

A Novel Catalytic Synthesis Method of Carbon Nanomaterials in the Organic Liquids

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ABSTRACT

We have developed a novel catalytic method for synthesizing a wide variety of carbon nanomaterials in the organic liquids [1]. There is no need for a vacuum reactor. The method realized a simple, speedy, and a high-purity growth of aligned carbon nanotubes in alcohol liquids [2]. At the interface between the liquid and the catalyst-supported substrate surface, a large gradient of the temperature exists. The nonequilibrium condition is a characteristic feature of the liquid phase synthesis method. This method is superior to a gas phase synthesis methods as it allows to use various choices of the organic liquids. Kinds of catalyst metal also affect the structure of the grown carbon materials, i.e. the combination of a carbon source and a catalyst metal leads to a great variety of morphologies. In this study, we investigated to grow and control the various morphologies of the grown materials by using octane (C_8H_{18}), 1-octanol ($CH_3(CH_2)_7OH$; OcOH), and methanol for a carbon source, and a small amounts of Co or Pd as a catalyst. The morphology of the grown carbon nanomaterials depended both on kinds of the catalyst metal and the organic liquid source.

Keywords: carbon nanomaterial, liquid phase synthesis, catalyst, Pd, Co

1 INTRODUCTION

Fibriform carbon nanomaterials synthesized by catalytic chemical vapor deposition have been known for a long time as vapor-grown carbon fibers [3]. These materials are catalytically grown with using the type of transition metal catalysts such as Fe, Co, and Ni. The effects of the differences in the metal type and reaction conditions on the fibriform carbon nanomaterial growth have been studied since the 1950s [4].

We have developed a novel catalytic method for synthesizing a wide variety of carbon nanomaterials, for example, a carbon nanotube, a carbon nanofilament, and a carbon thin film in an organic liquid [5]. Different from the CVD system, there is no need for a vacuum reactor. A catalyst-supported substrate is electrically heated around at 1000 K in the organic liquid. A catalytic decomposition of

the organic liquid yields carbon nanomaterials. At the substrate-organic liquid interface, a large gradient of temperature exists, in other words, a non-equilibrium thermal condition exists. A side reaction hardly occurs at the reaction site. This method is also superior to a gas phase synthesis methods as it allows to use various choices of the organic liquids. Kinds of catalyst metal also affect the structure of the grown carbon materials, i.e. the combination of a carbon source and a catalyst metal leads to a great variety of morphologies.

In this study, we have tried to grow and control the various morphologies of the grown nanomaterials by using octane (C_8H_{18}), 1-octanol ($CH_3(CH_2)_7OH$; OcOH), and methanol for a carbon source, and a small amounts of Co or Pd as a catalyst.

2 EXPERIMENTAL

The schematic drawing of the apparatus for the liquid phase deposition is shown in Fig. 1. As a catalyst metal, Co or Pd was deposited on the silicon substrate with using a magnetron sputtering system. The catalyst-loaded silicon substrate was heated by applying a direct current through the substrate to achieve a desired temperature. In order to control the physico-chemical states of the Co catalyst, the substrate was heated in air as a thermal pre-oxidation prior

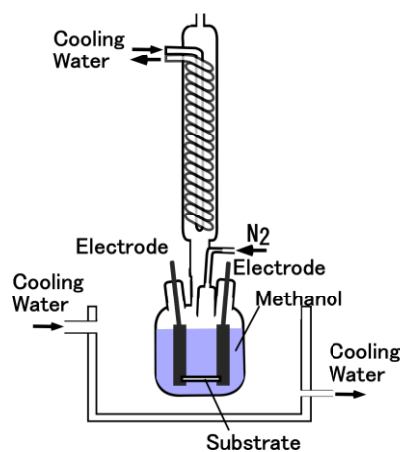


Figure 1: Schematic drawing of the apparatus for the liquid phase deposition system.

to the liquid phase deposition. The growth conditions were shown in Table 1. The morphology and fine structure of the grown materials were observed by Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy .

Table 1: Growth condition

Substrate	n-type Si(100), 7 x 22 x 0.5 mm
Catalyst	A Cobalt or Paradium target was sputtered onto the substrate in the Ar DC discharge.
Amount of the catalyst	1 - 10 nm (A weight gain of the substrate by the sputtering was measured and converted to the catalyst thin-film thickness.)
Organic liquid source	Methanol, 1-Octanol, Octane
Growth temperature	873 K ~ 1173 K
Input power	100 ~ 130 W

