Electronic Supplementary Information

Dopamine assisted PMOXA/PAA brushes for their switchable protein adsorption/desorption

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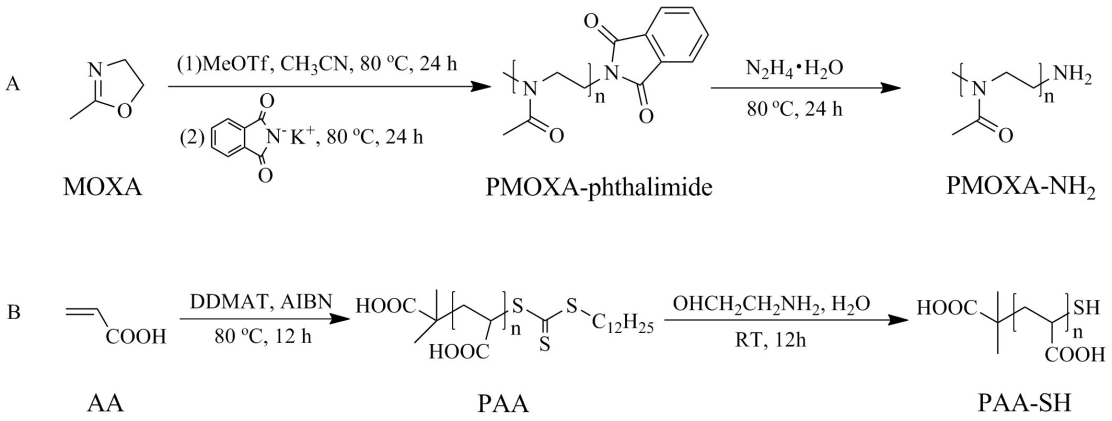

Fig. S1 Synthesis of (A) PMOXA-NH_2 and (B) PAA-SH.

Synthesis of S-1-Dodecyl- S-(α, α-dimethyl-α-acetic acid)trithiocarbonate (DDMAT) [1]

1-Dodecanethiol (20.19 g, 0.10 mol), acetone (48.1 g, 0.83 mol), and tricaprylylmethyl-ammonium chloride (1.62 g, 0.004 mol) were mixed in a three-necked flask cooled to 10 °C under a nitrogen atmosphere. Sodium hydroxide solution (50%) (8.4 g, 0.11 mol) was added over 20 min. The reaction was stirred for an additional 15 min before carbon disulfide (7.61 g, 0.10 mol) in acetone (10.09 g, 0.17 mol) was added over 20 min, during which time the color turned yellow. Ten minutes later, chloroform (17.81 g, 0.15 mol) was added in one portion, followed by dropwise addition of 50% sodium hydroxide solution (40 g, 0.5 mol) over 30 min. The reaction was stirred overnight. 150 mL of water was added, followed by 25 mL of concentrated HCl (caution! gas, odor) to acidify the aqueous solution. Nitrogen was purged through the reactor with vigorous stirring to help evaporate off acetone. The solid was collected with a Buchner funnel and then stirred in 250 mL of 2-propanol. The undissolved solid was filtered off and was identified as S, S-bis(1-dodecyl)trithiocarbonate. The 2-propanol solution was concentrated to dryness, and the resulting solid was recrystallized from hexanes to afford 20.12 g of yellow crystalline solid;

Preparation of phthalimide end-capped PMOXA (PMOXA-phthalimide) [2]

A solution of initiator (MeOTf), monomer (MOXA), and solvent (ACN) was prepared with a total monomer to initiator ratio of [M]/[I] = 25. The total monomer concentration was adjusted to 4 M. The solution was kept at 80 °C for 22 h. After cooling to room temperature a 5-fold excess of potassium phthalimide was added and the reaction mixture was stirred at 70 °C for 12 h. The reaction mixture was filtered and the solvent was removed. The residue was dissolved in chloroform and washed twice with a saturated aqueous solution of $NaHCO_3$ and once with brine. The organic phase was dried over sodium sulfate. After filtration, the polymer was concentrated under reduced pressure, precipitated into ice-cold diethyl ether, and dried at 40 °C under reduced pressure. The phthalimide end-capped PMOXA (PMOXA-phthalimide) was then confirmed by the ^{1}H-NMR spectroscopy (Fig. S2 (A)). When the integral area of the peaks for the protons of the methyl (a) at the end of PMOXA was 3.0, the integral area of the peaks of the protons from the phthalimide end group (e, f) were 4.2 calculated by the software of MestReNova, very similar to the theoretical value of 4.0 for PMOXA-phthalimide, which suggested that almost all of the obtained PMOXA chains are ended with phthalimide group.

