Sculpting Silica Colloids by Etching Particles with Nonuniform Compositions

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** Supporting Information

ABSTRACT: We present the synthesis of new shapes of colloidal silica particles by manipulating their chemical composition and subsequent etching. Segments of silica rods, prepared by the ammonia catalyzed hydrolysis and condensation of tetraethylorthosilicate (TEOS) from polyvinylpyrrolidone loaded water droplets, were grown under different conditions. Upon decreasing temperature, delaying ethanol addition, or increasing monomer concentration, the rate of dissolution of the silica segment subsequently formed decreased. A watery solution of NaOH (∼mM) selectively etched these segments. Further tuning the conditions resulted in rod–cone or cone–cone shapes. Deliberately modulating the composition along the particle’s length by delayed addition of (3-aminopropyl)-triethoxysilane (APTES) also allowed us to change the composition stepwise. The faster etching of this coupling agent in neutral conditions or HF afforded an even larger variety of particle morphologies while in addition changing the chemical functionality. A comparable step in composition was applied to silica spheres. Biamine functional groups used in a similar way as APTES caused a charge inversion during the growth, causing dumbbells and higher order aggregates to form. These particles etched more slowly at the neck, resulting in a biconcave silica ring sandwiched between two silica spheres, which could be separated by specifically etching the functionalized layer using HF.

INTRODUCTION

Instead of selectively adding material to build up a nanoparticle, it is also possible to selectively remove material of already formed particles to change their size and/or shape. Due to their high potential in chemical, electrical, and optical applications,1−3 a large variety of anisotropic particles have been developed following this principle. A common method used to create more complicated shapes is by making use of a template. Typically, colloidal templates are coated with a layer consisting of a different material than the template, so that the latter can be removed by chemical dissolution. Examples of anisotropic particles created this way are hollow spindles, cubes, ellipsoids, and peanuts but also particles with protrusions and cavities.4,5 Instead of using chemical dissolution, one can also make use of calcination. Here, a sacrificial layer is used consisting of a material that is eliminated a heat treatment. In such a way Nagao et al. were able to remove a polymer layer from between a silica core and a silica shell, in order to prepare hollow asymmetrical silica dumbbells.6

Instead of making use of the unequal solubility and/or rate of dissolution of two different materials, one can also make use of the different dissolution rates of certain sites on a nanoparticles consisting of only one material. Differences in chemical composition and structure within one particle result in different etching rates within the same particle. The local rate of dissolution of colloidal particles depends on the exact local composition and structure and is the product of a thermodynamic driving force as given by the solubility but also a kinetic factor that depends on accessibility and diffusion rates. Many nanocrystals show distinct anisotropic dynamics in their dissolution in low concentration of acid: reactive and highly accessible sites at the ends are etched first, resulting in the deformation of these nanocrystals, of which many examples are given in a recent review.7 In the presence of silver ions, etching of gold nanorods mostly takes place at the sides of the gold rod resulting in dumbbell shaped particles.8 By first embedding these gold nanorods in a mesoporous silica shell, one can change the size of the rod inside the silica matrix by oxidative etching. Subsequent overgrowth with a different metal resulted in new material properties.9

The extent of the condensation reaction in the formation of silica particles, also known as the degree of condensation, also influences the local rate of dissolution. Silica with a low degree of condensation dissolves faster than silica with a high degree of condensation, simply because fewer siloxane bonds need to be broken.10,11 Differences in the degree of condensation between different synthesis methods were found for Stöber silica and silica particles grown in a microemulsion. For microemulsion particles 55% of the silicon atoms were found to be fully condensed as compared to >60% for Stöber silica.12 Some
parameters that influence the condensation rate and degree of silica are the pH and the temperature. Besides a change in reaction conditions during growth, one can also apply a composition step during the growth of silica. Organo-silica co-condensed from tetraalkoxysilanes and alkyltrialkoxysilanes was found to dissolve faster in HF solutions than silica prepared from tetraalkoxysilanes alone as the degree of condensation will be lower than 4.

Differences in resistance to etching or differences in the rate of dissolution of the silica network have been used for the preparation of various types of particles. A well-known example is the rattler type particle: a silica shell that encapsulates a movable core. One way of preparing these particles is by exploiting the differences in structure and composition of the silica network. The silica grown lately in the synthesis was found to be more resistant against etching than silica grown at the start. This difference in the structure of the silica network was used to selectively etch the inner layer around a central gold core, while the outer layer was etched at a significantly lower rate and remained until the end. The outer layer of silica was found to be hardened by the reagents present in the preparative solution. Growing multiple shells around the particles resulted in a layered chemical structure, where upon etching each layer dissolved except for the silica at the boundaries between layers. It was found that this difference in dissolution rate became smaller upon incubating the particles in the preparative solution at 60 °C. In addition, it was found that even the solution in which Stöber silica is washed or stored after synthesis can have significant effect on dissolution rates of the particles.

