

Modification of colloidal particles by unidirectional silica deposition for urchin-like morphologies

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1. Materials

Tetraethyl orthosilicate (TEOS) and ammonia (28%) were purchased from Alfa Aesar. Polyvinylpyrrolidone (PVP, Mw. 40k) was purchased from Sigma Aldrich. *n*-Pentanol ($\geq 99\%$) was purchased from Acros. Silica and polystyrene microspheres were purchased from Tianjin BaseLineChromTech Research Centre. Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. All of the reagents were of analytical grade and used without further purification. The water used throughout all the experiments was purified with the Millipore system.

2. Synthesis of seed particles

2.1 Hematite cubic colloids: The synthesis of hematite colloidal particles with controlled size was achieved by a process based on a modified method developed by Sugimoto et al.¹ In a typical synthesis of 2 μm cubic hematite colloidal particles, FeCl_3 (2 M, 100 mL) was firstly added to NaOH solution (90 mL, 6 M) in a 250 mL Pyrex bottle, and agitation was continued for an additional 10 min. $\text{Fe}(\text{OH})_3$ gel in a tightly sealed bottle, typically containing $\text{Fe}(\text{OH})_3$ (0.9 M), Fe^{3+} (0.1 M) was placed in an oven preheated to 100 °C, and aged for 8 days. After the treatment, red products were collected by filtration and washed three times with deionized water and ethanol (1:1) before drying at 50 °C overnight. The procedure of the synthesis of

hematite cubic particles with a size of 800 nm was similar to the preparation of the 2 μ m particles except for shortening the reaction time to 5 days.

Reference 1. Sugimoto, T.; Khan, M. M.; Muramatsu, A. *Coll. Surf.* **1993**, *70*, 167–169.

2.2 Hematite micro-cake colloids: Cake-shaped particles were fabricated using a modified method reported by Song et al.² Iron chloride (1.5 mmol) was dissolved in deionized water (30 mL) as solution A. Sodium silicate (0.375 mmol) was homogeneously dispersed in deionized water (20 mL) as solution B. Both solutions were prepared at room temperature. The two solutions were then mixed to form a transparent orange colored solution, which was transferred into an autoclave (70 mL) and heated for 24 h at 140 °C. The red product was collected by centrifugation and rinsed with deionized water several times. Finally, the product was dried in oven at 80 °C overnight. Analysis was performed with a scanning electron microscopy (SEM, Hitachi S-4800 at 15 kV).

Reference 2. Qu, J.; Yu, Y.; Cao, C.-Y.; Song, W.-G. *Chem. Eur. J.* **2013**, *19*, 11172–11177.

2.3 Hematite quasi-cube colloids: Quasi-cube colloids were fabricated according to Gao's report.³ In a typical procedure, a mixture solution of zinc acetate (0.219 g) in Fe(NO₃)₃ solution (10 mL; 0.2 M) was prepared firstly. Then ammonia solution (10 mL; 25%) was added under magnetic stirring. After 10 min of stirring, the mixture was transferred to and sealed in a Teflon-lined autoclave (50 mL), kept at 160 °C for 16 h, and finally cooled to room temperature. The precipitate was collected by centrifugation (5000 rpm, 10 min), and washed alternately with deionized water and ethanol before being dried in air under ambient conditions.

Reference 3. Liu, R.; Jiang, Y.; Fan, H.; Lu, Q.; Du, W. and Gao, F.; *Chem. Eur. J.*, **2012**, *18*, 8957

2.4 Hollow nanoporous Au nanoparticles: A one-step synthetic protocol was applied here based on a method reported by Ling et al.⁴ In a typical synthesis, hydroquinone

solution (28mM, 160mL), AgNO₃ solution (10 mM, 60 mL) andHAuCl₄ solution (40 mM, 100mL) are added in sequence to aPVP solution (90 mM, 4.5mL) on gentle stirring at room temperature. The solution turned colorless immediately, changed to light green within the next 30s and eventually to reddish in 3min. After that, the solution was washed with concentrated NH₃•H₂O to remove residual AgCl formed during the reaction, and purified by repeated centrifugations and redispersed in water.

