Continuous Production of Carbon Nanostructures Using Plasma Jet

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We have developed a continuous synthesis technique to produce carbon nanostructures using a well-controlled plasma jet. In this method, numerous fiber-like structures can be produced readily using CH_4 gas and H_2 gas without a catalyst. Without a catalyst, carbon nanostructures that have small diameters in the range of about 10-100 nm are mostly produced. The effect of metal catalysts on carbon nanostructure synthesis is also studied. The yields of carbon nanostructures are dramatically increased using Ni substrate and/or Ni powders in the gas-phase synthesis of CH_4 and H_2.

KEYWORDS: thermal plasma processing, plasma jet, continuous fabrication, carbon nanotubes, carbon nanofibers

1. Introduction

Recently, much attention has been paid to both the control of the growth direction and mass production of high-quality carbon nanotubes (CNTs) owing to their possible applications, such as in field emission devices.[1] An arc discharge method and plasma-enhanced chemical vapor deposition (PECVD) are widely used for the preparation of carbon nanostructures.[2,3] CNTs prepared by the arc discharge method have a higher degree of crystallinity and a lower number of defects than those prepared by PECVD.[4] Nevertheless, CNTs produced by the arc discharge method also exhibit a wide diameter distribution. Furthermore, those methods are based on a discontinuous process. Therefore, we have studied the continuous synthesis method of CNTs using a thermal plasma reactor based on a forced constricted-type plasma jet generator.[5]

Thermal plasma processing using a plasma jet with a high speed and a high heat capacity is one of the most promising methods for synthesizing new materials. So far, we have reported the rapid synthesis of ferrite and diamond films from powders or gases using this reactor.[6,7] The synthesis of carbon nanostructures or CNTs using a plasma jet was studied by some authors[8-11]: in these studies, catalysts are needed for the preparation of carbon nanostructures and the arc current is high (-300 A). We have also tried the synthesis of carbon nanostructures without a catalyst using a low-power jet. We have confirmed that carbon nanostructures are synthesized readily using only CH_4 gas as a material.[11] By adding H_2 gas as an assist gas, the level of production of carbon nanostructures is increased.

Based on our previous results, in this study, we further investigate optimum conditions for carbon nanostructure synthesis and discuss gas-phase synthesis techniques

with a continuous process in detail. The effects of Ni substrate and Ni powders on the synthesis of carbon nanostructures are also discussed to produce uniform-sized and well-aligned carbon nanostructures.

2. Experimental Methods

The schematic diagram of the plasma jet reactor system used in this study is shown in Fig. 1. The reactor consists of a forced constricted-type plasma jet generator (Cu nozzle anode of 5 mm in diameter, Cu-insulated constrictor nozzle of 5 mm in diameter, and rod cathode made of 2 % Th–W), a feed ring (nozzle of 5 mm in diameter), a reaction chamber (370 mm in width, 390 mm in depth, 610 mm in length) and a substrate holder.

Experiments are performed under continuous pumping and flowing of Ar gas. The plasma jet is produced by direct-current arc discharge. As the insulated constrictor nozzle is set between the nozzle anode and the cathode, arc length is always kept constant and the nozzle wall strongly constricts the arc with the working gas. Then, a stable plasma jet with high heat capacity is produced under various operating conditions.[5] For synthesis of carbon nanostructures, CH_4 gas is used as material gas and H_2 gas is used as assist gas. The gas mixtures are injected into the plasma flow of a high-temperature region directly through two capillary feeding ports of the feed ring.

Experiments have been performed under the following conditions: working gas (Ar) flow rate Q_w is 20 l/min; jet power W_j range is 5-8 kW; distance from the feed ring exit to substrate L is 100 mm; pressure in the reaction chamber P_t is 760 Torr; material gas (CH_4) flow rate Q_m range is 0.2-0.3 l/min; assist gas (H_2) flow rate Q_a range is 3-8 l/min; processing

duration time T range is 30 s-10 min; and materials of the substrate are stainless steel (SUS304), Ni, and Si.

Prepared soot is characterized by scanning electron microscopy (SEM), energy dispersing X-ray (EDX) analysis for consistency and Raman spectroscopy.

