Supporting Information

1 Experimental procedures

1.1 Materials

The monomer *tert*-butyl methacrylate (tBMA, Aldrich, 98%) was passed through a column of activated basic alumina prior to use. Copper (I) bromide (CuBr, Fluka) and Copper (II) bromide($CuBr_2$, Aldrich) were recrystallized before use. 3-Aminopropyltriethoxysilane (APTES, Aldrich), bromoisobutyryl bromide (BIBB, Fluka) and 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, Aldrich) were used as received. Silicon wafers were purchased from Guangzhou Semiconductor Materials (Guangzhou, China). Deionized water purified by a Millipore water purification system to give a minimum resistivity of 18.2 MΩ·cm was used in all experiments. Lysozyme (MW=14.7 kDa, pI=12) was obtained from Sigma Chemical Co. (St. Louis, MO). Fibrinogen (MW= 341 kDa, pI=5.5) was purchased from Calbiochem (La Jolla, CA).

1.2 Preparation of Silicon nanowire arrays

The silicon nanowire arrays (SiNWAs) were prepared by chemical etching of crystalline silicon in $HF/AgNO_3$ aqueous solution. Briefly, silicon wafers were cleaned in a freshly prepared piranha solution (H_2SO_4:H_2O_2=7:3(v/v) **Caution: piranha solution reacts violently with organic materials and should be handled carefully!**) at 90 °C for 2 h and were then rinsed with distilled water and dried in a stream of argon. The cleaned silicon wafers were immersed in the etching solution containing 5.0 $mol \cdot L^{-1}$ HF and 0.015 $mol \cdot L^{-1}$ $AgNO_3$ at 50 ^oC for 30 min. The resulting surfaces were immersed in 20 % nitric acid for 1 min and then rinsed copiously with deionized water.

1.3 Preparation of SiNWAs-poly(MAA)

The initiator was immobilized on the SiNWAs followed the procedures reported previously [1]. ATRP grafting of tBMA was carried out as follows. tBMA (4 mL, 25 mmol), $CuBr_2$ (3.3 mg, 0.015 mmol), CuBr (7.15 mg, 0.05 mmol), PMDETA (0.031 mL, 0.15 mmol) and 3 mL acetone were mixed in a flask. The heterogeneous reaction solution was degassed with three freeze–pump–thaw cycles and then stirred at 60 ^oC for 20 min until it became clear and homogeneous. The solution was then transferred to a Schlenk flask containing the initiator functionalized SiNWAs via syringe. The polymerization was allowed to proceed at 60 ^oC for 4 h. Afterwards the wafers were taken from the polymerization solution, rinsed thoroughly with acetone and finally dried under an argon flow. The poly(t-BMA) modified SiNWAs were then placed in a flask containing a mixture of 1,4-dioxane (20 mL) and concentrated HCl (37 %, 3 mL). The reaction was carried out at 80 ^oC for 2 h to hydrolyze poly(t-BMA) to poly(MAA). The resulting surfaces were thoroughly rinsed with acetone and ethanol and dried under an argon flow. The attachment of poly(MAA) onto

smooth silicon surfaces was carried out in the same manner. The nanostructures and surface morphology of SiNWAs and SiNWAs-poly(MAA) were observed using a field-emission scanning electron microscope (FESEM, S-4800, Japan) and a transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin, American) .

2 Surface characterization

2.1 XPS

The chemical composition of the modified SiNWAs was determined with an ESCALAB MK II X-ray photoelectron spectrometer (XPS) (VG Scientific Ltd.). All XPS data were analyzed using XPS Peak 4.1 software. The survey spectra and the C/O ratio of the SiNWAs-poly(tBMA) and SiNWAs-poly(MAA) grafted surfaces are shown in **Figure S1** and **Table S1**.

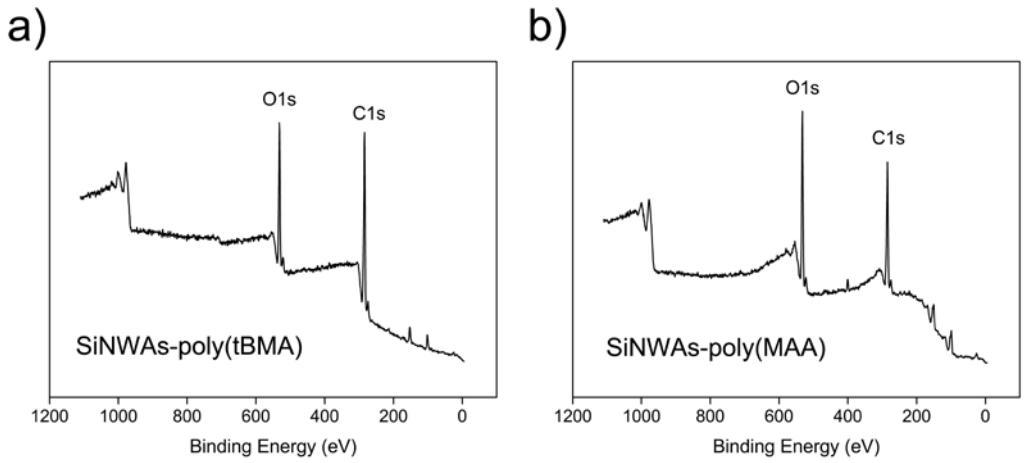

Figure S1. XPS survey spectra of a) SiNWAs-poly(tBMA) and b) SiNWAs-poly(MAA) surfaces.

