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Seeded-Growth of Silica Rods from Silica-Coated Particles

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S *Supporting Information*

ABSTRACT: Seeded growth of silica rods from colloidal particles has emerged as a facile method to develop novel complex particle structures with hybrid compositions and asymmetrical shapes. However, this seeded-growth technique has been so far limited to colloidal particles of only a few materials. Here, we first develop a general synthesis for the seeded-growth of silica rods from silica particles. We then demonstrate the growth of silica rods from silica-coated particles with three different cores which highlight the generality of this synthesis: fluorescently labeled organo-silica (fluorescein), metallic (Ag), and organic (PS latex). We also demonstrate the assembly of these particles into supraparticles. This general synthesis method can be extended to the growth of silica rods from any colloidal particle which can be coated with silica.
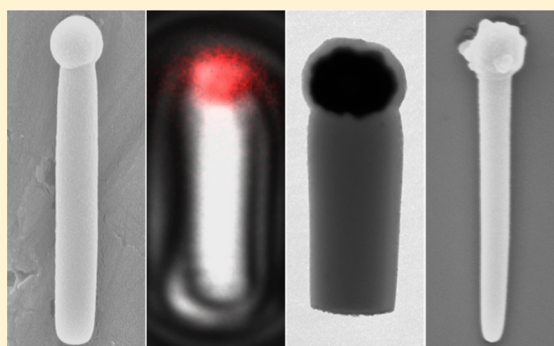
■ INTRODUCTION

Fine control of the composition and shape of building blocks at the nano and (sub) micron scale is a route to novel functional materials with unique properties. Particularly interesting colloidal building blocks are colloidal silica rod-like structures. Silica rods with high uniformity can be made via a one-pot wet-chemical synthesis method,[1] are low-cost, inert, biocompatible, and highly tunable and already show great potential for many novel materials such as advanced coatings (superhydrophobic[2] and nonfouling[3]), thin films for solar cells,[4] porous composites,[5,6] and advanced optical materials because of their ability to form liquid crystal[7−9] and plastic crystal phases.[10−12] In addition, they find applications as interesting model systems to study the influence of anisotropy on phase behavior on the single particle level in 3D.[7,9−12]

An increase in the breadth of these potential applications as well as the complexity of potential novel materials can be achieved by increasing the complexity of the building blocks themselves. Two ways to increase the complexity of silica rods are by introducing: (i) heterogeneity in composition (e.g., composites/hybrid structures) and (ii) anisotropy in composition (e.g., creating asymmetry). An introduction of heterogeneity in the composition of silica rods adds functionality which broadens the potential properties of the material, while asymmetry in these structures is essential for some potential applications in active matter,[13−17] directed assembly,[9] and advanced optical materials.

Currently, the most effective experimental conditions to prepare silica rods exploit the emulsion-droplet based growth of anisotropic silica structures, which was developed in our group.[1,18] In this method, silica rods grow from the ammonia-catalyzed condensation of tetraethylorthosilicate (TEOS) in water emulsion droplets stabilized by sodium citrate and poly(vinylpyrrolidone) (PVP) in a 1-pentanol continuous phase. This method reproducibly results in highly uniform silica rods with tunable aspect ratio. Moreover, with this method, the silica rods can even be shaped by modifying conditions during growth[3,19] or via post-treatment to create even more complex particles.[20,21] Subsequent research then found that when certain colloidal particles (e.g., TiO_2, FeO_x, and MnO_x) are also present in the synthesis, the silica rods can grow from the water droplets attached to (or Pickering stabilized by) the colloidal "seed" particles, resulting in anisotropic composite silica rods.[14,15,19,22−24] This is known as "seeded-growth", and the resulting particles are known as "matchsticks". Alternatively, functional polymer particles can be regiospecifically attached to silica rods by an inverse seeded-growth method, where silica rods are used as seeds in a dispersion polymerization reaction.[25] Despite the seeded-growth synthesis technique being very effective for growing anisotropic composite silica rods with certain functionalities, the synthesis has so far been limited to only a few colloidal particle compositions, e.g., FeO_x, TiO_2, and MnO_x. This is probably because the colloidal particle "seeds" must adhere to

certain requirements, e.g., be dispersible in 1-pentanol and interact in a specific way with the water emulsion droplets in order to facilitate growth of a silica rod. In practice, this means that seed particles and growth conditions must be optimized for each desired material. In fact, the use of this method along with colloidal silica and silica-coated particles has shown to result in isotropic shapes with multiple silica rods grown from the seed.[19,26] It is difficult with some colloidal particles to facilitate silica rod growth at all, where instead pure silica rods grow independently of the dispersed colloidal seeds. Therefore, there is a need for a general synthesis of silica rod growth from colloidal particles. This general synthesis will allow facile experimental preparation of advanced anisotropic composite silica rods with a wide range of functionalities.

