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Supporting Information

Assembly of Silica Rods into Tunable Branched Living Nanostructures Mediated by Coalescence of Catalyst Droplets

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1. Synthesis of Branched Structures

1.1. Materials and Regents

Sodium dihydrogen cirate (99%, Alfa Aesar), 1-pentanol (99.0%, TCI), polyvinylpyrrolidone (PVP, M_W = 40,000, Energy chemical), benzyl alcohol (99.0%, TCI), tetraethylorthosilicate (TEOS, 99.9%, Alfa Aesar). Iron(III) chloride($FeCl_3$, 99%), ammonium hydroxide solution (NH_4OH, 29 %), absolute ethanol (C_2H_5OH), isopropanol, butanol, heptanol, octanol, cyclopentanol, cyclohexanol, sodium hydroxide (NaOH), sodium sulfate (Na_2SO_4) were purchased from Adamas-beta.

1.2 Synthesis of silica branched structures

In a typical experiment, in Step 1, H_2O (140 μL), sodium citrate (0.18 M, 20 μL), absolute ethanol (500 μL), NH_4OH solution (100 μL) and 50 μL TEOS were successively added to a solution of PVP (0.5 g) in pentanol (5 mL) in a 20 mL glass vial and shake the vial for 1 min after each addition forming a stable emulsion system at the room temperature. After condensation of TEOS for 6 h in Step 2, 5 mL of benzyl alcohol (BA) was added to the mixture and vortex the reaction mixture (benzyl alcohol/pentanol, v/v = 1/1) followed by resting for a period time. Finally, the mixture was centrifuged at 2500 rpm for 30 minutes and washed with ethanol and water three times.

1.3 Preparation of seed particles

Hematite (α-Fe_2O_3) particles were prepared by a method reported by Sugimoto et al.[1] In a typical experiment (α-Fe_2O_3 ellipsoid-shaped particles), 90 mL NaOH solution (6.0 M) was added into 100 mL $FeCl_3$ solution (2.0 M) under magnetic stirring (about 10 min). After adding 10 mL Na_2SO_4 solution (0.06 M), the gel was stirred for another 10 min, then transfer into in a Pyrex bottle. The Pyrex bottle was kept at 100 °C for 12 days.[2] The products were obtained by washing with

water and repeating centrifugation for three times. The products were dispersed in water and used as the stock solution for seeded growth of silica. Similar processes were used to prepare rod-shaped and cube-shaped α-Fe_2O_3 particles by changing the amount of Na_2SO_4 solution.[3]

1.4 Synthesis of hybrid structures

In a typical experiment, 30 μL of seed stock solution, H_2O (140 μL), sodium citrate (0.18 M, 20 μL), absolute ethanol (500 μL), NH_4OH solution (100 μL) and 50 μL TEOS were added to a solution of PVP (0.5 g) in pentanol (5 mL) in a 20 mL glass vial, forming a stable emulsion system by stirring and sonication.[4] After keeping standing for a certain period, a certain amount of BA was added to the mixture and vortex the reaction mixture, followed by resting for a period time. The products were obtained by washing with water and repeating centrifugation for three times. Finally, the products were kept in ethanol.

2. Characterizations and Measurements

Scanning Electron Microscopy (SEM). The surface profile of the aggregates was obtained from Field Emission SEM (S4800, Hitachi) operated at an accelerating voltage of 15 kV. The sample was prepared by placing drops of solution on a Si Wafer and then were dried at room temperature. Before observation, the samples were sputtered by gold.

Transmission Electron Microscopy (TEM). The morphologies of the aggregates were examined by TEM (JEM-1400) operated at an accelerating voltage of 100 kV. Drops of sample solution was placed on a copper grid coated with carbon film and then was dried at room temperature.

Dynamic Light Scattering (DLS) Measurements. DLS measurements were performed at a scattering angle of 90° on a commercial LLS spectrometer (ALV/CGS-5022) equipped with an ALV-High QE APD detector and an ALV-5000 digital correlator using a He−Ne laser (the wavelength λ = 632.8 nm) as light source. In DLS measurements, the intensity correlation function was measured at a scattering angle of 90° using all viscosity as 4 cp (the viscosity of the solution of PVP in BA measured was the same with that of pentanol),[5] and refractive index basis as 1.409 (pentanol) and 1.5396 (BA). All the measurements were carried out at room temperature, and the original reagents were filtered before mixture.

