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CVD for the Facile Synthesis of Hybrid Nanobiomaterials Integrating Functional Supramolecular Assemblies

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In this letter, we present a simple one-step, versatile, scalable chemical vapor deposition (CVD)-based process for the encapsulation and stabilization of a host of single or multicomponent supramolecular assemblies (proteoliposomes, microbubbles, lipid bilayers, and photosynthetic antennae complexes and other biological materials) to form functional hybrid nanobiomaterials. In each case, it is possible (i) to form thin silica layers or gels controllably that enable the preservation of the supramolecular assembly over time and under adverse environmental conditions and (ii) to tune the structure of the silica gels so as to optimize solute accessibility while at the same time preserving functional dynamic properties of the encapsulated phospholipid assembly. The process allows precise temporal and spatial control of silica polymerization kinetics through the control of precursor delivery at room temperature and does not require or produce high concentrations of injurious chemicals that can compromise the function of biomolecular assemblies; it also does not require additives. This process differs from the conventional sol−gel process in that it does not involve the use of cosolvents (alcohols) and catalysts (acid or base).

Introduction

The widespread study of biological and biomimetic phospholipid assemblies and related noncovalent supramolecular architectures (e.g., cellular components, phospholipid vesicles and supported lipid bilayers) has revealed the potential for recreating a plethora of unique biological phenomena (e.g., selective and active transport,[1,2] sensitive molecular recognition,[3,4] signal and energy transduction,[5,6] light harvesting,[6,7] and biocompatibility[8,9]) in synthetic functional materials. The fragility of such assemblies, however, has typically precluded their incorporation as functional elements into rugged devices[10] in potential applications include controlled release,[11] biosensing,[2,12] and artificial photosynthesis.[13] This has resulted in the development of several methods to stabilize supramolecular structure into and out of aqueous environments. However, such stabilization methods often require the addition of exogenous components to the assembly, which limit the dynamic properties of phospholipid assemblies (e.g., intramembrane diffusivity) and thus may hinder their functionality. Methods that have been explored to enhance the durability of such structures include (i) the incorporation of stabilizing agents in the phospholipid assembly (e.g., cholesterol[14] and tocophorol[15]); (ii) cross linking of constituent molecules in the assembly;[16] and (iii) tethering lipid bilayer architectures to solid supports.[1] Encapsulation in sugars has also been used to stabilize lipid assemblies toward freezing[17] and drying.[17,18] The encapsulation of phospholipid-based supramolecular assemblies in gels can preserve their biological function and provide enhanced thermal and mechanical stability. For example, agarose has been used to encapsulate and stabilize functional freestanding lipid bilayer architectures.[2] Such synthesis approaches are typically not amenable to the formation of nanoscopically thin protective layers around or on top of functional biomolecular assemblies. Ultrathin layers may be desirable, for example, in situations where rapid solute transport to and/or from the bioactive assembly is necessary for optimal function.

