Supporting Information

A Highly Efficient Bactericidal Surface Based on the Co-Capture Function and Photodynamic Sterilization

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The method for preparing silicon nanowire array (SiNW)[1, 2]

Firstly, silicon wafer was ultrasonically cleaned with acetone, ethanol and DIW by 5 min in each solution. Then the cleaned silicon wafer was immersed into the piranha solution (98% sulfuric acid: 30% hydrogen peroxide = 7:3) boiled on heater at 2 h. Afterward, it was rinsed by massive DIW and obtained the superhydrophilic silicon wafer surface (Si-OH). Secondly, we put the wafer into 5% HF aqueous resting for 10 min and the silicon wafer was shown up as superhydrophobic, then immersed it into Ag nanoparticle deposited solution of 5 M HF and 0.02 M $AgNO_3$ mixture at 60°C about 2 min. And finally, it was soaked in the chemical etching solution of HF-H_2O_2-H_2O for 2 h, thereafter put it into the boiling aqua regia (HCl: HNO_3 = 3:1) for 30 min to remove the Ag nanoparticle, dried with argon to obtain SiNW.

The synthesis of 1-adamantan methyl methacrylate (AdMA)[3]

Briefly, 2.5 g 1-adamantan methanol was added into the 250 mL round-bottom flask which contained 3 mL triethylamine and 60 mL dichloromethane under the ice bath, and then 2.3 mL methacryloyl chloride in 20 mL dichloromethane solution was added dropwise into the flask via dropping funnel. Removing the ice bath when the

solution was added finish, and reacted another 24 h at temperature. Then, 0.1 M $NaHCO_3$, 0.1 M HCl and cold saturated NaCl should be used to extract the resultant, removing the organic solution by rotary evaporation and using petroleum: acetic ether = 40 : 1 as the eluant to purify the products by column chromatography, finally obtained the white crystalline substance.

The synthesis of heptad-azide β-CD.

The heptad-azide β-CD was prepared by our previous reports.[4] Before we utilized β-CD, standard method to purify it had been described above. 3.68 g triphenylphosphine was dissolved in 25 mL DMF, and then 3.56 g iodine was added into it at 50°C stirring for 20 min. After that, 1.14 g β-CD was put into the solution under protecting of argon and reacting at 70°C for 24 h. When most of DMF had been removed by rotary evaporation and being viscous, 13 mL (3 mol/L) sodium methanolate was added dropwise to adjust the pH value of the solution nearly at 8 and keeping stirred 1 h under the ice bath circumstance for safety. Afterward, precipitating the products by substantial methanol, collecting the white substance after centrifugation and repeated three times, and finally put the products into oven at 60°C over night to obtain iodine substituted β-CD (β-CD-I_7). 432mg β-CD-I_7 was dissolved in 5 ml DMF excluding oxygen, and 148 mg NaN_3 was thrown into the reactor for stirring 24 h at 70°C. And then pour into DIW to quench the reaction, collecting the white solid after centrifugation and dried under the oven at 60°C over night to get the heptad-azide β-CD (β-CD-$(N_3)_7$).

The synthesis of alkynyl mannose.

The synthesis of alkynyl mannose is describing as the report.[5] Owing to the different reactivity of the C-6 on the pyranose ring, we can protect partial group on it to realize accurately substituting the hydroxyl of the C-6 by propynol. The synthesis route of alkynylmannose is shown as the scheme 2. 5 g D-(+)-mannose was dissolved in the 25 mL acetic anhydride and 25 mL pyridine mixture solution at 100 mL round-bottom flask via magnetic stirring uniformly under the ice bath. 0.5 g DMAP was

slowly added into the flask and stirring until the mixture solution became clarify, keeping reaction at room temperature overnight. After removing massive solution by rotary evaporation, 200 mL cold water and 50 mL dichloromethane were poured into the residual slurry and stirring vigorously about 3 h. The results can be separated from the mixture solution through extraction method. Using 50 mL dichloromethane to extract the water layer three times and combing the organic layer, then dried by anhydrous Na_2SO_4, evaporated the solvent and obtained per-acetyl-mannose (5AcO-mannose). 10 g 5AcO-mannose and 2.59 g propynol were dissolved in 20 mL dichloromethane and therewith added slowly 10 mL dichloromethane containing 6.4 mL $BF_3 \cdot Et_2O$ into it under the ice bath, reacted at room temperature for 24 h. Washing the reaction solution by $NaHCO_3$ aqueous and rotating the solvent to evaporate fully to get the acetyl-alkynylmannose (4AcO-alkynylmannose). 1 g 4AcO-alkynylmannose was dissolved in the ethanol at room temperature and stirring for 3 h, among this period 3 M NaOH aqueous was added dropwise into it and thereafter adjusted the pH value at 4 by 1 M HCl, reacted more 10 min to adequately hydrolyze. And finally removed solvent by rotary evaporation and purified the products via column chromatography with dichloromethane: methanol = 4 : 1 as the elution to obtain alkynyl-mannose.