Differences in the chemical composition can also be used to prepare anisotropic particles by etching. The etching rate of an organo-silica layer is different from that of a pure silica layer. The etching rate is increased due to the lower number of siloxane bonds of a silane coupling agent. As already mentioned, this principle was used to create rattler type particles. These particles consist of a pure silica core, an organo-silica layer, and a pure silica shell. Upon etching these particles in aqueous hydrofluoric acid (HF), the organo-silica layer etched significantly faster and could be removed through the outer silica layer which became only slightly more porous. The selectivity of differences in dissolution rates for different types of etchants can also be exploited to modify the particle shape further: double-shelled silica spheres were prepared by alternately using the base Na2CO3 and HF etching.

Instead of changing the chemical composition or structure, another way to change the dissolution rates is to protect the surface layer from etching. The polymer polyvinylpyrrolidone (PVP) was found to protect the surface and prevent etching whereas the inner parts dissolved much more easily. Instead of using a polymer, one can also prevent access to part of the silica interface of particles more drastically. Adsorbing modified silica spheres at a wax–water interface of a Pickering emulsion resulted in the etching of the hemisphere in contact with the aqueous phase. The part of the particles embedded in the wax was protected and remained unetched.

Recently, a new colloidal system consisting of silica rods was introduced. These rods grow from water rich emulsion droplets dispersed in a water poor continuous oil phase. The silica precursor requires water for the hydrolysis and subsequent condensation reaction. Therefore, growth mainly takes place from inside the water rich droplet and not from the water poor oil phase. This anisotropic supply of the precursor results unidirectional growth of a rodlike particle. The particles consist of a rounded end and a flat end; the silica at the flat end is grown last. Due to slow growth of silica from the oil phase as well, a thin shell is also grown on that part of the rod that is in contact with the oil. Because of the longer exposure to the growth solution of the tip and the shorter exposure of the end, this outer shell decreases in thickness along the length of the rod. The particles are monodisperse enough that they readily form smectic liquid crystal phases. They can be easily functionalized during or after synthesis. Incorporation of a dye coupled to 3-aminopropyltriethoxysilane (APTES) from the start of the reaction results in a fluorescent gradient pattern. Close inspection of this fluorescence pattern has shown that the dye is mainly located in an outer thin silica shell. However, upon incorporating APTES alone, followed by the fluorescent labeling with FITC (fluorescein isothiocyanate) afterward, a homogeneous distribution of fluorophores was found. This pattern of fluorescence indicates that the local chemical composition of the particle can be tuned by changing the properties of the reacting species.

Recent advances in the synthesis of silica rods, using the above-mentioned emulsion based procedure, have resulted in a variety of experimental methods to change the shape of the particles during their growth. Two important parameters that influence the growth of these particles are temperature and ethanol concentration. Upon increasing the temperature or the ethanol concentration, the diameter of the rod decreases from that point onward in the reaction, which is thought to be the result of a decrease in the water droplet size. The concentration of base has also been found to influence the locus of growth; an increased growth at the interface results in the growth of hollow rods. Even without changing any of these conditions externally, it is expected that the reaction conditions change in time anyway as during particle growth water and silicon alkoxide are consumed and ethanol is produced. These changes in the reaction conditions lead to a subtle gradient in degree of condensation along the rod’s length. This gradient was previously used for the transformation of rods into cone shaped particles, while, depending on the reaction conditions, biconcave rods could also be synthesized.

Here, we significantly expand on the possibilities of sculpting silica colloids by changing the reaction temperature, precursor concentration, and ethanol concentration. Temperature, reagent concentration, and ethanol concentration were found to influence the local chemical structure. We show that these gradients in composition and structure can be used to change the shape of the particles by etching the particles in low concentrations of etchant (using NaOH, HF, or even pure water solutions). These methods were also combined in one synthesis to form more complicated gradients and, through these, an even larger variety of new shapes in silica particles. The chemical composition of silica rods could be modified by the incorporation of APTES, and the segment grown was found to dissolve faster in water than regular silica. In this paper, we not only demonstrate sculpting of rod-like silica particles but also illustrate with spherical silica particles that the methodology can be generally applied to all kinds of silica structures. For instance, under certain etching conditions dumbbell shaped core–shell particles, formed by aggregation during the growth of layers around silica spheres, were found to etch from the outside specifically. The middle segment where the spheres met dissolved more slowly than the rest of the spheres. The
resulting biconcave segment could be easily detached by subsequently etching the particles in HF.

