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Supporting Information

Tadpole-like Janus Nanotubes

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1. Experimental Section

1.1 Chemicals and reagents.

1,2-bis(triethoxysilyl)ethane (BTEE), 1-pentanol and sodium tetrachloropalladate (II) (Na_2PdCl_4) were purchased from J&K, n-octyltriethoxysilane (OTES) was purchased from Acros Organics, polyvinylpyrrolidone (PVP-K30) was obtained from Sinopharm Chemical Reagent, trisodium citrate dihydrate ($Na_3C_6H_5O_7 \bullet 2H_2O$), ammonium hydroxide (25 wt%), hydrochloric acid (37 wt%), hydrogen peroxide (30 wt%), absolute ethanol, hexane, sodium borohydride were purchased from Beijing Chemical Works, fluorescein sodium was obtained from Tianjin Guangfu Fine Chemical Research Institute, PEG-Fe_3O_4 nanoparticles (20-40 nm) is homemade, deionized water produced by the Millipore system. All chemicals were used as received.

1.2 Characterization.

In order to avoid aggregation among the samples, absolute ethanol was used as a dispersant, a small amount of dispersion was dropped on a silicon slice with a 10 μL locomotive pipette, and dried it at room temperature. Scanning electron microscopy (SEM) equipped with an energy dispersive X-ray (EDX) measurements were performed with a FEI QUANTA FEG 250 apparatus operated at an accelerating voltage of 15 kV. A small amount of dispersion was dropped on a carbon-coated

copper mesh, and dried it at room temperature. Morphologies of the samples were characterized by transmission electron microscopy (TEM) with a JEOL JEM-1011 apparatus operated at an accelerating voltage of 100 kV. 899 KF Coulometer Karl Fischer Moisture Titrator was used to measure water contents of emulsion and solvent. The aqueous phase of reaction emulsion was labelled with fluorescein sodium, a small amount of reaction emulsion was dropped on a glass slide with a glass cover, morphologies of the samples were observed by confocal laser scanning microscopy (CLSM) with a Nikon TI2-S-HU CLSM at a laser wavelength of 488 nm. Optical microscopy: the self-swimming phenomenon of tadpole-like Janus Pd-nanotubes was observed with an Olympus BX51 microscope. The sizes of water droplets in inverse-emulsions and solutions were measured by dynamic light scattering (DLS) with a Malvern Nano ZSE. Zeta potential of tadpole-like Janus nanotubes and nanotubes were measured with a Malvern Nano ZSE. Temperature variation curves of the samples dispersion with irradiation time were recorded with a thermal infrared imager, the samples dipersion was irradiated by 808 nm near-infrared light.

1.3 Preparation of tadpole-like nanotubes and nanoparticles.

In a 25 mL round-bottomed flask, 1 g PVP-K30 was dissolved in 10 mL 1-pentanol, and the solution was sufficiently dissolved by ultrasound to obtain a light yellow slightly viscous solution. Subsequently, 100 μL $Na_3C_6H_5O_7 \bullet 2H_2O$ aqueous solution (180 mM), a certain amount of ammonium hydroxide (25 wt%) and deionized water were added to the solution. The emulsion was vortexed for 1 min. After standing for 5 minutes to remove air bubbles, 50 μL BTEE was added, and the emulsion was slightly shaken for 0.5 min. The hydrolysis-condensation of BTEE was allowed to proceed without stirring at room temperature for several hours. The mixture was centrifuged and washed with absolute ethanol. Morphologies of the samples with different reaction time, water contents, NH_4OH and HCl concentration were observed.

1.4 Preparation of tadpole-like Janus nanotubes.

In a 25 mL round-bottomed flask, 1 g PVP-K30 was added in 10 mL 1-pentanol to

obtain a light yellow slightly viscous solution by ultrasound. Subsequently, 100 μL $Na_3C_6H_5O_7 \bullet 2H_2O$ aqueous solution (180 mM), 350 μL deionized water, and a certain amount of ammonium hydroxide (25 wt%) were added to the solution. The emulsion was vortexed for 1 min. After standing for 5 minutes to remove air bubbles, 50 μL BTEE and a certain amount of OTES were added simultaneously, and the emulsion was slightly shaken for 0.5 min. The hydrolysis-condensation of BTEE and OTES was allowed to proceed without stirring at room temperature for several hours. The mixture was centrifuged and washed with absolute ethanol.

