Supercontinuum Generation in Naturally Occurring Glass Sponges Spicules

Hermann Ehrlich, Manuel Maldonado, Andrew R. Parker, Yuri N. Kulchin, Jörg Schilling, Benjamin Köhler, Ulrich Skrzypczak, Paul Simon, Henry M. Reiswig, Mikhail V. Tsurkan, Eike Brunner, Sergey S. Voznesenskiy, Alexander V. Bezverbny, Sergey S. Golik, Ivan G. Nagorny, Denis V. Vyalikh, Anna A. Makarova, Serguei L. Molodtsov, Kurt Kummer, Michael Mertig, Christiane Erler, Denis V. Kurek, Vasilii V. Bazhenov, Filipe Natalio, Alexander E. Kovalev, Stanislav N. Gorb, Allison L. Stelling, Johannes Heitmann, René Born, Dirk C. Meyer, and Konstantin R. Tabachnick*

The complex process of supercontinuum generation (SG) is known to be exploitable for designing spatially coherent white light sources emitting light simultaneously in the ultraviolet, visible, and infrared ranges. Herein the first natural material able to generate in laboratory conditions a supercontinuum similar to those known from man-made photonic crystal fibers is described. The ability resides in siliceous 20–50 cm long spicules of the glass sponge *Sericolophus hawaiicus*. By shedding into the spicules optical peak intensities ranging from 1 to 100 TW cm^{-2} the generation of a SG is revealed. The SG involves wavelengths between 650 and 900 nm and shows a maximum spectral spread for excitation at a wavelength of 750 nm. It is hypothesized that the SG is favored by spicules being a biocomposite that incorporates together isotopically pure biogenic silica (δ^{30}Si = −3.28) and 15.2 ± 1.3 µg *N*-acetyl-glucosamine (chitin) per mg of silica. The internal organization of these spicules is distinguished by a solid silica core with a 1 µm wide axial channel as well as a highly ordered silica–chitin composite. Such a composition and organization pattern may be of potential interest for the design of low temperature synthesis of future materials for light guidance.

1. Introduction

The peculiar fiber-optical features of sponge spicules have attracted the attention of a large section of the scientific community recently. Yet, the first report on their remarkable optical properties dates back nearly 154 years.[1,2] More recently, spicules from hexactinellid sponges, such as *Rossella racovitzae*,[3] *Euplectella aspergillum*,[4,5] *Hyalonema sieboldi*, and *Monorhaphis chuni* (for review see ref. [6]), demonstrated the ability to transmit light very efficiently within the spectral range from 600 to 1300 nm wavelength.[6] This demonstrated ability of silica spicules to function as waveguides for light[7] relies on total internal reflection, the same mechanism on which light propagation in commercial silica optical fibers is based, confining photons in either a single-mode

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Prof. H. Ehrlich, Prof. S. L. Molodtsov, Dr. V. V. Bazhenov,
Prof. D. C. Meyer
Institute of Experimental Physics
TU Bergakademie Freiberg
Leipziger Str. 23, 09599 Freiberg, Germany
E-mail: Hermann.Ehrlich@physik.tu-freiberg.de

Prof. M. Maldonado
Department of Marine Ecology
Centro de Estudios Avanzados de Blanes (CSIC)
Acceso Cala St. Francesc 14, E-17300 Blanes, Girona, Spain

Prof. A. R. Parker
Department of Life Sciences
Natural History Museum
Cromwell Road, London SW7 5BD, UK

Prof. Y. N. Kulchin, Prof. S. S. Voznesenskiy,
Prof. A. V. Bezverbny, Prof. S. S. Golik,
Prof. I. G. Nagorny
Institute of Automation and Control Processes of the
Far Eastern Branch of the Russian Academy of Sciences
Radio Str. 5, 690041 Vladivostok, Russia

Prof. J. Schilling, B. Köhler, U. Skrzypczak
Centre for Innovation Competence SiLi-nano
Martin-Luther-Universität Halle-Wittenberg
Karl-Freiherr-von-Fritsch-Str. 3, D-06120 Halle (Saale), Germany

