)ZnSe QDs (the nanophosphor) are located at ($x = 0.6854$ and $y = 0.2722$) on the CIE colour chromaticity diagram. The fabricated red light emitting hybrid device of (CdSe)ZnSe and a NUV GaN LED showed a good luminance of 5 mcd out of 8 mcd. We demonstrated that the (CdSe)ZnSe QDs are promising red nanophosphors for NUV excitation and that a red LED made of QDs and a NUV excitation source was a highly efficient hybrid device.

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References