Controlling the photoluminescence spectroscopy of quinacrine dihydrochloride by SiO_2 inverse opal photonic crystal*

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Manipulation of the photoluminescence spectra of light-emitting materials doped in three-dimensional (3D) inverse opal photonic crystals is investigated. Quinacrine dihydrochloride molecules doped highly ordered SiO_2 inverse opal is successfully synthesized by co-assembly combined with double-substrate vertical infiltrate method. The quinacrine dihydrochloride-doped and -undoped SiO_2 inverse opals each exhibit an apparent photonic band gap (PBG) in the visible light region. Significant suppression of the emission is observed when the PBG is overlapped with the quinacrine dihydrochloride emission bands. The mechanism of suppression effect of PBG in inverse opal on the fluorescence intensity of quinacrine dihydrochloride molecules is studied.

Keywords: inverse opals, photonic stop band, photoluminescence

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1. Introduction

Photonic crystal exhibiting a three-dimensional(3D) periodic modulation of the dielectric constant has attracted much attention since it was introduced by Yablonovitch[1] and John[2] in 1987. The periodic electromagnetic modulation created by a photonic crystal can yield a gap of forbidden photon energies, which is the same as an electronic band gap created by the periodic arrangement of atoms in a semiconductor.[3] When the refractive index of the dielectric material is sufficiently large, a complete photonic band gap is formed in which Bragg diffractions inhibit a range of wavelengths from propagating through the photonic crystal over all directions.[4–7] However, when the refractive index contrast is low, an incomplete photonic band gap is obtained in which a range of wavelengths is partially inhibited from propagating over certain directions. Colloidal crystal is a kind of photonic crystal which has an incomplete photonic band gap (PBG) at visible or near-infrared wavelength, and this PBG position can be tuned by changing system structural parameters. The refractive index ratio of a colloid (such as polystyrene (PS), polymethyl methacrylate (PMMA) or SiO_2) to the background of the air in colloidal crystal is often low, hence, we obtain a pseudo-PBG in most cases.[8] If a high dielectric constant material infiltrates into the voids of colloidal spheres and then removes the colloids by hyperthermia or chemical etching, a high refractive index ratio of inverse opal structure material is obtained. In a photonic crystal with a complete PBG, spontaneous emission is inhibited fully because the optical electromagnetic mode does not exist in the PBG frequency range.[9,10]

Inverse opal can exhibit a high-degree interconnected porosity (approximately 75%) with an extremely uniform size (average size normally in the range of 100 nm–1000 nm) and a periodic distribution of pores, which is achieved through colloidal monodispersity.[11] This structure can have many potential applications, such as, in the areas of gas sensing,[12] color fingerprinting,[13] and fabricating functionalized polymeric films,[14] adjustment of the intensity of up-conversion emission bands of the rare earth ions,[15] and directional fluorescence spectra of laser dye,[16] etc. According to Bragg diffraction law, the optical properties of the inverse opal can be tuned by modifying the dielectric components of the system. The PBG in opal or inverse opal results from the periodic dielectric field on the scale of optical wavelength. This physical environment provides a possibility to modify the behavior of photoelectron, such as photovoltaic conversion, energy transition, spontaneous emission, etc.

In this paper, the fluorescence emission spectra of quinacrine dihydrochloride molecules doped in SiO_2 inverse opal are investigated. Quinacrine dihydrochloride molecules with high fluorescence quantum yields are often used as fluorescence labeling in the field of molecular biology.[17] We also study the suppression effect of PBG on the photoluminescence intensity of quinacrine dihydrochloride molecules.

2. Experiment

2.1. Materials

All reagents, including potassium persulfate ($K_2S_2O_8$), sodium bicarbonate ($NaHCO_3$), sodium dodecyl benzene sulfonate (SDBS), sodium hydroxide (NaOH), tetraethoxy silane

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(TEOS), ethanol, 0.1-M HCl, 100-μg/mL quinacrine dihydrochloride aqueous solution, were used without further purification. The styrene was purified with NaOH and then washed with pure water to pH∼7. We used ultrapure water (18.25 MΩ·cm) for synthesis.

