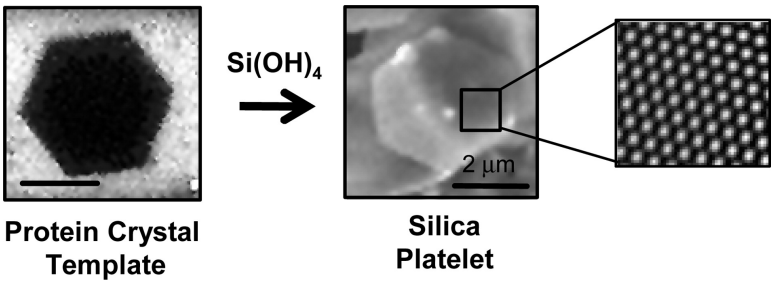
Article

Polypeptide-Templated Synthesis of Hexagonal Silica Platelets

Melanie M. Tomczak, Diana D. Glawe, Lawrence F. Drummy, Charles G. Lawrence, Morley O. Stone, Carole C. Perry, Darrin J. Pochan, Timothy J. Deming, and Rajesh R. Naik

J. Am. Chem. Soc., **2005**, 127 (36), 12577-12582• DOI: 10.1021/ja0524503 • Publication Date (Web): 19 August 2005



More About This Article

Additional resources and features associated with this article are available within the HTML version:

- Supporting Information
- Links to the 22 articles that cite this article, as of the time of this article download
- Access to high resolution figures
- Links to articles and content related to this article
- Copyright permission to reproduce figures and/or text from this article

View the Full Text HTML

J|A|C|S
ARTICLES
Published on Web 08/19/2005

Polypeptide-Templated Synthesis of Hexagonal Silica Platelets

Melanie M. Tomczak,[†] Diana D. Glawe,[‡] Lawrence F. Drummy,[†] Charles G. Lawrence,[†] Morley O. Stone,[†] Carole C. Perry,[§] Darrin J. Pochan,[||] Timothy J. Deming,[⊥] and Rajesh R. Naik*,[†]

Contribution from the Materials and Manufacturing Directorate, Air Force Research Laboratory, Dayton, Ohio 45433, Department of Engineering Science, Trinity University, San Antonio, Texas 78212, Department of Chemistry and Physics, The Nottingham Trent University, Nottingham NG11 8NS, U.K., Department of Materials Science and Engineering, University of Delaware, Newark, Delaware 19716, and Department of Bioengineering, University of California at Los Angeles, Los Angeles, California 90095

Received April 15, 2005; E-mail: rajesh.naik@wpafb.af.mil

Abstract: Several studies have demonstrated the use of biomimetic approaches in the synthesis of a variety of inorganic materials. Poly-L-lysine (PLL) promotes the precipitation of silica from a silicic acid solution within minutes. The molecular weight of PLL was found to affect the morphology of the resulting silica precipitate. Larger-molecular weight PLL produced hexagonal silica platelets, whereas spherical silica particles were obtained using low-molecular weight PLL. Here we report on the polypeptide secondary-structure transition that occurs during the silicification reaction. The formation of the hexagonal silica platelets is attributed to the PLL helical chains that are formed in the presence of monosilicic acid and phosphate ions. Hexagonal PLL crystals can also serve as templates in directing the growth of the silica in a manner that generates a largely mesoporous silica phase that is oriented with respect to the protein crystal template.

Introduction

The synthesis of inorganic materials using biomimetic approaches has become an important area of research. Biomimetic synthesis is a potential route for the synthesis of inorganic materials under mild conditions, and numerous studies have already demonstrated the use of biotemplates in the synthesis of inorganic materials.[1−6] In the biological world, the organic matrix (proteins, carbohydrates) plays an important role in the synthesis and morphology of inorganic materials.[1,2,5,6]

Proteins play an important role in synthesis of intricate silica structures in marine organisms such as sponges and diatoms. The silicatein[1] and silaffin[2] proteins identified in marine sponges and diatoms, respectively, are involved in the formation of the elegant silica structures observed in these organisms. Furthermore, the addition of silicatein or silaffin to a silicic acid precursor solution in vitro results in the formation of silica under ambient conditions.[1,2] These studies have been extended to show that synthetic peptides and polyamines can also be used to mimic the biosilicification reactions that occur in living organisms.[7−11] Biomimetic approaches have some distinctive advantages over the traditional sol−gel methods for the synthesis of silica. Most importantly, the benign reaction conditions and the ability to manipulate the (bio)template are key attributes that differentiate biomimetic approaches from traditional chemical methods.[12−16] The ability of organisms to carry out the biosilicification process in "one pot" has also led to the development of biomimetic strategies for the encapsulation of biomolecules and nanoparticles.[17−19]

[†] Air Force Research Laboratory.
[‡] Trinity University.
[§] The Nottingham Trent University.
[||] University of Delaware.
[⊥] University of California at Los Angeles.

