White-light light-emitting device based on surface plasmon-enhanced CdSe/ZnS nanocrystal wavelength conversion on a blue/green two-color light-emitting diode

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The authors demonstrate the implementation of a white-light device by spin-coating CdSe/ZnS nanocrystals (NCs) on the top of a blue/green two-color InGaN/GaN quantum-well light-emitting diode for converting blue and green emissions into red light through the absorption/reemission process. Meanwhile, Au nanoparticles are mixed with CdSe/ZnS NCs for generating localized surface plasmon (LSP) modes to couple with the CdSe/ZnS NCs. The LSP modes can absorb green emission and effectively transfer the energy into the CdSe/ZnS NCs through the coupling process for enhancing red emission. With the LSP coupling process, the conversion efficiency from the blue/green range into red light can be increased by around 30%. The conversion quantum efficiency can reach 52.8%. © 2008 American Institute of Physics. [DOI: 10.1063/1.2890730]

Semiconductor nanocrystals (NCs), such as CdSe/ZnS core/shell quantum dots, can be used for effectively converting high-energy photons into longer-wavelength lights. Their absorption and emission spectra can be tuned by controlling their sizes and core/shell dimension ratios.¹ The use of such NCs for color conversion has several advantageous features, including spectral tunability, high quantum efficiency, and photostability. They have been used for implementing multi-color and white-light devices by using a blue or ultraviolet InGaN/GaN quantum-well (QW) light-emitting diode (LED) as the pump source.²⁻⁷

Recently, the coupling of a light absorber/emitter with surface plasmons (SPs) on a nearby dielectric/metal interface for enhancing absorption/emission efficiency has been widely discussed.^{8,9} Basically, in the coupling process, the energy of the light emitter can be transferred into SP modes and then radiates such that the effective emission efficiency can be enhanced. On the other hand, the SP modes can absorb incident light and transfers the energy into a light absorber such that its effective absorption is enhanced.¹⁰ Such studies include the coupling between an InGaN/GaN QW and SP polaritons for enhancing LED efficiency.¹¹ They also include the coupling of light-emitting NCs with SPs (LSPs) on metallic nanoparticles (NPs). LSPs can create strong localized electromagnetic field, which can be used for enhancing the absorption and emission of a nearby material.^{12,13} CdSe/ZnS NCs have been widely used for studying the behavior of such an LSP-coupling induced absorption/emission enhancement.¹⁴ In such studies, CdSe/ZnS NCs were spin coated on rough Au surfaces for observing the photoluminescence (PL) enhancement.^{15,16} The PL enhancement of CdSe/ZnS NCs was also implemented by mixing with Au NPs.^{17,18} Although the PL enhancement of CdSe/ZnS NCs through LSP coupling has been widely observed, such a mechanism has not been applied to practical devices. In this letter, we report the implementation of a white-light device by using the coupling mechanism between CdSe/ZnS NCs,

which are utilized for converting the output of a blue/green two-color LED into red light and Au NPs for enhancing red light conversion. The white light is obtained by mixing the residual blue and green photons from the LED and the red light converted by the NCs.

The used CdSe/ZnS NCs have a CdSe core diameter of 5 nm and a ZnS shell thickness of 0.2 nm. The absorption (in toluene solution) and PL emission (coated on sapphire) spectra of the NCs are shown in Fig. 1. Here, the absorption spectrum of Au NPs in toluene solution is also shown. In Fig. 1, one can see the PL spectral peak of the NCs around 620 nm. Between 450 and 525 nm, there is a shoulder in the absorption spectrum for effectively absorbing the emission of the fabricated blue/green two-color LED. In fabricating the device, first, a four-QW LED epitaxial structure was grown with metalorganic chemical vapor deposition on *c*-plane sapphire substrate. In the growth process, after a 30 nm GaN nucleation layer was grown at 535 °C, followed by a 3 μm *n*-type GaN layer (grown at 1080 °C), three blue-emitting InGaN/GaN QWs with 3 nm in the well thickness (grown at 740 °C) and 12 nm in the barrier thickness (grown at 840 °C) were deposited. Then, a green-emitting InGaN/GaN QW with 3 nm in the well thickness (grown at 680 °C) and 5 nm in the barrier thickness (grown at 840 °C) was grown. To complete the growth of this LED epitaxial structure, a 20 nm *p*-Al_{0.2}Ga_{0.8}N layer, followed by a 120 nm *p*-GaN layer (both grown at 950 °C), was grown. The blue-and green-emitting QWs lead to PL spectral peaks

FIG. 1. Absorption and emission spectra of the CdSe/ZnS NCs. The absorption spectrum of Au NPs is also shown.

