Abstract

A simple Microreactor was fabricated by vertically-aligned multi-walled carbon nanotubes (MWCNTs) on the mc-Si substrate. MWCNTs were synthesized by homemade equipment aided with chemical vapor deposition (CVD). The wettability of the surfaces of Microreactor with the synthesized MWCNTs, Au coating and plasma irradiation were investigated, respectively. Results show that the initial surface with the MWCNTs film behaves as a super-hydrophobic surface. However, it changes to a super-hydrophilic surface after coated with Au or irradiated by plasma. It shows that Microreactor with treated MWCNTs film can be used as potential applications for bioanalysis.

Keywords: bioanalysis microreactor, wettability, hydrophobic, hydrophilic, plasma, x-ray lithography

Concept of fabricated 3D surface by vertically-aligned MWCNTs for micro reactor based µTAS

Since CNTs have high-aspect ratios, in micro total analysis systems (µTAS), they can form a much wider reaction field on the surface, which is useful for biological applications. The micro reactors in these systems have been proposed to be micro channels or micro wells based on the droplets. All of these systems have surfaces with a very high surface-to-volume ratio. From this point-of-view, a reactor with MWCNTs can improve existing Microreactor capabilities obviously. In order to achieve a high quality µTAS reactor, synthesis of MWCNTs with a high density is required. Figure 1 shows the concept of a Microreactor with MWCNTs. The relevant proposed method is to locate primary antibodies on the CNTs surface. Thus, primary antibodies are located in three dimensions. Furthermore, the representative size (L in the Figure 1) will be changed (cf. Figure 1A & 1B). In a traditional Microreactor, L is the depth or width of a micro channel or a micro well. However, L in the new reactor becomes the length between vertically aligned CNTs if the reaction field height is coincident with the CNT length. Consequently, the basic diffusion can be expressed as, where D is the diffusion coefficient and t is the diffusion time. By decreasing the value of L, t decreases as well. When the primary antibodies are located in three dimensions, appropriate decreases in the size will lead to higher sensitivities and reaction speed. It is well known that etching-based processes are used for the fabrication of µm–nm size structures. The advantage of etching is that it can be used to fabricate structures with high accuracy. However, it is difficult for etching to make under several nanometers just like CNTs. UV and X-ray lithography can make structures or patterns within 100nm, but these methods are expensive. On the other hand, synthesis of CNTs currently can be achieved easily at low cost. In this research, MWCNTs are synthesized only by the catalyst pre-deposited...
by CVD and ethanol with the home-made equipment. Furthermore, CNTs unique structures such as high aspect ratios and densities cannot be fabricated by etching techniques. Therefore, the new Microreactor with CNTs proposed in this work will have a promising potential application in μTAS for bioanalysis.

**Figure 1** Concept of a microreactor based μTAS with CNTs. A. Traditional bioanalysis microreactor B. New bioanalysis microreactor

### Experimental procedure

**Catalyst coated for synthesizing vertically-aligned MWCNTs**

The catalyst (Fe) was deposited on the substrate (mc-Si) by electron cyclotron resonance (ECR) and the related deposition parameters are listed in Table 1.

| Parameters       | Values                                      |
|------------------|---------------------------------------------|
| Substrate        | Si (100)                                    |
| Catalyst         | Fe/Al                                       |
| Irradiation time | 60, 150, 300, 600 s                         |
| Accelerated voltage | 2,500V                                     |
| Ion current density | 12.0mA/cm²                   |
| Gas              | Ar                                          |
| Gas flow rate    | 0.6SCCM                                     |
| Vacuum           | 1.5×10⁻⁴ Pa                                 |

### MWCNTs synthesis

For vertically-aligned MWCNTs synthesis, the schematic diagram of the home-made equipment is shown in Figure 2. The size of vacuum chamber and the heater is Φ100×150mm and 50×30mm respectively. The electrical resistance is taken as the heating resource. The maximum temperature can be reached to 1680°C. Ethanol in a ceramic container is located under the heater and the specimen deposited with the catalyst is placed on the heater in the vacuum chamber. A DC power supplier is applied to heat the specimens in the vacuum (1×10⁻² Pa) under 38~40A.

