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Surface-Plasmon-Coupled Emission of Rhodamine 110 in a Silica Nanolayer

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The first observation of strong directional surface-plasmon-coupled emission (SPCE) of Rhodamine 110 in silica nanofilms deposited on silver nanolayers is reported. The preparation of the material is described in detail. The intensity of SPCE exceeds 10 times that of free space fluorescence and total linear

light polarization in the SPCE ring is observed. A new experimental setup and an original data collection method is presented. Our material completely preserves its fluorescence properties for at least eight months.

1. Introduction

Luminescent hybrid materials have been drawing much attention recently as potential lasing media for compact tunable lasers, host–guest systems playing an important role in drug delivery, solar cells and concentrators, to name a just few.^[1–4] One of most frequently used ways for obtaining hybrid organic–inorganic materials makes use of the sol–gel process. This is a convenient and versatile method for the preparation of transparent optical thin films due to good mixing of the starting compounds at low temperatures. Moreover, this method is attractive, as it ensures negligible diffusion losses and high product quality. Besides, the method offers a new level of control over microstructure. This is very important in view of material engineering, since the performance of micro- and nano-scale devices can be determined by the local structure around the optically active ion.^[1]

The sol–gel process is based on the hydrolysis and polycondensation of molecular precursors such as metal alkoxides $M(OR)_n$. The classical sol–gel route takes advantage of a sequence of reactions: hydrolysis of the alkoxy groups and condensation. Precursors react in a liquid medium and lead to partially cross-linked three-dimensional particulates suspended in the liquid, which is called the sol. The viscosity of the sol increases as the polymer network grows and all reactions can be carried out at room temperature. Further reactions, during aging and curing of the sol, lead to the solid amorphous state called the gel. Remaining solvents and water evaporate, before the amorphous material is built up. The evaporation under normal conditions converts the material into xerogel. Hydrolysis and condensation reactions can be influenced by many parameters. Changing the temperature, pH, catalyst, solvent and water/silane ratio influences the formation of many intermediate states such as dimers, oligomers or higher condensation products. A number of different gradually hydrolysed species condense together, and the direction of a reaction can be influenced by an appropriate choice of parameters. The characteristics of the final thin films or bulk materials depends on the storage time, curing manner and properties of the surface.^[2]

Materials obtained by the sol–gel process include hybrid siloxane matrices that can be doped with organic dyes,^[4] rare earth ions^[5] or transition metal ions.^[6] On the other hand, immense interest emerged over the last years in enhanced fluorophore emission induced by the interaction of surface plasmons on metallic nanofilms with neighbouring fluorophores located closer than 200 nm to the metal surface.^[7,8]

Surface-plasmon-coupled emission (SPCE) can simply be provoked by illuminating the sample through the glass prism and metal film (Kretschmann configuration) or direct excitation of fluorophore thin film spread over the metal nanolayer (reverse Kretschmann configuration).^[9,10] Anyway, bright directional emission passing through the metallic film and back into the prism is observed. For the sake of observation comfort and simplicity in the detection part of the experimental setup a hemispherical prism is often used. This leads to the appearance of SPCE in a form of colorful rings observed in the detector plane. This directional character of SPCE results from a near-field interaction between the excited fluorophore and vi-

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cial surface plasmons at the metal nanolayer. It should be stressed that SPCE carries the same spectral information as the normal fluorescence, but can be more efficiently collected. These unique features of SPCE lead to various attractive applications. By now, most of them are related to these problems where there is a need to detect very weak fluorescence signals, that is, in biosensing, antigen–antibody reactions, energy transfer in special systems, and many others.^[3,7,8,11]

The aim of our paper is to demonstrate for the first time extremely strong SPCE in a hybrid luminescent material. For the purpose of our paper we have chosen the strongly fluorescent Rhodamine 110 molecule (fluorescence quantum yield $\eta = 0.95$). This strongly fluorescent and photostable molecule can easily be excited by ordinary diode lasers and incorporated into various polymer or glassy matrices. As a host matrix we have chosen a xerogel nanolayer spread over 50 nm thin silver film. An alternative and more efficient method of SPCE signal collection is also presented and described in detail.