3. Results and Discussion

We have reconfirmed that carbon nanostructures are synthesized continuously using only CH_4 gas.[11] Figure 2(a) shows an SEM image of the products on the substrate (SUS304). Numerous fiber-like structures can be clearly observed. The diameters of the products were distributed over a wide range from 40 nm to 200 nm. Figure 2(b) shows the results of an EDX analysis of the products. As shown clearly, only the characteristic peak of carbon (C) is observed, and other peaks of electrode or substrate metals are not observed. Therefore, the products are made of carbon, and are synthesized using a well-controlled plasma jet with no catalyst metals.

The yields of the products of carbon clusters similar to those of amorphous carbon increase with increasing processing time. In diamond synthesis, hydrogen plays an important role.[7] Graphite and amorphous carbon prepared on the substrate are removed by etching with atomic hydrogen. As a result, product yield is enhanced. We also expect these effects in the present experiment. With the injection of H_2 gas, amorphous carbon is removed and the production of carbon nanostructures is enhanced. The synthesis of carbon nanostructures with H_2 gas is tested.

Figures 3 and 4 show SEM images of products for two different conditions of H_2 gas

flow rate. One condition is Q_a = 3.0 l/min in Fig. 3, and the other is Q_a = 8.0 l/min in Fig. 4. Innumerable small seam marks exist on the substrate, and carbon nanostructures are formed along these marks. When H_2 gas is injected, the carbon clusters similar to amorphous carbon are hardly observed with processing time. In addition, product yields are increased with the H_2 gas injection compared with using only CH_4 gas. Therefore, H_2 gas injection is effective for the continuous synthesis of carbon nanostructures. In this case, the production of nanostructures with the highest yield is achieved when Q_m/Q_a = 1/25 l/min. At the same time, the yield is increased by about a factor of ten compared with that without H_2 gas injection. Therefore, in the following experiments, the preparation of nanostructures is examined with H_2 gas injection at this rate.

The effect of metal on carbon nanostructure synthesis is studied. Because Ni is one of the catalysts commonly used in the synthesis of CNTs, carbon nanostructures are prepared using Ni powders or Ni substrates. Although carbon nanostructure synthesis using substrates as the catalyst is a general step in PECVD, the effect of Ni powders can also be studied using our plasma jet device. We have tried carbon nanostructure synthesis with two methods using Ni. In both methods, the production of carbon nanostructures is enhanced.

First, the results of using Ni powders are shown in Fig. 5. In this case, Ni powders are injected into the plasma jet through the feed ring with CH_4 gas and H_2 gas. Figure 5(a) shows an SEM image of the products. In Fig. 5(a), it can be observed that many straight products have grown. The diameters of the products are nearly equal, and are about 250 nm. The Ni particles can be observed in the center of the carbon nanostructures. Figure 5(b) shows the results of an EDX analysis of the products. The spectra of Ni can also be observed clearly

unlike in Fig. 2(b). According to the quantification by EDX analysis, the products are composed of two elements, namely, C: 90.5% and Ni: 9.5%. The diameter of the carbon nanostructures is nearly the same as the diameter of the catalysts.[12] Therefore, the diameter (about 250 nm) of the synthesized carbon nanostructures might depend strongly on the size of Ni particles in the plasma flow and plasma jet. Figure 5(c) shows the Raman spectrum of the products. Peak spectra near 1600 cm^{-1} in the G-band and near 1400 cm^{-1} in the D-band are well confirmed. The peak spectrum near 1400 cm^{-1} is presumed to be due to defects of carbon. The crystallinity of the products is determined by the intensity ratio of the peak spectrum in the G-band (I_G) to the peak spectrum in the D-band (I_D). The intensity ratio between the two peaks (I_G/I_D) is 1.41. A general crystallinity level is estimated using the ratio I_G/I_D. When the ratio is high, crystallinity is also high. The intensity ratio of 1.41 corresponds to the intensity ratio of typical carbon nanofibers (CNFs)[13] (The intensity ratio of CNTs is 10 or more).

