



# 希少元素に頼らない 永久磁石の開発

## Rare-metal-lean permanent magnet

## 磁性材料研究拠点

The Elements Strategy Initiative Center for Magnetic Materials (ESICMM)



GL: 三宅 隆  
産業技術総合研究所  
GL: Takashi Miyake,  
CD-FMat, AIST



### 研究の背景 Background to the research

- 高性能磁石材料の市場の拡大
- ネオジム磁石の特性を超える新材料が待望
- 希少元素に頼らない新材料への期待
- Growing market for high-performance permanent magnets
- Anticipation for novel materials beyond neodymium magnet
- Anticipation for novel magnet materials that do not include critical elements

### 研究のポイント Points of the research

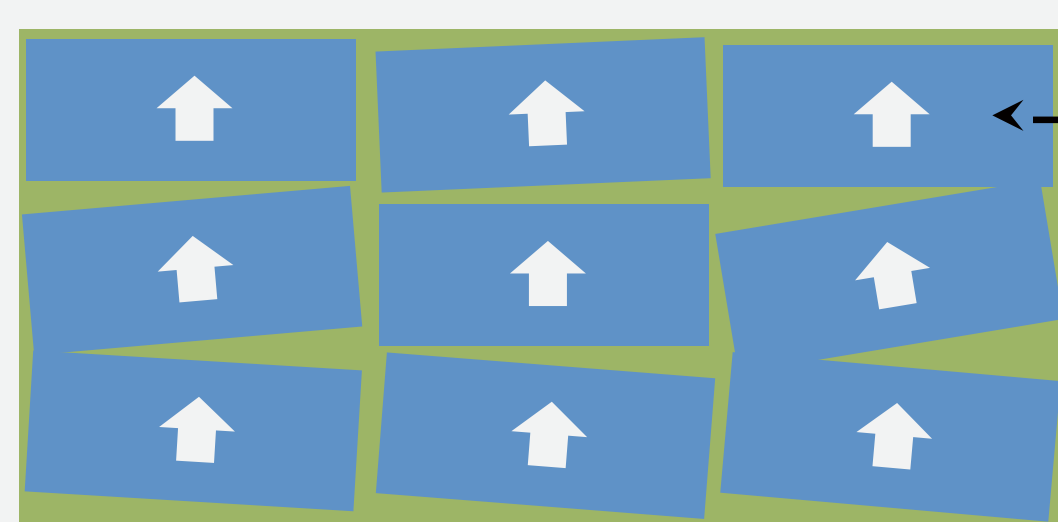
- 電子論に基づいた高飽和磁化と高結晶磁気異方性の解明へ向けた理論構築
- 計算、データ駆動、理論を組み合わせた効率的な新物質探索
- 高鉄濃度希土類化合物  $\text{NdFe}_{12}\text{N}$  の高磁気特性の計算予測と見える化
- Understanding high saturation magnetization and high magnetocrystalline anisotropy based on quantum theory
- Efficient materials discovery using a combination of computational, data-driven, and theoretical approaches
- High magnetic properties of Fe-rich rare-earth magnet compound  $\text{NdFe}_{12}\text{N}$ : prediction by first-principles calculations and visualization

### 研究概要 Outline of the research

1

## 高性能磁石に求められる条件 Requirements for high-performance magnet materials

### 微細構造 Microstructure



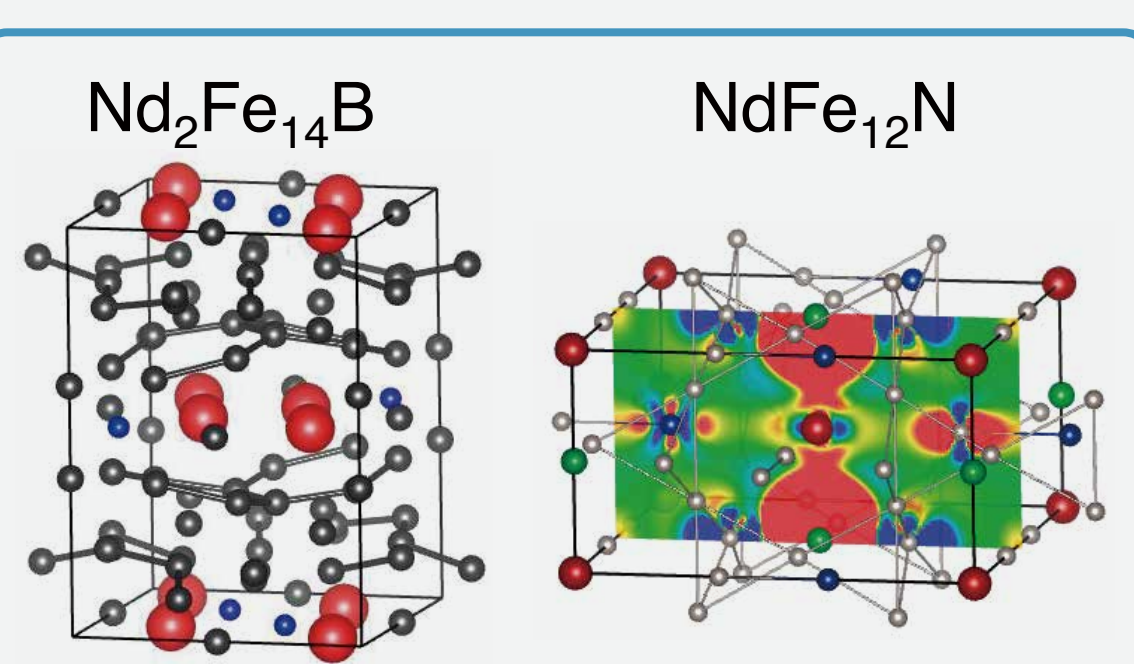
### 副相化合物 Sub phases

- Nd酸化物等  
Neodymium oxides
- アモルファス相  
Amorphous

### <副相の要件> Sub phases

- 高保磁力を発現する微細組織  
(磁化反転抑制など)
- Optimized microstructures for high coercivity

### 主相化合物 Main phase



### <主相の要件> Main phase

- 高飽和磁化
- 高結晶磁気異方性
- 高キュリー温度
- High saturation magnetization
- High magnetocrystalline anisotropy
- High Curie temperature

図1 高性能永久磁石の主相には、高飽和磁化、高結晶磁気異方性、高キュリー温度が、副相には、主相間磁気結合を分離して磁化反転を抑制する効果が求められる。

Figure 1 High-performance permanent magnet materials require a main phase having high saturation magnetization, high magnetocrystalline anisotropy, high Curie temperature, and a sub phase that blocks the magnetic coupling among main phases. Coercivity has strong positive correlation with the microstructure.

### 研究概要 Outline of the research

2

## 希土類磁石化合物の磁性の発現機構 Mechanism of magnetism in rare-earth magnet compounds

### 遷移金属 Transition metal

3d 電子軌道  
3d electrons

S: 電子スピン  
Spin magnetic moment

L: 軌道磁気モーメント  
Orbital magnetic moment

$S_{3d}$   $S_{5d}$

希土類元素  
Rare earth element

$S_{4f}$   $L_{4f}$

4f 電子軌道  
4f electrons

5d 電子軌道  
5d electrons

図2 希土類元素の4f電子軌道は、周囲にある5d電子軌道で結晶場を感じ、軌道磁気モーメントの方向が決まる。この4f電子の軌道磁気モーメントが、スピン軌道相互作用、原子間交換結合、軌道混成を通じて、飽和磁化やキュリー温度と関連する遷移金属の3dスピンの影響を与えている。

Figure 2 High saturation magnetization and high Curie temperatures in rare-earth magnet compounds come from the 3d electrons of transition metals, whereas the 4f electrons of rare-earth elements are the source of strong magnetocrystalline anisotropy. The direction of the orbital magnetic moment of the 4f electrons is affected by the crystal field produced by the surrounding charge distribution.

### 研究概要 Outline of the research

3

## 第一原理計算データで探る 磁化とキュリー温度の最大値 Search for maximum performance of magnets through ab-initio data

### 材料予測手順 Procedure for materials design

ハイスループット計算で数百点のデータを可視化  
Several hundreds of data points obtained by high-throughput ab-initio calculation are visualized.

→ピーク近傍の条件を満たす材料を探索し、結晶構造の安定性を計算して候補物質を絞る  
Materials located around the peak position in performance are searched and targeted as candidate materials after their structural stabilities are examined.

→合成の可能性がある範囲のものを抽出し詳細な特性を計算  
Among candidates, those possibly synthesized are further investigated theoretically in detail.

→実際に化合物を合成し特性評価  
Syntheses of thus predicted materials and their characterizations are tried out.

破線より左側では強磁性が不安定  
Ferromagnetism is unstable in the region to the left of the dashed line.

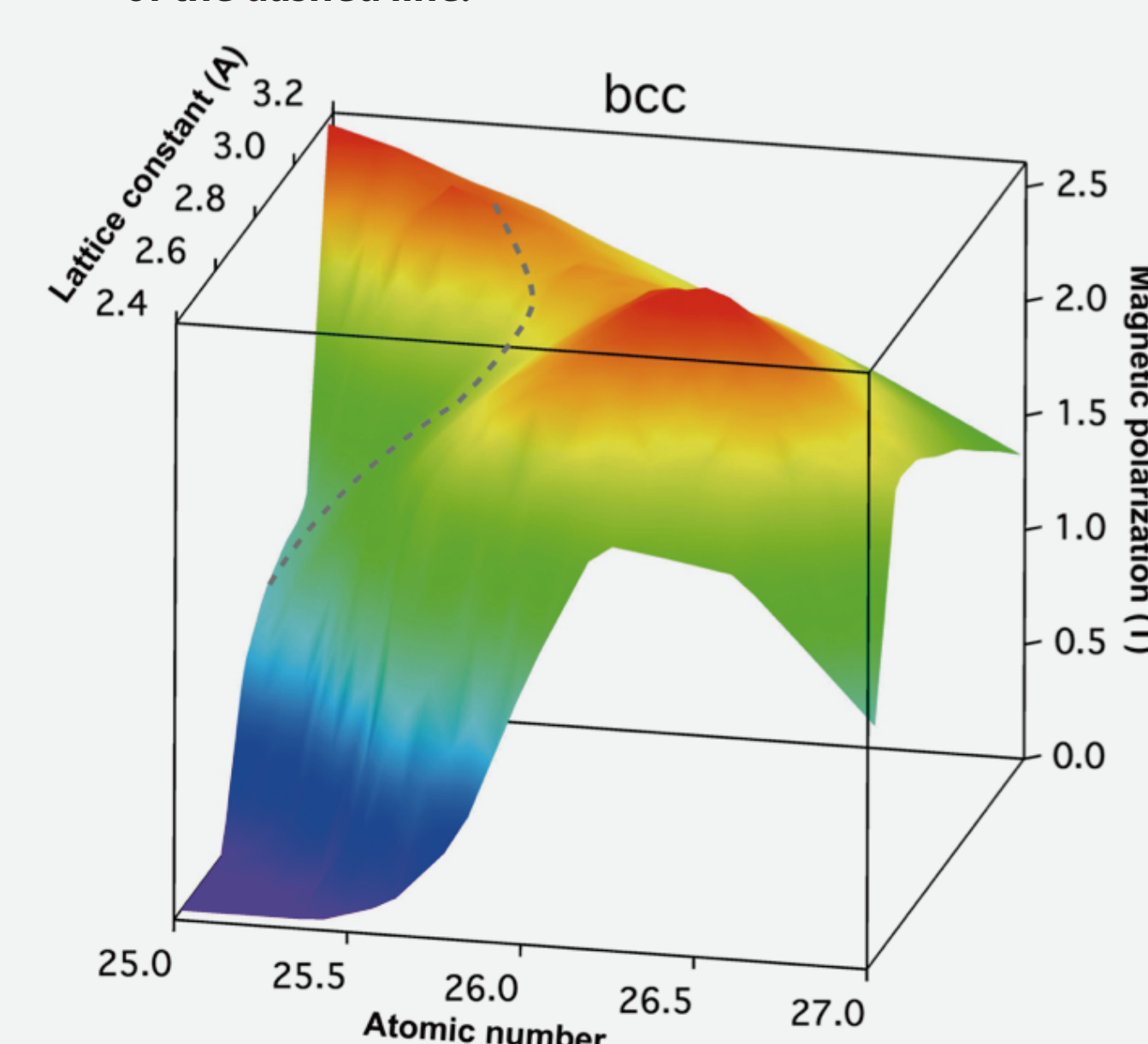


図3 bcc構造を仮定し、格子定数と仮想的な原子の原子番号の関数として計算された磁化の値。磁化は $a = 2.65 \text{ \AA}$ 、 $Z = 26.4$ のあたりでドームのような構造のピークを持っており、最大値は $\text{Nd}_2\text{Fe}_{14}\text{B}$ よりもはるかに大きい2.66 Tを示す。

Figure 3 Saturation magnetic polarization  $J_S$  of the system plotted against the lattice constant  $a$  and atomic number of a fictitious atom  $Z$ . The ferromagnetic state is unstable in the region to the left of the dashed line. Here a bcc structure is assumed, and the electron number corresponds to the atomic number of fictitious atoms. A dome-like structure appears around  $a = 2.65 \text{ \AA}$  and  $Z = 26.4$ , where  $J_S$  takes the maximum value of 2.66 T, which is much larger than that of  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , is seen.

### 研究概要 Outline of the research

4

## 磁性発現機構の見える化 Visualization in Mechanism of magnetism

- 磁石特性に影響を与える電子スピン密度だけを可視化  
Visualization of electron spin-density that may affect the magnetic properties.
- 透明樹脂の中に結晶構造と電子を描写する3Dプリント技術を開発  
Development of 3D-Printing technology that enables us to depict the crystal structure and electron density in the transparent resin.

→理解や議論が深まり、新しいアイデア創出をサポート  
This helps us to get better understanding and deep insights, supporting the creation of new ideas.

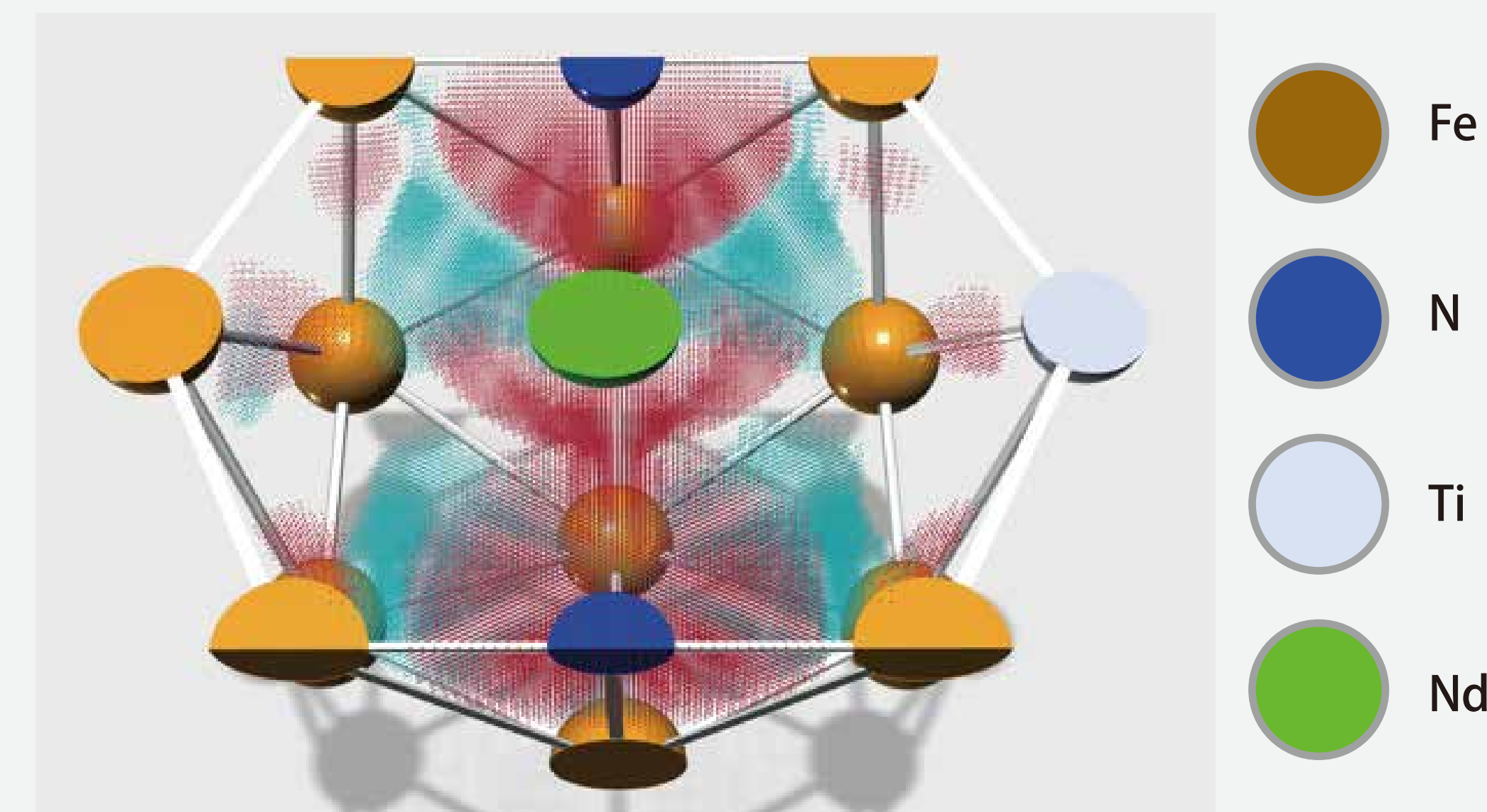


図4  $\text{NdFe}_{12}\text{TiN}$ と $\text{NdFe}_{11}\text{Ti}$ の電子スピン磁気モーメントの差は、窒素原子に近いところより顕著であることが可視化されている。  
Figure 4 Difference in the electron spin-density is obtained by subtracting that of  $\text{NdFe}_{11}\text{Ti}$  from that of  $\text{NdFe}_{12}\text{TiN}$ . The difference near the N atoms is conspicuous, is seen.

