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研究課題名（和文）Concurrent development and assessment of emerging technology: a case study on carbon nanotube production

研究課題名（英文）Concurrent development and assessment of emerging technology: a case study on carbon nanotube production

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研究成果の概要（和文）：カーボンナノチューブ（CNT）の商品化は、CNTを効率的に合成するための化学蒸着（CVD）法の改善に不可欠です。材料科学で、環境影響が定量化されることはほとんどありません。
ですから、2つの新たなCNT合成方法（基板上および流動層CVD）のライフサイクル温室効果ガス（GHG）排出に関する体系的な調査を提案します。実験に基づいて、重要な構成の影響を示します。CNT生産のライフサイクルGHGは、28.55（基板上）から0.48（流動層）kgCO2e/gCNTの範囲がわかりました。工業レベルを考慮すると、CNTの生産は、炭素繊維（0.02 kgCO2e）と同じくらい低くなる可能性があります。

研究成果の学術的意義や社会的意義
This research promotes an environmentally-conscious framework to develop emerging nano-materials in laboratory. We ensure the recommended CNT synthesis pathway is practical and well-aligned with the Japanese vision of achieving a low-carbon society for sustainable future.

研究成果の概要（英文）：Improvement in chemical vapor deposition (CVD) methods to efficiently synthesize high-quality carbon nanotubes (CNTs) is critical to commercialization of CNTs. Methods with less environmental impacts are preferable for sustainable chemistry. However, in the field of material sciences, the environmental impacts are rarely quantified. Here we provide a systematic investigation on the life cycle greenhouse gases (GHGs) emission of two emerging CNT synthesis methods: on-substrate and fluidized-bed CVD. Based on years-long experiments, we show the impacts of important configurations. We find that the life cycle GHGs of CNT production ranged from 28.55 (on-substrate) to 0.48 (fluidized-bed) kg CO2e/g CNTs. Considering the scale-up effects to industrialized levels, CNT production can be as low as to present carbon fiber (0.02 kg CO2e/g materials).

研究分野：Life Cycle Assessment (LCA)

キーワード：single-wall CNT　CVD synthesis　LCA　industrial ecology　nanotechnology

様　式　Ｆ－１９－２

１．研究開始当初の背景

Carbon nanotubes (CNT) is a novel material with wide applications. Lab-based experiments have been fast developing to improve the CNT synthesis technology. For chemical vapor deposition (CVD) method, this often means a trial-and-error of different experiment variables. However, this approach neglects the prospective environmental impact of production. The consequences can be significant as CNT synthesis is energy and materially intensive. Hence, the anticipated application of CNT to create next generation renewable energy devices such as solar cells and batteries might have reverse impacts.

２．研究の目的

This study aimed to propose a novel concurrent development and assessment framework that takes environmental impact into account at early-stage of technology development. Therefore, driving the emerging synthesis technology towards a low-carbon direction. We collaborated with an experimental-based CNT synthesize laboratory to achieve the following objectives:

- To construct lifecycle inventory data for the famous on-substrate CVD methods.
- To construct lifecycle inventory data for the easily scalable fluidized-bed CVD methods.
- To identify environmental hotspots of the CNT synthesis methods.
- To compare life cycle greenhouse gas (GHG) emissions of CNT synthesis methods.

３．研究の方法

We applied life cycle assessment (LCA), a methodology that comprehensively accounts the environmental impacts from a product cradle-to-grave perspective. The foreground experimental data were acquired from the collaborators as well as direct measurements in the laboratory. The background data were obtained from Ecoinvent v3.6 LCA database to supplement the model. An important originality of this study is the empirical data we analyzed. As the nature of timescale of experimental research is often much longer than assessment modelling work, we had looked into data accumulated over ten years in the laboratory. This allowed us to compare a realistic set of scenarios and to provide insights into various CNT synthesis methods.

４．研究成果

(1) Structural Scenarios Analysis. Overall, we had selected 12 set of experiments from the laboratory, which previously published in three journal papers [1,2,3], to perform the LCA. **Table 1** summarizes the selected cases. These structural scenarios highlight the effect of changing form 2D (on-substrate) to 3D (fluidized-bed) synthesis methods, and the effect of changing from sputtering to CVD reactions. The functional unit is defined as 1 g single to few-wall CNT with purity >99%.

Table 1. Selected experiments for LCA in this study.