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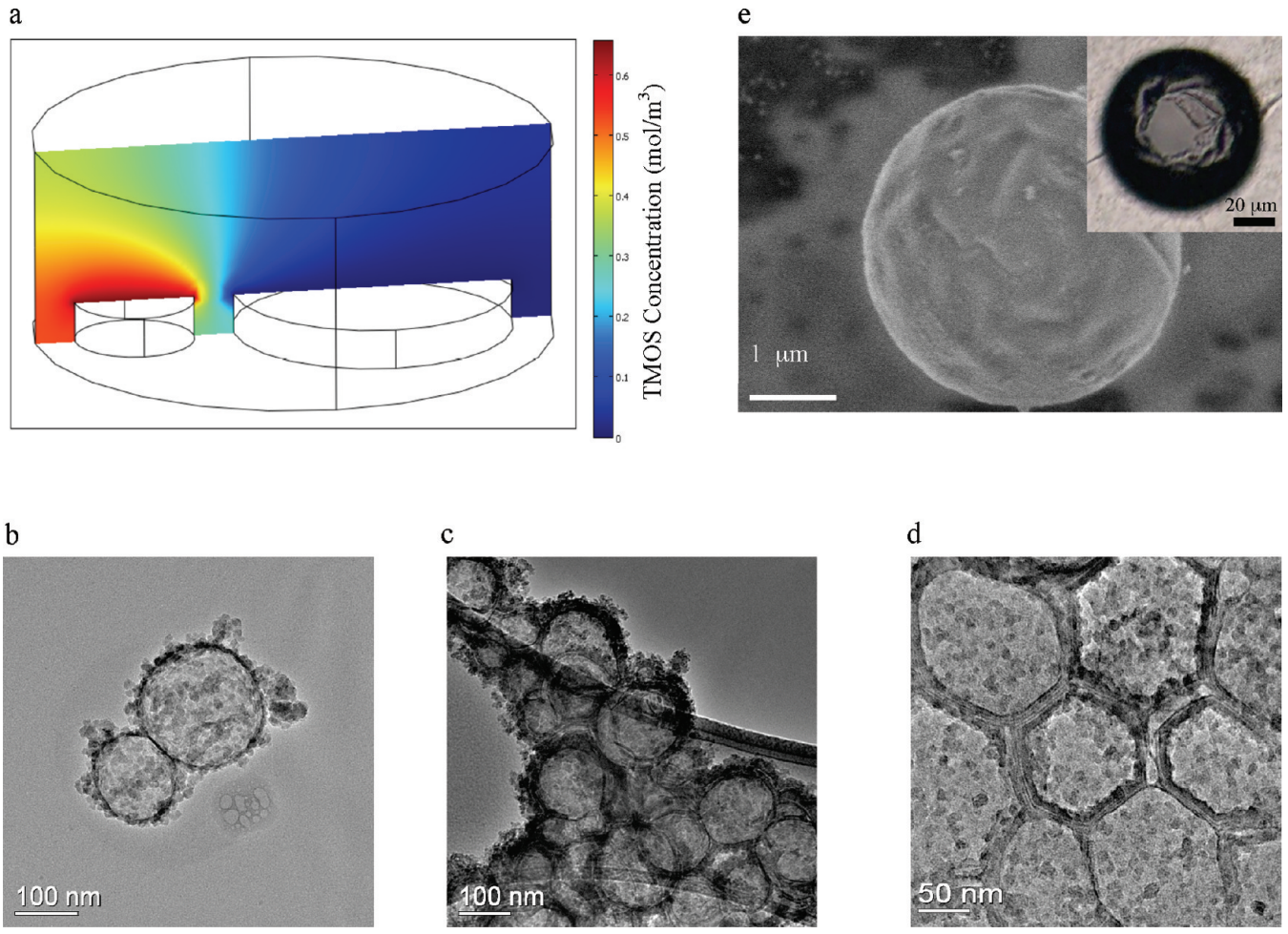

Figure 1. Encapsulation of supramolecular assemblies by the deposition of silica precursors into aqueous solutions. (a) Schematic of the reactor used to synthesize silica gels and the results of 3D finite element simulation of TMOS diffusion from the source container to the aqueous sink; within the reaction chamber (6.5 cm diameter, 2.5 cm height), TMOS is placed in a vessel (left) next to a vessel containing aqueous solution or suspensions of biomolecular assemblies (right). The steady-state concentration gradient of TMOS in the plane of symmetry of the reaction system is shown. (b, c) TEM images of thin silica shells obtained by deposition in a suspension of DMPC liposomes at a lipid concentration of 1 mg/mL. Exposure times are (b) 2 h and (c) 12 h. (d) TEM of gel obtained by the exposure of DMPC liposomes (10 mg/mL) for 12 h. The solution was not optically clear before exposure to silica precursors. (e) SEM image of a silica shell obtained after 2 h of exposure of air microbubbles stabilized by DMPC. (Inset) Optical image of a cracked microbubble.

Silica gels have been studied extensively as matrices for the encapsulation and stabilization of functional enzymes,[19] liposomes,[12,20,21] proteoliposomes,[6] and whole cells.[22] Whereas some of the methods that we describe below represent a new approach to sol−gel synthesis methods, sol−gel methods used previously to form such hybrid bioinorganic gels are generally more complex in comparison to the methods described herein because of the immiscibility of silica precursors (e.g., tetraethyl orthosilicate) and aqueous buffers that are used to solubilize or suspend active biomolecular architectures.[23] This inherent incompatibility has generally necessitated the development of two-step processes in which catalysts and products of precursor hydrolysis (typically ethanol) that are deleterious to biological structure and function must be removed from the reaction mixture before complex biomolecules and assemblies are introduced.[6,19] It is also often necessary to include polymers or other additives in the reaction mixture to make the gelation process more biocompatible.[23] By comparison, the CVD-based methods presented in this letter allow precise control of the delivery of precursors to aqueous solutions that can vary widely in pH and electrolyte concentration while limiting the exposure of biomolecules to methanol, which is the most volatile component in the reaction mixture.