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FIG. 2. EL spectra showing the relative intensities at three injection current levels in the BG LED.

at 445 and 510 nm, respectively. The epitaxial sample was processed for fabricating a two-color LED of the conventional configuration following the standard procedures.^{4,5} Figure 2 shows the electroluminescence (EL) spectra of the LED at three injection current levels. One can see that the EL intensity of the green band is stronger than that of the blue range at low injection current levels. As injection current increases, the blue emission becomes stronger. This trend is due to the slow hole migration in nitride compounds. When the injection current level is low, holes are mainly distributed in the first QW (green emitting) leading to the stronger green emission. As injection current increases, more holes migrate into the deeper QWs (blue emitting) for stronger blue emission.¹⁹

Then, toluene solution of CdSe/ZnS NCs with 5 wt % in weight concentration was spin coated (speed at 100 rpm) on a fabricated LED. The thickness of the coated layer is around 200 nm. The synthesis process of such NCs of up to 85% in internal quantum efficiency has been reported in literature.²⁰ Figure 3 shows the EL spectra of the coated device at 5, 10, and 15 mA in injection current. Here, the red emission peaks around 620 nm can be clearly seen. Because of the strong absorption of blue light by the NCs for converting into red light, the relative intensity of the blue band with respect to the green range becomes weaker. To generate the effect of LSP coupling, the toluene solution of CdSe/ZnS NCs (5 wt %) and Au NPs (0.05 wt %) was spin coated on the same LED after the coating layer of pure NCs was washed out. The Au NPs have the dimension of 10–20 nm leading to the LSP resonance energy in the spectral range of 500–560 nm, as indicated by the hump of the NP absorption curve in Fig. 1. The used concentrations of NCs and NPs were optimized based on PL measurement. When the NP weight concentration is higher than 20% that of NC, the NCs may effectively contact with metallic NPs such that carriers can be directly transferred from NCs into NPs, resulting in emission quenching.²¹ Figure 4 demonstrates the comparisons of the EL spectral pattern and intensity between the blue/green LED (BG-LED), the device of CdSe/ZnS NC

FIG. 3. EL spectra showing the relative intensities at three injection current levels after the CdSe/ZnS NCs are coated on the BG LED.

FIG. 4. EL spectra showing the relative intensities of the BG-LED, the CdSe/ZnS NC coating device (NC coating), and the device of mixed coating of CdSe/ZnS NCs and Au NPs (NC/NP coating) at the fixed injection current of 15 mA.

coating (NC coating), and the device of CdSe/ZnS NC and Au NP coatings (NC/NP coating) at the fixed injection current of 15 mA. Here, one can first observe that the integrated intensity of red emission is increased by 58% after the Au NPs are added to the CdSe/ZnS NC solution. Also, after adding the Au NPs, the green intensity is significantly reduced even though the blue one is almost unchanged, implying that the LSP coupling enhances green light absorption. In other words, the energy for the increase of red intensity through the LSP coupling originates from the green emission. Therefore, the contrast between blue and green intensities becomes larger after the addition of the Au NPs, as clearly shown in Fig. 5, in which the EL spectral patterns and intensities of the NC/NP-coating device at three injection current levels are shown. Note that the chromaticity coordinate of the device emission shown in Fig. 4 is shifted from (0.22, 0.27) into (0.27, 0.24) when the Au NPs are added to the NC coating.

Table I shows the conversion power and quantum efficiencies from blue/green photon into red light under various device conditions. Generally, either the conversion power or quantum efficiency increases with increasing injection current because of the increasing intensity in the blue range, in which the absorption of CdSe/ZnS NCs is stronger. However, in the NC-coating case, the conversion efficiency seems to saturate as injection current reaches 15 mA. Either the power or quantum efficiency is increased by a factor ranging from 12 to 34% after adding the Au NPs for generating the LSP coupling. At 15 mA in injection current, the LSP coupling can result in a conversion quantum efficiency of 52.8%. This conversion quantum efficiency for red light generation is significantly higher than the reported value of phosphor for converting high-energy photon into red light.²²

In summary, we have demonstrated the fabrication of a white-light device based on a blue/green two-color InGaN/GaN QW LED by spin-coating CdSe/ZnS NCs on the top for converting blue and green lights into red emission. By adding Au NPs for generating LSP modes to couple

FIG. 5. EL spectra showing the relative intensities at three injection current levels in the device of mixed coating of CdSe/ZnS NCs and Au NPs.

TABLE I. Conversion power efficiency and quantum efficiency under various device fabrication and operation conditions. The numbers within the parentheses represent the increase percentages after the LSP coupling effect is included.

NC coating			NC/NP coating	
Injection current	Power efficiency	Quantum efficiency	Power efficiency	Quantum efficiency
5 mA	0.261	0.340	0.308 (18%)	0.400 (18%)
10 mA	0.327	0.442	0.369 (13%)	0.497 (12%)
15 mA	0.292	0.400	0.391 (34%)	0.528 (32%)

with the CdSe/ZnS NCs, the conversion efficiency was enhanced. The enhanced color conversion energy mainly came from the green light because the LSP resonance energy covered only the green range in the concerned spectral distribution. The conversion quantum efficiency could reach 52.8%.

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