(1) Cha, J. N.; Katsuhiko, K.; Zhou, Y.; Christiansen, S. C.; Chmelka, B. F.; Stucky, G. D.; Morse, D. E. *Proc. Natl. Acad. Sci. U.S.A.* **1999**, *96*, 361−365.
(2) Kroeger, N.; Deutzmann, R.; Sumper, M. *Science* **1999**, *286*, 1129−1132.
(3) Naik, R. R.; Stringer, S. J.; Agarwal, G.; Jones, S. E.; Stone, M. O. *Nat. Mater.* **2002**, *1*, 169−172.
(4) Lee, S.-W.; Mao, C.; Flynn, C. E.; Belcher, A. M. *Science* **2002**, *296*, 892−895.
(5) Shankar, S. S.; Rai, A.; Ankamwar, B.; Singh, A.; Ahmad, A.; Sastry, M. *Nat. Mater.* **2004**, *4*, 482−488.
(6) Perry, C. C.; Keeling-Tucker, T. *J. Biol. Inorg. Chem.* **2000**, *5*, 537−550.
(7) Coradin, T.; Durupthy, O.; Livage, J. *Langmuir* **2002**, *18*, 2331−2336.
(8) Naik, R. R.; Brott, L. L.; Clarson, S. J.; Stone, M. O. *J. Nanosci. Nanotechnol.* **2002**, *2*, 95−100.
(9) Patwardhan, S. V.; Mukherjee, N.; Steinitz-Kannan, M.; Clarson, S. J. *Chem. Commun.* **2003**, 1122−1123.
(10) Knecht, M. R.; Wright, D. W. *Langmuir* **2005**, *25*, 2058−2061.
(11) Coradin, T.; Livage, J. *Colloids Surf. B* **2001**, *21*, 329−336.
(12) Cha, J. N.; Stucky, G. D.; Morse, D. E.; Deming, T. J. *Nature* **2000**, *403*, 289−292.
(13) Naik, R. R.; Whitlock, P. W.; Rodriguez, F.; Brott, L. L.; Glawe, D. D.; Clarson, S. J.; Stone, M. O. *Chem. Commun.* **2003**, 238−239.
(14) Rodriguez, F.; Glawe, D. D.; Naik R. R.; Hallinan, K. P.; Stone, M. O. *Biomacromolecules* **2004**, *5*, 261−265.
(15) Glawe, D. D.; Rodriguez, F.; Stone, M. O.; Naik, R. R. *Langmuir* **2005**, *21*, 717−720.
(16) Coffman, E. A.; Melechko, A. V.; Allison, D. P.; Simpson, M. L.; Doktycz, M. J. *Langmuir* **2004**, *20*, 8431−8436.
(17) Luckarift, H. R.; Spain, J. C.; Naik, R. R.; Stone, M. O. *Nat. Biotechnol.* **2004**, *22*, 211−213.
(18) Naik, R. R.; Tomczak, M. M.; Luckarift, H. R.; Spain, J. C.; Stone, M. O. *Chem. Commun.* **2004**, 1684−1685.
(19) Roth, K. M.; Zhou, Y.; Yang, W.; Morse, D. E. *J. Am. Chem. Soc.* **2005**, *127*, 325−330.

10.1021/ja0524503 CCC: $30.25

Controlling the experimental conditions during the in vitro silicification reaction has been shown to affect the morphology of the silica product.[13,14] The inclusion of chemical additives[13] in the silicification reaction has been used to influence the overall morphology of the silica structures. Polypeptide secondary structure can be used as a means to tune the porosity of the silica structures using poly-L-lysine (PLL).[20] Another interesting observation is the effect of polymer chain length on the morphology of the resulting silica precipitate. Larger-molecular weight (long-chain) PLL has been shown to produce hexagonal silica platelets, whereas spherical silica particles are obtained when low-molecular weight (short-chain) PLL is used.[9,14−15] In this study we demonstrate that long-chain PLL undergoes a secondary structure transition in the presence of the silicate precursor and phosphate anions, resulting in the formation of helical chains. These helical PLL chains then pack into a hexagonal lattice as the silicification reaction proceeds, giving rise to fused silicified hexagonal platelets. When preformed hexagonal PLL crystals were used in the silicification reactions, the PLL crystals favor the growth of silica whose nanostructure follows that of the underlying protein template.

