Colloidal Synthesis of Metallodielectric Janus Matchsticks

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ABSTRACT

Metallodielectric Janus particles, due to their dual composition and anisotropic properties, have found applications in catalysis, actuation, and optical applications. Their practical applications are limited by the difficulty of controlling their structures while allowing mass production. In this work, we introduce a gram-scale synthesis of matchstick-shaped metallodielectric Janus particles, which feature a gold-coated silica sphere and a straight silica rod. SiO_2 Janus matchsticks are synthesized in one batch by growing amine-functionalized SiO_2 spheres at the end of SiO_2 rods. The amine groups on the sphere surface provide nucleation sites for the chemical deposition of a gold nanolayer that yields the Au-SiO_2 Janus matchsticks. We show that the aspect ratio of the Janus matchsticks can be controlled by the length of the SiO_2 rods. As both silica growth and gold coating can be performed in large reaction volumes, gram-level metallodielectric Janus matchsticks can be produced for potential use as functional colloidal materials.

INTRODUCTION

Janus particles feature an asymmetric structure with two distinct physical and/or chemical characteristics.[1-3] They have been studied in a wide range of fundamental investigations including stabilization of multiphasic mixture,[4-6] micromotors and active colloids,[7-9] and colloidal self-assembly.[10-12] Metallodielectric Janus particles are a particular type of anisotropic colloids that comprise metallic and dielectric regions. They have been studied as active colloids that exhibit dynamic propulsion and assembly activated by chemical or external field.[13] For instance, platinum-coated Janus spheres are able to self-propel by decomposing a fuel such as hydrogen peroxide.[14-15] Gold-coated Janus and patchy colloids have been demonstrated with a variety of propulsion and assembly behaviors when activated by AC electric field.[16-18]

A straightforward way of making these particles is by physical vapor deposition (PVD), whereby a thin metal film is coated on a monolayer of dielectric spheres while enabling the shape of the metal patch via glancing angle deposition.[19-20] The method, however, is limited by scalability and does not provide much control over the particle geometry. Recent developments in colloidal synthesis have provided metallodielectric Janus particles with more sophisticated shape control.[21-22] For instance, the platinum−polystyrene Janus dimers have been synthesized by a sequential chemical deposition of gold and platinum onto the lobe with amine groups.[23] Recently, a “cluster-encapsulation-dewetting” method has been developed for making Janus particles (two lobes) and patchy particles (multiple lobes).[24-26] The aspect ratio of Janus particles can be controlled by the dewetting degree of the two lobes. After coating gold on the lobes, these particles can be stimulated to propel or rotate, and form spinning clusters or colloidal molecules under AC electric field.[27] However, the current synthetic methods involve multiple steps and are not suitable for mass production of metallodielectric Janus particles. Therefore, while these particles offer a great model system for exploring the dynamic behaviors of active colloids, their material functions have been largely overlooked due to the lack of facile and scalable synthetic methods.

Herein, we develop a gram-scale colloidal synthesis of gold-silica Janus matchsticks with a tunable aspect ratio. These Janus matchsticks are made of a gold-coated silica sphere and a straight silica rod. SiO_2 Janus matchsticks are synthesized by sequentially adding a silane ((3-aminopropyl)triethoxysilane, APTES) and the silica precursor (tetraethyl orthosilicate, TEOS) to the as-synthesized SiO_2 rod suspension. The APTES hydrolyzes and remains soluble in the water droplet attached to the SiO_2 rod, which not only increases the droplet's volume and transforms the rod to the matchstick shape, but also modifies it with amine groups. The condensation of TEOS with APTES solidifies the water droplet and fixes the matchstick shape. A gold nanolayer is selectively coated on the amine-functionalized SiO_2 sphere, resulting in the Au-SiO_2 Janus matchsticks. Our work will enable future studies on their active propulsions and potential applications in optical devices.

