Optics and Photonics Journal, 2023, 13, 243-250
https://www.scirp.org/journal/opj
ISSN Online: 2160-889X
ISSN Print: 2160-8881

Fabrication of High Color Rendering Index White Light Emitting Diodes from Gold Nanoclusters

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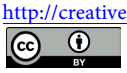
How to cite this paper: Lee, Y.-C., Chen, C., Lin, C.-A.J., Huang, C.-Y. and Lin, C.-H. (2023) Fabrication of High Color Rendering Index White Light Emitting Diodes from Gold Nanoclusters. *Optics and Photonics Journal*, **13**, 243-250.
https://doi.org/10.4236/opj.2023.1311022

Received: October 1, 2023
Accepted: November 27, 2023
Published: November 30, 2023



Abstract

We demonstrated gold nanoclusters as color tunable emissive light converters for the application of white light emitting diodes (WLEDs). A blue LED providing 460 nm to excite gold nanoclusters mixed with UV curable material generates broad bandwidth emission at the visible range. Increasing the amount of gold nanoclusters, the correlated color temperature of WLEDs tuned from cold white to warm white, and also results in the variation of color rendering index (CRI). The highest CRI in the experiment is 92.

Keywords

Gold Nanocluster, White Light Emitting Diodes, Color Rendering Index, Color Temperature

1. Introduction

White light emitting diodes (WLED) have attracted great attention due to their compactness, energy efficiency, environmental soundness and long operational lifetime compared with conventional incandescent and fluorescent lamps. There are two conventional methods to produce WLEDS, one is to properly mix red, green and blue discrete LEDs (RGB-LEDs) and the other is based on phosphor optically excited by LEDs (PC-LEDs). The disadvantage of RGB LEDs is the instability of color temperature due to degradation of different color LEDs, therefore different driving currents are required. More complex optics design is also required to collect the lights of different color LEDs. Current commercial

PC-LEDs use blue InGaN LED to pump Ce doped yttrium aluminum garnet ($Y_3Al_5O_{12}$:Ce, YAG:Ce) yellow phosphor which was developed by Nichia Chemical Co. [1]. Although YAG:Ce PC-LED has high luminous efficacy, poor color rendering index (CRI) is its main inferiority because of the red-deficiency of YAG:Ce phosphor. To get over this problem, red phosphor excited by blue LED [2] or integrating red, green and blue phosphors with UV LED to adjust the color ratio [3] could be used to compensate the red spectra region. The impact of the fluorescent materials and the position of the recombination zone on the change direction and range of color temperature variations by adding the interlayer or varying the doping concentration and the thickness of the emitting layer were also investigated in organic light emitting diodes [4] [5].

Recently, semiconductor quantum dots (QDs) is considered to replace the phosphors due to tunable optical emission can be achieved by controlling the size or the composition of QDs [4], optical scattering loss can be remarkably reduced for their nanometers in size [5], and also high feasibility of mass production. High CRI QDs-WLED was already introduced in 2006, Chen *et al.* [6] combined green-emitting, and red-emitting CdSe-ZnSe QDs into a blue InGaN chip to fabricate a three-band RGB WLED with CRI 91. Many researches focus CdSe QDs for WLED due to its superior quantum yield and high lighting quality, however, cadmium is a *toxic* heavy metal which will hinder its commercialization on the illumination. Therefore, other environmental-friendly non-Cd QDs were synthesized for lighting application, such as $CuInS_2$ [7], $AgInS_2$ [8], InP-based QDs [9], etc.

In addition to the semiconductor QDs, gold nanoparticles were attached on the YAG:Ce phosphors to augment the photoluminescent intensity due to the enhancement of local surface plasmonics of gold nanoparticles [10]. In this study, gold nanoclusters (Au NCs) comprised of several to hundred atoms were directly used to replace conventional phosphors and semiconductor quantum dots. Instead of local surface electromagnetic field of Au nanoparticles, Au NCs (usually less than 2 nm) have molecular-like properties showing discrete energy state and strong fluorescence [11]. In this study, this non-toxic, chemical and photo-stable material was used to fabricate WLED.

