様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

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研究課題名（和文）一次元ファンデルワールスヘテロ構造の創成と評価

研究課題名（英文）Creation and characterization of one-dimensional van der Waals heterostructures

研究代表者
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研究成果の概要（和文）：化学気相成長法で単層カーボンナノチューブ（SWCNT）の外層に窒化ホウ素ナノチューブ（BNNT）、さらに二硫化モリブデンナノチューブ（MoS2NT）を同軸に成長した一次元ファンデルワールスヘテロ構造の合成に実現した。詳細な構造と形成メカニズムについて、透過型電子顕微鏡を用いた包括的な研究を行った。異なる形状のBNNTのエッジ構造を識別し、同一箇所に対して電子線回折によりそれぞれのカイラル角と極性が厳密に相関を持つことを見出した。SWCNTとBNNTの対掌性の相関を明らかにした。これは一次元ヘテロ構造という新材料群の知見に留まらず、将来の電子デバイスへの応用も期待される。

研究成果の学術的意義や社会的意義
One-dimensional van der Waals heterostructures are a class of new materials. Because of the unique 1D geometry, these heteronanotubes can host new physics and therefore have interesting properties. It may be used in future electronic devices including transistors, solar cells and nanolasers.

研究成果の概要（英文）：By chemical vapor deposition, we have realized the synthesis of one-dimensional van der Waals heterostructurenanotubes, in which boron nitride nanotubes (BNNT) and molybdenum disulfide nanotubes (MoS2NT) are coaxially grown on the outer layer of single-walled carbon nanotubes (SWCNTs). A comprehensive study using a transmission electron microscope was conducted on the detailed structure and formation mechanism of the synthesized heteronanotubes. We identified the edge structures of BNNTs of different shapes and found that they are closely associated with the chiral angles and polarities of the tube. In addition, the correlation between the SWCNT template and BNNT chirality was clarified. This is not limited to the knowledge of the new material group of one-dimensional heterostructure, but from a more general point of view, it is expected to be applied in future electronic devices.

研究分野：ナノ材料

キーワード：一次元ファンデルワールスヘテロ構造　カーボンナノチューブ　透過型電子顕微鏡

１．研究開始当初の背景

The demonstration of two-dimensional (2D) van der Waals (vdW) heterostructures, in which atomic layers are stacked on each other and different 2D crystals are combined beyond symmetry and lattice matching, represents a way of manipulating crystals to enable both the exploration of physics not observable in conventional materials and of device applications. These 2D heterostructures have been fabricated with by transferring preprepared layers (transfer approach) or by synthesizing layers onto a base layer (synthesis approach). Whether such artificial materials and interfaces can be fabricated in other dimensions remains an open question. In one-dimensional (1D) materials, for example, an ideal vdW heterostructure would be a coaxial structure with different types of nanotubes. Such ideal structures have been investigated in theoretical studies and would appear to require a synthesis approach. Experimental attempts to fabricate coaxial nanotube structures have yielded only amorphous or very poorly crystallized coating.

２．研究の目的

Therefore, the first purpose of this study is to develop a method to synthesize one-dimensional van der Waals heterostructures. If these coaxial heterostructures consisting of different nanotube crystals can be generated, the growth of these heteronanotubes will be likely shell by shell, a very different growth process from conventional growth of 1D homo-material nanotubes where multiple walls are formed simultaneously from a nanoparticle. Accordingly, the second purpose of this study is to investigate the nucleation and crystal growth behaviors in 1D vdW heterostructures, which is of fundamental research interest but is challenging as all processes occur on tiny (only a couple of nm) and highly curved surfaces.