Dr. P. Simon
Max Planck Institute of Chemical Physics of Solids
D-01187 Dresden, Germany

Prof. H. M. Reiswig
Department of Biology
University of Victoria, and Natural History Section
Royal British Columbia Museum
Victoria, British Columbia, V8W 3N5 Canada, Canada

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or a multimode optical signal. It has also been reported that light transmitted through silica spicules is cut off below 600 nm and above 1310 nm, in a similar manner to that is seen in combined high-/low-pass filters.[6] Therefore, there is enormous interest in imitating the structure of sponge silica spicules to incorporate those advantages into the manufacturing technology of optical fibers.[7,8]

The spicules of most modern hexactinellid sponges are usually elaborated in complete darkness at bathyal depths[9] and also under so-called psychrophilic biomineralization conditions, with temperatures ranging from −1.5 to about 12 °C. However, before Cretaceous times (about 65 mya), hexactinelllid sponges were able to live in comparatively shallower and better illuminated environments on the continental shelves.[10,11] It remains unresolved whether the optical properties of their silica spicules are accidental and spurious or it was favored by any biological selective advantages at a time when these sponges grew on illuminated continental-shelf habitats. In the ocean, sunlight can be used for vision to about 1000 m maximum.[12] Even in the present-day bathyal, dark habitats of hexactinellids, a functionality has been hypothesized for the optical property of the long spicules. It has been suggested that associated bacteria might produce bioluminescent light that could be channeled through the spicules to a light-responsive harvesting system in the sponge's cells for a subsequent but yet unknown biological purpose.[13] Alternatively, some sponges are able to generate bioluminescent light endogenously,[6] and it could have a biological function that awaits to be discovered. The hexactinellid sponge *Sericolophus hawaiicus* collected for this study (**Figure 1**) lives at depths of 350–450 m, on the continental slope of Kona Island (Hawaii, USA). Their populations receive exclusively the blue wavelengths from sunlight, and most putative bioluminescence is also expected to be blue at that depth range. Surprisingly, despite the potential biological and biotechnological interest, the detailed optical properties of these spicules remain poorly investigated.

Spicules can function as waveguides for light,[7] relying on total internal reflection to confine photons in either a single-mode or a multimode optical signal. During preliminary work examining the optical properties of the large (20–45 cm long) anchoring spicules of *S. hawaiicus,* we discovered that laser light could be efficiently coupled into the polishing ends of the spicules using an aspheric lens. The spicule then acts like a multimode optical fiber, transmitting light through all of its layers (see Figure S1, Supporting Information). Interestingly, the internal structure of the natural spicules showed some

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Dr. M. V. Tsurkan
Leibniz Institute of Polymer Science and Max Bergmann Centre of Biomaterials
Budaperster Str. 27, 01067 Dresden, Germany

Prof. E. Brunner
Institute of Bioanalitical chemistry
TU Dresden
Bergstrasse 66, D-01062 Dresden, Germany

Prof. D. V. Vyalikh, Dr. A. A. Makarova
Institute of Solid State Physics
Dresden University of Technology
Zellescher Weg 16, D-01062 Dresden, Germany

Prof. D. V. Vyalikh
Department of Physics
Saint Petersburg State University
198504 St. Petersburg, Russia

Prof. D. V. Vyalikh
Donostia International Physics Center (DIPC)
Departamento de Fisica de Materiales and CFM-MPC, UPV/EHU
20080 San Sebastian, Spain

Prof. D. V. Vyalikh
IKERBASQUE
Basque Foundation for Science
48011 Bilbao, Spain

Dr. A. A. Makarova
Department of Physics
St. Petersburg State University
198504 St. Petersburg, Russia

Prof. S. L. Molodtsov
European XFEL GmbH
Albert-Einstein-Ring 19, 22761 Hamburg, Germany

Prof. S. L. Molodtsov
Transnational Scientific and Education UniFEL Center for Advanced Methods of Materials Research
ITMO University
Kronoverskiy pr. 49, 197101 St. Petersburg, Russia