Herein, we demonstrate a general synthesis for growing silica rods from silica seeds with potentially any functionality, by optimizing the experimental conditions of the seeded growth approach. Then, we use the principle that almost all colloidal particles can be coated with silica.[27] Subsequently, as a proof-of-principle for the generality of this method, we prepare composite matchstick particles from core/shell silica particles with (i) a fluorescent silica core, (ii) metallic Ag core, and (iii) organic polystyrene (PS) core, using the same experimental conditions for the seeded growth. These three cores were specifically chosen in order to demonstrate the generality of the synthesis, highlighting that these matchsticks can potentially be prepared with a huge diversity of functionality/composition. The first anisotropic composite matchstick particles we prepare with a fluorescent core in the head are particularly interesting for applications which can utilize the fluorescent anisotropic nature of these particles, including confocal fluorescence microscopy in which single particle orientations and positions can be determined even in concentrated systems,[28] cell imaging, and the investigation of flow behavior. The second anisotropic composite matchstick particle we prepare introduces a catalytically active and electrically conductive and plasmonic material (Ag) into the rod head. The former property makes these potentially self-propelling particles with applications in active matter,[13−17] while the latter introduces the possibility of fine and anisotropic manipulation of the rods via dielectrophoretic trapping.[29] The seeded growth method presented here is able to incorporate the silver head, while reliably maintaining a shape resembling a high aspect ratio rod. Current methods to incorporate metals into rod heads require Pickering stabilization of water droplets, which results in polydisperse mixtures of particles (size range of smallest dimension generally between 100−1000 nm) with nonuniform shapes.[15] The third anisotropic composite matchstick particles we prepare with organic PS in the heads are potentially very versatile because organic polymers—and therefore these particles—can be made with a huge range of functionality.

We then also demonstrate the assembly of the matchsticks with PS heads into supraparticles. Supraparticles are clusters of smaller particles which themselves have a defined structure.[30−32] The formation of supraparticles commonly utilizes the technique involving the slow drying of particle-containing emulsion droplets in a nonvolatile continuous phase, and recently our group extended this technique to the formation of supraparticles also from rod-like nanoparticles.[28,33] These hybrid matchsticks with PS heads therefore have the potential to form advanced hierarchical structures, because supra-particles can be used as building blocks themselves for hierarchically ordered structures which combine original functionalities at different length scales.[30,31] These supra-particles assembled from the matchsticks with PS heads are particularly interesting for advanced supraparticles with tunable porosity, because the organic PS can be burned away.[34] Such structures are potentially interesting for catalysis and sensing applications.

We believe these results have implications for the develop-ment of novel complex composite particles for applications toward novel advanced materials, and they are fundamentally of great interest.

■ EXPERIMENTAL SECTION

Materials. Sodium citrate dihydrate (99%), 1-pentanol (99%), tetraethylorthosilicate (TEOS, 98%), ammonium hydroxide (NH$_4$OH, 25 w/w%), polyvinylpyrrolidone-40 (PVP, Weight-Average Molecular Weight MW = 40 kg/mol), PVP-360 (MW = 360 kg/mol), (3- aminopropyl)-triethoxysilane (APTES, 98%), fluorescein iso-thiocyanate isomer I (FITC, > 90%), AgNO$_3$ (>99%), L-ascorbic acid (>99%), and Span80 were purchased from Sigma-Aldrich. Ethanol (100%) was purchased from Interchema, and pure water was used from a Millipore system. Gum arabic was obtained from Fluka. n-Hexadecane (for synthesis) was obtained from Merck.