３．研究の方法

The template SWCNT film used in this project was synthesized by aerosol CVD. Typically ferrocene was used as the catalyst precursor and CO was used as the carbon source. The growth temperature was 1000-1200°C. The SWCNTs were formed in gas phase and collected onto a filter paper. SWCNT-BNNT heterostructures were synthesized by a low pressure thermal CVD using ammonia borane (H_3NBH_3) as the BN precursor. Briefly, the starting SWCNT prepared in the previous section was placed at the center of the furnace. 30 mg BN precursor was loaded at the upstream and heated to 70-90°C. Vapor of BN precursor was taken by a flow of 300 sccm Ar (with 3% H_2) to the hot zone to form BNNT on surface of SWCNTs. The reaction temperature was 1000-1100°C and the chamber pressure was maintained at 300 Pa. The coating time in this study varied from a few min to 1 hr. SWCNT-BNNT-MoS_2NT heterostructures were synthesized by a low-pressure CVD using MoO_3 and S powder as precursors. S powder were placed at the upper stream and heated to 100-130°C, and MoO_3 is placed at next to S and heated to 500-600°C. The vapor was carried in by a flow of 50 sccm Ar to SWCNTs or SWCNT-BNNT heterostructures at the center. The temperature was maintained at 400-600°C, and typical growth time varied from 5-70 min.

Conventional HRTEM images were taken by a JEM-2800 at an acceleration voltage of 100 kV. EDS and selected area electron diffraction (SAED) patterns of the entire film were taken by the same TEMs with a typical selected area aperture diameter of a few μm and a camera length of 60 cm. Nano area electron diffraction (NAED) patterns of individual SWCNT-BNNT heterostructure were obtained by JEM-ARM200F STEM with a cold field-emission gun operating at 80 kV. In this case a near parallel beam is used together with a small convergence lens aperture (10 μm in diameter) to obtain a small-area electron beam size (~10 nm in diameter). Additionally, the samples were heated at 300 °C during the measurement to avoid carbon contamination using a heating holder (EM-31670SHTH) and a controller unit (EM-08170HCU). HAADF-, ABF-STEM images and corresponding EELS mapping of SWCNT-BNNT-MoS_2 heterostructures were obtained in the same TEM or GRAND-ARM^{TM} STEM operating at 80 kV. Aberration corrected TEM images are taken at a different JEM-ARM200F TEM with a cold field-emission gun operating at 120 or 60 kV.

４．研究成果

We present the initial growth step, the formation of the SWCNT-BNNT 1D heterostructure. We used SWCNTs as a template and synthesized additional hexagonal BN layers by chemical vapor deposition (CVD). Figure 1C shows a representative high-resolution transmission electron microscope (HRTEM) image of this coaxial heterostructure. In a conventional HRTEM image, this nanotube is not distinguishable from a triple-walled pure carbon nanotube. The aberration-corrected HRTEM image of a similar tube revealed a contrast of stacking of two perfect nanotubes (Fig. 1, D and E). However, given the starting material is purely single-walled before we performed a post BN coating, we expect that the outer wall or walls were BN. This is supported by electron energy loss spectroscopic (EELS) mapping (Fig. 1F). Because the reaction occurs on the outer surface, unlike previous attempts

inside a nanotube, we achieved continuous coating and highly crystallized outer BNNTs. The number of outer BNNT walls can be adjusted from a minimum of 1 to a maximum of 5 to 8 depending on the duration of BN CVD. These different layers grow independently, but the first layer is always longest. The walls of our SWCNT template are very clean, so the nucleation is usually observed at the end of a suspended region, where a SWCNT is connected with another SWCNT or a SWCNT bundle. Occasionally, nucleation also occurs simultaneously at both ends of suspended SWCNT region. Nucleation from middle of a SWCNT is rarely observed.

