

Supporting Information

Janus Particles with Tunable Coverage of Zinc Oxide Nanowires

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Experiment detail:

Instruments and Reagent: The morphology of the samples was observed using a LEO 1530 thermally-assisted field emission SEM. All the samples were sputtered with gold before the test. EDX was used in conjunction with the SEM scans to determine the chemical composition. PS microspheres with diameter of 6 μm were purchased from Sigma Aldrich. SiO_2 microspheres with diameter of 5.2 μm were purchased from Bangs Laboratories, Inc. All chemicals were analytical grade.

Synthesis of poly(butyl acrylate): The reaction was carried out in a flask equipped with a reflux condenser and a stirrer. 20 g of butyl acrylate was dissolved in 100 mL of toluene. The mixture was stirred for 20 min at ambient temperature under nitrogen flow. Then 0.4 g of azobisisobutyronitrile (AIBN) in 4 mL of tetrahydrofuran (THF) was injected in the reaction mixture, and meanwhile, the temperature was raised to 70 $^{\circ}\text{C}$ under nitrogen for 4 h.

Synthesis of hydrophobic Ag nanoparticles (According to Chem. Mater. 2008, 20, 6939): 0.85 g of AgNO_3 and 2 mL of oleylamine were dissolved in 50 mL of toluene in a 100 mL flask. The mixture was heated to 80 $^{\circ}\text{C}$ under nitrogen and kept at this temperature for 6 hrs before it was cooled down to room temperature. A total of 50 mL of ethanol was added into the solution after the reaction, and the suspension was centrifuged at 6000 rpm for 10 min. The supernatant was discarded. The precipitation was redispersed in 50 mL of toluene to give a brown-yellow dispersion.

Synthesis of the Janus PS microspheres with controlled ZnO nanowires: To introduce Zn^{2+} on the PS surface, the PS microspheres were pretreated by mixing them with 2 M ZnCl_2 at 100 $^{\circ}\text{C}$, followed by centrifugal separation, washing and drying at 50 $^{\circ}\text{C}$. For comparison, the PS microspheres treated in the same way but dried at room temperature were also used. 0.1 mL of the above hydrophobic Ag nanoparticle solution was added to 0.1 g of poly(butyl acrylate) in 10 mL of CHCl_3 at the room temperature. A bare ITO glass ($0.5 \times 1.0 \text{ cm}^2$) was cleaned thoroughly by sonication in ethanol for 10 min and dried in air. Then above poly(butyl acrylate) solution with Ag nanoparticles was dropped onto the clean ITO substrates and spun coating with a spin

coater with different spinning speed. By varying the concentration and the spinning speed, the masking polymer layer can be adjusted (Figure S1)

Thanks for the referee's valuable suggestion. In order to show how the polymer concentration and spin speed are adjusted to achieve varied thicknesses, as an example, we investigate the polymer thickness by using different concentration of polymer and spin speed. The thickness is determined by SEM as shown in the following pictures. We added these to the Supporting information (Figure S1).

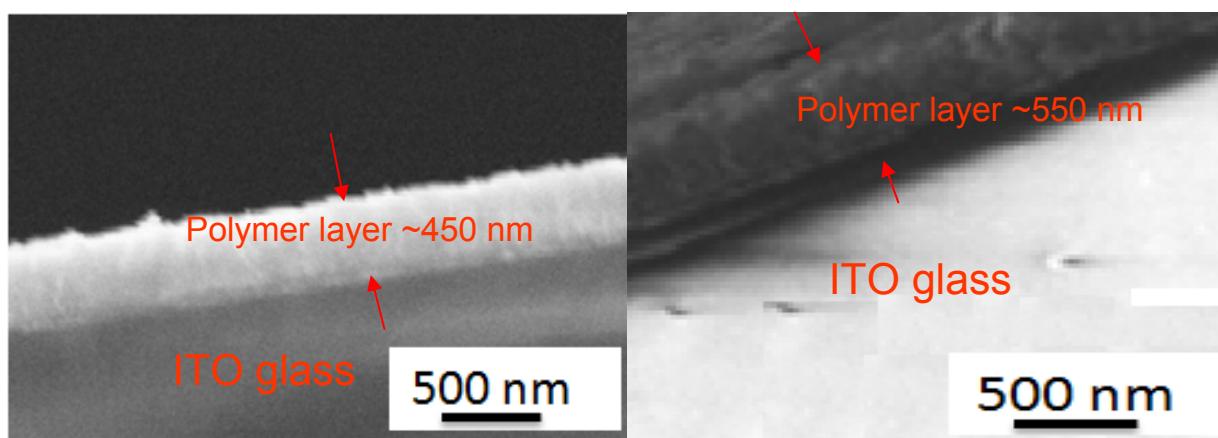


Figure S1: Adjusting the masking polymer layer thickness by polymer concentration and spinning speed. Left: Poly(butyl acrylate): Poly(butyl acrylate): 0.06g; CHCl₃: 10 mL; Spin speed: 5000 rpm; Polymer thickness: ~ 450 nm; and Right: 0.06g; CHCl₃: 10 mL; Spin speed: 2000 rpm; Polymer thickness: ~ 550 nm.

