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Dispersion of metal nanoparticles for aligned carbon nanotube arrays

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We report that Co metal nanoparticles (an average diameter of 4 nm) chemically synthesized by a reverse micelle method catalyzes the growth of multiwall carbon nanotubes (MWNTs) aligned perpendicular to a substrate. The surface of the nanoparticles is covered with surfactants so that the nanoparticles can be dispersed in organic solvent. The dispersion of the nanoparticles was cast directly onto a plane Si substrate for thermal pyrolysis of acetylene. We have found that the pretreatment of the metal nanoparticles with hydrogen sulfide before the pyrolysis straightens the MWNTs, suggesting sulfurization of the nanoparticle catalyst plays an important role in regular growth of the MWNTs. The dispersion of the nanoparticles offers a conventional and processible approach to synthesize large area aligned MWNT arrays. © 2000 American Institute of Physics. [S0003-6951(00)05327-4]

Carbon nanotubes either in their single wall or in multiwall form have been extensively studied for macroscopic applications in many areas, such as electronics, mechanics, and energy storage.¹ As a method to synthesize carbon nanotubes, chemical vapor deposition (CVD) in the presence of a transition metal catalyst has attracted a great deal of interest, because the CVD proceeds at relatively lower temperature (below 1000°C) with less carbon impurities compared with arc discharge or laser ablation methods.²⁻⁷ Moreover, the catalytic CVD method offers a new route to control over the alignment and/or direction of carbon nanotubes. Recently, it has been shown that the CVD method enables directional growth of carbon nanotubes, which could be developed into nanoscopic integrated circuits using nanotubes.⁸

In the catalytic CVD method, metal nanoparticles are essential for the growth of carbon nanotubes, because they work as a catalyst of the nanotube growth; the size and chemical composition of the metal nanoparticle determines diameter and structural perfection (degree of graphitization) of the nanotube.² It is also noted that metal nanoparticles are indispensable for the nanotube growth not only in the CVD method but also in arc discharge or laser ablation methods.^{1,2} Metal nanoparticles employed in the CVD synthesis of carbon nanotubes have been prepared mainly by the following two methods. One method is to use nanoporous or mesoporous substrates, such as zeolites,⁵ porous Si,⁶ and anodized Al₂O₃,⁹ in which metal nanoparticles are confined through evaporation or impregnation. Another method is to etch a metal substrate or a metal-coated substrate by laser ablation³ or plasma treatment.⁴ The physical etching generates metallic nanoparticles, which play a role as a catalyst for nanotube growth. For future development, a more simple synthetic method applicable to plane and large area substrates is very important.

In this letter, we have synthesized Co metal nanoparticles by a reverse micelle method and applied them for the CVD synthesis of carbon nanotubes. We show that straight and aligned multiwall carbon nanotubes (MWNTs) were formed from the nanoparticles pretreated with hydrogen sulfide (H₂S) on a plane Si substrate. This array of the MWNTs has potential applications, especially to field emission displays (FEDs), because the density of the present MNWT array is relatively low and the array can be developed to a large area.

In a reverse micelle method, metal chloride is reduced in a nanoscale water pool surrounded by surfactants to form the metal nanoparticles stabilized by the surfactants. We employed didodecyldimethylammonium bromide (DDAB) and sodium borohydride (NaBH₄) as the cationic surfactant and reducing agent, respectively.¹⁰ First, DDAB was dissolved in toluene with a 10 wt % concentration, followed by dissolving cobalt chloride (CoCl₂ 6H₂O) to a concentration of 0.005 M. Under vigorous stirring, 5 M NaBH₄ aqueous solution was added to the toluene solution with a concentration of $[BH_4^-]/[Co^{2+}] = 3:1$. The solution turned from light blue to black, suggesting the formation of a colloidal dispersion of Co nanoparticles. All the above procedures were performed in a glove box filled with nitrogen gas to avoid oxidation. The Co nanoparticles were purified by repeating centrifuge and redispersion in toluene and acetone. The final dispersion of the Co nanoparticles in acetone was cast onto a plane crystalline Si substrate and dried at room temperature.

In order to activate and sulfurize the Co nanoparticles, their cast film was heated in H₂S and H₂ gas diluted with nitrogen at 400 °C for 2 h prior to the pyrolysis. For comparison, we also examined H₂ gas without H₂S for the activation under the same condition. The pyrolytic reaction was carried out at 800-900 °C in acetylene (C₂H₂) gas diluted with nitrogen for 1 h.

Figure 1 shows Co nanoparticles synthesized by the reverse micelle method. It is seen that Co nanoparticles are well separated with a certain distance due to the presence of the surfactants that cover the surface of the nanoparticles. In the present condition, an average diameter of the nanoparticles was estimated to be 4 nm from the TEM image. We note that these nanoparticles can be dispersed in organic sol-

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FIG. 1. TEM micrograph of Co nanoparticles prepared by a reverse micelle method. Dispersion of the nanoparticles in toluene was cast onto a polymer-coated TEM grid for the TEM measurement.

vent and their size is tunable by the water concentration of $NaBH_4$ aqueous solution,¹¹ which promises processibility and wide variation of the nanoparticles made by the reverse micelle method.

