

Energy transfer in porous-silicon/laser-dye composite evidenced by polarization memory of photoluminescence

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The optical properties of nanocomposites are studied for rhodamine B (RhB) dye molecules embedded in nanoscale porous silicon (PS) and porous silica (*P*-silica). The samples are prepared by simple immersion of porous matrix substrates in RhB solutions. Fourier transform infrared spectroscopy suggests that RhB molecules fully penetrate into the porous matrix. Efficient photoluminescence has been observed in all experimental nanocomposites. The measurement of the polarization memory (PM) effect provides a clear evidence for the presence of an excitation energy transfer from PS to RhB molecules, in contrast to the PM behavior in RhB/*P*-silica composite. © 2007 American Institute of Physics. [DOI: 10.1063/1.2814051]

The incorporation of organic dyes into solid-state matrix is attracting wide interest because of useful applications such as light concentrators in solar cells, optical waveguides, laser materials, sensors, and nonlinear materials.^{1–5} Embedding those molecules in a rigid matrix leads to isolation of active species that suppresses intermolecular interaction and intermolecular rearrangement, protects the active molecule from the environmental attack and/or photofragmentation, and increases the life of the material.⁶ Different methods to trap organic molecules within solid substrates have been developed, including direct soaking of the host material with dye solutions.^{7–9} It has been shown that porous Si (PS) acts as a host matrix for dyes.^{10–13} However, the dye/PS composites show photoluminescence (PL) instability under laser irradiation, and the excitation mechanism is yet to be clarified.

To make the excitation-relaxation process in nanocomposites clear, the degree of polarization memory (PM) in PL, including the dependence of the PL intensity on the excitation energy, has been studied here for PS and porous silica (*P*-silica) samples impregnated with dye molecules.

PS layers were formed by electrochemical anodization of (100)-oriented lightly doped *p*-type (resistivity: 1–4 Ω cm) Si wafers in an electrolyte solution composed of HF (40 wt %): C₂H₅OH: H₂O=2:1:1. The current density and etching time were 10 mA/cm² and 5 min, respectively. The PS layers have typical porosity of 60%–65% and pore sizes in the range 2–5 nm.¹⁴ The samples are regarded as partially oxidized ones, since they were kept in air for 2 months.

For the preparation of *P*-silica samples, (100)-oriented heavily doped silicon substrates (10⁻³–10² Ω cm) were used. These substrates were anodized at 20 mA/cm² for 4 min in the same HF solution as that used above. Then,

these samples were partially oxidized at 300 °C in O₂ for half an hour, followed by full oxidation of the Si structure at 1000 °C in O₂ for 2 h in order to obtain *P*-silica. Before oxidation, the porosity was about 70%–75% and the pore size in the range of 5–10 nm. Both the porosity and pore size decrease upon full oxidation due to volume expansion.¹⁵ The final pore sizes are about 5 nm.^{16,17}

PS and *P*-silica have been chosen because they exhibit very different PL properties. The PL of PS is efficient whereas that of *P*-silica is extremely weak because it does not include any luminescent Si nanocrystals.

All samples (PS and *P*-silica) were immersed for 1 h in a solution of rhodamine B (RhB) in ethanol (5 × 10⁻⁴ mol/l). Then, the formed nanocomposites were rinsed in ethanol in order to remove all residual dye molecules at the top surfaces of the samples. The PS and *P*-silica samples impregnated with dye molecules are denoted here as RhB/PS and RhB/*P*-silica, respectively. Fourier transform infrared (FTIR) spectra were measured using a Bruker IFS 66 v/s FTIR spectrometer with a resolution of 4 cm⁻¹. PL and PM spectra were measured using a fiber-optic spectrometer (Ocean Optics USB 2000). The excitation source was an argon laser (457.9 or 514.5 nm). All the spectroscopic measurements were performed at room temperature.

The FTIR spectrum of RhB/PS nanocomposite is shown in Fig. 1(a). The relatively intense peaks around 800 and 1050 cm⁻¹ are related to Si—O vibrations. This confirms that PS was partially oxidized by exposition to air. The bands at 1370 and 1460 cm⁻¹, together with these at 2900 and 1730 cm⁻¹, are characteristics of the stretching mode vibrations of the C—N, —CH₂—, and C=O species in RhB molecules, respectively. These results are an indication of the penetration of RhB molecules into the pores of PS.

