Supporting Information

Seeded-Growth of Silica Rods from Silica-Coated Particles

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1. Preparation of Silica Particles

Silica particles (**Figure S1**) were prepared by a modified Stöber method, as described in the Experimental Section. Particle size average as determined from 25 particles in **Figure S1**: 325 nm, δ = 6%.

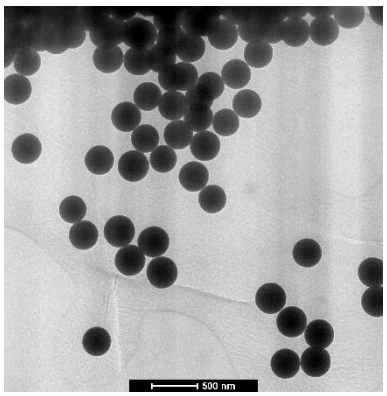

Figure S1. TEM image of silica particles used as seeds for the rods in **Figure 1**.

2. Growth of Silica Rods from Silica Particles

When we first increased the amount of water used in the silica rod growth reaction, we found that this facilitated the growth of fewer spikes per seed particle, but also shortened the length of the rods (**Figure S2**).

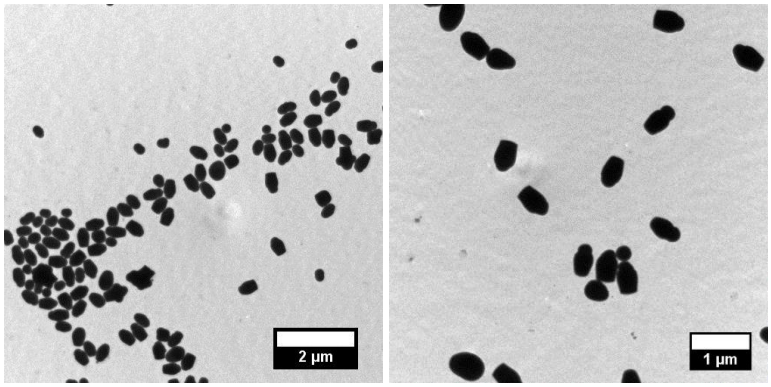

Figure S2. TEM image of short and fat silica rods grown from silica particles.

When using much larger seed particles with an average size of 1.5 µm, we found that multiple rods would grow from the particles (**Figure S3**).

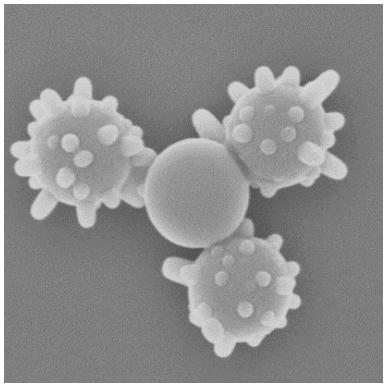

Figure S3. SEM image of larger silica spheres (average size 1.5 μm) with rods grown from the surface of some of the particles.

3. Preparation of Silica Particles with a Fluorescent Core

Silica particles with a fluorescent core had an average size of 441 nm, δ = 3%, as measured from 50 particles in **Figure S4**.

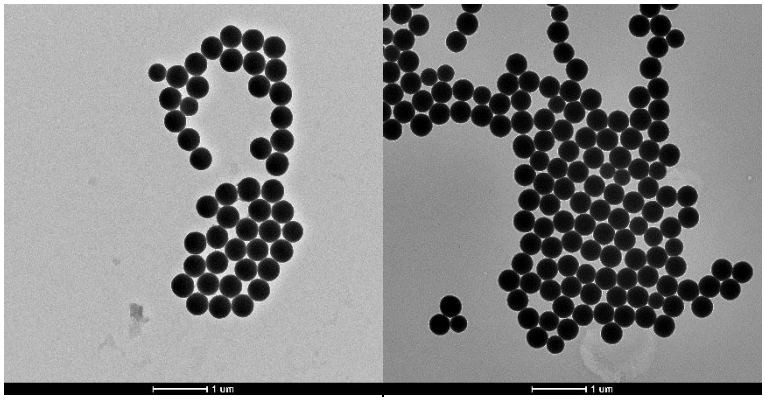

Figure S4. TEM images of silica particles containing a fluorescent core.

