Supplementary Material (ESI) for Polymer Chemistry

Oxidant-induced dopamine polymerization for multifunctional coatings

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Supporting Information

Materials

Dopamine·HCl (DA·HCl, 99%) was purchased from Alfa Aesar. Bovine serum albumin (BSA; fraction V) was obtained from Sigma Chemical Co. Other reagents, purchased from Chengdu Kelong Reagent Company (P.R. China), were of analytical grade and used as received.

Characterization of the dopamine polymerization by UV-vis spectra

The reactivity of dopamine was measured at room temperature using UV-vis spectroscopy (U-200A, Shanghai Spectrum Instruments Co., Ltd, shanghai, China) at the wavelengths from 250 to 600 nm.

The DA·HCl concentration was 2mg/ml (the same concentration as reported in the literature of 'pH-induced') in all experiments. The molar ratios of DA to ammonium persulfate (AP) were 0.5:1, 1:1, 1.5:1, 2:1, 3:1, 4:1 and 5:1, respectively. For the UV spectroscopy measurements, the samples were prepared by 1:19 (v/v) dilution of the DA solution with double distilled water. In the 'pH-induced' control experiment, 2mg/ml DA·HCl was added into the Tris-HCl buffer (pH8.5), other operations were the same as the 'oxidant-induced' experiment.

To investigate the DA polymerization in weak acidic, neutral and weak alkaline aqueous media, 2mg/ml DA and 1.2mg/ml AP (the molar ratio of AP to DA was 1:2) were added into the buffer solutions of pH5.5 (Disodium hydrogen phosphate- citric acid buffer), pH7.0 (Disodium hydrogen phosphate- citric acid buffer) and pH8.5 (Tris-HCl buffer) for 2h polymerization. For the UV spectroscopy measurements, the operation was the same as above.

The experiments for sodium periodate and potassium chlorate induced DA polymerization was the same as for AP.

Discussion of quantitative analysis of the PDA formation

In fact, it is hard to do the quantitative analysis of the PDA formation in the solution. The PDA molecular weight cannot be accurately determined by GPC, due to the cross-linked structure, the aggregation and the precipitation like melanin did. Also, light scattering methods for determining molecular weight are not possible since the refractive index of PDA is unknown.

Polydopamine coating

The cleaned substrates were immersed in the solution of 2 mg/ml dopamine·HCl mixed with 1.2 mg/ml AP (the molar ratio of AP to DA was 1:2) at pH 7.0 (Disodium hydrogen phosphate- citric acid buffer) for several hours. After the coating, the substrates were rinsed with double distilled water, and then freeze-dried.

To measure the stability of the polydopamine-coatings, the eluent from the membrane was assayed by UV-vis absorbance spectra. The results showed that polydopamine-coating was not detached from substrate surface by simply washing, unless that the membrane was scratched, treated by ultrasound, or dipped in a strong acid/ alkali solution.

Surface Characterization

An XPS (KRATOS XSAM800, Britain) instrument using Al Kα (1486.6 eV) as radiation source was used to determine the composition of the films. The take-off angle of the photoelectron was set at 70° for XPS measurements.

The surface structures of the coatings were investigated with atomic force microscopy (AFM, SPI4000 Probe Station, SIINT Instruments Co., Japan) and field-emission scanning electron microscope (FSEM, FEI Sirion-200, USA) at ambient condition. The multimode AFM instrument was operated in a tapping mode, and the height and phase contrast images were collected. Olympus tapping mode cantilevers with the spring constants ranging from 51.2 to 87.8 N/m (as specified by the manufacturer) were used.