Experimental Section

Materials and Methods: Thin films of silica gel doped with Rhodamine 110 were prepared by the sol–gel process and the spin-coating method. The starting compounds used herein were of at least analytical grade. Tetramethoxysilane $\text{Si}(\text{OCH}_3)_4$ (TMOS) was from Aldrich, methanol from POCh (Poland) and Rhodamine 110 from Aldrich. First, TMOS and methanol with Rhodamine 110 were mixed together. After a while, deionised water was added to the solution. The molar ratio TMOS/methanol/water was 0.013:0.05:0.055. The final concentration of Rhodamine 110 in sol was 0.002 M. Then, three drops of NaOH (0.1 M) were added to promote the reaction of the sol–gel process. The mixture was stirred at room temperature for several minutes and a highly transparent sol was obtained, which was subsequently used for film deposition. Glasses with silver from EMF (USA) were used as substrates. They were cleaned with spectroscopically pure methanol. Reference glasses without metal (used to absorption spectra measurements) were kept in a mixture of 33% H_2O_2 and H_2SO_4 in the molar ratio 2:1 over 24 h. Next, they were bathed in water and dried. The Rhodamine 110-doped sol was deposited on the thoroughly cleaned substrates with or without silver using the spin-coating technique. In the spin-coating process, the deposited coating material on the substrate (silver nanolayer on the glass) spins around the fixed axis. The coatings were rotated at 3600 revolutions per minute (rpm) for 60 seconds. Thereafter, the samples were cured.

Spectroscopic Measurements: SPCE and fluorescence free space spectra were measured with the SPCE spectrofluorometer designed and constructed in our laboratories. The setup for the observation of SPCE is presented in refs. [7, 11]. The setup of the whole equipment is presented in Figures 1 a,b.

In the case of Rhodamine 110 the observations were made upon excitation at $\lambda_{\text{exc}} = 473$ nm with a diode-pumped solid-state laser DPSS473 (CNI, China). The average beam power was set to 25 mW and the monochromator slit was set to 0.75 mm. The monochromator Sp300i (Acton, USA) grating was 300 lines mm^{-1} . For light detection the photomultiplier H5783–20 (Hamamatsu, Japan) was used. Camera shots of the pictures were taken with an exposure time of $\tau = 4$ s. The distance from the sample to the screen was set to 0.04 m. During observations, to eliminate the excitation light, the cut-off filter G495 (Edmund Optics, USA) was used.

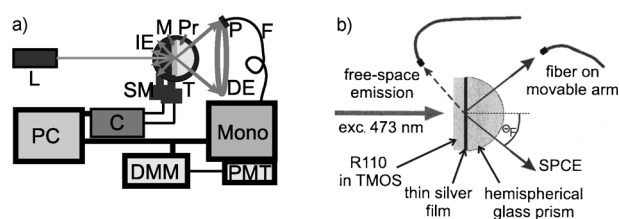


Figure 1. a) Experimental setup for measuring the angular distribution of SPCE from fluorophores in a TMOS nanolayer distributed on thin metal films. A diode-pumped solid-state laser (L) operating at $\lambda_{\text{exc}} = 473$ nm is used to excite Rhodamine 110 molecules (M) in tetramethoxysilane deposited on a 50 nm silver thin film. The substrate is in contact with the hemispherical glass prism (Pr) due to immersion oil and located on a rotatable table (T). IE and DE stands for the isotropic emission and directional emission originating from fluorophores, respectively. Photon emission is collected by a single fiber cable (F) positioned on the precisely moving arm and directed towards the monochromator input slit. A photomultiplier tube (PMT) is used to measure intensity of incoming light. A personal computer (PC) with originally written software based on the LabVIEW package is used to steering stepper motors (SM) by the controller (C), setting the monochromator (Mono) and the reading signal from digital multimeter (DMM) via a general purpose interface bus (GPIB) connection. b) Setup for the observation of SPCE in the reverse Kretschmann configuration. Directional SPCE emission propagates at a small spatial angle at the surface of the cone of emission forming characteristic rings on the observation screen.

Thickness measurements: Ellipsometric investigations were carried out with a phase-modulated ellipsometer Jobin–Yvon UVISSEL (HORIBA Jobin–Yvon Inc., Edison, USA) in the photon energy range from 1.8 eV up to 4.8 eV at an angle of 60° , due to the Brewster's angle of the silver-coated glass substrate. In order to determine the thickness and the optical properties of films we assumed a single-layer optical model based on a mixture layer of Rhodamine 110– SiO_2 calculated by effective medium approximation.^[12] The Tauc–Lorentz (TL) dispersion model^[13] of the dielectric function of the Rhodamine 110-doped layer was utilized.^[14,15] The optical indices of silver and SiO_2 were obtained from the database.^[16] The optical model was fitted to the experimental data using the Levenberg–Marquardt nonlinear least-squares algorithm.^[17] The thickness of 81 nm was obtained.

