

Supporting Information

Flexible Method on Fabricating Protein Patterns Over Superhydrophobic Platforms Controlled by Magnetic field

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EXPERIMENTAL SECTION

Preparation of superhydrophobic substrates: PS superhydrophobic surfaces were prepared using a phase inversion method [27]. 70 mg/ml PS solution (Aladdin Industrial Inc., China) in tetrahydrofuran was mixed with ethanol (1:0.65 v/v). The mixture was coated dropwise onto smooth PS substrate in air for 1min, that was then immersed in ethanol for 1min and dried with a gentle nitrogen flow. For controlling the adhesion force on the superhydrophobic PS substrate, further fluoridization was carried out on the superhydrophobic substrate. After UV irradiation on PS substrate for 120s, it was modified with PFOTS solution (1% v/v in ethanol, Aldrich) for 1h, 2h, 3h, 6h, 12h, 18h and 24h.

Superhydrophobic nanocupule PS substrate with high adhesion force was fabricated using a methodology described in [29]. In brief, 33 wt% mixture solution of PS (Aladdin Industrial Inc., China) (99:1, w/w) in THF was added dropwise onto a AAO template (pore diameter ~ 200nm, thickness ~ 60µm, Watman Int. Ltd, England). After 12h solidification, the AAO

template was removed by immersion in 4M NaOH solution, the prepared nanocupule substrate was fully washed by deionized water and dried in air.

The adhesion force and the magnetic force acted on CHS-MP were measured using a micro-electrodynamic balance system (Data-Physics DCAT 11, Germany). For the adhesion force measurement, a 2 μ l water droplet was fixed on the thin metal loop, which was hung on the microbalance. The PS substrate was fixed on the microbalance. Before PS substrate contacted with the droplet, the adhesion force was zero as showed in Figure S1. When the PS substrate contacted with the droplet, it would move away automatically. The adhesion force would increase till the droplet leave off the substrate which adhesion force became zero again. Similar procedure was carried out for measuring the magnetic force acted on the CHS-MP; here the CHS-MP was fixed on a plastic loop, and the magnet was placed on the microbalance. The force was measured when the CHS-MP just contacted with magnet.

Preparation of hydrogel sphere encapsulated magnetic Fe₃O₄ particles: the magnetic hydrogel spheres were fabricated according to our previous work [26]. In brief, the mixture solution of magnetic microparticles Fe₃O₄ (5mg/ml, diameter ranging from 50-100 nm, Aldrich), chitosan (10mg/ml, medium molecular weight, Aldrich) and cross-linker genipin (2mg/ml) in 1% acetic acid solution was dropped on the SH PS substrate with controlled volume of 4 μ l, 6 μ l and 8 μ l by using a micropipette. The drops were placed in a saturated humidity environment at 25°C for preventing the evaporation process. After 12h the obtained chitosan hydrogel spheres encapsulating magnetic Fe₃O₄ particles (CHS-MP) were freeze-dried.

Preparation of aqueous CdTe NPs: CdTe NPs with green and red emission were synthesized in aqueous solution according to our previous method [30] using 3-mercaptopropionic acid as the capping ligand. The concentration of NPs is 10⁻³ M referring to the concentration of Cd²⁺, and the molar ratio of Cd²⁺/MPA/HTE⁻ was fixed at 1:2.4:0.2. UV-visible absorption spectra were obtained using a Lambda 800 UV-vis spectrophotometer. Photoluminescent (PL)

spectroscopy was performed with a Shimadzu RF-5301 PC spectrophotometer. The excitation wavelength was 400 nm. Transmission electron microscopy (TEM) was conducted using a Hitachi H-800 electron microscope at an acceleration voltage of 200 kV with a CCD camera.