The hydrophilicity of the film surface was characterized on the basis of static contact angle measurement using a contact angle goniometer (OCA20, Dataphysics, Germany) equipped with video capture. A piece of 2 cm×2 cm film was stick on a glass slide and mounted on the goniometer. A total of 3μl droplet was dropped on the airside surface of the film at room temperature, and the contact angle was measured after 15s. Advancing (θa) and receding contact angles (θr) were measured by increasing 1μl droplet or decreasing 2μl droplet to ensure the three phase boundary line moved over the surface. Double distilled water was used as the polar liquid and methylene iodide was used as the apolar liquid. The surface energy of the surfaces was calculated from the contact angle data by Wu method. At least five measurements were averaged to get a reliable value.

BSA immobilization on the polydopamine layer

The polydopamine-coated substrates were immersed in the solution of 5mg/ml BSA, at pH 7.8 (PBS buffer). After 12h conjugation reaction, the substrates were washed by using 2%wt SDS solution for 3 times, followed by double distilled water for 3 times to remove the unimmobilized BSA.

Figure S1 UV-vis spectra of DA after 24h running time by mixed with sodium periodate (red line), potassium chlorate (blue line) and without oxidant (green line).

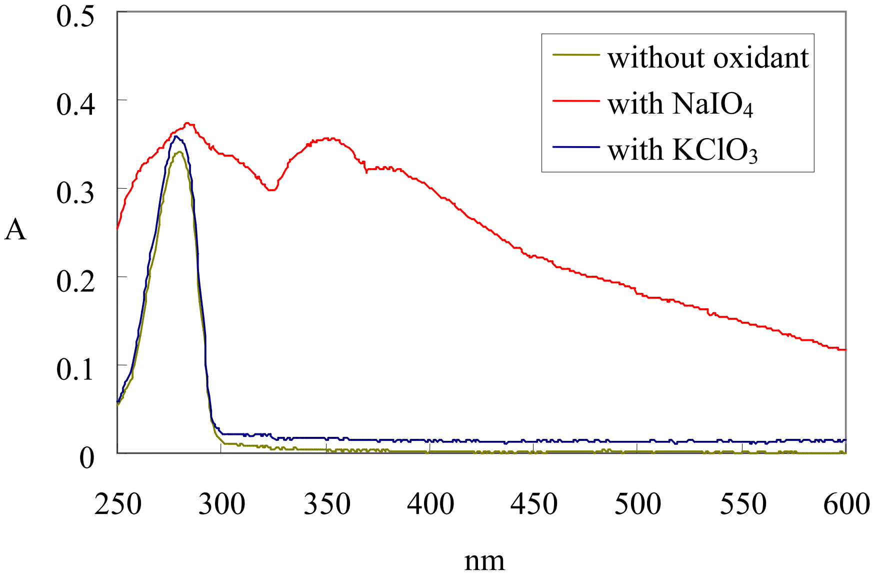


Figure S2 UV-vis spectra of DA after 4h running time by mixed with AP (blue line) and without AP (red line) at pH5.5 (a), pH7.0 (b) and pH8.5 (c). (d) Absorption intensity at 350 nm of DA after 4h running time by mixed with and without AP.