## RESULTS AND DISCUSSION

Rodlike silica particles with steps in degree of siloxane cross-linking were synthesized by varying the temperature, ethanol concentration, and TEOS concentration at different stages of the rod growth (see Experimental Section). This reaction protocol resulted in silica rods with segments of different compositions along the length of the rod. These different segments along the length of the silica rods therefore also had a different sensitivity to the etchant NaOH. Exposure to the etching solution thus produced sculpted colloids.

We initially investigated the effect of varying the temperature, ethanol concentration, and TEOS concentration on the resulting shape of the silica rod. Thereafter, we explored how the shapes were further changed by etching of these particles.

We found that not only the degree of local silica condensation but also the accessibility of sections of the particles to the etchant are of great importance to the resulting silica rod morphology. A balance between the rate of dissolution as determined by the degree of siloxane bonds formed or the degree of condensation and the accessibility of the base in a colloidal silica particle was then used to obtain a new shape by a simple two step etching protocol.

**Effect of Modifying Temperature at Various Times during the Silica Rod Growth on the Resulting Morphology.** It is known that decreasing the temperature during the growth of silica rods results in an increase of the diameter of the rod, and an increase in reaction temperature results in a decreased diameter. These effects are explained by a change of the water droplet size in accordance with the diameter change of the rods. By designing a procedure with multiple growth steps at various temperatures, segmented rods can be prepared, as has been previously shown by Datskos et al.28

First, we prepared silica rods, consisting of a segment grown at 50 °C followed by a segment grown at 5 °C (Figure 1a and scheme in Figure 1). This resulted in rods with two segments. Etching these silica rods, with 1 mM NaOH, resulted in particles in which the second segment is etched so much faster that it ends up being etched almost completely even though it was initially thicker, whereas the first segment seems to have remained untouched (Figure 1b). We hypothesize that this selective etching occurs because of the varying microstructure of the silica network in the segments. This varying microstructure arises from growing the silica rod segments at varying temperatures, which influences the degree of condensation of silica. A lower temperature resulted in a decreased degree of condensation with a faster dissolution rate, whereas an increased temperature resulted in an increased degree of condensation and thus the network that dissolves more slowly.11,12,31

Looking more closely at the etched segment in the particles in Figure 1b, we see that it shows “growth rings”. We hypothesize that these “growth rings” arise from the inhomogeneous cooling of the sample during the silica rod growth. Thus, various growth conditions actually exist in the solution as a result of the rapid cooling down process. Furthermore, the slow gradient in composition, which was initially observed for silica rods grown at room temperature,27 cannot be observed in these particles; the first segment of the rod does not transform into a concave shape upon etching with the mild base. This is probably caused by the higher temperature during the growth of the first segment that makes this segment more resistant against etching.

By programming a sequence of temperatures during the growth of silica rods, we tuned the degree of silica condensation present in the particles and thus obtained a large variety of new particle morphologies after etching in a NaOH solution. In the following, we illustrate this general method with some specific examples: we prepared silica rods with a segment grown at 5 °C followed by a segment grown at 25 °C. Upon etching these particles in a 1 mM NaOH solution (Figure 2a), the tips of the particles preferentially etched, while at the boundary between the two segments the particles etched less. The remaining part of the rod etched as explained and shown in a previous paper in a cone shape.27 As mentioned, the lower temperature during the first 2 h of the reaction lowered the degree of condensation of the silica network and caused an increase in the etching rate of the segment. Moreover, a thin silica shell surrounded the empty first segment grown at 5 °C. This thin shell was also observed in etching “regular” silica rods in 2 mM NaOH and was explained by the condensation of some of the silica precursor directly from the oil phase, but with a higher degree of siloxane cross-linking than the silica grown from the water droplet.27 This shell becomes thinner when going from the rounded end to the flat end, because the exposure time to the growth solution decreases in this direction. The slight chemical gradient present in the bulk of the silica rods prepared using the general reaction procedure was not affected. Solely the part grown at lower temperatures was affected.

