Mimicking Biosintering: The Identification of Highly Condensed Surfaces in Bioinspired Silica Materials

Joseph R. H. Manning, Brant Walkley, John L. Provis, and Siddharth V. Patwardhan*
additive’s initial incorporation and subsequent removal. By comparing this against amine-free industrially precipitated silica (IPS) and IPS, which has been exposed to additive, we show the lasting impact additive has on silica polymerization and how this may relate to other nanocomposite silica materials.

### EXPERIMENTAL SECTION

#### Silica Synthesis and Modification

Silica was synthesized according to methods previously published by the authors. Briefly, solutions of sodium silicate pentahydrate (Fisher Scientific, technical grade) and pentaerythritolhexahexamine (PEHA; Sigma-Aldrich, technical grade) were separately prepared corresponding to final reaction concentrations of 30 mM each of Si and N. These were then mixed, neutralized in a single step using 1 M HCl (Fisher scientific, stabilized), and allowed to react for 5 min under stirring.

After 5 min, 1 M HCl was further added to the silica coagulum to reduce the pH from 7 to either 5 or 2. After the pH had subsequently stabilized (ca. 1 min unless otherwise noted), the samples were isolated by centrifugation at 5000g for 15 min. The supernatant was then decanted, and this centrifugation procedure was repeated twice using deionized water to wash the samples of any salts and unreacted reagents. After the last wash, the supernatant was decanted, and the silica was allowed to dry in an oven at 80 °C overnight.

For the IPS samples, 100 mg of premade silica (Grace, Syloid AL-1 FP grade) was suspended in 100 mL deionized water. The samples were titrated using 1 M HCl and 2 M NaOH (prepared from sodium hydroxide pellets, Fisher Scientific, analytical grade) to the same pH as for the BIS materials. Because of the low initial electrolyte concentration, the pH was allowed to equilibrate overnight before separation, followed by washing and drying as described above.

Premade IPS was also exposed to PEHA to assess any impact the additive has on the surface chemistry of premade silica. This was performed at two concentrations; one in which the additive concentration was approximately equal to that used in the BIS synthesis procedure and the other in which the additive concentration was significantly higher. For the lower concentration, 100 mg of IPS was added to 95 mL of 5 mM PEHA solution (corresponding to 30 mM dissolved nitrogen, as before). This suspension was then neutralized with 1 N H₂SO₄, and the final volume made up to 100 mL. The higher concentration was prepared by suspending 100 mg of IPS in 0.5 mL of 250 mM PEHA solution, which was then neutralized as before and made up to a total volume of 2 mL. Solutions were aged for 1 h using magnetic stirrer bars before being left to stand for a further 18 h at an ambient temperature (ca. 20 °C) and isolated as described for BIS. For comparison, as-made BIS samples containing PEHA were also aged overnight, and CHN experiments were performed on these “aged-BIS” samples as described previously (see ref 35).

#### Solid-State NMR Experiments

Solid-state single pulse ²⁹Si MAS NMR and ¹H−²⁹Si CP MAS NMR spectra were acquired on a Bruker AVANCE III HD 500 spectrometer at 11.7 T. ²⁹Si MAS NMR spectra were acquired using a 4 μs nonselective (π/2) excitation pulse, a measured 90 s relaxation delay, a total of 256 scans, and spinning at 12.5 kHz. ¹H−²⁹Si CP MAS NMR experiments were performed using the same instrument with a spinning frequency of 12.5 kHz, a 20 μs nonselective (π/2) pulse width of 4.0 μs, an initial ¹H nonselective (π/2) pulse width of 2.5 μs, a recycle delay of 3 s, and Hartmann–Hahn contact periods of 2 ms. A nominal ¹H decoupling field strength of 80 kHz was employed during acquisition and 1456 scans were collected per experiment. ¹H MAS NMR spectra were acquired using a 2.5 μs nonselective (π/2) excitation pulse, a single scan, and spinning at 12.5 kHz. All ²⁹Si spectra were referenced to tetramethylsilane (TMS) at 0 ppm, and all ¹H spectra were referenced to liquid H₂O at 4.7 ppm. Gaussian peak profiles were used to deconvolute the ²⁹Si MAS NMR and ¹H−²⁹Si CP MAS NMR spectra. The minimum possible number of peaks were fitted, and the chemical shift (δₚₑ㎜) and peak full width at half maximum (fwhm)
of each resonance were required to be consistent in both the $^{29}\text{Si}$ MAS NMR and $^1\text{H}$–$^{29}\text{Si}$ CP MAS NMR spectra. When fitting the data, $\delta_{\text{iso}}$ and $\delta_{\text{ppm}}$ were held constant for each site within the same sample (i.e., only peak intensity was allowed to vary). NMR parameters for all spectra are shown in Table S1–S4 for BIS, aged BIS, IPS, and modified IPS respectively.