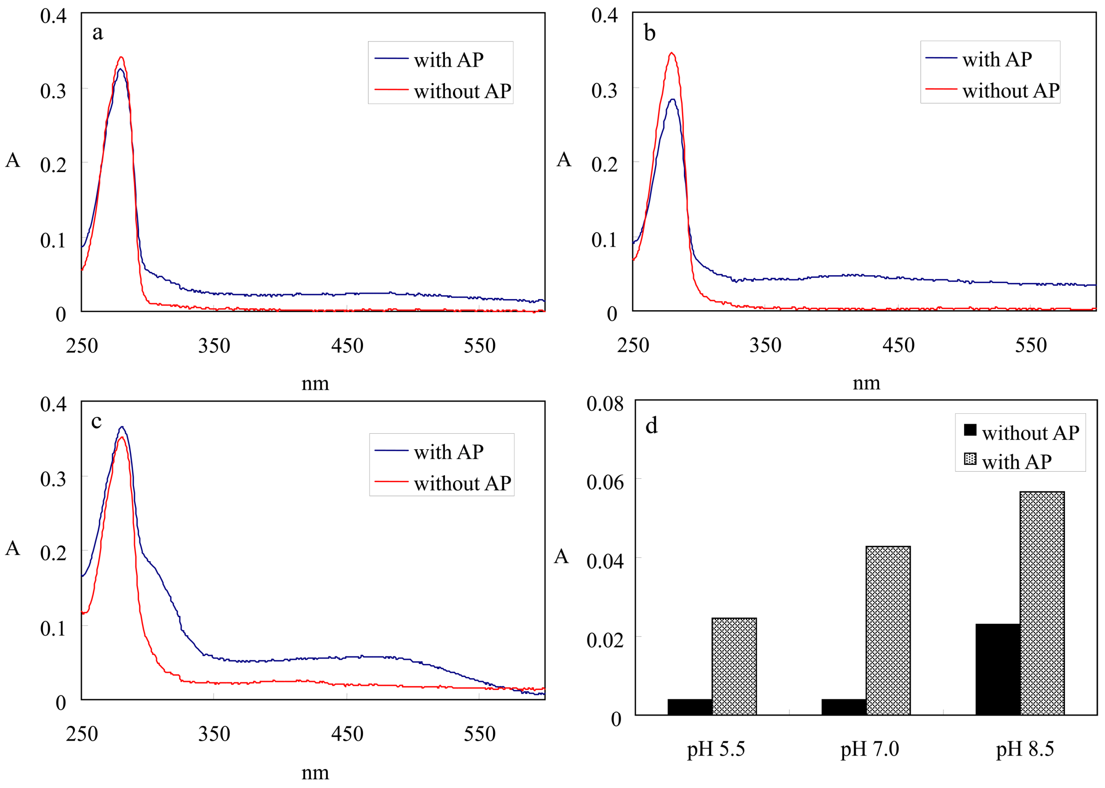
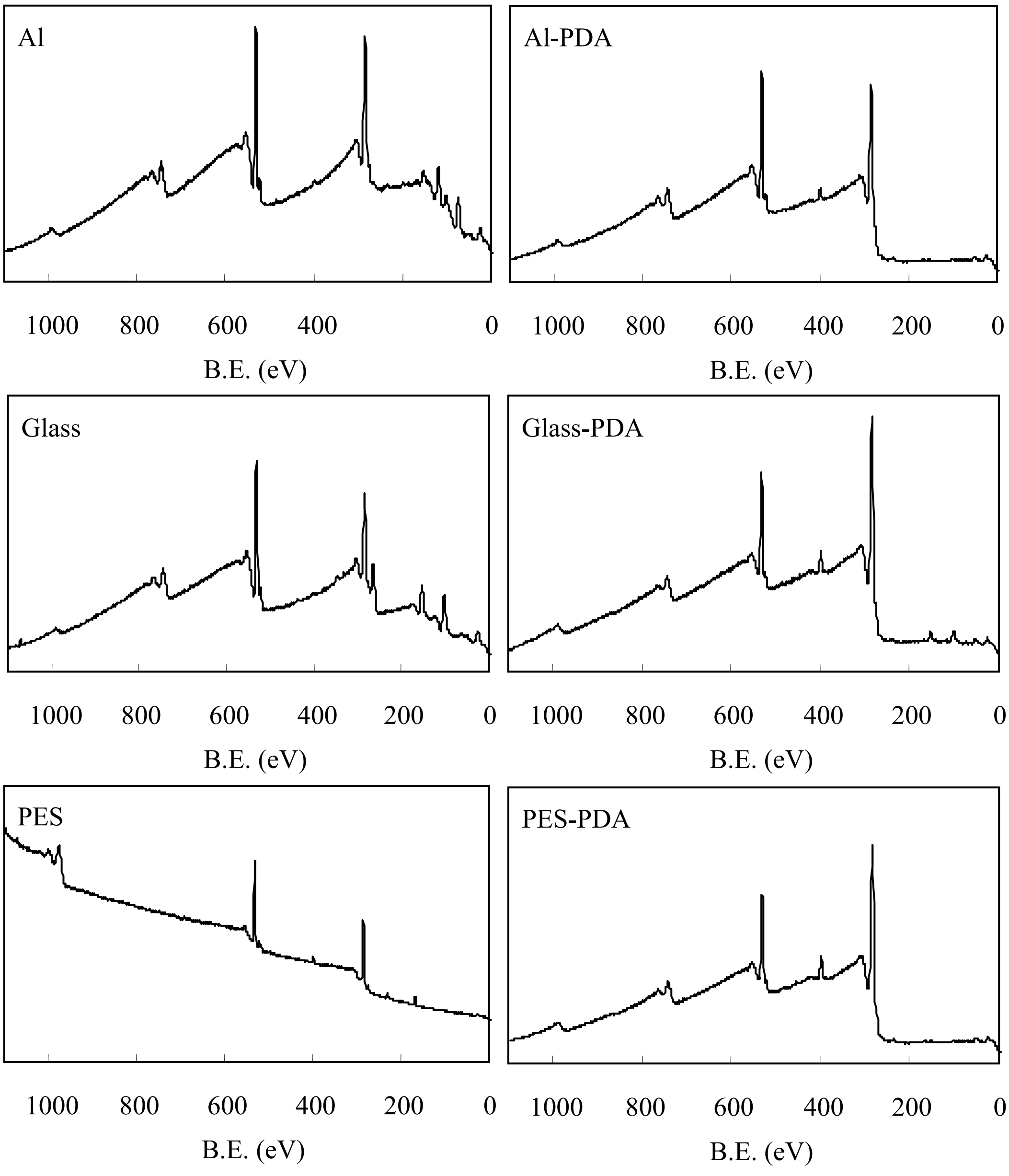
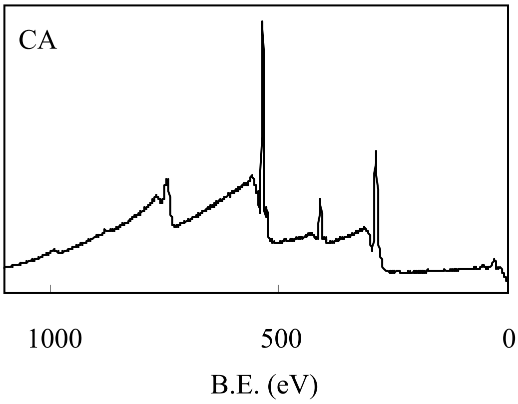
