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Photoluminescence and energy transfer investigation from SiO_2: Tb, Au inverse opals to rhodamine-B dyes

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ABSTRACT

Energy transfer has attracted extensive attention due to its widespread applications in medical diagnostics, DNA analysis and lighting devices. There are few reports on the energy transfer from rare earth ions to dyes. In the present work, the SiO_2:Tb inverse opals with and without Au nanoparticles were prepared, and the organic rhodamine-B (RhB) dyes were filled into the voids of SiO_2:Tb inverse opals. Non-radiative and radiative energy transfer processes from the SiO_2:Tb inverse opals to the RhB were observed. The influence of Au nanoparticles and photonic band gap on the energy transfer from SiO_2:Tb inverse opals to the RhB was investigated. The Au nanoparticles enhanced energy transfer was observed due to the surface plasmon resonance effects of the Au nanoparticles. When the emission peaks from the SiO_2:Tb inverse opal is overlapped with the photonic band gap, the emission suppression of the SiO_2:Tb inverse opal as well the emission enhancement of the RhB dyes were obtained, which is attributed to improved energy transfer caused by the photonic band gap. The steady state rate equations were used to explain enhancement of energy transfer caused by the photonic band gap.

1. Introduction

Energy transfer is a unique phenomenon in photoluminescence process, in which a donor active center transfers its energy to an acceptor active center, resulting in the photoluminescence from an acceptor. Energy transfer can be mainly divided into two classes: non-radiative energy transfer and radiative energy transfer. Non-radiative energy transfer takes place in the photoluminescence materials through long-range dipole-dipole interactions between donor luminescent centers and acceptor active centers. Radiative energy transfer is that virtual photons emitted by excited donor molecules are absorbed by acceptor molecules. During the past decades, energy transfer had attracted extensive attention due to its widespread applications in medical diagnostics, DNA analysis and lighting devices [1–4]. For example, the energy transfer between rare earth ions was extensively used to increase photoluminescence efficiency of rare earth ions due to their weak 4f–f absorption cross section [5–7]. The energy transfer from quantum dots or organic dyes to rare earth ions were investigated in order to extend the excitation spectrum of rare earth ions with narrow excitation band [8–10]. However, to our knowledge, there are few reports about energy transfer from rare earth ions to organic dyes.

In recent years, inverse opal photonic crystals doped with rare earth ions have attracted much attention due to their potential applications in the solid-state laser, lighting, displays and biosensor and so on [11–13]. Based on the photonic band gap of inverse opal, the photoluminescence property of rare earth ions can be modified [14,15]. However, the lower luminescence efficiency of inverse opal doped with rare earth ions caused by the small absorption cross-section from the rare earth ions limits their practical applications. At present, considerable efforts were devoted to enhancing the photoluminescence intensity of the inverse opals doped with rare earth ions [16–18]. Noble metal nanoparticles possess unique optical properties such as surface plasmon resonance (SPR) effect in contrast to bulk materials, which were extensively applied in the biological labeling and SPR enhanced luminescence, etc [19–22]. Previously, Cai et al. reported the preparation of inverse SiO_2 opals "doped" with gold nanoparticles by a self-assemble method combined with subsequent removal of polystyrene spheres by calcination [23]. However, the influence of gold nanoparticles on the luminescence property of active centers was not investigated. Very recently, our works demonstrated that metal nanoparticles enhanced photoluminescence intensity of inverse opals doped with rare earth ions could be obtained [24–26]. In the present work, the

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SiO_2:Tb inverse opals with and without Au nanoparticles were prepared, and the organic rhodamine-B (RhB) dyes were filled into the voids of the SiO_2:Tb inverse opals with and without Au nanoparticles. The prepared Au nanoparticles including SiO_2:Tb inverse opal infiltrated with the RhB dyes have several advantages. First, the energy transfer from the SiO_2:Tb inverse opals to the RhB dyes was investigated [27,28]. Second, the Au nanoparticles embedded in the SiO_2:Tb inverse opals have the influence on the photoluminescence of rare earth ions and the energy transfer from the rare earth ions to the rhodamine-B owing to the surface plasmon resonance effects of Au nanoparticles [23,29–31]. Third, the photonic band gap may have the influence on the energy transfer from the SiO_2:Tb inverse opals to RhB dyes, thus this photo-physical process can be simultaneously investigated in the SiO_2:Tb inverse opals infiltrated with RhB dyes.

2. Experimental

Ordered opal templates were fabricated on quartz substrates using the polystyrene (PS) microspheres with mean diameter of 470 nm by the self-assembly technique [32]. The SiO_2: x mol% Tb(x = 1, 2, 3, 4, 5) and SiO_2: 2 mol% Tb, 0.1 mol% Au inverse opals were synthesized by colloidal crystal template method using above opals as templates. The $Tb(NO_3)_3$ was prepared by dissolving the Tb_4O_7 into hot HNO_3. The stoichiometric amounts of $Tb(NO_3)_3$ and $HAuCl_4$ were dissolved in ethanol solution, respectively. The $Si(CH_3CH_2O)_4$ was dissolved in ethanol solution to form a transparent and clear 0.5 mol/L SiO_2 sol. The $Tb(NO_3)_3$ and $HAuCl_4$ ethanol solution in a well-designed molar ratio were introduced into the aforementioned sol with the stirring, and the SiO_2: x mol % Tb(x = 1, 2, 3, 4, 5) and SiO_2: 2 mol%Tb, 0.1 mol% Au homogeneous sol were obtained. The ordered PS templates were infiltrated by the prepared SiO_2: x mol %Tb(x = 1, 2, 3, 4, 5) and SiO_2: 2 mol% Tb, 0.1 mol% Au precursor sols, then sintered at 750 °C for 2 h in an air furnace until the PS were completely removed, the SiO_2:Tb inverse opals with and without Au nanoparticles were prepared. The 2.08×10^{-4}, 6.24×10^{-4}, 1.04×10^{-3}, 1.46×10^{-3} mol/L RhB solutions were prepared by dissolving various amount RhB dyes into the ethanol, respectively. In order to investigate the energy transfer possibility from the SiO_2:Tb inverse opals to the RhB dyes, the various concentration RhB solutions with volume of 40 μL were completely infiltrated into the SiO_2:Tb inverse opals with and without Au nanoparticles, then the RhB was absorbed on the silica network surface of inverse opals.