3. TEM Observation of Branched Structures

The branched structures were investigated by monitoring the original state of the branched structures without extra handling in the WPN system. As shown in the TEM image of Fig. S1a, the original rod possesses an attached catalyst droplet on the flat end. When the BA was added in Step 2, the connected structure with a liquid core was observed (Fig. S1b and S1c). Therefore, the branched structure was formed by the end-to-end coalescence of rod-like silica units with liquid attachment. The extra incubation, which continues to yield silica solid, led to robust branched colloids showing in Fig. S1d.

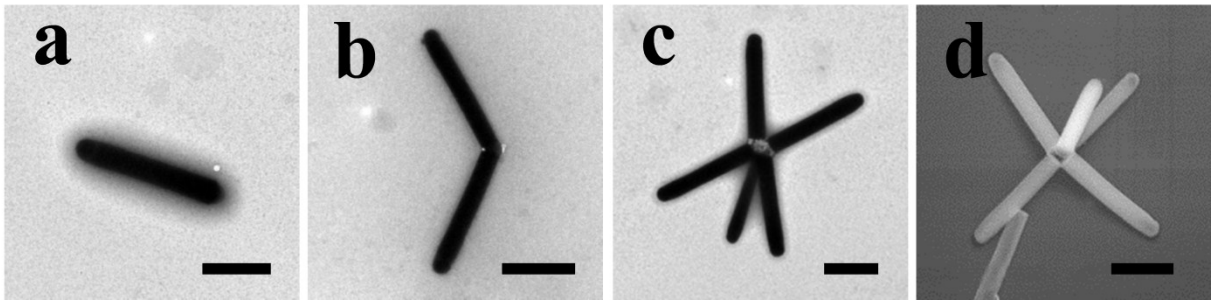

Fig. S1 TEM images for silica structures before washing and the sample was prepared immediately after adding BA. (a) The rod with attached catalyst droplet. (b) Bipods with a liquid central core. (c) Penta-pods with a liquid central core. (d) SEM image of penta-pods corresponding to TEM image of penta-pods(c). Scale bars: 1 μm.

As shown in Fig. S2a, the schematic intuitively shows the formation process of typical branched particles, bipods. In the growth process, the catalyst droplets are the sites of hydrolysis reaction of the precursor (TEOS), hence, the droplets are attached to the silica rods from beginning to end. Delayed addition of BA enables the catalyst droplets coalescence, resulting in the connecting branched structures. This formation process can be directly observed by SEM, as shown in Fig. S2b-f.

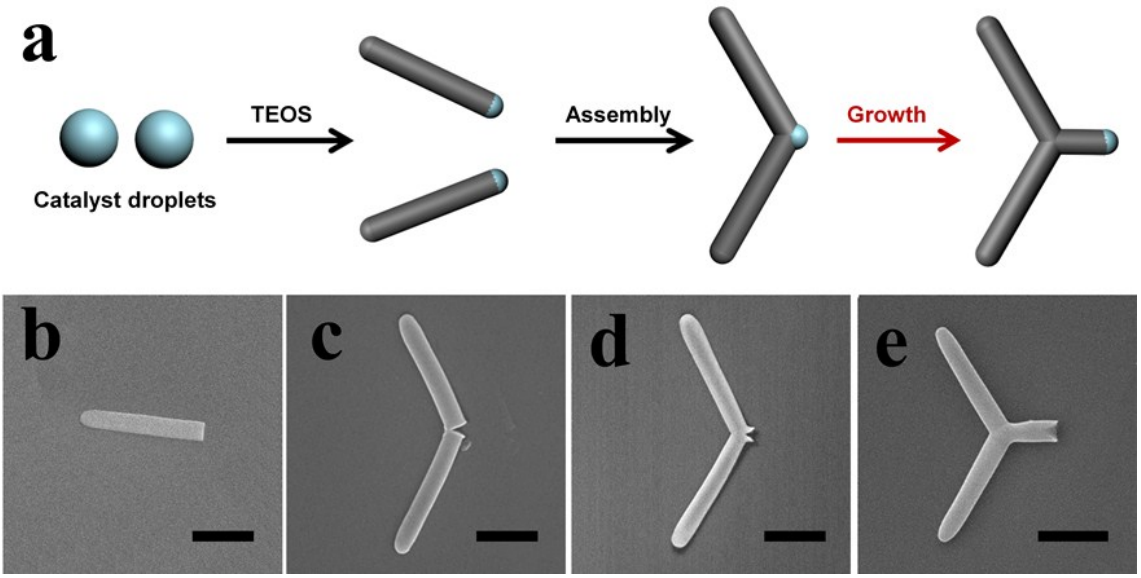

Fig. S2 (a) Schematic of the formation process of branched particles**.** (b-f) SEM observation for the formation process of bipods. The reaction time from adding BA: (b) 0 min, (c) 10 min, (d) 30 min, (e) overnight. Scale bars: 1μm.