Dr. K. Kummer
European Synchrotron Radiation Facility
F-38043 Grenoble, France

Prof. M. Mertig, C. Erler
Institute of Physical Chemistry
Dresden University of Technology
D-01069 Dresden, Germany

Prof. M. Mertig
Kurt Schwabe Institute for Sensor Technology
Kurt-Schwabe-Straße 4, D-04736 Waldheim, Germany

Dr. D. V. Kurek
Centre "Bioengineering"
Russian Academy of Sciences
117312 Moscow, Russia

Prof. F. Natalio
Institute for Chemistry
Martin-Luther-Universität Halle-Wittenberg
Kurt Mothes Strasse, 2, 06120 Halle (Saale), Germany

Dr. A. E. Kovalev, Prof. S. N. Gorb
Zoological Institute
Christian-Albrechts Universität zu Kiel
Am Botanischen Garten 1-9, 24098 Kiel, Germany

Dr. A. L. Stelling
Center for Materials Genomics
Mechanical Engineering and Materials Science
Duke University
144 Hudson Hall, Durham, NC 27708, USA

Prof. J. Heitmann
Institute of Applied Physics
TU Bergakademie Freiberg
Leipziger Str. 23, 09599 Freiberg, Germany

R. Born
EKF-Diagnostik GmbH
R&D Chemistry
Ebendorfer Chaussee 3, 3917 Barleben, Germany

Prof. K. R. Tabachnick
International Institute of Biomineralogy GmbH
Talweg 26, 09599 Freiberg, Germany

Prof. K. R. Tabachnick
P. P. Shirshov Institute of Oceanology of Academy of Sciences of Russia
Nahimovky 36, Moscow 117218, Russia

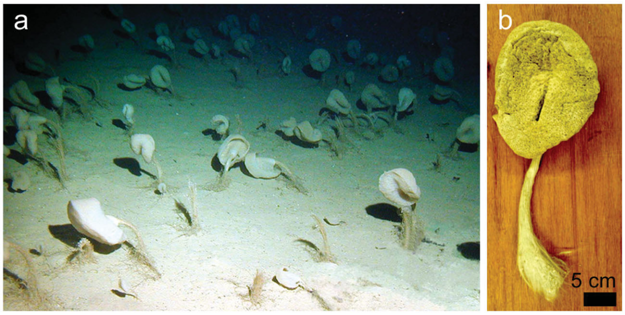

Figure 1. Glass sponge *Sericolophus hawaiicus*. a) In situ view of *S. hawaiicus* at bathyal depths in Kona Island (Hawaii), forming a dense population. b) Dried individual of *S. hawaiicus* showing the flattened body and the anchoring stalk formed by long and highly flexible needle-like spicules.

similarity to those of artificial photonic fibers used for supercontinuum generation (SG). This motivated us to investigate in greater detail the *S. hawaiicus* spicules as a potential source for SG.

2. Results and Discussion

2.1. Structural Characterization

It is well established that glass sponge spicules incorporate organic elements in two ways that makes them biocomposites. The first is a central protein filament of glassin and/or silicatein, which enzymatically controls the initiation of silica polycondensation[14] and the second is the structured organic matter represented by collagen, or chitin.[9,15] Our initial demineralization of the spicules (**Figure 2**) revealed high resistance to 2.5 M NaOH treatment, even after two months of immersion. This outcome raised suspicion that chitin, an organic material highly resistant to alkali digestion and known to occur in silica spicules and skeletal spongin-containing fibers of other sponges,[16,17] could also be integrated into the spicules of *S. hawaiicus*.

