

Electronic Supplementary Information

A facile photopolymerization method for fabrication of pH and light dual reversible stimuli-responsive surface

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1. Experimental details

1.1 Materials and Equipment.

p-Phenylazophenol was purchased from TianJing HEOWNS Co., Ltd. 3-methacryloxypropyltrimethoxysilane (γ -MPS) was obtained from NanJing Capatue Chemical Co., Ltd. Dimethylaminoethyl methacrylate (DMAEMA) and β -cyclodextrin (β -CD) was purchased from Aladdin Company. Trimethylolpropane triacrylate (TMPTA) was donated by Sartomer Co., Ltd. Photoinitiator 2-Hydroxy-2-methylpropiophenone (1173) and isopropyl thioxanthone (ITX) was donated by Changzhou Runtec Chemical. They all were used without further purification. OmniCure series 1000 (EXFO, Canada) was used as the light source. The radiation intensity was measured by UV-A Radiometer (Photoelectric Instrument Factory of Beijing Normal University).

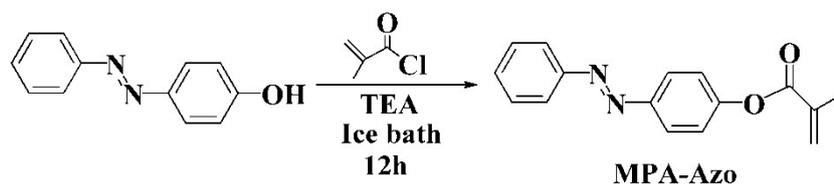
¹H NMR spectrum was recorded on a 400 MHz NMR instrument (Bruker Corporation, Germany) at 298 K with TMS as internal standard and CDCl₃ as solvent. XPS (ESCALAB 250, Thermo Fwisher Scientific, USA) was employed to study the chemical composition and element content change of modified surface. Hitachi U-3010 UV-vis spectrophotometer (Hitachi High-Technologies Corporation, Tokyo, Japan) was used to investigate the absorption spectra of quartz modified by different chemical. The surface wettability of the modified quartz was determined by the contact angle instrument (Data physics OCA 20 optical contact angle meter): a small drop of aqueous solution of different pH value (5 μ L) was injected onto the different modified quartz slides. The contact angle values of the examined quartzes were all the arithmetic average values of five repetitive tests on the same quartz sheet.

1.2 Synthesis of MPA-Azo.

The synthesis route of MPA-Azo was outlined in Scheme 1. *p*-Phenylazophenol (4.9550 g, 25 mmol), triethylamine (3.7946 g, 37.5 mmol), and 250 mL chloroform were added into a 500 mL three-necked round bottom flask fitted with an overhead stirrer, a thermometer and an addition funnel. A mixture of methacryloyl chloride (3.1359 g, 30 mmol) and chloroform (100 mL) was added dropwise in an ice water bath. After stirring for 12h, the organic phase of the mixture was extracted thrice with 1 M hydrochloric acid, 1 M sodium bicarbonate solution and water sequentially, then dried overnight with MgSO₄. A yellow product was obtained after the solvent was evaporated by rotary evaporator. The product was washed by ethanol and water for three times. Finally, the

solid product was purified by column chromatography with dichloromethane as eluent. The yield of MPA-Azo was 4.9936 g (75%).

^1H NMR (400 MHz, CDCl_3) δ (ppm): 7.995–8.017 (2H, -ArH), 7.935–7.952 (2H, -ArH), 7.552 (3H, -ArH), 7.310–7.331 (2H, -ArH), 6.418 (1H, -H), 5.826 (1H, -H), 2.036 (3H, - CH_3).



Scheme S1. Synthetic route of the MPA-Azo.

1.3 Fabrication of stimuli-responsive surface.

Hydroxylation. The quartz sheets were ultrasonic cleaning with acetone, ethanol and ultrapure water sequentially, 10 min for each process, and dried with nitrogen stream to remove the impurities. Then the dried quartz sheets were cleaned by being immersed in a “piranha” solution [H_2SO_4 (98% wt. %) / H_2O_2 (30% wt. %) 7:3 v/v] and heated to 90°C for 2 h. The hydroxylated substrates were then rinsed with ultrapure water and dried under a flow of ultrapure N_2 .

Silanization. γ -MPS (100 mg) was added in toluene (100 mL) solution. The mixture was stirred for 2 min at room temperature. Then the rich hydroxylated quartzes were dipped into this solution for 12 h. After the reaction, the quartz sheets were washed with toluene to remove the surplus γ -MPS, then washed thoroughly with ethanol and dried under a flow of ultrapure N_2 . The silane coupling agent γ -MPS which contains double bonds has been grafted on the quartz surfaces.