4. Effect of BA Content on the Branching Number

It was found that the branching number of the branched structures can be roughly controlled by the amount of the BA solvent. Generally, the more the BA content is, the more the arms are. As shown in Fig. S3a-c, when adding BA from 1 mL to 3 mL in Step 2, the proportion of bipods (consisting of rod and bipods) is generally increasing. When 4 mL BA was added, the tripods (dominant) were obtained (Fig. S3d). Further increasing the BA content, the multi-armed colloids was prepared (Fig. S3e). However, the excess BA can also damage the attached catalyst droplets, which will limit the formation of branched particles with more arms showing in Fig. S3f.

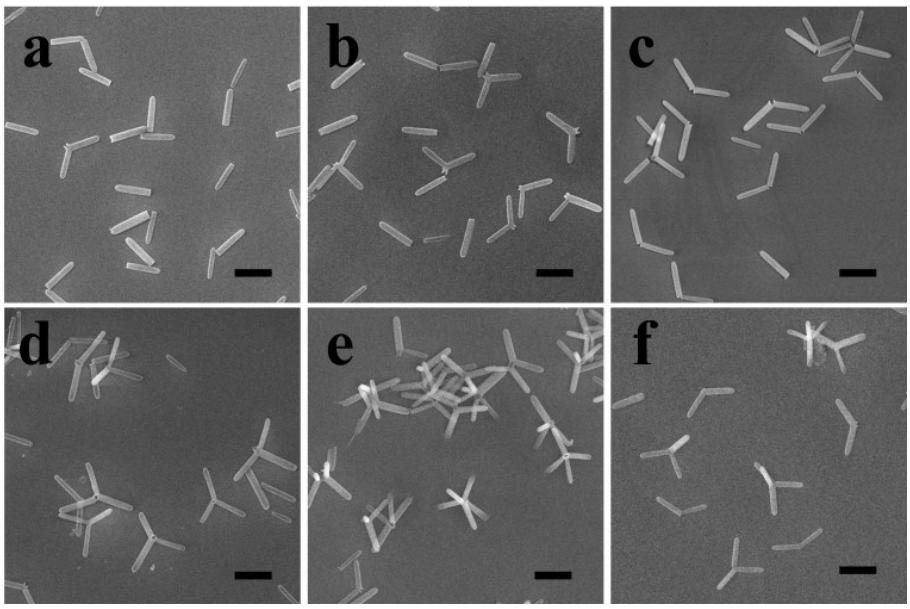

Fig. S3 SEM images of branched particles by varying the amount of BA. (a) 1 mL, (b) 2 mL, (c) 3 mL, (d) 4 mL, (e) 5 mL, (f) 8 mL. Scale bars: 2μm.

5. Effect of the Concentration of the Silica Rods on the Coalescence

The concentration of the silica rods in solution also affects the coalescence behavior of the silica rods. For example, maintaining the same proportion of benzyl alcohol to the solution of PVP in pentanol (3/5.5), when the concentration of silica rods was decreased, the yield of branched products decreases (Fig. S4). The result can be explained as follows: firstly, the lower concentration of silica rods decreases the probability of collision; secondly, the stable size of catalyst droplets decreases in the diluted solution, which would decrease the coalescence ability of the silica rods.

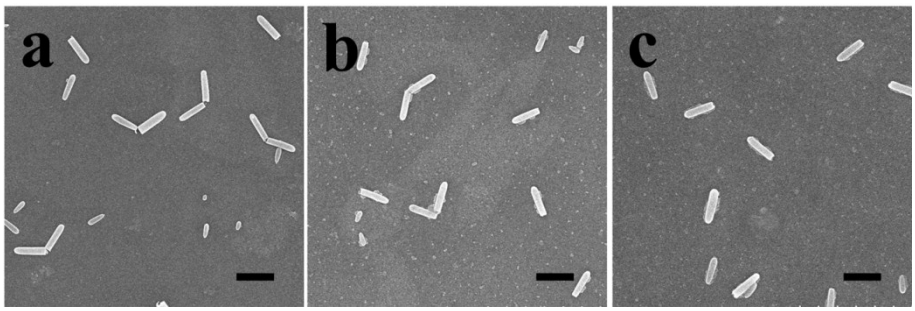

Fig. S4 SEM images of assemblies obtained at various concentrations of silica rods (c_0 is the initial concentration of silica rods in original solution): (a) c_0; (b) $0.8c_0$; (c) $0.6c_0$. The volume ratio of benzyl alcohol to pentanol maintains 3/5.5. The incubation time is 6 h. Scale bars: 1 μm.