4. Preparation of Silica Particles with an Ag Core

The Ag particles and Ag particles coated in silica which were used as seeds for the preparation of the structures shown in **Figure 3** are shown in **Figure S5 and Figure S6,** respectively. We do not quote an average value for the size of the silica layer because the sample is so polydisperse. This means that the silica layer for each particle will likely be very different, and light scattering techniques will also not give an accurate value for particle sizes. Despite this, we can see for the individual particles in **Figure S6** that the thickness is approximately between a few nanometers and 30 nm.

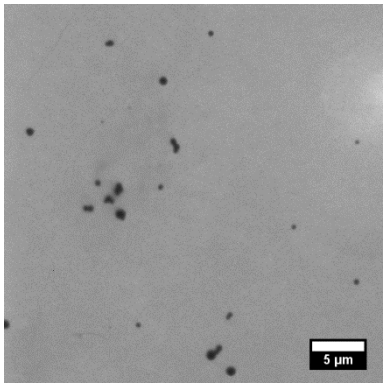

Figure S5. TEM image of Ag particles.

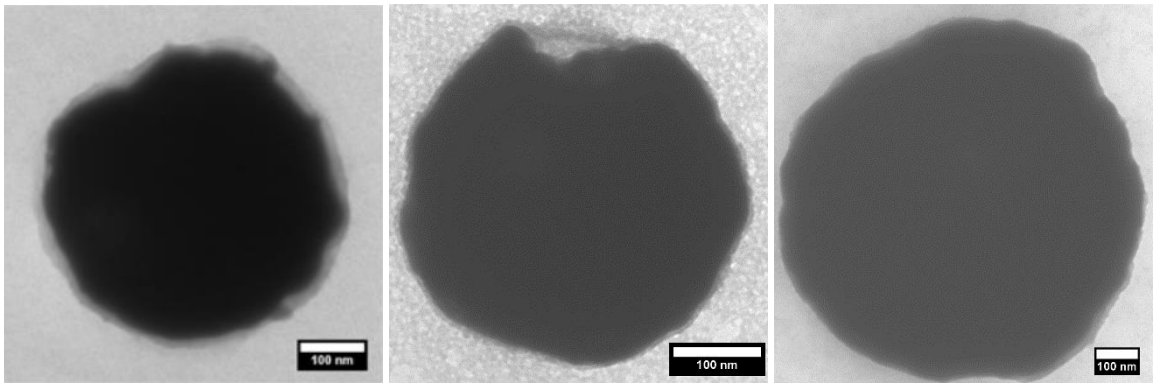

Figure S6. TEM images of silica coated Ag particles. These particles were used as seeds for the rods grown in **Figure 3**.

5. Preparation of Silica Particles with a PS Core

The PS particles and PS particles coated in silica which were used as seeds for the preparation of the structures shown in **Figure 4** are shown in **Figure S7** and **Figure S8** respectively. In the right hand image of **Figure S8** it appears there are also some very small silica nanoparticles which have likely formed as a result of secondary nucleation. These particles are discarded upon washing by centrifugation, which is why they are not observed in **Figure 4**.