Synthesis of amine end-capped poly(2-methyl-2-oxazoline) (PMOXA-NH_2) [2]

PMOXA-phthalimide was dissolved in ethanol and a 10-fold excess of hydrazine monohydrate was added. The reaction mixture was stirred at 70 °C for 12 h. After cooling to room temperature, a concentrated hydrochloric acid was added to adjust the pH value to 2-3. The precipitate was removed by filtration and the ethanol was evaporated. The residue was dissolved in water and aqueous sodium hydroxide solution until the pH value reached 9-10. The aqueous solution was extracted thrice with chloroform. The organic phase was dried over sodium sulfate, concentrated, and precipitated into ice-cold diethyl ether. The white precipitate was filtered off and dried at 40 °C under reduced pressure. As shown in Fig. S2, the peaks of protons from the phthalimide end group (e, f) disappeared thoroughly after removing the phthalimide end group, which illustrated that almost all of the PMOXA chains were successfully terminated with a primary amine.

Synthesis of thiol end-capped polyacrylic acid (PAA-SH) [3, 4]

Polymerizations were performed in glass vials which were placed in an oil bath thermostated at 80 °C. At first, AA,

DDMAT, AIBN, and dimethylformamide were added into a 100 mL glass flask and mixed for 2 h. Then, the reactor's contents were transferred into the glass vials by means of a syringe and was then degassed under the nitrogen atmosphere, sealed and placed in an oil bath. Polymerizations were run during 10 h for AA. The polymerizations were stopped by cooling the reaction mixture in an ice bath after distinct time periods. Then, the reaction solution was diluted in ethanol and precipitated into ice-cold diethyl ether. The light yellow precipitate was filtered off and dried at 40°C under reduced pressure. Various molar ratios of AA, DDMAT and AIBN were designed as 30:1:0.25, 50:1:0.25, and 100:1:0.25.

The resulting polymer was converted to the thiol-terminated polymer (PAA-SH) by aminolysis with ethanolamine. A typical procedure was as follows: PAA was dissolved in deionized water and then the polymer solution was added to a three-necked, round bottom flask equipped with a Teflon coated magnetic stir bar. After that, 20 mol equiv. ethanolamine was added to the polymer solution. The reaction mixture was deoxygenated by bubbling with nitrogen. The solution was then stirred at ambient temperature for 12 h, after the reaction the pH of the solution was adjusted to about 4 immediately, and then the solution was filtered. PAA-SH was obtained after purification of the polymer solution by dialysis in deionized water for 5 days and lyophilization. The obtained samples were then kept in valve bag and used immediately. The obtained PAA with different molecular weights was characterized by ^{1}H-NMR spectroscopy. As shown in Fig. S 2, after the aminolysis of PAA by ethanolamine, the peaks (d, e) of the protons of $-C_{12}H_{25}$ disappeared completely from the spectroscopy, which indicated that almost all of the end groups of $-C_{12}H_{25}$ were removed. In addition, according to the previous study,[5] there will be a shoulder peak in GPC trace of PAA-SH if the end thiol group of PAA-SH was oxidized. In our work, the GPC trace (Fig. S3) of PAA-SH presented only one peak for each polymer, suggesting that almost all of the end groups of PAA chains were transformed to -SH groups and few of the obtained PAA-SH was oxidized.

