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Fluorescence and $^1O_2$ generation properties of porphyrin molecules immobilized in oxidized nano-porous silicon matrix

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Abstract

Recently it has been shown that nano-porous silicon (pSi), synthetic material produced by electrochemical etching of monocrystalline silicon, is able to provide an efficient electronic energy transfer to molecular oxygen, thus producing singlet (i.e. excited) oxygen in gaseous and liquid environment that opens the possibilities for application of pSi in Photodynamic Therapy (PDT). Here, we study the photophysical properties, including an ability of singlet oxygen ($^1O_2$) generation, of a modified pSi matrix impregnated with cationic (TMPyP(4)) or anionic (TPPS) porphyrins, which are known as effective photosensitizers of $^1O_2$ production in solution.

It is shown that a use of oxidized pSi matrix instead of as-prepared one results in an increase of an ability of the porphyrins to be immobilized in the matrix by orders of magnitude. A matrix of pSi formed in (1 0 0)-oriented Si wafers ensures, after pSi oxidation, better uptake of porphyrins into the pores as compared with oxidized pSi(1 1 1). The fluorescence decay kinetics of the immobilized porphyrins are found to be non-exponential, and the effective fluorescence lifetime shortens with an increase of the porphyrin concentration. It evidences in favour of a moderate annihilation-type concentration quenching of the fluorescence rather than in favour of any quenching effect of oxidized pSi matrix. It opens perspectives for application of the hybrid material for $^1O_2$ generation. An ability of immobilized TMPyP(4) to generate $^1O_2$ is shown experimentally by direct $^1O_2$ luminescence measurements.

Keywords: Porphyrins; Nano-structured porous silicon; Photoluminescence; Generation of singlet oxygen

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1. Introduction

Nano-porous silicon (pSi) is a synthetic material produced by electrochemical or chemical etch of mono- or polycrystalline Si [1]. It is a porous matrix with pores of varying diameters (10 nm–10 μm) and shapes, the pore walls being composed of crystalline Si nano-clusters [2]. Known mainly for its very interesting non-linear optical properties, this material has recently found application in controllable and targeted drug delivery into humans due to its bio-degradability and bio-compatibility [3]. Another very exciting property of porous silicon that has been recently discovered is its ability to generate an electronically excited singlet oxygen (molecule denoted as $^1O_2$ with anti-parallel spins of electrons) while being irradiated by visible light [4]. Photosensitizing properties of pSi are based on a specifics of its electronic states, surprisingly similar to those of porphyrins [5] which are known for their efficient photogeneration of singlet oxygen, very strong oxidant of organic molecules and living cells and therefore, useful active substance for Photodynamic Therapy (PDT) of cancer and other diseases [6].

The idea to use pSi as in vivo $^1O_2$ photosensitizer in Photodynamic Therapy of cancer and other deceases has arisen in the literature [4–5]. However, one of possible difficulties on this way is that pSi exhibits most intensive light absorption in the blue-UV part of the spectrum, where a skin and tissues absorb light very strongly. In connection with this, the idea of this study is to use pSi as a platform carrying an immobilized organic photosensitizer, which exhibits intensive absorption of light in the red—near IR region, where a skin and tissues have the "transparency window". Combination of photosensitising activity of an organic photosensitizer with bio-degradability of pSi and its ability to form solid particles of different size can result in interesting PDT applications of such a hybrid material. It has also been shown earlier that photosensitizers embedded into the nano-particles of silica ensure better delivery of $^1O_2$ to cells

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as compared with organic photosensitizers [7]. We hope that replacement of porous silica by pSi would ensure higher flexibility of $^1O_2$ delivery to the cells.

In this study, porphyrins were used as photosensitizers because of their high efficiency of the singlet oxygen formation and ease of adjustment of their physicochemical (hydrophobicity and hydrophylity) as well as optical (absorption and emission spectra) properties to the researcher's requirements by means of chemical modifications of the porphyrin structure. Particularly, we focused on finding those forms of porphyrins and porous silicon, which would ensure best photosensitising properties of the hybrid material.

We did not find in the literature other studies of photophysical properties of the porphyrin/porous silicon composites. There is only a series of works concerned with a study of the related hybrid materials (metallo)porphyrin/mesoporous silica composites [8–18]. These works, however, are mostly devoted to study catalytic activity of the composites and only in a little extent concern with the study of the guest (porphyrin)–host (porous matrix) interactions (see Section 4).

Obtained results show unambiguously that by using pSi in combination with post-growth treatments, and cationic forms of porphyrins, it is possible to create a hybrid porphyrin/pSi material, which is able to immobilize porphyrins at sufficiently high concentrations, the inorganic pSi matrix has no quenching effect on the porphyrin fluorescence state. It opens perspectives for application of the material for singlet oxygen generation.

2. Experimental techniques

We have used two types of porphyrins in the experiments. One was water-soluble cationic porphyrin 5,10,15,20-tetrakis-(*N*-methyl-4-pyridyl)porphyrin tetrachloride (hereafter, TMPyP(4)), and water-soluble anionic porphyrin 5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin Na salt (TPPS), purchased from Mid-Century Chemicals. Molecular structure of these typical representatives of porphyrins family is shown in Fig. 1.

The pSi samples were prepared by anodic polarization (anodization) of p-type (1 0 0) and (1 1 1)-oriented Si wafers with a resistivity of 10–20 Ω cm. Anodization was performed using electrochemical potentiostat PAR273A in 48% HF:95% ethanol 1:1 solution (by volume) for 10 min at a current density of 30 mA/cm^2. The thickness of the pSi layers was estimated by using an optical microscope and was found to be about 20 μm for (1 0 0)-oriented Si and about 10 μm for (1 1 1)-oriented Si. Typical morphology of the pSi samples grown at (1 0 0)-oriented Si wafers is presented in Fig. 2. The pores are aligned along the crystallographic axes of Si wafer and have medium pore diameter of about 45 nm. After anodization, thermal oxidation of pSi samples was performed at 500 °C in air ambient for 1.5 h using Programat P200 vacuum micro-oven.