	Product	Reactor Type	Catalyst Deposition	Reactor Size	Substrate Size	CNT Yield per Batch
Sato et al. 2018	Vertically-aligned single-wall CNT arrays	Fixed bed	Radio frequency magnetron sputtering	Tubular hot-wall reactor: 34 mm inner diameter, 300 mm heating zone length	Flat silicon substrate: 10 mm × 10 mm	3.9 – 4.0 mg (1 substrate), 4.7 – 25.6 mg (18 substrates)
Kim et al. 2012	Vertically-aligned single-wall CNT arrays	Fluidized bed	Radio frequency magnetron sputtering	Tubular hot-wall reactor: 22 mm inner diameter, 300 mm heating zone length	Aluminum oxide bead: 0.5 mm diameter	90 – 230 mg
Kim et al. 2011	Few-wall CNTs (~3 walls)	Fluidized bed	Chemical vapor deposition	Tubular hot-wall reactor: 22 mm inner diameter, 300 mm heating zone length	Aluminium oxide bead: 0.5 mm diameter	260 mg

(2) On-substrate CVD. Adding small amount of oxidative additive such as H2O and CO2 is the key to prevent premature catalyst deactivation and thus increase the CNT yield drastically. We examined the case of a single substrate of 1 cm^2 and scale-up to 18 substrates [1].

Figure 1a shows the LCA results of 1 g CNT synthesized via the selected on-substrate CVD methods. For the single-substrate, the GWP impacts of H2O- and CO2-assisted growths were equally high, 55.34 and 53.87 kg CO2e/g CNT, respectively. For 18 substrates, the impacts ranged from 28.55 to 158.36 kg CO2e/g CNT. CO2-assisted growth clearly outperformed H2O-assisted growth due to much higher CNT yield. In addition, the impacts were shown in two categories: catalyst deposition and CNT growth. CNT growth had higher impact in the single-substrate cases, but catalyst deposition dominated in the 18-substrate cases.

Figure 1b shows the relative contribution of GWP impact based on input materials and energy and direct emission in the on-substrate CVD methods. Electricity, silicon, and argon gas together accounted for more than 99% of the impact in all cases. Vacuum pumping of the sputtering chamber was the most energy intensive, 50% of the total impact in the optimal case. The minor addition of oxidative agents, H2O or CO2, direct emissions, and rest of the processes contributed to less than 1% of overall impact. This showed that regardless of the additive choice, CNT yield per batch was the determining factor for environmental performance of on-substrate CVD methods.

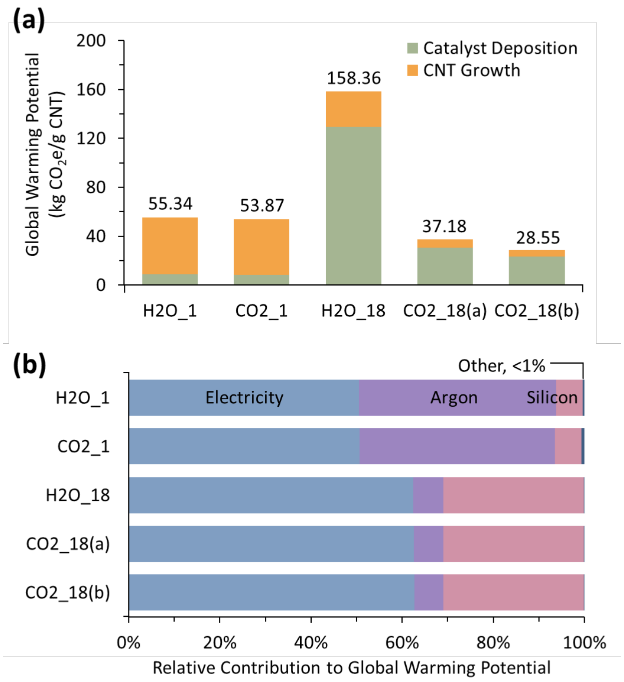

Figure 1. (a) **Life cycle** GHG emissions of 1 g CNT synthesized via on-substrate CVD methods (additive choice_number of substrate). (b) Relative contributions to the GHG of input materials and energy, and direct emissions.

(3) Fluidized-bed CVD. Fluidized-bed CVD method is effective in expanding the reaction space from two dimensions (2D, monolayer stack of flat substrates) to three dimensions (3D, bed of spherical beads) therefore increasing CNT yield and lowering the overall cost. We analyzed the experiments conducted by Kim et al. [2] and Kim et al. [3]. First, the experiments applied a sputtering method for catalyst deposition similar to the previous on-substrate CVD to contrast the effect of 3D to 2D. Then, energy-intensive sputtering process was replaced via a combined catalyst deposition and CNT growth method, using CVD in a single fluidized-bed reactor.

Figure 2a shows the LCA results of 1 g CNT synthesized via the fluidized-bed CVD methods. In comparison to 2D growth, the GWP impact of 3D growth reduced to about one-third, 9.94 kg CO2e/g CNT with sputtered catalyst in fluidized bed. Changing to chemical vapor deposited catalyst further reduced the impact to 2.59 kg CO2e. Reusing aluminum beads twenty times would mitigate about 20% of the impact but the effect of extending the beads use to infinite cycles was minimal. Lastly, substituting argon with nitrogen reduced the impact significantly to 0.48 kg CO2e.