1.5 Preparation of Pd or Fe_3O_4 composed tadpole-like Janus nanotubes.

Polyethylene glycol (PEG) modified Fe_3O_4 nanoparticles were prepared by coprecipitation method.[1] In a 25 mL round-bottomed flask, 1 g of PVP-K30 was dissolved in 10 mL 1-pentanol, and the solution was sufficiently dissolved by ultrasound to obtain a light yellow slightly viscous solution. Subsequently, 100 μL $Na_3C_6H_5O_7 \bullet 2H_2O$ aqueous solution (180 mM), 350 μL Na_2PdCl_4 aqueous solution (1 mg/mL) or PEG-Fe_3O_4 nanoparticles (20-40 nm) dispersion and a certain amount of ammonium hydroxide (25 wt%) were added to the above solution. The emulsion was vortexed for 1 min. After standing for 5 minutes to remove air bubbles, 50 μL BTEE and a certain amount of OTES were added simultaneously, and the emulsion was slightly shaken for 0.5 min. The hydrolysis-condensation of BTEE and OTES was allowed to proceed without stirring at room temperature for several hours. Sodium borohydride was add into the above emulsion in order to reduce the Na_2PdCl_4, and sonicate for several hours, the color of emulsion was slightly darkened. The mixture was centrifuged and washed with absolute ethanol.