Reference 4. Pedireddy, S.; Lee, H. K.; Tjiu, W. W.; Phang, I. Y.; Tan, H. R.; Chua, S. Q.; Troadec, C.; and Ling, X. Y.; *Nat. Commun.*, **2014**, 5, 4947.

2.5 Magnetic Fe₃O₄ microspheres: a modified solvothermal reduction method was used to synthesis monodisperse Fe₃O₄ microspheres. FeCl₃ · 6H₂O (1.89 g, 7 mmol) was dissolved in a mixture of ethylene glycol (30 mL) and diethylene glycol (10 mL) to form a clear solution, followed by the addition of deionized water (1 mL), NaAc (3.6 g) and polyethylene glycol (1.0 g). The mixture was stirred vigorously for 30 min and then sealed in a Teflon-lined stainless-steel autoclave (50 mL capacity). The autoclave was heated to and maintained at 200°C for 6 h, and allowed to cool to room temperature.

The black products were washed several times with ethanol and dried at 60°C for 6 h.

Reference 5. Deng, H.; X. Li; Q. Peng; X. Wang; J. Chen and Y. Li; *Angew. Chem. Int. Ed.*, **2005**, 44, 2782.

2.6 Prussian blue microcubes: Preformed Prussian blue (PB) microcubes were synthesized according to Lou's report. In a typical procedure, polyvinylpyrrolidone (PVP, K30, M_w ~ 40000, 3.8 g) and K₄Fe(CN)₆·3H₂O (0.11 g) were added to a HCl solution (0.1 M, 50 mL) under magnetic stirring. After stirring for 30 min, a clear solution was obtained. The bottle was then placed into an electric oven and heated at 80°C for 24 h. The obtained blue product was filtered and washed several times with distilled water and absolute ethanol and finally dried in a vacuum oven at 25°C for 12 h.

Reference 6. Zhang, L.; Wu, H. B.; Madhavi, S.; Hng, H. H. and Lou, X. W.; *J. Am. Chem. Soc.*, **2012**, 134, 17388.

3. Modifying colloidal particles with silica rods

In a typical process, PVP (3g) was dissolved in 1-pentanol ($\geq 99\%$, 30 mL) by sonication for 1 h. When PVP was dissolved, a dispersion of hematite cubes in water (20% w/v, 50 μL) was added, and sonicated for a further 2 h before adding a mixture of ethanol (3 mL), deionized water (350 μL) and sodium citrate dihydrate solution (0.18 M, 200 μL). The resulting mixture was shaken by hand for 5 min to form a water/1-pentanol emulsion. Ammonia (28%, 675 μL) was then added and the flask was shaken for another 3 min before adding TEOS ($\geq 98\%$, 500 μL) to the emulsion. After a further shaking for 1 min, the flask was left to rest and the reaction was allowed to proceed overnight. Next, the resulted mixture was centrifuged several times with water and ethanol (1:1) before being transferred into pure water.

Various shapes and materials of seed particles (or Plane) were synthesized in a similar process except the amount of water and aqueous ammonia used in the process were varied. For the spherical hollow nanoporous Au nanoparticles, Fe_3O_4 , silica and polystyrene particles, 0.545 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 0.350 mL of H_2O were used for silica wires growth. For micro-box Prussian blue and PDMS plane, 0.675 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and 0.840 mL of H_2O were used for straight silica rods modified on the surface. The parameters of other seeds or plane used in this report were labeled on the figure comments.

