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Catalytic growth of carbon nanofilament in liquid hydrocarbon

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Carbon nanofilaments were grown on silicon substrates by using a novel catalytic method in an organic liquid hydrocarbon. Nonequilibrium catalytic deposition gave significantly pure carbon nanofilaments with very little soot within a few minutes in n-octane. Scanning electron microscope images indicate that the nanofilaments are grown perpendicular to the Si substrate surface. This very rapid and dense production of carbon nanofilaments can be attributed to the great difference of chemical potential between the substrate surface and reactant liquid.

KEY WORDS: catalytic growth; carbon nano filament.

1. Introduction

The production and utilization of nano-carbon materials such as fullerene, filament, and carbon nanotubes (CNTs) have attracted much recent attention [1–3].

In general, various methods of synthesizing carbon filaments or CNTs – such as the disproportionation of CO [4–8], the thermal decomposition of hydrocarbons [9–15], arc discharge [16,17], laser ablation [18], and plasma CVD [19], – have been reported. Until now, however, these have been no satisfactory method for the production of carbon filaments or CNTs.

Recently, we proposed one of the most effective method for synthesizing CNT using liquid-phase nano-amorhozo [20,21]. In the liquid-phase nano-amorhozo method, CNTs were grown in organic liquids such as methanol and ethanol. This liquid-phase synthetic method enables great chemical flexibility and synthetic tunability, and the synthesis process is compatible with the existing semiconductor processes and easily adaptable to industrial production levels. CNTs produced by arc discharge must be separated from many impurities such as soot by various purification steps. In contrast, carbon nanomaterials produced using the liquid-phase nano-amorhozo technique do not need to be separated from products. Moreover, because carbon nanomaterials can be formed with high efficiently in large yields on Si substrate, they might be applied to the development of new and unique electronic devices.

In this paper, we designed on effective technique for synthesizing of carbon nanofilament on Si substrate in liquid hydrocarbon using n-octane, an important ingredient in chemical feedstock. In our method, the organic liquid is rapidly converted into solid carbon nanofilament.

2. Experimental

The apparatus consisted of a quartz chamber with outside cooling (figure 1). A direct current (DC) electric power supplier was used to apply a controlled current to the substrate. High-purity n-octane (99.7%) was used as the organic liquid source. Fe-loaded Si (100) substrates of low resistance (0.002 Ω·cm) and a size of $10 \times 20 \times 1\ \mathrm{mm}^3$ were placed perpendicularly on the center of the chamber in the liquid and connected to the electric power supplier. Then the Fe-loaded Si substrate was heated up to 1073 K by applying electrical current through the Fe-loaded Si substrate. The heating rate was 300 K/min. Substrate temperature was measured by optical pyrometers.

2.1. *Catalyst preparation*

The Si (100) substrate was ultrasonically cleaned in acetone and coated with Fe film 5 nm thick in a magnetron sputtering system using low-DC electric voltage (0.4 kV, 30 mA) and low Ar pressure (0.6 torr) for the production of nucleation sites for carbon nanofilament growth. After the chamber was filled with organic liquid, N_2 gas was introduced into the chamber for several minutes.

2.1.1. *Characterization*

Scanning electron microscopy (SEM) results were observed using a HITACHI S-4500. Transmission electron microscope (TEM) results were performed using a JEOL JEM-2010 (200 kV) on samples so that the morphology of the deposited carbon could be determined.

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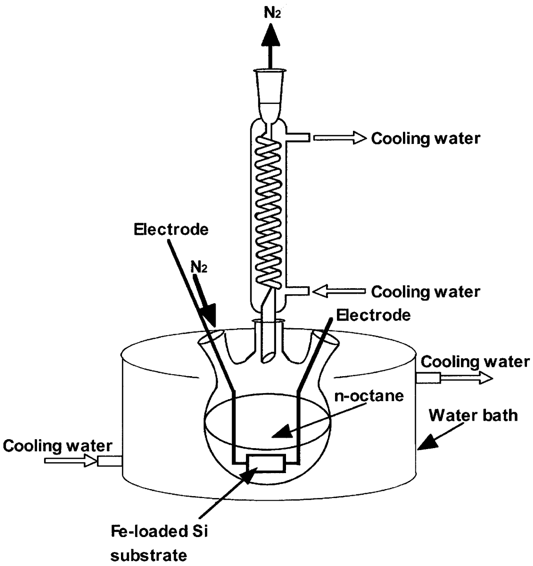


Figure 1. Schematic of the experimental setup chamber used to synthesize carbon nanofilament in liquid hydrocarbon. Substrate temperature was measured by optical pyrometers.