The dry powder of PS microspheres after Zn²⁺ treatment was then spread on the masking polymer that was pre-coated on ITO glass. The sample was then centrifuged at 6000 rpm for 15 minutes to force the PS particle moving down to the bottom of the polymer layer and to directly contact with surface of the ITO glass. The unembedded PS microspheres on the samples were then blown out with pressure air leaving a monolayer of PS microspheres on the masking polymer coated ITO glass.

The SiO₂ microspheres were modified by ZnCl₂ with a similar process as used for treating the PS microspheres except that the final SiO₂ particles were calcined at 400 °C for 4 h.

The ITO glass with modified PS microspheres was used as the working electrode with an Au flake as the reference electrode in the electrochemical deposition process. 5 mM of Zn(NO₃)₂·6H₂O (zinc precursor) and 7.5 mM of NH₄NO₃ (supporting electrolyte) were used as the electrochemical reaction solution. The electrochemical deposition was performed at a constant electric potential (-1.36 V). The electrochemical deposition temperature was kept at 85 °C.

After 10 min, the ITO sample was washed with distilled water and dried in vacuum at 50 °C. In the end, the sample was immersed in isopropyl alcohol for 24 h to remove the polymer masking layer and release the Janus particles into the solution.

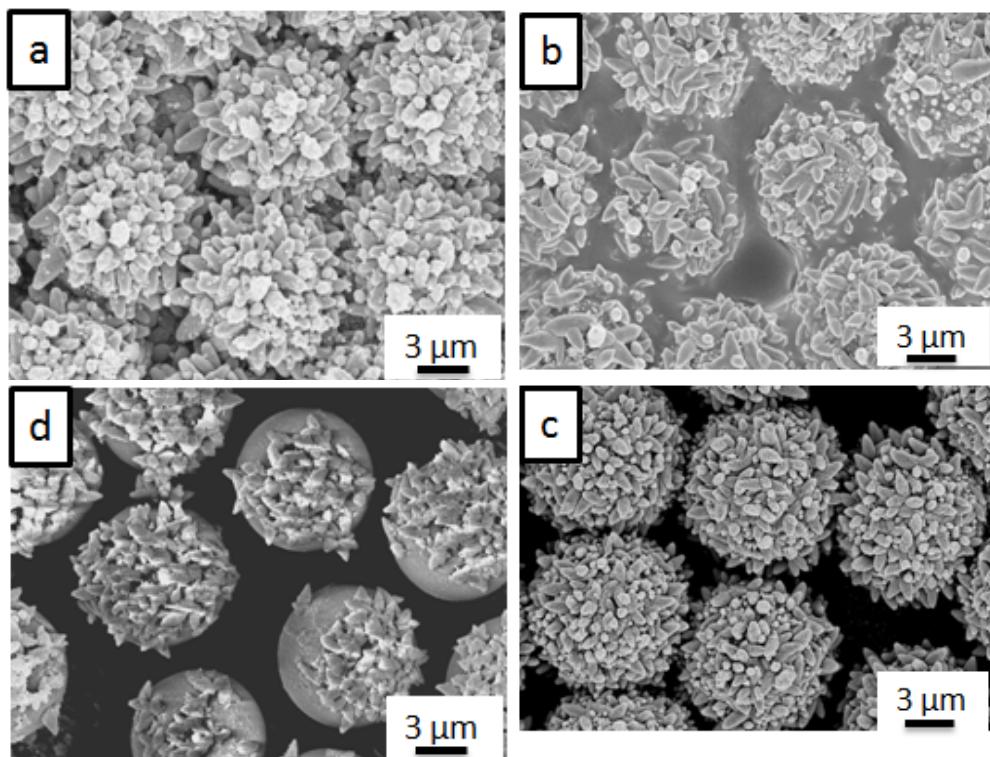


Figure S2. SEM images of the Janus PS microspheres with ZnO nanowires embedded in the masking polymer thin layer with different layer thicknesses (a and b), and of that after removing the masking polymer layer *in situ* (c and d). Experimental condition: 5 mM of $\text{Zn}(\text{NO}_3)_2$ and 15 mM of NH_4NO_3 .

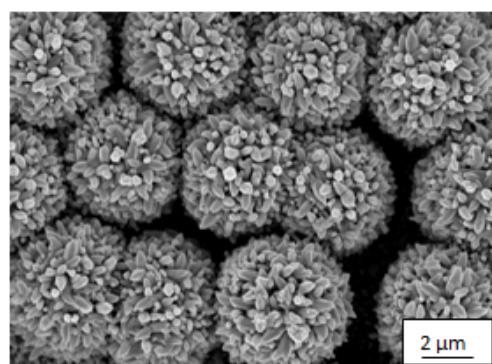


Figure S3. SEM images of SiO_2 microspheres with ZnO nanowires. Experimental condition: 5 mM of $\text{Zn}(\text{NO}_3)_2$ and 15 mM of NH_4NO_3 .