Supplementary Information

Coumarin-Driven Switchable Superhydrophobic Silica Surface by Photochemistry

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Experimental Sections

Materials: 7-hydroxycoumarin (98%), 6-chloro-1-hexanol (95%) and fumed silica (14nm) were purchased from Sigma Aldrich. Potassium iodide, anhydrous potassium carbonate, 2, 4-toluene diisocynate (TDI), and all solvents used were purchased from Sinopharm Chemical Reagent Co Ltd.

Synthesis of 7-(6-hydroxy hexyloxy) coumarin:[1] In a typical experiment, 7-hydroxycoumarin (2.5 g, 15 mmol), 6-chloro-1-hexanol (4.2 g, 41 mmol), potassium iodide (1.2 g, 7 mmol) and anhydrous K_2CO_3 (4.4 g, 32 mmol) was added in *N, N*-dimethylformamide (DMF) (50 mL). Then the mixture was heated to 60 ^oC for 24 h. The obtained precipitate was filtered off and washed with DMF. Water was added to the solution, and then stirred for 6 hours at room temperature. The residue was extracted with water (3×100 mL) and evaporated in vacuum drying oven at room temperature, and then the final product was obtained as a white solid of 3.5 g (yield, 86.6%, mp 52.1-53.1 ^oC). FT-IR (KBr) of 7-(6-hydroxy hexyloxy) coumarin: 3417 cm^{-1} (O-H), 2935 cm^{-1}, 2858 cm^{-1} (-CH_2-), 1734 cm^{-1} (O-C=O), 1057 cm^{-1} (R-CH_2-OH), 1012 cm^{-1} (R-O-R'). ^{1}H NMR ($CDCl_3$) δ [ppm]: 1.2-1.9 (m, 8H, CH_2), 3.677 (t, 2H, CH_2OR), 4.020 (t, 2H, -OCH_2), 6.23 (d, 1H, aromatic) .6.79-6.84 (m, 2H, aromatic), 7.36 (d, 1H aromatic) 8.02 (d, 1H, aromatic), 7.64 (d, 1H, aromatic).

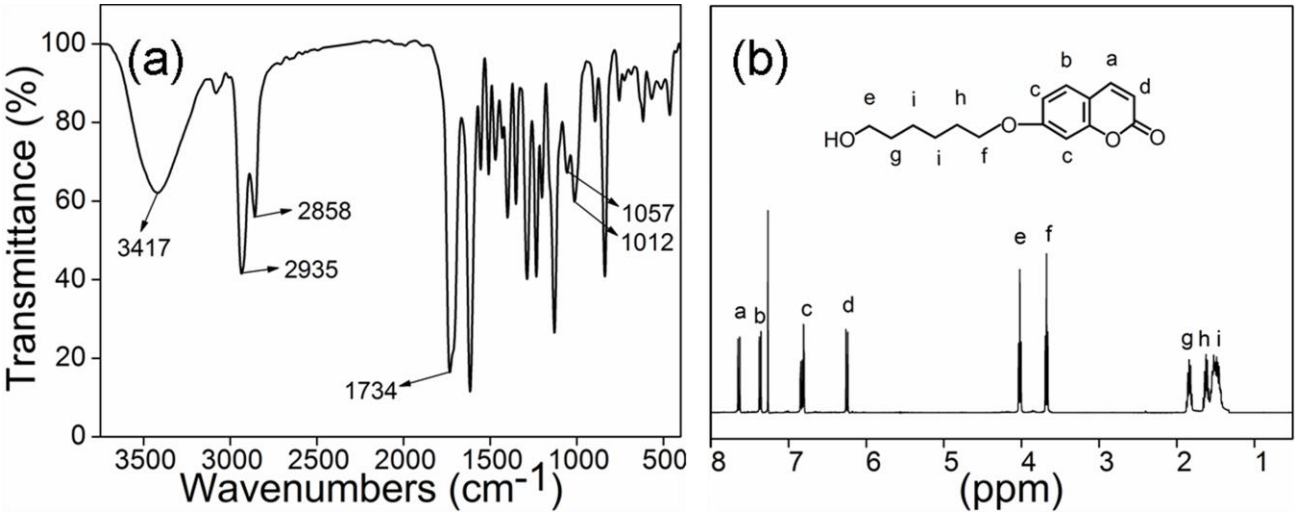

Fig. S1 FT-IR (a) and ^{1}H NMR (b) of 7-(6-hydroxy hexyloxy) coumarin in $CDCl_3$.

Synthesis of SiO_2-TDI: A mixture of fumed silica particles (0.5 g) and 0.52 g TDI was dispersed in 120 mL ethyl acetate by ultrasonication for 10 min, and the reaction mixture was stirred at 60 ^{o}C for 4 h under nitrogen atmosphere.[2] The product was separated by centrifugation and carefully washed with DMF to remove the unreacted and physical-absorbed TDI. The product, TDI modified silica (SiO_2-TDI), was dried in vaccum at 80 ^{o}C for 12 h. FT-IR (KBr): 2297 cm^{-1} (-NCO), 1655 cm^{-1}, 1545 cm^{-1} (-NHCO-), 1616 cm^{-1} (C=O) (Fig. 1b).

Synthesis of CMFST nanoparticles: A suspension of 0.25 g SiO_2-TDI particles dispersed in 50 mL DMF was placed in an ultrasonic bath for 10 min, and 0.2 g 7-(6-hydroxy hexyloxy) comaruin was added, then the suspension was placed in an oil bath at 80 ^{o}C for 4 h with stirring. The product was isolated by centrifugation, redispersed in DMF and centrifuged again, finally dried in vacuum drying oven. FT-IR (KBr): 2925 cm^{-1}, 2856 cm^{-1} (-CH_2-), 1695 cm^{-1} (lactonic -C=O carbonyl), 1545 cm^{-1} (-NHCO-) (Fig. 1c).

