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Optical fibres based on natural biological minerals – sea sponge spicules

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***Abstract*. A complex study of spicules of glass sponges *Hyalonema sieboldi* and *Pheronema sp*. is performed. It is shown that skeletal spicules represent a bundle of composite fibres cemented with silicon dioxide, which imparts a high mechanical strength to spicules. The presence of a layered organosilicon structure at the nanometre scale in the spicule cross section gives rise to a periodic spatial modulation of the permittivity of the spicule material, which allows one to treat spicules as one-dimensional photonic crystals. Upon excitation of basal spicules by second-harmonic pulses from a Nd : YAG laser, we observed a considerable increase in the fluorescence intensity in the long-wavelength region with a maximum at 770 nm, saturation and anomalously large fluorescence lifetimes.**

Keywords: *optical fibres, organosilicon sea sponge spicules, new materials for quantum electronics.*

1. Introduction

During the evolution process biological systems have found the unique ways providing their survival, from the means to frighten predators and to ensure the mechanical strength to complicated photosynthesis. The skeletons of some sea organisms are constructed from various minerals such as calcite, aragonite, apatite, and silica [1]. Sea organisms such as diatoms, Radiolaria, and sponges with skeletons based on silica attract special attention [2]. This is explained by the fact that silicon and its oxides are basic materials used in micro- and optoelectronics for solving a variety of problems. Optical communication based on the use of silica fibres is now widely used in our everyday life. However, the 'idea' of using silica fibres has been realised by the Nature long before the appearance of a man on the Earth. Glass sponges of the class *Hexactinellida* (*Porifera*) represent a group of ancient multicellular animals inhabiting predominantly deep-sea regions of all oceans. The skeleton of such sponges consists of peculiar filament silicon-containing structures, the so-called silica hexactinal spicules. The geometrical dimensions of spicules can vary, depending on their type and age, in a broad range: their diameter varies from 0.01 to 30 mm and their length varies from a few millimetres to 5 m and more [3].

From a practical point of view, the most attractive object for studies is sea sponges, whose skeleton is formed by long spicules of length no less than a few centimetres, which consist of amorphous hydrated quartz deposited around the protein base. It seems that an understanding of the growth mechanisms of such elements and light propagation processes in them will allow one not only to lay the foundations of a new low-temperature manufacturing technology of optical fibres but also to create new functional elements for optoelectronics. Sponges of this type include glass sponges *Euplectellidae, Hyalonema sieboldi* (Fig. 1), and *Pheronema sp*. (Fig. 2) inhabiting cold seas of the Pacific Ocean at depths from 30 to 5000 m. The studies of basal spicules of glass sponges *Euplectella aspergillum* [2, 3] have

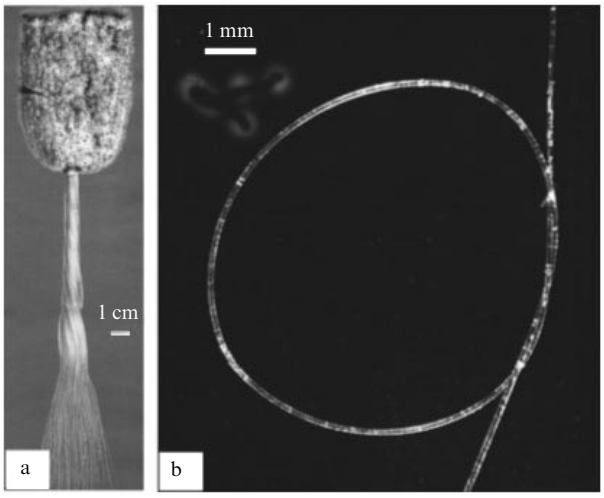

Figure 1. Glass sponge *Hyalonema sieboldy* (a) and its basal spicule (b).

