Atomistic Growth Mechanisms & Property Optimization of Two-Dimensional Materials

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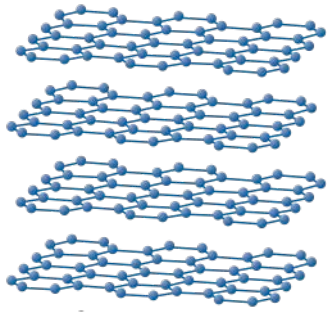
University of Science and Technology of China

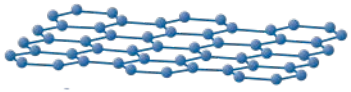
Funding

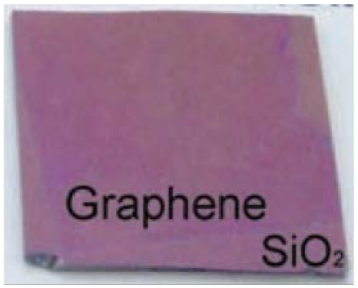
NSFC, MOST, CAS

Golden Period of Two-dimensional (2D) Materials: A Fast and Ever Expanding Materials Family

Mechanical Exfoliation

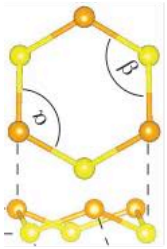




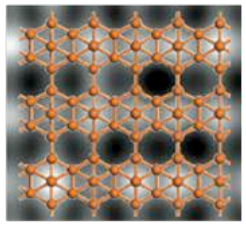


Epitaxial Growth

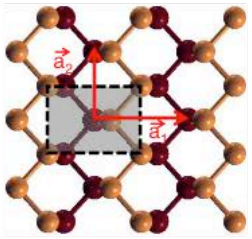
More and more branches of the large 2D family tree



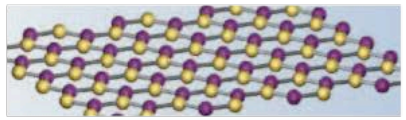
Silicene



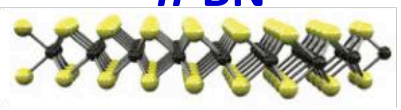
Borophene



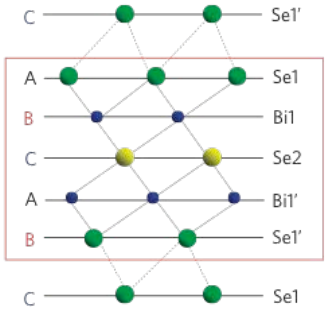
Phosphorene



h-BN

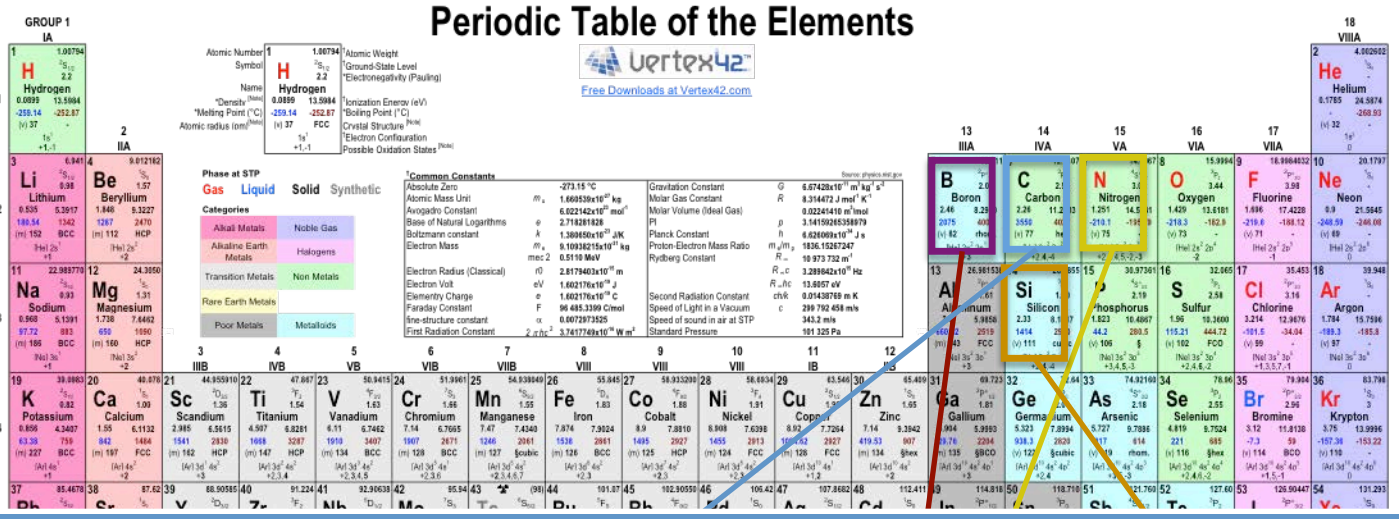


MoS_2 (TMDs)

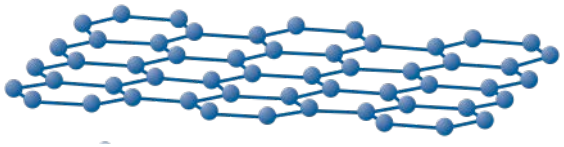


Bi_2Se_3 (Topological insulators)

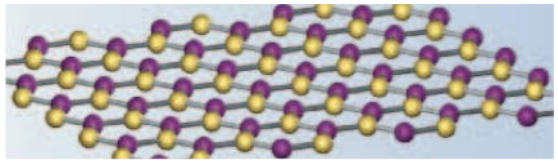
Each Member Possesses Its Characteristic Properties



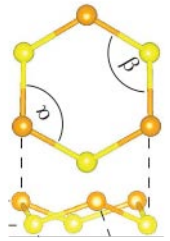
Different chemical identities prefer different structures, demand different growth mechanisms, and inherently define their rich and characteristic properties



Semimetal



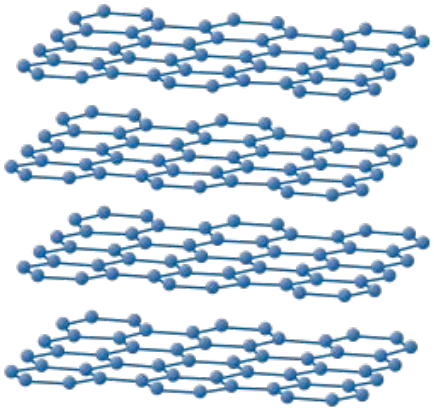
Insulator



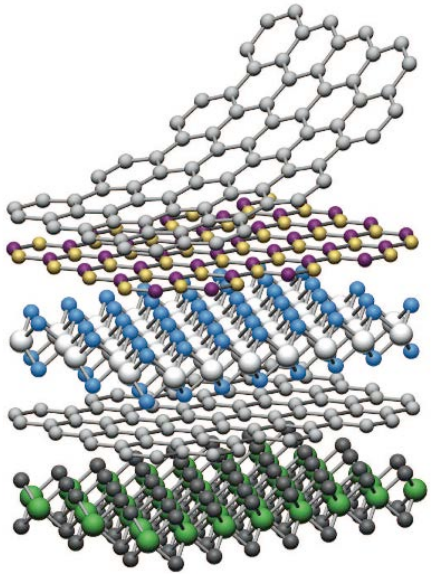
“more bumpy”

Commonalities

The interlayer coupling is predominantly of weak, van der Waals (vdW) nature.



Graphite



vdW heterostructures

A. Geim and I. Grigorieva, *Nature* **499**, 419 (2013).

vdW Heteroepitaxy: Structural control is crucial to property optimization.

Commonalities

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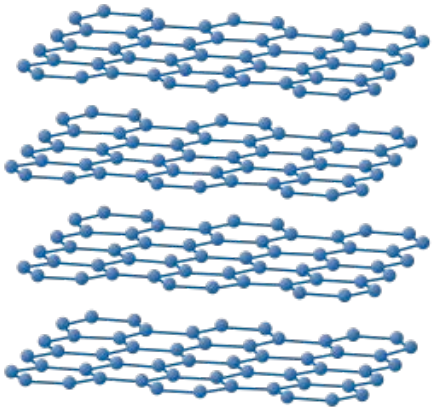
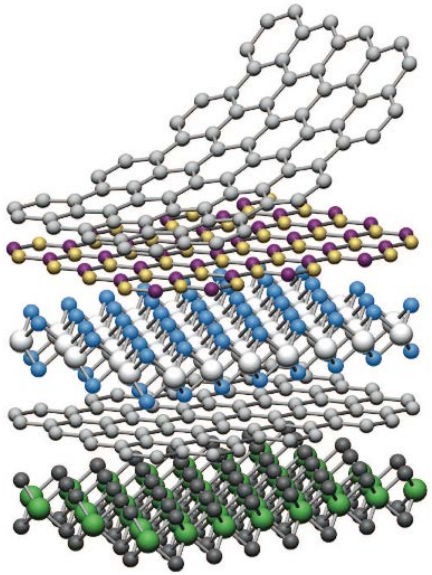


Graphite



vdW heterostructures

A. Geim and I. Grigorieva, *Nature* **499**, 419 (2013).

vdW Heteroepitaxy: Structural control is crucial to property optimization.

“一叶知秋”(The falling of one leaf heralds the autumn)

Walking into/onto Graphene

走　近/进　石墨烯

Where to grow?　在哪长？

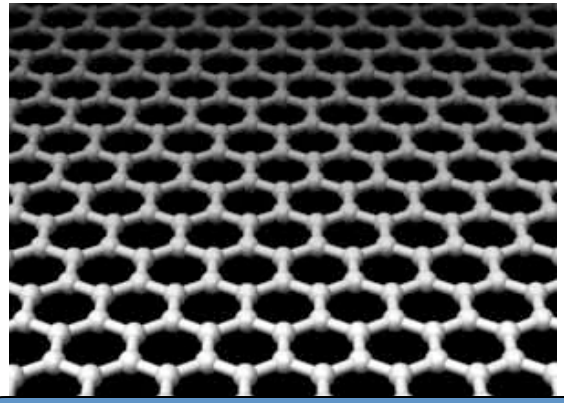
How to grow better?　怎么长好？

How to growth faster? 怎么长快？

How to grow large?　怎么长大？

How to grow SUPER large?　怎么长超大？

Graphene: Hot Topic, Big Prize, & "Simple Tool"



Going Beyond the "Scotch-Tape" Approach:

Fundamental Growth Science Towards
Mass Production of High Quality Graphene on Various Substrates

"Physics Nobel Prize Winners' Secret: Scotch Tape"

$t_{zz}=0$:

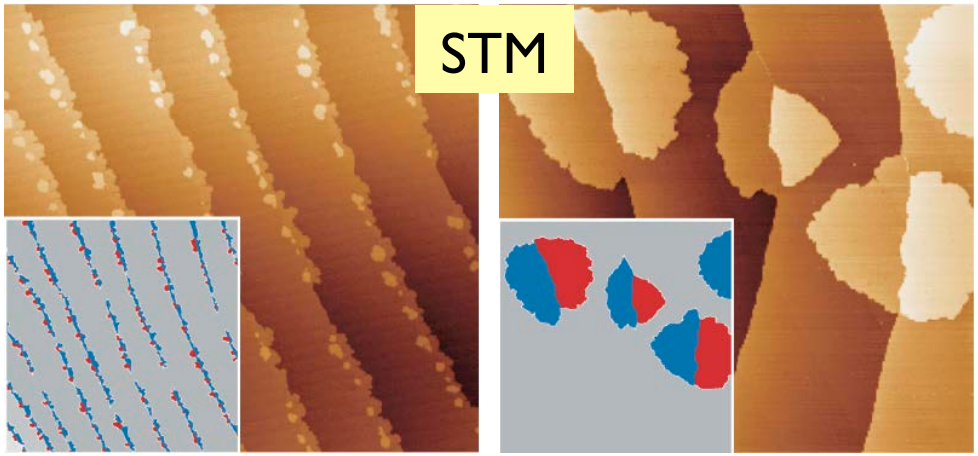
Beautiful Site, Stimulating Workshop, and Inspiring Lectures

VIth Stranski-Kaischew Surface Science Workshop
"Nanophenomena at Surfaces - Fundamentals of Exotic Condensed Matter Properties"
"Sunny Beach", Black Sea Coast, Bulgaria, September 20-26, 2008

Thomas MICHELY
Graphene as a Template for Cluster Lattices

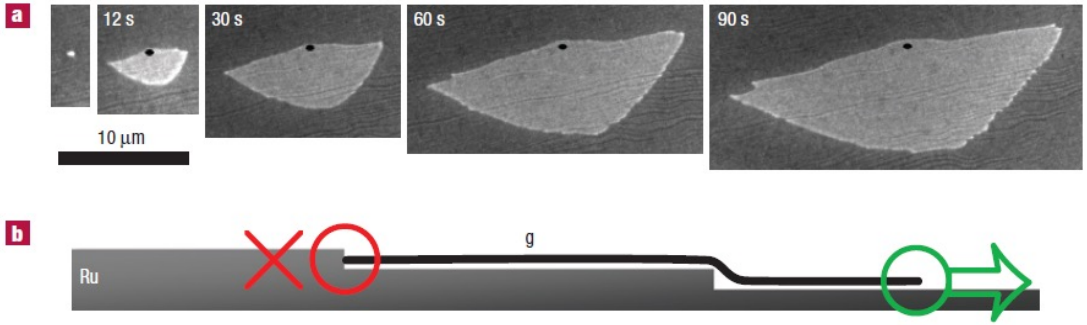
Eli SUTTER
Metal Catalyzed sp2 Bonded Carbon Assemblies -
from Nanoscale Pipettes to Macroscopic Graphene Sheets

Step-edge Initiated Growth on Ir(111) and Ru(0001)



Graphene on Ir(111)

J. Coraux, T. Michely et al.,
New J. Phys. 11, 023006 (2009)



Graphene on Ru(0001)

P. W. Sutter, J.-I. Flege, & E. A. Sutter
Nature Mat. 7, 406 (2008)

Atomistic Processes and Morphological Evolution on Stepped Substrates

New playground:

Nucleation and growth of carbon islands on stepped metal surfaces

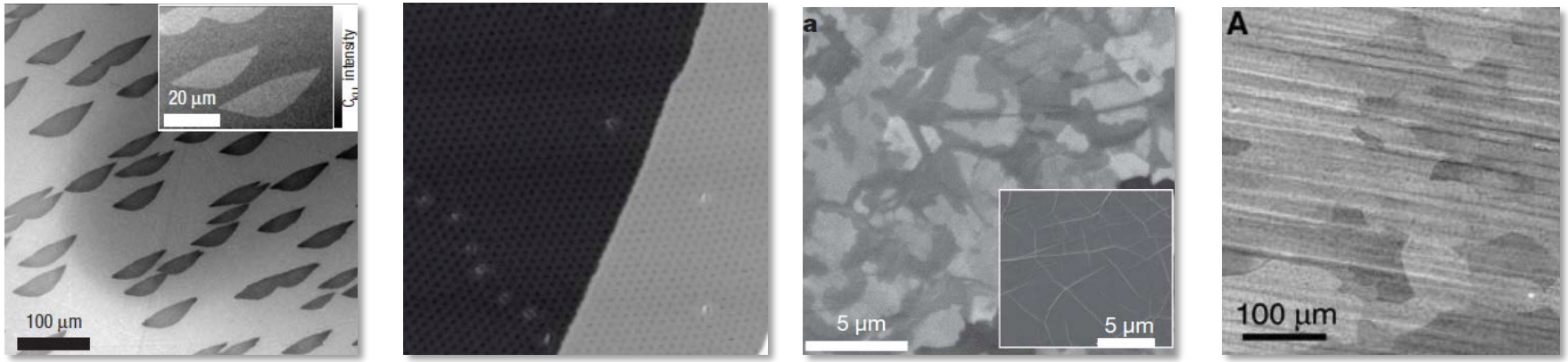
To start with, stay away from the graphene "theory rush"

Metiu, Lu, & Zhang, *Molecular epitaxy and the art of computer simulations,* Science (review article), 2002

Zhang and Lagally, *Atomistic processes in the early stages of epitaxial growth,* Science (Review Article), 2007

Epitaxial Graphene on Metal Substrates: From Islanding to Micron-Sized Monolayers

Ru(0001) Ir(111) Ni(111) Cu(111)



Ru(0001):
Sutter, Flege, and Sutter, *Nature Mater.* **7**, 406 (2008).
Pan *et al.*, *Adv. Mater.* **21**, 2777 (2009).
Marchini, Gunther, and Wintterlin,
Phys. Rev. B **76**, 075429 (2007).
Loginova, Bartelt, Feibelman, and McCarty,
New J. Phys. **10**, 093026 (2008); **11**, 063046(2009).

Ir(111):
Coraux, N'Diaye, Busse, and Michely,
Nano Lett. **8**, 565 (2008).
Coraux *et al.*, *New J. Phys.* **11**, 023006 (2009).

Ni(111)
Kim *et al.*, *Nature* **457**, 706 (2009).
Yu *et al.*, *Appl. Phys. Lett.* **93**, 113103 (2008).
Reina et al., *Nano Lett.* **9**, 30 (2009).

Cu(111):
Li *et al.*, *Science* **324**, 1312 (2009).
Li et al., *Nano Lett.* **9**, 4268(2009).
Gao, Guest, and Guisinger, *Nano Lett.* **10**, 3512 (2010).
Bae et al., *Nature Nanotech.* **5**, 574 (2010).
Cao et al., *Appl. Phys. Lett.* **96**, 122106 (2010).

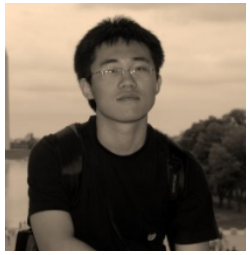
Distinctive merits and potentials for graphene electronics:
Mass production, transferrable, "good" quality

Outline

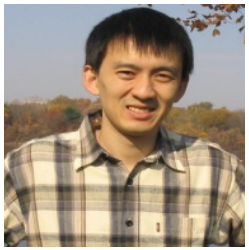
- Brief Introduction on Motivation
- Atomistic Mechanisms of Epitaxial Growth of Graphene:
  - Why Cu is the preferred substrate? (Hua Chen)
  - Suppression of grain boundaries (Wei Chen)
  - Low-temperature growth (Jin-Ho Choi)
- Going beyond graphene
- Functionalization of 2D materials
  - A few highlights

"Facebooked" Collaborators (Partial List)

Dr. Hua Chen, *UTK/UT Austin*

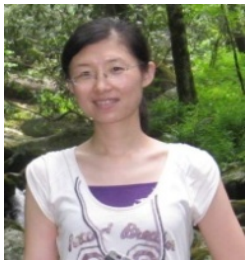


Dr. Wenguang Zhu, *UTK/ USTC*



Robert Van Wesep, *UTK*

Dr. Ping Cui, *USTC*



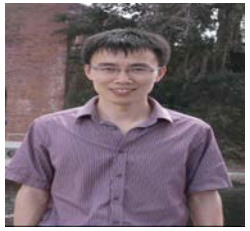
Dr. Wei Chen, *UTK/USTC*

Dr. Tim Schulze, *UTK*

Dr. Jin-Ho Choi, USTC

Dr. Changan Zeng, *USTC*

Dr. Shifei Qi, *Shanxi Normal U*



Dr. Xiaohong Xu, *Shanxi Normal U*

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  - A few highlights

Graphene synthesis by CVD on Cu substrates

Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils

Xuesong Li,[1] Weiwei Cai,[1] Jinho An,[1] Seyoung Kim,[2] Junghyo Nah,[2] Dongxing Yang,[1] Richard Piner,[1] Aruna Velamakanni,[1] Inhwa Jung,[1] Emanuel Tutuc,[2] Sanjay K. Banerjee,[2] Luigi Colombo,[3]* Rodney S. Ruoff[1]*

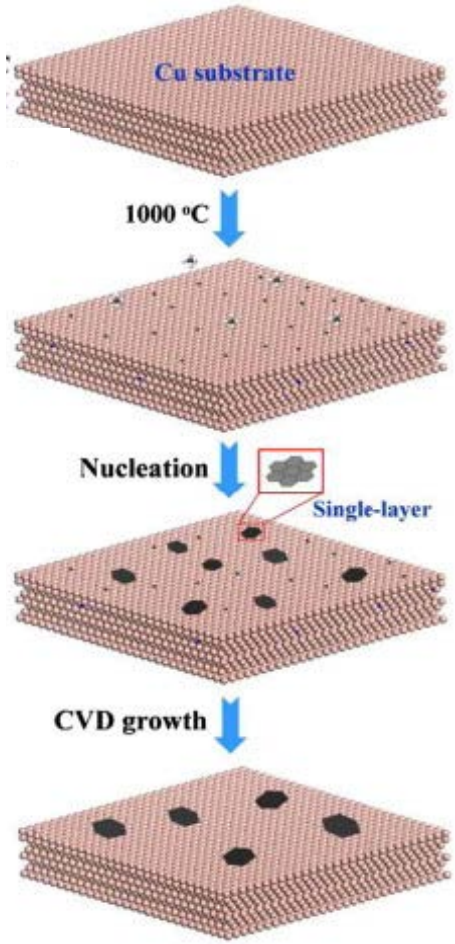
Science 324, 1312 (2009)

Chemical vapor deposition (CVD) on Cu substrates

Graphene films of the order of centimeters

Most of the synthesized graphene films are monolayer in thickness (more than 95%).