2. Results and Discussion

Figures 2a,b shows the SPCE ring obtained in the reverse Kretschmann configuration (also see Figure 1b) for Rhodamine 110 at a bulk concentration of $C = 0.02$ M in a rigid thin xerogel film distributed over a silver nanolayer. Images were captured through the paper screen.

Figure 2a presents the picture taken without the polarizer, whereas Figure 2b was taken with the polarizer placed between the screen and the sample. Figure 2c shows the angular intensity distribution of the polarized light in the ring at the observation wavelength $\lambda_{\text{obs}} = 530$ nm corresponding to the maximum of monomer fluorescence band of Rhodamine 110 in the silica matrix. The measurements were performed with the equipment shown in Figure 1 with two different orientations of the polarizer (horizontal, H, and vertical, V) placed before the entrance to the fiber. The ring for which the maximal emission intensity of H polarization is located in the upper and lower parts of the screen (characteristic bows in Figure 2b), is s polarized with the electric vector tangent to the

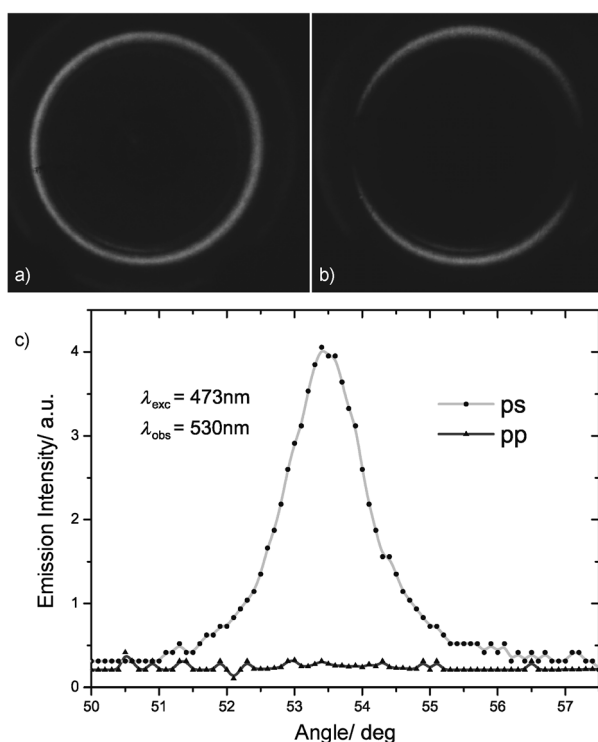


Figure 2. Pictures of SPCE rings with the filter cutting off the excitation wavelength: a) without polarizer, b) with polarizer, c) polarized intensity components in SPCE rings. There is a strong ps component and no pp component, evidencing total linear polarization of SPCE radiation (ps: s polarization, pp: p polarization; the beam power was set to 15 mW).

ring everywhere. It should be stressed that the light polarization in the SPCE ring does not depend on the exciting light polarization, which is in agreement with previous observations.^[7,18] As a result of angle-dependent (radial) SPCE intensity measurement, only one polarization component is recorded (see the curve with triangles in Figure 2c). The results presented together in Figures 2b,c prove the total linear polarization everywhere in the SPCE ring. The visible strong contrast between the bright ring and the screen background has not been manipulated in any way and represents the really observed intensity of the emitting sample. The residual red ring seen inside the green one (Table-of-Contents picture) corresponds to the weak aggregate emission of Rhodamine 110 in silica matrix.^[19]

Figure 3 shows angle-resolved spectra of SPCE. This kind of observation of the SPCE signal improves the method of signal collection for directional emission. Contrary to other reports on SPCE, in the method proposed herein, the entrance end of the fiber optics is fixed on an automated moving arm at a much smaller distance from the lens, yielding angular scanning resolution even up to 0.01 degree. This improvement not only gives a much better angle resolution, but also a better signal-to-noise ratio as a result of more efficient signal collection.