Further on, pSi layers were immersed in water solutions of TMPyP(4) or TPPS with porphyrin concentration of about 3×10^{-3} M for 1 h and then dried at room temperature for 24 h. The presence of porphyrins in pSi matrix was controlled using infrared spectrometry (System 2000 FTIR spectrometer from Perkin-Elmer) operating in a diffuse reflectance mode. Further increase of the pSi matrix impregnation time did not result in increase of the immobilized porphyrin amount, the last being controlled by its fluorescence intensity.

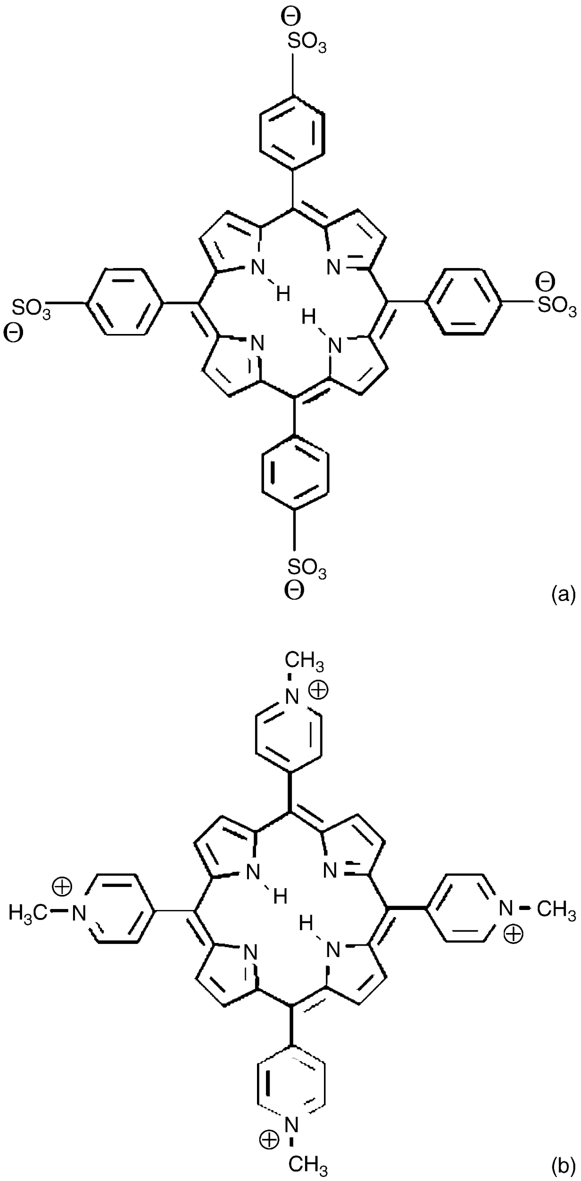

Fig. 1. Molecular structure of TPPS (a) and TMPyP(4) (b).

Corrected steady state fluorescence and fluorescence excitation spectra were recorded on a SDL-2 fluorimeter (LOMO). The fluorescence parameters of porphyrin-doped pSi samples were quite stable after keeping them at open air for weeks, thus showing good environmental stability of the synthesized materials.

Fluorescence lifetimes were measured with use of subnanosecond-pulsed source PLS 400 (PicoQuant) for excitation, photomultiplier tube model 1551 (Photochemical Research Associates) and computer module TCC900 (Edinburgh Instruments) for time-correlated single-photon counting.

In view of a finite duration of the excitation pulse and limited time resolution of the registration system of the spectrometer,

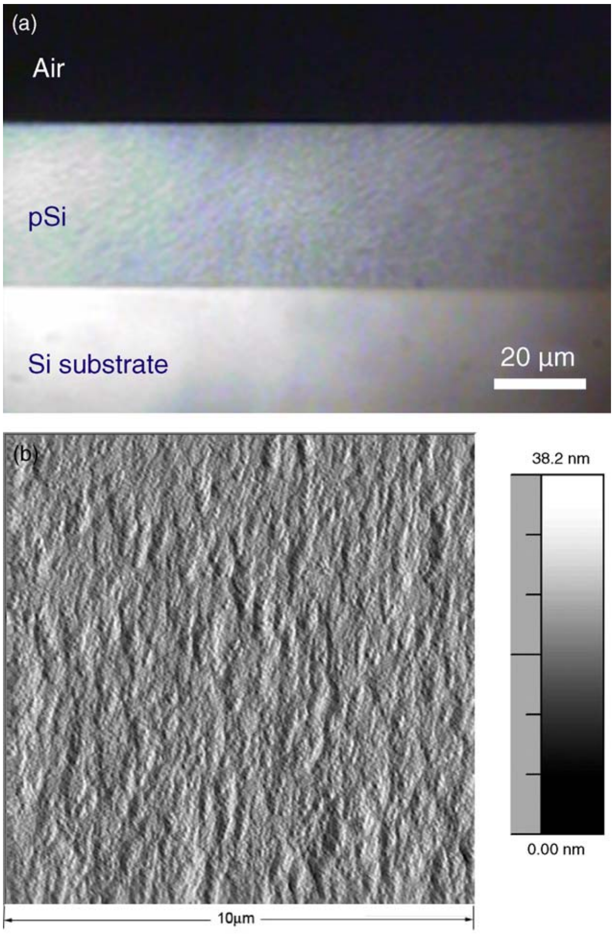

Fig. 2. Cross-sectional view of porous silicon film grown at pSi(1 0 0) wafer as yielded from optical microphotography (a) and AFM measurements (b).

the experimentally measured kinetics *I*(*t*) is a convolution of the spectrometer response function *R*(*t*) and the "true" kinetics *F*(*t*), the former is a response of the sample to the δ-function excitation:

$$I(t) = \int_0^t R(t - t')F(t')\,\mathrm{d}t' \qquad (1)$$

Since we found experimentally that the "true" function of the fluorescence intensity decay *F*(*t*) is non-exponential for both immobilized porphyrins, we modeled it in the first approximation as a bi-exponential decay function

$$F(t) = A_1 \exp\left(\frac{-t}{\tau_1}\right) + A_2 \exp\left(\frac{-t}{\tau_2}\right), \qquad (2)$$

where τ_i and A_i are the time constant and the relative amplitude of the *i*th component, respectively ($i = 1, 2$). The goodness of the fit was evaluated by statistical parameters (reduced χ^2) and graphical methods (autocorrelation function and weighted residuals, not shown lest the figures be overloaded).

