Enhancement of 1.54-μm emission from Er-doped sol-gel SiO2 films by Au nanoparticles doping

Fukushima, Masanori
Managaki, Nobuto
Fujii, Minoru
Yanagi, Hisao
Hayashi, Shinji

(Citation)
Journal of Applied Physics, 98(2):24316-24316

(Issue Date)
2005-07

(Resource Type)
journal article

(Version)
Version of Record

(URL)
https://hdl.handle.net/20.500.14094/90000276

JOURNAL OF APPLIED PHYSICS **98**, 024316 (2005)

Enhancement of 1.54-μm emission from Er-doped sol-gel SiO_2 films by Au nanoparticles doping

Masanori Fukushima, Nobuto Managaki, Minoru Fujii,[a] Hisao Yanagi, and Shinji Hayashi
The Graduate School of Science and Technology, Department of Electrical and Electronics Engineering, Faculty of Engineering, Kobe University, 1-1 Rokkodai, Nada, Kobe 657-8501, Japan

(Received 22 October 2004; accepted 10 June 2005; published online 29 July 2005)

A 1.54-μm emission from erbium-doped sol-gel SiO_2 was strongly enhanced by doping Au nanoparticles. The enhancement factor depended on Au concentration and was the largest at the concentration of 1.0 mol %. The photoluminescence enhancement was accompanied by the lengthening of the lifetime, suggesting that the enhancement is caused by the decrease of hydroxyl groups. In addition, enhancement due to strong fields induced by localized surface plasmon of Au nanoparticles was observed. © *2005 American Institute of Physics*. [DOI: 10.1063/1.1990257]

I. INTRODUCTION

One of the key technologies that support modern optical telecommunication networks is an Er-doped silica fiber amplifier, which amplifies light signals attenuated during the transmission through optical fibers.[1–3] Er doped into SiO_2 ($Er-SiO_2$) is in a trivalent ionic state (Er^{3+}), which exhibits an emission line at 1.54 μm. This wavelength corresponds to a minimum loss band of silica-based optical fibers. The standard method to produce Er-doped silica fiber is a melting method. An alternative method is a sol-gel method,[4–8] which does not require expensive instruments and high-temperature treatments. However, the quality of sol-gel silica films is usually very poor. The silica matrix leaves a lot of hydroxyl groups. Since two vibrations of hydroxyl groups are enough to bridge the gap of about 6500 cm^{-1} between the ground $^4I_{15/2}$ state and the first excited $^4I_{13/2}$ state of the Er^{3+},[9] the excited Er^{3+} efficiently transfers energy to the vibration of hydroxyl groups and relaxes nonradiatively.[10] In order to reduce the amount of hydroxyl groups, several attempts have been performed. Biswas *et al.* doped potassium ions (K^+) into sol-gel SiO_2 films and succeeded in reducing the amount of hydroxyl groups and realizing the enhancement of Er^{3+} luminescence.[11] K^+ replaces hydrogens with substitution reaction and reduces hydroxyl groups. The enhancement of luminescence from $Er-SiO_2$ films is also achieved by doping silver ions.[12] In this case, silver ions are thought to act as a photosensitizer to excite Er^{3+} and enhance the effective absorption cross section.

In this work, we attempt to realize the enhancement of Er^{3+} luminescence in sol-gel silica films by a different approach. We dope Au nanoparticles into sol-gel $Er-SiO_2$ films. Unlike K^+, Au does not reduce the amount of hydroxyl groups in a sol-gel film. However, hydroxyl groups are known to be preferentially coordinated around Au nanoparticles,[13] and thus Au nanoparticles are expected to act as chemical absorbents for hydroxyl groups. This may increase the number of hydroxyl-group-free Er^{3+} and thus improve the luminescence efficiency. In addition, absorption cross sections of Er ions are considered to be enhanced by the strong field accompanied by the surface plasmon of metal nanoparticles.[14–16] In this paper, we report the results of detailed optical studies of Au nanoparticles and Er-doped sol-gel silica films. We will show that the luminescence intensity of Er^{3+} is strongly enhanced by doping Au nanoparticles.