RESULTS AND DISCUSSION

The synthesis of metallodielectric Janus matchsticks is schematically illustrated in Figure 1. A key step for creating the matchstick shape is to modify the silica growth in the water droplet from the rod by sequentially adding (3-aminopropyl)triethoxysilane (APTES) followed by tetraethyl orthosilicate (TEOS). Given the different chemical structures, APTES and its hydrolyzed products are soluble in the water droplet which expands its size; this process transforms the rod into the matchstick shape. If TEOS is added first, however, its hydrolysis in the water droplet would simply extend the rod length. The introduction of different silanes, such as hexadecyltrimethoxysilane, to the rod suspension has also been used to make amphiphilic Janus particles.[28-29] In this case, the silane and TEOS are added as a mixture, by which the rods become partially functionalized by the silane.

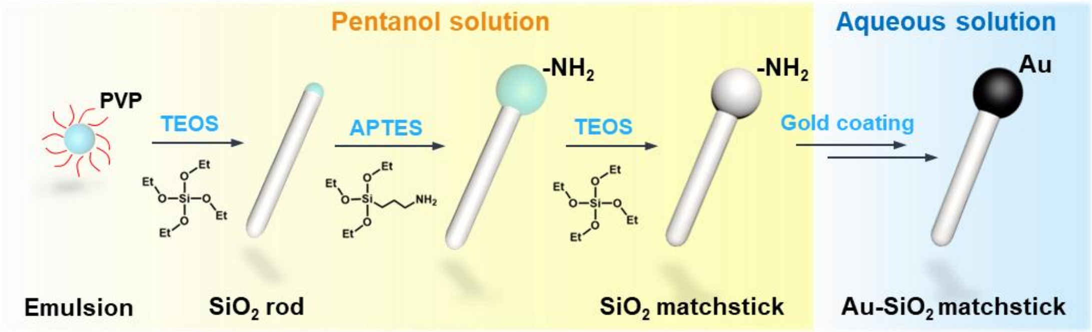

Figure 1. Schematic showing the synthesis of the SiO_2 matchstick with an amine-functionalized head and the site-specific gold coating to form the Au-SiO_2 matchstick.

A detailed description of the synthesis is as follows: First, SiO_2 rods are synthesized following a previous method.[30] Water-in-oil (W/O) emulsions are generated in a solution mixture containing water, pentanol, polyvinylpyrrolidone (PVP), ammonia, and sodium citrate. The addition and hydrolysis of the silica precursor, TEOS, forms solid SiO_2 in the water droplets. The water droplet partially engulfs the solid SiO_2 rather than fully wetting it; thus, the subsequent silica growth occurs at the interface of this solid SiO_2 and the droplet and occurs along one dimension, producing a straight SiO_2

rod.

After the growth of SiO_2 rod, a silane, APTES, is added to the rod suspension of same batch. APTES hydrolysis in the water droplet forms soluble oligomers, which do not induce further growth of the rod but rather introduce amine groups in the droplet. At the same time, the size of the water droplet increases with the addition of APTES, converting the SiO_2 rod into a matchstick particle. To solidify the water droplet and fix the matchstick shape, TEOS is added again and its condensation with APTES oligomers forms the crosslinked SiO_2 sphere (i.e., the head of the matchstick).