3. Supplementary SEM images called for manuscript

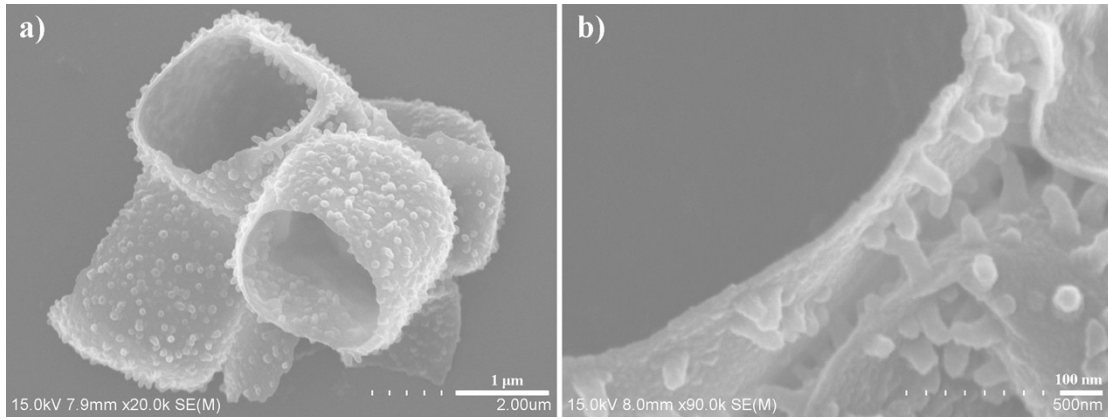


Fig.S1 SEM images of the urchin-like structure of $\text{Fe}_2\text{O}_3@\text{SiO}_2$ when limited water was used. a) the cracked cubic silica with urchin-like structure; b) the enlarged SEM image of the surface silica rods. The hematite cores were etched by HCl for clear observation of the microstructure.

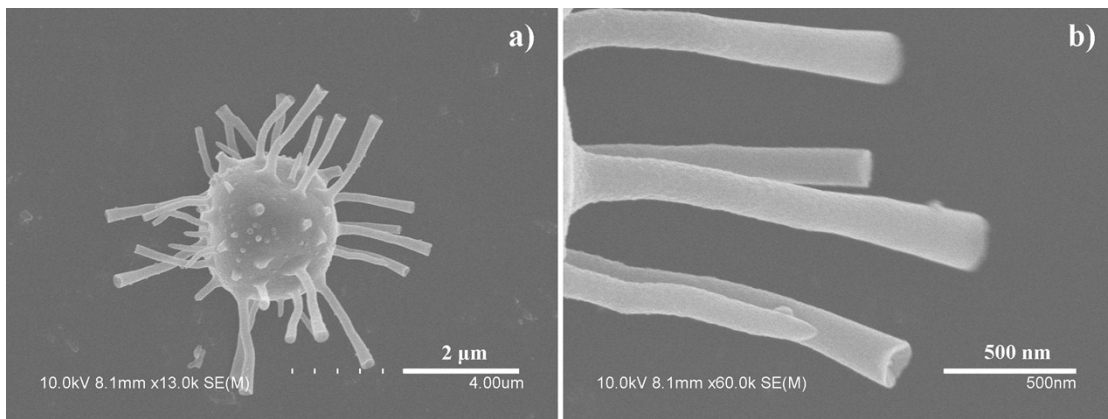


Fig.S2 SEM images of one urchin-like particle and its silica antennas when plenty of TEOS was used. a) SEM image of an integrated urchin-like particle; b) enlarged SEM image of silica rods on the surface of the seed particle. The silica antennas have an average length of $1.5\mu\text{m}$.