Scanning electron microscopy (SEM) examination of *S. hawaiicus* spicules that had been immersed in cold 2.5 M NaOH for weeks confirmed previous reports[16] that this demineralization treatment leads to only partial loss of spicule integrity (Figure 2a). SEM approach indicates that, in section, the spicules show 3 very obvious regions: a) a central, 1µm-wide, hollow channel (i.e., axial channel) of square section, b) a surrounding, 25 to 100 µm thick solid region of silica were lamination is not obvious, hereafter referred to as “protosiphon”, and c) an outermost region where concentric nanostructured silica-chitin layers were found. SEM examination corroborated that the alkali-resistant material was consistently located around the axial siliceous protosiphon (Figure 2a–d) and showed unique nanolamellar, periodic structure (Figure 2f). To provide evidence that the spicular nanostructured remnants (Figure 2f) persisting after demineralization were chitinous, we conducted a battery of assays for chitin identification. Solid-state ^{13}C nuclear magnetic resonance (NMR), near-edge X-ray absorption fine structure spectroscopic method (NEXAFS), Fourier transform infrared spectroscopy (FTIR), high-resolution transmission electron microscopy (HR-TEM), and electron diffraction measurements, as well as Electrospray ionization mass spectrometry (see section 1, Supporting Information) consistently agreed in showing unambiguously that α-chitin is an essential component of the 50 µm thick outermost layer of *S. hawaiicus* spicules. Quantification methods revealed 15.2 ± 1.3 µg *N*-acetyl-glucosamine per mg of spicule of *S. hawaiicus*. The spaces localized between chitinous nanolamella within spicules show strongly perpendicular orientations to each other (see Figure S7, Supporting Information), and are filled with silica (Figure S8, Supporting

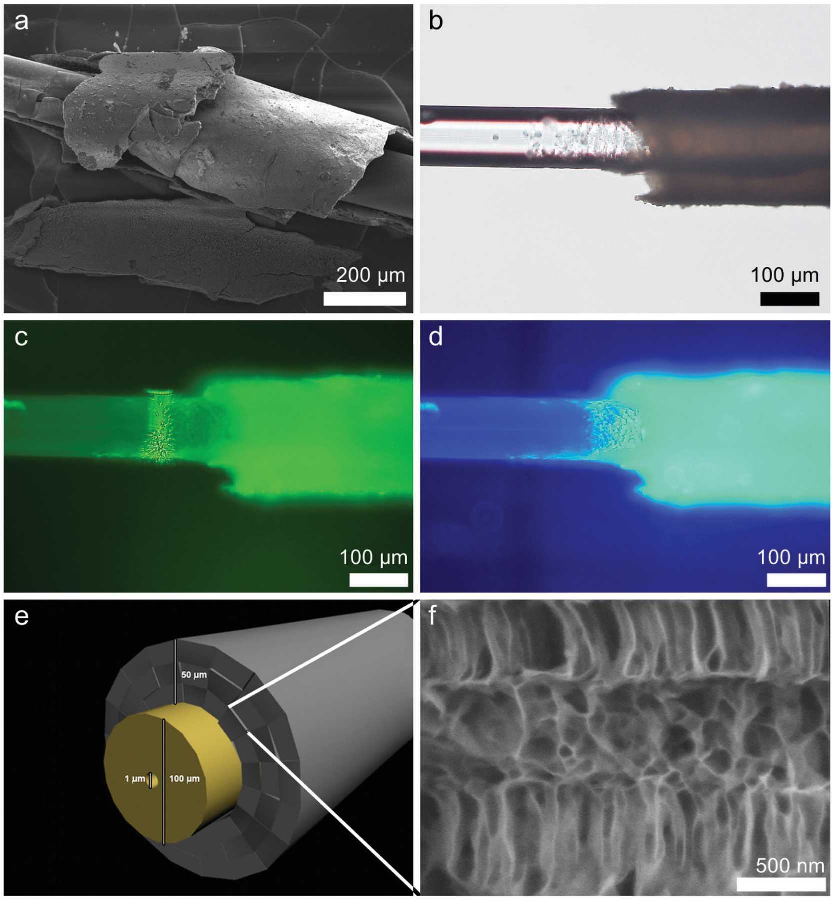

Figure 2. Structural properties of *S. hawaiicus* spicules. Alkali treatment leads to partial dissolution of the siliceous matrix of the spicule, leaving alkali-resistant layers. a) SEM image; b) light; and c,d) fluorescence microscopy images, in which the Calcofluor White staining (d) indicates the presence of chitin. e) Schematic illustration of the general spicule structure based on the observations made using SEM, showing the 1 µm wide axial channel, the surrounding protosiphon region (in brown), and the outermost region of specifically laminated silica. f) SEM detail of the organic material intercalated between the concentric silica layers of the outmost spicule region, made evident after silica digestion (see also Figure S7, Supporting Information).

