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Silica-Deposited Phospholipid Tubules as a Precursor to Hollow Submicron-Diameter Silica Cylinders

Subhash Baral*,† and Paul Schoen‡

Geo-centers Inc., 10903 Indian Head Highway, Fort Washington, Maryland 20744
Naval Research Laboratory Washington, D.C. 20375-5000

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Although sol–gel methods have been widely applied to deposit thin films on various macroscopic and microscopic substrates,[1,2] they are not common[3] on unsupported self-organized substrates, i.e., molecular aggregates held together by weak intermolecular interactions. In nature, however, sol–gel type deposition on self-organized assemblies probably accounts for the formation of intricate structures of some biominerals.[4] We have coated silica film on self-organized phospholipid tubules in an attempt to mimic such in vivo processes and to stabilize their tubular structure.

Phospholipid tubules[5] are hollow, open-ended cylinders (0.5 μm in diameter and about 50–100 μm in length) formed by spontaneous self-aggregation of certain chiral phospholipid molecules.[6] The walls (6–50 nm thick) of the cylinders consist of one to about eight phospholipid bilayers. The tubule structure is stable in aqueous dispersions below the chain melting transition temperature (typically 35–60 °C depending on the acyl chain length[7] of the phospholipid molecule). Despite their limited stability, the structural features (hollow open-ended cylinder of high aspect ratio) of the phospholipid tubules made them attractive for certain potential applications.[8,9] In the present work, the mechanical strength and thermal stability of this cylindrical microstructure have been found to improve through silica film deposition. Subsequent curing at high temperature decomposed the organic phospholipid molecules and produced a silica replica. In the past, hollow ceramic silica cylinders of 2–4-μm diameters have been obtained by impregnating porous carbon fibers with silicon compounds followed by calcination and sintering.[10] Silica coating has also been used in the past[11] as a support for poly(acrylonitrile) fibers during pyrolysis to graphite fibers.

Silica film deposition was carried out by mixing about 100 mL of phospholipid[12] tubule dispersion (containing

* To whom correspondence should be addressed.
† Geo-centers, Inc.
‡ Naval Research Laboratory.

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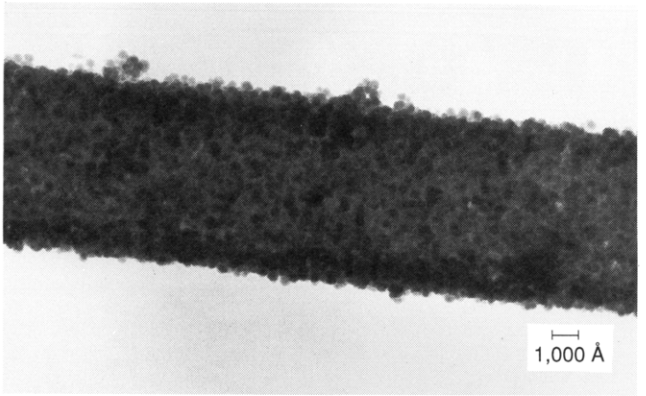

Figure 1. Transmission electron micrograph of silica coated $DC_{8,9}PC$ phospholipid tubules (no staining).

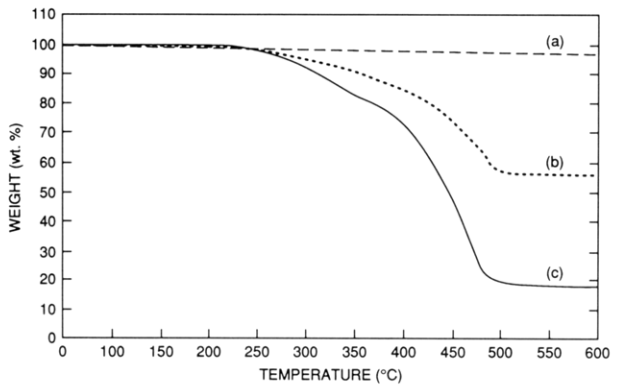

Figure 2. Thermogravimetric analysis of (a) silica powder (dry gel from Ludox), (b) silica coated phospholipid tubules, and (c) pristine phospholipid tubules.

