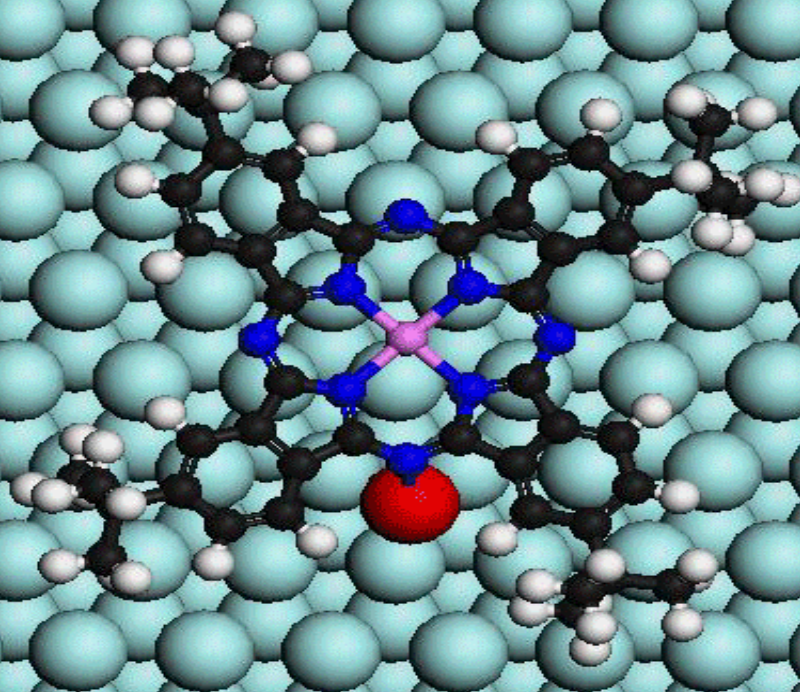


*Construction of an Anchored and Off-centered  
Single Molecular Rotor Array*

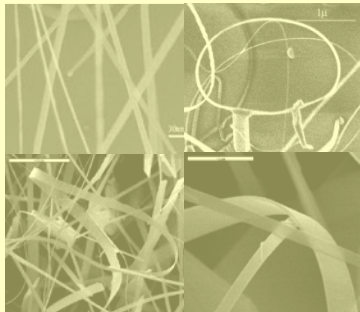


H.-J. Gao Group (高鸿钧), IOP-CAS, China

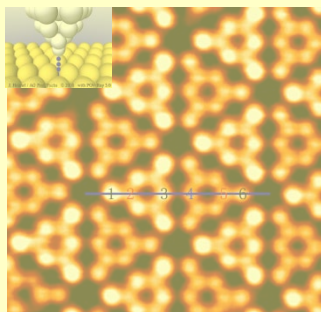
# 纳米量子结构的构造与物性

高 鸿 钧

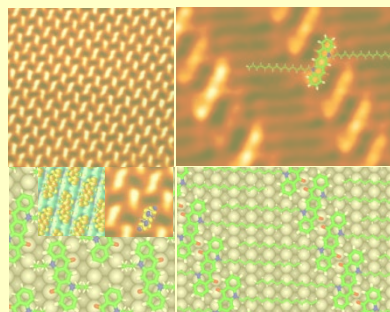
中国科学院物理研究所



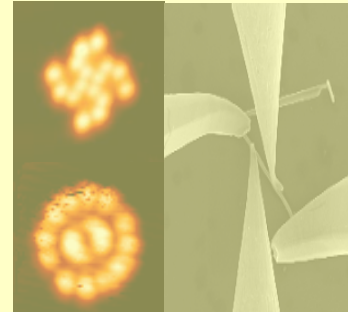
“Structuring”



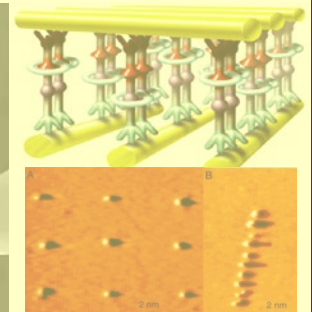
“Seeing”



“Understanding”

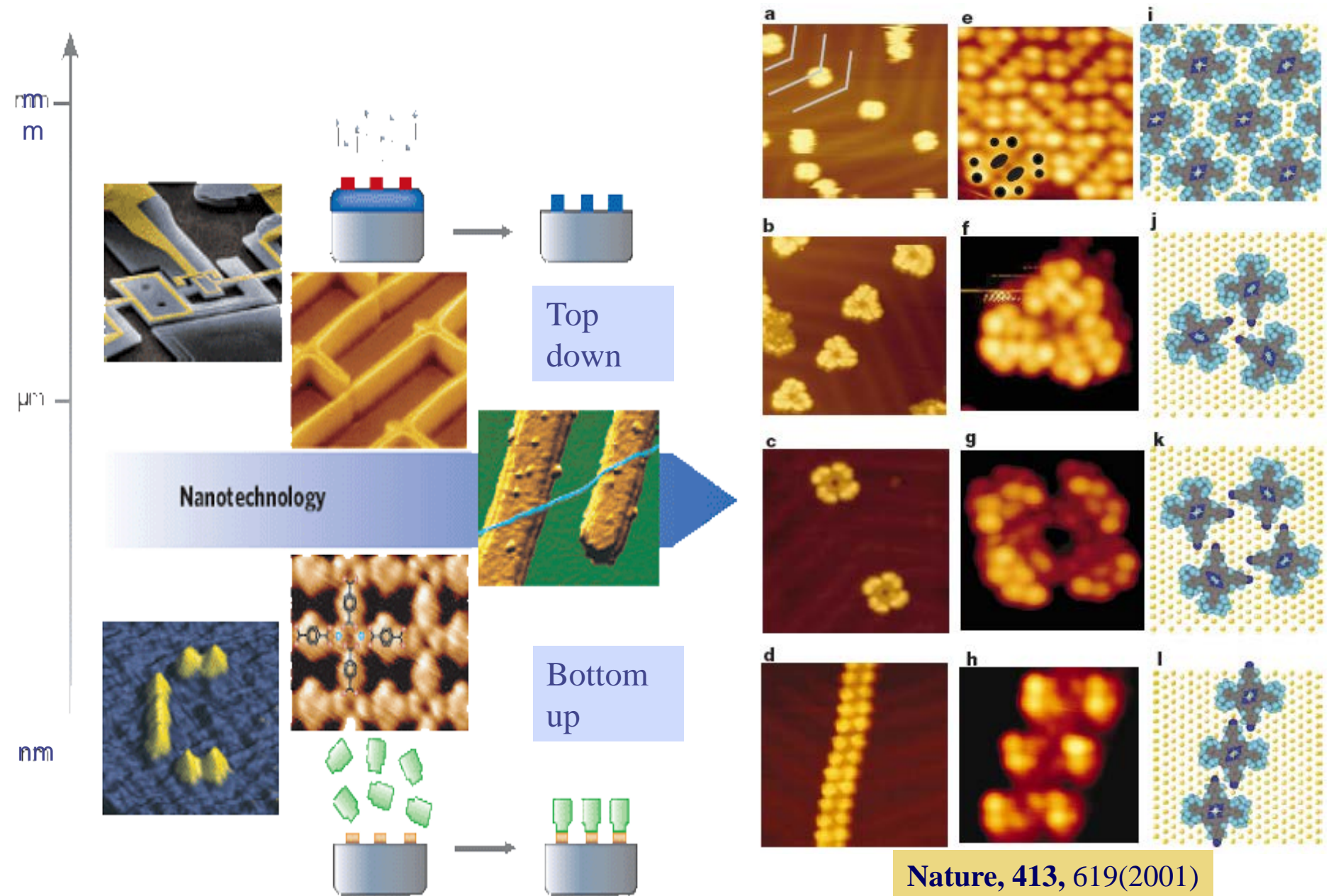


“Controlling”

