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https://doi.org/10.15017/16707

出版情報：九州大学大学院総合理工学報告. 25 (3), pp.365-367, 2003-12. Interdisciplinary Graduate School of Engineering Sciences, Kyushu University
バージョン：
権利関係：

九州大学大学院総合理工学報告
第25巻 第3号 365－367 頁 平成15年12月

Engineering Sciences Reports, Kyushu University
(KYUSHU DAIGAKU SOGORIKOGAKU HOKOKU)
Vol. 25, No. 3 pp. 365－367 DEC. 2003

Synthesis of Carbon Nanotube Using Ni Catalyst Prepared by Laser Ablation in Water

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(Received October 9, 2003)

Nano-size Ni particles prepared by laser ablation in water were used as catalyst for synthesizing carbon nanotubes by a thermal CVD method. The width of synthesized CNT was almost the same as the size of the Ni particles. It was found that hydrogen-reduction treatment of the Ni particles was necessary to obtain nanotubes, suggesting that surface of the colloidal particles were oxidized in the laser ablation process.

Key words: *Laser ablation in water, Nano-size particle, Carbon nanotube, Thermal CVD*

1. Introduction

Recently, applications of laser ablation techniques have been extended from the gas phase to the liquid phase. Especially laser ablation in solution has been concentrated as a new technique for preparing nano-size metal particles. So far, it has been found that stable nanoparticles of noble metals were efficiently prepared by laser ablation of metal plates and films in such a solution as water or alcohol.[1)] An advantage of this technique is that surface of prepared nanoparticles is pure, i.e. no stabilizer or ion is contained in the colloidal solution. Thus, it can be expected that colloidal particles prepared by a laser ablation technique will possess a high catalytic ability. Another advantage of application of the laser ablation technique on colloid synthesis is that the size of colloidal particles can be easily controlled by changing wavelength,[2-4)] intensity,[5)] and pulse duration[6)] of ablation laser.

In this letter, we have reported on the first application of nanoparticles, which were prepared by laser ablation in liquid phase, to a catalyst for synthesizing carbon nanotubes (CNTs). Ni nanoparticles used for CNT synthesis were prepared by laser ablation in water.

2. Experimental

The experimental setup for preparing Ni colloids by laser ablation in water is shown in Figure 1. A piece of Ni plate was settled in a glass cell containing deionized water. The fundamental pulse (wavelength: 1064 nm pulse duration: 10 ns, repetition rate: 10 Hz) of a Nd:YAG laser (Spectra Physics GCR-100) was used as ablation laser light. The

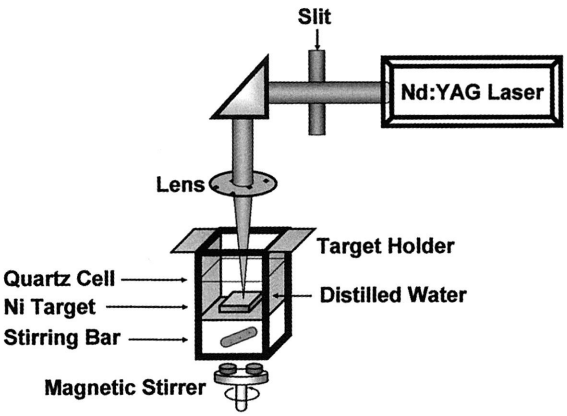

Figure 1. Laser ablation cell of Ni plate in water.

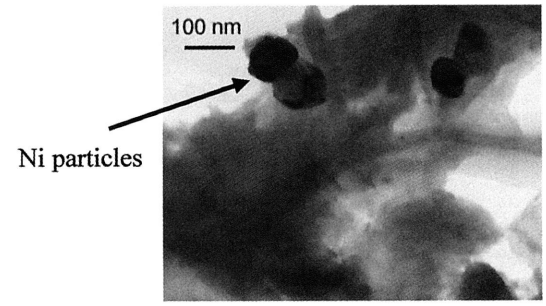

Figure 2. A TEM image of Ni colloids prepared by laser ablation in water. (1064 nm, 12 mJ/pulse, 30 min)

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ablation light was focused on the surface of the Ni plate. After ablating the target for 30 min, a gray colloidal solution of Ni was obtained. Figure 2 shows a TEM image of Ni particles prepared by laser ablation in water. The size of particles was 10 – 100 nm. These particles were used as catalyst for synthesizing CNTs.

Figure 3 shows thermal CVD chamber for synthesizing CNT. A small amount of the colloidal solution was dropped on a silicon substrate and dried in vacuum. The silicon substrate on which Ni particles were deposited was settled in a silica tube with an inner diameter of 24 mm. The silica tube was heated by an electronic heater. A mixture of acetylene/H_2 gas was used as carbon source. In the case of performing reduction of the surface of Ni particles, hydrogen gas was introduced into the tube before CVD of carbon for 60 min. In order to determine the optimum thermal CVD conditions in our apparatus, CNT was prepared by using various mixtures of C_2H_2/H_2 and $Ni(NO_3)\cdot mH_2O$ catalyst at 700 – 900 °C.[7] We found that the best CNTs were obtained at 900°C for 60 min and C_2H_2/H_2 flow rates of 10/50 sccm (standard cubic centimeter per minute). Thus, experimental conditions summarized in Table 1 were used, when $Ni(NO_3)\cdot mH_2O$ catalyst was replaced by Ni catalyst prepared by laser ablation in water. The products of CVD were analyzed by using a scanning electron microscope (SEM) (JEOL JSM6320F) and a transmission electron microscope (TEM) (JEOL JEM-2000FX in HEVEM of Kyushu University).