We have developed a simple, one-step synthesis process that circumvents the above limitations of previous methods for the stabilization of functional suprabiomolecular assemblies. Though we focus here on the silica encapsulation of phospholipid-based architectures, the process is general and can be used to form a wide range of hybrid nano- and microcomposite materials. The process is based on low temperature, atmospheric pressure CVD of silica precursors in solutions, suspensions, and thin films containing biomolecular assemblies. To our knowledge, this is the first documented application of CVD in bulk liquid phases for material synthesis and for the direct encapsulation of functional supramolecular assemblies. Silica accumulation can occur preferentially at nanoscopic interfaces, and encapsulated biomolecular materials can retain their biological functionality (including lipid bilayer fluidity).

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Results and Discussion

The synthesis details of each hybrid material are provided in Supporting Information. In brief, for a standard gel synthesis, 10 mM sodium phosphate (pH 7.0) buffer was used in all encapsulation experiments unless otherwise specified. Buffer (2 mL) containing the relavent supramolecular assembly is placed in a 3.5-cm-diameter Petri dish. Tetramethyl orthosilicate (TMOS) (Sigma, 0.5 mL) was placed in a 1.5-cm-diameter Petri dish. Both dishes, one containing buffer and one containing the TMOS solution, were placed in a closed container (diameter = 6.5 cm, height = 2.5 cm) for 2 h at room temperature, unless otherwise specified.

Figure 1a quantitatively depicts the process of CVD of TMOS in an aqueous suspension containing biomolecular assemblies. Three-dimensional finite element simulation of the transient vapor diffusion process in the reaction chamber assumes that TMOS molecules impinging on the surface of the aqueous solution immediately hydrolyze (i.e., the aqueous solution is a perfect sink for TMOS). Simulation demonstrates that a stable steady-state concentration gradient is quickly established (in <100 s) between the TMOS source and the aqueous sink at room temperature (Figure S1) that leads to the deposition of material into the aqueous solution at a constant rate. For the system depicted, simulation with no adjustable parameters accurately predicts experimental mass uptake by the aqueous solution (Figure S1). This simple model can also predict the rate of deposition observed at different temperatures.

Provided that exposure to TMOS or other precursors is continued for a sufficient length of time, the entire aqueous volume will be converted to a silica gel. By controlling the time of exposure, pH, and electrolyte concentrations, the kinetics of gelation[24] and porosity (and thus opacity and solute transport characteristics of the gel) can be controlled (Figure S2). If a thin shell or a layer of silica is desired around a biomolecular assembly (rather than a bulk gel), then the time of exposure to the precursor source can be appropriately limited. It is likely that polymerized silica accumulates preferentially around phospholipid assemblies because of favorable electrostatic interaction and hydrogen bonding between silica-associated silanol groups and polar groups associated with the phospholipid assembly.[20,21]

Figure 1b,c shows TEM micrographs of silica structures resulting from CVD in an aqueous suspension of unilamellar liposomes ($\sim$100 nm diameter) at a concentration of 1 mg/mL via their exposure to vapors of TMOS at room temperature for 2 and 12 h, respectively. After 2 h, the liposome suspension remained liquid, but after 12 h, a soft gel was formed. Samples were subsequently dried and imaged. In both cases, the silica shells remained intact upon exposure to high vacuum. In contrast, liposomes exposed for 1 h or less resulted in ruptured shells upon TEM imaging (data not shown). These results indicate that CVD can result in the formation of thin silica shells or bulk gels around intact liposomes. These results demonstrate that this synthesis method also represents a facile staining technique for imaging the structure of liposomes (and perhaps other nanobiomaterials) by TEM that may represent a viable alternative to other painstaking techniques that use heavy metals or cryogenic preservation.[25] Early results from in vitro studies with Jurkat cells indicate that cells are capable of taking up silica-coated liposomes (Figure S3). Figure 1d shows a micrograph of material formed by exposing liposomes at a concentration of 10 mg/mL to vapors of TMOS for 12 h. A porous silica framework containing ordered multilamellar structures is visible, likely corresponding to the presence of ordered multilamellar lipid bilayers between which silica has polymerized. Hybrid materials containing phospholipid assemblies encapsulated in silica may be useful in a number of studies and applications,[11,23] including the study of active transport processes, as briefly described below.