2. Results and Discussion

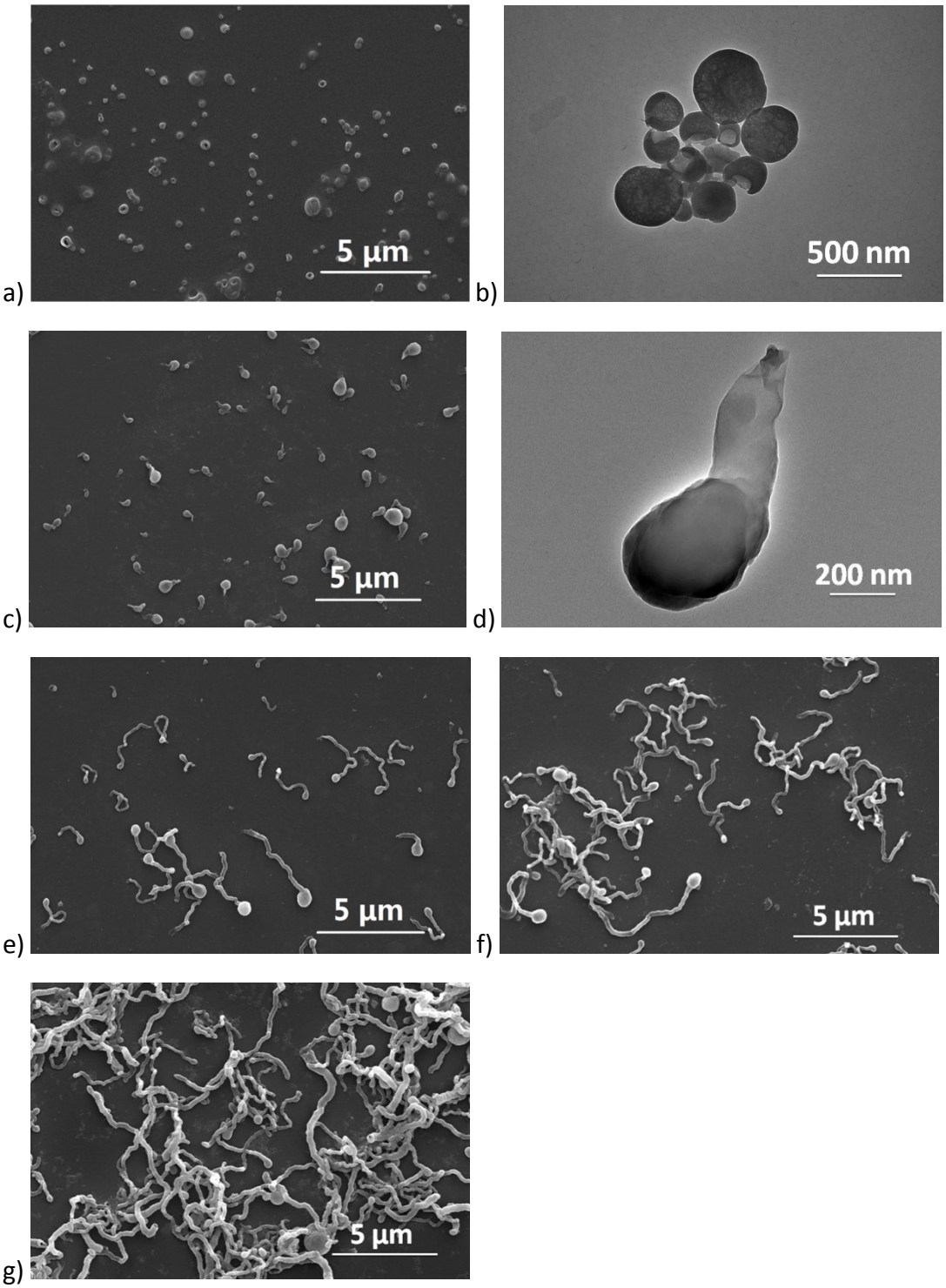


Figure S1. SEM and TEM images of the tadpole-like nanotubes with different reaction time (h): a, b) 0.5; c, d) 1; e) 5; f) 16; g) 48. The aqueous phase content is 59 mg/mL, and the NH_4OH concentration in the aqueous phase is 122 mmol/L.

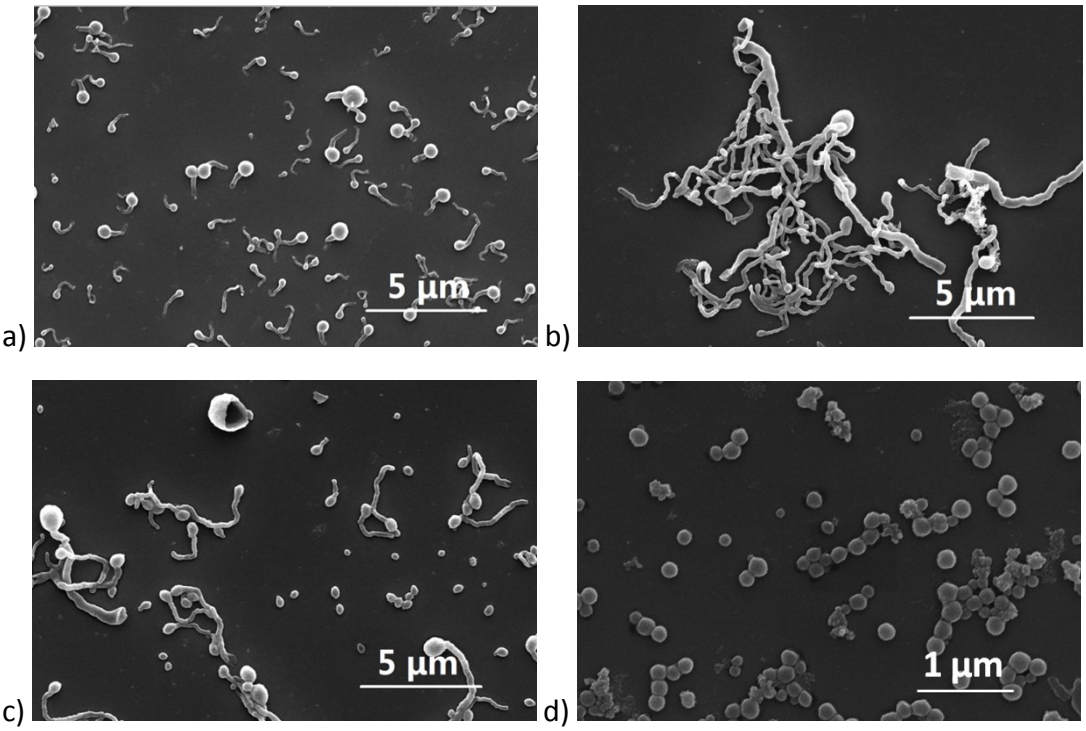


Figure S2. SEM images of the tadpole-like nanotubes with different aqueous phase contents (mg/mL): a) 29; b) 59; c) 74; d) 224. The NH_4OH concentration in the aqueous phase is 122 mmol/L, and the reaction time is 24 h.