Estimation of grafting density [6]

For the pure PMOXA or PAA brush on PDA-coated surface, the grafting amount of each polymer was calculated by $A = d\rho$, and the grafting density $\Sigma = AN_A/M_w$, where d is the ellipsometric dry thickness of brush, ρ is the density (for simplicity we took always $\rho = 1$ g cm^{-3}), N_A is Avogadro's number, and M_w is the molecular weight. For the calculation of the grafting density of the polymer chains in the mixed brush (PDA/M9h/A), it was assumed that $d_{mix} = d_M + d_A$ for simplicity, where d_{mix} is the thickness of mixed brush, d_M is the thickness of pure PMOXA brush and d_A is the thickness of PAA in the mixed brush, and then $\Sigma = AN_A/M_w$ was also used for the calculation of grafting density in mixed brush. The catechols existed in PDA could be able to react with thiols and amines via Michael addition or Schiff base reactions to form covalent bond, indicating that the tethered PMOXA-NH_2 by the covalent bond is not easily displaced by other polymers. In addition, the grafting conditions for PMOXA-NH_2 are the same for all the mixed brushes. Therefore, the grafting density of PMOXA-NH_2 in mixed brush is assumed to be the same of 0.63 nm^{-2} in all the mixed brushes.

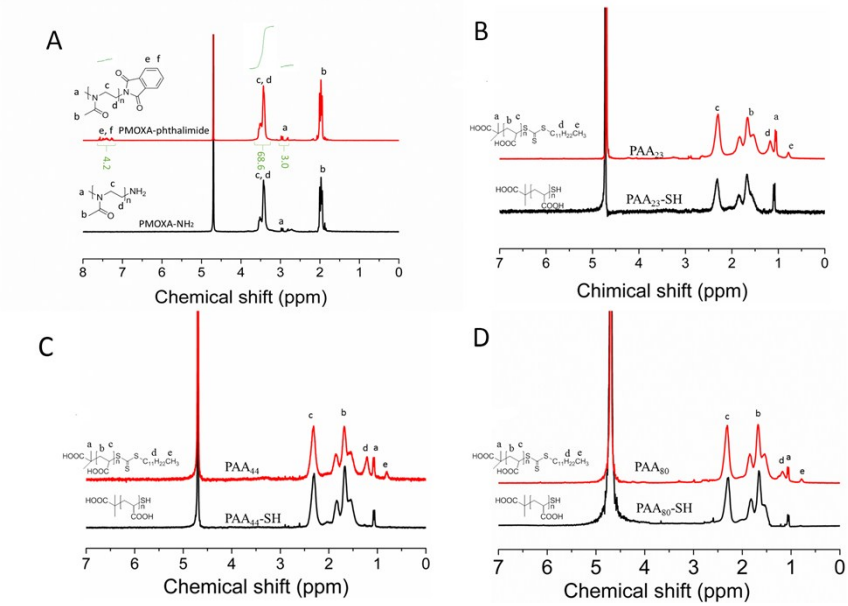

Fig.S2 ^{1}H NMR spectra of (A) PMOXA-phthalimide and PMOXA-NH_2 and (B-D) PAA and PAA-SH with different molecular weight in D_2O.

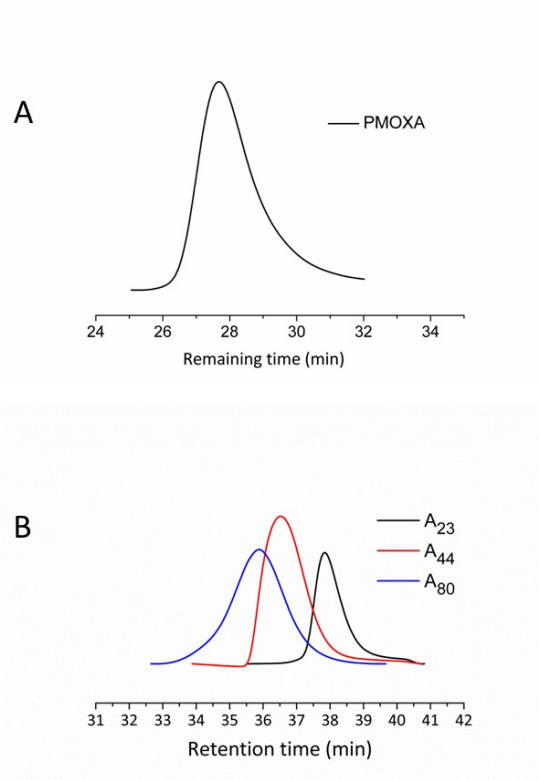

Fig.S3 GPC trace of (A) PMOXA and (B) PAA-SH with different molecular weight.