Fabricating soluble proteins pattern on the SH substrate: Solutions including BSA-FITC and IgG-RBITC (Zhongkechenyu Company Ltd. China) was dripped on the superhydrophobic substrate, with volumes of 4 μ l, 6 μ l and 8 μ l. Then a CHS-MP was added into the droplet. During this process the CHS-MP would be wetted by the protein solution first, and subsequently surround by the solution. When a magnetic field of 5000G (WD-50, the British General Magnetic Technology Development Co., Ltd. China) was turned on, the CHS-MP fixed on the substrate. At that moment the protein dot was stamped on the SH substrate. When the drop moved straightly on the superhydrophobic substrate droved by an electronic displacement, the protein line was produced over the substrate. The pattern size could be regulated by the volume of protein solution and the diameter of the CHS-MPs. A similar patterning process was also performed using suspensions of CdTe QDs.

Application on the controlled cells adhesion: SH substrate was sterilized by immersion in 75% ethanol for 24h and dried in nitrogen flow. A fluorescent-labeled fibronectin (Cloud-Clone Corp. China) line was prepared on the superhydrophobic substrate using the abovementioned method. Subsequently the substrate was immersed in a 3T3 cells (Purchased from the cell bank, Chinese academy of sciences, Shanghai, China) suspension with a density of 20000 cells/ml. After 15min culture, it was moved to a new well and washed by PBS for 3 times.

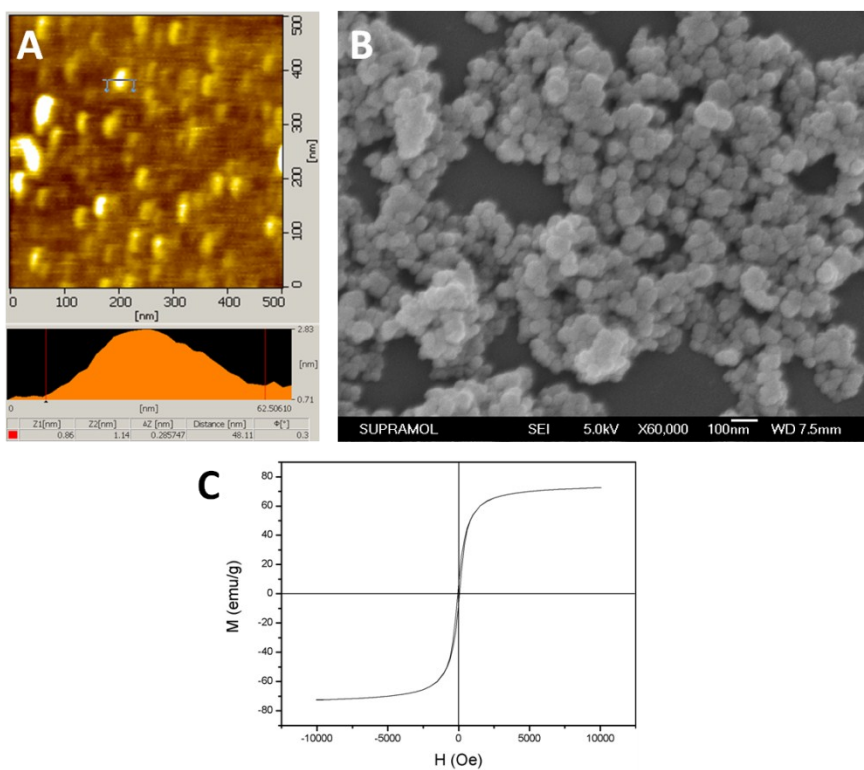


Figure S1 A) and B) represented the AFM and SEM images of the magnetic Fe_3O_4 nanoparticles; C) the magnetic hysteresis curve of the magnetic Fe_3O_4 nanoparticles.

