



Multiple energy transfer in porous silicon/Rh6G/RhB nanocomposite evidenced by photoluminescence and its polarization memory

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ARTICLE INFO

Available online 21 October 2009

Keywords:

Porous silicon
Laser dyes
Photoluminescence
Polarisation memory
Excitation transfer

ABSTRACT

Porous silicon (PSi)-laser dye composites were obtained by simply immersing PSi in ethanolic solutions of rhodamine 6G (Rh6G), rhodamine B (RhB), and RhB:Rh6G mixture. Partially oxidized PSi was also used as a host matrix. Fourier transform infrared spectroscopy suggests that the dye molecules fully penetrate into the porous matrix. Efficient photoluminescence (PL) was observed in all nanocomposites. The study of the polarization memory of PL provides a clear evidence for the presence of energy transfer from PSi to Rh6G molecules. The energy transfer was found more efficient in oxidized PSi. In RhB:Rh6G/PS composite, energy transfer from Rh6G molecules to RhB molecules was demonstrated. Rh6G molecules play the role of an intermediate radiative center in the excitation energy transfer from PSi to RhB molecules.

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1. Introduction

In the current context of nanotechnology, obtaining nanometer scale features on large area is an important requirement. Nanocrystalline porous silicon (PSi), which can be formed widely on the surface of Si wafers, is very attractive for optoelectronic applications because of its tunable optical properties and visible luminescence [1]. PSi can be prepared so that it could emit very efficient red photoluminescence (PL) resulting from the recombination of excitons in Si nanocrystals [2,3]. Very recently, efficient blue PL [4] and phosphorescence lasting several seconds [5] was demonstrated in oxidized PSi. Besides, PSi can also be used as a host matrix for various functional molecules.

The incorporation of organics dyes into solid matrix is attracting wide interest because of such useful applications as lights concentrators in solar cells, optical waveguides, lasers materials, sensors and nonlinear materials [6–10]. Especially, laser dyes have been included in solid matrices such as minerals [11], polymers [12], sol–gel hosts [13] and porous inorganic materials in order to increase their photostability [14]. Embedding molecules into a rigid matrix leads to isolation of active species that hinders intermolecular interaction and intermolecular rearrangement, protects the active molecule from the environmental attack and/or photofragmentation and thus increases the life of the material [15]. Different methods to trap organic molecules within solid substrates have been developed, including the direct soaking of the host material with dye solutions [16–18].

For decades, energy transfer dye lasers using numerous donor (D)–acceptor (A) pairs and mechanisms have been demonstrated [19–23]. Dye mixtures have already been used in solutions in order to improve laser performance and produce multicolor output [24–31]. In this type of laser, one kind of dye molecule, which is referred to as the donor dye, absorbs pumping light and is thus optically excited first. The excited donor dye molecule relaxes by transferring the energy to another kind of dye molecule, which is referred to as the acceptor dye. The acceptor dye molecule is thus indirectly pumped by the pumping source. In this way, the acceptor dye molecules may act as a laser source.

In a previous work [32], we have shown that significant energy transfer occurs in rhodamine B (RhB)-impregnated PSi by using polarization memory (PM) of PL. In the absence of energy migration, the emitted light would tend to have the same polarization as that of the excitation light. However, when excitation energy is transferred to a new molecule with a different physical orientation, the memory of the initial excitation polarization should be lost [33]. We observed a significant decrease in the degree of PM that demonstrated the presence of energy transfer in the RhB-PSi composite [32]. The degree of PM is determined from the following formula [34]:

$$P = (I_{\parallel} - I_{\perp}) / (I_{\parallel} + I_{\perp})$$

where I_{\parallel} and I_{\perp} are the PL emission components polarized parallel and perpendicular to the polarization direction of the excitation light, respectively.

In this paper, we report on the excitation process of PSi impregnated with either rhodamine 6G (Rh6G) or RhB:Rh6G mixture. Effects of host and guest materials on their PL and PM were investigated. In

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addition to the energy transfer from Si nanocrystals to Rh6G molecules, we investigated the possibility of energy transfer from Rh6G to RhB in PSi solid matrix.