Figure 1(b) shows the FTIR spectrum of the RhB/*P*-silica nanocomposite. The peaks at 860 and 1100 cm⁻¹, assigned to Si—O vibrations, come from the

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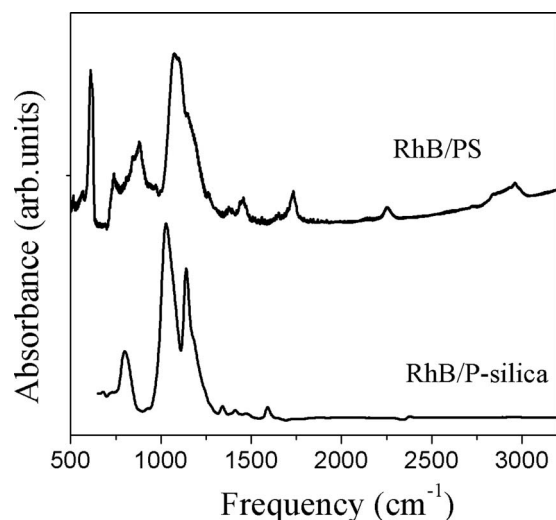


FIG. 1. FTIR spectra of RhB/PS and RhB/*P*-silica.

P-silica matrix. The absence of signals from Si—H wagging modes ($650\text{--}700\text{ cm}^{-1}$), SiH_2 wagging (856 cm^{-1}), and SiH_2 scissor (906 cm^{-1}) supports the fact that PS has been completely oxidized and turned into *P*-silica. The bands at 1340 , 1468 , and 1590 cm^{-1} , which are characteristics of the stretching mode vibrations of the C—N—, — CH_2 —, and C=C species of the RhB molecules, respectively, confirm the incorporation of rhodamine molecules inside the *P*-silica matrix. The dye molecule has a length smaller than 1 nm . Therefore, its incorporation into the pores of PS and *P*-silica is reasonable. Actually, the immersion method used in this study was previously shown to lead to homogeneous incorporation of dye molecules in the depth of PS.¹⁸

The PL of the *P*-silica host layer is very poor [Fig. 2(a)]. In contrast, the PL of the RhB/*P*-silica nanocomposite [Figs. 2(b) and 2(c)] is strong with a common spectral shape regardless of excitation at 457.9 or 514.5 nm . Therefore, this emission mainly originates from direct excitation of RhB molecules. The mutual difference in the PL intensity can be attributed to that the absorption of RhB molecules at 457.9 nm is much weaker than that at 514.5 nm .¹⁹ There is

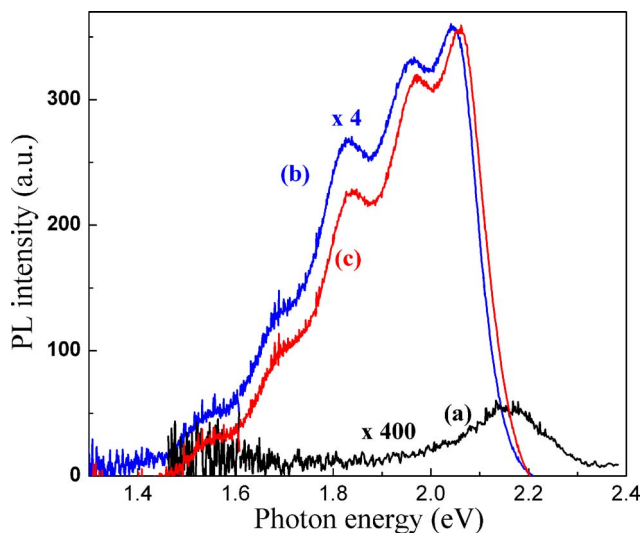


FIG. 2. (Color online) PL spectra of *P*-silica for the excitation wavelength of (a) 514.5 nm and of RhB/*P*-silica for the excitation wavelengths of (b) 457.9 nm and (c) 514.5 nm .