Finally, we study the effect of Ni substrates on the synthesis of carbon nanostructures. Figures 6(a) and 6(b) show an SEM image and a Raman spectrum of the products, respectively. Numerous bundles and intricate structures can be observed in Fig. 6(a). The products are distributed over large areas on the Ni substrate. The diameters of the products are smaller than those shown in Fig. 5(a) and these are about 100 nm. In Fig. 6(b), the intensity ratio between the two peaks (I_G/I_D) is 1.31. This intensity ratio corresponds to the intensity ratio of typical CNFs as products using Ni powders. As the characterization of carbon nanostructures by EDX analysis is almost the same as that shown in Fig. 5(b), Ni is also included in the products of carbon nanostructures. Therefore, there are no qualitative differences between the two carbon nanostructures shown in Figs. 5(a) and 6(a). By using Ni

substrates or Ni powders, the synthesis of CNFs with almost uniform size was possible performed. However, the quality of the products is not high because, as shown in the Raman spectra of the products in Figs. 5(c) and 6(c), the half-widths of the G-bands are wide. In the future, details in production mechanism should be clarified for synthesizing high-quality carbon nanostructures.

4. Conclusions

We have studied the synthesis of carbon nanostructures in the gas phase using our newly designed thermal plasma reactor. By using H_2 gas as an assist gas, the production of carbon nanostructures is enhanced and carbon clusters similar to amorphous carbon are hardly observed. Thus, our thermal plasma process enables a continuous synthesis of carbon nanostructures without catalysts. Furthermore, products with nearly the same diameters are synthesized using Ni substrate and Ni powders. The crystallinity of the products synthesized using our thermal plasma reactor corresponds to the crystallinity of CNFs. In the future, the optimum conditions for the mass production of high-quality CNTs and CNFs should be further discussed.

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Figure Captions

Fig.1 Schematic diagram of thermal plasma reactor system with forced constricted-type plasma jet generator.

Fig.2 Characterization of carbon nanostructures prepared on substrate (SUS304) : (a) SEM image and (b) EDX analysis. The experimental conditions are as follows : working gas (Ar) flow rate $Q_w = 20$ l/min, pressure in the reaction chamber $P_t = 760$ Torr, jet power $W_j = 5$ kW, distance from the feed ring exit to substrate $L = 100$ mm, material gas (CH_4) flow rate $Q_m = 0.3$ l/min, assist gas (H_2) flow rate $Q_a = 8.0$ l/min and processing duration $T = 10$ min.

Fig.3 SEM images of carbon nanostructures prepared on substrate (SUS304), where $Q_a =$ 3.0 l/min : (a) Image and (b) magnified view of large quantity of products.

Fig.4 SEM images of carbon nanostructures prepared on substrate (SUS304), where $Q_a =$ 8.0 l/min : (a) Image and (b) magnified view of large quantity of products.

Fig.5 Characterization of carbon nanostructures prepared on Si substrate with Ni powders, where $T = 30$ s : (a) SEM image, (b) EDX analysis results, and (c) Raman spectrum.

Fig.6 Characterization of carbon nanostructures prepared on Ni substrate : (a) SEM image and (b) Raman spectrum.