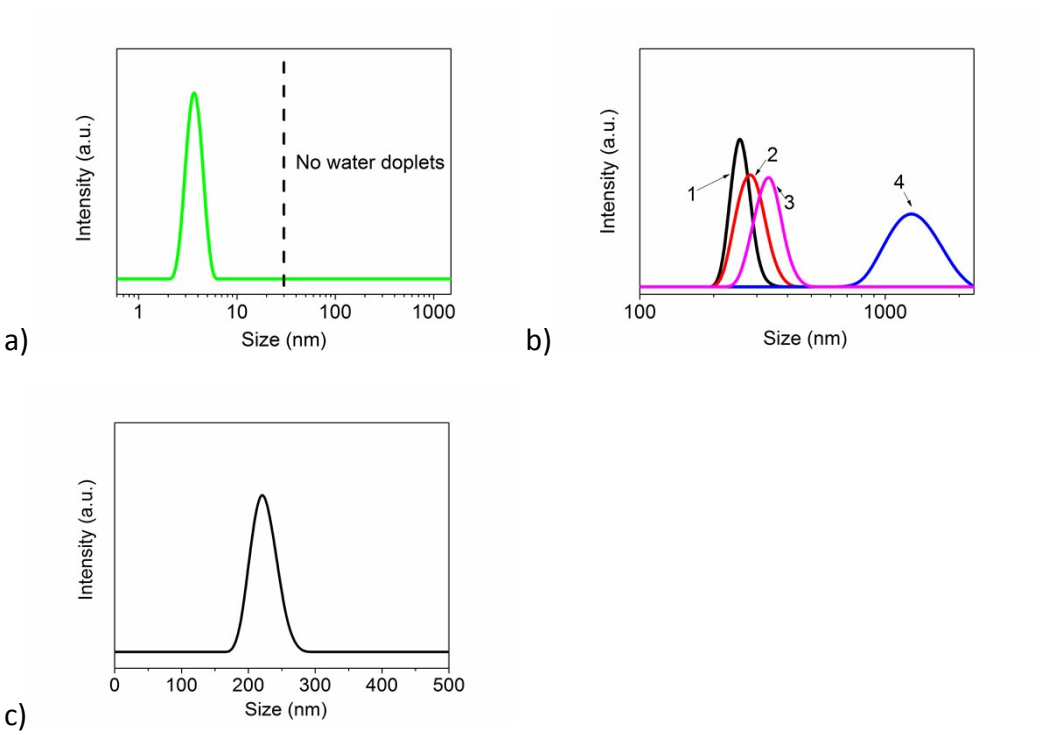


Figure S3. DLS size analysis of 1-pentanol solution of PVP (a) and the water droplets in the water in 1-pentanol emulsion with different aqueous phase contents (mg/mL) (b): line 1) 26; line 2) 34; line 3) 59; line 4) 84; the water droplets in 1-pentanol phase when 224 mg/mL aqueous phase contents is used (the upper 1-pentanol phase) (c).

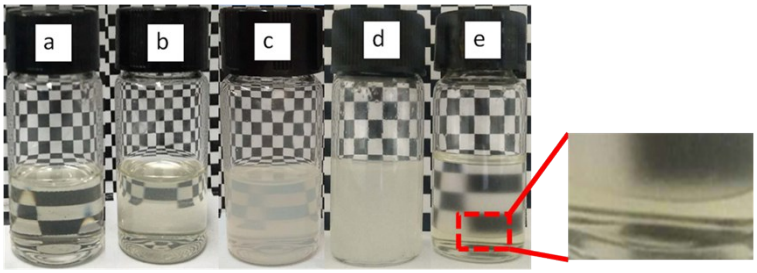


Figure S4. Emulsions photographs with aqueous phase contents (mg/mL): a) 0; b) 26; c) 74; d) 84; e) 224, 1-pentanol and aqueous phase were separated.

