Supporting Information

Synthesis of Monodisperse, Rodlike Silica Colloids with Tunable Aspect Ratio

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Synthesis procedure

Rods with a length of 1.7 μm and a diameter of 225 nm were prepared as follows. In a closed 500 ml glass laboratory bottle, 30 g of PVP (average molecular weight M_n = 40.000, Sigma-Aldrich) was dissolved in 300 ml of 1-pentanol (≥99%, Sigma-Aldrich) by sonication for 2 hours (Branson 8510). When all PVP had been dissolved, 30 ml absolute ethanol (Baker), 8.4 ml ultrapure water (Millipore system) and 2 ml of 0.18 M sodium citrate dihydrate (99%, Aldrich) solution in water was added to the pentanol. The flask was shaken by hand to mix the content. Then, 6.75 ml of ammonia (25 mass percent in water, Merck) was added, the flask was shaken again and 3 ml of TEOS (≥98%, Fluka) was added to the mixture. After shaking again, the bottle was left to rest and the reaction was allowed to proceed overnight. Next, the reaction mixture was centrifuged at 1500 g for 1 hour. The supernatant was removed and the particles in the sediment were redispersed in ethanol. This centrifugation procedure was repeated at 1500 g for 15 minutes, 2 times with ethanol, 2 times with water and finally again with ethanol. To remove small rods and improve monodispersity, the rods were centrifuged three times at 700 g for 15 minutes and redispersed in fresh ethanol. An extra (30 nm) silica shell was grown around the particles by dispersing the particles after the last cleaning step in 100 ml of ethanol. Under magnetic stirring, 12 ml of ammonia, 10 ml of water and 1 ml of TEOS were added. After reacting for several hours the mixture was centrifuged at 700 g for 30 minutes and washed with ethanol three times. The formation of a fluorescent shell was achieved by letting 25 mg of FITC (isomer I, ≥90%, Sigma) react overnight with 35 μl APS (≥98%, Sigma-Aldrich) in 5 ml ethanol and adding this mixture together with the TEOS for shell growth.

Synthesis conditions

All syntheses were performed at room temperature (~20°C). Experiments at 5°C resulted in shorter rods, experiments at 50°C in longer rods.

It was found that the concentration of ammonia in the storage bottle is extremely important: while ammonia from a fresh bottle results in the described rods, a bottle of a few months old results in less and shorter rods. We hypothize this is due to CO_2 dissolved in the basic solution of the bottle that was opened several times and which increased the ionic strength.

The reagent concentrations that can be used to grow rods are summarized in the graphs below. Tests were done with a standard of: 1g PVP, 10 ml Pentanol, 0.28 ml water, 0.1 ml (0.18 M) sodium citrate solution, 0.2 ml ammonia, 1 ml ethanol and 0.1 ml TEOS. For most reagents there are 3 concentration regimes: one that results in sphere formation, one that results in rods and one that results in curly rods (Figure 1). Most likely, the curliness of the rods results from the changed reaction conditions that disturbed the process in such a way that surface tension is no longer able to keep the angle between the emulsion droplet and the growing silica rod constant during growth.