about 2 mg/mL of lipid) with 100 mL of 20% Ludox[13] solution. The mixture (pH 8.2–8.4) was allowed to stand undisturbed for 6–9 days. During this period silica-coated tubules settled to the bottom as a white solid. These were collected, washed five or six times with water (by light centrifugation and decantation), and redispersed in 10 mL of water. Transmission electron micrographs (TEM) of this sample indicate the presence of a film of aggregated silica particles on the phospholipid tubule (Figure 1). Their appearance is very similar to that of silica particles adsorbed on dark green algae cells (1 μm wide and 2 μm long), reported by Iler.[14]

The silica film on the tubule surface remained continuous after extensive washing with water, indicating a strong adherence of the silica film to the tubule surface. TEM micrographs indicated that the inside of the tubules remained hollow. Comparing the external diameters of these silica coated tubules (600 nm) with that of pristine phospholipid tubules (500 nm), the average film thickness was approximated to 50 nm (four or five silica particles).[13] X-ray diffraction measurements showed that the silica film was amorphous.

A strong affinity between biological cell surfaces and various silica surfaces has been noted in the past.[15] This

Figure 3. SEM of residue from the TGA experiment on silica-coated phospholipid tubules. The residue in the pan was redispersed in water, dried in air on an SEM stage, and sputter-coated with a thin layer of gold before the micrograph was taken.

has been attributed to electrostatic attraction between the negatively charged silica surface[14] and positively charged quaternary tetramethylammonium headgroup of the phosphatidylcholine lipid present in the cell membranes.[16] The phospholipid $DC_{8,9}PC$ has the same headgroup as phosphatidylcholine, and therefore the adsorption of silica particles on the tubule surface can also originate from electrostatic attraction. That the silica particles on the tubule surface gel, leading to a thin film, indicates significant neutralization of their charges[17] subsequent to adsorption on the tubule surface.

An aqueous suspension of silica-coated tubules was freeze-dried (*Caution*: The dry material is very light and easily becomes airborne). The white powder was subsequently heated in air at 150 °C for 5 h. SEM micrographs indicate that the silica coated tubules retained their hollow cylindrical geometry, although some of them were broken. When pristine $DC_{8,9}PC$ phospholipid tubules are heated, either as a freeze-dried solid or in aqueous dispersion, the tubular structure completely disappears at 43 °C.

Heating the silica coated tubules to 600 °C in a nitrogen atmosphere results in about 40% weight loss over the temperature range 250–500 °C on a thermogravimetric balance (Figure 2). Results from separate control experiments using pristine phospholipid tubules and dry gel from Ludox are also shown in Figure 2. With silica gel the weight loss was only 3% and took place below 200 °C. The pristine phospholipid showed no weight loss up to 200 °C but between 250 and 500 °C underwent more than 80% weight loss, indicating a thermal decomposition. The residue from the lipid tubule was a small amount of black tarry material strongly bonded to the pan. On the contrary, the residue from the silica coated tubules was a gray, light fluffy solid. SEM micrographs indicated the presence of hollow tubular silica[18] cylinders in this residue (Figure 3).

(12) The phospholipid, $DC_{8,9}PC$ (1,2-bis(10,12-tricosadiynoyl)-*sn*-glycero-3-phosphocholine), was used as obtained from Avanti polar lipid (Birmingham, Al). Tubules are formed by precipitation from an aqueous ethanolic solution (ethanol:water = 70:30) as described in ref 5.

(13) Ludox was obtained from Du Pont Chemical Co (Wilmington, DE). The stable sol had a pH of 9 and contained 40% silica (particle of 10–15-nm diameter) by weight.

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(17) The isoelectric points of aqueous silica sols are around pH 2 (ref 14, pp 355 and 367). With increasing pH (in the range 3.5–10.5) hydroxyl ions are increasingly adsorbed on the silica surface rendering the surface charge increasingly negative.

(18) Thin silica films with thickness up to 1 μm are usually sintered around 500–600 °C (ref 1b, p 52).