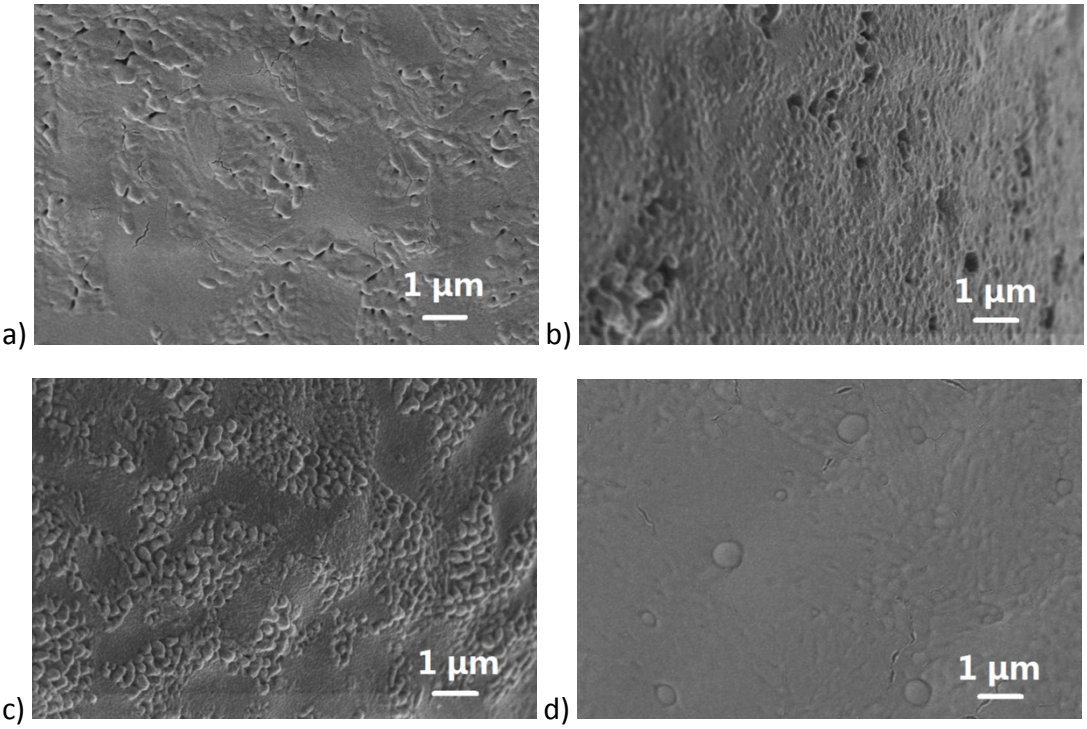
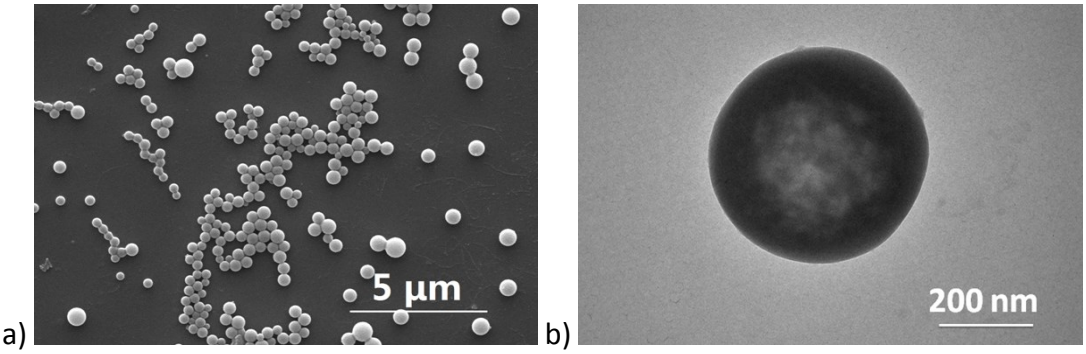


Figure S5. Cryo-SEM images of emulsions with aqueous phase contents (mg/mL): a) 26; b) 34; c) 59; d) 84.



