

Supporting Information

3D Networked Polydiacetylene Sensor for Enhanced Sensitivity

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1. Procedures for 3D networked polydiacetylene sensor

The networked carbon nanotubes (CNTs) was synthesized on the micro-pillar structure. Micro-pillar structure was made on p-type silicon (100) substrate by silicon deep etching process. The micro-pillar structure with diameter of 1 μm , height of 5 μm , and the inter-pillar gap of 4 μm was prepared. Micro-pillar structure was soaked in a piranha solution ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 7 : 3$) for 30 min in order to clean and modify the surface with hydroxyl group. The micro-pillar substrate was fully rinsed with de-ionized (DI) water to remove acid residue and dried with nitrogen gas. 100 μL of 3-aminopropylmethyldiethoxysilane (APMDES) was diluted in 10 mL of toluene (Junsei) in N₂ air condition and the piranha treated micro-pillar substrate was dipped in the APDMES solution for one hour. The substrate was rinsed with toluene for 2 min and it was baked at 120 °C for 10 min. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Junsei), Mo solution (ICP / DCP standard solution, Aldrich), and HPLC grade ethanol (Daejung) was used to make Fe/Mo (molar ratio 7:1) catalyst solution by ultrasonication. Amine terminated micro-pillar substrate was soaked in the catalyst solution for 1 hour and then the substrate was dipped in ethanol for 10 min to remove excess amount of Fe/Mo catalyst. The networked CNTs was synthesized by thermal chemical vapor deposition method.

The substrate was placed in quartz tube reactor and the reactor was heated up to 850 °C for thermal annealing in air. When the reactor reached 850 °C, NH₃ gas (300 sccm) was injected into the reactor for 10 min and followed by 10 sccm of C₂H₂ gas for 20 min. Synthesized networked CNTs was cooled down to the ambient temperature and to enhance the network, the whole networked CNTs was coated with Al₂O₃ by atomic layer deposition.

PDA vesicles were coated on two substrates: 3D networked chip and two-dimensional silicon planar substrate. Both Al₂O₃ coated 3D networked chip and 2D planar substrate were treated with UV O₃ (Jaesung, UVC-30) for 15 min to introduce hydroxyl group on the surface and after they were soaked in APMDES solution to modify the surface with amine group. 10,12-Pentacosadiynoic acid (PCDA) and n-hydroxysuccinimide modified PCDA (PCDA-NHS) were mixed in DI water at 9:1 molar ratio to make 1 mM PDA solution. The PCDA / PCDA-NHS mixture were stabilized at 4 °C for 12 h and the PDA monomers formed vesicles by ultrasonication for 10 min. The PDA solution was diluted to make 0.25 mM PDA solution and the both substrates were incubated in the PDA solution with stirring (800 rpm) for 30 min. After 30 min, the substrates were rinsed with DI water for 2 min and were irradiated with 254 nm UV light (1 mW/cm²) for 2 min to induce polymerization.