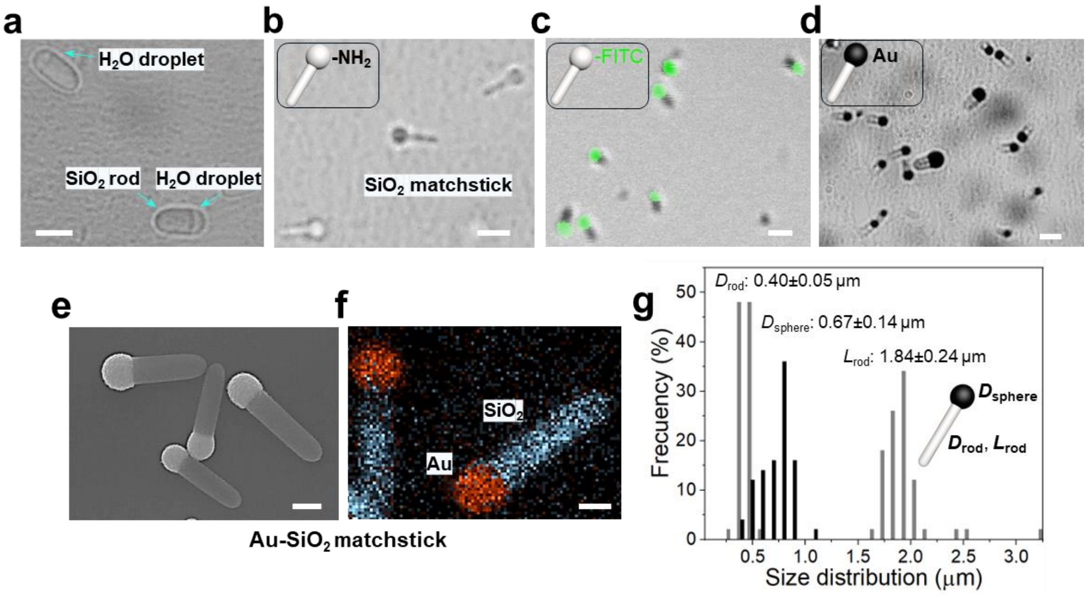

Figure 2. a Optical microscope image showing water droplets attached at the end of SiO_2 rods. **b** Microscope image of the SiO_2 Janus matchsticks. **c** Confocal microscope image showing that the fluorescent dye, fluorescein isothiocyanate (FITC-NCS) is selectively grafted to the spherical heads of matchstick particles. **d** Microscope image

of the Au-SiO_2 Janus matchsticks. Scale bars = 1 µm. **e** Scanning electronic microscope (SEM) images of the Au-SiO_2 Janus matchsticks. **f** Energy dispersive X-ray (EDX) image of gold and oxygen. Scale bars = 0.5 µm. **g** Distribution of length of rod, diameter of rod and sphere based on counting at least 50 Au-SiO_2 Janus matchsticks from Figure 4c.

Water droplets attached at the rod end can be observed under an optical microscope in some SiO_2 rods with large diameters (Figure 2a). After the subsequent addition of APTES and TEOS, the SiO_2 Janus matchsticks are obtained, as shown in Figure 2b. To verify that only the spherical heads are functionalized with amine groups, we use a fluorescent dye, fluorescein isothiocyanate (FITC-NCS), where the NCS group forms a covalent bond with the NH_2 group. Confocal microscopy of these particles clearly shows that the fluorescence signal is only detected on the spherical head of the matchstick as shown in Figure 2c.

The SiO_2 sphere with amine groups is selectively coated with a gold nanolayer, yielding the Au-SiO_2 Janus matchsticks. The gold coating is performed by a two-step seeding and growth protocol.[24] Specifically, the amine groups can chemically bind a gold precursor (chloroauric acid, $HAuCl_4$),[31] which is reduced to gold nanoparticles on the surface of the silica sphere. The gold nanoparticles serve as seeds for the further growth of the gold nanolayer covering the spherical SiO_2 head (Figure 2d). Scanning electronic microscopy (SEM) and energy dispersive X-ray (EDX) images of these particles clearly demonstrate the formation of gold layers on the spherical heads of matchstick particles as shown in Figure 2e-f. The average rod length is 1.84±0.24 µm and the average diameter of rod and sphere is 0.40 ± 0.05 and 0.67 ± 0.14 µm, respectively, as shown in Figure 2g.

