*Biomimetic Structures Through CVD*

# Exact Replication of Biological Structures by Chemical Vapor Deposition of Silica**

*Gary Cook, Peter L. Timms, and Christine Göltner-Spickermann**

Biological species produce a rich variety of structures or forms that serve their needs of adaptation and survival. The success of these forms often depends on the underlying organization of their structure from the nanometer scale upwards.[1,2] The superb performance of biologically derived inorganic materials is usually not reproduced in synthetic analogues, which is why the biomimetic or bio-inspired approach towards new functional materials is currently a topic of research interest.[3,4] The mechanisms of formation of most biological structures are often extremely complex, therefore the exact imitation of biological form in a chemistry laboratory is difficult. However, the synthetic replication of evidently useful biological structures by a simple casting process is expected to introduce some of the superb properties of biological structures into man-made materials. Wet-chemistry techniques, as applied to polymer gels[5] or microfibers,[6] can cause considerable damage to a delicate biological specimen, but chemical vapor deposition (CVD) has greater potential. Herein we demonstrate that the controlled vapor-phase oxidation of silanes on the surface of biological structures produces an exact, inorganic oxide replica of the natural form.

At room temperature and under pressures in the range between 1 and 5 hPa, silane reacts with an excess of vaporized hydrogen peroxide to deposit silica on almost any material by a surface-phase process.[7–9] This reaction was initially developed for depositing a smooth dielectric layer of silica on silicon wafers, but is now shown to be an outstandingly effective way of coating delicate biological specimens. Conventional CVD processes create a stream of oxide particles in gas-phase reactions, which cannot uniformly coat a three-dimensional object because of shadowing. Other techniques employ surface reactions, but at elevated temperatures detrimental to delicate (biological) specimens. The apparatus for the reaction of hydrogen peroxide and silane is shown in Figure 1. The CVD of silica is known to produce silica primary clusters. These clusters have extraordinary flow properties and are capable of "creeping" into smallest gaps within the substrate,[9] which makes the method promising for the replication of intricately structured objects. The biological specimens used in this study were chosen for their structure-related function, for example, optical properties, mechanical stability, or surface energy.

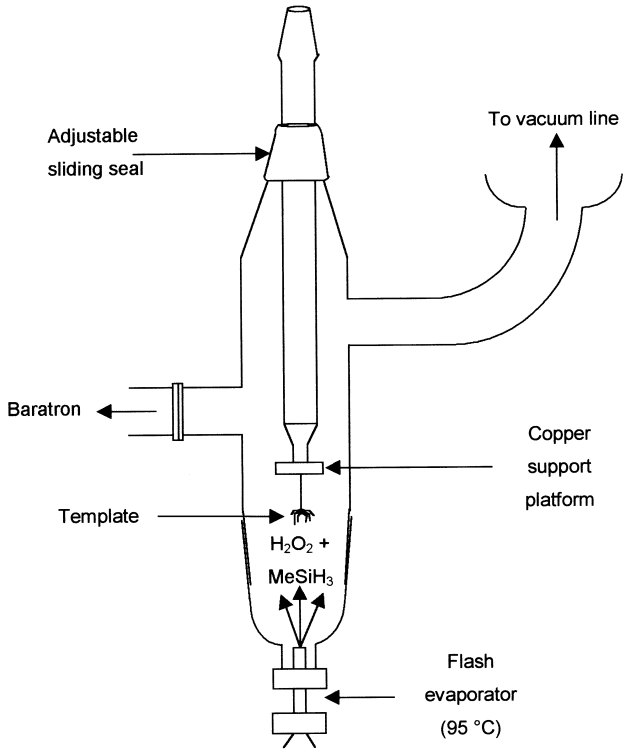


***Figure 1.*** Experimental apparatus for the chemical vapor deposition of silica.

In all cases the relatively soft templates are substantially harder after the deposition of silica and brittle after removal of the biological structure through calcination (combustion of the organic material at 500 °C in air). However, the coated materials as well as the calcined, all-inorganic products can be handled easily with tweezers. Depending on the thickness of the silica layer, the film is either invisible, translucent, or white. The true character of the replication process is revealed by scanning electron microscopy (SEM). The beautifully iridescent 2D-photonic bandgap material[10] of a butterfly wing (Figure 2a), designed by nature for aerodynamics, light weight, protection, and finding a suitable mate (color!), can be replicated by CVD of silica. Figure 2b shows the hollow silica replica obtained from a Peacock butterfly. The overall dimension of the wing is reduced by 25% due to shrinkage during calcination, which also causes slight creasing, but the structural features of the 100–150 nm thick replica are clearly visible (Figure 2b, inset). In contrast, if the same type of butterfly wing is subjected to dip-coating with a sol–gel precursor solution, there is a very evident lack of compatibility (dewetting) between the wing and the inorganic coating, and catastrophic cracking of the coating occurs because of shrinkage (not shown here).

