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Photoinduced electro-optics measurements of biosilica transformation to cristobalite

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ABSTRACT

In this paper we studied the photoinduced electro optics effects in the thermal transformation process of biosilica to cristobalite, at a relatively low temperature and ambient pressure. This process was characterized by a variety of *standards* techniques with emphasis on linear electro optic effect measurements. Overall we demonstrated that photoinduced electro optics measurements are very sensitive to the transformation from amorphous structure of silica in the natural sponge samples to laminar string morphology of cristobalite. With this technique we could probe the change in the samples chirality from achiral bio silica to chiral cristobalite structure. Furthermore it is shown that natural biosilica have photoinduced linear electro optics respond indicating *the chiral* natural of biosilica.

1. Introduction

Silicon and his oxides forms are major members in the earth's crust, therefore it has been a long lasting focus in using silicon base materials for commercial products such as filling material, filtering agents, catalyst support, and ion-exchange material [1–3]. This demand of SiO_2 based substances has driven the production of new material and new products in order to improve the capacity, selectivity and productivity of the known products in to new frontiers [4]. One of these new prospect products are based on the sources of silica produced by a biological systems such as plants, animals and microbial systems [5]. Recent studies in biology of marine organisms such as diatoms and marine sponges, which produce a great amount of silicified structure, showed that Silicatein is one of the main proteins that are responsible for the formation of silica structure in the marine organisms. Silicatein is comprises of nearly 70% in mass of the filaments inside the organism [6]. The demosponge categorized into the cathepsin L family showed an enzyme functionality in the biosilica formation, and even capable of polycondensation in the case of inorganic source of alkoxy groups such as tetra ethyl ortho silicate (TEOS) [7–10]. In numerous papers it was shown that Silicatein has the ability to produce controlled mineralization of SiO_2 and can determined the morphology, shape and size of the biomineral skeleton. Although the molecular mechanism of this effect has proved to be elusive, much is known of the structure and functional groups of the silicatein [11], and using this macromolecule features, a new line of functionalized material such as TiO_2 [12], SnO_2 [13] and even bone regeneration scaffolding [14] were shown. Another interesting feature of this biosilica to work as a fiber-optical device has been shown by Aizenberg et al. [15]. This preliminary work showed that the skeleton of the sponges, although constructed from amorphous hydrated silica, is able to act as light refracting material such as fiber-optic, thus indicating the optical capability and prospect of bio-silica material to work as an optical material in the optics field.

With the on growing use of porous silica material, the use of chiral entrapment molecules as a base for chiral porous silica has been in focus in the past decade [16,17]. In previous work [18], we have demonstrated that biosilica such in a marine sponges with high content of silicatein, can undergo structural rearrangement to high polymorphs of silica, especially to cristobalite, in relative low temperature and ambient atmospheric pressure. This use of silicatein as surface directing agent (SDA) was also capable of making this rearrangement in inorganic material such as sol–gel matrix embedded with the silicatein to exclude any other prospects of external influence and the demonstrate the importance of silicatein as an hierarchical moiety in the transformation process.

In order to further investigate the role and impact of silicatein in the transformation of bio silica to cristobalite and the effect of silicatein for the preparation of mesoporous silica we decided to use a photoinduced electro-optics technique to probe this

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transformation. Photoinduced electro-optics measurements are effective in the studies of the chiroptical behavior of different organic compounds. In photoinduced electro-optics measurements the additional photo stimulation of the intrinsic defect states favors an enhancement of the liner effect described by the third polar tensor (d_{22}) and defined by the local electronic charge density non-centrosymmetry. Therefore we can use photoinduced electro-optics measurements to explore the transformation of biosilica that is achiral material to the cristobalite, a crystalline form of silica with crystal system of $P4_12_12$ (for α-cristobalite and $Fd3m$ for β-cristobalite) [19] which should be sensitive also to the chiroptical features [20,21]. The additional photoillumianton of the intrinsic defect states favors an enhancement of the liner electro-optics effect described by the third rank polar tensor [22] and defined by the local acentricity.

2. Experimental

2.1. Biological specimen collection

The spicules used in this work were isolated from *Cinachyrella levantinensis* marine sponge harvested at Ma'agan Michael bay in the Mediterranean Sea (32°29′77N; 34°53′23E) from a depth of 2 m. Samples were cute in to small cubes (4 cm^3) then gently shaken in 5% $NaOCl_3$ for 24 h, followed by a rinse with water and filtered in 200 μm filters. To ensure the absence of organic substance around the spicules, a mixture of cold (4 °C) HNO_3: H_2SO_4 1:4 solution was prepared and the specimen was immersed in it for 12 h, followed by extensive wash in cold Millipore water until it reached a neutral pH level.