### ロードマップ Roadmap

- 機械学習・AIによる新磁石化合物探索と組成最適化
- 保磁力機構の解明
- Discovery of novel magnet compounds and optimization of chemical composition by machine learning / AI
- Mechanism elucidation of coercivity

### 応用分野 Applications

- 電動車用駆動モータ
- 風力発電機
- 家電
- 産業用ロボット
- ドローン 等
- Electric motors for xEVs (hybrid vehicles, electric vehicles etc.)
- Wind turbines
- Home electric appliances
- Industrial robot
- drone etc.

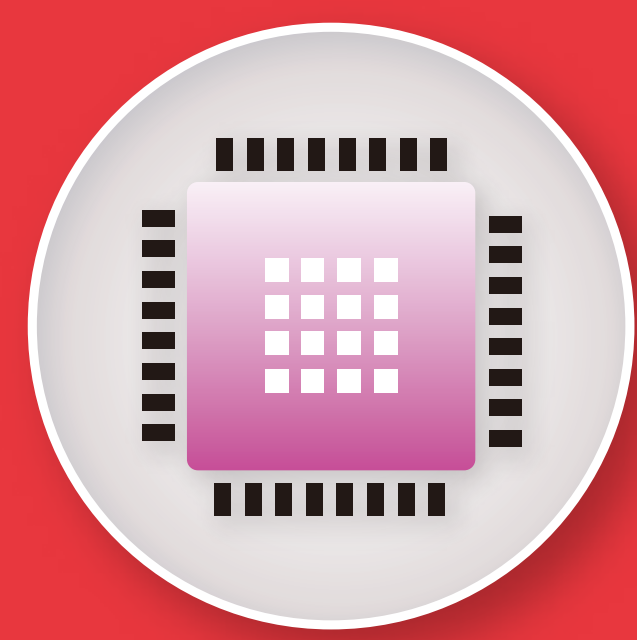
## 問い合わせ先 Contact us here

物質・材料研究機構 元素戦略磁性材料研究拠点 企画室  
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元素戦略  
Element Strategy Initiative:  
To Form Core Research Centers





# 新しい材料設計指針と 新機能高性能電子材料

Creation of Novel-Function & High-Performance Electronic Materials based on Novel Concepts for Materials Design

## 電子材料研究拠点

Tokodai Institute for Element Strategy (TIES)



GL: 細野秀雄  
東工大元素戦略拠点代表  
GL: Hideo Hosono,  
Representative, TIES



### 研究の背景 Background to the research

- GDPへの寄与の大きい電機・電子産業を支える電子材料の大型国家プロジェクトは多数
- 旧来の材料設計指針は半導体ならダイヤモンド構造、誘電体ならペロブスカイトと固定化
- 従来の成功体験に拠る固定化した攻め方から意図的に離れた多存元素の新しい視点が必要
- There have been numerous large-scale national projects on electronic materials to date.
- Materials design has become fixated on just a few concepts, such as diamond-structure semiconductors and perovskite dielectrics.
- There is a need for novel perspectives on abundant elements independent of obsolete approaches based on previous successes.

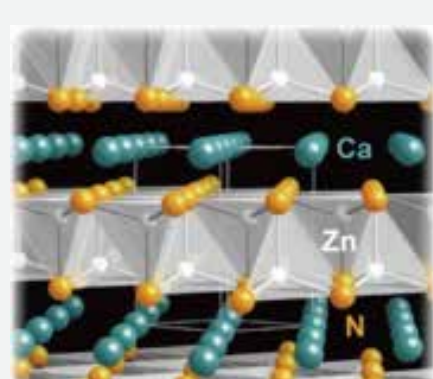
### 研究のポイント Points of the research

- 物性論、電子論、計算化学、インフォマティクス等を駆使して新材料候補と合成法を探索
- 超高圧や超高真空等の極限環境を含む材料合成で迅速な試料試作
- 放射光(KEK-PF, SPring-8)、中性子線、ミュオン(J-PARC)を駆使する先端解析で迅速なフィードバック
- Exploring novel material candidates making full use of condensed matter physics, electron theory, computational chemistry, materials informatics (M. I.), etc.
- Rapid syntheses of candidate materials utilizing such extreme experiments as super-high pressure and super-high vacuum.
- Rapid feedback of material property analyses using synchrotron radiation (KEK-PF and SPring-8), neutrons, and muons (J-PARC).

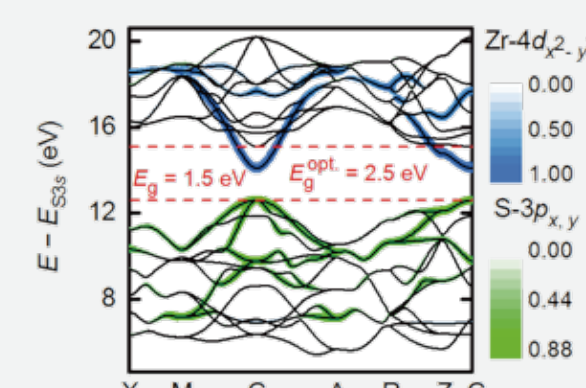
### 研究概要 Outline of the research

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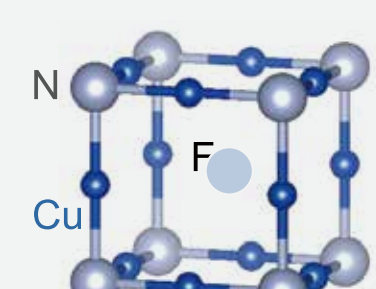
## M. I.や分子軌道等の新コンセプトによる 新しい直接遷移型両極性半導体 Novel Direct Band-Gap, Bipolar Semiconductors derived from New Concepts of M. I. and Molecular Orbitals



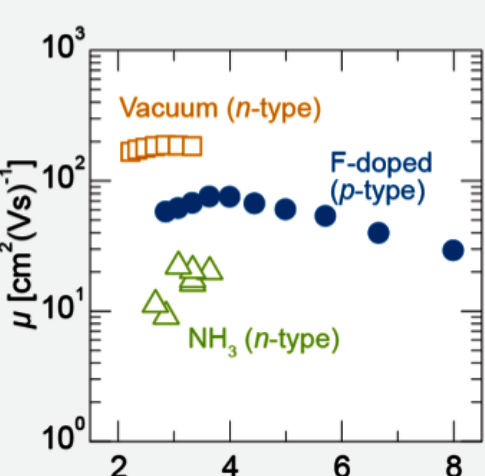
結晶構造  
Crystal Structure



バンド構造  
Band Structure



理論予測による  
格子間フッ素p型ドーピング  
p-type Doping by Theoretically  
Derived Interstitial Fluorine



両極性ドーピング  
Bipolar Doping

図1 M. I.で見出し高圧合成した窒化物半導体新物質CaZn<sub>2</sub>N<sub>2</sub>  
Figure 1 Novel nitride semiconductor, CaZn<sub>2</sub>N<sub>2</sub>, discovered by M. I. and synthesized under high pressure

図2 分子軌道の観点で設計した前周期遷移金属の硫化物半導体  
Figure 2 Oxyulfide semiconductor based on early-transition metals, ZnO<sub>s</sub>, designed under molecular orbital concepts

図3 格子間フッ素によりp型ドーピングした太陽電池応用を狙う窒化物半導体Cu<sub>3</sub>N  
Figure 3 A new nitride semiconductor, Cu<sub>3</sub>N, for solar-cell applications by p-type doping with interstitial fluorine

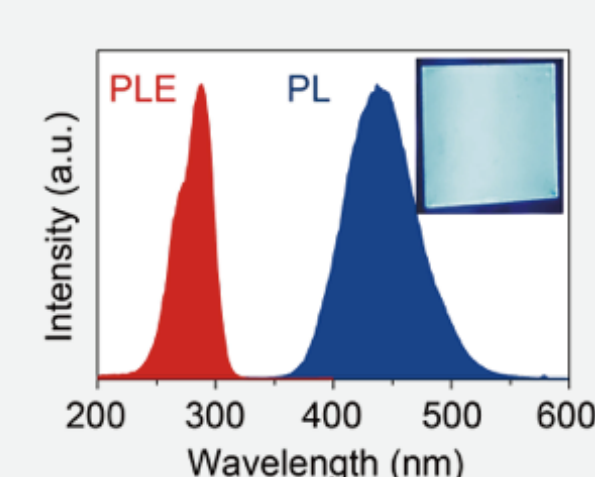
### 研究概要 Outline of the research

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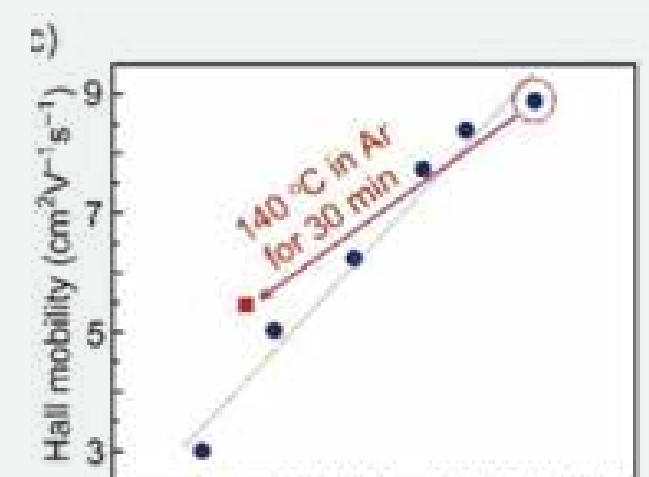
## 次世代自発光平面ディスプレイ用半導体新材料 Novel Semiconductor Materials for Next-Generation Light-Emission-Type Flat-Panel Displays



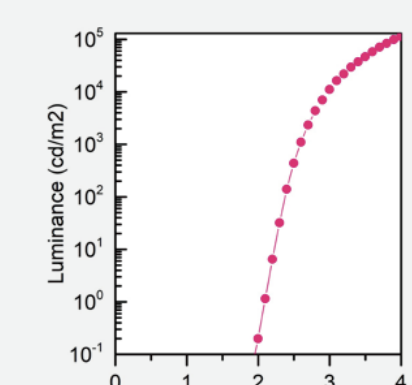
半値幅16 nm、最高輝度180,000 cd m<sup>-2</sup>の  
緑色エレクトロルミネッセンス  
Green Electroluminescence with  
FWHM of 16 nm and  
Maximum Intensity of 180,000 cd m<sup>-2</sup>



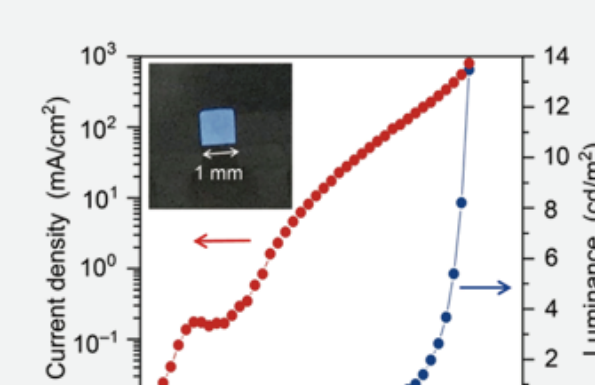
フォトルミネッセンススペクトル  
Photoluminescence Spectre



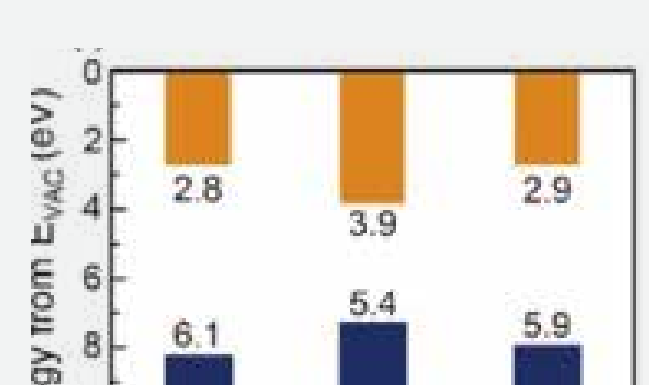
ホール移動度  
Hall Mobilities



注入電流効率30 cd A<sup>-1</sup>の  
低電圧高効率発光  
Low-Voltage, High-Efficiency  
Luminescence with current  
efficiency of 30 cd A<sup>-1</sup>



Zn-Si-Oからの電流注入による  
エレクトロルミネッセンス  
Electroluminescence by  
electron injection from Zn-Si-O



隣接発光層との  
バンドアラインメント  
Band Alignment with Adjacent

図4 新酸化半導体Zn-Si-Oを電子輸送層に用いる低電圧高輝度ペロブスカイトハロゲン化合物半導体LED  
Figure 4 Low-voltage, high-brightness LED based on halide perovskite semiconductors with the novel oxide semiconductor Zn-Si-O as an electron-transport layer.

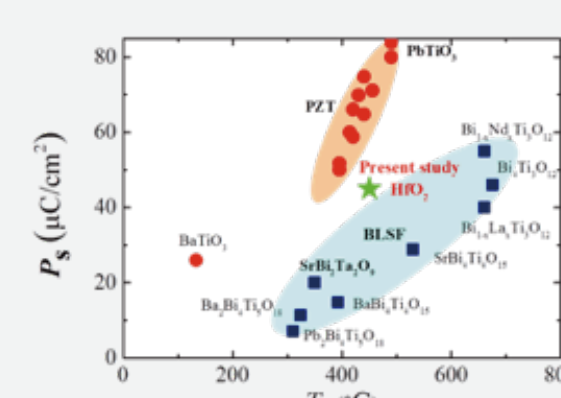
図5 0次元電子構造の高効率青色発光鉛フリー無機ヨウ化物半導体: Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>  
Figure 5 High efficiency blue-light emitting lead-free inorganic iodate semiconductor, Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>.

図6 低温塗布形成可能な高移動度p型透明アモルファス半導体: Cu-Sn-I  
Figure 6 Low-temperature, printable, high-mobility, p-type, transparent, amorphous semiconductor: Cs<sub>3</sub>Cu<sub>2</sub>I<sub>5</sub>.

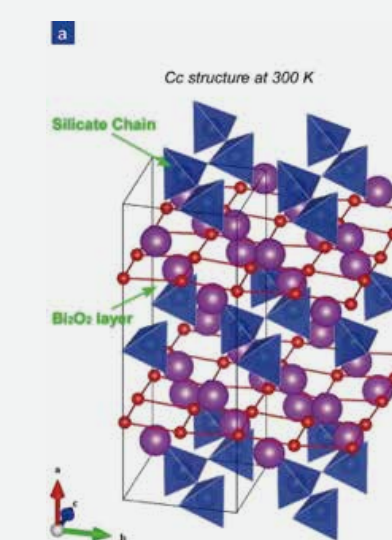
### 研究概要 Outline of the research

3

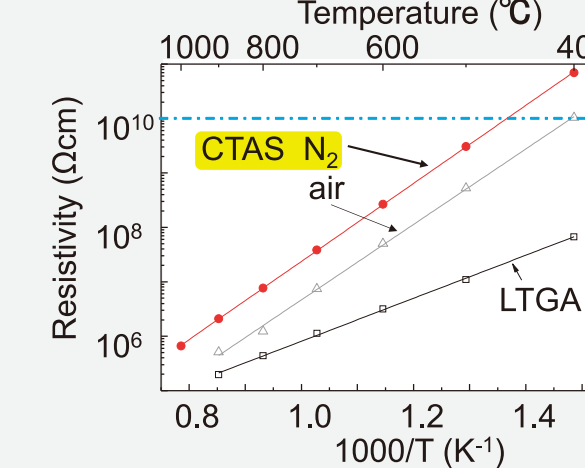
## パワーエレクトロニクス用 高温安定高誘電率非ペロブスカイト系誘電体 High-temperature stable, high dielectric constant, non-perovskite dielectrics for power-electronics applications



従来材料より高T<sub>c</sub>で高P<sub>s</sub>  
Higher T<sub>c</sub> and Higher P<sub>s</sub>  
than conventional materials



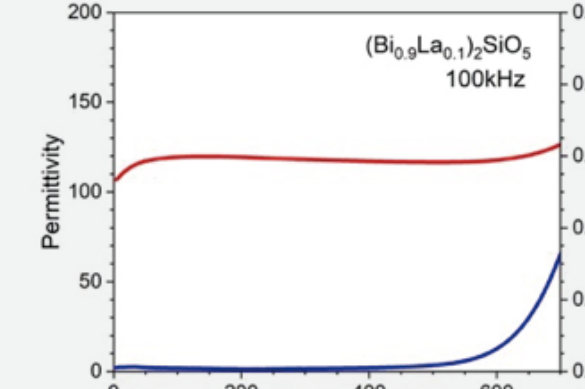
結晶構造  
Crystal Structure



抵抗率の温度依存性  
Temperature Dependence  
of Resistivity



厚膜【対数表示】(nm)  
Thick Films for Industrial Use



温度安定性  
Thermal Stability



2インチ単結晶とセンサーモジュール  
2-inch Single Crystal and  
Sensor Module

図7 高いT<sub>c</sub>とP<sub>s</sub>を示す蛍石構造強誘電体: HfO<sub>2</sub>Y  
Figure 7 Fluorite ferroelectrics with high T<sub>c</sub> & P<sub>s</sub>: HfO<sub>2</sub>Y.

