Electronic Supplementary Material (ESI) for Biomaterials Science.

Supporting Information

Biomimetic Honeycomb-patterned Surface as the Tunable Cell Adhesion Scaffold

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Attenuate total reflectance-Fourier-transform infrared spectroscopy (ATR- FTIR) was recorded using a Perkin-Elmer Spectrum 100 (USA).

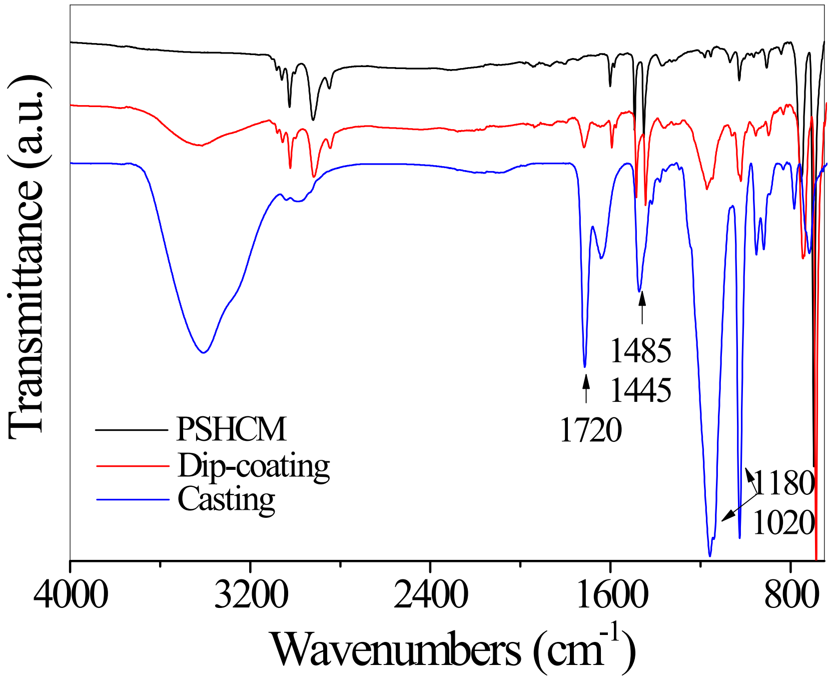

Figure S1. The ATR-FTIR spectra of PSHCM and the modified membranes by dip-coating and casting.

Similar peak information of membranes was obtained via ATR-FTIR compared with FTIR. The bands at ν=1180 and 1020 cm^{-1} can be assigned to antysimmetric and symmetric vibrations of the sulfonyl group ($-SO_3$) and 1720 cm^{-1} is the typical peak of carbonyl group (C=O), both groups are of the SBMA segment. Moreover, an obvious difference in intensity of the two characteristic peaks, where the stretching vibration peak of C=C in the benzene ring (ν=1490 cm^{-1}) is chosen as a reference, could be seen in the spectra of the two decorated membranes: the peak intensity in the spectrum of the polySBMA-decorated membrane obtained by direct casting was stronger than that in the spectrum of the dip-coated membrane, implying a difference in SBMA grafting density.

The X-ray Photoelectron Spectroscopy (XPS) was measured on PHI-5000 Versaprobe II (Japan). The scanning area is 200×200μm.

Table S1. XPS results of membranes.

Membranes	S 2p		C 1s		N 1s		O 1s	
	Peak/eV	Atomic %	peak/eV	Atomic %	peak/eV	Atomic %	peak/eV	Atomic %
PSHCM	166.7	0.00	283.5	97.09	400.4	0.00	530.6	2.91
Dip-coating	165.75	3.36	283.5	64.82	400.4	5.80	530.6	26.02
Casting	166.7	4.22	283.5	64.79	400.4	5.51	530.6	25.68

As shown in Table S1, the peaks of polySBMA (N and S elements) can't be observed on PSHCM, which is attributing to that the chemical property of PSHCM only contains carbon and hydrogen elements. After modification by polySBMA, both on the dip-coating and casting PSHCM exhibit the information of S and N elements. The XPS furthermore demonstrated the grafting of polySBMA on the membranes.

The wettability of membranes was measured using an OCA 20 apparatus (Dataphysics, Germany).

