



Research paper

Impacts of different sulfur sources as a promoter on the growth of carbon nanotubes in chemical vapor deposition

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HIGHLIGHTS:

- Impacts of different sulfur sources on CNT growth were investigated.
- Activation energy required for CNT growth was estimated by Arrhenius equation.
- Activation energy required for CNT growth depended on sulfur source.
- Interpretation on the differences among sulfur sources was provided.

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ABSTRACT

Different kinds of sulfur sources which acted as a growth enhancer of carbon nanotube (CNT) were employed in chemical vapor deposition (CVD) process. Influences of sulfur sources, sulfur powder and thiourea, were investigated. The production of CNTs was facilitated when sulfur source was added, but its degree depended on sulfur source. Results showed that the smallest activation energy for CNT growth was obtained in sulfur powder, and an intermediate value between Co/Mo without sulfur source and with sulfur powder was obtained in thiourea. We attempted to interpret the difference in activation energy, especially between thiourea and sulfur powder.

1. Introduction

It has been reported that sulfur-included materials were employed for promoting the growth of carbon nanotube (CNT), in particular chemical vapor deposition (CVD) technique [1–5]. Although sulfur is undoubtedly effective for facilitating CNT synthesis, the reason of growth enhancement is still in controversy in spite of some proposals such as the reduction of melting temperature of catalytic nanoparticles [6], the decreasing of interface energy between catalyst surface and graphite layer [7], and others. Sulfur brings about not only promoted CNT growth but also changes in CNT morphology [8], CNT diameter [9], CNT chirality [10], and so on. The reason why these changes are caused by the presence of sulfur is also under investigation. A variety of sulfur sources has been used in CVD process to investigate effects of sulfur on CNT synthesis until now, for instance, thiophene [2,11,12], pure sulfur [7,11], carbon disulfide [13], and hydrogen sulfide [14]. However, the comparative study to employ different sulfur sources in the same system and to investigate its impacts on CNT synthesis is very

limited. Lee et al. varied both carbon and sulfur source in floating catalyst CVD method and provided the implication that the formation of catalytic nanoparticles and nucleation of CNT were affected by the combination of carbon and sulfur source [11]. On the other hand, to our knowledge, there is hardly reported on the influences of different sulfur compounds on CNT synthesis in substrate catalyst CVD process. It is of quite importance to grasp advantage/disadvantage brought by various sulfur species in order to improve the structure of grown CNTs and/or CNT production, leading to making CNT synthesis process more sophisticated.

In this study, we employed two kinds of sulfur-containing compounds, sulfur powder and thiourea, and examined the effects of sulfur sources on CNT growth, especially CNT production. Since the activation energy necessary for CNT growth may present useful information for understanding the effect of sulfur, the Arrhenius relation between CNT growth rate and CVD temperature was prepared in this study. We believe that findings obtained in this work stimulate the understanding of CNT synthesis using sulfur.

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2. Methods

Catalyst layer was prepared by means of dip-coating technique. Dip-coating method was a developed technique to synthesize high-quality CNTs directly on a substrate [15]. Two types of sulfur species, sulfur powder and thiourea, were used in this study. We prepared three types of samples for a comparison study, namely, Co/Mo alone, Co/Mo/S derived from thiourea, and Co/Mo/S derived from sulfur powder. As a first step, cobalt acetate 0.05 wt% (95%, Wako Pure Chemical Industries, Ltd.) and molybdenum acetate dimer 0.05 wt% (98%, Sigma-Aldrich) which functioned as co-catalyst were dissolved in super dehydrated ethanol (99.5+%, Wako Pure Chemical Industries, Ltd.). When Co/Mo/Thiourea catalyst layer was prepared, thiourea 3.5 wt% (98.0+%, Wako Pure Chemical Industries, Ltd.) was put into an ethanol solvent besides cobalt and molybdenum source. After immersion into tailored solution, quartz substrate was calcined in air at 400 °C for 5 min. In case of Co/Mo and Co/Mo/Thiourea catalyst system, the substrate was then moved to a furnace to carry out a next reduction operation. Although one may have a concern that sulfur from thiourea does not remain on a substrate because thiourea is thermally decomposed ~220 °C which is significantly lower than the calcination temperature in this study, we confirmed through X-ray photoelectron spectroscopy that sulfur could remain on a substrate by forming chemical bonds with metal catalyst (not shown here). On the other hand, for preparing Co/Mo/Sulfur powder catalyst system, an additional dip-coating was required to load sulfur on a substrate because sulfur powder can hardly dissolve into ethanol. Quartz substrate was again dip-coated into the tailored solution that sulfur powder 2.0 wt% (98.0+%, Wako Pure Chemical Industries, Ltd.) was dissolved in a toluene as a solvent (99.5+%, Wako Pure Chemical Industries, Ltd.). Then, the sample, Co/Mo/Sulfur powder, was moved to a next reduction operation. The reduction operation was performed in a furnace under Ar (60 sccm)/H₂ (40 sccm) atmosphere at 800 °C for 30 min in order to make catalyst nanoparticles active. After the reduction operation was completed, CVD was initiated at given temperature under Ar (45 sccm)/CO (155 sccm) atmosphere. The schematic showing dip-coating operation and experimental setup for reduction/CVD is presented in Fig. 1.

