Fabrication of Carbon Nanotubes Monolayer Film Using Liquid/Liquid Interface

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Introduction
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 and biological sensors, field-effect transistors (FET) and transparent conductive film 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. Here, we report a fabrication of CNT monolayer thin film using liquid-liquid interface. The multivalved carbon nanotube (MWCNT), which was synthesized by the alumina template method formed a monolayer at liquid-liquid interface after sonication the MWCNT water-oil dispersion. Moreover, with the addition of ethanol in to the dispersion, MWCNT monolayer was also formed at the liquid-liquid interface. The monolayer is transferable onto solid substrates and the transferred film was observed using atomic force microscopy (AFM).

Results and Discussion
MWCNTs were synthesized by chemical vapor deposition of acetylene onto an anodic aluminum oxide template. The MWCNTs synthesized using the template method have many oxygen functional groups, such as alcohol, ester, and carboxyl and carbonyl groups, which formed during alkali treatment to dissolve the template. The MWCNT synthesized by the template method is easily dispersed in hydrophilic solutions such as ethanol, water, and so on. Figure 1 shows an AFM image of the MWCNT, cast onto silicon substrate from ethanol dispersion. The length of MWCNTs was shorter than the template, which indicates that MWCNTs were cut during the purification process. The partially cut MWCNTs were used to fabricate monolayer thin film.

![Figure 1. SEM image of MWCNT cast from ethanol solution onto a silicon substrate](image)

Two processes were applied to prepare MWCNT monolayer using the liquid-liquid interface (Figure 2). One process used sonication (named as “sonication process”) and the other used a second organic solvent, which mixed with water such as ethanol (named as “ethanol dropping process”) to prepare MWCNT monolayer at liquid-liquid interface. Figure 2 shows the processes to prepare MWCNT monolayer. 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 ethanol aqueous dispersion to create the water-toluene liquid-liquid interface. In the “sonication process”, the vessel was sonicated for 20 min using sonicator and leave 24 h. In the “ethanol dropping process”, 10 wt% (against water) of ethanol was added into the vessel at the addition speed of 0.1 mL/min. The monolayer formed at the liquid-liquid interface was transferred onto a silicon substrate by vertically dipping the substrate into the interface.

![Figure 2. Procedure to fabricate MWCNT monolayer at the liquid-liquid interface](image)

Figure 3 shows an AFM image of the assembled film using the “sonication process”. The AFM image indicates that a densely packed MWCNT thin film is transferred onto the silicon substrate. Moreover, analysis of the height profile of 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. Similar AFM image was obtained using the “ethanol dropping process” to fabricate MWCNT monolayer at the liquid-liquid interface.

![Figure 3. AFM image of the MWCNT monolayer film transferred onto a silicon substrate and height profiles across the sample surface](image)

Several groups have been reported that nanoparticles were self-assemble at liquid-liquid interface. It was reported when the surface contact angle of nanoparticles become close to 90°, the nanoparticles were assembled at the liquid-liquid interface. In the “ethanol dropping process”, MWCNT surface charge was decrease with adding ethanol, very likely because of competitive adsorption of ethanol molecules onto the MWCNT surface. We think, with the addition of suitable amount of ethanol the surface contact angle of MWCNT become close to 90° and the MWCNTs were assembled at the liquid-liquid interface. In the “sonication process”, a middle phase micro emulsion formation was observed after sonication the water-toluene dispersion. After the micro emulsion formation, the MWCNTs may form a sheet-like aggregate. The surface contact angle of the sheet-like aggregate may close to 90° and the MWCNT were assembled at the liquid-liquid interface.

In conclusion, a monolayer film of MWCNT was fabricating using 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

References