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Carbon Nanotube Growth from Diamond

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Precise control of the structure and density of carbon nanotubes (CNTs) is indispensable for applying them to nanoelectronics. Metal particles have been used as catalysts for CNT growth by chemical vapor deposition (CVD). Conventional catalysts Fe, Co, and Ni and noble metals, such as Au, Pt, and Pd, mediate CNT growth via their nanoparticles in the liquid phase or highly mobile solid phase with the bulk diffusion of carbon.[1] Since the structure of these particles fluctuates, precise structure control of CNTs is difficult. Additionally, the density of grown CNTs is limited because the density of the catalyst particles must be suppressed to avoid particle aggregation and fusion, which significantly reduce the catalytic activity of the nanoparticles. To overcome these problems, we have explored CNT growth from particles in the stable solid phase and discovered that semiconductor and oxide solid particles, such as SiC and Al_2O_3, act as CNT growth nuclei.[2] The CNT growth from solid particles may offer new avenues for structure-controlled CNT growth based on the epitaxial relationship between CNTs and crystalline solid particles. However, the mechanism of CNT nucleation on a solid surface has not been fully understood, and the limitation of catalyst density remains a crucial unresolved issue.

Here, we show that diamond can solve the above issues. We found that nanosized diamond particles act as CNT growth nuclei effectively in CVD. Since the CVD growth process and surface structure of the diamond have been extensively studied,[3] the diamond is an ideal material to elucidate the CNT growth mechanism from solid particles. Moreover, the nonfusion characteristic of nanodiamond particles helps to improve the particle density and will change the paradigm of CNT growth from nanoparticles.

We used nanodiamond particles 4−5 nm in size produced by the detonation method (NanoCarbon Research Institute Co., Ltd., Japan) to promote CNT growth.[4] Since diamond does not have the ability to decompose carbon-bearing molecules such as CH_4 and ethanol, the term “catalyst” as used for metal particles is unsuitable for nanodiamond particles. We therefore refer to a nanodiamond particle for CNT synthesis as a growth “seed”. The nanodiamond particles were dispersed in ethanol (0.01−1.0 wt %) and spread on a substrate. By controlling the concentration of nanodiamond particles in the ethanol solution, we prepared isolated, two-dimensionally packed and three-dimensionally accumulated nanodiamond particles. Nanodiamond particles are enclosed in amorphous carbon or graphite, even if the particles are purified.[4] Samples were heated in air for 1−15 min at 600−700 °C to remove residual carbonaceous materials and impurities. This treatment also decreased the size of the nanodiamond particles. After heat treatment in air, CNTs were grown at 850 °C by CVD using ethanol as a carbon source. The high-temperature growth condition promotes ethanol decomposition. With this pyrolysis of ethanol, nanodiamond particles act well as CNT growth seeds.

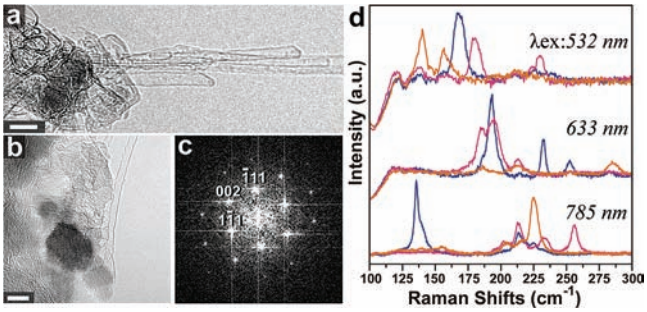

Figure 1. (a) TEM image of single-layer tubes and caps. (b) TEM image of SWCNT and nanodiamond growth seed. (c) Fourier transform pattern obtained from b. Diffraction spots originating from ($\bar{1}11$), (002), and ($1\bar{1}1$) surfaces of diamond crystal. Scale bars in Figure 1a,b are 5 nm. (d) Raman spectra in the low-wavenumber range of SWCNTs.

The transmission electron microscopy (TEM) images of grown CNTs and diamond particles are shown in Figure 1a,b, and a Fourier transform image of Figure 1b is shown in Figure 1c. Figure 1a indicates that CNTs grown from nanodiamond seeds are single-walled carbon nanotubes (SWCNTs) without amorphous carbon adhesion. Grown SWCNTs have caps like metal-catalyzed SWCNTs,[5] but the caps do not have a hemispherical shape. This may reflect the mechanism of CNT nucleation from diamond as described later.

These figures prove that crystalline nanodiamond particles are the seeds of CNT growth. Raman scattering spectra in Figure 1d reveal that SWCNTs 1−2 nm in diameter were synthesized.[6] Additional analysis of the grown CNTs and seed particles by scanning transmission electron microscopy, energy dispersive X-ray spectroscopy, and X-ray fluorescence spectroscopy indicate that diamond can act as CNT growth seeds (Supporting Information: Figures S1 and S2; Table S1).

The scanning electron microscopy (SEM) images in Figure 2a−d highlight the large advantage of diamond for CNT growth. Aggregated nanodiamond particles do not fuse to each other in the CNT growth temperature and preserve their ability for CNT growth seeds, as shown in Figure 2a (before CNT growth) and 2b (after CNT growth). CNT growth from accumulated seeds without fusion is tangible proof that CNTs are synthesized from diamond particles in the solid phase, not in the liquid phase.