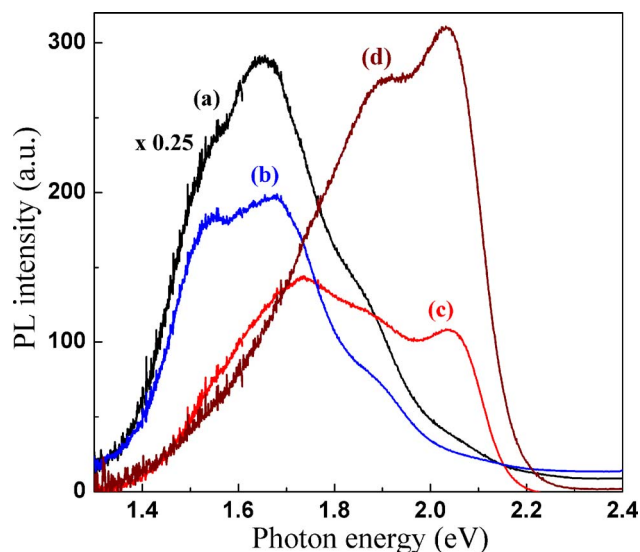


FIG. 3. (Color online) PL spectra of PS for the excitation wavelengths of (a) 457.9 nm and (b) 514.5 nm . Also represented are the PL spectra of RhB/PS for the excitation wavelengths of (c) 457.9 nm and (d) 514.5 nm .

no evidence of excitation transfer between *P*-silica and RhB molecules, as expected.

Figure 3 shows the influence of the impregnation of RhB molecules into PS on the PL. The PS sample exhibits a PL spectrum with a peak at about 1.6 eV . For the RhB/PS nanocomposites, the respective contributions of PS and RhB molecules can be analyzed. For the excitation line at 514.5 nm , the PL intensity is blueshifted compared to that of PS, and comparable to that of RhB/*P*-silica, with in addition, a small contribution from PS. This shows that the contribution of RhB to the PL is strong. However, for the excitation wavelength line at 457.9 nm , the PL spectrum of RhB/PS exhibits a PL spectrum with a shape intermediate between that of PS and that of RhB. The emission of RhB (particularly around $1.8\text{--}2.2\text{ eV}$) is surprisingly strong, because RhB absorbs excitation photons only slightly at this wavelength and most of the excitation light must be absorbed by PS. Therefore, there is a high possibility of energy transfer from PS to RhB. This is supported by the fact that most of the area under the emission line shape of PS overlaps with the absorption line shape of RhB (the absorption spectra of RhB molecules in solution and in solid matrix are similar to each other¹⁹).

In the absence of energy migration, the emitted light would tend to have the same polarization as the excitation laser. However, when energy is transferred to a new molecule with a different physical orientation, the memory of the initial excitation polarization should be lost.²⁰ The PM measurements are effective to confirm the hypothesis of energy transfer in RhB/PS. The PM degree is determined from the following formula:²¹ $\text{PM} = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$, where I_{\parallel} and I_{\perp} are the emission components polarized parallel and perpendicular to the polarization direction of the excitation light, respectively.

Figure 4 shows the PM spectra of PS, RhB/PS, and RhB/*P*-silica when the excitation was either at 457.9 nm or at 514.5 nm and polarized along the $[001]$ crystallographic orientation. It can be seen that the degree of PM does not depend on the excitation energy in the case of PS [Fig. 4(a)]. This is consistent with the results reported previously.²² The PM degree obtained for RhB/*P*-silica [Fig. 4(b)] corre-