### RESULTS AND DISCUSSION

$^{29}\text{Si}$ MAS NMR. BIS was synthesized by room-temperature precipitation at pH 7 using PEHA as a bioinspired additive. These samples of IPS were acidified to change the surface charge and hence PEHA surface concentration in the case of BIS (see Supporting Information and ref 35 for details). Samples were therefore titrated to pH 7 (corresponding to as-made BIS), pH 5 (partial PEHA removal), and pH 2 (full PEHA removal). These were then analyzed by $^{29}\text{Si}$ MAS NMR to study how PEHA removal affected the silica structure itself (Figure 1, below). $^{29}\text{Si}$ MAS NMR enables distinction between these and samples of IPS were acidiﬁed to change the surface charge and hence PEHA surface concentration in the case of BIS (see Supporting Information and ref 35 for details). Samples were therefore titrated to pH 7 (corresponding to as-made BIS), pH 5 (partial PEHA removal), and pH 2 (full PEHA removal). These were then analyzed by $^{29}\text{Si}$ MAS NMR to study how PEHA removal affected the silica structure itself (Figure 1, below). $^{29}\text{Si}$ MAS NMR enables distinction between

![Figure 1](https://dx.doi.org/10.1021/acs.langmuir.0c03261)

Figure 1. $^{29}\text{Si}$ single-pulse MAS NMR spectra for (A) BIS and (B) IPS washed at pH 7 (top), 5 (middle), and 2 (bottom) and associated deconvolutions. Overlaid are representative schemes (adapted from ref 31) of BIS: silica primary particles (gray circles) containing PEHA molecules (red lines) at as-made concentration (top), partially extracted (middle), and fully extracted (bottom). The NMR spectra shown are for the original data (black), individual resonance contributions (green), fitted sum of individual contributions (red), and residual (blue).

fully saturated silicon centers ($Q^4$ at $\delta_{\text{iso}} = -110 \text{ ppm}$) with singly hydroxylated ($Q^3$, ca. $\delta_{\text{iso}} = -100 \text{ ppm}$) and doubly hydroxylated ($Q^2$, ca. $\delta_{\text{iso}} = -90 \text{ ppm}$) Si centers and hence quantiﬁcation of their relative abundance in the material. From this, the degree of polymerization in BIS was observed to be higher than that in industrial silica (Table 1). This is unexpected, as polymerization of silica from $Q^3$ to $Q^4$ is generally considered to occur through syneresis— the slow condensation of silica to expel water from the framework— which should be more prevalent in the industrial silica material because of its signiﬁcantly longer reaction times (2–3 h vs 5 min)$^{12}$ and similar micron-scale aggregate sizes compared to BIS. Upon modification of pH, the surface Si speciation of IPS changed slightly to include fewer $Q^2$ sites (from 55% relative abundance at pH 7 to 48% relative abundance at pH 2) and correspondingly more $Q^3$ and $Q^2$ sites (Figure 2). This is in good agreement with previous studies on the acid treatment of precipitated silicas, which found an increase in $Q^3$ relative abundance of up to 10% under similar conditions. For BIS, such pH-based changes were not seen ($Q^4$ sites remained at approximately 60% relative abundance across all pH values).

PEHA has been shown to be effective at “passivating” silica surfaces to prevent dissolution in undersaturated Si solutions. Therefore, IPS modification with PEHA was attempted to observe its effect on the surface chemistry of premade silica and determine if the difference in measured $Q^3$ ratios resulted from the presence of PEHA in solution or was intrinsic to the BIS materials. To ensure direct comparison between modified

![Figure 2](https://dx.doi.org/10.1021/acs.langmuir.0c03261)

Figure 2. Relative abundance of Si $Q^3$ species (determined from the $^{29}\text{Si}$ single-pulse MAS NMR spectral deconvolutions) against extraction pH for IPS (open shapes) and BIS (filled) silica materials (with greater degree of extraction at lower pH). Overlaid bars are equivalent relative abundance for PEHA-modified IPS materials. Black squares represent $Q^3$ species, red circles represent $Q^2$ species, and blue triangles represent $Q^4$ species.