The synthesis of heptad-mannose β-CD (β-CD-mannose$_7$).

The synthesis of heptad-mannose β-CD (β-CD-mannose$_7$) was prepared as the report.[3] 349 mg (1.6 mmol) alkynyl-mannose, 262 mg (0.2 mmol) β-CD-$(N_3)_7$ and 50 mg 2-2’ bipyridine was dissolved in 5 mL DMSO, and then using freeze-pump-fill argon-thaw method to remove oxygen of solution. 23 mg (0.16 mmol) CuBr was added into the deoxygenation solution and reacted at 50°C under the argon atmosphere for 24 h. After removed the DMSO and precipitated by methanol, white substance(β-CD-mannose$_7$) could be obtained by centrifugation and dried in oven for 24 h.

The synthesis poly(HEMA-AdMA)-ppix

The ppix grafted on the poly(HEMA-AdMA) was synthesized according to the reports with mirror emendation.[6] 47 mg (83.5μmol) ppix, 20 mg (104.4 μmol)

EDC·HCl and 11.7 mg (104.4 μmol) DMAP were added into 10 mL DMSO under the argon steam bubbling 30 min to activate the carboxyl groups of ppix. 300 mg poly(HEMA-AdMA) was thrown into the vessel and reacting 24 h at 35°C protected from light. After finished, DMF and methanol mixture solution was applied to dialyze the reaction liquid until the dialysis cylinder didn't exist color then exchanged DIW to dialyze about 1 d, after freezing-drying the solution we can obtain the polymers modified by ppix (poly(HEMA-AdMA)-ppix).

Characteristic of ^{1}H NMR and FT-IR for poly(HEMA-AdMA) and β-CD-mannose$_7$

The random polymer of 2-hydroxyethyl methacrylate (HEMA) and 1-adamantan methyl methacrylate (AdMA) can be obtained on the SiNW surface (SiNW-polymer) via atom transfer radical polymerization (ATRP).[7]

Because it was difficult to measure the structure of poly(HEMA-AdMA) on the surface of SiNW-polymer, we could employ the sacrificing initiator method to simulate the composition of it through analyzing the polymer which initiated by EBIB in the solution. The ^{1}H NMR of poly(HEMA-AdMA) was shown in Figure S1. Through calculating the integral area of peak a_1, b_1 and c_1, we found that the ratio among them was 70 : 70 : 2, that was equivalent as m : n = 70 : 2. Although it had some deviation compared with the initially feed ratio (98 : 2), that was enough to realize the subsequent modification on the wafer.

Then ^{1}H NMR and FT-IR were applied to examine the structure of β-CD-(mannose)$_7$ to testify our guest molecules as shown in Figure S2-5. Compared with the 5AcO-mannose (Figure S2(a)), 4AcO-alkynylmannose had an obvious single peak at 2.47 ppm, which contributed to the H chemical shift of end alkynyl (Figure S2(b)). Furthermore, the value increased to 2.85 ppm after acetyl hydrolysis into hydroxyl and the other chemical shift of the carbons on pyranose ring had minor variation (Figure S2(c)). To examine the structure in more accurate manners, FT-IR was employed to examine it. Both of 4AcO-alkynylmannose and alkynylmannose had an absorbed peak at 2117 cm^{-1} owing to the alkynyl (Figure S3), hence we may conclude that the

alkynylmannose had been synthesized. After interaction with β-CD-$(N_3)_7$ via click chemistry reaction, the β-CD-mannose$_7$ was obtained. ^{1}H NMR and FT-IR were given in Figure S4-5. Compared to the chemical shift of β-CD-$(N_3)_7$, the β-CD-mannose$_7$ had a strong peak at 7.9 ppm which contributed to the H of triazolyl according the report.[3] To further confirm the reaction successfully performed, FT-IR was also employed to examine it. At the 2107 cm^{-1}, there were no absorbed summit in β-CD and β-CD-I_7, but it extremely appeared in β-CD-$(N_3)_7$ and finally entirely disappeared in β-CD-mannose$_7$. Thus we could claim that our guest molecules had been successfully prepared.