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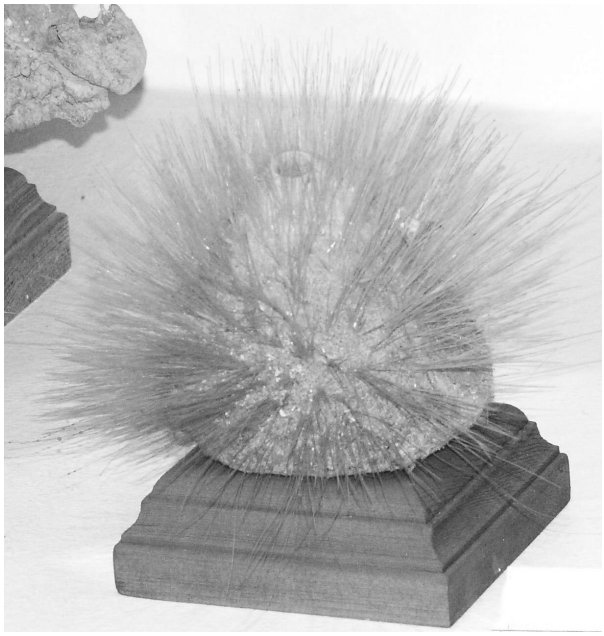

Figure 2. Glass sponge *Pheronema aspergillium*.

shown their unique optical properties. In this paper, we investigated the structural and optical properties of spicules of sponges *Hyalonema sieboldi* (hereafter, I) and *Pheronema sp*. (II) in order to understand the principles of creation of natural structures with unusual optical properties and to elucidate the possibility of the development of artificial technologies for manufacturing new materials for applications in optoelectronics.

2. Peculiarities of the structure of glass sea sponge spicules

We studied spicules of sea sponges of types I and II of length 1 – 5 cm and diameter 40 – 150 μm. It was found that, depending on their functions and location in the sponge, spicules have some differences in the structure; however, the principles of their organisation are the same.

There exist two types of spicules in sponges: basal (anchor-type) spicules and skeletal spicules. Basal spicules represent thin filaments consisting of a central organic fibre surrounded by silica layers. The main function of these spicules is probably to provide the mechanical coupling with the environment and to ensure responses to variations in the life conditions. Unlike basal spicules, skeletal spicules have a more complicated mechanical structure providing the shape of a spicule and the strength of its skeleton. In all cases, spicules have an intricate composite structure consisting of silica and a protein component. The composite structure of glass sea sponge spicules is demonstrated by the method of X-ray photoelectron spectroscopy. Figure 3 presents the typical photoelectron spectrum of sponge spicules obtained by using an ultrahigh-vacuum SPECS spectrometer (Germany) with a 1253.6-eV monochromatic $K_{\alpha}Mg$ X-ray source. The X-ray photoelectron spectra of spicules demonstrate the presence of various organic compounds and silicon dioxide.

More detailed microscopic studies of basal spicules showed that all spicules contain a central core – an axial fibre of diameter 1 – 2 μm, which controls the polymerisation of silica [4]. The axial fibre is located in the central channel of a spicule, which is distinctly demonstrated in photographs of optically magnified images of the ends of sponge spicules I and II (Figs 4a and 5).

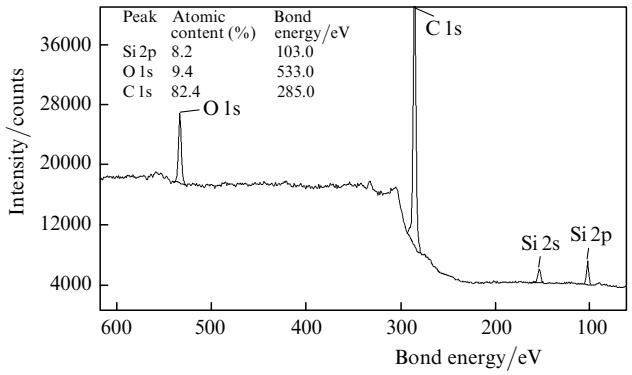

Figure 3. X-ray photoelectron spectrum of spicules of type II sea sponges.

The control mechanism of the polymerisation process and concentration of silica in spicules is inadequately studied at present, although it seems that this mechanism is based on the operation of silicatein protein. Silicatein is a unique enzyme contained in a more complex protein – spongin, which catalyses hydrolysis and performs polycondensation of siliconferroalgolate, which serves as a matrix for formation of a highly-ordered spicule structure [5, 6]. It was shown in [7] that spicules are formed around the axial protein fibre consisting of silicon dioxide nanoparticles of