To detect a characteristic luminescence band of $^1O_2$ (that corresponds to 1270 nm wavelength), the samples were excited by a light from a high-pressure xenon lamp (1000 W) focused to the 3 mm diameter spot on the sample surface through a 10 cm water filter and a band-pass glass filter transmitting the light in the 300–800 nm interval. The fluorescence output of the porphyrin/pSi sample was focused onto an entrance slit of MDR-23 U monochromator (600 lines/mm grating fabricated by LOMO) and then onto a liquid N_2-cooled InGaAs photodiode (Hamamatsu).

3. Results

3.1. Dependence of luminescence yield on the pSi oxidation state

It was earlier shown in the literature for dye-impregnated pSi layers that the fluorescence of the dyes deposited into an oxidized pSi matrix is higher by orders of magnitude than that of the dyes immobilized into a freshly prepared pSi matrix [19–21]. To check either this effect is observed in our case, we have compared the fluorescence ability of the porphyrins deposited into freshly prepared and oxidized (at 500 °C in the air atmosphere) pSi. Indeed, the fluorescence intensity of both porphyrins, TMPyP(4) and TPPS, deposited in the oxidized pSi matrix turned to be at least two orders of magnitude more intensive. Therefore, all our further experiments were carried out with the porphyrins immobilized in the oxidized pSi matrix. It is worth to note that an inherent pSi luminescence is quenched in oxidized pSi layer.

It was suggested in the literature that the above-mentioned low intensity of emission of the dyes adsorbed in the freshly prepared pSi matrix is caused by the energy/electron transfer processes, which occur between the semiconductor matrix and the dye [19]. On the other hand, it was also concluded in another work [21] that this effect is caused by an increased ability of the oxidized pSi matrix to adsorb dye molecules resulting in a higher dye concentration in the matrix. It should be pointed out here that the oxidized pSi matrix consists mainly of hydrophylic S–OH and Si–O_2 groups, whereas the freshly prepared pSi matrix contains mainly hydrophobic Si–H groups.

To determine the mechanism responsible for more intensive porphyrin fluorescence observed in case of oxidized pSi matrix, the porphyrin concentrations were qualitatively compared by FTIR spectroscopy for both types of matrixes. Diffuse reflectance IR spectra were obtained for freshly prepared and oxidized pSi(1 0 0) layers impregnated in 3.2×10^{-3} M TMPyP(4) solution. Only for the latter case the porphyrin vibrational bands were detected. Fig. 3 shows FTIR spectra of the oxidized pSi(1 0 0) layer before (dotted line) and after (solid line) its impregnation in TMPyP(4) solution. The porphyrin vibration bands appear in the regions of 600–1000 cm^{-1} (out-of-plane deformation vibrations of the pyrrole and methyne bridge CH groups) and 1300–1600 cm^{-1} (skeletal pyrrol vibrations, out-of-plane CH deformation vibrations as well as C=C vibrations of the methylpyridyle ring, see, for example [22]). No such vibrations appeared after an impregnation of freshly prepared pSi(1 0 0) matrix. Similar results were obtained for the anionic porphyrin TPPS.

These data imply that: (1) different fluorescence intensity of the porphyrins immobilized in freshly prepared and oxidized pSi matrixes is most likely a result of different ability of these matrixes to adsorb porphyrin molecules; (2) the ability of a

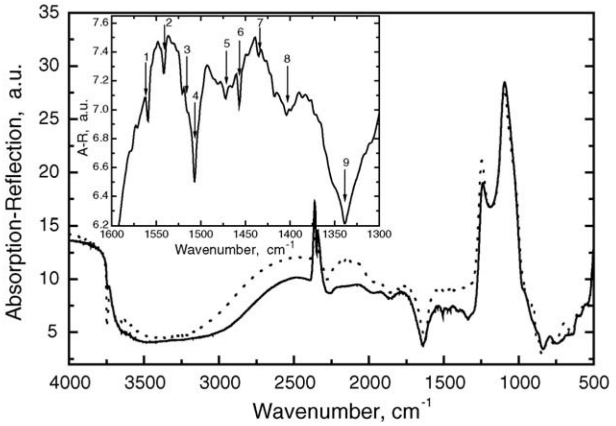

Fig. 3. FTIR transmission spectra of the oxidized pSi(1 0 0) layer before (dotted line) and after (solid line) its impregnation in 3.2×10^{-3} M TMPyP(4) solution. An inset shows a part of the spectrum after impregnation where the porphyrin vibration modes are clearly observed.

hydrophobic surface of the freshly prepared pSi matrix to adsorb cationic and anionic water-soluble porphyrins is considerably smaller than an adsorption ability of a hydrophylic surface of the oxidized pSi.