Calculation the mounts of ppix on poly(HEMA-AdMA)-ppix

Before detected the ROS production, we have roughly calculated the ppix content grafted on the poly(HEMA-AdMA). The gel permeation chromatography (GPC) measurement can provide the molecular weight of pure poly(HEMA-AdMA) (M_n=22000 g/mol) and poly(HEMA-AdMA)-ppix (M_n=28500 g/mol) as shown in Table S1. The ratio between HEMA and AdMA was 70 : 2 from the chemical structure in Figure S1(a). The molecules increasement from 22000 g/mol to 28500 g/mol could be attributed the ppix grafted on the hydroxyl pendant in HEMA. Thus, the mounts of ppix on poly(HEMA-AdMA)-ppix was estimated as 7.5%, which could produce enough ROS to kill bacteria.

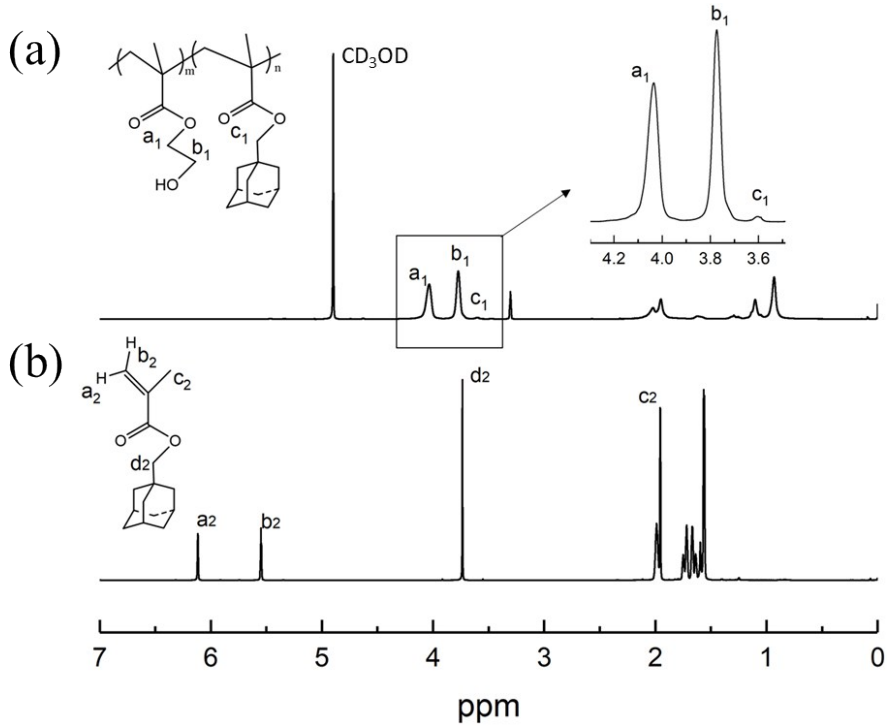
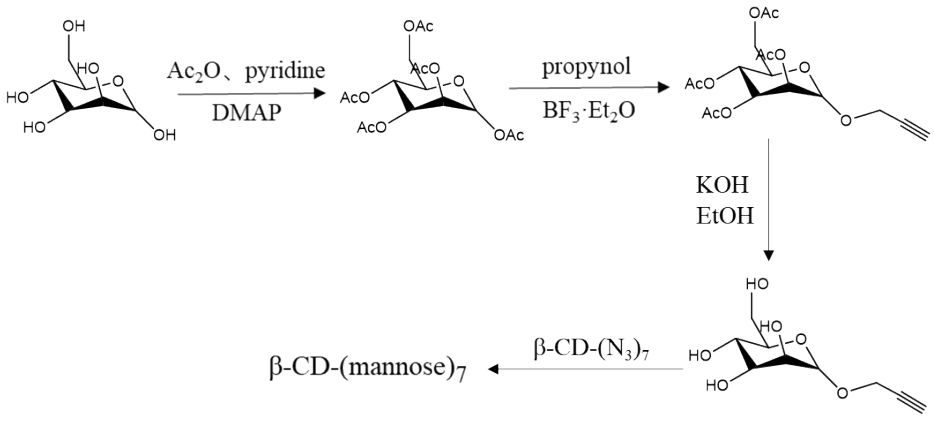


