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様　式　C－１９、F－１９－１、Z－１９　（共通）

# 科学研究費助成事業　　研究成果報告書

令和　５ 年　６ 月　６ 日現在

機関番号：１７１０２
研究種目：挑戦的研究（萌芽）
研究期間：2021～2022
課題番号：２１Ｋ１８６９３

研究課題名（和文）固体の熱電変換素子を超える熱流体発電素子の創出

研究課題名（英文）Creation of thermofluidic energy harvesting elements to surpass the solid-state thermoelectric energy conversion

研究代表者

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交付決定額（研究期間全体）：（直接経費）　　4,900,000円

研究成果の概要（和文）：本研究では、数十から数百ナノメートルの深さを持つナノチャネル内の流れの正確な測定方法を開発した。更に、グラフェンコーティングされたナノチャネルにおける毛管流れと表面電荷の相互関係を解明した。また、様々な液体をカーボンナノチューブ単体の内部に充填する方法を確立した。これらの成果は、ナノ空間における流れ、電気、熱的効果に関わる複雑な物理現象の完全な理解を促進し、「熱流体発電素子」の創出の可能性を示した。

研究成果の学術的意義や社会的意義
本研究にて得られた成果は、ナノ空間における流れ、電気、熱的効果に関わる複雑な物理現象の完全な理解を促進し、熱工学および応用物理学の新たな展開に貢献した。また、「熱流体発電素子」の創出の可能性を示し、環境発電およびセンサへの応用は期待でき、脱炭素社会および高度な情報化社会の達成に貢献できる。

研究成果の概要（英文）：Throughout this project, we have developed an accurate method for measuring flow in nanochannels with depths ranging from tens to hundreds of nanometers. We have further elucidated the reciprocal relations between capillary filling and surface charge in graphene-coated nanochannels. We have also established efficient methods for filling various liquids into individual carbon nanotubes. These achievements pave the way for a complete understanding of the multi-physical phenomena involving flow, electric and thermal effects in nanoconfined spaces, as well as the creation of an electricity generator utilizing thermofluids.

研究分野：熱工学

キーワード：ナノチャネル　グラフェン　発電素子

## １．研究開始当初の背景

It had been reported in several high-impact papers that liquid flow and evaporation in carbon-based porous materials could generate a high voltage up to about 1 V, which can find wide applications including energy harvesting and sensors. (Nature Nanotech. 12, 2017; Nature Nanotech. 13, 2018; Joule 4, 2020; Nano Energy 77, 2020; *etc.*) However, the mechanisms of this direct electricity generation have not been fully unveiled yet, due to the complexity of this multi-physical phenomenon involving flow, electric and thermal effects. Based on this background, this research project aimed to unveil the mechanism of the electricity generation from liquid flow and evaporation by nanochannel experiments instead of using porous materials.

## ２．研究の目的

This research project aims to decouple the multi-physical phenomena of the electricity generation from liquid flow and evaporation in the nanosized space confined by carbon-based materials. By fully understanding the mechanisms behind, the final goal of this project is to create "thermofluid-based electricity generators" that can beat the solid-state thermoelectric conversion devices based on the Seebeck effect.

## ３．研究の方法

We fabricated graphene nanochannels with tens to hundreds of nanometers in depth for the study of flow, evaporation, and electrification in nanoconfined space. The graphene nanochannels were fabricated on $SiO_2$/Si wafers using electron-beam lithography and wet-etching, followed by graphene transfer from the copper substrate and anodic bonding of the glass cover. As shown in Fig. 1, by recording the liquid meniscus movement changing with time driven by the capillary force, we can experimentally elucidate the slip flow and evaporation under nanoconfinement. Further, we connected graphene to electric instruments including power supply and high-precision voltage meters, and studied the interplay between flow, evaporation, and graphene surface charge.

