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Fluorescence resonance energy transfer between conjugated molecules infiltrated in three-dimensional opal photonic crystals

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ABSTRACT

Fluorescence resonance energy transfer (FRET) from Coumarin 6 (C-6) to Sulforhodamine B (S-B) infiltrated into opal PMMA (poly-methyl-methacrylate) photonic crystals (PCs) has been studied in detail. The intrinsic mesh micro-porous structure of opal PCs could increase the luminescent efficiency through inhibiting the intermolecular interaction. Meanwhile, its structure of periodically varying refractive indices could also modify the FRET through affecting the luminescence characteristics of energy donor or energy acceptor. The results demonstrate that the FRET efficiency between conjugated dyes was easily modified by opal PCs.

1. Introduction

Three-dimensional photonic crystal (PC) is a type of periodic dielectric composites, where the refractive index varies periodically on the optical wavelength scale [1–3]. Thus it will provide a photonic stop band (PSB), where the light propagation is modified. This exceptional characteristic leads to a new specific physical environment, which can affect the spontaneous emission of embedded luminescent guests such as organic dyes [4], quantum dots [5] and rare earth ions [6]. Recently, a series of works have shown many interesting phenomena, such as photon localization [7], modulation of energy transfer [8], Lamb shift [9], and the improvement on luminescent quantum yield [10]. Therefore, PCs can be used in the optoelectronic device applications, such as all optical switches [11], laser [12], light emitting diode [13], solar cells [14] and fluorescence-based biosensors [15].

In this investigation, we chose three-dimensional opal PMMA photonic crystals as research objects. PMMA PC is a type of organic polymer opal PCs, where PMMA microspheres are tightly arranged. Due to the refractive index difference between PMMA and air, the propagation of light in PMMA PCs is easily modified by the photonic stop band (PSB). Compared with other kinds of PCs, PMMA PC owns many advantages, such as easily being processed, good orderliness and adjustable band gaps [16]. Therefore, the opal PMMA PC often acts as a model PC to investigate the effect of PCs on the photophysical process of fluorescence species [17].

Fluorescence resonance energy transfer (FRET) [18] is a physical phenomenon in which the energy absorbed by a fluorophore transfers to another fluorophore through a nonradiative pathway [19]. This phenomenon could be used in the field of beacon biosensors [20] and optoelectronic devices [21]. In previous reports, people reported that the efficiency of the FRET could be increased while the PSB of PCs is overlapped with the fluorescence spectrum of the energy donor [22,8].

In this paper, we investigated the effect of the PSBs on the fluorescence resonance energy transfer from Coumarin 6 (Donor: C-6) [23] conjugated molecules to the Sulforhodamine B (Acceptor: S-B) [24], as both of the donor and the acceptor were infiltrated in the opal PMMA PCs which could be obtained through the vertical self-assembled deposition method [25,3]. The role of PCs on the FRET has been studied in detail. This investigation could be beneficial to further understanding the principle of FRET process and utilizing the PCs to control the energy transfer.

2. Experimental part

Materials: Sodium hydroxide (Fengchuan, Tianjin), potassium peroxydisulfate (Huadong, Tianjin), methyl methacrylate (Guangfu, Tianjin), C-6 and S-B (J&K Chemica, Beijing) were utilized. MMA (methyl-methacrylate) was purified before utilized, while other chemical reagents were utilized directly.

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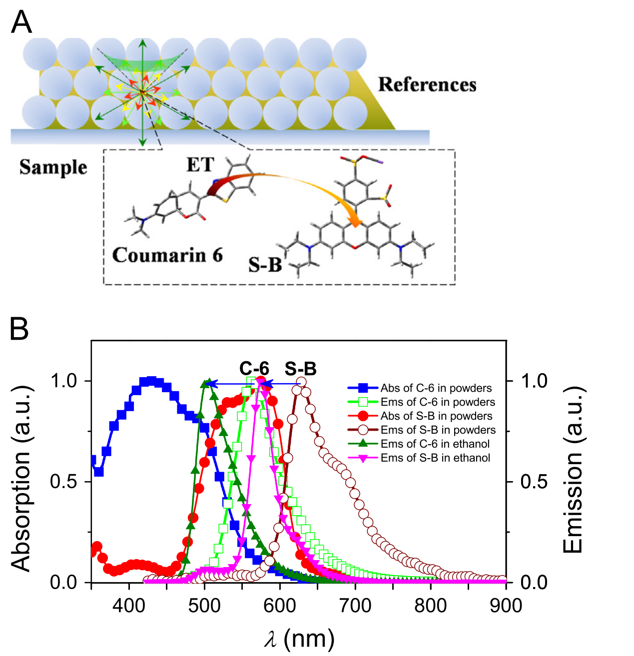

Fig. 1. (A) Schematic diagram of PMMA PCs infiltrated with C-6 and S-B (B) absorption and fluorescence spectra of C-6 (the blue and the light green lines, respectively) and S-B (the light red and the dark line, respectively) in aggregation state and the fluorescence spectra of C-6 (the dark green line) and S-B (the pink line) in ethanol solution. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this article.)