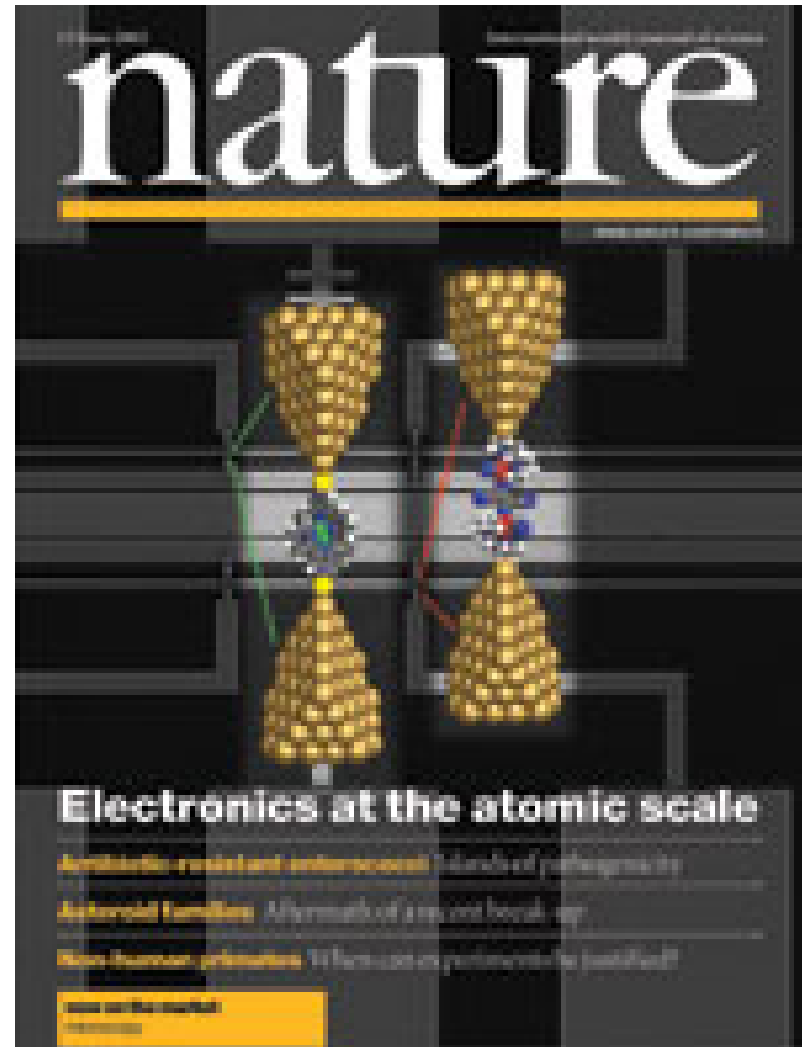


“Functionalizing”

# 纳米量子结构的构造及其特性



# 纳米量子结构组装与物性



## Challenges:

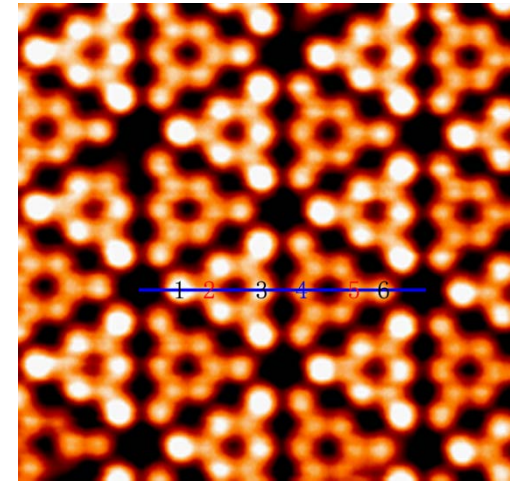
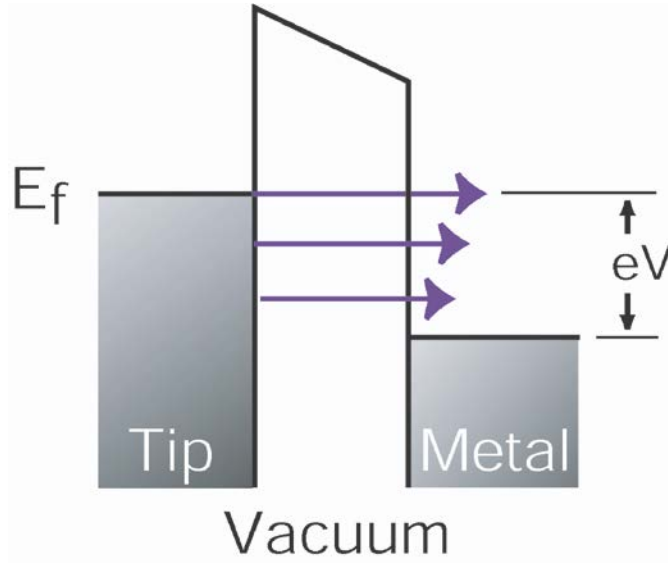
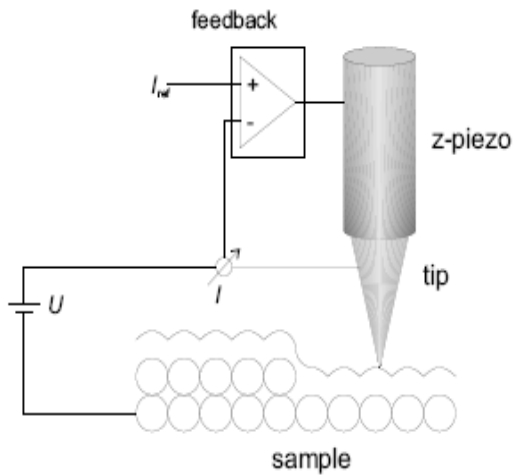
- 1) Novel Nanostructures and nanomaterials;
- 2) Interface and self-assembly;
- 3) Physical properties of the unit cells

# *Construction Nanostructures*

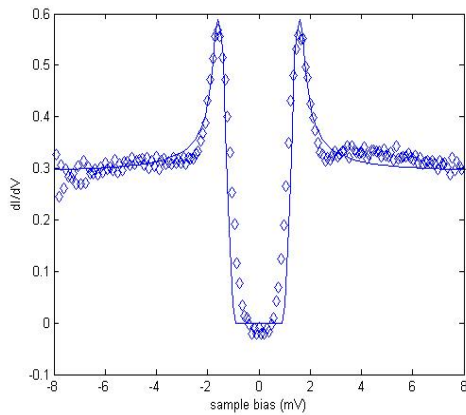


- ◆ Very difficult to control the junctions
- ◆ Environmental impact on magnetic and electrical properties
- ◆ Very young but promising field

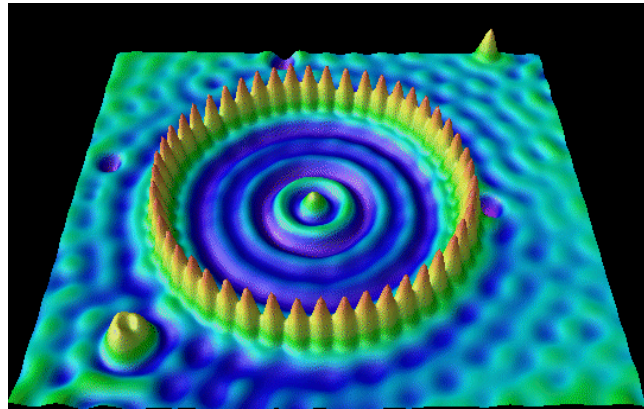
# Scanning Tunneling Microscopy and Spectroscopy