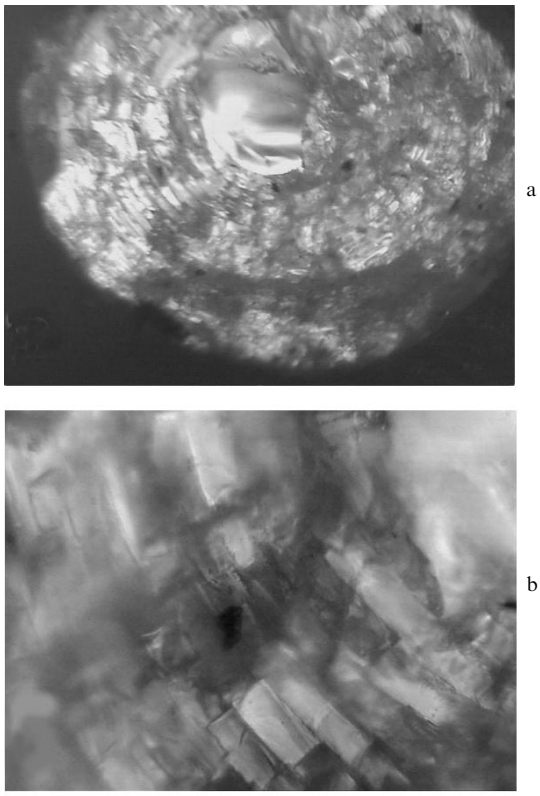

Figure 4. Photography of a cleaved unpolished end of spicule I (magnification 297×) (a) and a fragment of its circular structure (magnification 1157×) (b).

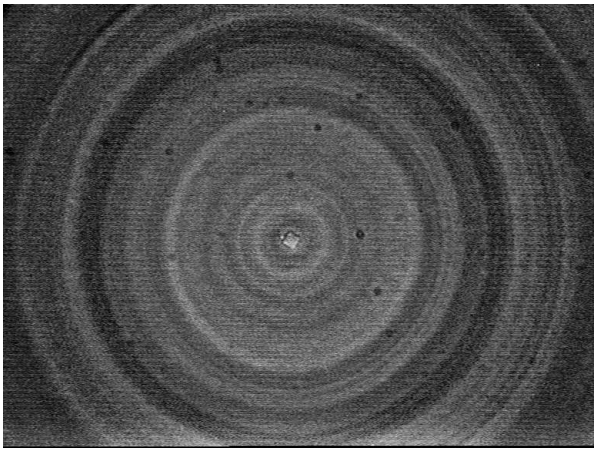

Figure 5. Photography (in transmission) of a central cylinder of spicule II with a channel for a protein fibre (magnification 1157×).

size 10 – 20 nm, which are then combined to microparticles, by forming a dense layer of silicon dioxide, which is also confirmed by our studies. When the silication process ends, special cells, spongiocytes, release fibrils of spongin around the fibre formed and the next layer of silicon dioxide grows. Thus, processes of silication and spongin release alternate during the spicule growth. The photograph of the spicule cross section in Fig. 4b demonstrates microparticles of silicon dioxide, which are structured in the form of separate blocks. These blocks form axially symmetric periodic layers of size 40 – 300 nm (depending on the sponge age), each of the layers being surrounded from the external sides by a protein matrix of thickness up to several nanometres, which is also well demonstrated by photographs of spicule ends (Figs 4b and 5).

The detailed study of important operation parameters of materials such as the microhardness and Young modulus by the method of Oliver – Pharr on cross sections by using the Berkovich pyramid (with the tip angle 115°) have shown (Fig. 6) that the values of these parameters for basal spicules of sea sponges are close to those for fused silica [8]. At the same time, the distributions of the microhardness and Young modulus are inhomogeneous over the spicule cross section, decaying from the spicule centre to its periphery. The analysis of Figs 4 and 5 shows that this is explained by