Microbubbles stabilized by phospholipids are commonly used as ultrasound contrast agents and are currently being investigated for a number of medical applications including ultrasound-mediated drug and gene delivery.[11] A major challenge in the development of microbubbles in such applications is their instability.[26] Figure 1e shows an SEM micrograph of a silica structure formed by CVD of a suspension of air bubbles stabilized by phospholipids in a sucrose solution. The inset of Figure 1e shows an optical micrograph of a silica-encapsulated microbubble. We have examined the stability of such silica-coated bubbles to high pressure over time. Although air bubbles without silica coatings typically disappear under a pressure of 80 psig, silica-coated bubbles are much more stable. We observed that silica-coated microbubbles can remain even when exposed to higher pressures (at least 120 psig) and when stored for long periods of time (at least 6 months). In comparison, air bubbles in control samples are lost after 4 h. These results show that CVD can be an effective means to stabilize evanescent structures such as microbubbles. They also represent a new synthesis route to hollow silica particles.

Supramolecular assemblies with characteristic optical properties that are indicative of their intact structure are especially useful as probes for verifying the benign (or harsh) nature of encapsulation processes. As a first such example, we incorporated bacteriorhodopsin in the form of a purple membrane into proteoliposomes encapsulated in silica gels via CVD. We have observed that the structure of the holoprotein is sensitive to encapsulation conditions and that alcohols produced in conventional sol−gel synthesis procedures can induce the loss of the characteristic purple color of proteoliposomes containing bacteriorhodopsin.[27] As shown in the inset of Figure 2a, CVD results in the formation of gels that retain the characteristic purple color (similar to that observed for control purple membrane) over a period of 50 days.

The conservation of proteoliposome structure upon encapsulation can be probed by examining the light-activated proton-pumping capability of liposomes containing the purple membrane.[6] Figure 2a shows the light-induced pH change for gels encapsulating liposomes with and without bacteriorhodopsin. A clear and sustained reduction in pH was observed for hybrid gels containing bacteriorhodopsin (rate $= -6.6 \times 10^{-2}\ \Delta$ pH/min). A similar reduction in pH was observed for bacteriorphodosin-containing liposomes not encapsulated in silica, thus indicating the effectiveness of immobilization and the minimal effect of the porous shell on proton transport. By comparison, there is only a slight pH drop for gels without bacteriorhodopsin, which might be due to heating by the light source. Although the slight pH drop in the latter case is observed to be largely reversible, it is not for the samples with bacteriorhodopsin. These results provide further evidence that liposomes are not disrupted upon CVD and that hybrid gels that incorporate intact liposomes containing functional transmembrane proteins can easily be obtained.

