AOARD Report

Fabrication of Carbon Nanotube Channels on Three-Dimensional Building Blocks and Their Applications

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- Past AOARD or US government support

Report Documentation Page

Form Approved
OMB No. 0704-0188

1. REPORT DATE **22 SEP 2011**	2. REPORT TYPE **Final**	3. DATES COVERED **10-06-2010 to 09-07-2011**

4. TITLE AND SUBTITLE
Fabrication of Carbon Nanotube Channels on Three Dimensional Building Blocks and their Applications

5a. CONTRACT NUMBER
FA23861014106

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
Haiwon Lee

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Hanyang University,Haengdang-dong, ,Seongdong-gu,Seoul,KR,133-791

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AOARD, UNIT 45002, APO, AP, 96338-5002

10. SPONSOR/MONITOR'S ACRONYM(S)
AOARD

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
AOARD-104106

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited

13. SUPPLEMENTARY NOTES

14. ABSTRACT
We report shape control of 3D SWNT networks using a multi-patterned template. 3D SWNT networks were applied to solar-cell, functional filters and sensors in microfluidic device. Therefore, three-dimensionally networked structures using CNTs with high surface area on pre-patterned substrates enhanced the conductivity and sensitivity of detectors. In addition to these enhanced electrical and chemical sensing properties, a mechanical filtration of submicron components is shown.

15. SUBJECT TERMS
Carbon nano tubes, Nanotechnology

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT **unclassified**	b. ABSTRACT **unclassified**	c. THIS PAGE **unclassified**	**Same as Report (SAR)**	**12**	

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std Z39-18

1. Introduction

Carbon nanotubes (CNTs) are the most attractive material in the fields of nanoscience and nanotechnology due to their chemical, physical and electrical properties. CNTs are being applied in transistors, electrodes, sensors and filters because of semiconducting, metallic, optical and structural properties. In general CNTs are mostly synthesized, grown and dispersed on the plat substrates. However, it is not easy to fabricate and manipulate CNTs on a particularly structured substrate. In the case of CNTs growth on planar substrate, it is hard to get high conductivity, because of physical disconnection and low surface area due to random orientation on the two dimensional structure. Therefore, three-dimensionally networked structure of CNTs with high surface area on pre-patterned substrates enhances the conductivity and sensitivity. In addition to these enhanced electrical and chemical sensing properties, a mechanical filtration of submicron components is also possible.

Here, we report the shape control of 3D SWNT network using a multi-patterned template. And also 3D SWNT network was applied to solar-cell, functional filters or sensors in microfluidic device.

2. Approach and Results

2-1. Structure Variation of 3D SWNT Networks by Patterned Substrate

To synthesize 3D SWNT networks between pillars, catalyst nanoparticles need to be deposited uniformly on the whole surface area. In case of catalyst deposition, the dipping method is easier than the evaporation method. Figure 1 shows that 3D SWNT networks were well synthesized between pillars using a dipping method.

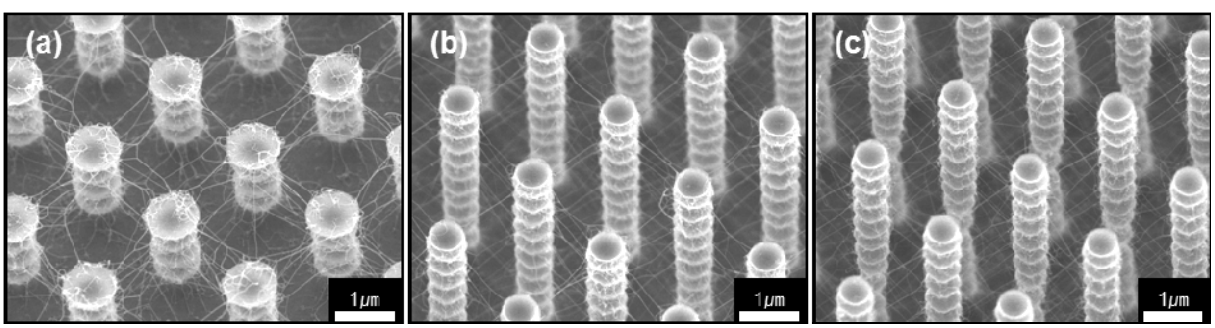

Figure 1. 3D SWNT Networks on the different height of pillars. : (a) 2 ㎛, (b) 5 ㎛ and (c) 7 ㎛ pillars.

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In order to develop a variety of different shape networks for bio-chip application, the structure variation of 3D SWNT networks is important. The variety of structures on Si substrate was made by using photolithography process. After making variety patterns of template, catalysts were deposited on the template by dipping method using inorganic catalyst solution. Then, CNTs were grown on the template using a CVD method.

