Electronic Supplementary Material (ESI)

Cellular-membrane Inspired Surface Modification of well aligned ZnO nanorods for Chemosensing of Epinephrine

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Reagents and Chemicals

L-α-Soybean phosphatidylcholine (SBPC, purity≥99%), was purchased from sigma Aldrich. Calix[6]arene (CX) supplied by the Tokyo Chemical Industry, Japan. Dopamine and epinephrine hydrochloride are purchased from the sigma Aldrich. 1-octadecanthiol (1 mM) purchased from sigma Aldrich.

All commercial reagents were of analytical grade and used as received. Electrolyte containing the 100 mM NaCl, 2 mM imidazole and 1.5 mM $CaCl_2.2H_2O$ at pH 7.2. Phosphate buffer was prepared by using the Na_2HPO_4 0.05 M pH 7.2 as supporting electrolyte. Further during the sensing layer analysis McIlvaine buffer system was used at pH 5. All solutions were prepared with deionized water (18 MΩ cm^{-1} resistivity; MiliQ, Millipore, USA).

Sensor Layer Preparation

A sensing layer is prepared on the surface of the 1-octadecantiol layer of the ZnO NRs. Calixarene (CX) was used as the receptor molecule incorporated in the liposome layer for preparing the sensing layer. The sensing layers are prepared in 1:100 CX to soybean phosphatidylcholine (SBPC) molar concentration. Such layers are prepared by dissolving 20 mM/mL of CX and SBPC in chloroform. Subsequent amounts of CX and SBPC were taken respectively in a round bottom flask which was dried under a steady stream of nitrogen gas to form a uniform layer at the bottom of the round bottom flask. A 5 mL aliquot of the electrolyte solution (100 mM NaCl, 2 mM imidazole hydrochloride, 1.5 mM $CaCl_2.2H_2O$, pH=7.2) was added to the round bottom flask containing the dried layers of CX and the SBPC, and left for incubation for 30 minutes. Then it was sonicated at room temperature for 20 minutes to form the liposomes containing the calix[6]arene molecules dispersed in the electrolyte solution. A small volume of the solution containing the CX and SBPC was used for the formation of self-assembled sensing layer on the already existent layer of the 1-octadecanthiol layer on the ZnO NRs.

Table S1 Surface depth analysis of the ZnO NRs with the NanoScope Analysis software

Without modification	After modification
47.7 nm	6.4 nm

Table S2 Data fitting results with the Equivalent Circuit

Surface	R_{SC} (kΩ)	C_{SC} (nF)	R_M (kΩ)	C_M (nF)	R_{CT} (kΩ)
Bare ZnO	1.0	1.0	0.85	8.6	7.2
ZnO/3s ODT	2.6	304.0	1.45	139	1.7
ZnO/1 hr. ODT/CX:SBPC (1:100)	28.4	792.0	46.4	3330.0	29.8

Where SC = space charge, M = membrane, CT = charge transfer, R = resistance and C = capacitance