Experimental Section

All chemicals and poly-L-lysine hydrobromide were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). Poly-L-lysine (PLL) was resuspended at concentrations of 1.0 or 10 mg mL^{-1} in a solution of 0.1 M sodium phosphate buffer at pH 7.5 or 11.2. The average chain length of PLL was provided by the manufacturer. To the PLL solution (10 μL of 1−10 mg mL^{-1}) was added 80 μL of 0.1 M sodium phosphate buffer at pH 7.5 containing 50−100 mM silicic acid. The freshly prepared stock solution of silicic acid was obtained by the addition of 1700 μL of 1 mM HCl to 300 μL tetramethyl orthosilicate (99%, Sigma-Aldrich) and mixed for 5 min. Over the course of the silicification reaction, the pH of the reaction mixture remained fairly constant (Supporting Information Figure S1). Circular dichroism measurements were performed using a Jasco J-715 spectropolarimeter. The CD Pro software package was used to fit the spectrum and to deconvolute the data. For in situ CD measurements, the silicic acid was introduced to the cuvette containing PLL in sodium phosphate buffer. PLL crystals were grown from an aqueous solution of 0.2 M ammonium monohydrogen phosphate (AMP) buffer incubated overnight at room temperature[21] or in 0.1 M sodium phosphate buffer pH 7.5 at 4 °C. The PLL crystals grown in AMP buffer were dialyzed into 0.1 M sodium phosphate buffer pH 7.5 before use in the silicification reaction as described above. Scanning electron microscopy analysis was performed on FEI XL30 Environmental Scanning Microscope equipped with an EDAX Genesis elemental analysis system. High-resolution transmission electron microscopy (HRTEM) was performed using a Philips CM200 FEG TEM operating at 200 kV and equipped with a Noran Voyager energy-dispersive X-ray (EDX) analysis system.

Results and Discussion

When PLL (1 mg mL^{-1}) is added to a 50 mM silicic acid solution (hydrolyzed tetramethyl orthosilicate) in 0.1 M sodium phosphate buffer pH 7.5, a silica precipitate is formed within minutes (Figure 1). Other polyamines such as polyarginine and polyallylamine are also known to precipitate silica.[7,22,23] The proposed mode of action of PLL-mediated silica precipitation involves a combination of electrostatic interactions and hydrogen bonding between PLL and the negatively charged silicate species that bring in close proximity the reactive silicate precursors so that condensation can occur.[7,24] PLL chain length can be used to tune the silica morphology.[14,15] PLL chain lengths between 100 and 840 amino acid residues resulted in the formation of fused silica platelets. In contrast, PLL of chain lengths <100 amino acids gave rise to a network of fused silica spheres.[14,15] As shown in Figure 1B, addition of PLL_{222} (chain length = 222 amino acid residues) to the silicic acid solution in 0.1 M sodium phosphate buffer pH 7.5 resulted in the formation of fused platelets of silica (Figure 1B, inset). Closer examination of silica precipitate revealed the presence of hexagonal silica platelets that fuse to form the sheet structure. The width of the hexagonal silica platelet was anywhere between 0.5 and 5 μm and 18−30 nm in thickness. In comparison, silica structures obtained using PLL_{20} (chain length = 20 amino acid residues) exhibited spherical morphologies (Figure 1A). The hexagonal silica platelets obtained in our experiments are amorphous, similar to previously published reports.[9,14]

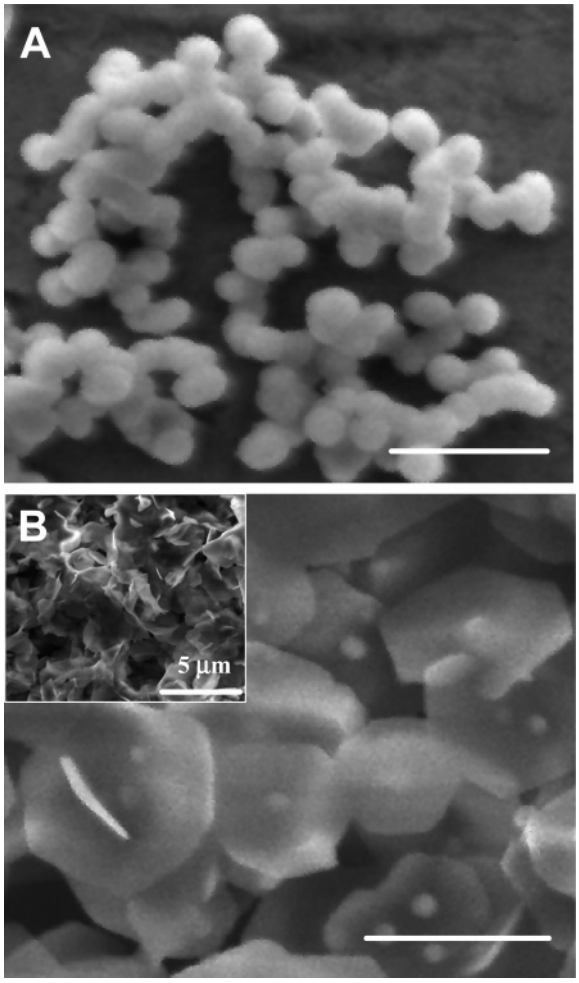


Figure 1. SEM micrographs of silica structures using PLL_{20} and PLL_{222}. (A) Network of fused silica spheres using PLL_{20}. (B) Hexagonal silica platelets obtained using PLL_{222}. Scale bar 2 μm. (Inset) Low-magnification micrograph showing the aggregation of PLL_{222}-derived silica platelets.

