resonance frequency 307–367 Hz, Digital Instruments). Solution UV-vis spectra were obtained on a HP 8452A diode array spectrophotometer. Spatially resolved UV-vis microextinction measurements were performed using a previously published procedure [56]. EDX spectra were obtained on a Hitachi 4500 FE-SEM operating at 20 kV. A He–Ne laser (λ = 632.8 nm, 5 mW, Uniphase) was used for the diffraction measurements. A digital zoom camera (Kodak) was used to capture the diffraction pattern.

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Fast Magic-Angle Spinning and Double-Quantum ^{1}H Solid-State NMR Spectroscopy of Polyelectrolyte Multilayers[**]

By *Leonard N. J. Rodriguez*, *Susan M. De Paul*, *Christopher J. Barrett*, *Linda Reven*,[*] and *Hans W. Spiess*[*]

The alternate adsorption of anionic and cationic polymers has become an increasingly important method for producing uniform thin polymer films.[1] Since a wide variety of charged molecules and polymers are amenable to this approach, polyelectrolyte multilayers (PEMs) are being explored for applications ranging from photonics to enzyme immobilization.

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The ability to reproducibly control the thickness of the layers through variation of preparative parameters such as the ionic strength is another attractive feature. Although flat surfaces are most commonly employed, non-planar substrates are being increasingly used. In particular, Möhwald and co-workers have deposited a wide variety of polyelectrolyte films on latex spheres and have shown that even enzymes can be encapsulated by this method.[2]

Although there has been considerable progress towards understanding the microscopic structure of these films through techniques such as neutron scattering,[3] the polymer chain conformation and dynamics have not been directly probed. The dependence of the film structure (stratification, thickness) on various preparative parameters is usually rationalized in terms of their effect on chain conformation and mobility. The charge overcompensation, observed through ζ potential measurements, is attributed to the presence of dangling loops and tails in the outermost polymer layer. The flaccidity of the layer adjacent to the aqueous phase can then lead to deep interpenetration of the next polyelectrolyte layer, resulting in a non-stratified film.[1,3] The nonlinear growth of multilayer films close to the substrate is also interpreted in terms of a roughening of the polymer/polymer interface, which creates a progressively larger number of adsorption sites for subsequently deposited layers. The formation of thick layers in the presence of salt has been explained by charge screening, which leads to the adsorption of polymer coils rather than extended chains.[3,4]

Solid-state nuclear magnetic resonance (NMR) techniques are regularly used to characterize the chain conformation and mobility in bulk polymers.[5] Although ^{1}H NMR has the advantage of the highest signal sensitivity, it has the disadvantage of poor resolution in organic solids. Therefore ^{13}C NMR has normally been employed to obtain high-resolution spectra of solid polymers. However, relatively few solid-state ^{13}C NMR studies have been carried out on adsorbed polymers due to sensitivity problems.[6] The recent introduction of very fast magic-angle spinning (MAS) NMR probes now permits high-resolution solid-state ^{1}H NMR spectra to be routinely obtained. In addition, multiple-quantum techniques have been developed to measure proton–proton proximities and to probe polymer chain conformation and dynamics.[7–10] In this communication, we demonstrate the application of these new techniques to probe the structure of PEMs deposited onto silica colloids.

Multilayers of poly(diallyldimethylammonium chloride) (PDADMAC) and poly(sodium 4-styrenesulfonate) (PSS) were deposited onto silica colloids using a procedure developed by Donath and co-workers that employs extensive washing and centrifugation to remove any unadsorbed polymer.[2a] The ζ-potential measurements, carried out after each layer was deposited, showed the expected surface charge reversal of the silica colloids as the outermost layer alternated between the cationic PDADMAC and the anionic PSS. A 1:1 PSS/PDADMAC polyelectrolyte complex (PEC) was produced by precipitation from an aqueous solution.