Typical CVD method



Dosing carbon source
eg) methane (CH_4)

Dehydrogenation of the carbon sources

Carbon coalescence

Formation of large high-quality graphene

Atomistic Mechanisms: Back to "Arithmetics"

- N=1: Rest areas of monomers
- N=2: Preferred nucleation sites of dimers
- N=3, 4, 5, …:
  - * Carbon Nanoarches
  - * 1D ⟹ 2D transition
- N=6 and beyond:
  - * On Cu(111): Good islands, bad islands
  - * On alloyed Cu(111):
    - # Good islands
    - # Minimal grain boundaries

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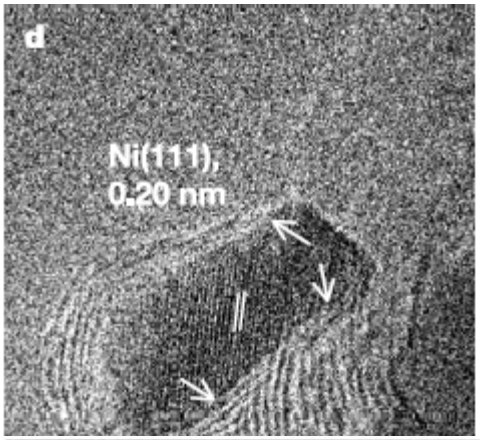
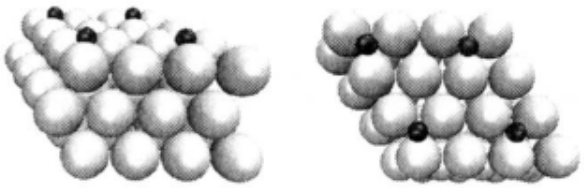
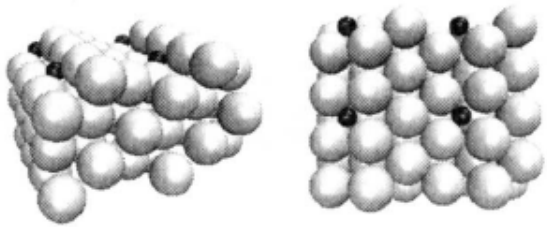
1st Thought: C monomers prefer step edges (as shown on Ni(111))



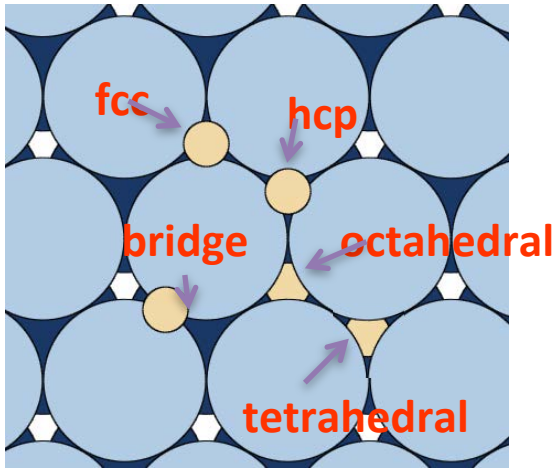
S. Helveg et al., Nature 427, 6973 (2004)

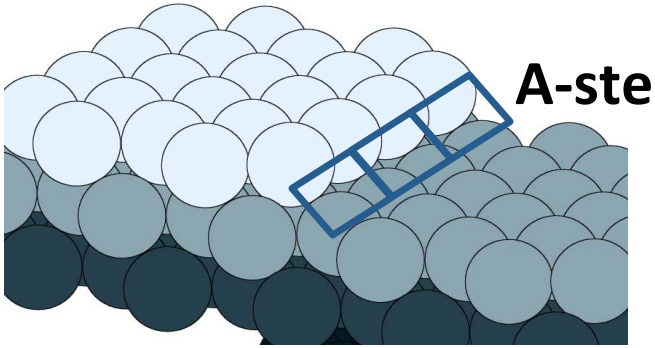
F. Abild-Pedersen et al., PRB 73, 115419 (2006)

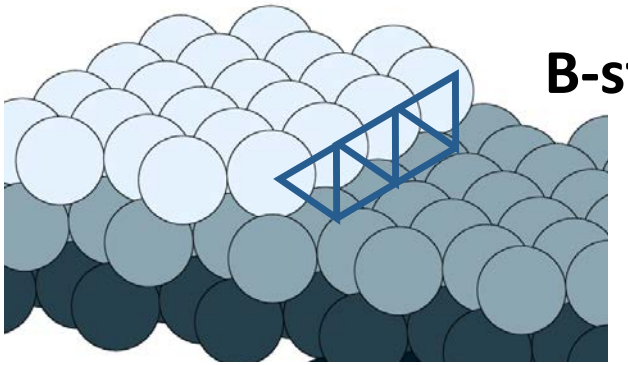
Structure	E_{ads}(eV)	Structure	E_{ads}(eV)
1  Ni(111) hcp site with $\theta_C = \frac{1}{4}$ML.	0.55	2  Ni(211) step-edge with $\theta_C^{st} = \frac{1}{2}$.	-0.45

1 eV difference

Methods

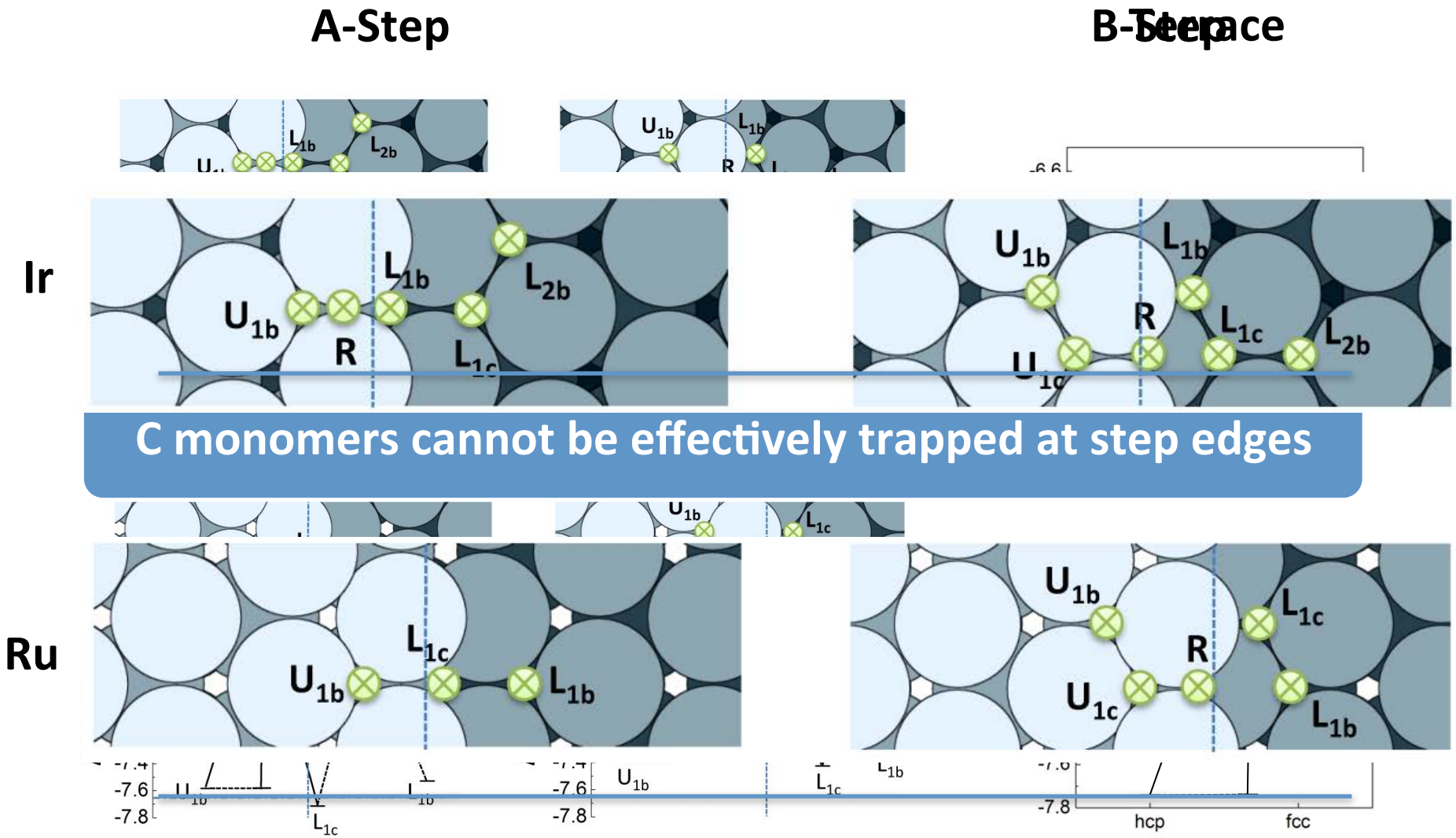






- VASP
- PAW-PBE
- Nudged Elastic Band
- Ir, Ru, Cu
- 6-layer slab
- 2x4 square surface unit cell

Energetics of C Monomers at Step Edges on Ir(111) and Ru(0001)



C monomers cannot be effectively trapped at step edges

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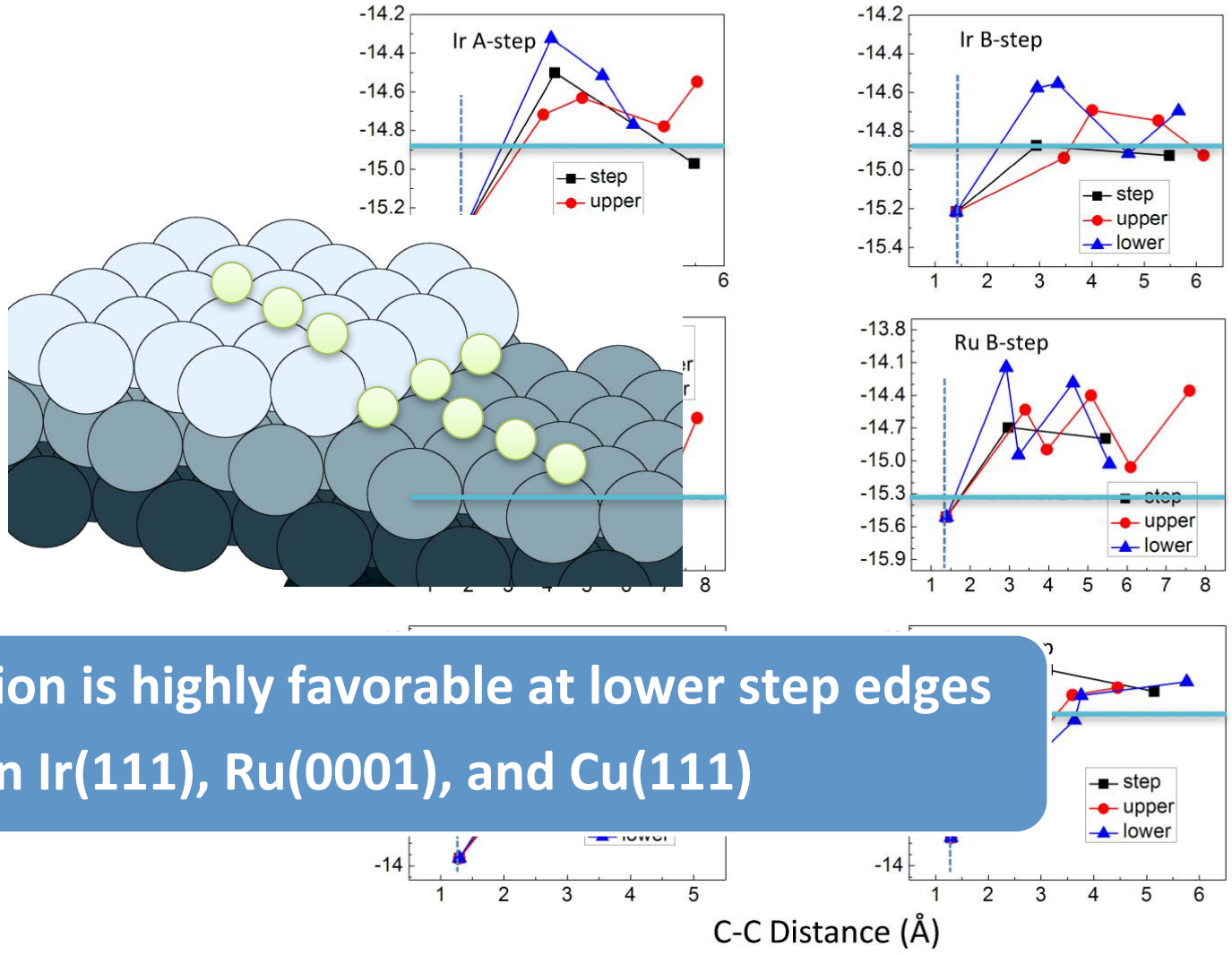
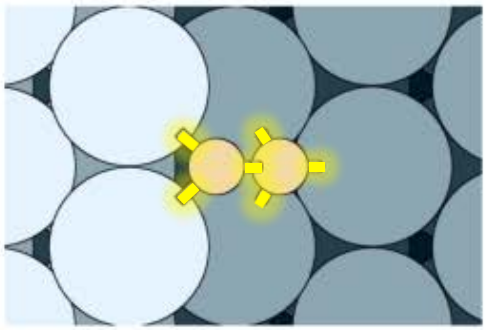
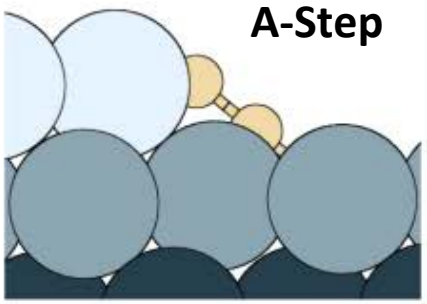
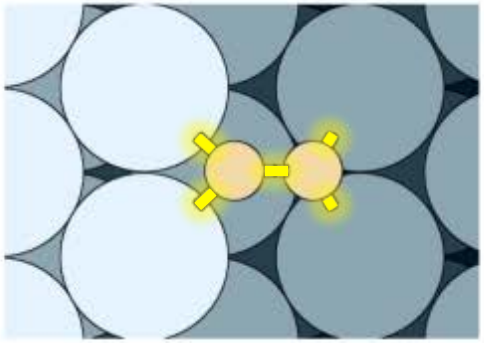


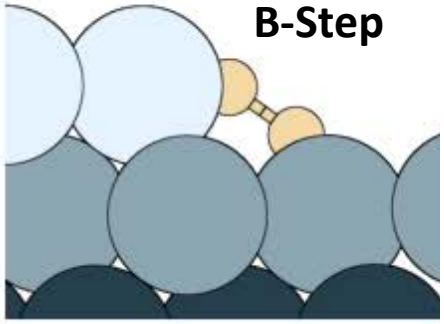
C dimerization is highly favorable at lower step edges on Ir(111), Ru(0001), and Cu(111)

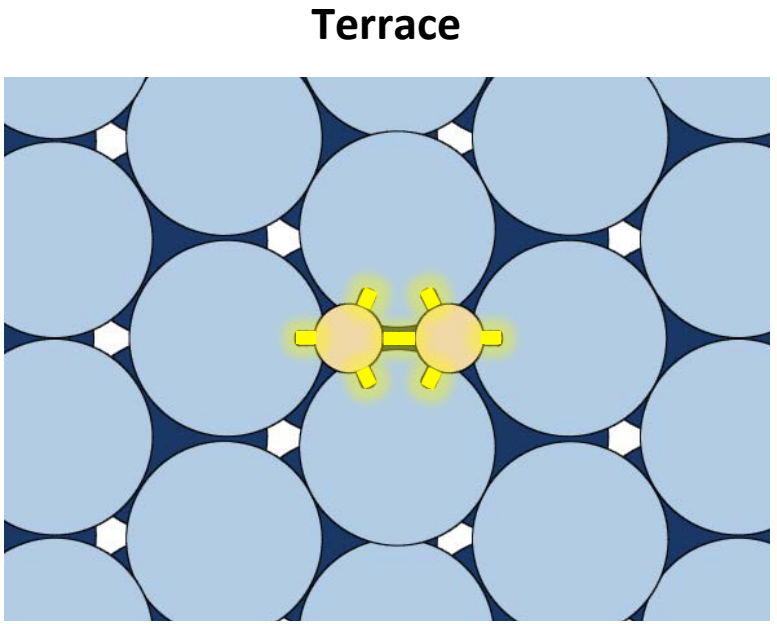
Why are C dimers more stable at step edges?