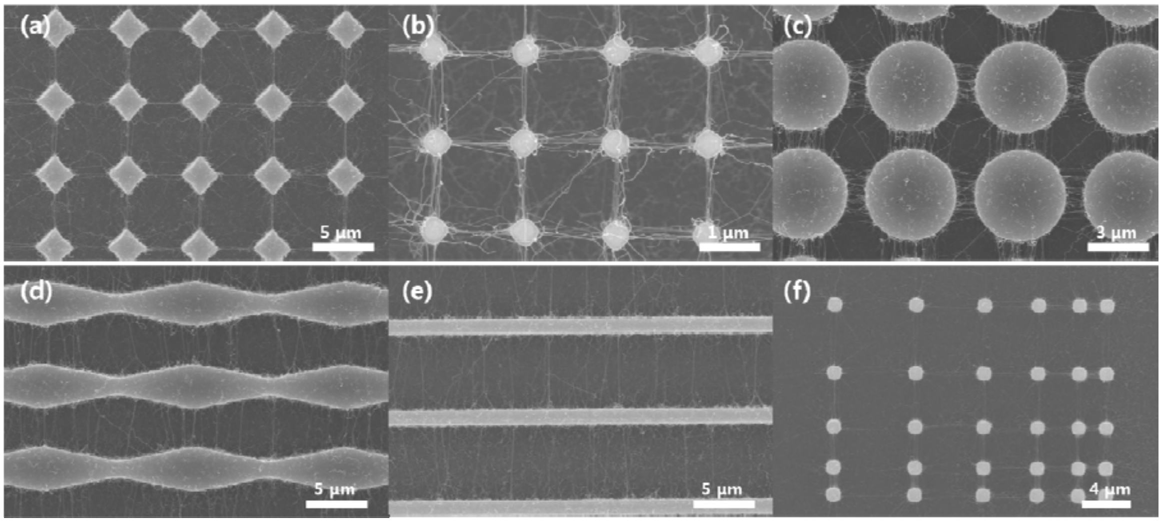


Figure 2. SEM images of 3D SWNT Networks on patterned substrates.

The SEM images in Figure 2 show that SWNTs were successfully grown on the patterned substrate. The shape of the 3D SWNT networks on the substrate depends on the shape of templates. Especially, Figure 2c-f show that the bridging probability strongly depends on pillar distance. The SWNTs density decreases as the pillar distance becomes wider, and this trend was confirmed as shown in Figure 3.

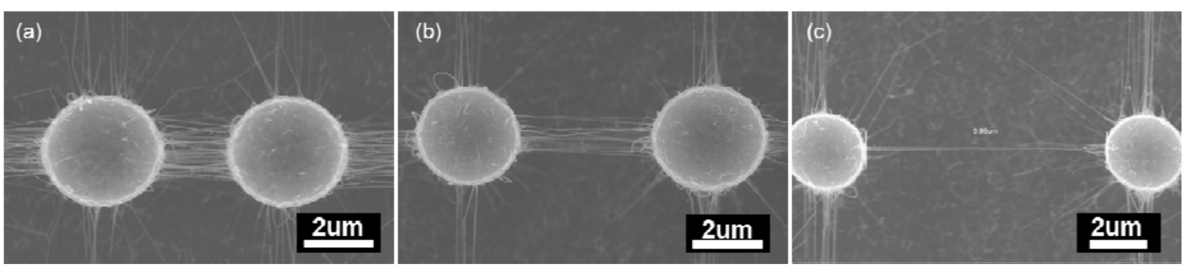


Figure 3. SEM images of SWNTs grown for interconnection between pillars with different gap distance.

2-2. Surface Modification of 3D SWNT Networks by Chemical Treatment

The coaxial coating of 3D SWNT networks with functional materials is essential and necessary for practical applications. The physical, chemical, and electrical properties of 3D SWNT networks can be enhanced by coating the 3D SWNT networks with various functional materials. Figure 4 shows that the 3D SWNT networks are easily bundled and collapsed during the wetting and drying process because the capillary forces of the solution drew the suspended SWNT channels closer together as the solution dried and evaporated. This bundling effect of 3D SWNT networks should be avoided for 3D SWNT networks to be used for nano-electrodes with large active surface area. Thus, the 3D SWNT networks were coated with metal or metal oxide by atomic layer deposition (ALD) in Figure 5 and electro chemical deposition (ECD) in Figure 6.

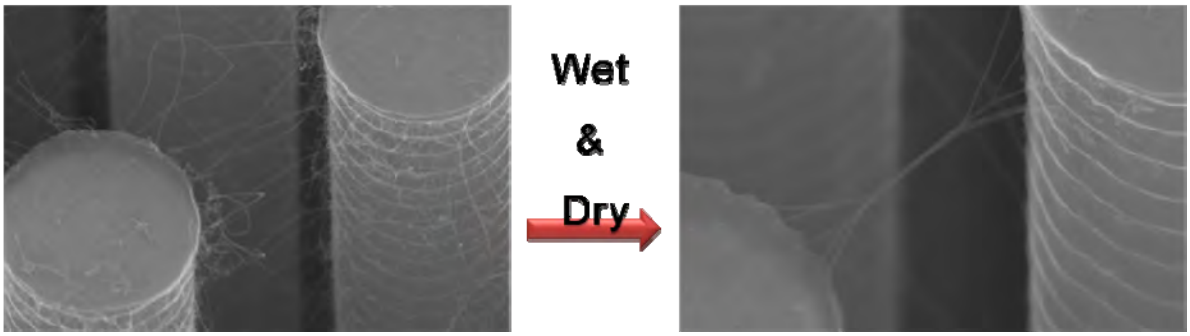


Figure 4. 3D SWNT networks were aggregated after dipping in the liquid and dried.