2. Experimental

PSi layers were obtained by electrochemical anodization of (100) oriented p-type silicon substrates ($1\text{--}4\ \Omega\ \text{cm}$) in an electrolyte solution composed of HF: $\text{C}_2\text{H}_5\text{OH}:\text{H}_2\text{O}=2:1:1$ by volume. The current density and etching time were $10\ \text{mA}/\text{cm}^2$ and 5 min, respectively. The PSi layers had typical porosity of 60%–65% and pore sizes in the range 2–5 nm. Some samples were regarded as partially oxidized ones, since they had been kept in air for 2 months. These samples were named OPSi. All samples were impregnated in a Rh6G ($5.10^{-4}\ \text{M}$), RhB ($5.10^{-4}\ \text{M}$), or RhB:Rh6G mixture (3:5 by volume) solution for one hour. The formed nanocomposites were then rinsed in ethanol in order to remove all residual dyes molecules at the top surfaces of the samples.

Fourier Transform Infrared (FTIR) spectra were recorded in absorption mode using a Bruker IFS 66 v/s FTIR spectrometer at $4\ \text{cm}^{-1}$ resolution. The PL and PM spectra were measured using a fiber-optic spectrometer (Ocean Optics USB 2000). The excitation source was an argon laser (514.5 or 457.9 nm) or a laser diode (410 nm). All the measurements were performed at room temperature. The excitation light was polarized along the (001) crystallographic direction of the Si substrate.

3. Results and discussions

Fig. 1 shows the FTIR spectrum of Rh6G/OPSi composite. The relatively large and intense bands at $860\ \text{cm}^{-1}$ and $1100\ \text{cm}^{-1}$ are assigned to Si–O vibrations in OPSi. The presence of the band at $614\ \text{cm}^{-1}$ that is related to Si–H wagging modes proves the partial only oxidation of porous silicon after exposition in free air for two months. The bands peaked at $1370\ \text{cm}^{-1}$, $1460\ \text{cm}^{-1}$; $2900\ \text{cm}^{-1}$, and $1730\ \text{cm}^{-1}$ are characteristic of the stretching mode vibrations of the C–N, $-\text{CH}_2-$ and C=O species of the Rh6G molecules, respectively. These bands are attributed to vibration modes in dye molecules. These results indicate the penetration of Rh6G molecules into the pores of OPSi. Similar results were observed in our previous work concerning RhB/OPSi composites [32].

Fig. 2a displays the PL spectra of Rh6G/PSi obtained using different excitation wavelengths. The component of the emission that is peaked

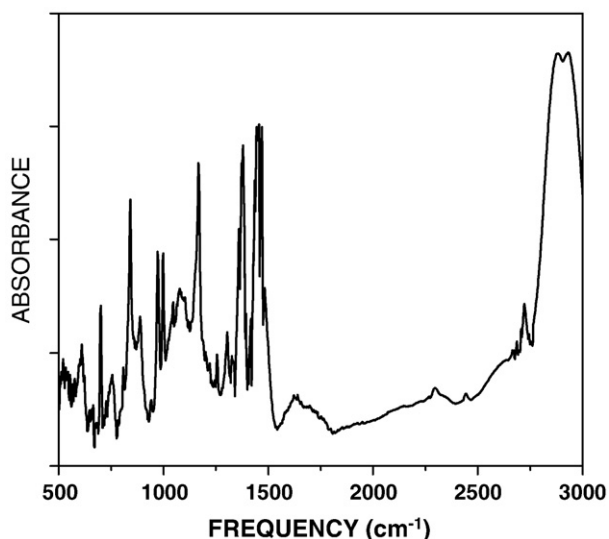


Fig. 1. FTIR spectra of Rh6G/OPSi composites.

