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Supporting Information

A Spiropyran-Decorated Nanocoating for Dynamically Regulating Bacteria/Cell Adhesion and Detachment

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Experimental Section

Materials and Methods

10-(2-Hydroxyethyl)-30,30-dimethyl-6-nitrospiro(2H-1-benzopyran-2,20-indoline) (SP-OH), acryloyl chloride, acridine orange (AO), and γ-methacryloxypropyltrimethoxysilane (MPS) were purchased from Tianjin Heowns Biochem Technologies LLC. (Tianjin, China). Azobis(isobutyronitrile) (AIBN, Aladdin) was recrystallized from ethanol. *N*, *N*-Dimethylformamide (DMF) was dried over calcium sulfate and distilled at reduced pressure. SP was prepared as previous report.[32] ^{1}H NMR (400 MHz, $CDCl_3$ δ, ppm): 1.15 (s, 3H, -CH_3), 1.27 (s, 3H, -CH_3), 1.90 (s, 3H, -CH_3), 3.37-3.62 (m, 2H, -N-CH_2-), 4.31 (t, 2H, -O-CH_2-), 5.55 and 6.07 (s, 2H, =CH_2), 5.87 (d, 1H, -CH=), 6.68-6.80 (q, 2H, Ar-H and –CH=), 6.85-6.96 (q, 2H, 2Ar-H), 7.07-7.14 (d, 1H, Ar-H), 7.17-7.25 (m, 1H, Ar-H), 7.97-8.06 (m, 2H, 2Ar-H). All other reagents with analytical grade were obtained from Tianjin Chemical Reagent Co. and used without further purification. Reversible addition-fragmentation transfer (RAFT) has recently emerged as a promising controlled radical polymerization technique due to its versatility and simplicity, and the polymer is free from the contamination of metal catalysts.[33]

RAFT Polymerization of PSP

The RAFT polymerization of PSP was conducted in a sealed tube. In a typical run, SP (1.7 g, 4.2 mmol), 4-cyanopentanoicacid dithiobenzoate (CPADB) (20 mg, 0.07 mmol) and AIBN (8 mg, 0.05 mmol) were charged into the glass tube containing DMF. The mixture was degassed through three freeze-thaw cycles and the tube was then

sealed under vacuum and kept in an oil bath at 70 ℃ to conduct the polymerization. After 24 h, the tube was put into liquid nitrogen to quench the polymerization. Afterwards, the mixture was added to a large amount of dry hexane and then further dried under high vacuum. To obtain the finally copolymer (PSP-*b*-PMPS), distilled MPS and AIBN were added to the solution of PSP. The mixture was degassed through three freeze-thaw cycles, and warmed to 70 ℃ to conduct the polymerization. After 24 h, the reaction flask was put into liquid nitrogen to quench the polymerization. The mixture was added to a large amount of dry hexane to precipitate the resulting polymer. The final product was dried in a vacuum oven at room temperature for 12 h.

General Procedures for Micellization and Sol-Gel Process

The micelles are conducted by adding 1 mL of 2 mg/mL PSP-*b*-PMPS solution into 4 mL of deionized water under vigorous stirring. Then, the mix solution was dialysis against deionized water.

Preparation of Self-Assembled Nanocoating

To immobilize PSP-*b*-PMPS micelles onto the surface of a silica gel, surface modification was required to provide hydroxide group. The PSP-*b*-PMPS micelles were homogeneously coated on a silica gel and dried at 60 ℃ for 30 min. After being washed with phosphate buffer saline (PBS) three times, the coating was obtained.

Cell Culture

The NIH 3T3 cells were cultured at 37 ℃ in an atmosphere of 5% CO_2/air in Dulbecco's modified Eagle's medium (DMEM) supplemented with 5% fetal bovine serum (FBS). The medium was changed every 2 days, and the cells were digested by

trypsin and resuspended in fresh medium before plating.

In Vitro Cytotoxicity Measurement

Cell viability was examined by the MTT assay as previous report with minor modification.[34] NIH 3T3 cells were seeded in a 96-well plate at an initial density of 1 × 10^4 in 100 μL of DMEM. After incubation for 24 h, the medium was replaced with fresh medium containing different concentrations of PSP-*b*-PMPS nanoparticles. After incubation for further 24 h, MTT reagent was added to each well, and the cells were further incubated at 37 ℃ for 4 h. The culture medium in each well was removed, and replaced by 150 μL dimethyl sulfoxide (DMSO). The plate was gently agitated for 20 min, and the absorbance values were recorded at a wavelength of 490 nm using a plate reader. The cells treated without the addition of micelles were used as control, and their cell viability was set at 100%. Each sample was repeated five times.