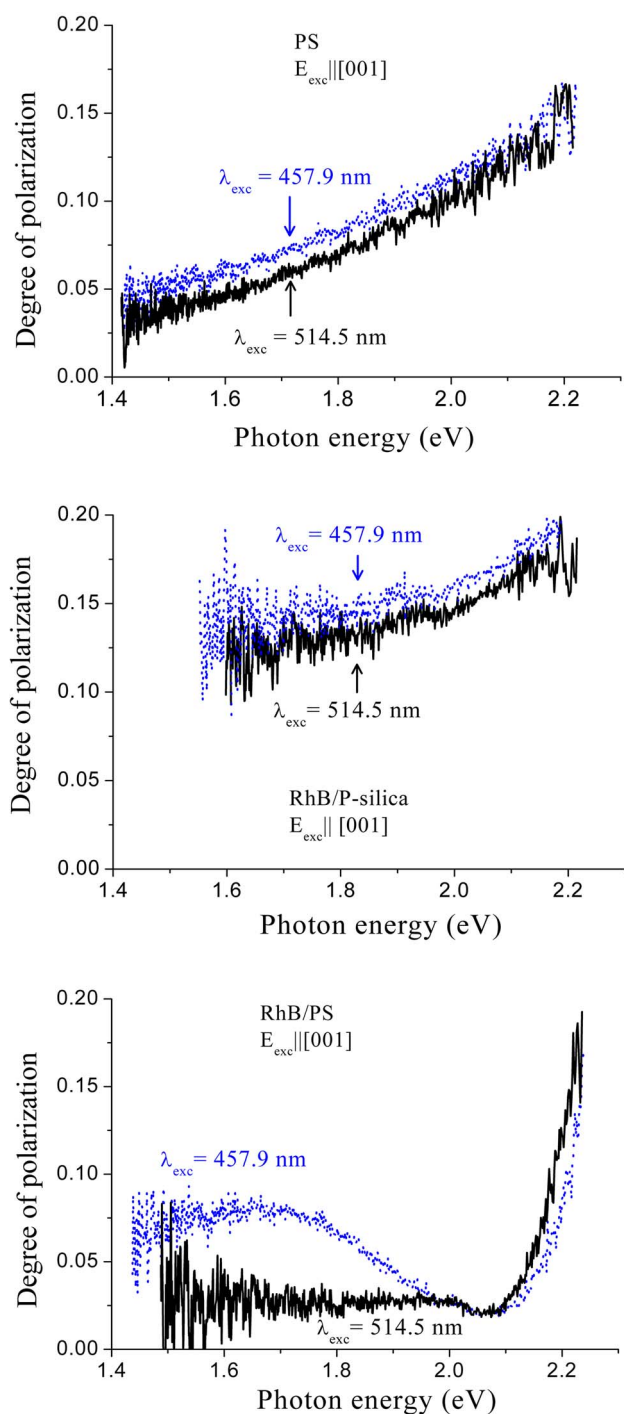


FIG. 4. (Color online) PM spectra of PS, RhB/*P*-silica and RhB/PS for both excitation wavelengths of 457.9 and 514.5 nm. The excitation was polarized along the [001] crystallographic orientation.

sponds well to that of RhB, since *P*-silica does not contribute to the PL. In RhB/*P*-silica, RhB molecules are isolated and adsorbed along the surface of the nanopores, making their rotation and diffusion difficult. This increases the fluorescence anisotropy and polarization of RhB.²³ The process of energy transfer between RhB molecules is very unlikely. As a consequence, a relatively large degree of PM can be observed in this system.

For RhB/PS [Fig. 4(c)], the presence of some PM in the photon-energy range of 1.4–1.75 eV under excitation at 457.9 nm can be attributed to the PL from PS itself. In the spectral range of 1.8–2.1 eV, a significant decrease in PM is

observed for excitation at both the 475.9 and 514.5 nm lines. This spectral range coincides well with the spectral overlap between the emission of PS and the absorption of RhB molecules. This result strongly supports the presence of a significant amount of energy transfer from PS to RhB molecules. In fact, the structure of PS has a spongelike network. The dye molecules in PS are randomly oriented inside the porous matrix. Since the emission dipole of the dye depends on its orientation, it is reasonable to assume that an energy transfer from PS to dye molecules should induce a loss of PM.

Above 2.1 eV, the degree of PM increases and approaches the values obtained for RhB/*P*-silica. In this energy range, the PL intensity of PS is rather weak, and then it decreases as the energy increases. So the increase in PM can be explained as a result of a decrease in energy transfer from PS to RhB molecules.

To conclude, the optical energy transfer in nanocomposites has been analyzed in terms of PM for RhB/PS and RhB/*P*-silica samples prepared by simple immersion of the porous matrices in RhB solution. FTIR spectroscopy suggests the incorporation of the RhB molecules into the pores of the matrices. The observed clear correlation between PL and PM spectra gives evidence of the excitation energy transfer from PS to the RhB molecules. The present results indicate that PS is useful not only as a luminescent material but also as an active host matrix for guest dye molecules.

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