

2015年3月12日 サーフワークショップ@筑波大学

## 物質変換材料研究部門の研究

筑波大学 数理物質系 中村潤児

### 講演内容

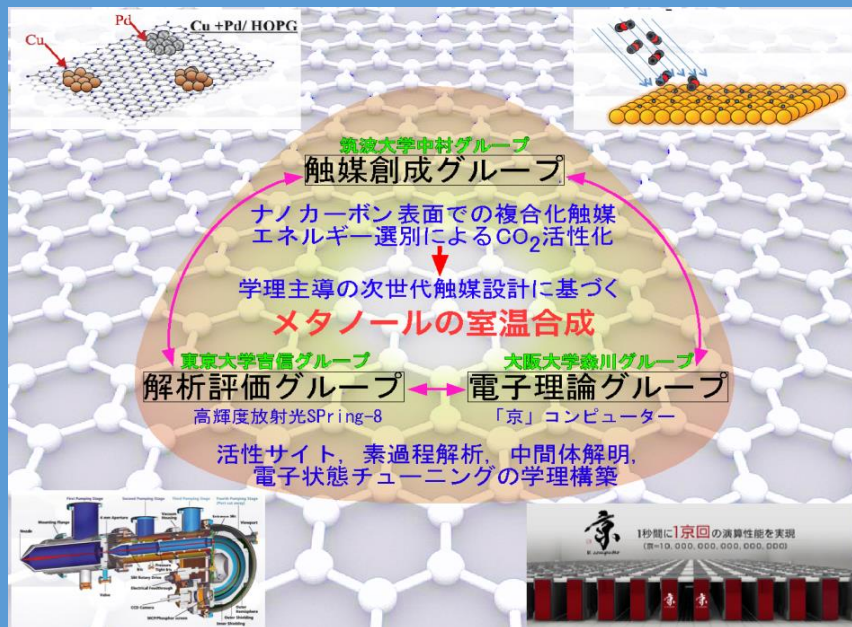
- ▶ 物質変換材料研究部門の研究内容
- ▶ CO<sub>2</sub>削減用の触媒開発
- ▶ 燃料電池における白金触媒量の削減

# 物質変換材料研究部門

## 触媒学理に基づく環境エネルギー材料の創成

PI: 中村潤児 共同研究者: 神原教授、山本准教授 他14名 (Prof. Barcikowski in Univ of Duisburg-Essen, Prof. Schlögl in Max Plank Inst., Prof. Wang in 南開大学, 吉信東大教授、森川阪大教授)

### 二酸化炭素のメタノールへの転換

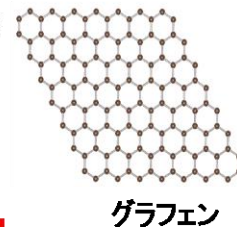
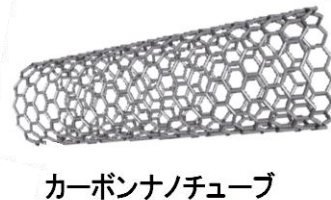
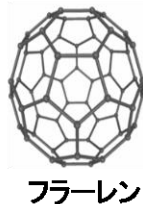


JST ACT-Cプロジェクト進行中 平成24~29年

計算科学, 先端物質解析などの学理  
 に基づく環境エネルギー材料の開発

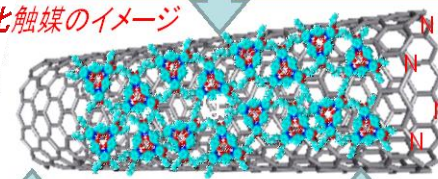
### ナノカーボンを用いた環境エネルギー触媒開発

π共役系ナノカーボン: π電子によるd電子系の電子状態制御



触媒担体

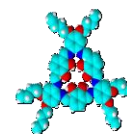
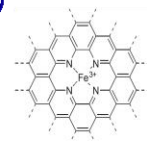
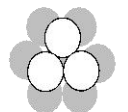
新規CO<sub>2</sub>水素化触媒のイメージ



触媒成分

触媒担体ドーパント

金属触媒  
 (Cu, Fe, Co, Ni等)



s,p電子系ドーピング剤

N, B, Sなどの典型元素を  
 ナノカーボンにドーブして  
 π電子系の電子状態を  
 制御する

# 物質変換材料研究部門の研究内容

## 1. CO<sub>2</sub> のメタノールへの転換

CO<sub>2</sub> 活性化機構解明、グラフェン触媒の応用、計算科学(阪大)と放射光実験(物性研)の共同研究

## 2. 燃料電池用カーボン触媒の開発

炭素/白金界面相互作用の解明、カーボンアロイ触媒の機能と設計

## 3. 触媒機能の学理構築

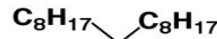
グラファイト系炭素の酸塩基性の起源、担体効果の解明、物性物理と反応性の橋渡し

## 4. 藻類産生油の触媒的転換

C<sub>30</sub> - C<sub>40</sub> 化学の構築、クラッキング、異性化、重合、ハイブリッド化

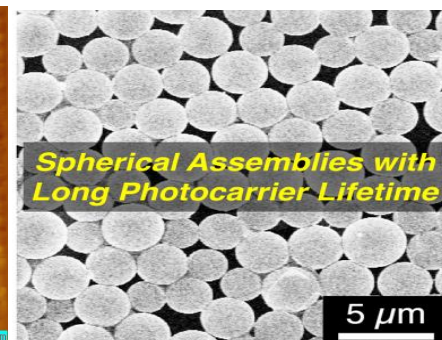
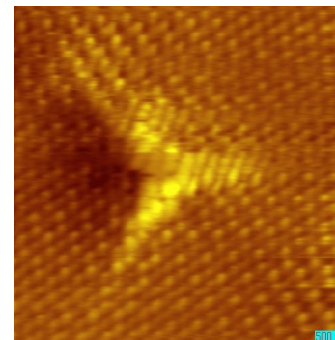
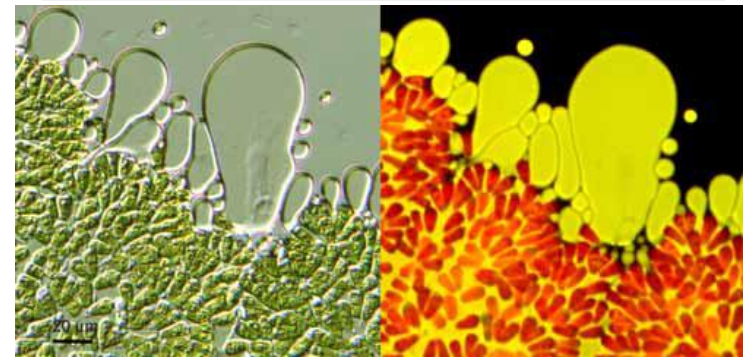
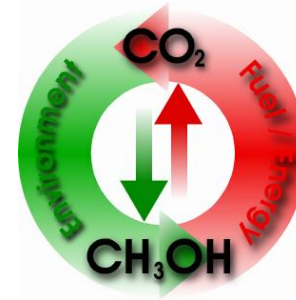
## 5. 光デバイスのための材料合成

ポリマーやグラフェンを用いた発光・レーザー、太陽電池材料



## 6. 新分光法と新物質

ヘテロダイン分光法のSTSへの応用、新二次元物質の創出



# 部門の特色：学理主導の触媒材料設計

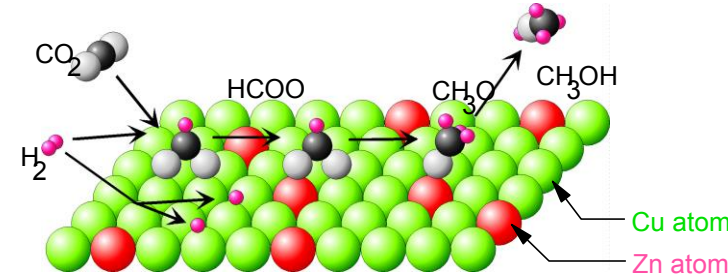
メカニズムを解明し、表面素過程の詳細を調べ、それらを再構築して活性触媒を予測する

**表面素過程：吸着、解離、表面拡散、会合反応、脱離**

**触媒表面は極めて複雑**

1. 表面では多くの素過程が同時に進行
2. 触媒成分元素も複数、表面構造の変化
3. 反応条件によって速度論が変化

触媒活性は素過程の速度バランスで決まる

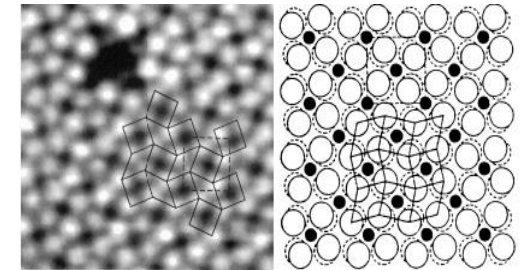
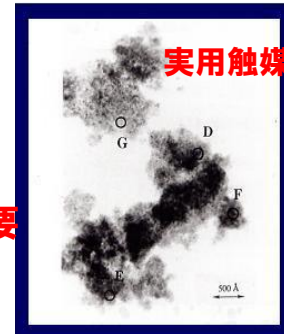


触媒は表面積をかせぐために触媒担体上に微粒子化して使用する

实用触媒そのものを研究しても素過程レベルで  
メカニズム解明は不可能  
したがって

単結晶表面などのモデル触媒を使った表面科学実験が必要

放射光施設を用いた表面科学実験は高度になっている



表面の構造は吸着種の存在によって変化する

**不均一系触媒の学理の実験面では表面科学実験が不可欠**

さらに計算科学では、素過程の速度論的・電子的情報を集積し、大規模シミュレーションによって触媒設計

**コンピュータ「京」の導入によって触媒開発シミュレーションは新たな時代へ突入**

表面科学を熟知する計算物理研究者の協力が必須、我々のプロジェクトが先駆けとなる

# 講演内容

- ▶ 物質変換材料研究部門の研究内容
- ▶ CO<sub>2</sub>削減用の触媒開発
- ▶ 燃料電池における白金触媒量の削減

# CO<sub>2</sub>を反応物とする不均一系触媒反応



Cu/ZnO触媒, 523K、5 MPa  $\Delta H = -49.4$  kJ/mol (発熱)

メタノール  
(化学原料、燃料として極めて有用)



Ni, Rh触媒, 800-1000K、0.01-0.1 MPa  $\Delta H = 247.3$  kJ/mol (吸熱)

合成ガス



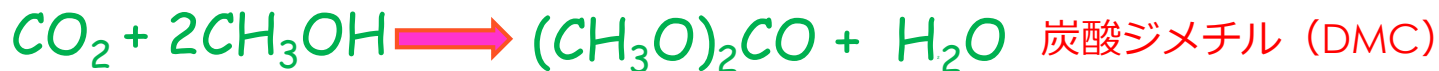
Cu触媒, 523K、 $\Delta H = -41.1$  kJ/mol (発熱)

一酸化炭素



Ru, Ni 触媒, 450-573K、 $\Delta H = -252.9$  kJ/mol (発熱)

メタン



CeO 触媒, 400 K、5 MPa、 $\Delta H =$  kJ/mol (吸熱)

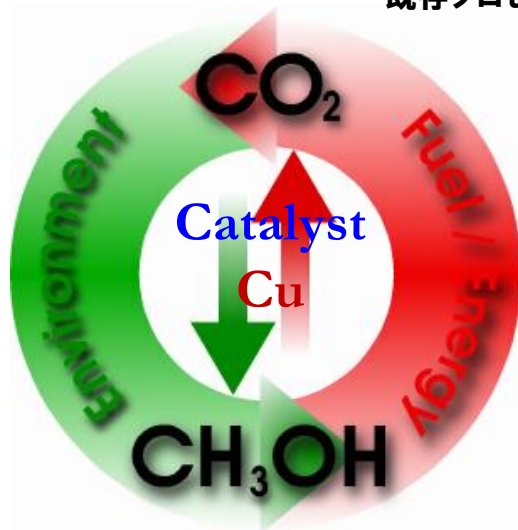
炭酸ジメチル (DMC)

## 二酸化炭素活性化機構の学理に基づく メタノール室温合成触媒の創成

**研究代表者:** 筑波大学 数理物質系 教授 中村潤児 (触媒設計・表面科学)  
**主要共同研究者:** 東京大学物性研究所 教授 吉信淳 (放射光実験・表面科学)  
大阪大学工学研究科 教授 森川良忠 (第一原理計算)



既存プロセス: Cu/ZnO触媒, 523K, 5 MPa  $\Delta H = -49.4 \text{ kJ/mol}$  (発熱)



### 研究目標

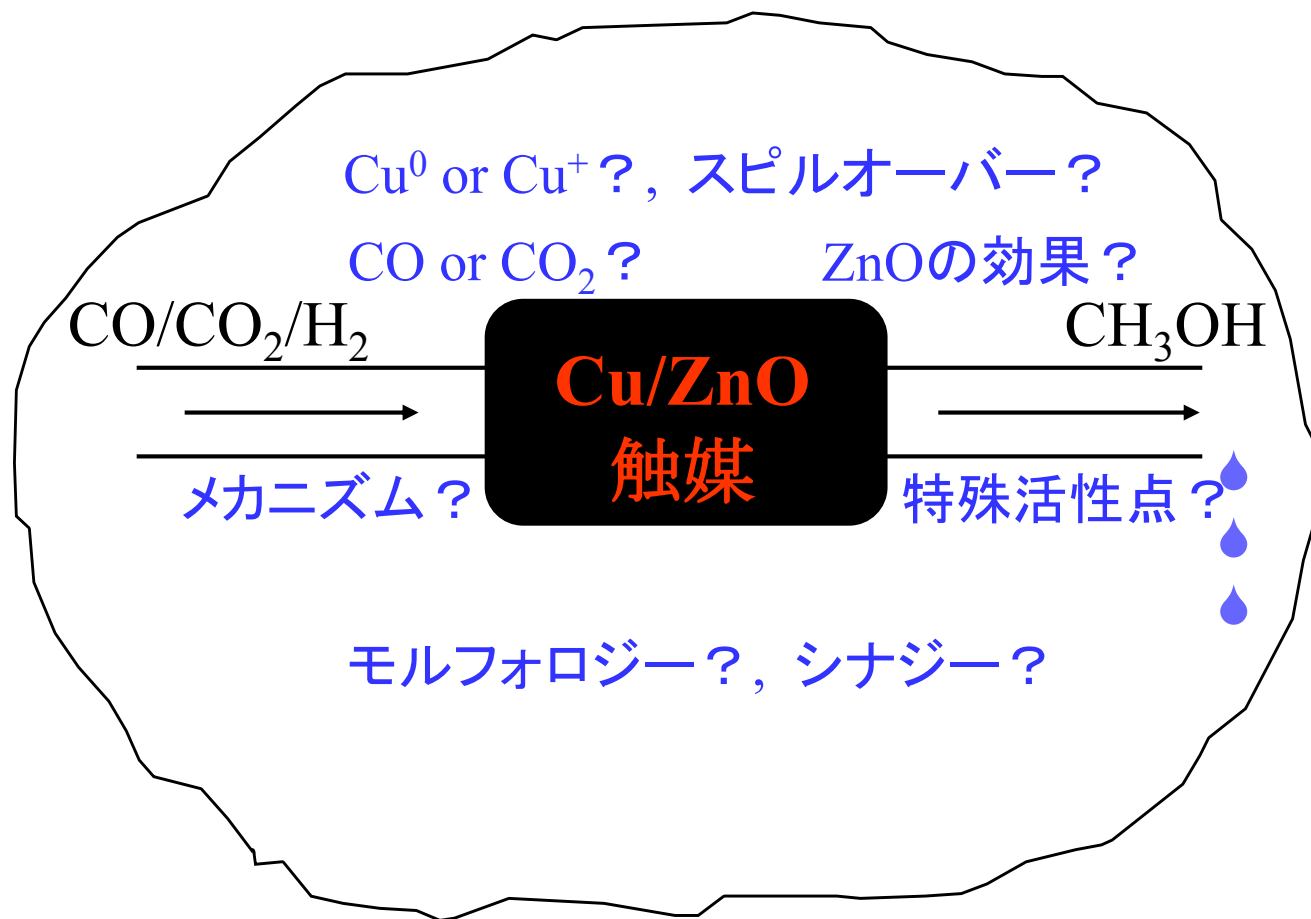
学理主導の触媒設計でメタノール室温合成を実現  
(メタノール製造に要するエネルギーを大幅に削減)

### 研究の意義

1. 社会的意義: 二酸化炭素の燃料・化学原料への転換
2. 学術的意義: 学理主導の触媒設計

触媒調製・表面科学・計算科学の三位一体  
(経験則に基づく既存の触媒開発から脱却)

# メタノール合成反応のメカニズムは長い間不明





# Cu系メタノール合成触媒研究の歴史と中村の貢献

## メタノール合成化学工業

- 1923 ZnO/Cr<sub>2</sub>O<sub>3</sub> Catalyst by BASF ,  
MeOH synthesis start  
1925 Patard : Discovery of Cu-based Catalyst  
1928 Frolich : CuO/ZnO catalyst  
1947 Blasiak : Cu/ZnO/SiO<sub>2</sub> (Patent, Poland)  
1960 MeOH synthesis, ICI  
combined with CH<sub>4</sub> reforming process

## 表面科学的研究

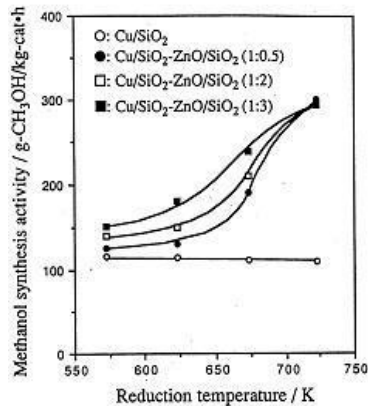
- 1991 Goodman :  
Cu(100), CO/CO<sub>2</sub>/H<sub>2</sub>, Cu<sup>+</sup> is active  
1994 Chorkendorff :  
CO<sub>2</sub>/H<sub>2</sub>, Cu(100), metallic Cu  
1995 Campbell :  
CO<sub>2</sub>/H<sub>2</sub>, Cu poly, metallic Cu  
Nakamura, Fujitani :  
CO<sub>2</sub>/H<sub>2</sub>, Zn/Cu poly  
CO<sub>2</sub>/H<sub>2</sub>, Zn/Cu(111), Zn/Cu(110)  
1996 Campbell :  
Cu(110), Morphology effect