Preparation of Silica Particles. Silica particles (325 nm, δ = 6%) were prepared via a modified Stöber method. Briefly, NH$_4$OH (4.0 mL), water (3.0 mL), ethanol (22.0 mL), and TEOS (1.1 mL) were added to a 50 mL round bottomed flask. The mixture was stirred for 24 h before the particles were isolated via centrifugation and dried before then being redispersed in water to make a 2.5 wt % dispersion. Polydispersity values were obtained from 25 particles in the TEM image in Figure S1.

Preparation of Silica Particles with a Fluorescent Core. The silica particles with a fluorescent core (441 nm, δ = 3%) were synthesized by first coupling the FITC dye to APTES, followed by the addition of ammonia and TEOS using a syringe pump until the desired particle size was reached, as described by Vlug.[35,36] Polydispersity values were obtained from 50 particles in the TEM image in Figure S4.

Preparation of Silica Particles with an Ag Core. The silica particles with an Ag core were synthesized by first synthesizing Ag colloidal particles and subsequently coating them with silica. The Ag particles were synthesized as follows: First, gum arabic (0.35 g) and ascorbic acid (5.86 g) were dissolved in water (50 mL). Then a separate solution of gum arabic (0.35 g), AgNO$_3$ (1.41 g), and water (50 mL) was prepared. The second solution was quickly poured into the first solution in a 250 mL round bottomed flask and left to react for 12 h. The Ag particles were then isolated by centrifugation. Next, these Ag particles were coated with silica as described by Graf et al.[27] Briefly, 5.0 mL of a 4.72 g/L solution of Ag particles in water was added to 8.7 mL of a 9.5 g/L PVP (40 kg/mol) solution in water in a 50 mL centrifuge tube, and the tube was slowly rotated for 24 h. Then, the PVP-coated Ag particles were centrifuged, the supernatant was discarded, and the particles were redispersed in a solution of NH$_4$OH in ethanol (4.2 vol %, 8.63 mL). Then TEOS (87.2 µL, as a 10% solution in ethanol) was added to coat the particles with a thin layer of silica. Next, double the amount of the TEOS solution (10% in ethanol) was continuously added stepwise every 60 min (174.4, 348.8, 697.6 µL, and so on) for 6 additions. The resultant silica coated Ag particles were then isolated via centrifugation.

Preparation of Silica Particles with a PS Core. Cationic polystyrene (PS) particles (372 nm, δ = 1%) were prepared by a surfactant-free emulsion polymerization as described by Goodwin et al.[37] These particles could be readily dispersed in ethanol. The PS particles were then coated with silica as described by Graf et al.[27] The PS particles were sedimented, the supernatant was discarded, and a 4.75 mL solution of particles in ethanol (0.41 g/L) was then added to 4.75 mL of a 7 g/L PVP solution (360 kg/mol) in ethanol. Then, ammonia (0.25 mL) was added along with 500 µL TEOS (10% in

water) in order to coat the particles with a thin layer of silica. Next, double the amount of the TEOS solution (10% in ethanol) was continuously added stepwise every 60 min (1.0, 2.0, 4.0 mL, and so on) for 6 additions. The resultant silica coated PS particles (436 nm, δ = 1%) were then isolated via centrifugation.

Growth of Silica Rods from Silica Particles. Silica rods were grown via a modified procedure described by Datskos et al.,[19] which is a modification from the silica rod growth procedure originally described by Kuijk et al.[1] First, a PVP/1-pentanol stock solution was made with concentration of 100 g/L. Then 9.11 g of this stock solution was added to a 15 mL centrifuge tube. Next, 300 μL of the seed particles (2.5 wt % in water) were dispersed in the PVP/1-pentanol solution via sonication. We found that the seed particles needed to be aged in water for at least 24 h before use in the reaction to ensure growth of silica rods from the particles. Ethanol (1.5 mL) and aqueous sodium citrate (0.18 M, 100 μL) were then added, and the mixture was vigorously shaken by hand. Ammonia (200 μL, 25%) was then added, and the mixture shaken again. TEOS (100 μL) was then added followed again by vigorous shaking. The mixtures were then left to stand for 12 h. In the case of the Ag cores, the mixture was slowly rotated for the 12 h reaction period to prevent sedimentation. After the 12 h reaction, the mixtures were centrifuged at 800g for 45 min, the supernatant was discarded, and the particles were redispersed in ethanol. The particles were then washed by two rounds of centrifuging at 500 g for 15 min, discarding the supernatant and redispersing in ethanol. The Ag matchsticks were further isolated simply by letting the particles sediment for an hour and removing the supernatant.