Table 1. Comparison of Relative Peak Integral Areas for Silicon Species within IPS and BIS Materials against pH for Both Single-Pulse $^{29}\text{Si}$ MAS NMR and $^1\text{H}$–$^{29}\text{Si}$ CP MAS NMR Data

| Relative peak area (%) | pH 7—precipitated | pH 7—bioinspired | pH 7—bioinspired (aged 24 h) | pH 5—precipitated | pH 5—bioinspired | pH 2—precipitated | pH 2—bioinspired |
|------------------------|-------------------|-----------------|-----------------------------|-------------------|------------------|------------------|-----------------|
| $Q^4$                  | 6 14              | 7 12            | 4 ± 0 12 ± 1                | 8 20              | 5 8              | 9 20             | 5 13            |
| $Q^3$                  | 39 77             | 34 47           | 32 ± 1 65 ± 1              | 42 71             | 34 53            | 43 72            | 33 69           |
| $Q^2$                  | 55 9              | 59 41           | 64 ± 1 17 ± 1              | 50 9              | 61 39            | 48 9             | 62 18           |

“Error bars are one standard deviation around the mean (n = 3 silica samples), rounded to the nearest integer.”

https://dx.doi.org/10.1021/acs.langmuir.0c03261
Langmuir 2021, 37, 561–568
IPS and BIS, more BIS samples were synthesized and aged at ca. pH 7 for a similar time (i.e., untreated for 24 h) prior to isolation.

After exposing IPS to PEHA, the relative Q^4 concentration was again slightly lowered, compared to the pH 7 sample (from 59 to 48 or 53% relative abundance at low and high [PEHA], respectively, see Table S3), with concurrent increases in Q^2 and Q^3 prevalence. This runs counter to the stabilization observed in the previous study, although the effect could be due to higher overall [Si] (ca. 30 mM herein, cf. 1 mM in ref 44) or higher ionic strength during IPS modification (see Table S5). Regardless, it is clear that addition of PEHA to silica materials postsynthesis did not replicate the high and sustained condensation states observed in BIS. A similar behavior was not observed during aging of BIS samples (Table S2), wherein Q^3 prevalence remained the same (32 ± 1%, cf. 34% for unaged BIS) and Q^4 prevalence increased slightly at the expense of Q^2 species (64 ± 1 and 4 ± 0% cf. 59 and 7% for unaged BIS). Despite the increased silica condensation, aged BIS samples exhibited an unexpected decrease in PEHA content—from 0.64 to 0.12 mmol/g (ca. 80% removal, see Table S6)—indicative of significant leaching of the additive.

Overall, the ^29Si MAS NMR data indicate that BIS was in fact more stable than IPS. This is significant because even after removal of the PEHA by elution to pH 2 or 24 h of aging, BIS maintained a high Q^4 concentration, indicating that the structures have a higher hydrothermal stability even after purification. This provides the first direct comparison of BIS hydrothermal stability against industrial silicas, showing that the use of bioinspired additives creates more stable materials.

Given that BIS was found to be more condensed than IPS even after PEHA extraction/leaching, we hypothesize that the additive (PEHA) might be causing these effects during the initial synthesis. In order to test this hypothesis, we probed the interaction between silica and the adsorbed additive to determine the localization of PEHA surface interaction and why this causes lower susceptibility to attack by acidic medium even after full PEHA loss.

^1H MAS NMR. Initially, ^1H MAS NMR data for the three silica materials were gathered to observe any changes to the silanol chemical environment upon addition of PEHA. For IPS, a single well-defined peak was observed at approximately δiso = 5.5 ppm for all samples (Figure 3a), indicating a uniform chemical environment for the silanol species therein (corresponding to water molecules hydrogen bonded to silanol groups). Introduction of PEHA to IPS led to significant broadening of the ^1H MAS NMR resonance as well as peak shifting to higher ppm values (ca. δiso = 6.5 ppm, corresponding to previous reports of ammonium hydroxide in silica zeolites, Figure 3b). Peak broadening was even more pronounced for as-made BIS (Figure 3c), indicating that PEHA encapsulated during synthesis led to a wider range of local Si chemical environments. Upon extraction of PEHA from BIS by lowering the pH the peak broadening reduced until, at pH 2, a ^1H MAS NMR spectrum was observed that exhibited a lineshape similar to that of IPS.