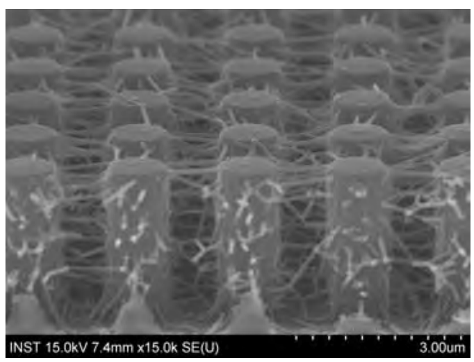


Figure 5. SEM image of Al_2O_3 coated 3D SWNT networks by ALD.

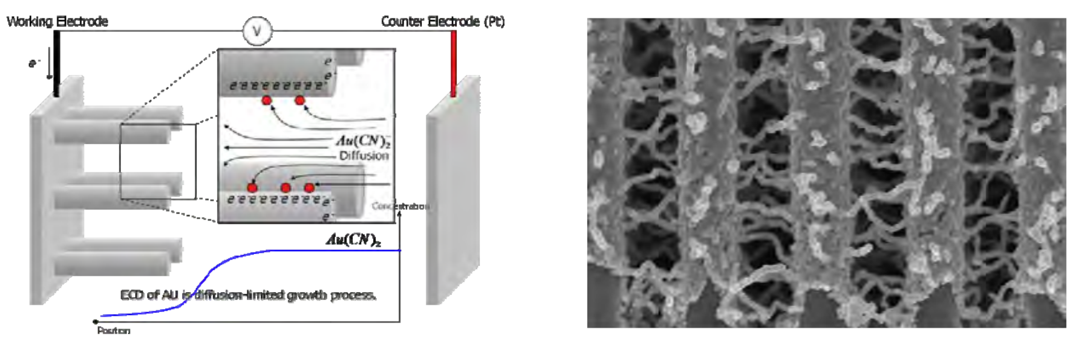


Figure 6. Scheme for ECD (left), and SEM image of Au-coated 3D SWNT networks by the ECD (right).

The 3D SWNT networks were coated with Al_2O_3 by chemical modification. Figure 7 shows a general process of self-assembly for aminopropyltrimethoxysilane (APS) modification. Figure 8 shows the XPS data of 3D networks before and after APS modification. The ending group of APS is $-NH_2$ which is able to be linked to the binding group with polar-materials or bio-materials.

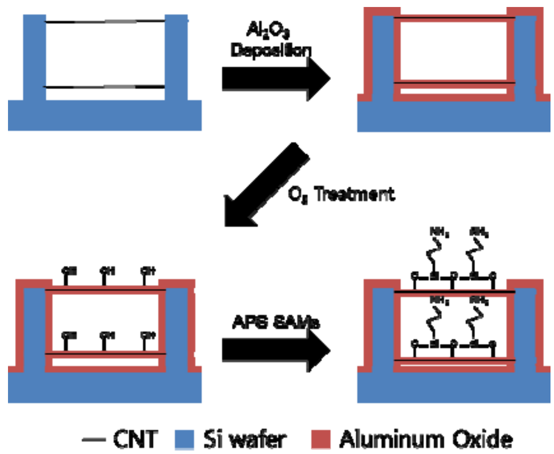


Figure 7. Schematic illustrations of the modification process with APS on Al_2O_3 coated 3D networks.

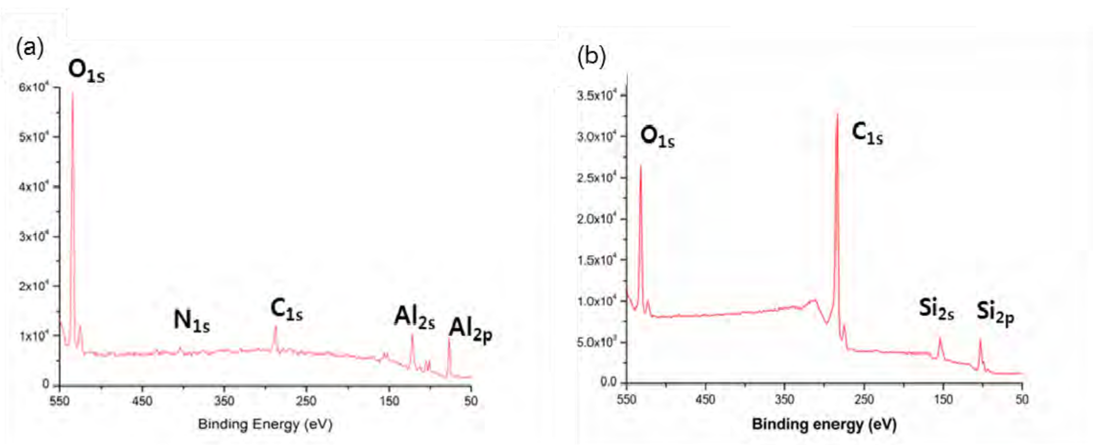


Figure 8. XPS data of (a) bare 3D network and (b) modified 3D network.