Interestingly, the morphology of the silica structure obtained using larger-molecular weight PLL resemble single crystals of

(20) Hawkins, K. M.; Wang, S. S.-S.; Ford, D. M.; Shantz, D. F. *J. Am. Chem. Soc.* **2004**, *126*, 9112−9119.
(21) Padden, F. J.; Keith, H. D.; Giannoni, G. *Biopolymers* **1969**, *7*, 793−804.
(22) Patwardhan, S. V.; Mukherjee, N.; Clarson, S. J. *J. Inorg. Organomet. Polym.* **2001**, *11*, 193−198.
(23) Mizutani, T.; Nagase, H. H.; Fujiwara, N.; Ogoshi, H. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 2017.
(24) Coradin, T.; Lopez, P. J. *ChemBioChem* **2003**, *4*, 251−259.

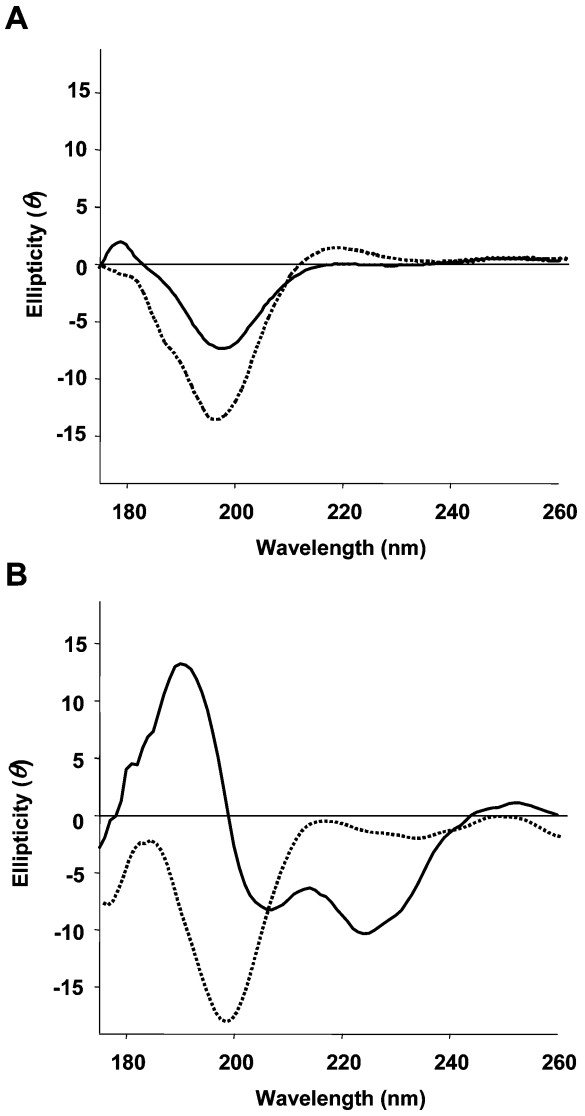


Figure 2. Circular dichroism spectra of (A) PLL_{20} and (B) PLL_{222} in sodium phosphate buffer pH 7.5 (dotted line) or pH 11.2 (solid line).

PLL previously described by Padden and co-workers[21,25] and more recently by the Pochan and Deming groups using PLL_{200} (chain length = 200).[26,27] The formation of hexagonal PLL crystals is suggested to occur due to the supramolecular assembly of α-helical chains of PLL that assemble in the presence of phosphate counterions. Supramolecular assembly failed to occur in solutions when PLL was either in the random coil or β-sheet conformation.[26]

The secondary structure of proteins is commonly determined using circular dichroism (CD) spectroscopy. PLL can adopt three different secondary conformations depending on pH and temperature.[28,29] PLL adopts a random coil conformation at pH 7.0, an α-helical conformation at pH 11, and a β-sheet structure after heating to 52 °C.[29] The CD spectra of the two PLL representative chain lengths used in this study at pH 7.5 and pH 11 are shown in Figure 2. The shorter-chain PLL_{20} adopts a random coil conformation in both pH 7.5 and pH 11 (phosphate buffer solutions), as evidenced by the minima around 200 nm (Figure 2A). In comparison, the longer-chain PLL_{222} assumes a random