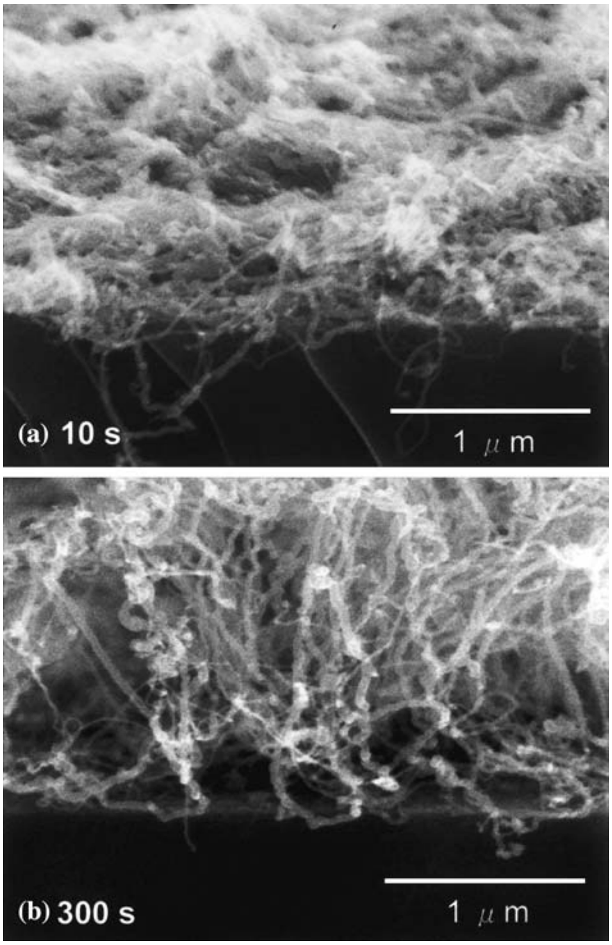


Figure 2. SEM images of carbon nanofilaments on a Si surface formed in n-octane.

Raman spectroscopy with a 1-μm depth resolution by Ar^+ laser excitation (NR-1800 MB, Jasco) was used.

3. Results and discussion

n-Octane was the only liquid hydrocarbon source used in our experiments. The as-grown carbon nanofilaments appeared as a dark black film on the Si substrate. Scanning electron microscope (SEM) images revealed that the sample consisted almost entirely of carbon nanofilaments (figure 2). The carbon nanofilaments were prepared in n-octane liquid at 1073 K. The reaction times were 10 and 300 s, respectively. Although their diameters and lengths differed, both nanofilaments had a zigzag structure.

Figures 3 and 4 show TEM images of carbon nanofilaments produced by 300 s reaction. The carbon nanofilaments were prepared in n-octane liquid at 1073 K. According to HRTEM image, the carbon nanofilaments partially have a coaxial hollow channel such as multi-walled or cup stacked structures, however graphite layers were not clear.

We previously reported carbon nanotube formation in liquid methanol [20,21]. In liquid methanol, carbon nanotube had a straight, fine, and coaxial hollow channel. However, in liquid n-octane, the carbon nanofilaments had a meandering and comparatively thick structure. Although it is premature to discuss the role of feeding or the state of the catalyst, these observations might suggest that the formation mechanisms and characteristics of the carbon nanomaterials, which were formed over Si substrates strongly depended upon the reaction conditions. Especially, presence of oxygen species in liquid hydrocarbons might have an important role for the oxidization state of iron catalysts. For nanocarbon synthesis in liquid hydrocarbon, oxidic iron phases would synthesize carbon nanotubes, on the other hand, metallic iron phases would form carbon nanofilaments.

The critical role of the catalytic Fe film was confirmed by the fact that, when Fe film was absent on the Si substrate, there was no growth of carbon nanofilaments, although a carbon film did grow. Morphologically, the carbon nanofilaments were very sensitive to both the substrate temperature and the thickness of the Fe film on the Si substrate. When the thickness of the Fe film on the Si substrate was 3 nm, the density of the synthesized carbon nanofilaments on the substrate surface was low.