Supraparticles from Matchsticks with PS Heads. Supraparticles were made using a water-in-oil (W/O) emulsion method, in which charge stabilized colloids were compressed inside aqueous droplets dispersed in a nonvolatile organic phase.[32] The matchstick particles with PS heads obtained from the synthesis were centrifuged and redispersed in deionized water (10 mL). A 0.5 mL portion of this dispersion was then pipetted into hexadecane (5 mL) containing nonionic surfactant Span 80 (1 wt %) in a small glass vial (20 mL). Parafilm was then used to seal the top of the glass vial, which was then punctured with a few holes (to allow slow evaporation of the aqueous dispersed phase). The vial was then left to shake gently (IKA KS 260 basic, 250 rpm) for 2 weeks. The shaking was then stopped to allow the formed supraparticles to sediment. After 1 h, sediment was visible on the bottom of the vial, so the supernatant was carefully removed using a glass pipet. The supraparticles were then washed twice with cyclohexane (cyclohexane added, solution vortexed, left to sediment, solvent removed), eventually leaving a relatively concentrated supraparticle dispersion in <0.5 mL cyclohexane.

Characterization. Imaging of the particle morphology was performed with TEM, SEM, and confocal microscopy. TEM was performed with an FEI TECNAI 20 electron microscope in which samples were prepared by pipetting a drop of the particle dispersion in ethanol onto a Formvar/Carbon Films 200 Mesh Copper (100) grid. SEM was performed with an FEI XL30SFEG, FEI Phenom in which samples were prepared by pipetting a drop of the particle dispersion onto an aluminum stub (Figure 1) or silicon wafer on top of an aluminum stub and subsequently sputter-coated with a platinum layer of approximately 4 nm. Confocal microscopy was performed with a Leica SP8 confocal microscope (100× oil immersion lens) with excitation by a 488 nm laser line. The reflection signal was recorded at 488 nm, and the fluorescence was in the range 500−600 nm. To prepare the samples, the rods with fluorescent heads were dried from ethanol on a #1.5 coverslip before adding a drop of refractive index matching liquid (glycerol/water mixture, 85:15 by mass) on top.

■ RESULTS AND DISCUSSION

Seeded Growth of Silica Rods from Silica Particles. The seeded growth of silica rods from silica particles has previously been shown to result in isotropic star-shaped particles in which multiple rods are grown from the silica seed particles.[19] Using this synthesis as our starting point, we then
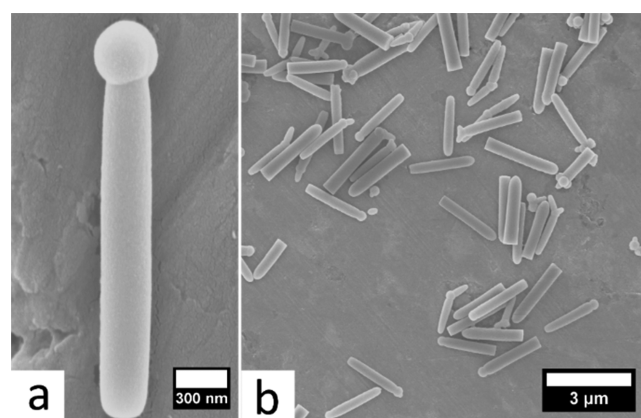

Figure 1. SEM images of matchsticks grown from silica particles.

optimized the conditions of silica rod growth in order to grow singular silica rods from pure silica particles (average size 325 nm, polydispersity δ = 6% where δ = (standard deviation)/(mean diameter), Figure S1). We reduced the number of rods grown from the silica seed particles by using more water in the emulsion. The effect of increased water content of the emulsion has recently been shown with FeO_x structures to better facilitate the growth of one rod onto one seed.[14] However, the increasing amount of water is also known to reduce the rod aspect ratio (Figure S2).[1] We therefore compensated for this rod shortening by increasing the amount of ethanol present, which is known to increase rod length up to a certain point, beyond which no rods are formed at all, only spheres.[1] The amount of each reagent in the recipe is a delicate balancing act, which is all the more reason why a general synthesis is necessary. By using more water and more ethanol in our recipe, we were successfully able to facilitate the growth of a singular silica rod from the silica seed particles (Figure 1a). The synthesis results in a highly uniform set of matchsticks (Figure 1b).