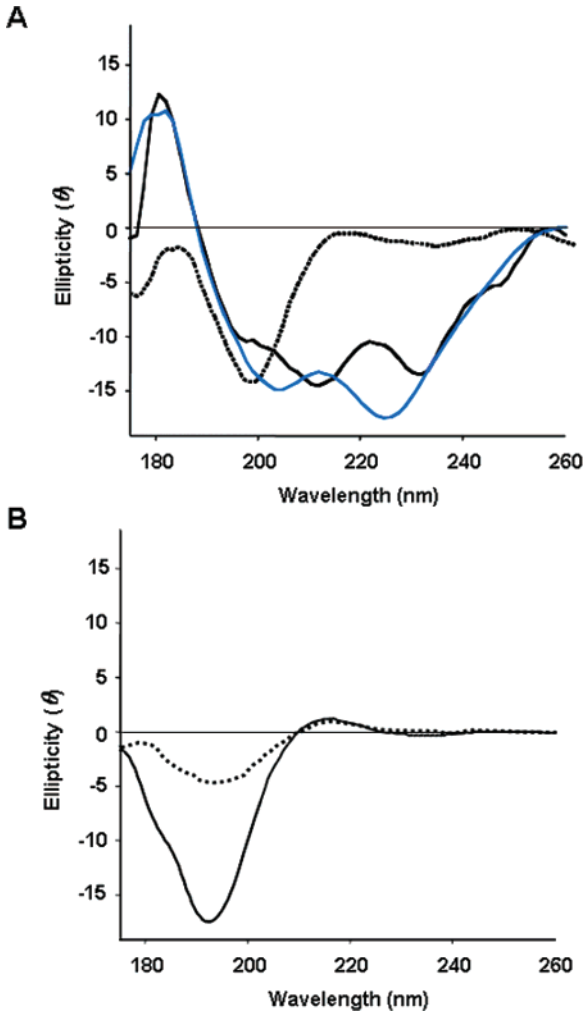


Figure 3. In situ circular dichroism spectra of PLL_{222} in the presence of silicic acid in sodium phosphate buffer pH 7.5 at $t = 0$ (dotted line), 0.5 min (solid line), and 1 min (blue line). (B) In situ CD spectra of PLL_{20} in the presence of silicic acid at $t = 0$ (dotted line) and $t = 1$ min (solid line).

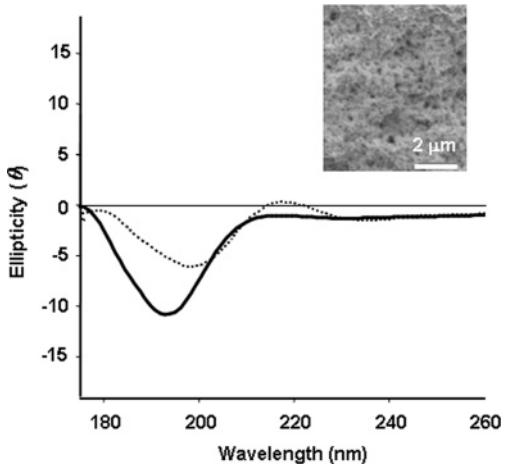


Figure 4. In situ circular dichroism spectra of PLL_{222} in the absence (dotted line) or in the presence (solid line) of silicic acid in 10 mM Tris buffer pH 7.5. (Inset) SEM micrograph of the silica precipitate obtained using PLL_{222} in Tris buffer.

(25) Padden, F. J.; Keith, H. D. *J. Appl. Phys.* **1965**, *36*, 2987−2995.
(26) Cui, H.; Thompson, J.; Nowak, A. P.; Deming, T. J.; Pochan, D. J. *Polym. Mater. Sci. Eng.* **2004**, *91*, 461.
(27) Cui, H.; Krikorian, V.; Thompson, J.; Nowak, A. P.; Deming, T. J.; Pochan, D. J. *Macromolecules* **2005**, *38*, DOI 10.1021/ma050776q.
(28) Satoh, M.; Hirose, T.; Komiyama, J. *Polymer* **1993**, *34*, 4762.
(29) Grigsby, J. J.; Blanch, H. W.; Prausnitz, J. M. *Biophys. Chem.* **2002**, *99*, 107−116.