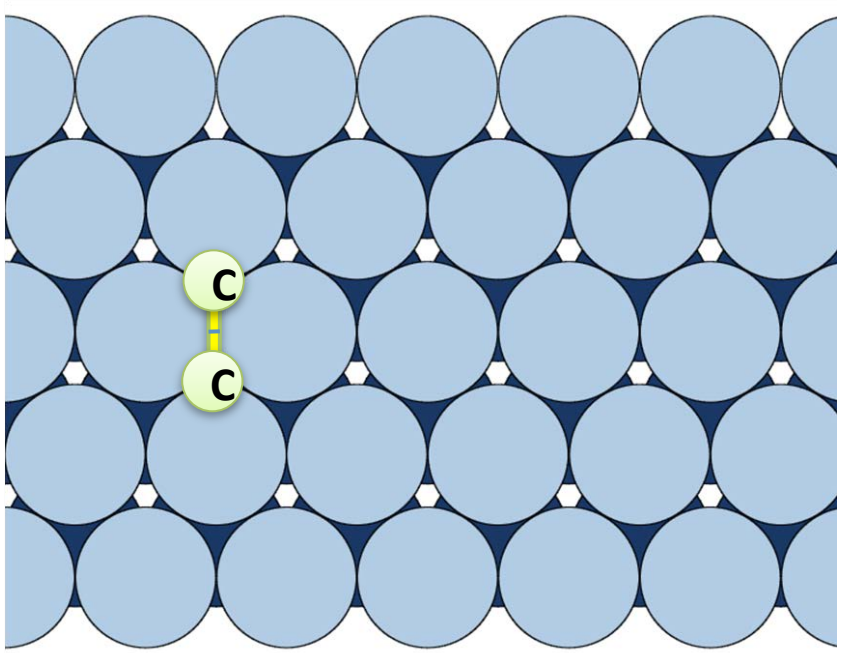


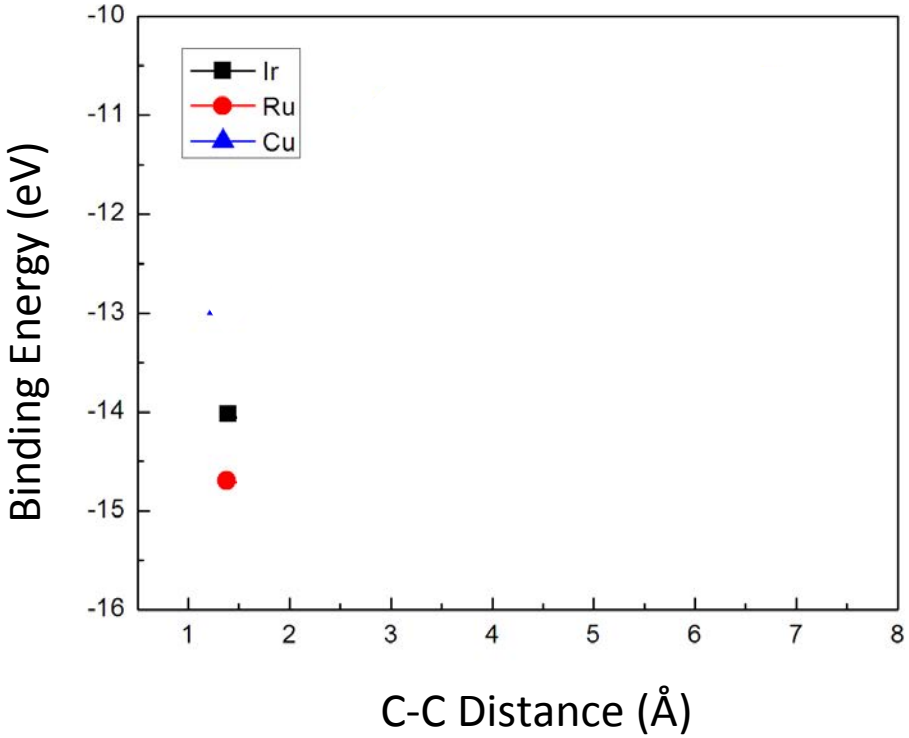


Step edge can accommodate energetically more favorable dimer configurations

“Napping” effect

Energetics of Carbon Dimers on Terraces



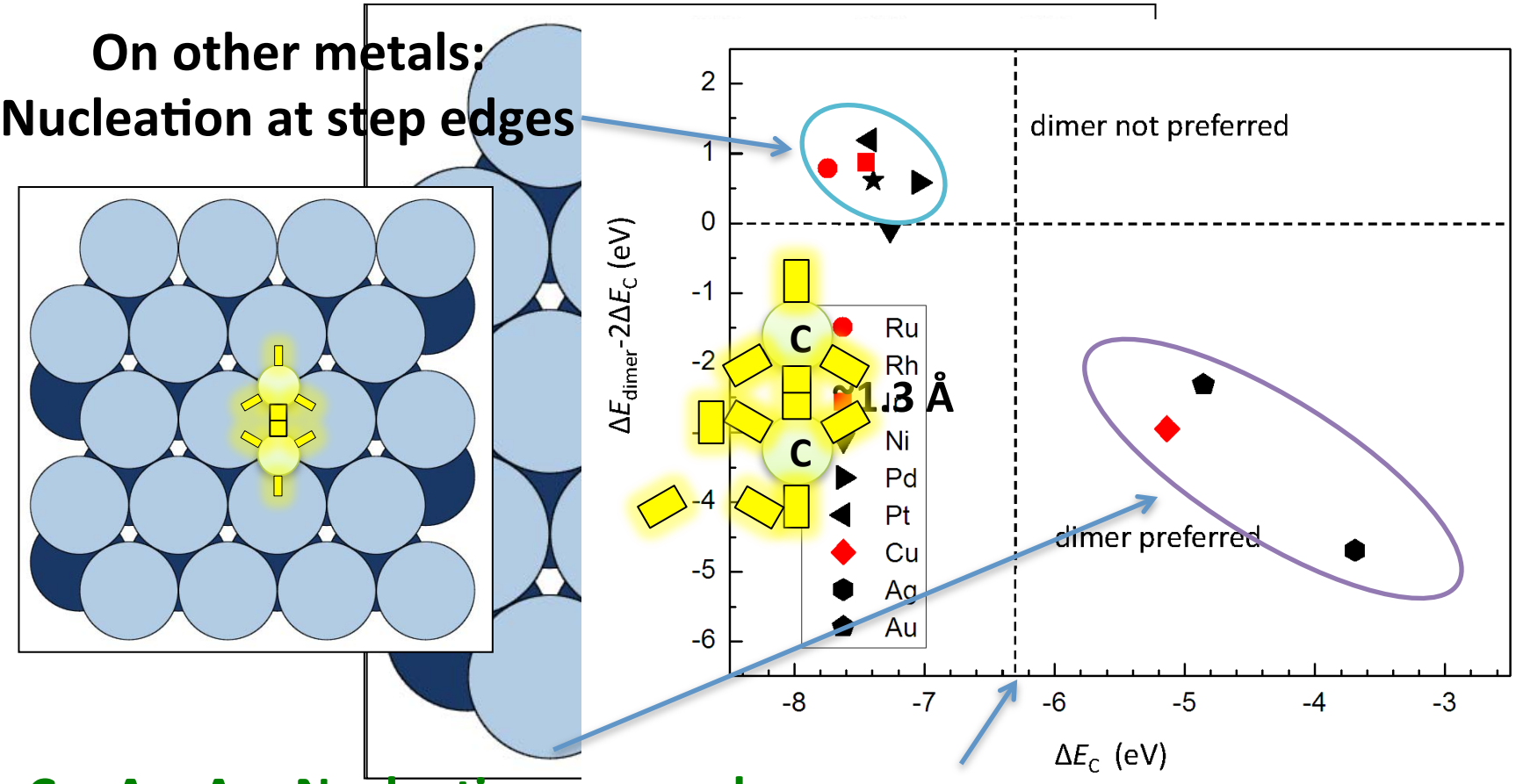


C dimerization is unfavorable on Ir(111) and Ru(0001), but is strongly favorable on Cu(111)

"Good" substrate for mass production: Cu(111)

Why dimer formation is preferred on Cu(111), but not on Ir(111) and Ru (0001)

On other metals:
Nucleation at step edges



On Cu, Ag, Au: Nucleation everywhere

C double bond

Hua Chen, Wenguang Zhu, ZZ, PRL 104, 186101 (2010)

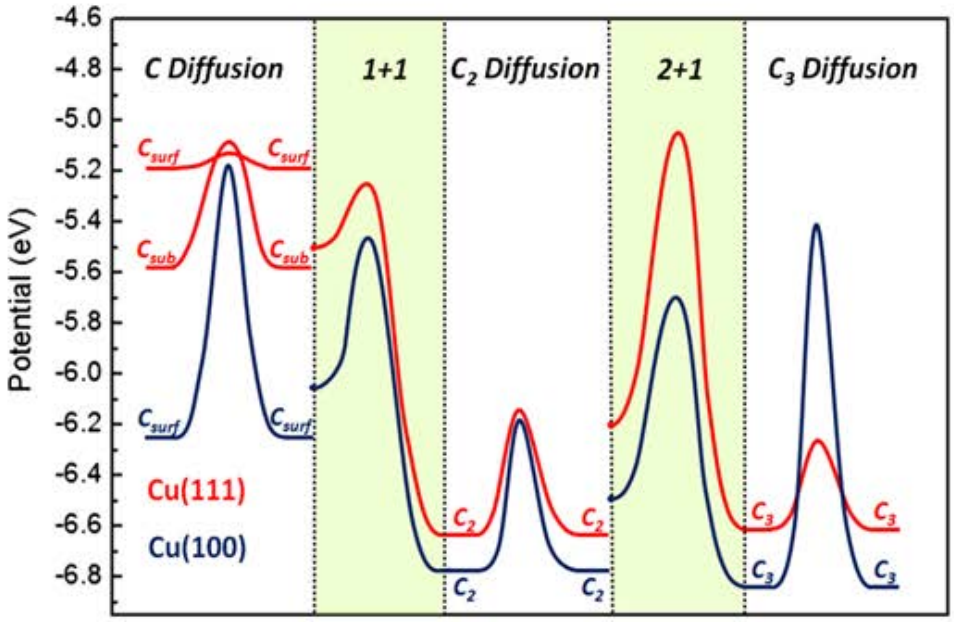
Carbon Dimers as the Dominant Feeding Species in Epitaxial Growth and Morphological Phase Transition of Graphene on Different Cu Substrates

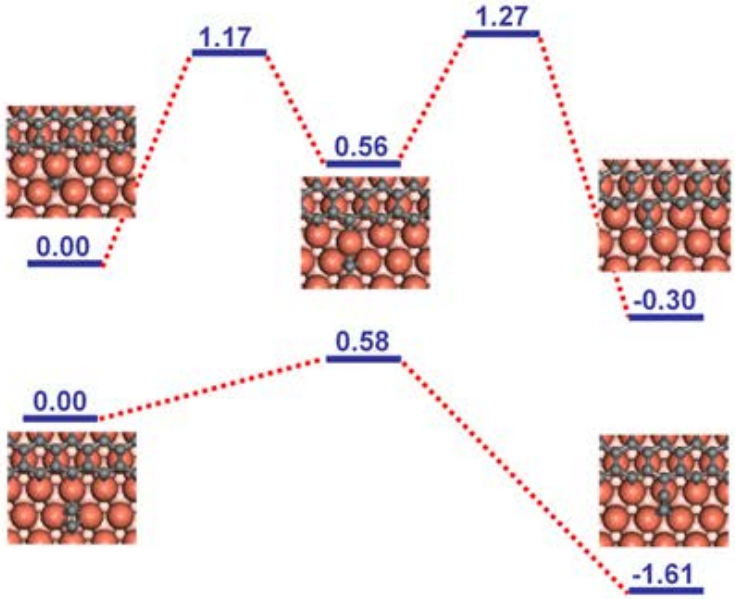
Ping Wu, Yue Zhang, Ping Cui, Zhenyu Li,* Jinlong Yang, and Zhenyu Zhang†

Hefei National Laboratory for Physical Sciences at Microscale, CAS Centre for Excellence and Synergetic Innovation Center of Quantum Information & Quantum Physics, and International Center for Quantum Design of Functional Materials (ICQD), University of Science and Technology of China, Hefei, Anhui 230026, China

(Received 18 February 2015; published 28 May 2015)

Cu substrates are highly preferred for the potential mass production of high-quality graphene, yet many of the important aspects of the atomistic growth mechanisms involved remain to be explored. Using multiscale modeling, we identify C-C dimers as the dominant feeding species in the epitaxial growth of graphene on both Cu(111) and Cu(100) substrates. By contrasting the different activation energies involved





Atomistic Mechanisms: Back to "Arithmetics"

- N=1: Rest areas of monomers
- N=2: Preferred nucleation sites of dimers
- N=3, 4, 5, …: (skip)
  - * Carbon Nanoarches
  - * 1D ⟹ 2D transition
- N=6 and beyond:
  - * On Cu(111): Good islands, bad islands
  - * On alloyed Cu(111):
    - # Good islands
    - # Minimal grain boundaries

Atomistic Mechanisms: Back to "Arithmetics"

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    - # Minimal grain boundaries

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- Brief Introduction on Motivation
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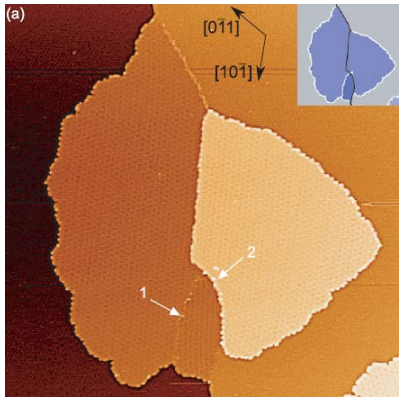
  - Why Cu is the preferred substrate? (Hua Chen)
  - Suppression of grain boundaries (Wei Chen)
  - Low-temperature growth (Jin-Ho Choi)
- Going beyond graphene
- Functionalization of 2D materials
  - A few highlights

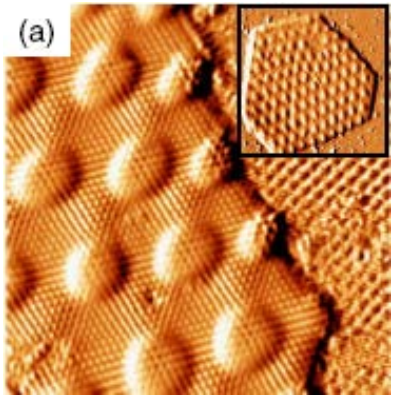
CVD Growth on Transition Metals: Go for Cu!!!

Ir(111), Co(0001), Pt(111), Ru(0001), Ni(111)…

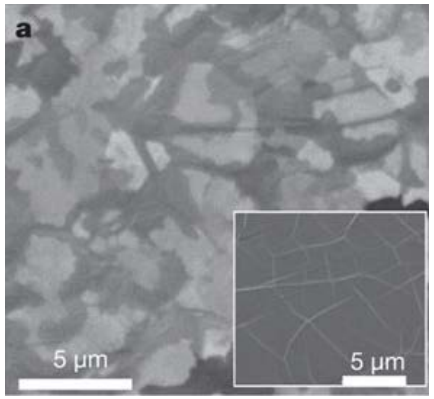
Cu(111)



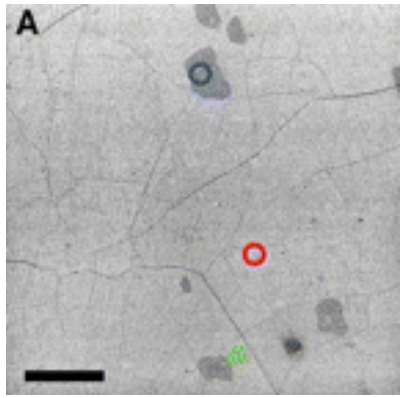
J. Coraux et al., *New Journal of Physics (2009)*



A. L. Va´zquez de Pargaet al., PRL (2009)



K.S. Kim et al., Nature(2009)

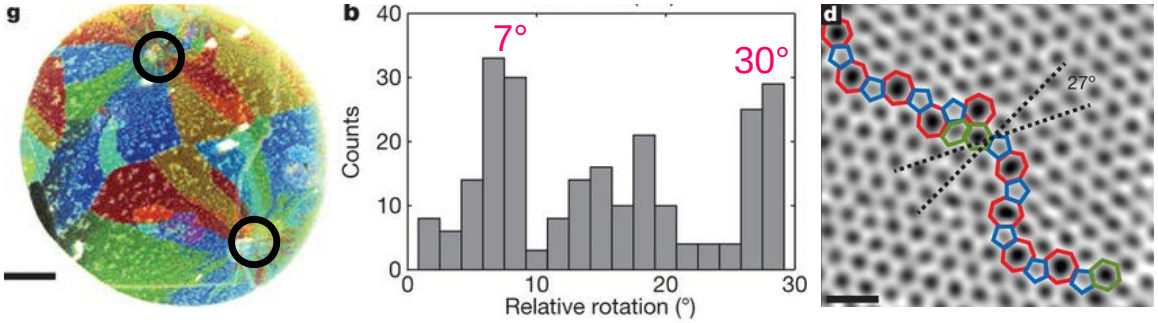


X. Li et al., Science (2009)

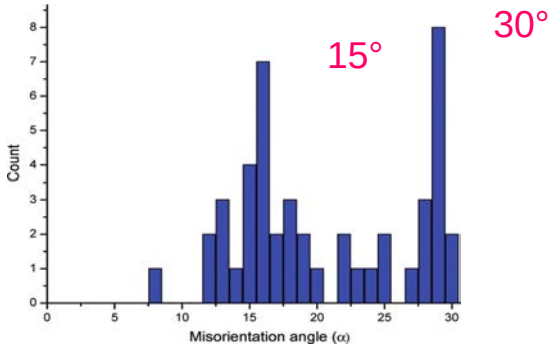
Factors determining growth rate, thickness & uniformity:

- ➡ Carbon solubility in Metals: low: Pt,Ru,Ir,Cu; high: Ni,Co
- ➡ Lattice mismatch: small: Ni 1.24% Cu 3.72%
- ➡ Carbon-Metal bond strength (nucleation sites)
- ➡ Experimental conditions: gas concentration, pressure, temperature, cooling rate…

Daunting Challenge: Populous Grain Boundaries



P.Y.Huang et al., Nature (2011)



J.H. An et al., ACS Nano(2011)

* Grain boundaries are undesirable (in general)

* Grains of different orientations originate from nucleation site

* 12-fold periodicity diffraction data shows 2 main families of grains rotated by ~30°

How to reduce the ~30°rotational defects at the initial nucleation stage?

What are the elemental **building blocks** of different grains?

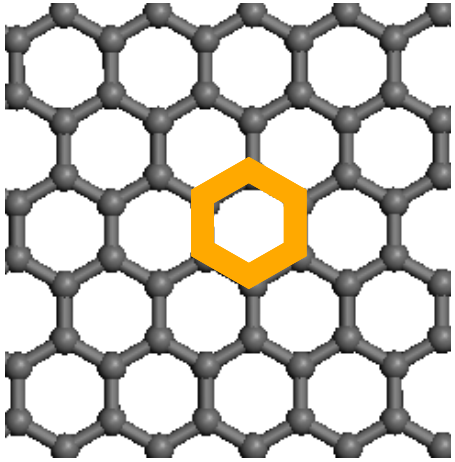
Diagnosis: Nearly degenerate orientations of C_6 Rings on Cu

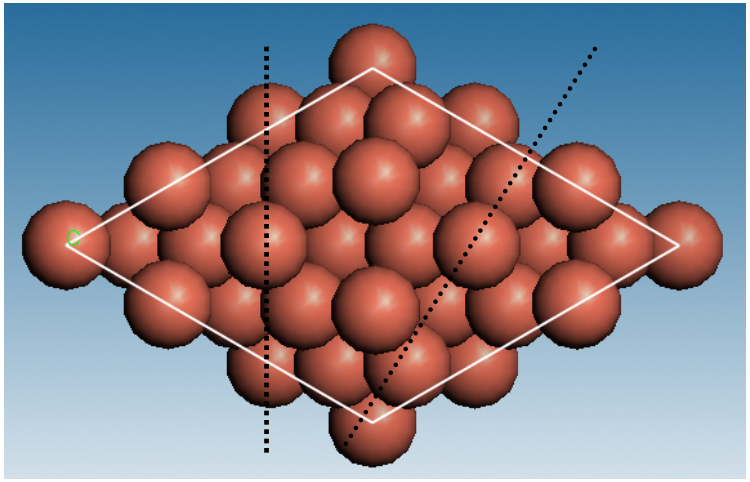
VASP

PAW-PBE

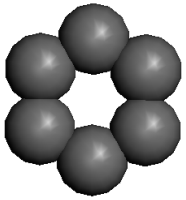
5-layer slab

3x3 unit cell





building blocks: 6-Carbon rings



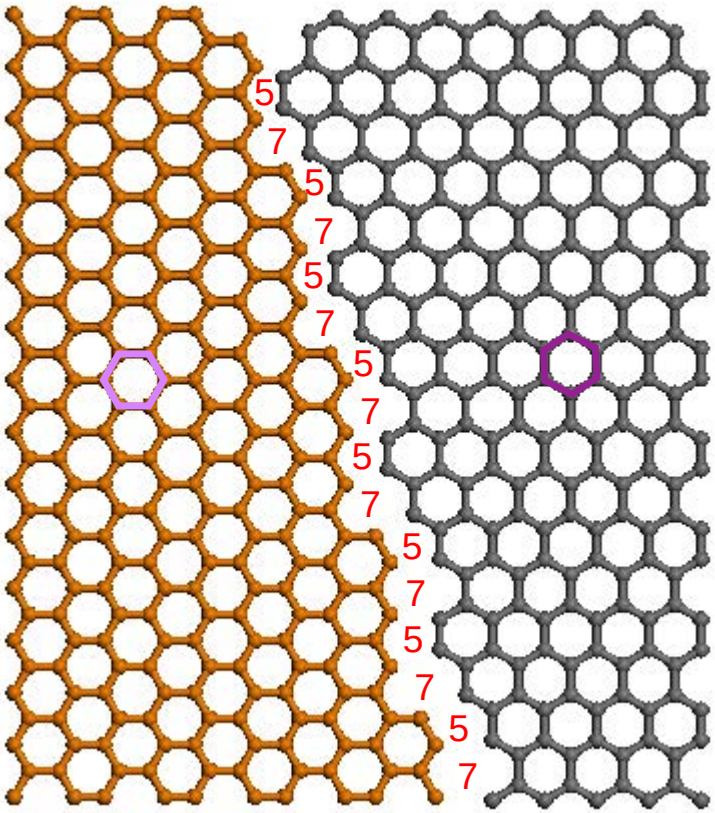
Two stable geometries rotated by 30°

30 °

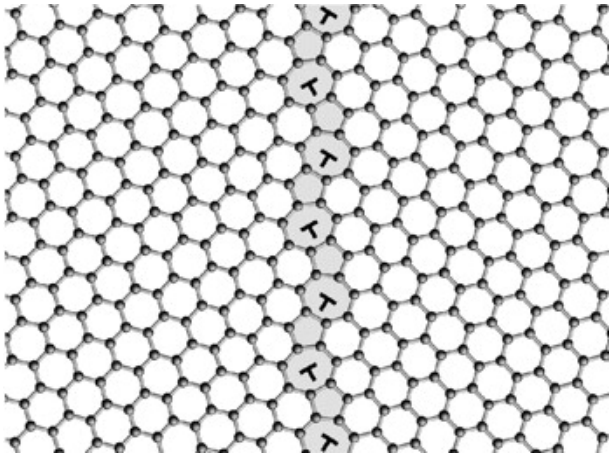
△E = 0.08eV → Nearly degenerate orientations