3.2. Fluorescence emission and excitation spectra of porphyrins immobilized in pSi matrixes of different crystallographic orientations

Fluorescence emission spectra of free TMPyP(4) in solution as well as of TMPyP(4) immobilized in pores of oxidized pSi(1 0 0) and pSi(1 1 1) matrixes are shown in Fig. 4a. While free TMPyP(4) in solution possesses asymmetrical single-band spectrum, the same porphyrin deposited in oxidized pSi shows two-band spectrum, which is known to be more typical for the porphyrin compounds. Similar effect of TMPyP(4) adsorption on its fluorescence spectrum is well-known for the case of the porphyrin binding to DNA [23]. For both cases the reason of this is likely a decrease of the environment polarity as compared to that of a bulk water, because similar fluorescence spectrum changes are observed when TMPyP(4) is dissolved in solvents with lower polarity (e.g. methanol) [24]. It is seen also in Fig. 4a that crystallographic orientation of Si wafer has some influence on the shape of TMPyP(4) emission spectrum, altering relative intensities of the fluorescence bands. Positions of the fluorescence band maxima of the adsorbed TMPyP(4) exhibit some dependence (within ca. 4 nm) on the wavelength of excitation within the Soret band profile.

Crystallographic orientation of initial Si crystal has also a drastic impact on the *intensity* of the fluorescence of the immobilized porphyrin. Under identical impregnation conditions, fluorescence intensity of TMPyP(4) deposited in pSi(1 0 0) matrix turned out to be at least one order of magnitude higher than that of TMPyP(4) deposited in pSi(1 1 1) matrix. We believe that this effect is caused by different porphyrin concentrations in these two pSi matrixes.

Fig. 5a shows the fluorescence excitation spectra of TMPyP(4) immobilized in oxidized pSi(1 0 0) and pSi(1 1 1) matrixes. Similarly to the emission spectra, the excitation spectra reveal moderate inhomogeneous broadening, which manifests itself through the dependence of a position of the excitation bands maxima on the registration wavelength (within ca. 5 nm).

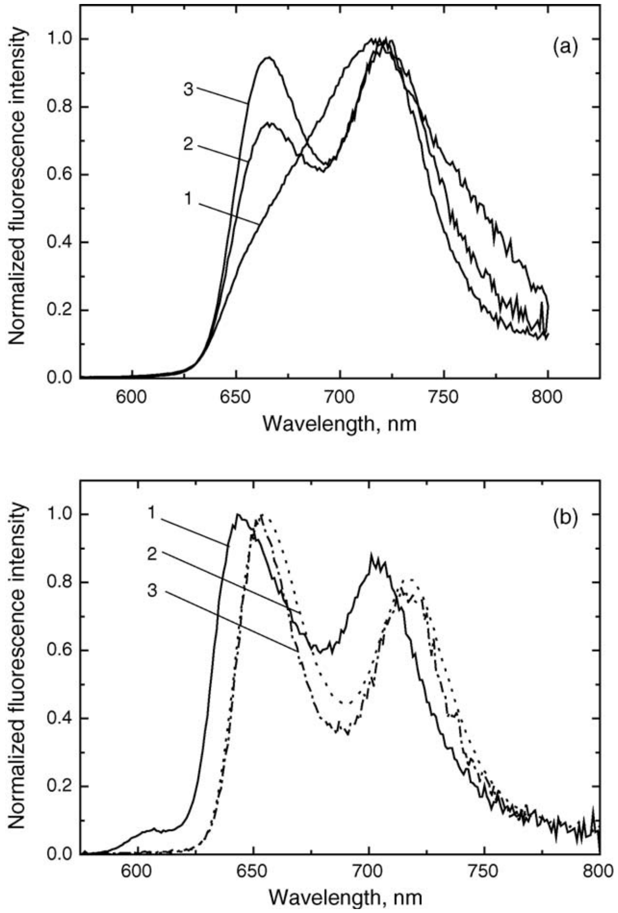

Fig. 4. Fluorescence emission spectra of TMPyP(4) (a) and TPPS (b). Panel (a): 1 - in solution, 2,3 - immobilized in oxidized pSi(1 1 1) and pSi(1 0 0) matrixes. Panel (b): 1 - in solution, 2,3 - immobilized in oxidized pSi(1 0 0) and pSi(1 1 1) matrixes.

As compared to TMPyP(4) in solution, fluorescence excitation spectrum of TMPyP(4) immobilized in pSi(1 1 1) matrix exhibits slightly broader and red-shifted Soret band, the Soret/Q band intensity ratio being much lower for the case of the immobilized porphyrin. This is most likely a result of the Soret band inhomogeneous broadening due to differences in the guest–host interactions in different porphyrin immobilization sites.

In case of TMPyP(4) immobilized in oxidized pSi(1 0 0) matrix an additional absorption appears in the 250–450 nm region with a visible maximum near 260 nm besides a broadening of the Soret band longwavelength slope. Such intensive absorption in this region is not a characteristic of the porphyrins. We are inclined to ascribe this absorption to the pSi(1 0 0) matrix itself, so that the fluorescence excitation signal in this region is a result of an electronic excitation energy transfer from the matrix to the porphyrin guest. Noteworthy is that an absorption in this region is a characteristic of silicas [11,12].

The fluorescence emission spectra of free TPPS in solution as well as of TPPS immobilized in pores of oxidized pSi(1 0 0) and pSi(1 1 1) matrixes are shown in Fig. 4b. One can see that the