2-3. Fabrication of 3D SWNT Networks at Low Temperature

In case of our thermal CVD process, 3D SWNT networks were synthesized at 800℃. Due to the high temperature process, it is difficult to use 3D SWNT networks directly to device application, which needs a low temperature process condition. The PECVD has an advantage for the synthesis of CNTs at the low temperature compared to the thermal CVD process, because PECVD uses plasma to decompose hydrocarbon gases. However, CNTs synthesized by PECVD have many defects and the length of CNTs are short compared to those prepared by a thermal CVD due to the chemical etching effect of plasma ions. Plasma etching induces the breakage of the SWNT in 3D network structure as shown in Figure 9. In order to successfully fabricate 3D SWNT networks using PECVD, the plasma etching effect should be decreased or avoided, because one or two graphene sheets of CNTs are easily broken by accelerated ions during PECVD process.

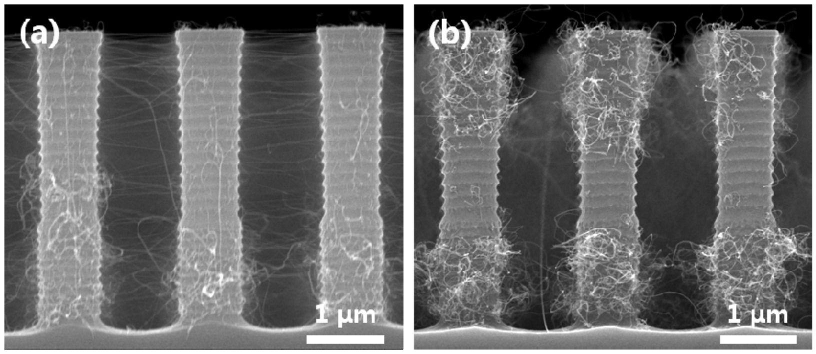


Figure 9. SEM images of 3D SWNT networks of (a) before plasma treatment and (b) after plasma treatment.

Figure 10 shows the SEM images of the effects of metal mesh against plasma etching effect under H_2 gas plasma. Before exposing to the plasma, many SWNTs formed bridge between pillars as shown in Figure 10b. However after plasma exposure without a mesh in the PECVD chamber, all SWNTs were removed by plasma. By using a mesh, most of interconnected SWNTs were remained after plasma treatment. Figure 11a shows the variation of CNTs interconnection density by plasma treatment with and without a mesh. This result of controlling SWNTs etching supports that the mesh structure successfully reduces the ion bombardment effect by lowering the kinetic energy of ions.

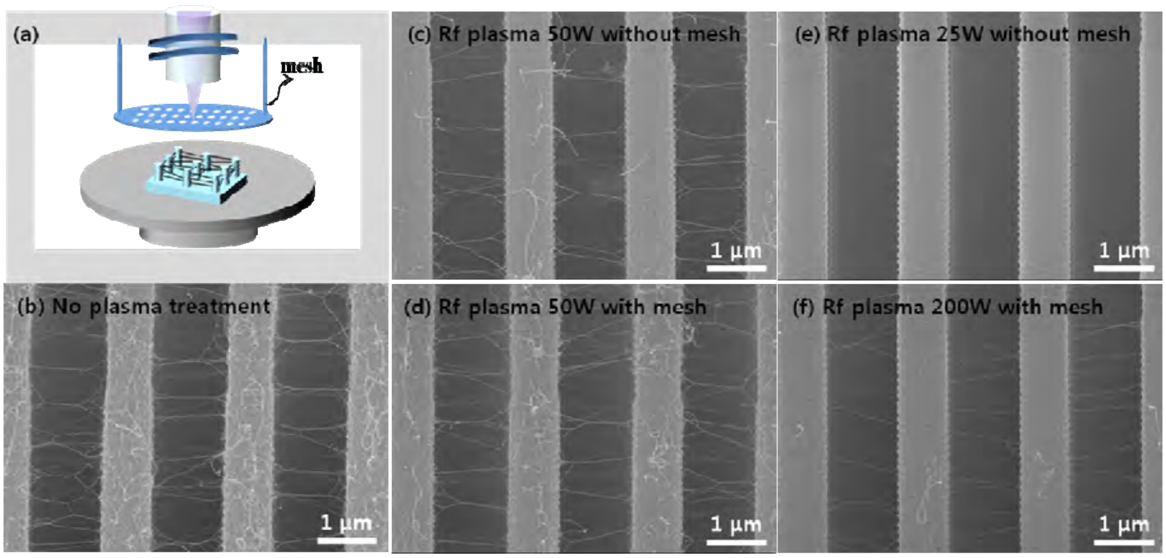


Figure 20. (a) Scheme of plasma etching experiment using a mesh installed PECVD, (b-f) SEM images of comparing plasma etching effects on the SWNT 3D network structure.

Figure 12b shows the ratio between G-peak and D-peak (I_G/I_D) of Raman spectra under the plasma treatment. In case of plasma treatment with a mesh, the I_D/I_G ratio was a little increased compare to that from the original 3D SWNT networks. This indicates that the ion bombardment was effectively decreased on the surface of SWNTs. In contrast, the I_D/I_G ratio of without a mesh increased compared to others. This is caused by the defects of SWNTs.