→ May explain the experimentally observed 30°rotational defects

Conjecturing from Building Blocks to Grain Boundaries

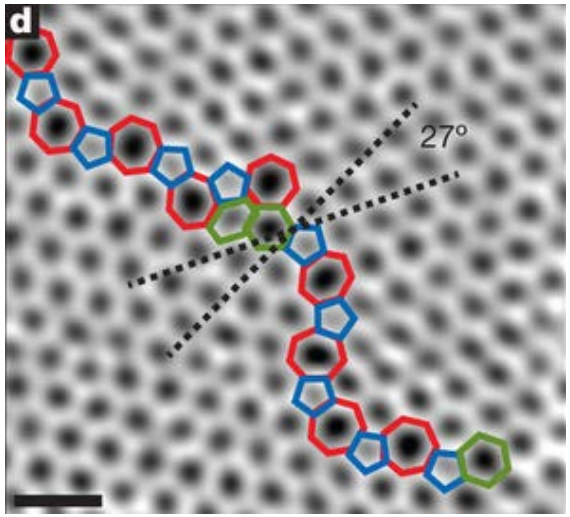


30°rotational defects → GB's with 5&7-membered rings and distorted hexagons



28.7°

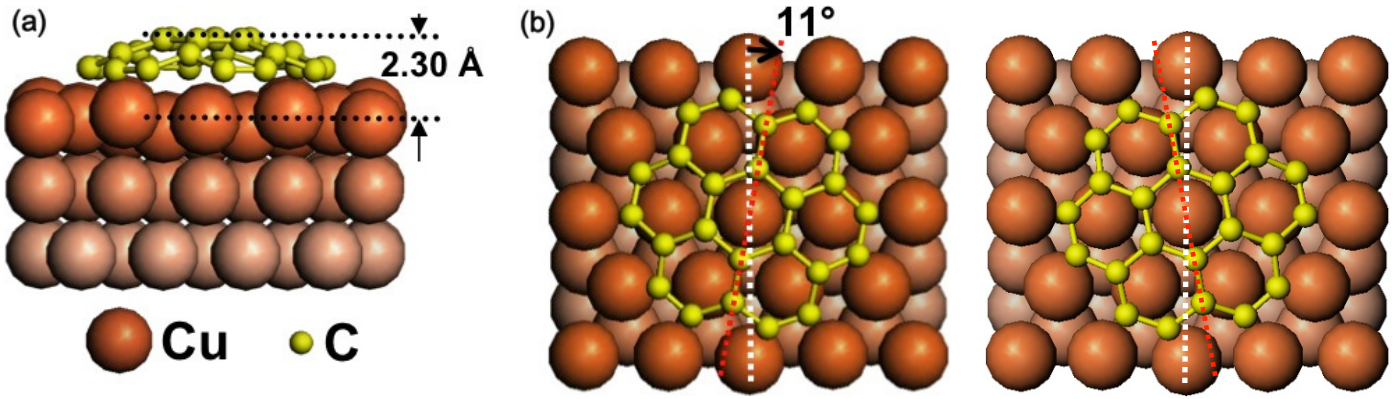
Rassin Grantab et al., Science(2010)



P.Y.Huang et al., Nature(2011)

Going Beyond C_6: Effects of Substrates on $7C_6$

VASP
PAW-PBE
5-layer slab
6x6 unit cell
Spin polarized

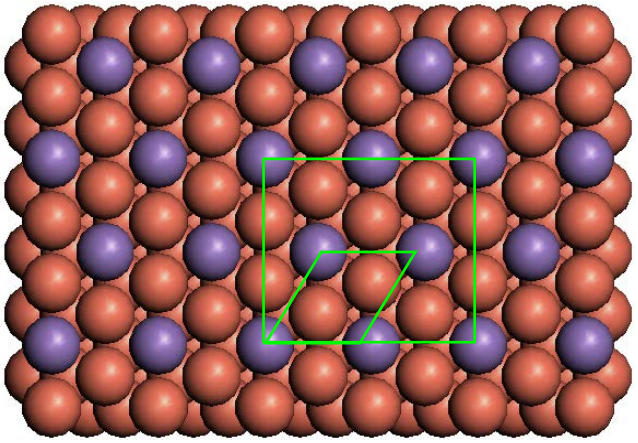


A $7C_6$ island still prefers to rotate away from the high-symmetry orientation.

Two such $7C_6$ islands have degenerate energies.

Grain boundaries with 22^0 orientational angle expected.

Prescription: Graphene Growth on Patterned Substrate (Ordered Nails)



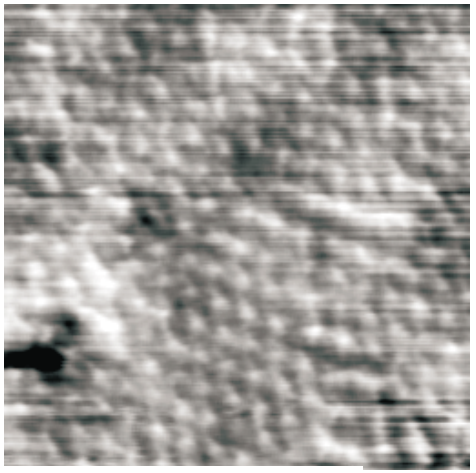
$(\sqrt{3}\times\sqrt{3})$ R30° superstructure

$V_{Carbon\text{-}X} > V_{Carbon\text{-}Cu}$ Search among transition metals with strong bond to carbon : Ru, Fe, Co, Ni, Mn

Only Mn atoms are repulsive at nearest-neighbor sites: Mn-Cu(111) patterned surface

Experiment:

J. Schneider et al., Applied surface science(1999)



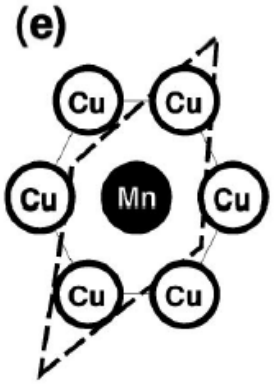
Theory:

PHYSICAL REVIEW B VOLUME 62, NUMBER 7 15 AUGUST 2000-I

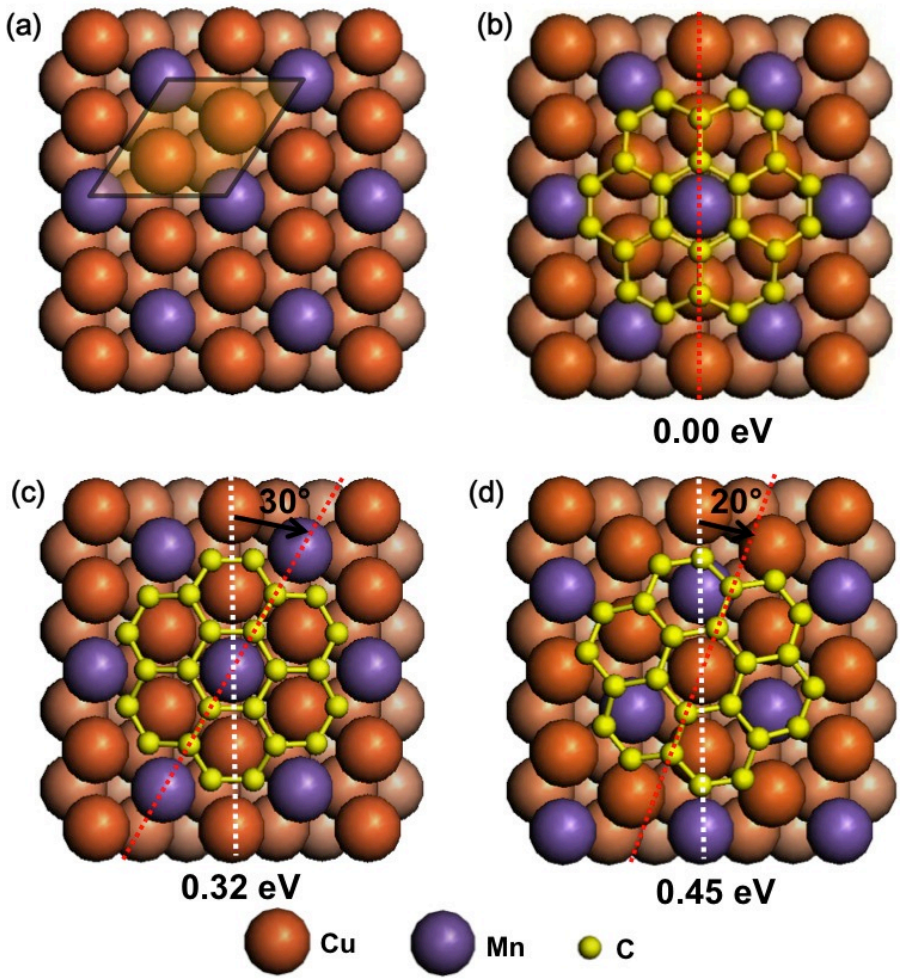
Overlayers, interlayers, and surface alloys of Mn on the Cu(111) surface

G. Bihlmayer,* Ph. Kurz, and S. Blügel
Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany
(Received 26 January 2000)

The energetics of various surface alloys of manganese on copper (111) are calculated and their stability against clustering and/or interdiffusion is determined by an *ab initio* method. The interplay between stoichiometry, chemical, and magnetic ordering allows for a large variety of ordered alloys; only two are found to be stable against clustering: a 33% alloy and a 50% alloy of antiferromagnetically ordered Mn chains. Thermodynamic considerations indicate that only the 33% alloy will be formed at temperatures typical for epitaxial growth. The results are compared to recent scanning tunneling microscopy experiments

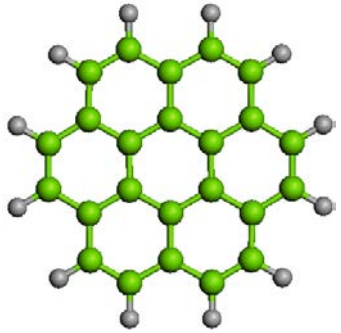


Adsorption of $7C_6$ on Mn-Cu (111)

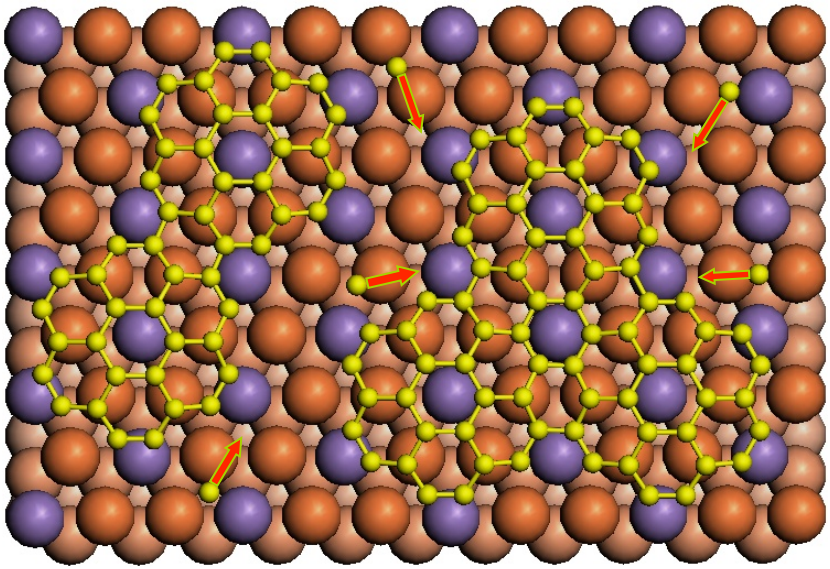


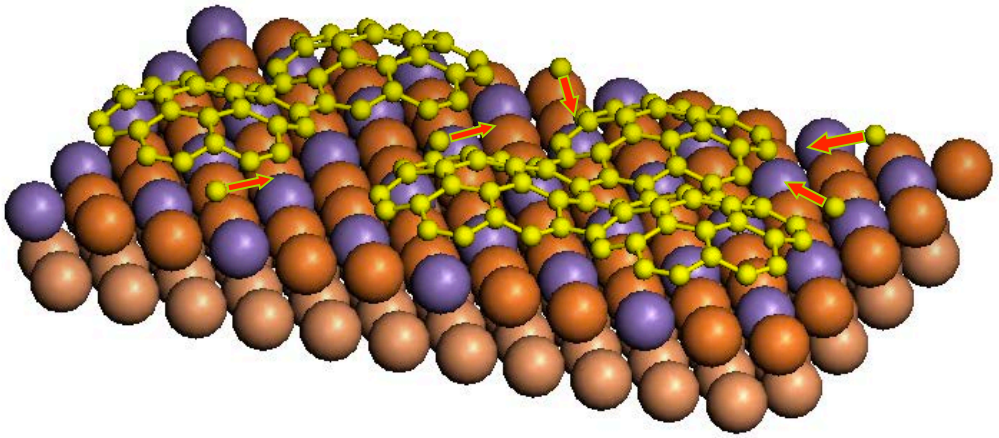
- A $7C_6$ island is pinned at the high-symmetry orientation due to stronger C-Mn interaction
- Enhanced binding energy of 0.24 eV per edge atom compared to Cu(111)
- No grain boundaries when coalescing

Two-Step Kinetic Pathway (SEED & GROW)



- Coronene ($C_{24}H_{12}$): seed molecule
- C-H bond strength vary little from that of benzene, which is used for low-T growth → coronene could also dehydrogenate easily
- Enlargening and gap filling: back to CH_4



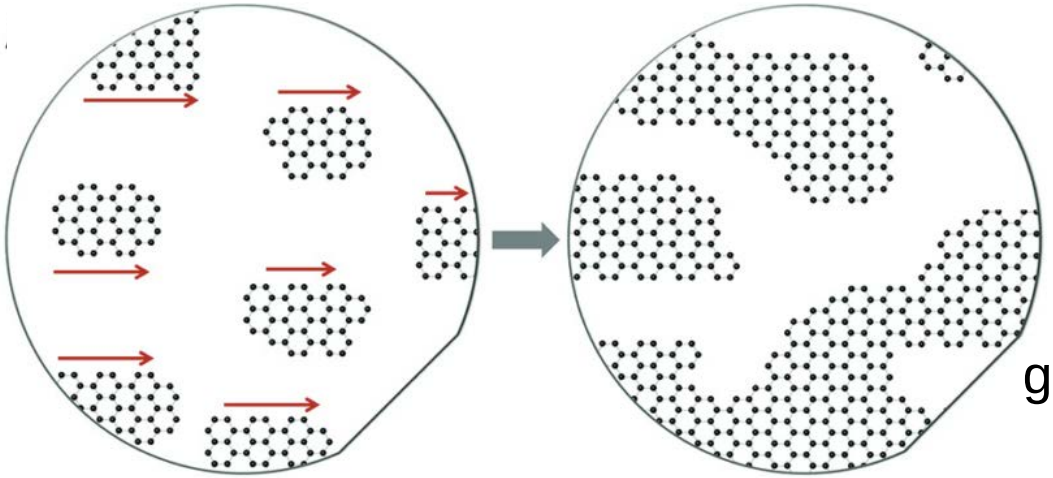


Wei Chen, Haiping Lan, Hua Chen, Ping Cui, Tim Schulze, Wenguang Zhu, ZZ, PRL 109, 265507 (2012)

Major experimental progresses based on the same spirit

substrate - cluster interaction ⇒ lift degeneracy
nucleation of islands everywhere, without misorientations

Wafer-Scale Growth of Single-Crystal Monolayer Graphene on Reusable Hydrogen-Terminated Germanium



growth on H-Ge(110)

J.-H. Lee *et al.*, *Science* **344**, 286 (2014)

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- Brief Introduction on Motivation
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- Going beyond graphene
- Functionalization of 2D materials
  - A few highlights

Graphene synthesis by CVD on Cu substrates

Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils

Xuesong Li,[1] Weiwei Cai,[1] Jinho An,[1] Seyoung Kim,[2] Junghyo Nah,[2] Dongxing Yang,[1] Richard Piner,[1] Aruna Velamakanni,[1] Inhwa Jung,[1] Emanuel Tutuc,[2] Sanjay K. Banerjee,[2] Luigi Colombo,[3]* Rodney S. Ruoff[1]*

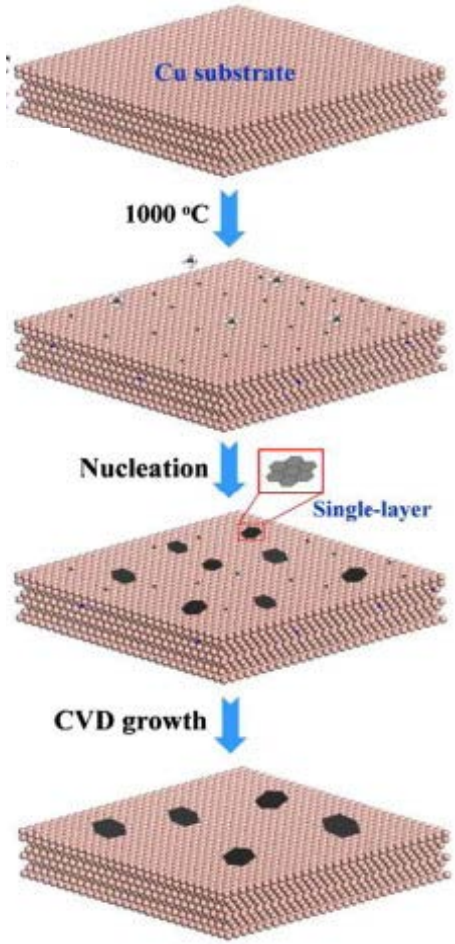
Science 324, 1312 (2009)

Chemical vapor deposition (CVD) on Cu substrates

Graphene films of the order of centimeters

Most of the synthesized graphene films are monolayer in thickness (more than 95%).