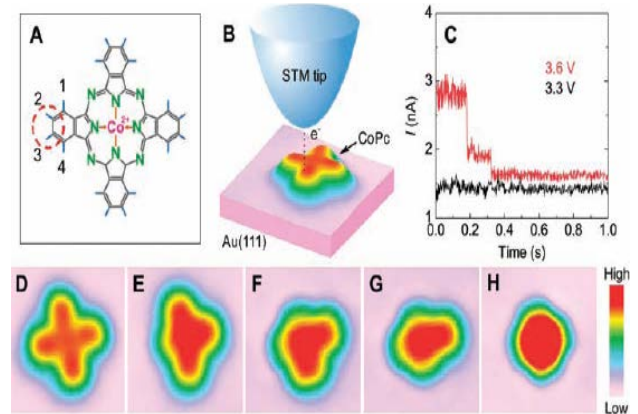
**Imaging**



**Spectroscopy**



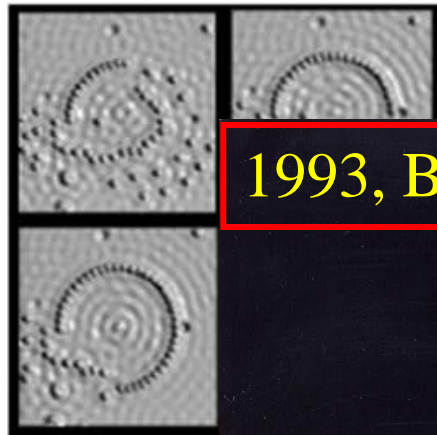
**Manipulation**



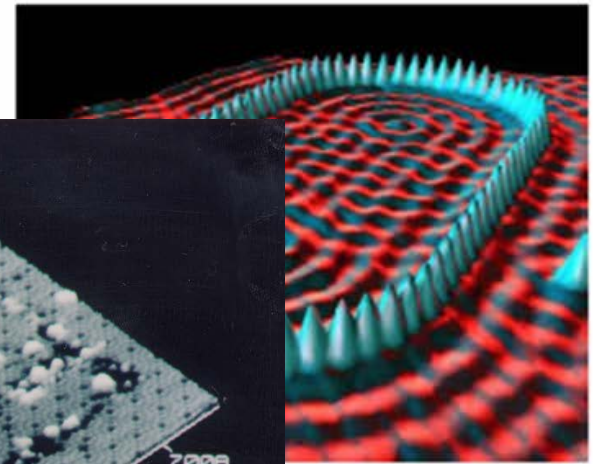
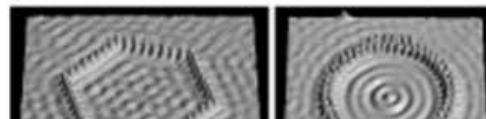
**Modification**

# 纳米量子结构的构造及其特性

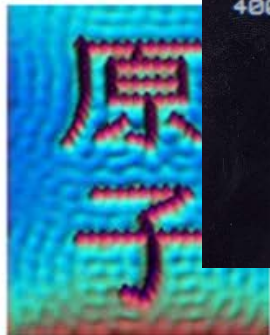
1993, BLVP, CAS



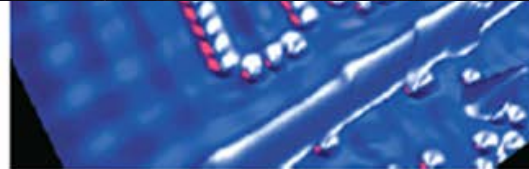
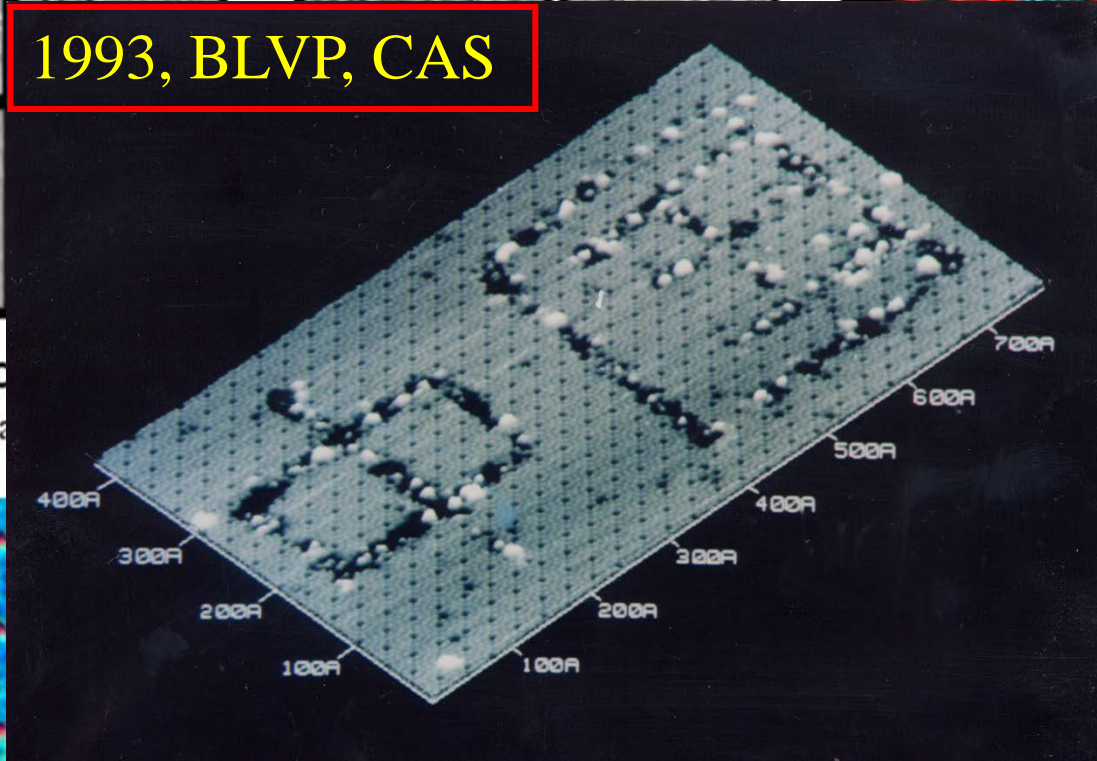
Atomic  
(iron atoms on a copper surface)



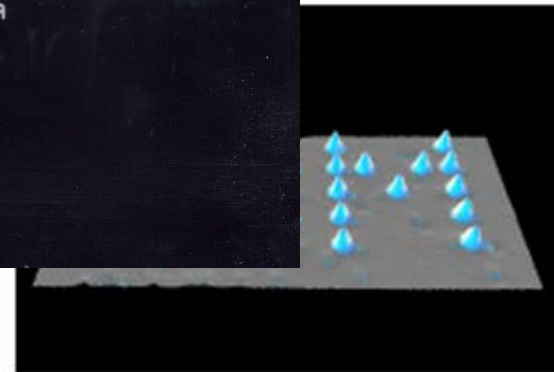
Stadium  
(on a copper surface)



Atomic Words  
(iron atoms on a copper surface)



