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Enhancing selectively red spectral region by photonic crystals toward white light emission

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ABSTRACT

The combination of red, green, blue (RGB) dyes and photonic crystals (PCs) is explored for white light application. The results show RGB emission is difficult to program by fluorescence resonance energy transfer, which is impossible to achieve the white light emission. When the PCs is used as an optical substrate, the green and blue spectral components obtain 2.7–3.5 times enhancement compared with the control sample due to large surface area of PCs. More importantly, the enhancement ratio of red spectral component is higher than that of the other color in the case of the stopband of PCs overlapping emission wavelength of Nile red, resulted from the enhanced light extraction of PCs, which makes up for the lack of red light, so that CIE coordinates are approaching to the white light region. The strategy will be of great guideline toward white light emission and play an important role on developing novel lighting devices.

1. Introduction

Phosphor-converted white light-emitting diodes (LEDs) have received considerable attention because of their potential applications in solid-state lightings and display systems [1]. Three typical combinations exist for the formation of white LEDs: (i) red, green and blue LEDs; (ii) near-ultraviolet LED+red/green/blue fluorescence, and (iii) blue LED+yellow phosphorescence [2]. At present, the most popular commercial phosphors for white LEDs mainly rely on a combination of a blue light source and the YAG:Ce yellow phosphor. This type of LED shows a low color rendering index because of their weak emission in the red spectral region, which will deteriorate the illumination quality and environmental friendliness [3,4]. To overcome the problems, three approaches have been proposed in the literature. One is to develop quantum dots (QDs) considered as promising phosphor converters in white light fabrication due to their outstanding virtues, such as good optical stability, facile color tenability and solution processability, [5,6] but they are hazardous and expensive owing to their difficult synthesis method, and their long-term stability has not been verified [7]. The second method consists in mixing YAG:Ce phosphor with red or orange-emitting phosphors including oxide and sulfide phosphors [8,9]. Although this method has been widely adopted to achieve warm white LED, moisture instability of sulfide, and high thermal quenching at elevated temperatures of oxide-based phosphors are critical problems [10–12]. The third is fluorescence resonance energy transfer (FRET). With the help of partial FRET in a multicomponent donor-acceptor assembly one can be tune the emission property and generate white light emission [13–18]. An efficient FRET from donor to acceptor needs to fulfill some criteria including, spectral overlap, distance between chromophore, and relative orientation between transition dipoles of the involved molecules. However, obtaining the appropriate spatial organization for efficient energy transfer is a key challenge; a structural matrix is required that furnishes both orientation and proximity between donor and acceptor molecules. Therefore, how to achieve white light with satisfactory luminous quality is still an important and challenging task.

As we know, photonic crystals (PCs) have emerged as the most promising candidate in photonics applications owing to its unique properties [19–21]. Near the stopband of PCs, light propagates at reduced group velocity owing to resonant Bragg scattering, which can enhance optical gain leading to stimulated emission [22]. Amplified spontaneous emission has been observed when PCs are used as a matrix for emitters, such as dyes, polymers, semiconductors [23–25]. Importantly, PCs can act as photonic environment to modify the spectral properties of the FRET via stopband [26–29]. Furthermore, the PCs present large surface-to-volume ratio for the effective dispersion of phosphors, which can avoid the concentration quenching effect. Thus, PCs as the excellent optical substrate are a powerful tool to manipulate and improve

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luminescent signal. Herein, we suggest a simple fabrication method for emissive composites composed of PCs as an optical substrate and red, green, and blue (RGB) dyes as fluorophores at various ratios, which enable a facile white light emission via control of interactive energy transfer between dyes. Unlike the conventional use of physically dispersed color dopants, FRET between fluorophores is difficult to program. As the optical substrate, the PCs not only has large surface area, resulting in 2.7–3.5 times enhancement of the green and blue spectral components, but also possesses extraordinary light extraction ability, leading to selective enhancement of red spectral component, which makes up for the lack of red light, so that chromaticity parameters are approaching to the white light region.

2. Experimental

2.1. Materials

Styrenes (St), methyl methyacrylate (MMA), arylic acid (AA) were purified by distillation under reduced pressure. The initiator of $(NH_4)_2S_2O_4$ (APS) was recrystallized three times. Milli-Q Water (18.2 MΩ/cm) was used for all experiments. All reagents and materials were purchased from Aldrich unless otherwise noted.

2.2. Fabrication of the crosslinked PCs film

Monodisperse latex spheres of Poly(St-MMA-AA) were synthesized via our previous method [30]. The resulting latex spheres were used directly without purification. The polydispersity of the latex spheres was about 0.5%, which was detected by ZetaPALS BI-90plus (Brookhaven Instrument). The PCs film was prepared on glass substrates by a vertical deposition method at constant temperature (80 °C) and humidity (80%). After the samples were dry, they were sintered at 85 °C for 30 min to increase the stability of the samples. Photo-crosslinkaged PCs film was fabricated by immersing arylamide solution for illumination of UV light [31].