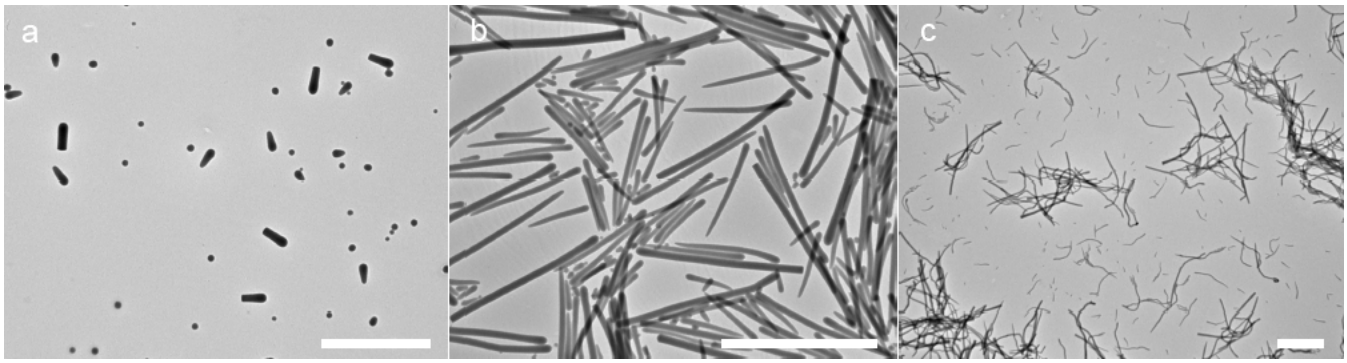
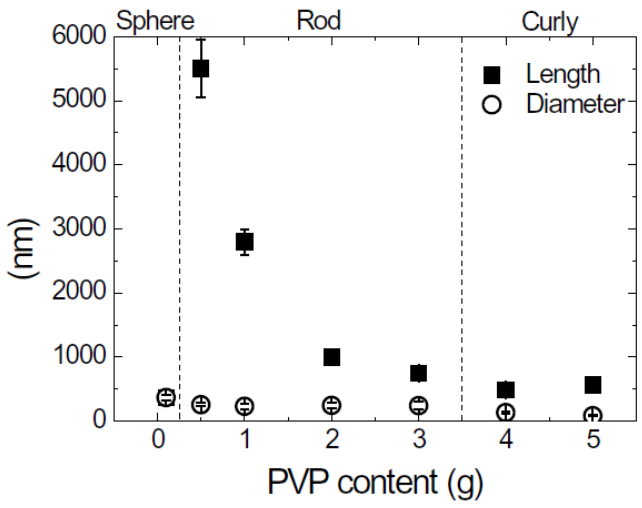
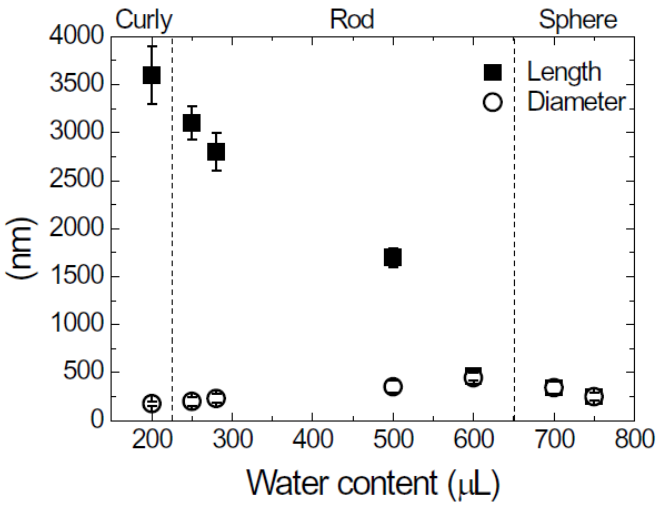
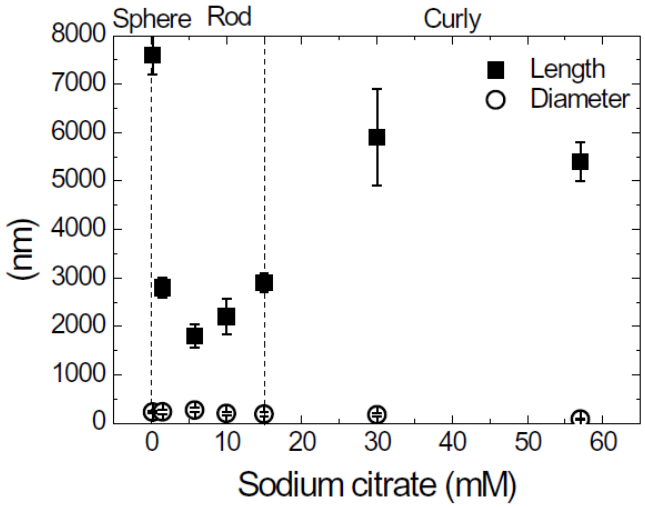
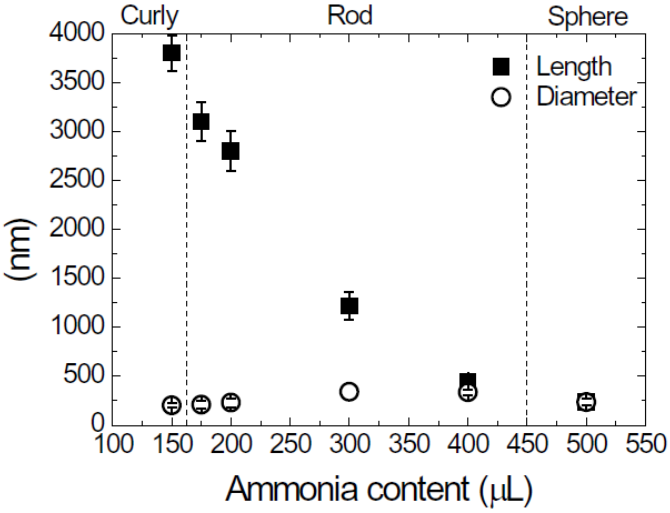