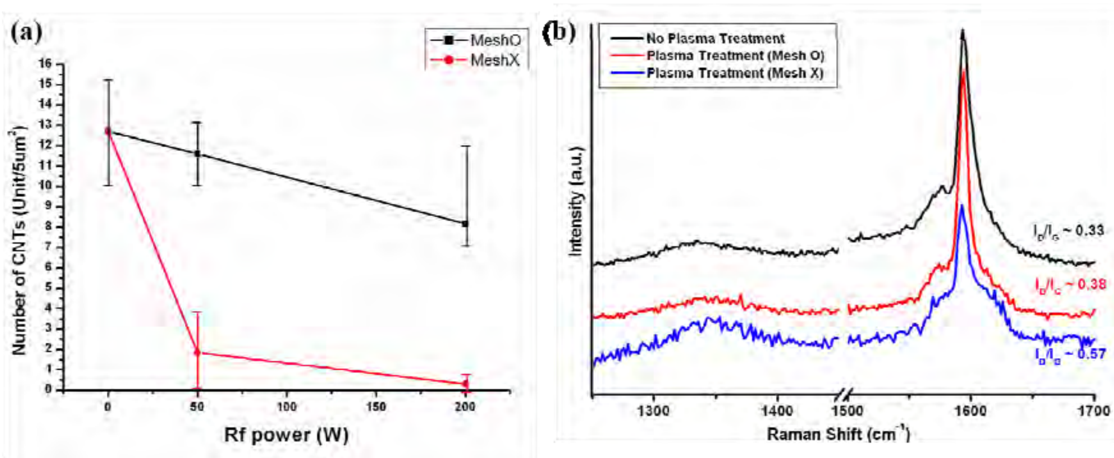


Figure 11. Plasma etching effects on 3D SWNT networks : (a) SWNT density variation versus Rf plasma power with and without mesh. (b) Raman spectra of SWNT as plasma treatment method.

However, the structure of MWNTs synthesized by PECVD process was different from those prepared by the thermal CVD process. For the best network structure, the synthesis conditions should be optimized. The number of CNT walls depends on the catalyst particle size. The size of catalyst particles is related to substrate temperature, annealing time and pretreatment plasma power during PECVD process. Both annealing and pretreatment steps were conducted to decrease the catalyst size effectively unlike as a conventional CVD process. The size of catalyst particles was decreased by plasma etching effect as shown in Figure 12.

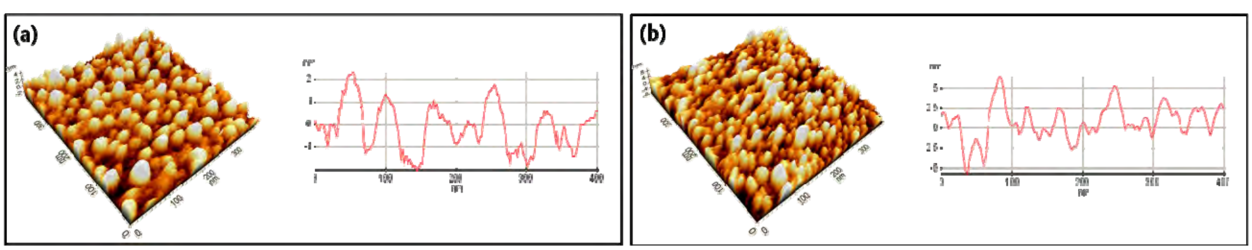


Figure 12. AFM topography images of catalyst formed on the substrate. : (a) Without plasma treatment and (b) H_2 plasma treatment.

Under the optimized conditions, 3D SWNT networks were successfully fabricated on the pillar patterned substrate by mesh installed PECVD as shown in Figure 13.

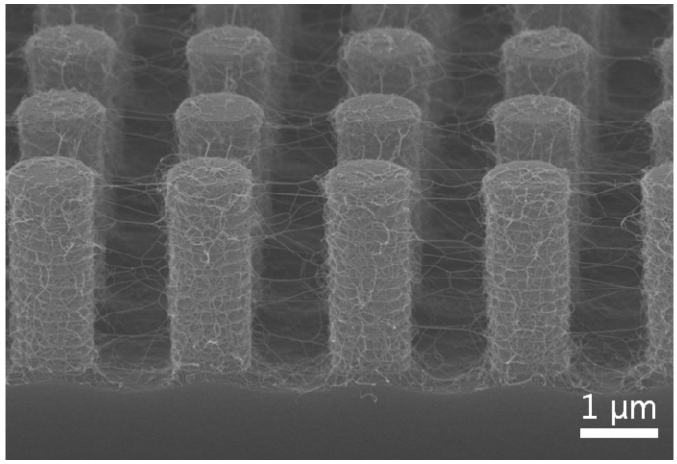


Figure 13. SEM image of SWNT 3D networks fabricated by mesh installed PECVD.