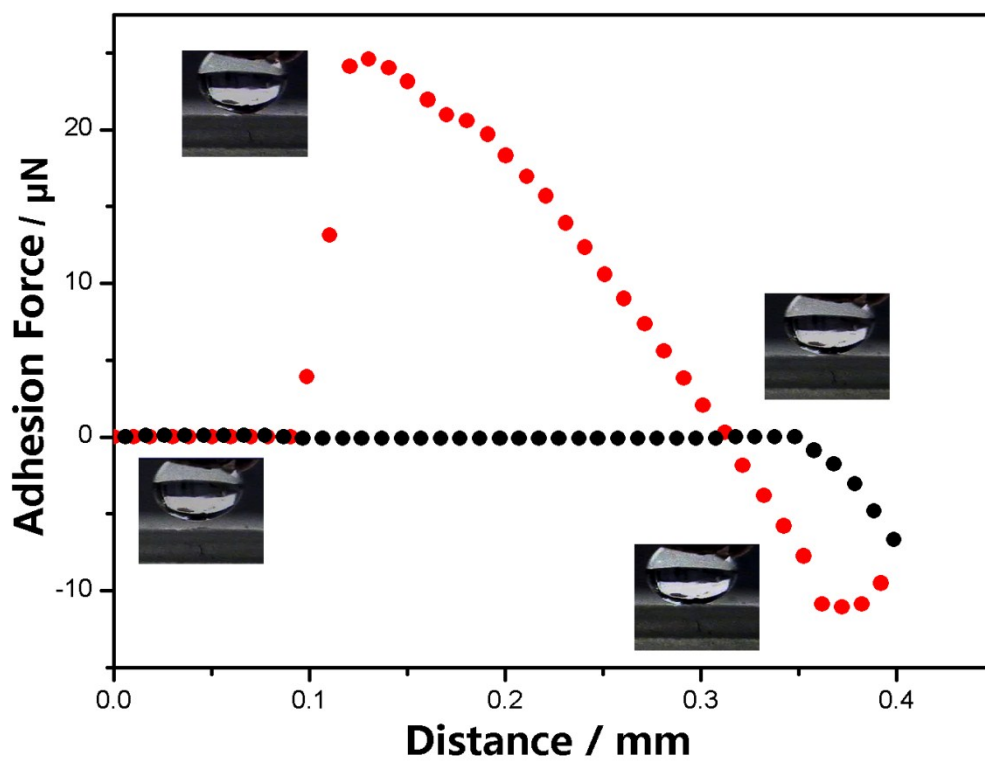


Figure S2 Representative adhesion force profiles measured on PS superhydrophobic substrate.

