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Assembly of silica rods into tunable branched living nanostructures mediated by coalescence of catalyst droplets†

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Branched nanostructures with tunable arm numbers were prepared through the assembly of silica rods mediated by coalescence of catalyst droplets on the end of the rods. The formed primary branched colloids retain living characteristics similar to the original ones, that is, they can further assemble into multilevel and hierarchical branched structures.

Self-assembly of colloidal particles into hierarchical complex structures has attracted considerable research interest in recent years.[1–4] The complex structures possessing controlled geometries and functions may find applications in photonic devices, electronics, porous membranes, drug/gene delivery, and other fields.[5–8] The diversity of building blocks in composition (inorganic, polymeric, and inorganic/polymeric hybrid) and morphology (such as spherical and rod-like) results in complex assembled structures.[4,9–11] Compared to direct fabrication methods based on growth modes,[12–14] for example, epitaxial growth,[13] the self-assembly approach is more suitable for a greater number of potential complex structures such as chains, molecules, and branched clusters.[15–18]

Currently, the majority of the self-assembled structures are analogues of chains[2,15,19,20] and molecules,[21] and few studies have addressed branched structures. Well-defined branched particles have unique potential applications in electronics/optics and as building blocks that usually possess greater programmed and directional self-assembly information for the creation of new complex objects, which inspired us to investigate the preparation of branched structures.[12,22–24] In view of their architectures, the assembly of rod-shaped building blocks *via* an end-to-end connection strategy has been considered as a facile method for preparing branched structures.[25,26] However, a major obstacle in this approach is that it lacks sufficient control of the topology of the assembled structures. A mixture of various branched architectures is usually obtained *via* uncontrolled random collision of the building rods. The synthesis of branched nanostructures with controlled architectures through the assembly approach is still a challenge.

Herein, we report the preparation of branched nanostructures with tunable branching numbers *via* an end-to-end assembly of rod-shaped silica colloids mediated by coalescence of catalyst droplets on the ends of the rods. The preparation process is illustrated in Fig. 1a. First, the silica rods were synthesized by a solution–liquid–solid (SLS) method,[27] which starts with the condensation of tetraethylorthosilicate (TEOS) in catalyst droplets containing polyvinylpyrrolidone (PVP), and ammonia dispersed in a solution of PVP in pentanol (water/PVP/*n*-pentanol (WPN) system).[28,29] In the second step, the introduction of benzyl alcohol (BA) causes the catalyst droplets on the silica rods to coalesce with each other into a new liquid droplet, which mediates the assembly of the silica rods into branched structures. After resting the solution for a short time (typically 0.5 h), these branched particles were collected by centrifugation.

Fig. 1b shows a scanning electron microscopy (SEM) image of the initial silica rods (approximately 1.90 μm in length and approximately 313 nm in diameter). In the inset transmission electron microscopy (TEM) image, a liquid droplet on one end of a silica rod was observed. Upon addition of BA, the silica rods assembled into branched structures, which is mediated by coalescence of the catalyst droplets on the ends of the rods. Such a process is well supported by the TEM and SEM observations (Fig. S1 and S2, ESI†). The branching number of the structures could be controlled by tuning the amount of BA added to the original solution of silica rods. When 1 mL BA was added to 5.5 mL of the original solution of silica rods (volume ratio of BA to pentanol, VR, was 1/5.5), bipod-like silica structures coexisting with a lot of single rods were observed (Fig. S3a, ESI†). As shown in Fig. 1c, when 3 mL BA was added

