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## **Electronic Supplementary Information (ESI)**

## **Colloidal Synthesis of Metallodielectric Janus Matchsticks**

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**Supplementary Figures** 

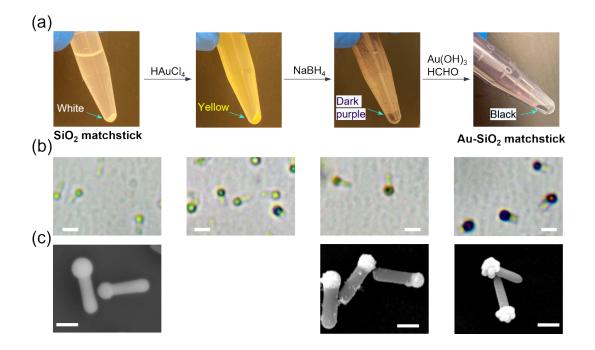
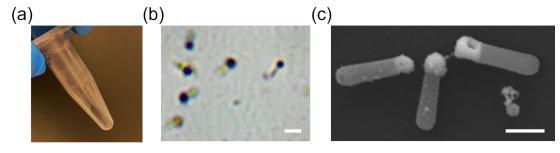
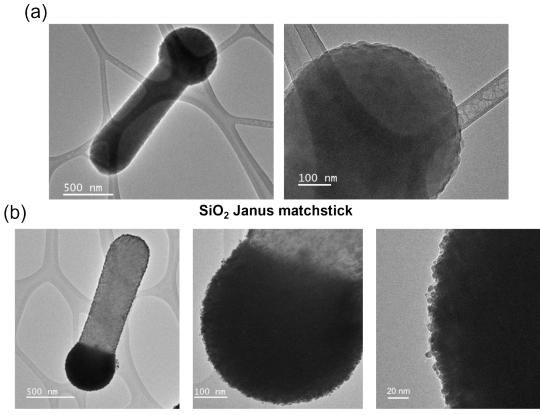


Fig. S1 (a) Photos showing the color change of particles during the gold coating. (b-c) Optical microscope and SEM images showing Janus matchsticks on each step of the gold coating. Scale bars =  $1 \mu m$ .



Au(OH)<sub>3</sub> reduced by NaBH<sub>4</sub> for gold coating

Fig. S2 (a) Photo showing particles after gold coating. (b-c) Optical microscope and SEM images showing Au-SiO<sub>2</sub> Janus matchsticks; these matchsticks were produced by reducing Au(OH)<sub>3</sub> with NaBH<sub>4</sub>. Scale bars = 1  $\mu$ m.



Au-SiO<sub>2</sub> Janus matchstick

Fig. S3 (a) TEM images of different magnifications showing a  $SiO_2$  Janus matchstick. Scale bars from left to right are 500 and 100 nm, respectively. (b) TEM images of different magnifications showing an Au-SiO<sub>2</sub> Janus matchstick. Scale bars from left to right are 500, 100 and 20 nm, respectively.

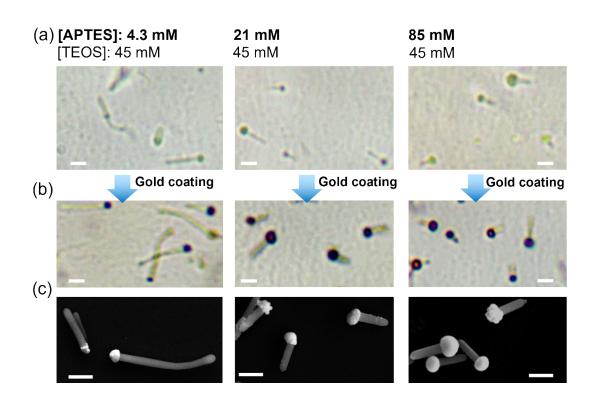


Fig. S4 (a) Optical microscope images showing SiO<sub>2</sub> Janus matchsticks by adding different concentrations of APTES while the concentration of TEOS is kept constant. (b-c) Optical microscope and SEM images showing corresponding Au-SiO<sub>2</sub> Janus matchsticks. Scale bars =  $1 \mu m$ .