This indicates that, although the quantity of Si−OH moieties was different between BIS and IPS at pH 2, the chemical environment in each of those moieties was similar. Furthermore, with regards to the goal of using acid elution of additives as a means of controlling organic localization within a silica matrix, we note that PEHA-modified IPS appears qualitatively similar to BIS treated to pH 5, but not as-made (pH 7) BIS (Figure 3b,c, respectively). The emergence of more well-defined peaks after partial extraction agrees with the authors’ earlier supposition that more loosely held additives are extracted first and therefore suggests that partial extraction can indeed be used as a tool to ensure uniform organic entrapment within a BIS matrix.

^1H−^29Si CP MAS NMR. Although both the ^29Si and ^1H MAS NMR data provide insights into the effect of PEHA on BIS chemistry, no specific details about the PEHA−silica binding were revealed. To better elucidate this, the bonding environment of Si with its proximate protons was measured using ^1H−^29Si CP MAS NMR. In the absence of any additives, we expect that Q^2 and Q^3 Si signals will be amplified as they are covalently connected to hydroxyl groups (hence protons), while Q^4 Si resonances will be dampened because of the absence of any protons within close proximity. Indeed, for the IPS, ^1H−^29Si CP MAS NMR data exhibited amplified Q^2 and Q^3 silica signals and suppressed Q^4 signals (Tables 1, S2 and Figure 4) regardless of the treatment pH. For BIS, ^1H−^29Si CP MAS NMR data showed significant differences for all pH treatments due to the presence (or absence) of PEHA (Figure 4). Compared to the IPS, ^1H−^29Si CP MAS NMR spectra (Figure 5) showed that the surface hydroxylation of PEHA-modified IPS differed from that of both unmodified IPS and BIS, with only minor suppression of the Q^3 signal to ca. 55% cf. 75% in IPS and ca. 47% in BIS (as well as concurrent Q^4 amplification, see Figure 5).

The ^1H−^29Si CP MAS NMR data suggest that in addition to creating more Q^2 species in BIS, PEHA forms an adduct with
Q³ Si sites in general; Q⁴ signals were enhanced in both BIS and modified IPS materials. This agrees with the results reported by Folliet et al., which proposed amine-Q⁴ hydrogen bonding as part of quantum chemical simulations.34 However, these findings appear to contradict previous simulations and experimental results for artificial templated silica systems, which show electrostatic or ion-pairing interactions only during surface adsorption of PEHA (or other amine molecules), that is, onto deprotonated Q³ Si centers only.27,35,49,50 Previous studies of dried silica surfaces have shown secondary interactions with surrounding moieties are possible;26 therefore, PEHA-Q⁴ adducts may be the result of secondary interactions on (partially) dried BIS surfaces.

However, this explanation for the detected ¹H-Q⁴ adducts cannot explain why the absolute Q⁴ concentration is enhanced in BIS materials compared to either IPS or modified-IPS materials. To explain this, we first note that PEHA has been shown to act as a catalyst in the initial condensation of silicic acid monomers, presumably through proton transfer. This was previously assumed to occur only in the solution phase during synthesis⁴⁹,⁵¹ where PEHA can freely disassociate from any silicate center after condensation due to weaker interaction with the now covalently saturated oxygen atom. Based on our findings, we posit that this catalysis continues after the amine molecule is physically trapped within the silica matrix (analogous to the “embedded” state recently proposed by Montagna et al.²⁷). In this case, desorption of PEHA after the Q³ sites have been polymerized is hindered, leading to the higher initial ¹H-Q⁴ adduct concentration, which disappears after 24 h.

The varying representation of surface additive silica reactivity is visualized in Figure 6. In the absence of additives, silica condensation is known to occur through charged SiO⁻ moieties nucleophilically attacking Si–OH centers, eventually leading to the elimination of OH⁻ (A); given the reported pKₐ of 6.8, these moieties are approximately equally abundant at pH 7.5²,⁵³ Prior MD results indicate that PEHA attaches to such SiO⁻ surface sites during silica synthesis (B), and that the SiO⁻ density is sufficiently low that PEHA can only “see” one such site. This predisposes us to think that further surface condensation only leads to PEHA dissociation (C) and presumably re-association at a different Q³ site. The results we have found, combined with the recently published report by Montagna et al.,²⁷ indicate that this is not the case. Instead, PEHA interacts with multiple surface sites, facilitated by the embedded configuration (D). These SiO⁻ moieties then polymerize further (E), leading to the unexpected PEHA-Q⁴ adducts seen in unaged BIS samples. PEHA then slowly leaches away from the surface, bringing the CP MAS results in line with modified IPS, while retaining the highly condensed surface chemistry.