2012 Science誌  
フリッツハーバーG( +Norskov) は我々のモデルを支持

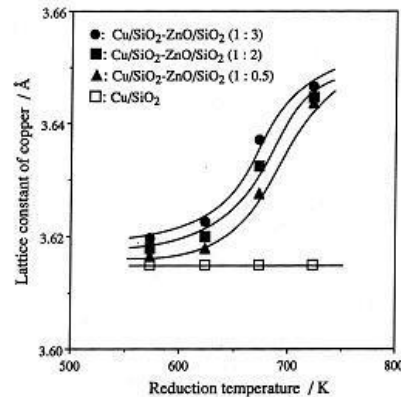
## 活性点、メカニズム、ZnOの効果

- 1962 Kotowski : addition of CO<sub>2</sub>  
1975 Ya : MeOH from CO<sub>2</sub> rather than CO, isotope  
1982 Klier : Cu is inactive, CO/CO<sub>2</sub>/H<sub>2</sub>  
1986 Chinchen(Waugh) : Cu<sup>0</sup> is active species,  
Cu/ZnO, Cu/Al<sub>2</sub>O<sub>3</sub>, Cu/MgO  
1987 Waugh(Chinchen, Spencer): CO<sub>2</sub> is intermediate  
Chinchen : MeOH from CO<sub>2</sub> rather than CO, isotope  
Amenomiya : CO<sub>2</sub>/H<sub>2</sub> support effect  
1988 Burch : physicals mixture, synergy, Morphology  
CO/H<sub>2</sub>, CO/CO<sub>2</sub>/H<sub>2</sub>, different specific activity .  
1989 Burch : spillover, King : K-promotor  
1990 Burch, Spencer : CO/CO<sub>2</sub>/H<sub>2</sub>, Cu/ZnO, yield vs area  
Mol : Cu/ZnO/Al<sub>2</sub>O<sub>3</sub>, CO/H<sub>2</sub>, nonlinear  
Joyner : Comment on Burch paper.  
Ponec : CO/H<sub>2</sub>, Cu is inactive  
1991 Klier : Cu/SiO<sub>2</sub>, CO/CO<sub>2</sub>/H<sub>2</sub>, CO/H<sub>2</sub>  
1992 Rochester : special site – Cu/ZnO interface.  
Baiker : Cu/ZrO<sub>2</sub>, CO<sub>2</sub> is intermediate  
1994 Fujitani, Kanai, Nakamura : Cu-O-Zn active site  
1997 Waugh : morphology, Norskov : morphology  
1997 Fujitani, Nakamura : Cu-Zn active site  
1999 Morikawa, Nakamura : DFT (Cu-Zn active site)  
2000年以前に中村らは活性点を解明

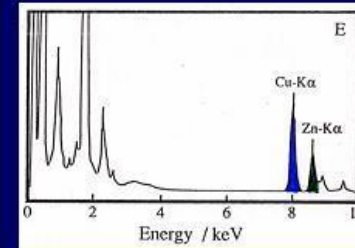
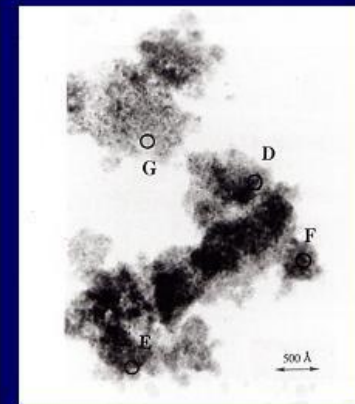
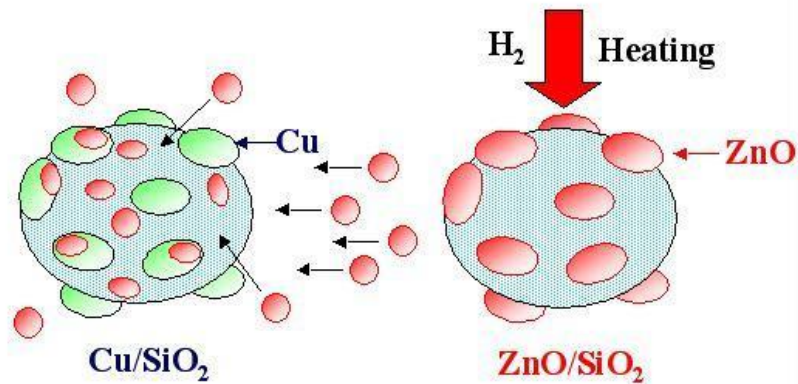
# Cu/SiO<sub>2</sub>+ZnO/SiO<sub>2</sub> 粉体触媒からの触媒モデルの導出



Activity increase

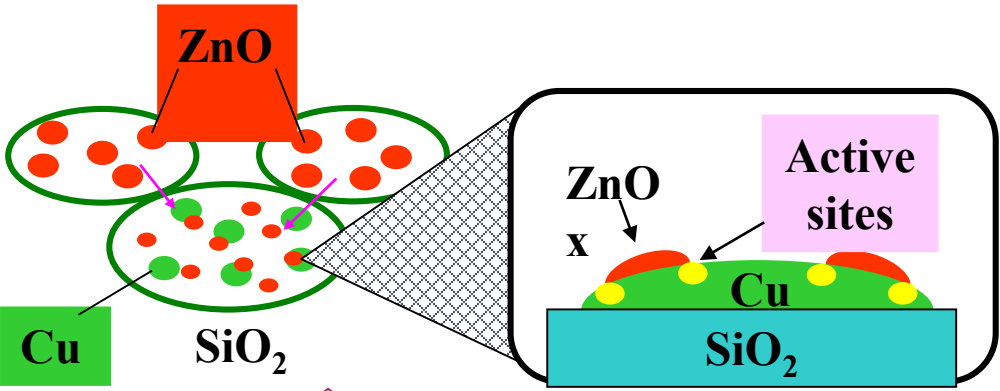


Cu-Zn alloy formation



Evidence of Zn migration

# 粉体触媒のモデルを単結晶表面に構築

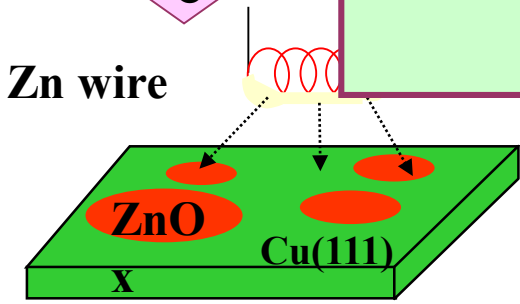


**Powder catalyst**  
(FT-IR, EDX, XRD,  
Oxygen Coverage  
measurements)

ZnOの役割は活性点の形成

consistent

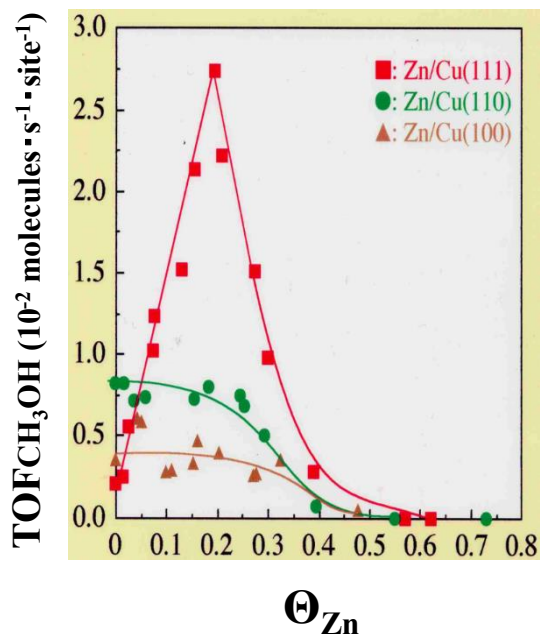
Active sites form on the  
ZnO<sub>x</sub>-covered Cu surfaces



**Model catalyst**  
(XPS, AES, STM, )

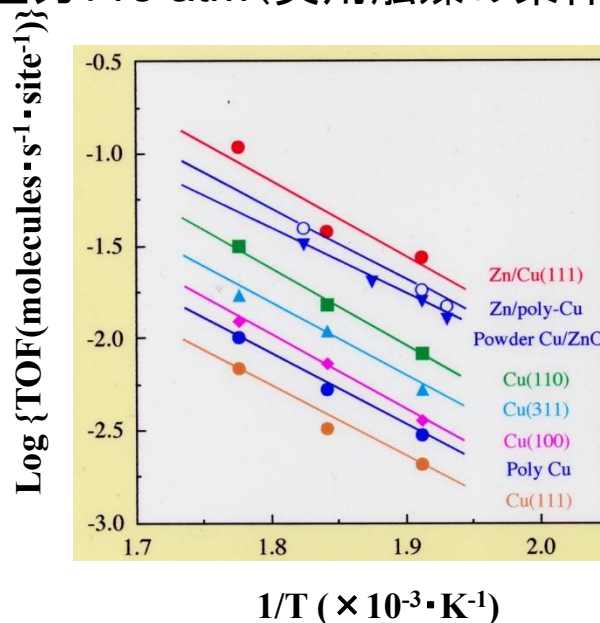
# Zn/Cu(111)モデル触媒の構築

超高真空XPS装置に高圧反応器を接続しモデル触媒の活性を評価



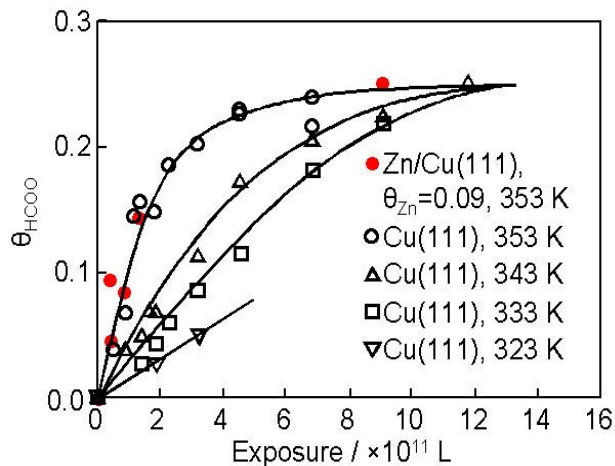
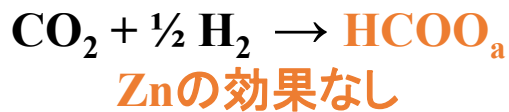
Cu(111)のみZnの促進効果

圧力: 18 atm (実用触媒の条件)

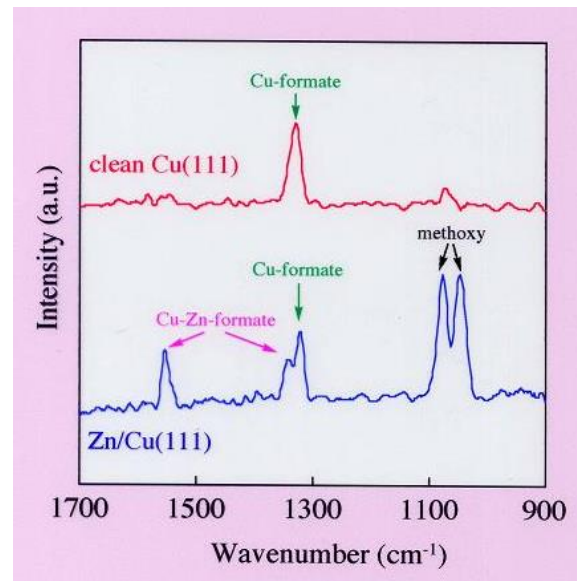


活性化エネルギーが等しい  
ターンオーバー頻度(TOF)が等しい

# Formateを室温で合成し、室温で水素化する



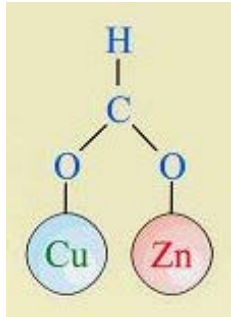
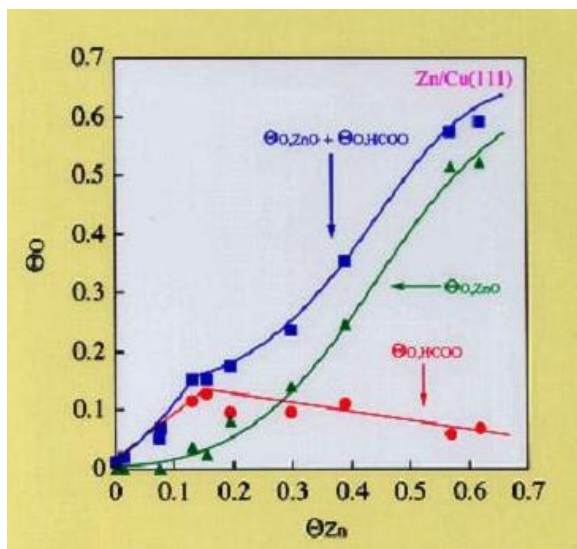
(XPS測定)



(in-situ IR測定)

# 活性点は何か、いかにしてformateを活性化するか

メタノール合成反応後のXPS測定

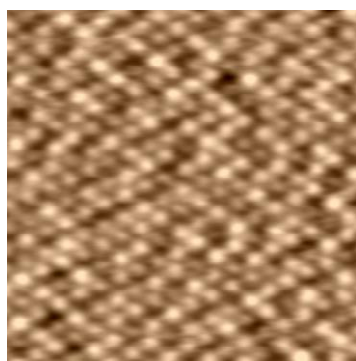


Cu-Zn上のformateが活性種

活性点はCu-Zn合金サイト

Zn原子がCu表面原子と置換する

表面合金がバルク合金よりも安定

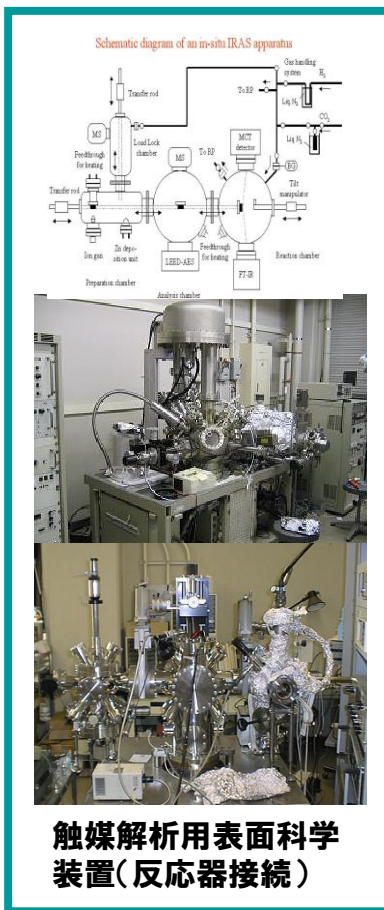


Zn/Cu(111) 表面はメタリック formateが検出

STM image of Zn/Cu(111)

annealed at 560 K ,  $\theta_{Zn} = 0.25$   $40 \times 40 \text{ \AA}^2$

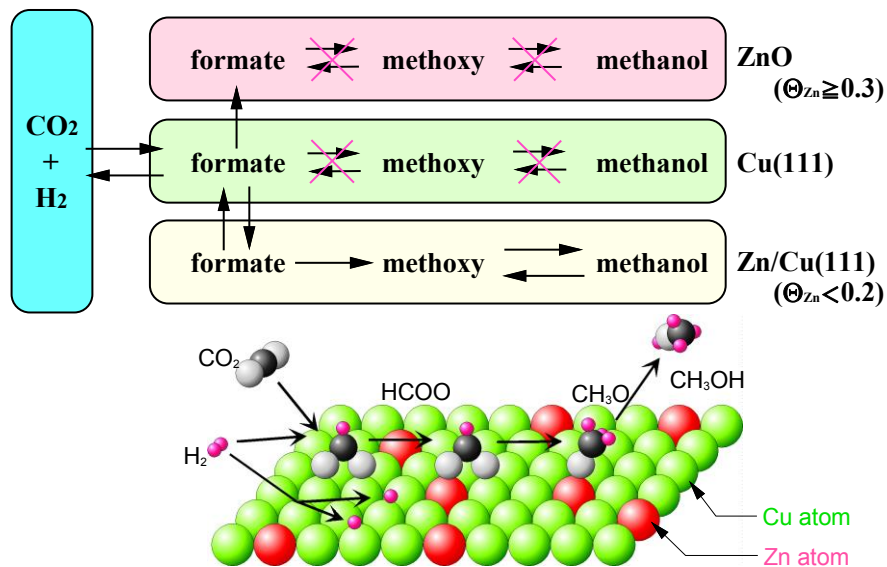
# 表面科学的手法でメタノール合成の活性サイトと反応機構を解明



触媒解析用表面科学装置(反応器接続)

RITEプロジェクト (1994-2003年で34報発表)

Cu-Zn 合金活性サイトを提案し実験的・理論的証拠を示してきた



研究実績を基盤にして、“**室温合成**”に挑戦  
 この10年間に発展した最先端の表面分析手法と大規模計算科学の連携により学理主導で達成する

## なぜメタノール合成反応は遅いか

Comparison of TOF of model catalysts and powder catalysts

	Cu(111)	Zn/Cu(111)	Cu/SiO <sub>2</sub>	Cu/ZnO
Temperature (K)	523	523	523	523
Pressure <sup>a</sup> (atm)	18	18	20	18
Feed rate or SV	5.56 cm <sup>3</sup> /min (at 18 atm)	5.56 cm <sup>3</sup> /min (at 18 atm)	1.8×10 <sup>5</sup> h <sup>-1</sup> (at 1 atm)	1.2×10 <sup>5</sup> h <sup>-1</sup> (at 1 atm)
TOF <sub>(CH<sub>3</sub>OH)</sub> <sup>b</sup>	0.2×10 <sup>-2</sup>	2.7×10 <sup>-2</sup>	0.8×10 <sup>-2</sup>	1.7×10 <sup>-2</sup>
TOF <sub>(CO)</sub> <sup>b</sup>	90	70	5.65	1.12
Reference	[15]	[15]	Unpublished	[15]

<sup>a</sup>H<sub>2</sub>/CO<sub>2</sub> = 3.

<sup>b</sup>TOF (molecules/site/s).