Preparation of the monodispersed PMMA latex: First, the MMA was purified by sodium hydroxide solution. Then, a finite amount of MMA was added into a flask (multiple necks) which held 40 ml deionized water. When stirring this mixture, we added potassium peroxydisulfate into the flask, which acted as the initiator. Finally, the liquid was stirred with a magnetic stirrer at 90 degrees centigrade for 90 min. During this process, three necks of flask were sealed up with one condenser pipe (neck in the middle) and two glass stopper (necks on the sides).

Sample preparation and spectral measurement: Three-dimensional PMMA PCs were prepared by the vertical self-assembled deposition method. C-6 and S-B acted as the energy donor and acceptor, respectively, and both purchased from Sigma without further purification. In the blend ethanol solutions, the concentration of S-B is always 10^{-4} M, but that of C-6 in solution is 1×10^{-4}, 3×10^{-4}, 5×10^{-4}, 1×10^{-3}, 1.5×10^{-3}, 2×10^{-3} M, respectively. So, the ratios between donor and acceptor in solution are 1:1, 3:1, 5:1, 10:1, 15:1, 20:1, when we take the same volume of C-6 and S-B. The reference samples were the C-6 and S-B in blended powders (the aggregation state) out of PCs. Blend powders out of PCs represented the residues after the evaporation of solvent. Steady-state transmittance measurements were performed by a UV–Vis spectrophotometer (Purkinje, TU-1810PC). Photoluminescence (PL) spectra were recorded by a fiber optic spectrometer (Ocean Optics, USB4000). The laser source is a continuous laser with the excitation wavelength of 400 nm. The angle-dependent spectral measurement could be considered in Ref. [18]. All the measurements are performed at room temperature.

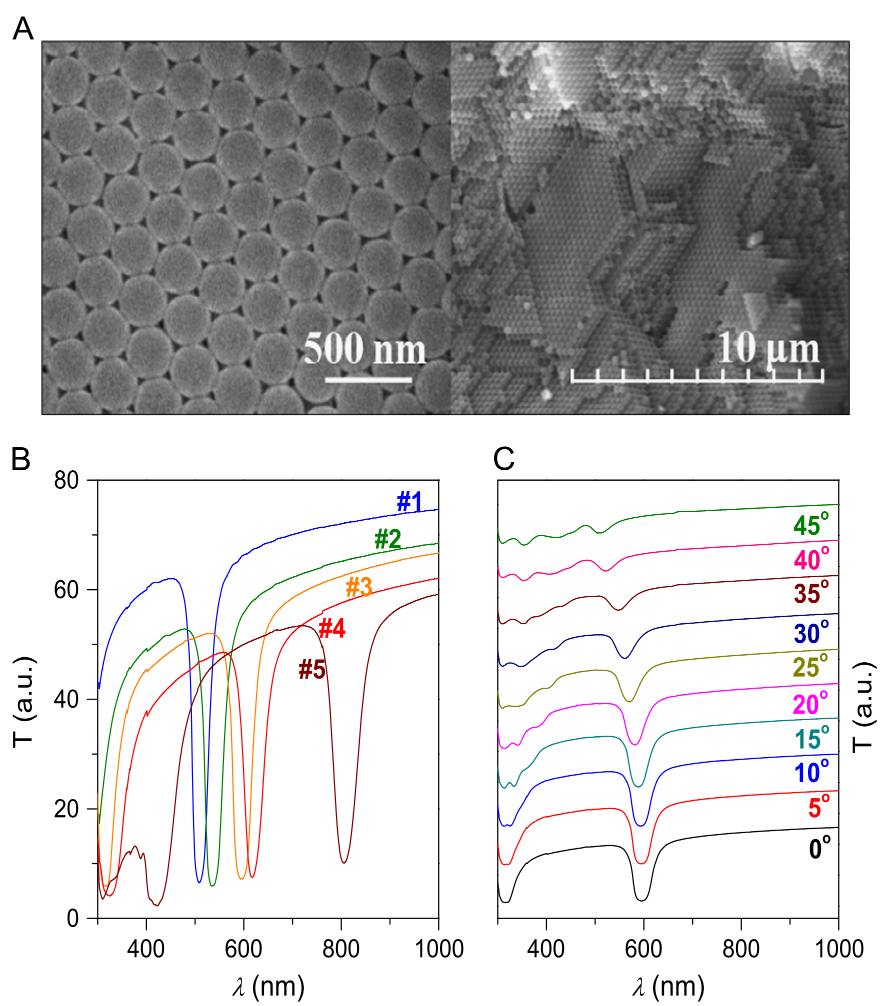

Fig. 2. The SEM images of surface (500 nm) and section (10 μm) of PMMA opal PCs; (B) Transmittance spectra of PMMA PCs; (C) angle-dependent transmittance spectra of PC#3.