More interestingly, this process can be applied to replicate hierarchical structure, such as the hairy, protective surface of a

[*] C. Göltner-Spickermann, G. Cook, P. L. Timms
School of Chemistry
University of Bristol
Bristol BS8 1TS (UK)
Fax: +44 1179251295
E-mail: goltner@supanet.com

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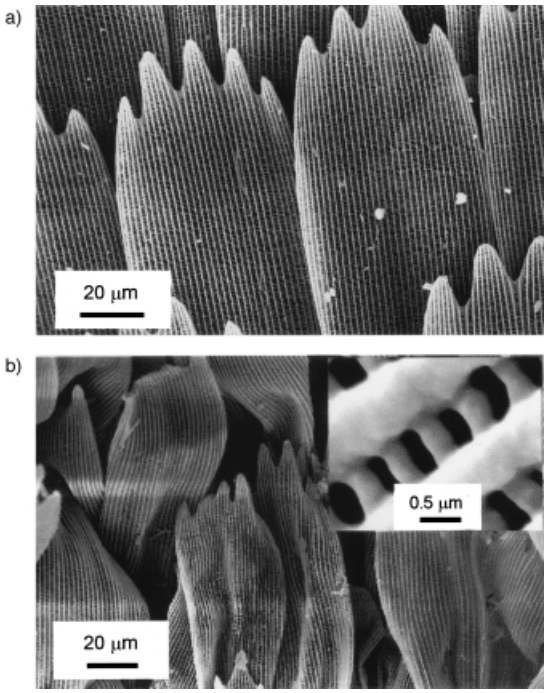


***Figure 2.*** a) Details of a peacock butterfly wing revealed by SEM. b) Calcined silica replica showing a slight degree of creasing as a consequence of heat treatment. Insert: high-magnification image.

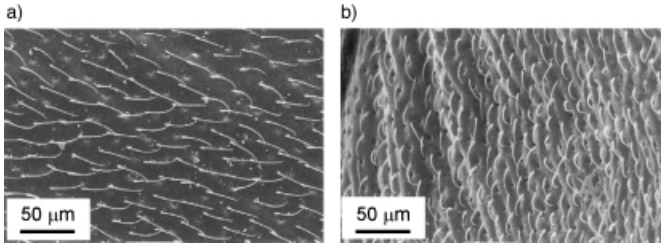


***Figure 3.*** The hairy wing of a housefly can be replicated precisely by CVD of silica. a) Original specimen, b) The hollow silica replica not only maintains structural identity, but is also macroscopically iridescent.

housefly wing, a structure designed by nature to be self cleaning in that dust particles are repelled from the wing. The specimen (see Figure 3a) consists of a smooth surface with periodic indentations 2 μm wide and almost 2-μm-thick hairs protruding from it, which are periodically spaced, approximately 20 μm apart. This structure is precisely replicated (Figure 3b) in a hollow silica cast, again allowing for a slight degree of shrinkage as a result of heat treatment (calcination). It can be imagined that the function of such surfaces (optical properties, repellency) could be preserved in the inorganic replica, which in turn would introduce specific properties, such as a particular refractive index or sorption behavior. Indeed, the all-inorganic replica of the house-fly wing shows the same iridescence as the biological specimen.

The replication of ultrahydrophobic, self-cleaning plant leaves (*colocasia esculenta*, see Figure 4a, and common pond weed, Figure 4b) is equally successful and produces an exact cast of the leaf structure.[11] The comparison of contact angles

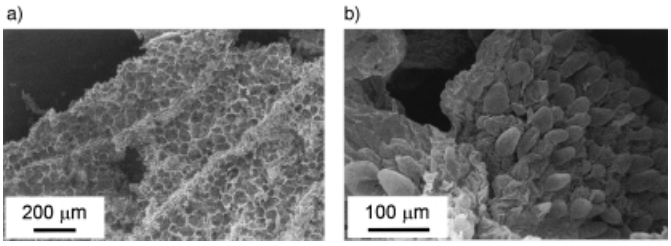


***Figure 4.*** a) Figure 4a: SEM image of a silica cast obtained from the leaf surface of *colocasia esculenta*, a self-cleaning plant. b) SEM image of the silica replica obtained from a common pond-weed leaf, likewise an ultrahydrophobic surface.

of water on a silica layer structured like this with those of water on a smooth blank is expected to provide information on the extent of structural contribution to the ultrarepellency of rough surfaces (lotus effect). Regardless of surface polarity, the CVD of silica from silane provides a means of faithfully replicating the most intricately structured biological specimens without the occurrence of artifacts. This universal behavior can be explained in two ways, partly by the reaction conditions, as the vacuum in the reaction chamber would remove nanoscopic air bubbles, which are held responsible for the ultrahydrophobic character of many surfaces[12] and partly by the variety of ways hydrogen peroxide can bind to surfaces, creating sites at which the oxidation of silane can occur.