Acidity- and Light-Mediated Cell Adhesion

The PSP-*b*-PMPS micelles modified surface was placed into a 24-well plate. NIH 3T3 cells were added to each well and cultured at 37 ℃ for 5 h. Then, the platform was examined for UV- and pH- triggered release. After UV irradiation or pH treatment for 4 min, the surface was gently washed with PBS three times to remove the released cells, and the cells number adhered on the surface were counted by a hemacytometer. AO dye was used to stain the cells on the substrate. After being washed with PBS three times, the substrates were supervised using fluorescent microscope. To evaluate the self-cleaning capability upon light exposure or pH treatment, the eight-step NIH 3T3 cells fouling cycle was succeeded by UV light exposure or pH treatment on the silica gel

surface.

The PSP-*b*-PMPS functionalized silica gel was immersed in 1.5 mL of the bacterial suspension at 37 ℃ for 6 h in 24-well microtiter plate wells, and then washed with PBS three times to remove loosely attached bacterial cells. For bacteria self-cleaning, the above surfaces were immersed in PBS and exposed to 365 nm UV light or pH 5.7 solution for 4 min, and then washed with PBS for three times. All samples were treated with 2.5% glutaraldehyde, and 30%, 50%, 70%, 80%, 90%, 95%, and 100% ethanol dehydration for SEM.

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Human Blood Adsorption

The human blood was obtained from Tianjin Medical University. The silicone tube with PSP-*b*-PMPS nanoparticle coating was placed in individual wells of a 24-well plate and each well was equilibrated with 1 mL of blood for 60 min at 37 ℃. All samples were rinsed five times with 1 mL of PBS and incubated in PBS. Then, all samples were exposed to 365 nm UV light or pH 5.7 solution for 4 min, and then washed with PBS three times. All samples were observed using SEM.

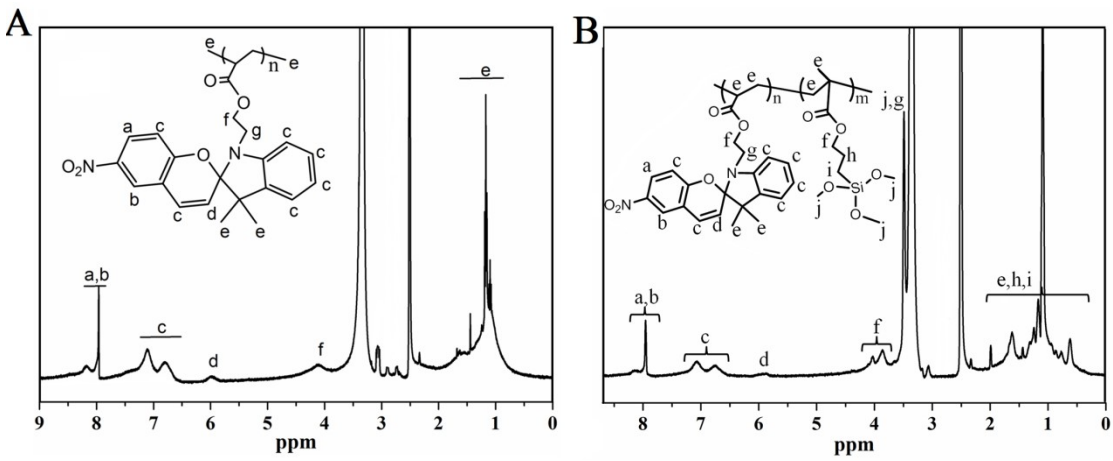

Figure S1. ^{1}H NMR spectra of PSP (A) and PSP-*b*-MPS (B), respectively.