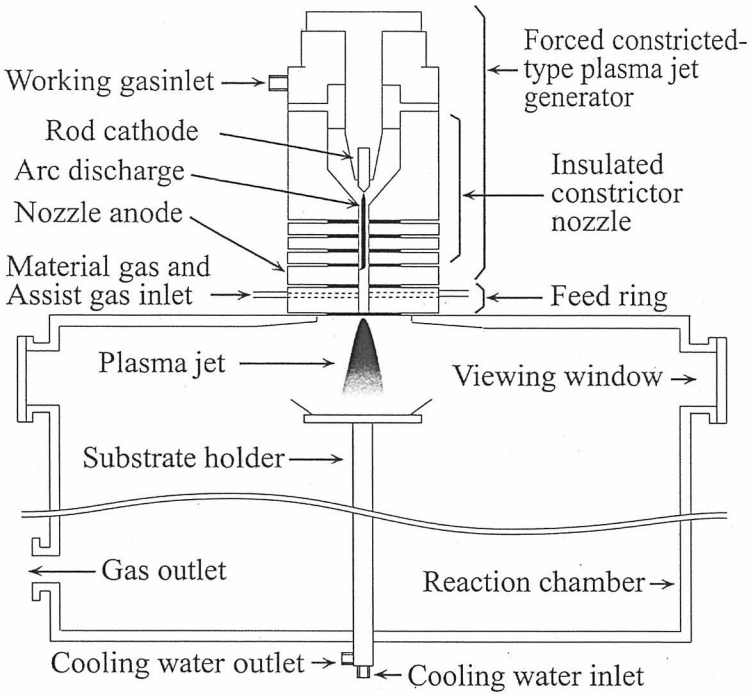

Fig.1

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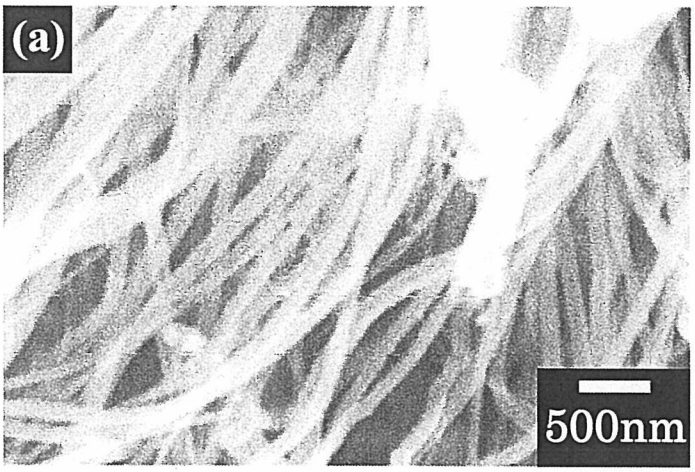

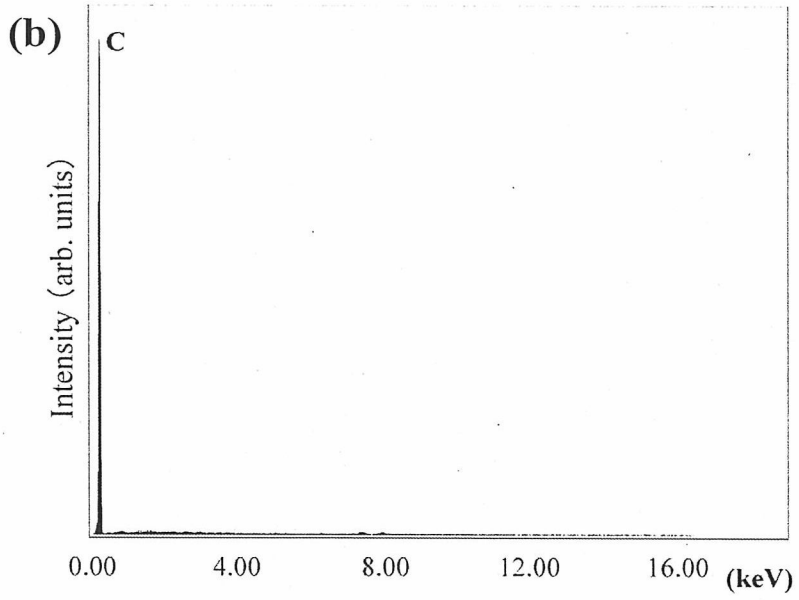

Fig.2

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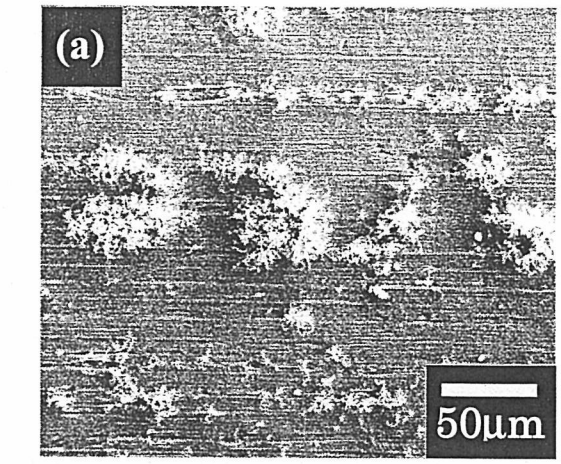