Information). After the silica is dissolved, the chitinous matrix looks like a regularly nanoporous system (Figure 2f).

To our knowledge, this work is the first demonstrating the presence of chitin within the long spicules that make the anchoring stalk of *S. hawaiicus*. We cannot discard the possibility that the incorporation of chitin into the large spicules enhances their flexibility (see section 4, Supporting Information), substantially improving the resistance of the sponge attachment and also its ability to reorient the body in response to changes in the direction of the prevailing water currents that bring the particulate food to these sponges.[18] It has been suggested[19] and it is herein further supported, that the chitin supplement to the biogenic silica framework increases by several orders of magnitude the resistance of this matrix to dissolution. In addition, we are demonstrating that the incorporation of oriented chitin into the biogenic silica matrix enormously improves its mechanical strength.

The spectroscopic analysis of the Silicon (Si) isotopes composition revealed that the *S. hawaiicus* sponge fractionates Si isotopes available in seawater when producing its spicules. It was found that biogenic silica is notably purified in terms of isotopic composition (δ^{30}Si = −3.28 ± 0.03; δ^{29}Si = −1.65 ± 0.01).

The δ^{30}Si of silica in modern hexactinellids and demosponges is known to range from +0.4‰ to −5.7‰,[20] which indicates that on average the capability of modern sponges to fractionate Si isotopes is about three times larger than that observed during silica formation by diatoms and terrestrial plants. We suggest that this high isotopic purity of the *S. hawaiicus* spicules favors light transmission with minimum energy dissipation.

2.2. Optical Properties

For our nonlinear optical experiments, we used two needle-like spicules of the same type. Hundreds of these 10–50 cm long spicules are normally placed in parallel to each other to make a thick (1–2.5 cm in diameter) stalk, which serves to anchor the sponge body to the soft bottoms where the animal lives (Figure 1a).[21,22]

To investigate the white light generation from 30 to 50 mm long fragments of spicules, we used two different fs-pulsed laser setups (see the Experimental Section for details). Different optical peak intensities, ranging from 1 to 100 TW cm^{-2}, were coupled into the spicules. The resulting white light emission was collected from the exit facet of the spicules and recorded with a fiber-coupled spectrometer with ≈1 nm spectral resolution.

Supercontinuum generation was observed for excitation wavelengths between 650 and 900 nm wavelengths, showing a maximum spectral spread for excitation at a wavelength of 750 nm (**Figure 3** and Figure S5 (Supporting Information)). This corresponds well with the spectral range of high transmission for wavelengths below the characteristic dip at 960 nm, which is observed in our linear transmission spectrum of the fiber (**Figure 4**a). In addition, the increasing spectral broadening with rising excitation intensity proves that the white light generation is indeed based on the nonlinear optical SG but not on pure fluorescence (Figure S2, Supporting Information). Furthermore, the spectral broadening increases with the distance the laser propagates within the fiber (Figure S3, Supporting Information). This confirms that the white light generation really happens within the fiber along its whole length and not only close to its entrance facet, where the laser is focused.

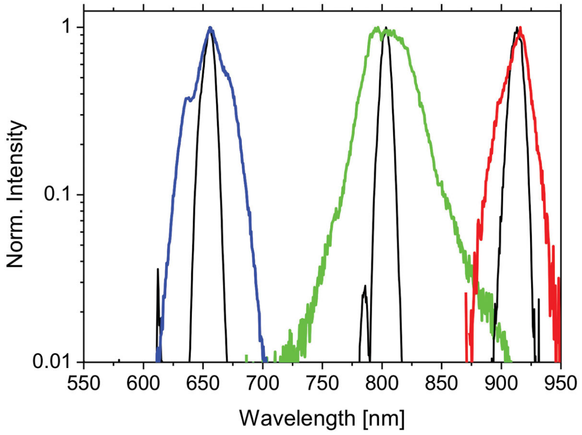

Figure 3. Spectral variation of supercontinuum probed by different excitation laser wavelengths. Black: normalized spectrum of excitation laser. Colored: the corresponding supercontinua. The widest supercontinuum spectrum of *S. hawaiicus* spicule was observed when exciting between 800 and 820 nm.