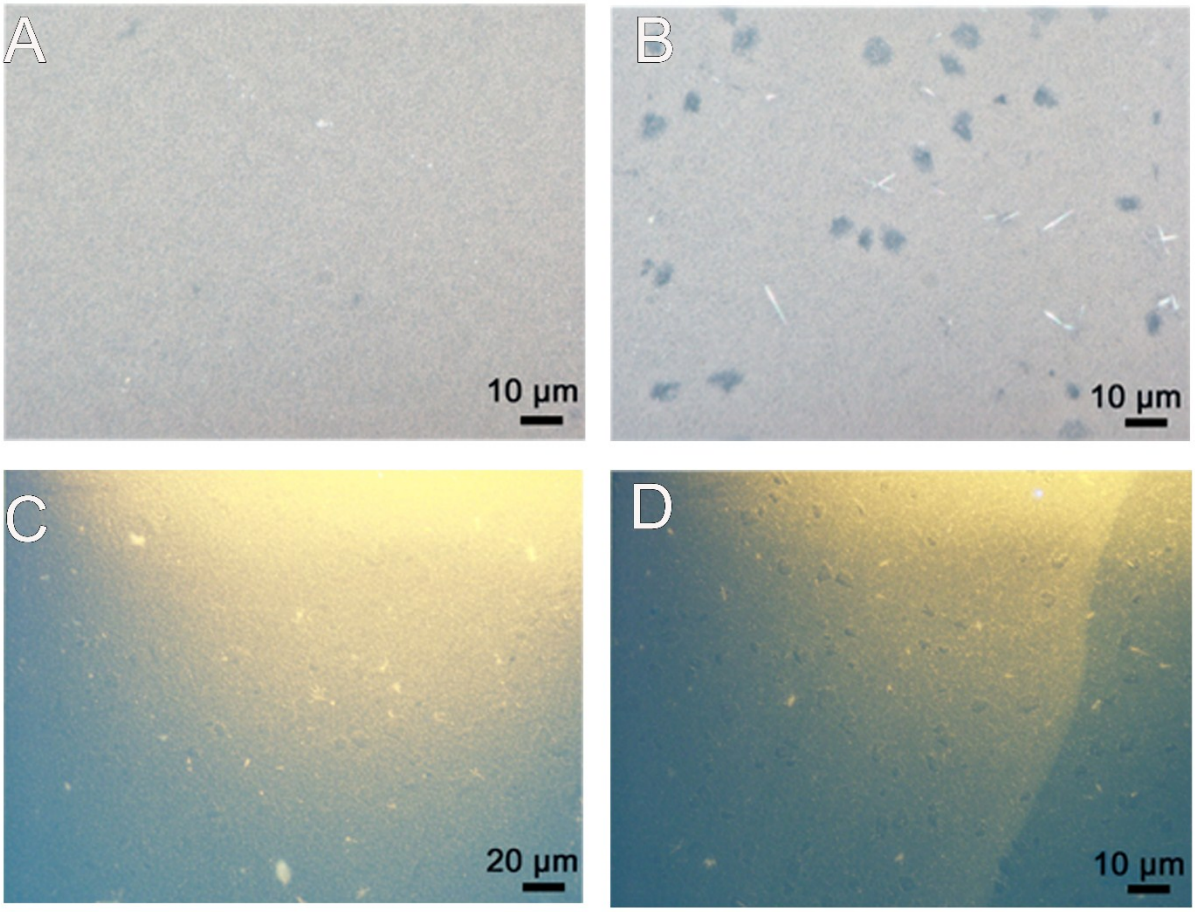


Fig. S1. (A & C) are the optical microscope images of the bare ZnO NRs and (B & D) are the images after modification with the 1-ocadecanthiol for 24 hours. Where (A & B) are the taken under visible light and (C & D) are captured under ultra-violet light.

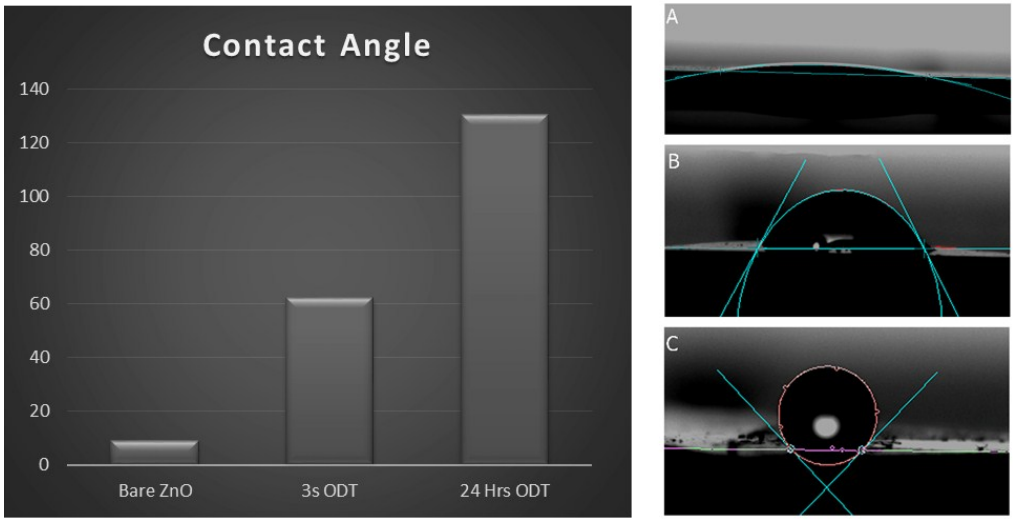


Fig. S2. Contact angle measurements for the ZnO NRs (A) bare ZnO NRs with contact angle = 9.1° (B) 3s ODT contact angle = 62.4° treatment and (C) 24 hours ODT modification contact angle = 130.5°.