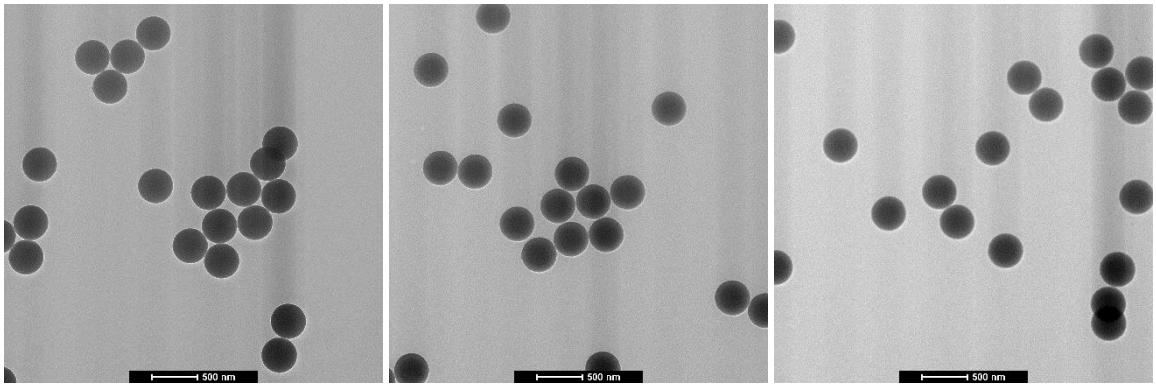

Figure S7. TEM images of PS particles. Particle size as determined from 25 particles in the images: 372 nm, δ = 1%.

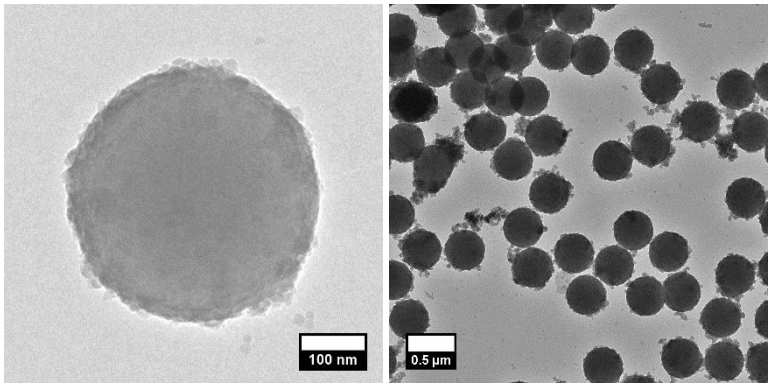

Figure S8. TEM images of silica coated PS particles. Particle size average as determined from 25 particles in the image: 436 nm, δ = 1%.

6. TEM images of matchsticks with PS heads

TEM images of the matchsticks shown in **Figure 4** are shown in **Figure S9** below, where the PS cores inside the matchstick heads are more obvious.

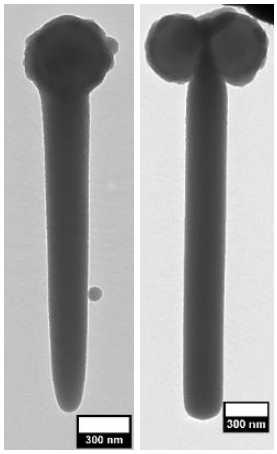

Figure S9. TEM images of matchsticks with silica-coated PS heads.

7. Reducing the Number of Multiple-Headed Matchsticks

We experimented to see the effect of lowering the concentration of silica-coated PS "seed" particles on the ratio of multiple-headed matchsticks to single-headed matchsticks. We kept the total volume of added particle dispersion equal for all experiments (300 µL), varying only the concentration of silica-coated PS particles within. We found that when matchsticks are prepared from 300 µL of a 1 wt% silica-coated PS particles in water, the ratio of multiple-headed matchsticks to single-headed matchsticks was reduced to ~27% (**Figure S10a**), which is lower than the value of 37% from Figure 4 when a 2.5 wt% was used. When matchsticks are prepared from 300 µL of a 0.1 wt% silica-coated PS particles in water, the ratio of multiple-headed matchsticks to single-headed matchsticks reduced to ~12% (**Figure S10b**). However, the amount of independent silica rods (which grow independently of seed particles) increases from <15% to >80%. When matchsticks were prepared from 300 µL of a 0.01 wt% silica-coated PS particles in water, no multiple-headed matchsticks were found in the synthesis whereas some (<2%) single-headed matchsticks can still be found (**Figure S10c**). Here, the amount of independent silica rods (which grow independently of seed particles) increases even further to >98%. The ratio of multiple-headed matchsticks to single-headed matchsticks can therefore be controlled to a certain extent by varying the concentration of "seed" particles. However, this is a delicate balancing act because when concentrations of seed particles are too low then many independent silica rods form.