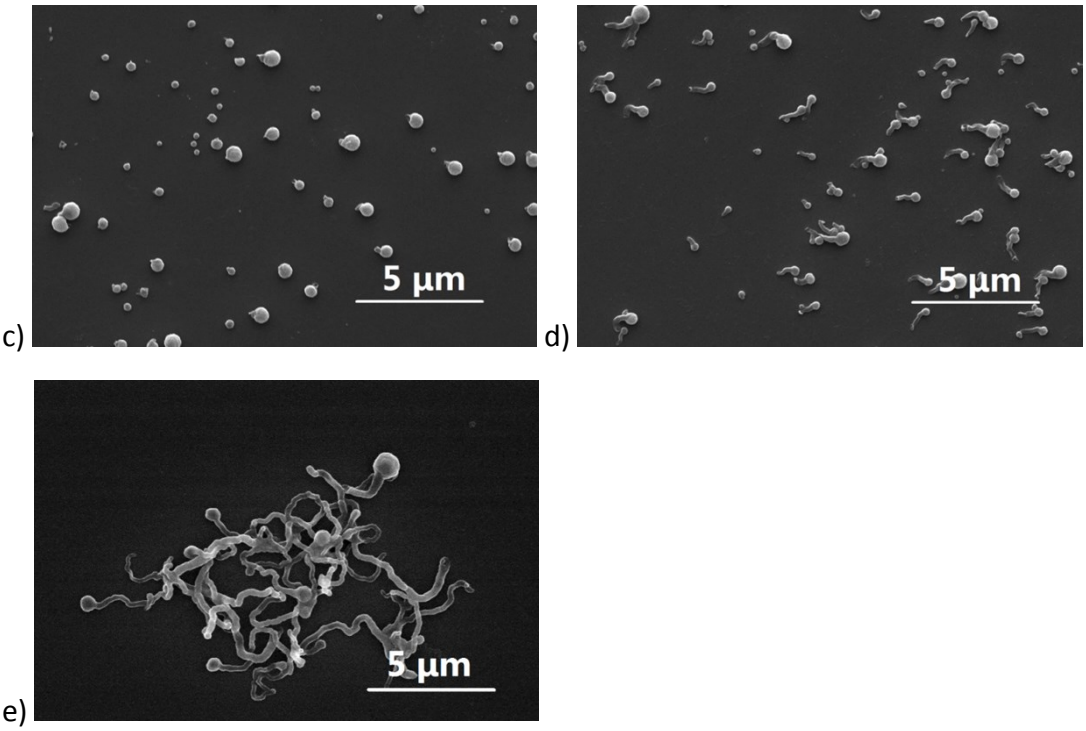


Figure S6. SEM and TEM images of the tadpole-like nanotubes with different NH_4OH concentration in the aqueous phase (mmol/L): a, b) 0; c) 8.71; d) 17.42; e) 226.46. The aqueous phase content is 59 mg/mL, and the reaction time is 24 h.

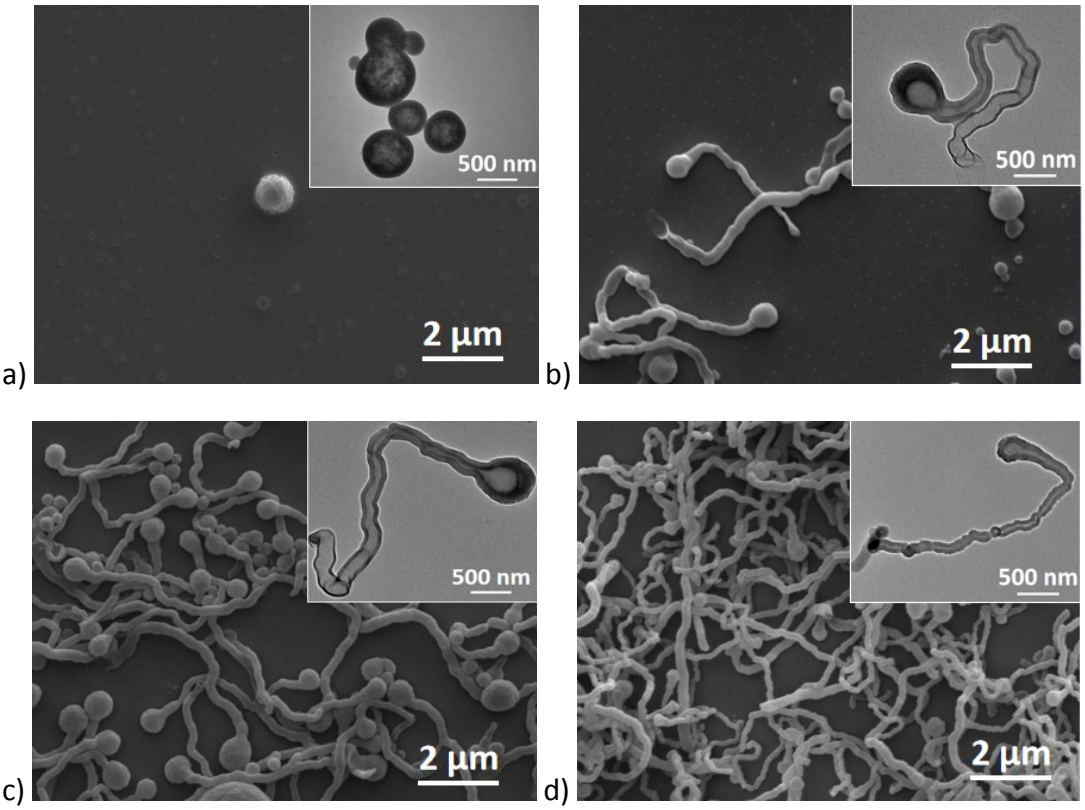


Figure S7. SEM and inset TEM images of the tadpole-like nanotubes with different NH_4OH concentration in the aqueous phase (mmol/L): a) 0; b) 8.71; c) 17.42; d) 226.46.

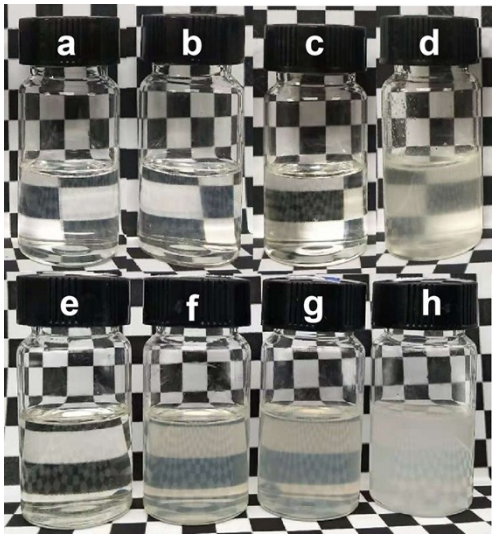


Figure S8. Emulsions photographs of the tadpole-like nanotubes with different NH_4OH concentration in the aqueous phase (mmol/L): a, e) 0; b, f) 8.71; c, g) 17.42; d, h) 226.46. The aqueous phase content is 59 mg/mL, and the reaction time is 24 h (a-d) and 72 h (e-h), respectively.