2.2. Preparations of SiO_2 inverse opal and SiO_2 disordered films

Monodispersed colloidal spheres PS (334 nm in diameter, standard deviation approximately 1.2%) were synthesized by surfactant-free emulsion polymerization through using potassium persulfate as initiator.[18] The glass substrates each were 1.25 cm×4 cm scale pieces and underwent hydrophilic processing. The preparation method of SiO_2 inverse opal was modified from the method of Hatton *et al.*[11] The precursor hydrolyzed TEOS solution, which consists of TEOS, 0.1-M HCl, and absolute EtOH (1:1:1.5 of weight ratio, respectively), was stirred for 1 h to mix at room temperature. 0.125-mL hydrolyzed TEOS solution made above was added into 20-mL distilled water and stirred for 1 h, then 1-mL 2.5-wt% PS aqueous suspension was added, and stirring continued for 30 min. The prepared hydrophilic substrates were vertically dipped on the suspension and self-assembled in a 65-°C vacuum oven for two days. When co-assembly thin film was obtained, the thin film was placed in an oven that was kept at 500 °C for 5 h to remove PS colloidal template and form SiO_2 inverse opal structure. After cooling down to room temperature we obtained sample 1. According to the same procedure except to change the volume of precursor hydrolyzed TEOS solution to 0.150 mL, we obtained sample 2.

The reference sample 3 of SiO_2 film, which is in an amorphous state at which the directionality of bonding becomes disorganized, was prepared with the same precursor hydrolyzed TEOS solution. In order to make the quantity of SiO_2 on the substrate close to the other two samples, 0.137-mL hydrolyzed TEOS solution was added to 20-mL distilled water. Then the treating process is the same as the procedure of SiO_2 inverse opal except to use the polydispersity PS spheres as "template".

2.3. Preparations of quinacrine dihydrochloride molecules-doped SiO_2 inverse opal and SiO_2 disorganized film

In this process, 100-μg/mL quinacrine dihydrochloride solution was used as dipping solution to infiltrate into the SiO_2 inverse opal and disordered structure film. In order to reduce the damage degree to the film structure in infiltration processing, we used double-substrate vertical deposition method to infiltrate. The up-substrate was also hydrophilic. The double-substrate was immersed in dipping solution for 24 h to make quinacrine dihydrochloride molecules sufficiently infiltrate into the voids and surface of the film, then it slowly lifted out of the solution. After that, the double-substrate was placed in a 80-°C oven for 10 min to evaporate the solvent. Then the up-substrate could be readily removed and the quinacrine dihydrochloride molecules-doped SiO_2 inverse opal and SiO_2 disordered film were obtained.

2.4. Characterizations

The morphology of the thin films was studied by field emission scanning electron microscope (FESEM, Hitachi S–4800). The optical properties of the films were investigated by UV-VIS spectrophotometer (Hitachi U–3900), and fluorescence spectrophotometer (FL, Hitachi F–7000, 220 –240 V).

3. Results and discussion

3.1. SEM images

Figure 1 shows that the average diameter of polystyrene (PS) sphere is ∼ 334 nm, and after calcination the mean diameter of air sphere in SiO_2 inverse opal is reduced to ∼ 280 nm. The average diameter of air sphere, compared with that of initial PS sphere, is reduced by 16.17%, which is caused by PS colloid volume shrinkage during calcinations. The inverse opal shows in Fig. 1(b) highly ordered triangular arrangement which corresponds to the (1 1 1) plane of an fcc structure. We can see that the inverse opal is of well ordered multilayer structure in Fig. 1(c), which is an essential guarantee for the existence of a photonic stop band in inverse opal. Figure 1(d) shows that reference sample 3 is quinacrine dihydrochloride molecules-doped disorganized SiO_2 film. The SEM image of sample 2 is similar to that of sample 1, but not shown in this paper. The average diameter of air sphere in sample 2 is ∼ 271 nm, and the shrinkage rate is 18.86% due to the difference in hydrolyzed TEOS concentration. The averagediameter of air sphere in quinacrine dihydrochloride molecules-doped SiO_2 inverse opal is similar to that in undoped inverse opal.