Typical CVD method



Dosing carbon source
eg) methane (CH_4)

Dehydrogenation of the carbon sources

Carbon coalescence

Formation of large high-quality graphene

LT graphene growth by CVD using solid & liquid C sources

Low-Temperature Growth of Graphene by Chemical Vapor Deposition Using Solid and Liquid Carbon Sources

Zhancheng Li, Ping Wu, Chenxi Wang, Xiaodong Fan, Wenhua Zhang, Xiaofang Zhai, Changgan Zeng,* Zhenyu Li,* Jinlong Yang, and Jianguo Hou

ARTICLE

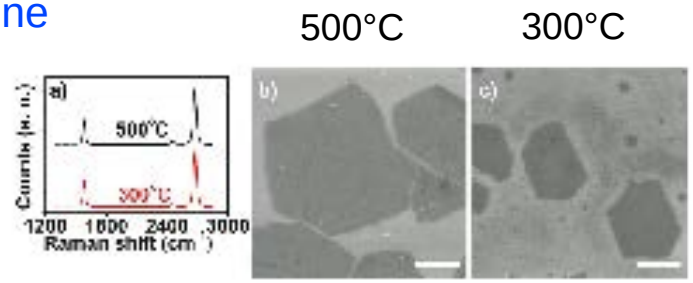
ACSNano 5, 3385 (2011)

A revised CVD method using solid (PMMA) & liquid (benzene) instead of CH_4 gas

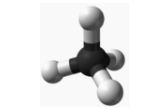
→ enabling low-temperature graphene growth around 300°C (significantly reduced from typical growth temperature of ~1000°C)

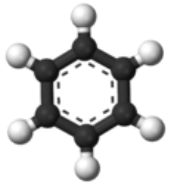
Synthesized graphene from benzene

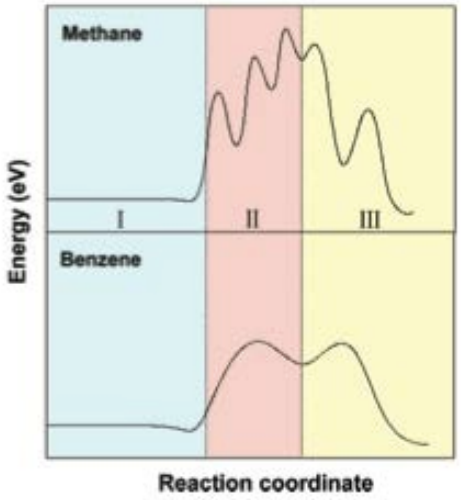
Raman spectra & SEM images



Previous related theoretical studies







ACS Nano 5, 3385 (2011) (no vdW)

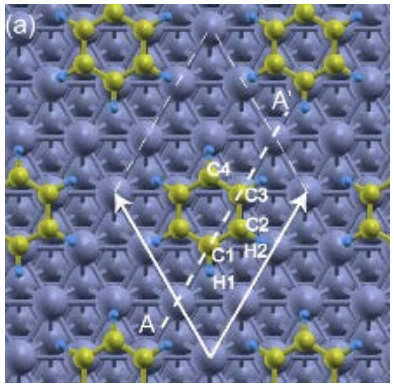
Density functional theory calculations (PBE)

Adsorption energy

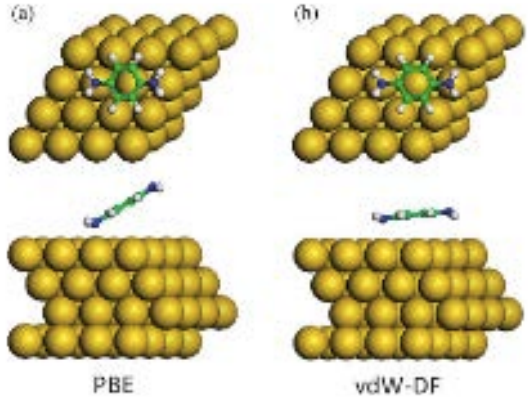
methane: 0.02 eV | benzene: 0.09 eV (exp. ~0.6 eV)

Activation energy of the dehydrogenation

methane: 1.77 eV | benzene: 1.47 eV



Surface Science 603, 2912 (2009)



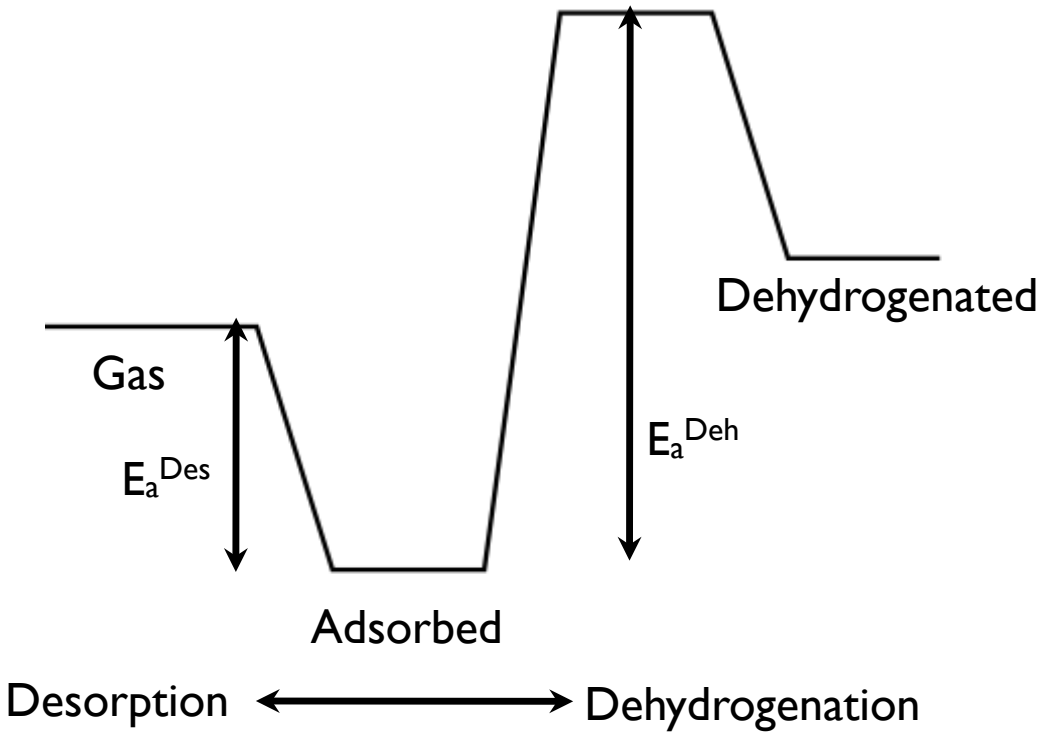
G. Li, et al., PRB 85, 121409(R) (2012)

Inclusion of London dispersion forces

The van der Waals density functional (vdW-DF) provides adsorption energies consistent with experiments.

Central Idea: Desorption vs dehydrogenation

For the adsorbed hydrocarbon molecules, desorption and competes with dehydrogenatic



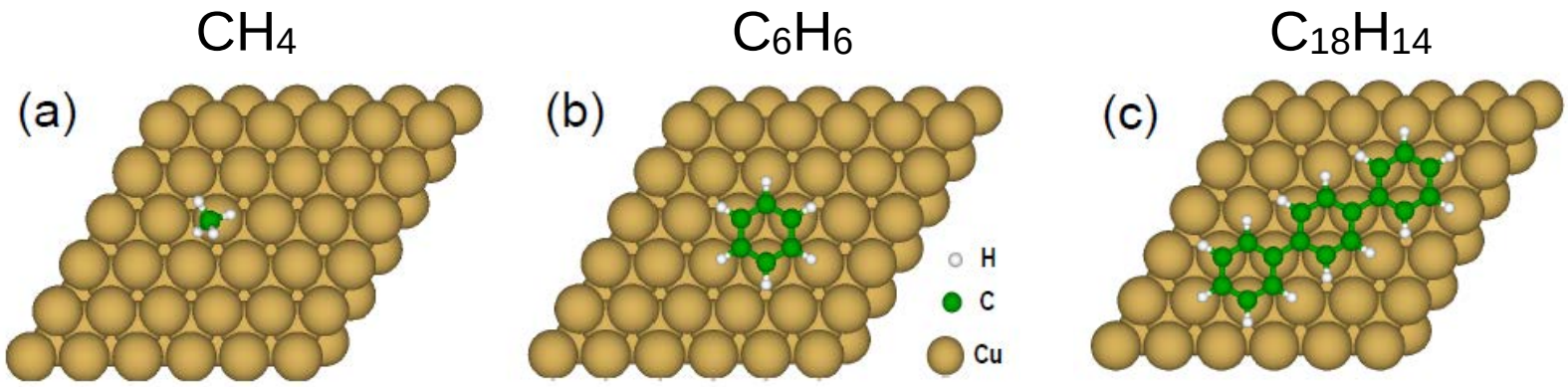
Easy desorption can make the dehydrogenation slow, while enhanced adsorption will prevent easy desorption.

Expectations and Approaches

Enhanced binding due to London dispersion forces leads to the followings:

→ preventing easy desorption of the adsorbed molecule

→ enabling the LT graphene growth from C_6H_6 and $C_{18}H_{18}$



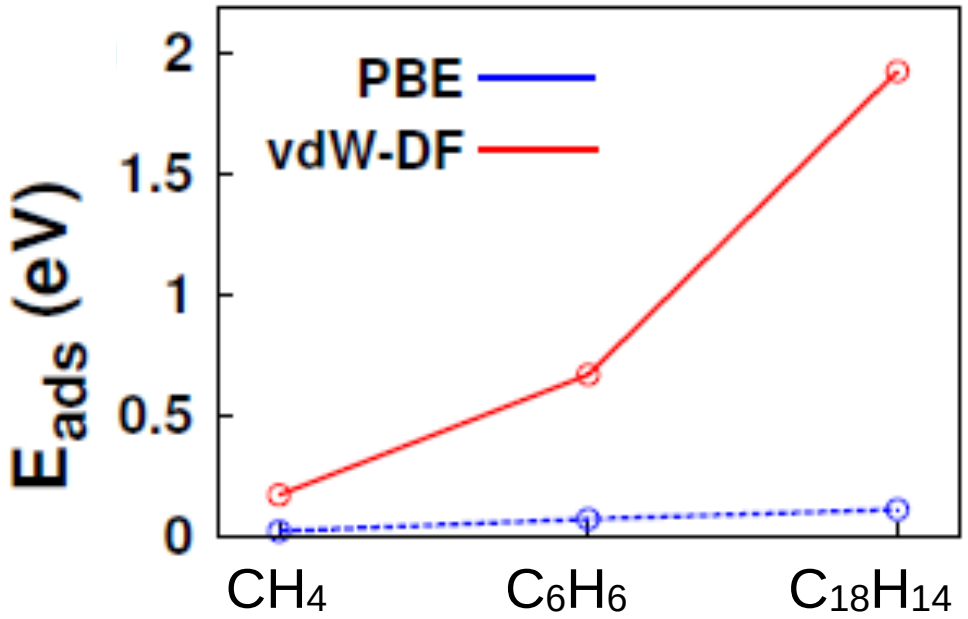
Vienna Ab-initio Simulation Package (VASP)

Cu(111) 6x6, 5layers, 2x2x1 kpoints

PAW pseudo-potentials, 400 meV

PBE, vdW-DF

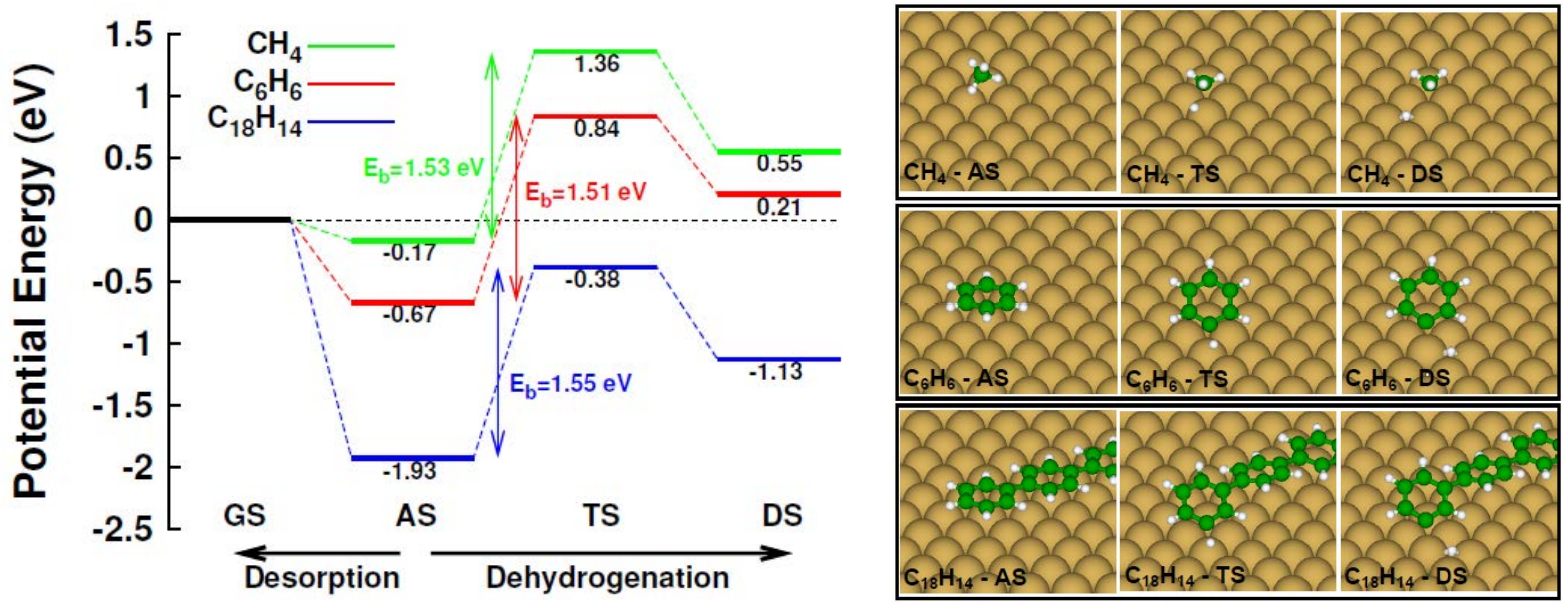
Enhanced binding due to London dispersion forces



vdW-DF calculations show a steep increase in E_{ads} with the molecular size.

- larger molecule → more electrons → larger fluctuating dipole moment
- aromatic structures → arranging parallel to surface → atoms close to the surface

Calculated energetics & kinetics for the three different molecules



Dehydrogenation activation energies for the three molecules are very close.

CH_4 and C_6H_6

$E_a^{Des} < E_a^{Deh}$

$C_{18}H_{14}$

$E_a^{Des} > E_a^{Deh}$

London dispersion forces prevent easy desorption and facilitate further dehydrogenations of the adsorbed molecules.

Time scales for one dehydrogenation event (T_D)

Temperature	estimated T_D (in seconds) CH_4	C_6H_6	$C_{18}H_{14}$
1000°C	0.18	8.4×10^{-4}	5.2×10^{-8}
800°C	1.6 (√)	3.2×10^{-3}	8.5×10^{-7}
600°C	43 (×)	2.3×10^{-2}	4.9×10^{-5}
400°C	8.1×10^{3}	0.57	2.9×10^{-2}
300°C	4.4×10^{5}	6.5 (√)	3.6 (√)
200°C	1.4×10^{8}	1.2×10^{3} (×)	3.3×10^{3} (×)

√: growth success ×: growth failure

——— Temperature boundary of graphene growth

T_D is obtained from calculated reaction rates.

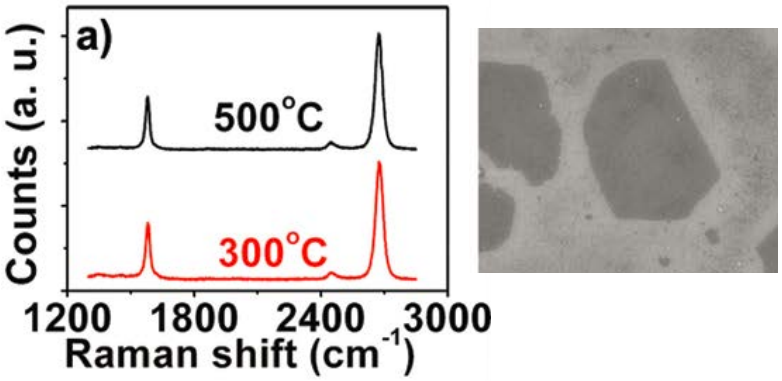
Typical experimental graphene growth time: 15 min ~ 1 hour

Graphene can grow from $C_{18}H_{14}$ at 300°C.

Below 200°C, E_a^{Deh} of ~1.5 eV is too large to overcome.

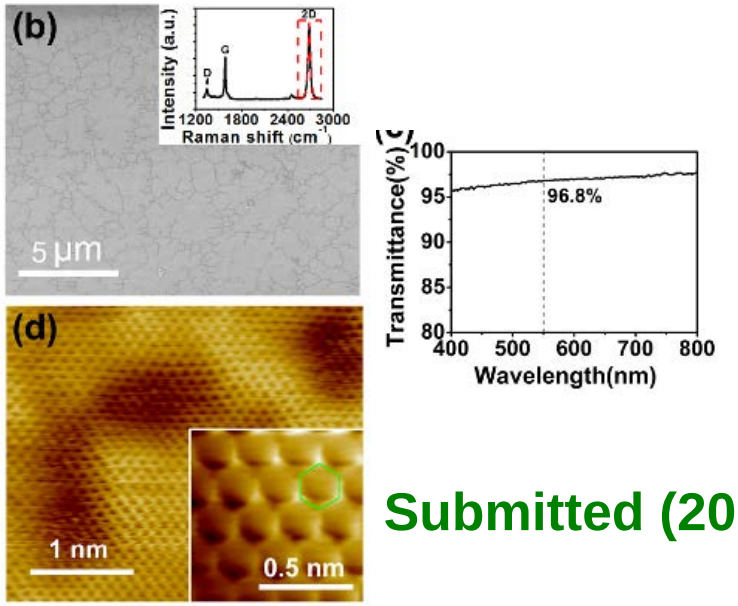
New experimental validations

C_6H_6



ACS Nano 5, 3385 (2011)

$C_{18}H_{14}$



Submitted (2013)

We achieved graphene films from $C_{18}H_{14}$ at low temperature as low as 300°C.

Experiments are consistent with the theoretical predictions.

The grown graphene films are monolayer in thickness.

Main Findings: ~1000 ^{o}C => ~300 ^{o}C!!!

