

# Promoted growth of carbon nanotubes by sulfur addition in chemical vapor deposition shown via Arrhenius law

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## ABSTRACT

We have employed a chemical vapor deposition (CVD) process to grow carbon nanotube (CNT) on a substrate where cobalt and molybdenum binary catalyst system and carbon monoxide were used as a catalyst source and carbon source, respectively. In addition to Co/Mo catalyst, we added sulfur powder into a catalyst layer as a growth promoter. From scanning electron microscopy (SEM) images, production of CNT was enhanced in the presence of sulfur compared with Co/Mo alone even when oxygen was used as one of feed gas. CNT growth rate obeyed Arrhenius equation, showing that the activation energy required for CNT growth was drastically reduced in the use of sulfur. In this study, based on the activation energy in different catalyst conditions, we attempted to consider the rate-controlling step in each case and to interpret the enhancement of CNT synthesis by sulfur addition.

## 1. Introduction

In order to increase carbon nanotube (CNT) production, some approaches such as introducing additives in gas phase or into a catalyst layer have been considered till now. As an example of a gas phase additive, chlorine was employed as a CNT growth enhancer in arc discharge [1] and chemical vapor deposition (CVD) process [2]. Phosphorous also exhibited promotion effects of carbon fiber growth [3] and CNT synthesis [4] probably due to interaction with catalyst. Further interestingly, Huang et al. [5] and Mas et al. [6] employed selenium as an enhancer in arc discharge and floating-catalyst CVD, respectively. However, the most well-known and frequently used promoter is sulfur or sulfur-included compounds like hydrogen sulfide and thiophene for the growth of carbon fiber [7,8] and CNTs [9,10,11,12,13,14,15,16,17,18]. The addition of sulfur-containing compounds is a versatile approach because it hardly limits the catalyst choice according to preceding articles, namely the performance of Fe [8,9,11,12,13,14,15,16,18], Fe/Cu/quartz [17], Co [7,19] and Co/Mo [10] was improved via a sulfur addition. Hence, influences caused by sulfur on CNT synthesis are able to be regarded as generalized phenomena. In our previous study which synthesized CNTs during combustion in a diesel engine instead of CVD, the addition of sulfur powder into feedstock was critical for the successful synthesis of CNTs in spite of the presence of oxygen in reaction regions [20,21]. Not only our research but also other group reported recently that the presence of both Fe catalyst and sulfur increased CNT production in a diesel engine system [22]. The approach to form CNTs via an internal combustion

system is very similar with floating catalyst CVD in terms of the mechanism of catalyst particle formation and CNT growth. Works to study the influence of sulfur on the growth of CNTs have been mainly dedicated to floating catalyst CVD method till now. Although a lot of efforts have been devoted to find the role of sulfur during CNT growth mainly in CVD system, it is still an open question even today. In this study, a CVD process where CNTs were grown on a substrate with catalytic nanoparticles fixed on it was employed, and we utilized sulfur powder as a sulfur source in order to explore the promoted growth of CNT by the addition of sulfur because this process made it relatively easy to tailor experimental parameters and analyze samples. Then, Arrhenius model which showed the correlation between CNT growth rate and CVD temperature was prepared to attempt to find insight on the role of sulfur during CNT synthesis.

## 2. Methods

In this study, cobalt-molybdenum co-catalyst was employed as a base catalyst because this catalyst has been authorized and practically enabled commercial production of CNTs [23,24]. Although we wanted to use Fe-base catalyst in this study since Fe catalyst was employed for CNT synthesis in our motivating study, CNT growth was hardly found in the employment of Fe alone or Fe/Mo co-catalyst formed on a substrate even in similar conditions/procedures with those in Co/Mo. On the other hand, because Co/Mo was compatible with CO as a carbon source for growing CNTs, we employed Co/Mo binary system in this work. The usage of CO was high priority due to the implication that CO might be

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<https://doi.org/10.1016/j.diamond.2018.08.012>

Received 3 May 2018; Received in revised form 9 July 2018; Accepted 21 August 2018

Available online 23 August 2018

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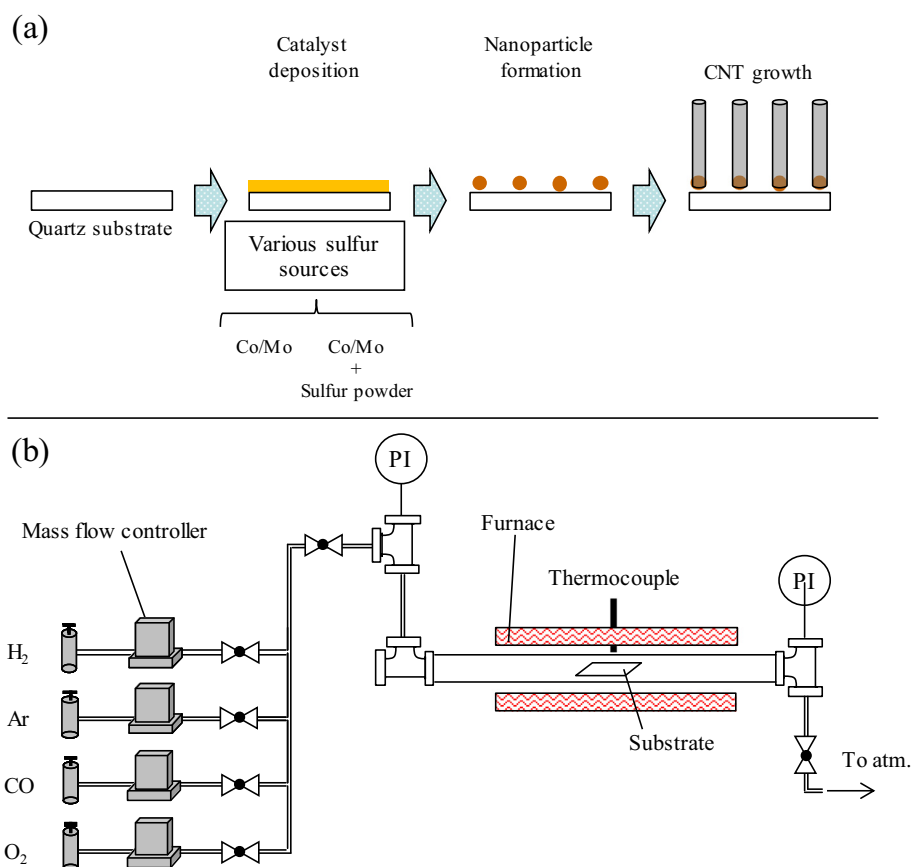