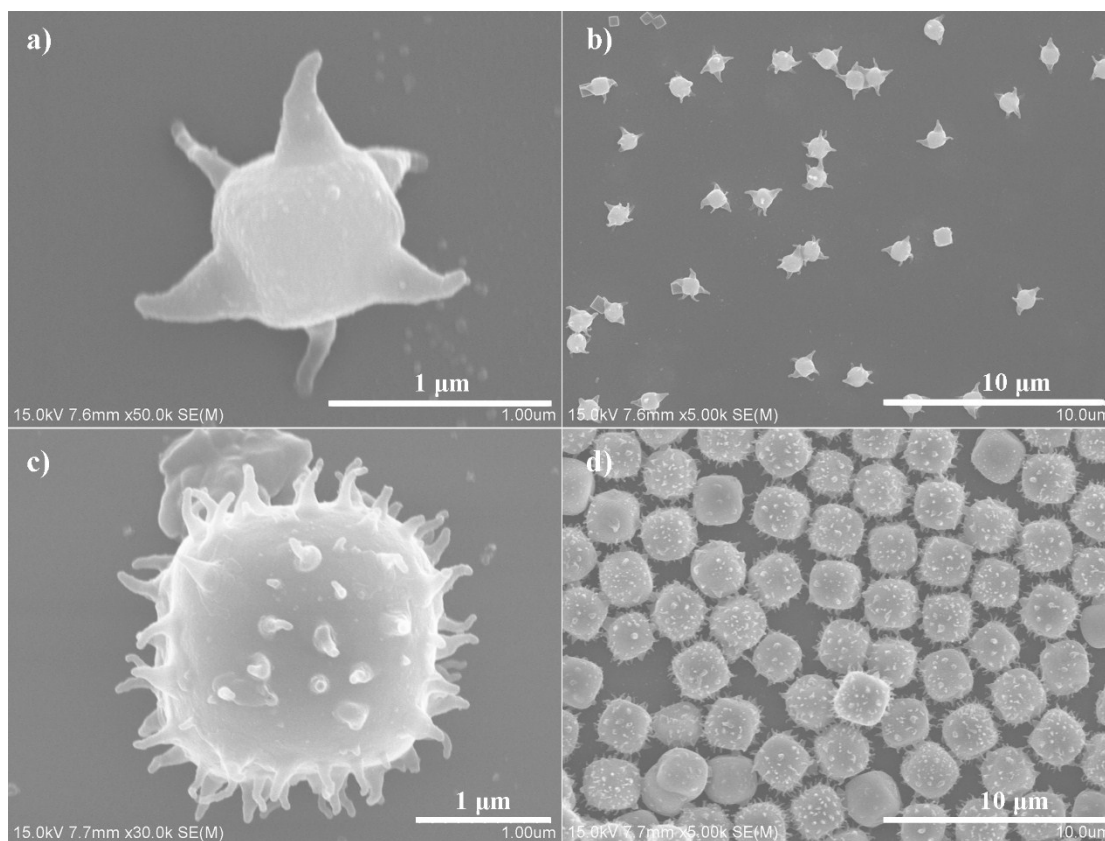


Fig.S3 SEM images of $\text{Fe}_2\text{O}_3@\text{SiO}_2$ urchin-like structure when two typical sizes of hematite cubes (a, b, 800 nm and c, d, 2 μm) were used under the same hydrolysis condition. When the smaller colloids were selectively modified by silica antennas on six faces, the bigger colloids exhibited abundant of silica antennas modified on each face forming a perfect urchin-like structure. ($\text{NH}_3 \cdot \text{H}_2\text{O}$: 545 μL, H_2O : 295 μL)