Preparation of PDMAEMA polymer network by stage I photopolymerization. DMAEMA (1.0 g), TMPTA (0.03 g), 1173 (0.01 g) as the monomer, cross-linker and cleavage-type photoinitiator respectively were mixed together and stirred for 2 min. This mixing solution (10 μL) was coated on the silanized quartz sheets, then the sheet was irradiated by UV irradiation with the intensity of $40 \text{ mW}/\text{cm}^2$ for 180 s, after that, washed thoroughly with ethanol to remove the unreacted monomer. The cross-linker TMPTA (3 wt.%) was introduced to promote the formation of a cross-linked network between amino monomers and double bonds on the surface so that the PDMAEMA reticulate membrane could be successfully grafted on the surface by covalent bonds performed good adhesive strength and stability. And the PDMAEMA containing tertiary amine groups could be used as coinitiator for the next step photopolymerization.

Grafting of MPA-Azo via stage II photopolymerization. MPA-Azo (0.3 g), ITX (0.003 g) as the monomer and hydrogen abstraction-type photoinitiator were dissolved in acetone (0.7 g) and sonicated for 5 min. Through photopolymerization, PDMAEMA on the substrate as coinitiator, MPA-Azo was grafted on the PDMAEMA. As a result, a layer of yellow film was fixed on the surface.

Due to the grafting of MPA-Azo, the classic host–guest recognition self-assembly of MPA-Azo and β -CD on the surface to verify the change of wettability properties under irradiation of different wavelength could be conducted. β -CD (100 mg) was added in solution[water/ DMF 1:1 v/v (100 mL)]. This mixture was heated to 50°C .

The modified substrate was immersed in the above solution and irradiated by visible light for 5 min, then dried under a flow of ultrapure N₂, the β-CD was anchored on the modified surface with MPA-Azo through host-guest recognition self-assembly. For the desorption process, it was carried out by irradiating the substrates with wavelength of 365 nm in the solution [water/ DMF 1:1 v/v (100 mL)].

2. Composition changes of modified quartz surfaces

The chemical compositions of the quartz surfaces with different grafting modification were investigated by XPS analysis.

Table 1. The composition changes of modified quartz surfaces

Modified surface	Atomic percent (%)			
	C 1s	N 1s	O 1s	Si 2p
-OH	20.94	0	49.77	29.29
-MPS	31.84	0	40.9	27.26
-DMAEMA	59.25	3.93	29.54	7.29
-MPA-Azo	67	4.86	21.39	6.76
-β-CD	67.15	4.8	24.67	3.38
-UV365	65.94	4.73	23.5	5.83

Table 2. The composition changes of -MPA-AZO modified surface soaked in different pH solution

-MPA-Azo modified	Atomic percent (%)					
	C 1s	N 1s	O 1s	Si 2p	Cl 2p	Na 1s
pH=3	64.74	4.65	21.56	5.86	3.19	-
pH=11	65.18	5.03	23.68	4.9	-	1.19

3. Wettability properties

3.1 The CA decay under different pHs with the increase of time.

Figure.S1 shows that the different pH conditions have significant effect on the surface wettability properties of thin films. With the increase of time (0-30 s), the contact angle was reduced significantly from $54^{\circ} \pm 2^{\circ}$ to $20^{\circ} \pm 2^{\circ}$ under low pH solution (HCl, pH=3). However, the contact angles were almost the same as initial surface when they were at pH=7 or higher pH solution (NaOH, pH=13). The data of CAs in our work were all measured at 10 seconds later after the solution was injected onto the different modified quartz.