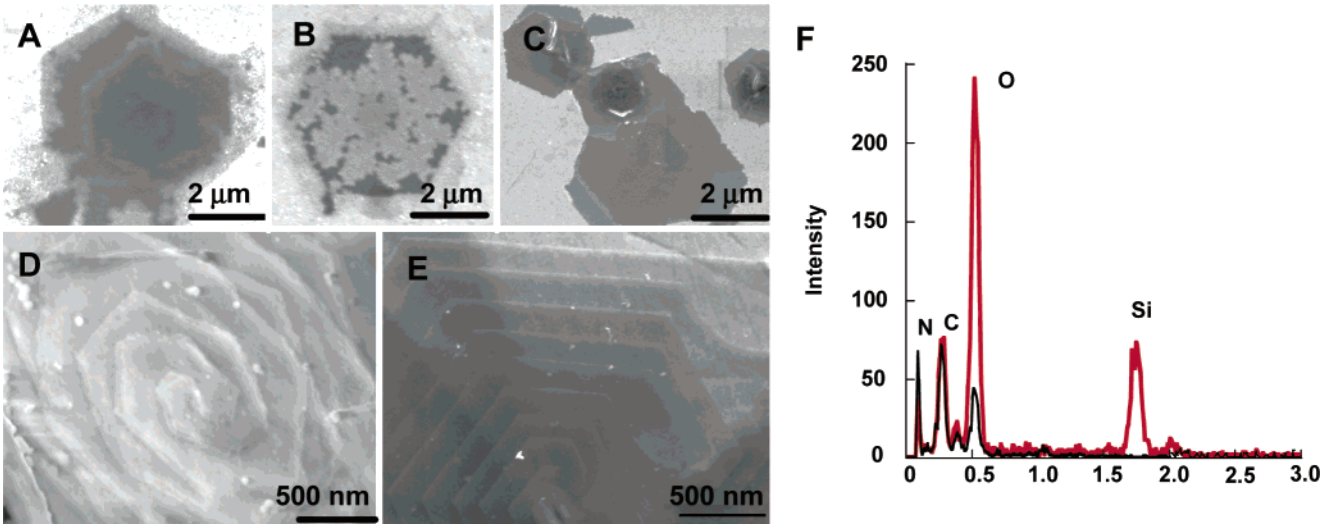


Figure 5. (A) SEM micrograph of PLL_{222} crystals. (B) SEM micrograph showing the sensitivity of the PLL crystal to the electron beam upon extended exposure. (C) SEM micrograph of PLL crystals after the silicification reaction. (D, E) Higher-resolution SEM micrograph of the silica-coated PLL structures that retain the multilamellar (with a central screw dislocation) features of the PLL protein crystal. (F) Elemental analysis of PLL crystal (black line), same as in (A) and the PLL crystals after silicification (red line) same as in (C).

coil conformation at pH 7.5 but is predominantly α-helical at pH 11.2, as evidenced by the two well-defined minima at 205 and 222 nm (Figure 2B). This result suggests that, in the case of PLL_{222}, the polypeptide does not assume a helical conformation under the buffer conditions used for the silicification reaction (pH 7.5).

We next performed in situ CD measurements of PLL_{222} in the presence of the silicate precursor (silicic acid). This was done to determine whether the addition of silicic acid affects the secondary structure of PLL_{222}. As seen in Figure 3A, the in situ CD measurements in the presence of silicic acid showed a dramatic change in the secondary structure of PLL_{222}. PLL_{222} undergoes a random coil to helix transition when silicic acid is introduced into the phosphate buffer solution (pH 7.5). The helical content based on the deconvolution of the CD spectrum using a standard software tool was estimated to be ~80% in the presence of silicic acid and <30% in the absence of silicic acid. The CD spectra after the first minute were unobtainable since the silicification reaction proceeds rapidly and the solution quickly becomes opaque due to the presence of silica particles. In contrast, in situ measurements of phosphate-buffered PLL_{20} solution in the presence of silicic acid under identical solution conditions showed no significant secondary structure transition (Figure 3B). The short-chain PLL fails to form helical chains even in the presence of the negatively charged silicate precursor.

In situ CD measurements of the silicification reaction using PLL_{222} in the absence of phosphate buffer showed that PLL_{222} failed to undergo a secondary structure transition into a helical conformation (Figure 4). Therefore, the secondary structure transition at pH 7.5 of PLL_{222} from a random coil to a predominantly α-helix occurs only in the presence of the silicate precursor and phosphate. Unlike polyamine-directed silicification,[30] PLL_{222} in the absence of phosphate ions did exhibit silica-precipitating activity, albeit at reduced levels. The silica precipitate was composed of a network of spherical nanoparticles (Figure 4, inset). On the basis of these results, we determined that phosphate ions are necessary but not sufficient for inducing