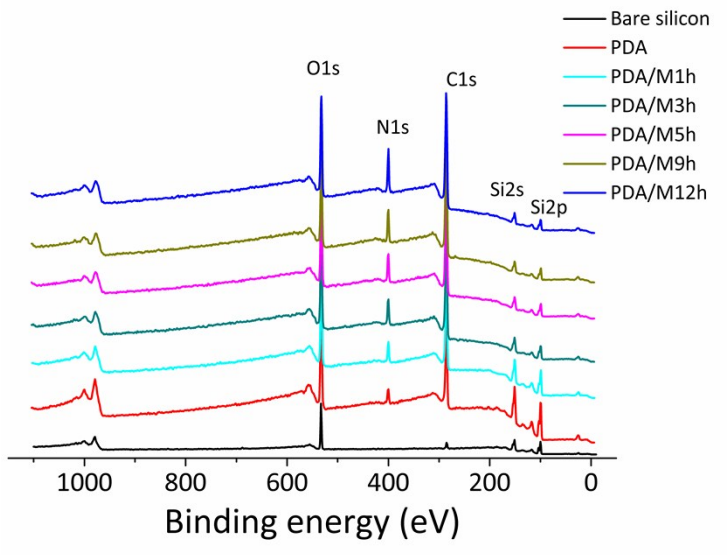

Fig. S4 XPS spectra of wide scan for the bare silicon and silicon surfaces modified by PDA, PDA/M1h, PDA/M3h, PDA/M5h, PDA/M9h, and PDA/M12h.

Table S1 The atomic percentage of elements on the bare and modified silicon surfaces based on XPS and the thickness of prepared coatings obtained by elipsometer

	Element mole percent (atom%)					
	Si(2s)	C(1s)	N(1s)	O(1s)	N/O (%)	d (nm)
Bare silicon	41.74	16.39	1.05	40.82	2.60	-
Silicon-PDA	21.69	45.06	4.56	28.69	15.9	19.71±0.56[a]
Silicon-PDA/M1h	15.68	53.3	6.6	24.42	27.0	0.86±0.21[b]
Silicon-PDA/M3h	9.18	59.97	8.53	22.32	38.2	1.52±0.12[b]
Silicon-PDA/M5h	8.06	60.72	9.74	21.48	45.3	1.85±0.28[b]
Silicon-PDA/M9h	6.55	63.66	10.29	19.50	52.8	2.06±0.25[b]
Silicon-PDA/M12h	4.59	66.27	10.43	18.71	53.1	2.01±0.36[b]