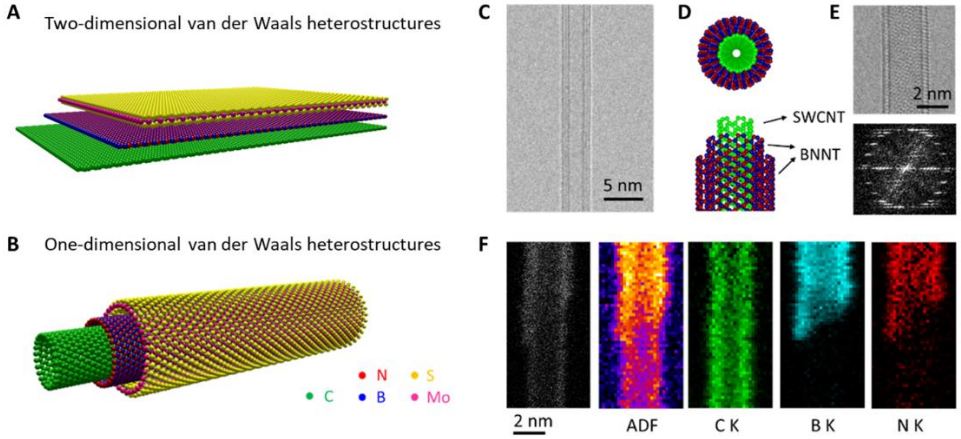

Fig. 1 Overview of 1D vdW heterostructures.

MoS_2 2D sheets have been studied intensively as the representative transmission metal dichalcogenide (TMD) material in recent years. Multi-walled MoS_2 nanotubes with diameters usually > 20 nm and their hybrid materials are well known, but single-walled, single-crystal MoS_2 nanotubes have not been convincingly demonstrated in previous studies. Thus, we explored growth of MoS_2 on SWCNTs. Figure 2, A to C, shows the atomic structure, TEM, and scanning TEM (STEM) images of SWCNT-MoS_2 coaxial nanotubes obtained after applying our growth strategy. The MoS_2 nanotube has much stronger image contrast than carbon in both TEM and STEM images. Single-walled MoS_2 nanotubes were predicted to have direct band gap distinctive from multiwalled nanotubes and to exhibit strong quantum confinement effects.

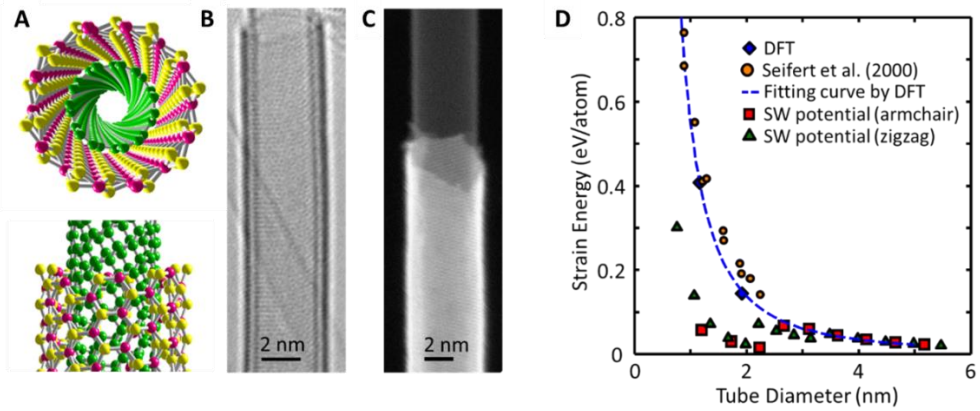

Fig. 2 SWCNT-MoS_2 1D vdW heterostructure.

As heterostructures were directly synthesized on Si/SiO_2 TEM grid, this "heterostructure-on-grid" sample can be brought from our CVD chamber to the TEM column without further processing. Many intrinsic details of the heterostructure can be thereby preserved. The first thing we noticed is that the open ends of BNNTs can be visualized by TEM. Under-focused images, even by conventional high resolution TEM (HRTEM), can reveal the shape of a tube edge, and this shape is found to be different from tube to tube. Fig. 3A represents three typical types of open edges we observed. These edges of BNNTs usually have sharp-cut shapes but are cut diagonally with various inclination angles from the circumference of the nanotube. For example, NT#1 has a clear spiral end and the edge inclination angle (between the edge and tube circumference) is roughly 30°, while NT#2 has an edge nearly perpendicular to the SWCNT axis. To distinguish the difference between these two tubes, nano-area electron diffraction (NAED) was employed to determine the chiral angle (crystal orientation) of outer BNNTs. NAED patterns in Fig. 3B suggests that NT#1 is a near-armchair BNNT with the chiral angle of 28°, while NT#2 is a near-zigzag BNNT with chiral angle of 2°. Plotting the atomic arrangement of these nanotubes in Fig. 3C immediately reveals that, in both cases, the sharp cuttings