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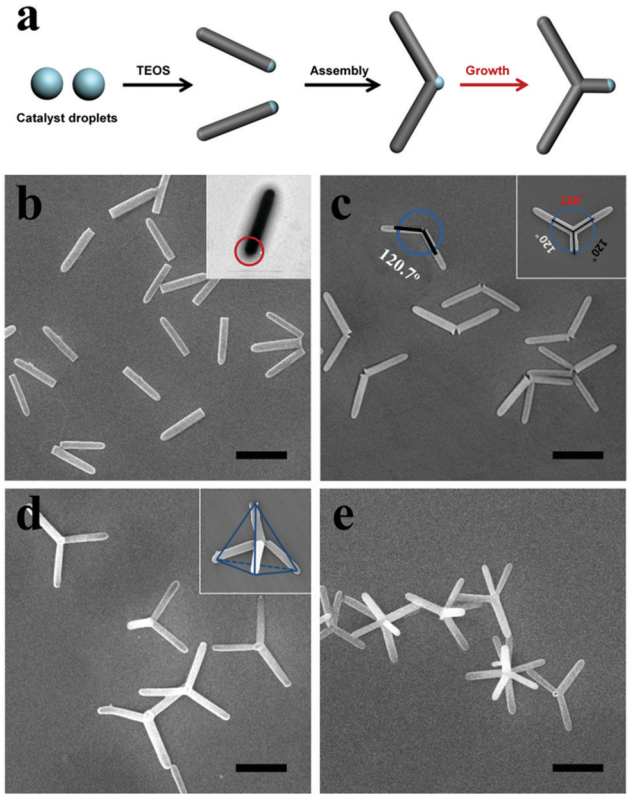

Fig. 1 (a) Scheme for the self-assembly of silica rods into branched structures. (b) SEM image of the initial silica rods. The inset shows the TEM image. (c–e) SEM images of branched structures prepared with various volume ratios of BA to pentanol (VR): (c) VR = 3/5.5, bipods (the inset shows a complete tripod); (d) VR = 4/5.5, tripods (the inset shows a complete four-armed star); and (e) VR = 6/5.5, a mixture of multipod structures. Scale bar: 2 μm.

(VR = 3/5.5), most of the rods assembled into bipods. Increasing the VR to 4/5.5 resulted in the formation of tripods (Fig. 1d, 4 mL BA), and further increasing the amount of BA produced a mixture of various multipods (Fig. 1e, VR = 6/5.5). These formed branched particles were found to possess specific architectural topologies. For the bipods, as shown in Fig. 1c, the average angle between the two arms was about 120°, which is the ideal value for two-dimensional (2D) regular three-armed stars. Such results are reasonable because the newly generated liquid droplets exhibit steric hindrance similar to that of the rods (Fig. 1c and Fig. S1d, S5, ESI†). Details regarding the dependence of the branching number on the BA amount are presented in Fig. S3 (ESI†). In addition to the BA amount, the concentration of the silica rods also affects their coalescence behaviors. For example, at lower concentrations, fewer branched nanostructures were formed (Fig. S4, ESI†).

Furthermore, the newly generated droplets retain the living characteristics similar to the original droplets on the silica rods, *i.e.*, they can still direct the growth of silica rods. As shown in the inset of Fig. 1c, a tripod-like silica particle was generated upon incubation for 2 h. Similarly, for the tripod-like silica colloids, the steric hindrance of the liquid droplets results in incomplete regular four-armed stars (Fig. 1d). Further incubation allows the growth of an additional rod to complete a regular four-armed branched particle (the inset of Fig. 1d). For multipod colloids (Fig. 1e), although it is difficult to recognize their three-dimensional architectural topologies, the arms are still arranged in the patterns typical of regular multiarmed stars.

The self-assembly of silica rods into tunable branched structures by adding BA is a striking finding. No similar phenomenon has been observed in WPN systems. We next investigated the formation mechanism of the branched structures. Fig. 2a shows the size of the newly grown silica rods following the addition of BA to the original solutions. The diameter of the newly grown silica rods is smaller than that of the original rods and decreases with increasing amounts of BA. This phenomenon indicates a gradual shrinkage of the droplets on the silica rods upon the introduction of BA, which is commonly observed in typical WPN systems. However, for similar original systems without TEOS, the size of the droplet increases with increasing BA content. As shown in Fig. 2b, dynamic light scattering (DLS) tests revealed that the stable size of the droplets increases gradually from 371 nm (original droplets) to 441 nm (following the addition of 3 mL BA) and then to 537 nm (following the addition of 7 mL BA). The details of the DLS results are presented in Fig. S6 (ESI†).