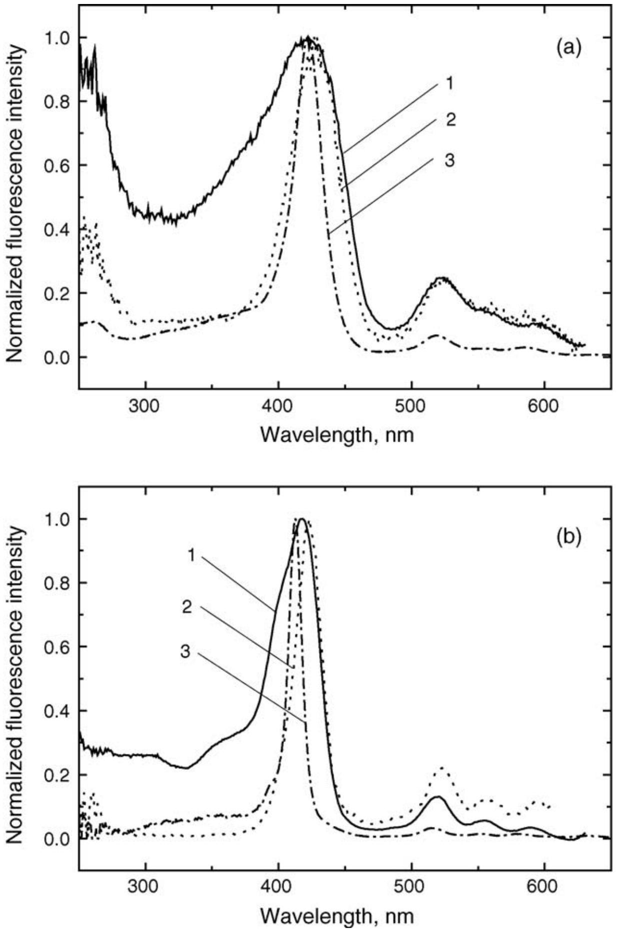

Fig. 5. Fluorescence excitation spectra of TMPyP(4) (a) and TPPS (b) immobilized in oxidized pSi(1 0 0) (1) and pSi(1 1 1) (2) matrixes and in solution (3).

porphyrin immobilization results in 15 nm longwavelength shift of the Soret band, and some dependence of a shape of the spectrum on crystal orientation of Si wafer has been observed. Again, the fluorescence intensity was at least one order of magnitude higher for TPPS/pSi(1 0 0) as compared to TPPS/pSi(1 1 1).

A comparison of TPPS/pSi(1 1 1) and TPPS/pSi(1 0 0) fluorescence excitation spectra points to the Soret band broadening in the latter case, which manifests itself as an additional shoulder at the shortwavelength side of the Soret band. An appearance of the shoulder is believed to be a result of interaction of closely spaced porphyrin molecules. This is confirmed by the fact that the shoulder disappears when TPPS concentration considerably drops (see TPPS/pSi(1 1 1) fluorescence excitation spectrum, where TPPS concentration is at least one order of magnitude smaller). It is also worth to note that this shoulder can be ascribed to the porphyrin aggregate, but these are fluorescing aggregates since the shoulder manifests itself in the fluorescence excitation spectrum.

3.3. *Fluorescence decay kinetics*

The fluorescence kinetic spectroscopy can be very informative in studying excited state interactions for dye molecules deposited on opaque surfaces, because a comparison of the fluorescence decay kinetics obtained for a dye in solution and for the same dye immobilized into the porous material can provide an adequate information on quenching (or enhancing) influence of the surface on the dye fluorescence efficiency.

Fluorescence kinetics measurements were done with freshly prepared samples and with the same samples after they were kept in open air conditions at room temperature for approximately 4 months. All measurements were done in air atmosphere. For a comparison, for both porphyrins the fluorescence decay kinetics were measured in water in the presence of air oxygen, the porphyrin concentrations were used as low as ca. 10^{-6} M to avoid aggregation and concentration quenching effects.

Fig. 6a shows the experimental fluorescence decay kinetics for the oxidized pSi(1 0 0) sample after maintaining it during 1 h in TMPyP(4) solution with the porphyrin concentration $C = 3.2 \times 10^{-3}$ M (curve 1) and for the same sample after 4-month standing (curve 2). Fitting the experimental data (dots) by the model function (1) (solid line) results in the following decay parameters: $\tau_1 = 1.55$ ns ($A_1 = 0.64$), $\tau_2 = 4.45$ ns ($A_2 = 0.36$), $\chi^2 = 1.19$ for the freshly prepared sample and $\tau_1 = 2.75$ ns ($A_1 = 0.46$), $\tau_2 = 7.80$ ns ($A_2 = 0.54$), $\chi^2 = 1.25$ for the sample

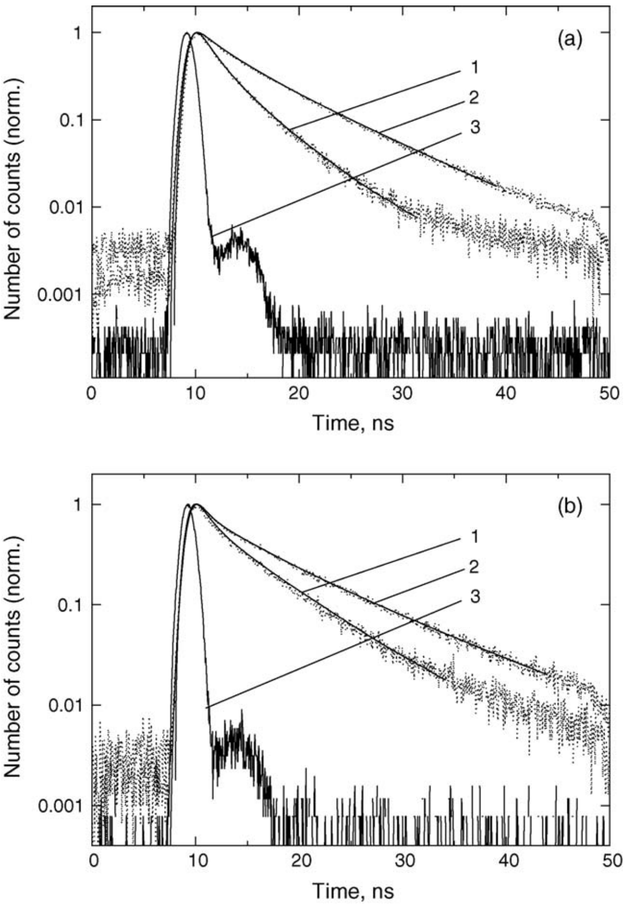

Fig. 6. Normalized fluorescence decay kinetics of TMPyP(4) (a) and TPPS (b) immobilized in oxidized pSi(1 0 0) matrix (1 and 2, dots) and model bi-exponential curves (1 and 2, solid lines) for freshly prepared samples (1) and for the same samples after 4-month aging (2). The instrument response function (3) is also shown.