Figure S1. ^{1}H NMR spectrum of (a) poly(HEMA-AdMA), ^{1}H NMR (400 MHz, CD_3OD) *δ 3.95 (s, 70H), 3.69 (s, 70H), 3.51 (s, 2H)*; (b) 1-Adamantane-methanol, ^{1}H NMR (400 MHz, $CDCl_3$) *δ 6.18-6.04 (m, 1H), 5.55 (p, J = 1.5 Hz, 1H), 3.74 (s, 2H), 1.96 (dd, J = 7.7, 6.6 Hz, 6H), 1.78-1.49 (m, 13H).*

Table S1 The GPC results of polymer and ppix grafted polymer (polymer-ppix).

Sample Name	Retention Time (s)	M_n (g/mol)	Polydispersity
A	20.4	22000	1.20
B	19.5	28500	1.20

A = poly(HEMA-AdMA); B = poly(HEMA-AdMA)-ppix



Scheme S1. Synthesis route of heptad-mannose modified β-CD (β-CD-mannose$_7$).

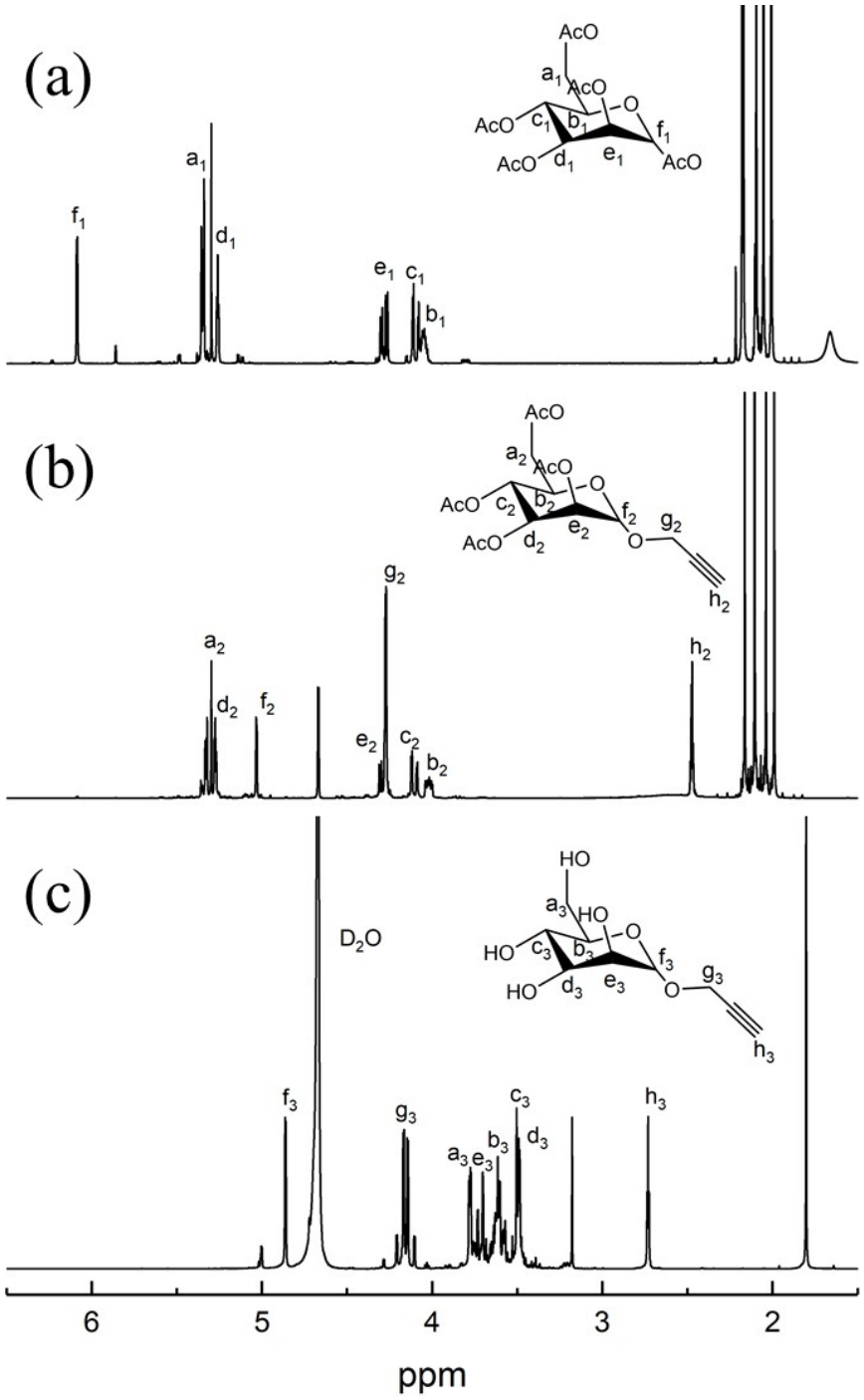