Table S2. Water and diiodomethane contact angle

Surfaces	Water	Diiodomethane
Smooth PS	97±1°	41±1°
PS-HCM	106±5°	37±4°
Casting HCM	30±2°	56±1°
Dip-coating	25±4°	64±3°

The surface energy was calculated based on Owens, Wendt, Rabel and Kaelble (OWRK) method. The Surface free energy of water and diiodomethane was provided by Busscher as showed in Table S2.

Table S3. The surface free energy and component of water and diiodomethane

Liquids	SE(mN/m)	Dispersion(mN/m)	Polar(mN/m)
Deionized water	72.10	19.90	52.20
Diiodomethane	50.00	47.4	2.60

The OWRK method is a standard method for calculating the surface free energy of a solid from the contact angle with several liquids. In doing so, the surface free energy is divided into a polar part and a disperse part.

The OWRK equation

$$\gamma_{sl} = \delta_s + \delta_l - 2(\sqrt{\delta_s^D \cdot \delta_l^D} + \sqrt{\delta_s^P \cdot \delta_l^P})$$

And the Young's equation

$$\delta_s = \gamma_{sl} + \cos\theta \cdot \delta_l$$

Where,

γ_{sl}: Solid-liquid interfacial tension;

δ_s, δ_l: Surface energy of solid and liquid, respectively;

$\delta_s^D \cdot \delta_l^D$: Disperse part of surface energy;

$\delta_s^P \cdot \delta_l^P$: Polar part of surface energy;

$\cos\theta$: Contact angle.

The above two equations can be consolidated. When a solid was tested with two liquids whose δ_l^D and δ_l^P has been known. Three unknown parameters need to be solved, namely θ, δ_s^D and δ_s^P. The contact angles would be obtained by experiment and plugged into the equations to solve the equations.

In our systems, the surface energy results were showed in Table S3.

Table S4. Surface energy and components of membranes

Liquids	SE(mN/m)	Dispersion(mN/m)	Polar(mN/m)
Smooth PS	40.43	40.42	0.01
PS-HCM	46.07	45.31	0.76
Casting HCM	59.98	16.45	43.13