3. Results and Discussion

Figure 4 shows a SEM image of a silicon substrate after the CVD procedure. Growth of CNTs was found where Ni colloids were deposited. Figure 5 shows a TEM image of the CNTs. The width of the CNTs is almost the same as diameter of the Ni particles which are also observed in the picture. These findings suggest that the CNTs were synthesized on the surface of the Ni particles,[8] and propose that the width of CNT can be controlled by size of Ni particles.

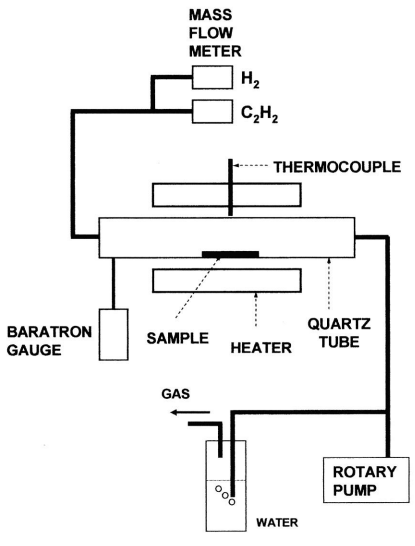

Figure 3. Thermal CVD apparatus for synthesizing CNT.

Table 1. Typical experimental conditions of thermal CVD procedure for CNT synthesis.

Temperature and reaction time	Gas and flow rate (sccm)	Reduction treatment
900°C for 60 min	C_2H_2/H_2 (10/50)	No treatment
900°C for 60 min	C_2H_2/H_2 (10/50)	H_2 (10 sccm), 900 °C for 60 min

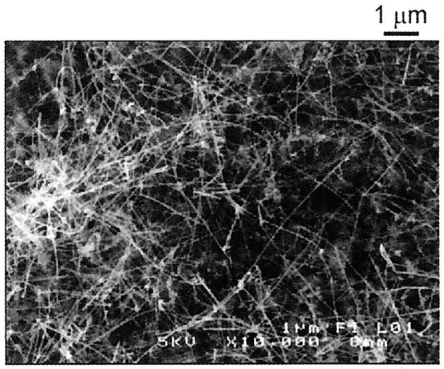

Figure 4. A SEM image of CNT grown on Ni colloids deposited on silicon substrate. (5 kV, ×10,000)

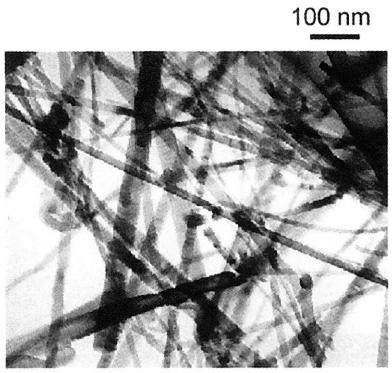

Figure 5. A TEM image of CNT synthesized by using Ni catalysis prepared by laser ablation in water. (200 kV, ×100,000)

It must be noted that CNTs could not be grown without the hydrogen-reduction treatment. The need for the hydrogen-reduction treatment suggests that pu-

for the hydrogen-reduction treatment suggests that purity of the surface of the Ni colloids was insufficient to catalyze CNT growth. As analogous with Cu particles prepared by laser ablation in water,[9] the surface of Ni colloids must be oxidized in the ablation process in which melted hot Ni particles (clusters) can react with O_2 and/or H_2O molecules in water. This assumption was supported by absorption spectra of the Ni colloidal solution. The surface plasmon absorption band of Ni particles, which appears at 300 – 400 nm region,[10,11] was diminished in absorption spectra of the Ni colloidal solution produced by laser ablation in water.

4. Summary and Conclusion

In summary, Ni nanoparticles prepared by laser ablation in water could be used as catalyst for the synthesis of CNTs. The hydrogen-reduction treatment was necessary to activate Ni catalyst, indicating that the surface of Ni particles was oxidized in the ablation process. Since the size of metal particles can be easily controlled by changing such an experimental parameter as wavelength, intensity, or pulse duration of ablation laser, laser ablation in solution is a new promising way of preparing the catalyst for CNT synthesis.

Acknowledgments

Authors thank Prof. Hiroki Ago (Kyushu Univ.) for useful discussion, and Prof. Isao Mochida and Mr. Atsushi Tanaka (Kyushu Univ.) for allowing us to use SEM. This work was partially supported by a Grant-in-Aid for Scientific Research No. 15651046 from the Ministry of Education, Science, Sports and Culture.

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