Table S1. Chemical composition of modified SiNWAs

Surface	C/O (experiment)	C/O (theory)
SiNWAs-poly(tBMA)	3.54	3.50
SiNWAs-poly(MAA)	1.95	2.00

2.2 Contact angle measurement

Static water contact angle measurements were performed using the sessile drop method with a C201 optical contact angle meter (Solon Information Technology Co., Ltd.). The smooth Si-poly(MAA) and SiNWAs-poly(MAA) surfaces were immersed in PBS at a specified pH (either 4 or 9) for 30 min and then dried immediately in an argon flow followed by water contact angle measurement. The oil (1,2-dichloroethane, CH_2Cl_2) contact angles in PBS with different pH were also measured. The results are summarized in **Table S2** and **Figure S2**. The results showed that the SiNWAs-poly(MAA) surfaces were superhydrophilic (water contact angle $<5\ ^{o}$) and superoleophobic (oil contact angle $>150\ ^{o}$) independent of pH.

Table S2. Contact angle of samples at different pH

Surface	Contact angle (°) [a]			
	at pH 4		at pH 9	
	water	CH_2Cl_2	water	CH_2Cl_2
Si-poly(MAA)	48.9	136.4	12.1	>150
SiNWAs-poly(MAA)	< 5	>150	< 5	>150

[a] Each value is the average of six parallel measurements. The standard error is less than 2 °.

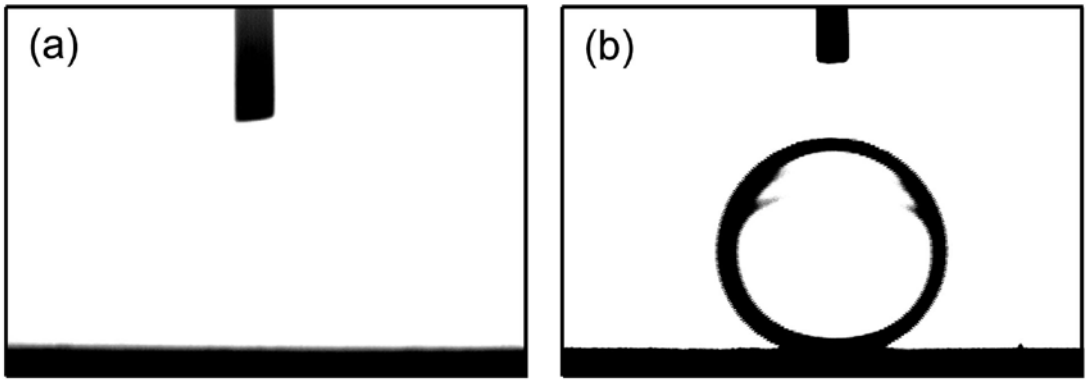

Figure S2. Water (a) and CH_2Cl_2 (b) contact angles of SiNWAs-poly(MAA) surface. The contact angles are independent of pH.

3 Preliminary experiments of protein adsorption

Phosphate buffered saline (PBS, 10 mM) solutions of different pH were used to prepare protein solutions. The pH of the PBS was preadjusted by adding aqueous NaOH or HCl solution until the desired values were reached. Lysozyme or fibrinogen adsorption from PBS buffer (1mg/mL) at room temperature (23 °C) was determined by radiolabeling with ^{125}I using a Wizard 3″1480 Automatic Gamma Counter (Perkin-Elmer Life Sciences) [1]. Protein desorption tests were performed on samples that were adsorbed with radiolabeled proteins at pH 4. These samples were transferred to fresh PBS at pH 9 and incubated for 3 h at room temperature; the quantity of protein remaining on the surfaces was measured. In all cases, radioactivity was converted to adsorbed protein amount. Because it is very difficult to calculate the absolute surface area of SiNWAs, the amount of protein adsorption is expressed as μg /disc (for one disc the "apparent" surface area is 0.5 cm^2).

3.1 Selection of adsorption time

The kinetics of lysozyme adsorption on SiNWAs-poly(MAA) surface was investigated (**Figure S3**). The time course of adsorption was typical with relatively rapid adsorption initially, gradually leveling off to a plateau after ~3 h. Therefore, we chose 3 h period as adsorption time for the following protein adsorption measurements.