In Figure 1a, the solid-state ^{1}H MAS NMR spectra of the bulk polymers and complex are compared to a four layer PEM deposited on silica colloids. In addition to the signals of the respective polymers (vide infra) adsorbed water peaks in PSS and PDADMAC are detected with chemical shifts of 3.66 and 4.29 ppm, respectively. The water in the PSS/PDADMAC complex shifts to an intermediate value of 3.85 ppm. In the spectrum of the PEM on silica, two sharp peaks are observed: a strong peak at 4.9 ppm for protons associated with the silica surface and a second peak at 3.85 ppm assigned to water adsorbed within the multilayer film. The peak at 3.85 ppm was observed to increase in intensity and shift slightly downfield (~0.3 ppm) when the sample was stored under ambient conditions, due to further uptake of water. The 3.85 ppm peaks and most of the peak at 5 ppm from the silica substrate disappeared when the complex and multilayer samples were dried under vacuum at 100 °C. A neutron reflectometry study of PSS/polydiallylamine (PAH) multilayers determined that

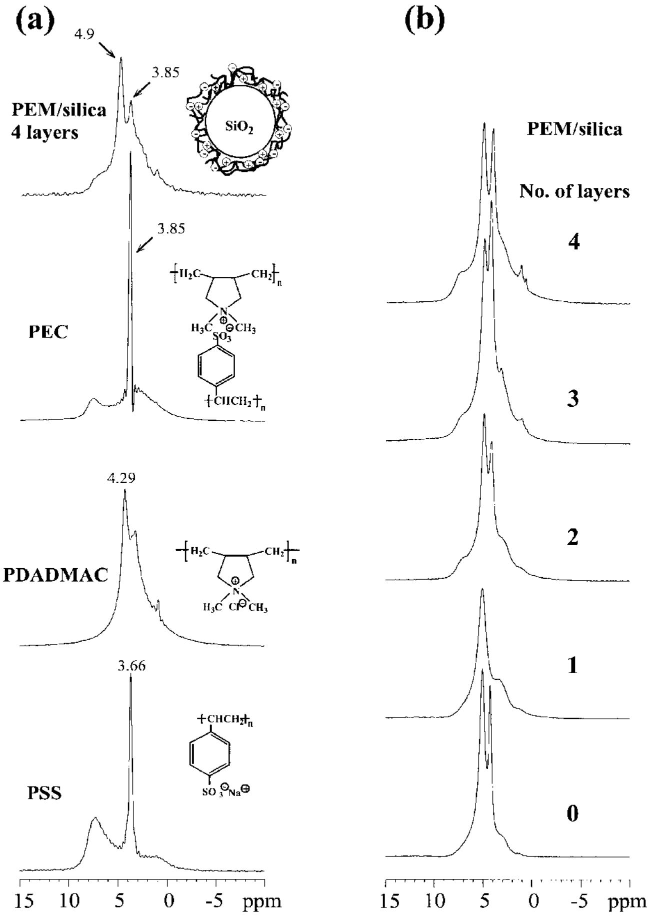

Fig. 1. a) ^{1}H MAS NMR spectra, recorded with a spinning frequency of 30 kHz, of PSS, PDADMAC, the 1:1 PSS/PDADMAC PEC, and the PSS/PDADMAC multilayers on silica colloids (PEM/silica). The chemical shifts of the adsorbed water are indicated. b) ^{1}H MAS NMR spectra at 30 kHz of the bare silica colloids (layer 0), silica colloids with adsorbed PDADMAC (layer 1), silica colloids with one layer each of adsorbed PDADMAC and PSS (layer 2), silica colloids with sequential adsorption of PDADMAC, PSS, and PDADMAC (layer 3), and silica colloids with sequential adsorption of PDADMAC, PSS, PDADMAC, and PSS (layer 4).

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twice as much water, volume-wise, is associated with PSS as with PAH.[3] Our observed value of 3.85 ppm, assuming that the water is in rapid exchange within the complex, suggests that PSS/PDADMAC complexes behave similarly (2/3(3.66) + 1/3(4.29) = 3.87 ppm).

The conventional single-quantum solid-state ^{1}H MAS NMR spectra for the bare silica and for different numbers of polymer layers are given in Figure 1b. The bare silica has two strong signals at 5.0 and 4.0 ppm and a shoulder at 3.0 ppm. Previous ^{1}H MAS NMR studies of hydrated silica samples detected peaks at 5.0, 4.1, 3.5, and 2.0 ppm, which are respectively assigned to hydrogen-bonded silanols, liquid-like water without any direct interaction with the silica surface, physisorbed water, and isolated silanols.[11] The position of the 4.1 ppm water peak observed in humidified silica samples was proposed to be due to rapid proton exchange between liquid-like water (4.9 ppm) and the physisorbed water (3.5 ppm).[11] When the first layer of PDADMAC is deposited, the peak at 4.0 ppm vanishes and the peak at 5 ppm broadens, presumably due to displacement and/or rearrangement of surface water. A peak at 4.0 ppm reappears when PSS is added as layer 2. This peak shifts slightly downfield when PDADMAC is added as layer 3 and upfield again when the last layer of PSS is added. Based on these observations, we tentatively assign this peak to water associated with the polymer or water in rapid exchange with water associated with the polymer. However, the nature of the water and silanol peaks will need to be further explored with dried and deuterium-exchanged samples.

