Fabricating Super-hydrophobic Lotus-leaf-like Surfaces through Soft-lithographic Imprinting

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Synthesis of BP-AZ-CA

The synthetic scheme of the epoxy-based azo polymers (BP-AZ-CA) is given as:

![Synthetic route of azo polymer BP-AZ-CA.](image)

**Scheme 1 Synthetic route of azo polymer BP-AZ-CA.**

**BP-AN.** Epoxy-based precursor polymer BP-AN was prepared through the step polymerization between the epoxide monomer diglycidyl ether of bisphenol-A and aniline.[1] Analytical data: IR (KBr): 3380 (O-H, m), 1600 1510 1463 (Benz. ring, s), 1250 cm$^{-1}$ (C-O, s). $^1$H NMR (DMSO-$d_6$): d= 7.07 (6H, d), 6.82 (4H, d), 6.72 (2H, d), 6.54 (1H, m), 4.03 (2H, m), 3.87 (4H, s), 3.34-3.75 (4H, m), 1.55 (6H, s).

**BP-AZ-CA.** BP-AN was functionalized to introduce the azo chromophores through azo-coupling reaction.[1] In the reaction, BP-AN (0.97 g, 2.0 mmol) was dissolved in DMF (66 mL) at 0 °C.
4-Aminobenzoic acid (0.330 g, 2.4 mmol) and NaOH (0.096 g, 2.4 mmol) were dissolved in 3 mL water, then 0.67 mL hydrochloric acid (38%) was added into the solution at 0 °C. After 1 min, the aqueous solution of sodium nitrite (0.199 g, 2.88 mmol in 0.6 mL of water) was added dropwise into the mixture above. The mixture was stirred at 0 °C for 1 min and then added dropwise into the BP-AN solution. The solution was stirred at 0 °C for 12 h. Then the solution was poured into plenty of water and the precipitate was collected by filtration. The product was washed with water for several times and dried. The obtained BP-AZ-CA was dissolved in 40 mL THF and precipitated into 400 mL petroleum ether. The final product was vacuum dried at 70 °C for 24 h. Analytical data: IR (KBr): 3350 (O–H, m), 1700 (C=O, s), 1598 1508 1460 (Benz. ring, s), 1240 cm⁻¹ (C–O, s). ¹H NMR (DMSO-d₆): δ= 8.05 (2H, d), 7.80 (2H, d), 7.75 (2H, d), 7.08 (4H, d), 6.91 (2H, d), 6.84 (4H, d), 4.11 (2H, m), 3.70–4.00 (6H, br), 3.40–3.70 (2H, m), 1.54 (6H, s). GPC: Mn= 41000, PDI= 2.2.

Other Materials
PDMS kit was purchased from Dow Corning (Sylgard 184). When using, the elastomer base and curing agent were mixed in a proper ratio (10:1, wt/wt). Glass slides and silicon wafers (GRITEK, crystallographic orientation (100), n-type) were used as substrates in the imprinting. Solvents, such as tetrahydrofuran (THF) and N,N-dimethylformamide (DMF), were commercially purchased and used without further purification. The Milli-Q water (resistivity >18 MΩ·cm) used in the experiment was supplied by a water-purifying system (Milli-pore).

Characterization
The SEM measurements were performed on a field emission scanning electron microscope (Hitachi S-4500) with the accelerating voltage of 15 kV. The samples were spurted by an ion sputter of JEOL-JFC-1100 with current of 5 mA for 5 min. A thin gold layer of about 10 nm was coated on the samples. Photographic images were taken by using a digital camera of Nikon Coolpix E4500 connected to an Olympus BH-2 optical microscope.

The Atomic Force Microscopy (AFM) images were obtained by using a Nanoscope-IIIa Scanning Probe Microscope in the tapping mode. AFM images of the spin-coated film of BP-AZ-CA are shown below (Figure S1):
Contact angles were measured by Contact Angle System OCA-20 (Dataphysics) under the ambient condition, where water droplet volumes were 4 µL. The advancing and the receding water contact angles were measured by using a standard procedure on Dataphysics OCA-20 contact angle system. The data were obtained by first dropping 4 µL water on the surface and then injecting or retracting a water droplet (2 µL) through an automatic syringe in a rate of 0.6 µL/s. A typical curve of advancing and receding angles of water on the imprinted BP-AZ-CA film is shown below (Figure S2). The figure shows the water contact angles measured when the water droplet was injected and then retracted as the time increase, which gives the advancing and receding water contact angles.