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Study of the photoluminescence properties of two-dimensional dye doped photonic crystals based on localized surface plasmon resonance

Lu Zou[a], Ying-Hui Wang[a,b,*], Ning Sui[a], Wen-Yu Ji[a], Ming-Rui Tan[a], Mou-Cui Ni[a], Han-Zhuang Zhang[a,**]

[a] *Femtosecond Laser Laboratory, Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012, PR China*

[b] *Department of Chemistry, University of California, Irvine, CA 92697-2025, USA*

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ABSTRACT

We introduce the preparation process of two-dimensional coumarin 6 (C-6) doped poly-methyl-methacrylate (PMMA) photonic crystals (2D C-6 PCs) in detail. We also cover the 2D C-6 PC with translucent Ag shells. By analyzing the system of 2D C-6 PCs and hemispherical Ag shells, we find that resonance energy transfer and local surface plasmon resonance (LSPR) can affect the photoluminescence (PL) characteristics of 2D C-6 PCs. When we cover the 2D C-6 PC with translucent Ag shell, there is energy transfer between the 2D C-6 PCS and the hemispherical Ag shells. The data of photoluminescence and the corresponding decay curves reveal that resonance energy transfer and localized surface plasmon resonance could effectively manipulate the PL properties of 2D C-6 PCs.

1. Introduction

With the development of technology, scientists found many ways to manipulate light depending on the nanophotonics principles. One of the most important purposes of latest nanophotonics is to modify the shapes and intensities of light by using small scale structures composed of dielectric materials or heavy metal with Plasmon [1]. These kinds of structures could provide a periodic dielectric environment where the refractive index varies periodically on the nanometer length scale. In this situation, heavy metal nanoparticles could successfully modify the light by localizing the light in a subwavelength volume due to the collective oscillations of electrons. Meanwhile, photonic crystal (PC) with a spatially periodic variation of the dielectric permittivity also plays an important role in modifying light [2–4], since its structures could provide a photonic bandgap which could forbid light within a certain frequency range to propagate in the PC [5]. Therefore, PCs can show a huge potential in the optoelectronic device applications, such as solar cells [6], all optical switches [7], light emitting diode [8], laser [9] and fluorescence-based biosensors [10].

If we combine the two-dimensional (2D) PC with thin heavy metal film, a novel type of optical materials would be obtained which owns the advantages of the plasmon and the photonic crystal. In this optical material, the excitation of surface plasmon polaritions (SPPs) originates from heavy metal, such as Ag, and would propagate along the metal-dielectric interface on the 2D PCs [11–13]. Such structures also show distinct dispersive features in their transmission [14] and reflection spectra [15]. Therefore, this novel optical material is called plasmonic photonic crystals (PPCs) and can be used in a lot of fields, such as photovoltaics [16], waveguide [17], biosensing and metamaterials [18,19]. If PPCs is coupled with the optoelectronic materials, the fluorescence properties of optoelectronic materials could interact with the resonant modes of the PPCs. So some optical properties of the optoelectronic materials could be affected, such as the fluorescence lifetimes [20,21], the spectral shape [22–24] and spatially direction [25–29].

In this paper, we built a hybrid system. In this system, the coumarin 6 (C-6) molecules were doped in the poly-methyl-methacrylate (PMMA) microspheres, which form 2D PCs. This kind of 2D PCs was further covered with different thicknesses of translucent Ag shells. Final, the photoluminescence properties of dyes manipulated by the PPCs have been investigated in detail.

* Corresponding author at: Femtosecond Laser Laboratory, Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), College of Physics, Jilin University, Changchun 130012, PR China.
** Corresponding author.
E-mail addresses: yinghui_wang@jlu.edu.cn (Y.-H. Wang), zhanghz@jlu.edu.cn (H.-Z. Zhang).

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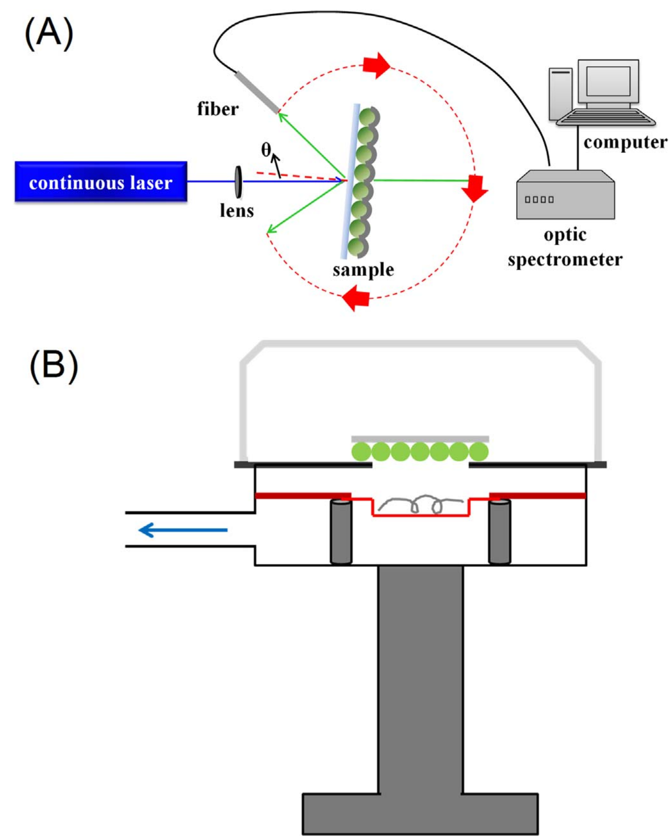

Fig. 1. (A) The schematic of experimental devices which was used for the angle-dependent steady photoluminescence measurement. (B) The schematic of thermal evaporation system.