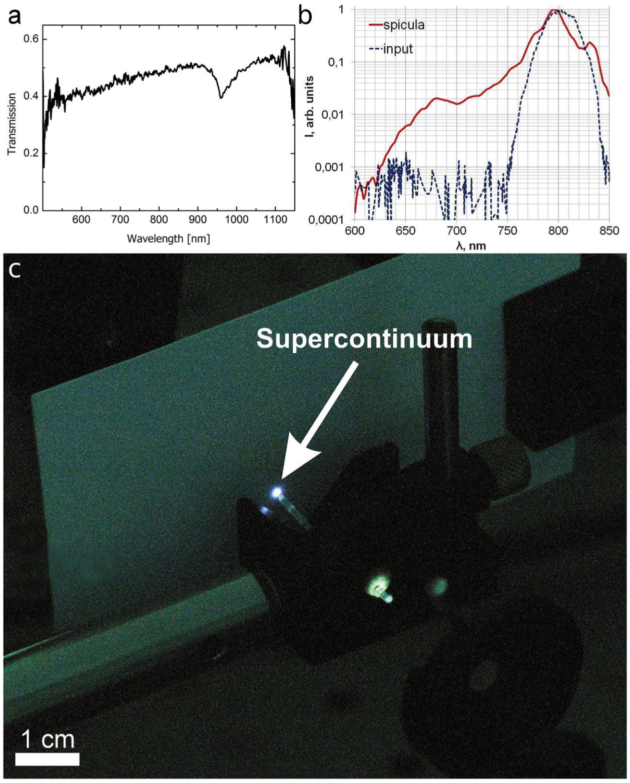

Figure 4. Supercontinuum properties of the *S. hawaiicus* spicules. a) Transmission spectrum for light guided through a ca. 400 µm thick spicule sample at low intensities in the linear optical regime. b) Normalized initial USP (blue curve) and supercontinuum spectra (red curve) in 30 mm long *S. hawaiicus* spicule. c) Supercontinuum (arrow) generated using the selected spicule.

To observe the maximum spectral spread of the supercontinuum, we pumped the spicules in the second setup with 35 fs-pulses from a Ti-sapphire laser (see the Experimental Section for details) resulting in an intensity of ≈70 GW cm^{-2} at the spicule. The shape of the detected spectra in Figure 4b demonstrates major changes, indicated by the broadening and the development of a dip. There is also the formation of a markedly strong anti-Stokes component in the output spectrum of the transmitted ultrashort pulses (USP).

The confluence of several nonlinear optical effects appears to be responsible for the generation of a supercontinuum (for a review of the general process, see refs. [23–27]). Often, the intensive laser pulse leads to a temporal change in refractive index due to third order nonlinear optical properties of the material which causes compression and stretching of the phase during pulse propagation. This nonstationary nonlinear optical effect is known as self-phase modulation and generates an optical "shock wave" at the back edge of the light pulse. This in turn brings about intensification of the higher frequency part of the pulse spectrum; meanwhile spatial self-focusing and noninstantaneous contributions to the nonlinear refractive index increase dramatically leading to the observed spectral broadening.