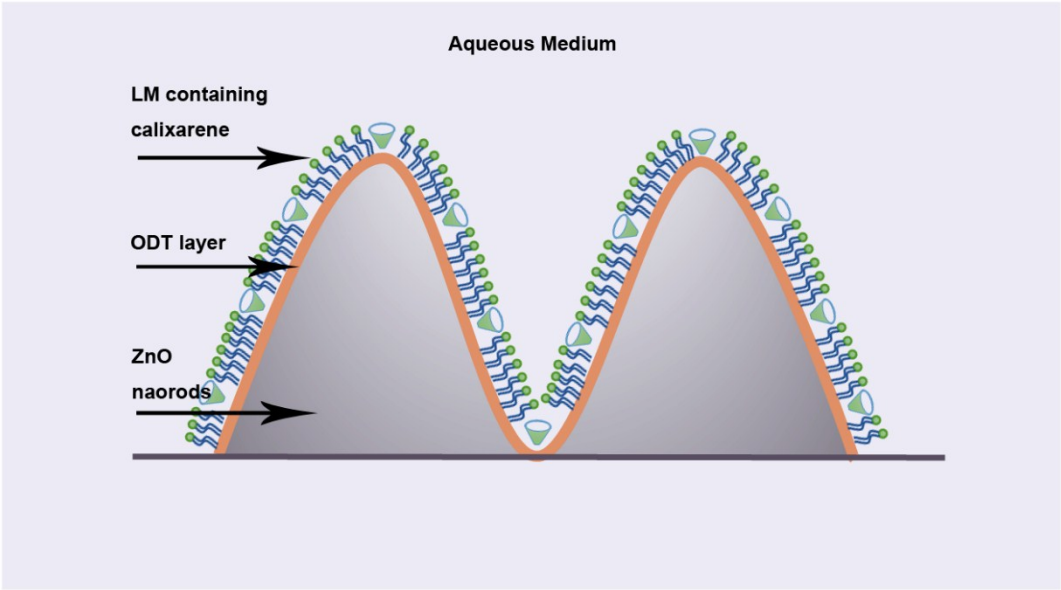


Fig. S3. Schematic illustration for the formation of LM containing the calixarene on the two adjacent nanorods