Figure S2. ^{1}H NMR spectrum of (a) 5AcO-mannose, ^{1}H NMR (400 MHz, $CDCl_3$) *δ 6.09 (s, 1H), 5.34 (s, 2H), 5.26 (t, J = 2.4 Hz, 1H), 4.26 (s, 1H), 4.11 (s, 1H), 4.04 (ddd, J = 9.1, 5.7, 2.3 Hz, 1H)*; (b) 4AcO-alkynylmannose, ^{1}H NMR (400 MHz, $CDCl_3$) *δ 5.32 (s, 2H), 5.28 (d, J = 1.9 Hz, 1H), 5.04 (s, 1H), 4.34-4.28 (m, 1H), 4.27 (s, 2H), 4.10 (d, J = 12.3 Hz, 1H), 4.03 (ddd, J = 7.6, 6.9, 4.4 Hz, 1H), 2.47 (s, 1H)*; and (c) alkynylmannose; ^{1}H NMR (400 MHz, D_2O) *δ 4.98 (d, J = 1.6 Hz, 1H), 4.31-4.24 (m, 2H), 3.93-3.84 (m, 2H), 3.83-3.80 (m, 1H), 3.73-3.70 (m, 1H), 3.62 (t, J = 5.3 Hz, 1H), 3.61-3.56 (m, 1H), 2.85 (t, J = 2.4 Hz, 1H)*.

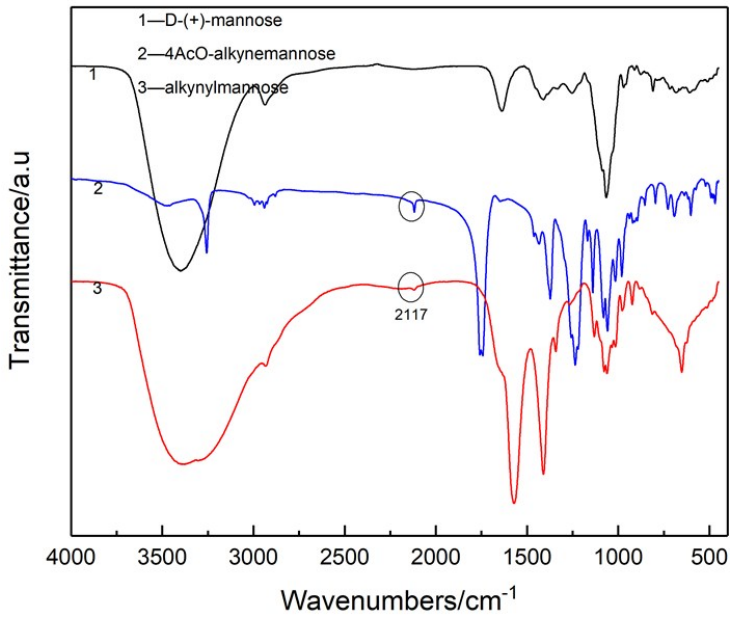


Figure S3. The FT-IR spectrum of alkynylmannose and its intermediate product.