2.3. Preparation of RGB films based PCs

The mixture of perylene, coumarin 6 and Nile red loaded PMMA films for tuning the white light were prepared by spin-coating the chloroform solution of perylene, coumarin 6, Nile red and PMMA mixture (m_{PMMA}: m_{dyes} = 50: 1) onto the crosslinkaged PCs film and glass substrates (as the control sample) at 1200 rpm for 20 s. Proportion of three dyes (perylene, coumarin 6 and Nile red) can be adjusted.

2.4. Characterization

The scanning electron microscope (SEM) images were obtained with a field-emission SEM (JEOL JSM-4800, Japan), after sputtering the samples with a thin layer of gold. Atomic force microscopy (AFM) characterization was performed with an SPI 3800N multimode scanning probe microscope (Seiko Instruments). Topographical images were obtained in contact mode with a silicon cantilever having a nominal spring constant of 0.02 N/m and at a scan rate of 1.0 Hz. The Ultraviolet–visible (UV–vis) absorbance spectrum was obtained by an UV–vis spectrophotometer (UV-2600, Japan). The fluorescence spectra were measured by a Hitachi F-4500 fluorescence spectrophotometer, samples were excited at 400 nm. The micro-reflectance spectra observation of the PCs were carried out by combining a reflected microscope (Olympus MX40, Japan) and a fiber optic UV–vis spectrometer (Ocean Optic HR 4000, USA). The illuminating light was focused onto the PC through an objective lens and the reflected light was collected by the same lens and then transported to the spectrometer through the optic fiber. The reflectance spectra were recorded normal to the hkl = 111 planes of the PCs.

3. Results and discussion

By tuning the overlap of the absorption and emission spectra, using appropriate materials act as both the converter and emitter simultaneously. Here, three types of commercially available light-emitting dye molecules: Nile red (R), coumarin 6 (G), and perylene (B) were prepared for red, green, and blue emissions, respectively [32]. Absorption and PL spectra of RGB dyes in chloroform solutions are illustrated in Fig. 1. The emission of B and the absorption of G and the emission of G and the absorption of R have good overlap, which means that energy transfer between donor (B or G) and acceptor (G or R) dyes will occur if they are in close proximity. The spectral overlap between the emission and absorption of chromophores indicates that photons emitted from the chromophore could definitely be absorbed and converted by the other. This chromophores energy transfer should be more important in the case of randomly mixed PMMA.

We are able to control the mixing of the three RGB colors in order to tune the white light. Fig. 2 shows emission spectra of three dye containing varying concentrations of perylene, coumarin 6 and Nile red. The control of luminescence of multiple dyes in a single solution deposition process has proved elusive. It is clear that on gradual addition of R to the aqueous solution there is a gradual decrease of PL intensity of G indicating energy transfer from G to R. Nevertheless, it is to be noted that the intensity of emission peak of R starts to rise, then to reduce slightly, consistent with the formation of dye aggregates with low fluorescence quantum yield [33]. Similarly, no significant red part of PL is observed when B: G: R ratio is 3:3:3 because of the absence of energy transfer. Although the doping concentration of R dye is increased, the solid film shows a similar trend in the solution evolution of the photoluminescence, where it can be seen that the conversion to red light is fairly inefficient. In this spectral region, the eye sensitivity is also lowest, hence an enhancement in this region is required. Indeed, emission color tuning becomes difficult if RGB dyes are located altogether within the same matrix [15,34]. This is presumably due to scare chance of energy transfer resulting from the large separation between dyes, leading to the need for more population of red dye molecules. However, at low dye concentrations FRET will occur either with poor efficiency or not at all, and at higher concentrations the signal will be quenched as a result of aggregation. As shown in Fig. 2, the emission color is varied according to the RGB ratios, indicating the inadequacy for emission color tuning, even enhancing the dosage of red dyes. The results prove unsuitable for control of the desired emission due to extensive and undesirable Förster transfers between perylene, coumarin, and Nile red. In fact, it is reported that partial FRET between physically dispersed color dopants does not conform to a simple “linear” model and therefore is difficult to program. For a tricolor system, inadvertent FRET, for instance between green and red dyes, makes color tuning difficult [32]. Thus, we try to introduce PCs as the optical substrate to manipulate red emission.

According to our previous work, the PCs film used as the substrate of optical devices was fabricated, which involved the self-assembly of latex spheres, the infiltration of monomers and photopolymerization. The step of photopolymerization can greatly improve solvent resistance of the PCs film. Fig. 3a shows the SEM image of poly(styrene-methyl methacrylate-acrylic acid) (P(St-MMA-AA)) PCs film. The SEM image illustrates that the colloid spheres are in a face-centered cubic arrangement with a close-packed plane (111) oriented parallel to the substrate. From the