[a] Thickness of the PDA coating modified on silicon surface

[b] Thickness of prepared PMOXA brush on PDA-coated surface

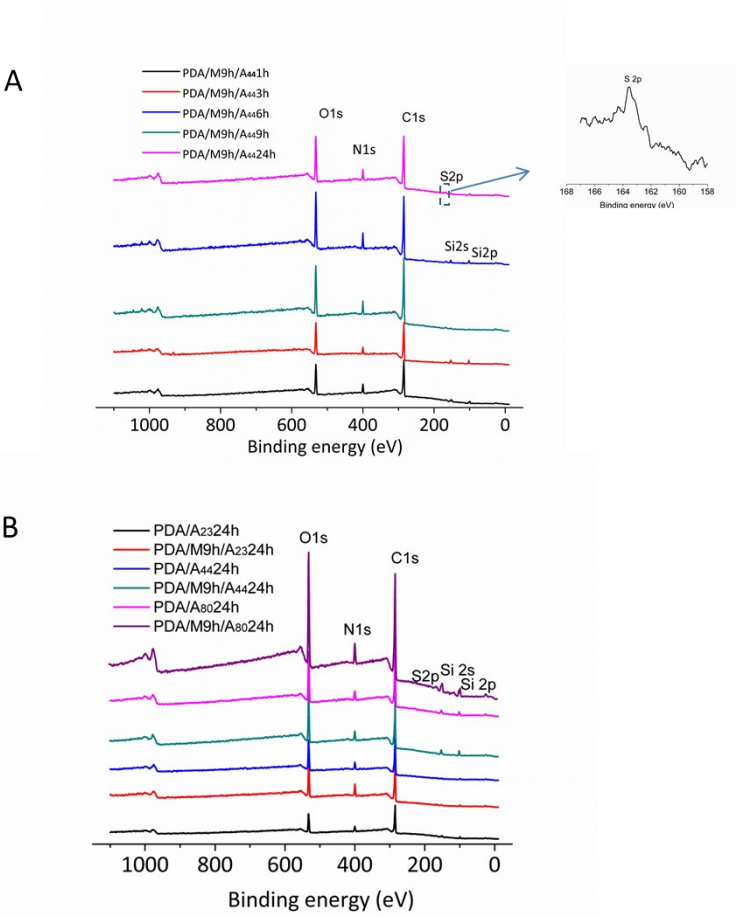

Fig. S5 XPS spectra of wide scan of (A) PDA/M9h/A_{44} with different grafting time of A_{44} as well as (B) PDA/A24h and PDA/M9h/A24h modified silicon surfaces with different molecular weights of PAA.

Table S2 The atomic percentage of elements on the bare and modified silicon surfaces based on XPS and the thickness of prepared coatings as well as the grafting density of tethered polymer chains

	Element mole percent (atom %)							
	Si(2s))	S(2p)	C(1s)	N(1s)	O(1s)	N/O (%)	d (nm)[a]	Σ (nm^{-2})[b]
Silicon-PDA/M9h/A_{44}1h	4.35	0.14	65.79	8.96	20.76	43.3	2.79±0.33	0.076
Silicon-PDA/M9h/A_{44}3h	5.75	0.26	65.57	7.38	21.05	35.1	3.15±0.27	0.11
Silicon-PDA/M9h/A_{44}6h	2.92	0.36	65.69	7.89	23.13	34.1	3.47±0.22	0.14
Silicon-PDA/M9h/A_{44}9h	1.12	0.46	68.91	7.37	22.14	33.3	3.59±0.29	0.16
Silicon-PDA/M9h/A_{44}24h	1.28	0.54	69.93	7.04	21.21	32.2	3.66±0.31	0.17

[a] The thickness of prepared brush on PDA-coated surface.

[b] The grafting density of tethered PAA chains in the mixed PMOXA/PAA brushes expressed by the chain number per square nanometer.

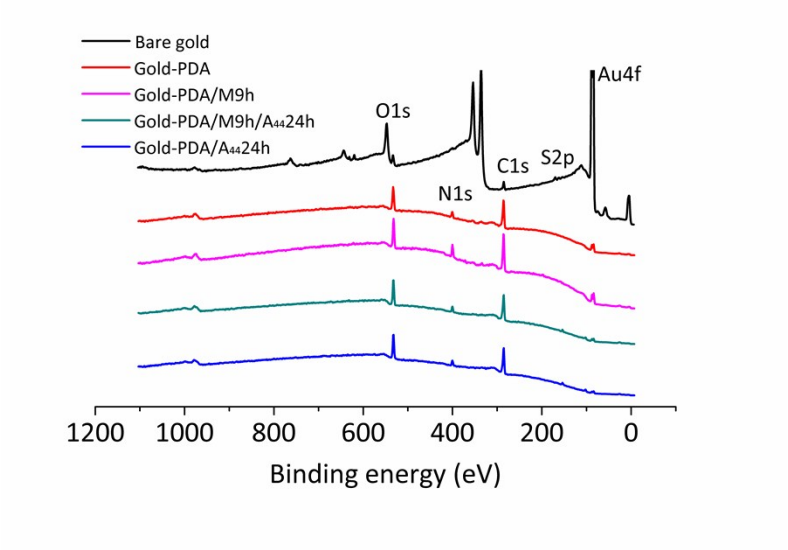

Fig. S6 XPS spectra of wide scan for bare gold surface and the gold surfaces modified by PDA, PDA/M9h, PDA/M9h/A_{44}24h, and PDA/A_{44}24h.