2. Experiments

2.1. Preparation of Gold Nanoclusters

Luminescent Au NCs were prepared through gold trichloride powder (37.5 mg $AuCl_3$, ACROS) mixed with Toluene (7.5 mg/mL) vigorously and removed all the insoluble parts by centrifugation. The supernatants containing $AuCl_3$/Toluene mixture were then sonicated by ultrasound (MISONIX with microtip, 20 kHz, 120W, and total process time: 30 mins (5 seconds ON, 1 second OFF)). After cooling to room temperature and removing the agglomerates (3000 r.p.m, 5 mins), trioctylphosphine (TOP, 50 μL, 0.5 M in toluene) was then added to protect the Au NCs, resulting in the bright yellow-emitted Au NCs. All the nanoc-

lusters were dried under evaporator for further use.

2.2. Preparation and Measurement of WLED

50 mg photoinitiator 2, 2-Dimethoxy-2-phenylacetophenone (DMPA) was dissolved in 5 ml poly (ethylene glycol) diacrylate (PEGDA) first to act as UV curable solvent. Then 7.5 mg, 5 mg, 3.75 mg and 2.5 mg of Au NCs was respectively mixed with 100 µl of UV curable solvent in the ultrasonic bath for 5 minutes. The obtained mixture was cured for 3 minutes under UV lamp to become a transparent material (**Figure 1(a)**) placed over the blue LED chip with the emission peak 460 nm to fabricate a WLED (**Figure 1(b)**).

The photoluminescent (PL) measurements were performed with a Horiba fluoromax-4 spectrophotometer equipped with a 150 W xenon lamp as the excitation source. The electroluminescent (EL) spectrum, Commission Internationale de l'Eclairage (CIE) chromaticity color coordinates, color rendering index (CRI), and correlated color temperature (CCT) were measured by Optimum ISP-050 under various forward currents.

3. Results and Discussion

The PL spectra in **Figure 2** shows a broad bandwidth emission at the visible range with a peak emission at 460 nm for 7.5 mg, 5 mg, 3.75 mg and 2.5 mg of Au NCs mixed with 100 µl toluene. The PL spectra intensity increases with the increase of Au NCs concentration in toluene and the emission peak appeared in the range of 600 - 660 nm. The broad bandwidth PL spectra attribute to size-dependent fluorescence in Au nanocluster, different size of Au NCs has discrete emission spectra, where larger NCs size induces to lower emission energy, and the relationship between the emission energy and Au NCs size is $E_{\text{Fermi}}/N^{1/3}$, which E_{Fermi} is the Fermi energy of bulk gold and N is the number of atoms [12].

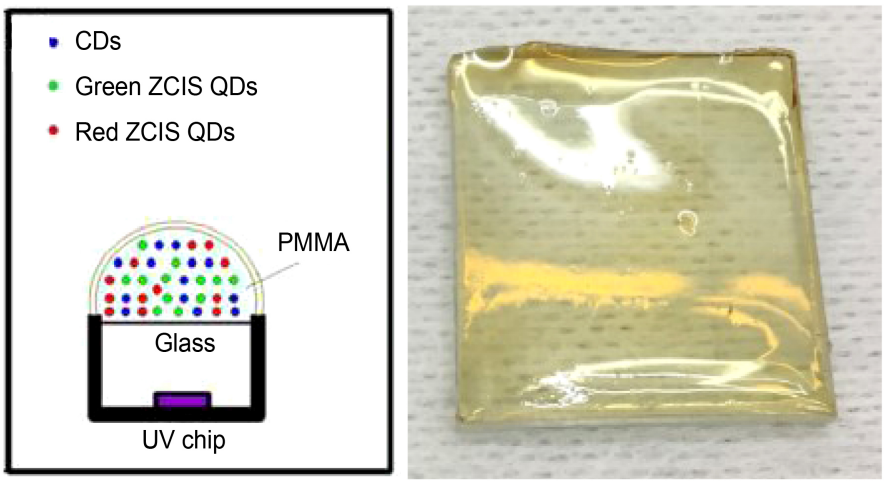


Figure 1. (a). Photograph of Au NCs mixed with UV curable material; (b) Scheme diagram of WLED.

