Electronic Supplementary Material (ESI) for Chemical Communications.

Supporting Information

One-Step Functionalization of Zwitterionic Poly[(3-(methacryloylamino)propyl)dimethyl(3-sulfopropyl)ammonium hydroxide] Surfaces by Metal-Polyphenol Coating

Suyeob Kim,[a] Seungjoo Kwak,[b] Seokchang Lee,[b] Woo Kyung Cho,[b] Jungkyu K. Lee,[c] and Sung Min Kang[a,*]

[a]*Department of Marine Biomaterials & Aquaculture, Pukyong National University, Busan 608-737, Republic of Korea,*
[b]*Department of Chemistry, Chungnam National University, Daejeon 305-764, Republic of Korea,*
[c]*Department of Chemistry, Kyungpook National University, Daegu 702-701, Republic of Korea*

* To whom correspondence should be addressed.

E-mail: smk12@pknu.ac.kr

Contents

Experimental Details

Materials: Iron(III) chloride hexahydrate ($FeCl_3,\cdot 6H_2O$, 97%, Sigma-Aldrich), tannic acid (TA, Sigma-Aldrich), copper(I) bromide (CuBr, 99.999%, Aldrich), copper(II) bromide ($CuBr_2$, 99.999%, Aldrich), 2,2'-dipyridyl (bpy, ≥ 99%, Aldrich), [3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium hydroxide inner salt (MPDSAH, 96%, Aldrich), poly(ethylene glycol) methacrylate (average M_n 360, Aldrich), fibrinogen (from human plasma, Sigma), lysozyme (from chicken egg white, Sigma), bovine serum albumin (Sigma), fibrinogen from human plasma Alexa Fluor® 488 Conjugate (Molecular Probes), (3-trimethoxysilyl)propyl-2-bromo-2-methylpropionate (95%, Gelest Inc.), absolute ethanol (Merck), absolute methanol (99.8%, J. T. Baker), toluene (HPLC grade, 99.94%, Burdick & Jackson), hydrogen peroxide (Daejung Chemicals & Metals, 30.0%), sulfuric acid (95.0%, Daejung Chemicals & Metals), and acetone (99%, Daejung Chemicals & Metals) were used as received. Silicon wafers (boron-doped p-type, <100> orientation, and thickness of 500 ± 25 μm) were purchased from ICM Engineering (Bulgaria). Ultrapure water (18.3 MΩ•cm) from the Human Ultra Pure System (Human Corp., Korea) was used.

Synthesis of poly(MPDSAH) surfaces: The silicon substrate was cleaned by immersion in a piranha solution (H_2SO_4:H_2O_2 = 7:3, *Caution: piranha solution reacts violently with most organic materials and must be handled with extreme care*) for 1 min and then thoroughly washed with water. The cleaned substrate was dried under a stream of argon and oxidized by oxygen plasma cleaner (Femto Science Cute, Power: 50 W) for 1 min to maximize the surface density of -OH groups. This was immersed into a 3.8 mM toluene solution of the polymerization initiator, (3-trimethoxysilyl)propyl-2-bromo-2-methylpropionate, for 24 h at room temperature. After the formation of self-assembled monolayers (SAMs) of the initiator, the silicon substrate was rinsed with toluene several times and then dried under a stream of

argon.

Both solvents used for the SI-ATRP procedure (water and methanol) were deoxygenated for 4 h by passing a continuous stream of dry argon through the solvent while stirring. $CuBr_2$ (0.0076 g, 0.034 mmol), bpy (0.1334 g, 0.854 mmol), CuBr (0.049 mg, 0.342 mmol), and MPDSAH (5.0 g, 17.1 mmol) were added to a Schlenk flask, and the mixture was degassed under vacuum and purged with argon. Water (8 mL) and methanol (2 mL) were added to this through syringes: this was the polymerization solution. The initiator-coated silicon substrate was placed in another Schlenk flask, degassed under vacuum, and purged with dry argon. The polymerization solution was transferred to the Schlenk flask containing the initiator-coated silicon substrate through a syringe, and the mixture was allowed to react for 24 h at room temperature. The resulting poly(MPDSAH) surface was rinsed with methanol and water, and dried under a stream of argon. To remove unreacted monomers and copper/ligand complex, which could be incorporated into zwitterionic polymer brushes, the poly(MPDSAH) surface was immersed in water for 4 days at 40 ^{o}C,[1] with the water being replaced every day. ***Synthesis of poly(PEGMA) surfaces***: SI-ATRP on the initiator-coated substrate was carried out in a solution of PEGMA (3.26 mL, 10 mmol), CuBr (143 mg, 1 mmol), and bpy (312 mg, 2 mmol) in water/methanol (2 mL/8 mL) overnight, at room temperature in an argon atmosphere. The synthesized poly(PEGMA) surface was washed with pure water and methanol to remove any remaining monomers and physisorbed polymers and then dried in a stream of nitrogen gas.