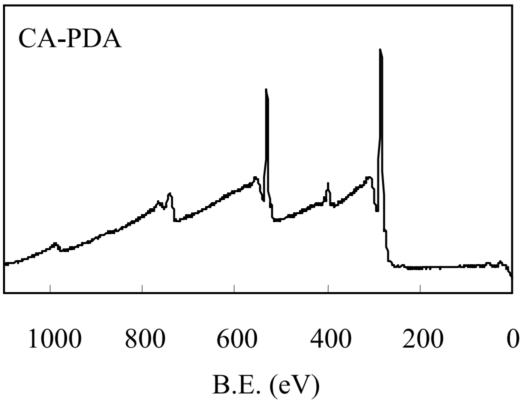
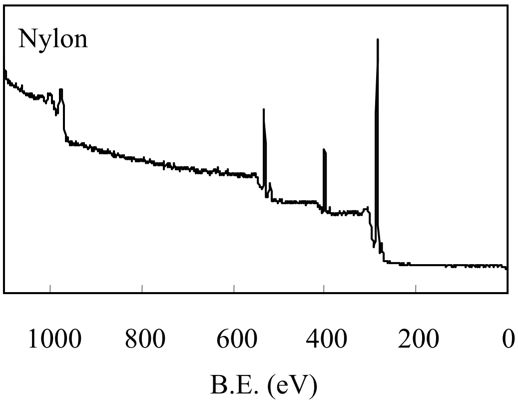