Three-dimensionally accumulated nanodiamond seeds can also contribute to the high-density CNT synthesis. Since accumulated nanodiamond particles take on porous structure as shown in inset of Figure 2a, not only the particles exposed on the layer surface but also the particles inside the layer can act as CNT growth seeds. This feature of nanodiamond seeds leads to high-density CNT growth. Figure 2c shows rolled-up-carpet-like CNT growth on a graphite substrate. High-density CNTs grown from accumulated

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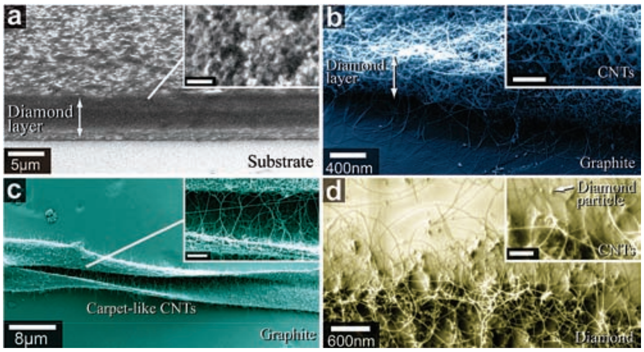

Figure 2. SEM images of grown CNTs from nanodiamond particles. (a) Nanodiamond particles after air (700 °C) and Ar/H_2 heating (850 °C). The particles can preserve own size in present CVD ambience. (b) CNT growth from three-dimensionally accumulated nanodiamond seeds on graphite substrate. (c) Rolled-carpet-like high-density CNT growth on graphite substrate. (d) CNT growth from nanodiamond seeds on diamond substrate. Insets in (a)−(d) are magnified images. Scale bars in inset images (a)−(d) are 30, 200, 800, 150 nm, respectively.

nanodiamond seeds are clearly observed in the magnified view. Isolated nanodiamond particles can also act as CNT growth seeds as shown in Supporting Information Figure S3.

In metal-catalyzed CNT growth on substrates that react with metal nanoparticles, metal nanoparticles do not act well as catalysts.[7] This limitation can be overcome by using the features of diamond. For example, as shown in Figure 2d, by using the nanodiamond as a CNT growth seed, CNTs can be synthesized easily on a diamond substrate, which reacts with metal particles in CVD ambience. Because of the very low reactivity of diamond with various materials compared with metals, more kinds of substrates become available for CNT growth.

Even if a material that reacts with diamond is used as a substrate, such as Si, CNTs can be synthesized by using accumulated nanodiamond particles. Nanodiamond particles in the upper part of the accumulation layer do not react with the substrate. This means CNTs can be synthesized on any kind of substrate, such as semiconductors (Si, SiC, etc.), insulators (SiO_2, sapphire, etc.), metals (Pt, Au, etc.), and metal-oxides (Al-oxide, Mg-oxide, etc.), as shown in the Supporting Information (Figure S4).

In metal-catalyzed CNT growth, metal catalysts form metal−carbon alloys, which can be either liquid phase or highly mobile solid phase.[1c,d] Similarly to the well-known growth mechanism of semiconductor nanowires, CNT growth from a liquid particle occurs via the so-called vapor−liquid−solid (VLS) mechanism, while the growth from a solid particle occurs via the vapor-solid−solid (VSS) mechanism.[8] In both cases, carbon atoms are supplied to the CNT through bulk diffusion of carbon in the particle. Diffusion of carbon in diamond is negligibly small compared with that in metal such as Fe.[9] It is therefore unlikely that bulk diffusion of carbon contributes to CNT growth. That is, CNT growth from nanodiamond particles must be promoted by surface diffusion of carbon. Here, we expediently call this growth mechanism "vapor−solid surface−solid" (VSSS). The VSSS mechanism of CNT growth on the nanodiamond surface is analogous to the mechanism of homoepitaxial diamond growth.

The mechanism of homoepitaxial diamond growth on diamond has been investigated extensively.[3] In homoepitaxial diamond growth, the diamond surface is kept in the sp^3 state by hydrogen termination. It has been proposed that homoepitaxial diamond growth is caused by substitution of the hydrogen on a diamond surface by CH_3, C_2H_2, or other C_nH_m species, which derived from carbon feedstock via complicated reactions induced by atomic hydrogen.[10,3] On the other hand, in the present CVD condition, hydrogen termination of the diamond surface is inhibited, because the density of atomic hydrogen is insufficient as discussed in Supporting Information and Figure S5. Since hydrogen termination is suppressed, the diamond surface becomes a π-bond (sp^2-type) relaxed surface instead of an sp^3 surface appropriate for homoepitaxial diamond growth.[11] Further, in the environment with depletion of atomic hydrogen, graphite is not etched. As a result, a small domain of graphite sheet (hereafter graphite island) is formed on the π-bond relaxed surface of the diamond. The grown graphite island including five-membered rings on a nanodiamond seed will have a nanosize curvature corresponding to or even smaller than that of the seed. The curved graphite island lifts off the diamond surface except the edge of the island and becomes a CNT cap.[2a,12] The edge of the CNT cap is chemically active and acts as incorporation sites for carbon adatoms, where CNT formation is induced. The difference in the homo- (diamond) and hetero- (CNT) growth between carbon allotropes would originate from an atomic hydrogen deficiency in a CVD ambience and the structure and curvature of the diamond surface. Thus, CNT growth from diamond can be explained by the VSSS mechanism with only the surface diffusion of carbon.

The mechanism of CNT growth from metal particles is very complex because it involves bulk diffusion and precipitation of carbon in binary catalyst particles, such as Au−C and Fe−C.[1c,d,13] On the other hand, the CNT synthesis from diamond with VSSS can be understood as a simple surface reaction system. Since it has been indicated that CNT-cap nucleation is influenced by the structure of a solid surface using *ab initio* calculation,[14] CNT growth in the VSSS mechanism would be useful for chirality control of CNTs.

Supporting Information Available: Methods, Table S1, and Figures S1−S5. This material is available free of charge via the Internet at http://pubs.acs.org.

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