However, 3D SWNT network structure did not be formed at 650℃. Because MWNTs were mainly synthesized on the pillar substrate as shown in Figure 14. It is known that the number of CNT walls related with catalyst diameter. In order to synthesize SWNT, the catalyst particles size should be decreased. According to Kelvin equation, radius of the particles is inversely proportional to temperature.

Kelvin equation

$$RT\ln\left(\frac{P}{P_0}\right) = \frac{2\gamma V_m}{r}$$

r : radius of the particle . T: temperature
γ : surface tension of metal layer
P: actual vapor pressure
P_0 : saturated vapor pressure

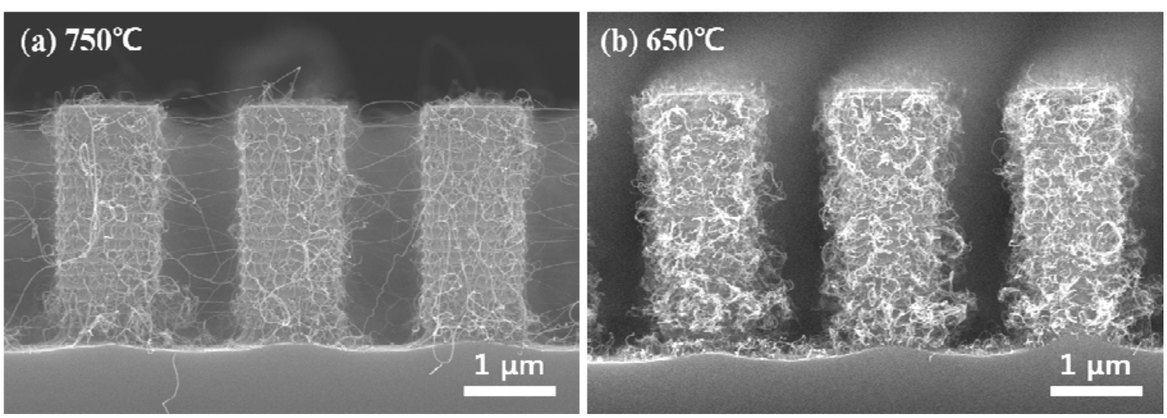


Figure 14. CNTs synthesis on the pillar substrate by mesh installed PECVD at (a) 750 ℃ and (b) 650 ℃.

2-4. Fabricating Dye-Sensitized Solar Cell using 3D SWNT Networks

DSSC(Dye-sensitized solar cell) based on semiconductor electrodes have been investigated. Pt is generally used as counter electrode. Although Pt has as high conductivity, stability, Pt is one of the most expensive components in DSSCs. Therefore, the development of finding alternative materials for the development of Pt-free DSSCs is expected to reduce the production cost for DSSCs. As a Pt-free counter electrode, carbon-based materials, such as graphite, carbon nanotube(CNT) and carbon black have been introduced.

In case of CNT electrode, vertical aligned CNTs or polymer mixed CNTs on the surface were announced. In order to increase contact-area with DSSC electrolyte and counter electrode, 3D SWNT network was applied as counter electrode. The performance of such counter electrodes can be compared directly with a Pt counterpart by fixing other parameters, such as the TiO_2 layer, dye, electrolyte, and conditions of cell assembly, as shown in Figure 15.

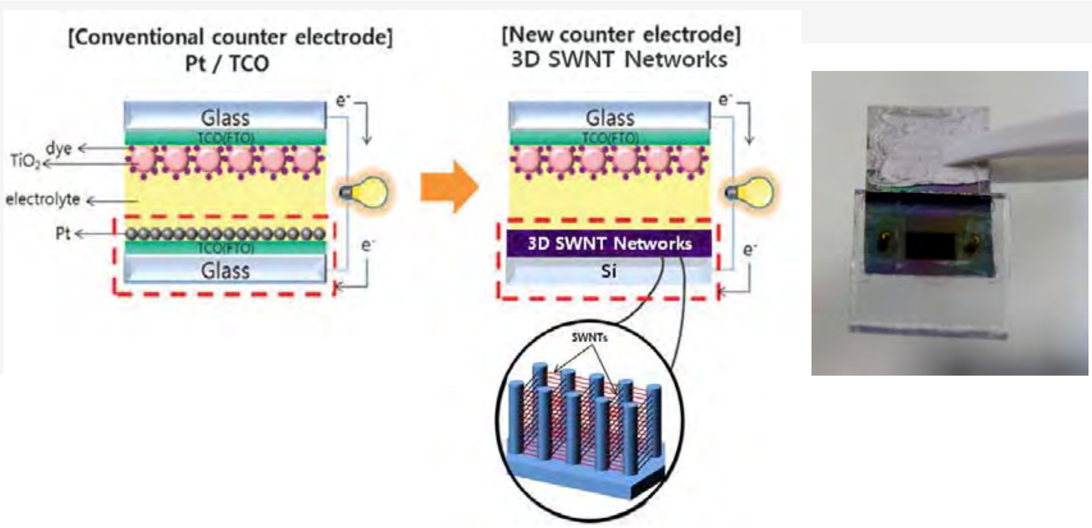
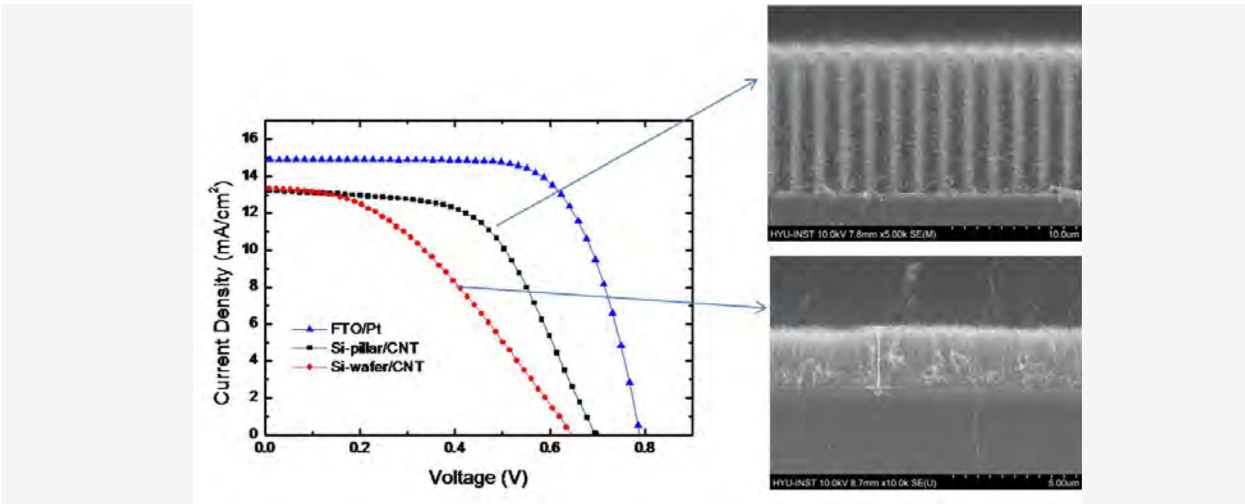