Figure S3 XPS spectra of uncoated (left) and PDA-coated (right) substrates.




CA
1000
500
0
B.E. (eV)


CA-PDA
1000
800
600
400
200
0
B.E. (eV)


Nylon
1000
800
600
400
200
0
B.E. (eV)

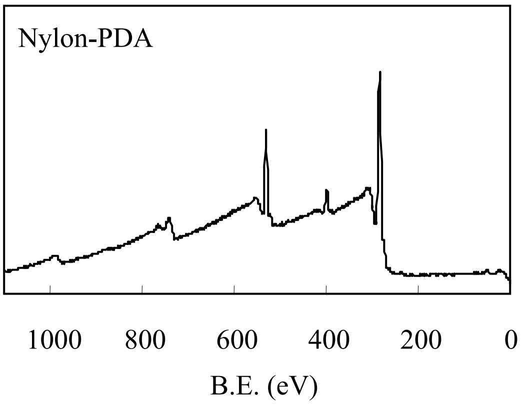

Nylon-PDA
1000
800
600
400
200
0
B.E. (eV)

Figure S4 C1s XPS spectra of (a) initial nylon substrate and (b) PDA-coated nylon substrate, and O1s XPS spectra of (c) initial nylon substrate and (d) PDA-coated nylon substrate.

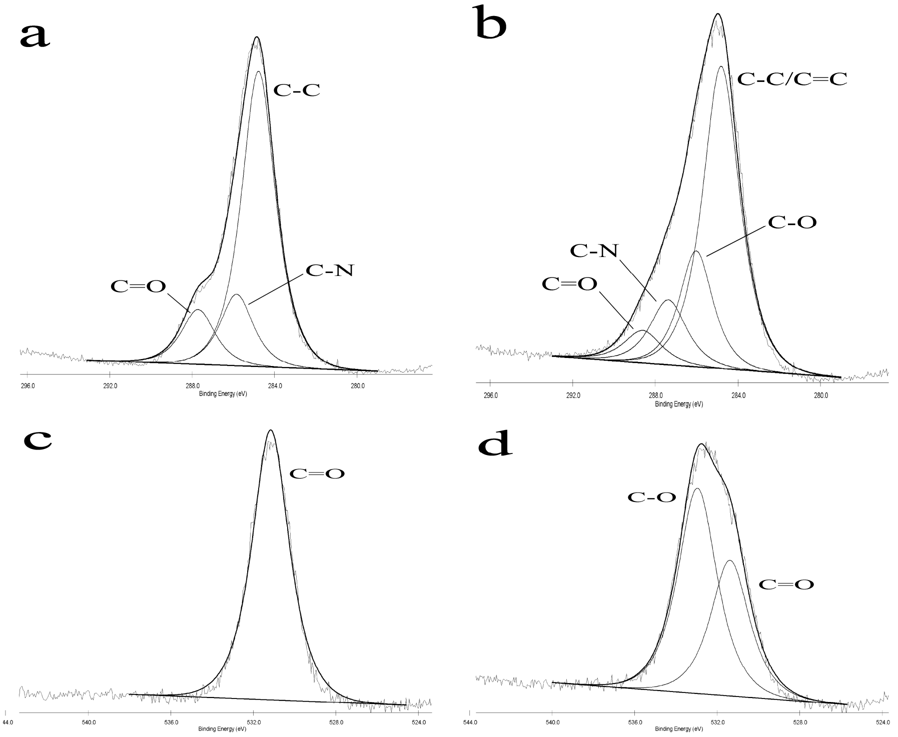


Figure S5 AFM images of uncoated (upper) and PDA-coated (lower) substrates.