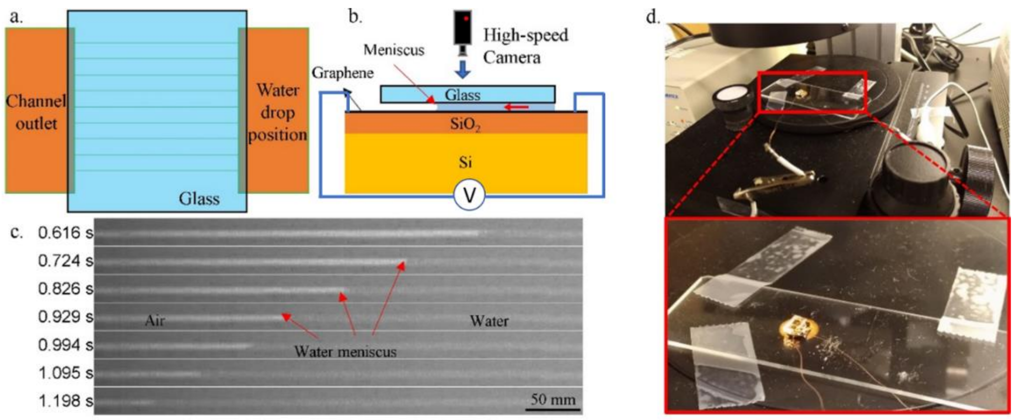


**Fig. 1** The experimental system for the flow, evaporation, and electrification measurements in graphene nanochannels. (a) top view, (b) side view, and (c) high-speed-camera images of the capillary filling in a 45-nm-deep and 5-μm-wide graphene nanochannel changing with time. (d) a photo of the graphene nanochannel device connected with electric instruments set under the high-speed camera.

Besides the graphene nanochannel experiments, we also filled various liquids into carbon nanotubes, and used carbon nanotubes as the nanochannel for the study of flow, thermal, and electrification phenomena.

４．研究成果

First, we have successfully measured the water slip length in graphene nanochannels with high accuracy. We developed a rigorous three-dimensional capillary flow model to measure the slip length, which considers the slip boundary conditions, a nonuniform velocity profile in both the width and depth directions, as well as the dynamic contact angle. By comparing the observed flow rates in two graphene nanochannels with the 3D flow model, we extracted the slip length of water on graphene to be 40±4 nm and 33±3 nm, respectively. Moreover, we used our 3D model to reevaluate the limited slip length data on graphene reported in the literature that neglected the 3D effect, and found that the existing experimental data of the water slip length on graphene approximately fall in the range of 30 to 50 nm, in agreement with some important MD simulation results. This work has been published in Carbon 189 (2022) 162-172.

Second, we systematically studied the slip flow in graphene nanochannels changing with surface electric charging. We found that the slip length of water and salt solutions on graphene decreases with increasing surface charge density, which can be well explained by recently developed theories.

Third, we studied the electric potential generated across the graphene nanochannel due to flow and evaporation. A voltage of several millivolts was generated from the spontaneous capillary flow of pure water in the graphene nanochannels. We used a heater to control the stage temperature for the evaporation experiments. We elucidated how the liquid flow and evaporation rates contribute to electricity generation at various confinements and temperatures.

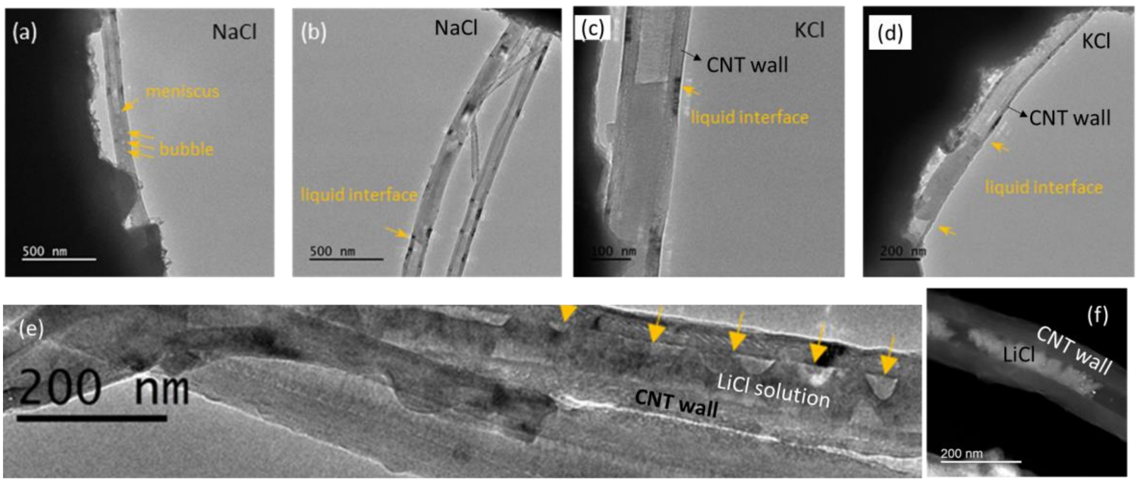


**Fig. 2** Transmission electron microscopy (TEM) images of various salt solutions filled in carbon nanotubes. (a) and (b), TEM images of NaCl solutions filled in carbon nanotubes; (c) and (d), TEM images of KCl solutions filled in carbon nanotubes; (e) and (f), TEM images of LiCl solutions filled in carbon nanotubes.