6. Influence Factors on the Angle between Two Arms

As shown in Fig. S5a, when the diameter of new generated rod is similar to that of the original rod, the angle between two arms is approximately 120°. When the diameter of the new generated rod is smaller, the angle is larger (approximately 140° in Fig. S5b). The sample in Fig. S5c was prepared by mixing the original catalyst droplets and silica rods mixture solution, the angle was about approximately 120°. Generally, the diameter of the rods is the same with the size of the catalyst droplets.[4] These results indicate that the angle depends on the diameter of conjoint catalyst droplets rather the length. The same steric hindrance leads to about 120° of angle, while the smaller steric hindrance corresponds to the larger angle.

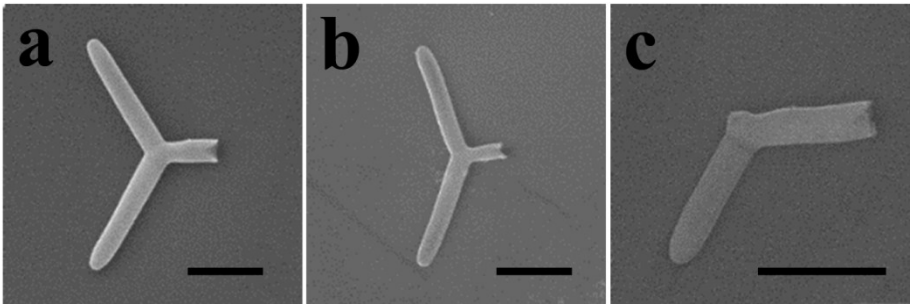

Fig. S5 Branched silica structures grown for longer time with different size of reconstituted liquid droplets: (a) the same diameter and the angle is approximately 120°. (b) Smaller diameter and the angle is approximately 140°. (c) Larger length and the angle is about 120°. Scale bars: 2 μm.

7. Effect of the BA Content on the Original Catalyst Droplets

To further understand the formation process, we investigated the change of the catalyst droplet size in the original solution without adding TEOS. The size distribution of the catalyst droplets, which was prepared from PVP/H_2O/citrate/NH_4OH/pentanol, followed by addition of different amounts of benzyl alcohol, was measured using DLS at 25 °C. Before measurement, the sample was resting for 15 min at 25 °C. As shown in Fig. S6, the finial average size of the catalyst droplets gets larger with the increased addition of benzyl alcohol. However, the system has a wide size distribution, as shown in Fig. S6b-d, which could limit the preparation of monodisperse branched particles with accurate arm number.

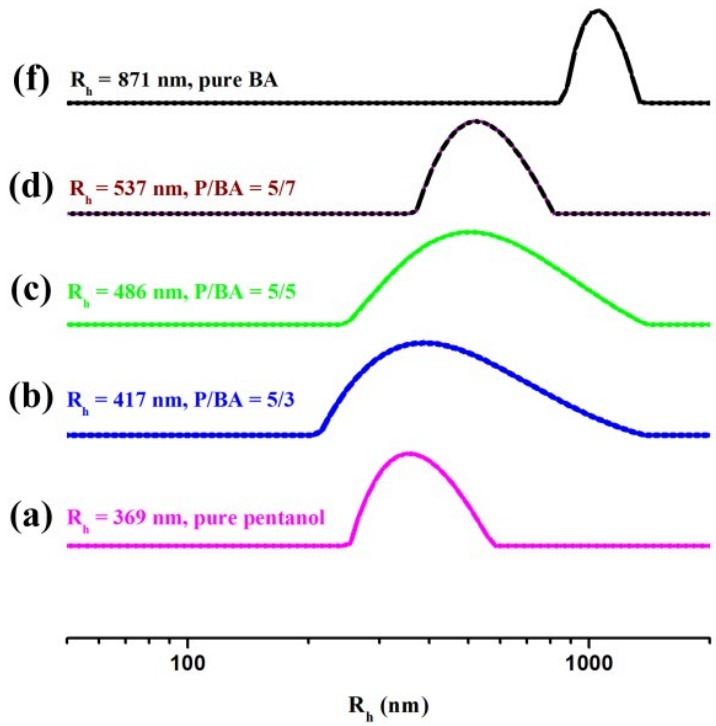

Fig. S6 The finial average size distribution of the catalyst droplets without TEOS varying with addition of different amount of BA measured by DLS. The final proportion of the pentanol (P)/benzyl alcohol (BA) is: (a) pure pentanol; (b) 5/3; (c) 5/5; (c) 5/7; (e) pure BA.