Fig. 1. (a) Schematic representation of the synthetic process for CNT from various catalyst layers. (b) Schematic of an experimental apparatus for operating a reduction and CVD in this work.

promising CNT precursor in our motivating study [21]. We suppose that the similar effect of sulfur on CNT growth in both Fe and Co catalyst may take place because CNT growth promotion was found in not only Fe but also Co according to preceding papers. Quartz with 0.3 mm thickness (Tokyo Glass Kikai Corp.) and carbon monoxide were used as a substrate and carbon precursor, respectively. We prepared two types of samples for a comparison study, namely, Co/Mo alone and Co/Mo/S derived from sulfur powder. A synthetic process of CNTs from two catalyst layers is schematically described in Fig. 1(a). Quartz substrate was calcined at 900 °C in air for more than 1 h before using in order to eliminate carbonaceous impurities on it. A dip-coating method was utilized for forming a catalyst layer on a substrate. Cobalt acetate (95%, Wako Pure Chemical Industries, Ltd.) and molybdenum acetate dimer (98%, Sigma-Aldrich) used as a Co and Mo precursor respectively were dissolved in super dehydrated ethanol (99.5 + %, Wako Pure Chemical Industries, Ltd.) through ultra-sonication. Co precursor of 0.05 wt% and Mo precursor of 0.05 wt% was added into ethanol. After immersing a substrate in a tailored solution for 10 min, it was drawn from the solution at a constant speed of 0.96 cm/min. Then, the substrate was calcined in air at 400 °C for 5 min to decompose precursors to form catalyst particles, and then cooled down to room temperature. For preparing Co/Mo/S derived from sulfur powder, an additional dip-coating was required to load sulfur on a substrate. This second dip-coating was carried out after calcination at 400 °C. Quartz substrate was again dip-coated into the tailored solution that sulfur powder (98.0 + %, Wako Pure Chemical Industries, Ltd.) was dissolved in a toluene solvent (99.5 + %, Wako Pure Chemical Industries, Ltd.). An immersion time in toluene and a drawing speed of a substrate from it were identical with that for forming a Co/Mo layer. Then, a substrate was inserted into a furnace and temperature was elevated up to 800 °C under Ar atmosphere. A reduction operation was carried out at 800 °C

for 30 min to form active catalyst particles under the condition that flow rates of Ar (> 99.999%) and H<sub>2</sub> (> 99.99%) were 60 sccm and 40 sccm, respectively. Temperature inside a furnace was adjusted to given temperatures for CVD under Ar atmosphere after a reduction operation was completed. CVD process to deposit carbon on a substrate was performed at given temperatures under the condition that flow rates of carbon monoxide (> 99.95%) and Ar were 45 sccm and 155 sccm, respectively. When impacts of oxygen on CNT synthesis were investigated, O<sub>2</sub> was also fed into a reactor besides CO and Ar. Both a reduction and CVD were carried out at atmospheric pressure. Schematic of an experimental set-up for a reduction and CVD operation is displayed in Fig. 1(b). When CVD was completed, a flow of carbon monoxide was stopped and a furnace was quenched to room temperature with Ar flowing. The substrate was then taken out from a furnace.

Field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F) was employed to know CNT production on the substrate after CVD. Samples were coated with a layer of Pt–Pd by sputtering (HITACHI E-1030) with a current of 15 mA for 60 s before observations. In order to obtain information about CNT morphology, high-resolution transmission electron microscopy at 200 kV (HR-TEM, JEOL JEM2010F) was performed. For CNT observations, CNTs grown on a substrate were directly scratched to a TEM grid. Raman spectroscopy (JASCO NRS-4100, 532 nm diode laser) was implemented to evaluate a CNT quality and speculate the presence of single walled carbon nanotube (SWNT) and its diameters. Laser was irradiated from a top direction on samples and a spot diameter was 100 μm. Measurement condition in Raman spectroscopy was identical in all samples and absolute intensity of each sample was normalized by the largest peak one. Top-view SEM micrographs were used to estimate CNT growth rate. SEM images were treated through ImageJ which is a freely available software, and CNT growth rates per substrate ( $k$ , μm<sup>2</sup>/cm<sup>2</sup>-substrate/min)

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