Samples obtained were analyzed via some characterizations. Field emission scanning electron microscopy (FE-SEM, JEOL JSM-7500F) was employed to explore CNT morphology grown on substrate. High-resolution transmission electron microscopy at 200 kV (HR-TEM, JEOL JEM2010F) was performed to investigate the internal structure of as synthesized CNTs. Raman spectroscopy (JASCO NRS-4100, 532 nm

diode laser) was implemented to evaluate CNT quality in our work. Three approaches to estimate CNT growth rate were employed. First one was to use top-viewed SEM micrographs and to treat them by image processing free software, ImageJ, and then to assess CNT growth rate per substrate (k , $\mu\text{m}^2/\text{cm}^2\text{-substrate}/\text{min}$) on the basis of the occupied area by CNTs in SEM images. Several images were employed for the purpose of ensuring reliability. Second approach was to use the transmission of substrate in nearly visible light (350–800 nm as wavelength) and to estimate CNT quantity on substrate by means of Lambert-Beer relation, then CNT growth rate was calculated. Relative CNT production on a substrate as a function of several experimental parameters was evaluated by this technique in the past [16]. Third approach was to use sheet resistance of grown CNT layer on a substrate. Since the thickness of CNT layer on substrate, namely CNT quantity, has inverse relationship with sheet resistance, CNT growth rate is able to be estimated by means of sheet resistance [17]. 4-Points probes resistivity processor was used for measuring resistance of CNT. All three methods possess advantages and disadvantages. For instance, there is the possibility that the evaluation via image treatment may underestimate CNT growth owing to overlapping of CNTs with each other, but the technique using image treatment is quite facile and simple. On the other hand, the evaluation through transmission has a potential to reflect information stemmed from not only CNTs but also amorphous carbon formed during CVD in the final result. It can be considered that electrical characteristics of grown CNTs may be affected by the change of CVD temperature, which may influence not only the graphitization of CNTs but also the chirality of them. Moreover, if there is no connecting path between CNTs, sheet resistance cannot be measured even when CNTs were formed on the substrate. By performing three approaches, there is increase in the possibility that we are able to gain highly reliable CNT growth rate and activation energy required for CNT synthesis.

3. Results and discussions

3.1. Results

Fig. 2 shows top-viewed SEM micrographs of the substrate when catalyst conditions and CVD temperature are altered. As an example of temperature effect, 750 °C and 650 °C were selected. CVD duration was 30 min except for Fig. 2(d), in which it was 60 min. Abundant CNTs were synthesized at 750 °C irrespective of catalyst conditions, Fig. 2(a)–(c). On the other hand, large difference was found among catalytic conditions at 650 °C, Fig. 2(d)–(f). The sample using thiourea

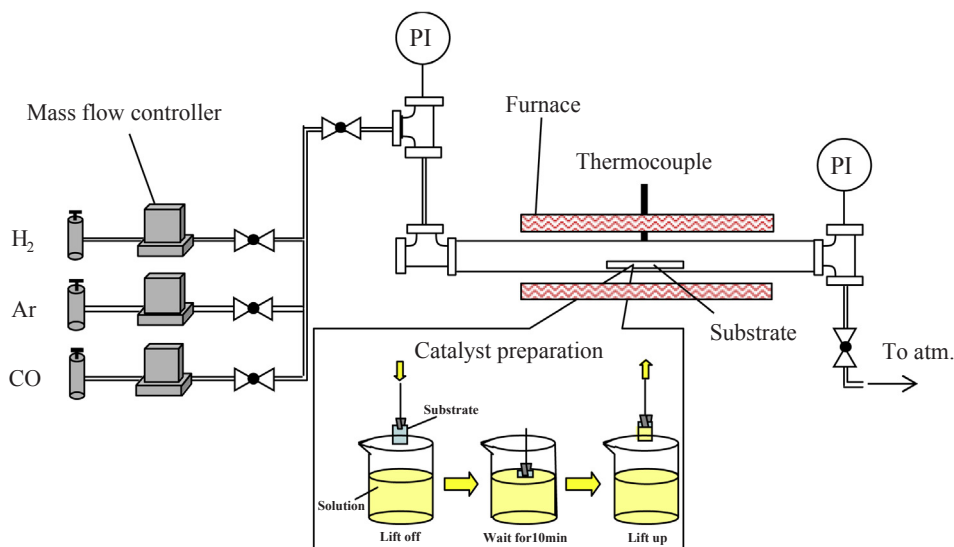


Fig. 1. Schematic showing the preparation way to form catalyst nanoparticles on substrate and experimental setup for CNT synthesis.

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