## **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<sub>4</sub>), formaldehyde (HCHO) and potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) were purchased from Sigma-Aldrich. Sodium borohydride (NaBH<sub>4</sub>) was purchased from Merck KGaA. Ethanol absolute was purchased from Decon Lab. Inc.. Deionized water (DI-Water) was obtained from a Nanopure Diamond water system purchased from Thermo Scientific.

**Characterizations.** Upright optical microscope (Carl Zeiss Axio Plan II), confocal microscope, scanning electron microscope (SEM, JEOL 7500F) and transmission electron microscope (JEOL F200 TEM-STEM) were used to observe and characterize the SiO<sub>2</sub> rods, SiO<sub>2</sub> Janus matchsticks and Au-SiO<sub>2</sub> Janus matchsticks. ImageJ was used for measuring the length and diameter of the rod and sphere in the matchstick.

Prior to SEM characterization, SiO<sub>2</sub> rods were purified with ethanol, and dispersed into DI-water; SiO<sub>2</sub> Janus matchsticks were purified with ethanol (matchsticks before gold coating should not come in contact with DI-water because the spherical head and the rod bear opposite charges, inducing uncontrolled aggregation). Au-SiO<sub>2</sub> Janus matchsticks were washed with 0.3 wt.% poly(vinylpyrrolidone) (PVP 29 K) aqueous solution for improving the particle dispersity. Subsequently, these particle suspensions were drop-casted on a silicon (Si) wafer for SEM characterization. For TEM characterization, particles were dispersed in ethanol and then deposited on copper grids.

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. The total volume of water (5 mL) for forming the water emulsion is based on the water amount from added DI-water and

water present in the ammonia solution. 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<sub>2</sub> 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<sub>2</sub> Janus matchsticks were washed with ethanol by the centrifugation-redispersion process 3 times.

Site-Selective Gold Coating on Silica Janus Matchsticks. As-synthesized Janus matchsticks were transferred into two 50 mL centrifuge tubes with each containing around 182 mg of particles. Next, 20 mL of 4 mg/mL chloroauric acid (HAuCl<sub>4</sub>) 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<sub>4</sub>) was added to reduce the Au<sup>3+</sup> 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)<sub>3</sub>) aqueous solution and 2 mL of formaldehyde (HCHO) aqueous solution. NaBH<sub>4</sub> can be also used for the

reduction of  $Au(OH)_3$  in the second gold coating step (Fig. S2). Note that the  $Au(OH)_3$  solution was freshly-made by dissolving 400 mg of  $K_2CO_3$  in 40 mL of HAuCl<sub>4</sub> solution and stirring overnight. Finally, the colloidal mixture was gently agitated overnight to avoid particle sedimentation. The resulting Au-SiO<sub>2</sub> Janus matchsticks were washed with PVP 29K solution by the centrifugation-redispersion process 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  $\mu$ L of H<sub>2</sub>O, 50  $\mu$ L of sodium citrate solution, 90  $\mu$ L of ammonia solution and 50  $\mu$ L of TEOS. For the growth of the spherical head, 50  $\mu$ L of APTES and 50  $\mu$ L of TEOS were sequentially added to the rod suspension. For gold coating, 3 mL of as-synthesized Janus matchsticks (~ 13 mg) were transferred into a 1.5 mL centrifuge tube by centrifugation. Then, the particles were washed with ethanol three times before adding the gold precursor. The amount of chemicals for gold coating were 1.5 mL of HAuCl<sub>4</sub> solution, trace amount of NaBH<sub>4</sub>, 500  $\mu$ L of PVP 10K, 800  $\mu$ L of Au(OH)<sub>3</sub> solution and 85  $\mu$ L of HCHO solution.

Selective Fluorescent Labelling on the Spherical Head.<sup>1</sup> Typically,  $SiO_2$  Janus matchsticks (~ 7 mg) were dispersed in 1.5 mL of ethanol. 5 mg of fluorescein isothiocyanate (FITC-NCS) was added to the particle suspension. The particle suspension was then agitated, and the reaction was allowed to proceed overnight.

## Reference

 Z. H. Shah, X. Xu, S. Wang, Y. Li, Y. Chen, H. Shan and Y. Gao, *Polymer*, 2019, 177, 91-96.