In Figure 2, the double-quantum-filtered (DQF) solid-state ^{1}H MAS NMR spectra of the bulk polymers, polyelectrolyte complex and multilayers are shown. In the presence of fast MAS, dipolar couplings between proton pairs can be detected through the excitation and reconversion of double-quantum (DQ) coherences, which are not directly observable, to single quantum coherences, which can be detected. Due to the r^{-6} dependence of the integrated DQ intensity, the appearance of a signal in the ^{1}H DQ-MAS NMR experiment indicates an effective proton–proton distance less than r = 0.35 nm.[7] In addition to establishing proton–proton connectivities, ^{1}H DQ-MAS NMR can be used to probe dynamics.[10] The more mobile components have smaller dipolar couplings and reduced intensities in DQF ^{1}H NMR spectra acquired with short excitation periods. The back-to-back (BABA) recoupling pulse sequence, which efficiently generates double quantum coherences in the presence of very fast MAS, was used.[9] The DQ filter strongly suppresses the signals from the mobile adsorbed water and the silanol groups. Two different DQ excitation periods are shown in Figure 2 to demonstrate the effectiveness of this technique to filter out overlapping resonances. One rotor period of BABA excitation, τ_{EXC}, is usually sufficient to maximize the signals of the most strongly coupled proton pairs (usually rigid methylene groups) and these signals will rapidly decay with increasing excitation times.[10] In Figure 2a, the ^{1}H DQF NMR spectrum of bulk PSS using one BABA cycle, τ_{EXC} = 33.3 µs, shows strong resonances for both the aromatic (7.5 ppm) and methylene (1.3 ppm) protons. When two BABA cycles are used, τ_{EXC} = 66.7 µs, the methylene resonance has almost completely decayed, leaving only the signal from the more weakly dipolar coupled aromatic protons. However, the peak at 3 ppm in the PDADMAC (primarily due to the methyl protons) remains. The net result is a complete separation of the peaks arising from the two different polymers in the ^{1}H DQF NMR spectra of the PEC and PEM/silica. Note also that the chemical shift of the methyl groups in PDADMAC at 3 ppm is significantly shifted from the CH_2 groups at 1.3 ppm.