TA-Fe^{III} coating: Ethanolic solutions of TA (5 mL, 10 mM) and $FeCl_3$ (5 mL, 10 mM) were freshly prepared and mixed. Poly(MPDSAH) surfaces were immersed in this solution mixture. After coating for 5 min at room temperature, resulting surfaces were rinsed with ethanol and dried under a stream of nitrogen gas.

Patterned TA-Fe^{III}coating: A PDMS stamp was prepared according to the literature method

using Sylgard 184 silicon elastomer (Dow Corning).[2] Prior to use, the PDMS stamp was oxidized by an oxygen plasma cleaner for 1 min and then inked by spin-casting with solution mixture of TA (10 mM in 50% ethanol) and $FeCl_3$ (10 mM in 50% ethanol) for 1 min at 2000 rpm. The inked stamp was brought into contact with poly(MPDSAH) and poly(PEGMA) surfaces, and the stamp was peeled off after 5 min. For visualization of the pattern, polymer surfaces were incubated in a solution of Alexa Fluor 488-conjugated fibrinogen (0.1 mg/mL) in PBS buffer (pH 7.4) at room temperature. After 15 h, the sample was taken, and washed several times with PBS buffer and distilled water.

Protein adsorption: For the protein adsorption study, poly(MPDSAH) surfaces were incubated in PBS buffer solutions of fibrinogen (0.1 mg/mL), BSA (1 mg/mL), and lysozyme (1 mg/mL), before and after TA-Fe^{III} coating. After 1 h, the resulting surfaces were washed with distilled water and dried under a stream of nitrogen gas.

Diatom adhesion: *Amphora coffeaeformis* was received from the Korea Marine Microalgae Culture Center (KMMCC) and grown in 100 mL of f/2 culture medium at 18 ^{o}C for 10 days. 15 mL of cell suspension (concentration of *chlorophyll a* = 4.0 μg/mL) was added to petri dishes containing solid substrates. After incubation at room temperature for 4 h, substrates were washed in sea water to remove unattached cells. Attached cells were characterized and counted by optical microscopy (Nikon, LV100ND).

Characterizations: XPS spectra were obtained using a MultiLab 2000 (Thermo VG Scientific, UK) with a Mg Kα X-ray source and ultrahigh vacuum (~10^{-10} mbar). The thickness of organic layers on solid substrates was measured using an M-2000D ellipsometer (J.A. Woollam Co., USA) and an Alpha-Step IQ surface profiler (KLA-Tencor Co.). Static water contact angle measurements were performed using a Phoenix-300 TOUCH goniometer (Surface Electro Optics Co., Ltd., Korea). Fluorescence images were acquired on an LSM 700 confocal microscope (Carl Zeiss, Germany). IR spectra were obtained in ATR mode

using a Bruker IFS 66V/S FT-IR spectrophotometer.

Table S1. Atomic composition (%) of poly(MPDSAH) and TA-Fe^{III}-coated poly(MPDSAH) surfaces.

	C 1s	N 1s	O 1s	S 2p	Si 2p	Fe 2p
Poly(MPDSAH)	51.37	6.78	22.45	6.00	13.40	0
TA-Fe^{III}-coated poly(MPDSAH)	57.45	4.61	27.49	3.58	5.30	1.57

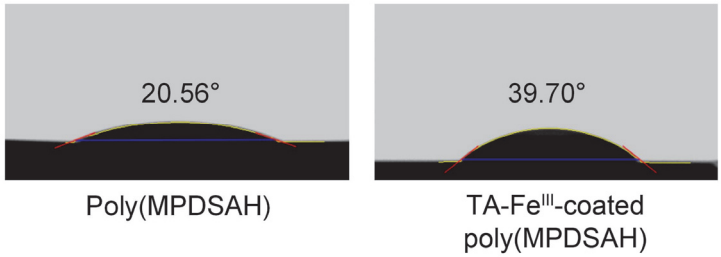

Figure S1. Static water contact angle images of poly(MPDSAH) surfaces before (left) and after (right) TA-Fe^{III} coating.