These findings continue a pattern where higher condensation is associated with multifunctional additives only (either biopolymers or artificial compounds).²⁵ Q⁴-template adducts have previously been detected in the cell walls of the diatom Thalassiosira pseudonana²⁶ as well as oligo³³ and monopeptides²² derived from the proteins therein. However, because the vast majority of artificially templated silica materials use monofunctional templates, which would be unable to make secondary interactions of these kinds with their silica surfaces, we conclude that polyfunctionality appears to be the key factor in determining if template-Q⁴ interactions can occur.

Accordingly, these results provide a useful indication of how template functionality may be employed to tailor surface chemistry. By taking advantage of the polyfunctional (and especially catalytically active) additive compounds, artificially templated silicas with higher degrees of surface condensation and hence hydrothermal stability could be designed without recourse to postsynthetic functionalization or changes to the material recipe itself—a key challenge in current templated silica design.⁵⁴ With regards to biosilica materials, this finding can provide a tentative explanation on a molecular level for complex and hard-to-analyze biological phenomena such as biosintering—the fusing of silica lamella in the core of sponge
formation. Given the range of di-BIS materials may be useful as model systems to study biosilica synthesis. Furthermore, this indicates that modifi-cations of the material postsynthetically while preserving the silica surface chemistry. Furthermore, this indicates that BIS materials may be useful as model systems to study biosilica formation. Given the range of different biosiliceous template structures, specific biological motifs or even general physical properties can be replicated and studied in isolation, providing reductionist insights into the more complex biological systems.

Finally, we believe that our results highlight a potentially important difference between current atomistic and ab initio simulations of silica surfaces. Our findings indicate that additive-Q^4 interactions, which have been positively identified during quantum chemical simulations but not in forcefield-based methods, are more prevalent than previously considered, and therefore current atomic simulations of solvated silica are not enough to fully describe the interfacial chemistry. Further simulations on partially or fully dewatered surfaces (such as those reported in ref 26) are needed to fully describe the more complex interfacial chemistry present in systems with polyfunctional templates. Future research focusing on solid-state NMR experiments directly probing ^13C and ^15N nuclei on isotopically labeled PEHA and other bioinspired additives, as well as experiments probing ^13C−^29Si and ^15N−^29Si inter-nuclear distances (e.g., ^13C−^28Si and ^15N−^28Si CP, HETCOR, or REDOR MAS NMR) will be vital to further resolve the surface PEHA–silica interactions and PEHA-mediated silica synthesis.

**SUMMARY AND CONCLUSIONS**

BIS materials were produced using the additive PEHA and analyzed by solid-state ^1H MAS, ^29Si MAS, and ^1H−^29Si CP MAS NMR after treatment to a range of different pH values. These were then compared against IPS (both treated to equivalent pH levels and after modification with PEHA), finding significantly higher condensation in the BIS, despite having a lower reaction time, even after modification with the catalytic PEHA template. This signifies that bioinspired synthesis methods can produce more hydrothermally stable silica than current industrial practices, a key property for the materials.

^1H−^29Si CP MAS data showed that the additional Q^4 sites associate with the PEHA additive, a phenomenon which has only been previously observed in biomolecule- or polymer-templated silica materials. We propose that these adducts arise because of secondary additive-silica interactions from organic additives in the “embedded” configuration, something which is impossible for more commonly studied monofunctional templates. These results highlight that BIS lies at the intersection between biosilica and artificially templated silica materials (as explained elsewhere^55), providing the advantages of catalytically active templating behavior to artificially templated silica materials while enabling systematic investigation into the more complex interfacial phenomena present in biosilicas.

Separately, our investigations of aged BIS materials show for the first time that the composition of BISs is not constant over time. The loss of additives from within the silica–amine composite over a 24 h period is highly surprising, especially given the author’s previous demonstration of highly consistent silica compositions after a range of postsynthetic modifications. This therefore necessitates further investigation of the kinetic stability of additive occlusion within BIS materials as a function of additive structure, solution composition, and synthesis conditions.