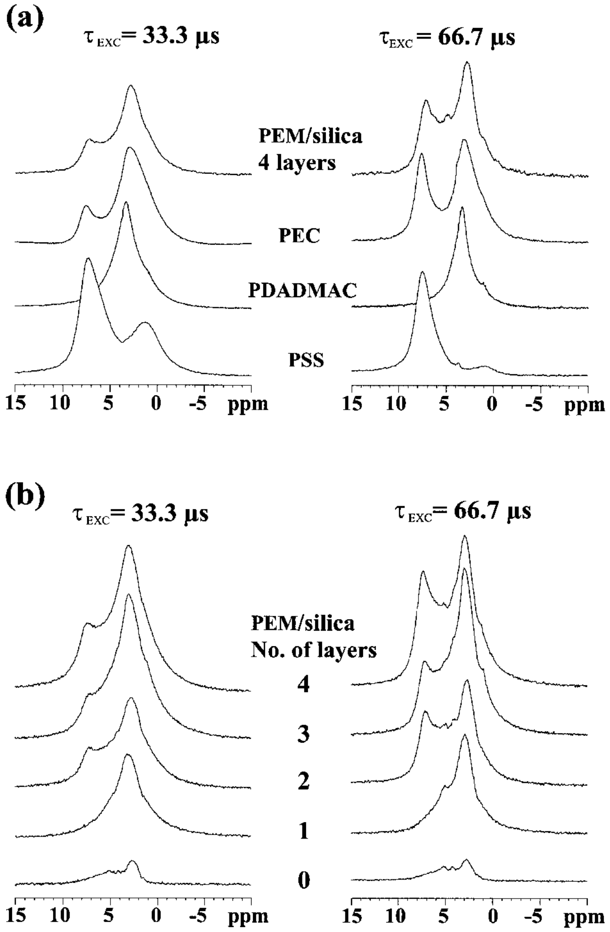

Fig. 2. ^{1}H DQF MAS NMR spectra, recorded with a spinning frequency of 30 kHz, of a) PSS, PDADMAC, the PEC, and the PSS/PDADMAC multilayers on silica colloids (PEM/silica) and b) layers 0 through 4 of the PEM/silica. Spectra acquired with one-rotor-period, τ_{EXC} = 33.3 µs, and two-rotor-period, τ_{EXC} = 66.7 µs, BABA recoupling sequences, are shown.

The ^{1}H DQF NMR spectra of the four layer PEM/silica sample in Figure 2a resemble those of the PEC, apart from intensity variations of the two dominant peaks and the presence of a small peak at 5 ppm from protons on the silica in the former for τ_{EXC} = 66.7 µs. Since the ^{1}H DQF NMR intensities depend on the size of the individual dipolar couplings, changes in the relative intensities between the PDADMAC and PSS components in the bulk PEC versus the PEM/silica may be due to differences in the chain mobilities. Solid-state ^{13}C cross polarization (CP) MAS NMR spectra (not shown) indicate that relative amounts of PSS and PDADMAC in the four layer sample are similar to the bulk PEC. However, since the ^{13}C CP MAS intensities also depend on the relative mobilities of different components, careful calibration of the cross polarization efficiencies would be required for an accurate quantitative analysis.[5]

In Figure 2b, the layer-by-layer growth of the multilayer is observed in the ^{1}H DQF NMR spectra of layers 0–4, acquired under identical conditions. The DQ filter greatly attenuates the contribution of water at the silica substrate and in the layers. The adsorption of a single layer of PDADMAC gives a peak at 3 ppm. In layer 2, the intensity of the 3 ppm PDADMAC peak remains similar that of layer 1, but a peak at 7.5 ppm appears due to the addition of one layer of PSS. In layer 3, the intensity of the PDADMAC peak again increases with the intensity of the PSS remaining constant relative to layer 2. Layers 2 and 4 are quite similar in appearance with the overall signal intensity of layer 4 being greater. This alternation of the relative intensities of the two polymers corresponds well to the observed charge reversal in the ζ potential measurements as subsequent layers are added. However, as mentioned above, a quantitative analysis is not possible since the chain mobilities, and thus the DQ efficiencies, may change as more layers are added.

In Figure 3, the 2D DQF spectra of the PEC and four layer PEM/silica acquired with τ_{EXC} = 66.7 µs are compared. These 2D spectra relate the single-quantum spectrum in the F2 (direct) dimension with the double quantum spectrum in the F1 (indirect) dimension. DQ resonances between two protons with the same chemical shifts (autocorrelation peaks) appear in the F1 dimension at twice the single-quantum chemical shift. DQ coherences between chemically inequivalent protons give rise to peaks at the sum of the two chemical shifts. The resonances along the diagonal (F1, F2) at 15.0, 7.5 ppm and at 6.0, 3.0 ppm are the autocorrelation peaks of PSS and PDADMAC, respectively. The off-diagonal peak visible at 10.5, 7.5 ppm is assigned to a double-quantum coherence between an aromatic proton of PSS and a methyl proton of PDADMAC. Since such coherences will only arise if the proton–proton distances are less than 3.5 Å, the appearance of this cross peak is strong proof of the intimate contact between the two polymers in the complex. The companion cross peak at 10.5, 3 ppm, which is not resolved at ambient temperature due to the large intensity of the PDADMAC autocorrelation peak at 6, 3 ppm, becomes visible upon heating the sample to ~70 °C. Note that a small cross peak between the aromatic and aliphatic protons at 8.8, 7.3 ppm is observed in the 2D DQ NMR of pure PSS only when the sample is completely dry, but the intensity is significantly suppressed due to the long excitation time. A 2D DQ NMR spectrum of the PEC was also recorded using a shorter excitation time (τ_{EXC} = 33.3 µs). A weak, unresolved shoulder at ~9, 7.5 ppm was present, presumably due to a contribution from the aromatic and aliphatic protons in PSS. Although the signal-to-noise is much weaker in the case of the adsorbed multilayer film, a cross peak at 10.5, 7.5 ppm is clearly visible and shows that the PSS and PDADMAC are also strongly complexed in the PEM/silica. This ^{1}H NMR manifestation of the complexation between the two polymers is useful in view of the fact that no significant change of the ^{13}C chemical shifts of PSS and PDADMAC occurs with complexation.