after aging. Similar data are presented in Fig. 6b for the oxidized pSi(1 0 0) sample impregnated in TPPS solution (the porphyrin concentration $C = 3.5 \times 10^{-3}$ M), and fitting the experimental data by bi-exponential decay function $F(t)$ gives the following parameters: $\tau_1 = 1.15$ ns ($A_1 = 0.50$), $\tau_2 = 5.75$ ns ($A_2 = 0.50$), $\chi^2 = 1.14$ for the freshly prepared sample and $\tau_1 = 1.55$ ns ($A_1 = 0.48$), $\tau_2 = 9.20$ ns ($A_2 = 0.52$), $\chi^2 = 1.30$ for the sample after aging. For both porphyrins in air-equilibrated water solution the fluorescence decay kinetics were found to be well-fitted by mono-exponential decay functions with the time constants of ca. 4.5 and 10.0 ns for TMPyP(4) and TPPS, respectively.

To evaluate quantitatively a possible quenching effect of pSi matrix on the porphyrin fluorescence state, one can introduce an effective fluorescence lifetime parameter $\tau_{\text{eff}} = A_1\tau_1 + A_2\tau_2$. The effective lifetime allows one to compare quantitatively bi- and mono-exponential decay kinetics. Thus, for TMPyP(4) in oxidized pSi(1 0 0) matrix the value $\tau_{\text{eff}} = 2.58$ ns can be obtained that is about 1.7 times shorter than the fluorescence lifetime of TMPyP(4) in solution. We neglect here a contribution from the porphyrin fluorescence quenching by oxygen. We believe, however, that this shortening is not due to quenching effect of the oxidized pSi(1 0 0) matrix itself but is rather caused by the so-called "concentration quenching" of the porphyrin fluorescence due to an interaction of closely spaced porphyrin molecules. Such kind of quenching is usually manifests itself by a non-exponential fluorescence decay, which is caused by a non-linear character of the annihilation mechanism of the fluorescence concentration quenching. Indeed, following this mechanism, the excitation energy migration occurs between closely spaced porphyrin molecules on the time scale compared with the fluorescence decay time. When two excitations meet at one molecule ($S_1 + S_1$), this results in a formation of highly excited state S_n followed by ultrafast $S_n \rightarrow S_1$ internal conversion and a loss of one excitation: $S_1 + S_1 \rightarrow S_n + S_0 \rightarrow S_1 + S_0 + \text{heat}$.

The above assumption is proved by our kinetic fluorescent measurements, which were carried out with the oxidized pSi(1 0 0) sample impregnated in TMPyP(4) solution of lower concentration (0.8×10^{-3} M, results are not shown). As is expected for the case of the annihilation-type mechanism of the fluorescence quenching, the porphyrin concentration decrease should result in lengthening of the short-lived decay time constant and a decrease of its contribution along with an increase of a contribution of the long-lived decay time constant without a marked change of its value. The measured decay parameters completely correspond to the above expectation: the values $\tau_1 = 1.50$ ns ($A_1 = 0.41$) and $\tau_2 = 5.65$ ns ($A_2 = 0.59$) were obtained, that results in $\tau_{\text{eff}} = 3.95$ ns.

It is worth to emphasize that the bi-exponential deconvolution of the experimental decay kinetics for the immobilized porphyrins does not imply that any real two species are available, but this is rather a *formal simplified method* to describe non-exponential fluorescence decay kinetics. Complex physical models can be applied to describe such annihilation processes in inhomogeneous media [25], but it was not a purpose of the present work.

Even more effective concentration quenching is found for anionic porphyrin TPPS immobilized in oxidized pSi(1 0 0) matrix (freshly prepared sample; Fig. 6b, curve 1). We have obtained $\tau_{\text{eff}} = 3.45$ ns in this case, that is about three times shorter than the fluorescence lifetime for the TPPS in solution. This fact, along with the above-mentioned observation of the additional blue-shifted shoulder in the Soret band profile, is likely a result of the well-known ability of anionic TPPS (but not cationic TMPyP(4)) to form aggregates even at moderate concentrations [26,27].

After the sample aging the effective fluorescence lifetimes increased up to 5.50 ns for immobilized TMPyP(4) and up to 5.05 ns for TPPS. Noteworthy is that profiles of fluorescence and fluorescence excitation spectra of the samples were practically unchanged as compared to the fresh samples. One of possible explanations of this effect consists in a partial decomposition of the porphyrin molecules on the oxidized pSi surface. Due to this, a decrease of the porphyrin concentration should occur, and, therefore, a decrease of the fluorescence annihilation losses. However, the mechanism of this effect is not yet conclusively established.

3.4. *Luminescence of singlet oxygen generated by immobilized porphyrins*

An ability of the immobilized porphyrin molecules to generate $^1O_2$ was studied in gas (open air) and liquid (toluene) environment. Toluene was used since, contrary to water, it provides sufficiently long $^1O_2$ luminescence lifetime and quantum yield [28] that facilitates its optical registration.