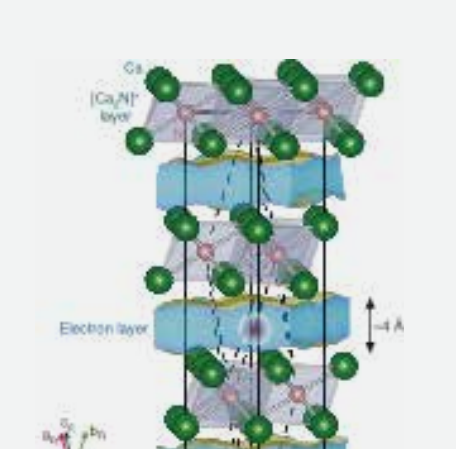
図8 車載用安定性規格を満たすケイ酸塩系強誘電体: (Bi<sub>0.5</sub>La<sub>0.5</sub>)<sub>2</sub>SiO<sub>5</sub>  
Figure 8 Silicate ferroelectrics satisfying requirements for vehicle applications: (Bi<sub>0.5</sub>La<sub>0.5</sub>)<sub>2</sub>SiO<sub>5</sub>.

図9 車載用圧電素子用ランガサイト材料: CTAS (Ca<sub>3</sub>TaAl<sub>3</sub>Si<sub>2</sub>O<sub>14</sub>)  
Figure 9 High-temperature stable piezoelectrics for vehicle pressure sensors: CTAS (Ca<sub>3</sub>TaAl<sub>3</sub>Si<sub>2</sub>O<sub>14</sub>).

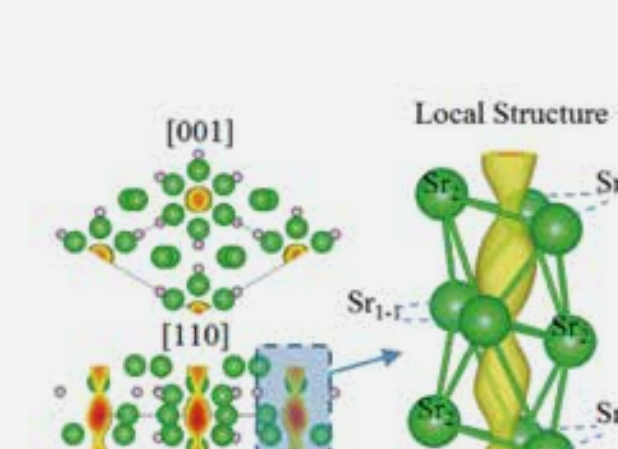
### 研究概要 Outline of the research

4

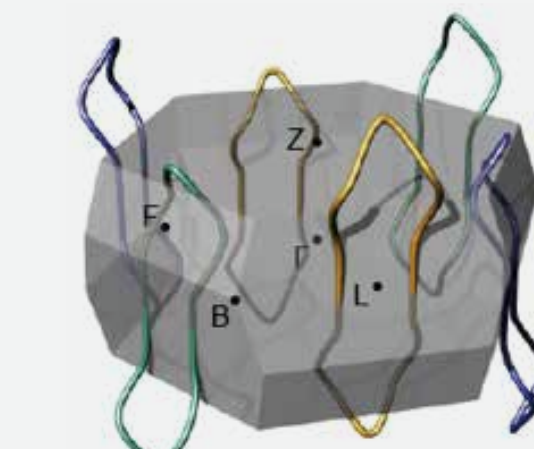
## 低温低圧アンモニア合成触媒への実用が近い 無機固体エレクトライド材料 Inorganic and Solid-State Electride Materials soon to be commercialized as catalysts for ammonia synthesis at low temperature and pressure



Ca<sub>2</sub>Nの結晶構造  
Crystal Structure of Ca<sub>2</sub>N



結晶構造と電子密度分布  
Crystal Structure and Electron  
Density Mapping



2次元エレクトライドY<sub>2</sub>Cの  
ノードルライン  
Nodal Lines of a 2D electride, Y<sub>2</sub>C

図10 実用化検討が進む材料系の基となった2次元エレクトライド  
Figure10 Two-dimensional electrides under consideration for the base of commercial material systems

図11 遺伝的アルゴリズムで探索した金属間化合物の新物質1次元エレクトライド: Sr<sub>5</sub>P<sub>3</sub>  
Figure11 A novel, intermetallic, one-dimensional electride explored using genetic algorithms: Sr<sub>5</sub>P<sub>3</sub>

図12 トポロジカルエレクトライドの概念の創出と候補物質の提案  
Figure12 A novel concept of "topological electrides" and their candidate materials.

### ロードマップ Roadmap

- 新コンセプトと新材料創出頻度の定常化
- 産業界への技術移転
- ポスト元素戦略へのコンセプト提案
- Stabilization of creation rates of novel materials and their design concepts
- Technical transfer to industries
- Concept proposal for post Element Strategy

### 応用分野 Applications

- 平面ディスプレイ用高効率・低コスト半導体材料
- 車載等パワーエレクトロニクス用高温安定高誘電率誘電体
- 触媒応用エレクトライド材料
- High-efficiency & low-cost semiconductor materials for flat-panel displays
- High-temperature, stable, & high-dielectric constant dielectrics for vehicle power electronics
- Electride materials for catalysts

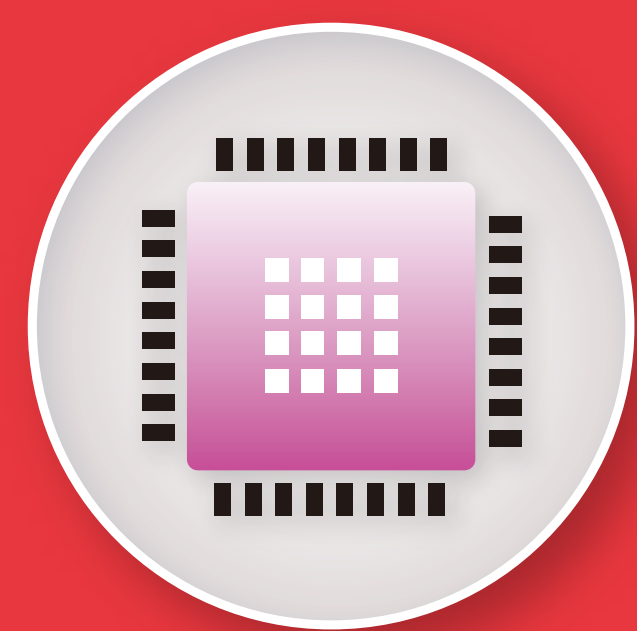
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東工大元素戦略拠点  
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元素戦略  
Element Strategy Initiative:  
To Form Core Research Centers





# 水素の役割・機能・状態の 解明と高感度定量

Unraveling the Roles, Functionalities, and States of Hydrogen in  
Condensed Matter and Establishing Highly Sensitive Quantification Methods

## 電子材料研究拠点

Tokodai Institute for Element Strategy (TIES)



GL: 細野秀雄  
東工大元素戦略拠点代表  
GL: Hideo Hosono,  
Representative, TIES



### 研究の背景 Background to the research

- 酸化物中に $\geq 10^{20} \text{ cm}^{-3}$ も含まれるにも関わらずその存在が無視されてきた水素
- 水素が物質の局所状態や電子状態を大きく左右することが実験的、理論的に示唆
- 水素の定量と状態特定、役割と機能の解明により機能性元素としての積極利用が重要
- The presence of hydrogen in oxides has often been ignored despite its high concentration ( $\geq 10^{20} \text{ cm}^{-3}$ ).
- Experimental and theoretical investigations have implied that the hydrogen strongly influences local and electronic structures of condensed matter.
- It is important to establish methods of quantification and state analysis for hydrogen and to unravel the roles and functionalities of hydrogen in order to utilize hydrogen as a key functional element.

### 研究の ポイント Points of the research

- 極限参照試料として超低水素濃度薄膜とその濃度を測定する超高感度定量法・装置を開発
- NMR、赤外吸収、中性子、ミュオン等の水素敏感プローブによる分析と第一原理計算を駆使
- 半導体薄膜中の水素量と状態とその薄膜を活性層とする電子素子の安定性の関係を調査
- Development of thin films with extremely low hydrogen content and a method and apparatus to quantify the hydrogen concentration with high sensitivity.
- Combined use of density functional theory calculations and analyses using hydrogen-sensitive probes, such as NMR, infrared absorption, neutrons, and muons.
- Investigations of relationships between the concentrations and states of hydrogen in semiconductor thin films and the stability of their electron devices.

### 研究概要 Outline of the research

1

## 水素の超高感度定量法と測定装置の開発 Development of a High-Sensitivity Method & Apparatus to Quantify the Hydrogen Concentration in Thin Films

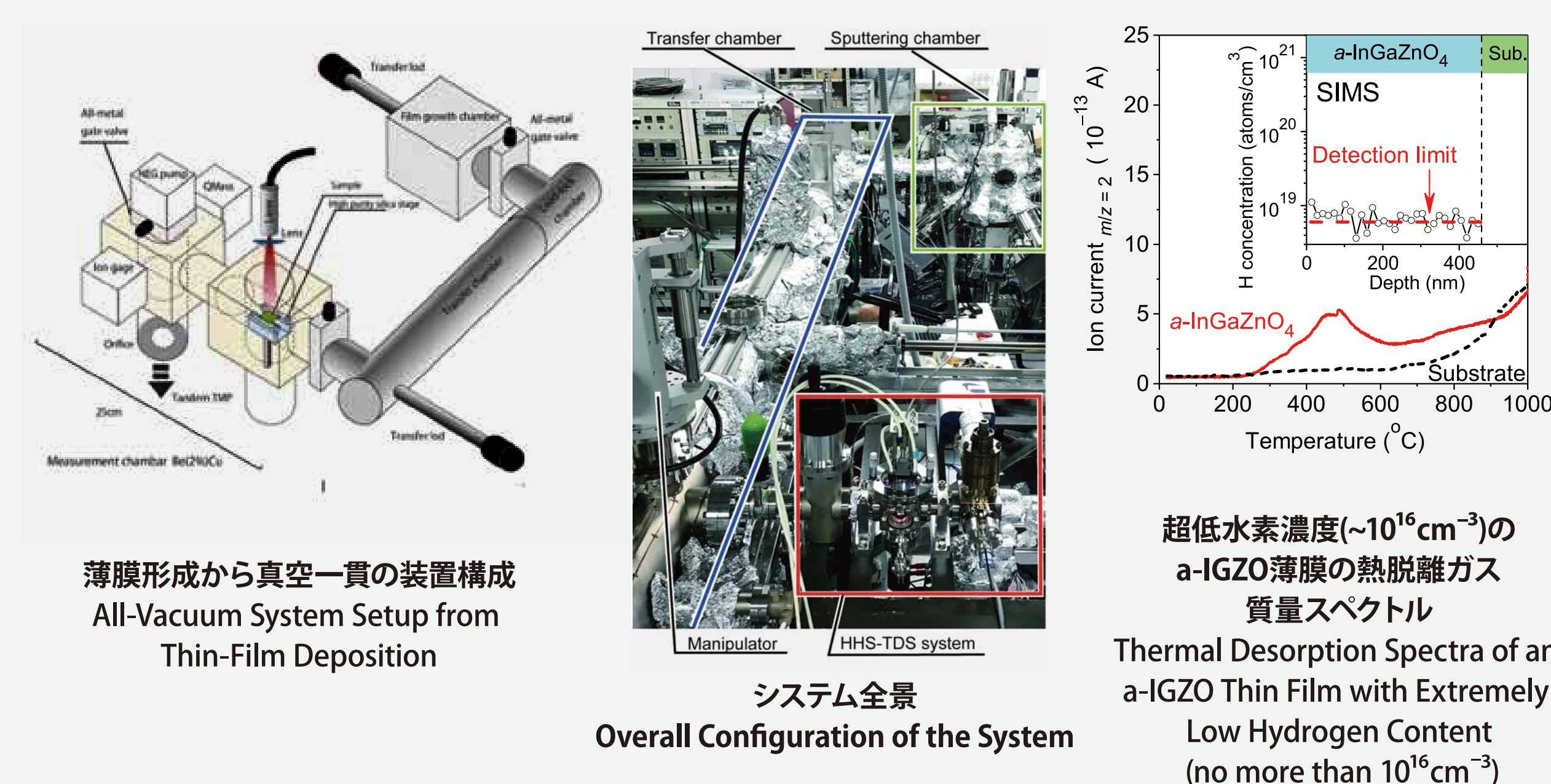


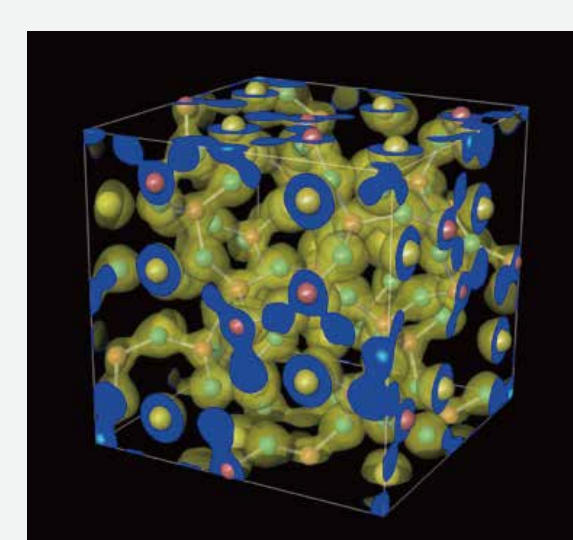
図1 SIMSを2桁以上回る高感度( $\sim 10^{16} \text{ cm}^{-3}$ )を実現した水素の超高感度定量法と測定装置と超低水素濃度a-IGZO薄膜での性能実証  
Figure1 High-Sensitivity method and apparatus for quantifying hydrogen concentration and their demonstration on a-IGZO thin films with extremely low hydrogen contents (under  $10^{16} \text{ cm}^{-3}$ ).  
・超高真空システム全体の徹底した低脱ガス化、成膜装置からの真空一貫システム、高精度イオン注入と極微量ガス導入による較正

法により実現。  
Implemented using an extremely low-outgassing, ultra-high vacuum system with all-vacuum transfer from the thin-film deposition chamber, and by performing calibration using high-accuracy ion implantation and the introduction of trace amounts of gas.  
極限低濃度参照試料の作成に活用  
Used for preparing reference samples with extremely low concentrations of hydrogen.

