Modification of Blue LED using Organic-Inorganic Hybrid Polymer Doped with Nile Red for Artificial Lighting of Photosynthesis

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Abstract. The photosynthesis process of chlorophyll absorbs only the light with wavelength in the blue and red ranges. The absorption peak of the chlorophyll-A is at 428 nm and 660 nm, while absorption peak of chlorophyll-B is at 453 nm and 643 nm. We report the modification of blue LED using hybrid polymer doped with Nile Red. In order to match the total absorption spectra of chlorophyll-A and chlorophyll-B, the emission spectrum of the modified blue LED was taken out by using the wavelength conversion material. We modified the blue LED by covering the blue LED of 450 nm as excitation source with precursor of red wavelength conversion material. The red wavelength conversion material was prepared by doped precursor of TMSPMA hybrid polymer with organic phosphor of Nile Red. The precursor of hybrid polymer was synthesized using sol-gel process and then it was doped with 0.1% Nile Red. In order to freeze the precursor of these conversion material, we employed UV photo-polymerization process. The modified blue LED has two emission peaks, which are at 448 nm (blue emission) and at 651 nm (red emission). The optimum spectrum profile of the modified blue LED has similar range as the total absorption spectra of chlorophyll-A and chlorophyll-B that obtain using Nile Red with the mass of 2.9 µg and the driven current of 60 mA. This result has a potential application for the artificial lighting in the photosynthesis process of horticultures at indoor plantation.

1. Introduction.
Currently it has been developed a horticultures arrangement in the room (indoor) that using modern horticultures technology. For this purpose, an artificial lighting was needed to fulfill requirement of photosynthesis process. The sufficient light is desperately needed to synthesize water and carbon dioxide into glucose. In the photosynthesis process, chlorophyll of the plants is functioned as a light absorber. The chlorophyll does not absorb the whole range of the sun light spectrum, but only absorb a particular wavelength range, that covers of red and blue wavelengths [1]. Based on chlorophyll absorption, it has been developed lights that can be used for plant growth. Many owned manufacturers have lighting products for plant growth from incandescent lamps, fluorescent lamp and a CFL, SSL lights up. Especially for SSL most products still use a combination of red LEDs and blue LEDs to meet the conditions of light emission of red and blue that will be absorbed by the plants, but the efficiency of the red LED is very small compared to the efficiency of blue LEDs [2].
Another way to get a combination of desired light emission color can be achieved by the color conversion using a wavelength conversion material. Besides being able to overcome the problem of efficiency red LEDs, the color conversion method also can streamline the distribution of color more evenly and especially more economical because it only uses a single excitation. Conversion materials most widely used in LED phosphor is an inorganic or organic. Phosphor organic hybrid polymer is integrated with one of the alternative material for converting the wavelength of the LEDs.

To meet the emission color red and blue light is required, has been created as an alternative hybrid LED manufacturing LEDs for plant growth. The hybrid LED using a combination of a blue LED with a peak emission of 450 nm and an organic chromophore Nile Red (9- (diethylamino) benzo [a] phenoxazin-5 (5H) -one) having absorption at 552 nm and emission at 636 nm [3]. Selection of the chromophore Nile Red LED and aims to produce a hybrid that has a pattern of LED emission curve approaching the curve pattern of absorption of chlorophyll-A and chlorophyll-B. In this paper, we reported the results of the fabrication and characterization of LED hybrid using single conversion approach for artificial lighting during photosynthesis process.

2. Experimental Methods

In this experiments, we used monomer TMSPMA (3-(Trimethoxysilyl) propyl methacrylate), organic chromophores NR (Nile Red) as photoluminescence material, Irgacure-819 as initiator on UV photopolymerisation process the network of organic link in hybrid polymer matrix, and a blue LED 450 nm as the excitation and source light. Other chemicals used are ethanol, DI water, hydrochloric acid and chloroform. The first step of experiment is to synthesize hybrid polymer precursors of monomer TMSPMA using sol-gel techniques. Sol-gel process is a part of inorganic phase polymerization of monomer, which is the main chain bonding (-Si-O-Si) formation. Precursors are made using a volume ratio of monomer: ethanol: DI water as 1 : 2 : 4. This ratio is based on the optimization of previous studies [4]. Sol-gel process results in the form of colored translucent and transparent gel. NR chromophore doping process on the hybrid polymer precursors begins by dissolving the precursor and the chromophore in chloroform. Furthermore, the chromophore solution (concentration of 0.1% by weight) were mixed with the precursor solution and stirred to form a homogenous solution. Before deposited, hybrid polymer precursor solution containing chromophore mixed with photoinitiator Irgacure-819 at a concentration of 0.1% by weight of the mass of the precursor. The second step is to make sample of modified blue LED as Hybrid LED, which is made by coating the blue LED with the mixture using a solution coating techniques. Finally, Hybrid LED pre-baked in an oven 50°C for 30 minutes to remove residual solvent following by UV photopolymerisation for 15 minutes and finishing with post-baked in an oven 50°C for 18 hours to complete the whole polymerisation process. The emission spectra of this Hybrid LED were characterized for several variations electric current drive from 10 mA to 80 mA and variation of the mass of the chromophore Nile Red performance films ranged 1.4 µg to 2.9 µg. Emission spectrum measurements has been done using Fluorescence USB4000FL Spectrometer and Spectra suite software from Ocean Optics.