8. Nanostructures formed by Delayed Addition of Other Alcoholic Solvents

Extra addition of other similar alcoholic solvents is able to quickly reduce the size of the emulsion droplet. The catalyst droplet size shrinkage has been discussed by Datskos et al,[6] who demonstrated that diameter reduction depends on ethanol itself, rather than the relative change of PH and TEOS concentration. A series of alcoholic solvents were added, from hydrophilic to hydrophobic, only segmented silica rods with decreasing thickness were obtained, no branched colloids were observed. Hence, we assumed the change of original composition (dilution and continuous phase component) breaks the balance of continuous phase and emulsion droplet causing the redistribution of the PVP molecules and water, which leads to shrinkage of catalyst droplet (Fig. S7). And different alcohol solvents have different effects on the catalyst droplets, as shown in Fig. S7a, 7c, 7g, 7i and 7k, that is, adding the same content, the more hydrophilic enables the more decreasing size. An overdose of alcohol solvents can even destroy the catalyst droplets, as shown in Fig. S7b. But beside benzyl alcohol, other alcoholic solvents only yield thickness gradient, not result in the coalescence. These results ruled out the possibility that the quick changed size directly leads to the coalescence and demonstrated the changed emulsion droplet is to adapt to the new outer environment.

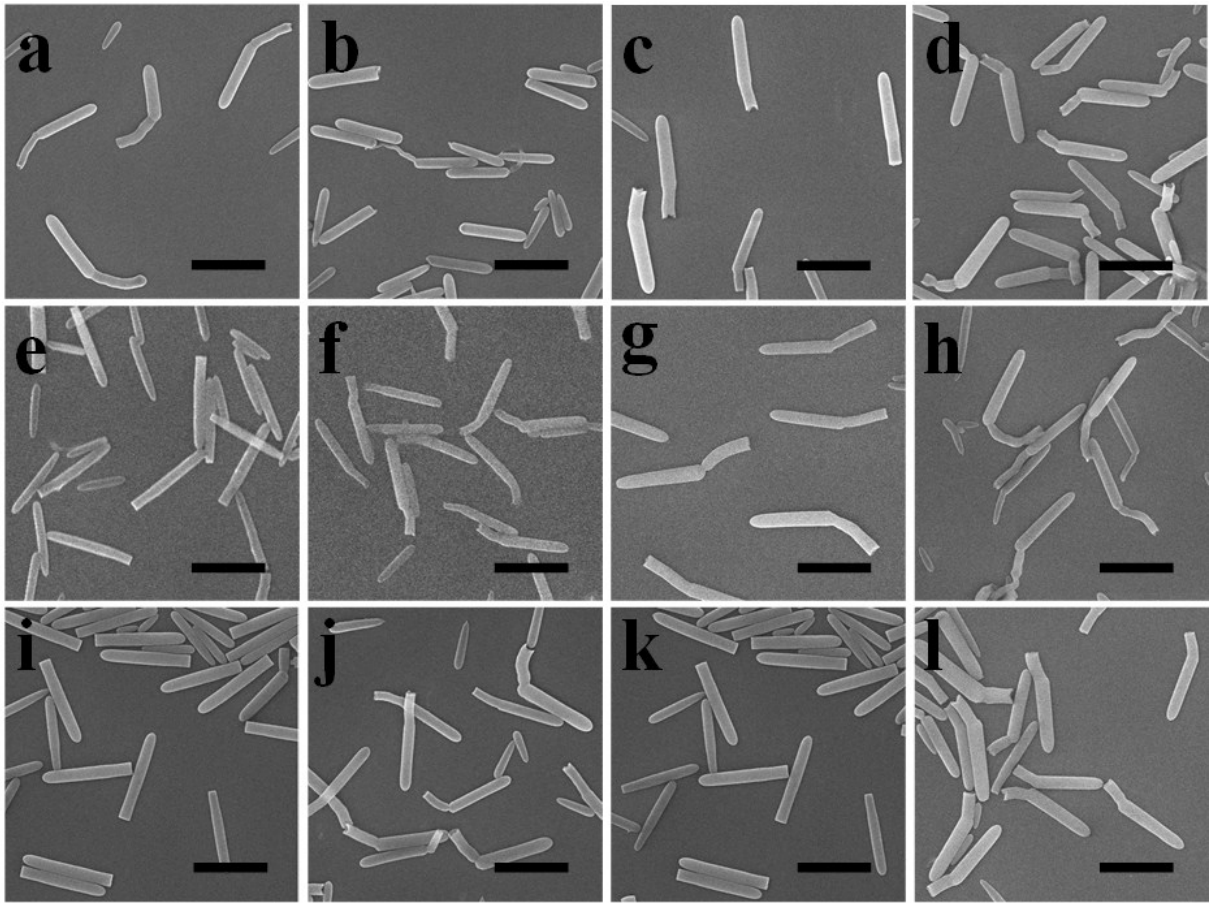