More complex shapes can be prepared by creating a more complicated sequence of growth steps with varying temper-
An interesting phenomenon can be observed upon growing a third segment at increased temperature (50 °C). These particles now consist of a thin segment grown at 50 °C, a thick segment grown at 5 °C, and another thin segment grown at 50 °C. After etching these particles in 1 mM NaOH we find that the second segment has hardly dissolved (Figure 3).

Varying the Precursor (TEOS) Concentration. Other subtle changes in the growth conditions are expected to also give rise to changes in the silica network. In earlier work we have shown that a gradual change in reaction conditions, due to the consumption of TEOS and the production of ethanol, resulted in a slight gradient in the degree of condensation of the silica present throughout the length of the particle. The main cause for this gradient was found to be the concentration of precursor, which decreased during the course of the reaction. To show the influence of the reactant concentration, here we changed the concentration of the precursor TEOS in steps. Upon injecting fresh, nonhydrolyzed TEOS 24 h after the start of the rod growth, we find that the particles continued growth, as described by Kuijk et al. Only the length of the particles increased, and no step in diameter was observed in this case. The segment was allowed to continue growth for another 24 h, after which the particle increased in length to 196 nm, ± 196 nm (b). Particles before etching are shown in Figure S11.

Figure 3. (a) Silica rods grown with a 5 °C (2 h), 5 °C (22 h), and 50 °C (18 h) segment, etched at 1 mM of NaOH. (b) The same particles at increased magnification. Scale bar indicates 1 μm (a) and 200 nm (b). Particles before etching are shown in Figure S11.

Figure 2. (a) Etched silica rods grown with a 5 °C (2 h) segment and a 25 °C (22 h) segment, etched at 1 mM of NaOH for 24 h. (b) Etched silica rods grown at 1 mM of NaOH for 24 h. (c) Etched silica rods grown at 50 °C (1 h), 5 °C (4 h), and 25 °C (22 h) segment, where the first segment is grown slightly longer, etched at 1 mM of NaOH for 24 h. (d) Particles shown in part c but etched at 0.5 mM of NaOH for 24 h. Scale bars indicate 1 μm. Particles before etching are shown in Figure S11.
more quickly dissolving (i.e., less condensed) silica. Immediately after the addition of fresh reactant, the conditions were quite similar to those at the start of the reaction. However, as the reaction continued the concentration of available TEOS fell gradually and therefore this segment contained a gradient in the chemical microstructure. Also in the first segment the gradient in the microstructure should still be present. However, due to a continued deposition of TEOS from the oil phase, the shell around the first segment became thicker and protected this part against etching. Careful inspection of the particles in Figure 4a shows the first signs of etching in the last part of the first segment, supporting our hypothesis. This is caused by the thinner outer shell present around this part of the particle.

**Sequential Steps.** It is also possible to combine these methods and to create more complicated chemical composition sequences throughout and thus morphologies throughout the particle. As an illustration, we synthesized particles that were first grown at 5 °C for 4 h and then at 25 °C for 22 h, and finally after injection of fresh precursor the growth was continued for another 24 h at 25 °C. According to the previously shown results this should lead to particles that consist of a highly soluble first segment, a segment with a gradient in structure, a sudden decrease in the degree of condensation, and finally a segment with a gradient in structure. Indeed, upon etching these particles in 1 mM NaOH solution we find that the first segment dissolved preferentially to a hollow shell, while the second and third segments both etched into cone shapes (Figure 4b). Comparing the result to Figure 4a, we find that the second segment now also transformed into a cone shape; due to the decreased amount of TEOS used for the extended growth of the silica rods, 100 μL versus 150 μL, the growth of the shell is less, making the inside of the particles more accessible to the etchant. Thus, we created a blunt cone with a second cone attached to its back. These results show that by changing the chemical composition in a smart way, the shape of the rod can be tuned by etching in low concentrations of NaOH.