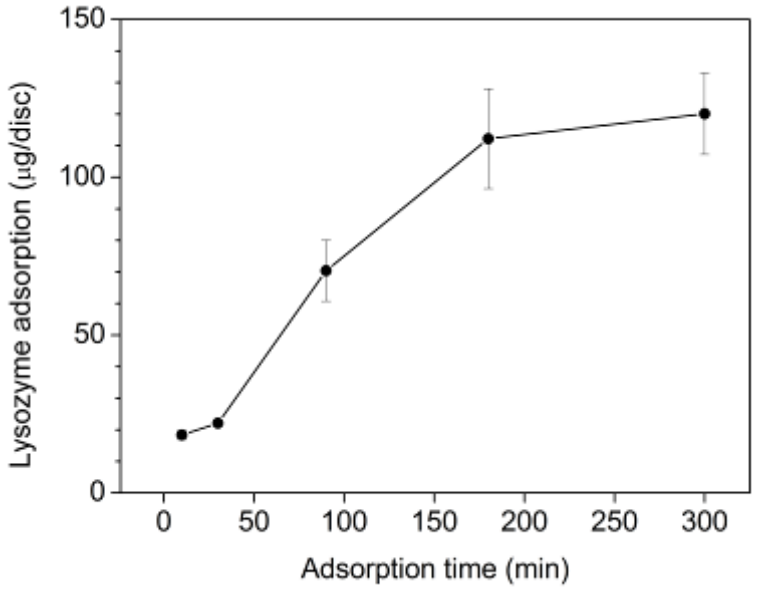

Figure S3 Kinetics of lysozyme adsorption on SiNWAs-poly(MAA) surface at pH 4. The "apparent" surface area of one disc is 0.5 cm^2. Data are means ± standard error (n=3).

3.2 Selection of adsorption pH and poly(MAA) chain length

PBS solutions of different pH (from 4 to 9) were used to prepare protein solutions. The chain length of grafted poly(MAA) was regulated via changing the polymerization time (30 min, 120 min and 240 min). Smooth Si-poly(MAA) surfaces were prepared as control, and the corresponding thickness of grafted layer is 2.3±1.5 nm, 12.8±1.8 nm, and 18.3±2.1 nm for the Si-poly(MAA) surface with polymerization time of 30 min, 120 min and 240 min. Lysozyme adsorptions from PBS buffer (1mg/mL) with different pH (from 4 to 9) on SiNWAs-poly(MAA) surfaces with different poly(MAA) chain length were shown in **Figure S4**. Based on the results, we chose 4 and 9 as test pH and the SiNWAs-poly(MAA) surface with polymerization time of 240 min for the further investigation.

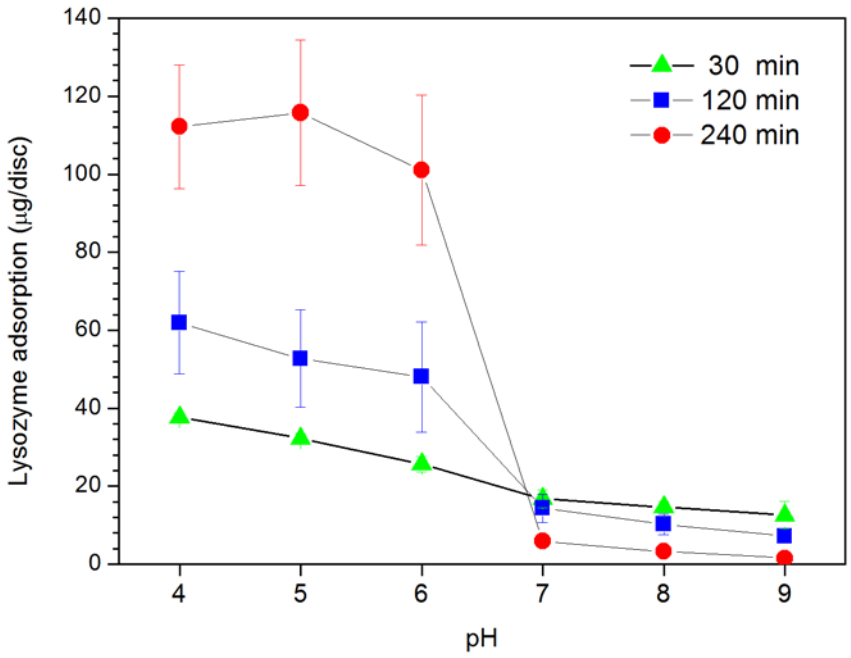

Figure S4 Lysozyme adsorptions from PBS buffer (1mg/mL) with different pH (from 4 to 9) on SiNWAs-poly(MAA) surfaces with different polymerization time. The "apparent" surface area of one disc is 0.5 cm^2. Data are means ± standard error (n=3).

4 Assay of lysozyme activity

The surfaces were incubated with lysozyme in PBS (pH 4) at 37 ^oC for 3 h with the final concentration of lysozyme at 1 mg/mL. The samples were then washed in PBS (pH 4), placed in reaction buffer (0.1 M sodium phosphate, 0.1 M NaCl, pH 7.5, containing 2 mM sodium azide) and mixed with the fluorescent substrate (EnzChek® Lysozyme Assay Kit, Invitrogen). The reaction was performed at 37 ^oC for 0.5 h, and the products of the fluorescent substrate were measured at Ex490/Em525. The activity of desorbed lysozyme after incubation with PBS (pH 9) for 3 h was measured in the same way.

References

[1] Yu, Q.; Zhang, Y.; Chen, H.; Wu, Z.; Huang, H.; Cheng, C. *Colloids and Surfaces B: Biointerfaces* **2010**, 76, 468-474.