We suggest that both the monolithic, high-purity silica-containing protosiphon with the axial channel and the nanoporous nature of strong oriented chitinous matrix within sponge spicule (Figure 2f) play a crucial role in the observed phenomenon. Most artificial photonic crystal fibers (PCFs) made of both silica and nonsiliceous materials are also microstructured.[28] Moreover, majority possess core holes.[29] It was reported that light confinement and average mode intensity within such holes is strongly dependent on hole size.[29] We hypothesize that the SG is favored by the global composite structure of the sponge spicule cross-section. The combination of an inner siliceous protosiphon and biosilica–chitin cladding appears to be responsible for generating the supercontinuum shown in Figures 3 and 4, rather than this effect deriving from the mere occurrence of the organic component alone. Recently, we showed SG within solid materials based on tetrakis(2-hydroxiethyl)orthosilicate, at which polysaccharide sodium hyaluronate was added.[30] Because the added polysaccharides played no crucial role within that material, we are here concluding that chitin (also a polysaccharide) cannot be by itself the cause of the observed SG. The silica matrix of the spicule seems to play a role too, as it is indicated from similar SG-spectra and SG-efficiencies been obtained for commercial glass fibers (Figure S4, Supporting Information). It is also interesting the fact that these spicules are the first biological material known to withstand the high light and energy intensities involved in the experimental generation of the supercontinuum, preserving their structure without appreciable damage through the assays.

3. Conclusions

Man-made multimaterial fibers of the structures with unique optical and optoelectronic properties have long been reported.[23–27] Moreover, supercontinua generated in specially designed PCFs under similar experimental conditions (lasers) are much wider due to diverse optimization steps which have been carried out after discovery of this phenomenon. However, the finding of SG in naturally occurring nanoorganized biosilica-based fiber-optic structures and the attempt to understand the mechanism of this phenomenon is an example of how Nature addressed our next challenge. In contrast to the temperature ranges at which artificially synthesized fibers with supercontinuum properties are made (between 1000 and 2000 °C), glass sponges produce siliceous fibers with similar properties at temperatures around 4 °C! To develop an in-depth understanding of supercontinuum generation in spicules, more studies of their dispersive and nonlinear properties should be carried out in the near future. It is likely that apart from the high-purity silica, the other components of the spicule material (such as polysugars and hydroxyl groups) strongly contribute to the dispersive and nonlinear properties of the spicule fibers.

Sponges are probably the earliest metazoans appeared on earth.[31,32] Spicules of hexactinellids have been unequivocally identified in strata at the border of the Late Ediacaran ca. 543–549 Ma.[33] To date, the oldest optical structures reported are the calcitic lenses of trilobite eyes, ca. 521 Ma,[34] and the diffraction gratings on the spines and setae of *Canadia* and *Wiwaxia* polychaetes from the Burgess Shale, ca. 508 Ma.[35] We cannot yet prove these spicules originally had a role related to light transmission to either sponge cells or symbionts. Should this be the case, the biocompositional structure of these spicules, which favors and resists the generation of a supercontinuum, may be as ancient as the emergence of the animal kingdom.

4. Experimental Section

The wavelength dependent white light continua were measured with a femtosecond laser source comprised of a collinear optical parametric white-light continuum amplifier (Light Conversion Orpheus), pumped by a Yb:KGW femtosecond laser (Pharos, Light Conversion). The system produced excitation pulses in the visible and the near-infrared spectral range with temporal widths between 170 and 190 fs, at a repetition rate of 1 kHz.

The experimental setup (see Figure S6, Supporting Information) was used based on a Ti-sapphire femtosecond laser system. A Spitfire Pro 40F (Spectra Physics) was used in our experiments on propagation of unfocused ultrashort laser pulses through *S. hawaiicus* spicules. Input pulse temporal width 38 fs was controlled by a standard technique of nonlinear autocorrelation with second harmonic generation. Other parameters of USP were as follows: central wavelength 800 nm, pulse width $\Delta\lambda_{\text{FWHM}} = 35$ nm, pulse energy 1 mJ, beam diameter $d = 7$ mm, repetition rate: 100 Hz. The power density of USP on the entrance of the sample was ≈70 GW cm^{-2}.

Analytical Methods: The analytical methods used in this work included NEXAFS, ^{13}C solid-state NMR, SEM, TEM, electron diffraction and HR-TEM, atomic force microscopy, fluorescence microscopy, FTIR, high-performance liquid chromatography, mass spectrometric methods, isotope analyses using MC-ICP-MS, Calcofluor White staining, and chitinase digestion test. These, as well as sample preparation, demineralization, and material properties techniques were described in detail in the corresponding section of the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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