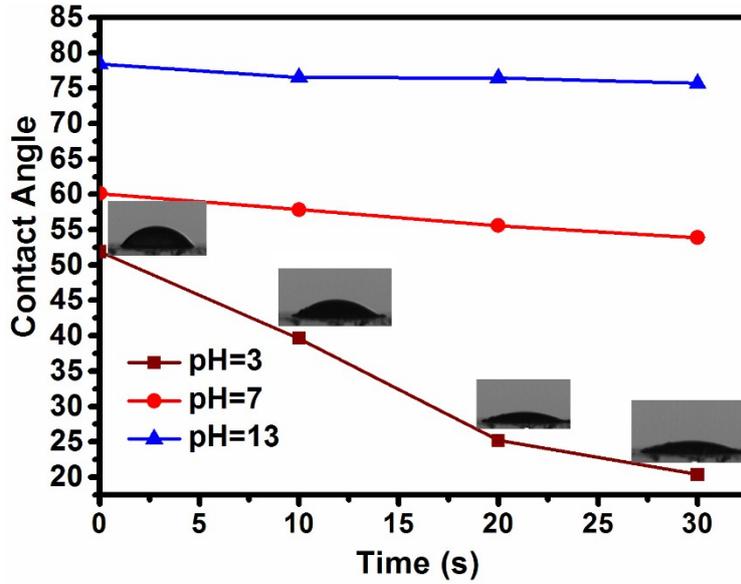


Figure.S1 The CA decay curve under different pH solution with the increase of time

3.2 The CAs of modified surfaces under different pH conditions and different UV irradiation

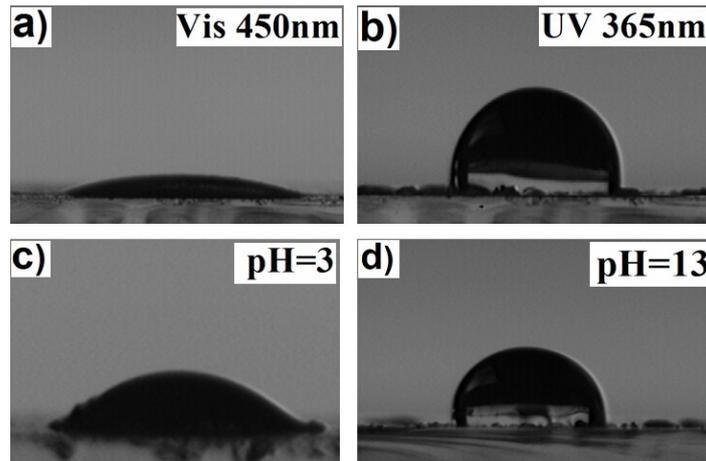


Figure.S2 CAs of the cycle experiments under different pH conditions and different UV irradiation

4. AFM topographic images

In order to further prove the feasibility of fabrication pH and light dual stimuli-responsive surface via our two-stage photo initiated radical polymerization mechanism, the following experiment has been finished. First, a PDMAEMA network utilized the stage I photopolymerization was prepared on the surface, then in the stage II photopolymerization, the photomask with stripes was used and only where the light transmitted was photopolymerized. AFM topographic images for patterned MPA-Azo polymer brushes grown from the PDMAEMA network were collected in tapping mode. Fig.S3a showed an image of structured MPA-Azo polymer brushes with 10 μm stripes that were spaced by 10 μm . A cross-sectional profile of the patterned brush showed that height difference between MPA-Azo brushes and the PDMAEMA polymer (Fig.S3b) was about 251 nm. Fig.S3c showed the 3D structure of the modified surface. This result also demonstrated that that the surface was modified successfully and our method was efficient to fabricate the patterned surface.

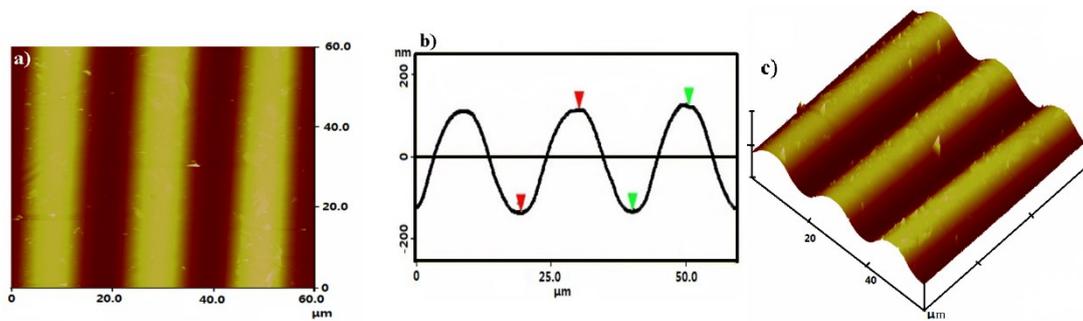


Figure S3: (a) AFM topographical image ($60 \times 60 \mu\text{m}$) of a patterned surface formed by combination of PDMAEMA (the dark areas) and PMPA-Azo (the bright areas). (b) AFM cross-sectional profile of the patterned MPA-Azo brush. (c) AFM 3D structure of the modified surface.