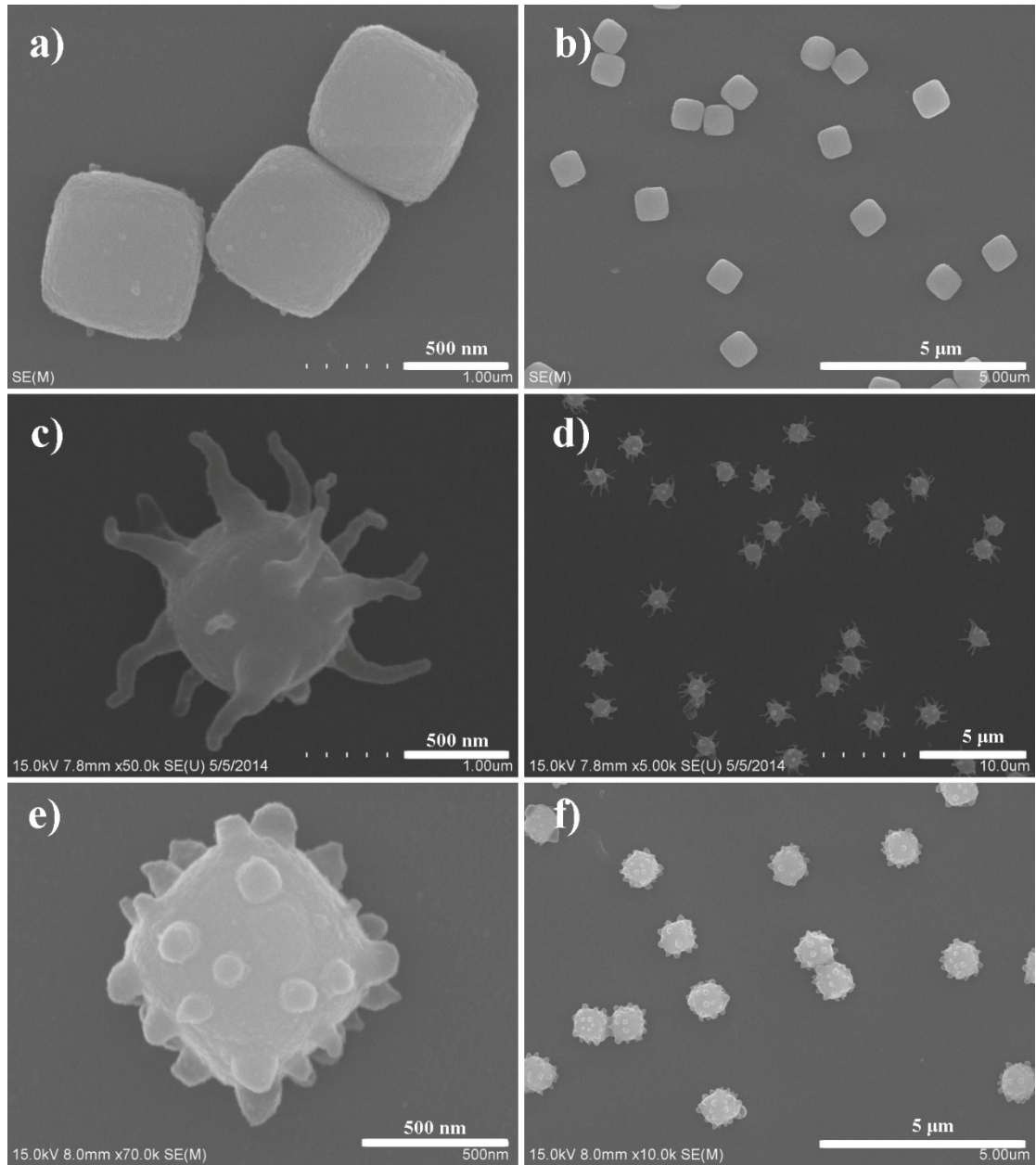


Fig.S4 SEM images of the 800 nm hematite cubes and their cosmetics by silica at varied ammonia concentration (a, b, the naked hematite colloids; c, d, $\text{NH}_3 \cdot \text{H}_2\text{O}$: 545 μL , H_2O : 245 μL ; e, f, $\text{NH}_3 \cdot \text{H}_2\text{O}$: 575 μL , H_2O : 245 μL).