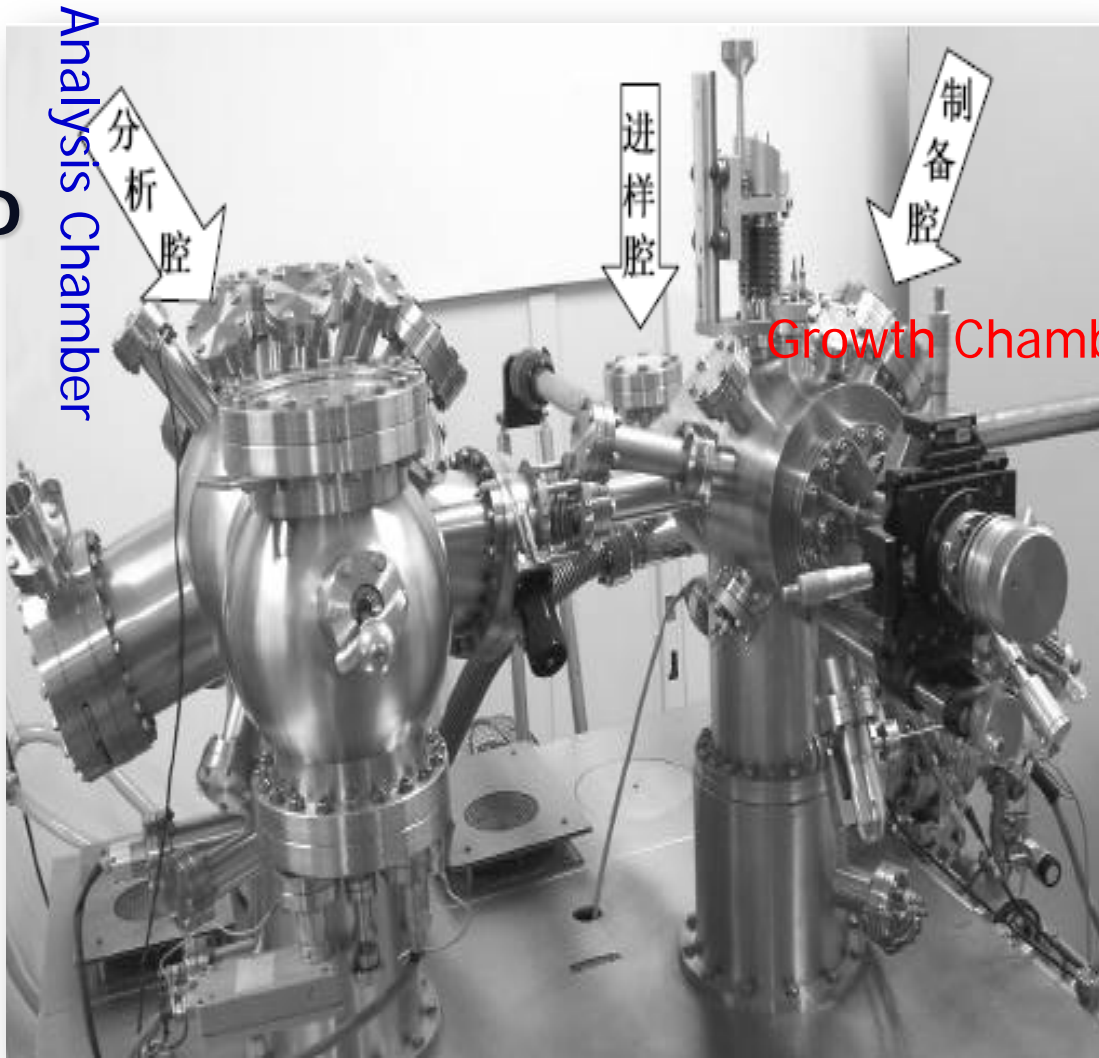
Molecular Words  
(CO on a copper surface)



Atomic Logo  
(Xe atoms on a Nickel surface)

# *Growth System with In situ Analysis Techniques*

- LEED
- AES
- STM



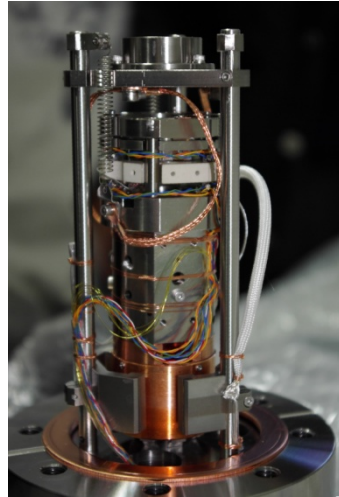
- Carbon Source
- Ar+ Ion gun
- Sample Heater
- Evaporator

**Ru, Pt, Ni, Cu, Ir metal crystals have been used**

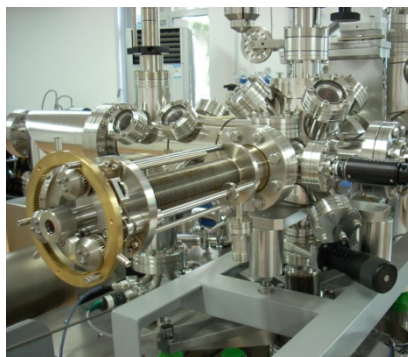


# 研究中的主要相关设备

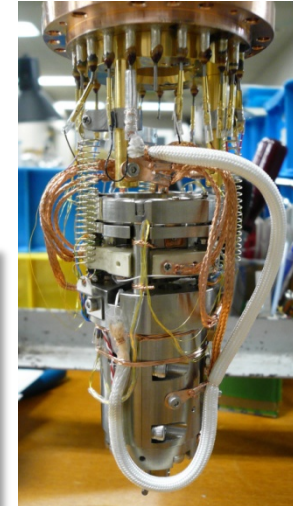
## 400 mK-11T UHV-STM with MBE-LEED



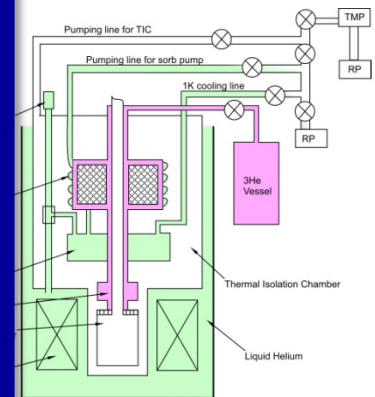
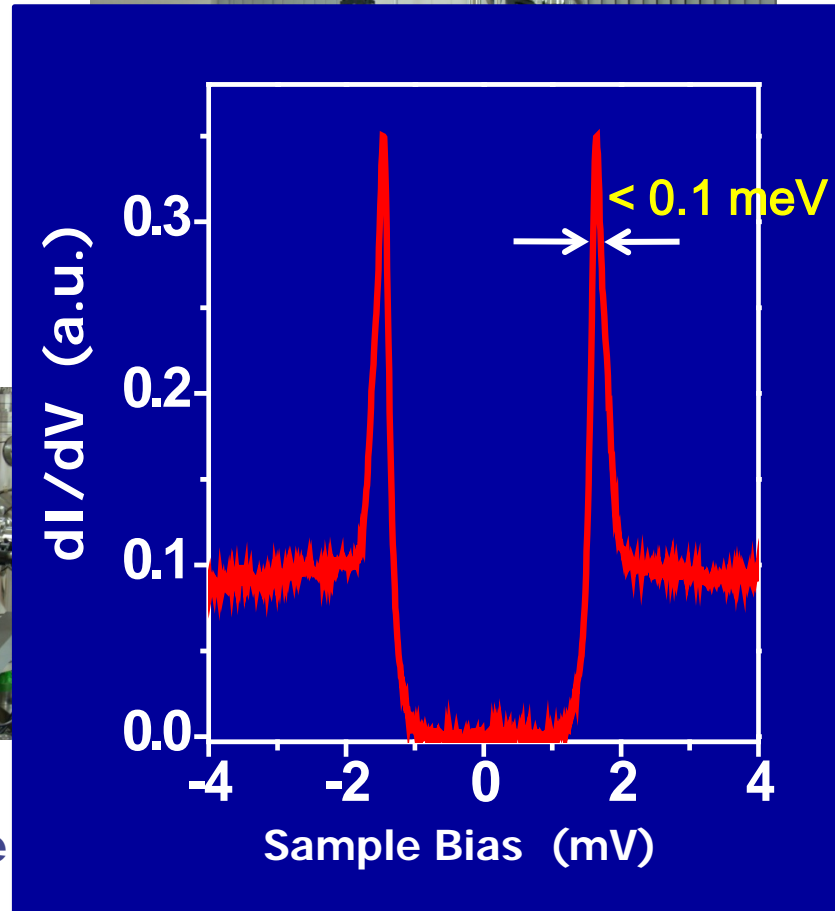
RT-STM Head