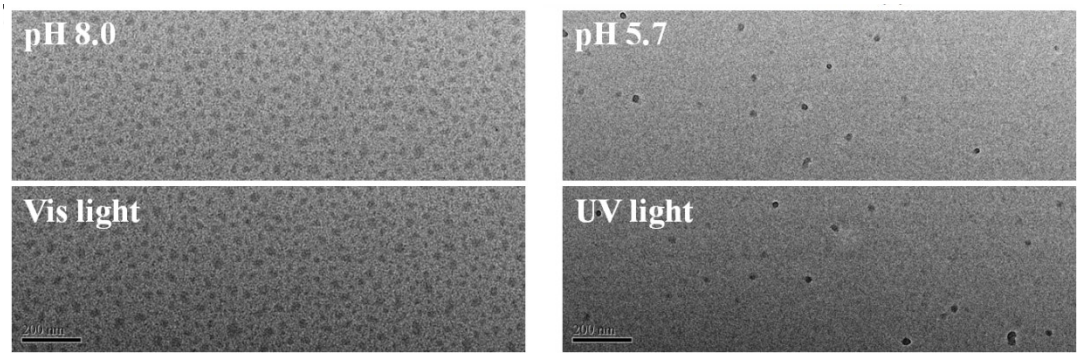

Figure S2. TEM images of the nanoparticles in weak alkaline and acid solution.

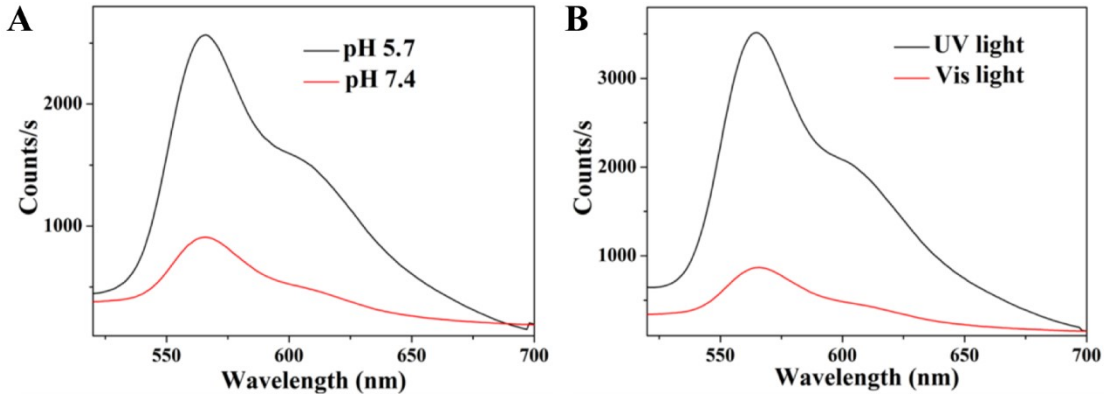

Figure S3. Fluorescence spectra of PSP-*b*-MPS in aqueous solution with different pH (A). Fluorescence spectra of nanoparticles in aqueous solution before and after UV light irradiation (B).

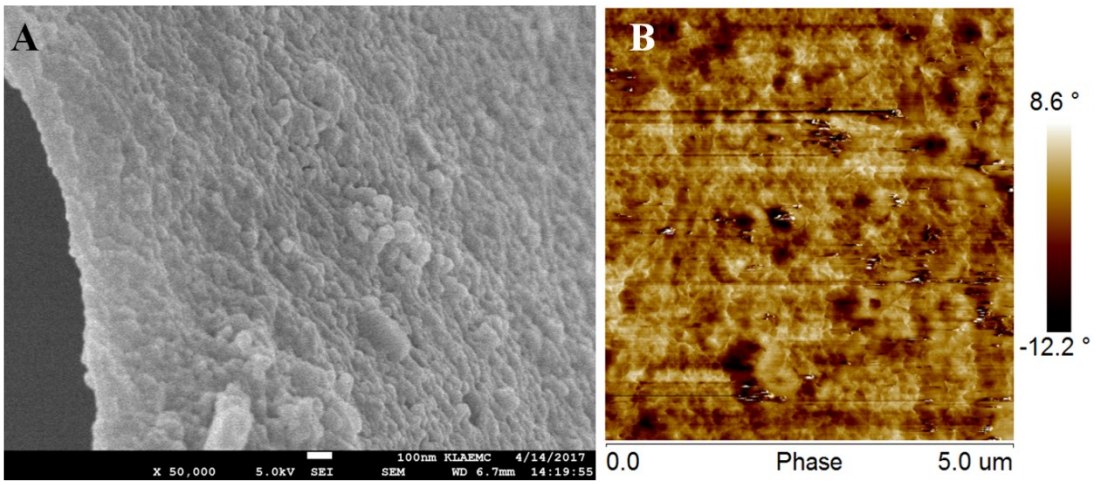

Figure S4. The SEM image of PSP-*b*-MPS nanoparticles assembled in the aqueous solution (A). AFM images of PSP-*b*-MPS nanoparticles coated on the silica gel (B).