Figure 16. Scheme of 3D SWNT networks based DSSC structure and the image of cell.

The J-V characteristics of the devices with Pt-coated, TCO counter electrodes and two different 3D SWNT networks-based counter electrodes with different conductivities are shown in Figure 16. At 1 sun illumination, the vertical aligned SWNTs DSSC exhibited a Jsc of 13.0 mA cm^2, a Voc of 0.64 V, a fill factor (FF) of 0.39, and an overall conversion efficiency of 3.39%. However, the performances of the DSSCs based on the 3D SWNT networks counter electrode were strongly dependent on the electric conductivity of the film. The DSSC with a 3D SWNT networks counter electrode had the highest fill factor of 0.57 and a Jsc of 13 mA cm^2, a Voc of 0.69 V, and a conversion efficiency of 5.23%, which is comparable to using the Pt/TCO electrode. The 3D SWNT networks were used as a counter electrode in the fabrication of DSSCs, resulting in a power conversion efficiency of 5.23% when a DSSC with a vertical aligned CNTs counter electrode was 3.39%. Although efficiency of 3D SWNT networks was less than Pt electrode, generally efficiency of carbon electrode DSSC was announced blew 5%. Therefore, if the electric conductivity of the 3D SWNT networks can be further increased through changing their structure and ratio of MWNT/SWNT, the performance of a 3D SWNT networks counter electrode can be improved, which eliminates the utility of Pt and TCO.



Sample	Jsc(mA/cm²)	Voc(V)	FF	Area(mm²)	CE(%)
Si-Pillar/CNT	13.2087	0.6962	0.5691	13.1915	5.23
Si-wafer/CNT	13.3151	0.6467	0.3937	12.6250	3.39

Figure 16. Dark current–voltage of the 3D SWNT counter electrode based DSSC and vertical aligned SWNT. And the current–voltage parameters of multi the 3D SWNT counter electrode based DSSCs.

2-5. Fabricating Functional Filter or Bio-sensor in Microfluidic Device

The 3D SWNT networks can be used as bio or chemical filter in microfluidic device. The coaxial coating technique was applied on the 3D SWNT networks to enhance their physical hardness using ALD and ECD. Because as-grow 3D SWNT networks could not endure in fluidic device. Once the basic performance of 3D SWNT networks was evaluated as a filter on a simple micro-fluidic structure, the 3D SWNT networks was filtered the 500 nm PS nanoparticles. Furthermore, 3D networks could be chemical modified by SAMs and plasma for using chemical filtration. The amine group is easily combined with bio and chemical material. Biotin is a well known linker molecule for bio applications. So, the Al_2O_3 coated 3D networks template was dipped in aminopropyltrimethoxysilane (APS) solution, then, the amine modified networks sample was dipped in 1 wt% biotin solution. Figure 17b shows the biotin immobilized 3D networks which seemed like a same structure of only Al_2O_3 coated on the template.