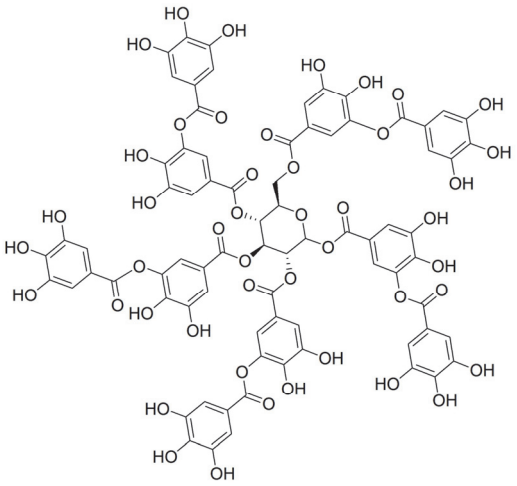

Figure S2. Chemical structure of tannic acid (TA).

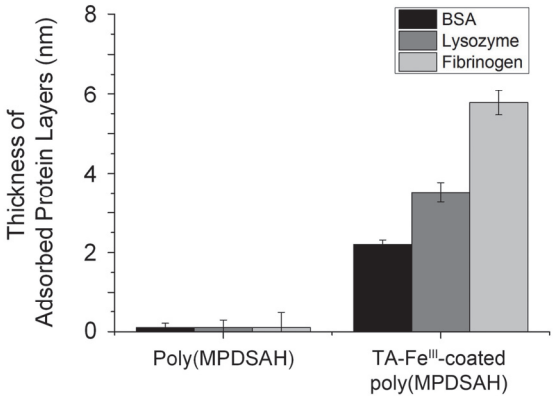

Figure S3. Thickness of adsorbed protein layers on poly(MPDASH) and TA-Fe^{III}-coated poly(MPDSAH) surfaces.

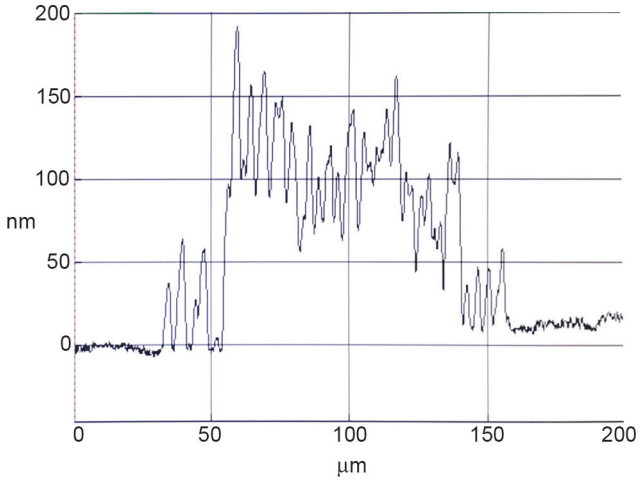

Figure S4. Thickness profile of the TA-Fe^{III}-patterned poly(MPDSAH) surface measured by Alpha-Step.

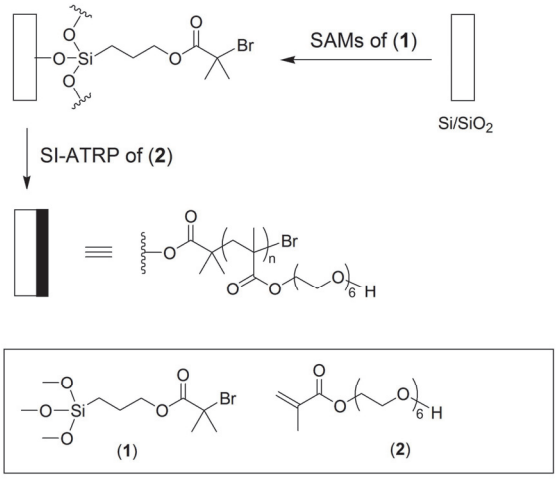

Figure S5. The procedure for the synthesis of poly(PEGMA) surfaces.

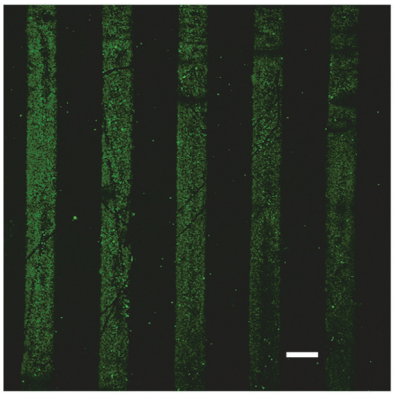

Figure S6. A fluorescence image of proteins selectively immobilized on the TA-Fe^{III}-patterned poly(PEGMA) surface. The scale bar represents 100 μm.

References

1. W. K. Cho, B. Kong and I. S. Choi, *Langmuir*, 2007, **23**, 5678.
2. B. S. Lee, Y. S. Chi, K.-B. Lee, Y.-G. Kim and I. S. Choi, *Biomacromolecules*, 2007, **8**, 3922.