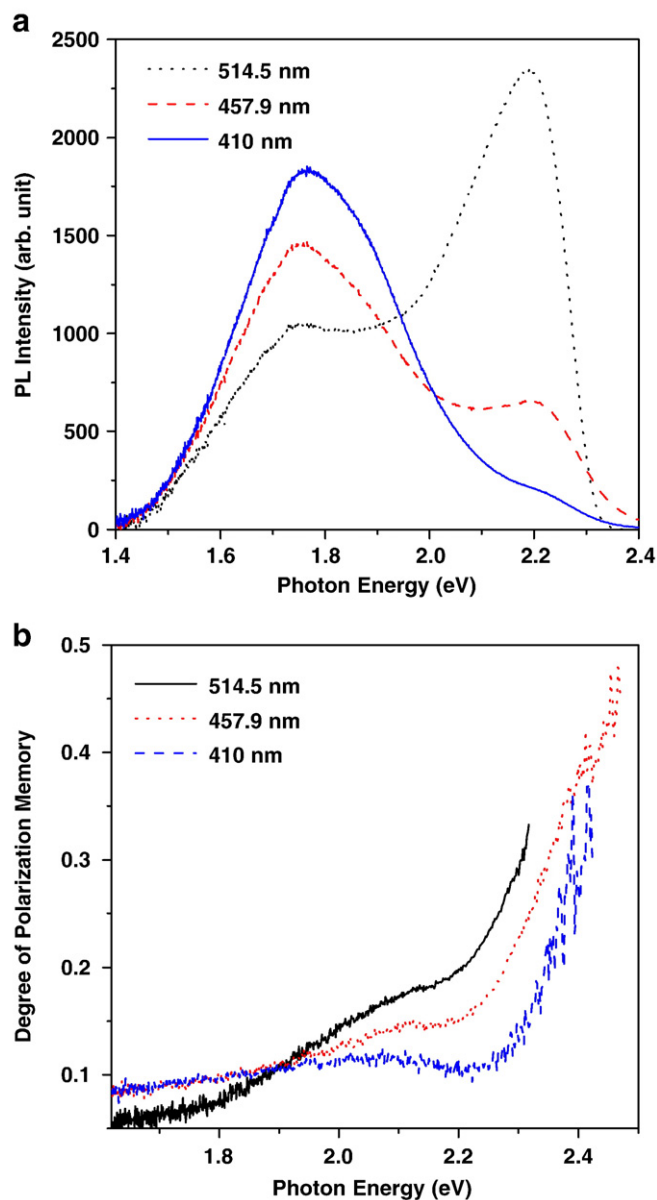


Fig. 2. PL (a) and PM (b) spectra of Rh6G/PSi for excitation wavelengths 410, 457.9 and 514.5 nm.

at about 1.8 eV is mainly due to the Si nanocrystallites. This emission dominates the whole PL spectrum, except for the one excited at 514.5 nm where the major part ($\sim 2.2\ \text{eV}$) of the emission is due to the dye. This is because the absorption of Rh6G is strong at 514.5 nm. In fact, the absorption band of dye molecules in a solid matrix is similar to that of in solution [35]. Nevertheless, it is important to notice that the emission of Rh6G can still be observed under excitation at 457.9 nm and 410 nm, despite its poor absorption at these excitation wavelengths. These results suggest possible energy transfer from PSi to Rh6G molecules. In order to investigate this possibility, we have measured the PM degree of these samples.

Fig. 2b shows the corresponding PM degree of Rh6G/PSi sample. A significant decrease of PM degree was observed at around 2.2 eV for both excitation wavelengths of 475.9 and 410 nm. This energy coincides the emission peak of Rh6G molecules. This result strongly supports the presence of a significant amount of energy transfer from PSi to Rh6G molecules, similarly to the case of RhB/PSi [32]. In fact, the structure of PSi has a spongelike network structure, and the dye molecules in PSi are randomly oriented inside the porous matrix.

Since the emission dipole of the dye depends on its orientation, it is reasonable to assume that the energy transfer from PSi to dye molecules should induce a loss of PM. Under the excitation at 514.5 nm (2.41 eV), only a small change was observed in the slope of the PM spectrum. This implies that most of Rh6G molecules are excited directly in this case.

The effect of the host matrix was investigated. The PL intensity and the degree of PM for the sample using OPSi as the host material are shown in Fig. 3. It can be seen that the PL of Rh6G/OPSi is mainly due to the emission of Rh6G molecules for any excitation wavelength, contrary to the case of Rh6G/PSi for which this trend is observed only for the excitation at 514.5 nm. This suggests that the excitation energy transfer from OPSi to Rh6G is more efficient than that from PSi to Rh6G.

In order to investigate this effect we have also measured the PM spectra for Rh6G/OPSi (Fig. 3b). As shown in the figure, the decrease in the degree of PM is more pronounced than in the case of Rh6G/PSi. This result can be explained by the aging effect on the PSi emission

band. In fact, after aging, the PL of PSi is intensified and blue-shifted compared to that of freshly prepared one [36]. This effect increases the overlapping between the absorption band of Rh6G and the emission band of OPSi, resulting in a higher efficiency of energy transfer. Also, another effect may play a significant role. It is well known that Rh6G is a cationic dye that preferentially interacts with oxygen-terminated OPSi surfaces rather than with hydrogen-terminated PSi surfaces. Thus the surface of OPSi can increase the interaction between Si nanocrystals and Rh6G molecules [37,38]. The same result was previously observed for RhB molecules [32].