The measurements carried out at open air atmosphere did not detect $^1O_2$ luminescence for TMPyP(4)/pSi(1 0 0) and TPPS/pSi(1 1 1) samples, whereas an immersion of TMPyP(4) (but not TPPS) sample in air-saturated toluene allowed to observe $^1O_2$ luminescence (Fig. 7). We suggest, that the absence of $^1O_2$ luminescence in case of TPPS immobilized in oxidized pSi(1 0 0) matrix is caused by TPPS aggregation. This effect provides more efficient annihilation quenching of the porphyrin

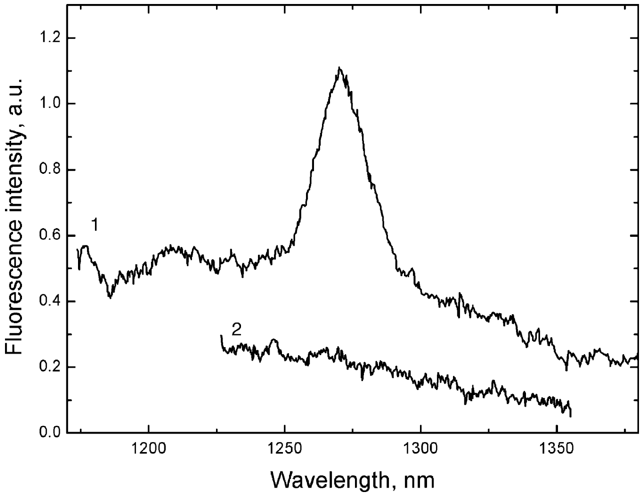

Fig. 7. Results of $^1O_2$ emission detection for freshly prepared samples of TMPyP(4) (1) and TPPS (2) immobilized in oxidized pSi(1 0 0) matrixes. The samples were immersed in toluene. For both cases, the same excitation conditions and spectrometer sensitivity were used.

S_1 state that results in less efficient population of the porphyrin triplet state, which is a donor of the electronic excitation energy for molecular oxygen.

4. Discussion

Previous studies have shown that pSi can be impregnated with different fluorescent dyes (Rhodamines, Fluorescein, Oxazine, Coumarin and Xanthene) [19–21]. Canham [19] was the first who showed that the fluorescent dyes immobilization into oxidized pSi (which is mostly SiO_2, or silica) results in much more intensive dye fluorescence as compared to the immobilization into the freshly etched pSi. It was explained as a result of the dye fluorescence quenching by means of energy transfer to luminescent crystallites in case of freshly etched pSi [19], but this idea was not confirmed later [21]. Excitation energy transfer in opposite direction, from pSi nano-crystallites of freshly prepared pSi to immobilized dye molecules, was also found [21].

Before we begun our studies, it was not a priori clear that porphyrin deposition into oxidized pSi matrix will not be accompanied by the porphyrin fluorescence quenching due to an interaction with the matrix. For example, it was found for Rhodamine B (RhB) immobilized in pSi that its fluorescence lifetime is about 100 ps for the case of immobilization into freshly prepared pSi and is much shorter than 100 ps for the case of oxidized pSi [20]. Taking into account that, in solution, RhB fluorescence lifetime is between 1.5 and 3.5 ns, depending on environment conditions [29], the pSi and oxidized pSi matrixes impose a strong quenching effect on the fluorescent state of this dye. Therefore, in the absence of systematic studies of the fluorescence decay kinetics of immobilized porphyrins the question remained unclear about possible quenching of the porphyrin fluorescence by the oxidized pSi matrix.

There is also a series of works in the literature [8–16] in which (metallo)porphyrin/mesoporous silica composites are studied, which are chemically similar to the porphyrin/oxidized pSi composites investigated in the present work. Although the (metallo)porphyrin/mesoporous silica composites were intended for the catalysis purposes, there are some common requirements imposed upon effective organic/inorganic photosensitizers and catalysts: the active center of the encapsulated organic molecule should remain essentially *unaffected* by the host.

The task to provide minimum host matrix influence on the porphyrin macrocycle was successfully solved in the work [8], where a porphyrin complex with a transition metal was embedded into mesoporous silica channels during the composite synthesis. In this case, the porphyrin absorption spectrum was practically unchanged by the matrix that was mainly achieved by use of four long and flexible pentane substituents connecting the porphyrin core with the silica channel walls.

In other works [9–16], where usual porphyrins were used of both water-soluble and hydrophobic types, the porphyrin immobilization into porous silica channels always resulted in marked changes of the Soret absorption band shape. These changes included both Soret band broadening and spectral shift and, since the changes increase with the porphyrin concentration, they are often ascribed to the porphyrin aggregation [17]. However, an alternative explanation may be that different binding sites may be populated at low and high porphyrin concentrations. Due to this effect an inhomogeneous broadening of the Soret band can be formed, the band shape being dependent on the porphyrin concentration. Evidences of such inhomogeneous broadening are found in the present work. Similar concentration dependent inhomogeneous broadening effects are observed when TMPyP(4) is bound with DNA [30].

It is also worth to mention the works [11,12], in which a photoinduced electron transfer reaction between Zn porphyrin and mesoporous silica was found. In the absence of fluorescence kinetic measurements it is difficult, however, to evaluate how strongly this photoionization reaction can quench the porphyrin excited states.

Therefore, the previous works concerned with the dyes and porphyrins immobilized on pSi (or oxidized pSi) and porous silicas do not provide an unambiguous answer to the question when and how strongly the host matrix can influence the fluorescent state responsible for the molecule sensitizing ability.

As our present investigation shows, the cationic and anionic water-soluble porphyrins TMPyP(4) and TPPS, respectively, effectively bind to the oxidized pSi matrix and the matrix does not quench the porphyrin S_1 state. The non-exponential character of the immobilized porphyrin fluorescence decay as well as some shortening of the effective fluorescence lifetime as compared to that in solution are due to the excitation annihilation between closely spaced porphyrin molecules. A decrease of the immobilized porphyrin concentration markedly cuts the annihilation losses.

Therefore, we expect that efficiency of a population of the immobilized porphyrins triplet state should be almost as high as it is in solution (the triplet state quantum yield is ca. 0.90 for TMPyP(4) and ca. 0.75 for TPPS [31]). As our preliminary transient diffuse reflectance measurements show the immobilized porphyrin *triplet state* is also not quenched by the matrix (will be published elsewhere). Since the triplet state is a precursor for $^1O_2$ formation, we expected to observe $^1O_2$ generation by immobilized porphyrins with a quantum efficiency approaching the triplet state quantum yield.

