Colloid Growth

DOI: 10.1002/anie.201308140

Synthesis of Segmented Silica Rods by Regulation of the Growth Temperature**

*Panos Datskos and Jaswinder Sharma**

***Abstract:** The control of the diameter of colloidal structures is of fundamental interest and practical importance. We synthesized segmented silica rods by regulating the reaction temperature while the rods were growing. With higher growth temperatures, the segment diameter became smaller. Longer incubation times gave longer segments at the same temperature. Similarly, high temperature for the same incubation time gave longer segments. It appears that the correlation between temperature and diameter results from the relation between temperature and the size of the emulsion droplet, that is, the higher the temperature, the smaller the emulsion droplet.*

Colloidal silica structures of controlled morphology are desired for applications ranging from photonics to surface coatings.[1–3] Several experimental parameters, such as the choice of precursors, catalysts, templates, stabilizer molecules, pH value, temperature, and relative concentration of the reagents, play a role in controlling the morphology of colloidal silica.[4–9] Employing combinations of these parameters, silica structures of varied morphologies, including spherical, tubular, fibrous, rodlike, and helical nanoribbons, have been synthesized.[4–10] Subsequent addition of precursors led to various hybrid structures, such as patchy particles and rods.[11,12] Despite tremendous progress in obtaining structures of predicted morphologies, it is still challenging to achieve control of the local diameter with correlating control of size. For example, there is no example demonstrating the synthesis of segmented (corrugated or grooved) silica rods, although they are highly desirable for applications such as antireflective coatings. This slow progress in the synthesis of segmented silica structures is either a result of the difficulty to control their growth in situ or due to the focus on predefining the reaction conditions such as pH value, concentration, and temperature to obtain predicted morphologies.[4–10] However, in nature many intricate structures emerge as a result of the changes in surroundings during growth, thus indicating that shape of the already growing structures can be modified by regulating the surrounding environment.[13] This manipulation of the surrounding environment or reaction conditions during growth provides a new possibility to create structures of extraordinary morphologies.[14]

Herein, we report the manipulation of the reaction temperature to achieve control of the local thickness of already growing silica rods. Recently, the groups of Ming[6] and Imhof[7] reported the synthesis of silica rods. Our strategy is unique, because 1) it does not include any etching or deposition to decrease or increase the local diameter of the rods, 2) it provides complete correlation of the diameter with the surrounding reaction temperature, and hence instead of providing only a few selected morphologies, it provides a broad spectrum of desired segmented rods (with a defined number of segments with controlled length, whereas the previously reported methods[6,7] only provide unsegmented rods, 3) it demonstrates that the rod diameter is not only determined by the initial droplet size,[7] but also by the reaction temperature, and 4) it provides a new method to control local morphology.

In a typical experiment, polyvinylpyrrolidone (PVP; MW = 40000, 0.5 g) was dissolved in pentanol (5 mL) in a 15 mL glass vial. H_2O (140 μL), sodium citrate (0.18 M, 50 μL), absolute ethanol (475 μL), and NH_4OH solution (28–30 %, 100 μL) were added to the glass vial and mixed (vortex stirrer) for 1 min after each addition. Tetraethyl orthosilicate (TEOS; 50 μL) was added and the solution was mixed (vortex stirrer) again. The incubation of the reaction mixture at 20 °C resulted in smooth silica rods (Supporting Information, Figure S1).[7] During our studies on silica rods, we observed that the rod diameter correlates with the reaction temperature (the higher the temperature, the smaller the rod diameter; 20 °C: ≈220 nm, 40 °C: ≈190 nm, 65 °C: ≈150 nm). Taking advantage of this correlation, we manipulated the temperature while the rods were still growing, that is, we modified the surrounding environment during growth. Figure 1 a–c shows SEM images of silica rods grown by incubating at 20 °C (2 h), 40 °C (a: 20 min, b: 40 min, c: 60 min), and 20 °C (16 h). Similarly, Figure 1 d–f shows SEM images of the rods grown by incubating at 20 °C (2 h), 40 °C (d: 20 min, e: 40 min, f: 60 min), and 4 °C (16 h). By changing the temperature from 20 °C to 4 °C, while keeping the other conditions the same as for d–f, the rods shown in Figure 1 g–i were obtained. By reversing the order of incubation temperature, rods with thick middle segments can also be obtained (Figure 1 j–l).