2.2. Isolation of silicatein filaments

Specimens of *Negombata magnifica* were collected, cut, and then cleaned using 5% $NaClO_3$ solution for 24 h. Then washed extensively in Millipore water (MP) (18 mΩ) followed by treatment with cold HNO_3/H_2SO_4 1:4 solutions for 12 h. after rinse with Millipore water to obtain neutral pH. The specimen immersed in cold NH_4F/HF 8 M/2 M overnight for dissolution of the silica matrix. The filaments was collected from the slurry and washed 5 times with MP water and dialyzed against 10 L of MP water at 4 °C overnight. The dialysate was collected using centrifugation at 10,000 rpm for 20 min at 4 °C, and kept in Et-OH at 4 °C for further use.

2.3. Sol–gel embedded with silicatein filaments

Silica matrix and entrapment of silicatein within was achieved by using the sol–gel process based on the entrapment method of alkaline phosphatase (AIP) proposed by Avnir et al. [23] with small adaptation for the silicatein, see our previous work [18] for more detailed information.

2.4. X-ray diffraction analyses

Powder X-ray diffraction (XRD) patterns were acquired with a Bruker AXS D8 Advance Diffractometer with Cu$K\alpha$ ($\lambda = 1.5418$ Å) operating at 40 kV 40 mA. Samples were mashed with Agate Mortar and placed in a PP holder. Data were collected from 5° to 80° with a step size of 0.01°, and rotation at 25 rpm.

2.5. Fourier transform infrared spectroscopy

(FT-IR/ATR) analyses were taken on a Bruker Alpha spectrometer (US). A diamond ATR crystal was used as the internal reflection element and the incident angle was fixed at 45°. The films were scanned 50 times at a 4 cm^{-1} resolution, in the region of 4000–450 cm^{-1}. The samples were placed on the reflection element, carefully pressed, and taken three times to ensure spectra accuracy.

2.6. Scanning electron microscopy

Surface morphology was characterized using high resolutions FEI, Magellan 400 L Scanning Electron Microscope (HR-SEM). Samples were prepared by sampling a small amount on double-sided carbon tape. For morphological examination the sample was coated with a layer of Ir to ensure conductivity, and when EDX was taken no coating was applied.

2.7. Transmission electron microscopy

Samples were examined with high resolution transmission electron microscope (HR-TEM, JEOL, JEM 2100, 200 kV). To observe by TEM a small amount of sub-sample dispersed in Et-OH was dropped onto a conductive holey carbon copper grid, letting the sample to dry out at room temperature. For selected areas electron diffraction patterns (SADP) were acquired.

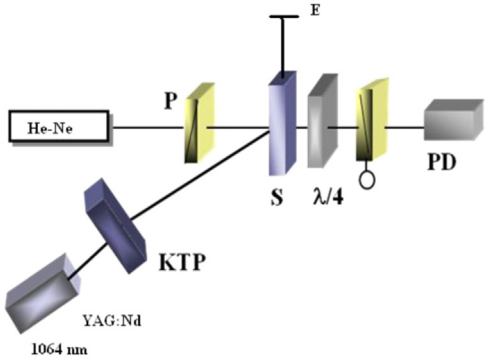
2.8. Temperature treatment

samples were taken as whole on a ceramic holder into open end horizontal tube furnace (Carbolite MTF 12/38/400) set to 850 °C in 5 °C/min steps, for 360 min, followed by controlled cooling.

3. Photoinduced electro-optics

Scheme 1. Principal set-up for the photoinduced dc-electric field stimulated electro-optical effect.

The principal set-up for the photoinduced electro-optic measurements is presented in Scheme 1. Photo inducing Nd:YAG laser is used with 12 ns pulse duration up to 60 mJ. The beam profile of this beam is Gaussian like and their frequency repletion is equal to about 1 kHz. The incident fundamental laser beam is incident on the KTP crystals cut under the angle satisfying the phase matching conditions. Some modified method is described in Ref. [24]. Simultaneously the crystal introduce some phase shift to the two beams, fundamental one at 1064 nm and its doubled frequency at 532 nm. The sample is treated simultaneously by the described above bicolor beam as well as treated by dc-electric field. Only such simultaneous treatment after 3–5 min and the saturation was controlled by saturation of the birefringence measured by Sénarmont method.



Scheme 1. Principal set-up for the photoinduced dc-electric field stimulated electro-optical effect.