Graphitization at Interface between Amorphous Carbon and Liquid Gallium for Fabricating Large Area Graphene Sheets

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We have found that liquid gallium exhibits good catalytic properties in graphitization for a large area graphene sheet. It is known that carbon generally does not dissolve in gallium, as indicated by the solubility diagrams of bulk carbon and gallium. Therefore, three-dimensional nanostructures of various shapes can be fabricated on diamond-like carbon (DLC) by using gallium species and a focused ion beam (FIB) system [1]. In addition, we have previously reported that a DLC structure gets instantly transformed into fragment and/or tubular graphite when a current discharge pulse is applied [2]. This crystallographic transformation could be speculated by the thermal graphitization induced at an extremely high temperature under nonequilibrium gallium plasma. We have found that this catalytic reaction is not a nonequilibrium reaction but an equilibrium reaction that is limited to a very narrow interfacial region between amorphous carbon and liquid gallium. This reaction is very useful for the fabrication of large area graphene sheets.

The experiment is very simple. A twisted single-walled carbon nanotube (SWNT) wire and an ultrathin amorphous carbon film were immersed in liquid gallium that was placed in an aluminum crucible (washer), as shown in Fig. 1. These specimens were annealed in an evacuated quartz tube for 30 min from 700 to 1000 ºC, at a back pressure of approximately 10^{-4} Torr. Such static annealing of the SWNT wire and amorphous carbon film leads to the formation of a few stack of graphene.

Figure 2(a) shows a typical HRTEM image of the twisted SWNT wire before gallium treatment. This image shows fibers of purified SWNTs with a diameter of approximately 2~4 nm. Further, soot and catalyst residues are not found. However, many graphitic layers are entangled with the fibers (Fig. 2(b)), and many of the CNT bundles appear to be adhered to the graphitic surroundings. Some of CNT single fibers that protrude from the bundle clearly show the presence of conical attachments at the bottom of the SWNTs, as shown in Fig. 2(c). A CNT bundle twisted in a hairpin shape would be the best site for chemical erosion. In fact, it appears that liquid gallium first reacts in the bent region, where the original SWNT fibers have been converted into entangled graphite. Figure 3 shows the image of a gap in a cleaved wire. The thin transparent film shown in the middle is found to be a graphite sheet comprising approximately 20 graphene sheets, and the electron diffraction pattern of this region has also confirmed that the sheet is indeed graphite; the spots indicated by red circles can be indexed as (0220), coinciding with the (0002) spots from the folding region.

Figure 4 shows the optical microscope image of the ultrathin amorphous carbon film fabricated on a template of an ethylene dichloride (EDC) film stretched on the aluminum washer with a diameter of 2 mm. The amorphous carbon film of a thickness of approximately 20 nm was coated by laser ablation and vacuum annealed at 600 ℃ to completely remove the template EDC film (Fig. 4(a)). Such amorphous carbon film was stamped on the gallium droplet so as to transform the film on the gallium surface, as shown in Fig. 4(b). It should be noted that the amorphous carbon film remained intact even after annealing it at 1000 ℃ for 30 min. The HRTEM image of the annealed film is shown in Fig. 4(c); the annealed film was separated from liquid gallium by soaking it in hydrochloric acid. Although the original amorphous carbon film had a thickness of approximately 20 nm, many of the folded parts formed on one side of the amorphous carbon film comprised approximately 3 to 5 graphene sheets (having a thickness of approximately 1~2 nm), and the other side of the amorphous

carbon remained intact. That implied that although liquid gallium covers a large area, the catalytic reaction was limited to the region just above the liquid surface. We believe that by optimizing this reaction, we can fabricate a true single graphene sheet with large area.