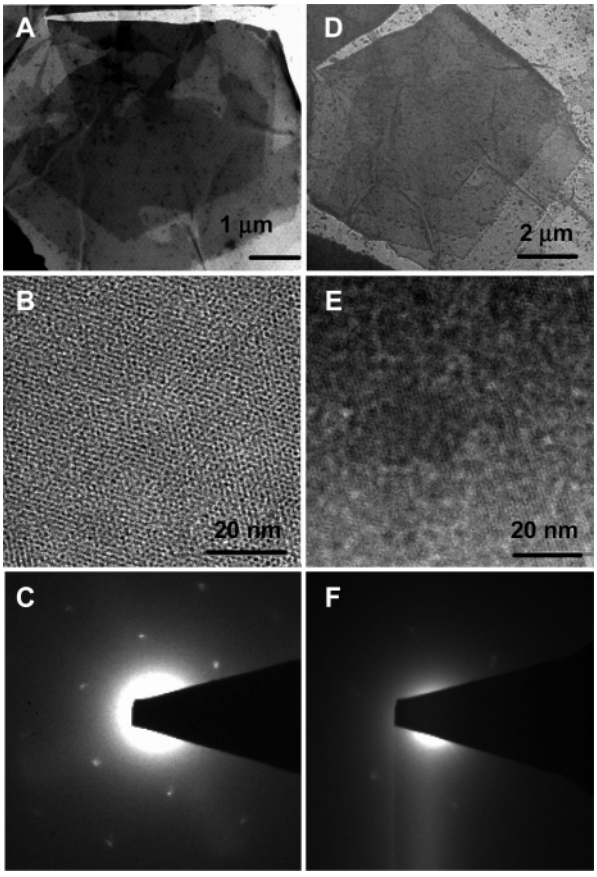


Figure 6. (A) TEM micrographs of a silica-coated PLL_{222} crystal before calcination. (B) High-resolution TEM micrograph of the PLL_{222} crystal before calcination. (C) Electron diffraction patterns of the silicified platelets with measured *d* spacing of (100) = 1.52 nm, (110) = 0.87 nm, (200) = 0.76 nm. (D) TEM micrograph of the PLL_{222} crystal after calcination at 300 °C for 2 h in air. (E) High-resolution TEM micrograph of the silicified PLL_{222} crystal after calcination. (F) Electron diffraction pattern of the calcined platelets showing only the (100) planes.

the α-helical transition of PLL_{222} at neutral pH and require the presence of the negatively charged silicate precursor. PLL[31] and polyallylamine (PAA)[32] can be induced into spherical assemblies

(30) Sumper, M.; Lorenz, S.; Brunner, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 5192−5195.

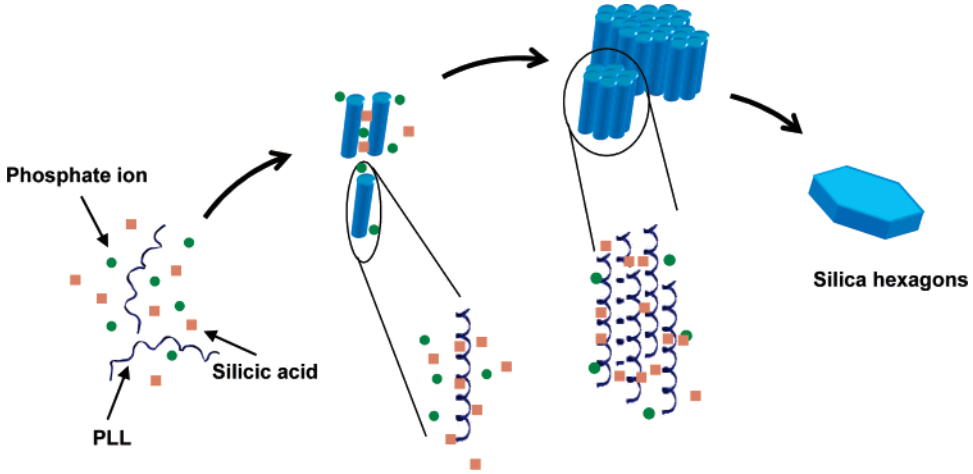


Figure 7. Proposed model for the formation of hexagonal silica platelets.

in the presence of counterions, which in turn exhibit silica-precipitating activity to produce silica spheres. In our case, long-chain PLL can be induced into a helical conformation in the presence of the silicate precursor and phosphate anions, which eventually results in the formation of hexagonal silica platelets.

Polypeptides and other silica-templating peptides have been previously shown to be entrapped within the silica matrix.[13,18,31] Thermogravimetric analysis (TGA) of the PLL_{222}-derived silica platelets shows that they contain ~20%/wt polypeptide. This suggests that PLL polypeptide chains are entrapped with silica matrix. Following this notion, we determined whether preformed hexagonal PLL crystals could serve as templates in the silicification reaction. PLL_{222} crystals were grown as previously described.[21,26,27] Figure 5A shows a SEM micrograph of the hexagonal crystals of PLL_{222}. Both lamellar and multilamellar hexagonal crystals of varying sizes could be observed in the SEM micrographs, similar to those in previously published reports.[21,26,27] We also observed that, in some cases, drying the crystals from aqueous suspension results in distortion and collapse of the crystals. In addition, the crystals also appeared to be sensitive to the electron beam. Prolonged exposure of the PLL_{222} crystal resulted in electron beam damage (Figure 5B).

The preformed PLL crystals were exposed to silicic acid to determine the silica-precipitating activity of the crystals. As shown in Figure 5, C-E, the PLL crystals become covered with silica during the silicification reaction, and EDX analysis confirmed the presence of a silica coating on the PLL crystal (Figure 5F). The silicified PLL crystals were also further analyzed by TEM. The TEM micrographs show that the hexagonal silica-coated PLL crystal appears to be mesoporous (Figure 6B). The *d* spacings of the silicified hexagonal platelets were calculated from the electron diffraction pattern to be 1.52, 0.87, and 0.76 nm corresponding to the (100), (110), and (200) planes, respectively, with a lattice parameter of $a = 1.76$ nm (Figure 6C). This diffraction pattern does not correspond to any of the silica polymorphs but rather reflects the *d* spacings of the underlying PLL crystal.[21,26,27] Similar behavior has also been observed for the templated formation of crystalline silica using plant bioextracts.[33,34] It should be noted that the crystallinity of the silica platelets could be attributed to that the fact that the silicification reaction is restricted to the surface of the preformed PLL crystal unlike that with the PLL polypeptide that results in amorphous hexagonal plates.[9,14]