Application of a fiber with a small radius allows one to obtain better spatial resolution at small distances from the emitting sample. Moreover, this results in the possibility of recording weaker emission signals than previously as the emitted

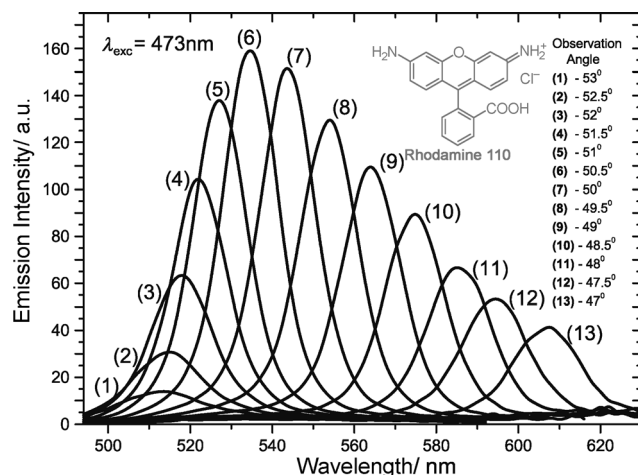


Figure 3. Angle-resolved spectra of SPCE for Rhodamine 110 in silica nanolayers on a silver substrate. Observations were carried out from 47° to 53°. For clarity, only selected angular spectra are presented.

light intensity is inversely proportional to the source–detector squared distance. The angle-resolved SPCE spectra presented in Figure 3 were obtained due to the described procedure, which in fact forms a kind of spatial filtering. We expect that this fact can be useful in studies of more complex multicomponent spectra. Simultaneously, SPCE collection with the fiber of small radius allows one strongly to restrict the inaccuracies connected with the light intensity changes dependent on the radiation angle. This is because the measurements during the movement of the fiber along the bow reflects the spherical symmetry of SPCE configuration.

Figure 4 shows the comparison between fluorescence intensities obtained with the SPCE technique (—) and as a free space fluorescence (FSE, ----). Both measurements were made under identical conditions. Due to the fluorophore transition moment interaction with surface plasmons, the emission signal becomes directional and is strongly enhanced. The peak-to-

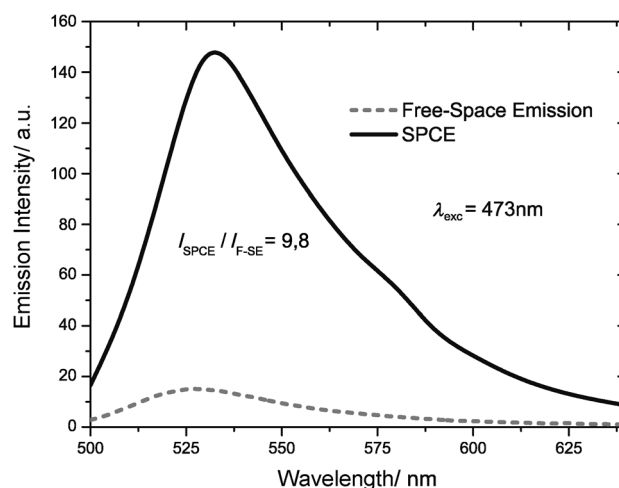


Figure 4. Emission enhancement of Rhodamine 110 in silica nanolayers by silver surface plasmons compared to the free space fluorescence signal obtained in the absence of the silver nanolayer. The peak-to-peak signal ratio I_{SPCE}/I_{FSE} amounts to 9.8, whereas the ratio of total intensities given by the respective areas amounts to 10.3.

peak intensity ratio of SPCE and FSE is 9.8 and the total signal ratio is equals 10.3, which means strong signal enhancement due to fluorophore–surface-plasmon near-field interaction. The total SPCE spectrum was obtained by summing up the intensities' distributions over the whole angle range for each observation wavelength with the maximal possible resolution.

3. Conclusions

The spectral properties of a new hybrid material based on silica nanolayer doped with Rhodamine 110 deposited on 50 nm thick silver plates were presented. The obtained material is characterized by strong directional luminescence upon excitation with a standard CW diode-pumped laser. It is also worthy to note that the material is extremely durable as it practically did not exhibit any signs of mechanical ageing or photobleaching after 8 months from its production. The setup for fully automated SPCE measurements was also presented. Our setup allows for higher angular and spectral resolution and better signal-to-noise ratio measurements. Next, we will present the application of the setup to study the aggregation phenomena in hybrid materials and its use in time-resolved equipment with a streak camera of ps temporal resolution.

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Keywords: fluorescence • rhodamine 110 • nanostructures • surface-plasmon-coupled emission • thin films

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