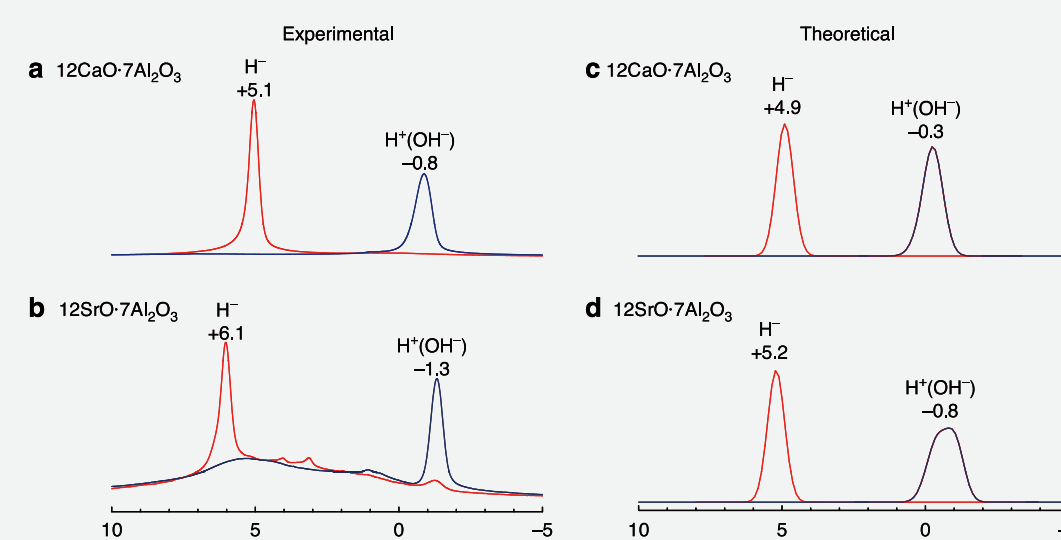
### 研究概要 Outline of the research

2

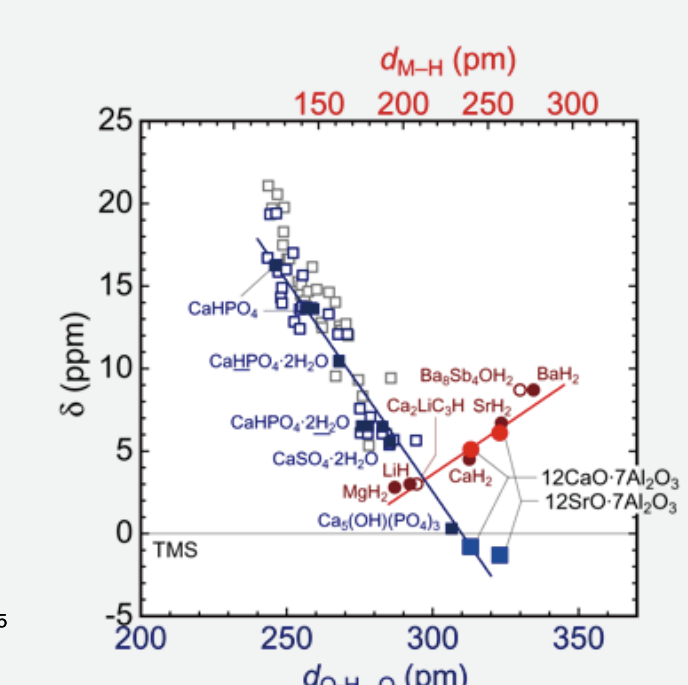
## 固体酸化物中の水酸化物に隠された 水素化物(ヒドリド、水素負イオン)の発見 Hydride Ions in Oxide Hosts Hidden by Hydroxide ions



ケージ構造を有する  
C12A7マイエナイト12CaO·7Al<sub>2</sub>O<sub>3</sub>の  
結晶構造  
Crystal Structure of C12A7  
Mayenite (12CaO·7Al<sub>2</sub>O<sub>3</sub>)  
Having a Cage Structure



実験データを再現する  
水素含有モデルの  
DFT計算に基づく1H NMRスペクトル  
1H NMR Spectra Derived from DFT  
Calculations of Hydrogen-Incorporated  
Structure Models, Which Reproduce  
the Experimental Observations



ホスト結晶の酸素-水素間距離、  
金属-水素間距離の拡大につれて  
H+とH-の化学シフトが逆転  
A reversal in Chemical Shifts of H+  
and H- accompanying an  
Increase in O-H and M-H Distances

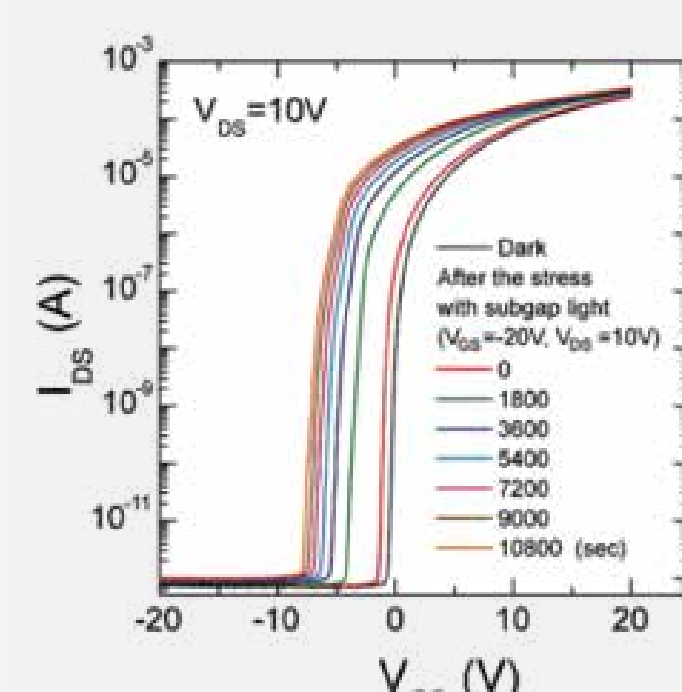
図2 固体酸化物中の水素化物(ヒドリド)の存在証明  
Figure 2 Demonstrating the presence of hydride in solid-state oxide crystals  
マイエナイトやアパタイト結晶の1H NMRスペクトルの分裂を観測  
Splits of 1H NMR spectra were observed in mayenite and apatite crystals

水素含有結晶構造モデルのDFT計算は従来の常識とは異なるH+とH-の化学シフト逆転の可能性を理論予測  
A reversal in chemical shifts of H+ and H- is predicted by DFT calculations based on crystal structure models with hydrogen incorporated.

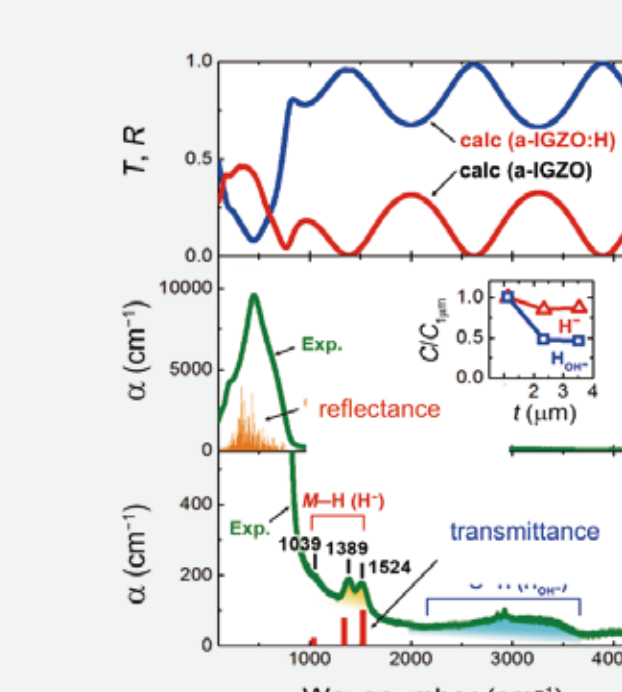
### 研究概要 Outline of the research

3

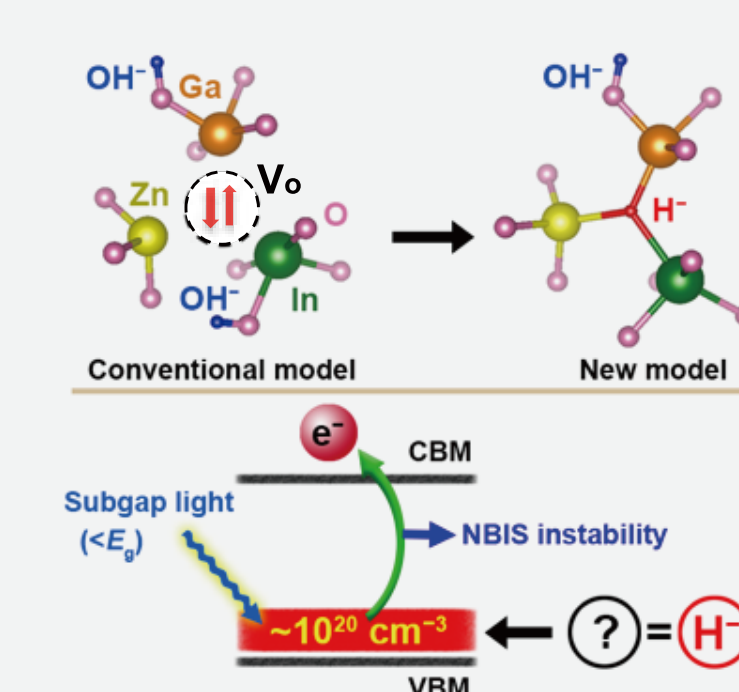
## アモルファス酸化物半導体中の水素負イオンの 発見と電子デバイス不安定性の起源の解明 Hydrides (hydrogen anions) in Amorphous Oxide Semiconductors and the Origin of Instabilities in their Electron Devices



光照射下負バイアスストレス  
印加時のa-IGZO TFTの閾値負シフト  
A Negative Shift of Threshold Voltage  
in a-IGZO TFT under Negative Bias  
Illumination Stress (NBIS)



赤外吸収スペクトルに現れた  
M-H結合(H-)に由来するピーク  
Extra Peaks Originating from  
M-H Bonds (H-) in the  
Infrared Absorption Spectrum



水素負イオンH-の局所構造と  
深いバンド間占有準位の形成  
Local Structure of Hydrogen Anions  
and Generation of  
Occupied Deep Subgap States

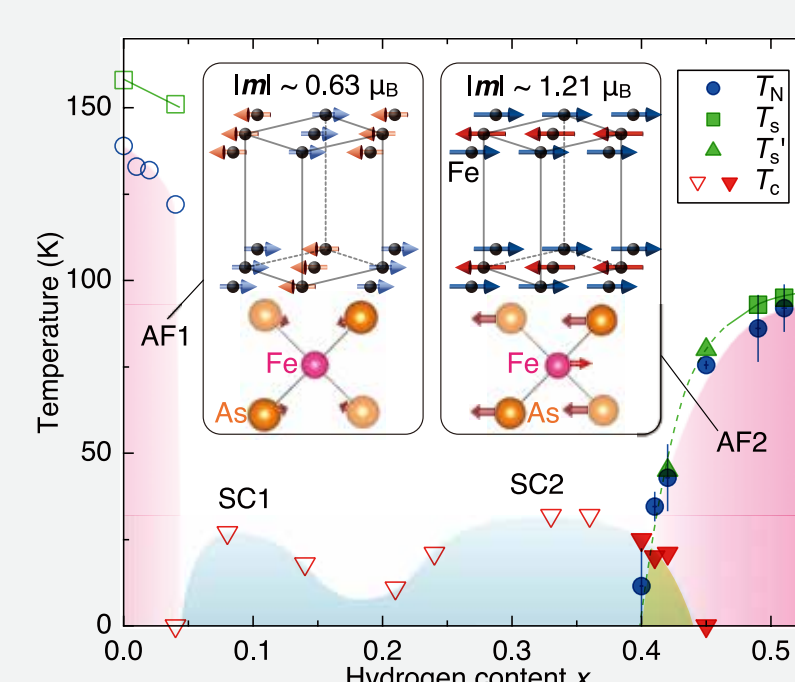
図3 a-IGZO薄膜中の水素負イオンとTFT不安定性の起源  
Figure3 Hydrides (hydrogen anions) in a-IGZO thin films and the origin of instabilities in their TFTs  
・a-IGZOをはじめとするアモルファス酸化物半導体TFTは光照射下負バイアス印加時に閾値の大きな負シフトを起こす  
・Amorphous oxide semiconductor TFTs such as a-IGZO exhibit large negative shifts in threshold voltage under illumination and negative bias stresses.  
・赤外吸収スペクトルと水素含有モデルのDFT計算で金属カチオンと水素が結合したヒドリド(水素は負イオンH-)を観測  
・Hydrides composed of metal cation-hydrogen anion bonds

are observed in infrared absorption spectra and identified by DFT calculations of hydrogen-incorporated models  
・酸素欠損Voの位置に取り込まれた水素原子が周囲の金属カチオンと結合し水素負イオンH-を形成し、これがNBIS不安定性の起源となる価電子帯直上の深い占有準位を形成  
・Hydrogen atoms incorporated into oxygen vacancies, Vo, bond to adjacent metal cations to form hydrides (hydrogen anions, H-), which generate occupied deep subgap states above the valence-band maximum (VBM) and cause NBIS instabilities in a-IGZO TFTs.

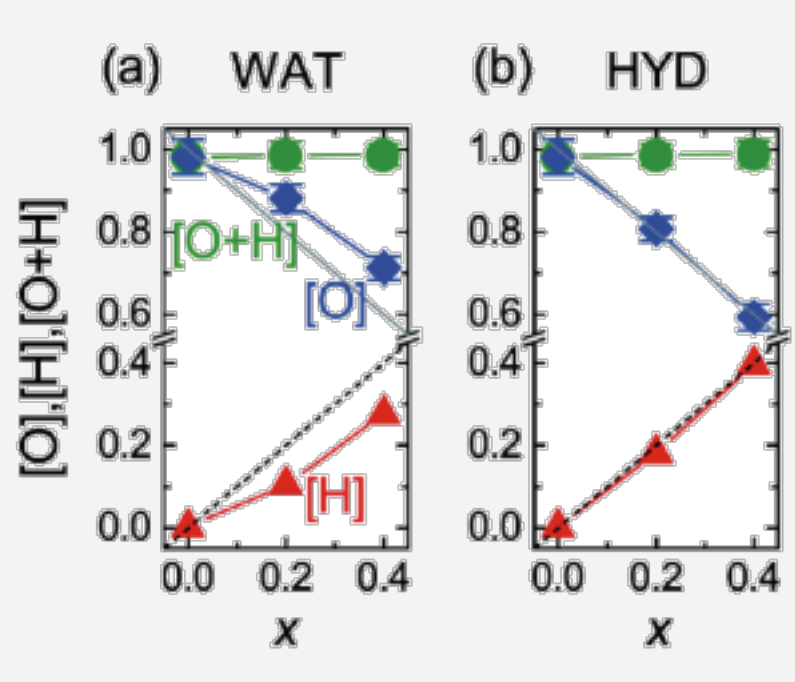
### 研究概要 Outline of the research

4

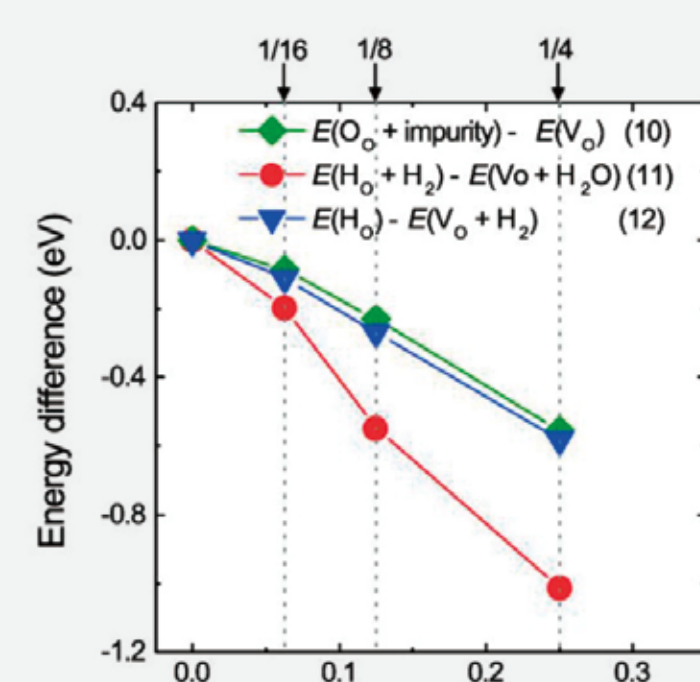
## 鉄系超伝導体に超伝導相を発現させる 水素による電子ドーピング Electron Doping by Hydrogen Incorporation in Iron Oxyprictides to Produce Superconducting Phase



放射光X線散乱、中性子散乱、  
ミュオンの量子ビームで解明した  
LaFeAsO1-xHxの結晶/磁気相図  
Crystalline/Magnetic Phase Diagram  
of LaFeAsO1-xHx. Unrevealed by  
Quantum Beams of SRX-ray Scattering,  
Neutron Scattering, and Muons



H2O (WAT), H2 (HYD) 雰囲気  
形成したLaFeAsO1-xHx試料に  
含まれる水素量と酸素量  
x-Dependence of Hydrogen and  
Oxygen Contents in a LaFeAsO1-xHx  
Specimen Formed under H2O  
(WAT), H2 (HYD) Ambient



安定性のx依存性の  
第一原理計算による理論予測  
Theoretical Prediction for  
x-Dependence of Stability by  
DFT Calculations

図4 鉄系超伝導体LaFeAsO1-xHxの水素ドーピングによる超伝導相発現と酸素を置換しない水素の状態  
Figure4 Superconducting phase generated by hydrogen doping in Iron Oxyprictide LaFeAsO1-xHx and states of the non-substituted hydrogen.  
鉄系超伝導体LaFeAsO1-xHxはドーピングする水素量に応じて二つの反強磁性の母相(AF1, AF2)を基にした二つの超伝導相(SC1, SC2)を有する  
Iron oxyprictide LaFeAsO1-xHx shows, depending on x, two superconducting phases (SC1, SC2) originating from two

antiferromagnetic mother phases (AF1, AF2).  
実験的に水素量と酸素量は相補的であることが判明  
Hydrogen and oxygen content were found experimentally to be complementary to each other.  
第一原理計算では酸素空孔の位置に水素負イオンH-が占める場合が最も安定で、酸素欠損はH-で安定化する描像の一般性を示唆  
DFT calculations predict that stability is greatest when hydrogen anions H- occupy the sites of oxygen vacancies Vo, which suggests the common image of Vo stabilization by H-.