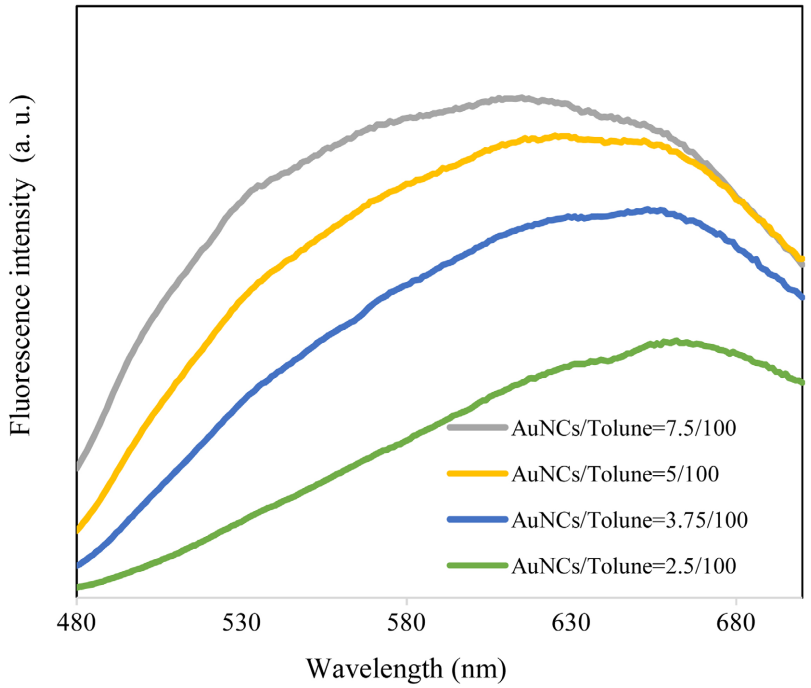


Figure 2. PL spectra for different concentration of Au NCs.

The electroluminescent (EL) spectrum, Commission Internationale de l'Eclairage (CIE) chromaticity color coordinates, color rendering index (CRI), and correlated color temperature (CCT) were measured by Optimum ISP-050 under various forward currents. The relative EL spectra of Au NCs WLED for Au NCs concentration 7.5/100 with input current measured from 2 mA to 30 mA of 460 nm blue LED pumping source is shown in **Figure 3**. As the input current increases, the peak emission wavelength remains unchanged, and the EL intensity step up gradually. **Figure 4** depicts relative EL spectra of Au NCs WLED with different Au NCs concentration including a bare blue LED under input current 20 mA of LED. It can be seen that the intensity of the EL spectra increased with the injection current. As like as PL spectra, the EL spectra also have broad bandwidth emission intensity at the visible range which shows Au NCs LED could be considered as a useful device for the application of illumination.

Table 1 shows the corresponding photographs, correlated color temperature (CCT) and color rendering index (CRI) of Au NCs WLED with different Au NCs concentration under input current 30 mA of blue LED. The color of UV curable material shifted from cold white to orange with the increase of Au NCs in PEGDA. By increasing amount of Au NCs shows a warm white generation, *i.e.*, the CCT of the Au NCs WLEDs could be tuned from cold white to warm white through the amount of Au NCs. This can be explained in EL spectra of **Figure 4** due to the same blue excitation and stronger broad bandwidth emission, the enhanced yellow, orange and red mission from more Au NCs lead to mixing light warmer. The strong emission and large broad bandwidth of EL