The Raman spectra are shown in figure 5a, b. The spectra of the samples were obtained after the synthesis of carbon nanofilament in liquid n-octane. Both the carbon nanomaterial produced with a reaction time 10 s and that produced by 300 s reaction showed two main bands at ca. 1400 (D band) and 1600 cm-1 (G band). The D band was considered to arise from the structural defects of graphite. In addition, the G band is ascribed to the in-plane carbon–carbon stretching vibration of graphite layers [21]. Both

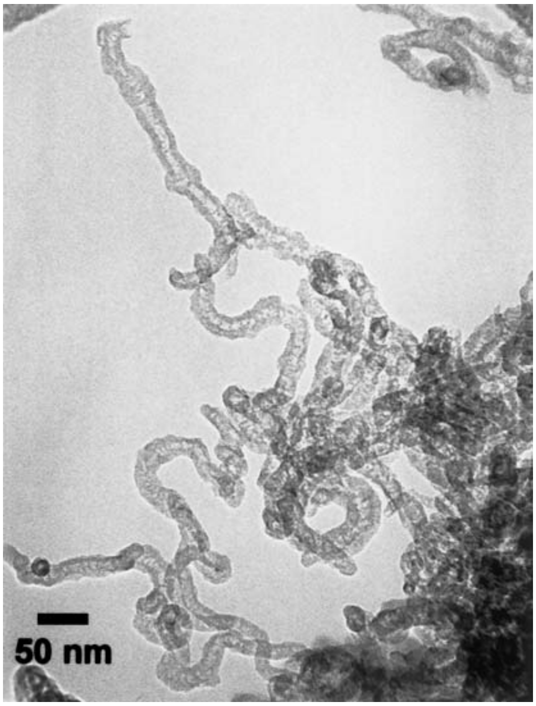


Figure 3. TEM image of carbon nanofilaments on a Si surface formed in n-octane.

bands were broad, and no graphite structures developed. This is the reason that the samples could be prepared at a temperature as low as 1073 K.

Scheme 1 shows a model of the growth mechanism of carbon nanofilaments in organic liquid hydrocarbon. The deposition of the precursor was essentially a heterogeneous process, which proceeded on the catalyst rather than in the bulk of the liquid. The temperature of the substrate catalyst surface was very high (approximately 1073 K), while the temperature of the reactant liquid was very low (below boiling point). Because the decomposition reaction can proceed only at the hot substrate surface and cannot occur in the bulk liquid phase, byproducts such as soot or other carbonaceous materials are not generated. Under these nonequilibrium reaction conditions, n-octane is a liquid, carbon nanofilament is a solid product, and H_2, which is another product, is gaseous (reaction 1).

$$C_8H_{18}\ (l) \rightarrow 8C\ (s) + 9H_2\ (g) \qquad (1)$$

Therefore, the large difference in interface temperature between the substrate catalyst and the liquid phase causes a large gradient of the chemical potential to give very high nucleation density and high growth rate. This large gradient also affects the direction of growth of the carbon nanofilament. On the substrate surface, hydrocarbon was absorbed and decomposed into carbon atoms and hydrogen gas in the catalyst Fe film. Carbon atoms then diffused through the catalyst to an outlet, forming nanofilament. In addition to n-octane, benzene was also tested in our experiments. In conclusion, the method presented herein might be used a wide range of research and industrial applications, such as synthesizing various carbon nanofilaments and films directly in liquids. This method of nanofilament synthesis has several important features. First, carbon nanofilaments were synthesized by a catalytic process under nonequilibrium thermal conditions on the Si substrate surface, where the temperature could be controlled in liquid hydrocarbon. Second, the large temperature gradient at the carbon nanfilament root perpendicular to the substrate surface may be an