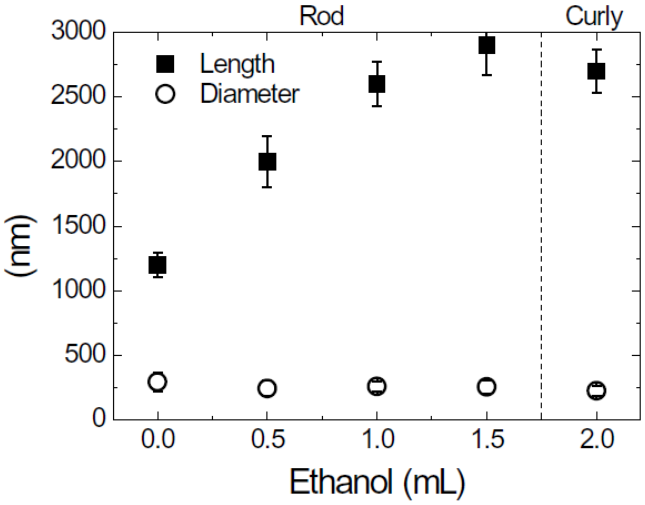
Figure 1.Variations in reagent concentrations produce rods from small aspect ratio (A) to large aspect ratio (B) to long an curly rods (C). Scale bars are 3 μm.


Sphere
Rod
Curly
Length
Diameter
(nm)
PVP content (g)


Curly
Rod
Sphere
Length
Diameter
(nm)
Water content (μL)


Sphere
Rod
Curly
Length
Diameter
(nm)
Sodium citrate (mM)


Curly
Rod
Sphere
Length
Diameter
(nm)
Ammonia content (μL)


Rod
Curly
Length
Diameter
(nm)
Ethanol (mL)

Scaling up the synthesis from the 20 ml described by Zhang et al. influences the size of the final rods. When going to larger volumes, we observed that the length of the rods decreased with increasing volume. Where 10 ml experiments resulted in 2 μm rods, 300 ml resulted in 1.3 μm rods and 750 ml in 760 nm. The diameter slightly increased to 400 nm for a 750 ml synthesis.

Stirring

Regarding the shape of the particles, we found that stirring is also an important parameter as is to be expected from our proposed mechanism. Straight rods were best grown without any stirring. When the reaction was performed in a round bottom flask and stirring with a magnetic stirring bar was applied, we observed two phenomena (Fig. 2). Initially, the rods grew stably until they were long enough for the shear caused by the stirring to affect them. At that point, the droplet at the end of the rod became unstable and shrank, after which the rod grew further with a smaller diameter (Fig. 2B). Secondly, the instability caused by the stirring can allow salt to crystallize from the emulsion droplets resulting in long needles with rods sticking out to the side (Fig. 2A). Regarding the reagents in our synthesis mixture and the work done by Wang et al. [1], we assume these are ammonium citrate crystals. Although stirring has a negative effect during the growth of the rods, the way of mixing the reagents at the start of the reaction did not matter at all. Sonication, shaking and stirring did not influence the size or polydispersity of the emulsion droplets and the resulting rod diameter. Addition of a surfactant (Igepal CO-520, up to 0.8 g per 10 ml pentanol) did not have any noticeable effect on the resulting emulsion or rod growth.