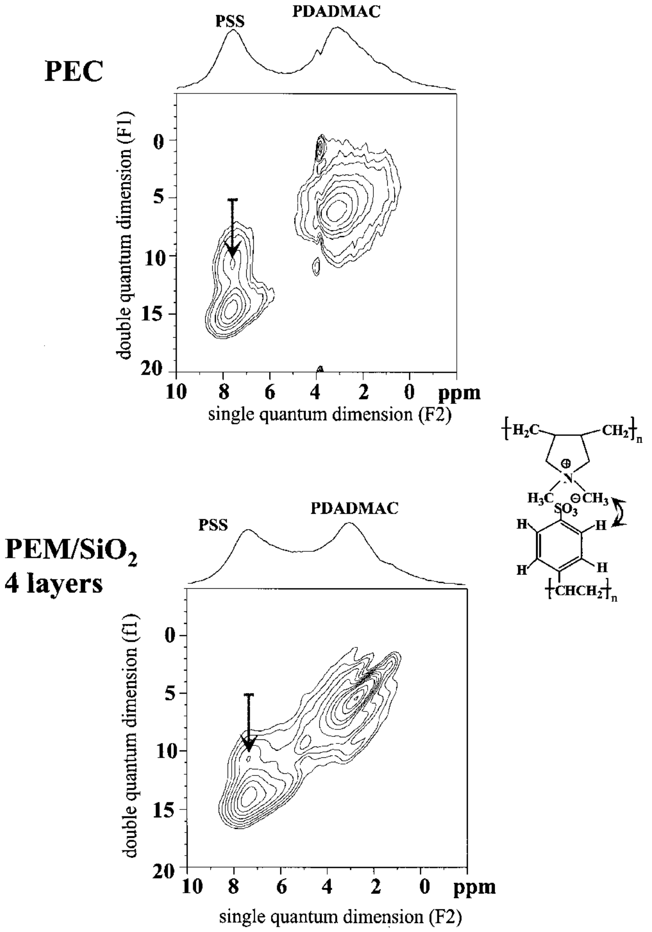

Fig. 3. 2D ^{1}H DQ MAS NMR spectra of the PEC and the PSS/PDADMAC multilayers on silica colloids (PEM/silica) recorded at 30 kHz using the BABA recoupling sequence with τ_{EXC} = 66.7 µs. The integrated intensities over the F1 dimension are shown on the top of each spectrum. Some T_1 noise at 3.85 ppm due to incomplete suppression of the water signal is present in the spectrum of the PEC.

To summarize, we report here the direct observation of the complexation between the two polymers in PEMs and show that the water associated with the multilayers can be distinguished in the single-quantum spectra and suppressed in the DQF spectra. These initial NMR results are consistent with other studies of PEM films. Dubas and Schlenoff also concluded, after using a variety of less direct experimental probes, that PSS/PDADMAC PEMs are structurally identical to the bulk PSS/PDADMAC PECs.[12] Future studies of PEMs using high-resolution ^{1}H solid-state NMR methods will focus on investigating the structure and dynamics as a function of number of layers, various preparative parameters, water content, and weak versus strong polyelectrolyte combinations.