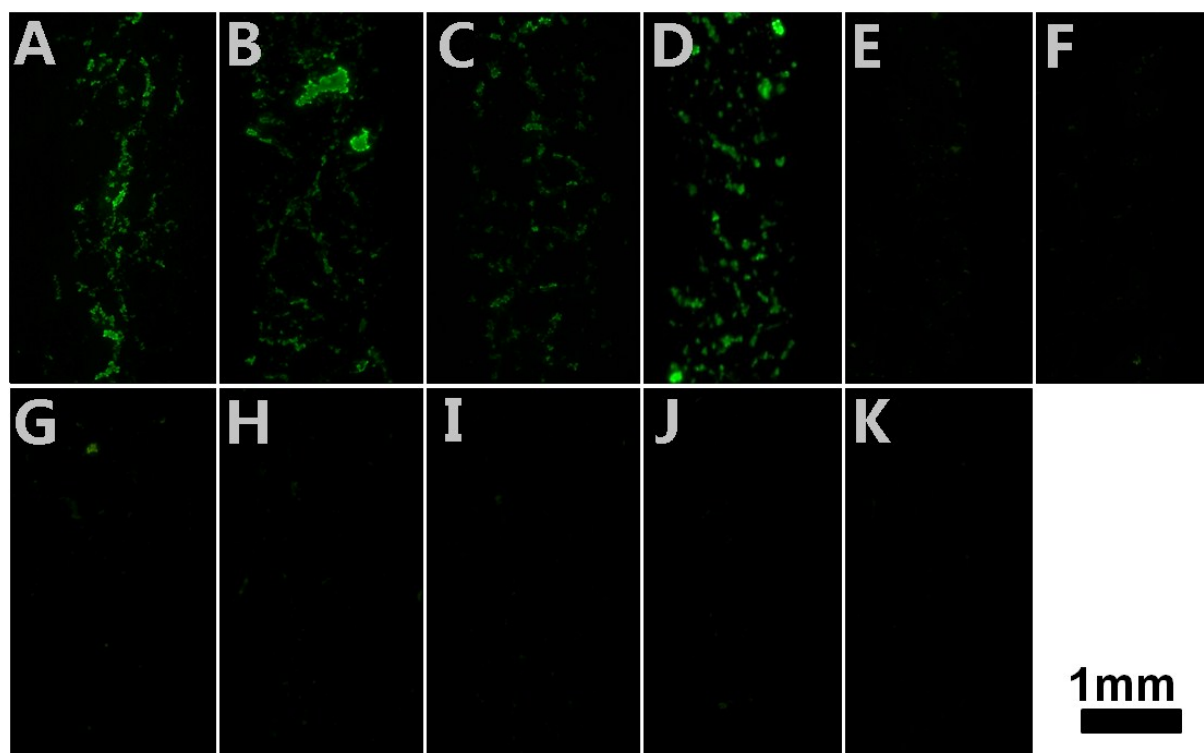


Figure S3 Fluorescent images of BSA-FITC lines prepared on different PS superhydrophobic substrates. A, B, C and D show the prepared BSA-FITC lines on the PS substrates treated by UV light for 60s, 30s, 15s and 0s respectively; E, F, G, H, I, J, K exhibit the fluorescent images of BSA-FITC lines on the PS substrates modified by a perfluorooctyltriethoxysilane solution (1% v/v in ethanol, Aldrich) for 1h, 2h, 3h, 6h, 12h, 18h and 24h.

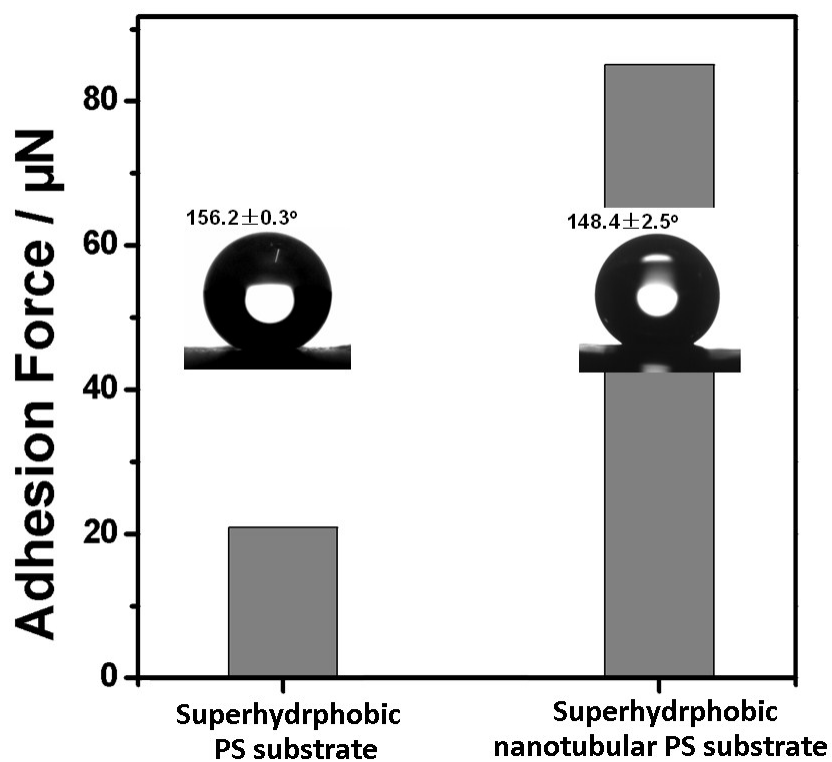


Figure S4 Adhesion force on the superhydrophobic PS substrate ($22.1 \mu\text{N}$) and nanotubular PS substrates ($85.1 \mu\text{N}$). The corresponding CAs on these two substrates were $156.2 \pm 0.3^\circ$ and $148.4 \pm 2.5^\circ$ respectively.