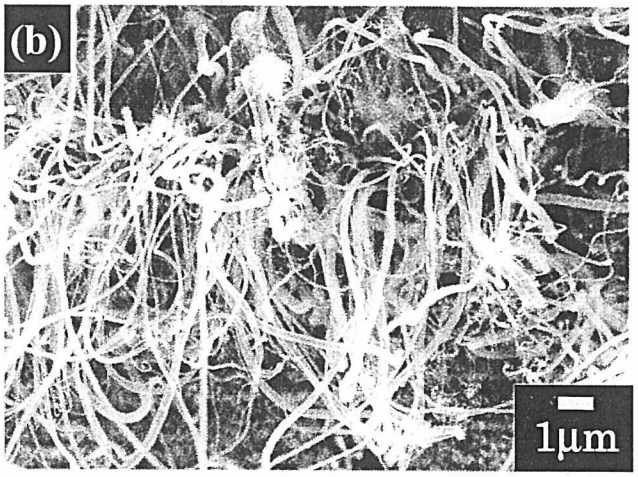

Fig.3

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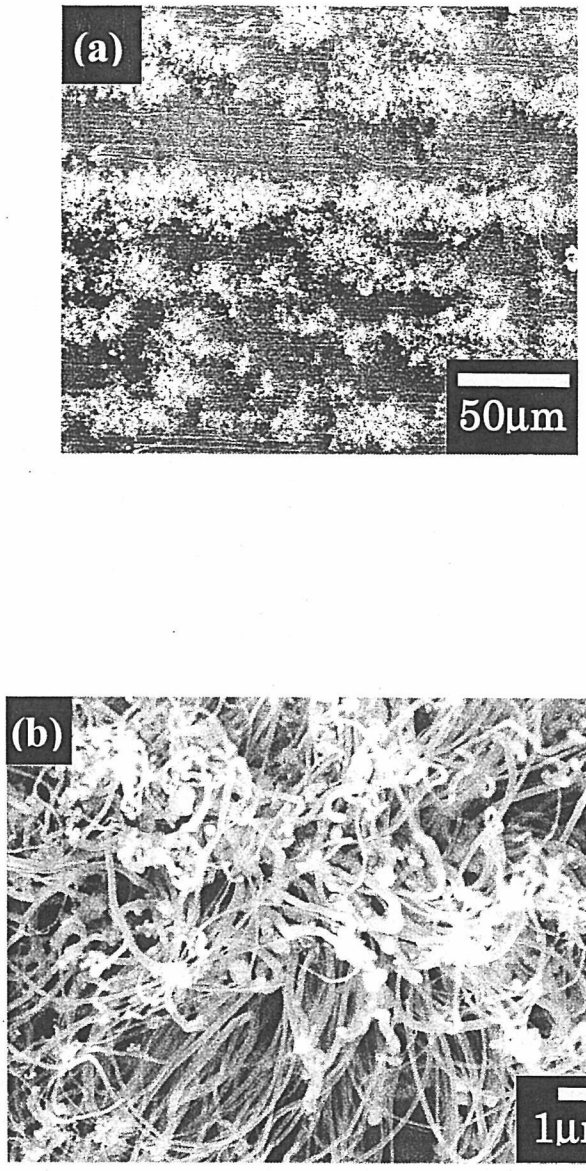

Fig.4

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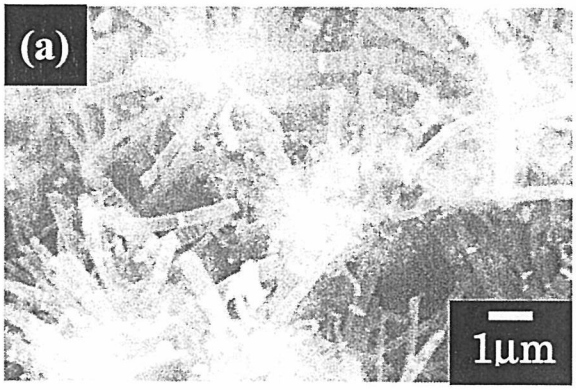