Notably, we also found that the size of the seed particle was important in facilitating singular silica rod growth. We found that using much larger seed particles sizes of >1.5 μm diameter facilitated the growth of many rods from one seed particle, resulting in rough particles with short spikes (Figure S3). We hypothesize that this is because the sizes of the emulsion water droplets from which the silica rods grow are ~200−500 nm,[1,19] therefore multiple emulsion droplets are able to form without coalescing on the surface of larger seed particles. In a similar way, urchin-like silica particles have been prepared.[26]

Seeded-Growth of Silica Rods from Silica Particles with a Fluorescent (FITC) Core. We then grew silica rods from silica particles with a fluorescent silica core containing fluorescein isothiocyanate isomer I (FITC). We chose a fluorescent core because this increases the utility of these particles for imaging applications. For example, this allows 3D tracking of one end of the particle from confocal image volumes, yielding information about the matchstick orientation and dynamics.

The silica particles with a fluorescent core (size 441 nm, δ = 3%) were prepared using established techniques, by a modified Stöber method, utilizing seeded-growth and the incorporation of silane coupling agents that were first reacted to a fluorescent dye (Figure S4).[35] The silica rods were then grown from these silica particles with a fluorescent core in the same way as with the pure silica particles. The resulting matchsticks displayed

fluorescence exclusively in the head of the matchsticks (Figure 2). Since our group has also developed the methodology to fluorescently label the silica rods, these matchsticks have real potential for advanced particle tracking studies.[1,18,28]
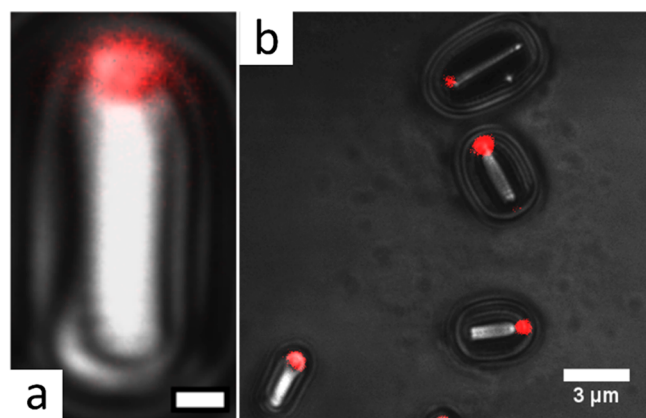

Figure 2. Confocal microscopy images of dried matchsticks. The fluorescence signal is overlaid in red on grayscale reflection images. The only appreciable fluorescence signal was found in the matchstick heads. Scale bar for part a is 500 nm.

Seeded-Growth of Silica Rods from Silica Particles with a Metallic (Ag) core. Next, we grew silica rods from silica particles with a core consisting of metallic silver (Ag). We chose Ag for the metallic core because silica rod matchsticks have not been prepared from large Ag colloidal particles, and colloidal Ag can be prepared with high yields. Moreover, Ag is (i) highly conductive as well as plasmonically interesting and (ii) highly catalytically active. The former means anisotropic hybrid rods with a Ag head would be responsive in an electric field and therefore have potential applications in directed assembly.[33] The latter means that these hybrid rods are interesting for the fields of active matter and catalysis (because the silica layer is porous).