3 RESULTS AND DISCUSSION

SEM observation revealed that the morphology of the grown carbon nanomaterials depended on the amounts of Pd catalyst as shown in Fig. 2 and Fig. 3, respectively. Fig. 2 shows the effect of the amounts of Pd on the morphology of the grown nanomaterials with using octane as the organic source. A fine fibriform materials were observed when Pd thickness was in the range from 2 nm to 4 nm. In the case of the Pd thickness was 4 nm, thicker fibriform materials which diameter was around at 30 nm increased. With increasing of the Pd thickness as shown in Fig. 2(c), a spiralled form of nanofilaments which diameter was around at 100 nm were mainly obtained. As the amounts of the supported Pd increased, the diameter of the obtained fibriform materials was increased and they varied in the form of a spiralled nanofilaments. In the case of using Octanol as the organic liquid source, as shown in Fig. 3, a diamter of the fibriform nanomaterials increased as the increasing of the Pd thickness in the range from 2 nm to 4 nm. Different from the case of using octane, the spiralled form was unclear and observed in the case of the Pd thickness was 4 nm. The excess amounts of Pd yielded both a fine and thick fibriform materials as shown in Fig. 3(c).

As shown in Fig. 2 and Fig. 3, the morphology of the obtained nanomaterials also depended on the kind of organic liquid. In the case of using 1-octanol (Fig. 3), the liquid-solid interface at the reaction site was suggested to be oxidative environment compared to the case of using octane (Fig. 2). Audier and coworkers[6] reported that the chemical nature of the catalyst strongly affected to the physical differences in the carbon nanofibers. A variety of

the organic liquid source, for example, it includes a different kind of functional groups, such as -OH, -SH, and -NH₂, is expected to affect both on the chemical nature of the catalyst and the impurity doping in the carbon nanomaterial structure. The catalytic growth of carbon nanomaterials in the organic liquid phase is indicative of yielding the wide variety of morphologies and a novel physico-chemical properties, as well.

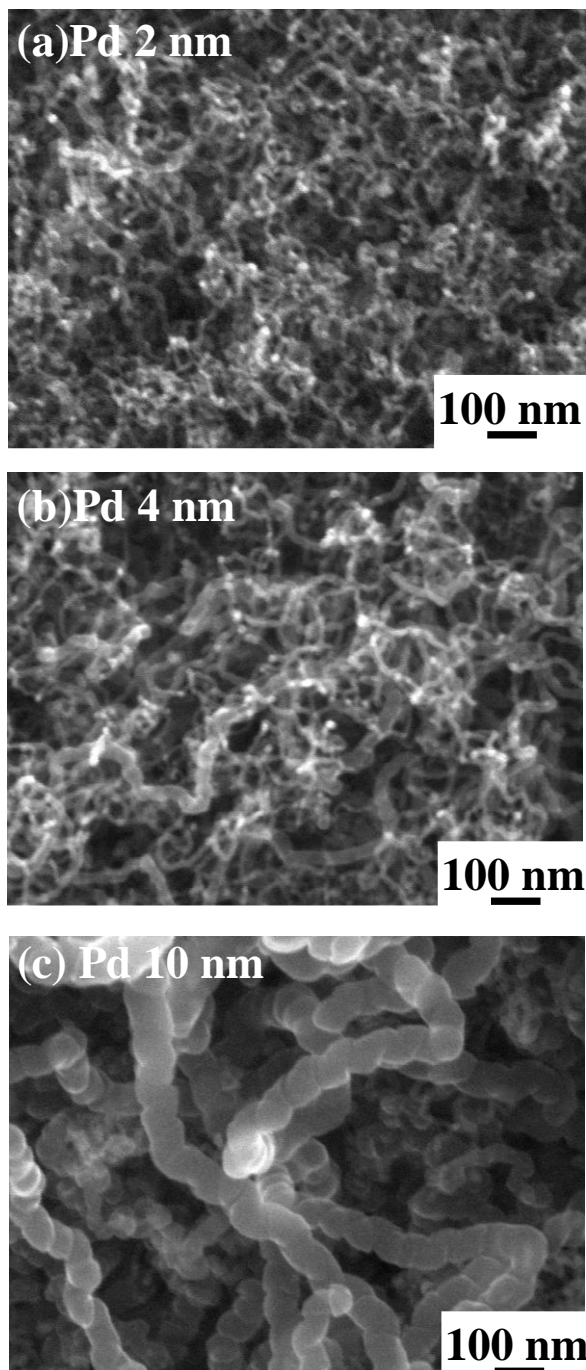


Figure 2: The effect of the amounts of Pd on the morphology at 923 K for 10 min with using octane.