References

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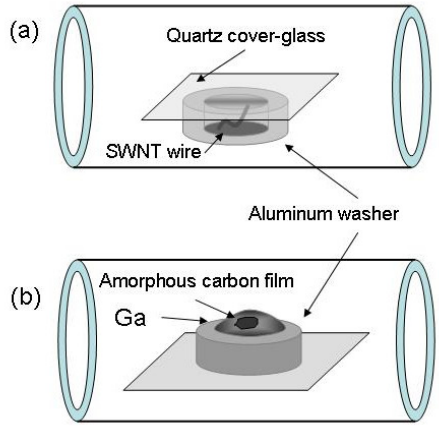

Figure 1 Schematic of gallium treatment of (a) twisted SWNT wire and (b) ultrathin amorphous carbon film. The quartz coverglass is used to prevent gallium evaporation during annealing.

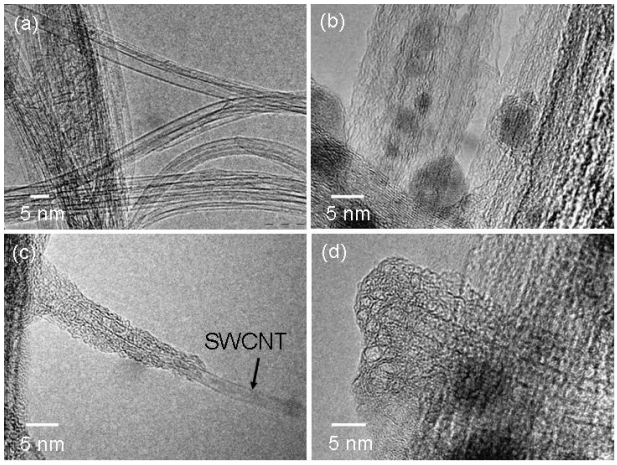

Figure 2 High-resolution TEM images of twisted SWNT wire (a) before and (b) and (d) after gallium treatment. The dark spots indicate gallium droplets that are covered with graphitic onions.

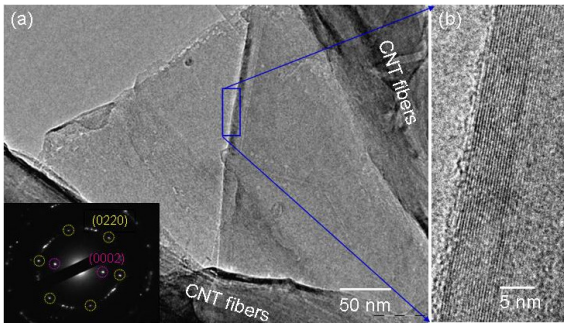

Figure 3 High-resolution TEM images of cleaved SWNT wire. Many parts of the SWNT wire appear to be covered with graphitic layers after gallium treatment. These layers are very thin, comprising approximately 20 graphene sheets.

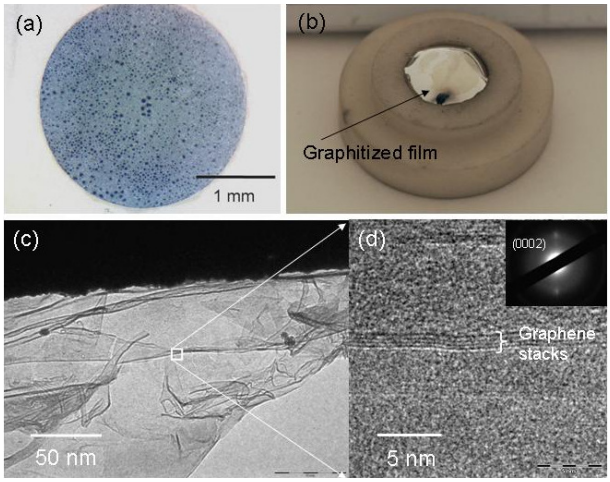

Figure 4 Optical microscope images of (a) EDC and (b) graphitized films on liquid gallium. The HRTEM images of the films treated with gallium show that a thin graphite layer comprising approximately 5 graphene sheets are formed on one side of the original amorphous carbon film.