The silica particles with a Ag core were synthesized by an established method involving the reduction of silver ions to metallic silver by ascorbic acid, which is known to result in polydisperse dispersions of Ag with diameter around 500 nm,[38] followed by subsequent washing and coating of the Ag particles with silica by an established method.[27] The resultant Ag particles were polydisperse (Figure S5) with an average diameter of 560 nm (from dynamic light scattering). Next, these particles were coated with silica (Figure S6). We then grew silica rods from these silica particles with a Ag core in the same way as with the pure silica particles. TEM images of the resulting matchsticks display an obvious darker region in the head of the matchstick, which is due to the presence of the Ag (Figure 3). Interestingly, matchsticks were successfully prepared from the seed particles of all sizes and the diameter polydispersity of the rods ($\delta = 10\%$), much lower than that of seed particles ($\delta = 22\%$) (Figure 3c). Furthermore, the rod diameter polydispersity is remarkably similar to that of the
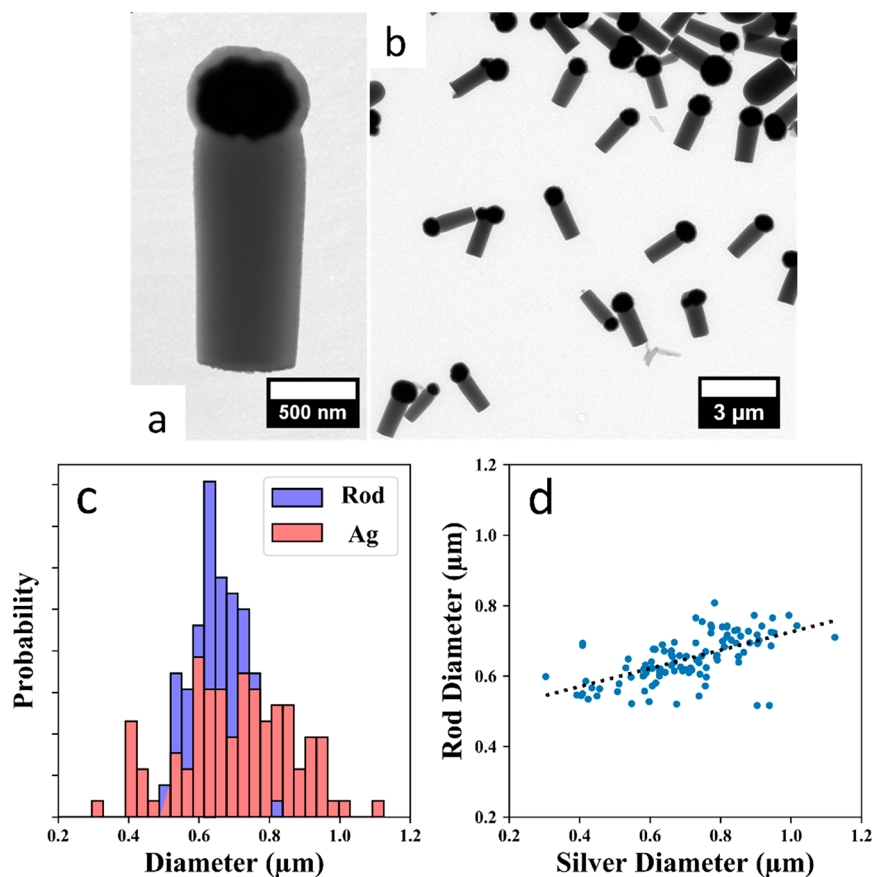