### ロードマップ Roadmap

- 材料機能やデバイス特性との関連解明の促進
- 誘電体材料への展開
- 水素機能性電子材料への展開
- Clarifying the relationships between material functionalities and device characteristics
- Extension to dielectric materials
- Exploration and creation of hydrogen-functionalized electronic materials

### 応用分野 Applications

- 電子材料・電子デバイスの性能向上や安定化
- 水素化物を含む水素機能材料
- 微量水素量分析
- Performance enhancement and stabilization of electronic materials and electron devices
- Novel hydrogen-functionalized materials including hydrides
- Analysis of low-hydrogen-content specimens

問い合わせ先 Contact us here

東工大元素戦略拠点  
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# 貴金属を減量した 新規自動車触媒の開発

## Novel Automotive Catalysts Using Less Noble Metals

## 触媒・電池材料研究拠点

Elements Strategy Initiative for Catalysts and Batteries (ESICB)



GL: 田中庸裕  
京都大学大学院工学研究科  
GL: Tsunehiro Tanaka,  
Graduate School of Engineering, Kyoto University



### 研究の背景 Background to the research

- 自動車触媒に用いる白金族元素 (PGM) の使用量節減
- 高活性な触媒ナノ粒子ほどシンタリングしやすく触媒寿命と二律背反する
- 触媒活性サイトは主に貴金属微粒子表面と考えられている
- Reducing the use of platinum-group metals (PGM) in automotive catalysts is of practical importance.
- Thermal sintering of metal nanoparticles poses a significant problem to catalyst life.
- Catalytic active sites are thought to be the surface of noble metal particles.

### 研究のポイント Points of the research

- プラズマ法によって調製した金属Rhナノ薄膜からなる高密度メタルハニカムを開発
- ナノ薄膜構造によりRhの触媒活性が飛躍的に向上
- サポート材の機能を利用した触媒の高機能化
- Plasma preparation for Rh nanofilm-coated metal honeycomb catalysts
- The catalytic activity of the Rh nanofilm is markedly superior to that of Rh nanoparticles.
- Improvement in catalytic performance using the function of a catalyst support.

### 研究概要 Outline of the research

1

## 触媒調製のパラダイムシフト Paradigm shift in catalyst preparation and structure

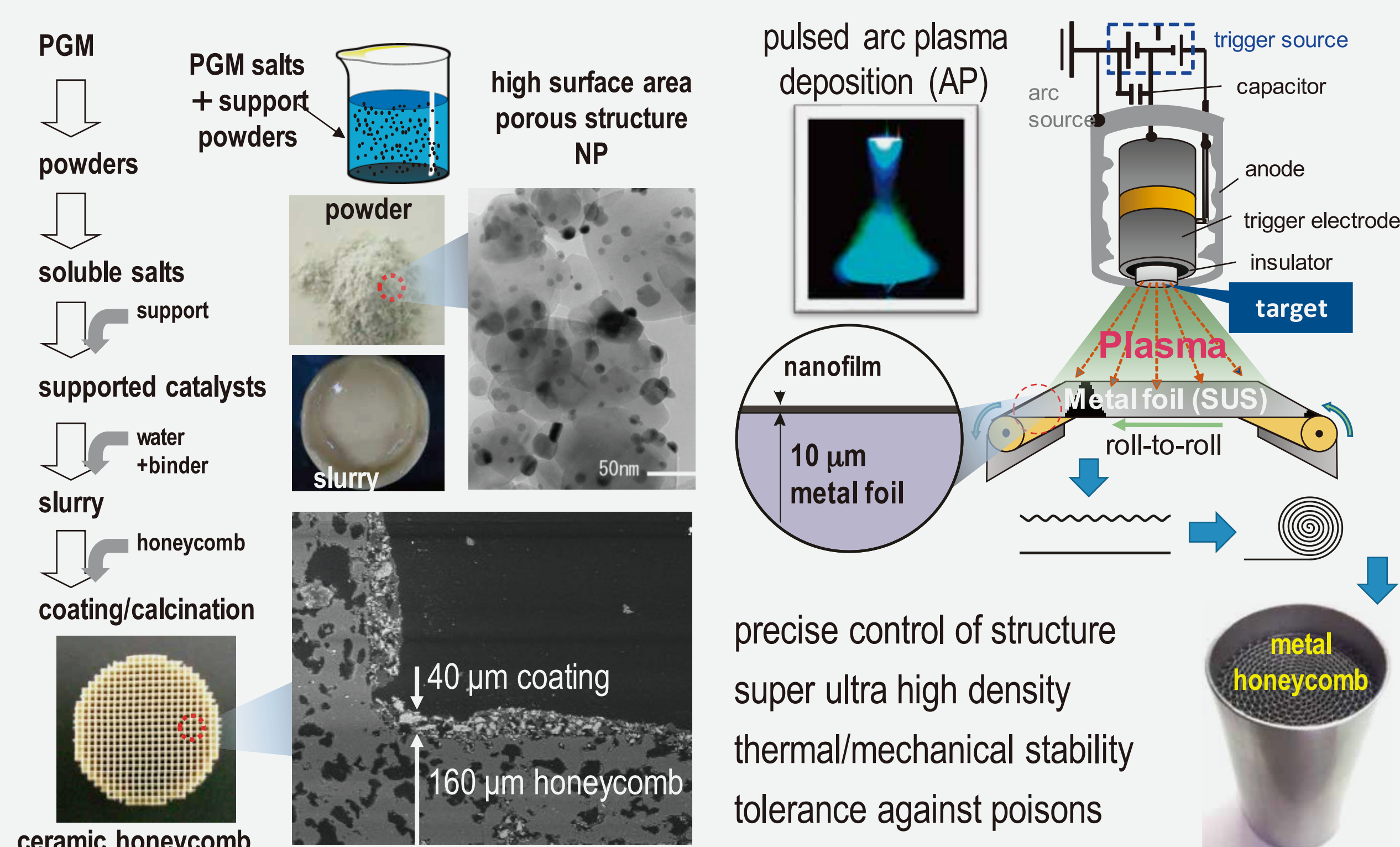


図1 (左)従来の湿式触媒調製法。金属ナノ粒子を含む触媒粉末からなるスラリーをセラミックハニカムにコーティングして得られる。(右)本研究で開発した乾式触媒調製法。金属をプラズマ化して金属箔上にナノ薄膜を形成後、ハニカム形状に成型する。

Figure 1 (Left) Conventional catalyst preparation via wet coating of powder containing metal nanoparticles. (Right) Novel catalyst preparation via pulsed arc plasma deposition of active metal nanofilms onto metal foil substrates.

### 研究概要 Outline of the research

2

## Rhナノ薄膜型ハニカム触媒の触媒特性 Catalytic performance of Rh nanofilm and Rh nanoparticle catalysts

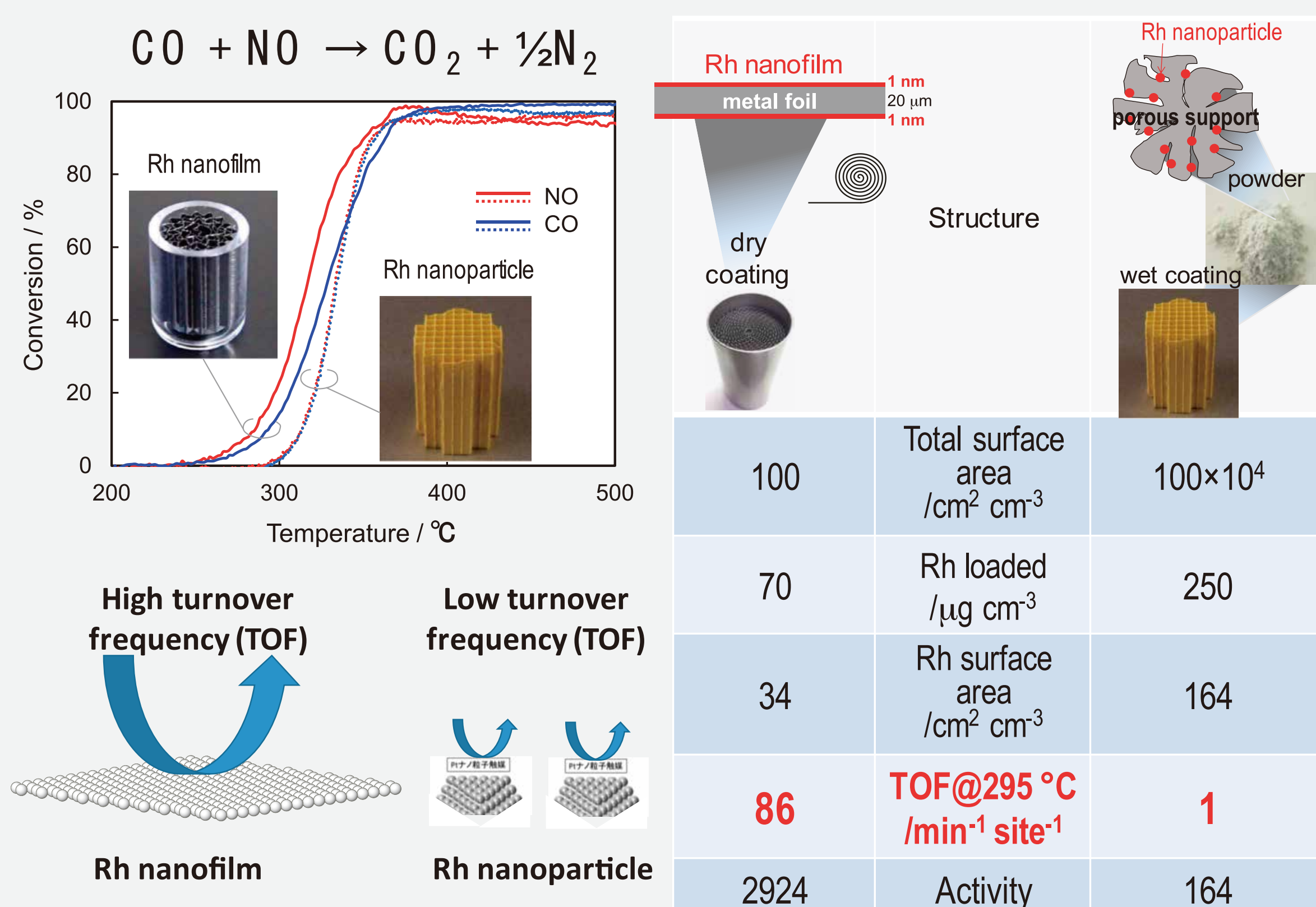


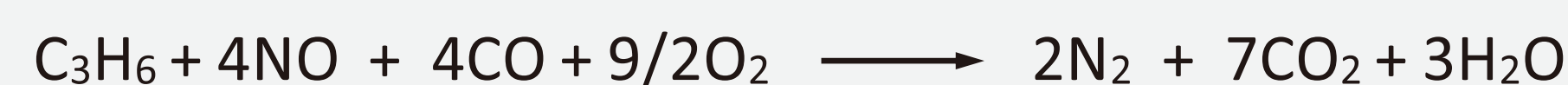
図2 Rh薄膜型メタルハニカムと従来型ハニカムの触媒性能。0.1% NO、0.1% CO、N<sub>2</sub> balance。GHSV = 1.2×10<sup>5</sup> h<sup>-1</sup>。  
Figure 2 Catalytic performance of a Rh nanofilm-coated honeycomb catalyst compared with a conventional honeycomb prepared by wet coating. 0.1% NO, 0.1% CO, N<sub>2</sub> balance. GHSV = 1.2×10<sup>5</sup> h<sup>-1</sup>.

### 研究概要 Outline of the research

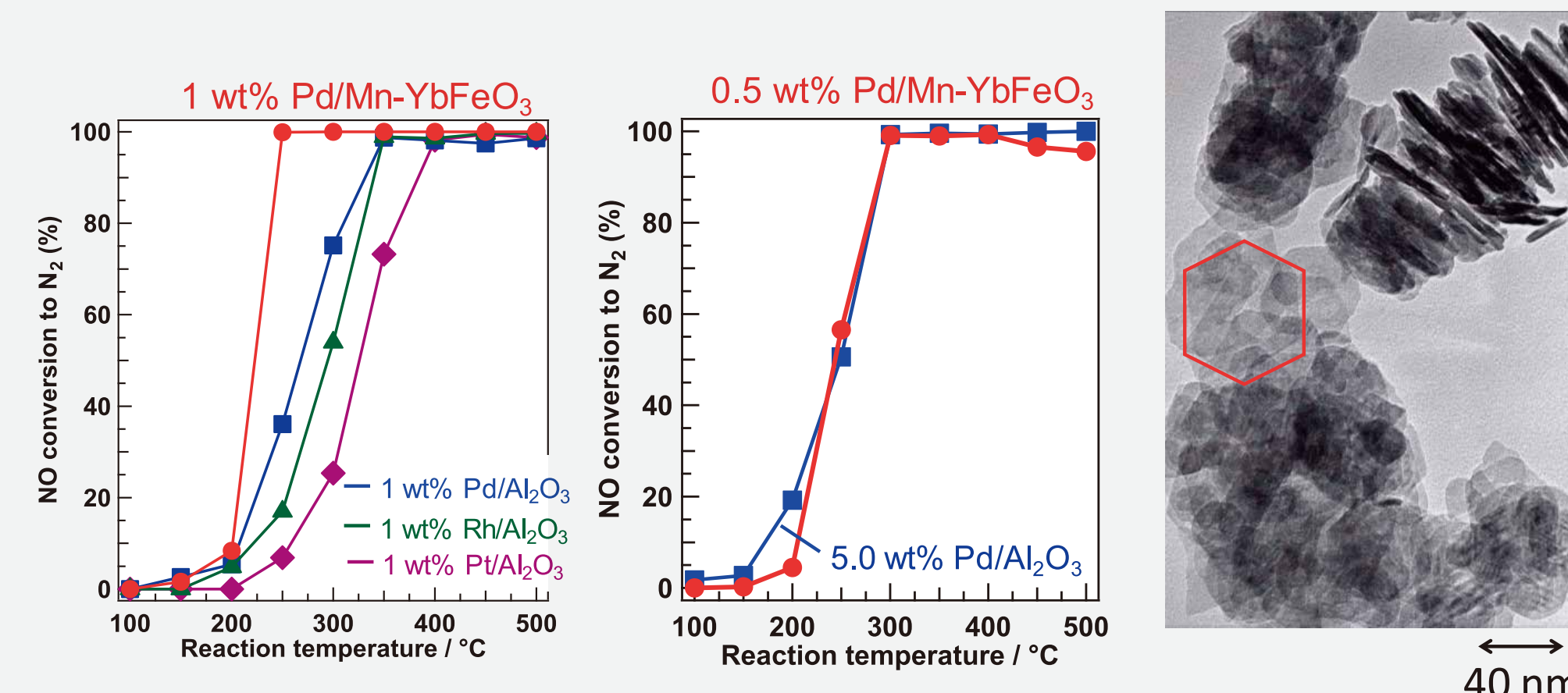
3

## 触媒担体の高機能化による Pd使用量低減型触媒 Reduction of Pd usage by improving a function of catalyst support

### Model Reaction for purifying automotive exhaust gas



C<sub>3</sub>H<sub>6</sub>: residual component due to gasoline, CO: component formed by incomplete combustion of gasoline  
NO: component formed under high temperature (> 1000 °C) in engine



The catalytic activity of 0.5 wt% Pd/Mn-YbFeO<sub>3</sub> is comparable to that of 5.0 wt% Pd/Al<sub>2</sub>O<sub>3</sub>.