3. Results and Discussions

The resulting Hybrid LED has a film on it’s surface containing Nile Red in organic groups of hybrid polymer TMSPMA that have been polymerized. Thin film hybrid polymers containing Nile Red looks red as shown in Figure 1.(a). There emission spectrum of the blue LED and Nile Red ( included its absorption spectrum) shown in Figure 1.(b).

In principle, this Hybrid LED is combining blue light emission of the blue LED as the excitation source then most of emission blue light is converted into red light by the chromophore Nile Red, which is indicated in Figure 2. Mass of thin films in Hybrid LED for each sample LED hybrid consist of 0.1 % Nile Red. Since we know the value of the thin film mass, Nile Red mass chromophore contained in each sample will be known, as shown in Table 1.
Figure 1. (a) Photograph of the modified blue LED as Hybrid LED, (b) the emission spectrum of blue LED and chromophores Nile Red (blue line indicate the absorption spectrum of its Nile Red).

Table 1. The mass of the coated wavelength conversion material on the surface of Hybrid LED and Nile Red mass that present in each sample.

| No. | Sample Code of Hybrid LED | Coated mass in mg | Nile Red mass in µg |
|-----|----------------------------|-------------------|---------------------|
| 1   | H-LED_1                   | 1.4               | 1.4                 |
| 2   | H-LED_2                   | 1.9               | 1.9                 |
| 3   | H-LED_3                   | 2.0               | 2.0                 |
| 4   | H-LED_4                   | 2.4               | 2.4                 |
| 5   | H-LED_5                   | 2.9               | 2.9                 |

Figure 2. The emission spectra of H-LED_1 at various driven electric current from 10 mA to 80 mA.

The Hybrid LED emission curve profile has match the total profile of absorption curve of chlorophyll-A and chlorophyll-B. The incorporation of Hybrid LED emission curve normalized with the normalization absorption curve of chlorophyll-A and chlorophyll-B. Its normalization absorption curve spectra was using an absorption curve of chlorophyll-A and B in the solvent diethyl ether [5,6].
All the five samples Hybrid LED has yield emission spectra curve mostly close to the total absorption curve of chlorophyll-A and B. The optimum emission spectra depend on NR mass content and driven current to the LED. Sample H-LED_3, H-LED_4, and H-LED_5 have optimum emission spectra with condition as shown in Table 2.

Table 2. Optimum parameter for Hybrid LED

| No. | Sample Code of Hybrid LED | Nile Red mass in µg | Driven current in mA |
|-----|--------------------------|---------------------|----------------------|
| 1   | H-LED_3                  | 2.0                 | 80                   |
| 2   | H-LED_4                  | 2.4                 | 60                   |
| 3   | H-LED_5                  | 2.9                 | 60                   |

The effectiveness of the emission curve Hybrid LED with optimum conditions as shown above has meet the absorption curve of chlorophyll in the blue and red wavelength region. This comparation results shown in Figure 3. The efficiency of Hybrid LED that meet the chlorophyll absorption curves in the blue and red wavelength region can be seen in Table 3.

Figure 3. The Optimum Hybrid LED emission curve that able to covering superposition absorption curve of chlorophyll-A and B.

Table 3. Efficiency of Hybrid LED

| No. | Sample Code of Hybrid LED | Driven current in mA | Efficiency in % |
|-----|--------------------------|----------------------|-----------------|
| 1   | H-LED_3                  | 80                   | 49.1            |
| 2   | H-LED_4                  | 60                   | 44.3            |
| 3   | H-LED_5                  | 60                   | 47.0            |

The performance of Hybrid LEDs were observed over eight hours at optimum condition of operation. The optimum operation condition, namely for samples H-LED_3 and H-LED_5 were driven with electric current of 80 mA and 60 mA, respectively. The measurement results are shown in Figure 4. From this figure, it can be observed that when Hybrid LED lighting continuously for eight hours, the total emission intensity of Hybrid LED were almost constant, it means Hybrid LED has good stability. Except in the first half hours after its turn on, this is due to the burnout process of the wavelength conversion material itself.
Figure 4. Hybrid LED performance, (a) total emission intensity of Hybrid LED, (b) emission intensity of blue light component, and (c) emission intensity of red light component.

The emission stability of blue and red light components, above two hours after Hybrid LED was turned on, tend to stable up to eight hours. Indicate the good stability on blue and red light emission of Hybrid LED. At the beginning the intensity changing on the blue region were slightly increases, however, on the red region seen the emission intensity slightly decreases when constantly lit. But after two hours is turned on, the emission intensity of blue and red LED hybrid tends to be stable. Also can be observed that when the supplied current to Hybrid LED has a great value, it made red light component curve was more lower as shown in H-LED_3 with driven current of 80 mA. Compare to H-LED_3, H-LED_5 with driven current of 60 mA has the red light component more higher and more stable.

4. Conclusion
Hybrid LEDs have been successfully made as an artificial lighting source that meet the purpose for the photosynthesis process. The emission spectrum of Hybrid LED has a peak at 450 nm in the blue region and a peak at 651 nm is the red region. Characteristics of the resulting hybrid LED has the best results for the mass of Nile Red 2.9 micrograms with the driven current of 60 milliAmperes.

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