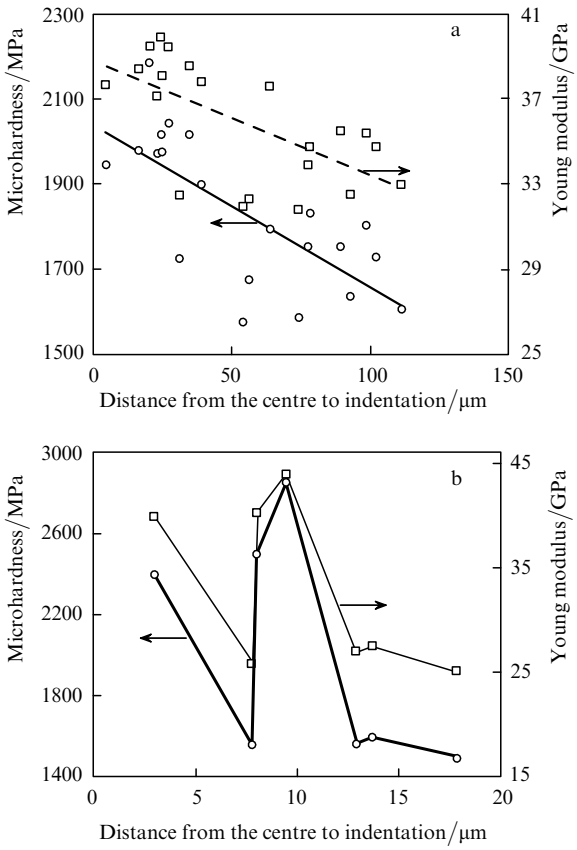

Figure 6. Transverse distributions of the microhardness and Young modulus of basal spicule I (a) and skeletal spicule II (b).

the spicule structure, in which silicon dioxide layers alternate with protein layers and become thinner at the periphery (Fig. 5). At the same time, the layered structure of spicules provides their enhanced mechanical strength and elasticity, which allows one to knot them without their destruction (Fig. 1b).

The microscopic study of skeletal spicules showed that they differ from basal spicules by the absence of a distinct central axial fibre. The atomic force microscope study of spicule cross sections revealed characteristic mineralization regions corresponding to the emergence of spongin on the

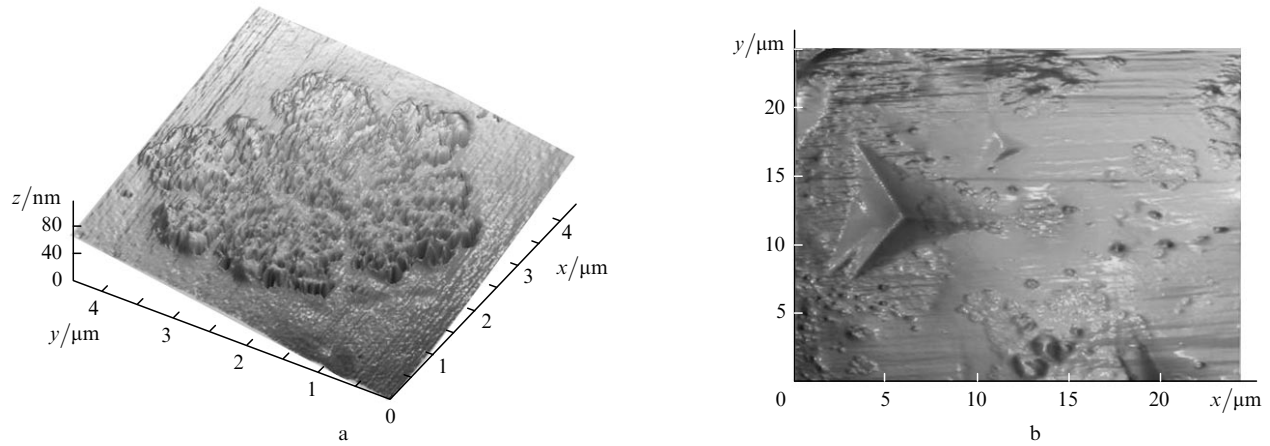

Figure 7. Atomic force microscope images of a protein fibre (a) and a fragment of a polished end (b) of skeletal spicule II.

surface of fibres (Fig. 7a), which are randomly distributed over the spicule cross section (Fig. 7b). This suggests that protein fibres covered with amorphous silica form during their growth a cylindrical bundle of composite fibres cemented with each other by silicon dioxide, thereby imparting a high mechanical hardness to spicules, which is required to support the sponge skeleton. The experimental dependences of mechanical parameters of skeletal spicules (Fig. 6b) demonstrate the large random scatter of the microhardness and Young modulus over spicule cross sections, thereby confirming the correctness of the assumption made above.

3. Optical properties of organosilicon spicules of glass sea sponges

The distribution of the refractive index over the cross section of spicules was measured with a Michelson interferometer by the method described in [4]. Because the cross section of spicules was very small, we have managed to measure only the integrated distribution of the refractive index over the cross section. The measurements showed that the refractive index at 633 nm for the axial fibre of basal spicules of sponges of both types of size 2–3 μm was 1.45–1.48, which is very close to the refractive index of amorphous quartz (1.458) and is in good agreement with data [4]. The region of diameter 15–20 μm around the axial fibre (well seen in Figs 4a and 5) has a lower refractive index ($\sim$ 1.4). This is explained by a high content of organic substances and a low degree of quartz packing. Further, in the region between 20 and 35 μm, the refractive index gradually increases from 1.4 to 1.45 due to a gradual change in the spicule composition and an increase in the diameter of silicon dioxide blocks in the layered region. Then, with distance from the spicule centre approaching the external diameter the refractive index decreased from 1.4 to 1.35–1.39. The difference in the refractive indices in these regions is also related to the thickness of organic layers between silicon dioxide layers, correlating with the distribution of microhardness over the spicule cross section (Fig. 6).

