Application of Magnetically Simulated Microgravity for Preparation of Thin Films with Carbon Nanotubes

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A poly(vinyl alcohol) (PVA) thin film in which multiwall carbon nanotubes (MWCNTs) were included was prepared in a magnetically simulated microgravity condition. The XRD pattern results and AFM observations showed that the nanotubes were oriented parallel to the surface of the film at the zero field. In contrast, they were oriented perpendicularly in the magnetic field.

Recently, a high magnetic field condition using a superconducting magnet has introduced the great creative potential of a new science, "Magneto-Science."[1] Especially, the high magnetic field gradient presents the possibility of simulating hypergravity and microgravity conditions. Microgravity can be simulated using a high magnetic field, as first reported for magnetic levitation of diamagnetic materials in 1991.[2] Although these conditions involve large potential, few applications have been reported.[3,4] In these conditions, we have prepared a large stable liquid water film and a bubble without surfactant. Moreover, the control of orientation of diamagnetic materials, carbon nanotubes, using a magnetic field is an important technique. The magnetic orientation of the diamagnetic material results not only from magnetic susceptibility anisotropy[5] but also from shape magnetic anisotropy.[6] That fact suggests that use of a magnetic field will enable orientation of almost any diamagnetic material. Some groups have reported magnetic orientation of carbon nanotubes in a polymer solution in a sample vessel.[7–11] However, the use of the sample vessel provides restrictions because of vessel properties: thermal tolerance, contamination by impurities from the vessel wall, and so forth. Magnetically simulated microgravity can achieve non-vessel conditions and magnetic orientation. We prepared poly(vinyl alcohol) (PVA) films with multiwall carbon nanotubes (MWCNTs) on glass plates to obtain fundamental data; we investigated the MWCNT orientation in the simulated microgravity condition.

A superconducting magnet (JMTD-LH15T40; Jastec, Inc.) was used. This magnet had a room-temperature 40-mm-diameter vertical bore tube. Its maximum magnetic flux density and the maximum magnetic force field (i.e., the product of magnetic flux density and its gradient) were, respectively, 15 T and $1500\,\mathrm{T^2\,m^{-1}}$.

Commercial distilled water and PVA (polymerization degree about 1500; Wako Pure Chemical Industries Ltd.) were used as received. The MWCNTs (80-nm diameter, ca. 10-μm length, VGCF-S; Showa Denko K.K.) were heat-treated at 2800 °C; the remnant iron was reduced to 20 ppm or less.

A 10 mL portion of aqueous PVA solution (3.8×10^{-2} g/mL) in which MWCNTs (0.026 g) had been dispersed was prepared using an ultrasonic homogenizer. Thin films were prepared using two methods: the PVA solution on a glass plate was held in the various magnetic fields, and the PVA film was prepared on the plate by drying on standing; alternatively, the thin films were prepared by soaking a ring in the solution placed in the bore tube, where the magnetic force field was about $-1200\,\mathrm{T^2\,m^{-1}}$; they were held in a magnetic field (about $-900\,\mathrm{T^2\,m^{-1}}$). A PVA film was prepared by drying the liquid films in the magnetic field overnight. Metal rings ($\phi = 14$–19 mm) were made from a tin-coated copper wire ($\phi = 1$ mm). The first one was used for X-ray diffraction (XRD) observation to characterize the MWCNT orientation because the dependence of the orientation on the magnetic field intensity was investigated and the film prepared using the second method was too thin (ca. 10 μm) to observe the XRD pattern. Since the whole thin film layer was examined, the concentration dependence by the distribution of the carbon nanotubes did not occur. The XRD patterns were measured (RINT2100; Rigaku Corp.); AFM images were obtained using a scanning probe microscope (SPI3800N and SPA-400; Seiko Instruments Inc.).