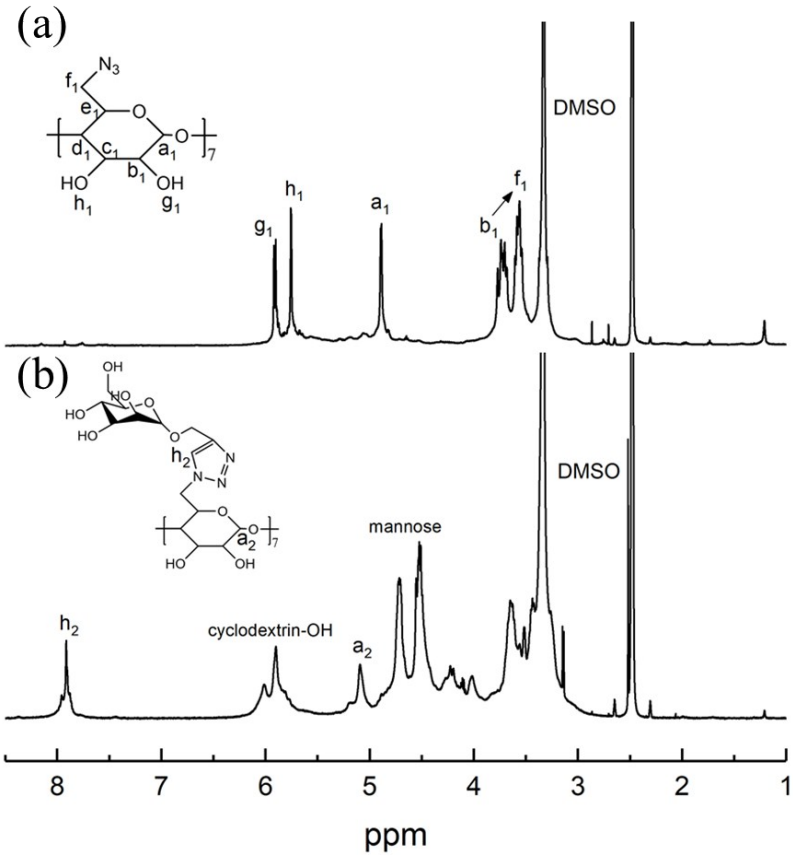


Figure S4. ^{1}H NMR spectrum of (a) β-CD-$(N_3)_7$, ^{1}H NMR (400 MHz, DMSO) *δ 5.90 (s, 7H), 5.72 (s, 7H), 4.89 (s, 7H), 3.98-3.40 (m, 42H)*; and (b) β-CD-mannose$_7$, ^{1}H NMR (400 MHz, DMSO) *δ 7.90 (s, 7H), 5.89 (s, 14H), 5.08 (s, 7H)*.

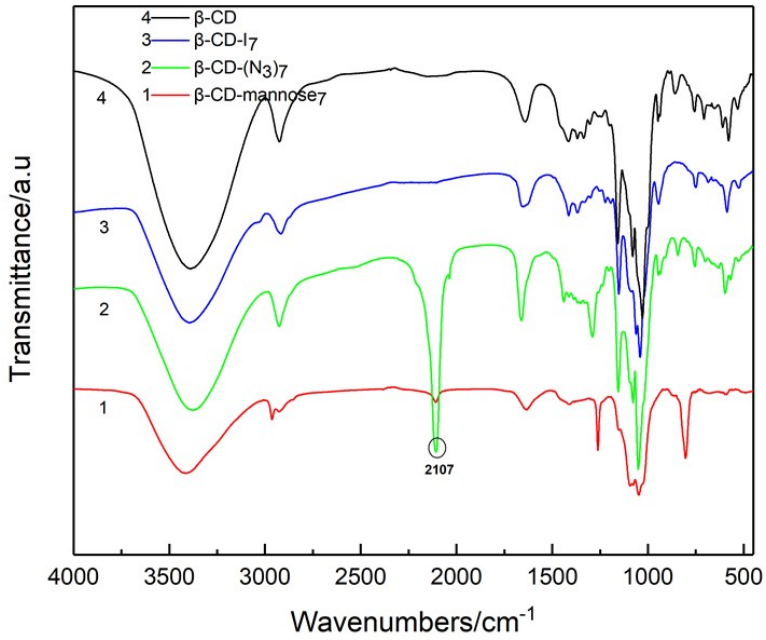


Figure S5. The FT-IR spectrum of β-CD-mannose$_7$ and its intermediate product.

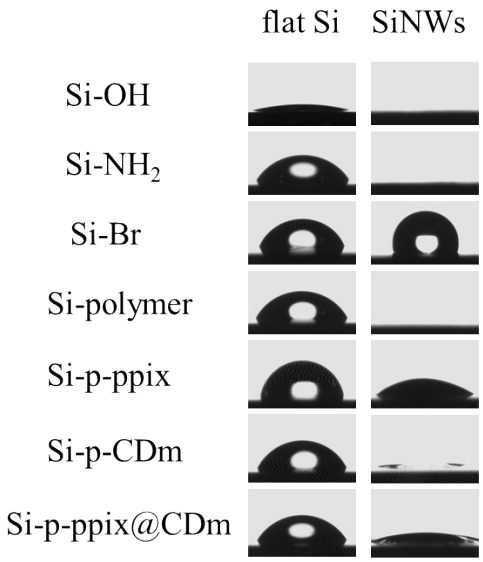


Figure S6. The WCA of droplet graph for different modification wafers at ambient temperature.