we observe correspond to the zigzag edge of a BN honeycomb lattice. That is, an open-ended BNNT in this study prefers a zigzag edge over an armchair edge. This is consistent with previous theoretical and experimental studies in 2D BN where zigzag edge is found to be energetically more favorable. With this ability of observing the edge shape and identifying the chiral angle for the same nanotube, we learned that the open end of a BNNT is aligned to its axis with an angle depending on its own chiral index. An armchair BNNT tends to have a spiral edge (NT#1) while a zigzag BNNT has a perpendicular edge (NT#2), both of which are due to the preference of a zigzag edge. This correlation is straightforward and clearly demonstrated by the above characterizations

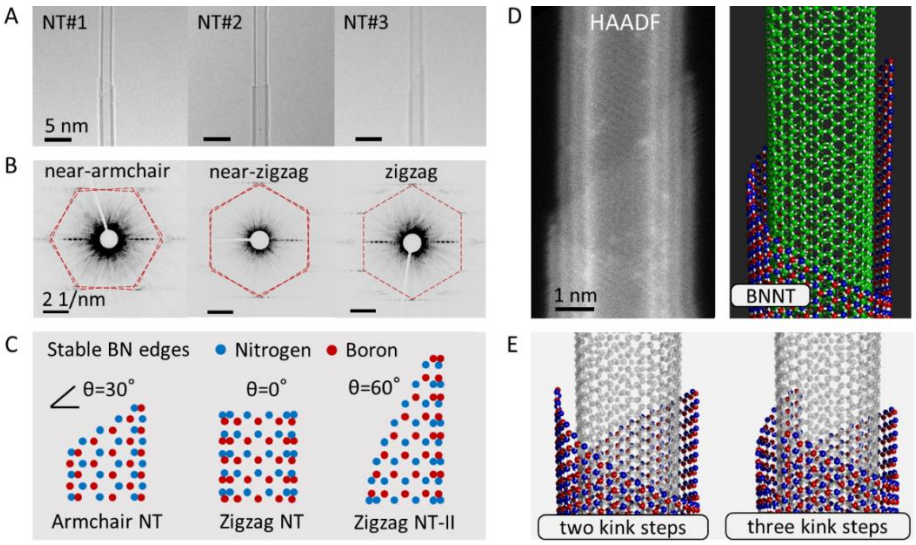

Fig. 3. Characterization of the open growing edge of the 1D vdW heterostructure.

However, one must take into account the difference in structural polarity when describing the edge of a BNNT (unlike in CNT where all atoms are carbon), and this polarity explains a second type of edge shape for zigzag BNNTs shown in NT#3. Because of the crystal symmetry, a zigzag BN edge can be either terminated with B (B-polar) atoms or N atoms (N-polar), and studies in 2D material indicated that the N-terminated zigzag edge formation is energetically more stable. Therefore, when a zigzag BNNT is N-polar in its growing direction, a flat cut edge is stable as shown in NT#2. However, when a zigzag BNNT is B-polar in its growing direction, a flat-cut edge becomes unstable and must grow to a 60° inclination angle to form the N-termination. This is exactly the case for NT#3. The chiral index of this BNNT is zigzag (34, 0), as suggested by the NAED pattern. Its chiral angle, 0°, is nearly the same as NT#2 but the edge shape is completely different. This indicates that the polarity of open ends in NT#2 and NT#3 are opposite, with NT#2 N-polar up and NT#3 B-polar up. Therefore, more generally, chirality of the BNNT, together with the polarity of the tube-growing direction, determines the stable edge structure of outer BNNTs. More discussions on this point, including the comparison between graphene and hexagonal BN, edge structure of a chiral BNNT and the method to extract the diffraction of BNNT from the two sets of patterns, are provided in the supporting information.