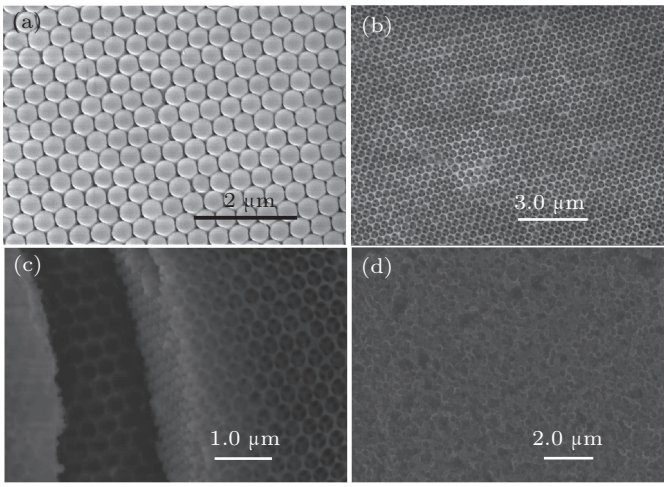


Fig. 1. SEM images of (a) co-assembly PS and SiO_2 precursor colloidal crystal of sample 1, panels (b) and (c) are after calcining quinacrine dihydrochloride undoped and doped SiO_2 inverse opal of sample 1, respectively, and (d) disordered SiO_2 film of sample 3.

3.2. Ultraviolet and visible (UV–vis) transmission spectra

Figure 2 shows that sample 1 has the central wavelengths of PBG at 511 nm and 507 nm before doped quinacrine dihydrochloride and after doping, and sample 2 has central wavelengths of PBG at 495 nm and 494 nm before and after doping, respectively. They all show green color when they are viewed with our naked eye in the direction perpendicular to the sample due to the limitation of the resolution of our eyes. The PBG position in inverse opal can be estimated by Bragg's law of diffraction combined with Snell's law[19,20] as follows:

$$\lambda = \frac{2d_{hkl}}{m}\sqrt{n_{\text{avg}}^2 - \sin^2\theta}, \tag{1}$$

where λ is the central wavelength of PBG; d_{hkl} is the interplanar spacing of (hkl) lattice plane, and

$$d_{hkl} = D\sqrt{2}/\sqrt{h^2+k+\bar{l}^2}$$

in which D is the pore spacing; m is the order of Bragg diffraction for which interference occurs; n_{avg} is the average refractive index of inverse opal, and $n_{\text{avg}} = \Phi \times n_{\text{sphere}} + (1-\Phi) \times n_{\text{interspace}}$, in which Φ is the volume fraction of spheres and generally $\Phi = 74\%$ in a fcc structure, and n_{sphere} and $n_{\text{interspace}}$ are the refractive indices of material of sphere and interspace, respectively; θ is the incident angle, so different colors can appear when we observe the inverse opal from different angles. According to Eq. (1), before doping, the PBG positions of inverse opal samples 1 and 2 are 510 nm and 494 nm respectively, which are consistent with the experimental results (511 nm and 495 nm). After being doped with quinacrine dihydrochloride, two samples both have the PBG positions with a little blue shift, which is because doped quinacrine dihydrochloride molecules change the average refractive index of the system.

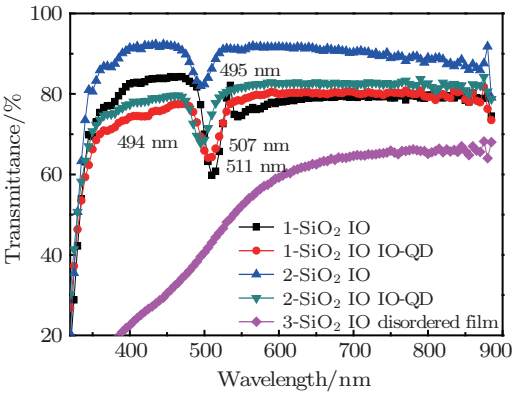


Fig. 2. (color online) UV-vis transmission spectra of SiO_2 inverse opal (IO), quinacrine dihydrochloride-doped SiO_2 inverse opal (IO–QD), and quinacrine dihydrochloride-doped disordered films.