### CO<sub>2</sub>の反応確率の比較

メタノール合成(523K)  $3 \times 10^{-12}$

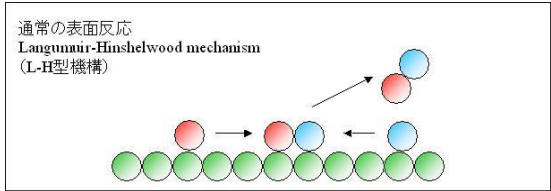
Formate 生成素過程(353K)  $2 \times 10^{-11}$

Formateは400K程度で分解するので、みかけのformate生成速度はメタノール合成速度に近い。

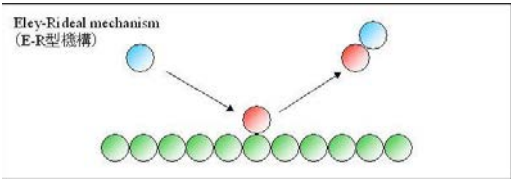
より低温でメタノールを合成するためにはformate生成も加速しなければならない。



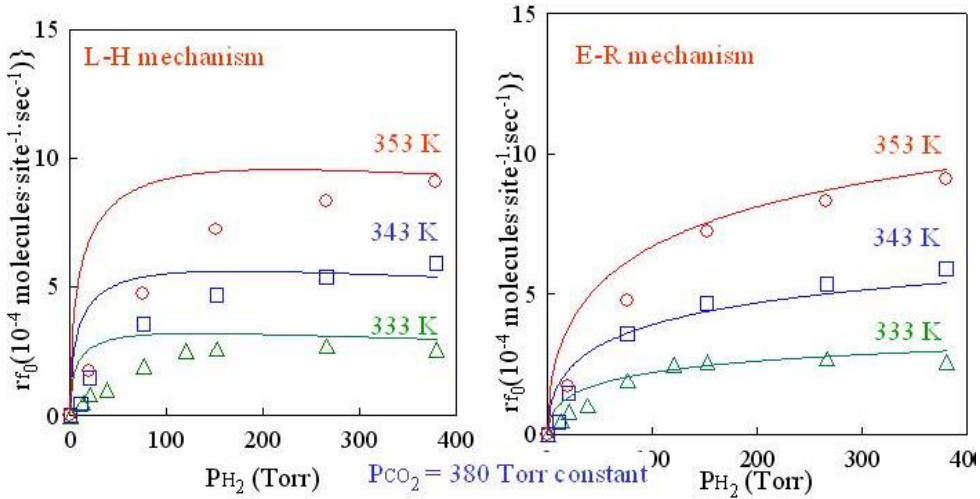
# Formate 合成はLangumuir-Hinshelwood型かEley-Rideal型か



$$r_{f_0} = \frac{k_1 k_2 k_3}{k_{-1} k_{-2}} \frac{P_{H_2}^{1/2} P_{CO_2}}{(1 + \frac{k_1}{k_{-1}} P_{H_2}^{1/2})^2}$$



$$r_{f_0} = \frac{k_1 k_3}{k_{-1}} \frac{P_{H_2}^{1/2} P_{CO_2}}{(1 + \frac{k_1}{k_{-1}} P_{H_2}^{1/2})^1}$$



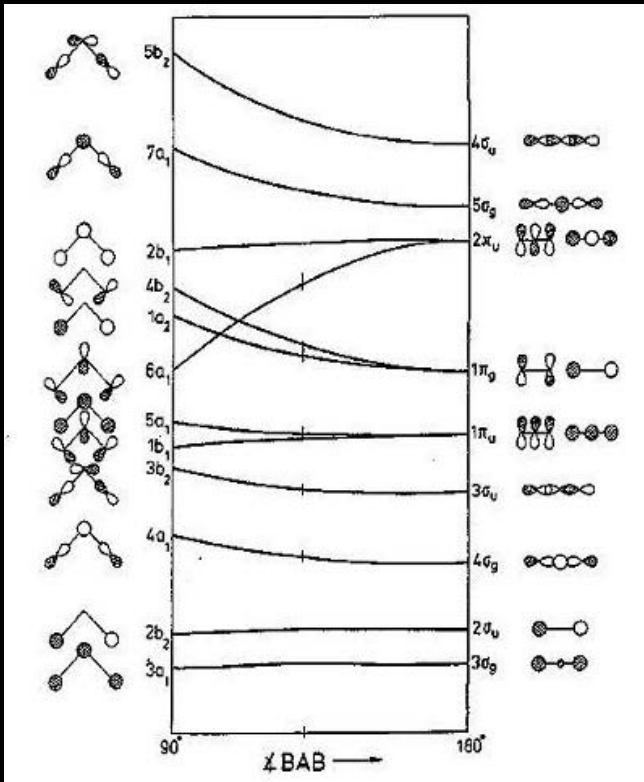
Formate生成速度の水素圧力依存性

実験結果はE-R機構に合う

表面反応ではほとんど知られていない

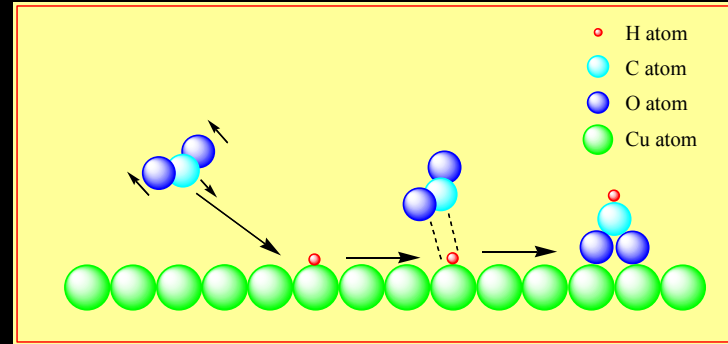
J. Phys. Chem. B **105** (2001) 1355

## CO<sub>2</sub>のWalshダイグラム



O-C-O 軸の変角に伴いLUMOが大きく  
低下

CO<sub>2</sub> は酸性分子(電子を受け取る)



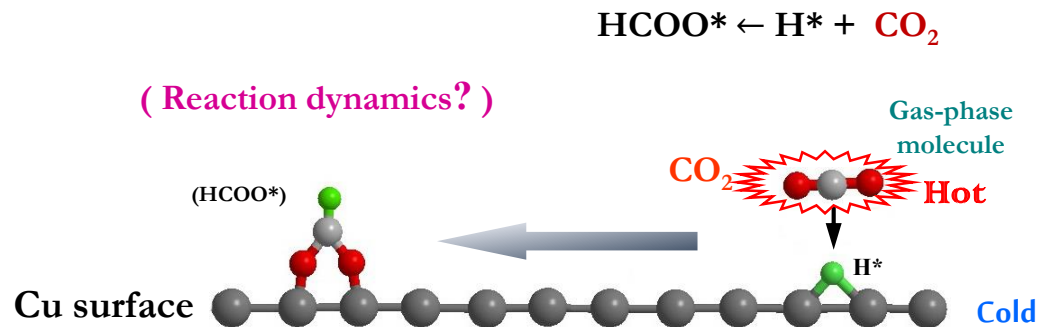
表面と分子が熱的平衡にならず  
とも反応が起こる

CO<sub>2</sub>の振動励起によって反応が  
起こる可能性が大きい

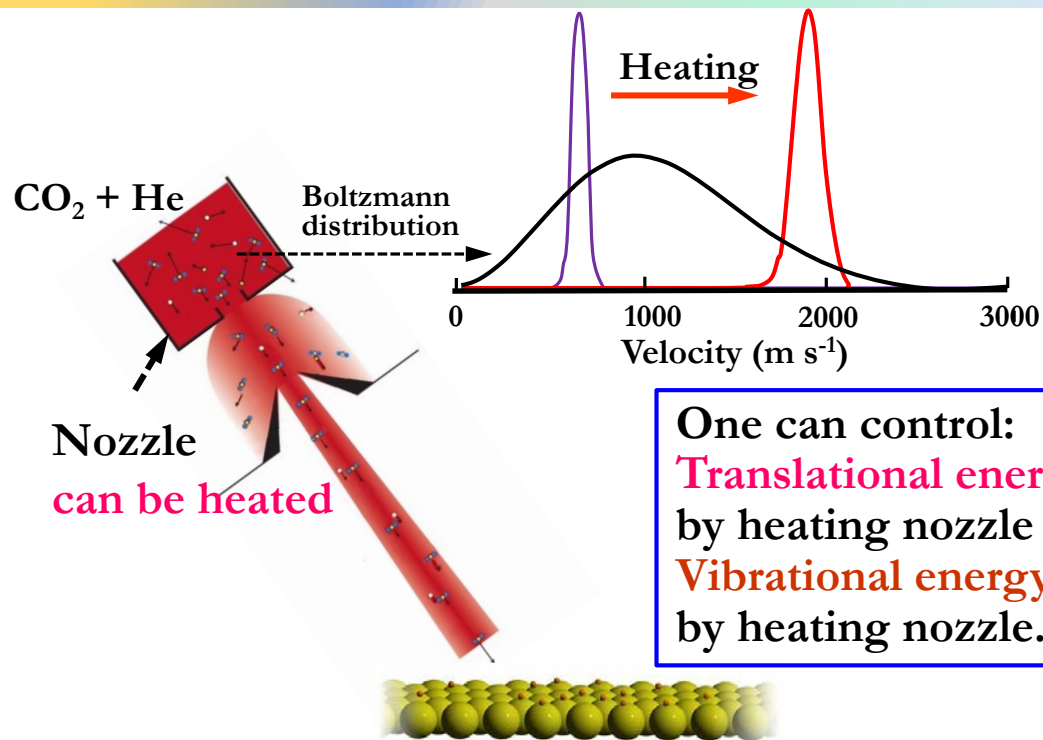
エネルギーの供給方法を変える事  
により反応を制御

## Eley-Rideal型反応を実証する分子線実験

If the reaction is *Eley-Rideal* type mechanism, formate could be synthesized through only supplying energy to CO<sub>2</sub> even at cold surface



# 加熱したCO<sub>2</sub>を冷やしたCu表面に照射する

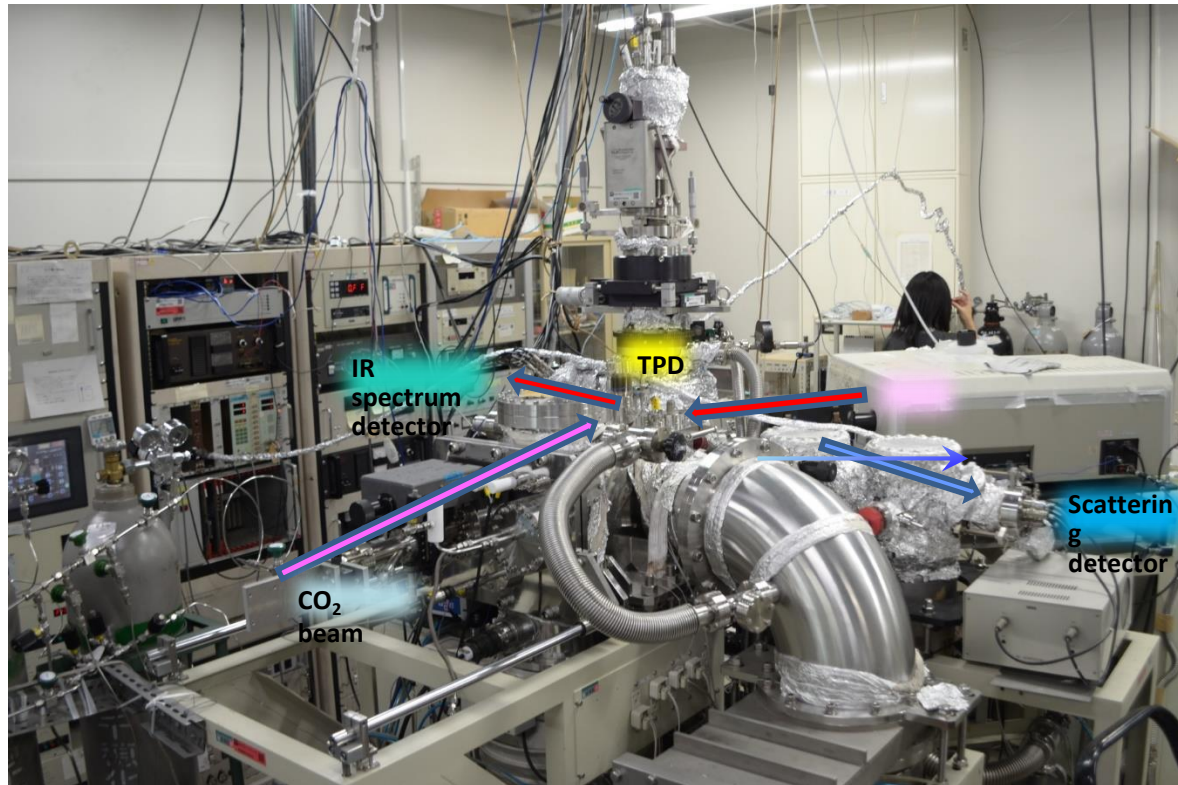


One can control:  
**Translational energy  $E_T$**   
by heating nozzle or mixing He,  
**Vibrational energy  $E_V$**   
by heating nozzle.

Cu at low temperature

# Experimental Setup

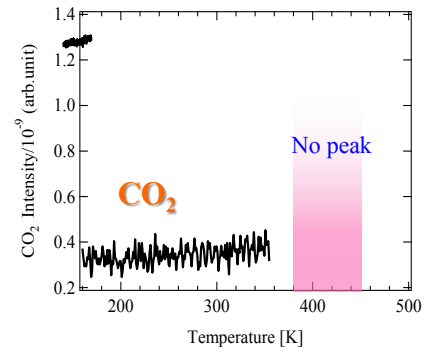
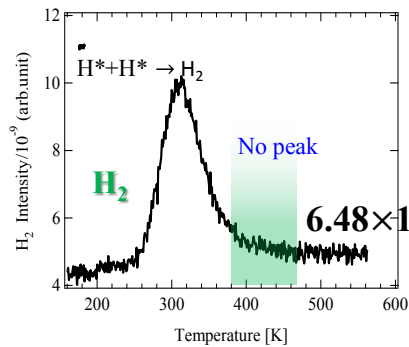
## Hot $\text{CO}_2$ preparation — Supersonic Molecular Beam



Ultra-high Vacuum System

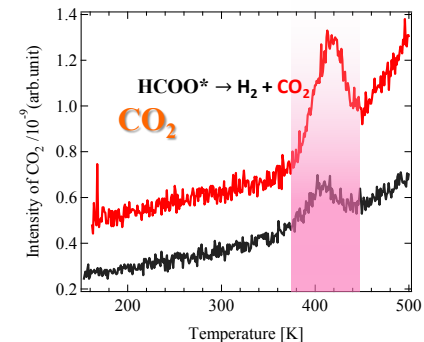
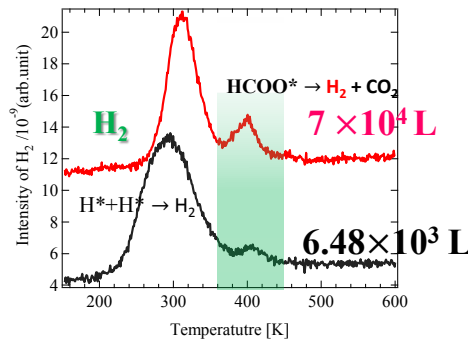
# 分子線実験 1050Kに加熱したCO<sub>2</sub>を150Kに冷却したH/Cu(111)に照射しformateを生成させることに成功した

(1) CO<sub>2</sub> (10% in He) beam:  $T_N = 300$  K, Exposure  $6.48 \times 10^3$  L



$6.48 \times 10^3$  L

(2) CO<sub>2</sub> (10% in He) beam:  $T_N = 1050$  K, Exposure  $6.48 \times 10^3$  L (black) and  $7 \times 10^4$  L (red)

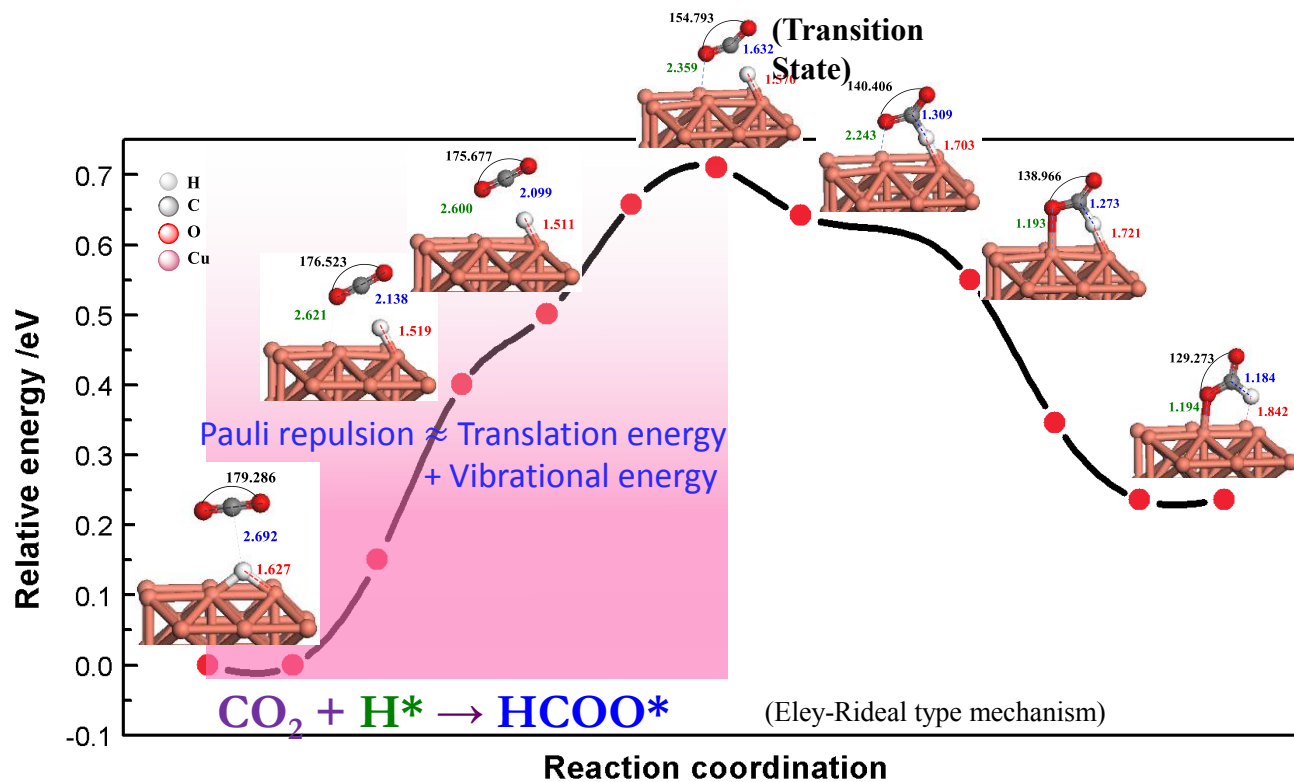


$6.48 \times 10^3$  L

The peaks of CO<sub>2</sub> and H<sub>2</sub> at 412 K result from the formate decomposition!

# DFT calculation

## Reaction path for formate synthesis on Cu(110)



➤ **Translational energy and vibrational energy** is favorable to  $\text{CO}_2$  to overcome the reaction barrier of formate synthesis.