Dip-coating	69.14	11.60	57.54

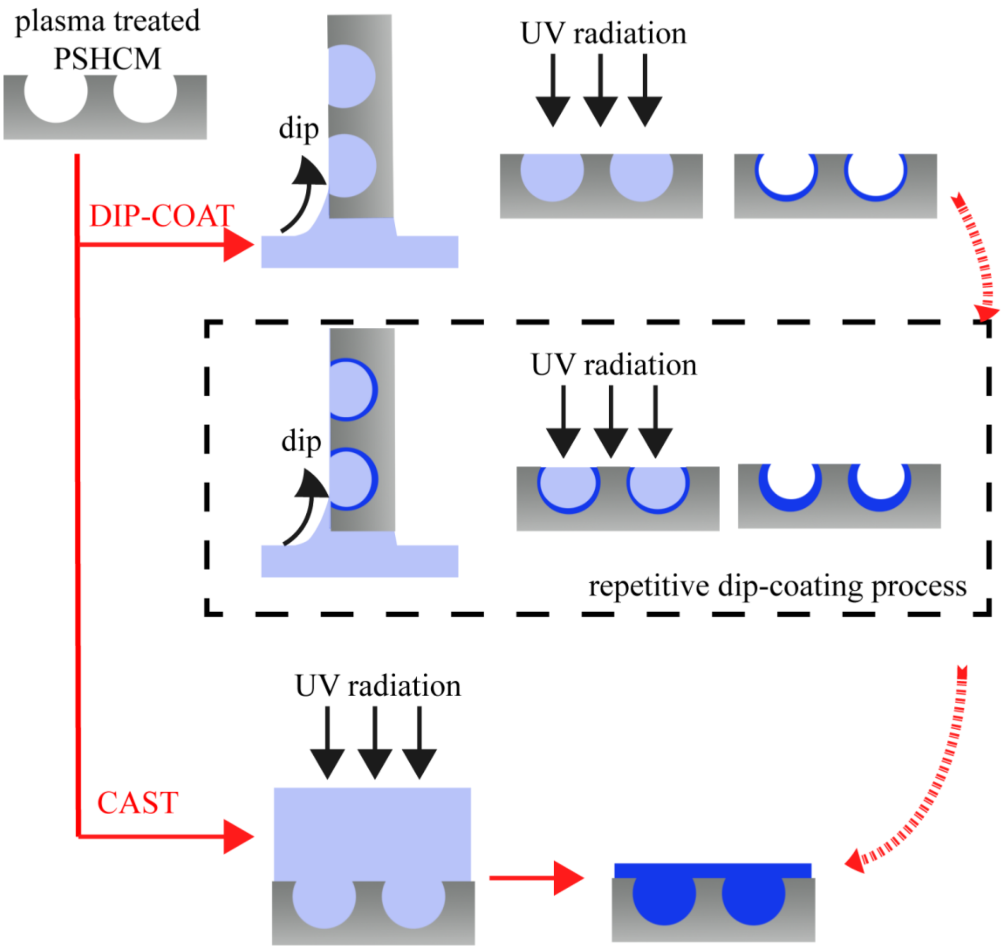

Figure S2. The Schematic illustration of the fabrication process of zwitterionic polySBMA grafted onto the honeycomb PS membrane.

The dip-coating and casting process can be applied to obtain different distribution of polySBMA as shown in Figure S1. After PSHCM being treated with plasma, the surface would be abundant with free radical. When modified by dip-coating method, the SBMA solution would aggregate in the honeycomb cavities for the capillary force. The film was further treated with UV radiation. Owing to the surficial free radical, the SBMA polymerized onto the wall of honeycomb hole. When modified by casting method, the SBMA solution would totally cover the surface of plasma treated PSHCM. After the UV radiation, the polySBMA would uniformly cover the surface.

Here, a mythological repetitive dip-coating process was exhibited. If the dip-coated membrane was retreated with dip-coating process, the hole of honeycomb would be decorated with more polySBMA. The conceivable result of repetitive dip-coating membranes is that the cavities would be fully filled with polySBMA until to be uniformly covered liking casting membrane.

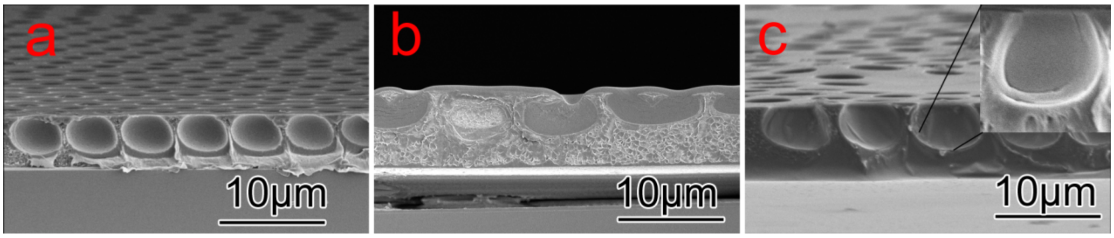

Figure S3. Cross-section SEM photographs of PSHCM (a), casting PSHCM (b) and dip-coating PSHCM (c). The hole of PSHCM after casting was filled with polySBMA, while that after dip-coating the porous structure was retained, and most of the polySBMA aggregated around the wall of the pores.