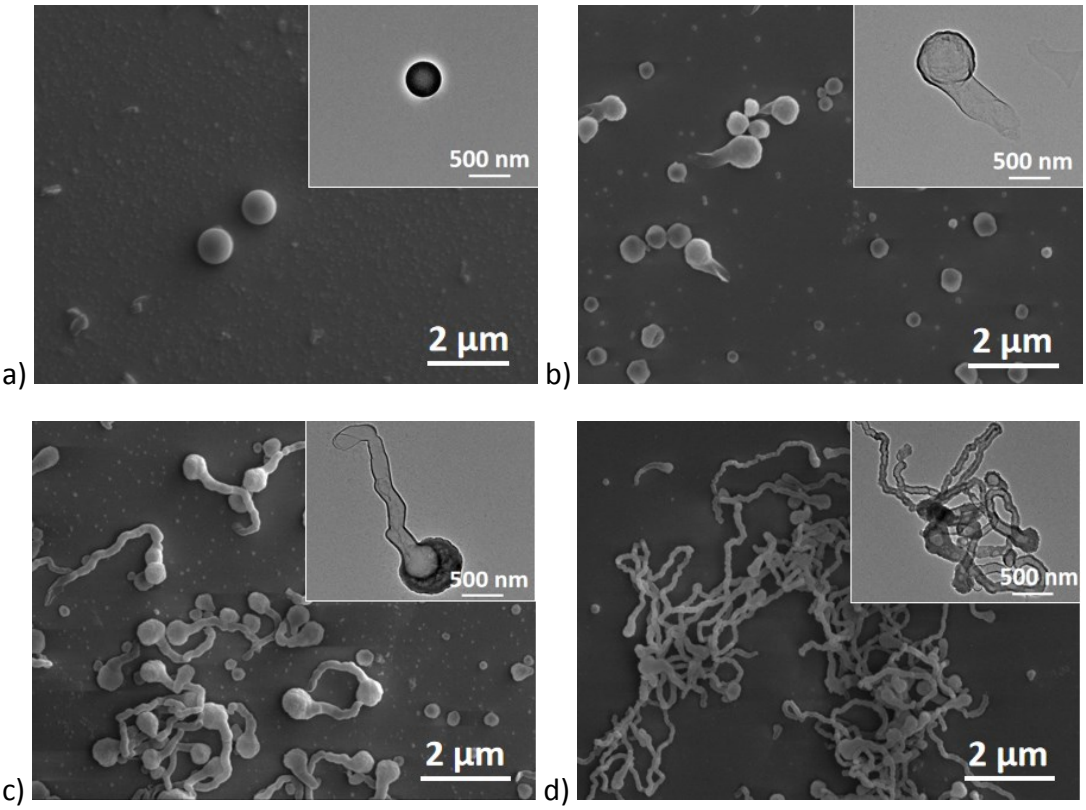
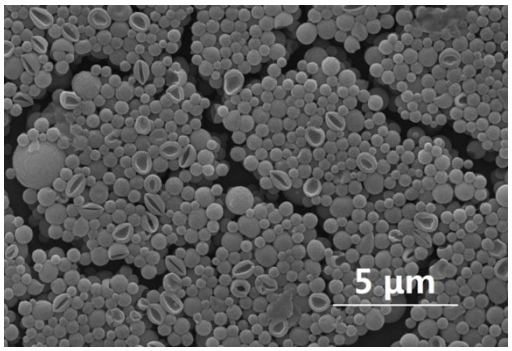
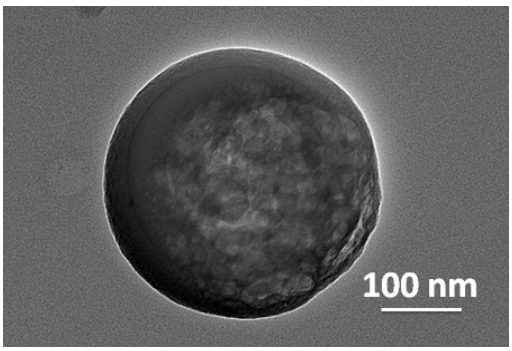