# 講演内容

- ▶ 物質変換材料研究部門の研究内容
- ▶ CO<sub>2</sub>削減用の触媒開発
- ▶ 燃料電池における白金触媒量の削減



# ナノカーボンを用いた白金量の削減

1. ナノカーボンを用いた電極触媒
2. ナノカーボンとPtクラスターの界面相互作用
3. カーボン表面の化学

キーワード: 界面相互作用、Pt 単原子層クラスター、窒素ドーピング、非結合性軌道

Acknowledgment



# Polymer Electrolyte Fuel Cell

## Fuel Cell (ENEFARM)



advantage

- Environmental friendly
- High efficiency of energy conversion

**Problem: Pt is so expensive (40 US\$/g)**

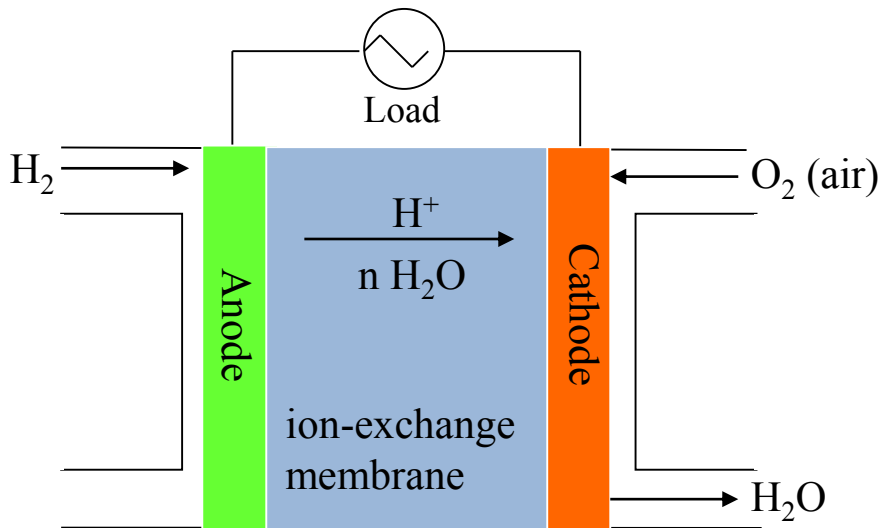
**Challenge:**

**1) Reduction of Pt usage**

→ **Promote catalytic activity of Pt**

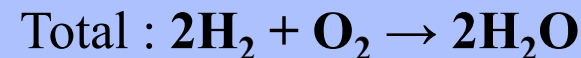
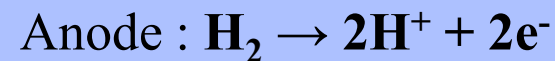
**2) Development of non-Pt catalyst**

## Principle of PEFC

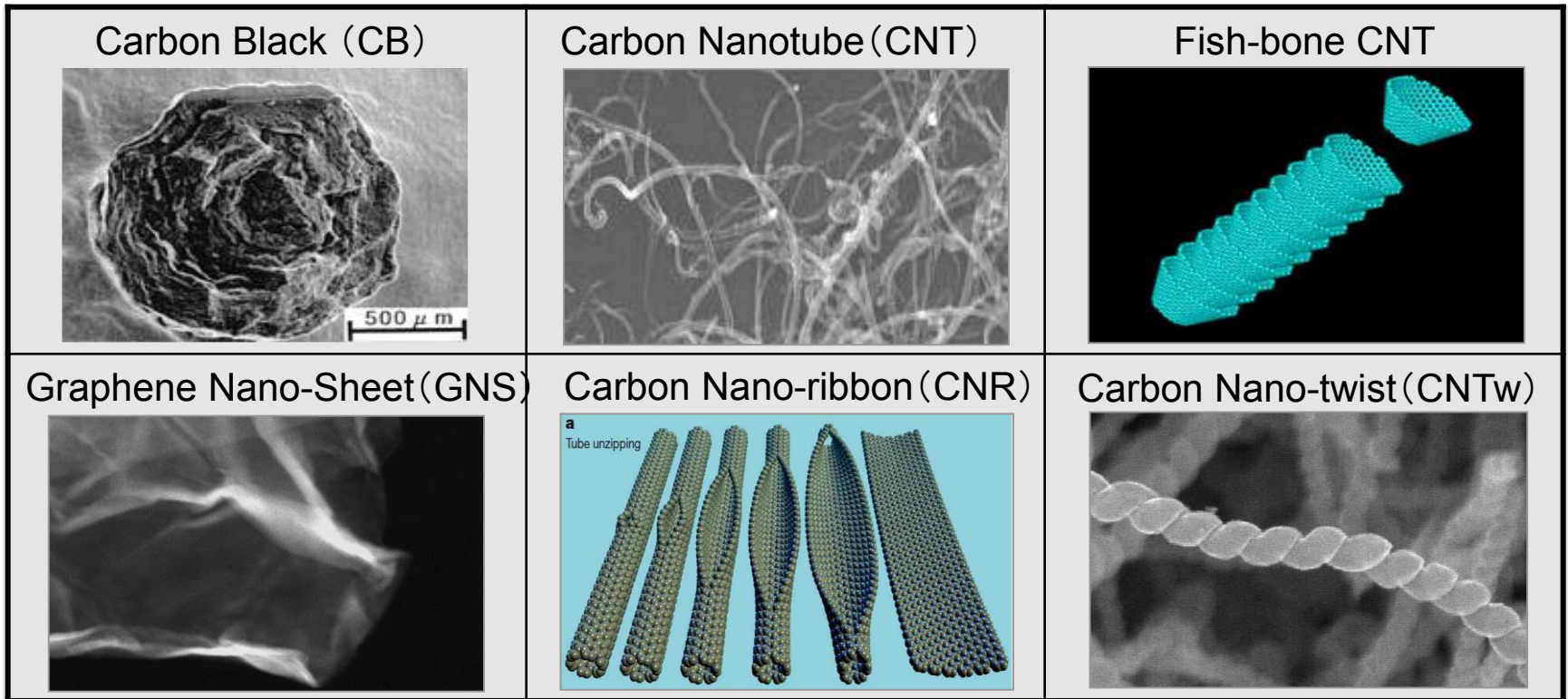


We use

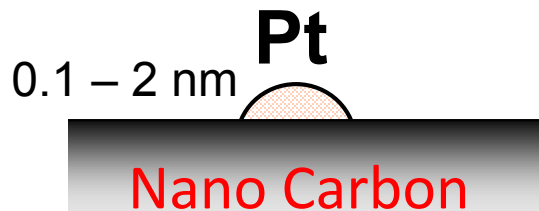
*“Nano carbon materials”*



# Graphitic Nano-carbon Family



**Concept:** Take advantage of Interface interaction between Pt and carbon



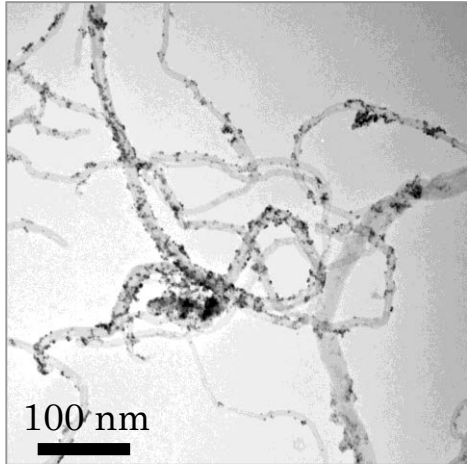
Chemical interaction

→ Modify electronic structure of Pt

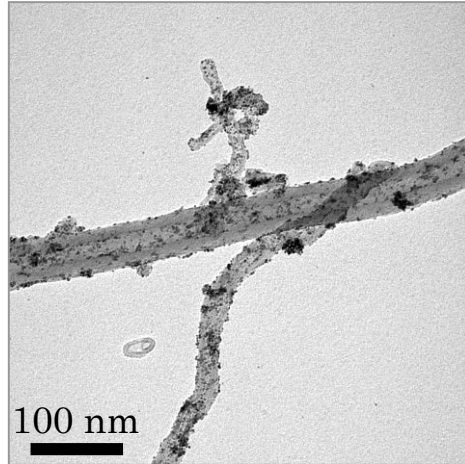
→ Improve activity → Reduce Pt usage

# TEM images of Pt(Ru) / Nano-Carbon

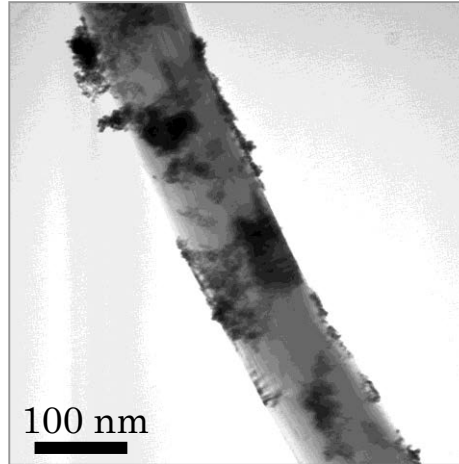
CNT (15 nm $\phi$ )



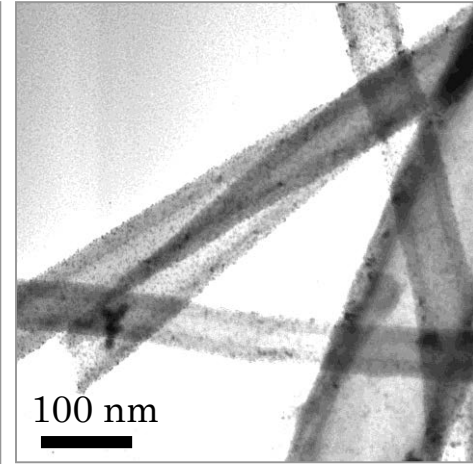
CNT (25 nm $\phi$ )



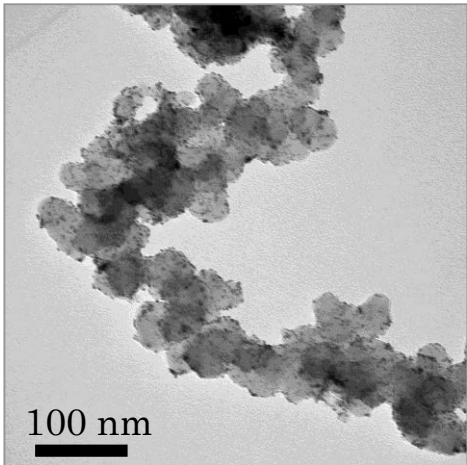
CNT (100 nm $\phi$ )



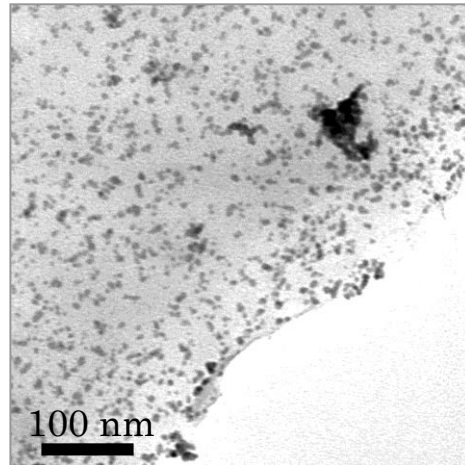
Fish-bone CNT



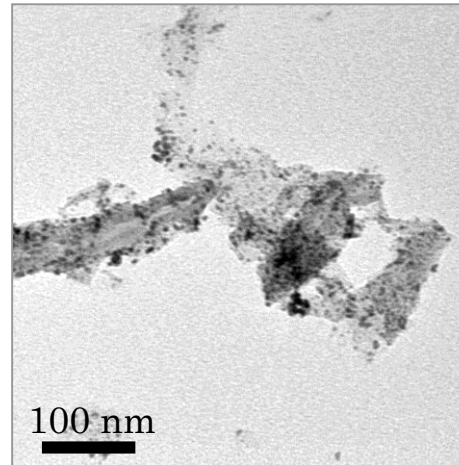
CB



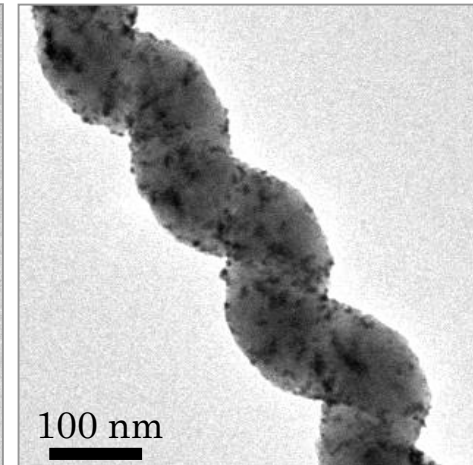
GNS



CNR

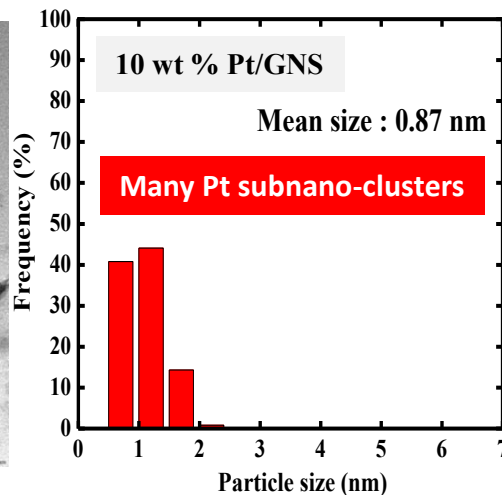
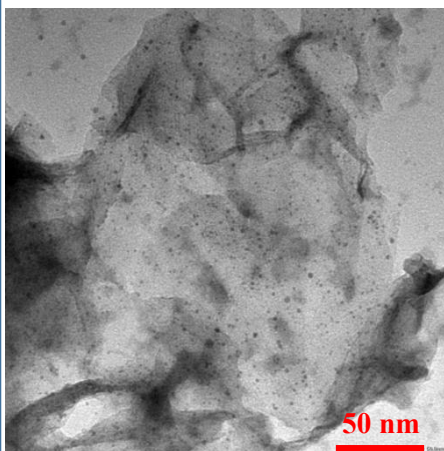


CNTw

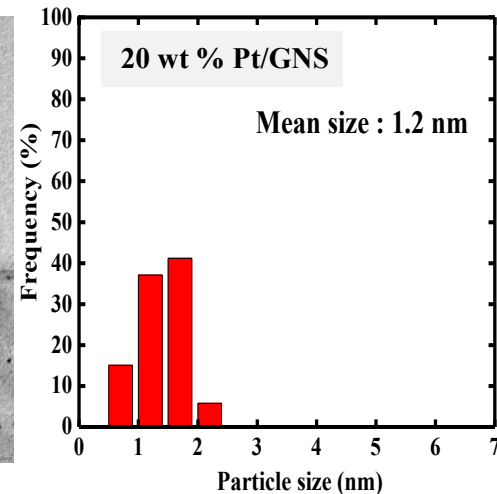
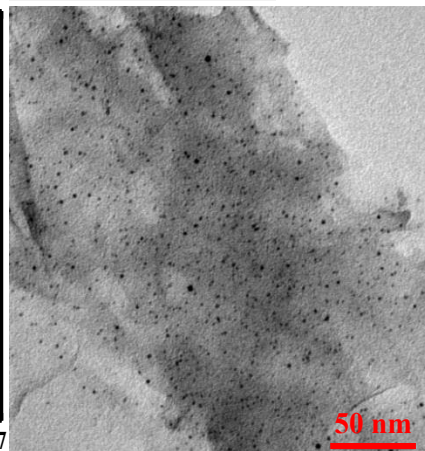


# Pt particle size of 10-70 wt % Pt/GNS by TEM

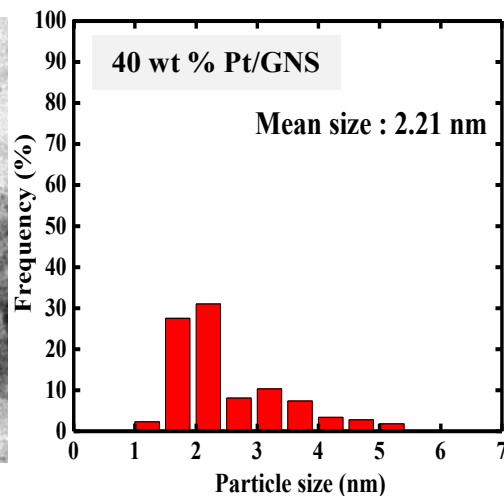
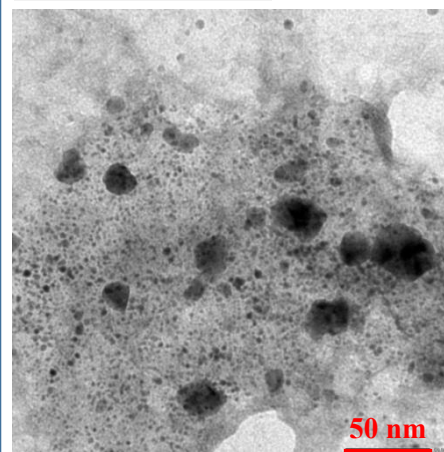
10 wt % Pt/GNS