From Fig. 2, no PBG is observed in reference sample 3 due to its disordered structure.

3.3. Photoluminescence properties

Figure 3 shows the fluorescence spectra of quinacrine dihydrochloride molecules-doped samples 1, 2, and reference sample 3 under 417 nm, which is the excited wavelength of quinacrine dihydrochloride molecules. Quinacrine dihydrochloride is one of the frequently used fluorescence indications in the field of molecular biology, and its excited wavelength $\lambda_{\text{ex}} = 417$ nm, and emission wavelength $\lambda_{\text{em}} = 496$ nm.

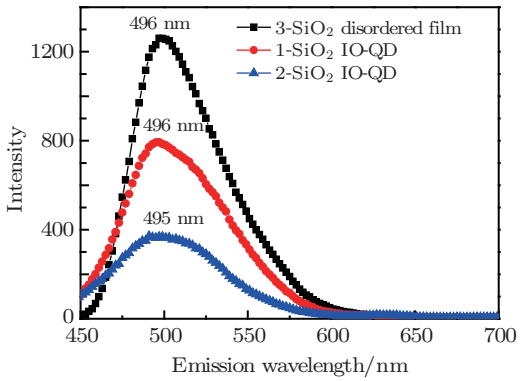


Fig. 3. (color online) Fluorescence spectra of quinacrine dihydrochloride-doped samples 1, 2, and reference sample 3 under the excitation wavelength of 417 nm.

Compared with samples 1 and 2, reference sample 3 has the highest PL intensity, because in the amorphous sample, the number of PL molecules located at or near the surfaces of SiO_2 particles is more than that of the inverse opal sample and the site symmetry of PL molecule in it should be much lower.[21] It can also be seen that in sample 2, the PL intensity at 496 nm is significantly suppressed compared with sample 1. As the luminescence of rare-earth ions is mostly dependent on the crystalline environment, which is mainly determined by the occupation of active ions,[22] the photoluminescence intensity of quinacrine dihydrochloride depends strongly on the relative position of the system PBG to its emission band. Obviously, the photonic stop band of sample 2 is better overlapped with the emission band than that of sample 1. They both have an ordered inverse opal structure, namely their physical environments with respect to the emitter photon are similar. Besides, as to the obtained PL intensity, the influences of different PBG locations relative to the emission band on the energy transition and diffusion of emission photon are the most important factors. For samples 1 and 2, with doping quinacrine dihydrochloride molecules, their PBGs are located at 507 nm and 494 nm, respectively. Apparently, the quinacrine dihydrochloride emission peak of 496 nm is closer to the PBG center of sample 2 at 494 nm. Generally, the suppression and the enhancement of the spontaneous emission can be understood in terms of redistribution of photonic density-of-states (DOS) caused by inhomogeneity and nontrivial boundary conditions imposed on the radiated field.[23] The suppressions of the light emission from the inverse opal have occurred due to the photon trapping caused by Bragg diffraction of lattice planes in

both sample 1 and sample 2.[24] A higher efficiency of trapping photons can be obtained when the PBG center of the inverse opal is closer to the emission central wavelength, which is in good consistency with the experimental observation in Fig. 3 in which sample 2 has a more obvious suppression of the spontaneous emission than sample 1.

In addition, we can see that the full width of PBG is about half of the full width of the fluorescence spectrum of quinacrine dihydrochloride. However, the PBG damps the emission over all instead of the local sink effect. This might be due to the defects in the SiO_2 inverse opal, which might diffuse the emitted light.[16] Another reason is that the PBG has less effect on the emission from the quinacrine dihydrochloride molecules on or near the surface of the sample.

4. Conclusion

In this paper, we use the co-assembly method to fabricate SiO_2 inverse opal and successfully dope the emitting material quinacrine dihydrochloride in it. Then we investigate the effect of PBG central position on the spontaneous emission of quinacrine dihydrochloride. When the quinacrine dihydrochloride emission band is overlapped with the PBG, significant inhibition of the emission can be observed. It demonstrates that photonic crystals can offer an effective way to regulate the PL intensity through changing the lattice parameter.

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