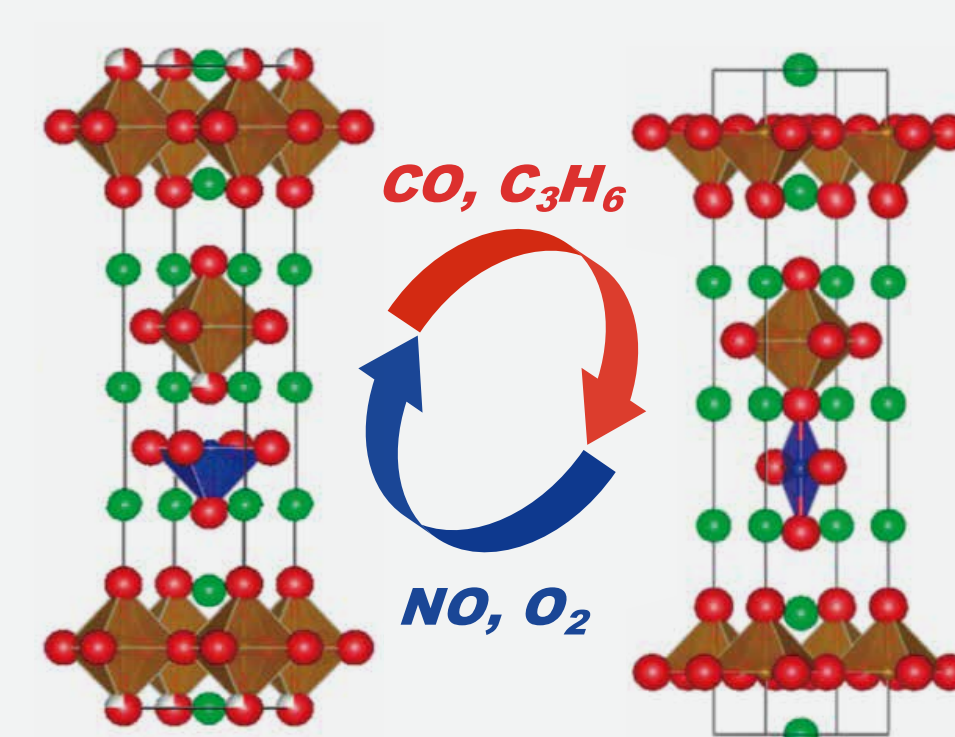
図3 (左) Mn修飾六方晶YbFeO<sub>3</sub>担持Pd触媒のNO還元活性(右)六角板状ナノ結晶の形態を有するMn-YbFeO<sub>3</sub>のTEM像  
Figure 3 (Left) NO conversion to N<sub>2</sub> over Pd catalyst supported on Mn-modified hexagonal YbFeO<sub>3</sub> (Pd/Mn-YbFeO<sub>3</sub>). (Right) TEM image of Pd/Mn-YbFeO<sub>3</sub> having hexagonal plate-like nanoparticles.

### 研究概要 Outline of the research

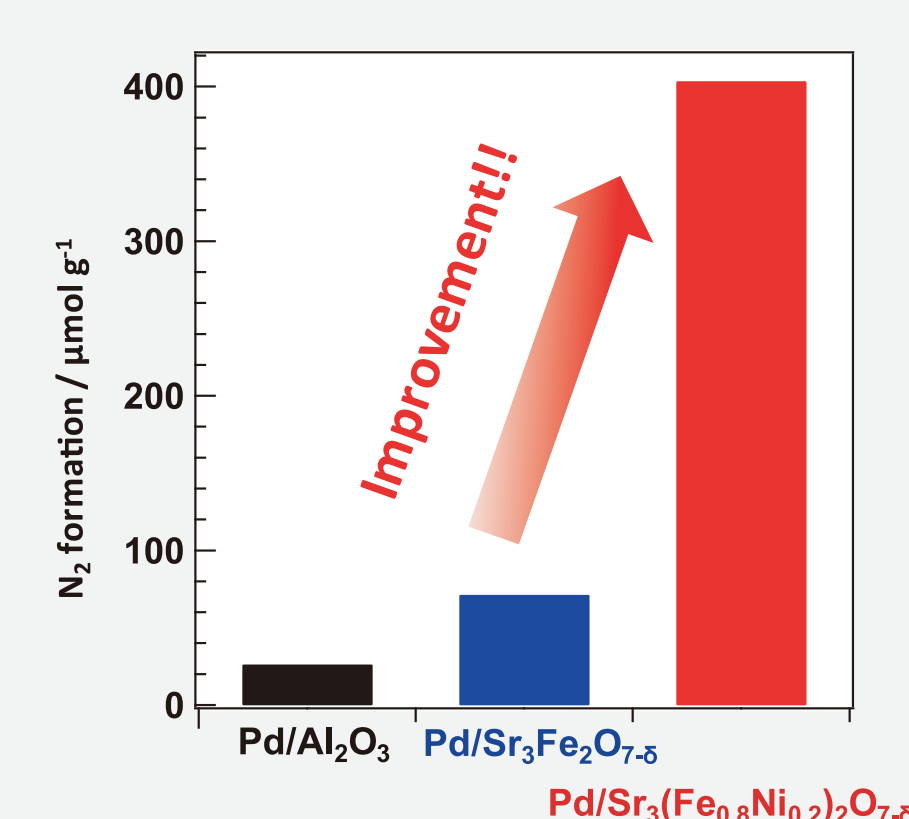
4

## 新規酸素吸蔵放出型触媒担体の開発 Development of novel catalyst support having oxygen storage capacity

### Redox behavior of Sr<sub>3</sub>(Fe<sub>0.8</sub>Ni<sub>0.2</sub>)<sub>2</sub>O<sub>7-δ</sub>



### Efficiency of NO reduction



### Mechanism for NO reduction on Sr<sub>3</sub>(Fe<sub>0.8</sub>Ni<sub>0.2</sub>)<sub>2</sub>O<sub>7-δ</sub>

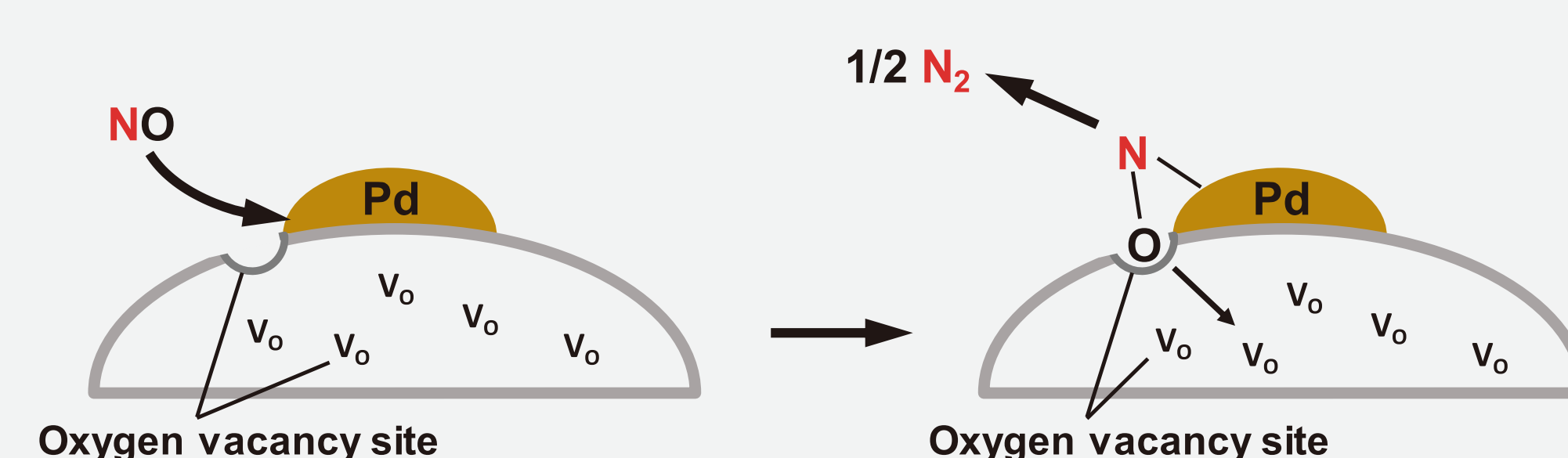


図4 (左上)自動車排ガス浄化反応時のSr<sub>3</sub>(Fe<sub>0.8</sub>Ni<sub>0.2</sub>)<sub>2</sub>O<sub>7-δ</sub>の構造変化(右上)Sr<sub>3</sub>(Fe<sub>0.8</sub>Ni<sub>0.2</sub>)<sub>2</sub>O<sub>7-δ</sub>中に存在する酸素欠陥サイトのNO還元効率(下)Pd/Sr<sub>3</sub>(Fe<sub>0.8</sub>Ni<sub>0.2</sub>)<sub>2</sub>O<sub>7-δ</sub>上でのNO還元メカニズム

Figure 4 (Upper left) Structural change of Sr<sub>3</sub>(Fe<sub>0.8</sub>Ni<sub>0.2</sub>)<sub>2</sub>O<sub>7-δ</sub> during the purification of automotive exhaust gas (Upper right) Efficiency of NO reduction at oxygen vacancy site in Pd/Sr<sub>3</sub>(Fe<sub>0.8</sub>Ni<sub>0.2</sub>)<sub>2</sub>O<sub>7-δ</sub> (Below) Mechanism for NO reduction in Pd/Sr<sub>3</sub>(Fe<sub>0.8</sub>Ni<sub>0.2</sub>)<sub>2</sub>O<sub>7-δ</sub>.

### ロードマップ Roadmap

- ナノ薄膜構造によって高活性が発現するメカニズムの解明
- 多様な化学反応に有効なナノ薄膜触媒の開発
- 触媒担体の結晶構造を利用した新規触媒材料の開発
- Elucidation of the reaction mechanisms for nanofilm catalysts
- Development of nanofilm catalysts for various chemical reactions
- Development of novel catalyst materials using the crystal structure of catalyst supports

### 応用分野 Applications

- 自動車排気浄化触媒
- 超小型触媒およびスマートリアクタ
- Automotive catalysts
- Microrreactors and smart reactors

## 問い合わせ先 Contact us here

京都大学 触媒・電池元素戦略研究拠点  
Elements Strategy Initiative for Catalysts and Batteries, Kyoto University  
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# 火を消してくれる安全な 二次電池用電解液

## Fire-Extinguishing Organic Electrolytes for Safe Batteries

## 触媒・電池材料研究拠点

Elements Strategy Initiative for Catalysts and Batteries (ESICB)



GL：山田 淳夫

東京大学大学院工学系研究科

GL：Atsuo Yamada,

School of Engineering, The University of Tokyo



### 研究の背景 Background to the research

- 二次電池には発火・爆発のリスクがある
- 電解液に難燃剤を加えると電池の充放電サイクル特性が大きく低下
- 難燃性と電池性能の両立を目標にした
- Fire incidents with explosions occurring in lithium-ion batteries have been problematic.
- The simple addition of flame-retardant solvents significantly degrades the battery cycle.
- How can we produce better batteries with a high level of safety?

### 研究の ポイント Points of the research

- 一般的な消火剤リン酸トリメチル (TMP) に通常の3倍濃度の特殊な電解質を溶かすと、負極に非常に安定な被膜ができる。
- これにより、充放電を1000回以上行ってもほぼ劣化ゼロの特性を達成
- 「京」コンピュータを用いた電子状態計算により、安定被膜形成メカニズムを解明
- Highly concentrated fire-extinguishing TMP-based electrolyte can form a very robust passivation film on the anode surface.
- This enables an excellent battery life of more than 1,000 charge-discharge cycles with negligible degradation.
- Computational analysis using the K computer has revealed the formation mechanisms of stable passivation film.

### 研究概要 Outline of the research

1

## 難燃性と反応可逆性の両立へ Toward ultimate safety while retaining repeated cycle stability

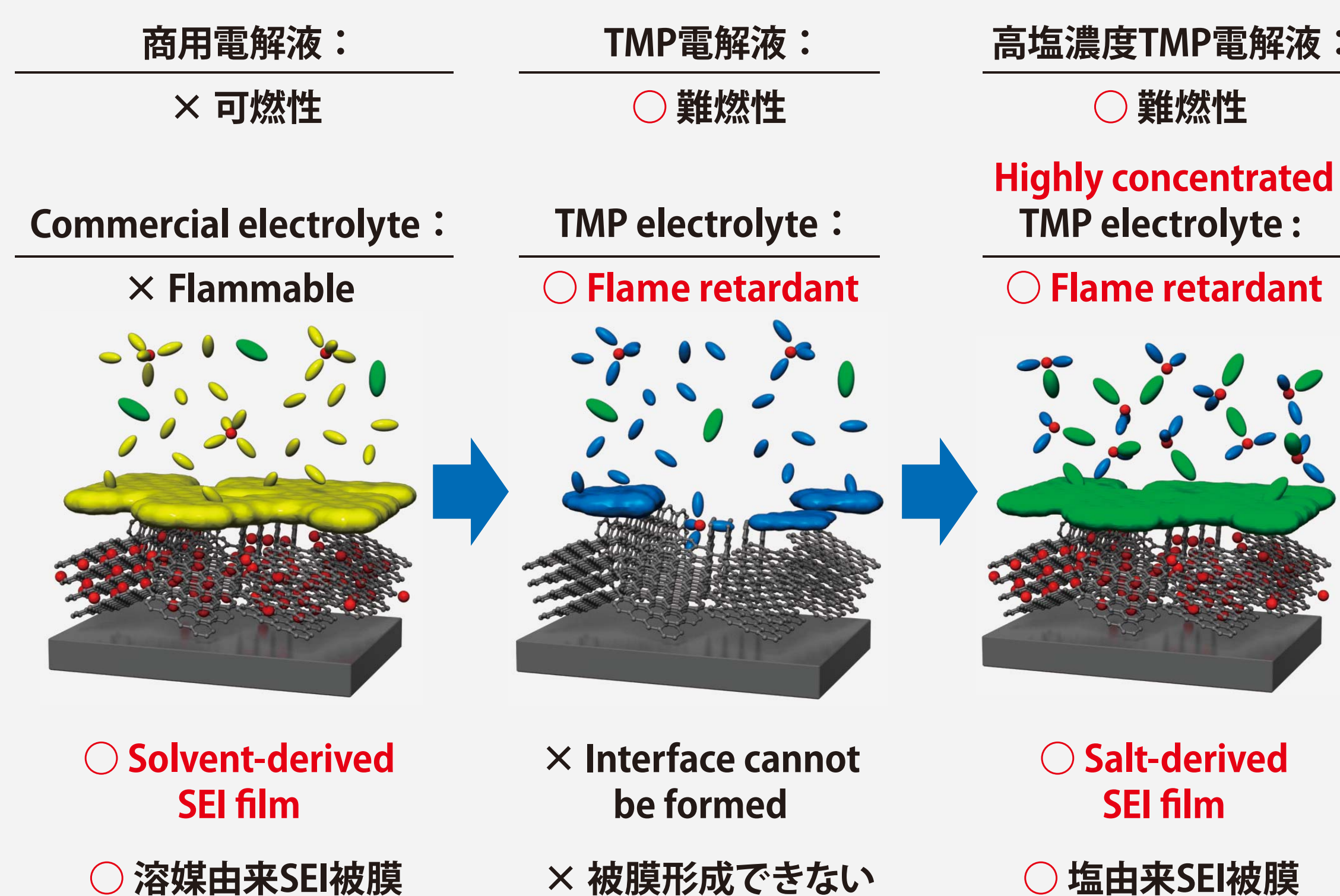


図1 安全な蓄電池電解液の設計概念。電解質塩を高濃度化するだけで、界面の性質が劇的に変化し、安定動作が可能となる。これまで使えなかった溶媒が機能する(今回は消火性TMP)。  
Figure 1 Electrolyte design concept for a safer battery. By ultimately simple strategy of increasing salt-concentration, interfacial character is dramatically modified to realize very stable operation, and many of the solvents are functionalized (fire-extinguishing TMP this time).