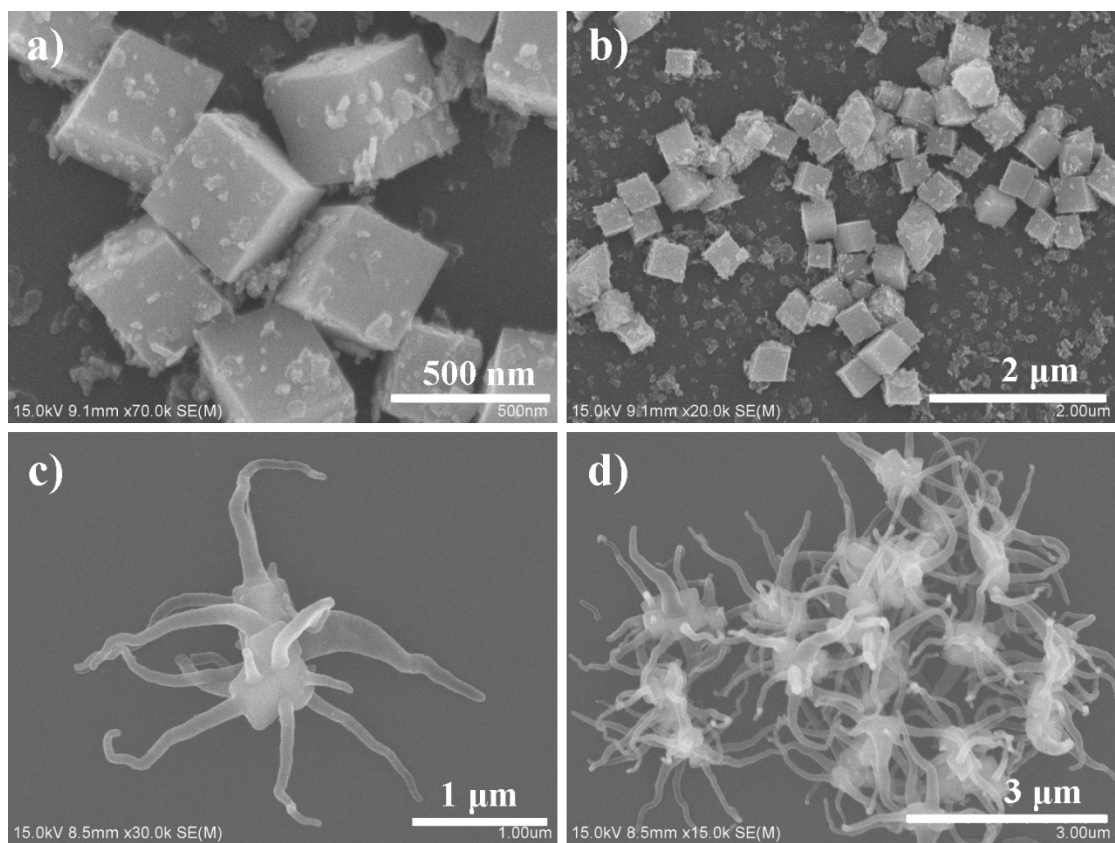


Fig.S5 SEM images of $\text{Fe}_2\text{O}_3@\text{SiO}_2$ urchin-like structure, (a, b) seed particles. (c, d) obtained urchin-link particles ($\text{NH}_3 \cdot \text{H}_2\text{O}$: 545 μL , H_2O : 350 μL).