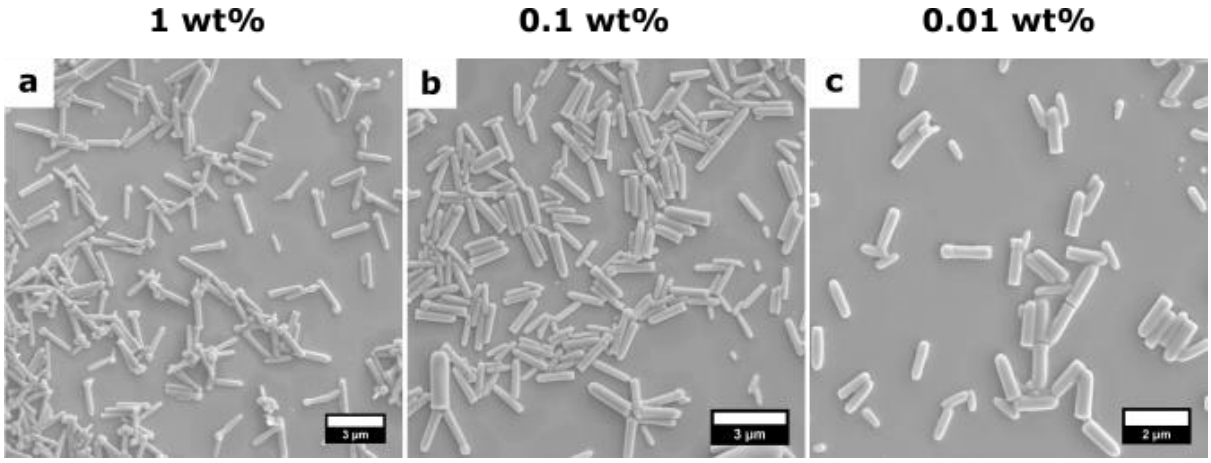

Figure S10. SEM images of matchstick particles prepared with various concentrations of silica-coated particles, where the total amount of colloidal solution was kept at 300 µL. (a) Matchsticks were prepared from 300 µL of a 1 wt% silica-coated PS particles in water. (b) Matchsticks were prepared from 300 µL of a 0.1 wt% silica-coated PS particles in water. (c) Matchsticks were prepared from 300 µL of a 0.01 wt% silica-coated PS particles in water.

8. Supraparticles from Matchsticks with PS Heads

Further SEM imaging of the assembled supraparticles (shown in **Figure 4**) is shown in **Figure S11**. The supraparticles ranged in size from ~3-15 microns, and we also observed some 'broken' supraparticles in the sample.

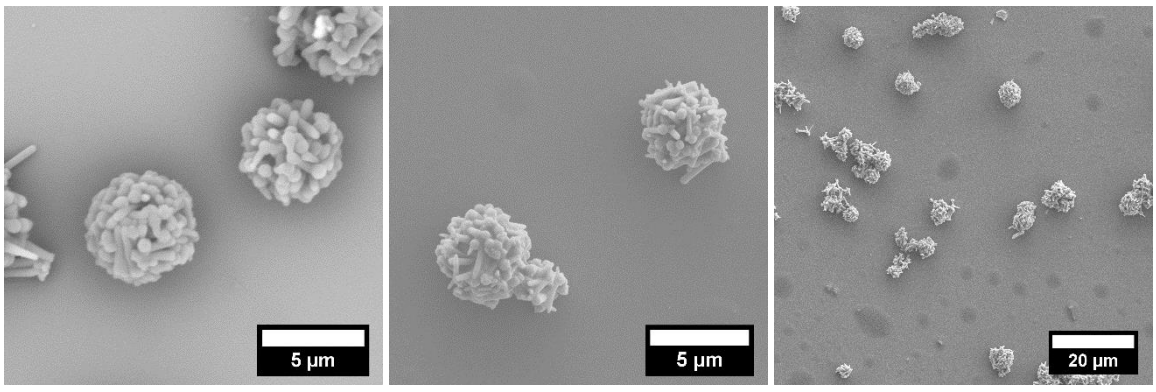

Figure S11. SEM images of supraparticles assembled from matchsticks with heads of PS.