Figure 3. (a, b) TEM images of matchsticks with a head containing an Ag core. (c) Size distributions of the silver seed particles and the rods grown from them. The rod and Ag mean values are 650 nm ($\delta = 10\%$) and 700 nm ($\delta = 23\%$), respectively. (d) Relation between the diameter of the silver particle and that of the rod grown from the same particle. The fit line has gradient 0.26 and intercept 0.47 μm.
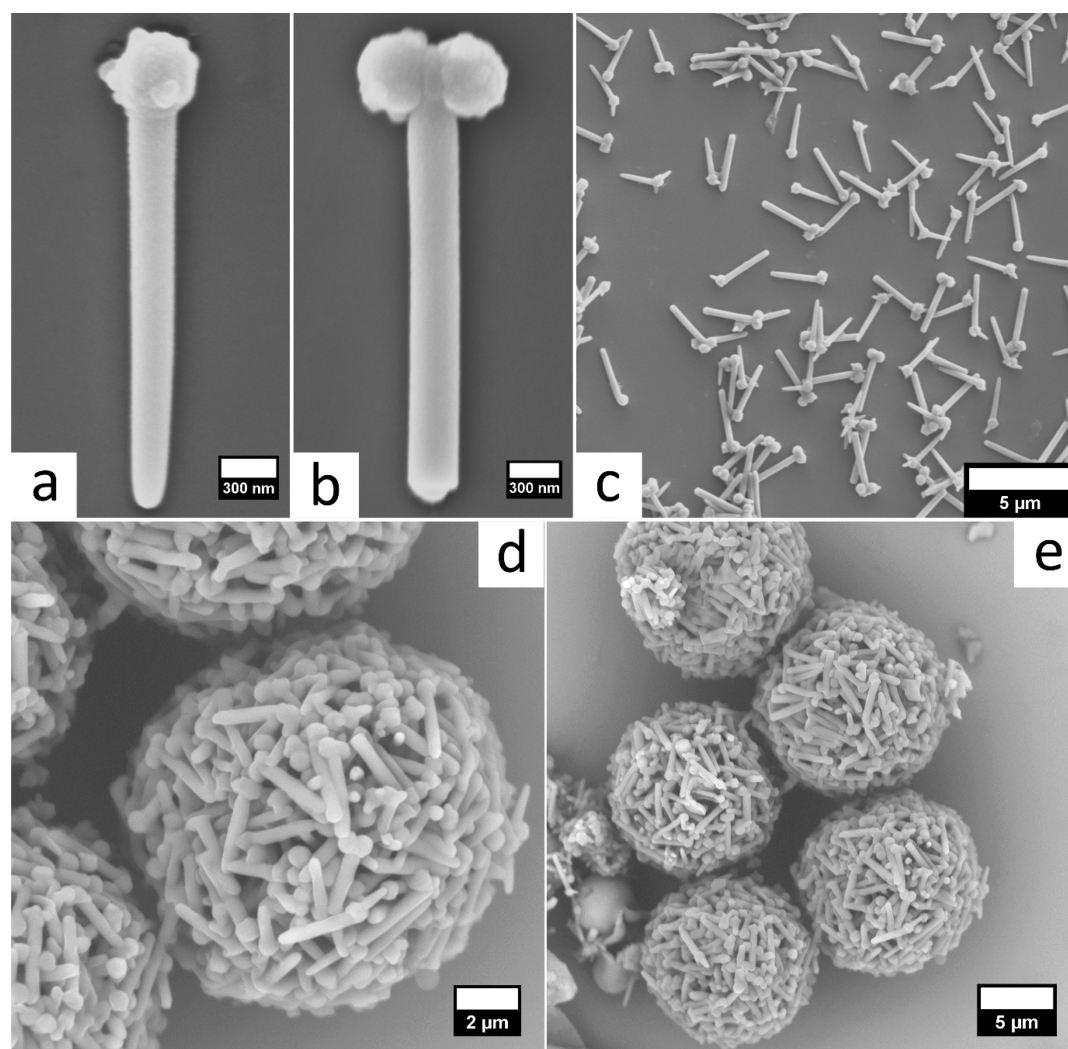
Figure 4. (a−c) SEM images of matchsticks with a head containing PS. (d, e) SEM images of supraparticles assembled from the matchsticks with PS heads.

unseeded synthesis.[1] This suggests that the relative width of the rod diameter distribution is still governed by a similar emulsion droplet size distribution as found in ordinary rod growth, while this slight increase in the mean rod diameter with larger seeds (approximately 26 nm with every 100 nm increase in seed size, Figure 3d) suggests a high contact angle of the droplet on the seed particle.

Seeded-Growth of Silica Rods from Core−Shell Silica Particles with an Organic (Polystyrene) Core and Assembly into Supraparticles. Finally, we grew silica rods from silica particles with an organic core of polystyrene (PS). We chose an organic core in order to fully demonstrate the generality of the synthesis. We chose PS as our organic core because monodisperse PS colloidal particles can easily be prepared. Moreover, polymers can have a huge potential range of functionality, which means the development of a synthesis for anisotropic composite rods with a polymer head could have many applications. Additionally, polymers can be selectively removed via heating[34] which means that the porosity of these particles could be tuned.

We chose to use cationically stabilized PS to further show the generality of the synthesis; silica itself is anionically stabilized and therefore we are demonstrating that we can also prepare matchsticks with colloids stabilized cationically, too.