II. EXPERIMENT

SiO_2 films containing Au nanoparticles and Er were prepared by a sol-gel method.[8] Tetraethylorthosilicate [$Si(OC_2H_5)_4$], ethanol, and hydrochloric acid (the volume ratio=1:10:0.01) were mixed to produce a sol solution. Erbium chloride ($ErCl_3$) and chloroauric acid ($HAuCl_4$) were then doped into the sol solution. The concentration of $ErCl_3$ in sol solution was 0.1 mol % and that of $HAuCl_4$ was changed from 0.1 to 7.0 mol %. Before the spin coating of the sol solution, a SiO_2 substrate was ultrasonicated and washed. The SiO_2 films containing Au ions and Er ions were then dried on a hot plate at 150 °C for 20 s. Finally, the films were annealed at temperatures between 700 and 1250 °C to reduce Au ions and grow Au nanoparticles in SiO_2 matrices. The thickness of the sol-gel films was about 260 nm.

The existence of Au nanoparticles in SiO_2 films is proved by transmission electron microscopy (TEM). Figure 1 shows a TEM image of a sample annealed at 900 °C. We can see spherical Au nanoparticles about 20 nm in diameter.

The photoluminescence (PL) spectra were measured using a single-grating monochromator and an InGaAs near-infrared diode array. The excitation source was an optical parametric oscillator (OPO) pumped by the third harmonic of a Nd:YAG (yttrium aluminum garnet) laser (pulse width of 5 ns and repetition frequency of 20 Hz). For the measurements of PL spectra and decay curves, 520- and 980-nm light were used for excitation. For the PL excitation spectra, the excitation wavelength was changed from 450 to 1050 nm. The PL decay curves were measured by a near-infrared photomultiplier (R5509-72 Hamamatsu) and a multichannel scalar (SR430, Stanford Research). The time resolution was better than 100 ns.

---

[a] Author to whom correspondence should be addressed; electronic mail: fujii@eedept.kobe-u.ac.jp

0021-8979/2005/98(2)/024316/4/$22.50

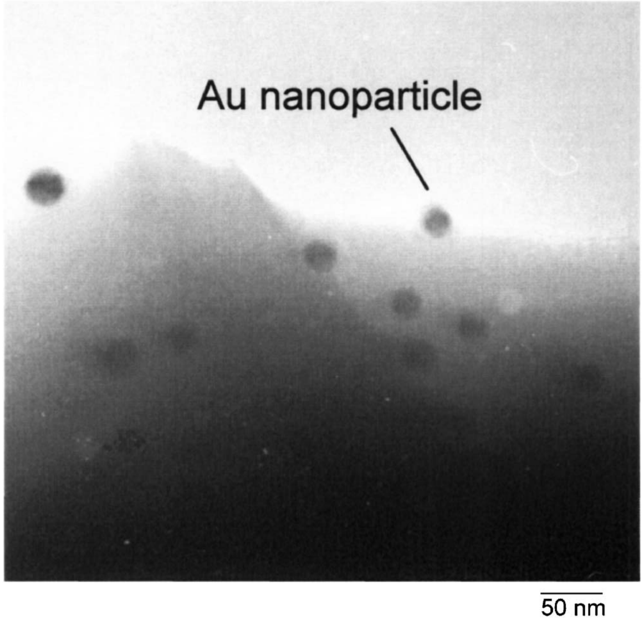

FIG. 1. TEM image of a Au and Er-doped SiO_2 sol-gel film annealed at 900 °C.

III. RESULTS

Figure 2 shows the PL intensities at 1.54 μm of $Er-SiO_2$ films containing Au nanoparticles ($Er/Au-SiO_2$) as a function of Au concentration. The annealing temperature is fixed to 700 °C. The intensities are normalized to that of the sample not containing Au nanoparticles. The vertical axis thus corresponds to the degree of PL enhancement by Au nanoparticle doping (enhancement factor). The PL intensity depends strongly on Au concentration and takes a maximum at 1.0 mol %. At this concentration, the enhancement factor is about 100. In the inset, the PL spectra of the samples with the Au concentrations of 0.3, 1.0, and 3.0 mol % are shown. In spite of strong variation of the PL intensity, the spectral shape is almost independent of Au concentration.

Figures 3(a) and 3(b) show the enhancement factor as a function of annealing temperature for the excitation wavelengths of 520 and 980 nm, respectively. The data are obtained by dividing the PL intensity of the samples containing Au nanoparticles by those without Au doping (see the insets). The wavelength of 520 nm corresponds to the energy difference between the $^2H_{11/2}$ state and the ground $^4I_{15/2}$ state of the 4f shell of Er^{3+}, and 980 nm to the $^4I_{11/2}$ and $^4I_{15/2}$ states (see the inset of Fig. 3). In both cases, the enhancement factor depends on the annealing temperature and is the largest at the annealing temperature of around 900 °C. However, the maximum value is different; it is about 500 in the case of 520-nm excitation, while about 200 in the case of 980-nm excitation. The reason for the excitation wavelength dependence of the enhancement factor will be discussed later.