[*] Dr. P. Datskos, Dr. J. Sharma
Nanosystems, Separations and Materials Research Group
Energy and Transportation Science Division
Oak Ridge National Laboratory
1 Bethel Valley Road, MS: 6054, Oak Ridge, TN 37831 (USA)
E-mail: sharmajk@ornl.gov

[**] J. Sharma is a Eugene P. Wigner Fellow at the Oak Ridge National Laboratory managed by UT-Battelle, LLC, for the U.S. Department of Energy under Contract DE-AC05-00OR22725. The work was supported by the Laboratory Director's Research and Development Program of the Oak Ridge National Laboratory. A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201308140.

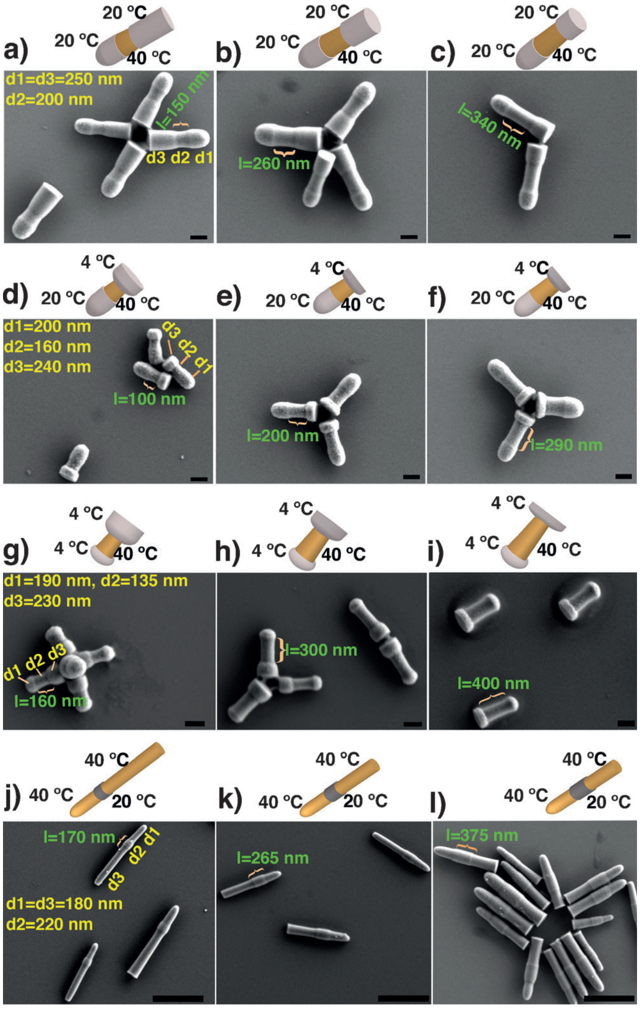

Figure 1. Cartoons and SEM images showing the effect of incubation temperature and time (at that temperature) on rod-segment diameter and size. Rods were grown at a–c) 20 °C (2 h), 40 °C (a: 20 min, b: 40 min, c: 60 min), and 20 °C (16 h); d–f) 20 °C (2 h), 40 °C (d: 20 min, e: 40 min, f: 60 min), and 4 °C (16 h); g–i) 4 °C (4 h), 40 °C (g: 20 min, h: 40 min, i: 60 min), and 4 °C (16 h); and j–l) 40 °C (40 min), 20 °C (j: 1 h, k: 2 h, l: 3 h), 40 °C (16 h). Scale bars: a–i) 200 nm, and j–l) 1 μm. Note: The length of the middle segment of a representative rod (in all panels, in green), and the diameter of each segment of a rod (only first panel of each set, in yellow) are provided.

The length of each segment correlated with the reaction time at that temperature (see Figure 1 a–l. Because of enhanced hydrolysis and condensation of TEOS at higher temperatures, larger segments were obtained in the same time frame compared to lower temperatures, at which both of these reactions are slower. At 4 °C, reactions are slowed to the extent that to achieve segment growth, a minimum time of 2 h is needed. The diameter of segments is inversely proportional to the incubation temperature, that is, the lower the temperature, the larger the diameter. It must be noted that in addition to the incubation temperature, the original size of the emulsion droplet also influences the achievable segment diameter.[7] However, for a rod growing from the same emulsion droplet, a change in temperature always results in a correlating change in its diameter.

