Synthesis of carbon nanotube in organic liquids carbon source on \( \text{La}_2\text{NiO}_4 \) ceramics catalyst

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Carbon nanotube was synthesized in organic liquids carbon source by using \( \text{La}_2\text{NiO}_4 \) ceramics catalyst. The \( \text{La}_2\text{NiO}_4 \) ceramics particles were deposited on a Si substrate by using electrophoretic deposition. The Si substrate supporting \( \text{La}_2\text{NiO}_4 \) ceramics particles was dipped in liquid ethanol, and then DC power current was applied to the Si substrate. After this reaction process, carbon nanotube was observed on the Si substrate. Next, various liquid organic compounds were applied as the carbon source for this method. All the organic compounds used in this study were effective for the synthesis of carbon material. However, the shape of the carbon material was depended on the kind of organic compound.

Key-words: Carbon nanotube, Ceramics catalysts, Liquid phase, Carbon material, \( \text{La}_2\text{NiO}_4 \)

1. Introduction

Nowadays, carbon nanotube has been studied by a lot of researchers. Carbon nanotube is a kind of carbon material, which is expected to have specific properties, such as field emission at al. Several methods have reported for the synthesis of carbon nanotube. So far, Zhang et al. reported that carbon nanotube was synthesized in liquid phase carbon source. In these studies, semiconducting Si substrate supporting metal catalyst, which was deposited by spattering process, was dipped in organic liquid compound such as alcohol, and then power current was applied to the silicon substrate for the heating of the catalyst. In the heating process, carbon nanotube was synthesized on the Si substrate. In these studies, metal catalyst, which was used as the metal catalyst for the synthesis of carbon nanotube. In the case of the method reported by Zhang et al., the concentration of carbon source around the catalyst condenses because the carbon source is liquid phase. Therefore, the carbon nanotube synthesis velocity is very large. Moreover, large amount synthesis of carbon nanotube may be achieved by using this method.

One of the popular methods for carbon nanotube synthesis is hot CVD system. In general, metal catalyst, which is deposited on other supporting material, is used as the synthesis catalyst for hot CVD system. So far, several papers reported that ceramics was used as the catalyst for carbon nanotube synthesis in hot CVD system. Liang et al. reported that \( \text{La}_2\text{NiO}_4 \) ceramics catalyst is effective for the synthesis of carbon nanotube in hot CVD system. In general, ceramics is stable in air. Electric furnace, which is more suitable for large amount of synthesis than vacuum system, is used for the synthesis of ceramics. Therefore, we attempt to use ceramics catalyst for carbon nanotube synthesis by using liquid phase synthesis. In this study, \( \text{La}_2\text{NiO}_4 \) ceramics, which is used as the catalyst for hot CVD system, was used as catalyst.

2. Experimental

2.1 Preparation of catalyst

Lanthanum oxide, \( \text{La}_2\text{O}_3 \), and nickel oxide, \( \text{NiO} \), was mixed in stoichiometrically by using alumina mortar. The mixed powder was heated at 1400°C for 10 h in air for the synthesis of \( \text{La}_2\text{NiO}_4 \). The crystal structure after the heating process was analyzed with XRD apparatus.

2.2 Deposition of catalyst

The powder after the heating process was grinded with an alumina mortar. After the grinding, the powder (0.01 g or 0.05 g) was dispersed in distilled water (130 mL). A Pt plate and a Si substrate were dipped in the water dispersing the \( \text{La}_2\text{NiO}_4 \) powder. The \( \text{La}_2\text{NiO}_4 \) particles were deposited on a Si substrate by using electrophoresis process. Electrical potential (DC 260 V) was applied for 0.01 g or 0.05 g for the deposit of the \( \text{La}_2\text{NiO}_4 \) particles on the Si substrate.

2.3 Synthesis process

After the deposition process, the Si substrate was dried in air, and then was dipped in organic liquid such as ethanol, methanol, and so on. DC power current was applied to the Si substrate supporting the particles for 5 min. – 20 min. to heat the catalyst on the Si Substrate. The synthesis apparatus used in this study is shown in Fig. 1. The temperature of the Si substrate was measured with infrared radiation thermometer. The DC power current was adjusted for the control the temperature of the Si substrate. After the synthesis process, the Si substrate was dried in air. The surface morphology of the catalyst on the Si substrate was observed with FE-SEM. The synthesized material by this study was measured TEM.

3. Results and discussion

3.1 Catalyst

In order to investigate the effect of catalyst, the Si substrates depositing \( \text{La}_2\text{O}_3 \) or \( \text{NiO} \) and the Si substrate depositing no material are used in the synthesis process. From the experimental results, Si surface, \( \text{La}_2\text{O}_3 \) and \( \text{NiO} \) are inactive.
for the synthesis of deposits in this condition. In the case of hot CVD process, it is known that Fe, Ni, Co metals are used as the catalyst for synthesis of carbon nanotube. These metal catalysts must be dispersed for acting as catalyst. From the experimental results of this study, we can confirm that NiO is not act as the catalyst for the synthesis of carbon nanotube in this synthesis process.