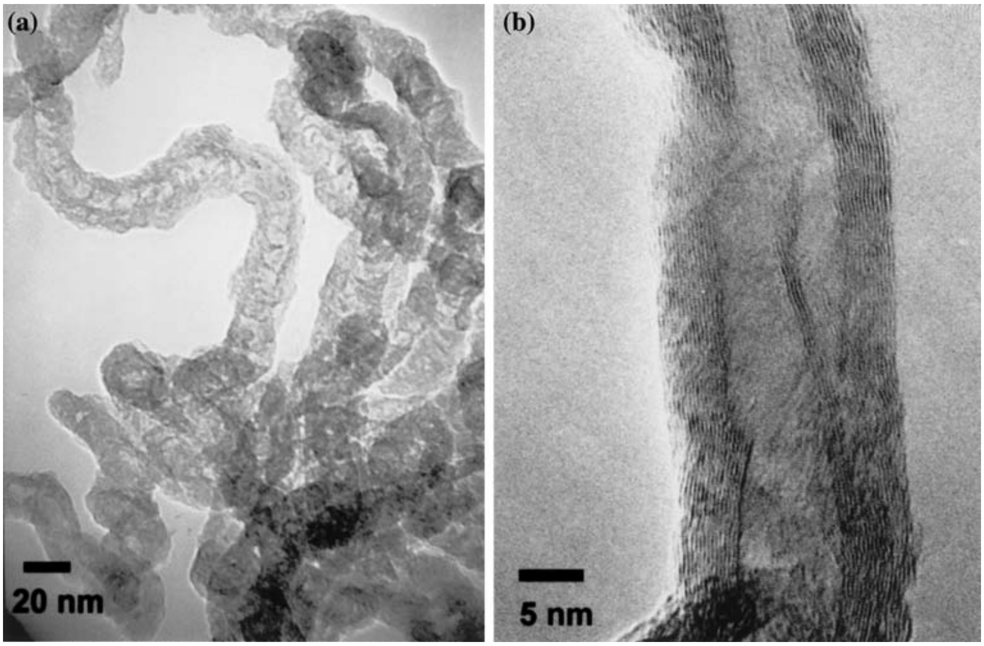


Figure 4. HRTEM images of carbon nanofilaments on a Si surface formed in n-octane.

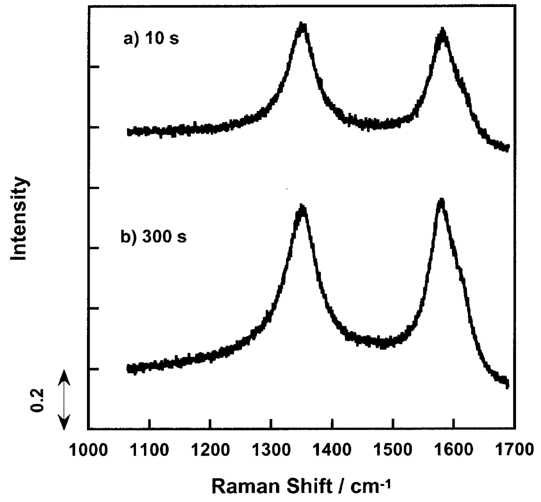
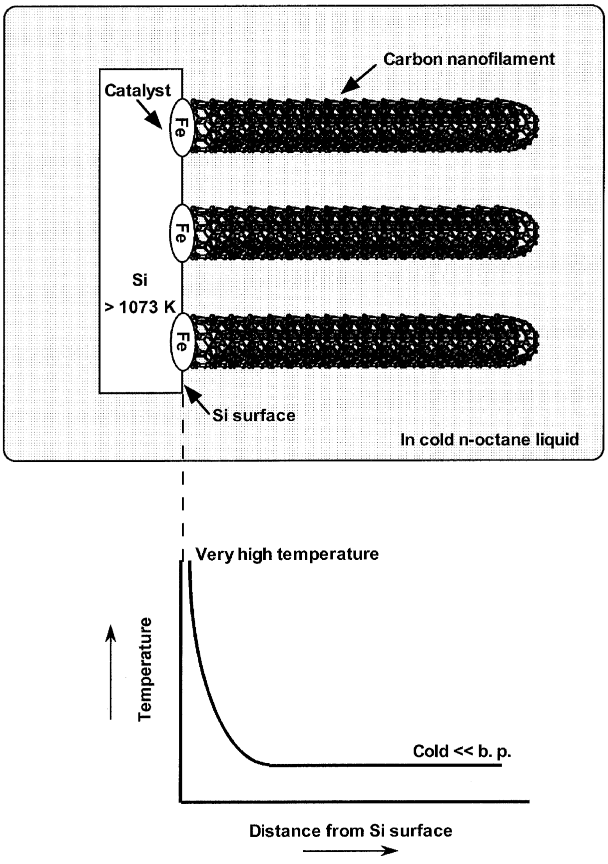


Figure 5. Raman spectra of carbon nanofilaments on a Si surface formed in liquid n-octane.

important force for the normal orientation of the carbon nanofilament because of the liquid surrounding the substrate. Third, our synthetic method is very simple; carbon nanofilament may be mass-produced, and easily introduces different elements into the liquid source for modified carbon nanofilaments production. Finally, the liquid phase synthesis process is entirely compatible with current Si technology.



Scheme 1. Model of rapid and selective synthesis of carbon nanofilament using liquid-phase nano-amorhozo.

4. Conclusions

In summary, we could synthesize carbon nanofilaments with rapid and selective growth using liquid-phase nano-amorhozo. In liquid-phase nano-amorhozo, the large difference in interface temperature between the substrate catalyst and the liquid phase causes a large gradient of the chemical potential to give very high nucleation density and high growth rate. Our new findings suggested that the present technique might be used to synthesize carbon nanomaterials in liquid hydrocarbon.

Acknowledgments

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