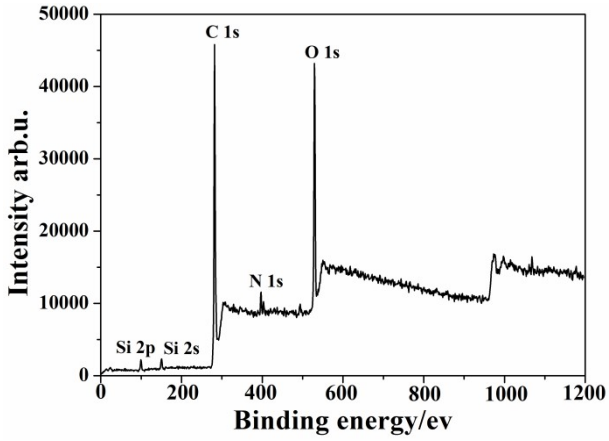

Figure S5. The XPS spectra of PSP-*b*-MPS.

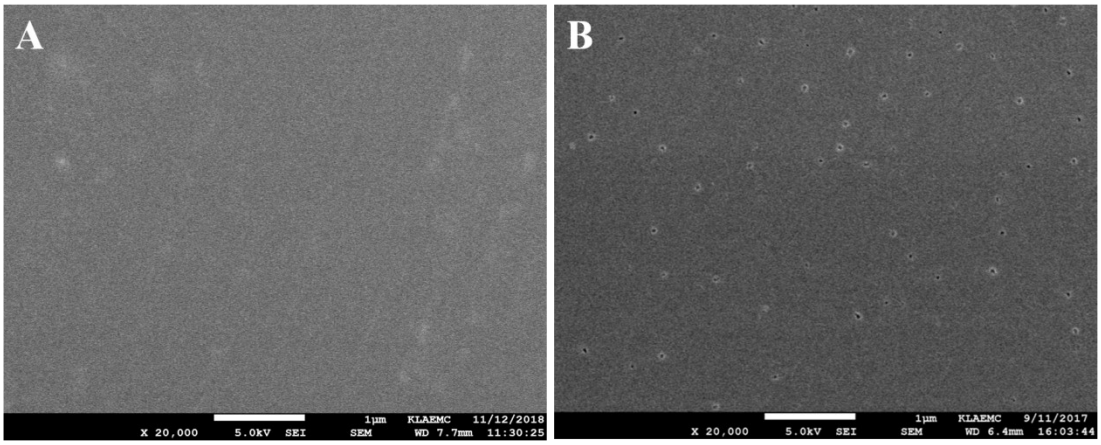

Figure S6. The SEM image of PSP-*b*-MPS nanoparticles after 8 switching cycles of

acid/base (A) and UV/vis light irradiation (B).

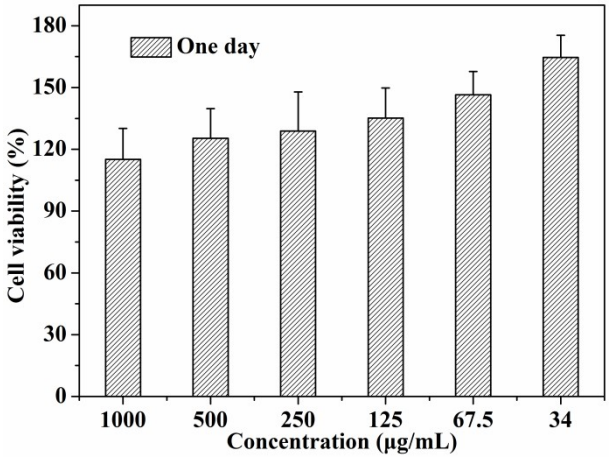

Figure S7. The viability of NIH 3T3 cell after treatment with PSP-*b*-MPS for 24 h.