Table S3 The atomic percentage of elements on the bare and modified gold surfaces based on XPS

	Element mole percent (atom%)						
	Au(4f)	Si(2s)	S(2p)	C(1s)	N(1s)	O(1s)	N/O (%)
Bare gold	51.5	1.83	2.74	27.25	2.98	13.7	21.8
Gold-PDA	1.02	-	-	70.54	8.04	20.4	39.4
Gold-PDA/M9h	0.94	0.89	-	67.2	12.39	18.57	66.7
Gold-PDA/M9h/A_{44}24h	0.39	2.83	0.46	64.76	8.08	23.49	34.4
Gold-PDA/A_{44}24h	0.26	3.87	0.41	63.07	7.53	24.86	30.3

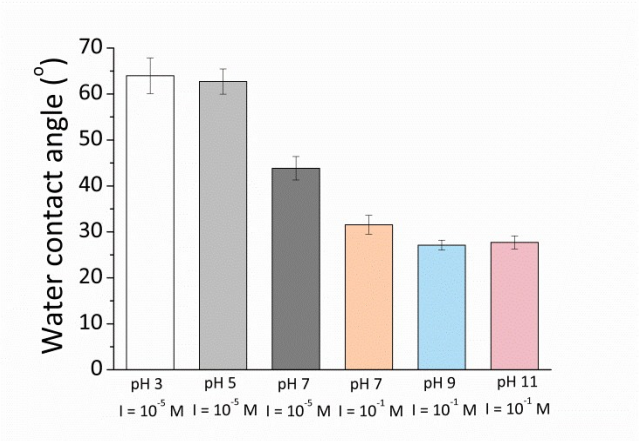

Fig. S7 Surface wettability variation for PDA/A_{44}24h modified silicon surfaces with the change of environment pH and I.

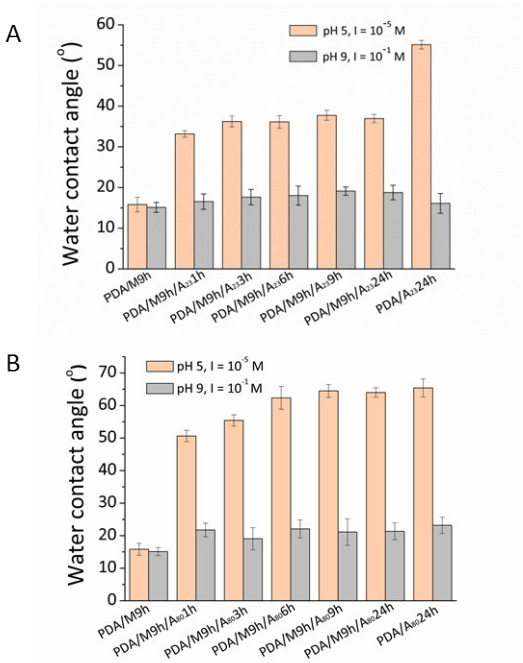

Fig. S8 Surface wettability for (A) PDA/M9h and PDA/M9h/A_{23} as well as (B) PDA/M9h/A_{80} modified silicon wafers in acid or basic conditions with different grafting time of PAA to PDA-coated silicon surfaces.

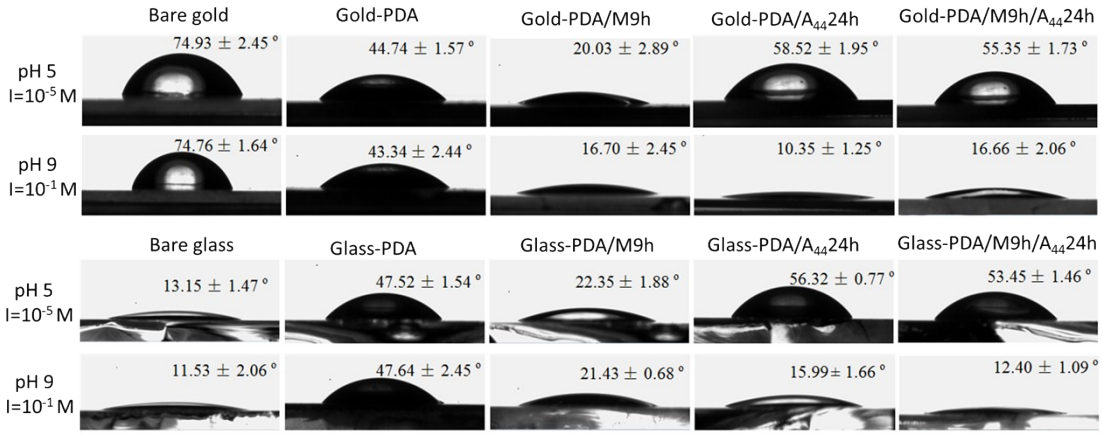

Fig. S9 Water contact angle changes on bare and modified glass and gold wafers along with the variation of pH and I.