### 研究概要 Outline of the research

2

## 電池用ハードカーボン負極のサイクル特性 Repeated cycle stability of hard carbon negative electrode for Na-ion batteries

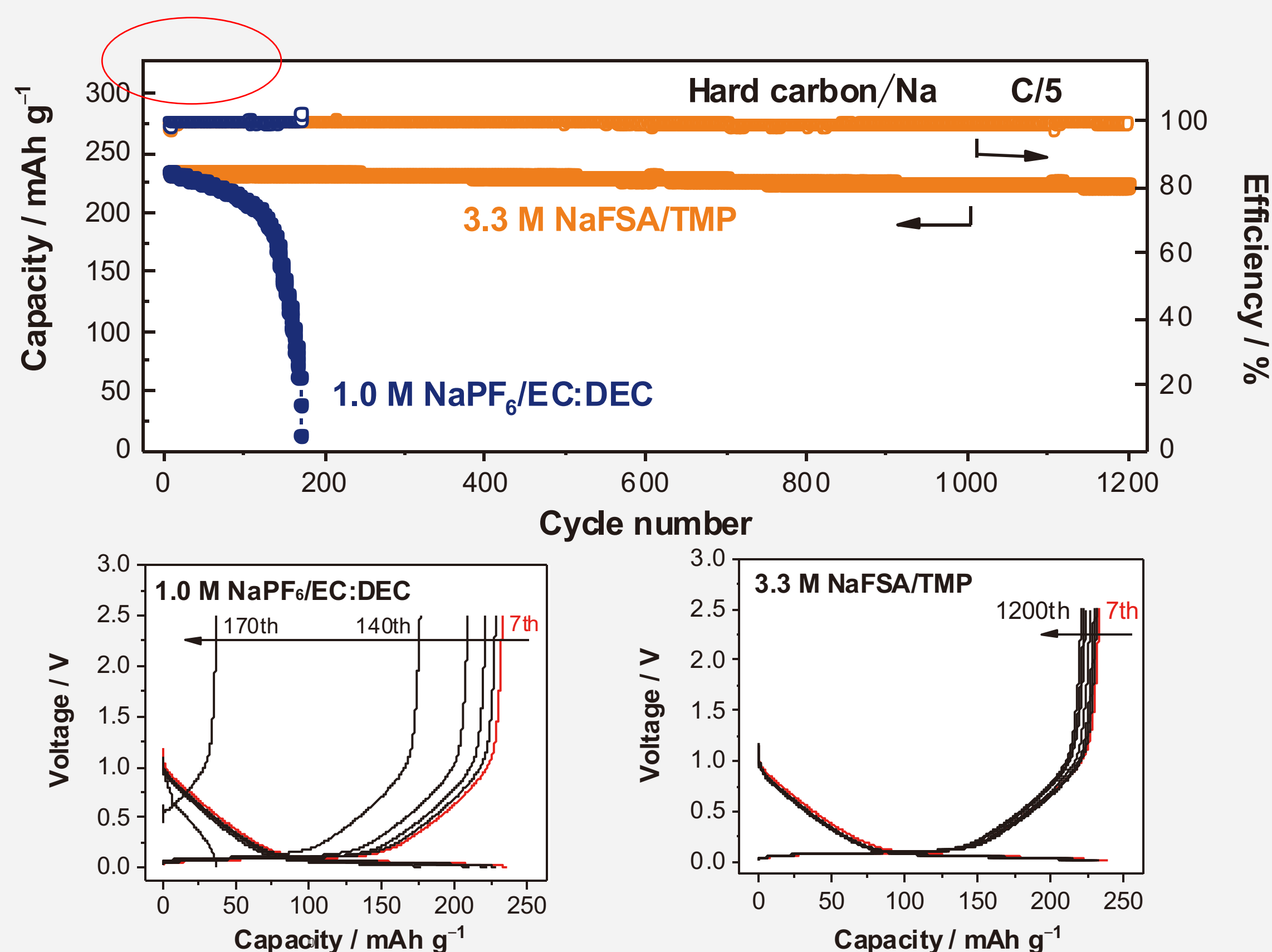


図2 Na-ion電池用ハードカーボン負極の繰り返しサイクルでの容量保持：本研究で開発された有機電解液は1200回以上(1年半以上)の安定な充放電サイクルを達成  
Figure 2 Capacity retention during repeated cycling of a hard-carbon anode for a Na-ion battery; the organic electrolyte developed in this study (3.3M NaFSA/TMP) achieved stable charging/discharging for more than 1,200 cycles (over a year and a half)

### 研究概要 Outline of the research

3

## 燃焼性の比較 Comparison of flammability

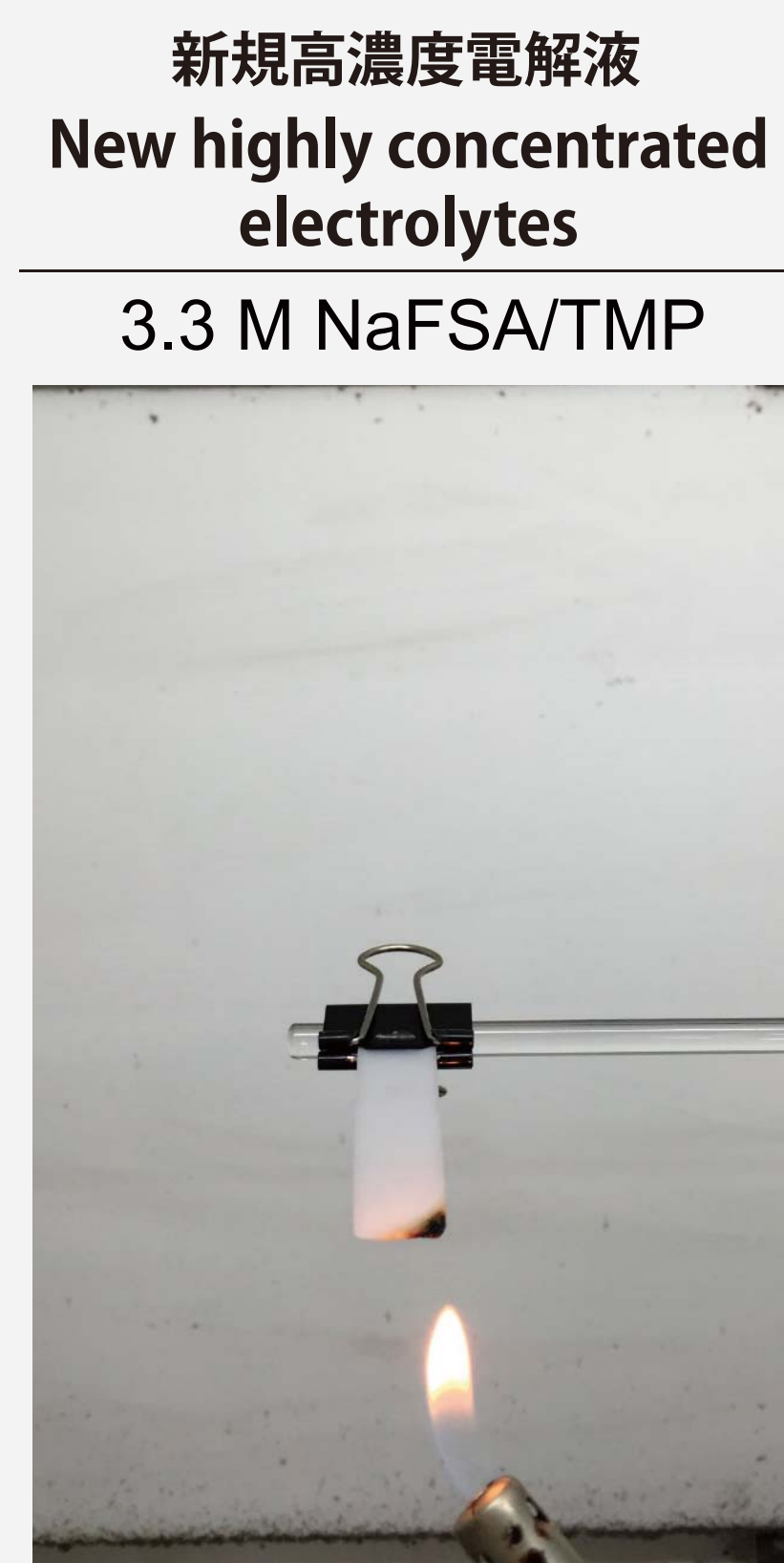


図3 (左)従来の1.0 M NaPF<sub>6</sub>/EC:DEC (1:1 by vol)電解液、(右)研究室で作製した3.3 M NaFSA/TMP電解液の燃焼テスト  
Figure 3 Flame tests on conventional 1.0 M NaPF<sub>6</sub>/EC:DEC (1:1 by vol) electrolyte (left) and laboratory-made 3.3 M NaFSA/TMP electrolyte (right)

### 研究概要 Outline of the research

4

## 高濃度電解液の電子状態 Electronic structures of highly concentrated electrolytes

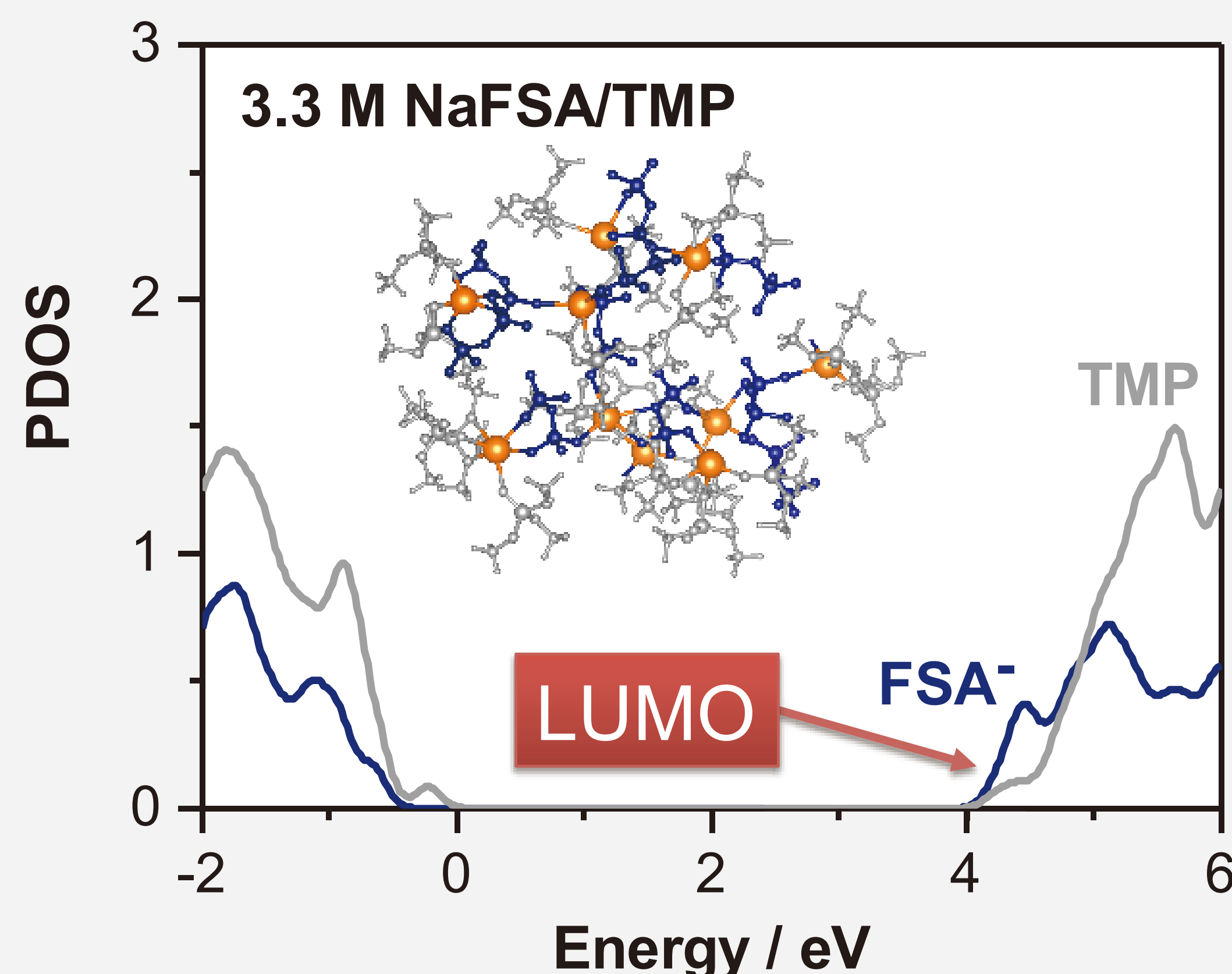


図4 DFT-MDシミュレーションで得られた3.3 M NaFSA/TMP溶液の電子状態と配位構造(挿入図)。Na<sup>+</sup>カチオン、FSA<sup>-</sup>アニオン、TMP溶液はそれぞれオレンジ色、青色、灰色で示す。射影状態密度(pDOS)は、LUMOがFSA<sup>-</sup>に局在しており、最初にFSA<sup>-</sup>が還元された結果、NaFSA塩由来の不動態被膜が形成されていることを示している。  
Figure 4 Electronic structures and coordination structures (insets) of 3.3 M NaFSA/TMP solutions obtained with DFT-MD simulations. Na<sup>+</sup> cations, FSA<sup>-</sup> anions and TMP solvents are shown in orange, blue and grey, respectively. The pDOS, projected density of states, shows that LUMO are located at FSA and that the FSA is attacked first upon reduction to form a passivation film.

### ロードマップ Roadmap

- 電解質に対する既存概念の打破
- 低コスト化と産業展開
- 量産に向けた最適化
- Paradigm shift of electrolyte concept
- Cost-cutting and industrial development
- Optimization for mass production

### 応用分野 Applications

- 民生用電池
- 自動車用電池
- 大型定置用電池
- Consumer batteries
- Batteries for vehicles
- Stationary batteries

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# 高強度と高延性を具備する バルクナノ六方晶金属材料

Concurrent enhancement of strength and ductility in bulk nanostructured hexagonal metals

## 構造材料研究拠点

Elements Strategy Initiative for Structural Materials (ESISM)



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### 研究の背景 Background to the research

- 安心・安全な社会を支える構造材料は、強度（つよさ）と延性（ねばさ）を具備することが不可欠である。
- チタンやマグネシウム合金は軽量で高い強度を有するが、六方結晶構造に起因して延性に乏しいため用途が限定される。
- 合金元素の添加ではなく、バルクナノ組織化による強度と延性両立を目標とした。
- Concurrent enhancement of strength and ductility in structural materials is essential for guaranteeing a safe and secure society.
- Applications for strong, light-weight titanium and magnesium alloys have been limited by poor ductility owing to their hexagonal crystal structures.
- Creation of innovative hexagonal metals through bulk nanostructuring rather than the addition of critical alloying elements is targeted.

### 研究のポイント Points of the research

- サブミクロンまでの様々な平均粒径を有する完全再結晶チタンおよびマグネシウム合金の作製に成功した。
- バルクナノメタル化することで、高強度と高延性を両立させることに成功した。
- バルクナノメタル材料における延性向上メカニズムを、電子顕微鏡、中性子回折実験と計算科学によって原子レベルから解明した。
- Fully recrystallized titanium and magnesium alloys with various average grain sizes down to the sub-micrometer scale were successfully fabricated.
- Concurrent enhancement of strength and ductility was successfully achieved in bulk nanostructured titanium and magnesium alloys.
- Atomistic mechanisms of the superior mechanical properties in bulk nanostructured materials were clarified through state-of-the-art experiments, such as transmission electron microscopy and neutron diffraction, as well as theoretical calculations.

### 研究概要 Outline of the research

1

## 様々な平均粒径を有する完全再結晶材料 Fully recrystallized magnesium alloys with various average grain sizes

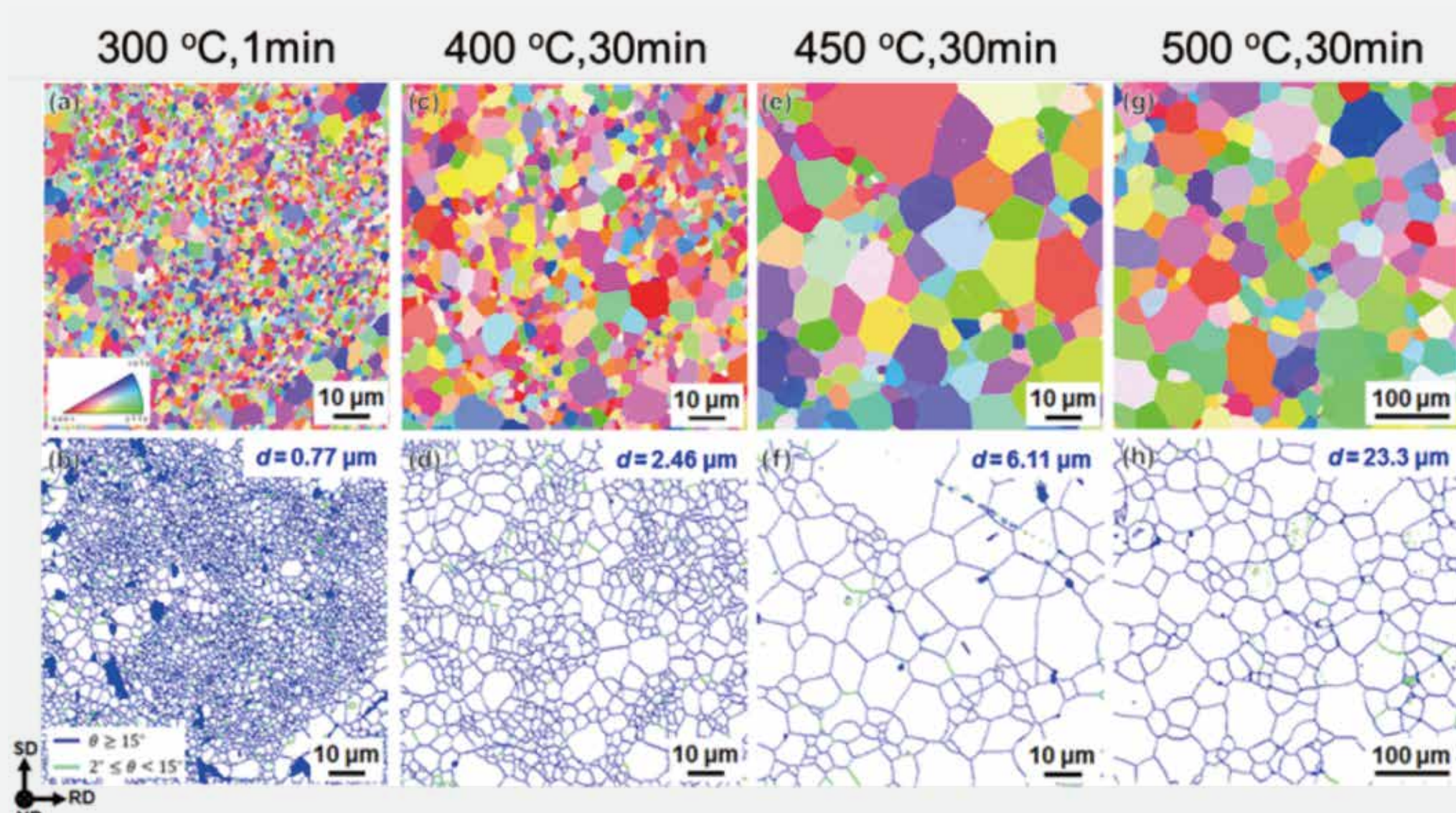


図1 高圧ねじり(HPT)法と焼鈍により作製した、種々の平均粒径を有する完全再結晶マグネシウム合金の電子線後方散乱回折(EBSD)法による微細構造、(上)逆局点図(IPF)マップ。結晶粒の結晶方位を色で識別している。(下)粒界(GB)マップ。青と緑の線は、それぞれ大角粒界および小角粒界を表す。

Figure 1 Magnesium-alloy samples having various average crystal grain sizes fabricated by high-pressure torsion (HPT) followed by recrystallization annealing treatments at the given temperatures and durations. (Top) Inverse pole figure (IPF) maps by electron backscatter diffraction (EBSD). Colors correspond to crystallographic orientations of grains. (Bottom) Grain boundary (GB) maps in which the blue and green lines correspond to high angle and low angle grain boundaries, respectively.