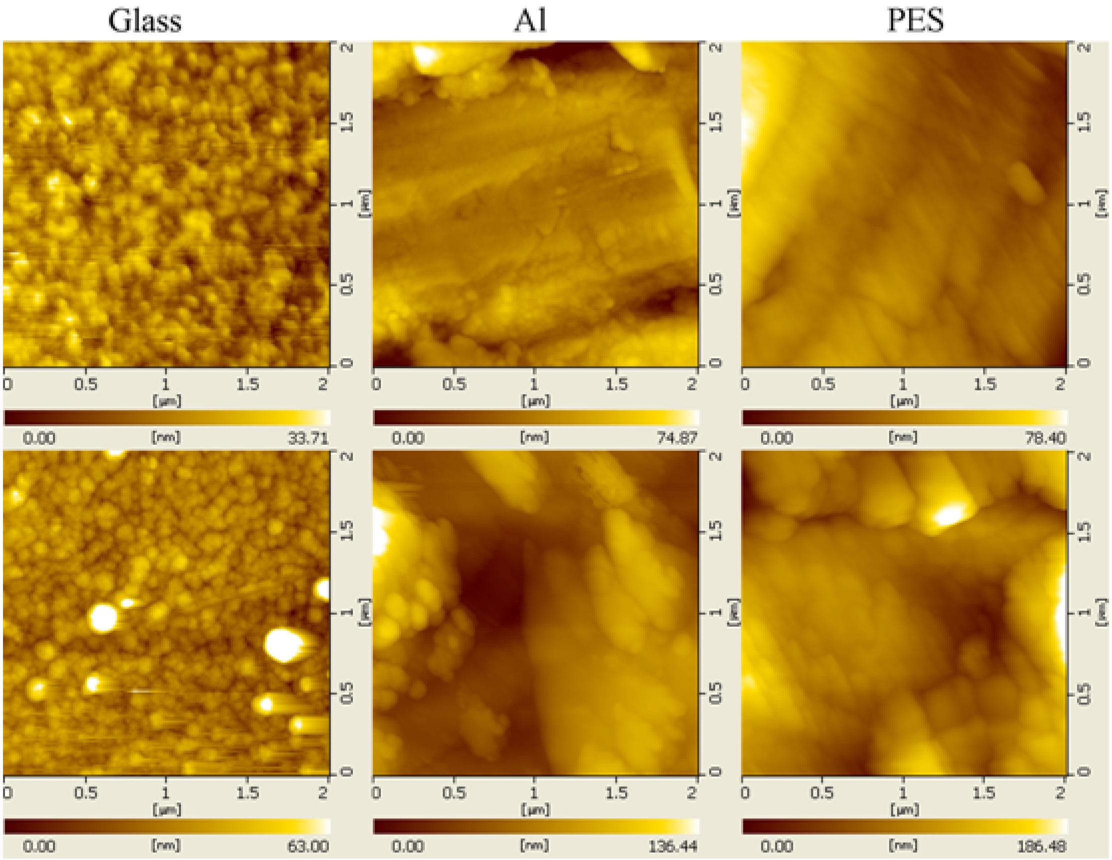


Figure S6 FSEM image of uncoated (A), oxidant-induced PDA-coated (B) and pH-induced PDA-coated (C) substrates. Magnification ×100,000