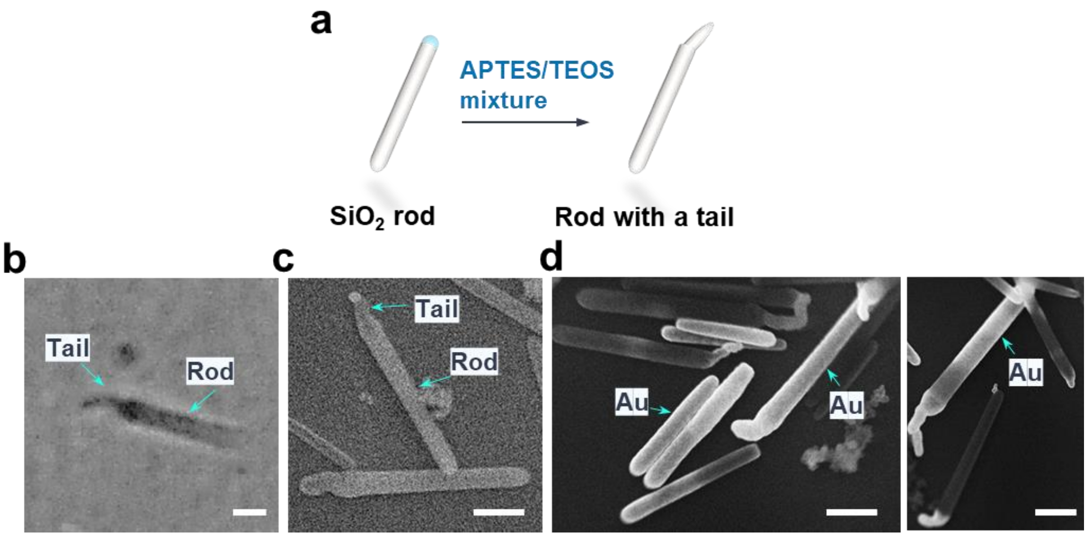

Figure 3. a-c Schematic and microscope images showing that adding APTES and TEOS as a mixture forms a silica tail at the end of rod. **d** The rods are found to be coated with gold. Scale bars = 1 µm.

We note that the addition of TEOS must follow the complete hydrolysis of APTES within water droplets, which normally takes a couple of hours (e.g., 5h). If TEOS and

APTES are added simultaneously as a mixture to the as-synthesized rod suspension, their condensation induces the growth of a tail-like silica tip at the rod end instead of a spherical head, as shown in Figure 3a-c. Under these conditions, the rods from the particles can be coated with gold, suggesting that the amine functionalization is not site-specific (Figure 3d). Taken together, our data suggests that the *sequential* addition of APTES and TEOS is essential for making the Au-SiO_2 Janus matchsticks.