Using this technique organic fibers of many types can be successfully coated with silica and then calcined to leave silica tube replicas of 200 nm thick nylon, spider silk of 2 μm diameter, sucrose-based "candyfloss" fibers of 5–10 μm diameter (not shown here). Even more complex, three-dimensional structures, such as the chitin skeleton of cuttlefish bone[13] can also be replicated precisely.

The thickness of the ceramic layer is controlled by the amount of silane added to the deposition chamber and the reaction time. Typical thicknesses are between 100 nm and 2 μm. Depending on the size of the object and the thickness of the layer the degree of shrinkage observed as a consequence of calcination lies between 5 and 40%, which is little compared with materials of similar dimensions derived by sol–gel processing. In addition, removal of the underlying template by heat treatment in air does not cause cracking of the inorganic coating, which is a common problem in sol–gel derived ceramic coatings.

The method presented here is chemically flexible, as mixing the silane with varying amounts of diborane, phosphane, or germane produces borosilicate, phosphosilicate, or germanosilicate coatings with maximum Si:B, Si:P, or Si:Ge ratios of about 3:1, 3:4 or 1:4, respectively.

We also propose this CVD technique as a novel tool for the generation of intricate and hierarchical structures on several length scales. As specimens do not appear to change shape, we propose the coating of biological structures with an invisibly thin film of silica as a possible means of conservation of delicate biological specimens (fixing). Nature provides an abundance of shapes which can be synthetically modified and preserved by this facile and inexpensive process.

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## Experimental Section

Liquid 60% hydrogen peroxide (3 mmol $H_2O_2\,min^{-1}$) was sucked through fine teflon tubing into a flash evaporator at 90 °C. The peroxide vapor mixed with gaseous silane (0.1–03 $mmol\,min^{-1}$) a few centimeters below where the template (substrate) was suspended in a pyrex glass reaction chamber. The sample and all internal surfaces of the reaction chamber became coated with silica at a rate of 50–200 $nm\,min^{-1}$. The layer thickness was adjusted through the amount of silane precursor and the reaction time. Subsequent pumping on the reaction chamber at 0.01 hPa assisted in removing side products as well as giving a highly condensed silica network. The organic template was removed by calcination at 500 °C in air. As known from earlier studies of the deposition on silicon wafers, silane can be replaced by the less pyrophoric methylsilane to give silica containing only a very small amount of organic groups.[6]

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*Patterned Polymer Brushes*

# Surface-Initiated Polymerization on Self-Assembled Monolayers: Amplification of Patterns on the Micrometer and Nanometer Scale**

*Ursula Schmelmer, Rainer Jordan,* Wolfgang Geyer, Wolfgang Eck, Armin Gölzhäuser,* Michael Grunze, and Abraham Ulman*

The application of highly ordered self-assembled monolayers (SAMs) as initiator systems for surface-initiated polymerization (SIP) allows the preparation of uniform and densely grafted polymer brushes. This so-called "grafting from" technique was demonstrated for nearly all types of polymerization,[1] including living anionic[2] and cationic SIP.[3] One important aspect offered by the use of SAM systems as two-dimensional initiator systems is the possibility to control the locus of the initiator sites within a SAM, for example, to finetune the grafting density of the resulting polymer brush by using mixed SAMs,[4] to prepare two-component gradients,[5] or to fabricate complex spatial structures at various length scales. The latter can be formed by various techniques, in particular by microcontact printing (μCP) for structures ranging from 0.1 to several hundred micrometers.[6,7] For patterning on the nanometer scale, SPM-based techniques for the manipulation of SAMs such as "dip-pen nanolithography",[8] "nanografting", or "nanoshaving"[9] were recently developed.

A combination of directed deposition of functionalized areas of SAMs and consecutive SIP allows a superior control of pattern formation and amplification of the patterns by creating polymer-brush layers at predefined sites. Surface defects, present in all SAM systems, as well as topological features of the substrate are covered by a significantly thicker layer of a flexible polymer brush. The resulting structures display a better contrast between the functionalized and

[*] Dr. R. Jordan, U. Schmelmer
Lehrstuhl für Makromolekulare Stoffe
Technische Universität München
Lichtenbergstr. 4, 85747 Garching (Germany)
Fax: (+49) 89-289-13562
E-mail: rainer.jordan@ch.tum.de
Dr. A. Gölzhäuser, Dr. W. Geyer, Dr. W. Eck, Prof. Dr. M. Grunze
Angewandte Physikalische Chemie, Universität Heidelberg
Im Neuenheimer Feld 253, 69120 Heidelberg (Germany)
Fax: (+49) 6221-546-199
E-mail: goelzhaeuser@uni-hd.de
Dr. R. Jordan, Prof. Dr. A. Ulman
Department of Chemistry, Chemical Engineering, and Materials Science, Polytechnic University
Six Metrotech Center, Brooklyn, NY 11201 (USA)

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