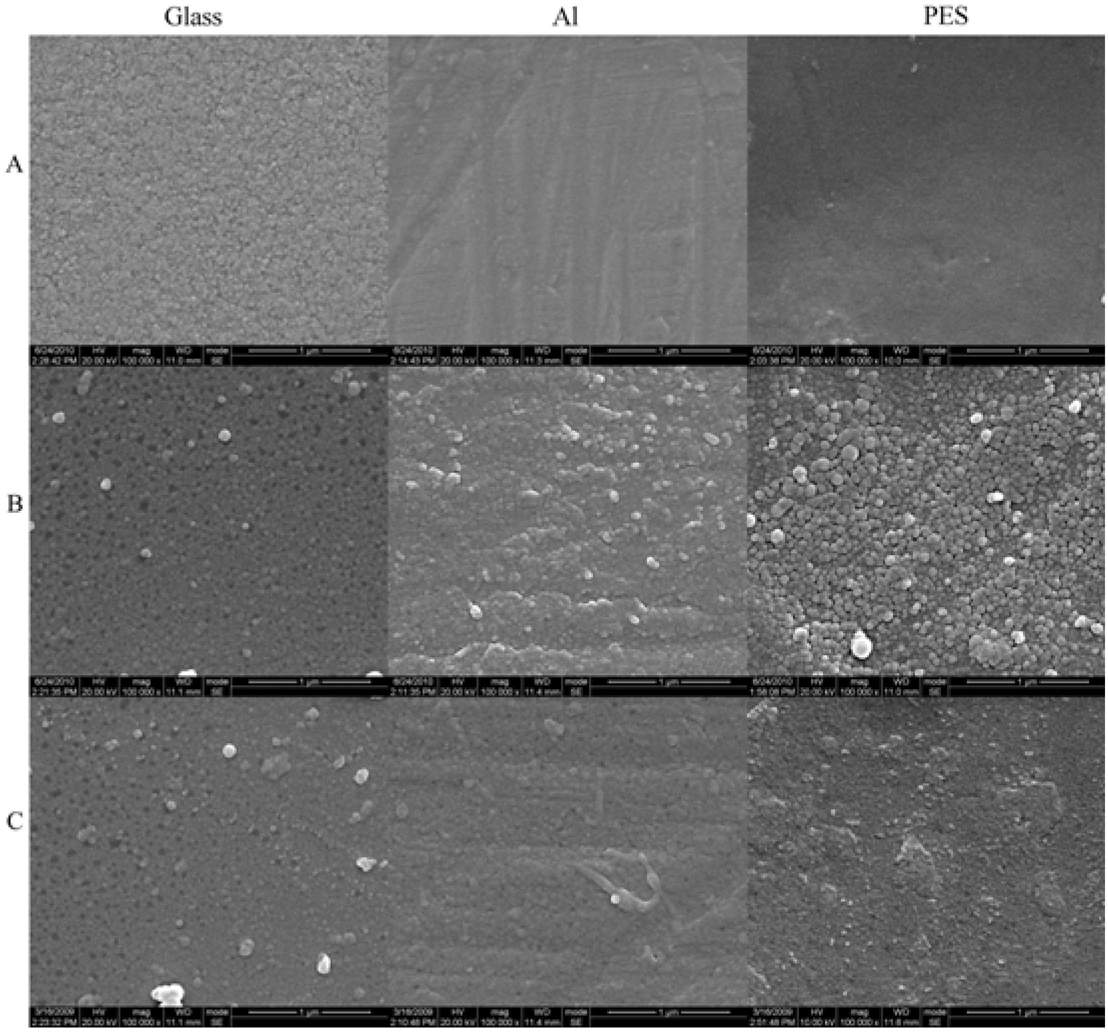


Table S1 Contact angles and roughness results of the PDA coated and uncoated glasses

Sample	θa	θr	(θa-θr)	Ra
PDA-coated glass	55.1°	41.5°	13.6°	7.20 nm
Glass	11.9°	8.8°	3.1°	3.95 nm

Table S2 Surface chemical compositions of the polydopamine-coated Nylon films before and after BSA immobilization. The data were obtained from the peak intensities of the XPS spectra shown in Figure S3 and S5.

Surface composition	C1s (%)	N1s (%)	O1s (%)
PDA-coated Nylon	70.95	8.28	20.77
BSA-PDA-coated Nylon	63.05	14.04	22.32