Fig. 4a shows the PL spectra of RhB/PSi and Rh6G/PSi samples at the excitation wavelength of 514.5 nm. These spectra show that the emission bands of Rh6G and RhB in the PSi matrix are centered at about 2.19 and 2.15 eV, respectively. The fact that the emission of Rh6G is slightly blueshifted compared to that of RhB is often observed in porous silica matrix [7]. The effect of mixing these two kinds of dye molecules was studied by using RhB:Rh6G/PSi composite. Fig. 4b shows the PL spectra of the RhB:Rh6G/PSi sample excited at three different wavelengths. It can be seen that the emission of the dye molecules is centered at 2.15 eV for any excitation wavelengths. This

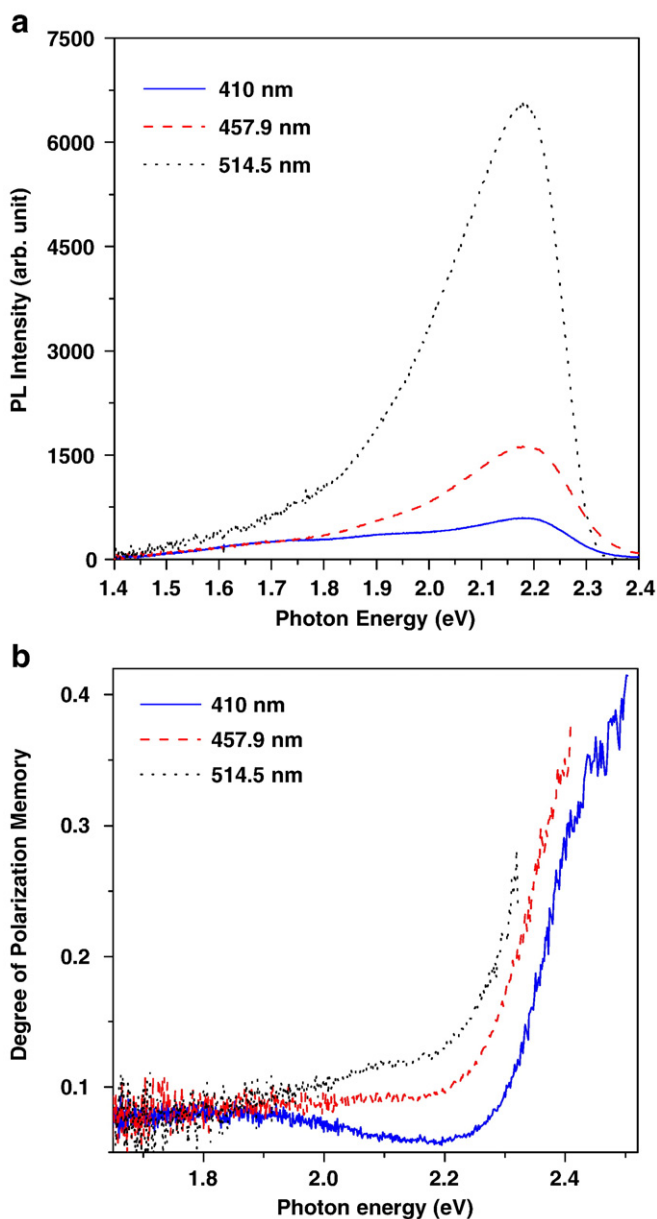


Fig. 3. PL (a) and PM (b) spectra of Rh6G/OPSi for excitation wavelengths 410, 457.9 and 514.5 nm.