Characterization: Fourier transform infrared spectra (FTIR) were measured with a Nexus 670 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a Mercury Plus 400 Hz spectrometer with trichloromethane solvent. Static water contact angles were measured at room temperature (21 ^{o}C) with deionized water (8 μL) on a contact angle goniometer (JC2001) instrument. All the contact angles measured at three different points on each sample surface were determined, and their average values were reported. UV absorption spectra of CMFST nanoparticles in trichloromethane ($CHCl_3$) solution were measured on a Shimadzu UV-260 spectrophotometer. Photochemistry of coumarin units on the CMFST nanoparticles was carried out by using a 500-W Xe lamp (CHF-XQ-500W, Beijing Trusttech. Co. Ltd) equipped with a cut filter 365 nm or 254 nm to produce special UV light. The morphological of CMFST nanoparticles and the exposed nanoparticles after irradiation UV light at different wavelength were analyzed by atomic-force microscope (AFM, diNaNoMan Vs). Thermal properties of the samples were measured using a HCT-1 (HENVEN, Beijing, China) comprehensive thermal analyzer in flowing (50 *mL/min*) nitrogen atmosphere.

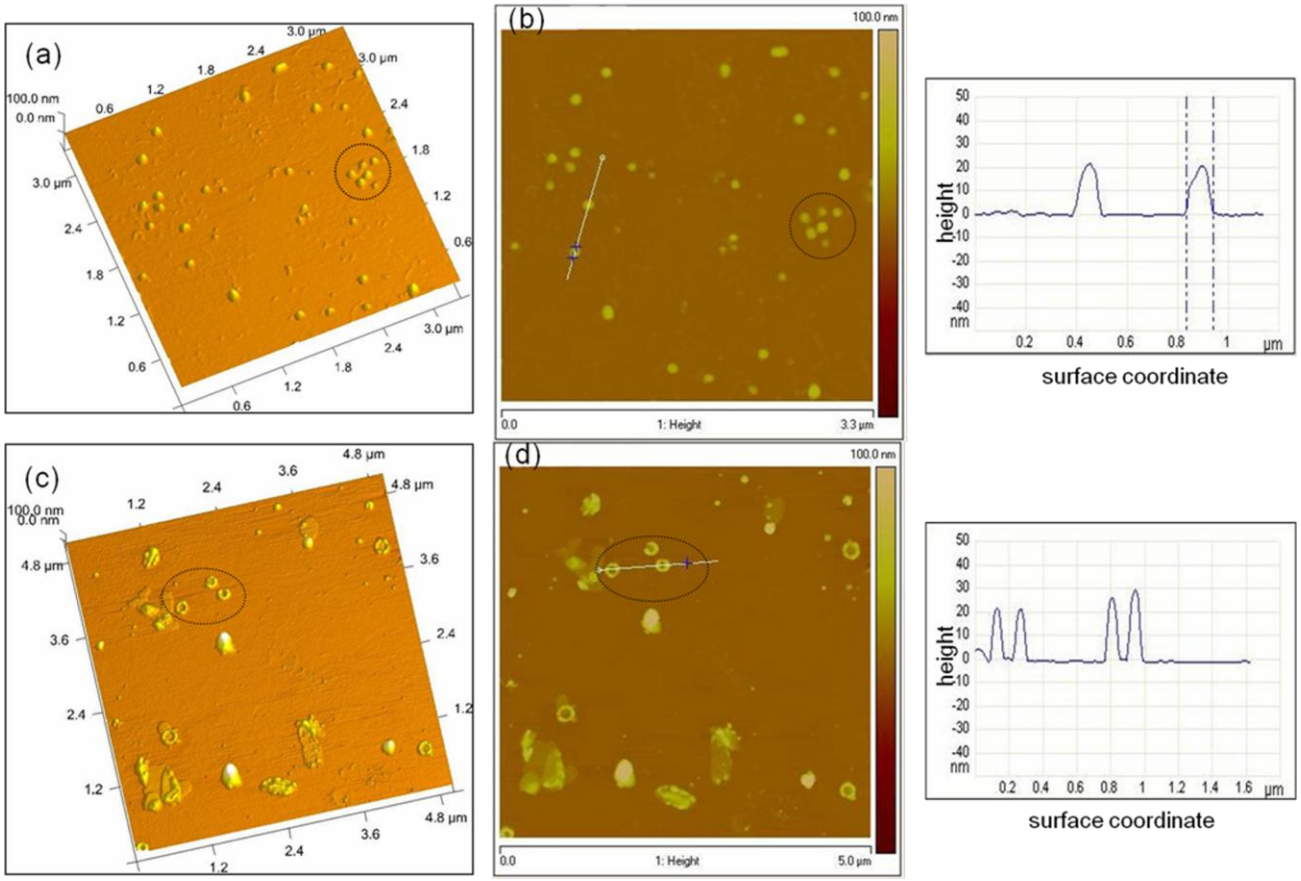

Fig. S2 Topographic AFM images of CMFST nanoparticles (a), (b) and BCMFST nanoparticles (c), (d); 3-D images (a), (c) and 2-D images (b), (d).

1. W. J. Li, V. Lynch, H. Thompson and M. A. Fox, J. Am. Chem. Soc., 1997, 119, 7211.

2. B. L. Ou, D. X. Li, Sci. China. Ser. B-Chem., 2008, 51, 51.