Moreover, PS is hydrophobic so we are also showing that hydrophobic materials can be incorporated into matchsticks. The silica particles with a PS core were prepared by an established surfactant-free emulsion polymerization method,[37] followed by subsequent washing and coating of the PS particles with silica by an established method.[27] The size of the PS particles from TEM imaging is 372 nm, δ = 1%, (Figure S7) and then this was coated with a 32 nm layer of silica (Figure S8). We then grew silica rods from these silica particles with a PS core in the same way as with the pure silica particles, resulting in composite matchsticks with PS heads (Figure 4a−c, Figure S9). Interestingly, we found many instances of silica rod growth from multiple silica-coated PS "seed" particles (Figure 4b, a ratio of ~37% for multiple- to single-headed matchsticks compared to <12% for the matchsticks from the "seeds" of silica-coated Ag, fluorescently labeled silica, or pure silica particles, respectively). The formation of these matchsticks with multiple heads can be explained by the favorable free energy of the water droplet attachment at concave regions, as has been previously observed.[39] We hypothesize that this higher ratio of multiple-headed matchsticks for the silica-coated PS "seeds" is a result of more silica-coated PS particles present in the synthesis than the other "seed" particles. There are more silica-coated PS particles because in all experiments

we use an equal 2.5 wt % dispersion of seed particles in water and these silica-coated PS particles are less dense than the other seed particles. Higher amounts of seed particles has previously been reported to result in more multiple-headed matchsticks,[19] and indeed we found that lowering the initial concentration of silica-coated PS particles reduces the ratio of multiple- to single-headed matchsticks in the synthesis (Figure S10). Another interesting observation is that the matchstick "heads" appear to have rough surfaces, which we believe to originate from the coating of the PS particles with silica. The coating of cationically stabilized PS particles has been previously observed to result in rough surfaces, while the coating of anionically stabilized PS particles did not.[27]

We then assembled the matchsticks with PS heads into supraparticles. We thus demonstrate that these matchstick particles have potential to form advanced hierarchical structures, which can lead to advanced materials in many applications. We found that the matchsticks with PS heads could be assembled into supraparticles simply by emulsifying the aqueous matchstick dispersion into a water-in-oil emulsion, followed by slow evaporation of the solvent in the suspended water droplets.[32] Here, the shrinking of the droplets slowly increases the concentration of matchstick particles confined within. At a certain point, the droplet shrinks so much that its shape is deformed by the closely packed particles within. This results in large capillary forces on the particles, pushing them together such that they stick. The result is a spherical supraparticle held together by van der Waals forces and stabilized on its surface by surfactant molecules.[32] The resultant supraparticles were composed solely of the matchstick particles (Figure 4d, e) and generally ranged in size from 3 to 15 μm (Figure S11). These supraparticles assembled from matchstick rods with PS heads are particularly interesting for the development of advanced supraparticles with tunable porosity, because PS can be easily be burned away from the cores of silica particles without damage to the silica.[34] Tunable porosity in supraparticles is particularly interesting because supraparticles are currently being studied for applications in catalysis, in which porosity is a key factor, as well as fundamental research which requires the formation of novel self-assembled structures. We believe that the other functional matchsticks prepared in this manuscript can also be assembled in the same way, because the assembly process relies on the dispersibility of the matchsticks in water. All the matchsticks are dispersible in water because their respective surfaces are silica, and the assembly of "pure" silica rods has also been demonstrated.[40]

CONCLUSIONS

In conclusion, we developed a general synthesis for the seeded-growth of silica rods from silica particles. We then demonstrated the potential of this synthesis to prepare anisotropic composite matchstick particles with a range of functionality by growing silica rods from other colloidal particles with a silica shell. We show the generality of this synthesis method by growing silica rods from three general types of colloidal particles as cores: (i) fluorescent (FITC), (ii) metallic (Ag), and (iii) organic (polystyrene, PS). We demonstrate the assembly of the matchsticks with a PS head into supraparticles, which are particularly interesting for the development of advanced supraparticles with tunable porosity. We believe that this general synthesis method can be extended to the preparation of matchsticks with a great range of

functionality for the development of advanced materials and the interest to study how the exact shapes of anisotropic particles affect their self-assembly.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.9b02847.

Characterization and analysis of the silica-coated particles, matchstick-shaped particles, and supraparticles; studies on the synthesis of the matchstick-shaped particles (PDF)

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Notes
The authors declare no competing financial interest.

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