Simple Fabrication of Carbon Nanotube Monolayer Film

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We report a simple fabrication method for creating a monolayer film of multiwalled carbon nanotubes (MWCNTs). The MWCNTs, which were synthesized using alumina template method, was dispersed in aqueous ethanol solution. Then toluene was added to the dispersion. After sonicating the solution, the MWCNTs form a monolayer at the liquid–liquid interface. The monolayer was transferred onto a solid substrate using simple dipping method. An AFM image showed the formation of a densely packed MWCNT monolayer film.

Carbon nanotubes (CNTs) represent an important group of nanomaterials with attractive electronic, chemical, and mechanical properties. Several kinds of electric devices, such as chemical sensors,[1,2] biological sensors,[3–5] field-effect transistors (FET),[6–8] and transparent conductive film[9] based on the unique electric properties of the carbon nanotubes have been reported. Implementation of CNTs for these applications requires methods to fabricate carbon-nanotube ultrathin film. Moreover, carbon-nanotube ultrathin film is important for understanding its basic electrical and optical properties. Several techniques, such as spraying,[10] self-assembly,[7,11,12] and the Langmuir–Blodgett technique[13–17] have been employed to produce a CNT thin film. Because the Langmuir–Blodgett technique is a suitable method for producing a densely packed film, we and other groups have worked to fabricate a monolayer film of CNT using the LB technique.[13–17] However, the CNT must be modified chemically to prepare the monolayer onto the air–water interface,[14–17] or mixed with surfactants.[13] Orikasa et al. synthesized water-dispersible and uniform multiwalled carbon nanotubes (MWCNTs) using template method.[20] The MWCNTs prepared by the template method have uniform length and diameter; they are water-dispersible without additional treatment after synthesis.[20]

Here, we report a simple method to fabricate CNT monolayer thin film. We found that the MWCNTs, which were synthesized by the alumina template method[18,19] formed a monolayer at the liquid–liquid interface after sonicating the MWCNT water–oil dispersion. The monolayer is transferable onto solid substrates and the transferred film was observed using atomic force microscopy (AFM).

Preparation of MWCNTs by the template method was carried out as described previously.[18,19] An anodic aluminum oxide plate, which has a nanochannel with 10–20 nm diameter and 1 μm length was used as a template. The MWCNTs synthesized using the template method have many oxygen functional groups, such as alcohol, ester, and carbonyl and carboxyl groups, which formed during alkali treatment to dissolve the template.[20] Therefore, the MWCNT synthesized by the template method is easily dispersed in hydrophilic solutions such as ethanol, water, and so on.[20] Figure 1 shows an AFM image of the casting of the MWCNT ethanol dispersion onto a silicon substrate. The MWCNTs are uniformly dispersed onto the substrate; each

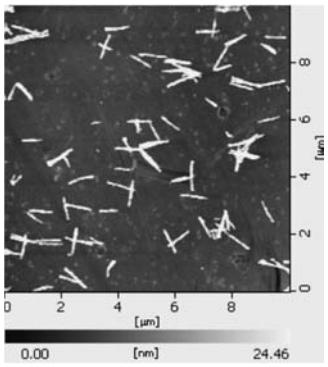

Figure 1. AFM image of MWCNTs cast from ethanol solution onto a silicon substrate.

MWCNT is about 1 μm long, which is the same length as the alumina pore used as a template. This fact indicates that well-defined MWCNTs with uniform length are produced.

Figure 2 shows the MWCNT monolayer formation process using the liquid–liquid interface. A round vessel was cleaned by O_3 treatment and rendered hydrophobic by immersion into octyltrichlorosilane chloroform solution. First, 100 μL of the MWCNTs (about 0.04 g/mL) ethanol dispersion was placed into the vessel, and 6 mL of distilled water was added to the ethanol dispersion. Then 2 mL of toluene was added to the aqueous ethanol dispersion and the vessel was sonicated for 20 min using sonicator (38 kHz; As One Corp.). Careful observation after sonication reveals that a black film is formed at the toluene–water interface.