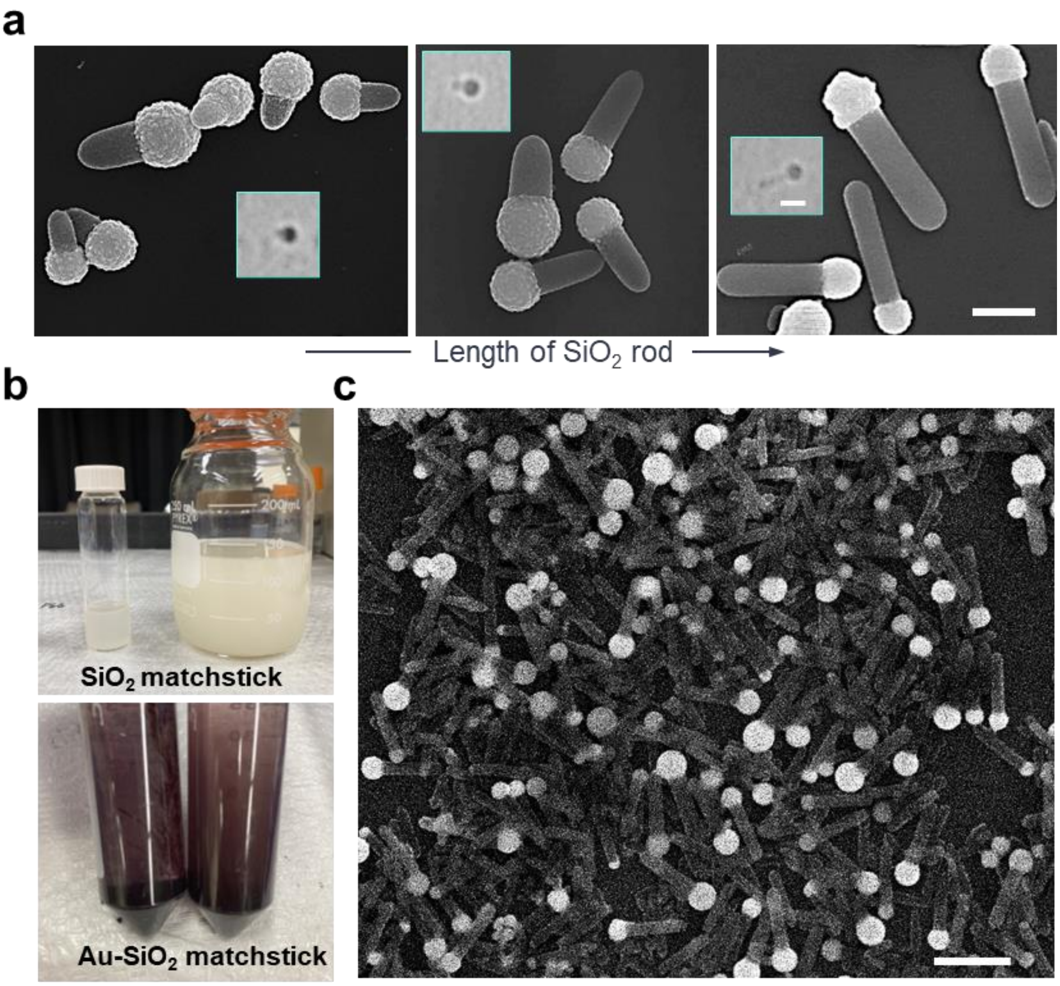

Figure 4. a SEM images of the Au-SiO_2 Janus matchsticks with a tunable aspect ratio. Insets are the corresponding microscope images of SiO_2 Janus matchsticks before gold

coating. Scale bars = 1 µm. **b** Pictures showing that the ability to increase the reaction volume and produce Au-SiO_2 Janus matchsticks in gram scale. **c** An SEM image showing the large quantity of Au-SiO_2 Janus matchsticks. Scale bar = 3 µm.

We further demonstrate that the aspect ratio of the gold and silica in the Janus matchsticks can be tuned by changing the length of SiO_2 rods. Specifically, the diameter of gold-coated sphere is generally fixed at around 0.7 µm as it is determined by the diameter of the SiO_2 rod (around 0.4 µm) shown in Figure 2g. The length of SiO_2 rod can be synthetically tuned from 0.8 µm to 2 µm by the volume of TEOS for the rod growth, as shown in Figure 4a. The colloidal synthesis protocol allows scale-up of the reaction volume of SiO_2 Janus matchsticks from 5 mL to 100 mL; subsequent gold coating following the same procedure as described above yields Au-SiO_2 matchstick particles in > 1 gram quantity (Figure 4b-c). Such scalability is critical for practical applications of these metallodielectric Janus matchsticks with shape and chemical anisotropy.

CONCLUSION

In summary, we have demonstrated a scalable colloidal synthesis of Au-SiO_2 Janus matchsticks consisting of a gold-coated sphere and a silica rod. We find that the sequential addition of APTES and TEOS to the SiO_2 rod suspension leads to growth of an amine functionalized sphere at the end of SiO_2 rod, therefore forming the matchstick geometry. Taking advantage of the anisotropic surface chemistry, gold is selectively coated on the spherical head of the matchstick. Both steps are scalable enabling gram-scale production of Au-SiO_2 Janus matchsticks. Our future studies will focus on investigating the optical and plasmonic properties of these metallodielectric Janus matchsticks.

EXPERIMENTAL SECTION

Materials. Polyvinylpyrrolidone (PVP 40K and 29K), pentanol, sodium citrate, tetraethyl orthosilicate (TEOS), (3-aminopropyl)triethoxysilane (APTES), ammonia (28-30 wt.%), fluorescein isothiocyanate (FITC-NCS), chloroauric acid ($HAuCl_4$), formaldehyde (HCHO) and potassium carbonate (K_2CO_3) were purchased from Sigma-Aldrich. Sodium borohydride ($NaBH_4$) was purchased from Merck KGaA.

Characterizations. Upright optical microscope (Carl Zeiss Axio Plan II), confocal microscope and scanning electron microscope (SEM, JEOL 7500F) were used to observe and characterize the SiO_2 rods, SiO_2 Janus matchsticks and Au-SiO_2 Janus matchsticks. Image J was used for measuring the length and diameter of the rod and sphere in the matchstick.