From the result of XRD measurement, the crystal structure of the prepared powder was La$_2$NiO$_4$ (main phase) and La$_2$O$_3$ (minor phase) when the heating temperature was above 1400°C. Because La$_2$O$_3$ is inactive for the synthesis of deposits in this condition, in this study we used the powder treated at 1400°C.

3.2 Ethanol
3.2.1 Synthesis temperature dependence
First, ethanol was used as the carbon source for the synthesis process, and the synthesis temperature dependence was investigated (synthesis time is 5 min.). After this synthesis process, the color of the major part the substrate surface was black. On the other hand, minor part of the substrate surface was the Si substrate. For the synthesis process, ethanol evaporated and gaseous ethanol generated on the Si substrate. The bubble gas separated the deposits with catalyst from the Si substrate. The SEM images of black part after the synthesis process were shown in Fig. 2. As shown in Fig. 2, when the temperature of the Si substrate was 700–900°C, rope type materials were synthesized on the Si substrate. Moreover, the condition of the deposits was not depended on the substrate temperature in the 700°C to 900°C range. Si surface, La$_2$O$_3$ and NiO are inactive for the synthesis of deposits in this condition. Therefore, these experimental results must mean that La$_2$NiO$_4$ ceramics is necessary for the synthesis of rope type material.

The diameter was measured from the SEM image as shown in Fig. 3. The diameter of the deposits was 15–60 nm, and the most frequently diameter of the material was ca. 25 nm. The lengths of the rope type materials cannot be measured because the rope type materials do not orient. The TEM image of the deposits is shown in Fig. 4. We can confirm
that the deposits have tubular structure. The inside diameter of the tubular material was ca. 10 nm. From the results of Figs. 3 and 4, it was confirmed that carbon nanotube was synthesized in the process of this study.

### 3.2.2 Synthesis time dependence

From the experimental results of section 3.2.1, we can confirm that La$_2$NiO$_4$ ceramics is effective for the synthesis of carbon nanotube in the process reported in this study. However, the amount of the synthesized carbon nanotube is

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**Fig. 4.** TEM images of synthesized materials.

**Fig. 5.** SEM images of the synthesized materials from various organic compounds.
small. In order to increase the amount of synthesized material, the synthesis time was increased (5 min→20 min). However, the amount of the synthesized material was not increased with increasing the synthesis time because the deposits with the catalyst were separated from the Si substrate for the synthesis process. When the Si substrate was heated for the synthesis, ethanol evaporated and gaseous ethanol generated on the Si substrate. The gas separated the deposits with the catalyst from the Si substrate. Therefore, the long time synthesis is ineffective for the increase in the amount of synthesized material as for the method of this study.

3.2.3 Dependence of the amount of La$_2$NiO$_4$ ceramics dispersed in distilled water

In order to improve the problem that the deposits with the catalyst separate from the Si substrate in the process of electrophoresis the amount of La$_2$NiO$_4$ dispersed in distilled water was changed to 0.01 g. However, the surface morphology after the synthesis process was basically independent of the amount of La$_2$NiO$_4$ ceramics dispersed in distilled water. Therefore, small amount of deposition of La$_2$NiO$_4$ ceramics is ineffective for the increase in the amount of synthesized material as for the method of this study.

For avoiding the separation of the deposits with the catalyst separate from the Si substrate, we have a few ideas,

1. Small particle of La$_2$NiO$_4$,
2. High voltage for electrophoresis,
3. Heat treatment after electrophoresis.

In future, we will try these methods for improving the problem that the deposits with the catalyst separate from the Si substrate.

3.3 Other organic compound

Next, various organic compounds were used as the carbon source in this method. The SEM images of the deposits synthesized from various organic compounds are shown in Fig. 5. All the organic compounds are effective for the synthesis of deposits. However, the structure of the deposits changed. From the experimental results, it is obvious that the shape of the generated material after the reaction process depended on the kind of the organic liquid used as the carbon source. However, the reason for the change is unclear at this point because there are few data of this synthesis method. It is necessary for the clarification of the synthetic mechanism of carbon nanotube to be continued the research work for getting data.

4. Conclusions

In this study, La$_2$NiO$_4$ ceramics was used as the catalyst for the synthesis of carbon nanotube. The ceramics particles were deposited on a Si substrate, and the Si substrate was dipped in organic liquid such as ethanol. The Si substrate was heated in the organic liquid by using DC power supply. From the experimental results, we can conclude that La$_2$NiO$_4$ ceramics acts as the catalyst for the synthesis of carbon nanotube in the synthesis method used in this study. The shape of the carbon material synthesized by using the method of this study was depended on the kind of organic compound.

References