20 wt % Pt/GNS

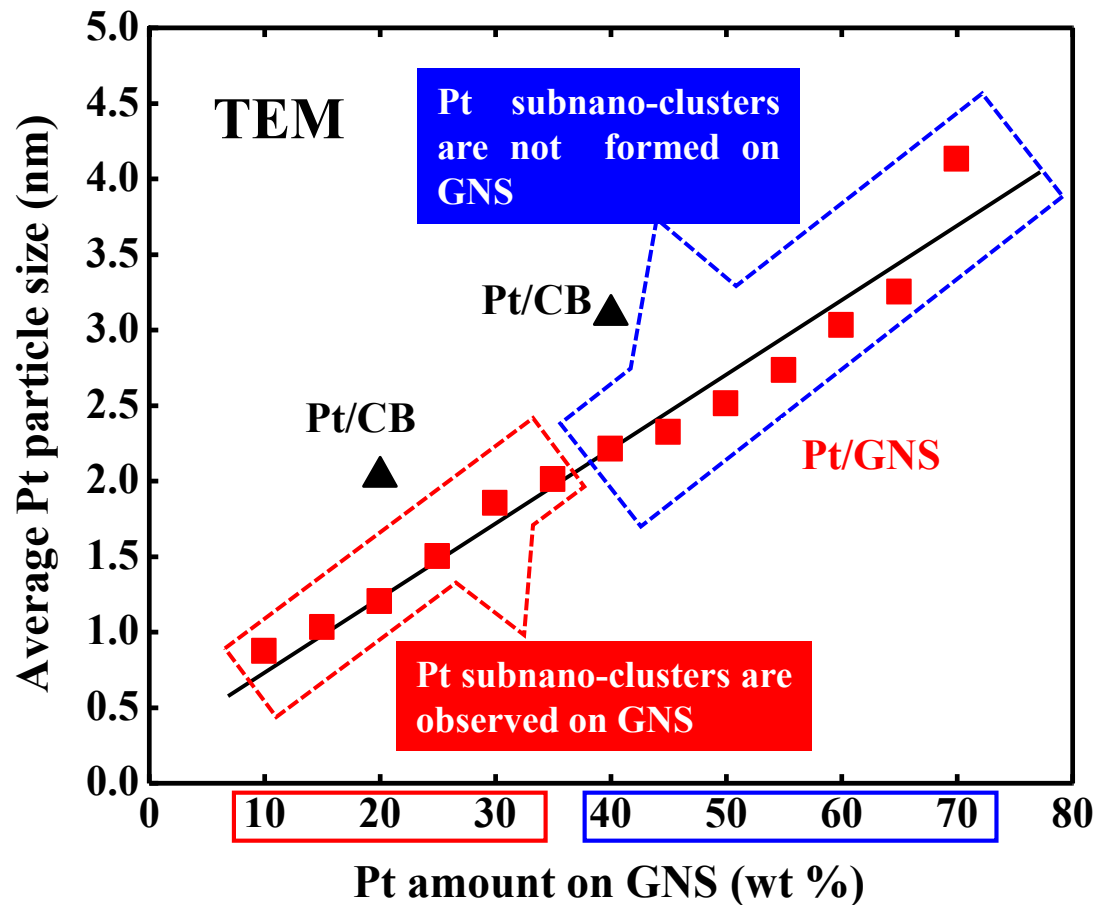


40 wt % Pt/GNS



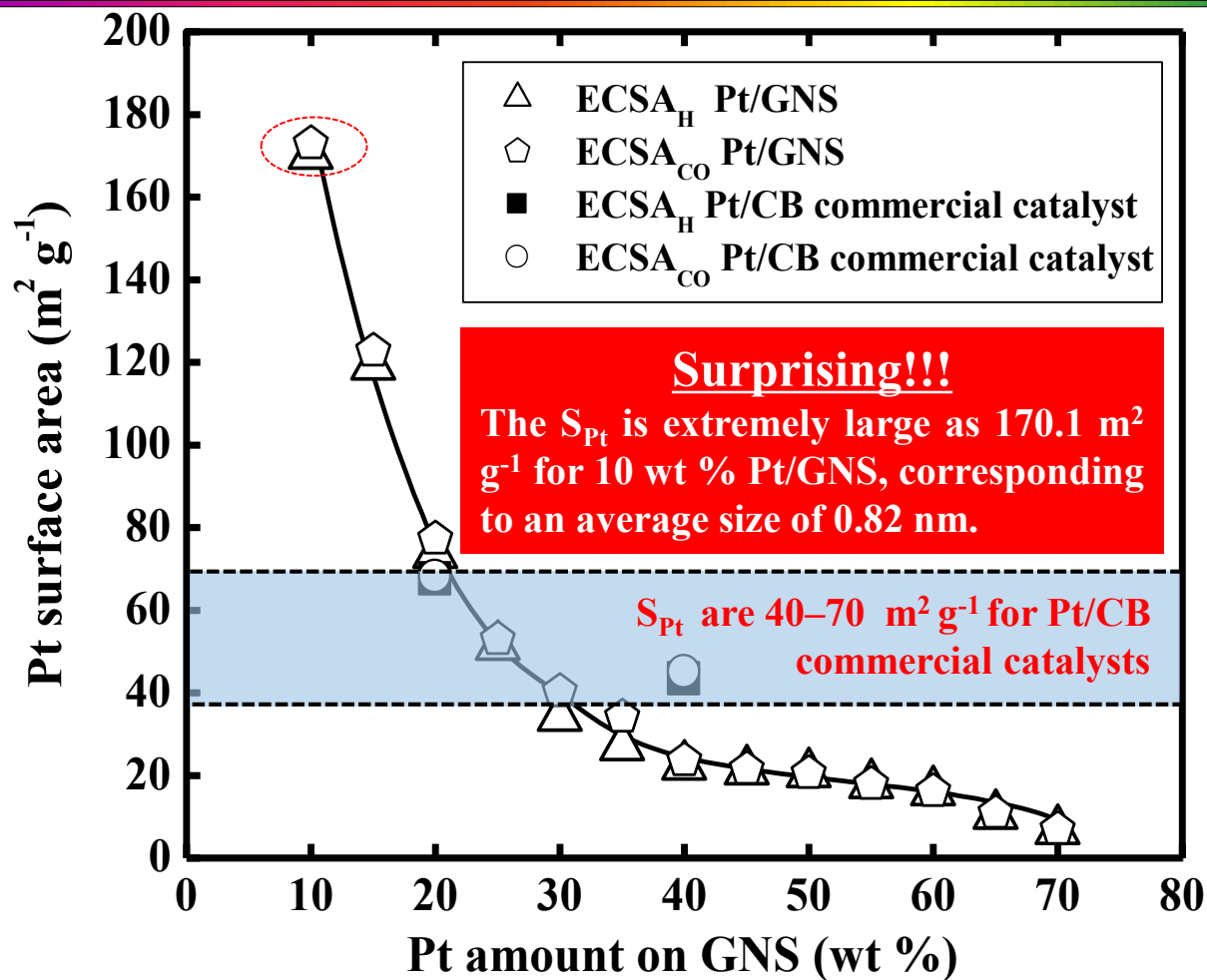
□ For 10 wt % Pt/GNS, many Pt subnano-clusters were formed on GNS.

# Pt particle size of 10-70 wt % Pt/GNS by TEM



The average particle size of Pt linearly increases with increasing Pt amount on GNS

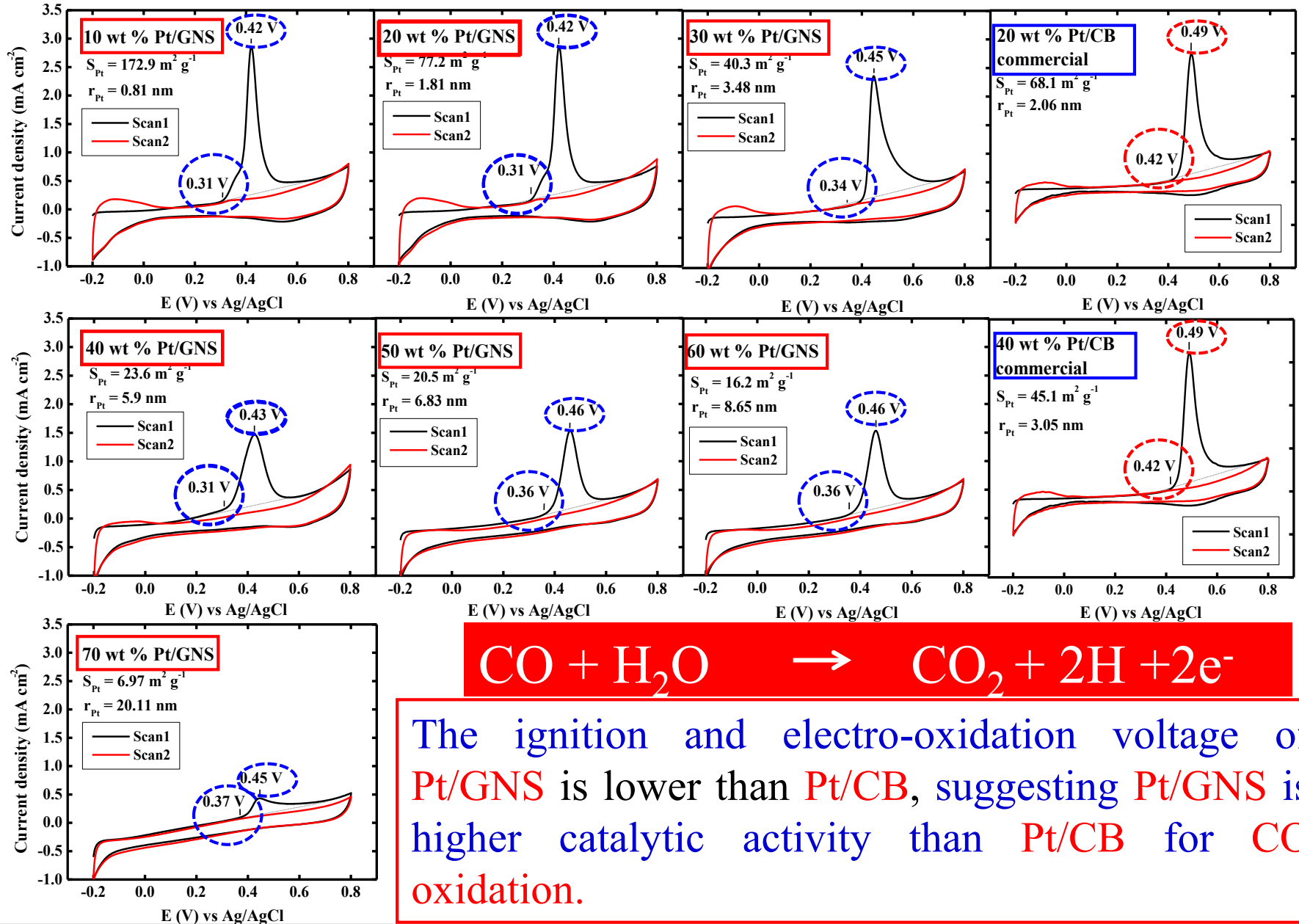
# ECSA of 10-70 wt % Pt/GNS



- If every Pt atom is exposed, the surface area is  $205 \text{ m}^2 \text{ g}^{-1}$ .
- For 10 wt % Pt/GNS, the surface area is  $170 \text{ m}^2 \text{ g}^{-1}$ .
- 83 % of Pt is exposed to gas phase.

The large ECSA of Pt subnano-clusters is promising as a cost-effective Pt catalyst.

# CO-stripping for 10-70 wt % Pt/GNS (catalytic activity)

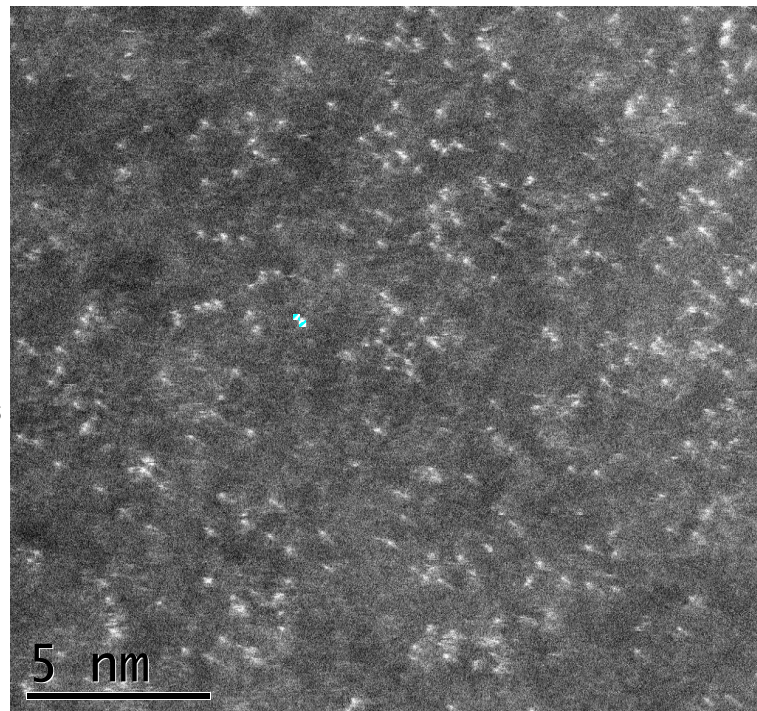
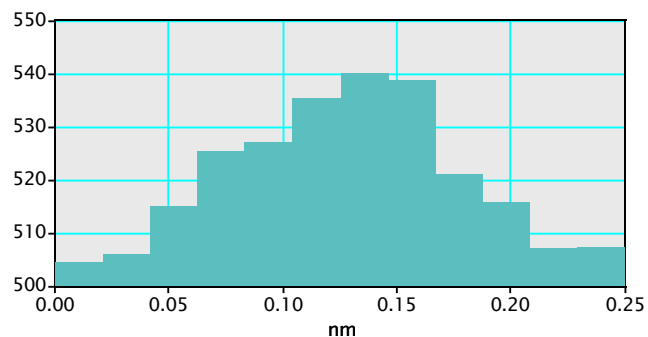




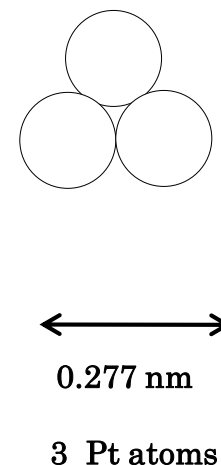
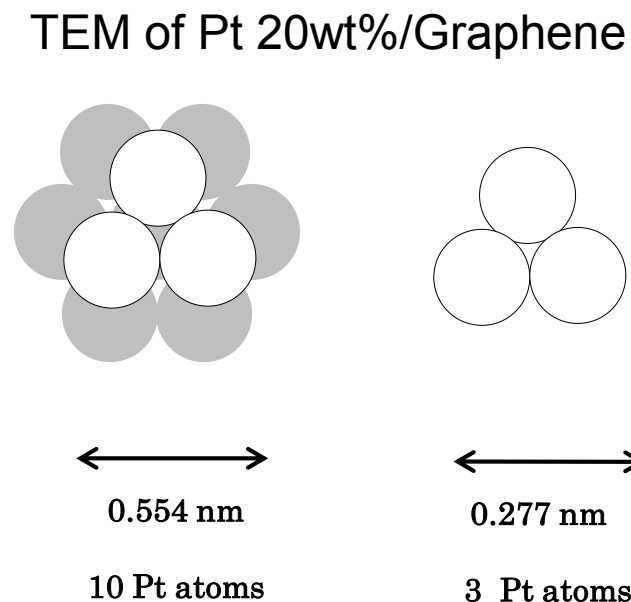
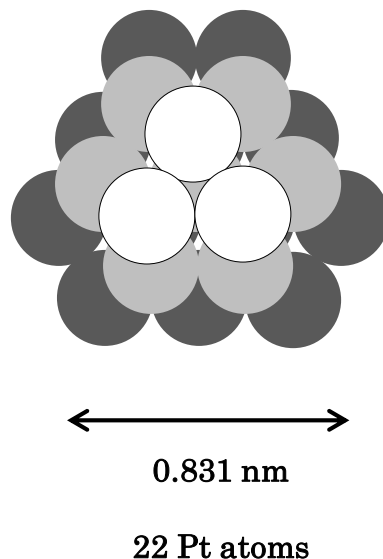
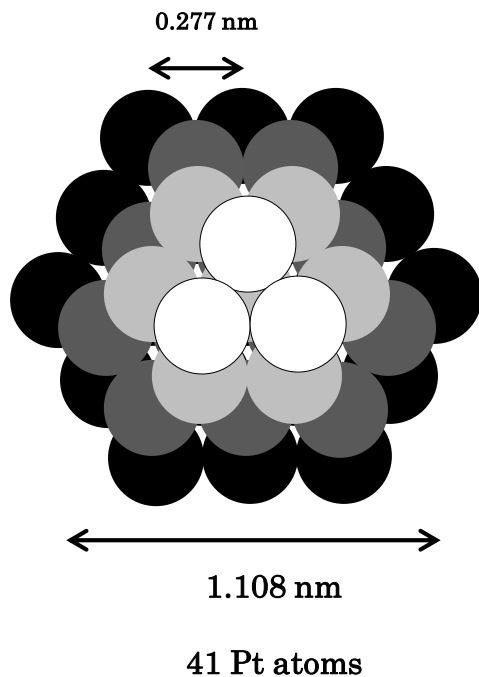
# Graphene supported Pt catalyst

*Very small !!*

*Strong interaction*



Sub-nano Pt Clusters are formed  
(1- 10 atoms)



TEM of Pt 20wt%/Graphene

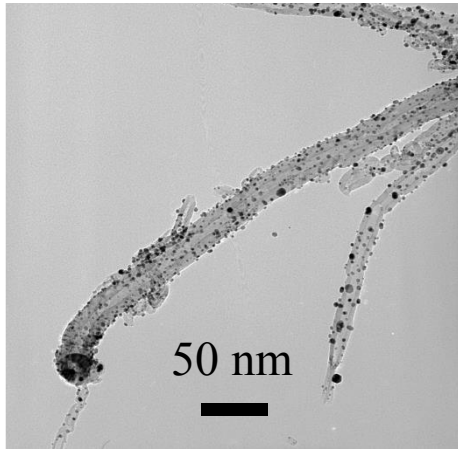
# Message 1

Usage of Pt (40 US\$/g) can be  
reduced by using CNTs (10 US ¢ /g)  
or GNS

# Reduction of Pt usage in fuel cells by using nano-carbons

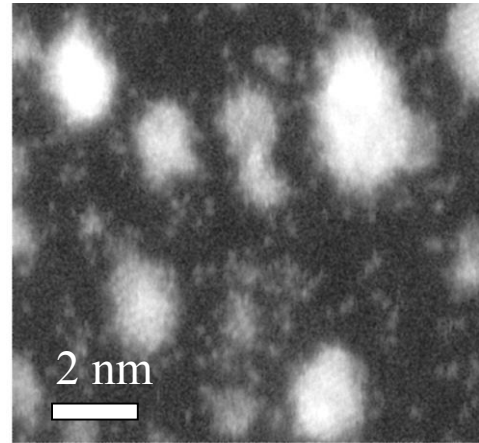
Carbon nanotube and Graphene are superior support materials

Pt/MWCNT



Activity is promoted

Pt/Graphene



Sub-nano Pt clusters are formed

## Why superior ?

Consists of **FLAT surface** of graphene sheets

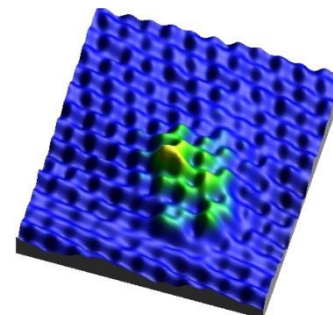
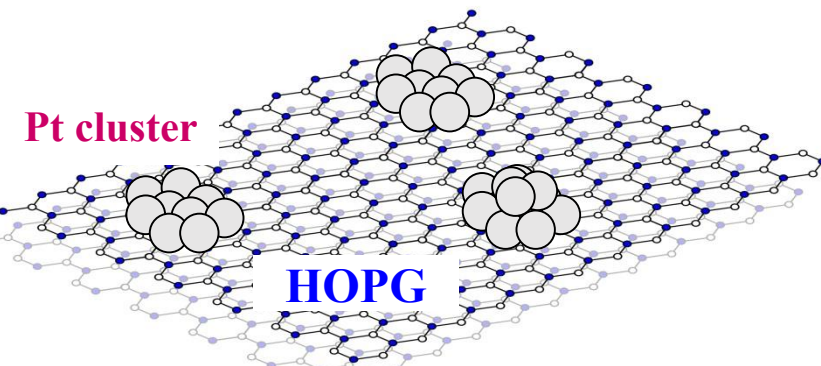
- Superior electronic conductivity
- Chemically stable (anticorrosion)
- **Pt-graphite interface interaction**