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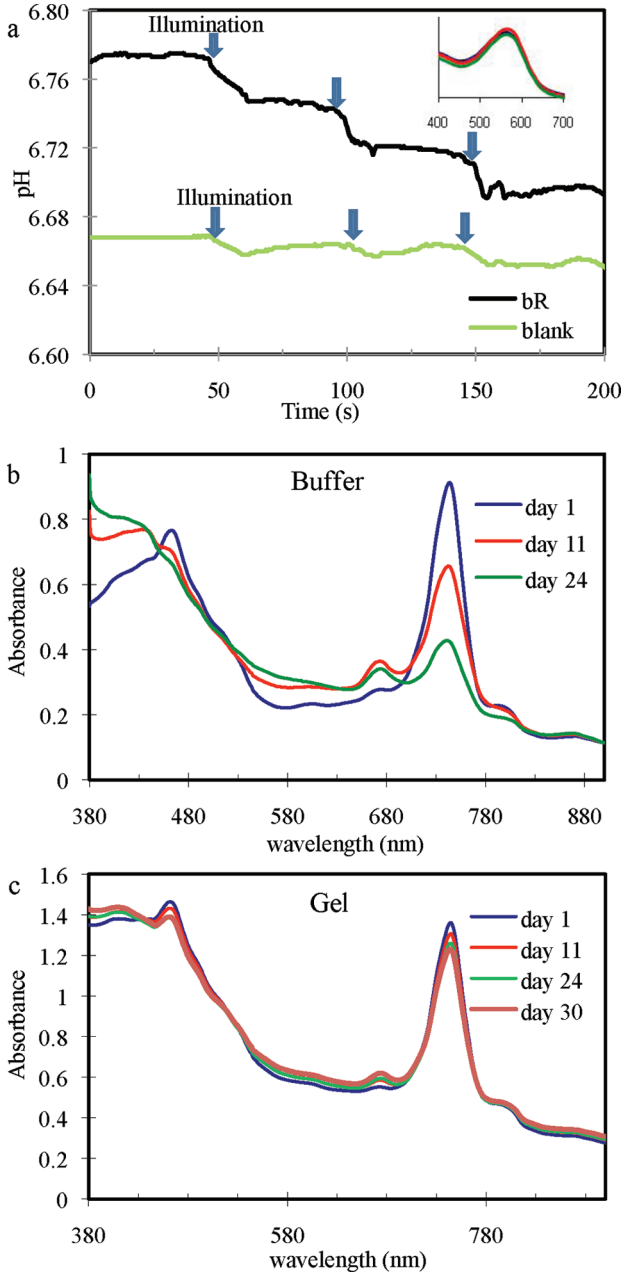

Figure 2. Stability and functionality of proteoliposomes and light-harvesting complexes in gels. (a) Electrochemical (pH) response of gelled liposomes (4:1 DOPE/ eggPC) with and without bacteriorhodopsin (purple membrane) upon excitation with light. The gels were kept in the dark for 1 h before electrochemical measurements were performed. The protons are pumped from inside of the liposomes to the exterior bulk gel. (Inset) UV−vis spectrum of the silica gels with the purple membrane (3, 12, and 50 days). Arrows indicate the onset of light exposure, which in each case lasted for 20 s. (b, c) UV−vis spectra of chlorosomes (light-harvesting complexes isolated from *Chloroflexus aurantiacus*) in buffer and in gels over a period of 30 days.

These results also point to the possibility to form hybrid materials that are capable of highly selective and active transport.

The second optically active biological assemblies that we examined are highly efficient light-harvesting antennae complexes, referred to as chlorosomes, isolated from the filamentous anoxygenic phototrophic bacterium *Chloroflexus aurantiacus*.[7] Chlorosomes contain intricately assembled bacteriochlorophyll (*bchl*) *c* chromophores (absorption at ~740 nm) encased in a lipid monolayer envelope and an integral membrane light-harvesting complex (the B795 baseplate) that contains *bchl a* coordinated by protein (characteristic absorption at ~795 nm). Figure 2b (day 1) shows the absorption spectrum of intact chlorosomes. An alteration in chlorosome structural membrane integrity results in noticeable decreases in the *bchl c* aggregate absorption at ~740 nm and corresponding rises in monomeric *bchl c* absorption at ~670 nm.[28] Figure 2b shows that, for chlorosomes kept in suspension at room temperature, noticeable reductions in absorbance for both *bchl c* aggregation and the baseplate can be observed within 11 days. Further reductions are evident by day 24, indicating, together with the concomitant increase in the absorption band at ~670 nm (monomeric *bchl c*), that significant chlorosome disruption has occurred. Continual baseline shifts, indicative of scattering due to chlorosome breakdown, are also observed but have been minimized by baseline correction at 900 nm for a comparison of chromophore peaks.

Figure 2c shows spectra of chlorosomes stabilized by CVD but otherwise kept under identical conditions to those studied in Figure 2b. After 30 days, spectral properties are preserved, indicating little to no change in chlorosome structural integrity. No spectral changes reminiscent of scattering due to breakdown can be observed as in Figure 2b, where no baseline correction was necessary. These data indicate that CVD is an effective means of stabilizing chlorosome components, including chromophore assemblies and integral membrane proteins of the baseplate. They also suggest a route for integrating chlorosomes as highly efficient antennae into light-harvesting devices.