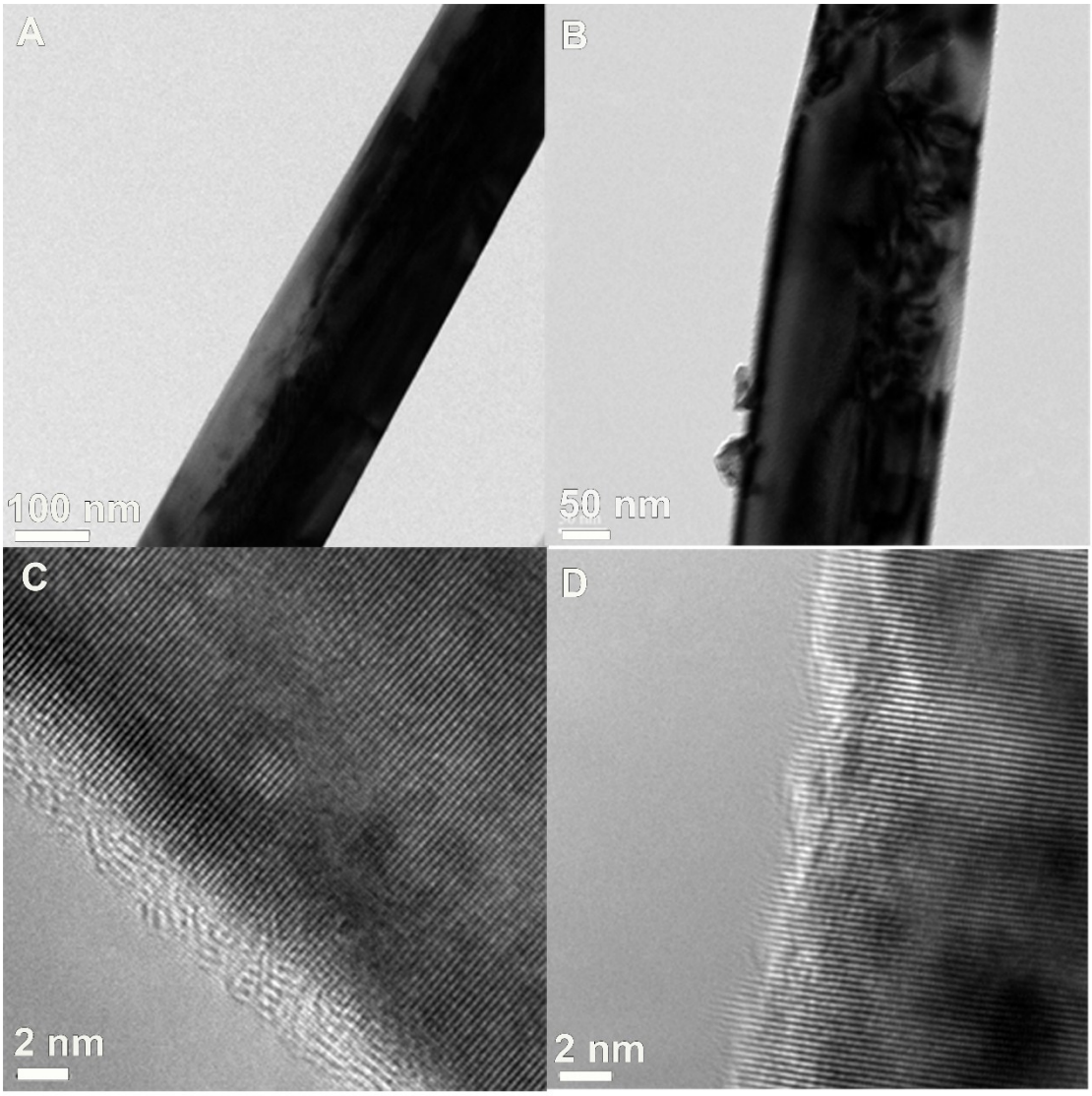


Fig. S4. TEM images of the ZnO NRs (A & C) are without ODT modification and (B & D) are with 30 min ODT modification.

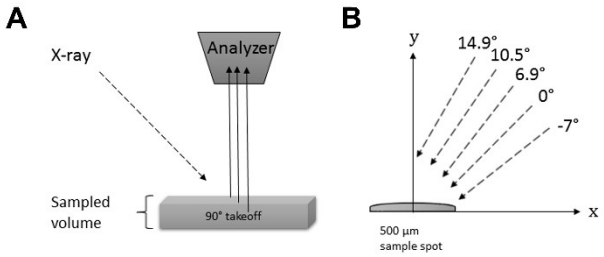


Fig. S5. Schematics of the ARXPS, showing the angles adopted for the surface analysis of the modified ZnO nanorods array