Fig. S7 SEM images of silica rods with thickness gradient obtained by adding various alcoholic solvents after 6h. For each alcoholic solvent, the amount, 2 mL and 4 mL, were chosen. (a,b) Isopropanol: (a) 2 mL; (b) 4 mL. (c,d) Isobutanol: (c) 2 mL; (d) 4 mL. (e,f) Pentanol: (e) 2 mL; (f) 4 mL. (g,h) Cyclohexanol: (g) 2 mL; (h) 4 mL. (i,j) Heptanol: (i) 2 mL; (j) 4 mL. (k,l) Octanol: (k) 2 mL; (l) 4 mL. Scale bars: 2 μm.

9. The Role of the BA on the Coalescence of Catalyst Droplets

To further understand the role of the BA, we used pure benzyl alcohol instead of pentanol to synthesize silica rods. As shown in Fig. S8a, a clutter of branched structures, rather than segmented silica rods with decreasing thickness, were observed, which demonstrates the BA itself plays an important role on the coalescence. Similar phenomenon has been observed in the growth process of germanium nanorods.[7] Therefore, we assumed the BA itself can destabilize the catalyst droplets and induce the attached droplets coalescence. It is noting that the length of arms and the times of coalescence (some have not only one branching point) are different, however, the total length is similar, as shown in Fig. S8b-h. Considering this result, we deem that the formation of branched structures in the BA system is due to the random coalescence of attached droplets which can be one or more times. But in the coalescence process, the catalyst droplets retain living character, yielding silica solid continuously.

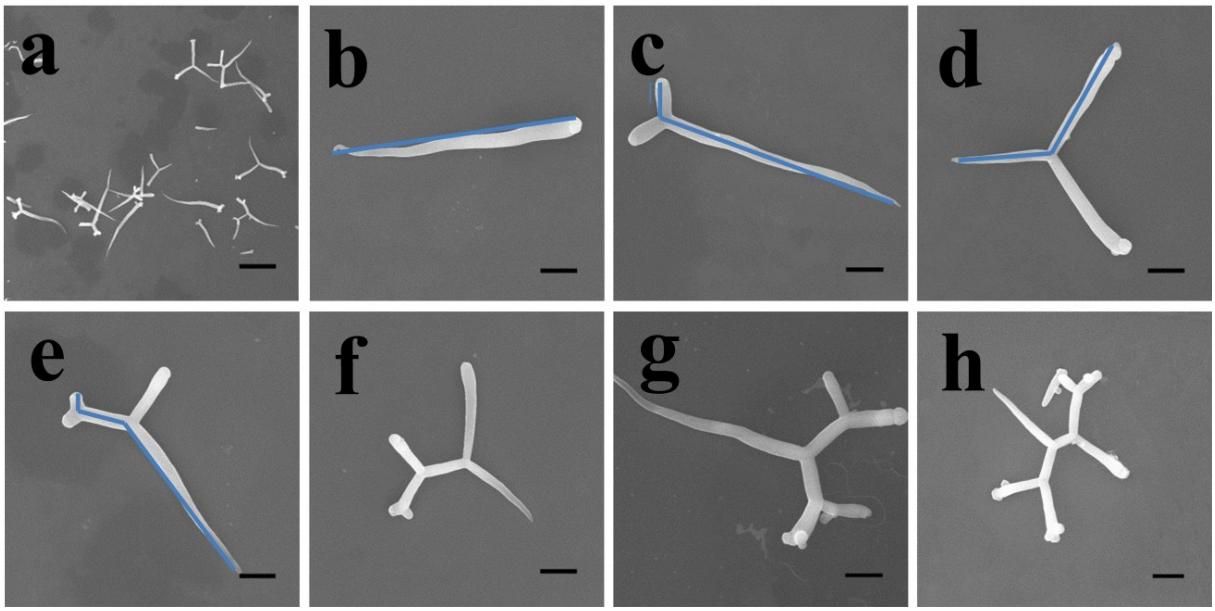

Fig. S8 SEM images of branched structures. The various structures were obtained in BA/PVP system by using BA instead of pentanol as solvent. Scale bars: (a) 10 μm; (b-h) 2 μm.