Cleaing and Cooling Stage



LT-STM Head



$^3\text{He}$  Circulatory Refrigeration



# 2014年度发表论文与会议邀请报告情况

## 共发表SCI论文**25**篇

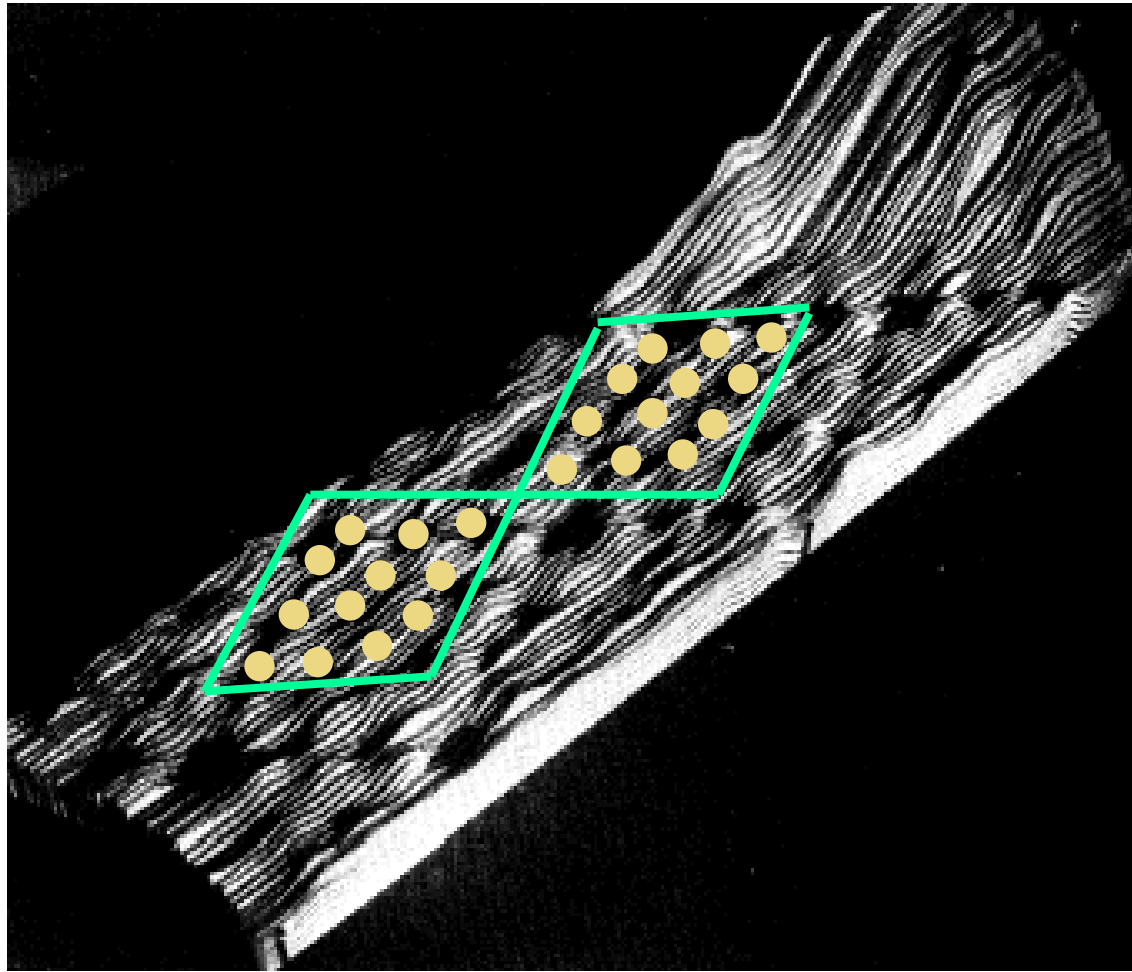
- Nature Physics 1 篇
- Adv. Mater. 1 篇
- Nano Lett. 2 篇
- J. Am. Chem. Soc. 1 篇
- Scientific Reports 2 篇

## Plenary/Invited Talk: 15次

- 美国MRS 秋季年会, Boston, Invited talk
- 美国AVS 年会, Baltimore, Invited talk
- The 2014 International Conference on Nanoscience + Technology (ICN+T) , Colorado, USA, Invited talk
- .....