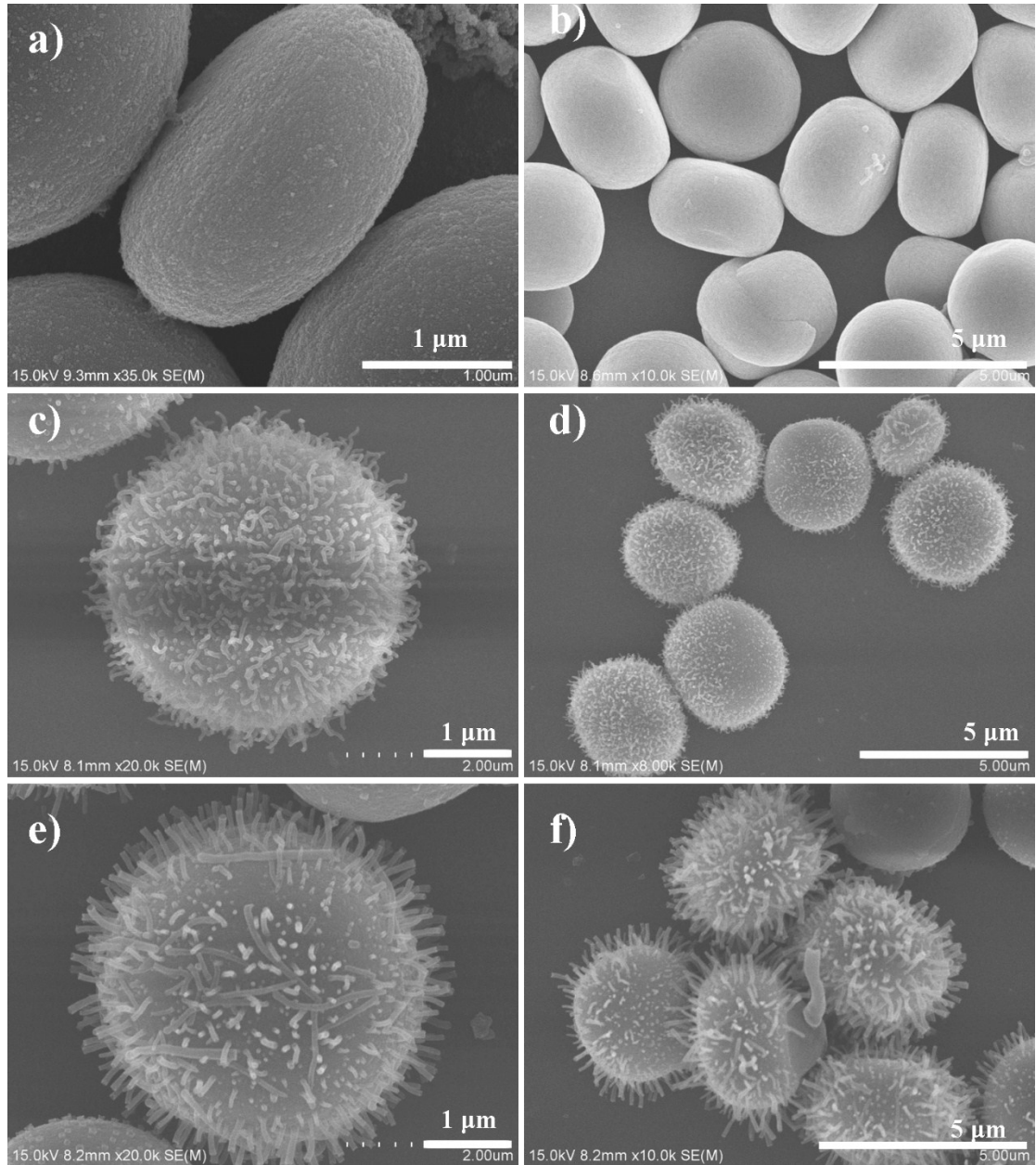


Fig.S6 SEM images of hematite cakes (a, b) and their cosmetics by silica at varied ammonia concentration for bent and unbent silica antennas (c, d, $\text{NH}_3 \cdot \text{H}_2\text{O}$: 545 μL , H_2O : 350 μL ; e, f, $\text{NH}_3 \cdot \text{H}_2\text{O}$: 675 μL , H_2O : 350 μL).