Previously we have confirmed that there is no obvious chirality correlation between the inner SWCNT and outer BNNT in a heterostructure, but the handedness correlations still remain unknown. Handedness is a unique structural feature for 1D tubular nanostructures and the experimental identification is extremely difficult. It is usually recognized as the ultimate structure characterization for a nanotube, as a left-handed nanotube and a right-handed nanotube have a mirror symmetry for their atomic arrangements, but are supposed to have exactly the same electronic and chemical properties (Fig. 4A). There are only a couple of techniques that have been proven capable of identifying handedness.

In TEM imaging, a right-handed (12,6) nanotube and left-handed (6,12) nanotube show similar contrasts. Electron diffractions, although capable of telling the chiral index of a nanotube, cannot distinguish a left-handed nanotube from right-handed one as their patterns are exactly the same. Despite the technical challenges, identifying the handedness is scientifically meaningful particularly in the case of a heterostructure. One reason is that, if one would unfold a double-walled heteronanotube (should have four different combinations as shown in Fig. 4B), even for the same configuration, e.g. (17,13)@(34,0), a left-left handed (L@L) and left-right handed (L@R) have completely different stacking angles and thus Moiré patterns. Considering the recent progress in moiré physics (e.g. in both graphene-graphene and graphene-hBN) for 2D crystals, and more recently 1D double-walled carbon nanotube (e.g. moiré-induced tube-tube coupling and new states), it is not only important to

satisfy fundamental scientific curiosity in crystallography, but also of great importance to understand how the properties of a heteronanotube may be affected by their atomic arrangements.

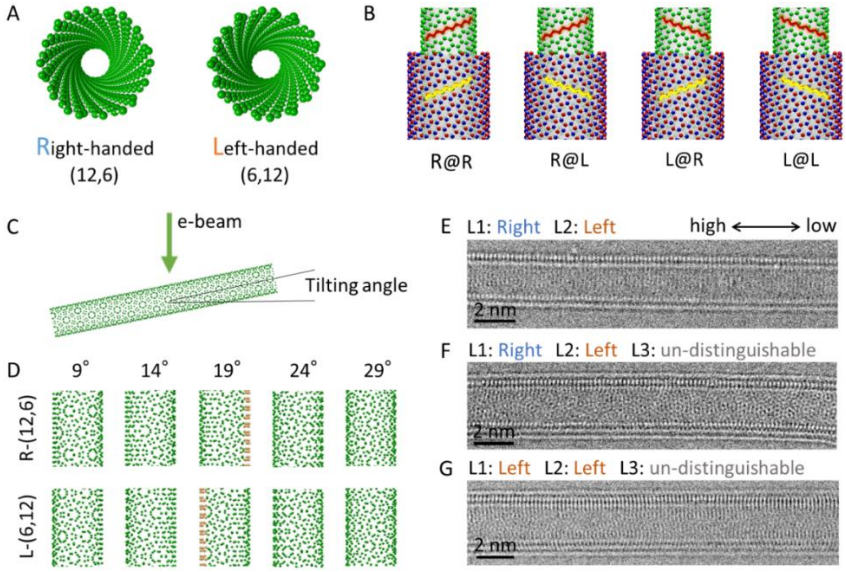

Fig. 4. Handedness relationship in 1D SWCNT-BNNT vdW heterostructures.