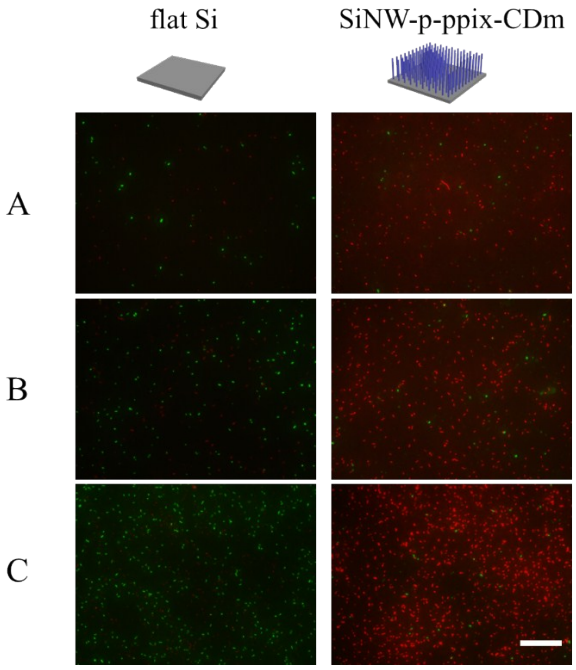


Figure S7. The fluorescence microscope image of flat Si wafer and SiNW-p-ppix@CDm incubated with different concentration of *E.coli* (the CFU of A, B, and C were respectively at 10^2, 10^4, and 10^6 mL^{-1}) and stained by Live/Dead bacteria kits after irradiation by 630 nm light for 10 min. Scale bar for all images is 20 μm.

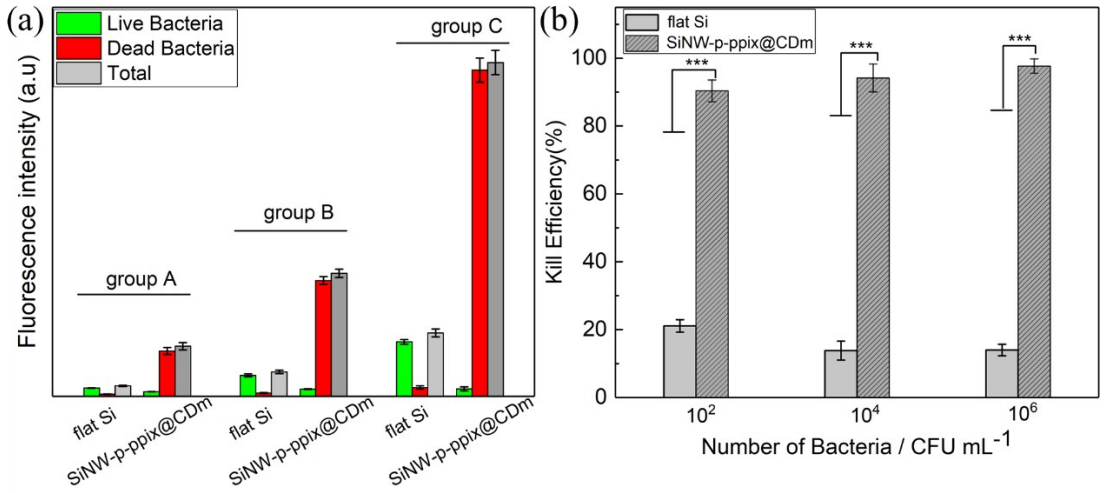


Figure S8. The histogram of fluorescence intensity (a) and kill efficiency (b) for bacteria attached on the flat Si and SiNW-p-ppix@CDm wafer analyzed by Image J. The CFU in group A, B, and C were 10^2, 10^4, and 10^6 mL^{-1} respectively. Standard error, n = 3, ***$p < 0.001$.