The concentrated dispersion of the Co nanoparticles was cast onto a plane Si substrate and subjected to pyrolysis of C_2H_2 gas. The pyrolysis in the presence of the H₂-pretreated Co nanoparticles resulted in a MWNT array as shown in Fig. 2(a). The MWNTs showed the outer and inner diameters of 20–40 and 8–20 nm, respectively. Because the diameter of the catalyst tends to correspond to the inner diameter of the MWNTs for the CVD method,⁵ the diameter which was ob-



FIG. 2. SEM micrographs of MWNTs grown from Co nanoparticles actitrans avated in H₂ gas prior to the pyrolysis (a) and MWNTs grown from H₃S-pretreated Co (b).



FIG. 3. High-resolution TEM image of a MWNT grown from H_2S -pretreated Co metal nanoparticles.

served of the MWNTs suggests that the as-prepared Co nanoparticles aggregate to form bigger clusters (we use the term "clusters" for aggregates of the original nanoparticles). Although the MWNTs are not perfectly straight, one can see that they have a tendency to grow perpendicular to the substrate.

We have found that pretreatment of the Co nanoparticles with H_2S gas straightens the MWNTs [Fig. 2(b)]. Moreover, the MWNTs grew almost perpendicular to the substrate. We have also found that the present MWNTs have a wider range of outer diameters (30–80 nm) than those of MWNTs generated from nonsulfurized Co nanoparticles (20–40 nm). The corresponding high-resolution transmission electron microscopy (HR-TEM) image of the MWNT shown in Fig. 3 indicates that some MWNTs have a well-graphitized structure.

To study the growth mechanism, bases of the aligned MWNTs synthesized from H₂S-treated Co nanoparticles have been investigated (Fig. 4). We note that the present nanoparticles are suitable for the study of the growth mechanism because the nanoparticles are not confined in nanoporous substrates. Figure 4(a) indicates a SEM image of the substrate in the initial stage of the MWNT growth. It is supposed that Co nanoparticles aggregated and formed Co clusters with a droplet-like shape during the heating and the following pyrolysis processes. Interestingly, we have found that the MWNTs grow from each tip of the droplet-like clusters as shown in Fig. 4(b). From TEM studies, a metal cluster was also found at a tip of the MWNT after the growth.

Based on the above observations, we propose a possible growth mechanism as follows. In the beginning, Co metal nanoparticles aggregate and react with C_2H_2 gas, leading to a droplet-like cluster [Fig. 4(a)]. The cluster should be metal or metal carbide. Co atoms located at the tip of the cluster is supposed to be the most reactive in the cluster, because the atoms at the tip have the highest surface area and, they are significantly exposed to C_2H_2 . Hence, we speculate from



FIG. 4. SEM micrographs of bases of MWNTs: (a) metal clusters with a droplet-like shape which can be regarded as seeds of the MWNTs, and (b) a boundary between an area with fully grown MWNTs and an area with droplet-like clusters.

SEM and TEM images that further pyrolytic reaction occurs at the tip of the cluster being similar to a standard tip-growth model.³ Finally, a MWNT is formed having a metal cluster at the MWNT tip. It is noted that metal-filled MWNTs were frequently found together with hollow MWNTs, suggesting the metal cluster at the MWNT tip can have a rod shape.¹²

The effect of H₂S treatment is also an important issue, because it may be closely related to the growth mechanism. We think the main effect of H₂S is the reduction of catalytic activity (poisoning) of the Co nanoparticles by sulfur.¹³ It is well known that sulfur blocks active surface sites of transition metal catalysts, such as Ni and Co, by forming chemical bonds with metal atoms. The poisoning reduces the number of catalytically active sites and would limit the direction of the MWNT growth. Another possible effect is a stimulation of forming droplet-like metal clusters [see Fig. 4(a)]. This effect was confirmed by a primary study of vacuumevaporated Co metal thin film treated with H₂S and H₂ gas at 400 °C (not shown here). The metal film treated with H₂S gas showed prominent change in the film morphology, resulting in grains of metal clusters somewhat similar to those obtained for the Co metal nanoparticles. On the other hand, the film treated with H₂ gas showed almost no change. It is interesting to note that the observed change of the diameter was also reported for SWNTs synthesized by an arcdischarge method.¹⁴ The arc-discharge method using a sulfur-doped graphite rod leads to the increase in the diameter of the SWNTs from 1.3–1.5 to 2.7–3.6 nm.¹⁴ The role

of sulfur atoms as well as the growth mechanism of the present MWNT arrays is interesting and a more detailed discussion will be reported elsewhere.

The present MWNT array is different from previous catalytically grown MWNT arrays in terms of the density of MWNTs. The present sample is less dense (10^7 cm^{-2}) compared with previous aligned MWNT samples.^{3,5,7} Davydov *et al.* pointed out that density of emission sites is essential for FED property and that the less dense array is better for FED applications.¹⁵ This is because an applied electric field tends to concentrate at each tip of the MWNTs for the lowdensity nanotube array. Therefore, we think the present MWNT array is promising for a FED application. We would like to note that the arrays can also be used for a high surface area metal electrode for macroscopic devices.¹⁶

In summary, we have shown that a cast film of dispersion of Co nanoparticles catalyzes growth of the MWNT. We have found that the addition of sulfur into the nanoparticles stimulates the straight growth of the MWNTs and increases the diameter of the MWNTs. Because the present method does not require porous substrates, it offers a simple and processible approach to a large area aligned MWNTs array. The nanoparticles here are available as dispersion in solvent so that they could be applied to an ink-jet method for micropatterning of nanotube arrays.

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¹See, for example, *The Science and Technology of Carbon Nanotubes*, edited by K. Tanaka, K. Fukui, and T. Yamabe (Elsevier, Oxford, 1999).

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