A simple TEM technique for the identification of handedness in 1D nanotubes is to use side-wall contrast. In brief, when a nanotube is tilted to a certain angle in TEM, a discontinuous, dots-like contrast, which originates from 0.21 nm zigzag atomic chain of the hexagonal honeycomb lattice, will appear at one side of projected TEM image depending on which handedness the nanotube is. Fig. 4C and 4D shows the scheme of this method. Historically when this method was proposed, a nanotube needed to be tilted to its nearly exact chiral angle to see a clear side contrast. For example, a (12, 6) nanotube needs to be tilted to 19° in order to see this side-wall armchair contrast. However, with recent development of aberration-corrected TEM and hence the improvement of the point resolution, we notice that even within ±5°, side-wall contrast of a nanotube can be observed in our aberration-corrected TEM. For a (12,6) nanotube having a chiral angle of 19°, within the range when the tube is tilted from 14 to 24°, the sidewall contrast can be distinguished. This decently large angle tolerance suggests that, in a SWCNT network where chiral indexes of SWCNTs are randomly distributed (as confirmed previously), we can roughly identify the handedness of 1/3 of the nanotubes among the whole population by only tilting the TEM holder to one angle. This is a convenient way to identify many nanotubes in the sample or many walls in one multi-walled heteronanotube. Occasionally we can also observe 0.12 nm armchair contrast at the wall (but this requires the nanotube to be titled in a very narrow angle range), which can help to further identify more nanotubes. Detailed explanation to this method, including the mechanism and examples of the side wall contrast are provided in supporting information.

Representative experimental data are shown in Fig. 4E-G. In all these three images, the sample is tilted as the left side is higher in TEM and the right side is lower. In the first image, clear contrast appeared at the bottom wall for the inner tube and at the upper wall for the outer BNNT, which suggests that the inner nanotube is a right-handed and the outer nanotube is a left-handed. The second example in Fig. 4F is a triple-walled heteronanotube. The inner and middle shells also have a contra-handedness, but the outer shell is undistinguishable as no obvious contrast appears at either side of the walls. This indicates the chiral angle of this outmost shell is beyond the range of tilting angle ±5°. The third heteronanotube however has a uni-handedness. Both the inner and middle shells are left-hand, while the outer shell is also undistinguishable.

Key publications:

1. R. Xiang*, T. Inoue, Y. Zheng, A. Kumamoto, Y. Qian, Y. Sato, M. Liu, D. Tang, D. Gokhale, J. Guo, K. Hisama, S. Yotsumoto, T. Ogamoto, H. Arai, Y. Kobayashi, H. Zhang, B. Hou, A. Anissimov, M. Maruyama, Y. Miyata, S. Okada, S. Chiashi, Y. Li, J. Kong, E. I. Kauppinen, Y. Ikuhara, K. Suenaga, S. Maruyama*, One-dimensional van der Waals heterostructures, *Science,* (2020), 367, 537-542.
2. Y. Zheng, A. Kumamoto, K. Hisama, K. Otsuka, G. Wickerson, Y. Sato, M. Liu, T. Inoue, S. Chiashi, D.-M. Tang, Q. Zhang, A. Anisimov, E. I. Kauppinen, Y. Li, K. Suenaga, Y. Ikuhara, S. Maruyama*, R. Xiang*, One-dimensional van der Waals Heterostructures: Growth Mechanism and Handedness Correlation Revealed by Non-destructive TEM, *P. Natl. Acad. Sci. USA,* (2021), 118-37, e2107295118-1-e2107295118-10.

５．主な発表論文等

〔雑誌論文〕　計7件（うち査読付論文　6件／うち国際共著　3件／うちオープンアクセス　1件）

１．著者名 Ya Feng, Henan Li, Taiki Inoue, Shohei Chiashi, Slava V. Rotkin, Rong Xiang, and Shigeo Maruyama	４．巻 15
２．論文標題 One-Dimensional van der Waals Heterojunction Diode	５．発行年 2021年
３．雑誌名 ACS Nano	６．最初と最後の頁 5600-5609
掲載論文のDOI（デジタルオブジェクト識別子） 10.1021/acsnano.1c00657	査読の有無 有
オープンアクセス 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 該当する