Large-Scale Synthesis of Silica Janus Matchsticks. In a 250 mL glass bottle, 10 g of PVP 40K was dissolved in 100 mL of 1-pentanol by sonicating for 2 hours. After completely dissolving the PVP, 9 mL absolute ethanol, 3.5 mL DI-water and 1 mL of 0.18 M sodium citrate aqueous solution were sequentially added to the glass bottle, which was shaken vigorously to mix the solution. Subsequently, 2.3 mL of concentrated ammonia solution was added. The bottle was shaken vigorously again and was left to rest for 20 mins until gas bubbles disappeared. Finally, 1 mL of TEOS was added to the mixture and the bottle was shaken gently. The bottle was left to rest, and the reaction was allowed to proceed overnight. After the successful growth of SiO_2 rods, 1 mL of APTES ((3-aminopropyl)triethoxysilane) was added to the bottle, which was shaken gently for mixing. The reaction was allowed to proceed over 5 hours. Finally, another 1 mL of TEOS was added and the reaction was allowed to proceed overnight. The resulting SiO_2 Janus matchsticks were washed with ethanol by the centrifugation-redispersion process for 3 times.

Site-Selective Gold Coating on Silica Janus Matchsticks. The as-synthesized Janus matchsticks were transferred into two 50 mL centrifuge tubes. Next, 20 mL of 4 mg/mL chloroauric acid ($HAuCl_4$) aqueous solution was added to each centrifuge tube. To complete the gold precursor absorption, the particle suspension was vortexed to mix, and then left to rest for 10 mins. The particle suspension was washed three times with

DI-water and was redispersed in 25 mL DI-water. Then, 10 mg of sodium borohydride ($NaBH_4$) was added to reduce the Au^{3+} to Au, which forms gold nanoparticles on the sphere of the matchstick particle. After 30 mins of the reduction reaction, the particle suspension was washed by DI-water for another 3 times and dispersed in 10 mL of 0.3 wt.% poly(vinylpyrrolidone) (PVP 29 K) aqueous solution. The gold nanoparticles served as seeds for the further growth of the gold nanolayer. In this case, the particle suspension was added with 20 mL of 4 mg/mL gold hydroxide ($Au(OH)_3$) aqueous solution and 2 mL of formaldehyde (HCHO) aqueous solution. Note that the $Au(OH)_3$ solution was freshly-made by dissolving 400 mg of K_2CO_3 in 40 mL of $HAuCl_4$ solution and stirring overnight. Finally, the colloidal mixture was gently agitated overnight to avoid particle sedimentation. The resulting Au-SiO_2 Janus matchsticks were washed with PVP 29K solution by the centrifugation-redispersion process for 3 times.

Small-Scale Synthesis of Gold-Silica Janus Matchsticks. The volume of the pentanol was set as 5 mL and the rest of the chemicals for the rod synthesis were 500 mg of PVP 40K, 475 mL of ethanol, 175 µL of H_2O, 50 µL of sodium citrate solution, 90 µL of ammonia solution and 50 µL of TEOS. For the growth of the spherical head, 50 µL of APTES and 50 µL of TEOS were sequentially added to the rod suspension. For the gold coating, the as-synthesized Janus matchsticks were transferred into two 1.5 mL centrifuge tubes. The amount of chemicals used were 1.5 mL of $HAuCl_4$

solution, trace amount of $NaBH_4$, 500 µL of PVP 10K, 800 µL of $Au(OH)_3$ solution and 85 µL of HCHO solution.

Selective Fluorescent Labelling on the Spherical Head.[32] The SiO_2 Janus matchsticks are dispersed in ethanol. 5 mg of fluorescein isothiocyanate (FITC-NCS) was dissolved in 1.5 mL of particle suspension. The particle suspension was then agitated, and the reaction was allowed to proceed overnight.

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Author Contributions

Y. M. and W. D. conceived the project. Y. M. and D. L. wrote the manuscript. W. D. and Y. W. participated in the manuscript revision. All authors have given approval to the final version of the manuscript.

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Notes

The authors declare no competing financial interest.

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