### 研究概要 Outline of the research

2

## バルクナノ材料において強度と延性の両立に成功 Concurrent enhancement of strength and ductility in bulk nanostructured materials

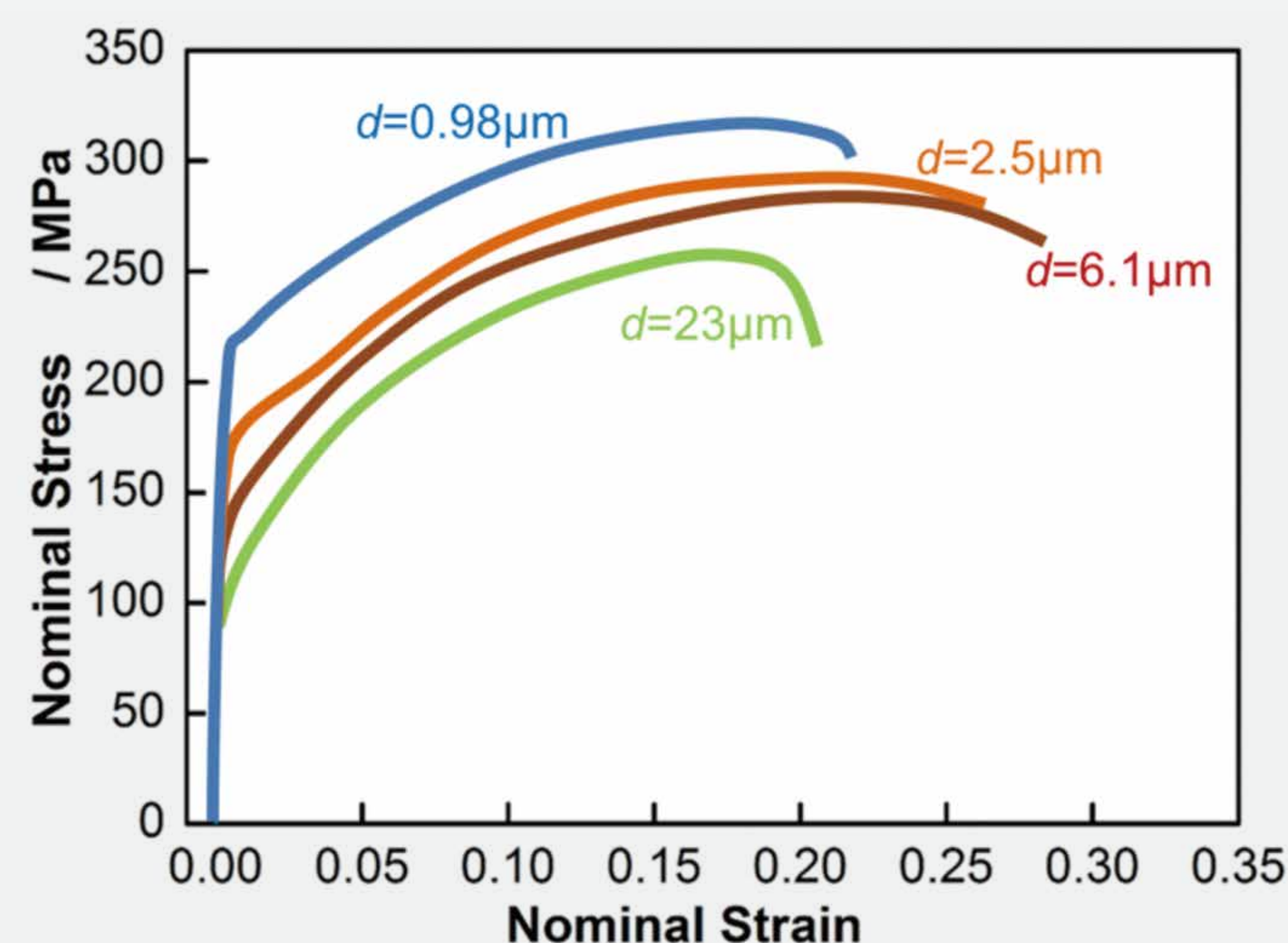


図2 4種の異なる結晶粒径dを有するマグネシウム合金の応力-ひずみ曲線。  
Figure 2 Comparison of stress-strain curves for Mg-alloy specimens having four different average grain sizes d.

### 研究概要 Outline of the research

3

## バルクナノ材料における延性向上機構の解明 Mechanism of enhanced ductility in bulk nanostructured materials

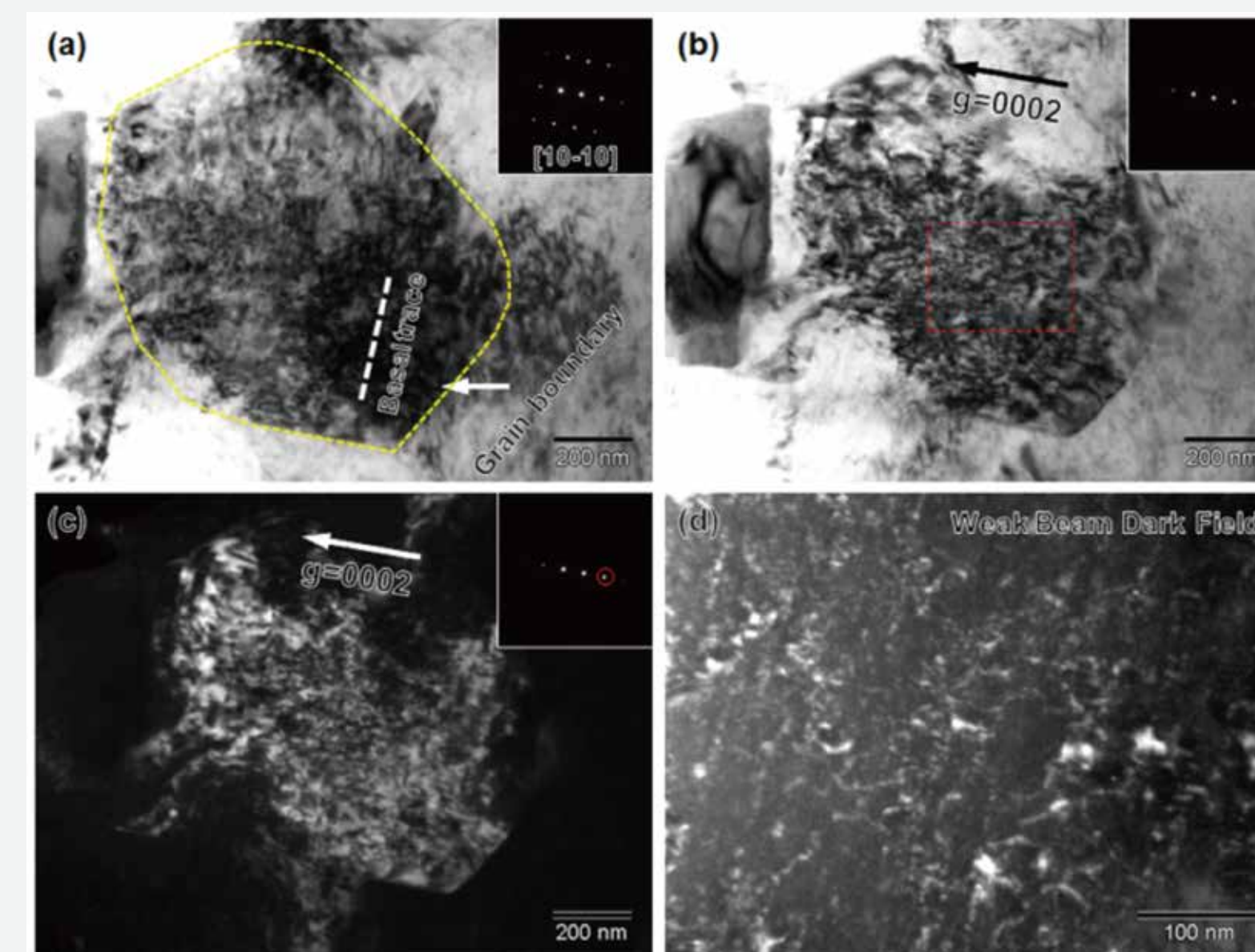


図3 平均粒径 $d=0.98\mu\text{m}$ の超微細粒マグネシウム合金試料をひずみ0.095まで引張変形させた後の透過電子顕微鏡観察結果。(a) [10-10]晶帯軸から観察した明視野像、(b)(c)回折ベクトル $g=(0002)$ での二波条件での明視野および暗視野像。(d) (b)図に示した領域を拡大しウィークビーム法で観察した結果。マグネシウムでは通常活動しないc成分を持つ転位が多数観察された。このような特異な転位は、応力レベルが高くなった時に粒界で核形成したものと考えられる。

Figure 3 Transmission electron micrographs of ultrafine grained magnesium alloy sample with average grain sizes of  $d=0.98\mu\text{m}$  after tensile deformation to a strain of 0.095. (a) Bright-field image observed along [10-10] zone axis. (b) Bright-field and (c) corresponding dark-field images observed under two-beam condition with diffraction vector  $g=(0002)$ . (d) Weak-beam dark-field image of the rectangular area in (b) at a higher magnification. Highly dense, unusual dislocations with c-component can be observed. Such dislocations are presumed to be nucleated at grain boundaries when the stress level increases.

### 研究概要 Outline of the research

4

## バルクナノメタルにおける延性向上機構の新しい変形子概念による包括的な理解 Comprehensive understanding of ductility enhancement in bulk nanostructured metals under the new concept of *plaston*

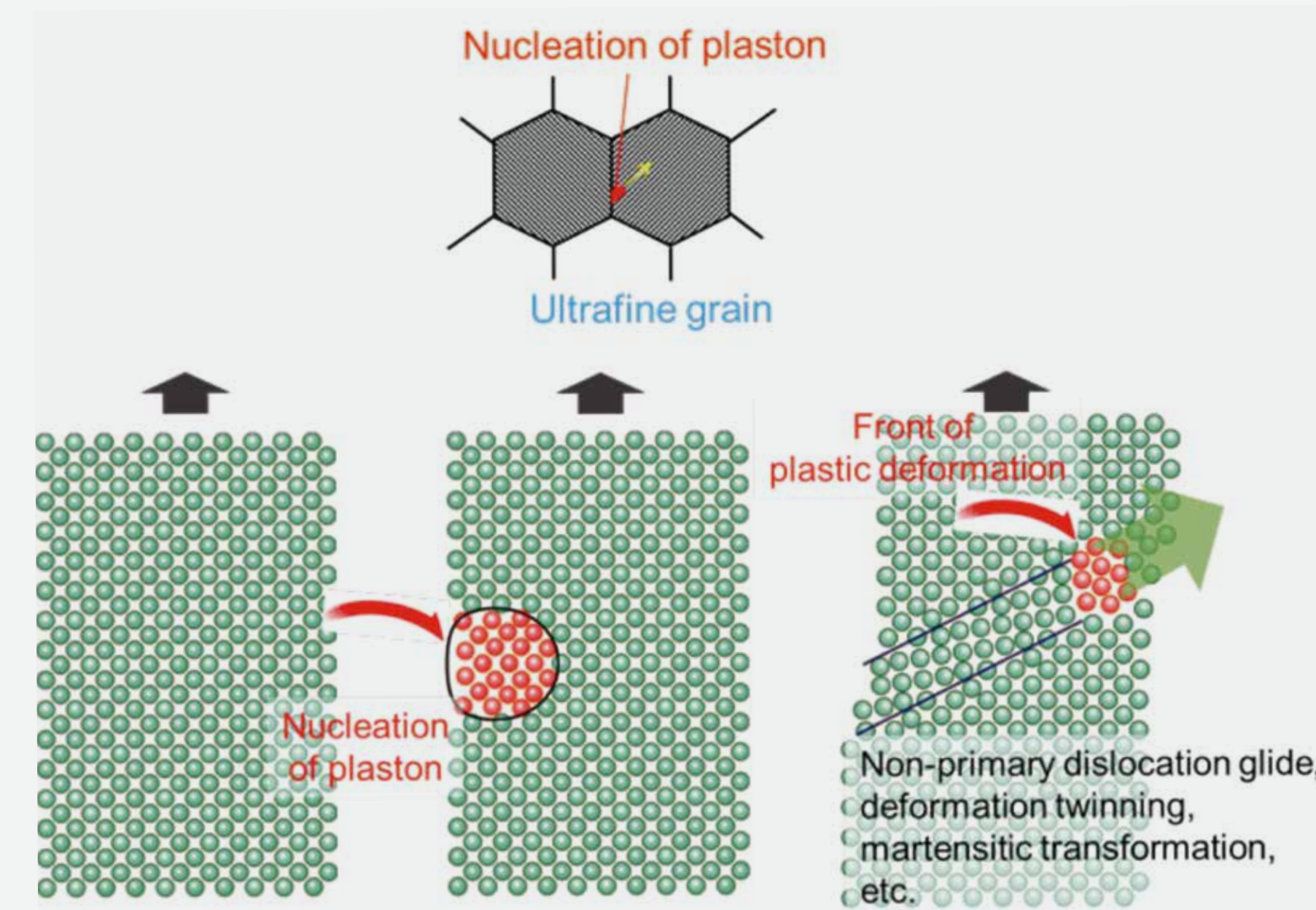


図4 バルクナノ材料では、非主すべり転位、変形双晶、変形誘起マルテンサイト変態のような特異な塑性変形機構が実験的に観察される。これらは、変形子という新しい概念により包括的に説明することが可能である。すなわち、十分に高い応力が印加されると、表面や粒界のように結晶格子が不完全な部分で集団的な原子の動きが起こり、変形子の核形成が生じる。塑性変形フロントにおいても、同様の現象が起こっていると考えられる。

Figure 4 Unique plastic deformation mechanisms different from primary dislocation glide, such as non-primary dislocation glide, deformation twinning, and martensitic transformation, have been experimentally found to take place in bulk nanostructured materials. These mechanisms can be comprehensively explained under the new concept of *plaston*. When a large enough stress is applied, collective atomic motion occurs at lattice imperfections such as surfaces and grain boundaries, which eventually leads to the nucleation of plastic deformation. Similar phenomena are thought to take place at the front of the plastic deformation.

### ロードマップ Roadmap

- 新しい変形子概念に基づく高強度と高延性を具備する鉄鋼材料の創製
- 多様な化学結合を有する構造材料における変形子解明と脆性克服への指針獲得
- Concurrent enhancement of strength and ductility in bulk nanostructured steels based on the new concept of *plaston*.
- Fundamental understanding of *plaston* in other materials having a variety of chemical bonds in order to overcome their brittleness.

### 応用分野 Applications

- 輸送用機器
- 建造物
- 生体材料
- Vehicles and aircrafts
- Structures
- Biomaterials

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