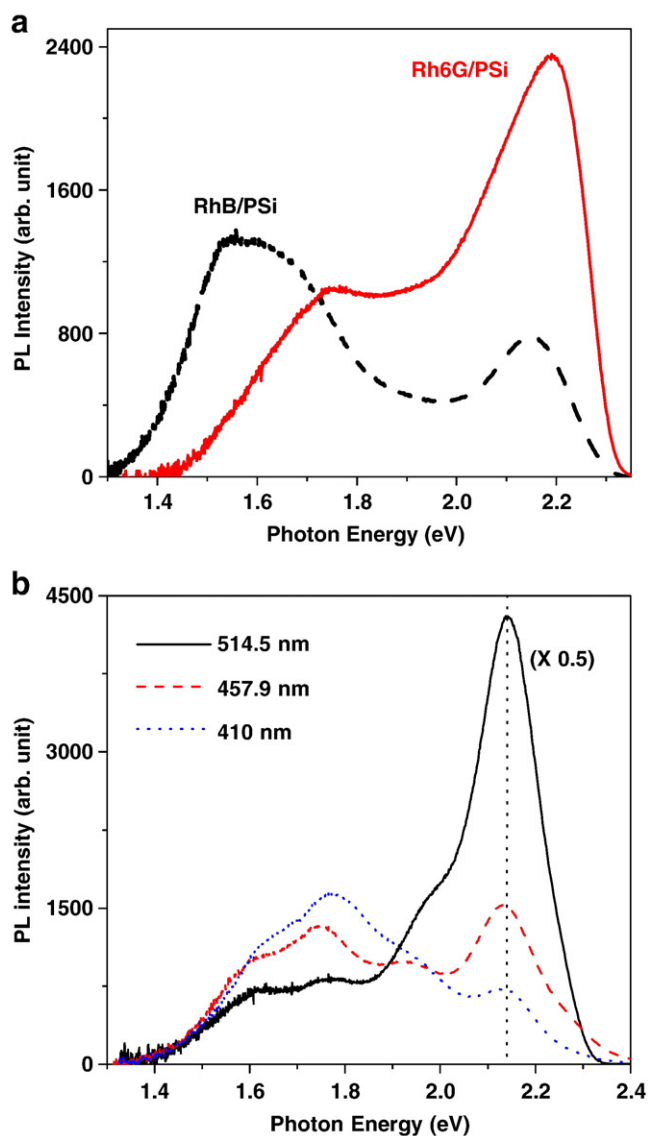


Fig. 4. PL spectra of Rh6G/PSi (solid line) and RhB/PSi (dash line) for excitation 514.5 nm (a). PL spectra of RhB:Rh6G/PSi for excitation wavelengths 514.5, 457.9 and 410 nm (b).

energy coincides well with the emission energy of RhB in the PSi matrix, as shown in Fig. 4a.

In order to explain the fact that the emission from RhB overcomes that from Rh6G, the excitation energy transfer from Rh6G molecules to the RhB molecules in the RhB:Rh6G/PSi system should be considered. The existence of this phenomenon enhances the participation of the RhB molecules in the photoluminescence of porous silicon-rhodamine dyes composites. In fact, this process contributes to the donor fluorescence quenching and enhances the acceptor fluorescence yield. Greater enhancement in the fluorescence intensity of the acceptor (RhB) could be attributed to the overlap between the fluorescence band of the donor (Rh6G) and the absorption band the acceptor (RhB). So, in addition to the direct excitation and to the excitation transfer from PS to both dye molecules, a possible energy transfer from Rh6G molecules to RhB molecules could take place.

The PL spectra of RhB/PSi, Rh6G/PSi and RhB:Rh6G/PSi for the excitation at 457.9 nm are compared in Fig. 5a. Except the band relative to PSi emission, the PL spectrum of RhB:Rh6G/PSi is similar to that of RhB/PSi. This suggests that the Rh6G molecules play the role of intermediate radiative centers which transfer the excitation to RhB molecules. In fact, the absence of Rh6G emission band indicates that the RhB is the acceptor dye and the Rh6G is the donor dye. This result strongly suggests the existence of excitation transfer from Rh6G molecules to RhB molecules.