**Ethanol Delay Time.** Datskos et al.29 showed that the diameter of the rod is strongly influenced by the ethanol concentration. By delayed addition of ethanol, steps in the diameter could be achieved. Here, we show that changes in the ethanol concentration also influence the degree of silica cross-linking. First, a segment was grown for 3 h in the absence of ethanol. Then, the usual amount of ethanol was carefully mixed into the solution and the remaining part of the rod was left to grow for 24 h. Upon etching these particles in 1 mM NaOH, we found that the first segment, grown in the absence of ethanol, dissolved faster than silica grown under regular conditions (Figure 5a), again despite being thicker than the part of the rod that dissolved more slowly. The second segment etched into a cone, indicating that, after the delayed addition of ethanol, the gradient in structure, which can be found in regular silica rods, still formed. The length of this segment can be easily changed by choosing a shorter or longer time of growth without ethanol, as shown in Figure 5b. We propose the following mechanism: ethanol is a cosolvent in the reaction but is not consumed. Therefore, it does not have a direct influence on the reaction itself. However, ethanol partitions between the oil phase and the droplet phase. Datskos et al.29 showed by dynamic light scattering that the volume of the droplet decreased upon the addition of ethanol to the reaction mixture. The addition of ethanol increased the solubility of water in the pentanol phase. Due to this increase in solubility, the concentration of water inside the droplet decreases, leading to a lower formation rate of hydrolyzed TEOS. In turn, this resulted in a lower concentration of hydrolyzed TEOS inside the water droplet. As we have seen in the TEOS addition experiments this results in silica that dissolves more slowly.

**Segmented Rods with Amine Functionality.** Extending the above results to particles grown partly from silane coupling agents, which allow incorporation of functional groups inside hybrid organo-silica structures, we altered the chemical
properties of the rods by the co-condensation of the APTES (3-aminopropyltriethoxysilane), which was added 3 h after the start of the reaction. APTES has a structural formula similar to TEOS, but with one of the four ethoxy groups replaced by an aminopropoxy group. This group lowers the degree of condensation to a maximum of three bonds per silicon atom. Similarly as in the condensation of TEOS, however, a significant number of the silicon atoms (~30%) is not fully condensed and stays attached to hydroxy and/or ethoxy groups.\textsuperscript{15,16} Therefore, the incorporation of APTES is expected to increase the etching rate of the particle w.r.t. those composed of TEOS alone. For instance, working with silica core–shell–shell spheres, Chen et al.\textsuperscript{14} showed that the incorporation of a similar silane coupling agent (N-[3-(trimethoxysilyl)-propyl]-ethylene-diamine, TSD) in an inner shell in between a central TEOS based core and outer shell led to silica core–void–silica shell particles after etching with hydrofluoric acid through the outer silica shell. The Haes group incorporated APTES in a layer of organo-silica grown around metal core–shell particles and etched this layer through an outside Stöber silica layer using ammonia as the etchant.\textsuperscript{32} We adapted this concept to our silica rods. Adding APTES 3 h after the synthesis had begun resulted in particles with a normal silica segment and an APTES functionalized segment.

Upon etching undyed versions of these segmented particles in Milli-Q grade water, the second segment partly dissolved, whereas the first half remained intact as we expected (Figure 6a). Furthermore, the transition between the two parts appears to be rather sharp, and the location of the step in diameter can be easily tuned by choosing shorter or longer reaction times. Surprisingly, etching in basic conditions (3 mM NaOH) left the APTES segment intact and etched only the first segment, leaving behind a thin shell (Figure 6b). Contrary to what we expected and to what was observed by others,\textsuperscript{32} the APTES containing tail segment etched more slowly than the unmodified silica, which etched, as before, through an outer shell. At present we do not have an explanation for this behavior, which seems contrary to the etching results in water without base.

The presence of the APTES functionalized end segment on the rods could be illustrated by post-modification of the unetched particles from Figure 6 with a fluorescent dye that links to the amino group. The resulting dyed particles were imaged using a form of super-resolution microscopy, stimulated emission depletion (STED) confocal microscopy (see Figure 6c). Here, one can see that the functional amine groups can be found on both the tail of the particle and in a thin outer shell. The thin shell again originates from the attachment of the precursor directly from the oil phase and is similar to the layer found in earlier work.\textsuperscript{27} The fluorescence from the shell is lower than that from the tail segment. The fluorescent segment appears to be shorter in length than the segment grown, but as described in earlier work, the dye cannot infiltrate the particle far enough. Nevertheless this confocal image gives a good indication that the functional group is distributed throughout the tail segment of the particles.\textsuperscript{27} In the following we illustrate how differences in the rate of silica etching in both base and HF can be used to achieve unusual silica morphologies from spherical core–shell particles.

**Silica Spheres—Different Etching Media.** We also used spheres to illustrate the difference in etching rates between various etching media: HF, neutral, and basic NaOH etching. These spheres contained an internal layer of organo-silica containing a silane coupling agent TSD (N-[3-(trimethoxysilyl)-propyl]ethylene-diamine) and a thin outer shell of pure silica, partially building upon Chen et al.\textsuperscript{14} (see schematic illustration in Figure 7). However, we used a higher concentration of TSD in the organo-silica segment. TSD is similar to APTES (used in the sections above), but its diamine arm is larger and contains an additional amine group.