J. Nakamura et al., Chem.Commun. (2004)

J. Nakamura et al.,  
Nano Letters 9 (2009) 2255.

# Surface science studies to clarify carbon support effect

Model catalyst : **Pt / HOPG**



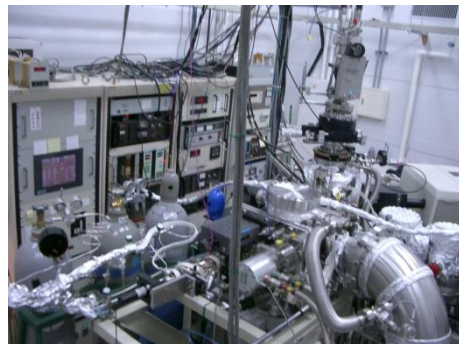
STM image

**Pt monolayer clusters** are formed, which are very active for H<sub>2</sub>-D<sub>2</sub> exchange reaction.

CO desorb from Pt at very low temperature as 270 K

# Experiments

## (1) Molecular beam scattering apparatus



He scattering

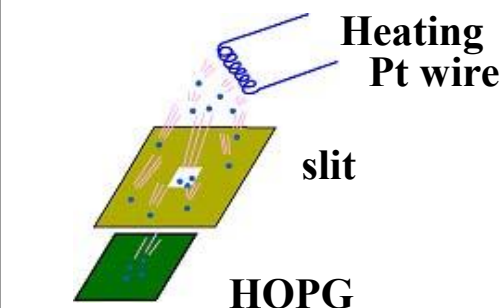
Monitor morphological change of Pt cluster

CO-TPD

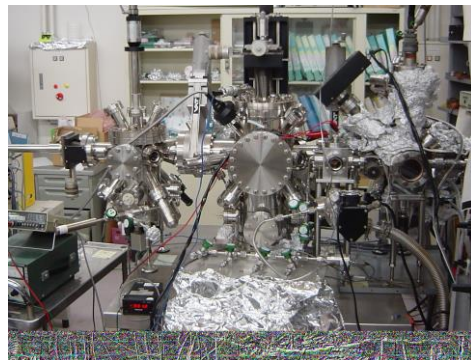
with He scattering at the same time

CO adsorption energy vs Pt morphology

Pt deposition at RT in UHV



## (2) UHV-STM with high pressure reactor cell



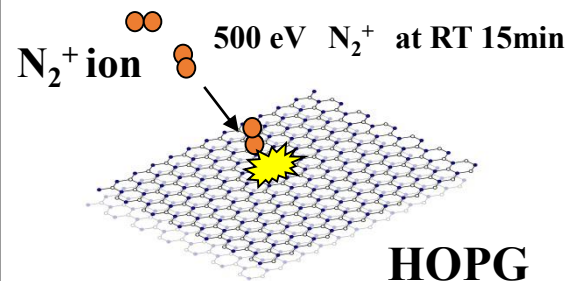
High Pressure Reactor

Measure catalytic activity of Pt/HOPG  
for HD exchange rxn at 12 Torr

STM

Observe atomic structure of  
Pt cluster before and after rxn

Sputtering by  $\text{Ar}^+$  or  $\text{N}_2^+$



## (3) Low temperature STM and STS



STS at 5K

Measure electronic state of local site

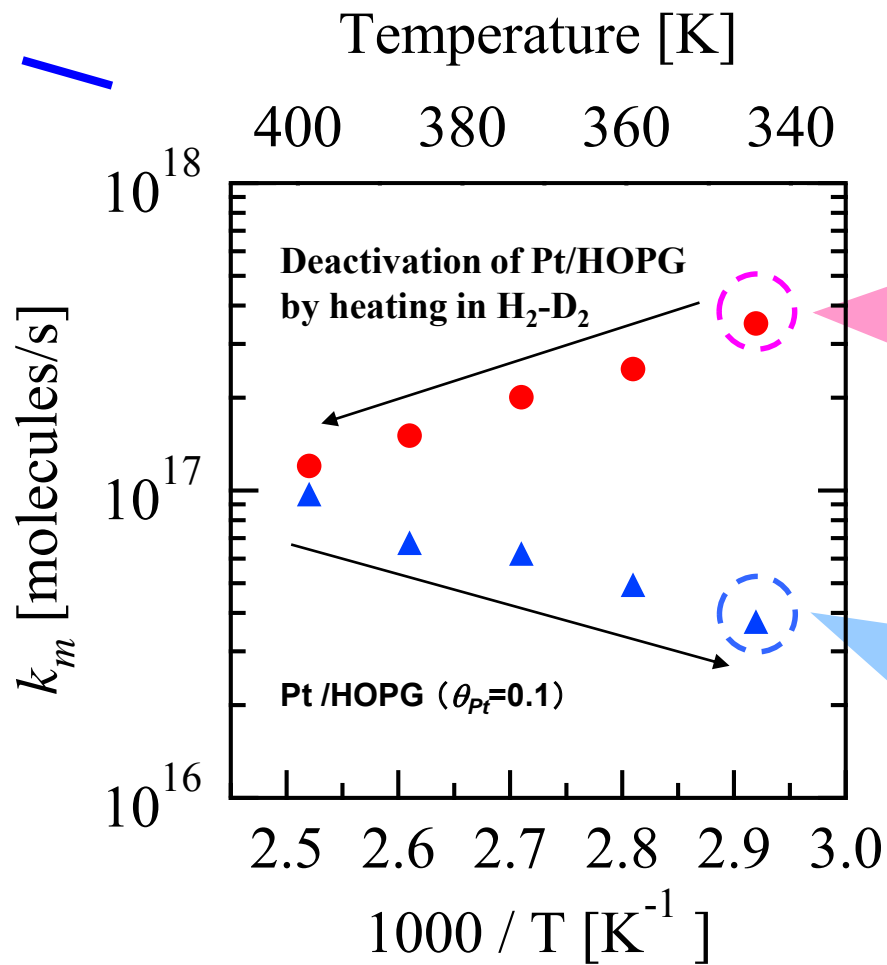
## (4) X-ray photoelectron spectroscopy

Measure core level of Pt cluster

## (5) RBS facility in Univ. Tsukuba

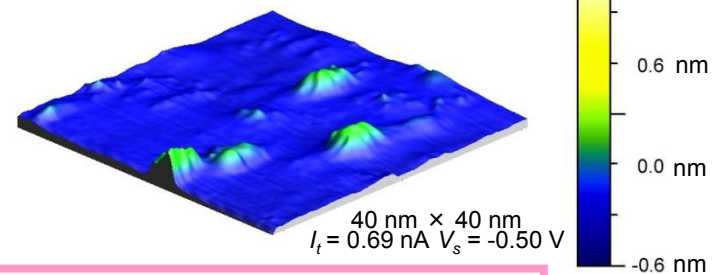
Determine Pt coverage

# Catalytic activity and morphology of Pt / HOPG



Active Pt

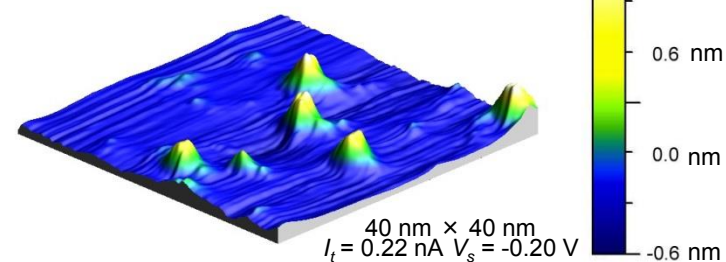
Flat cluster



1~2 atomic heights

Normal Pt

Taller cluster

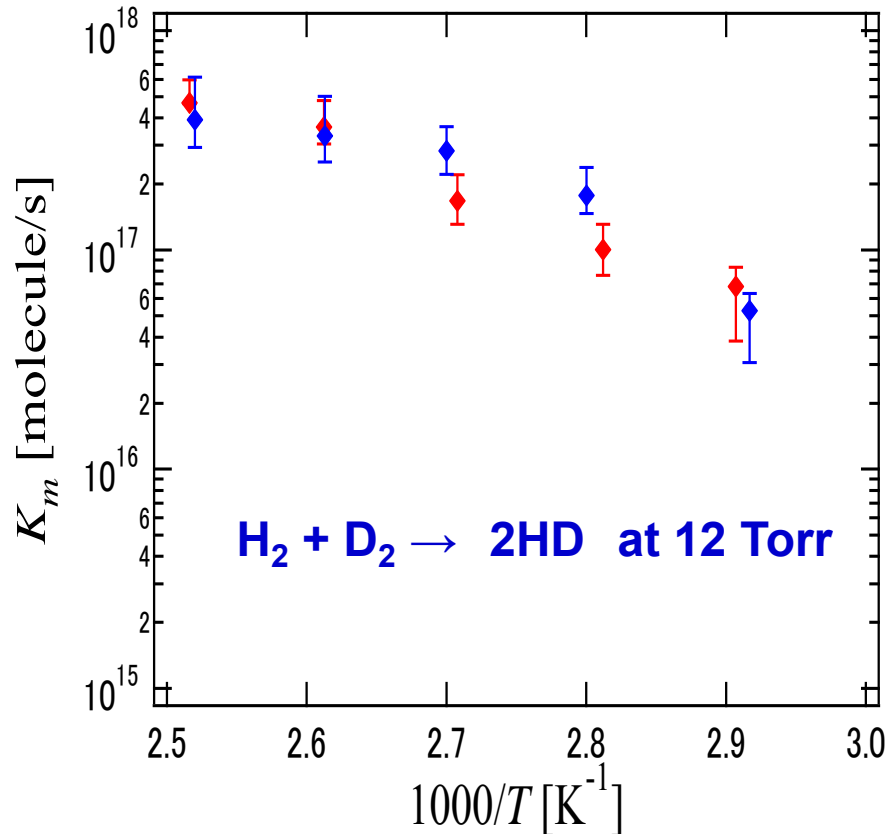


More than 3 atomic heights

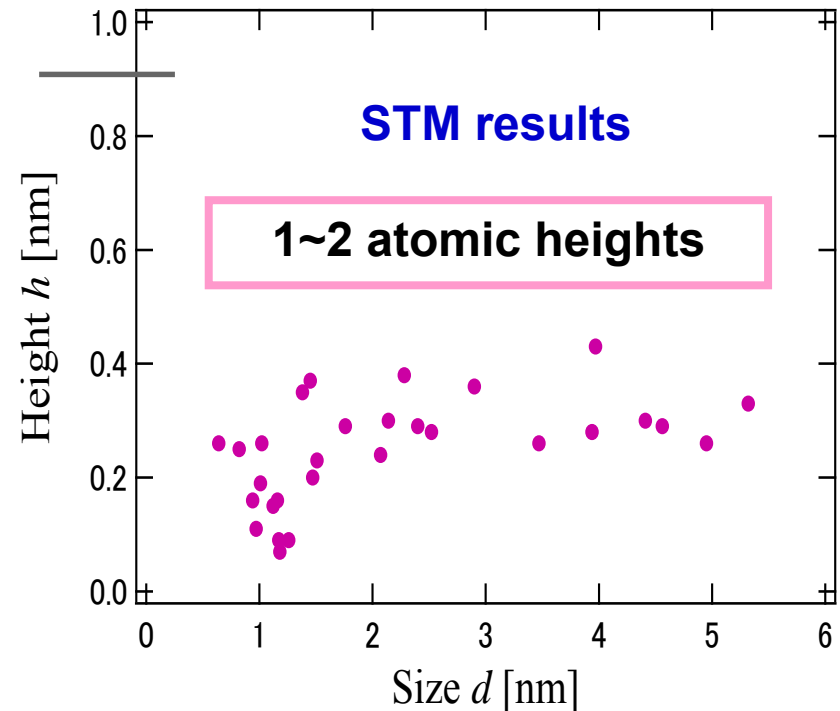
# H<sub>2</sub>-D<sub>2</sub> exchange reaction on Pt/ N-sputtered HOPG

No hysteresis is observed

Catalytic activity of Pt clusters



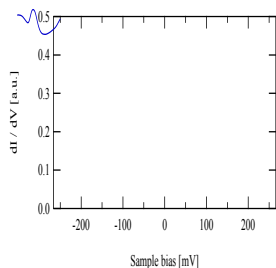
Height and size of Pt clusters



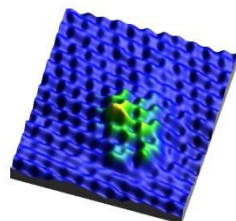
**Flat Pt clusters are stabilized on sputtered HOPG**  
**Interface interaction is significant**

# The origin of the promotion is due to the interface interaction between Pt and sp<sup>2</sup> carbon

New carbon electronic state (non-bonding state) was found by STS (Evidence of Pt-C hybridization)

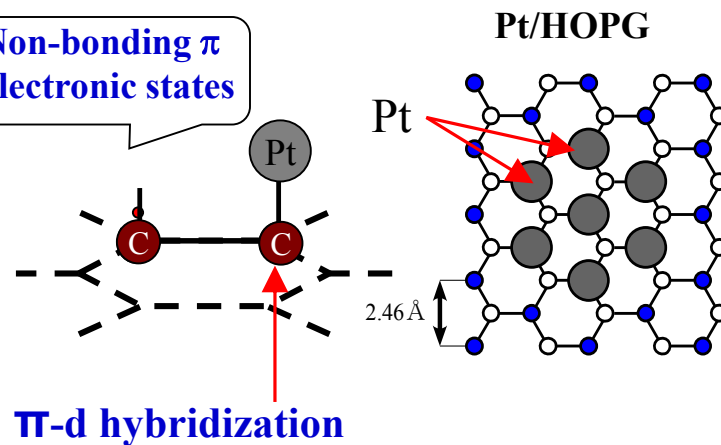


STS peak near  $E_f$  in the vicinity of a Pt cluster on HOPG



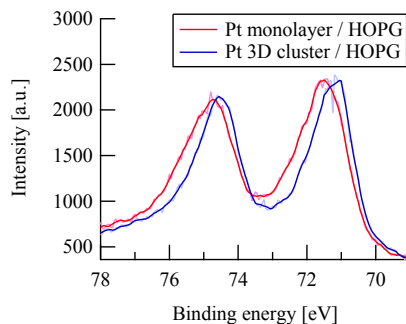
## Schematic of Pt cluster on HOPG

Non-bonding  $\pi$  electronic states



Proposed model for the promotion of Pt catalyst

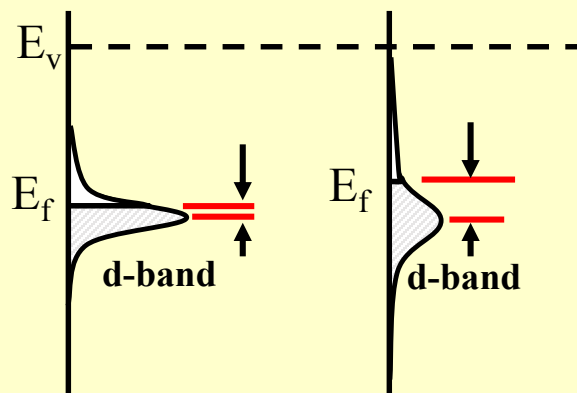
d-band center shift away from  $E_f$  by the  $\pi$ -d hybridization



XPS peak shift suggest the d-center shift

Lower adsorption energy of molecules on Pt

- $k_m$  of  $H_2$ - $D_2$  reaction increase !
- $E_a$  of CO on Pt decrease !