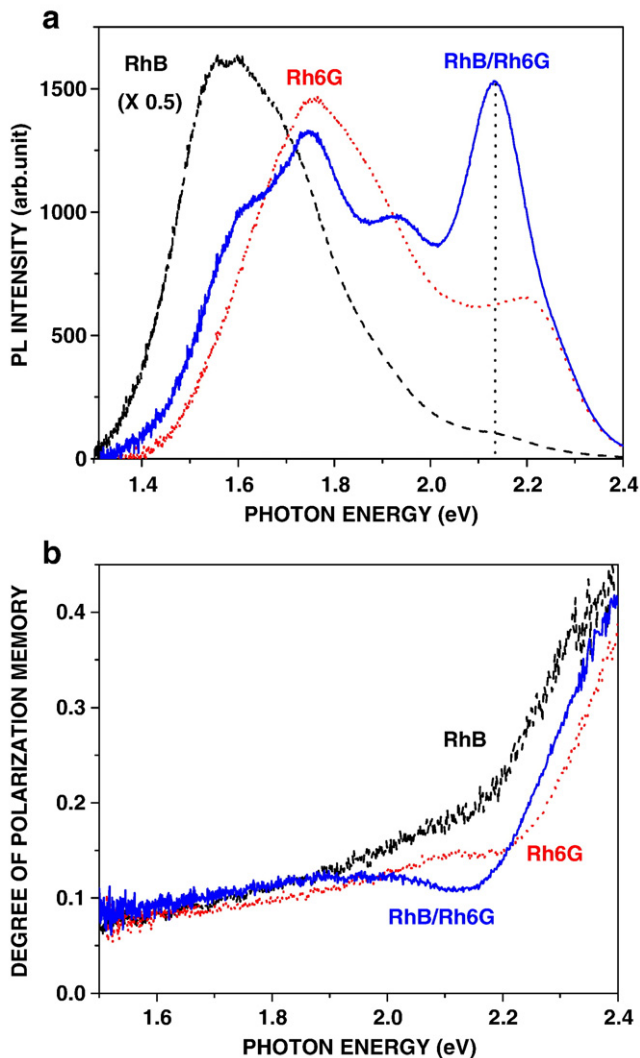


Fig. 5. PL (a) and PM (b) spectra of RhB/PSi (dash line) Rh6G/PSi (dots line) and RhB:Rh6G/PSi (solid line) for excitation 457.9 nm.

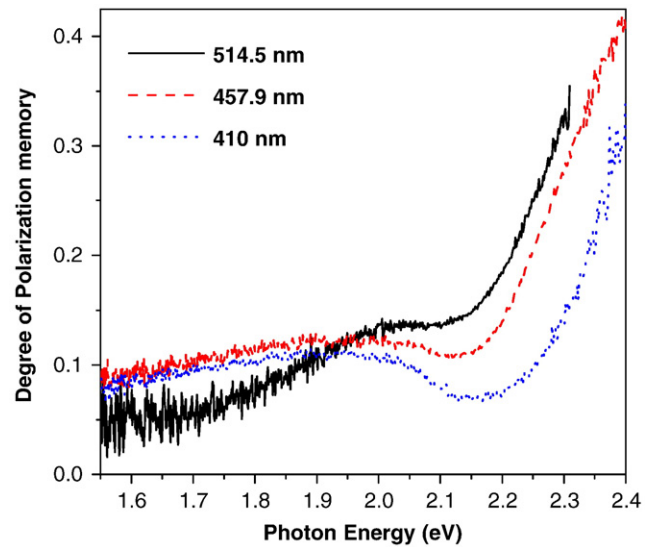


Fig. 6. PM spectra of RhB:Rh6G/PSi for excitation wavelengths 410, 457.9 and 514.5 nm.

In order to further support this hypothesis, the PM spectrum of RhB:Rh6G/PSi was measured. Fig. 5b shows the PM spectra of RhB/PSi, Rh6G/PSi and RhB:Rh6G/PSi for the excitation wavelength of 457.9 nm. The decreasing part of the PM spectrum for RhB:Rh6G/PSi coincides well with that of RhB/PSi. In addition, the decrease of the degree of PM for RhB:Rh6G/PSi is more pronounced than that for RhB/PSi alone and for Rh6G/PSi alone. This result confirms the energy transfer from Rh6G molecules to the RhB molecules. The PM experiments evidence that all conditions of this transfer are satisfied. In particular, the overlapping between the RhB absorption line shape and the Rh6G emission lines shape is established. Fig. 6 shows the increase of energy transfer when the direct excitation of dye molecules decreases. Similar result was previously reported for Rh6G:RhB system in PMMA matrix [39].

4. Conclusion

To conclude, the optical energy transfer in PSi/dye nanocomposites has been analyzed in terms of PM and PL. Rh6G/PSi and RhB:Rh6G/PSi samples were prepared by simple immersion of the porous matrices in dye solutions. FTIR spectroscopy suggests the incorporation of rhodamine molecules into the pores of the matrices. An energy transfer was demonstrated from Si nanocrystallites to Rh6G molecules. This phenomenon is enhanced in partially oxidized PSi. The observed clear correlation between PL and PM spectra gives evidence of an excitation energy transfer from Rh6G molecules to RhB molecules. The present results indicate that PSi is useful not only as a luminescent material but also as an active host matrix for guest dye molecules.

Acknowledgements

This work was partially supported by a Grant-in-Aid for Scientific Research from JSPS and from MEXT-Japan, and by SORST Program from JST.

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