1. Enhanced binding due to London dispersion forces

   - prevents easy desorption of the adsorbed hydrocarbon sources

   - therefore enables the LT graphene growth on Cu substrates

2. Comparison of three different hydrocarbon sources

   - shows the enhanced bindings with increasing molecular size

   - predicts the LT graphene growth from $C_{18}H_{14}$ (experimentally confirmed)

Jin-Ho Choi, Zhancheng Li, Ping Cui, Xiaodong Fan, Changgan, Zeng, and ZZ, Scientific Reports 3, 1925 (2013)

Outline

- Brief Introduction on Motivation
- Atomistic Mechanisms of Epitaxial Growth of Graphene:
  - Why Cu is the preferred substrate? (Hua Chen)
  - Suppression of grain boundaries (Wei Chen)
  - Low-temperature growth (Jin-Ho Choi)
- Going beyond graphene
- Functionalization of 2D materials
  - A few highlights

Walking into/onto Phosphorene
走　近/进　磷烯

Black phosphorene 黑磷？
Blue phosphorene 蓝磷？

PHYSICAL REVIEW LETTERS

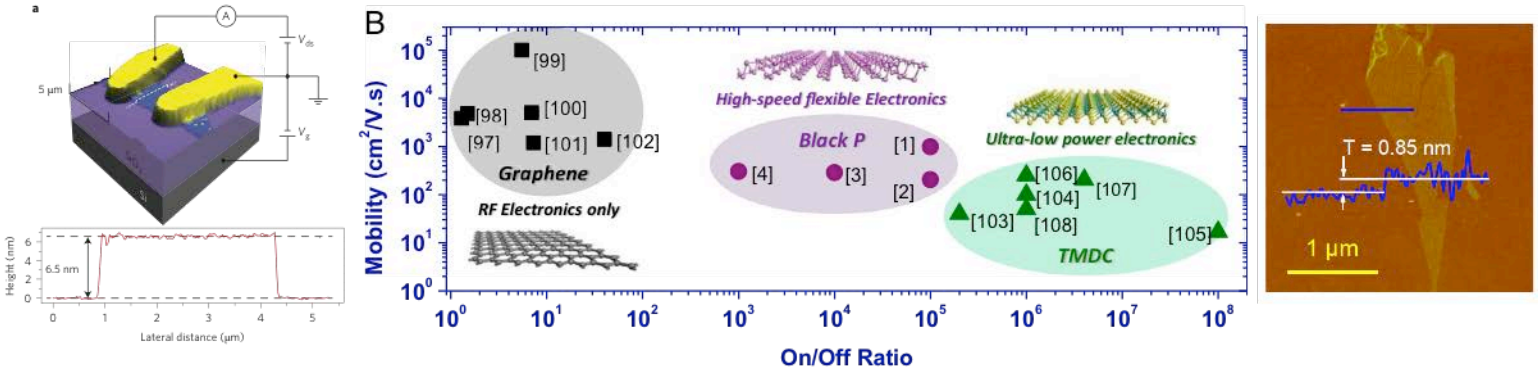
Half-Layer-By-Half-Layer Growth of a Blue Phosphorene Monolayer on a GaN(001) Substrate

Jiang Zeng,[1,2] Ping Cui,[1,*] and Zhenyu Zhang[1,†]
[1]*International Center for Quantum Design of Functional Materials (ICQD), Hefei National Laboratory for Physical Sciences at Microscale (HFNL), and Synergetic Innovation Center of Quantum Information and Quantum Physics, University of Science and Technology of China, Hefei, Anhui 230026, China*
[2]*Beijing Computational Science Research Center, Beijing 100094, China*
(Received 4 June 2016; revised manuscript received 5 December 2016)

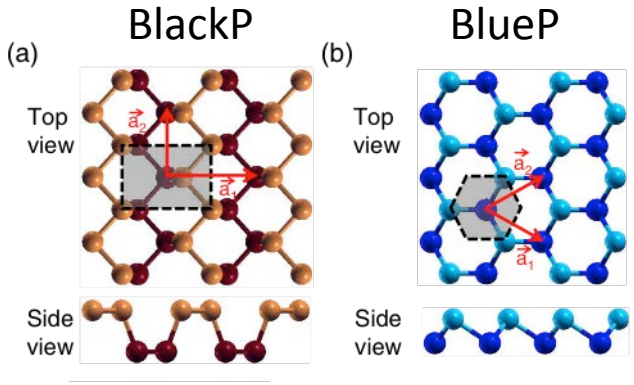
Black phosphorene (BlackP), consisting of a vertically corrugated yet single layer of phosphorus atoms, is a latest member of the expanding two-dimensional (2D) materials family with high carrier mobility and immense application potentials. Blue phosphorene (BlueP), an allotrope of BlackP with appealing

Phosphorene: a latest member of 2D family

Black Phosphorene: high carrier mobility and intrinsic band gap



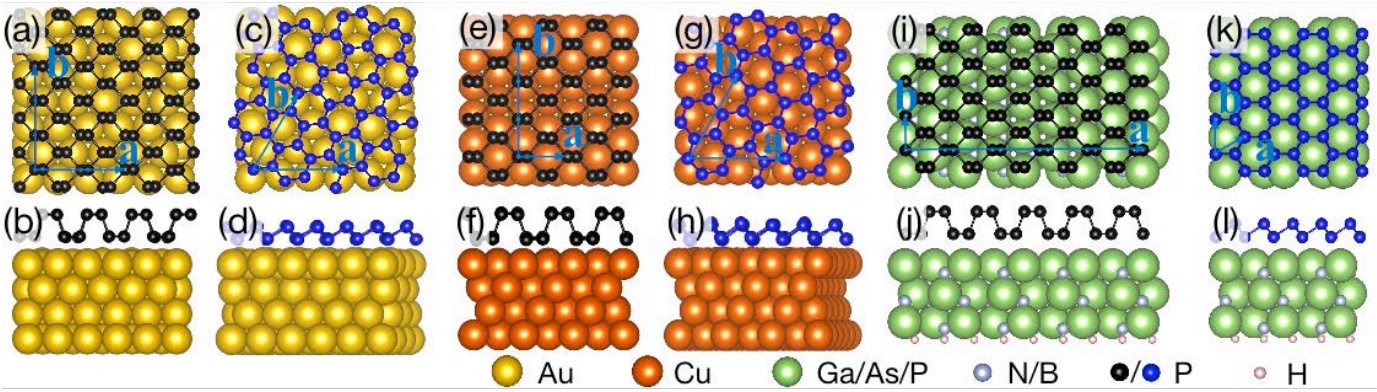
An allotrope: Blue Phosphorene



1. Energetically nearly degenerate
2. Tunable band gap
3. High carrier mobility
4. Flatter structural configuration

Xian Hui Chen, Yuanbo Zhang *et al.*, Nature Nanotech. 9, 372 (2014)
Zhen Zhu and David Tománek, PRL 112, 176802 (2014)
Han Liu *et al.*, ACS Nano 8, 4033 (2014)
Xi Ling *et al.*, PNAS 112, 4523 (2015)
Jin Xiao *et al.*, Scientific Report 5, 09961 (2015)

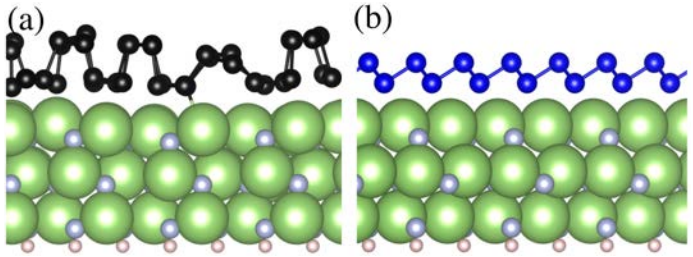
Epitaxial growth



Lattice mismatches and binding energies of BlackP and BlueP

		BAs	BP	Cu	Au	GaN
	a_0 (Å)	3.41	3.22	2.56	2.95	3.25
BlackP	δ_a (%)	4.35	-1.65	-1.78	-2.25	-0.60
	δ_b (%)	3.07	-2.86	3.42	2.99	-1.82
	$E_{\text{b-D2}}$ (eV)	0.42	0.56	0.69	0.76	0.71
	$E_{\text{b-TS}}$ (eV)	0.20	0.27	0.37	0.33	0.42
	$E_{\text{b-DF2}}$ (eV)	0.18	0.29	0.30	0.31	0.41
BlueP	δ (%)	3.70	-2.27	2.23	1.75	-1.22
	$E_{\text{b-D2}}$ (eV)	0.49	0.58	0.86	0.88	0.88
	$E_{\text{b-TS}}$ (eV)	0.23	0.32	0.53	0.37	0.49
	$E_{\text{b-DF2}}$ (eV)	0.20	0.31	0.44	0.33	0.45

AIMD simulations



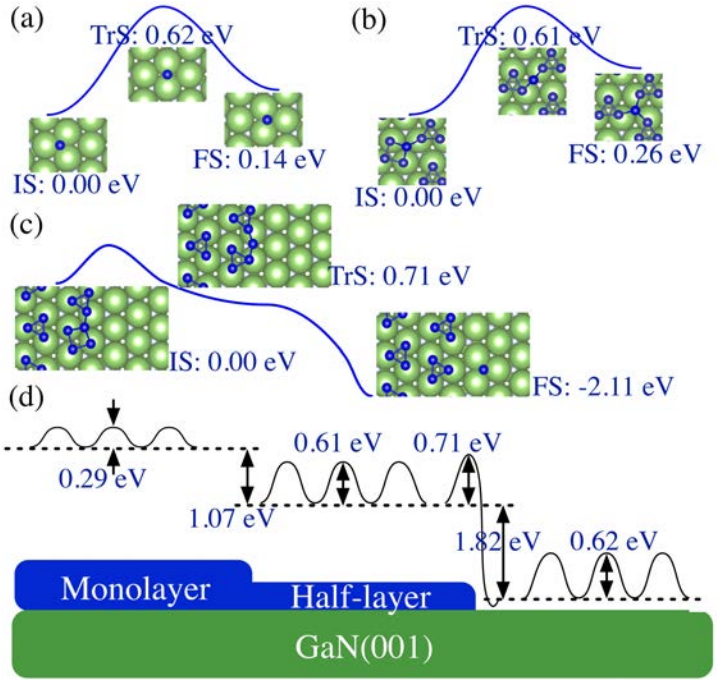
400 K: 1-ps 400K 50-ps

Due to the chemical activity and instability of both phosphorene, the chemical affinity and lattice mismatch become important factors for epitaxial growth of phosphorene on a substrate.

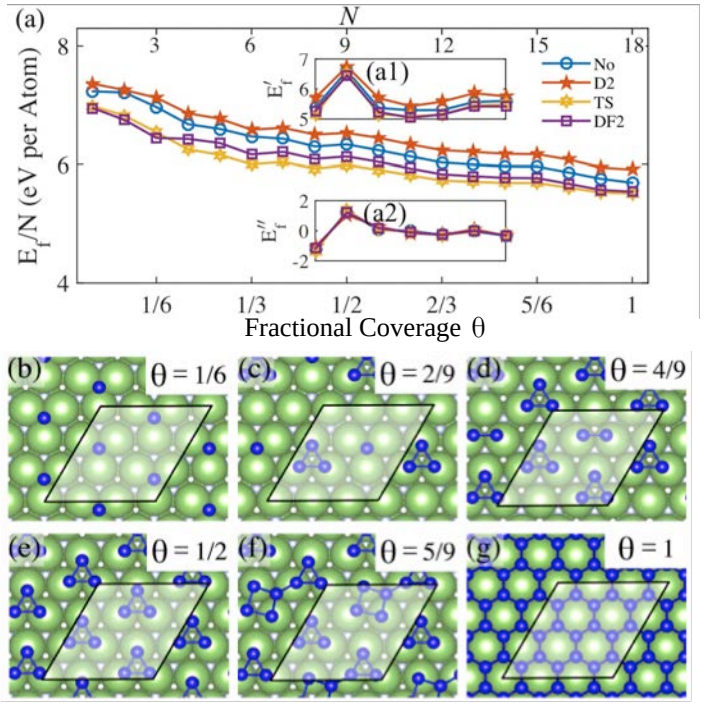
With flatter structural configuration, the BlueP is more stable than BlackP on GaN(001).

Xian Hui Chen, Yuanbo Zhang *et al.*, Nature Nanotech. 9, 372 (2014)
A. H. Castro Neto *et al.*, PRL 114, 046801 (2015)

Diffusion and metastable configuration

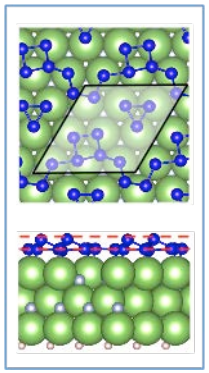


Diffusion barriers



Metastable configurations

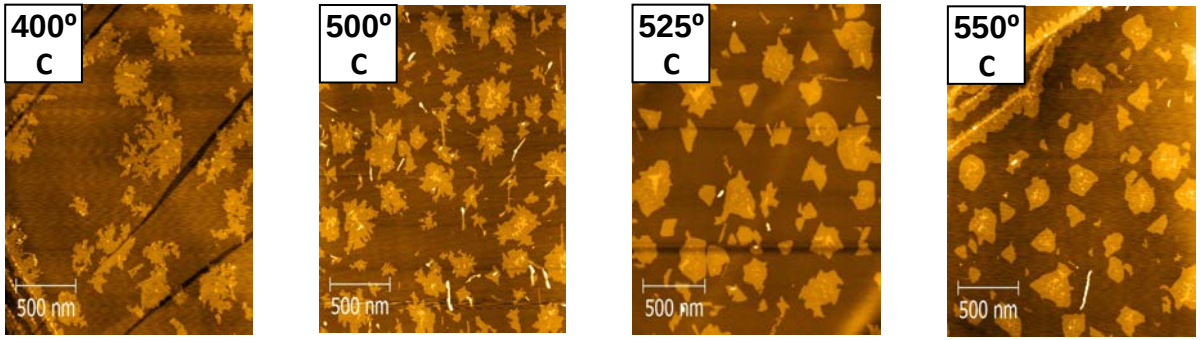
θ =11/18



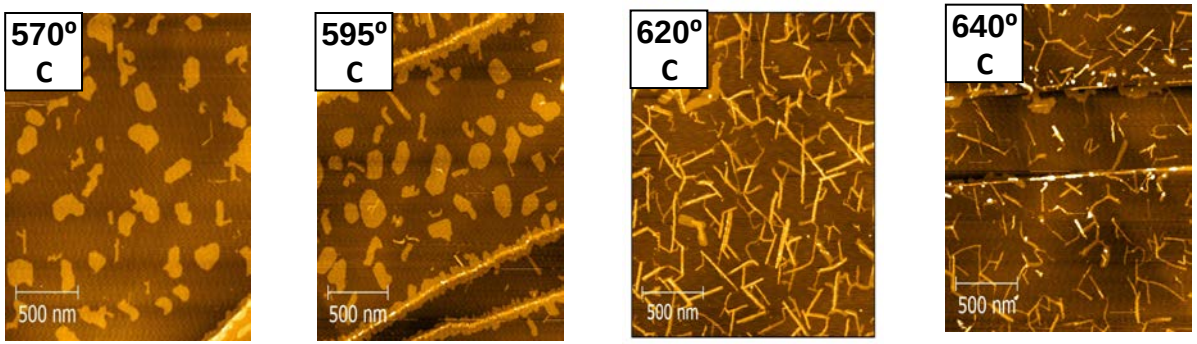
Half-Layer-By-Half-Layer

Controlled Fabrication of TMD Nanoribbons

Yuxuan Chen, Ping Cui, … Zhenyu Zhang, Chih-Kang Shih, Nature Comm. (to appear)



a b c d



e f g h

Outline

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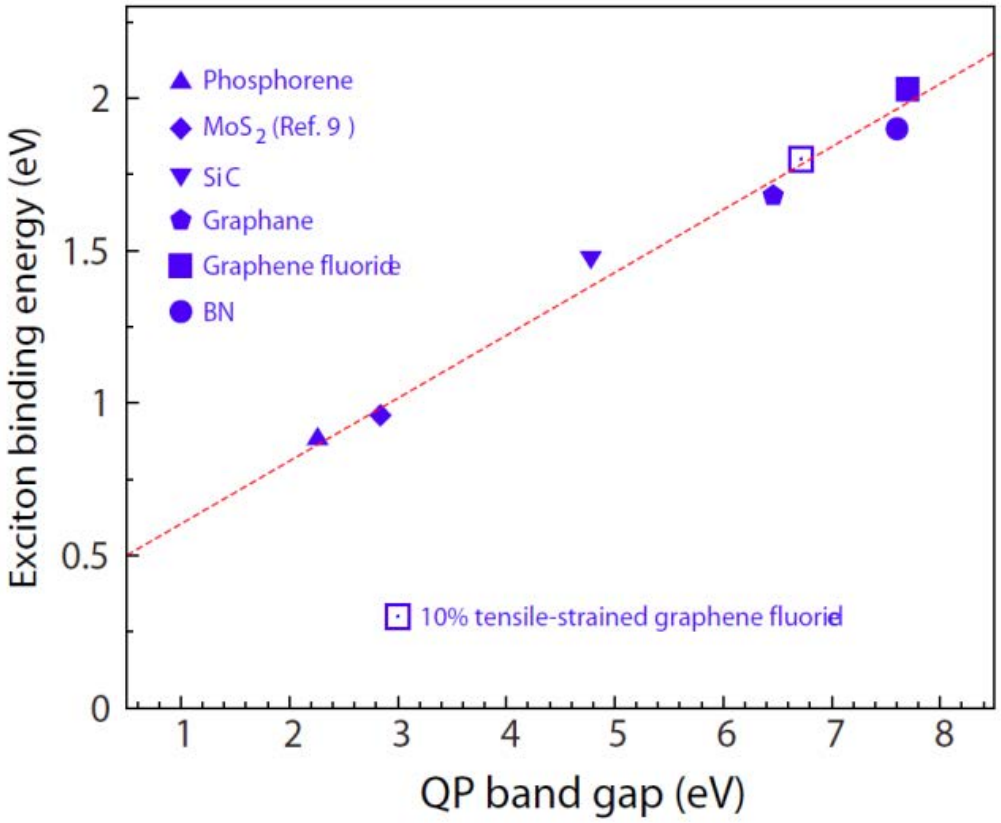
- Going beyond graphene (Jiang Zeng)
- Functionalization of 2D materials
  - A few highlights

几个例子，几个方面

光学响应
信息储存
能源催化
自旋磁性
量子输运

Linear Scaling of the Exciton Binding Energy versus the Band Gap of 2D Materials



Jin-Ho Choi, Ping Cui, Haiping Lan, ZZ, Phys. Rev. Lett. 115, 066403 (2015).

See also:

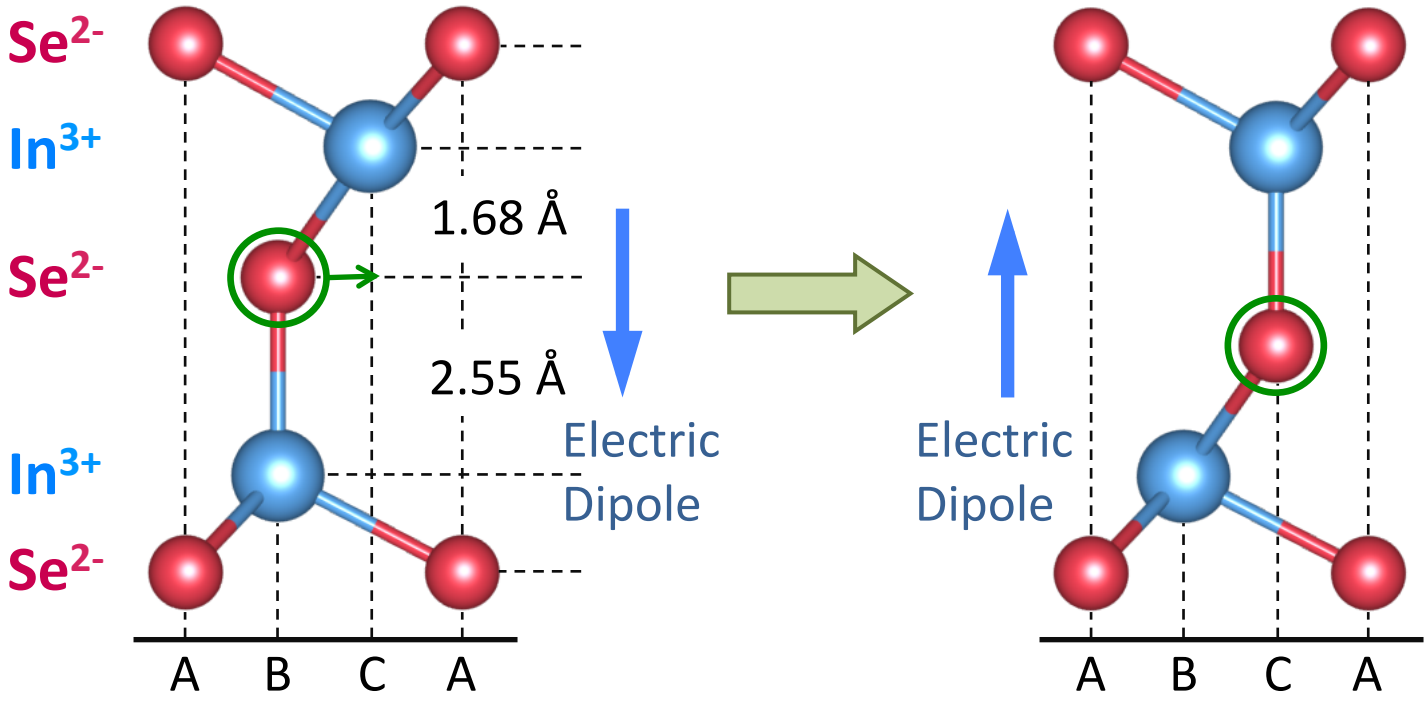
Olsen et al., , *Phys. Rev. Lett.* 116, 056401 (2016).