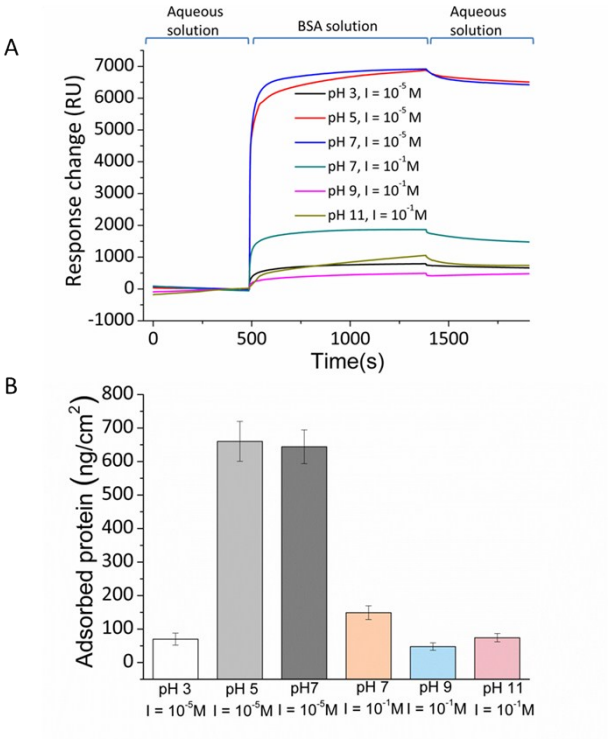

Fig. S10 (A) SPR sensorgram of BSA adsorption on PDA/A_{44}24h modified surfaces with the change of pH and I; (B) the corresponding bar graph for the amount of adsorbed proteins.

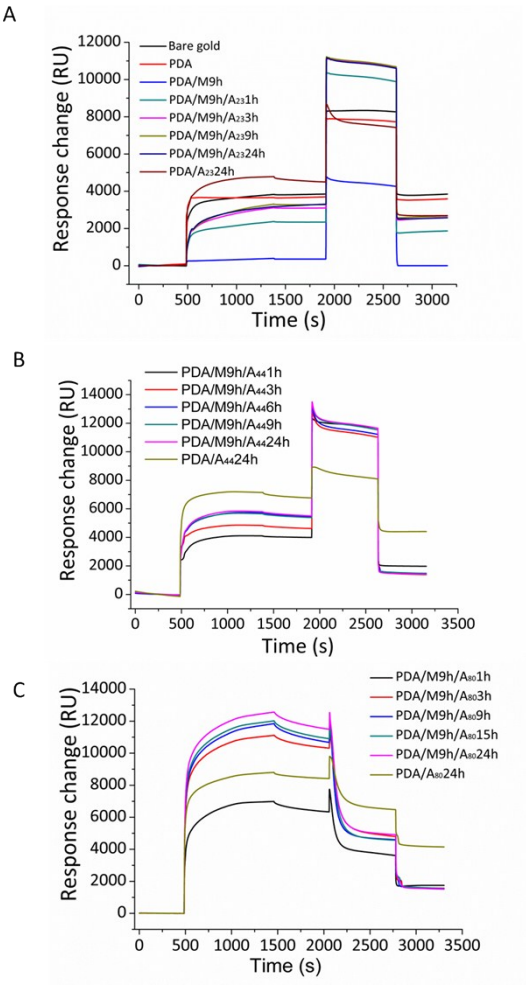

Fig. S11 SPR sensorgrams of BSA adsorption at pH 5, I= 10^{-5} M and release at pH 9, I= 10^{-1} M: (A) bare gold sensor and sensors modified by PDA, PDA/M9h, PDA/A_{23}24h, and PDA/M9h/A_{23} with different grafting time of A_{23}; (B) the gold sensors modified by PDA/A_{44}24h and PDA/M9h/A_{44} with different grafting time of A_{44}; (C) the gold sensors modified by PDA/A_{80}24h and PDA/M9h/A_{80} with different grafting time of A_{80}.