Last, we have developed efficient methods to fill various kinds of liquids into individual carbon nanotubes. Especially, as shown in Fig. 2, we have successfully filled various salt solutions into individual carbon nanotubes, which are ready for in-depth investigation of interfacial electrification effects.

In summary, during this project, we have developed an accurate method for the flow measurement in nanochannels with depths of tens to hundreds of nanometers, elucidated the reciprocal relations between the capillary filling and surface charge in graphene-coated nanochannels, and established efficient methods to fill various liquids into individual carbon nanotubes.

５．主な発表論文等

〔雑誌論文〕　計7件（うち査読付論文　3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 |
|---|---|
| Chen Kuan-Ting、Li Qin-Yi、Takahashi Koji | 31 |
| ２．論文標題<br>Slip Flow on Graphene: Current Status and Perspective | ５．発行年<br>2022年 |
| ３．雑誌名<br>Journal of Thermal Science | ６．最初と最後の頁<br>1115～1134 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1007/s11630-022-1668-8 | 査読の有無<br>有 |
| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>- |

| １．著者名 | ４．巻 |
|---|---|
| Chen Kuan-Ting、Li Qin-Yi、Omori Takeshi、Yamaguchi Yasutaka、Ikuta Tatsuya、Takahashi Koji | 189 |
| ２．論文標題<br>Slip length measurement in rectangular graphene nanochannels with a 3D flow analysis | ５．発行年<br>2022年 |
| ３．雑誌名<br>Carbon | ６．最初と最後の頁<br>162～172 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1016/j.carbon.2021.12.048 | 査読の有無<br>無 |
| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>- |

| １．著者名 | ４．巻 |
|---|---|
| Kimura Ryota、Teshima Hideaki、Li Qin-Yi、Takahashi Koji | 181 |
| ２．論文標題<br>Thermally induced mass transfer between nanobubbles and micropancakes | ５．発行年<br>2021年 |
| ３．雑誌名<br>International Journal of Heat and Mass Transfer | ６．最初と最後の頁<br>122001～122001 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1016/j.ijheatmasstransfer.2021.122001 | 査読の有無<br>無 |
| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>- |

| １．著者名 | ４．巻 |
|---|---|
| Hirokawa Sota、Teshima Hideaki、Solis-Fernandez Pablo、Ago Hiroki、Li Qin-Yi、Takahashi Koji | 37 |
| ２．論文標題<br>Pinning in a Contact and Noncontact Manner: Direct Observation of a Three-Phase Contact Line Using Graphene Liquid Cells | ５．発行年<br>2021年 |
| ３．雑誌名<br>Langmuir | ６．最初と最後の頁<br>12271～12277 |
| 掲載論文のDOI（デジタルオブジェクト識別子）<br>10.1021/acs.langmuir.1c01589 | 査読の有無<br>無 |
| オープンアクセス<br>オープンアクセスではない、又はオープンアクセスが困難 | 国際共著<br>- |

〔学会発表〕　計3件（うち招待講演　3件／うち国際学会　3件）

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| **1．発表者名**<br>Li Qin-Yi |
| **2．発表標題**<br>In-situ thermal measurement with electron microscopy |
| **3．学会等名**<br>The 13th Asian Thermophysical Properties Conference (ATPC 2022)（招待講演）（国際学会） |
| **4．発表年**<br>2022年 |

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| **1．発表者名**<br>Li Qin-Yi |
| **2．発表標題**<br>Nanoscale Thermal and Fluid Characterization with Electron Microscopy |
| **3．学会等名**<br>2022 International Forum on High-end Equipment and Intelligent Manufacturing（招待講演）（国際学会） |
| **4．発表年**<br>2022年 |

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| **1．発表者名**<br>Li Qin-Yi |
| **2．発表標題**<br>Controlling thermal conductivity of individual nanocarbon materials |
| **3．学会等名**<br>2021 International Forum on High-end Equipment and Intelligent Manufacturing（招待講演）（国際学会） |
| **4．発表年**<br>2021年 |

〔図書〕　計0件

〔産業財産権〕

〔その他〕

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**6．研究組織**

| | 氏名<br>（ローマ字氏名）<br>（研究者番号） | 所属研究機関・部局・職<br>（機関番号） | 備考 |
|---|---|---|---|
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**7．科研費を使用して開催した国際研究集会**

〔国際研究集会〕　計0件

８．本研究に関連して実施した国際共同研究の実施状況

| 共同研究相手国 | 相手方研究機関 |
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