According to the opposite trends in the size of the droplets observed in the silica rods and in the original systems upon adding the BA solvent, we inferred that in the new solution the shrunken droplets on the end of the silica rods are unstable.[30] The unmatched size of the droplets between the restricted state (on the silica rods) and the stable state (in the new solution) forces the shrunken catalyst droplets on the silica rods to coalesce with each other reaching a stable size (larger size) under the surface energy minimization. Therefore, the silica rods assembled into branched structures *via* an end-to-end connection. This self-assembly process is illustrated in Fig. 2c. Since the size differences between the droplets in the stable form and droplets on the ends of rods increase as the amount of BA added increases, more catalyst droplets should coalesce with each other, forming branched structures with more arms. These results

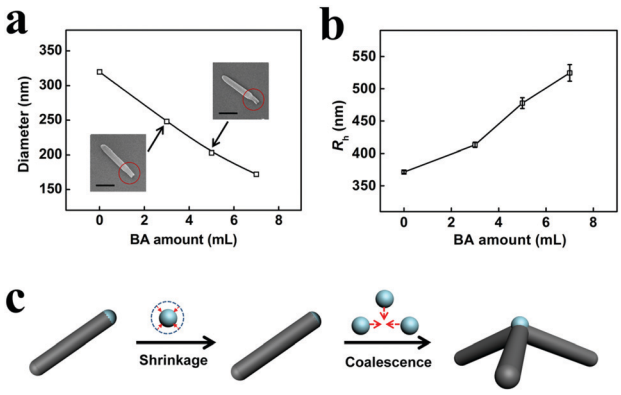

Fig. 2 (a) Effect of the BA amount on the diameter of newly grown silica rods. Scale bar: 1 μm. (b) DLS tests for effect of the BA amount on the hydrodynamic radius (R_h) of the catalyst droplets. The scattering angle is 90°. The volume of the original solution is 5.5 mL. (c) Illustration of the formation mechanism of tripod structures.

explain both the formation mechanism of the branched colloids and the dependence of the branching number on the BA content.

The formation of branched structures upon adding BA is exciting. It has been reported that changes in experimental conditions including temperature, pH, and delayed addition of ethanol usually result in changes in the silica linear morphology such as bent and segmented, but no branched structure has been observed.[31–34] Similarly, in the present system, the delayed addition of various alcoholic solvents only decreased the thickness of the silica rods (Fig. S7, ESI†). Therefore, we came to the conclusion that the BA solution not only decreased the size of the catalyst droplets but also destabilized the liquid domains. To verify this statement, we checked the structure of the silica colloids synthesized under similar conditions but using BA instead of pentanol as the solvent. As expected, branched structures other than rod-like colloids were prepared, which supports our viewpoint regarding the formation mechanism of the tunable branched nanostructures (Fig. S8, ESI†).

As mentioned above, the newly generated liquid droplets at the merging points of the branched structures can mediate the growth of new silica arms. Furthermore, these liquid droplets can also mediate the coalescence of primary branched particles into multilevel branched structures upon increasing the incubation time. This is the reason for choosing a short incubation time (“0.5 h”) for solidifying the newly formed nanostructures after adding BA. As shown in Fig. 3a–d, when the incubation time in Step 2 is increased, multilevel branched silica colloids with diverse structures are obtained. The corresponding cartoons specify both the building blocks and the merging points for these multilevel branched structures. Increasing the amount of BA produces branched silica colloids with more complex multilevel topologies, which indicates the probability of increasing secondary coalescence with increasing BA content (Fig. S9, ESI†). Note that the formation mechanism of these multilevel branched structures is different from that of the primary branched structures. The formation of primary branched structures was mediated by controlled coalescence of the catalyst droplets; while multi-level branched structures were formed by random collision of the liquid droplets. Such a random collision of the silica rods can also be achieved by vigorously shaking the solution (Fig. S10, ESI†). On the other hand, the addition of BA in multiple portions while maintaining its total content constant could also increase the complexity of the structures (Fig. S11, ESI†).

Furthermore, such a droplet-coalescence-mediated assembly strategy can be used to prepare hybrid branched structures from different building blocks with specific shapes and components. Fig. 4 shows typical hybrid structures consisting of α-Fe_2O_3 particles and silica rods. Firstly, the hybrid building blocks are prepared by growing silica rods from α-Fe_2O_3 particles with cubic, rod-like or ellipsoid-like shapes, which is mediated by the catalyst droplets post-adsorbed on the seed particles (Fig. S12, ESI†).[27,35] Subsequently, BA was added to induce the assembly of these building units. Fig. 4a and b show typical hybrid branched particles with two and three arms, respectively. Fig. 4c shows multicomponent quadruple-like particles generated from a variety of building blocks. Moreover, multiple droplets could adhere to one anisotropic particle yielding branched building units with multiple living points, which allows the construction of novel hierarchical nanostructures. For example, shown in Fig. 4d is a zig-zag-shaped α-Fe_2O_3/SiO_2 hybrid structure.