10. Effect of the BA Content on Formation of Multilevel Branched Structrues

In Step 2, adding a certain amonut of BA can yield primary branched particle by quick coalecence of attached droplets and the new generated droplets still retain the living character which is growth and secondary coalescence capicy. It was found that the possibilities of secondery coalescence varies with the additive BA content. As shown in Fig. S9a, when a small amount of BA was added, the newly generated catalyst droplets still retain better stability, which can mediate the simple epitaxial growth without connecting. While 6 mL BA was added, the new generated catalyst droplets tend to secondary coalescence in the growth process forming multilevel structures (Fig. S9b). In a word, incresing the proportion of BA provides more possibilities for secondary coalescence.

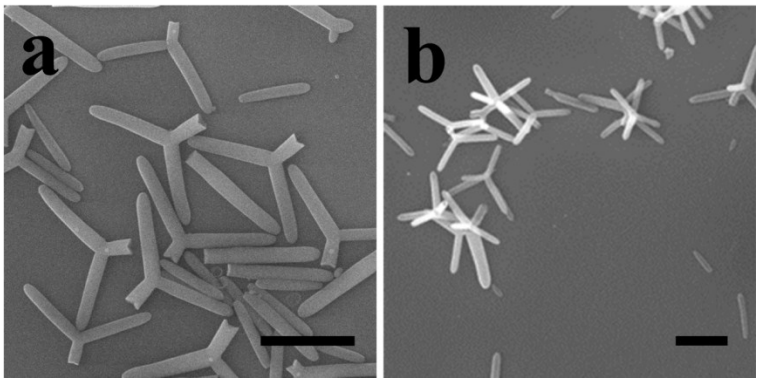

Fig. S9 SEM images of branched colloidal particles obtained by adding different amount of BA: (a) 2 mL; (b) 6 mL. BA was added after 6 h, and react overnight. Scale bars: 2 μm.

11. Branched Nanostructures formed by Shaking-Induced Coalescence

It was found that shaking vigorously of the solution could also induce the coalescence of the silica rods. As shown in Fig. S10, after shanking the solution of silica rods vigorously for 20 min, some “Y”-shaped nanostructures were observed. The driving force of this method is deduced to the random collision of the silica rods, which differs from that found in the present work. Note that the shaking-induced collision of the silica rods is uncontrollable, and the yield of branched nanostructure is very low.

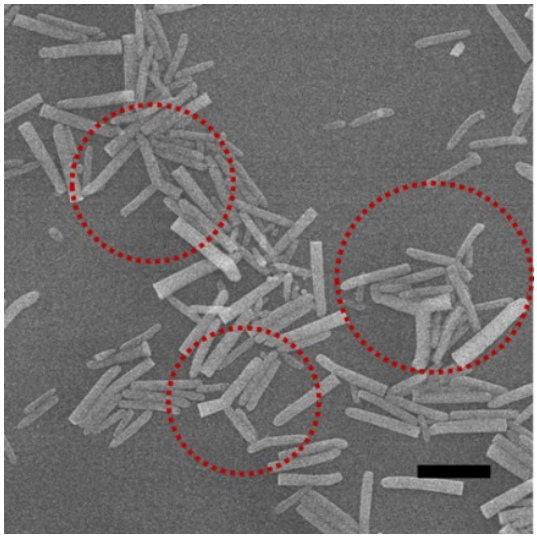

Fig. S10 SEM image of silica structures obtained after shaking vigorously about 20 min. Scale bar: 2 μm.

12. Effect of Addition Times of BA on Formation of Multilevel Structures

The resulting branched structures becomes complex by adding the constant volume BA via multiple times (Fig. S11b). The structures by prolonging the incubation time are formed by random collision, as shown in Fig. S11a. While the multiple times addition is more effective for preparing more complex colloidal structures by inducing coalescence. For example, when totally 4 mL BA was added by 4 times (1 mL each time) in 2 hr, dendritic structures were obtained (see Fig. S11b). As shown in Fig. S11, the formed structure is tree-like structure with multiple connecting points. However, the random collision coexists with induced coalescence. Hence the approach of multiple times addition is tricky to achieve accurate control.