2. Materials and methods

Sodium hydroxide (Fengchuan, Tianjin, China), methyl methacrylate (MMA; Guangfu, Tianjin, China), Coumarin 6 (C-6; Sigma Aldrich, Shanghai, China) and Ag wires (China New Metal Materials Tech. Co., Ltd, Beijing, China) are used. MMA was purified by sodium hydroxide (NaOH) aqueous solution before we used, while other chemical reagents were used directly. Steady-state absorption and transmittance measurements were carried out using a UV–Vis spectrophotometer (TU-1810PC). Steady photoluminescence (PL) spectra were recorded by a fiber optic spectrometer (Ocean Optics, USB4000) with a continuous laser at 400 nm. The emission wavelength-dependent PL dynamics curves were detected by a time-correlated single-photon counting spectrometer (Becker & Hickl GmbH, SPC-130), and excited by a picosecond pulse laser with an excitation wavelength of 405 nm (Becker & Hickl GmbH, BDL-SMN-405) [30]. The schematic of experimental devices was shown in Fig. 1(A). All the experiments were performed at room temperature.

3. Experimental

3.1. Preparation of two-dimensional dye doped plasmonic photonic crystals

First, C-6 was dissolved in methyl-methacrylate (MMA) with a concentration of 1.4 g/l. Then 1.4 ml of C-6 MMA solution was put into a multiple-neck flask with 40 ml deionized water. We used potassium peroxydisulfate as initiator. After stirring the mixed liquid with a magnetic stirrer at 90 °C for 90 min, we got the C-6 PMMA latex. 2D PMMA photonic crystals doped with coumarin 6 (C-6) were made by self-assembled method [31] using the C-6 PMMA latex. The scanning electron microscope (SEM) image of 2D C-6 PC is shown in Fig. 2(C), exhibiting that PMMA microspheres arrange closely in this kind of PC. Some 2D C-6 PCs were covered with different thicknesses of Ag shells. So, we could investigate the spectral reshaping of the fluorescence of the samples with and without Ag shells.

3.2. Preparation of Ag shell

As shown in Fig. 1(B), Ag shells were deposited onto 2D C-6 doped PCs by a thermal evaporation system. Ag wires with 99.99% purity were used as source materials directly and were loaded onto a molybdenum boat. The chamber was evacuated down to 5×10^{-3} Pa. The distance between the source and the 2D C-6 PCs was kept constant. The thickness of Ag shell was controlled by the quality of Ag wires. The qualities of Ag wires were 1.32, 2.36 and 3.32 mg respectively (the corresponding sample names were #1, #2 and #3).

4. Results and discussion

Fig. 1(A) shows the schematic of the experimental devices for angle-dependent steady photoluminescence measurements. A continuous laser (wavelength is 400 nm) is used to excite the sample from the glass substrate side with a fixed angle of incidence $\theta=5^{\circ}$ to the sample. The detecting angle (the angle between the vertical direction of the sample and the detecting direction) is varied from 25° to 330° with a step size of 10°. By using a fiber optic spectrometer, we could record the steady photoluminescence (PL) spectra at different detecting angles. Fig. 2(A) offers the absorption spectra of Ag shells with different thicknesses, whose peaks are located at 470 (#1), 513 (#2) and 570 (#3) nm. The pink dashed line is the steady-state emission spectrum of 2D C-6 doped PC. It can be seen from Fig. 2(A) that the emission spectrum is overlapped with the absorption spectra of these Ag shell samples. This phenomenon would cause energy transfer between Ag shells and 2D C-6 PCs. Because the Ag shell is tightly covered on 2D C-6 PCs, this structure allows the excitation of surface plasmon polaritions propagating along the metal-dielectric interface and causes the localized surface plasmon resonances (LSPRs). This process would cause resonance energy transfer between Ag shells and 2D C-6 PCs. The Ag shells could influence the PL properties of 2D C-6 doped PCs.

Fig. 2(B) shows the steady-state PL spectra of 2D C-6 PCs without and with different thicknesses of Ag shells at different detecting angles. Since the Ag shells resonate with 2D C-6 PCs, the steady-state PL spectra of 2D C-6 PCs covered with Ag shells are weaker than those of 2D C-6 PCs without Ag shells. As the thickness of the Ag shell increases, the energy transfer increases. Resulting in 2D C-6 PCs, the photoluminescence intensity is further weakened.

Without Ag shells, the peak values of the 2D C-6 PC are the same as the reflection direction and the transmission direction. When covered the 2D C-6 PCs with Ag shells, the energy of those excited C-6 molecules which coincide with the absorption spectrum of Ag shell will resonate with Ag shell at the interface of media and metal. The scheme of resonance energy transfer process in 2D C-6 PC with Ag shell is shown in Fig. 3(A).

The basic principle for resonance energy transfer requires close contact between the two materials, so we only analyze the photophysical processes of the C-6 molecules in close contact with the Ag shell. In the direction of reflection, the fluorescence spectrum of 2D C-6 PC consists of three parts. The first part is the fluorescence spectrum of C-6 which is far away from the Ag shell and does not undergo resonance energy transfer. The second part is the residual energy after the resonance energy transfer between Ag shell and C-6 molecules when C-6 molecules closely contact to the Ag shell. The third part is a small part of the reflected light which should originally propagate to the transmission direction without Ag shell. With the weak reflection effect of translucent Ag shell, this part of light changes the direction of propagation and could be collected in the reflection direction. So the fluorescence intensity of 2D C-6 PCs with Ag shells in the reflection direction is weaker than that of 2D C-6 PC without Ag shell. In terms of