Etching these particles with aqueous HF, the different etching rates of the organo-silica and pure silica became apparent. In the early stage of the etching process, the less condensed inner layer remained completely protected by the outer silica shell. However, as etching continued, the outer shell became progressively more porous and eventually the inner layer was exposed to the solution. Once the inner layer had become accessible, it was rapidly etched and removed (see Figure 7d) without the shells becoming more etched. When the inner layer was completely removed, a core–void–shell (or rattler) particle remained. We attribute the much higher dissolution rate of the inner organo-silica layer to its lower degree of condensation, similarly to the APTES segments in the silica rods described in the previous section.

The difference between the etching rates of the two types of silica depended strongly on the etchant. For HF etching, the difference was the largest. When the particles were etched in

![Figure 6](image-url)
pure water, the difference was smaller, although the inner layer still etched faster than the shell (see Figure 7a). When etching with NaOH, both types of silica etched at nearly identical rates. In 1 mM NaOH, the particles etched from the outside inward resulting in a uniform decrease in particle diameter, even beyond the thickness of the pure silica shell (see Figure 7b). The slight undercut of the inner layer under the silica shell, highlighted by the arrows in Figure 7c, indicates that the organo-silica etched slightly faster.

The silica etching rate was also affected by the geometric shape of the particle. This is clearly demonstrated by the etching behavior of dumbbell particles that were formed during the growth of the shell around the organo-silica layer (~23%). Upon etching these particles with 4 mM NaOH, the particles etched from the outside inward. However, a small segment of pure silica remained in the region between the two spherical lobes. This region is more secluded than the rest of the particle surface, and as a result it etched more slowly than the outer spherical parts. The dependence of the etching rates of different types of silica on etchant, geometry, and accessibility can be used to modify the shape of silica particles in new ways.

Silica Biconcave Platelets. The silica bridges visible for the dumbbell particles in Figure 7c are remnants of the silica shell and are sandwiched between two TSD functionalized layers. As described above, these layers etch much faster than pure silica in HF solution.14 By employing a second etching step using 0.03% HF, we specifically etched the organo-silica layer without significantly changing the shape of the bridge. This resulted in the release of biconcave platelets consisting of nonfunctionalized silica from the rest of the particle (Figure 8).

Some of these particles had an opening in the middle of the ring. This opening formed when the spheres had aggregated before the coating with the outer silica layer had commenced. In case there was no opening, the particles had aggregated after a thin silica layer had already grown between the two aggregated spheres. The biconcave platelets were monodisperse and had an approximate diameter of 346 ± 30 nm. The platelets had an approximate thickness of 10 nm at the middle and 100 nm at the edge and could in principle be separated from the other morphologies present by centrifugation.

CONCLUSIONS

In summary, we present a general method to change the chemical composition of rod-shaped and spherical core–shell silica particles. We found that a decrease in reaction temperature and an increase in precursor concentration result in a higher local rate of dissolution of the silica structure, when etched by NaOH solutions and vice versa. We found that an increase in the ethanol concentration during the reaction also resulted in an increased rate of dissolution of the grown segment. This allowed us to produce silica colloids in many new shapes: double cones, cylindrical rods, hollow middle segmented rods, rod–cone particles, and biconcave particles. A similar difference in dissolution rate could be induced by the incorporation of a silane coupling agent. Differences in local rates of dissolution were affected not only by the degree of condensation but also by other kinetic factors, such as the accessibility to the etchant used to create an even larger variety of particles. We used core–layer–shell silica spheres to illustrate the possibilities. These particles consisted of a core, an organo-silica layer, and a thin pure silica shell. Aggregates of these particles, formed during seeded growth, were found to etch anisotropically in NaOH solutions. The region close to the contact point between the spheres was found to etch more slowly due to its geometry. Using this finding, a silica platelet sandwiched between two silica spheres was obtained. More-
over, the resulting ring-like structures could be liberated from the organo-silica layer by a final HF etching resulting in biconcave ring shaped particles. We believe that these results open up new opportunities in the preparation and self-assembly of anisotropic particles.