# 功能化针尖提高STM的分辨能力

# 第一个Si(111)- $7\times 7$ 表面的STM图象

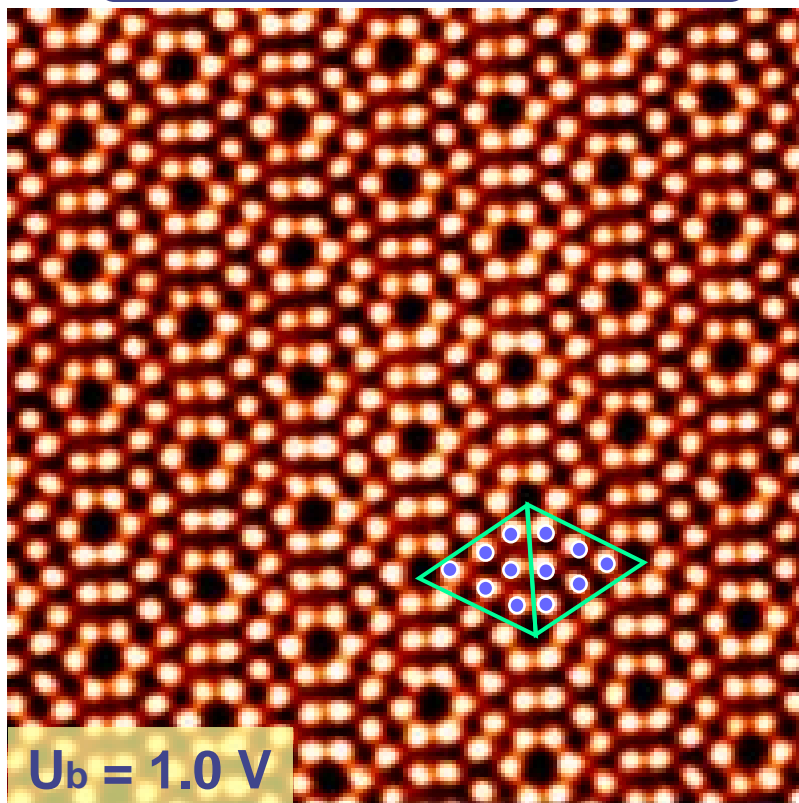


G. Binnig *et al.* Phys. Rev. Lett. 50,120(1983)

# 通常的Si(111)-7×7表面STM图象

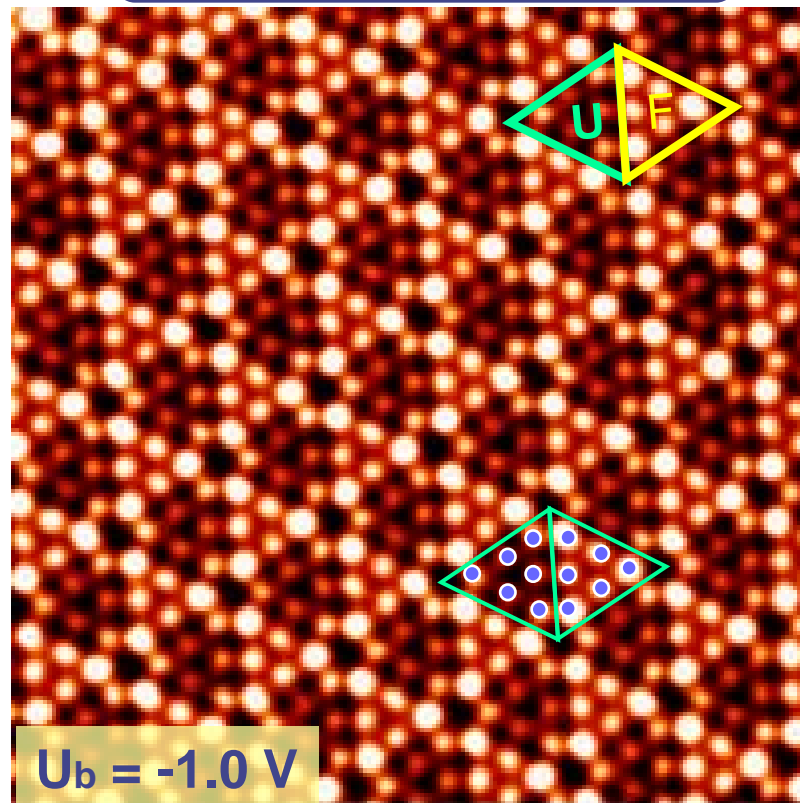
能看到 Si(111)7×7 单胞中的 12 个增原子(adatom)

正偏压下的STM图像



$16 \text{ nm} \times 16 \text{ nm}$

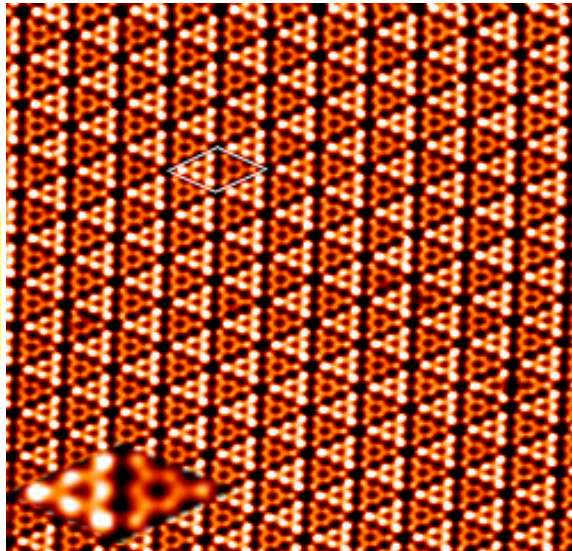
负偏压下的STM图像



$16 \text{ nm} \times 16 \text{ nm}$

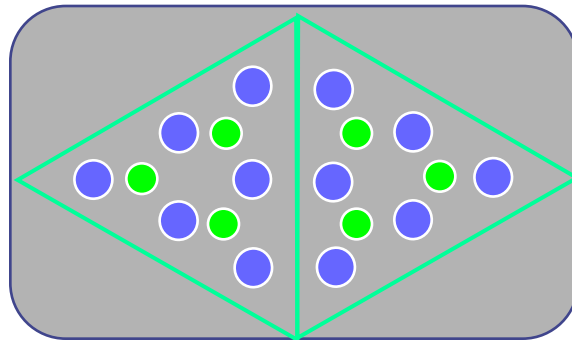
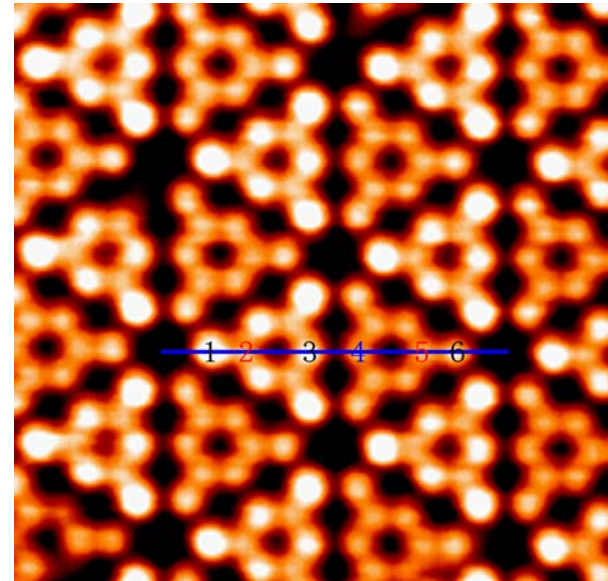
# Seeing the Rest Atoms and Adatoms Simultaneously

30 nm × 30 nm



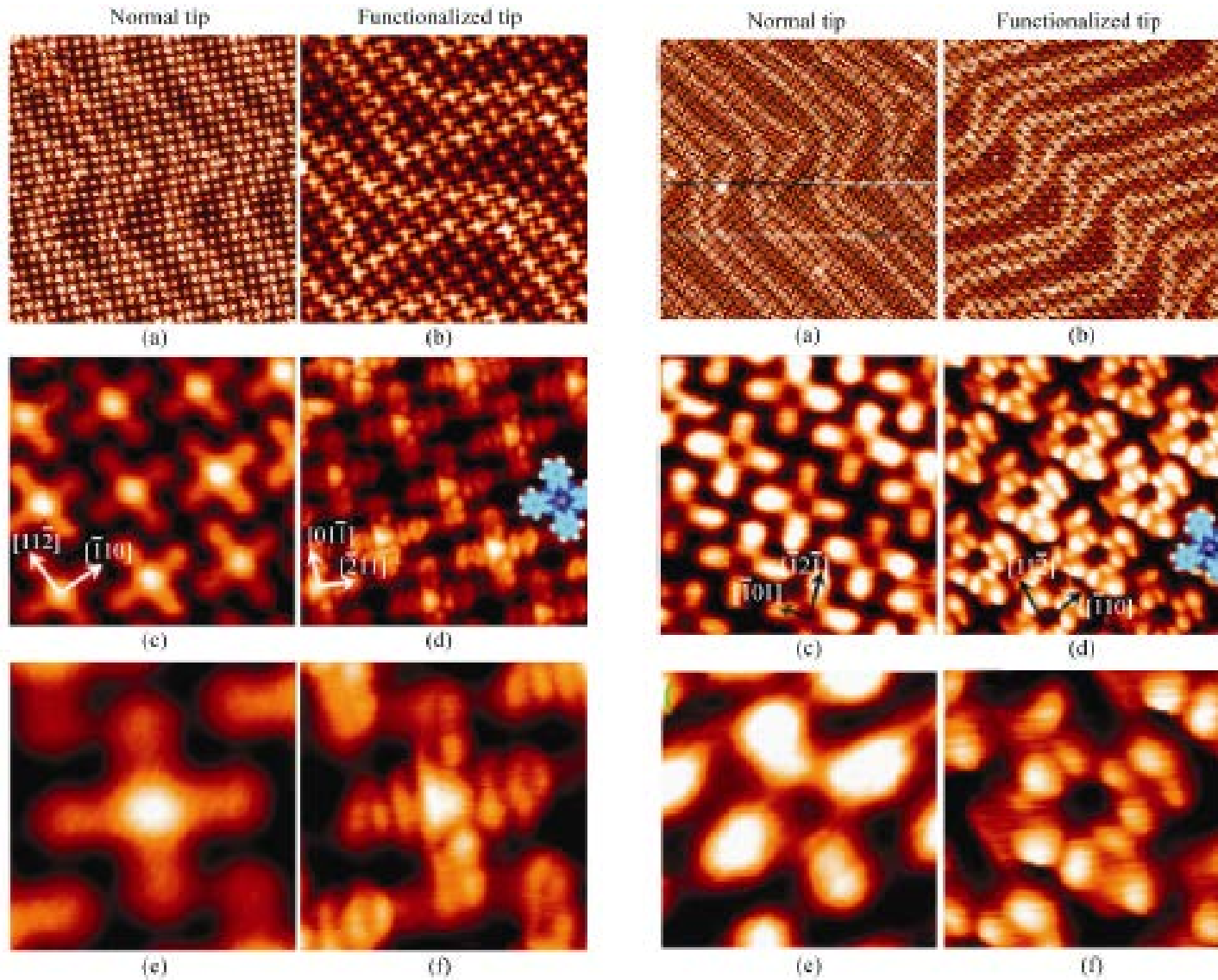
$U_b = -1.5 \text{ V}$   
 $I_t = 0.4 \text{ nA}$