１．著者名 P. Wang, Y. Feng, R. Xiang, T. Inoue, A. Anisimov, E. I. Kauppinen, S. Chiashi, S. Maruyama	４．巻 32
２．論文標題 Phenomenological model of thermal transport in films of carbon nanotubes and hetero-nanotubes	５．発行年 2021年
３．雑誌名 Nanotechnology	６．最初と最後の頁 205708-1-8
掲載論文のDOI（デジタルオブジェクト識別子） 10.1088/1361-6528/abe151	査読の有無 有
オープンアクセス 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 該当する

１．著者名 R. Xiang* and S. Maruyama*	４．巻 1
２．論文標題 Heteronanotubes: challenges and opportunities	５．発行年 2021年
３．雑誌名 Small Science	６．最初と最後の頁 2000039-1-5
掲載論文のDOI（デジタルオブジェクト識別子） 10.1002/smsc.202000039	査読の有無 有
オープンアクセス オープンアクセスとしている（また、その予定である）	国際共著 －

１．著者名 Xiang Rong、Inoue Taiki、Zheng Yongjia、et al.	４．巻 367
２．論文標題 One-dimensional van der Waals heterostructures	５．発行年 2020年
３．雑誌名 Science	６．最初と最後の頁 537～542
掲載論文のDOI（デジタルオブジェクト識別子） 10.1126/science.aaz2570	査読の有無 有
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1．著者名 Arai Hayato、Inoue Taiki、Xiang Rong、Maruyama Shigeo、Chiashi Shohei	4．巻 0
2．論文標題 Non-catalytic heteroepitaxial growth of aligned, large-sized hexagonal boron nitride single-crystals on graphite	5．発行年 2020年
3．雑誌名 Nanoscale	6．最初と最後の頁 0
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/D0NR00849D	査読の有無 有
オープンアクセス 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 －

1．著者名 Lim Hong En、Irisawa Toshifumi、Okada Naoya、Okada Mitsuhiro、Endo Takahiko、Nakanishi Yusuke、Maniwa Yutaka、Miyata Yasumitsu	4．巻 11
2．論文標題 Monolayer MoS2 growth at the Au-SiO2 interface	5．発行年 2019年
3．雑誌名 Nanoscale	6．最初と最後の頁 19700～19704
掲載論文のDOI（デジタルオブジェクト識別子） 10.1039/C9NR05119H	査読の有無 有
オープンアクセス 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 －

1．著者名 Zheng Yongjia、Kumamoto Akihito、Hisama Kaoru、Otsuka Keigo、Wickerson Grace、Sato Yuta、Liu Ming、Inoue Taiki、Chiashi Shohei、Tang Dai-Ming、Zhang Qiang、Anisimov Anton、Kauppinen Esko I.、Li Yan、Suenaga Kazu、Ikuhara Yuichi、Maruyama Shigeo、Xiang Rong	4．巻 118
2．論文標題 One-dimensional van der Waals heterostructures: Growth mechanism and handedness correlation revealed by nondestructive TEM	5．発行年 2021年
3．雑誌名 Proceedings of the National Academy of Sciences	6．最初と最後の頁 1-9
掲載論文のDOI（デジタルオブジェクト識別子） 10.1073/pnas.2107295118	査読の有無 無
オープンアクセス 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 －

〔学会発表〕　計1件（うち招待講演　1件／うち国際学会　1件）

1．発表者名 Rong Xiang, Yongjia Zheng, Ming Liu, Taiki Inoue, Shohei Chiashi, Shigeo Maruyama
2．発表標題 One-dimensional van der Waals heterostructures
3．学会等名 第81回応用物理学会秋季学術講演会（招待講演）（招待講演）（国際学会）
4．発表年 2020年

〔図書〕　計0件

〔産業財産権〕

〔その他〕

Website http://www.photon.t.u-tokyo.ac.jp/ http://www.photon.t.u-tokyo.ac.jp/index-j.html

6．研究組織

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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