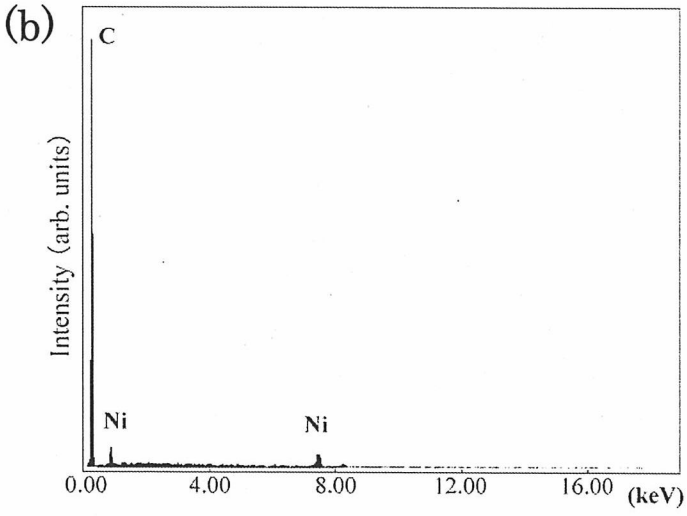

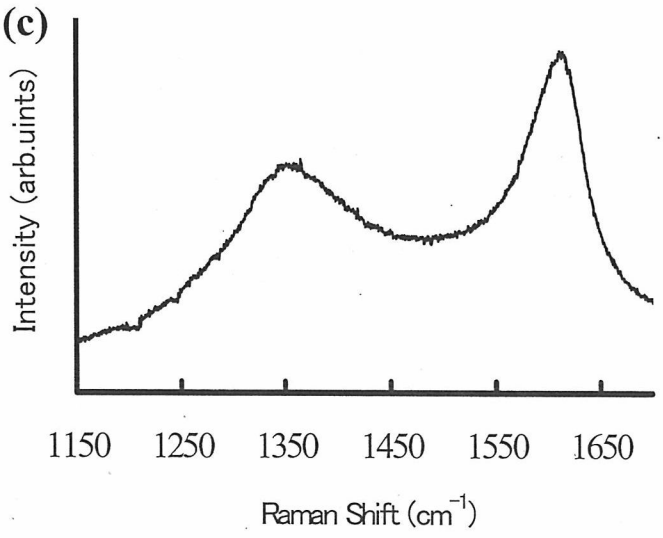

Fig.5

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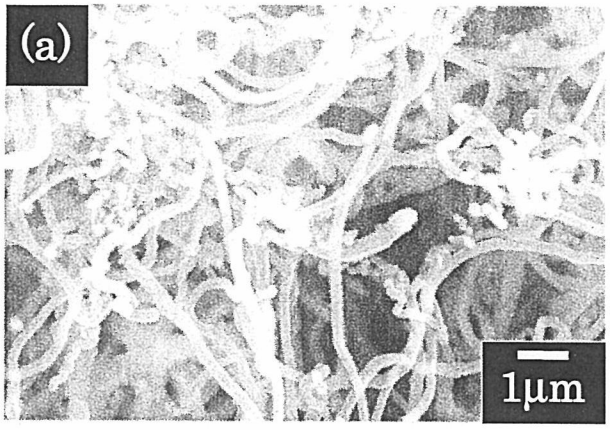

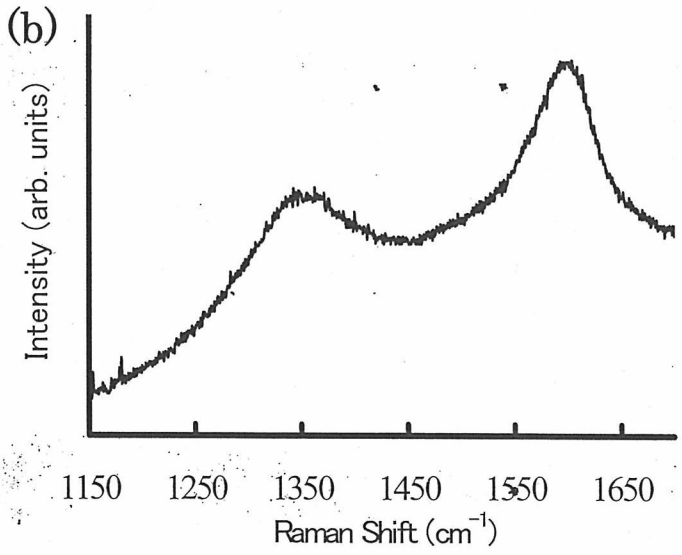

Fig.6

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