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Supporting Information

Polymeric Janus nanorods via anodic aluminum oxide templating

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A. Materials and Characterizations

Recrystallization was performed for 2,2'-azobis(isobutyronitrile) (recrystallised from methanol) and *N*-isopropylacrylamide (recrystallised from *n*-hexane) prior to their utilization. Pentafluorophenyl acrylate (PFPA) was prepared following reported procesures.[1] Aluminum discs was obtained from Goodfellow Cambridge Ltd. Other commercially available chemicals were purchased from Acros, TCI, Merck, and Roth and used without further purification.

Scanning electron microscopy (SEM) images were recorded with a Zeiss LEO 1530 and transmission electron microscopy (TEM) images were recorded using a Hitachi H600. The oxygen plasma treatment was carried out by plasma system type-ZEPTO from DIENER.

B. Preparation of Anodic Aluminum Oxide Template

The AAO templates were fabricated through a two-step anodization process.[1] High-purity

(99.999%) aluminum disks were mounted within a tetrafluoroethylene case and subjected to electro-polishing at 20 V, 5 °C for 6 min to attain a flat surface. This process was carried out in an electrolyte bath containing a mixture of ethanol and perchloric acid (V/V, 3:1). The first anodization process was conducted by cooling the electropolished aluminum disks at 3-5 °C and applying a voltage of 175 V for 3 h, followed by an increase in voltage to 195 V for 20 h. A bath solution consisting of 1 wt% phosphoric acid (H_3PO_4) was used. After the initial anodization treatment, the formed irregular layer of aluminum oxide pores was removed through etching by using a mixed aqueous solution of chromic oxide (1.8 wt%) and phosphoric acid (6.0 wt%) at 45 °C for 36 h. Subsequently, the chamber containing the aluminum disks was thoroughly washed with deionized water. Following the first step, a second anodization was performed at 195 V for 1h and 2 h, respectively, in 1 wt% phosphoric acid at 3~5 °C. The resulting AAO templates were washed and sonicated with acetone, then dried.

C. Fabrication of Janus PS-*b*-PNIPAm Nanorods

A styrene solution was prepared by dissolving styrene (100 mg) 2,2'-azobis(isobutyronitrile) (1 mg), 1,6-hexanediol diacrylate (10 mg) and 4-acryloylbenzophenone (10 mg) in 1,4-dioxane (100 µL). The solution was drop-cast onto the as-prepared AAO template followed by pressing the template between two glass slides and transfered into a vacuum oven. The oven temperature was increased to 80 °C and maintained for 8 h in the absence of light. Subsequently, the template was subjected to oxygen plasma treatment. A solution of *N*-isopropylacrylamide (NIPAm) (100 mg), 2,2'-azobis(isobutyronitrile) (1 mg), *N,N'*-methylenebis(acrylamide) (1 mg) and 4-acryloylbenzophenone (1 mg) in 1,4-dioxane (200 µL) was added to the prefabricated AAO template containing polystyrene, pressed in between two glass slides, and subjected to a vacuum oven at 80 °C for 8 h in with the exclusion of light. The template was further treated with UV (365 nm) for 1 h to afford the chemically bonded polystyrene-*block*-poly(*N*-isopropylacrylamide) (PS-*b*-PNIPAm) Janus nanorods. To release the Janus nanorods, the template was immersed in a 10 wt% aqueous phosphoric acid solution at 45 °C for 2 h. The released Janus nanorods were collected through filtration and thoroughly washed with deionized water.

D. Fabrication of Janus PNIPAm-*b*-PPFPA Nanorods

NIPAm solution was prepared following the same recipe as depicted in Section C. In a similar manner, the polymerization of NIPAm was carried out in the vacuum oven at 80 °C for 8 h without light exposure to provid poly(*N*-isopropylacrylamide) (PNIPAm) in the AAO template. Then, the template was treated with oxygen plasma. A solution of PFPA (100 mg), 2,2'-azobis(isobutyronitrile) (1 mg), 1,6-hexanediol diacrylate (2.5 mg), 4-acryloylbenzophenone (2.5 mg) in 1,4-dioxane (100 µL) was drop-cast onto the AAO template containing PNIPAm. The polymerization was conducted in a vacuum oven at 80 °C for 8 h in the absence of light. Subsequently, the template was treated with UV light (365 nm) for 1 h. The Janus poly(*N*-isopropylacrylamide)-*block*-poly(pentafluorophenyl acrylate) (PNIPAm-*b*-PPFPA) nanorods were obtained via dissolving the template with a 10 wt% aqueous phosphoric acid solution at 45 °C for 2 h followed by filltration and washing with deionized water.

E. Fabrication of Janus PPyNP-*b*-PMMA Nanorods

Polypyrrole nanoparticles (PPyNPs) were prepared using $FeCl_3$, NaOAc and pyrrole in distilled water. First, a solution was prepared by dissolving NaOAc (82 mg) and pyrrole (70 µL) in 5 mL of deionized water. Simultaneously, another solution was prepared by dissolving $FeCl_3$ (162 mg) in 5 mL of deionized water. Then, the two aqueous solutions were added to a glass vial containing a AAO template. PPyNPs were generated on the surface of and within the cannulas of the AAO template after sonication of 0.5 h at room temperature. The resulting PPyNPs had an average diameter of ≈180 nm, as depicted in Figure S1. Subsequently, oxygen plasma treatment was carried out for 30 min. Poly(methyl methacrylate) (PMMA) was then synthesized on top of PPyNPs in AAO cannulas. A solution of methyl methacrylate (MMA) (100 mg), 4-acryloylbenzophenone (10 mg) and Irgacure 2959 (5 mg) in 1,4-dioxane (100 µL) was drop-cast onto the as-prepared AAO template with PPyNPs followed by UV irradication (365 nm) for 1 h to form the of Janus polypyrrole nanoparticle-*block*-poly(methyl methacrylate) (PPyNP-*b*-PMMA) nanorods. Subsequently, the template was dissolved with a 10 wt% aqueous phosphoric acid solution at 45 °C for 2 h. The nanorods were collected via filtration and washed with deionized water.

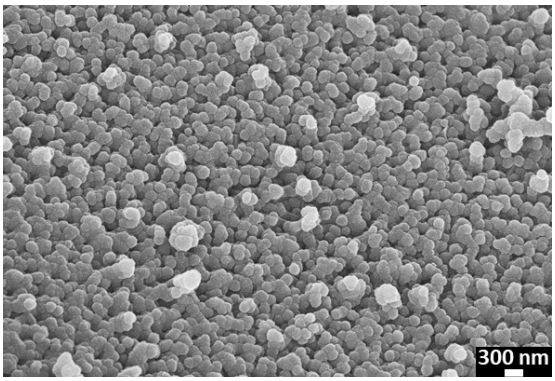

Figure S1. *SEM image of PPyNP.*

References:

1 X. Huang, H. Mutlu and P. Theato, Adv. Mater. Interfaces, 2020, **7**, 1–7.