It was tricky to obtain rods that have segments of decreasing thickness, while keeping the smallest-diameter segment with a round end. Incubation at increasing temperature at different time intervals gave rods with a smallest-diameter segment with a flat end (flat end results from the loss of the emulsion droplet at the end of the reaction, thus the last segment always has a flat end).[7] To address this issue, we grew rods in the opposite direction, that is, with higher temperature first. This resulted in rods that had a thickness gradient (stepwise increase in diameter, Figure 2 a–c), while retaining the round end on the smallest-diameter segment. By increasing the difference in incubation temperature between two consecutive steps, the sharpness of the thickness gradient could be increased (Figure 2 b–c).

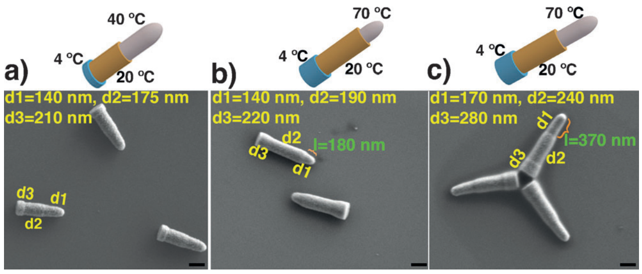

Figure 2. Cartoons and SEM images of rods that have segments with increasing diameter (gradient thickness). Rods were grown at a) 40 °C (40 min), 20 °C (2 h), and 4 °C (16 h); b) 70 °C (10 min), 20 °C (2 h), and 4 °C (16 h); c) 70 °C (20 min), 20 °C (2 h), and 4 °C (16 h). Scale bars: 200 nm. Note: The diameter of each segment of a representative rod (in all panels, in yellow), and the length of the tapered segment (in panel b and c, in green) are given.

The correlation between temperature and diameter is completely reversible. For example, an alternate incubation at low and high temperatures results in multisegmented rods that consist of alternate thick and thin segments. Taking benefit of this behavior, we synthesized a library of segmented rods by varying the temperature and incubation time (Figure 3 a–l). The length of each segment for the same time interval decreased because of the diminished supply of TEOS with time (Figure 3 a–f, h–k). More SEM images and experimental details are provided in the Supporting Information.

The exact mechanism of the effect of the temperature on the rod diameter is not clear, there are however three possibilities. First, the increased temperature results in enhanced TEOS hydrolysis and diffusion within the emulsion droplet, resulting in more deposition at the front end compared to the lateral sides. Second, the enhanced temperature decreases the molecular interactions between the PVP molecules and citrate and water. These diminished interactions result in expulsion of some of the PVP molecules in the bulk solution, which in turn reduces the size of the emulsion droplet. The similar phenomenon has been observed in the case of H_2O/Triton X-100/cyclohexane emulsions.[15] Third, enhanced temperature expels pentanol molecules that might have been intercalated in the micelles, in turn shrinking the emulsion droplet. Similar intercalation of cyclohexane molecules in Triton X-100/cyclohexane micelles has been