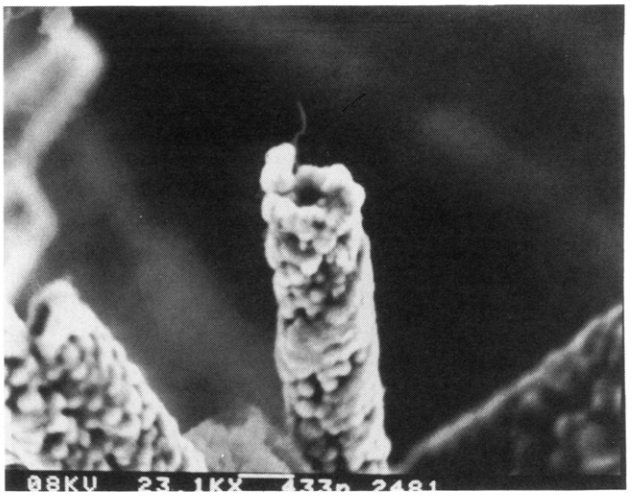

Figure 4. SEM of nickel–silica coated tubules. The sample was air-dried on the SEM stage from an acetone dispersion.

A number of silica tubules also appeared to have collapsed or broken into shorter tubules in the micrographs (this might have caused partly by the process of drying after redispersion during the sample preparation stage). Although these silica tubules did not have as high aspect ratio (their lengths varied between 15 and 25 μm) as the original phospholipid tubules starting material, the deposition of silica film certainly improved the mechanical and thermal stability of tubule microstructure.

An additional benefit of silica film deposition is that the new silica surface can be easily functionalized. We have palladized[19,20] silica coated tubules (by treating them with ammoniacal solution of palladium chloride) and subsequently deposited nickel metal (using an electroless[21] nickel plating bath, Niposit468 from Shipley Co, at 55 °C) to produce a magnetic black solid. When pristine phospholipid tubules are subjected to identical palladizing and plating treatments (at 22 °C), hardly any metal deposition takes place.

X-ray powder diffraction pattern shows the presence of nickel microcrystallites (average grain size 2.7 nm) with face-centered cubic structure in the nickel overcoated silica tubules. SEM micrographs of these tubules (Figure 4) indicate the presence of large spherical deposits of nickel (about 50–80 nm in diameter) on silica surface which coalesced in several places to produce small regions of apparently continuous nickel film. TEM micrograph of a 30–40-nm-thick cross section of these tubules (obtained after embedding the tubules in a polymer matrix and ultra microtoming in direction perpendicular to tubule axis) is shown in Figure 5. The tubular core appears to remain hollow and the total thickness of the nickel–silica film is estimated to be about 100 nm.

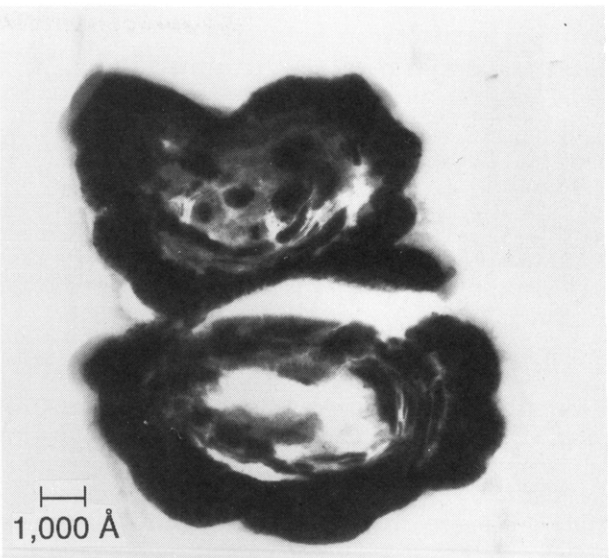

Figure 5. TEM of a cross section from a nickel–silica-coated tubule. The tubules were embedded in an epoxy polymer and cured, and the composite solid was subsequently microtomed into 300–400-Å-thick sections which were micrographed. The darker regions represent nickel metal (no staining).

In conclusion, we have utilized a self-organized molecular assembly, namely, an aqueous dispersion of phospholipid tubules as template for 50-nm-thick silica film deposition by a sol–gel method. The silica film substantially increased the mechanical and thermal stability of the tubule geometry. Freeze-drying followed by decomposition of the lipid by heating to 600 °C resulted in hollow silica cylinders. The cylinders were made ferromagnetic through nickel overcoating by electroless plating. Potential applications of these hollow silica cylinders for oriented composite formation, as vehicle for targeted controlled release, and as a sensor for stress, friction, and wear, etc., subsequent to the inclusion of suitable materials in the cavity, are being investigated.

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