In practice, however, the $^1O_2$ luminescence was difficult to detect for our samples, and only for TMPyP(4)/pSi system it was experimentally found at the limit of our setup sensitivity. Taking into account that approximately same quantities of photophysically similar lipophylic porphyrins (tetraphenylporphyrin and others) dissolved in toluene give at least two order of magnitude more intensive $^1O_2$ luminescence, we suggest that $^1O_2$ is effectively quenched on the surface of oxidized pSi. The mechanism responsible for the quenching is, most likely, the $^1O_2$ electronic energy transfer to the high-frequency vibrations of the surface groups. Such mechanism is responsible for the very short lifetime of $^1O_2$ luminescence in water, where OH vibrations play a role of accepting modes [27]. In our case OH stretching vibrations of SiOH groups (ca. $3500\,cm^{-1}$), if pSi is not fully oxidized, can play a role of such high-frequency accepting mode. Another very plausible acceptor of the $^1O_2$ excitation energy is, again, OH vibration mode of water, since water usually richly adsorbs on the oxidized pSi surface. The corresponding broad band absorption of water can be seen in the 2750–3750 cm^{-1} region of the FTIR spectrum shown in Fig. 3. (Similar visible decrease of $^1O_2$ generation ability caused by the photosensitizer immobilization in porous of powdered solid state supports was earlier recognized in the literature [32].)

It is worth to note, however, that the above-mentioned quenching of the singlet oxygen luminescence by the oxidized pSi matrix merely makes difficult a detection of the $^1O_2$ luminescence but cannot lower the photodynamic activity of the hybrid photosensitizer at in vivo conditions, because all in vivo processes occur in water environment.

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References

[1] L.T. Canham, Appl. Phys. Lett. 57 (1990) 1046.
[2] V. Parkhutik, Solid State Electron. 43 (1999) 1121.
[3] L.T. Canham, C.L. Reeves, D.O. King, P.J. Branfield, J. Crabb, M.C.L. Ward, Adv. Mater. 8 (1996) 850.
[4] D. Kovalev, M. Fujii, Adv. Mater. 17 (2005) 1–15.
[5] D. Kovalev, E. Gross, N. Künzner, F. Koch, V.Y. Timoshenko, M. Fujii, Phys. Rev. Lett. 89 (2002) 137401.
[6] S. Brown, E. Brown, I. Walker, Lancet Oncol. 5 (2004) 497–508.
[7] F. Yan, R. Kopelman, Photochem. Photobiol. 78 (2003) 587–591.
[8] B.T. Holland, C. Walkup, A. Stein, J. Chem. Phys. B 102 (1998) 4301–4309.
[9] S. Nakagaki, A.R. Ramos, F.L. Benedito, P.G. Peralta-Zamora, A.J.G. Zarbin, J. Mol. Catal. A: Chem. 185 (2002) 203–210.
[10] J. Poltowitz, E.M. Serwicka, E. Bastardo-Gonzalez, W. Jones, R. Mokaya, Appl. Catal. A: Gen. 218 (2001) 211–217.
[11] H.M. Sung-Suh, Z. Luan, L. Kevan, J. Phys. Chem. B 101 (1997) 10455–10463.
[12] Z. Chang, L. Kevan, Langmuir 18 (2002) 911–916.
[13] J.R. Choi, M. Yoon, Y.-H. Yim, S.C. Jeoung, Chem. Phys. Lett. 351 (2002) 391–396.
[14] Y. Kim, J.R. Choi, M. Yoon, A. Furube, T. Asahi, H. Masuhara, J. Phys. Chem. B 105 (2001) 8513–8518.
[15] V. Shunemann, A.X. Trautwein, I.M.C.M. Rietjens, M.C. Boersma, C. Veeger, D. Mandon, R. Weiss, K. Bahl, C. Colapietro, M. Piech, R.N. Austin, Inorg. Chem. 38 (1999) 4901–4905.
[16] M. Ogawa, H. Ishikawa, T. Kikuchi, J. Mater. Chem. 8 (1998) 1783–1786.
[17] A. Yoshida, N. Kakegawa, M. Ogawa, Res. Chem. Intermed. 29 (2003) 721–731.
[18] W. Xu, H. Guo, D.L. Akins, J. Phys. Chem. B 105 (2001) 1543–1546.
[19] L.T. Canham, Appl. Phys. Lett. 63 (1993) 337.
[20] P. Li, Q. Li, Y. Ma, R. Fang, J. Appl. Phys. 80 (1996) 490.
[21] S. Letant, J.-C. Vial, J. Appl. Phys. 82 (1997) 397.
[22] G.S.S. Saini, S. Sharma, S. Kaur, S.K. Tripathi, C.G. Mahajan, Spectrochim. Acta A 61 (2004) 3070–3076.
[23] J.M. Kelly, M.J. Murphy, D.J. McConnell, C. OhUgin, Nucleic Acids Res. 13 (1985) 167.
[24] F.J. Vergeldt, R.B.M. Koehorst, A. Van Hoek, T.J. Schaafsma, J. Phys. Chem. 99 (1995) 4397.
[25] D. Pines, D. Huppert, J. Phys. Chem. 91 (1987) 6569–6572.
[26] R.F. Pasternack, P.R. Huber, P. Boyd, G. Engasser, L. Francesconi, E. Gibbs, P. Fasella, G.C. Venturo, L. deC. Hinds, J. Am. Chem. Soc. 94 (1972) 4511.
[27] A. Iosif, U.-W. Grummt, J. Prakt. Chem. 339 (1997) 420–425.
[28] C. Schwitzer, R. Schmidt, Chem. Rev. 103 (2003) 1685.
[29] D. Magde, G.E. Rojas, P.G. Seybold, Photochem. Photobiol. 70 (1999) 737.
[30] I.V. Sazanovich, V.S. Chirvony, Quantum Electron. 35 (2005) 756–760.
[31] G.S. Nahor, J. Rabani, F. Grieser, J. Phys. Chem. 85 (1981) 697.
[32] W.R. Midden, S.Y. Wang, J. Am. Chem. Soc. 105 (1983) 4129–4135.