8 nm × 8 nm



- Adatom
- Rest atom

# 功能化针尖对分子纳米结构的成像与机制



Z.T. Deng/H.-J. Gao *et al.*, Phys. Rev. Lett. 96, 156102(2006)

Z.H. Cheng/H.-J. Gao *et al.*, Nano Res. 4, 780(2011)



**Dangerously beautiful**

Seeking the source of space weather

**Out of this world** The strange life of Hugh Everett III  
**Look, but don't touch** Seeing with scanning probe microscopy  
**Living the dream** UK-based duo scoops Nobel prize

Si (u) 10/23 14:40

# physicsworld

Mark Everett



Man in the multiverse – Hugh Everett III 36–40

Photoblibrary



Winning ways – physics prizes 46–47

**On the cover**

Seeking the source of space weather (NASA) 24–28  
 The strange life of Hugh Everett III 36–40  
 Seeing with scanning probe microscopy 29–34  
 UK-based duo scoops Nobel prize 6–7

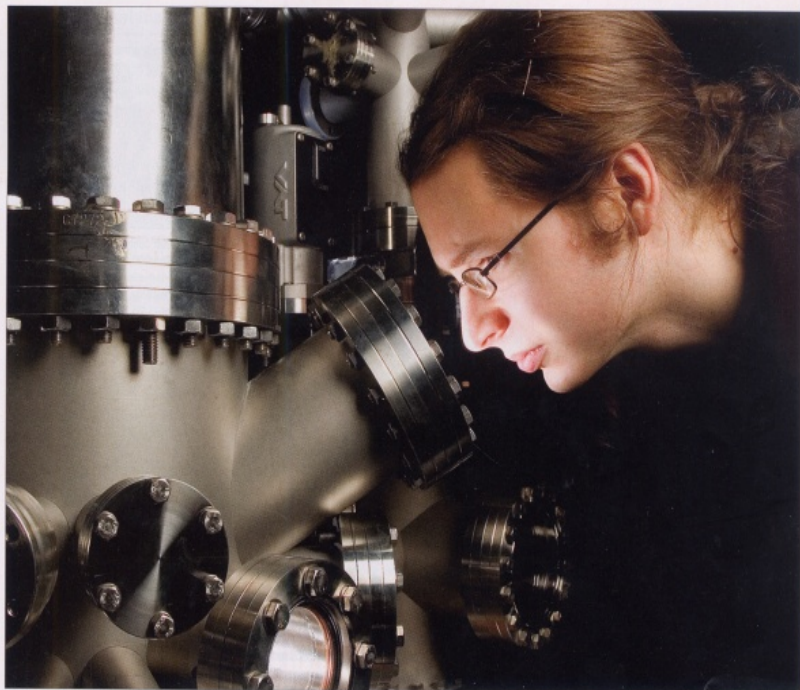
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<b>Lateral Thoughts</b> We all live in peculiar times <i>David J Miller</i>	56

15/10

2010-12-16



University of Nottingham

# Resolution frontiers

Now able to resolve details less than 100 picometres apart, scanning probe microscopes, which measure how a sharp tip interacts with a surface, keep smashing the record for how small we can see. **Philip Moriarty** explains how these instruments let us explore the nanoworld, and what it really means to “see” anyway

“I know what the atom looks like!” Ernest Rutherford’s excited announcement at a Sunday evening dinner party almost a century ago stemmed from his remarkable ability to distil the results of a series of painstaking scattering experiments into an elegant and appealing model of the atom. Despite the revolution in our understanding of the atom brought about by quantum mechanics, Rutherford’s iconic model persists. It is the Rutherford–Bohr picture of the atom that non-scientists, and quite a few scientists too, tend to hold in their head, rather than the probability density distributions for *s*, *p*, *d* and other orbitals. In the minds of most, an atom is a solar system writ small.

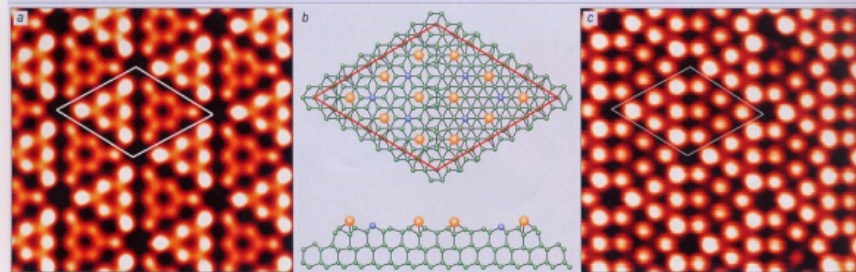
To see small things, we, of course, use a microscope. Indeed, the word microscope, which has Greek origins,

means “to see small”. But the traditional optical microscopes many of us have used to bring small structures into focus have a basic problem when it comes to resolving something as small as an atom: the wavelength of a photon of visible light is *huge* on the atomic scale. Visible light spans from about 400–750 nm and there is a fundamental limit – the diffraction limit – that dictates just how small an object we can resolve using photons of these wavelengths. It turns out that about the best we can do with traditional optical microscopy is to resolve objects about 200 nm across – almost three orders of magnitude larger than the diameter of an atom.

In order to get anywhere close to imaging on atomic length scales, a radically different approach is required, with the most logical step being to reduce the wave-

**Philip Moriarty** is a professor of physics at the University of Nottingham, UK, e-mail [philip.moriarty@nottingham.ac.uk](mailto:philip.moriarty@nottingham.ac.uk)

## 2 Silicon(111)-(7 × 7) diamonds are a scanning tunnelling microscopist's best friend



(a) The highest resolution scanning tunnelling microscope image of the silicon(111)-(7 × 7) surface acquired to date. (b) Both the uppermost atomic layer (represented by the yellow circles in the structural model) and the underlying, so-called rest-atom layer (blue circles) are clearly resolved. (c) Changing the bias voltage used to acquire the image modifies the energy range of the tunnelling electrons, thus producing a distinct change in image contrast.