Like particulate phospholipid assemblies, planar lipid membranes have received enormous attention as possible functional biomimetic materials. An important hallmark of cell membranes[29] and biomimetic planar lipid membranes[30] is lateral molecular diffusive mobility (fluidity). To examine the effect of encapsulation on membrane fluidity, we formed a supported lipid bilayer of POPC containing a small amount of a fluorescent phospholipid on a plasma-cleaned silicon wafer surface via vesicle fusion and subjected it to CVD for 2 h such that a silica gel (~5 mm in thickness) formed above the supported lipid bilayer. (See Supporting Information for details.) Figure 3 shows the results of a fluorescence recovery after photobleaching (FRAP) experiment conducted ~24 h after the formation of the gel. The bleached area recovers fluorescence over time at a rate ($D = 2.8 \pm 0.5\ \mu m^2/s$, mobile fraction ~50%) that is similar to that observed for uncoated supported POPC bilayers ($D = 2.9 \pm 0.3\ \mu m^2/s$, mobile fraction ~75%). This result suggests that the silica encapsulation of supported lipid bilayers can yield laterally diffusive assemblies while potentially enhancing the stability to allow a greater flexibility of manipulation than for typical untreated lipid bilayers, which are notoriously fragile. Further FRAP experiments have demonstrated that encapsulated lipid bilayers can remain diffusively fluid (although they often recover at slower rates) upon rehydration after storage under ambient conditions for long periods of time (at least 1 month) or after exposure to high temperatures (at least 90 °C).

Although we have focused here on phospholipid-based assemblies, the process is general and can be used to encapsulate and stabilize a wide range of biological materials including proteins (Figure S4) and cells in materials (shells, thin films, or bulk gels) that have controllable porosity, which allows solute access to the encapsulated biological species. Recent progress in cell-based

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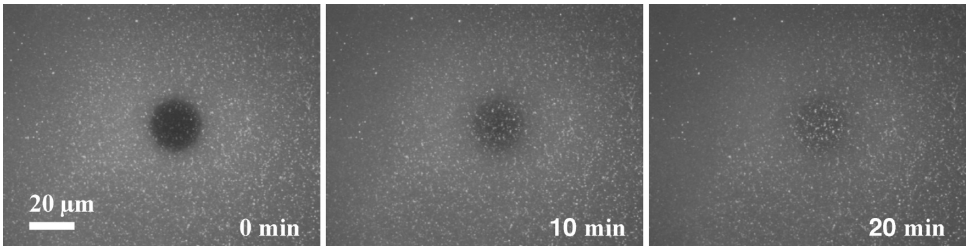

Figure 3. Fluidity of planar bilayers (POPC) in gels using fluorescence recovery photobleaching with laser excitation of 488 nm. Selected sequence of fluorescence images obtained from a lipid bilayer (with 0.1 mol % BODIPY-PC encapsulated in a silica network).