**EXPERIMENTAL SECTION**

**Silica Rods—General.** Silica rods were synthesized as follows. First, 20.0 g of PVP (Sigma-Aldrich, M_w = 40 kg/mol) was dissolved in 200 mL of 1-pentanol (99%, reagent-plus, Sigma-Aldrich). After the PVP had completely dissolved 20.0 mL of ethanol (100%, Interchima), 5.6 mL of Milli-Q grade water (Millipore system) and 1.24 mL of 0.18 M sodium citrate solution in water (99%, Sigma-Aldrich) were added. After vigorous shaking of the flask, 4.5 mL of ammonia (26.3%, Sigma-Aldrich) was added. Before the addition of TEOS, the emulsion was split in volumes of 40.0 mL. To each volume 300 μL of TEOS (tetraethyl orthosilicate, 98%, Sigma-Aldrich) was added, and the flask was shaken vigorously. If not mentioned otherwise, the particles were centrifuged after the reaction and dispersed in ethanol (100%, Interchima) and Milli-Q grade water (Millipore system) and again centrifuged and dispersed and stored in ethanol. The rods were used not older than one month.

**Silica Rods—Temperature.** In order to vary the chemical composition along the length of the rods, we changed the temperature during the course of the reaction. To this end we performed the reaction at a scale 40.0 mL of emulsion in a 40 mL vial. The vial was placed in a preheated hot air oven after the addition of TEOS. The temperature was changed during the reaction in the following schemes:

1. **50 °C (2 h), 5 °C (22 h)**
2. **50 °C (2 h), 5 °C (22 h), 50 °C (18 h)**
3. **5 °C (2 h), 25 °C (22 h)**
4. **50 °C (0.5 h), 5 °C (4 h), 25 °C (22 h)**
5. **50 °C (1 h), 5 °C (4 h), 5 °C (22 h)**

At the last step of reaction scheme 2, 70 μL of TEOS (98%, Sigma-Aldrich) was also added to continue the growth of the rod and the reaction was left to continue for the above indicated time. A TEM (transmission electron microscopy) image of the nonetched silica rods is shown in the Supporting Information Figure SII.

**Silica Rods—Precursor Concentration.** The composition was also modulated by increasing the concentration of precursor. To this end, first a rod was grown for 24 h at room temperature as described above. Then 150 μL of TEOS (98%, Sigma-Aldrich) was added, and the bottle was carefully homogenized. The synthesis was left undisturbed for another 24 h at room temperature. A TEM image of the nonetched silica rods is shown in Figure 4c.

**Silica Rods—Ethanol Addition Time.** The addition moment of ethanol during the reaction was used to vary the degree of cross-linking of the silica rods. To this end, first a rod was grown following the general rod synthesis procedure, but in the absence of ethanol. The addition of ethanol was delayed by either 1 or 3 h. The reaction mixture was then left undisturbed for 24 h at room temperature. A TEM image of the nonetched silica rods is shown in the Supporting Information Figure SII.

**Silica Rods—Sequential Steps.** The above methods were combined by growing rods following the general rod synthesis procedure. The reaction temperature was kept at 5 °C for the first 4 h and subsequently raised to room temperature for another 22 h. Then 100 μL of TEOS (98%, Sigma-Aldrich) was injected, and the mixture was carefully homogenized. The mixture was left to react for another 18 h. A TEM image of the nonetched silica rods is shown in Figure 4d.

**Silica Rods with an APTES Segment.** The procedure started with the general procedure described above. After mixing the content and the addition of TEOS, 40 mL of emulsion was transferred to a 40 mL glass bottle which was left to rest for 3 h. Then, 35.0 μL of APTES (98%, Sigma-Aldrich) was added, and the mixture was carefully homogenized and left to rest for 21 h. A TEM image of the nonetched silica rods is shown in the Supporting Information Figure SIII.

**Organo-Silica Spheres.** Silica spheres consisting of a fluorescently labeled silica core, an organo-silica layer, and a pure silica shell were synthesized as follows.

The preparation of the silica core consists of two phases. First the dye is coupled to the amine group on APTES. To this extent, 2 mL of absolute ethanol was added to 50.0 mg of FITC (98%, HPLC grade, Sigma-Aldrich) and stirred for 15 min. Then, 300 μL of APTES (98%, Sigma-Aldrich) was added, and the reaction mixture was stirred for 1.8 h in the dark. After coupling the dye to APTES, the fluorescein labeled core was prepared. In a round-bottom flask, 33.9 mL of ammonia (26.3%, Sigma-Aldrich) was mixed with 328 mL of absolute ethanol (Merck). To this mixture, 14.34 mL of TEOS (98%, Sigma-Aldrich) was added quickly while stirring vigorously. Finally, the mixture of FITC, APTES, and ethanol was added to the reaction mixture and left to react for 48 h.