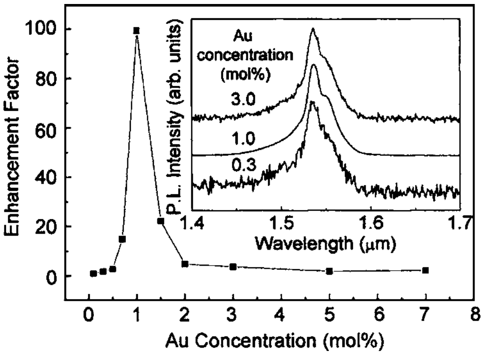

FIG. 2. The ratio of PL intensity of $Er/Au-SiO_2$ films to that of $Er-SiO_2$ film as a function of Au concentration. The excitation wavelength is 520 nm. The annealing temperature is fixed to 700 °C. The inset shows PL spectra for the samples with the Au concentrations of 0.3, 1.0, and 3.0 mol %.

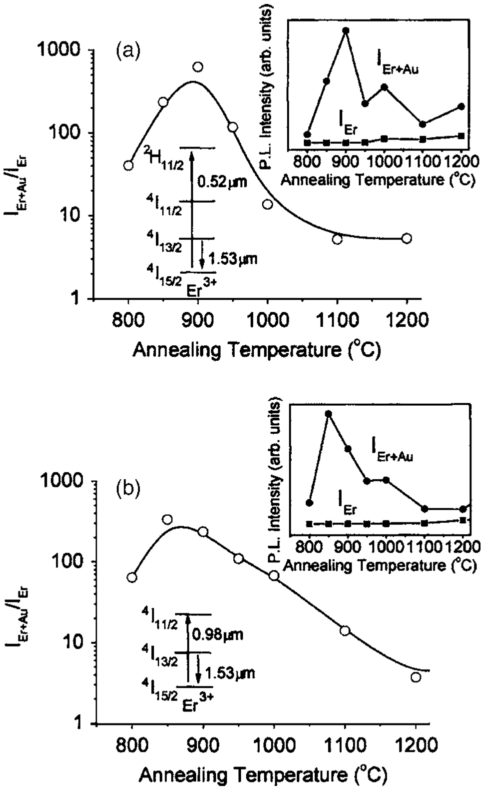

FIG. 3. The ratio of PL intensity of $Er/Au-SiO_2$ films to that of a $Er-SiO_2$ films as a function of annealing temperature. The Au concentration is 1.0 mol %. Insets are PL intensities of $Er/Au-SiO_2$ and $Er-SiO_2$ films. The Excitation wavelengths are 520 nm (a) and 980 nm (b). The energy diagrams of 4f shell of Er are drawn in the insets.

Figure 4 shows the absorption spectra of Au nanoparticles dispersed in $Er-SiO_2$ films at various annealing temperatures. For the samples annealed below 500 °C, the spectra are almost flat meaning that Au nanoparticles are not grown. Above 600 °C, a broadband appears at 520 nm. This band originates from the localized surface plasmon of Au nanoparticles, thus indicating the formation of Au nanoparticles. By increasing the annealing temperature above 1200 °C, the 520-nm band again disappears. This is probably due to the evaporation of Au nanoparticles because the temperature is higher than the melting point of Au (1063 °C).[17,18] In the inset of Fig. 4 the maximum value (a) and full width at half maximum (FWHM) of the absorption band (b) are plotted as a function of annealing temperature. The absorbance reaches maximum at 950 °C and then decreases due to the evaporation of Au particles. In Fig. 4, with