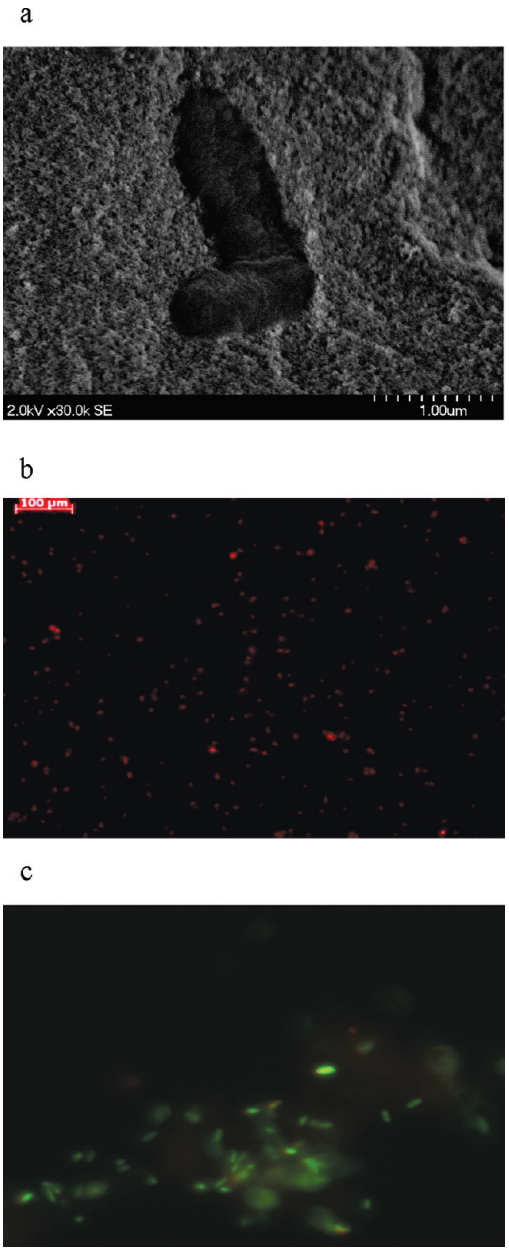

Figure 4. (a) SEM micrograph of cells encapsulated in silica gels. Epifluorescence images of *Pseudomonas aeruginosa* PAO1 obtained using SYTO 13 and 24 (green − all cells) and propidium iodide (red − dead cells) (b) without immobilization at 14 days and (c) after encapsulation at 100 days. The scale bar corresponds to 100 μm.

biotechnologies (e.g., bioreactors and cell-based biosensors) has generated a need for the development of new techniques for whole cell immobilization. A principal advantage of whole cell immobilization is that the cells can be stabilized with respect to degradation in adverse environments. In preliminary experiments, a marine bacterium, *Cobetia marina*, was encapsulated using the methods described above. Interestingly, it was found that such cells could survive for up to 1 month after encapsulation. Quantification of the fraction of cells that survived in this experiment was difficult because the high salt concentration needed in the media resulted in the formation of an opaque gel. We thus also examined cells that did not require a high salt concentration. We immobilized *Pseudomonas aeruginosa* PAO1 cells in the gels by exposing buffer (pH 7.0) to TMOS precursors for 2 h, followed by the addition of cells. Figure 4a shows an SEM micrograph of the resulting gels that clearly reveals the porous nature of the gels and the intimate contact of the gel and cell.

The survival of these cells was examined using a live−dead assay. SYTO 13 and 24 (green) permeate all cell membranes. Propidium iodide (red) permeates only cells with compromised membranes (i.e., dead cells). Fifty percent of the nonencapsulated cells survived after a period of 2 days in buffer (stored at 4 °C), and 90% of the cells died in a period of 2 weeks (Figure 4b). The cells encapsulated using the modified procedure survive for much longer periods of time. Ninety percent of the cells remain viable after 42 days of immobilization, and more than 80% of the cells remain viable 100 days after encapsulation (Figure 4c). Using this procedure, a soft gel is formed that can be disrupted by strong vortex mixing. Vortex-mixed gels containing bacteria were then returned to a rich nutrient medium (Tryptic Soy Broth), where they grew to a stationary phase in 18 h, thus confirming that at least some of the live cells retained their reproductive capacity. We note that when the PAO1 cell suspension is subjected to CVD directly, the cells are not stabilized and die at rates comparable to the control.

We present an exceedingly simple process for encapsulating phospholipid-based assemblies in thin silica layers or gels that stabilize the assemblies while allowing the preservation of their chemical, optical, electrical, and mechanical functions. The synthesis process is unique (i) in its simplicity, (ii) as the first application of chemical vapor deposition (CVD) in bulk liquids for materials synthesis, and (iii) in its applicability to the stabilization of a wide range of noncovalently assembled materials. The new implementation of CVD-based materials synthesis described accessible to nonspecialists and will have a significant impact by enabling the incorporation of delicate biological attributes into a host of functional hybrid nanomaterials. The process requires no specialized equipment, cosolvents, or additives and can be easily used to form a wide variety of gels, particles, thin films, and membranes. We are also investigating the use of this process as a general method of stabilizing a wide range of material assemblies that are not held together by covalent or ionic bonds. We are further examining the range of volatile precursors (inorganic and

organic) that can be implemented in CVD into liquids for nanomaterials synthesis.

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Supporting Information Available: Detailed synthesis procedures and characterization data for hybrid materials. This material is available free of charge via the Internet at http://pubs.acs.org.