Pt/HOPG

Active Pt/HOPG (monolayer Pt cluster)

T. Kondo, J. Nakamura, et al., J. Phys. Chem. C **112** (2008) 15607

T. Kondo, J. Nakamura et al., Phys. Rev. B **80** (2009) 233408.

J. Oh, T. Kondo, J. Nakamura et al., J. Phys. Chem. Lett. **1** (2010) 463.

# Message 2

Carbon can change Pt

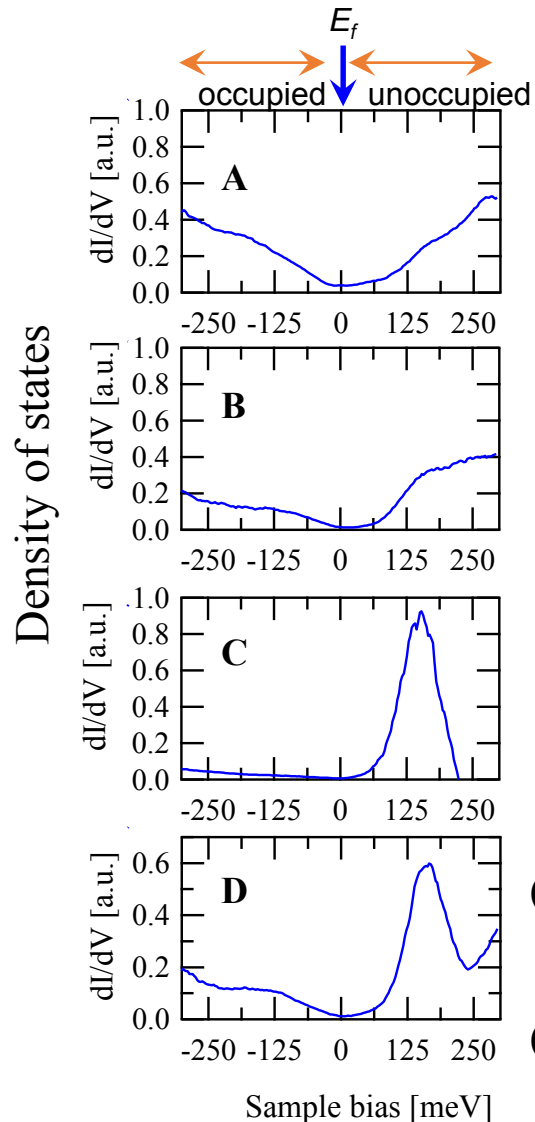
in terms of **electronic structure**

by **the interface interaction**

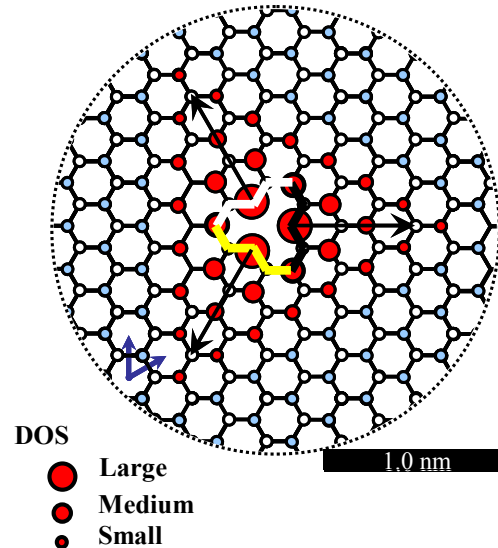
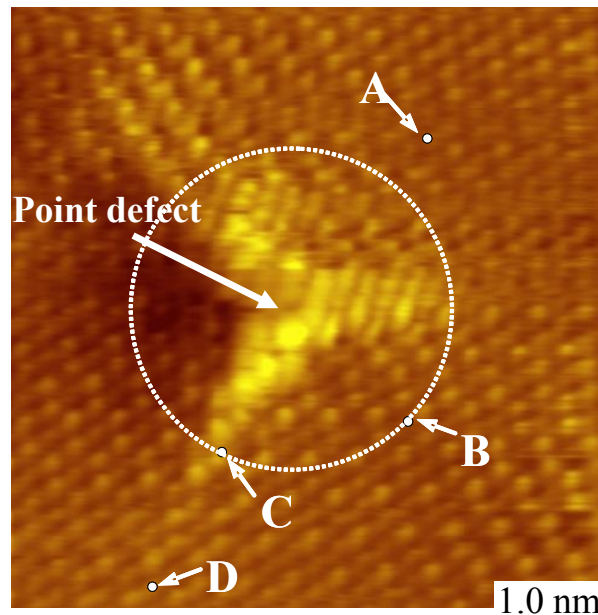


# STS measurements around a point defect

## Localized electronic state near $E_f$ propagating from a point defect



Non-bonding state formed by re-hybridization of  $\pi$  orbital, ( $p_z$  orbital)

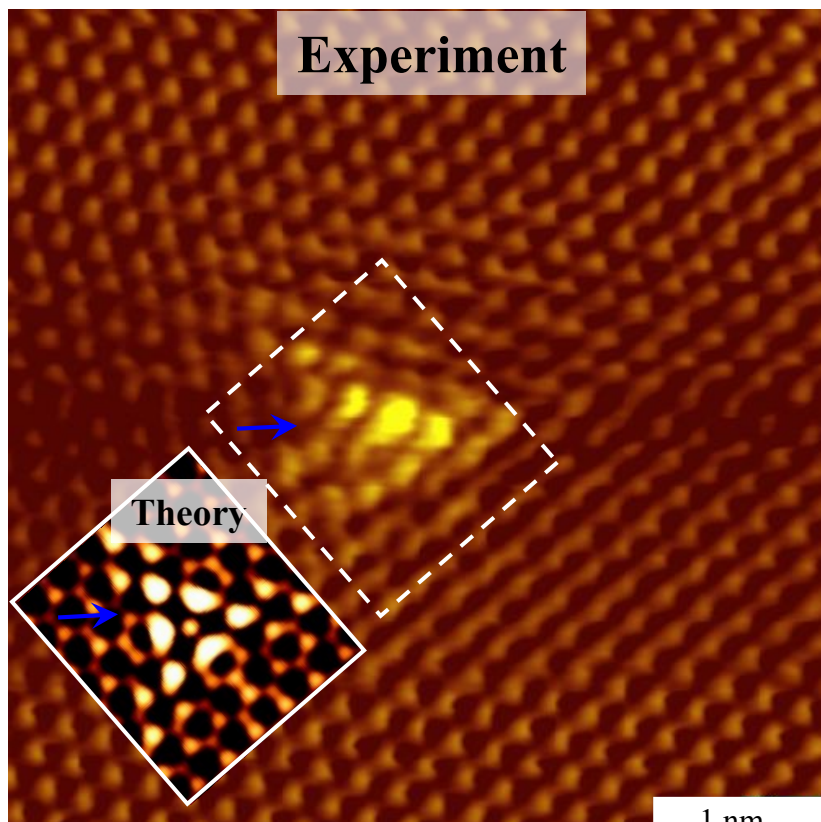


## Characteristics

- (1) Non-uniform propagation perpendicular to a small edge at the defect, **Edge state**, **Anisotropic propagation**
- (2) Appearing at unoccupied state

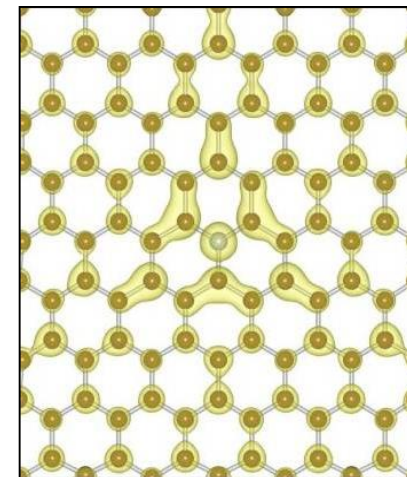
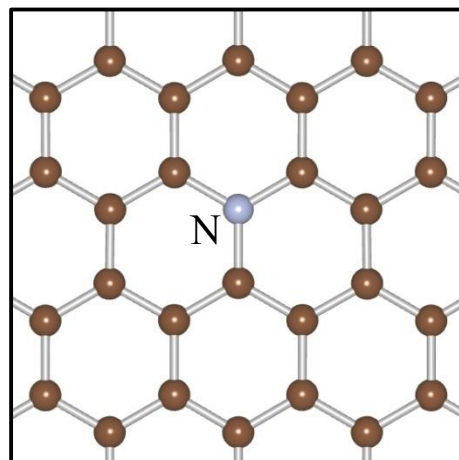
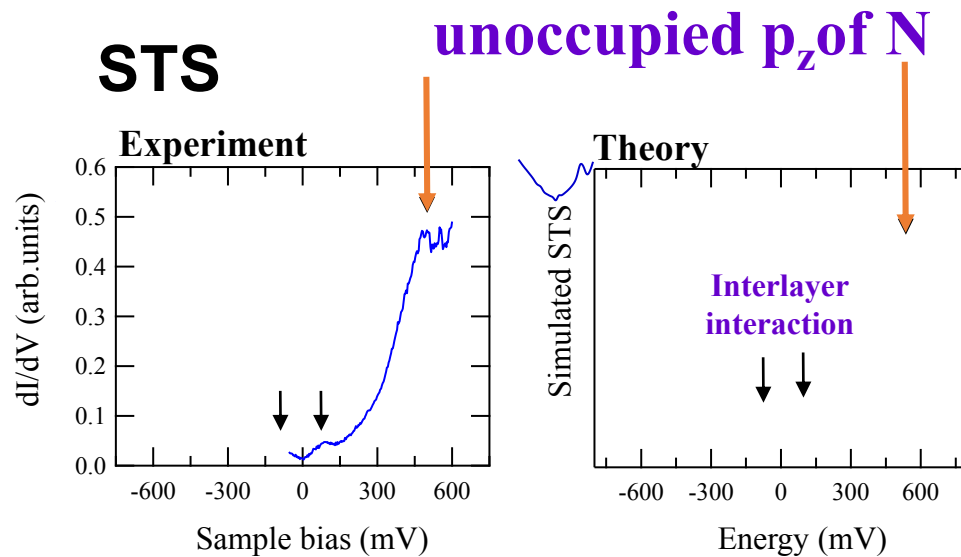
# STM & STS for N-doped HOPG: **graphitic N**

## STM image



Scan Size  $5 \times 5 \text{ nm}^2$   
 $I_t = 40 \text{ pA}$ ,  $V_s = +500 \text{ mV}$

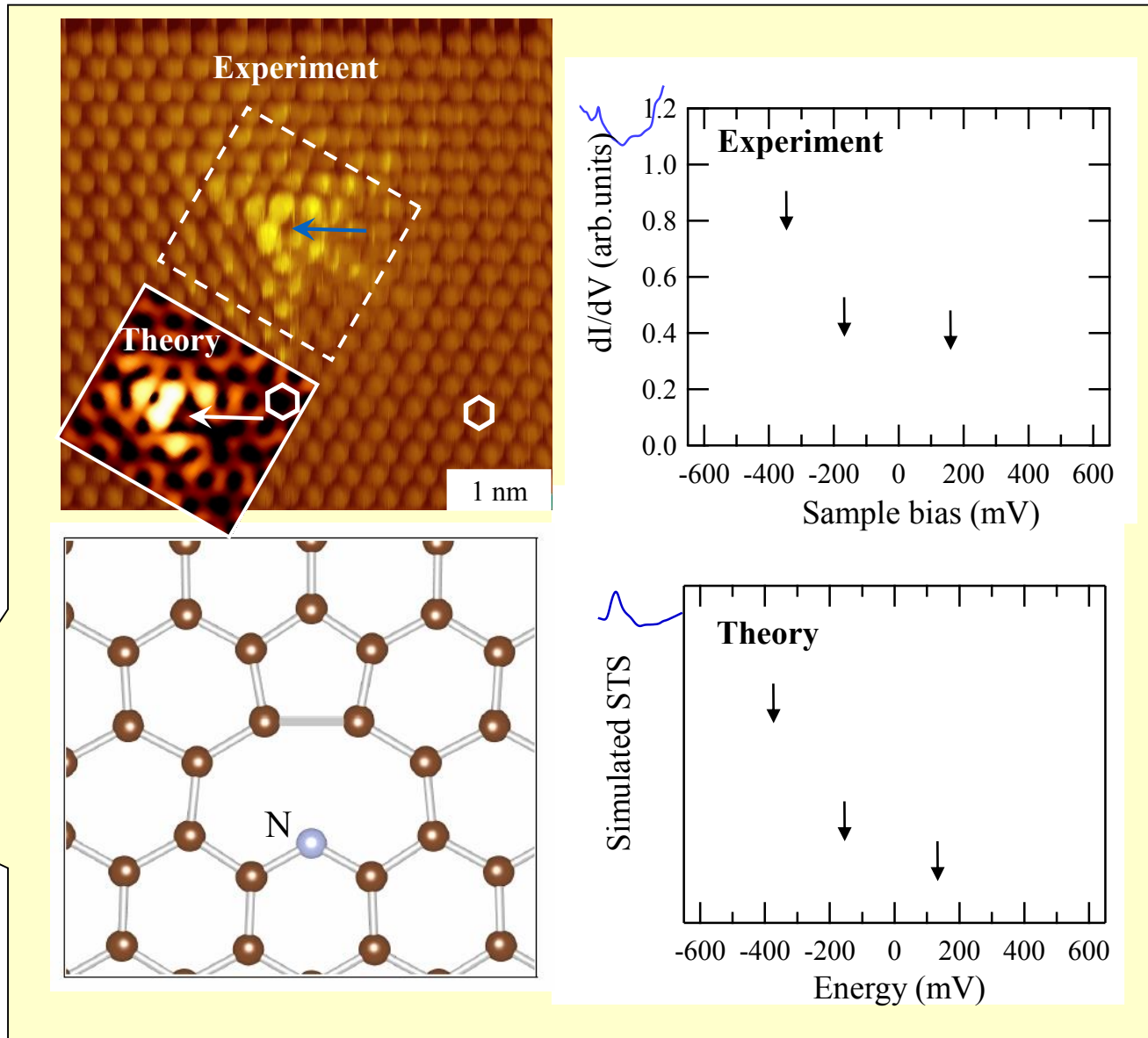
## STS



Calculated electron density

**Assignment based on STS and DFT**

# Pyridinic-N + vacancy



**Assignment based on STS and DFT**

# Message 3

Non-bonding states propagate from point defects or doped nitrogen atoms.

Atoms, molecules, and clusters will be interacted with the sites.

# 無磁場下で発現するランダウレベル

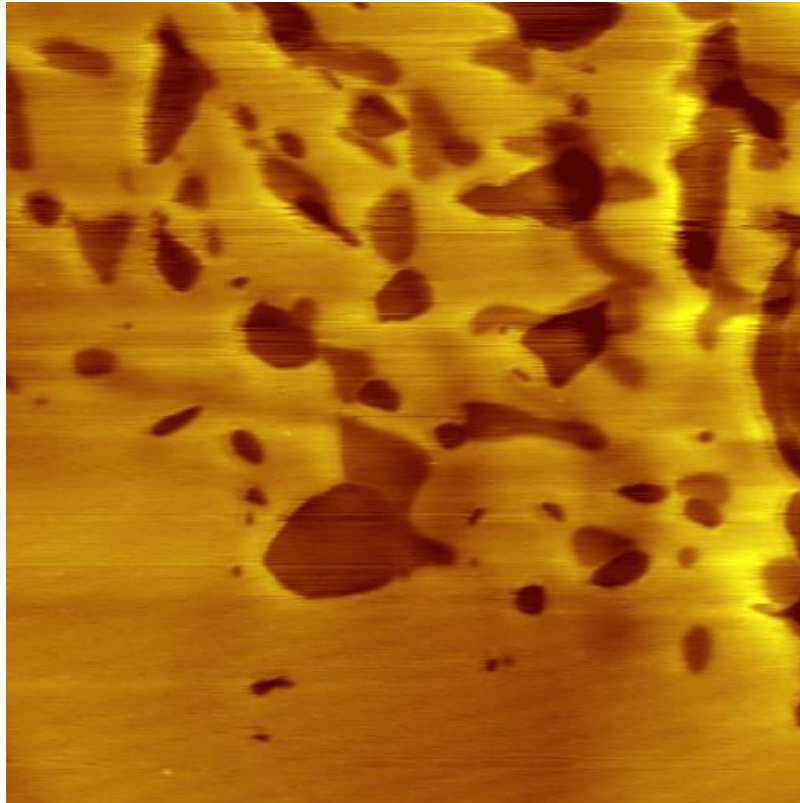
Nature Communications (2012)

K/ HOPG表面 のSTS

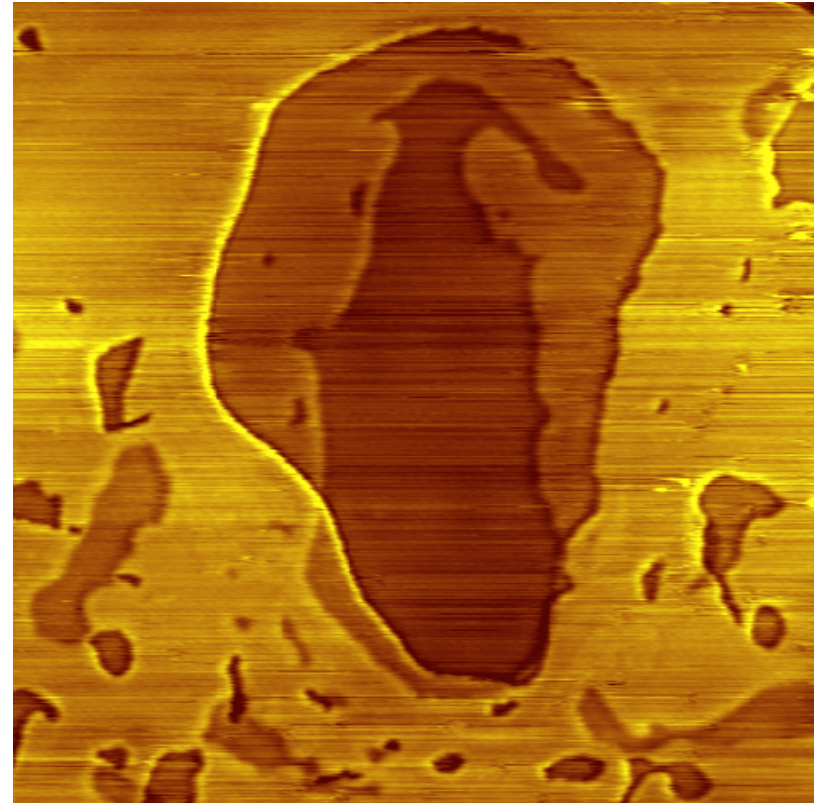
(Scanning Tunneling Spectroscopy)

# Potassium intercalated graphite

Large amounts of potassium (corresponding to over 10 ML)



-100 mV, 2.0 nA,  $150 \times 150 \text{ nm}^2$  4.6 K

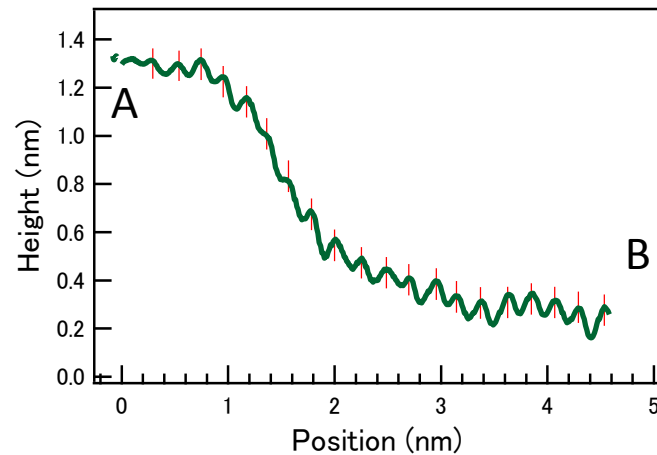
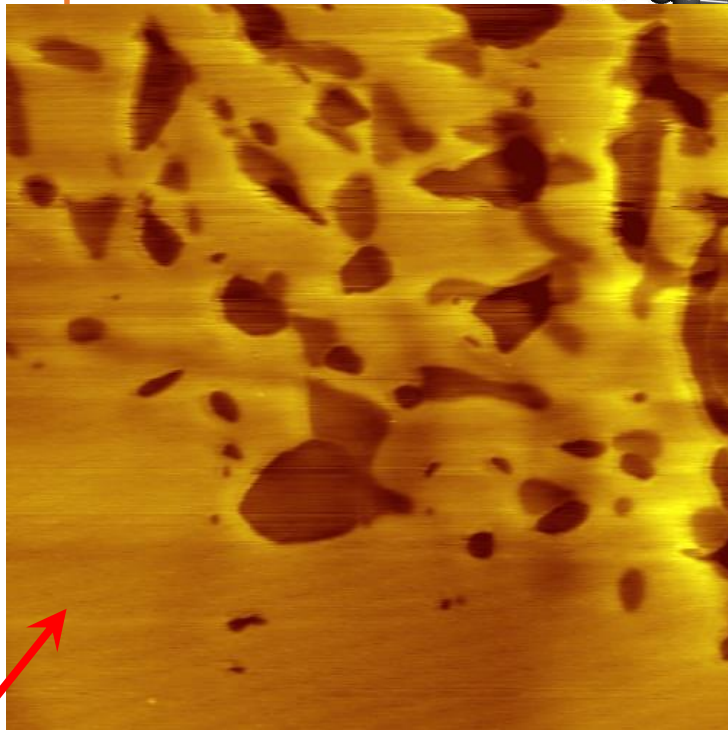
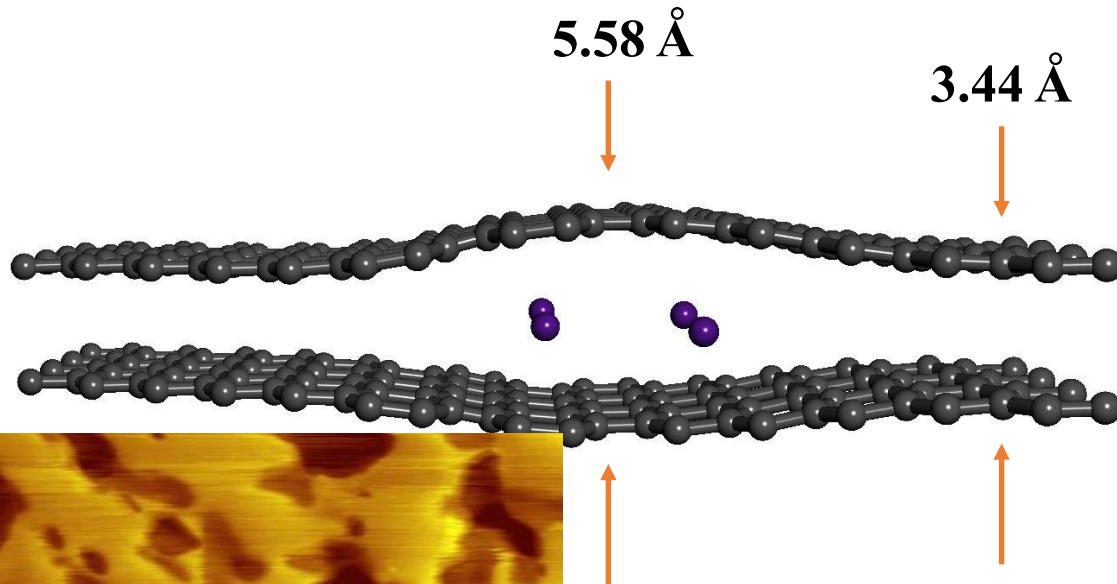