The lattice parameter of the PLL crystals dried from solution in our study was measured to be around 0.92 nm (Supporting Information Figure S2), much smaller than the previously measured lattice parameters of hydrated or freeze-dried PLL crystals.[21,27] Most likely, the crystals in our study are defective due to dehydration of the crystal, during imaging, that resulted in the collapse of the PLL side chains. In contrast, the silicified PLL crystals maintain their integrity due to the presence of a silica coating, and possibly due to the infiltration of the silicic acid into the interstices that effectively result in the cross-linking of the neighboring PLL chains. PLL crystals have been shown to be porous and can allow for the infiltration of small molecules.[21,27] Therefore, the PLL crystals can swell and change their lattice spacing depending on hydration, presence of counterions, and infiltration of silicate precursors into the crystal lattice. The silica platelets retain the shape and features of the underlying protein template after calcination in air. The electron diffraction pattern of the calcined platelet shows the (100) planes only (Figure 6D), and the *a* parameter of the hexagonal unit cell was calculated to be 1.59 nm. Although this suggests that lattice does shrink slightly when the protein template is removed, the silica platelet does retain the shape and mesoporous features of the crystal template. Retention of the meso/nanoporous structure in the calcined platelet suggests that the silicate precursor was also able to infiltrate the PLL crystal lattice.

Together, our results suggest that long-chain PLL undergoes a rapid secondary-structure transition from a random coil to a helical structure in the presence of silicic acid and phosphate ions. The negatively charged silicate precursor, along with phosphate ions, allows for the secondary-structure phase transition of PLL to occur at neutral pH. The formation of the helical PLL chains during the silicification reaction results in the formation of hexagonal silica platelets. Preformed PLL hexagonal crystals can also serve as templates to direct the growth of a mesoporous silica phase that is oriented in respect of the protein crystal template.

(31) McKenna, B. J.; Birkedal, H.; Bartl, M. H.; Deming, T. J.; Stucky, G. D. *Angew. Chem., Int. Ed.* **2004**, *43*, 5652−5655.
(32) Brunner, E.; Lutz, K.; Sumper, M. *Phys. Chem. Chem. Phys.* **2004**, *6*, 854−857.
(33) Keeling-Tucker, T.; Perry, C. C. *Chem. Commun.* **1998**, 2587−2588.
(34) Perry, C. C.; Keeling-Tucker, T. *Colloid Polym. Sci.* **2003**, *281*, 652−664.

Conclusions

Our proposed model for the formation of hexagonal silica platelets is shown in Figure 7. We propose that PLL polypeptide backbone interacts with the silicate species (monomers or small oligomers) in the solution via hydrogen bonding and electrostatic interactions. The interactions between PLL and the negatively charged silicate species can bring in close proximity neighboring reactive silicate precursors present on the polypeptide backbone or on neighboring PLL polypeptide chains so that condensation is favored. The condensation reaction between neighboring silicate precursors would in turn promote the formation of intramolecular hydrogen bonding on the polypeptide backbone, causing PLL to zip into a helical conformation. It reasonable to assume that the formation of ionic interactions, hydrogen bonding, and siloxane bridges across the polypeptide chains also facilitates the secondary structure transition. In addition, these interactions may also lead to cross-linking of the PLL chains. It is important to note that the rate of silica condensation is rapid at neutral pH. The combination of all the above results in the packing of the PLL chains into a hexagonal lattice as the silicification reaction proceeds. The presence of an inorganic network does significantly affect chain packing since the long-chain PLL may be able to accommodate defects. In contrast, low-molecular weight or short-chain PLL (<100 residues) are unstable and fail to adopt a helical structure since the number of intramolecular hydrogen bonds may not be sufficient to stabilize the helical structure. Further investigations are currently underway to verify our model. Results obtained with PLL crystals suggest that the protein crystals can serve as templates in the silicification reaction, and the mesoporous silica structures obtained retain the features of the protein crystal template. In conclusion, our results provide an insight into the role of polypeptide secondary structure in the formation of hexagonal silica platelets, and the use of homopolymer crystals as templates in the synthesis of mesoporous inorganic materials.

Acknowledgment. Funding for this work was provided by the Air Force Office of Scientific Research (R.N and C.C.P) and the National Science Foundation (D.J.P. and T.J.D.).

Supporting Information Available: The pH of silicification reaction, TEM micrograph of PLL crystal, and the electron diffraction pattern, and high-resolution TEM and Fourier filtered image of the silicified silica platelet. This material is available free of charge via the Internet at http://pubs.acs.org

JA0524503