The QUANTA200 scanning electron microscope (SEM) was used to observe the microstructures and morphologies of opals made of the PS microspheres and the SiO_2: Tb, Au inverse opals. The image of powder scrapped off SiO_2: Tb, Au inverse opals was measured by using the JEOL 2100 transmission electron microscope(TEM). The XRD patterns of the as-prepared SiO_2: Tb inverse opals with and without Au nanoparticles were determined using a powder X-ray diffraction (XRD) performed on a D/max-2200 diffractometer. The photoluminescence and absorption spectra were recorded by using the HITACHI F-7000 fluorescence spectrophotometer (Hitachi, Japan) and HITACHI U-4000 instrument (Hitachi, Japan), respectively. Lifetime decay curves of the samples were measured by the FLS-980 spectrophotometer (Edinburgh, UK) by using the microsecond flashlamp as light source.

3. Results and discussion

3.1. Energy transfer investigation from the SiO_2:Tb inverse opals to the rhodamine-B

The SEM image demonstrated that there is a successful preparation of the ordered PS opal templates by using 470 nm microspheres, as shown in Fig. 1(a). The SEM image of the SiO_2: 2 mol% Tb inverse opal prepared by opal template constructed with 470 nm PS microspheres exhibited typical inverse opal structure with three dimensionally ordered interconnected macrospores, as shown in Fig. 1(b). After infiltration of the SiO_2: Tb sols and calcination, the PS opal templates were completely removed and the SiO_2: Tb inverse opals were obtained. The thickness of wall and the center to center distance of hollow spheres in the inverse opal was measured based on SEM image with the higher magnification shown in the inset of Fig. 1(b), respectively. During the measurement, the wall thickness of inverse opal at 10 different sites and the center to center distance of hollow spheres of inverse opal at 10 different sites were measured, respectively. Then the average value was calculated. The average thickness of the wall of inverse opal is about 100 nm, and the center to center average distance of inverse opal is about 360 nm.

The crystal structures of the SiO_2: 2 mol% Tb inverse opals with and without Au nanoparticles were confirmed by the XRD, as shown in Fig. 1(c). No obvious peak from the SiO_2: 2 mol% Tb inverse opals were observed except a broad diffraction peak at the 22°, which suggested the prepared SiO_2: 2 mol% Tb inverse opals are composed of amorphous SiO_2 host.

The SiO_2: 2 mol% Tb inverse opals were infiltrated by using the 2.08×10^{-4}, 6.24×10^{-4}, 1.04×10^{-3}, 1.46×10^{-3} mol/L RhB solutions, which were denoted as the SiO_2: Tb-R1, SiO_2: Tb-R2, SiO_2: Tb-R3 and SiO_2: Tb-R4, respectively. Fig. 2(a) shows the absorption spectra of the SiO_2: 2 mol% Tb inverse opals infiltrated with various RhB concentrations. The absorption peak located at the 650 nm was assigned to the Bragg diffraction of light from the ordered porous structure, which was called as the photonic band gap. The

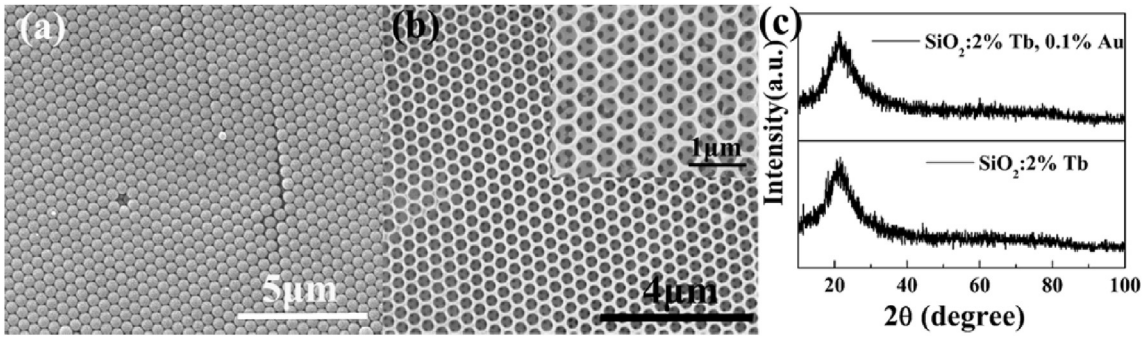

Fig. 1. The SEM images of opal template **(a)** and SiO_2:2 mol%Tb inverse opal **(b)**, **t**he inset is the highly magnified SEM image of SiO_2:2 mol%Tb inverse opal; The XRD patterns of SiO_2: 2 mol% Tb inverse opals with and without Au nanoparticles **(c)**.