**Figure 2** Schematic diagram of home-made equipment for MWCNTs.

### Raman spectroscopy analysis

The characteristics of the vertically aligned MWCNTs synthesized were evaluated by Raman spectroscopy analysis. Table 2 shows the conditions of the Raman spectroscopy analysis. Generally, typical Raman shifts (cm⁻¹) of CNTs include the G-band, the D-band and RBM, where the peak of the G-band is at about 1590cm⁻¹ and the D-band is 1350cm⁻¹. The CNTs is evaluated on the basis of the ratio between the G-band and the D-band.

| Conditions                  | Values         |
|-----------------------------|----------------|
| Laser wavelength            | 532nm          |
| Laser power                 | 30mW×0.5%      |
| Irradiation spot            | 5μm            |
| Integration times           | 30             |

### Microreactor fabrication with CNTs

Figure 3 shows the fabrication procedure for the Microreactor with MWCNTs, where unit reactor is machined by dice cutting after the catalyst deposition. Table 3 shows the corresponding parameters of dice cutting and Microreactor.

| Parameters                  | Values                  |
|-----------------------------|-------------------------|
| Size of Micro reactor unit  | 100μm×100μm             |
| Gap among reactors          | 35μm                    |
| Cutting speed               | 0.5mm/s                 |
| Cutting depth               | 50μm                    |

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Results and discussion

Morphology of synthesized vertically-aligned MWCNTs

The synthesized vertically-aligned MWCNTs are shown in Figure 4. It shows that the general growth direction was normal to the surface. They appeared wiggly due to CNTs tightly packed during growth. The TEM image of one typical CNT is shown in Figure 5. The image reveals that they were definitely multi-walled nanotubes. The diameter was about 3–5nm. Also, the lengths of the CNTs were estimated to be 10–35µm. Moreover, the morphology of the relevant Microreactor is shown in Figure 6.

Wettability of the vertically-aligned MWCNTs

The wettability of surface of Microreactor with MWCNTs was investigated by the droplet of pure water and the volume of the droplets was 1µl. Result shows that the contact angle on the vertically-aligned CNTs film was 146.6° resulted in super-hydrophobic as shown in Figure 8A and the related schematic diagram is shown in Figure 8B. For changing the wettability, the Au coating and plasma irradiation were carried out with the plasma irradiation time of 5 min and ion current of 6.5mA. Figure 9 shows the contact angles of the vertically-aligned MWCNTs surface coated with Au and irradiated with the plasma, respectively. Results show that the processed surface changed to a super-hydrophilic surface after Au coating and plasma irradiation. More attractively, the contact angle on the plasma-irradiated CNTs film was close to 0° as shown in Figure 9C and its corresponding schematic diagram is shown in Figure 9D. However, the contact angle of the vertically-aligned MWCNTs surface with Au coating (Figure 9A & 9B) was higher than that of surface with plasma irradiation which indicates the droplet cannot be infiltrated into CNTs completely with Au coating on the surface resulted in the successive application failure.

Result of raman spectroscopy analysis

The result of Raman spectroscopy analysis of the synthesized vertically-aligned MWCNTs is shown in Figure 7. It elucidates that the peak of D-band was higher than that of G-band and the ratio of IG/ID was about 0.75, which indicates that many CNTs were disordered. As the media in the Microreactor, the disordered MWCNTs will be inclined to catch the antibody more easily. Therefore, the Microreactor with such MWCNTs must be more effective for the practical applications than that of the traditional reactors.
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**Conclusion**

The simple Microreactor potential for bioanalysis was successfully fabricated with MWCNTs. Results show that the initial synthesized surface with the MWCNTs film behaves as a super-hydrophobic surface. After coating with Au or irradiating by plasma it changes to a super-hydrophilic surface. Moreover, the effect of plasma treatment on the wettability changed from super-hydrophobic to super-hydrophilic is definitely superior to that of Au coating. It indicates that Microreactor with surface treated MWCNTs can be more in favor of the potential applications for bioanalysis.

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**Conflict of interest**

The author declares no conflict of interest.

**Figure 8** Wettability of the vertically-aligned MWCNTs.

**Figure 9** Wettability of the vertically-aligned MWCNTs film with Au coating and plasma irradiation.

**Figure 10** Wettability of the vertically-aligned MWCNTs film with Au coating and plasma irradiation.