Figure S9. SEM and inset TEM images of the tadpole-like nanotubes with different NH_4OH concentration in the aqueous phase (mmol/L): a) 0; b) 8.71; c) 17.42; d) 226.46. The aqueous phase content is 59 mg/mL, the reaction time is 24 h, and the temperature is 40 °C.

a) 

b) 

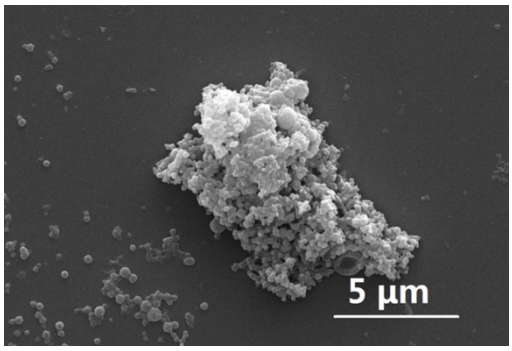
c) 

Figure S10. SEM and TEM images of the tadpole-like nanotubes with different HCl concentration in the aqueous phase (mmol/L): a, b) 9.66; c) 228.26. The aqueous phase content is 59 mg/mL, and the reaction time is 24 h.

Figure S11. Dispersions photographs of the tadpole-like Janus nanotubes (1, 3) and the tadpole-like nanotubes (2, 4) in water (1, 2) or hexane (3, 4).

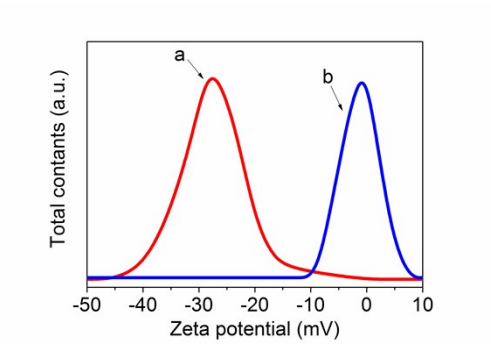
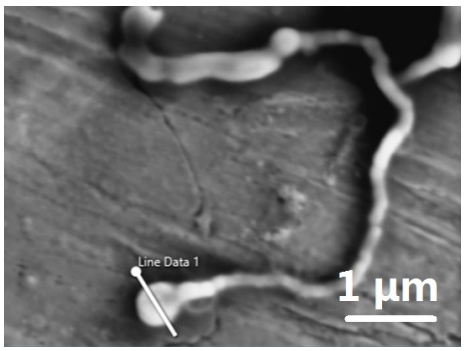


Figure S12. Zeta potential of the tadpole-like nanotubes (line a) and the tadpole-like Janus nanotubes (line b).

a) 

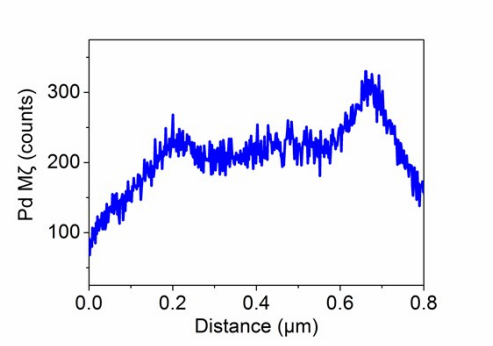
b) 

Figure S13. The SEM image (a) and EDX elemental line-scan profile (b) of the tadpole-like Janus Pd-nanotubes.

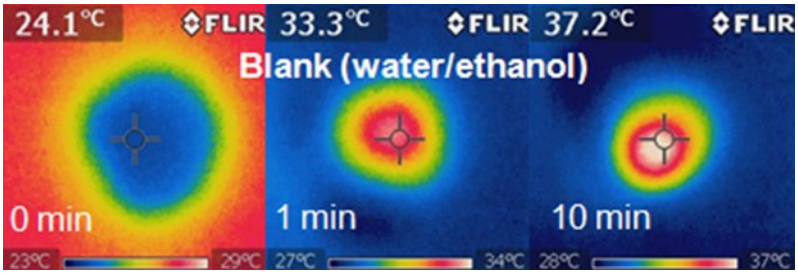


Figure S14. Infrared thermal images of blank (water/ethanol mixture).

Reference

1. J. H. Yang, P. Zou, L. L. Yang, J. Cao, Y. F. Sun, D. L. Han, S. Yang, Z. Wang, G. Chen, B. J. Wang and X. W. Kong, *Appl. Surf. Sci.*, 2014, **303**, 425-432.