The self-assembly of colloidal rods into tunable branched structures by coalescence of catalyst droplets observed in this work is an unprecedented finding. This work represents an emerging strategy for preparing branched nanostructures with controllable architectures. Taking the advantages of the end-to-end connection mechanism, a library of branched structures with multicomponent compositions could be synthesized using various starting colloidal building blocks. Compared with the commonly applied strategy of outward growth of colloids from

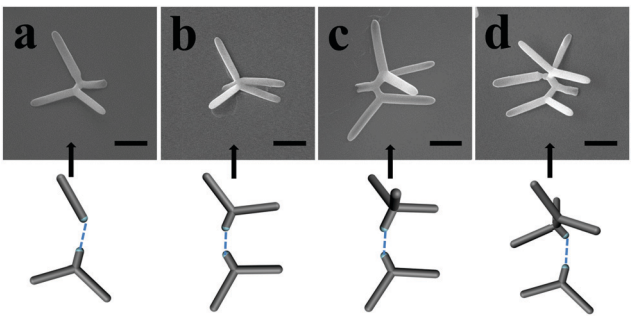

Fig. 3 Morphology and schematic of typical multilevel branched colloids prepared by increasing the incubation time in Step 2 (typically overnight). The building blocks for these multilevel branched colloids are: (a) single rod and bipod; (b) bipod and bipod; (c) tripod and bipod; and (d) multipod and bipod. The cartoons specify the building blocks and the merging points for these multilevel branched silica colloids. Scale bar: 1 μm.

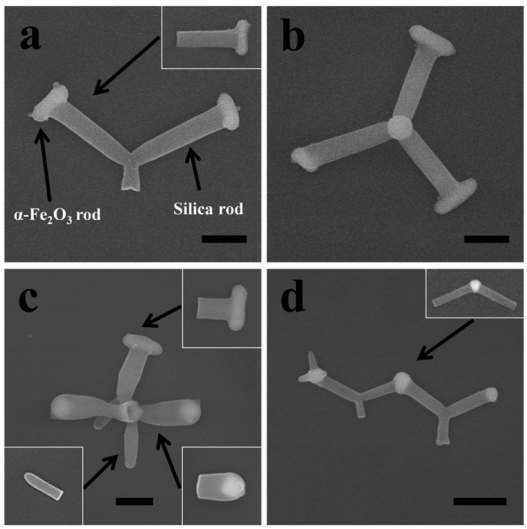

Fig. 4 Hierarchical hybrid structures. (a) Bipod-like particles and (b) tripod-like particles prepared from two and three SiO_2 rod@Fe_2O_3 rod hybrids as the building blocks, respectively. (c) Quadruple-like particles prepared from the SiO_2 rod@Fe_2O_3 cubic hybrid, SiO_2 rod@Fe_2O_3 rod hybrid, and SiO_2 rod@Fe_2O_3 ellipse hybrid, and silica rods as the building blocks. (d) A zig-zag-shaped Fe_2O_3 rod@SiO_2 structure. Scale bars: 1 μm for (a–c) and 2 μm for (d).

specific seed templates,[12] the assembly approach not only displays facile control of the topology but also releases us from the difficult task of preparing specific seed templates.

In summary, we demonstrated the preparation of tunable branched living nanostructures *via* the self-assembly of rod-shaped colloids. Upon adding BA to the original solution of rod-like silica colloids, the silica rods self-assembled into branched structures *via* an end-to-end connection mechanism. This process is mediated by coalescence of catalyst droplets on the ends of the silica rods, and the branching number is regulated by tuning the amount of BA added to the system. The newly formed droplets on the branching points can serve as a living point for the growth of silica rods and mediate further connection of branched structures into multilevel branched structures. Furthermore, this strategy was extended to the preparation of hierarchical hybrid structures. These branched particles may find applications in the fields of antibacterial materials and drug delivery based on their unique shape which could usually lead to special interactions with biological systems.[36,37] We anticipate that this catalyst-droplet-induced assembly approach will provide opportunities for creating various structures with controlled spatial morphologies and compositions.

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Conflicts of interest

There are no conflicts to declare.

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