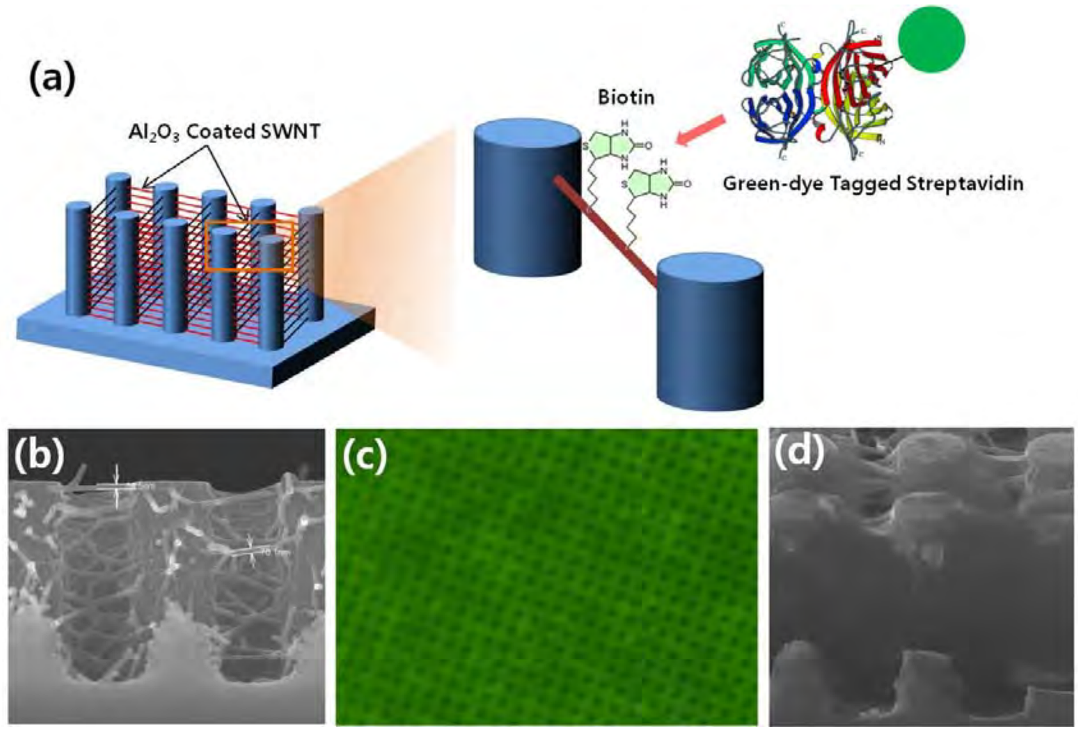


Figure 17. (a) Scheme of the streptavidin filtration using biotin modified 3D networks. And (b) SEM image of the biotin coated 3D networks. (c) Fluorescence image of the filtered streptavidin and (d) SEM image of filtered streptavidin on the biotin modified 3D networks.

The green-dye-tagged streptavidin was disembogued through modified 3D networks channel in order to chemical adsorb by biotin. Figure 17c and b show filtered streptavidin molecules. The sized of streptavidin is 3 nm. After rinsing the template several times, the strepatividin was remained on 3D networks. The result supports that 3D SWNT networks on a microfluidic chip could be quite effective for the practical application in bio sensor and chemo sensor.

3. Summary

The SWNTs were synthesized on various Si pillar structures. The interconnected SWNTs were successfully formed on Si pillars, and the shape of SWNT networks can be controlled using the different shape of templates. And bundling and collapsing of SWNTs in the networks were easily happened during the drying process after dipping in the solution. For preventing SWNTs collapse and microfluidic applications, both ALD or ECD methods are very promising for coaxial coating of the SWNT interconnection channels.

The chemical modification of SWNTs networks is necessary for bio application. The Al_2O_3 coated 3D networks were modified with an amine group using APS. Amine modified network structure was dipped in the biotin solution, and biotin molecules were well attached to the modified 3D networks. The biotin immobilized networks were confirmed with green fluorescent-tagged streptavidin. Steptavidin molecules strongly bind with biotin molecules. Green fluorescence from strepatavidin was stronger than that of biotin modified Si surface.

And also, in order to lowering the process temperature, the synthesis of 3D SWNT networks was carried out at 650℃. However, mostly MWCNTs were synthesized on the whole surface of pillars. It is known that the number of CNT walls is related to the catalyst diameter. To decrease radius of the catalyst particles on the substrate, catalyst particles were treated with H_2 in the plasma chamber. 3D SWNT networks was also applied to the DSSC as a counter electrode. Although efficiency was lower than that of Pt electrode, we suggest an alternative new counter electrode.

Publication

1. Jeongeun Seo, Taejea Lee, Haegu Yeo, Taeyong Noh, Bio Park, Simon Song, Myeongmo Seong, Haiwon, Tunable and hierarchical three-dimensional networks of carbon nanotubes as microfluidic applications, ***Angew. Chemi*** (To be Submitted)

2. Haegu Yeo, Jeongeun Seo, Seockjin Jo, Yongduck Jo, Haiwon Lee, Fabrication of single-walled carbon nanotube network structure by mesh installed plasma enhanced chemical vapor deposition, ***Carbon*** (Manuscript in preparation)

3. Taeyong Noh, Jeongeun Seo, Haegu Yeo, Jonghyeck Park, Haiwon Lee, Three-dimensionally nanostructured carbon nanotubes for counter electrode of dye-sensitized solar cell, ***Chem.comm.*** (Manuscript in preparation)