A pure silica shell was grown around these particles to improve their stability. To 250.0 mL of unwashed reaction mixture two solutions (A and B) were added at a rate of 0.25 mL/h. The solution was stirred slowly during the whole reaction. Mixture A contained 1 mL of TEOS (98%, Sigma-Aldrich) and 6.9 mL of absolute ethanol (Merck) and mixture B contained 6.9 mL of absolute ethanol (Merck), 0.92 mL of ammonia (26.3%, Sigma-Aldrich), and 2.34 mL of Milli-Q grade water (Millipore system). Finally, the particles were washed three times with ethanol (100%, Interchima).

An organo-silica layer was grown around the fluorescent silica spheres as follows: 619 mL of absolute ethanol (Merck), 85.0 mL of Milli-Q grade water (Millipore system), 33.6 mL of ammonia (26.3%, Sigma-Aldrich), and 12.5 mL of seed particles (7.3 g/L) were added to a two necked round-bottom flask. Through one neck solution A was added, and through the second neck solution B was added. Solution A consisted of 32.3 mL of absolute ethanol (Merck), 10 mL of Milli-Q grade water (Millipore system), and 4.1 mL of ammonia (26.3%, Sigma-Aldrich). Solution B consisted of 31.3 mL of absolute ethanol (Merck), 11.8 mL of TEOS (98%, Sigma-Aldrich), and 3.82 mL of TSD (97%, Sigma-Aldrich). To prevent condensation at the nozzle of solution B, a slight nitrogen flow was applied away from the nozzle. Solution A was added to maintain a constant concentration of base.

Finally, a pure silica shell was grown using a regular Stöber silica growth procedure. To 140 mL of organo-silica coated cores (3.0 g/L), 91.35 mL of absolute ethanol (Merck), 121.5 mL of Milli-Q grade water (Millipore system), and 47.9 mL of ammonia (26.3%, Sigma-Aldrich) were added. While stirring, 8.98 mL of TEOS (98%, Sigma-Aldrich) was added in steps of 808 μL every minute. Finally the particles were washed three times with ethanol (100%, Interchima). A TEM image of the nonetched silica rods is shown in the Supporting Information Figure SIII.

**Etching.** Silica rods were etched by dispersing 6 mg of preformed silica rods in 10 mL of NaOH (sodium hydroxide, Sigma-Aldrich, extra pure, pellets) solution and put on a roller bank for 24 h. The concentration of the base was varied at the mM level to change the degree of etching (see the Results and Discussion section).

Silica rods with an APTES segment were etched by transferring 6 mL of 1.4 g L^-1 silica rods in ethanol to 40 mL of Milli-Q grade water (Millipore system). The bottle was put on a roller bank for 27 h. Next, the particles were washed three times with ethanol (100%, Interchima).

Silica spheres were etched in mild base by dispersing 6 mg of particles to 10.0 mL of 4 mM NaOH (sodium hydroxide, Sigma-Aldrich, pellets) solution and put on a roller bank for 24 h. Afterward the particles were washed three times with ethanol (100%, Interchima). To obtain biconcave disks, the particles were further etched in a solution of HF. To this end, 2.0 mg of etched silica spheres were dispersed in 10 mL of Milli-Q grade water (Millipore system). To this solution, 6.0 μL of HF (40–45%, technical grade, Riedel-de Haën) was added and subsequently homogenized. The solution was immediately washed with ethanol three times. This last step was done quickly to stop the reaction immediately.
The images were taken at a resolution of 512 by 512 pixels (pixel size: 10.4 nm × 10.4 nm).

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b00687.

TEM images of the silica rods prior to etching with NaOH (PDF)

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**Author Contributions**

The manuscript was written through contributions of all authors. F.H. wrote the manuscript and performed the synthesis and analysis of rod-shaped particles. F.H. performed the etching of the rod-shaped particles. W.V. and C.R. performed the synthesis of the spherical particles. W.V., C.R., and F.H. performed the etching of the spherical particles. A.v.B. and A.I. supervised the research. All authors have given approval to the final version of the manuscript.

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**Notes**

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**ABBREVIATIONS**

APTES, 3-aminopropyltriethoxysilane; PVP, polyvinylpyrrolidone; STED, stimulated emission depletion; TEM, transmission electron microscopy; TEOS, tetraethyl orthosilicate; TSD, N-[3-(trimethoxysilyl)-propyl]ethylene-diamine

**REFERENCES**