Generalized to 51 TMD systems.

- Discovering a universal linear scaling relationship between the exciton binding energy and band gap of 2D materials within the first-principles *GW*–BSE approach.
- Underlying physics within within a generalized hydrogenic picture with anisotropic screening.

The 1st Known Class of 2D Ferroelectric Materials

Wenguang Zhu, ZZ, et al., ***Nature Comm.*** (2017, to appear)

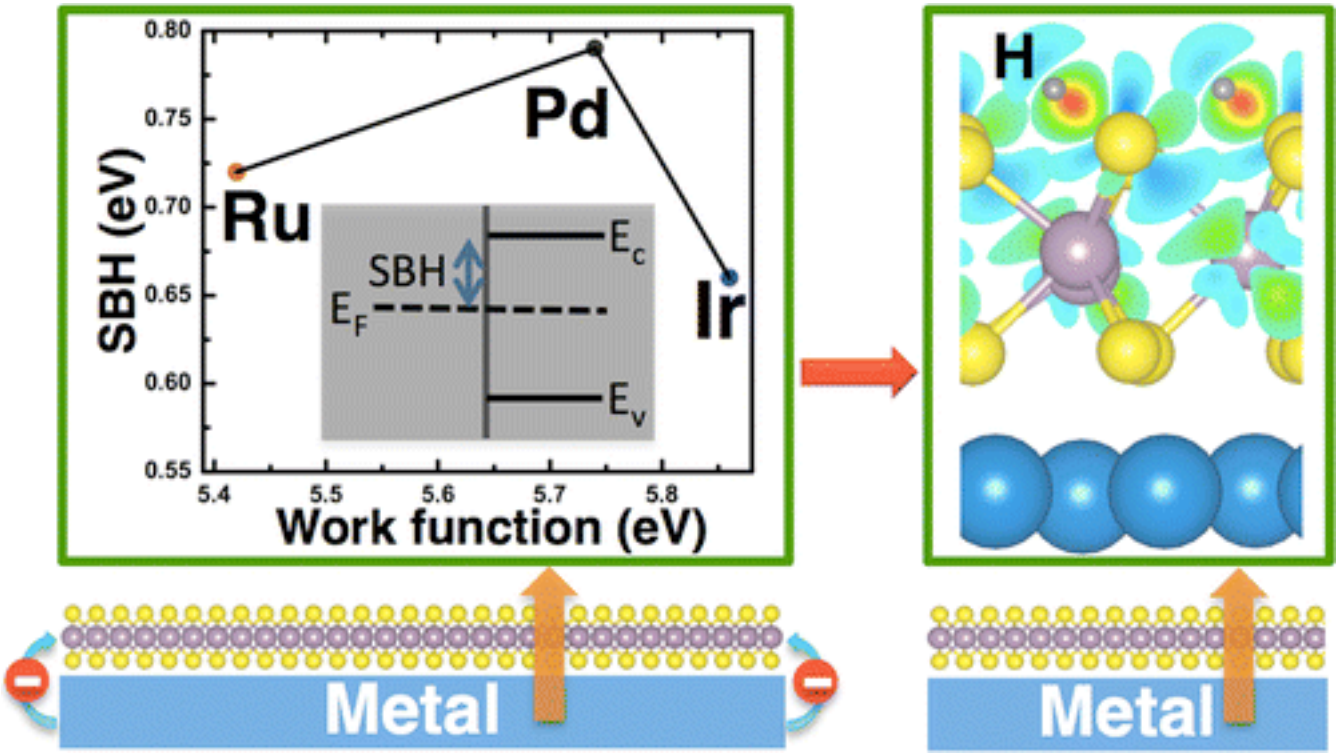


Predictive design of intrinsic 2D ferroelectrics in In_2Se_3 and other III_2-VI_3 vdW materials with
(a) vertical polarization, (b) easy reversibility

59

Electronic, Transport, and Catalytic Properties of MoS_2 on Precious Metal Substrates

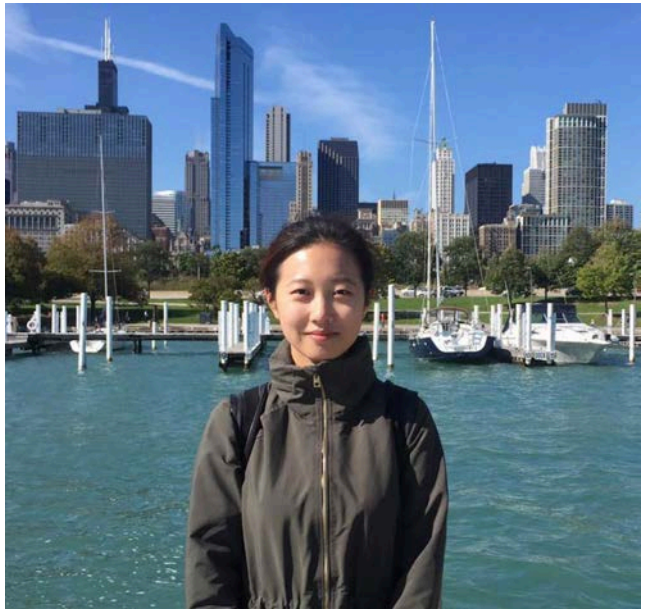
Wei Chen, Tim Kaxiras, ZZ, et al., ***Nano Lett.*** 13, 509 (2013)



- The contact nature of MoS_2 on three precious metal substrates is of Schottky-barrier type, exhibiting a partial Fermi-level pinning picture.
- The chemical reactivity of MoS_2 measured by the hydrogen binding energy is enhanced by the charge transfer from the substrates.

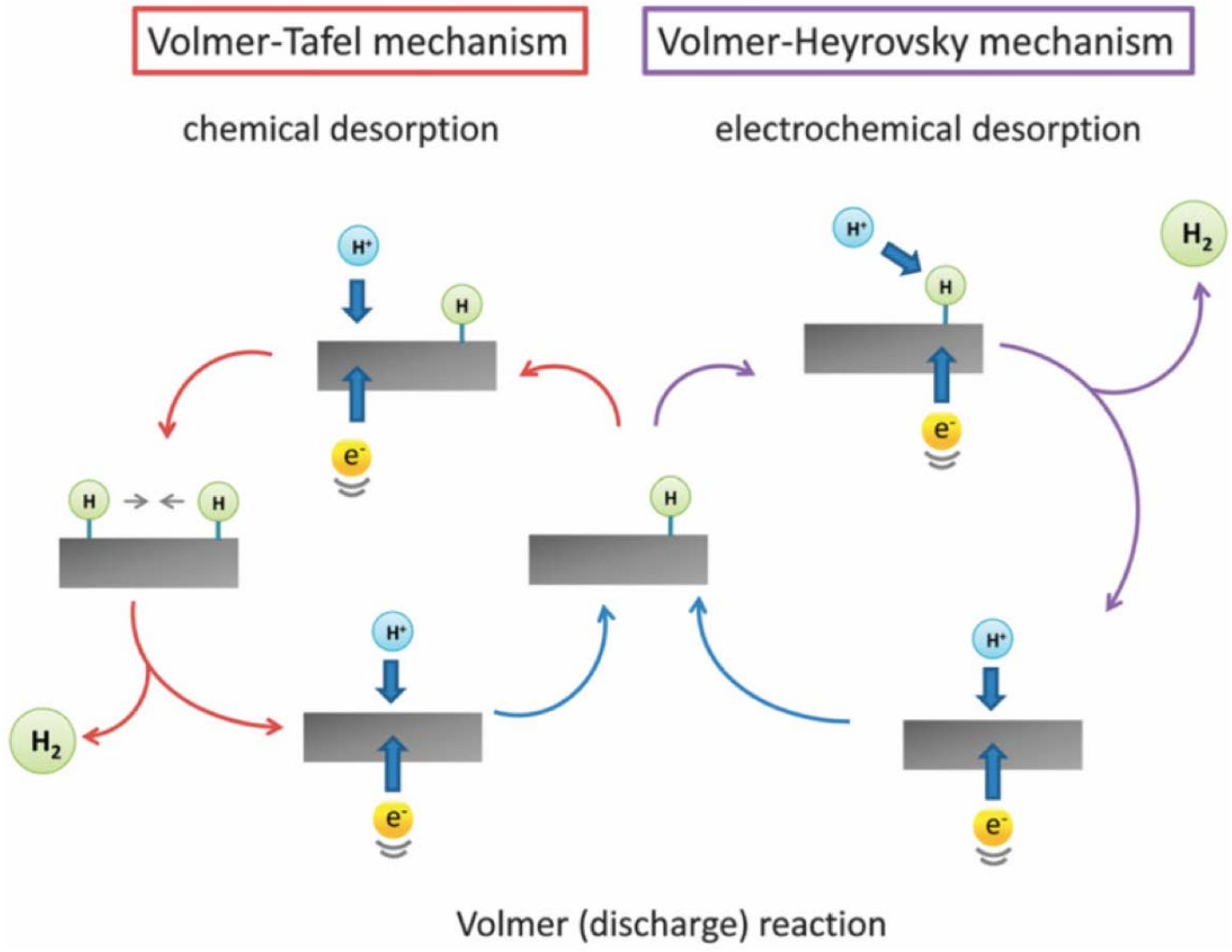
Enhancing the Hydrogen Activation Reactivity of Nonprecious Metal Substrates via Confined Catalysis Underneath Graphene

Yinong Zhou, Wei Chen, Ping Cui, Jiang Zeng, Zhuonan Lin, Efthimios Kaxiras, and Zhenyu Zhang, Nano Lett. (2016)



USTC Undergraduate Research Assistant

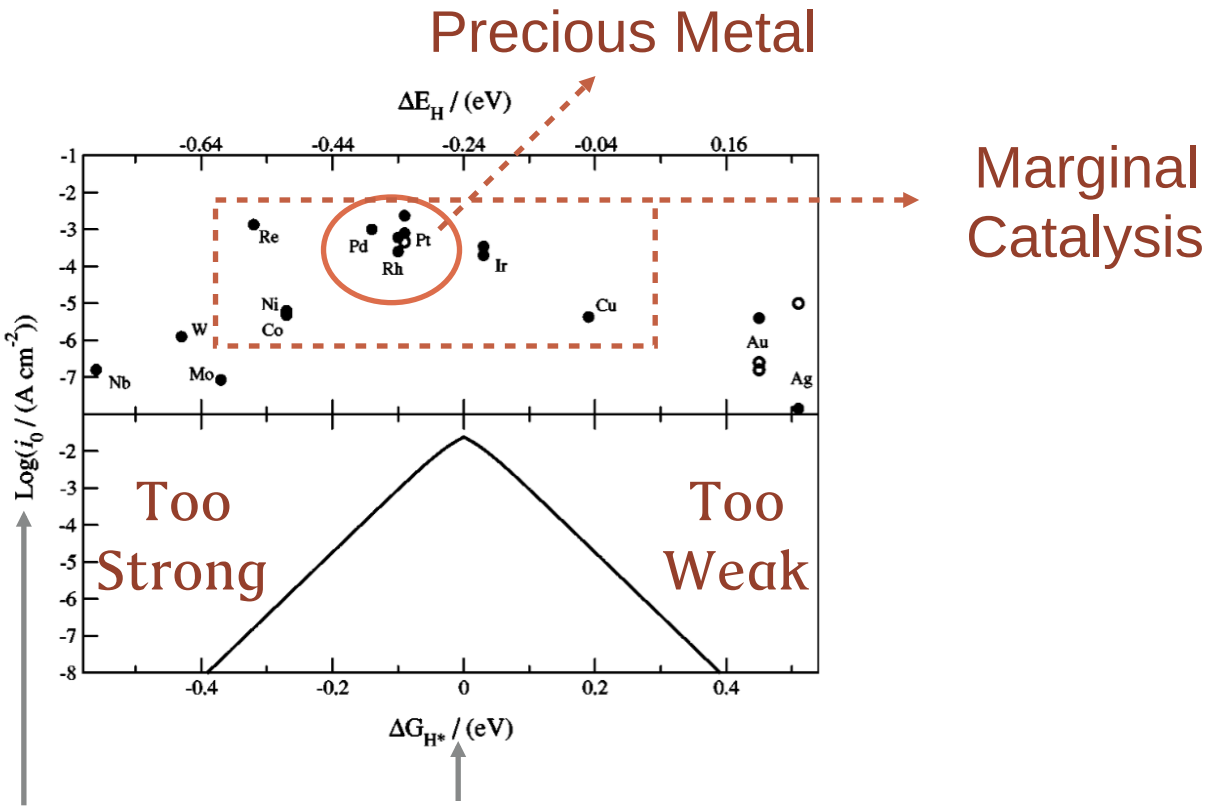
Background: Hydrogen Evolution Reaction (HER)



Morales-Guio CG, Stern LA, Hu X. Chemical Society Reviews. 2014, 43, 6555.

Volcano Curve for HER

Nørskov, J. K.. J. Electrochem. Soc. 2005, 152, J23.



Exchange current density

$$i_0 \propto \exp\left(-\left|\Delta G_{H^*} - \Delta G_{peak}\right| / kT\right)$$

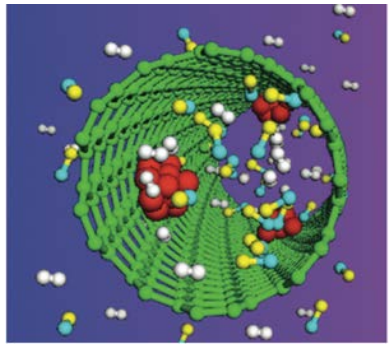
Adsorption free energy of hydrogen

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H = \Delta E_H + 0.24 \text{ eV}$$

How to convert non-precious metals or materials into efficient catalysts?

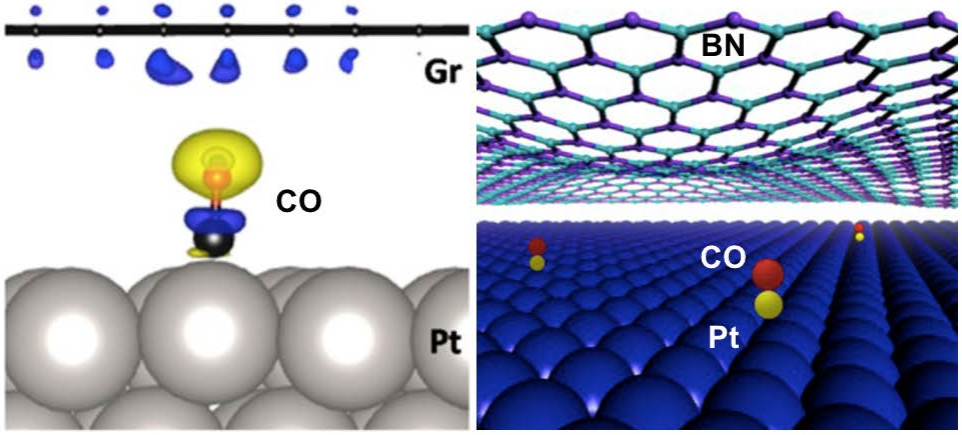
Confined Catalysis

Carbon Nanotube



Pan, X., & Bao, X. Acc. Chem. Res. 2011, 44, 553.

Graphene or h-BN Overlayer

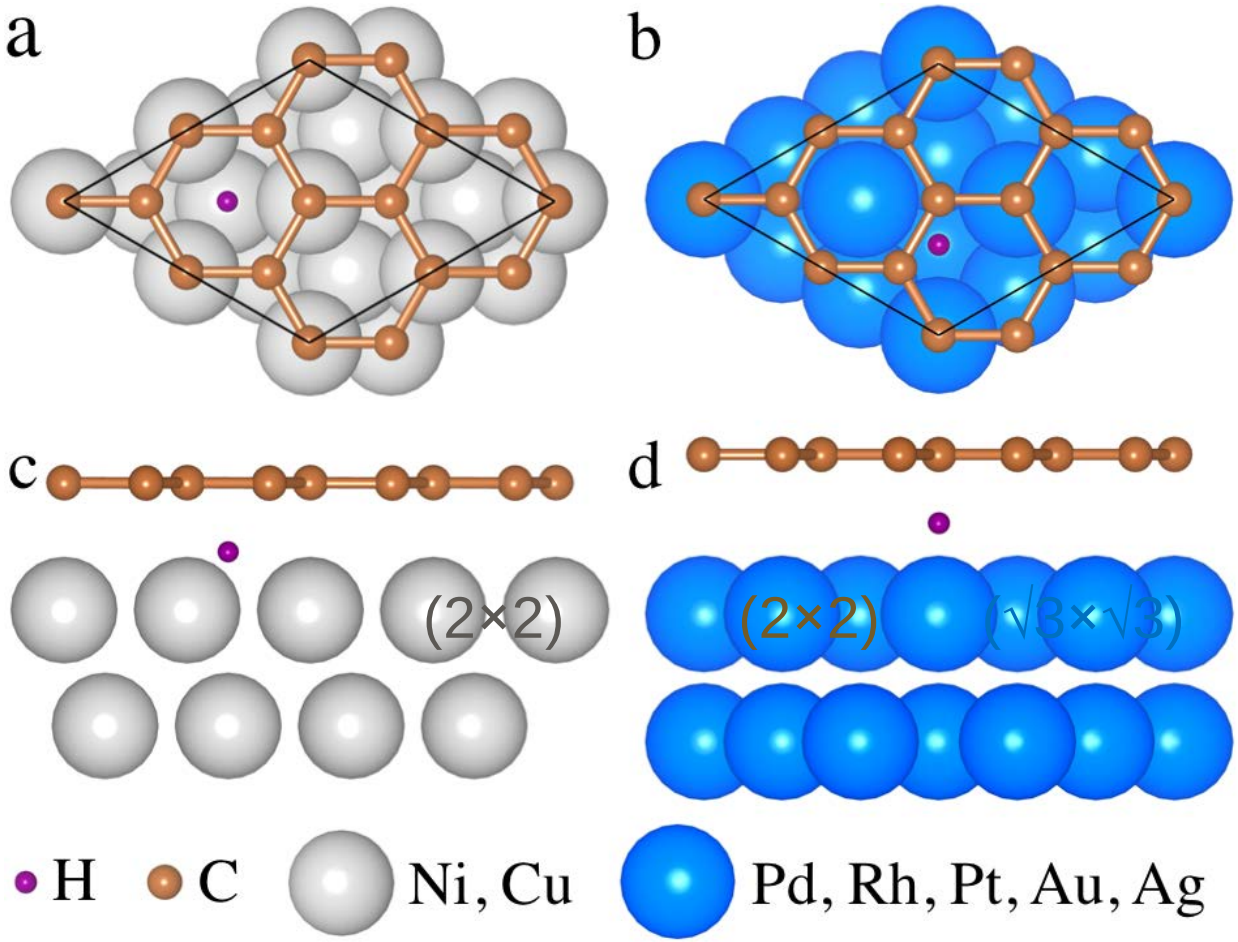


Yao, Yunxi, et al. PNAS. 2014, 111, 17023;
Bao, X, et al. Nano Lett. 2015, 15, 3616.

Q: With the assistance of graphene, which metal is best for HER?