-90 mV, 2.2 nA,  $200 \times 200 \text{ nm}^2$  4.6 K

**Irregular domains with overlapping feature  
suggesting subsurface information**

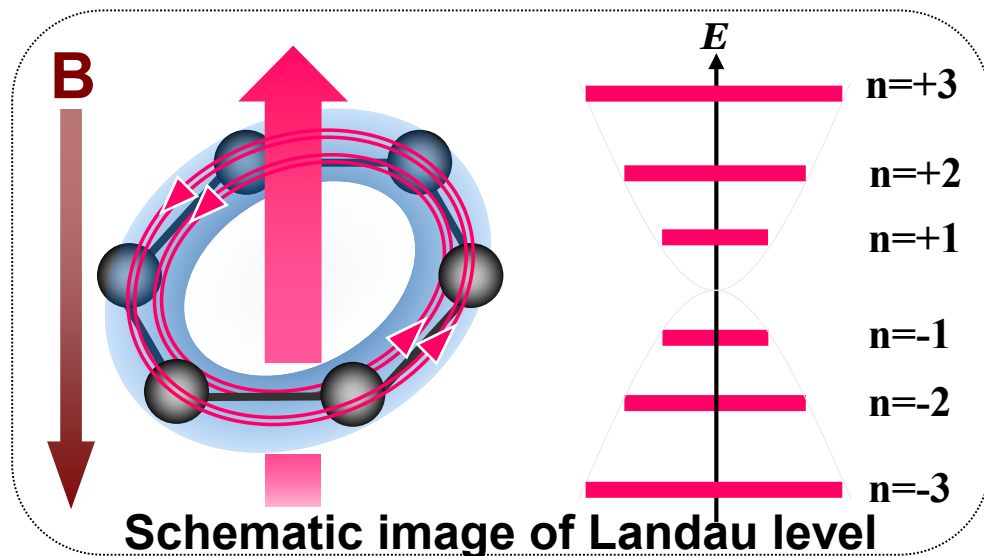
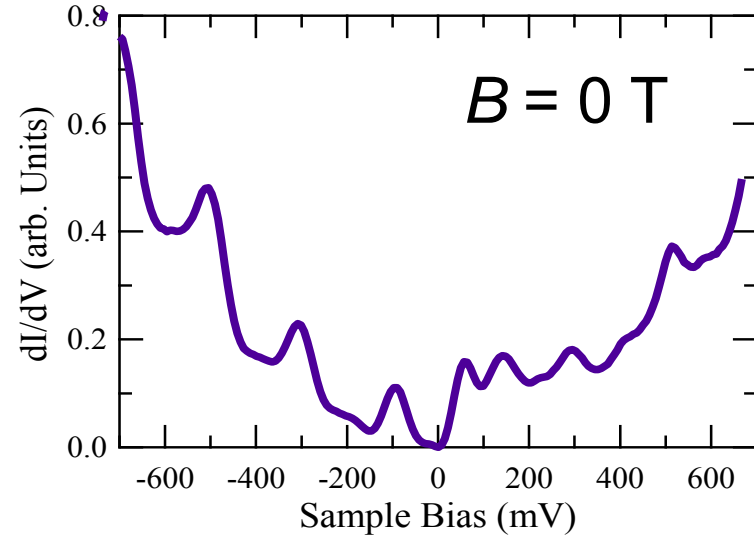
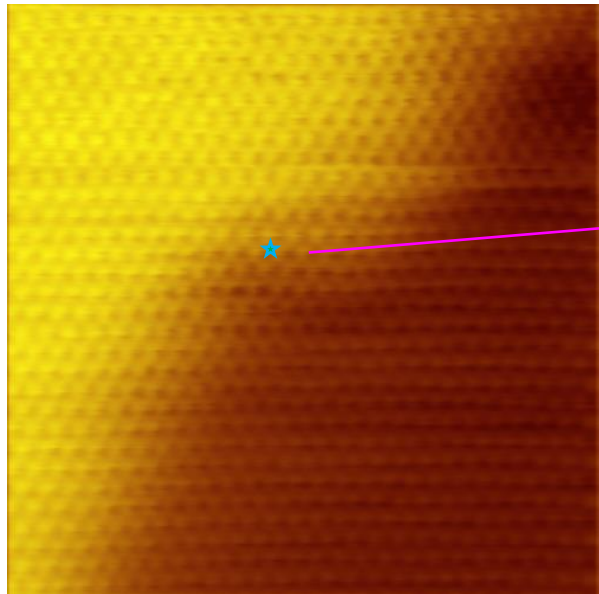
**Those should be due to K-presence and K-absence domains**

# DFT calculations

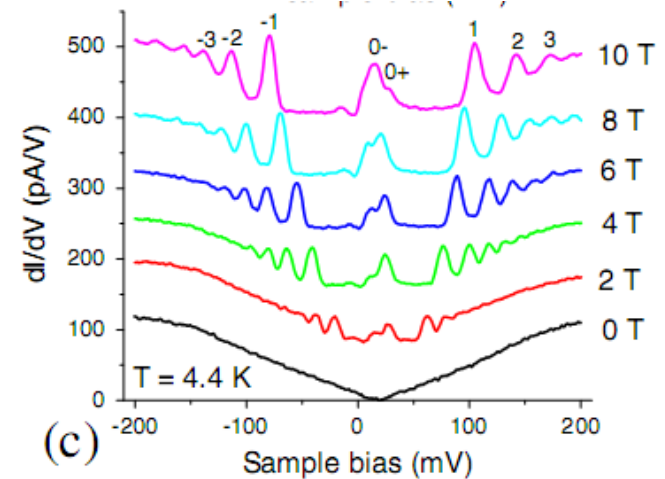


Potassium atoms are intercalated at the bright area

# STS on Potassium intercalated graphite



Similar to Landau level peaks

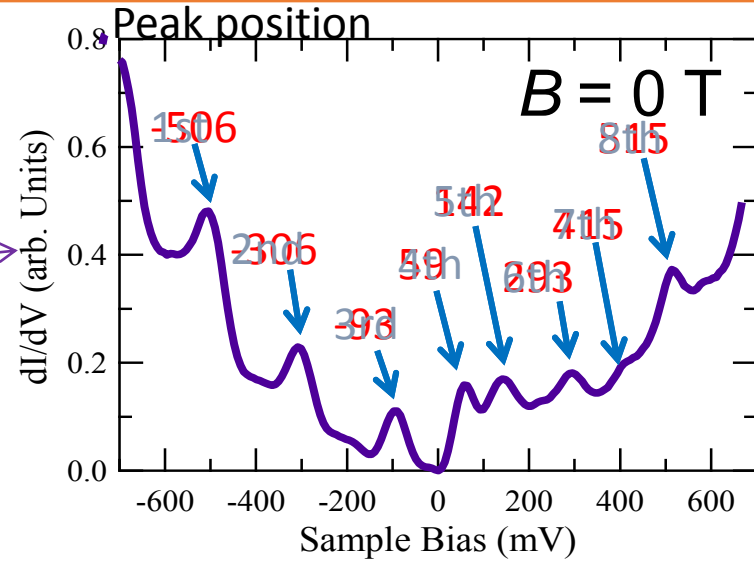
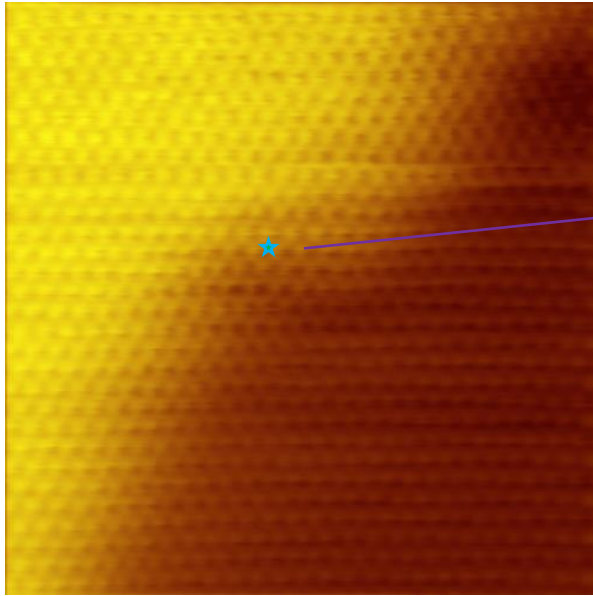


STS of Graphene on graphite under magnetic field

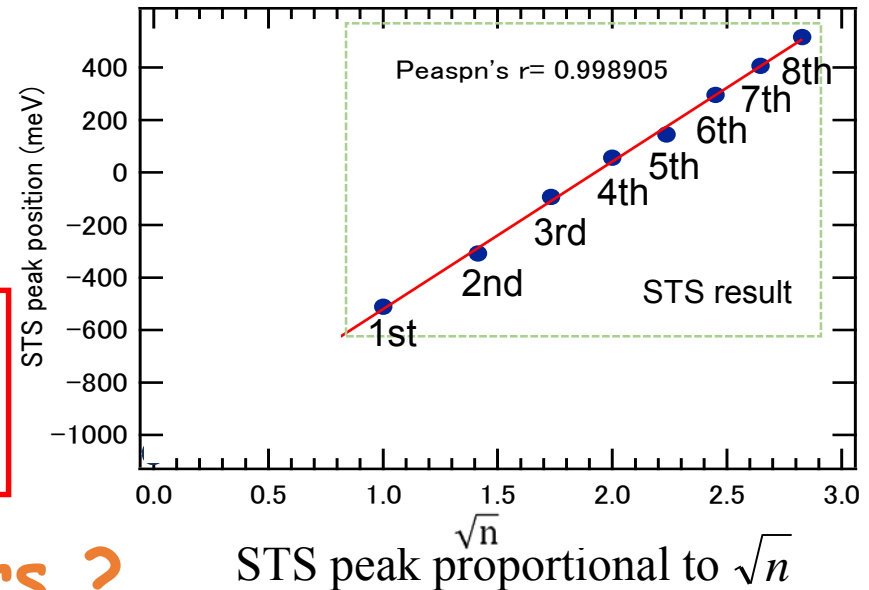
Li, *et al.* Phys Rev Lett 102 (2009) 176804



# Peak energy vs $\sqrt{n}$ : Dirac fermion



Peak energy against  $\sqrt{n}$



$$\omega_c = \sqrt{\frac{2ev_F^2 B_s}{\hbar}}$$

$$E_n = \text{sgn}(n)\hbar\omega_c\sqrt{|n|} + E_{\text{Dirac}}$$

Similar to the Landau level of graphene (Dirac fermion)

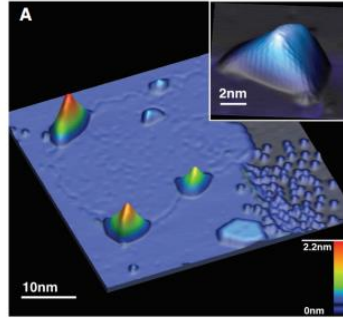
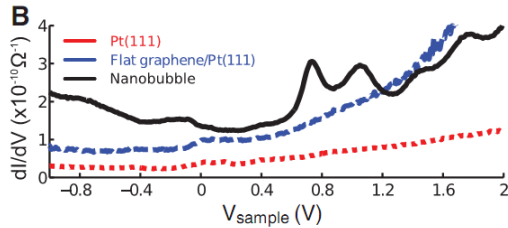
Graphene character appears ?

STS peak proportional to  $\sqrt{n}$

# Mechanism of the pseudo-magnetic field formation

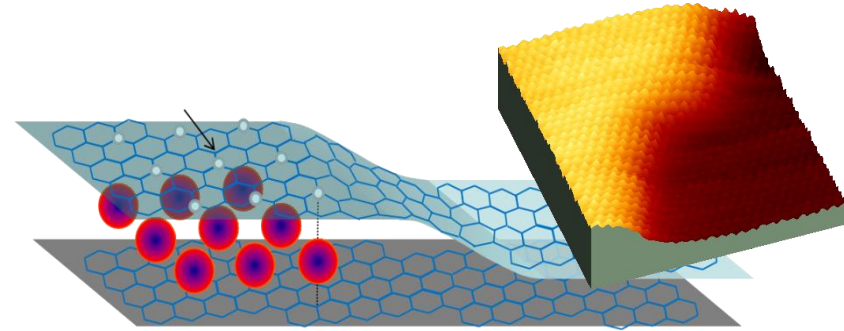
## Strain-Induced Pseudo-Magnetic Fields Greater Than 300 Tesla in Graphene Nanobubbles

N. Levy,<sup>1,2\*</sup> S. A. Burke,<sup>1\*</sup> K. L. Meaker,<sup>3</sup> M. Panlasigui,<sup>1</sup> A. Zettl,<sup>1,2</sup> F. Guinea,<sup>3</sup> A. H. Castro Neto,<sup>1</sup> M. F. Crommie<sup>1,2,5</sup>



Science 329 (2010) 544

Inhomogeneous strain appears due to corrugation



Non-uniform shear strain  
non-equivalent hopping

$$u_{xx} = \frac{\partial u_x}{\partial x}, \quad u_{yy} = \frac{\partial u_y}{\partial y}, \quad 2u_{xy} = \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}$$

Ando, et al., Phys. Rev. B **65** (2002) 235412.  
Neto et al., Rev. Mod. Phys. **81** (2009) 109.

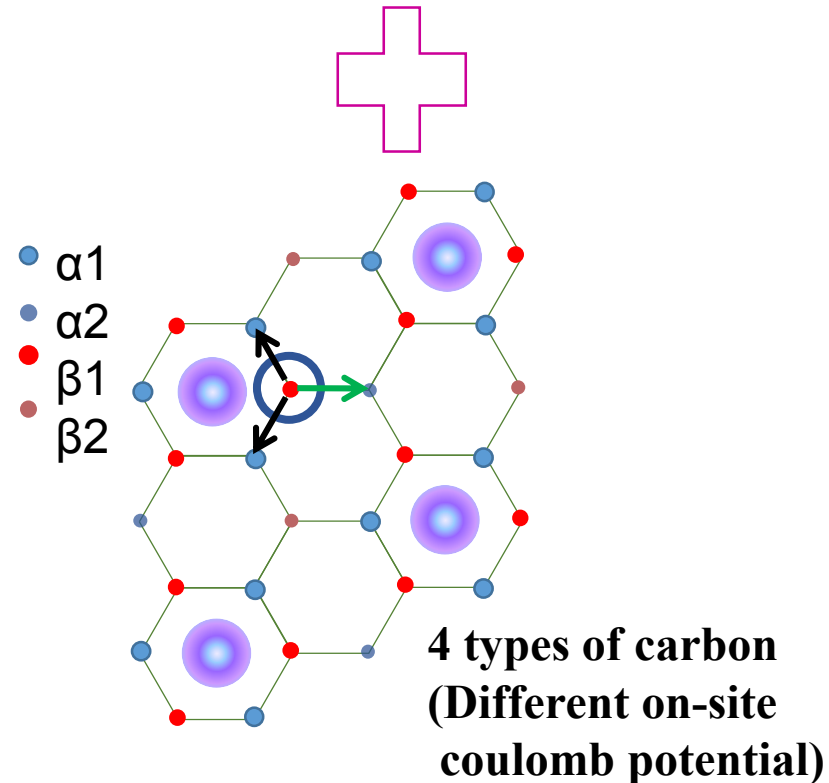
Gauge field

$$\mathbf{A} = \frac{\beta}{a} \begin{pmatrix} u_{xx} - u_{yy} \\ -2u_{xy} \end{pmatrix} \quad B_s = \frac{\partial A_y}{\partial x} - \frac{\partial A_x}{\partial y}$$

Geim, et al., Nature Phys. **6** (2010) 30

Pseudo-magnetic field

$$\vec{B}_s = \vec{\nabla} \times \vec{A}$$



# まとめ

## ▶ 物質変換材料研究部門の研究内容

CO<sub>2</sub>の化学的変換、燃料電池触媒、  
触媒学理の表面科学的研究、ナノカーボン化学の学理と応用

## ▶ CO<sub>2</sub>削減用の触媒開発

メタノール合成が有望、Cu/ZnO触媒、CO<sub>2</sub>活性化メカニズム

## ▶ 燃料電池における白金触媒量の削減

ナノカーボンの触媒応用、金属・炭素界面相互作用、炭素の反応性の起源解明、炭素の局所的電子状態の解明

*Thank you for your attention !*