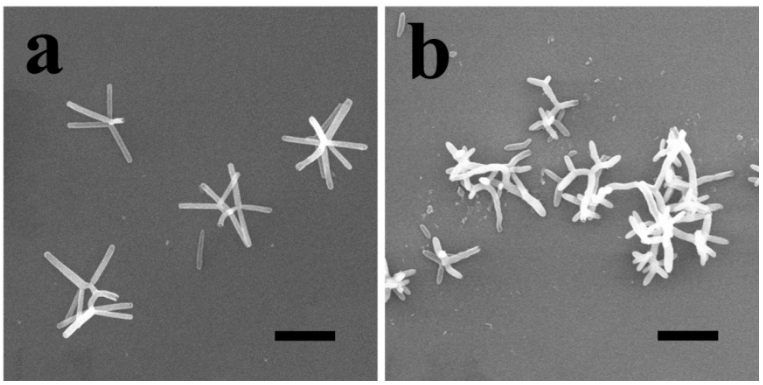

Fig. S11 SEM images of dendritic silica structures obtained by, in Step 2, (a) prolonging time (overnight); (b) Adding 1 mL BA every 1 hr, and repeating for 4 times, then react overnight. Scale bars: 3 μm.

13. The Adsorption and Growth of the Catalyst Droplets on the Seed Particles

It has been reported that the adsorption sites of the catalyst droplets are controlled by the local curvature of the seed particles.[1] Solution–liquid–solid (SLS) growth of silica rods from the attached droplets can prepare the hybrid building units with liquid attachment. As shown in Fig. S12, hierarchical nanostructures were obtained by growing out silica rod from the flat site of seed particles. These results indicate the well-defined hybrid units are easy to obtain, which greatly enriches the application of our strategy.

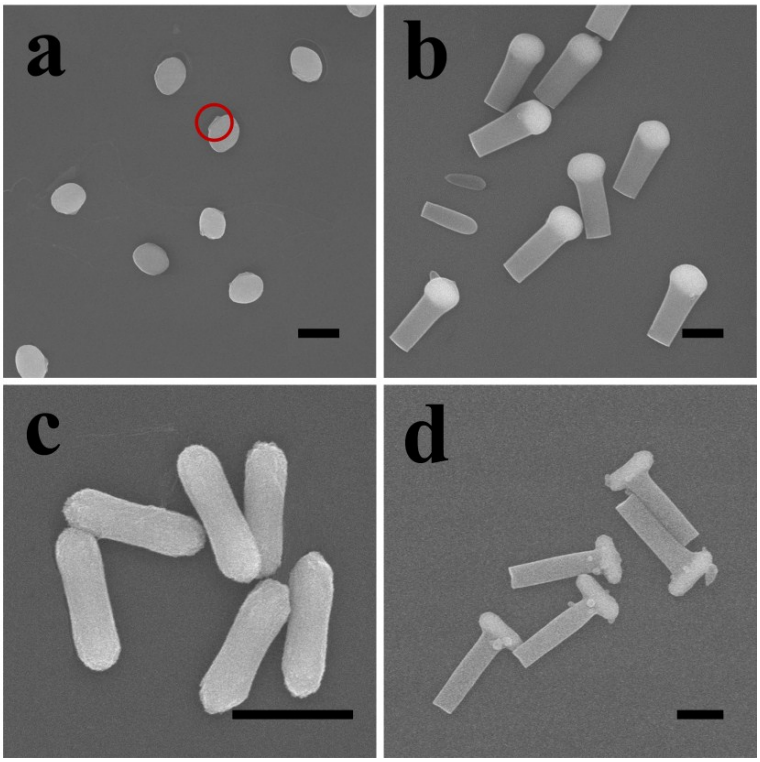

Fig. S12 SEM images of α-Fe_2O_3 particles after the growth of silica. (a) No extra addition of water, grow from elliptical α-Fe_2O_3 particles for 4 hr. (b) Extra addition of 140 μL of water, grow for 4 hr. (c) rod-like α-Fe_2O_3 particles; (d) α-Fe_2O_3@SiO_2 hammers, rod-like silica is grown from the side of the seed. Scale bars: 1 μm.

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