Figure 1 shows XRD patterns of the PVA films with

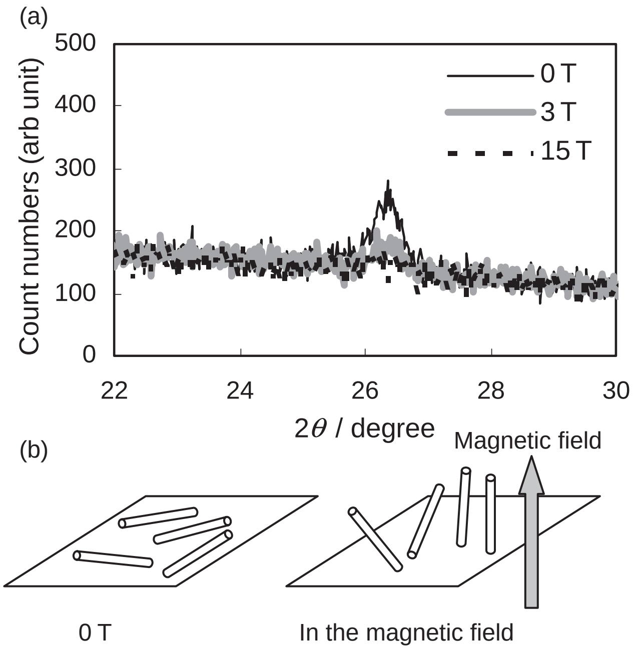

Figure 1. (a) XRD patterns of PVA films with MWCNTs. Solid line on the glass plates, 0 T; bold line, 3 T; dotted line, 15 T. (b) Possible structures of MWCNTs on the glass plates.

Figure 2. Photograph of a PVA thin film containing MWCNT prepared in the magnetically simulated microgravity (5 T, $-900\,\mathrm{T^2\,m^{-1}}$). The central area looks like a hole because of too thin thickness, but the clear layer with carbon nanotubes has been prepared.

MWCNTs on the glass plates. A sharp signal near 26 deg was observed at 0 T. This was attributed to the face-to-face distance of the MWCNT because this distance was estimated as 3.35 Å, which is nearly equal to the face-to-face distance of the graphite.[12] This signal intensity was dependent on the magnetic field strength; it decreased to less than the half at 3 T and nearly disappeared at 15 T. XRD patterns of the PVA films placed vertically showed that the sharp signal disappeared at 0 T and one appeared at 15 T, though it was weak. The result shows that the MWCNTs, at least over half of them, are oriented from 45 to 90 deg for the substrate over 3 T; these are parallel to the substrate at 0 T (Figure 1b).

Figure 2 shows a photograph of a PVA film ($\phi = 18$ mm) with MWCNTs prepared in the simulated microgravity created by the magnetic field. Although distribution of MWCNTs occurred because of the thickness difference between rim and central areas, a flat and smooth film was prepared easily. In earth gravity conditions, such a large thin film has never been prepared.

Figure 3 shows AFM images of the PVA films containing MWCNTs without the glass plate. The rod-like objects of the length over 5 µm were observed at 0 T (Figure 3a); these were assigned to MWCNTs. The result shows that MWCNTs are horizontally oriented to the face of the film. In contrast, the circular objects were observed in the simulated microgravity created by the magnetic field (Figure 3b), and these are correspondent to the tip of MWCNTs. Therefore, MWCNTs are oriented perpendicularly to the face of the film (Figure 3c). A similar AFM image to that presented in Figure 3b was obtained for the film on the glass plate. These results are consistent with those of the XRD patterns of the film on the glass plate. This indicates PVA's contraction stress does not affect the orientation seriously.

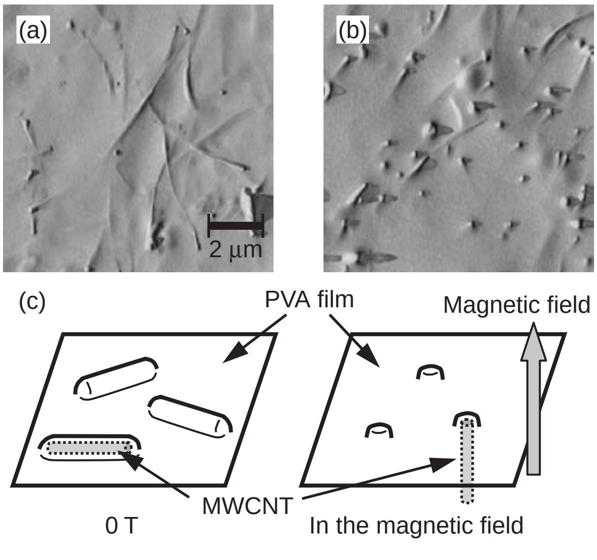

Figure 3. AFM images of PVA thin film containing MWCNT (a) 0 T, (b) 5 T, $-900\,\mathrm{T^2\,m^{-1}}$; (c) a simple sketch of the PVA films with MWCNTs.

We prepared a large PVA film with magnetic vertical orientation of MWCNTs in the simulated microgravity for the first time. Preparation of this large film without substrate is otherwise impossible under earth's surface gravity. Using this method, it is possible to produce a solid film with two clean surfaces because there is no substrate. The combination and interactive effect of the simulated microgravity condition and the magnetic orientation provide the large potential of production of new functional materials and wide application.

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