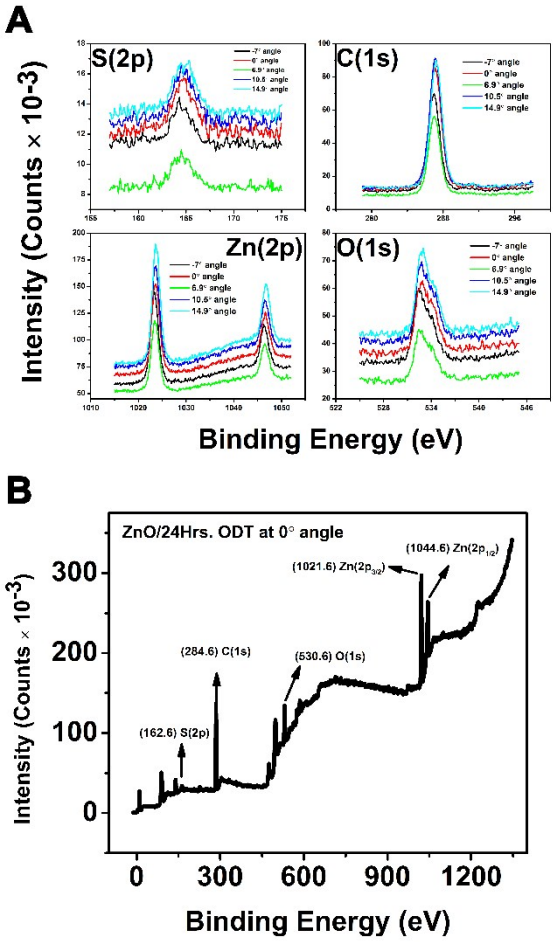


Fig.S6. (A) XPS spectra of ZnO NR modified with 24 Hrs. ODT at different angles and (B) XPS spectra at 0° angle of the modified ZnO referenced to C(1s)=284.7 eV

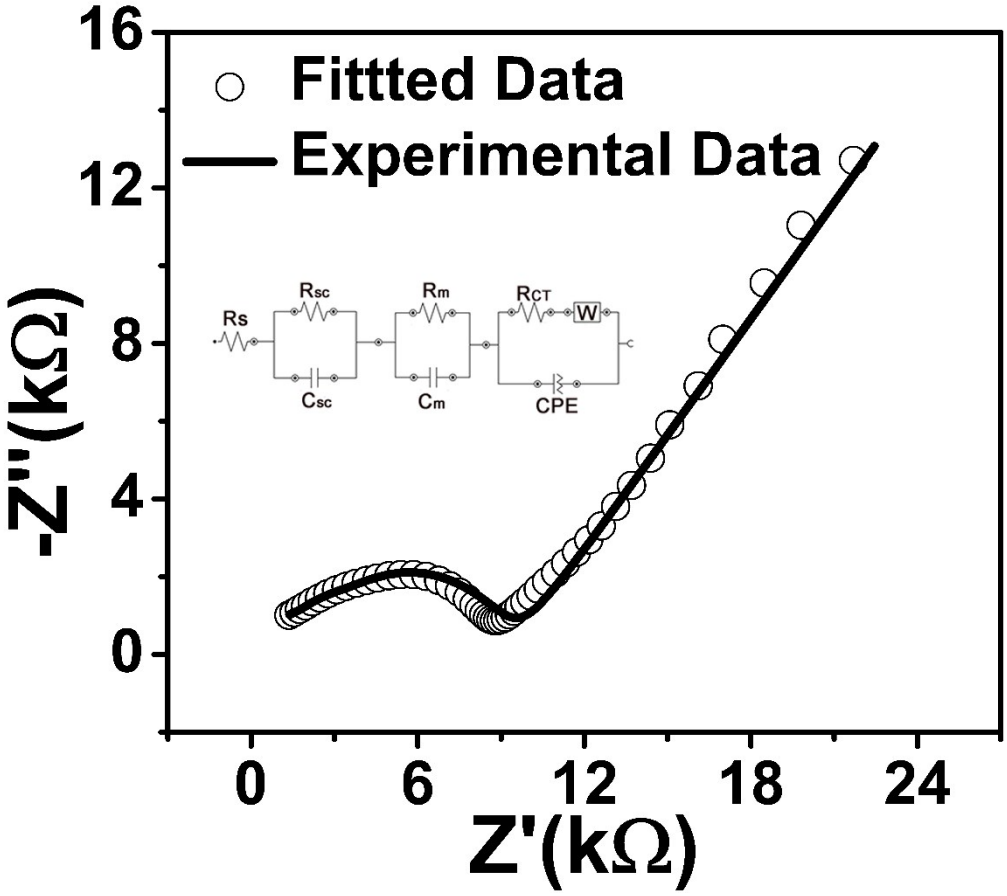


Fig. S7. Data fitting of the bare ZnO NRs with the Equivalent circuit.