Overall, these findings are significant, as they demonstrate an as-yet unexploited design space for artificially templated silica materials, wherein the catalytically active additives can be used to stabilize silica surfaces, even after their removal. Finally, this mechanism of surface catalysis by embedded additive compounds provides a potential explanation for the biological

---

**Figure 6.** Scheme visualizing potential mechanisms of surface silanol condensation of BIS materials at pH 7. (A) In the absence of organic additives, (B,C) at single silica surfaces wherein the additive can freely desorb after elimination of surface SiO^−^ moieties, and (D,E) in the “embedded” state, wherein additives remain in close contact with the surface after polymerization of some surface SiO^−^ moieties, before slowly leaching from the material. OH^- leaving groups are omitted in each case for clarity.
phenomenon of biosintering in sponge spicules and highlights the overlooked details in current atomistic simulations of templated silica interfaces which are incapable of predicting such reactions.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.langmuir.0c03261.

NMR peak deconvolution and relative integral area for all samples analyzed, graphs of $^{29}$Si MAS, and $^1$H$-^{29}$Si CP MAS NMR spectra of modified IPS and aged BIS samples (including peak deconvolutions), ionic strength for BIS and IPS samples prepared at different pH conditions, and CHN elemental analysis for aged BIS samples (PDF)

**AUTHOR INFORMATION**

Corresponding Author
Siddharth V. Patwardhan — Department of Chemical and Biological Engineering, The University of Sheffield, Sheffield S1 3JD, U.K.; orcid.org/0000-0002-4958-8840; Email: s.patwardhan@sheffield.ac.uk

Authors
Joseph R. H. Manning — Department of Chemical and Biological Engineering, The University of Sheffield, Sheffield S1 3JD, U.K.; Department of Chemical Engineering, The University of Bath, Bath BA2 7AY, U.K.; Department of Chemistry, University College London, London WC1E 6BT, U.K.

Brant Walkley — Department of Chemical and Biological Engineering, The University of Sheffield, Sheffield S1 3JD, U.K.; Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, U.K.; orcid.org/0000-0003-1069-1362

John L. Provis — Department of Materials Science and Engineering, The University of Sheffield, Sheffield S1 3JD, U.K.; orcid.org/0000-0003-3372-8922

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acs.langmuir.0c03261

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We thank the EPSRC SynBIM project (EP/P006892/1), EPSRC Fellowship (EP/R025983/1), and ERC GROWMOF project (Prof. Tina Düren, ERC grant no. 648283) for their financial support. We thank the departments of Chemistry, Chemical and Biological Engineering, and Materials Science and Engineering at the University of Sheffield for funding and access to facilities. We thank Dr Sandra van Meurs for very insightful discussions and assistance with performing the NMR experiments.

**REFERENCES**

(1) Duer, M. J. The Contribution of Solid-State NMR Spectroscopy to Understanding Bimetalization: Atomic and Molecular Structure of Bone. *J. Magn. Reson.* 2015, 253, 98–110.

(2) Hildebrand, M. Diatoms, Bimetalization Processes, and Genomics. *Chem. Rev.* 2008, 108, 4855–4874.

(3) Sumper, M.; Kröger, N. Silica Formation in Diatoms: The Function of Long-Chain Polyamines and Silaffins. *J. Mater. Chem.* 2004, 14, 2059–2065.

(4) Staniland, S. S.; Rawlings, A. E. Crystallizing the Function of the Magnesosome Mineralization Protein Mms6. *Biochem. Soc. Trans.* 2016, 44, 883–890.

(5) Dickerson, M. B.; Sandhage, K. H.; Naik, R. R. Protein- and Peptide-Directed Syntheses of Inorganic Materials. *Chem. Rev.* 2008, 108, 4935–4978.

(6) Patwardhan, S. V.; Patwardhan, G.; Perry, C. C. Interactions of Biomolecules with Inorganic Materials: Principles, Applications and Future Prospects. *J. Mater. Chem.* 2007, 17, 2875–2884.

(7) Coppage, R.; Slocik, J. M.; Sethi, M.; Pacardo, D. B.; Naik, R. R.; Knecht, M. R. Elucidation of Peptide Effects That Control the Activity of Nanoparticles. *Angew. Chem., Int. Ed.* 2010, 49, 3767–3770.

(8) Dang, X.; Yi, H.; Ham, M.-H.; Qj, J.; Yun, D. S.; Ladewski, R.; Strano, M. S.; Hammond, P. T.; Belcher, A. M. Virus-templated Self-Assembled Single-Walled Carbon Nanotubes for Highly Efficient Electron Collection in Photovoltaic Devices. *Nat. Nanotechnol.* 2011, 6, 377–384.

(9) Grand View Research. Speciality Silica Market Size, Share & Trend Analysis Report by Product, 2018.