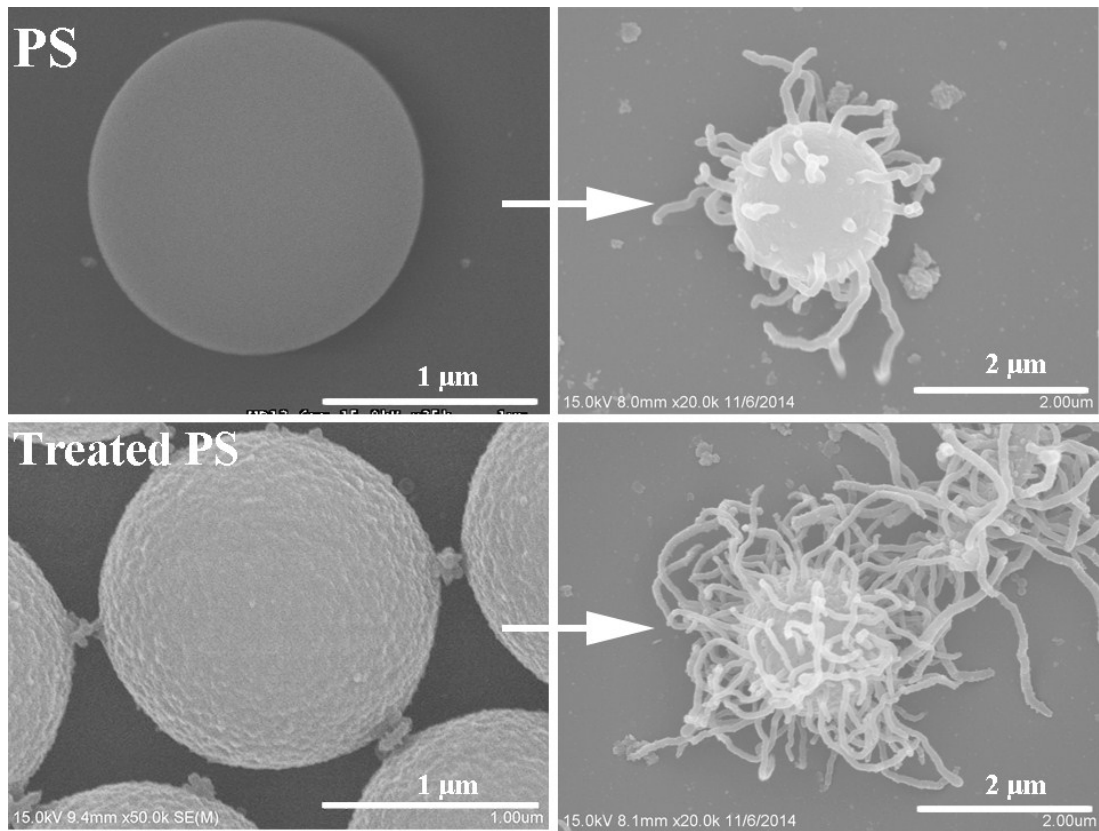


Fig.S7 SEM images of varied surface roughness PS and their urchin-like cosmetics after silica wires modification. The roughness PS particles were obtained by oxygen plasma etching ($\text{NH}_3 \cdot \text{H}_2\text{O}$: 545 μL , H_2O :350 μL).

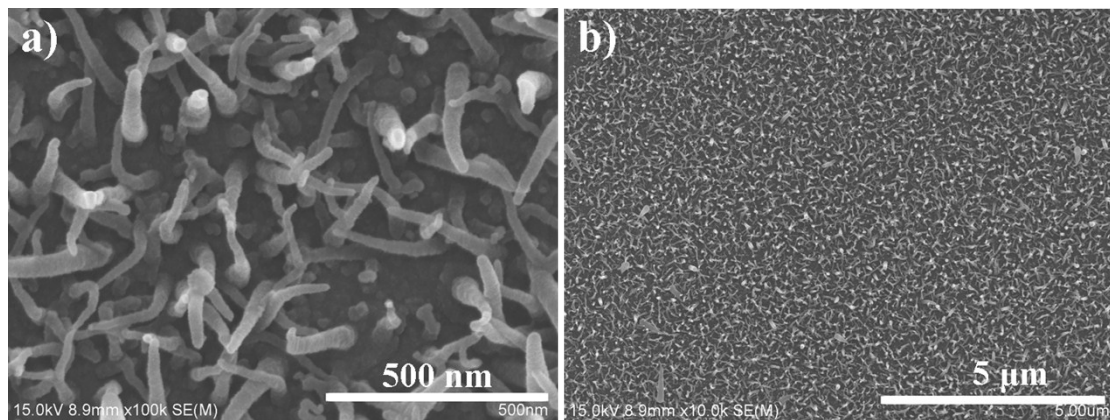


Fig.S8 SEM images of glass substrate (commercial glass slides cleaned by water, ethanol and acetone to remove the dust and oil on the surface, and dried by nitrogen) after silica wires modification. (a) enlarged location of glass modified by silica wires, (b) overall image ($\text{NH}_3 \cdot \text{H}_2\text{O}$: 545 μL , H_2O :350 μL).