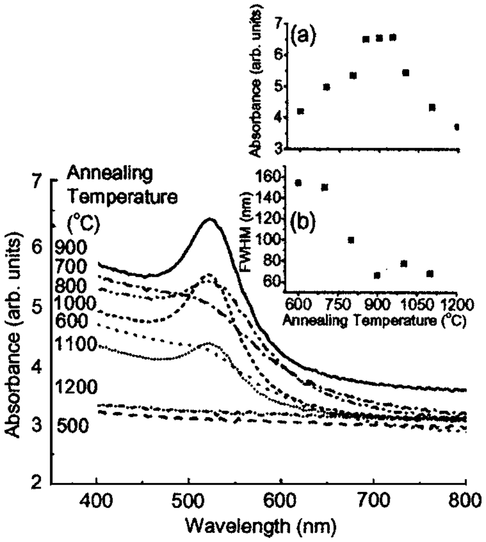

FIG. 4. Absorption spectra of Er/Au–SiO$_2$ films. The Au concentration is 1.0 mol %. Annealing temperature is changed from 500 to 1250 °C. Insets: Intensities (a) and FWHMs (b) of surface-plasmon resonances of Er/Au–SiO$_2$ films as a function of annealing temperature.

increasing annealing temperature the spectra become narrower, suggesting that damping of the surface plasmon becomes smaller due to the improvement of crystallinity in and on the surface of Au nanoparticles.

Figure 5(a) shows the photoluminescence excitation (PLE) spectra detected at 1.54 μm. The excitation wavelengths are changed from 450 to 1050 nm. The peak at around 520 nm corresponds to the transition between the $^4I_{15/2}$ and $^2H_{11/2}$ states, and that at around 980 nm to the $^4I_{15/2}$ and $^4I_{11/2}$ states. For comparison, the PLE spectrum of the Er–SiO$_2$ film without Au nanoparticles is also shown. In order to obtain an enhancement factor as a function of excitation wavelength, in Fig. 5(b), the PLE spectrum of the sample with Au nanoparticles is divided by that without Au nanoparticles. We can see a peak centered at around 520 nm. On the spectrum, an absorption spectrum is added (dashed curve). The spectrum coincides quite well with that of the enhancement factor, indicating that the peak is related to the surface-plasmon resonance of Au nanocrystals.

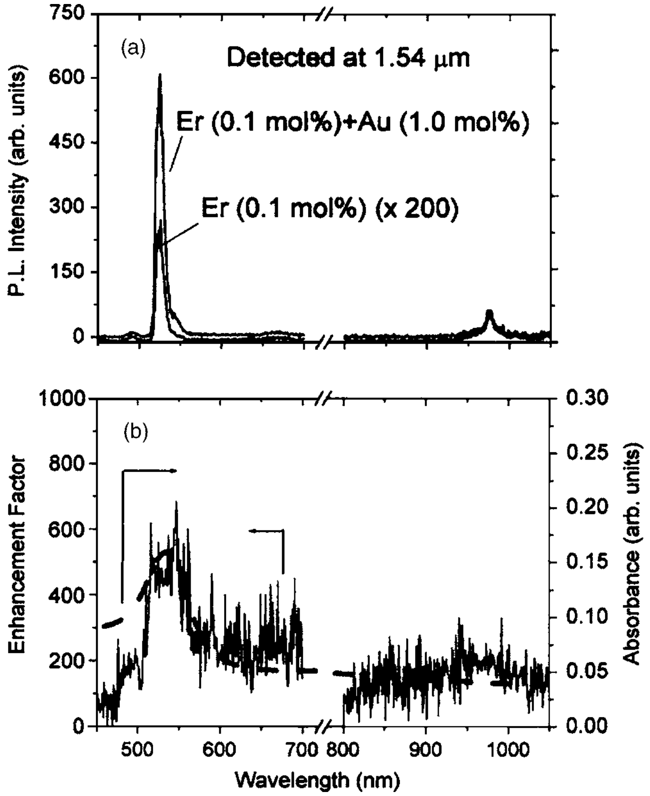

FIG. 5. (a) PL excitation spectrum (λ_{det}=1535 nm) of a Er/Au–SiO$_2$ film (Au concentration: 1.0 mol %) and a Er–SiO$_2$ sol-gel film. (b) The ratio of the two spectra and the absorption spectrum of a Er/Au–SiO$_2$ film are drawn. Annealing temperature is 900 °C.