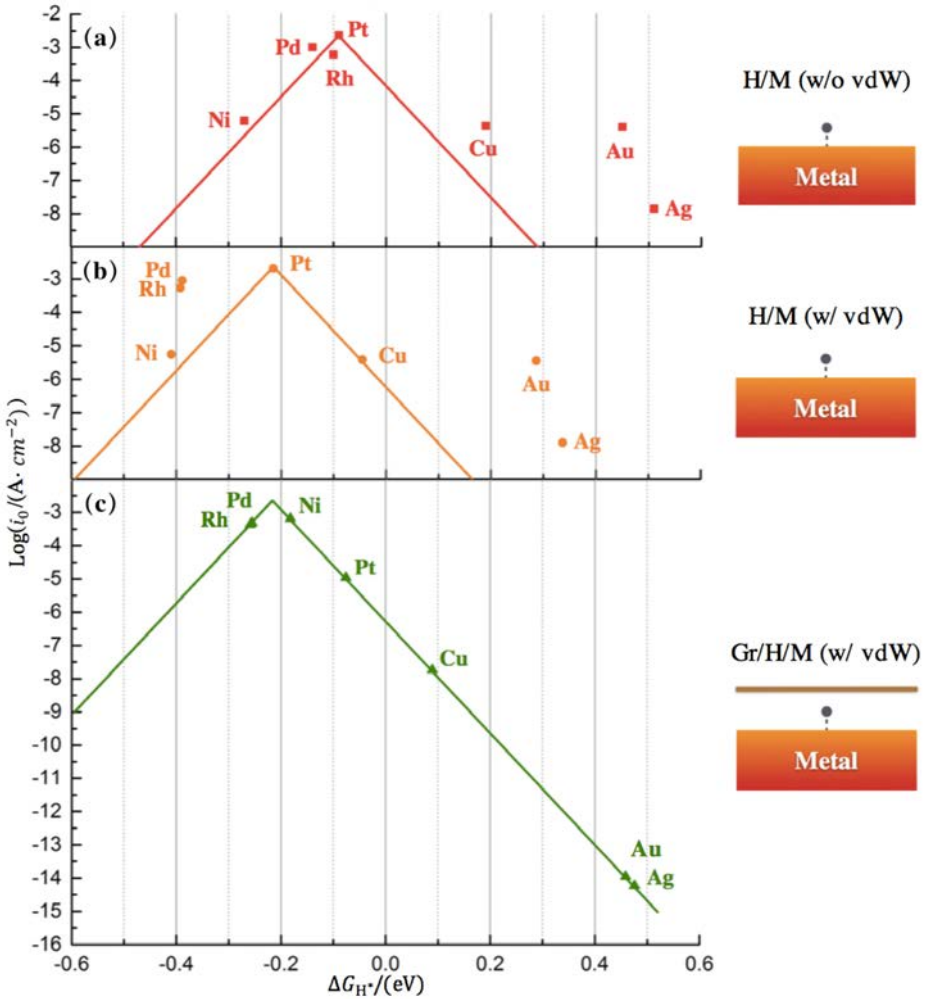
(Confined Catalysis + Marginal Catalysis)

Model Systems Considered



Confined Catalysis + Marginal Catalysis

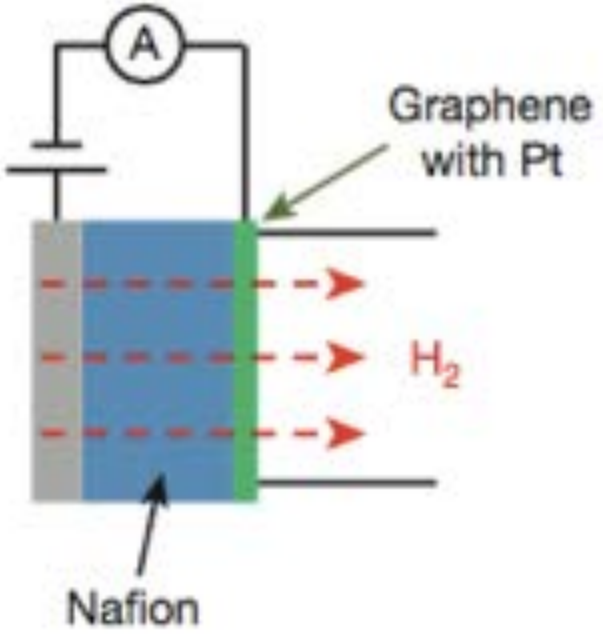
Central Finding



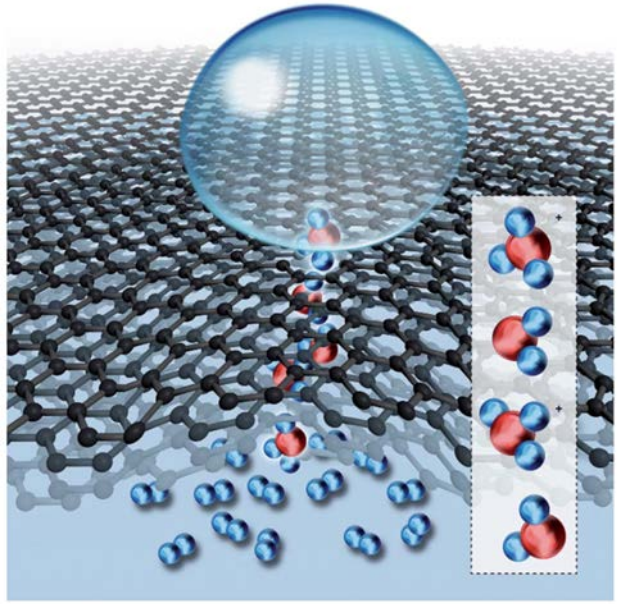
- The vdW corrections enhance the binding between H and metal,with the new peak still located at the most reactive metal Pt (ΔG_{H^*} = −0.21 eV).
- The graphene overlayer weakens the adsorption free energy of hydrogen on the metal surfaces by about 0.12−0.23 eV, with Ni showing the only reactive non precious metal for HER.

“点镍成金”

Experimental Aspects



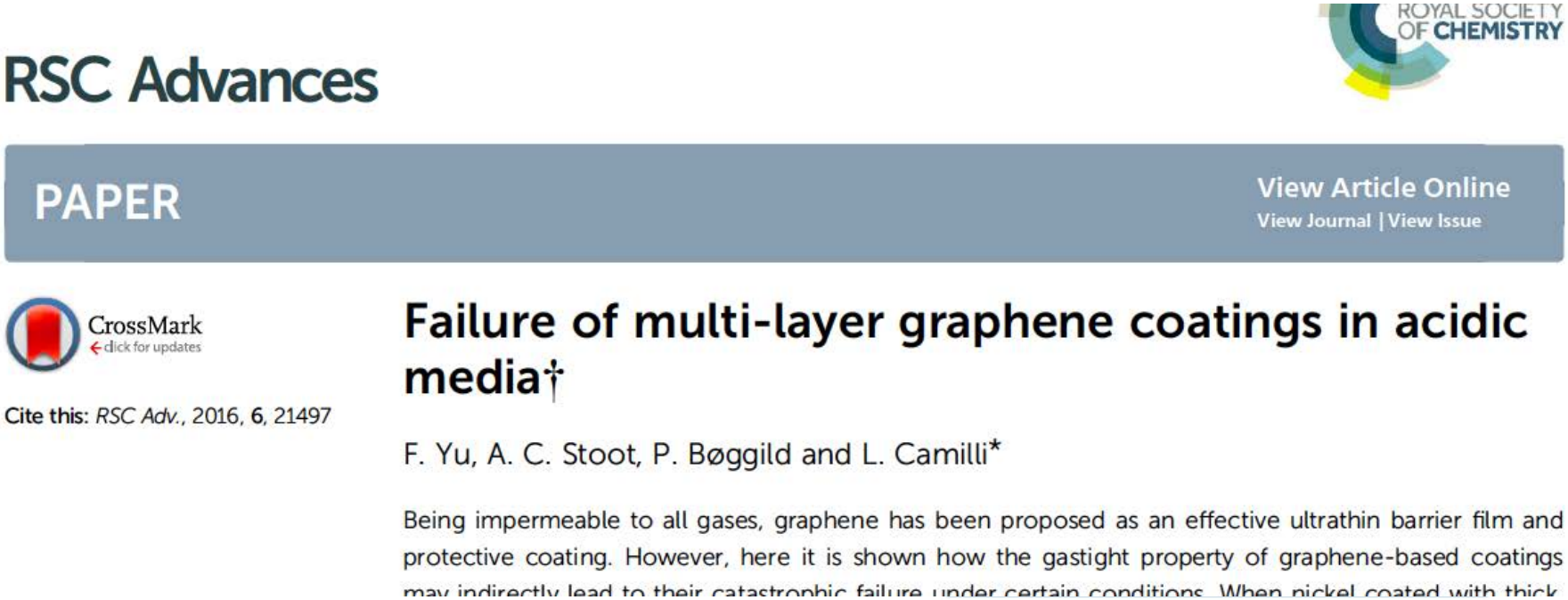
Hu, S., et al. Nature, 2014, 516, 227.



Yu, *et al.* RSC Advances, 2016, 6 21497.

Hydrogen ions readily in, hydrogen molecules easily out

Experimental Aspects



RSC Advances

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Cite this: *RSC Adv.*, 2016, **6**, 21497

Failure of multi-layer graphene coatings in acidic media†

F. Yu, A. C. Stoot, P. Bøggild and L. Camilli*

Being impermeable to all gases, graphene has been proposed as an effective ultrathin barrier film and protective coating. However, here it is shown how the gastight property of graphene-based coatings may indirectly lead to their catastrophic failure under certain conditions. When nickel coated with thick

Hu, S., et al. Nature, 2014, 516, 227.

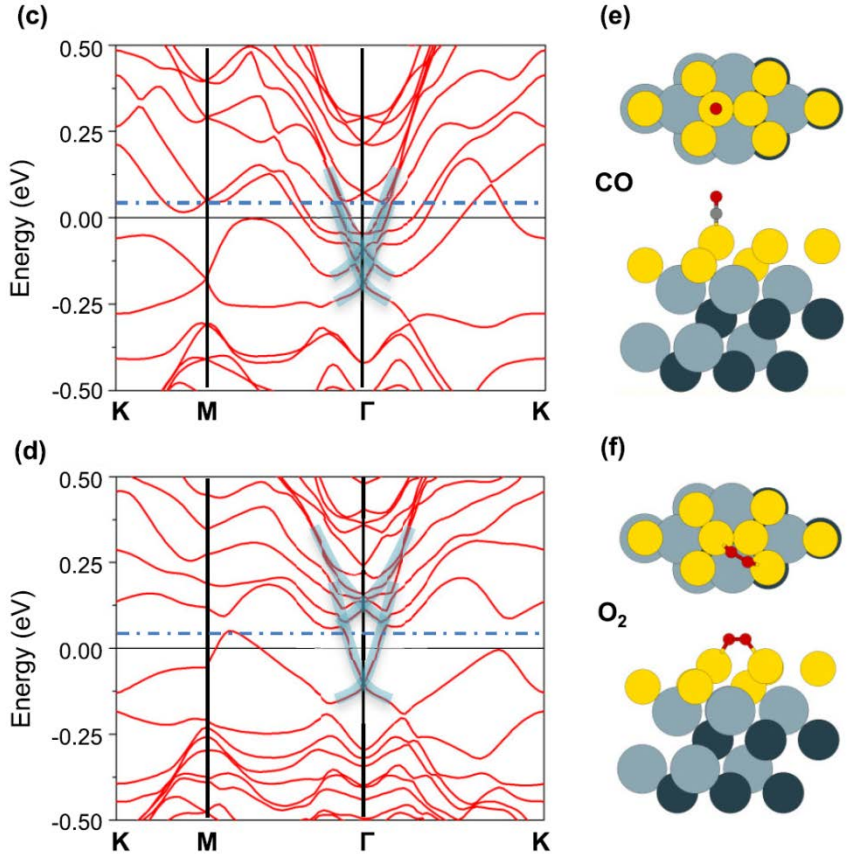
Yu, *et al.* RSC Advances, 2016, 6 21497.

Hydrogen ions readily in, hydrogen molecules easily out

Topological Catalysis via Robust Topological Surface State(s) (TSS) on Au-Covered Bi_2Se_3

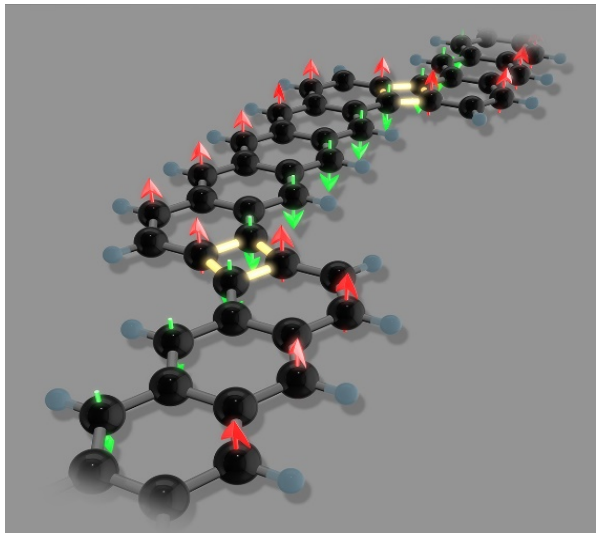
Hua Chen, Wenguang Zhu, Di Xiao, ZZ, ***Phys. Rev. Lett.*** 107, 056804 (2011)

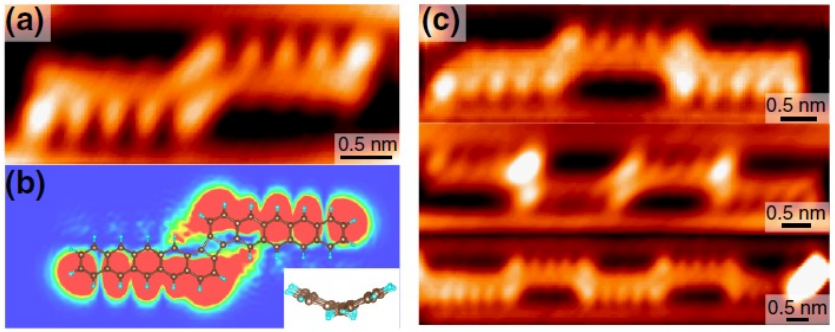
CO and O_2 on Au-covered Bi_2Se_3



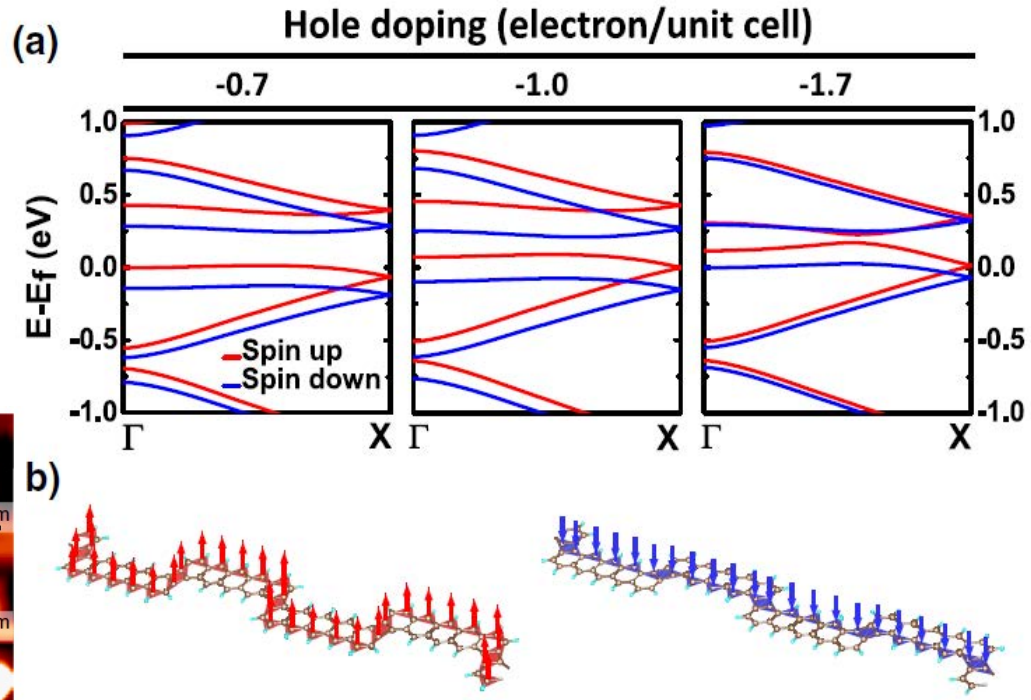
Protected TSS of topological insulators could be exploited to enhance surface reaction dynamics.

Carbon Quartets as Definitive Spin Switches in Narrow Zigzag Graphene Nanoribbons (ZGNRs)



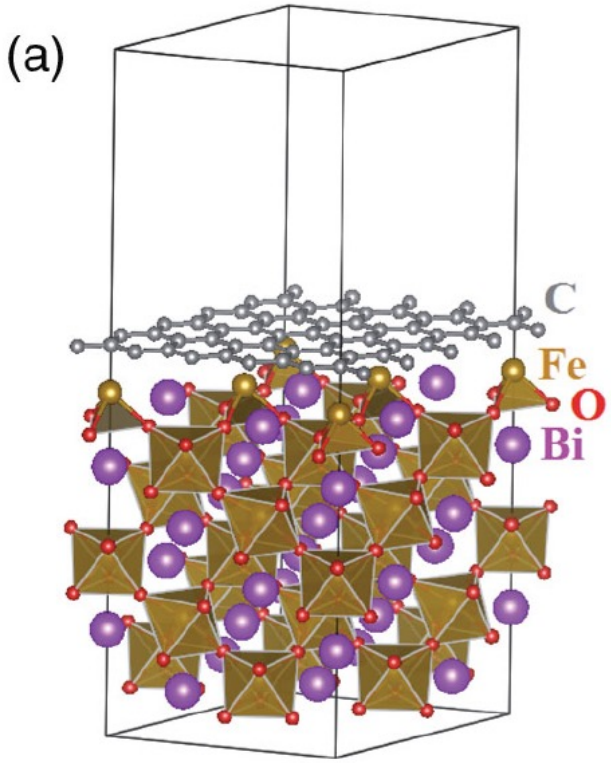


Ping Cui, Changgan Zeng, ZZ, et al.,
Phys. Rev. Lett. 116, 026802 (2016)



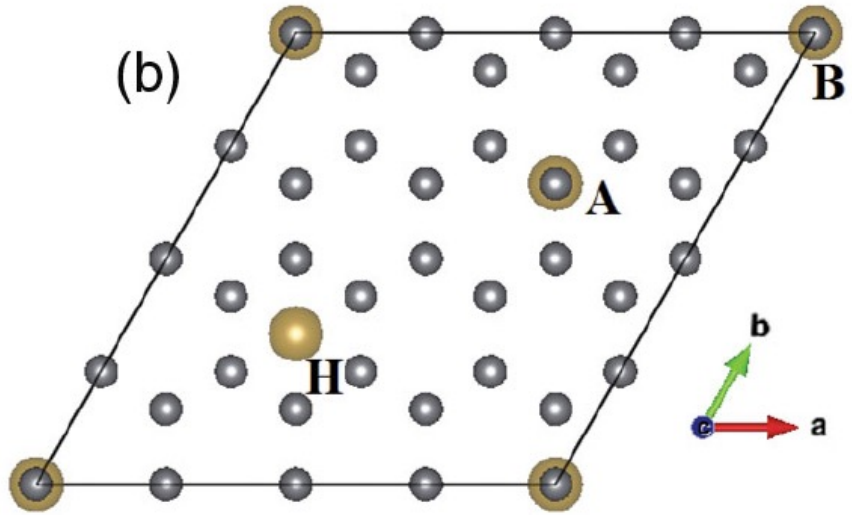
- Predictive design of a topological spin switch capable of regulating the spin channels along the two edges of ZGNRs.
- Demonstration of activated or suppressed spin channels via charge doping.

Predictive Design of Realizing Quantum Anomalous Hall Effect (QAHE) in Graphene



Graphene on a (111) $BiFeO_3$ surface

Zhenhua Qiao, ZZ, Qian Niu, et al.
Phys. Rev. Lett. 112, 116404 (2014)



One Fe layer on graphene

Realizing QAHE by proximity coupling graphene to an antiferromagnetic insulator

(a) Breaking time-reversal symmetry

(b) Enhancing Rashba spin-orbit coupling

Concluding Remarks

- **Growth of 2D materials and heterostructures via vdW epitaxy on various substrates provides an ideal new playground for the surface and thin-film growth community to make important contributions.**

- **Such contributions will likely make a difference, by advancing the field more towards fundamental growth science and beyond.**

- **Collectively, we may also help to deliver the high expectations in graphene electronics， spintronics， and other functional devices based on vdW heterostructures.**