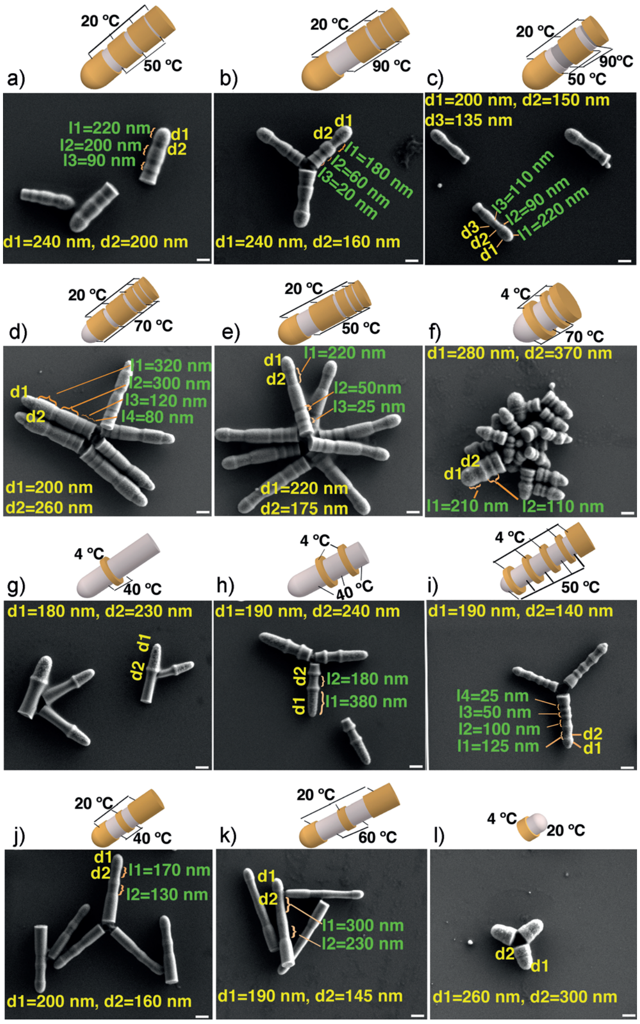

Figure 3. Cartoons and SEM images showing a library of segmented rods obtained by varying the reaction temperature and incubation time. a) Bε-Dβ-Bε-Dβ-Bε-Dβ-Bθ; b) Bε-Gβ-Bε-Gα-Bε-Gα-Bθ; c) Bε-Dβ-Gα-Bε-Dβ-Gα-Bθ; d) Fβ-Bε-Fβ-Bε-Fβ-Bε-Fβ-Bθ; e) Bε-Dβ-Bε-Dβ-Bε-Dβ-Bε-Dβ-Bθ; f) Fβ-Aη-Fβ-Aε-Fβ-Aθ; g) Cδ-Aη-Cθ; h) Cδ-Aη-Cδ-Aη-Cθ; i) Dβ-Aε-Dβ-Aε-Dβ-Aε-Dβ-Aε-Dβ-Aθ; j) Bε-Cγ-Bδ-Cγ-Bθ; k) Bε-Eγ-Bδ-Eγ-Bθ; l) Bε-Aθ (with A = 4 °C, B = 20 °C, C = 40 °C, D = 50 °C, E = 60 °C, F = 70 °C, G = 90 °C, α = 5 min, β = 10 min, γ = 20 min, δ = 40 min, ε = 2 h, η = 4 h, and θ = 16 h). Scale bars: 200 nm. Note: The diameter (in yellow) and length (in green) of selected segments (where length comparison helps in understanding the growth rate) of a representative rod is provided in each panel.

reported.[15,16] To study the second and third possibility, the size distribution of the emulsion droplets was measured using Dynamic Light Scattering (DLS) at 20 °C and 40 °C by preparing the samples without TEOS (addition of TEOS results in solid rods with the size changing continuously during the growth, and hence may interfere in the DLS studies). The DLS studies showed a decrease in the size of emulsion droplets with increased temperature (experimental details and data are provided in the Supporting Information, Figure S4). These results led us to believe that the shrinkage of the emulsion droplet with the rising temperature is the main factor that influences the decrease in rod-segment diameter. The change in diameter of contiguous segments (not the diameter of the same segment) is quick and reversible. Similarly, DLS studies showed the reversibility of the emulsion-droplet size with alternate decrease and increase in temperature (Supporting Information, Figure S4b).

At higher temperatures (≈ 65 °C and beyond), longer incubation times (> 20 min) result in the bending of the rod segments, and at around 145 °C, the emulsion droplets detach from the rods (Supporting Information, Figure S9). However, lower incubation times (10 min or less) can be employed up to 90 °C to control the rod-segment diameters. Generally, a change in the incubation temperature from 20 °C to 40 °C results in a decrease in diameter by around 40 nm, and to 90 °C in a decrease in diameter by around 80 nm, while incubation at 4 °C results in an increase in diameter by approximately 50 nm. The smallest diameter (≈ 90 nm) of a segment can be obtained at around 135 °C, but results in the "zigzag growth" of the next segment (Supporting Information, Figure S9). The rods grown at higher temperature are also longer than those grown at lower temperature. We assume that this effect results from the decreased diameter, because the total amount of TEOS deposited in a single rod seems almost the same (0.048 μm^3 at 20 °C, and 0.046 μm^3 at 50 °C, details the in Supporting Information, Figure S8), irrespective of the length, when the reaction was given sufficient time (48 h) so that all available TEOS got deposited. Additionally, the increased temperature enhances the reaction rate, which also affects the final rod length by depositing more TEOS in the given time frame (Figure S7 in the Supporting Information shows the rate of rod growth at different temperatures).