(10) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. A New Family of Mesoporous Molecular Sieves Prepared with Liquid Crystal Templates. *J. Am. Chem. Soc.* 1992, 114, 10834–10843.

(11) Gérardin, C.; Rebboul, J.; Bonne, M.; Lebeau, B. Ecodesign of Ordered Mesoporous Silica Materials. *Chem. Soc. Rev.* 2013, 42, 4217–4255.

(12) Drummond, C.; McCann, R.; Patwardhan, S. V. A Feasibility Study of the Biologically Inspired Green Manufacturing of Precipitated Silica. *Chem. Eng. J.* 2014, 244, 483–492.

(13) Belton, D. J.; Patwardhan, S. V.; Annenkov, V. V.; Danilovsvea, E. N.; Perry, C. C. From Biosilicification to Tailored Materials: Optimizing Hydrophobic Domains and Resistance to Protonation of Polyamines. *Proc. Natl. Acad. Sci. U.S.A.* 2008, 105, 5963–5968.

(14) Jantschke, A.; Spinde, K.; Brunner, E. Electrostatic Interplay: The Interaction Triangle of Polyamines, Silicic Acid, and Phosphate Studied through Turbidity Measurements, Silicomolybdic Acid Test, and $^{29}$Si NMR Spectroscopy. *Beilstein J. Nanotechnol.* 2014, 5, 2026–2035.

(15) Robinson, D. B.; Rognlien, J. L.; Bauer, C. A.; Simmons, B. A. Dependence of Amine-Accelerated Silicate Condensation on Amine Structure. *J. Mater. Chem.* 2007, 17, 2113.

(16) Babonneau, F.; Baccé, N.; Laurent, G.; Maquet, J.; Azais, B.; Gervais, C.; Bonhomme, C. Solid-State Nuclear Magnetic Resonance: A Valuable Tool to Explore Organic-Inorganic Interfaces in Silica-Based Hybrid Materials. *C. R. Chim.* 2010, 13, 58–68.

(17) Rimola, A.; Costa, D.; Sodupe, M.; Lambert, J.-F.; Ugliengo, P. Silica Surface Features and Their Role in the Adsorption of Biomolecules: Computational Modeling and Experiments. *Chem. Rev.* 2013, 113, 4216–4313.

(18) Ravera, E.; Martelli, T.; Geiger, Y.; Fragai, M.; Goobes, G.; Luchinat, C. Biosilica and Bioinspired Silica Studied by Solid-State NMR. *Coord. Chem. Rev.* 2016, 327–328, 110–122.

(19) Emami, F. S.; Puddu, V.; Berry, R. J.; Varshney, V.; Patwardhan, S. V.; Perry, C. C.; Heinz, H. Prediction of Specific Biomolecule Adsorption on Silica Surfaces as a Function of pH and Particle Size. *Chem. Mater.* 2014, 26, 5725–5734.

(20) Heinz, H.; Pramanik, C.; Heinz, O.; Ding, Y.; Misha, R. K.; Marchon, D.; Flatt, R. J.; Estrela-Lopes, I.; Llop, J.; Moya, S.; et al. Nanoparticle Decoration with Surfactants: Molecular Interactions, Assembly, and Applications. *Surf. Sci. Rep.* 2017, 72, 1–58.

(21) Jorge, M.; Milne, A. W.; Sobek, O. N.; Centi, A.; Pérez-Sánchez, G.; Gomes, J. R. B. Modelling the Self-Assembly of Silica-Based Mesoporous Materials. *Mol. Simul.* 2018, 44, 435–452.
(22) Baccile, N.; Laurent, G.; Bonhomme, C.; Innocenzi, P.; Babonneau, F. Solid-State NMR Characterization of the Surfactant—silica Interface in Templated Silicas: Acidic versus Basic Conditions. *Chem. Mater.* 2007, 19, 1343−1354.

(23) Tanve, P. T.; Pinnavaa, T. J. Mesoporous Silica Molecular Sieves Prepared by Ionic and Neutral Surfactant Templating: A Comparison of Physical Properties. *Chem. Mater.* 1996, 8, 2068−2079.

(24) Centi, A.; Manning, J. R. H.; Stivavea, V.; Van Meurs, S.; Patwardhan, S. V.; Jorge, M. The Role of Charge-Matching in Nonporous Nanoparticles Formation. *Mater. Horiz.* 2019, 6, 1027−1033.