The study of light transmission in basal spicules in the spectral range from 400 to 1600 nm (a halogen lamp was used as a radiation source) showed that spicules well transmit light in the spectral range between 500 and 1300 nm. A strong absorption was observed in the ranges 400–450 nm and 590–650 nm (attenuation in spicules of diameter 140 μm at a wavelength of 633 nm was ~ 0.1 dB m^{-1}) and also in the regions of 800, 1000, and 1150 nm, where spicules virtually did not transmit light. Experimental studies of transmission of white light through basal spicules of sponges I and II demonstrated the concentration of light near the axial region of size ~ 20 μm and the presence of a strong colour gradient (from white to red) over the spicule length. These results can be explained by the presence of a periodic layered organosilicon structure at the scale of a few hundreds of nanometres in glass sponge spicules, which causes the periodic spatial modulation of the permittivity of the spicule material with a period comparable with the light wavelength. Thus, glass sponge spicules can be treated as natural one-dimensional photonic crystals.

Upon excitation of basal spicules by 532-nm, 12-ns, 30-mJ second-harmonic pulses from a Nd : YAG laser at a pulse repetition rate of 10 Hz, a considerable increase in the fluorescence intensity in the wavelength region was observed. Figure 8 presents the normalised fluorescence spectra of basal spicules of sponges II of diameter 140 μm and length 5 cm obtained at different excitation intensities. One can see that the fluorescence spectra have a maximum at 770 nm whose position is independent of the laser excitation intensity. These spectra differ from the fluorescence spectrum of a usual multimode silica fibre [9]. The difference between the fluorescence spectra of organosilicon and silica fibres is probably explained by the fact that sea sponge spicules contain large organic inclusions of spongin. Our measurements showed that, as the excitation power was increased by an order of magnitude, the fluorescence band narrowed down and saturated (Fig. 8). According to [10], this also demonstrates the nonlinearity of the transformation of light energy in spicules due to the presence of inhomogeneously distributed organic inclusions.

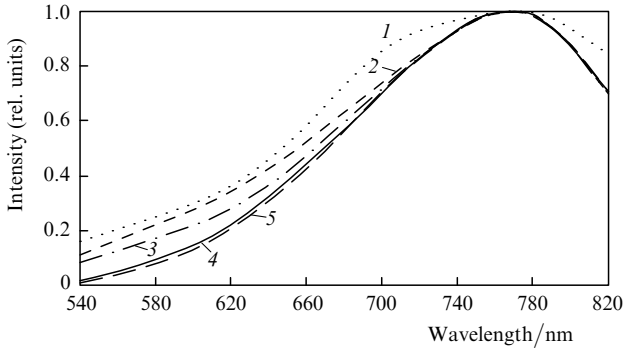

Figure 8. Fluorescence spectra of basal spicule I at the 532-nm excitation intensities 3 (*1*), 10 (*2*), 15 (*3*), 22.5 (*4*), and 30 MW cm^{-2} (*5*).

Organic inclusions in glass sponge spicules considerably change the fluorescence lifetime. The fluorescence lifetime of basal spicules measured at different laser excitation powers was tens of microseconds, considerably exceeding the fluorescence lifetime of organic substances dissolved in sea water or silica fibres ($10^{-7} - 10^{-9}$ s).

4. Conclusions

Our study has shown that the natural combination of spongin protein and silicon dioxide extracted from sea water by silicatein protein can be used to obtain at low temperatures a composite nanomaterial, which is promising for applications in optoelectronics, combining the protein elasticity and strength with the elasticity and strength of silica. It seems that optical fibres based on biomineral spicules of sea sponges will have a number of advantages compared to the known silica fibres due to their better mechanical parameters. In addition, the investigation of such fibres can help us to find simpler solutions of complicated technological processes and to develop the low-temperature manufacturing technology of optical fibres.

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