Experimental

Sample Preparations: Multilayers of PDADMAC (M_w = 200K–350K g/mol, Aldrich), and PSS (M_w = 70 000 g/mol, Aldrich) were deposited onto silica colloids (Snowtex, nominal diameter 70–100 nm). 3 g of silica colloid, previously dried for 12 h at 400 °C, was dispersed in 500 mL of a polymer/salt solution, comprised of 0.02 M PDADMAC and 0.1 M NaCl in Millipore Q water. This adsorption solution was left standing for 30 min, then centrifuged at 4300 rpm and the supernatant was removed. 500 mL water was added and the solution was sonicated and centrifuged. The supernatant was then removed to rinse the unadsorbed polyelectrolyte from the colloids. A total of three 500 mL washings were performed after the adsorption of each polymer layer. A small amount (~50 mg) of the coated colloid was then removed for characterization and dried at 65 °C for 12 h prior to measurement. The remaining colloid was then dispersed in 500 mL of a similar solution of the oppositely charged polymer (0.02 M PSS and 0.1 M NaCl), and the adsorption and washing steps repeated, until two layers of PDADMAC and two layers of PSS had been sequentially deposited. An insoluble PEC for reference was prepared by adding 2 mL of 20 wt.-% PDADMAC aqueous solution slowly to 200 mL of a 0.01 M PSS solution, under vigorous stirring. A precipitate formed immediately as a thick milky suspension in solution. This solution was centrifuged, and the supernatant removed by pipette. To remove uncomplexed polyelectrolyte, the complex was then washed with water, agitated to disperse, and centrifuged again as described for the colloids, for a total of three washings.

ζ-Potential Measurements: 30 mg of each dried colloid sample was suspended in 15 mL of 1 mM NaCl solution. The pH of each solution was found to be in the range of 7.4 to 7.7 for the multilayered samples, and 8.2 for the bare silica colloid. Electrophoretic mobilities were measured on a Microelectrophoresis Apparatus Mk II (Rank Brothers, Bottingham) and converted to ζ potentials using the Smoluchowski equation.

NMR Measurements: ^{13}C CP MAS NMR of the carbon spectra were recorded on a Chemagnetics CMX-300 spectrometer for the colloid coated with four layers, the precipitated complex, and both bulk polyelectrolytes. A total suppression of sidebands (TOSS) sequence with background suppression, a spinning speed of 3 kHz, and a contact time of 500 μs were used. Single- and double-quantum ^{1}H MAS NMR spectra were acquired either on a Bruker ASX500 or DRX700 spectrometer equipped with a 2.5 mm fast MAS probe.

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Silica Nanotubes and Nanofiber Arrays**

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The synthesis of one-dimensional nanostructures is of fundamental importance to nanotechnology. Nanowires are particularly interesting as they offer the opportunity to investigate electrical and thermal transport processes in size-confined systems, with the possibility of providing a deep understanding of physics at the nano-scale. Silicon and silica nanostructures have attracted considerable attention because of their potential application in mesoscopic research, the development of nanodevices, and the potential use of large surface area structures for catalysis.[1] Recently Lueber,[2] Lee,[3] Yu,[4] Korgel,[5] and co-workers have extrapolated on the vapor–liquid–solid (VLS) technique[6] employing variants of laser ablation and high-pressure synthesis to produce silica-sheathed crystalline silicon nanowires. Lee et al.[3] have shown that oxides play a dominant role in the nucleation and growth of these semiconductor nanowires by laser ablation, thermal evaporation, and chemical vapor deposition. Lieber et al.[7] have used catalyst-initiated growth to synthesize silicon–carbon nanotube heterojunctions. Zhu et al. have recently grown silica "nanoflowers".[8] We[9] have applied the techniques of high temperature synthesis to modify the approach of Lee et al.[3] and generate virtually defect-free SiO_2-sheathed crystalline silicon nanowires and silica (SiO_2) nanospheres which can be agglomerated to wire-like configurations impregnated with crystalline silicon nanospheres. Side-by-side biaxial nanowires of SiO_2–SiC have also been synthesized.[10] In the present report, we demonstrate that this nanoagglomeration can be extended to produce SiO_2 nanowire "bundles" and "brush-like" arrays. The growth appears to be dominated by vapor-phase processes, as the oxides can form a variety of interesting new nanostructures including silica nanobrushes and nanotubes.

The growth of the silica structures initiates from nanofibers composed of tiny amorphous particles. Aligned fiber arrays appear to grow from a single or biaxial nanofiber (Fig. 1a), and have a structure similar to a protozoa and its "flagellum". The width of the bundle is 300–500 nm. We observe that, after reaching a certain length, the silica fibers in the interior of the bundle cease growth while those in the outer regions continue to grow, forming a cylindrical chamber. Energy dispersive X-ray spectroscopy reveals small crystalline Si nanoparticles

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