(25) Spinde, K.; Pachis, K.; Antonakali, I.; Pasch, S.; Brunner, E.; Demadis, K. D. Influence of Polymethylene and Related Macromolecules on Silicic Acid Polycondensation: Relevance to “Soluble Silica Polys”? *Chem. Mater.* 2011, 23, 4676−4687.

(26) Brückner, S. I.; Donets, S.; Dianat, A.; Bobeth, M.; Gutierrez, R.; Cuniberti, G.; Brunner, E. Probing silica−biomolecule Interactions by Solid-State NMR and Molecular Dynamics Simulations. *Langmuir* 2016, 32, 11698−11705.

(27) Montagna, M.; Brückner, S. I.; Dianat, A.; Gutierrez, R.; Daus, F.; Geyer, A.; Brunner, E.; Cuniberti, G. Interactions of Long-Chain Polymethylene with Silica Studied by Molecular Dynamics Simulations and Solid-State NMR Spectroscopy. *Langmuir* 2020, 36, 11600−11609.

(28) Wisser, D.; Brückner, S. I.; Wisser, F. M.; Althoff-Ospelt, G.; Getzschmann, J.; Kasket, S.; Brunner, E. 1H-13C-29Si Triple Resonance and REDOR Solid-State NMR - A Tool to Study Interactions between Biosilica and Organic Molecules in Diatom Cell Walls. *Solid State Nucl. Magn. Reson.* 2015, 66−67, 33−39.

(29) Lutz, H.; Jaeger, V.; Schmücker, L.; Bonn, M.; Pfandtner, J.; Weidner, T. The Structure of the Diatom Silafin Protein RS within Freestanding Two-Dimensional Biosilica Sheets. *Angew. Chem., Int. Ed.* 2017, 56, 8277−8280.

(30) Roehrich, A.; Droby, G. Solid-State NMR Studies of Biominalerization Peptides and Proteins. *Acc. Chem. Res.* 2013, 46, 2136−2144.

(31) Abacilar, M.; Daus, F.; Haas, C.; Brückner, S. I.; Brunner, E.; Geyer, A. Synthesis and NMR Analysis of 13 C and 15 N-Labeled Long-Chain Polymethylene (LCPAs). *RSC Adv.* 2016, 6, 93343−93348.

(32) Ben Shir, I.; Kababa, S.; Schmidt, A. Binding Specificity of Amino Acids to Amorphous Silica Surfaces: Solid-State NMR of Glycine on SBA-15. *J. Phys. Chem. C* 2012, 116, 9691−9702.

(33) Geiger, Y.; Gottlieb, H. E.; Koscik, C. E. A.; Jacobs, P.; Martens, J. A.; Sels, B. F.; et al. Hierarchization of USY Zeolite by NH4OH. A Postsynthetic Process Investigated by NMR and XRD. *J. Phys. Chem.* 2014, 118, 22557−22582.

(34) Belton, D. J.; Patwardhan, S. V.; Perry, C. C. Spermine, Spermidine and Their Analogues Generate Tailored Silicas. *J. Mater. Chem.* 2005, 15, 4629.

(35) Patwardhan, S. V.; Emami, F. S.; Perry, R. J.; Jones, S. E.; Naik, R. R.; Deschaume, O.; Heinz, H.; Perry, C. C. Chemistry of Aqueous Silica Nanoparticle Surfaces and the Mechanism of Selective Peptide Adsorption. *J. Am. Chem. Soc.* 2012, 134, 6244−6256.

(36) Delak, K. M.; Sahai, N. Mechanisms of Amine-Catalyzed Organosilicate Hydrolysis at Circum-Natural PH. *J. Phys. Chem. B* 2006, 110, 17819−17829.

(37) Belton, D. J.; Deschaume, O.; Perry, C. C. An Overview of the Fundamentals of the Chemistry of silica with Relevance to Biosilicification and Technological Advances. *FEBS J.* 2012, 279, 1710−1720.

(38) Delak, K. M.; Sahai, N. Mechanisms of Amine-Catalyzed Organosilicate Hydrolysis at Circum-Natural PH. *J. Phys. Chem. B* 2006, 110, 17819−17829.

(39) Belton, D. J.; Deschaume, O.; Perry, C. C. An Overview of the Fundamentals of the Chemistry of silica with Relevance to Biosilicification and Technological Advances. *FEBS J.* 2012, 279, 1710−1720.

(40) Belton, D. J.; Deschaume, O.; Perry, C. C. An Overview of the Fundamentals of the Chemistry of silica with Relevance to Biosilicification and Technological Advances. *FEBS J.* 2012, 279, 1710−1720.