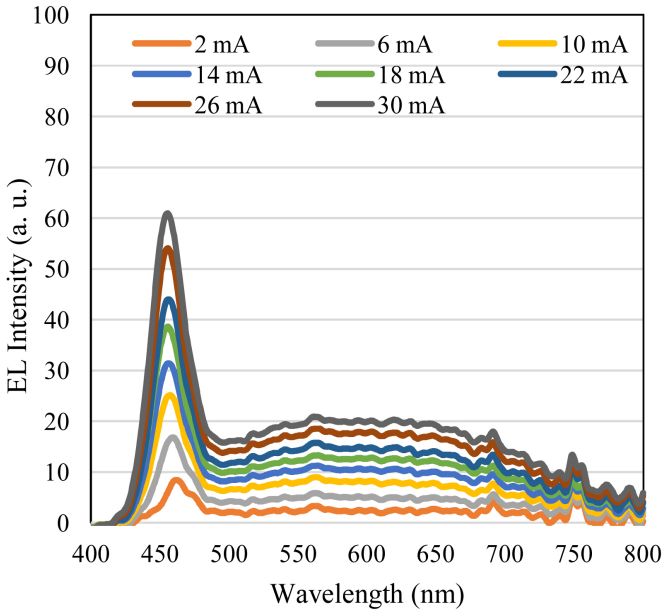


Figure 3. El spectra of AuNCs/PEGDA = 7.5/100 fabricated WLED with various operated current.

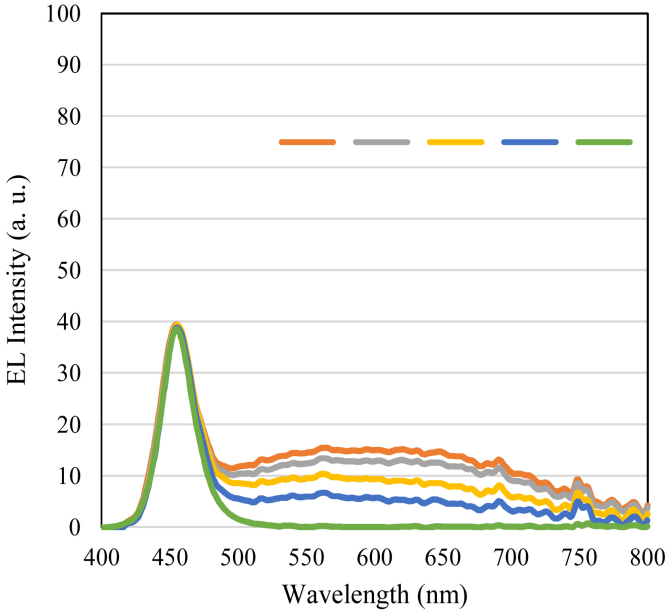


Figure 4. El spectra of Au NCs fabricated WLED with different Au NCs concentration and a bare blue LED.

emission spectra also possess the superiority to enhance the color rendering values of three devices, AuNCs/PEGDA = 7.5/100, 5.0/100 and 3.75/100 in **Table 1**, the highest color rendering index is shown 92 of 7.5/100 device. Although AuNCs/PEGDA = 2.5/100 also has broad bandwidth emission, the emission intensity is quite low to lead to a blue-rich white lighting. The CIE color coordinate of four devices, 7.5/100, 5.0/100, 3.75/100 and 2.5/100, are shown in **Figure 5**. The color coordinate of 2.5/100 locates at (0.272, 0.227) which is not at the

Table 1. Photographs of WLED fabricated with different Au NCs concentrations and their corresponding CCT and CRI.