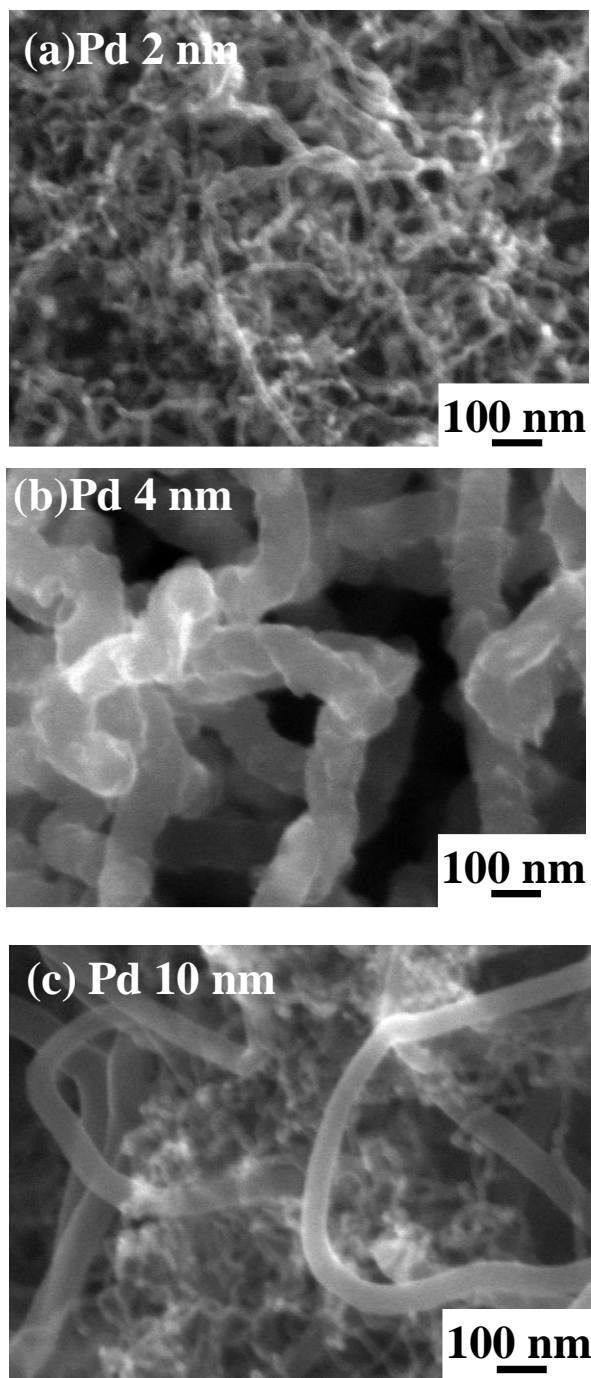


Figure 3: The effect of the amounts of Pd on the morphology at 923 K for 10 min with using 1-octanol.

Different kinds of the catalysts yielded a difference in the morphology of the obtained materials as shown in Fig. 4. A fibriform nanomaterials around at 100 nm diameter were obtained with using Co catalyst and OcOH (Fig. 4(a)). As a combination of the Pd catalyst and OcOH gave a thicker morphology of nanomaterials (Fig. 4(b)). The combination of kinds of an organic liquid as a carbon source and a

catalyst metal has a possibility for realizing a various morphologies in the grown nanomaterials.

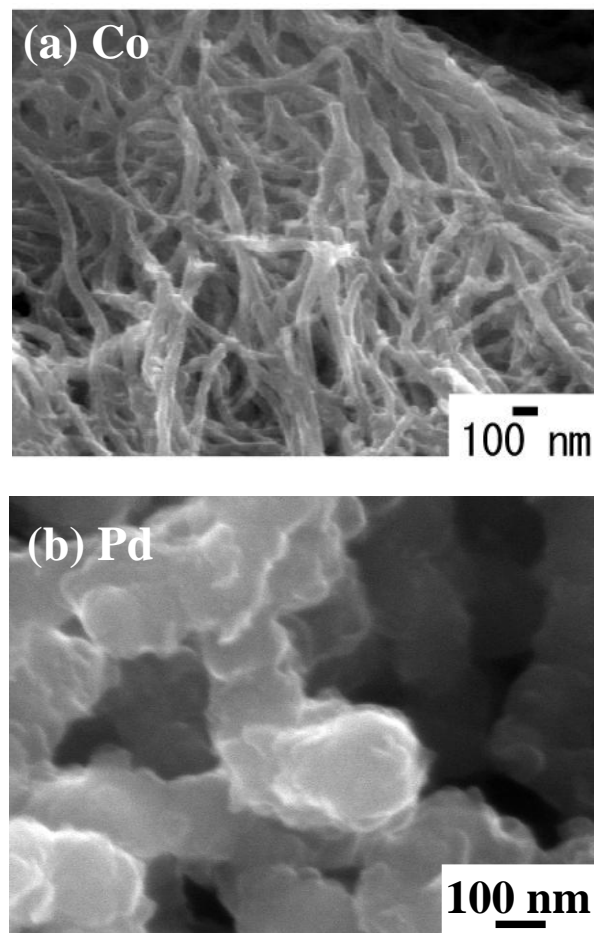


Figure 4: SEM images of the carbon nanomaterials synthesized with different kinds of catalysts (a) Co and (b) Pd, using 1-octanol as an organic liquid source grown at 1073 K for 10 min.

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