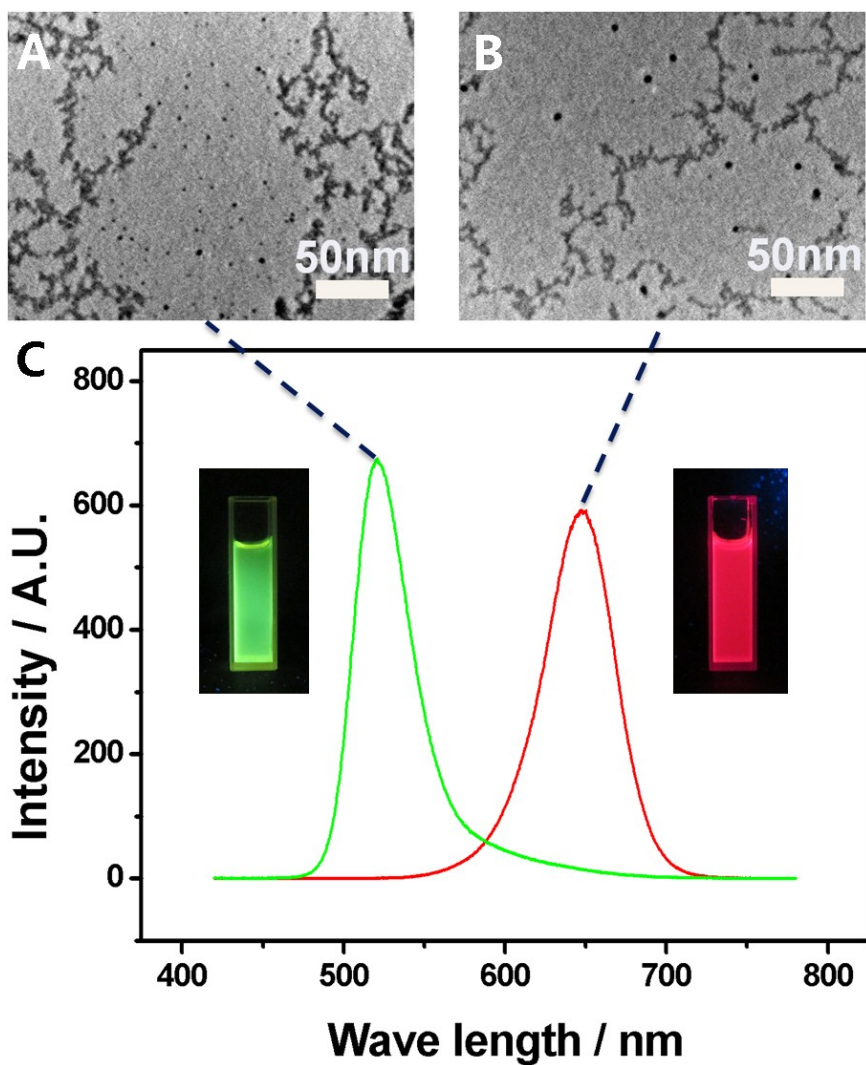


Figure S5 A) and B) TEM images of the as-synthesized CdTe QDs with diameter of 2.2 nm and 4.3 nm, respectively; C) fluorescent spectrum of the CdTe QDs.

Table S1. Width of the prepared BSA-FITC lines.

Volume of BSA-FITC(μ l)	CHS-MP4 (mm)	CHS-MP6 (mm)	CHS-MP8 (mm)
4	0.9	1.1	1.3
6	1.1	1.5	1.8
8	1.4	1.7	2.0

Table S2. Size of the prepared BSA-FITC dots.

Volume of BSA-FITC(μ l)	CHS-MP4 (mm)	CHS-MP6 (mm)	CHS-MP8 (mm)
4	1.2	1.5	1.8
6	1.6	1.9	2.1
8	1.7	2.0	2.4