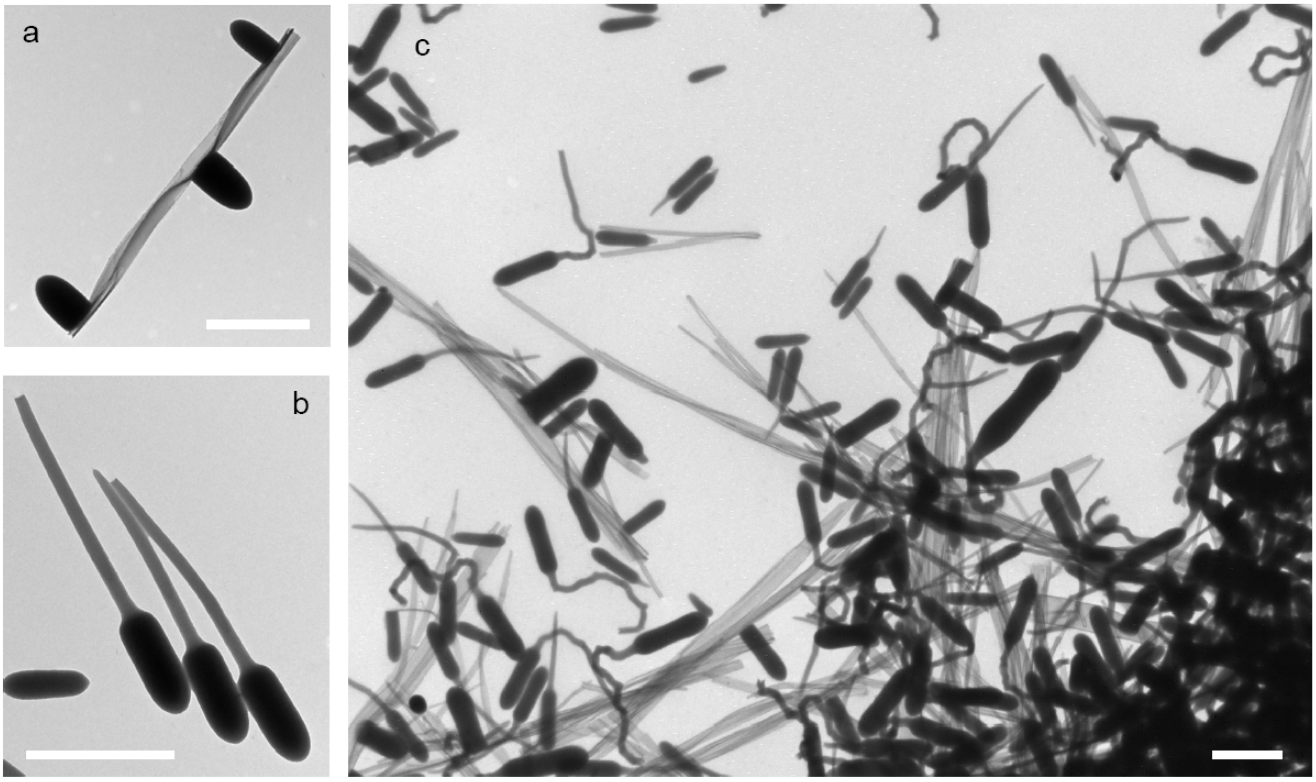


Figure 2. Peculiarly shaped particles due to instabilities induced by stirring. A) Rods joined by (silica coated) ammonium citrate crystals. B) Rods with a reduced diameter due to stirring. Scale bars are 1 μm.

Refractive index and density measurement

The refractive index of the particles was measured by dispersing them in oils of varying refractive index (using steps of 0.01, Cargille refractive index liquids, set RF 1/5, measured at 589.3 nm at 25°C). Observation with an optical microscope allowed us to determine whether the refractive index of the particles is higher or lower than that of the oil.

The density of the rods was measured by dispersing them in a mixture of bromoform and methanol and centrifuging them. The composition of the mixture was adjusted until the rods did not cream or sediment anymore. The density of the corresponding mixture was calculated using the data from Figure 1 in reference 2.

Electric field

The CLSM image of the rods aligned by an electric field was made of a dispersion contained in a cell that consisted of a 2 mm wide capillary with 0.05 mm thick metal wires running through with an inter wire distance of 1.65 mm. A 352 V peak to peak sinusoidal signal with a frequency of 1 MHz was applied to polarize the particles but not the double layer, as was done by us before to influence the ordering of silica spheres [3,4].

References:

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