A silicon substrate was dipped vertically into the interface to transfer the assembled film formed at the toluene–water interface onto the solid substrate. Deposition method is the same as the Langmuir–Blodgett technique. The silicon substrate was washed

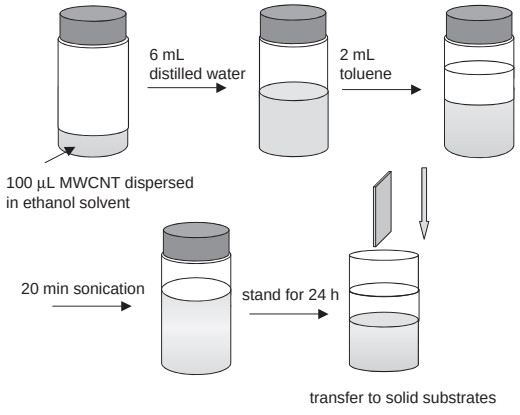

Figure 2. Procedure to fabricate MWCNT monolayer at the liquid–liquid interface.

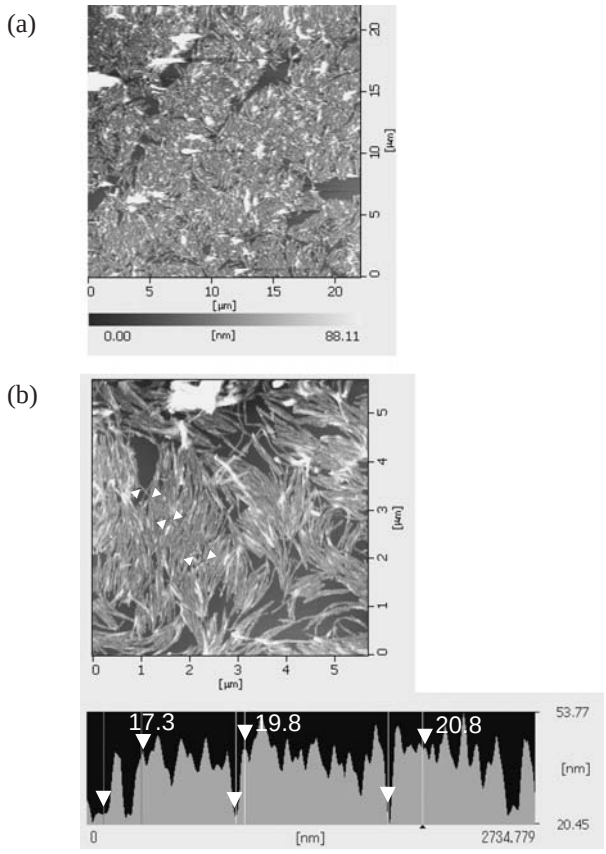

Figure 3. AFM images of the MWCNT monolayer film transferred onto a silicon substrate. a) Large area ($25 \times 25\,\mu m^2$) image. b) Small area ($6 \times 6\,\mu m^2$) image and height profiles across the sample surface.

with O_3 treatment and made hydrophilic before the dipping process. The substrate was dipped into the interface at the rate of 10 mm/min and withdrawn at the same rate. Figure 3a shows a large area ($25 \times 25\,\mu m^2$) AFM image of the assembled film. The AFM image indicates that a densely packed MWCNT thin film is transferred onto the silicon substrate. Moreover, analysis of the height profile of the small area ($6 \times 6\,\mu m^2$) AFM image (Figure 3b) indicated that the height of each MWCNT of the transferred film was determined as 17–20 nm, which is similar to the diameter of the template nanochannels, indicating that the assembled film that is formed at the liquid–liquid interface is an MWCNT monolayer and that the monolayer is transferable onto the silicon substrate using LB technique.

The formation mechanism of the MWCNT monolayer at the liquid–liquid interface remains unclarified. The MWCNT is presumed to aggregate during sonication. The MWCNTs have uniform length and a rod like structure. Therefore, the MWCNTs readily form a sheet-like aggregate. Because the sheet has a high surface-area-to-mass ratio, it will not precipitate: it floats at the liquid–liquid interface as a "raft."

In conclusion, we report a simple method to prepare a carbon nanotube monolayer using the liquid–liquid interface. The MWCNT monolayer is transferable onto solid substrates and the AFM image shows a densely packed MWCNT monolayer film. The monolayer film is anticipated to be useful not only for application to several devices, but also for understanding fundamental properties of the MWCNT.

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