IV. DISCUSSION

Figures 2–5 clearly demonstrate that the PL of sol-gel Er–SiO$_2$ films is enhanced by doping Au nanoparticles. As mentioned in the Introduction, two different mechanisms are expected. The first one is the chemical mechanism that will decrease nonradiative recombination centers such as OH bonds. The second one is the enhancement of absorption cross section of Er ions by the resonance with the localized surface plasmon of Au nanoparticles. These two mechanisms can be distinguished by the PLE spectrum. The enhancement due to chemical mechanism does not in principle depend on excitation wavelength, while that due to surface-plasmon resonance should be the most effective when the excitation wavelength coincides with the resonant wavelength. In the PLE spectra, we can see a clear peak of enhancement factor that coincides very well with the absorption spectrum of Au nanoparticles. This is the direct evidence that the PL from Er^{3+} is enhanced by the strong field accompanied by the surface plasmon of Au nanoparticles. However, it should be noted here that the observed enhancement cannot be fully explained only by this mechanism. In Figs. 3(b) and 5(b), we can see a very large enhancement about 200 even when the excitation wavelength is 980 nm, which is far from that of the surface-plasmon resonance. The enhancement in this wavelength is considered to come from pure chemical effects and that at 520-nm excitation is due to the mixture of the chemical and the physical effects. Therefore, we can conclude from Fig. 5(b) that the enhancement factor due to chemical effect is about 200, and that due to physical one is about 2.5, implying that the chemical mechanism is responsible for the major part of the enhancement and the physical mechanism is a small addition when excitation wavelength coincides with the surface-plasmon resonance wavelength.

If the PL is enhanced by the chemical mechanism, the enhancement should be accompanied by the recovery of PL lifetime. Figure 6 shows the PL decay curves at 1.54 μm for the sample containing and not containing Au nanoparticles. Since the PL intensity of the sample not containing Au nanoparticles was very weak and the decay curve was too noisy, we prepared a much thicker film only for the decay measurement. The annealing temperature is 900 °C, and the concentration of Au nanoparticles is 1.0 mol %. We can clearly see the recovery of the lifetime from 0.082 to 7.7 ms by doping Au nanoparticles.

As the origin of the chemical mechanism, suppression of the energy transfer to hydroxyl groups, which is efficient

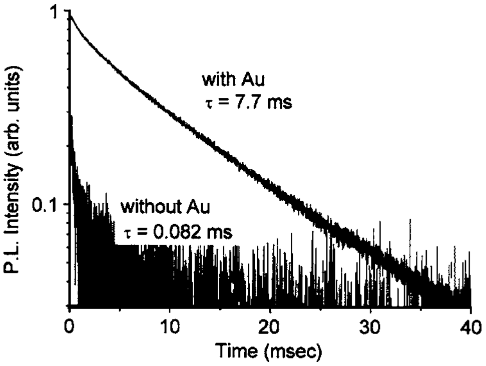

FIG. 6. Photoluminescence decay curves (λ_{det}=1535 nm) of a Er/Au–SiO_2 sol-gel film (Au concentration: 1 mol %) and a Er–SiO_2 sol-gel film excited at 520 nm. Annealing temperature is 900 °C.

nonradiative recombination centers for Er ions, is the most plausible. In order to study the amount of hydroxyl groups, IR absorption due to OH vibration signals is measured. Figure 7 shows the result. In spite of the strong enhancement of PL intensity, the amount of OH bonds does not change so much. This contradiction can be explained by considering the fact that Au nanoparticles in sol-gel SiO_2 films act as chemical absorbents for hydroxyl groups; OH bonds are preferentially coordinated on the surface of Au nanoparticles,[13] which increases the number of OH-free Er ions and the enhancement of PL intensity.

As can be seen in Figs. 2 and 3 emission of Er is maximum when Au concentration and annealing temperatures are optimum. We obtained a very sharp peak of the enhancement factor at Au concentration of 1.0 mol %. Since Au nanoparticles are responsible for the PL enhancement, the enhancement becomes large with increasing Au concentration when Au concentration is rather small. However, it should be noted that Au nanoparticles act as a quencher for Er ions when Er^{3+} is very close to Au nanoparticles due to the excitation of intra- and interband transitions, and also surface plasmons of Au nanoparticles by nonradiative energy transfer from Er^{3+}.[19] As Au concentration increases, the number of Er staying in close proximity to Au nanoparticles increases, resulting in the quenching of PL. The peak at 1.0 mol % in Fig. 2 is considered to arise from the competition between the enhancement and the quenching effects.