Figure 2b shows the relative contributions to GWP impacts of the input materials and energy and direct emission in the fluidized-bed CVD methods. The major impacts could be narrowed down to a few items, electricity, argon or nitrogen, and aluminum oxide. For sputtered catalyst, the energy demand was huge mostly due to the sputtering process (77%), thus unsuitable for scale-up production. The electricity demand reduced drastically to less than 11% in the case of CVD. For the combined CVD method, noticeable impact reductions were achieved by reusing the aluminum oxide beads; the impact from oxygen increased due to the treatment of used beads. The carrier gas, argon, was clearly the environmental hotspot. The impact of nitrogen production was about one sixth of argon. Therefore, by substituting argon with nitrogen, the relative contribution was more balance, highlighting opportunity for improvements.

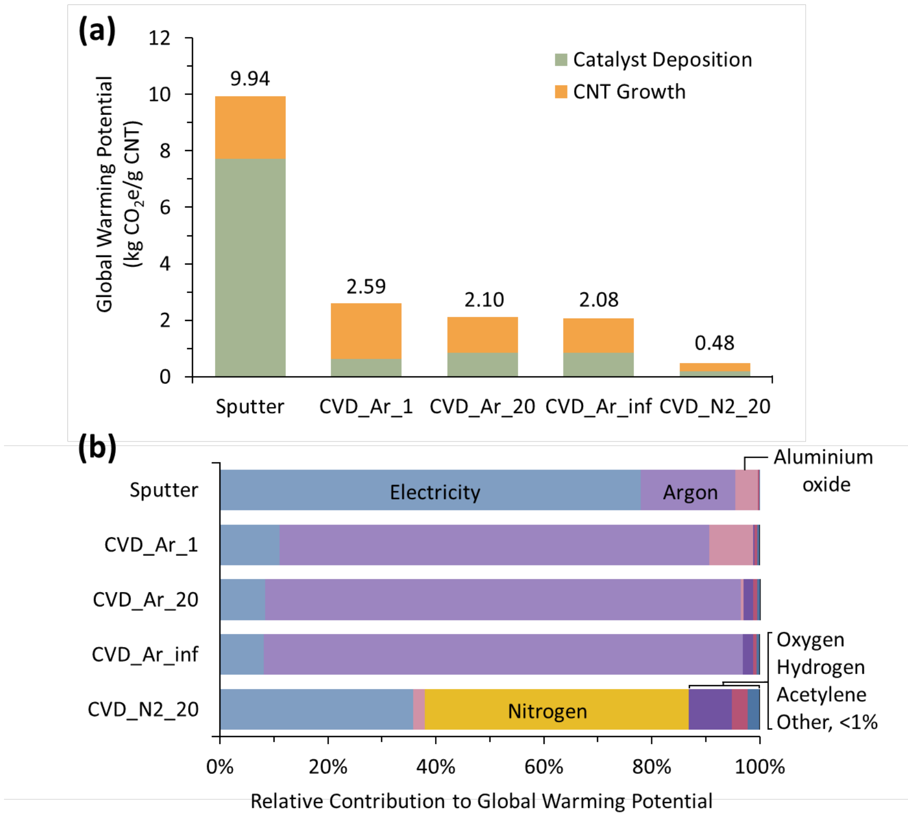

Figure 2. (a) Lifecycle GHG emissions of 1 g CNT synthesized via fluidized-bed CVD methods (sputter = sputtered catalyst and CVD growth) (catalyst deposition method_carrier gas_number of cycle), in catalyst deposition and CNT growth. (b) Relative contribution to the GWP of input materials and energy, and direct emission.

(4) Implications. We showed that with an active decision support of LCA, the CNT production can be potentially as competitive as current carbon fiber production (about 0.02 kg CO2e). This could be achieved by improving the method selection for synthesis including additives, reactors, carrier gases, and other factors.

(5) Publication. The results of this project had been published in ACS Sustainable Chemistry and Engineering. With the encouraging findings, our next goal is to expand towards the evaluation of the environmental benefits of CNT in realistic applications such as next generation solar cells and batteries.

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５．主な発表論文等

〔雑誌論文〕　計1件（うち査読付論文　0件／うち国際共著　0件／うちオープンアクセス　0件）

1．著者名	4．巻
Teah Heng Yi、Sato Toshihiro、Namiki Katsuya、Asaka Mayu、Feng Kaisheng、Noda Suguru	8
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3．学会等名
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Teah Heng Yi、Sato Toshihiro、Namiki Katsuya、Asaka Mayu、Feng Kaisheng、Noda Suguru
2．発表標題
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3．学会等名
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2．発表標題 Environmental Evaluation of Carbon Nanotube Production via On-Substrate and Fluidized-Bed Chemical Vapor Deposition
3．学会等名 sian Pacific Confederation of Chemical Engineering（国際学会）
4．発表年 2019年

1．発表者名 Teah Heng Yi
2．発表標題 Concurrent Development and Assessment of Emerging Technologies: Case of Carbon Nanotubes
3．学会等名 International Symposium on Chemical-Environmental-Biomedical Technology（招待講演）（国際学会）
4．発表年 2019年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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6．研究組織

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