In conclusion, we demonstrated that unprecedented silica structures can be obtained by manipulating the surrounding conditions while structures are still growing. This type of thickness control does not require any etching or post-synthesis processing. We anticipate that these results will open up opportunities for the fabrication of structures that are challenging to obtain by conventional techniques (pre-defined reaction conditions or post-synthesis etching), and will entice further interest in the control of local morphology of colloidal structures. We expect that these segmented rods may find applications in surfaces with a desired stepwise refractive index gradient, such as antireflective coatings, and for ceramic polymer composites.[3,17] Further efforts to understand the effect of the temperature on the rod diameter are in progress.

Received: September 16, 2013
Revised: October 11, 2013
Published online: November 24, 2013

Keywords: colloids · growth regulation · segmented rods · silicates · temperature control

[1] R. Ciriminna, A. Fidalgo, V. Pandarus, F. Beland, L. M. Llharco, M. Pagliaro, *Chem. Rev.* **2013**, *113*, 6592 – 6620.
[2] J.-Q. Xi, J. K. Kim, E. F. Schubert, *Nano Lett.* **2005**, *5*, 1385 – 1387.
[3] Y. Li, J. Zhang, B. Yang, *Nano Today* **2010**, *5*, 117 – 127.

[4] Y. Liu, J. Goebl, Y. Yin, *Chem. Soc. Rev.* **2013**, *42*, 2610 – 2653.
[5] X. Yang, H. Tang, K. Cao, H. Song, W. Sheng, Q. J. Wu, *J. Mater. Chem.* **2011**, *21*, 6122 – 6135.
[6] J. Zhang, H. Liu, Z. Wang, N. Ming, *Chem. Eur. J.* **2008**, *14*, 4374 – 4380.
[7] A. Kuijk, A. V. Blaaderen, A. Imhof, *J. Am. Chem. Soc.* **2011**, *133*, 2346 – 2349.
[8] C. Gao, Z. Lu, Y. Yin, *Langmuir* **2011**, *27*, 12201 – 12208.
[9] J. Wang, A. Suguwara, A. Shimojima, T. Okubo, *Langmuir* **2010**, *26*, 18491 – 18498.
[10] D.-M. Li, Y.-C. Chen, C. Zhang, S. Song, Y.-S. Zheng, *J. Mater. Chem. B* **2013**, *1*, 1622 – 1627.
[11] J. He, M. J. Hourwitz, Y. Liu, M. T. Perez, Z. Nie, *Chem. Commun.* **2011**, *47*, 12450 – 12452.
[12] J. He, B. Yu, M. J. Hourwitz, Y. Liu, M. T. Perez, J. Yang, J. Nie, *Angew. Chem.* **2012**, *124*, 3688 – 3693; *Angew. Chem. Int. Ed.* **2012**, *51*, 3628 – 3633.
[13] C. Costa, J. Aguzzi, P. Menesatti, F. Antonucci, V. Rimatori, M. Mattoccia, *J. Zool.* **2008**, *276*, 71 – 80.
[14] W. L. Noorduin, A. Grinthal, L. Mahadevan, J. Aizenberg, *Science* **2013**, *340*, 832 – 837.
[15] D.-M. Zhu, K.-I. Feng, Z. A. Schelly, *J. Phys. Chem.* **1992**, *96*, 2382 – 2385.
[16] D.-M. Zhu, Z. A. Schelly, *Langmuir* **1992**, *8*, 48 – 50.
[17] W. Li, K. Lu, J. Y. Walz, M. Anderson, *J. Am. Ceram. Soc.* **2012**, *95*, 398 – 406.