• AuNCs/PEGDA = 7.5/100 CCT ≒ 4000 K CRI = 92 	▪ AuNCs/PEGDA = 5.0/100 CCT ≒ 6500 K CRI = 89 
▲ AuNCs/PEGDA = 3.75/100 CCT ≒ 9000 K CRI = 83 	◆ AuNCs/PEGDA = 2.5/100 CCT > 20000 K NA 

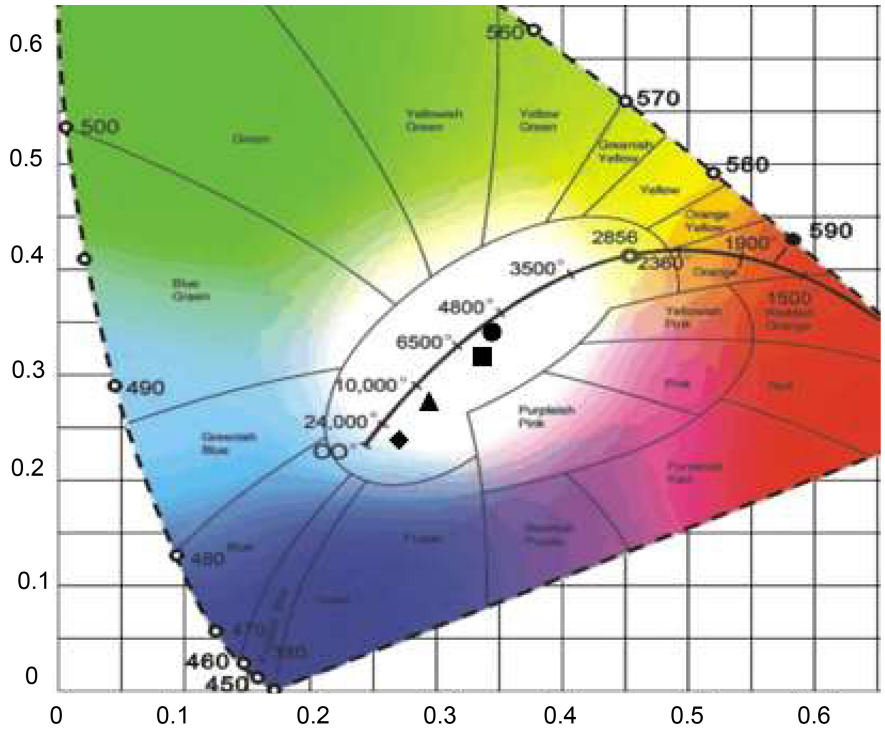


Figure 5. CIE chromaticity diagram of the Au NCs fabricated WLED with different Au NCs concentration (• AuNCs/PEGDA = 7.5/100; ▪ AuNCs/PEGDA = 5.0/100; ▲ AuNCs/PEGDA = 3.75/100; ◆ AuNCs/PEGDA = 2.5/100).

white region, hence, the CRI is not worth mentioning [13]. The CIE color coordinates of other three devices all laid in the white light region near with the Planckian locus. The color coordinate of 3.75/100 device locates at (0.296,

0.262), the color coordinate move to (0.338, 0.304) and (0.346, 0.323) while increasing more amount of Au NCs to 5.0/100 and 7.5/100, which is pretty close to the pure white coordinate (0.333, 0.333).

4. Conclusion

We have demonstrated the broadband visible emission of Au NCs under the blue LED pumping to generate the WLED. The color coordinate, CCT and CRI were investigated at different concentration of Au NCs. The results show the cold WLED of low Au NCs concentration turns into warm WLED from increasing NCs. The highest CRI appeared at the AuNCs/PEGDA = 7.5/100 which the CCT is around 4000 K and the color coordinate is quite close to the pure white light (CRI = 92). The current study used gold nanocluster films to produce white light, in the future it could directly combine gold nanoclusters with light-emitting diode chip packaging.

Funding Acknowledgement

This work was supported in part of the projects: NSC 100-2628-E-033-002-MY3, MOST 103-2221-E-033-014-MY3 and MOST 105-2622-E-033-008-CC3.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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