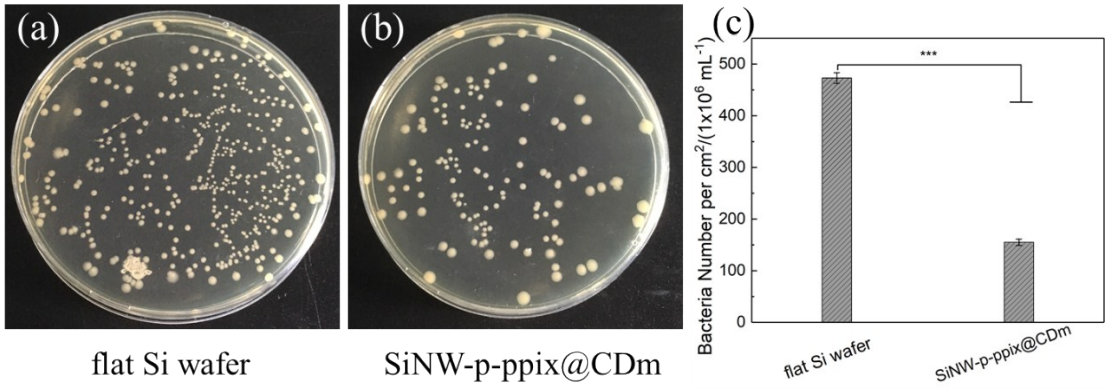


Figure S9. Photograph of the spread plate for bacteria of the culture medium incubating 12 h after removed the wafer which incubated for 24 h and then irradiated by 630 nm light for 10 min, and finally diluted into CFU = 1×10^{-6} mL^{-1}. (a) and (b) were the photograph of bacteria culture medium, removed flat Si and SiNW-p-ppix@CDm wafer respectively. (c) was the statistical data corresponded to the spread plate. They are mean ± standard error, n = 3, ***$p < 0.001$.

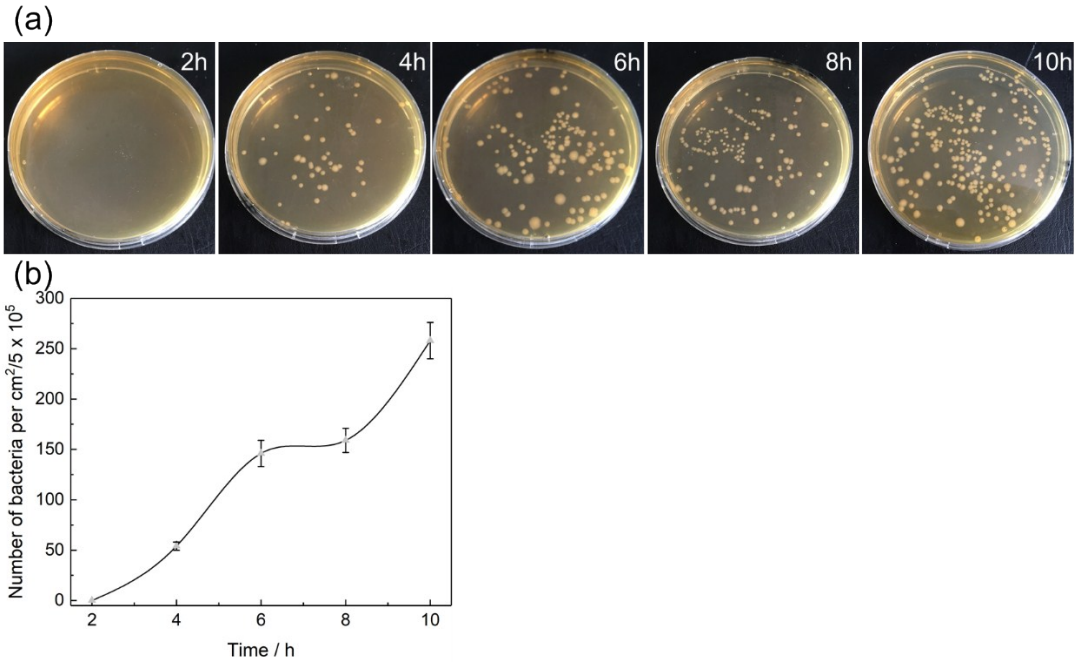


Figure S10. Photograph of the spread plate for bacteria at different incubation time on SiNW-p-ppix@CDm wafer after ultrasound in 1 mL PBS and diluted into 5×10^{-5} (a); And the corresponding bacteria capture absorption curve, (b). Standard error, n = 3.

References

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