Protein preconcentration

The synthesized PDA/M9h/A_{80}24h mixed brush could also be applied in protein preconcentration. A low concentration protein solution of BSA (2×10^{-3} mg mL^{-1}) was used for SPR test. As shown in Fig. S12, aqueous solution (pH 5, I = 10^{-5} M) was first flowed at a rate of 30 µL min^{-1} through the sensor for 460 s to obtain the baseline signal, and then the protein solution (BSA of 2×10^{-3} mg mL^{-1}, the same pH and I) was flowed for 500 s for the protein adsorption. Rinsing was performed by flowing the same saline solution as previously (pH 5 and I = 10^{-5} M) for 300 s, the above process of protein adsorption and rinsing was repeated four times. In above repeated process, the total time for BSA adsorption is 2000 s. After that, another saline solution (pH 9 and I = 10^{-1} M) was flowed through the sensor for 240 s to trigger the protein desorption, and subsequently, the saline solution (pH 5, I = 10^{-5} M) was flowed for 300s. It is found that there is a largely sharp decrease of RU in short time (t = 70 s) when the saline solution (pH 9 and I = 10^{-1} M) was flowed through the sensor. It was calculated that the amount of adsorbed BSA on the modified sensor surface was 794.5 ng cm^{-2}, and 709.7 ng cm^{-2} of adsorbed BSA could then be desorbed upon changing the pH and I to 9 and 10^{-1} M in 70 s. These results indicated that about 89 % of adsorbed proteins could be released in a short time. It is suggested that the coating could preconcentrate proteins and then release them in a short time which could improve the sensitivity of protein detection.

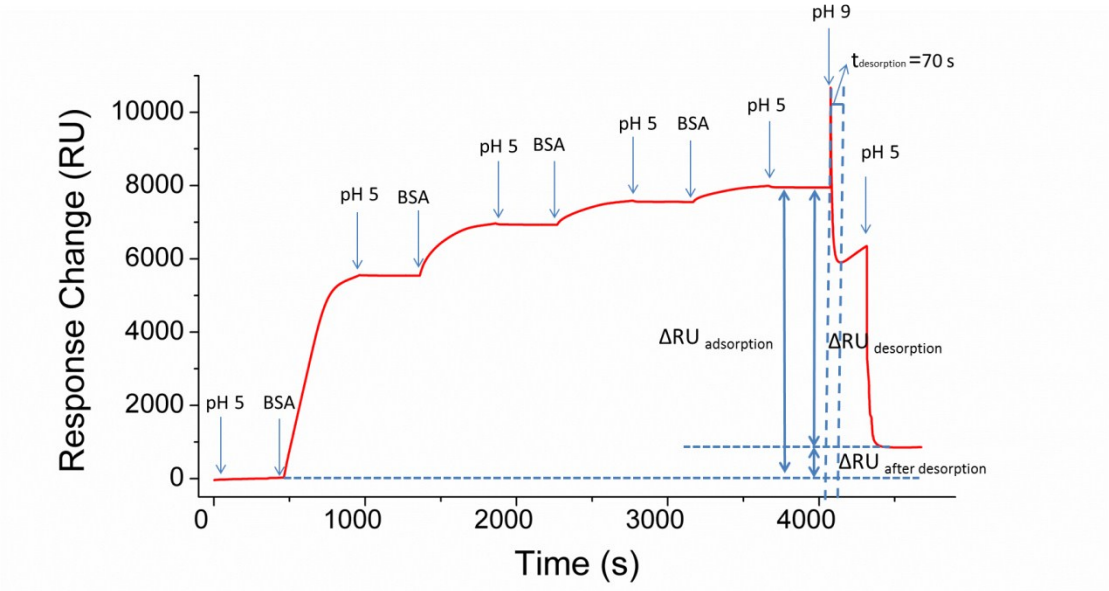

Fig. S12 SPR sensorgram of BSA (2×10^{-3} mg mL^{-1}) adsorption at pH 5, I= 10^{-5} M and release at pH 9, I= 10^{-1} M on the PMOXA/PAA mixed brush surface (Gold-PDA/M9h/A_{80}24h).

Notes and references

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