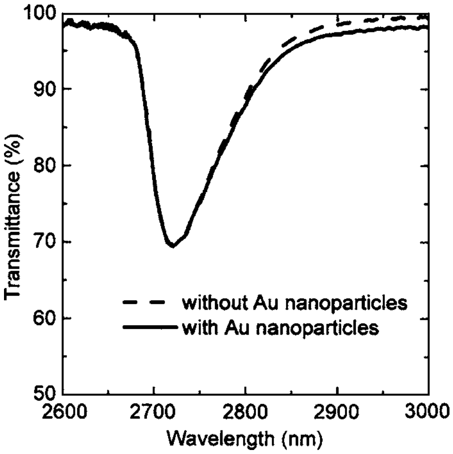

FIG. 7. Infrared absorption spectra of vibration signals of hydroxyl groups in Er–SiO_2 and Er/Au–SiO_2 sol-gel films.

The maximum PL enhancement at 900 °C annealing can be explained as follows. The increase in the PL enhancement factor with increasing annealing temperature is accompanied by the increase and narrowing of the absorption band of surface-plasmon resonance of Au nanoparticles. The stronger and narrower absorption band imply that the crystallinity of Au nanoparticles is improved. Furthermore, the number of defects in glasses is considered to be decreased and OH groups are more properly coordinated on the surface of Au nanoparticles. This enhances the chemical effects described in the above resulting in higher enhancement factor. The decrease in the enhancement factor above 900 °C is due to the decrease of the number of Au particles by evaporation.

V. CONCLUSION

We have succeeded in improving the PL properties of Er-doped sol-gel silica films. The PL intensity was at most 500 times enhanced by doping Au nanoparticles when Au concentration was 1.0 mol %. The analysis of PLE spectra revealed that there are two mechanisms contributing independently to the enhancement. The first one is the chemical mechanism; Au nanoparticles act as chemical absorbents of hydroxy groups and increase the number of OH-free Er ions. The other one is the enhancement of absorption cross section of Er^{3+} due to localized surface-plasmon resonances of Au nanoparticles.

ACKNOWLEDGMENT

This work is supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

[1] J. T. Ahn and K. H. Kim, Opt. Commun. **212**, 275 (2002).
[2] T. C. Teyo, M. K. Leong, and H. Ahmad, Opt. Laser Technol. **34**, 497 (2002).
[3] A. Polman and F. C. J. M. van Veggel, J. Opt. Soc. Am. B **21**, 871 (2004).
[4] H. Schoder, Phys. Thin Films **5**, 87 (1969).
[5] K. S. Mazdiyasni, R. T. Dolloff, and J. S. Smith, J. Am. Ceram. Soc. **52**, 523 (1969).
[6] H. Dislich, Angew. Chem., Int. Ed. Engl. **10**, 363 (1971).
[7] H. Dislich, J. Non-Cryst. Solids **73**, 599 (1985).
[8] H. Kozuka and S. Sakka, Chem. Mater. **5**, 222 (1993).
[9] R. Campostrini, G. Carturan, M. Ferrari, M. Montagna, and O. Pilla, J. Mater. Res. **7**, 745 (1992).
[10] C. Coutier, W. Meffre, P. Jenouvrier, J. Fick, M. Audier, R. Rimet, B. Jacquier, and M. Langlet, Thin Solid Films **392**, 40 (2001).
[11] A. Biswas, G. S. Maciel, R. Kapoor, C. S. Friend, and P. N. Prasad, Appl. Phys. Lett. **82**, 2389 (2003).
[12] C. Strohhöfer and A. Polman, Appl. Phys. Lett. **81**, 1414 (2002).
[13] W. Yan, B. Chen, S. M. Mahurin, E. W. Hagaman, S. Dai, and S. H. Overbury, J. Phys. Chem. B **108**, 2793 (2004).
[14] T. Hayakawa, S. T. Selvan, and M. Nogami, J. Non-Cryst. Solids **259**, 16 (1999).
[15] J. R. Lakowicz, J. Malicka, S. D'Auria, and I. Gryczynski, Anal. Biochem. **320**, 13 (2003).
[16] H. Nabika and S. Deki, J. Phys. Chem. B **107**, 9161 (2003).
[17] P. Buffat and J. P. Borel, Phys. Rev. A **13**, 2287 (1976).
[18] T. Castro, R. Reifenberger, E. Choi, and R. P. Andres, Phys. Rev. B **42**, 8548 (1990).
[19] E. Dulkeith, A. C. Morteani, T. Niedereichholz, T. A. Klar, J. Feldmann, S. A. Levi, F. C. J. M. van Veggel, and D. N. Reinhoudt, Phys. Rev. Lett. **89**, 203002 (2002).