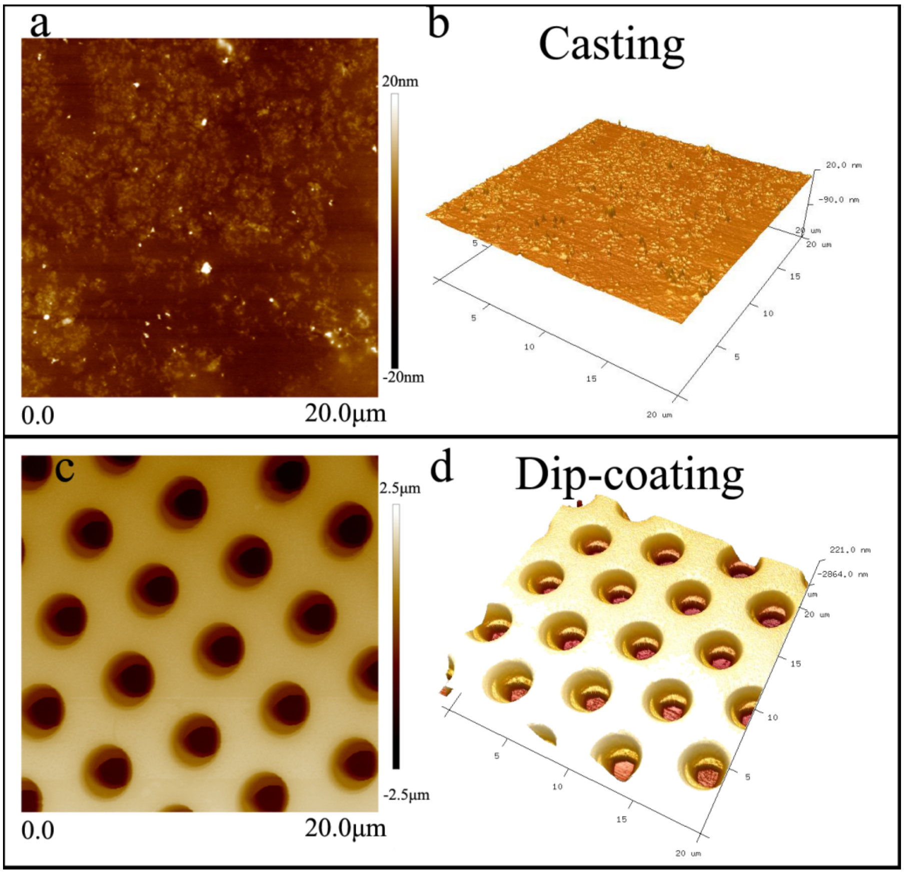

Figure S4. Plane AFM images (a,c) and 3D AFM (b,d) images of polySBMA casted PSHCM (top) and polySBMA dip-coating PSHCM (bottom). The hole of PSHCM after casting was filled with polySBMA. Thus, the AFM images showed a plane surface. While PSHCM after dip-coating retained the porous structure, and most of the polySBMA was aggregatively grafted around the hole of the pores.

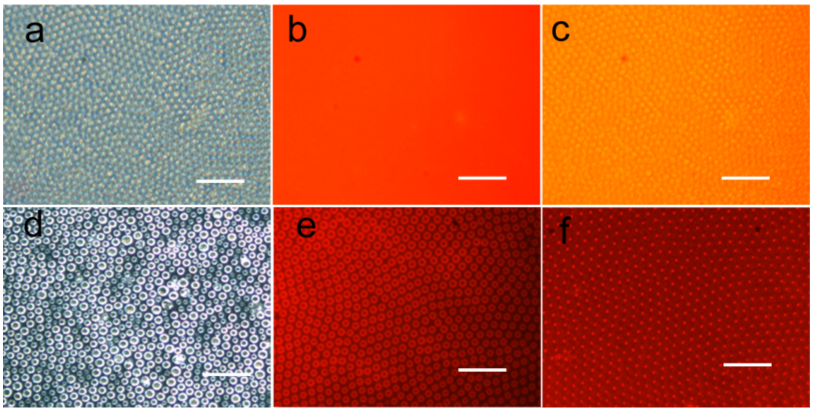

Figure S5. Fluorescence images of polySBMA modified PSHCM via casting (line 1) and dip-coating (line 2): a,d) the bright-field. b,e) fluorescent-field. c,f) bright/fluorescent composited field. Scale bar= 20 nm

PolySBMA contains a large number of ammonium (-NH_2^+-) and sulfonic (-SO_3-) groups, which could combine with the fluorescent dye (Rh-B). In contrary, the PS does not interact with Rh-B. It means that only the domain which had been decorated by polySBMA can emit fluorescent light in the exciting fluorescent field. Thus the Rh-B labelling can be applied to exemplify the distribution of polySBMA.

When observed under fluorescent field, the polySBMA casted PSHCM formed a uniform fluorescence layer. While that of dip-coated one was quite different from it. Only fluorescent circle around the honeycomb holes can be observed which indicating a micro-distribution of polySBMA. Due to the difference in refractive index between PS and polySBMA, porous structures can be observed on the casting membranes under optical field.