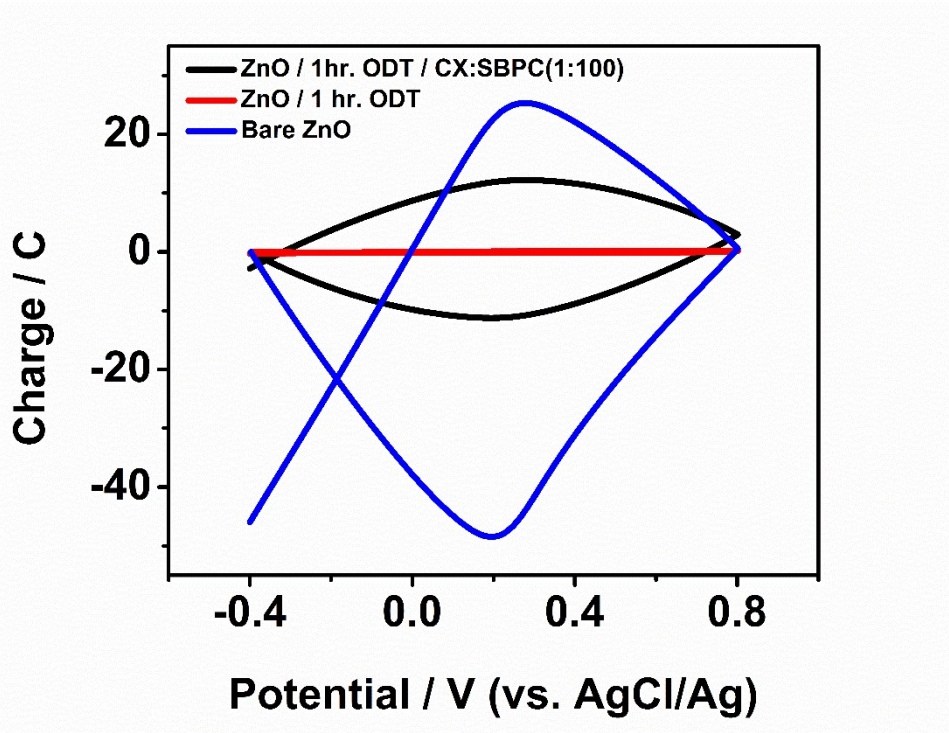
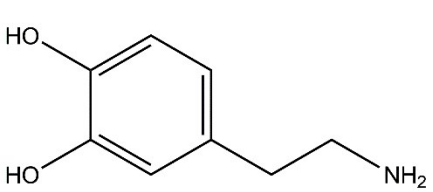
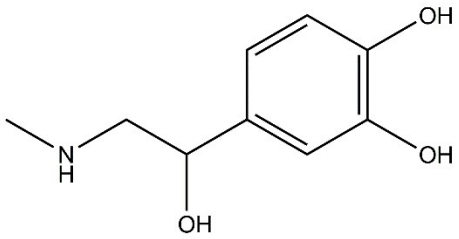


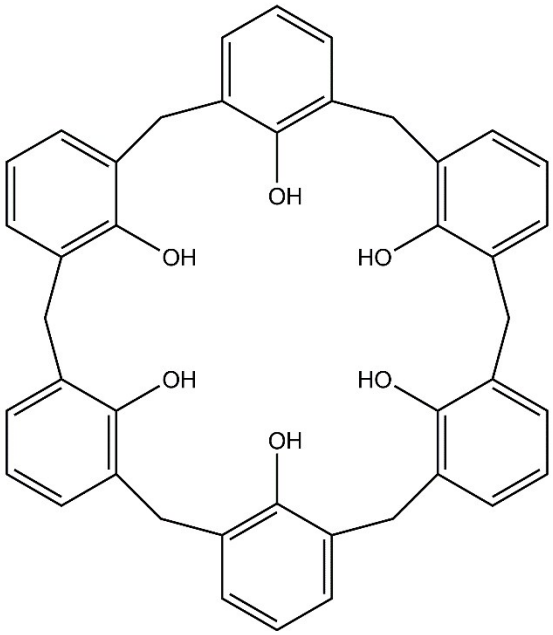
Fig. S8. Charge calculations from the CV measurement of bare ZnO NRs and those modified by ODT and sBLM incorporated with calixarene in CX: SBPC (1:100). Exp. conditions: 0.05 M Phosphate buffer pH 7.2 for bare ZnO and for the other modified surfaces McIlvaine Buffer pH 5 is used, (1:1) redox probe 10 mM, 120 s Ar gas, Ag/AgCl in 3 M KCl Ref Electrode



Dopamine



Epinephrine



Calix[6]arene

Fig. S9. Structure of DA, EP and Calix[6]arene.