Y. Wang et al., 2006, Phys. Rev. Lett. 97, 036102

rearrange themselves, to lower their energy, in a pattern made up of tessellating diamonds – the “unit cells” of the surface reconstruction (figure 2b). The two vectors that describe these unit cells are both seven times larger than those that describe the spacing of atoms on the uncut (111) plane – hence (7 × 7). Binnig and Rohrer focused their efforts on imaging this particular surface, which is *the* prototype surface for scanning-probe studies under ultrahigh-vacuum conditions.

Although FEM, FIM and STM all use a sharp tip from which electrons are emitted via quantum-mechanical tunnelling, the STM differs substantially from its field-emission predecessors in that electrons tunnel not from the tip into the vacuum, but through a tiny vacuum gap between the tip and a sample. The electrons can either travel from the tip to the sample or, with a change in polarity of the voltage, from the sample to the tip. The probability for electrons to tunnel increases exponentially as the gap between the tip and the sample decreases.

The SPM tip can be positioned with sub-angstrom precision above the surface using piezoelectric actuators. These devices are based on piezoelectric crystals that produce a voltage when mechanically stressed – an effect many of us are familiar with as it is exploited to generate the spark in cigarette and gas lighters. Conversely, a piezoelectric crystal will deform when a voltage is applied across it. It is this latter phenomenon that is exploited in scanning probe microscopes. With low-noise voltage sources and high-quality piezoelectric actuators, control of the tip position down to the picometre level is possible.

### Seeing atoms?

But what do the intensity maxima in an STM image actually represent? Each peak originates from the tunnel current flowing between the tip and sample, the magnitude of which is determined by the overlap of the electronic wavefunctions of the tip and sample. An STM image is, in essence, a map of the local density of electron states within an energy window defined by the bias voltage applied to the tip or sample. The overlap of tip and sample wavefunctions results in a convolu-

tion of tip and surface structure and deconvolving one from the other is generally a far from trivial task.

For the silicon(111)-(7 × 7) surface there is a fortuitous match between the positions of the surface atoms and the peaks in the STM image, largely because the dangling-bond orbitals of the silicon atoms are oriented so that they point directly out of (i.e. normal to) the surface. Nevertheless, a different voltage can produce a distinct change in the contrast of the image (figure 2c) because the energy window available for electron tunnelling is modified. With an STM we therefore do not see atoms as such, i.e. we do not map the nuclear positions, rather, we map out the variation in electron density.

It is in the field of *molecular* imaging where the most striking high-resolution images of electron-density variations are produced. Buckminsterfullerene, the football-shaped  $C_{60}$  molecule, has been particularly intriguing in this context, with a variety of fascinating STM studies revealing its internal electronic structure. Intramolecular contrast in STM images arises from the spatial distribution of the molecular orbital electron density. (Uniquely, STM is capable of mapping, with sub-nanometre resolution, both the orbitals occupied with electrons and those without.) A particularly impressive example of this is shown in figure 3. Taken from the work of Guillaume Schull and Richard Berndt at Christian Albrechts University in Kiel, Germany, the data show how the intramolecular contrast observed in the STM images varies with the orientation of the molecule on the surface.

### Feel the force

We are not constrained to just using tunnel current to probe the tip-sample interaction. Binnig and Rohrer, inspired by a talk by John Pethica at the first international workshop on scanning tunnelling microscopy in 1985, extended STM to the detection of atomic forces, inventing the AFM in 1986. The most significant recent advances in high-resolution imaging have come from a particular breed of AFM that uses a mode known as “non-contact” (figure 4).

Non-contact AFM (NC-AFM) is an excellent exam-

# 功能化STM针尖

- 提出了提高STM分辨能力的方法, 拓展了对STM成像机制的认识
- 观察到过去不能观察到的原子分子的精细结构和电子结构

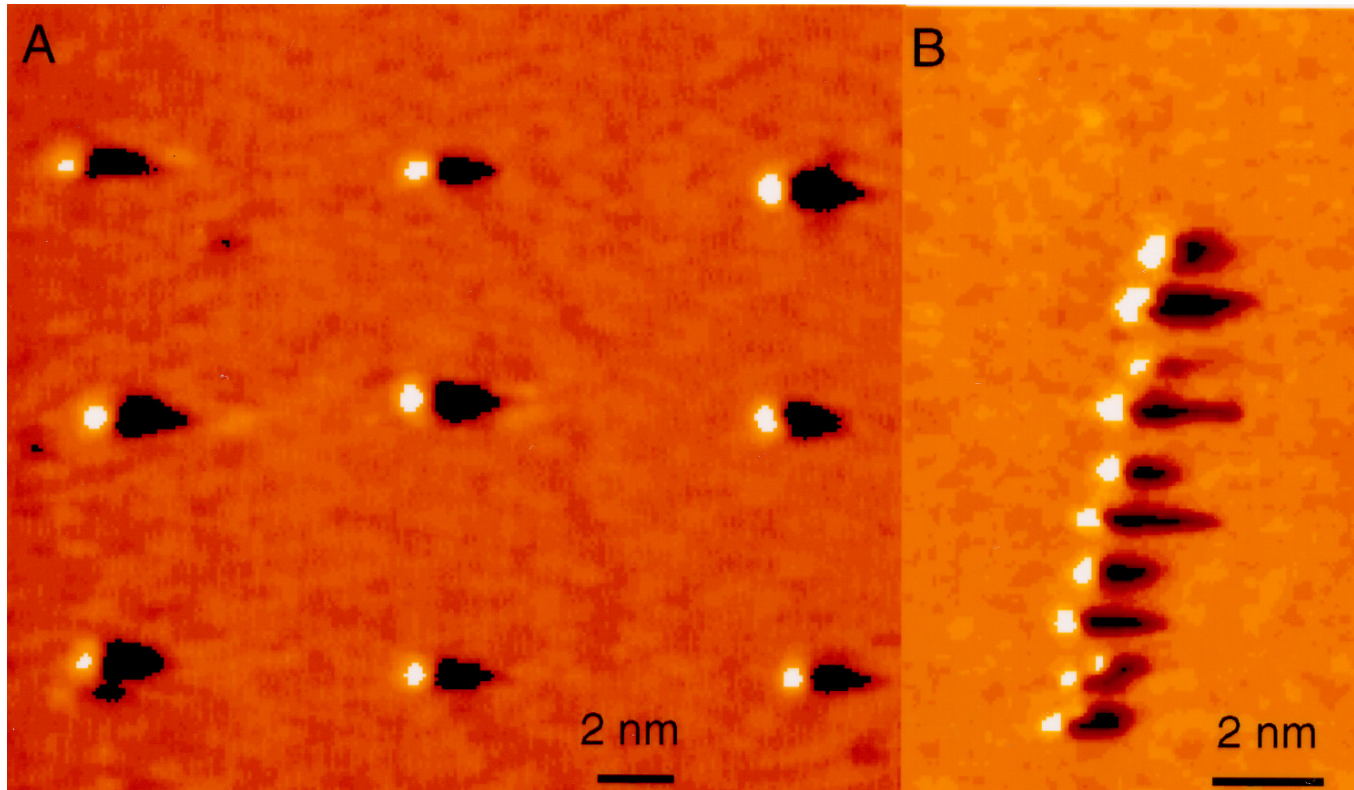
**基于对STM方法的深入认识与把握,**

**进而开展原子操纵和纳米量子结构的研究**

# 纳米量子体系的构建及其 物性研究

# Conductance Transition and Nanorecording

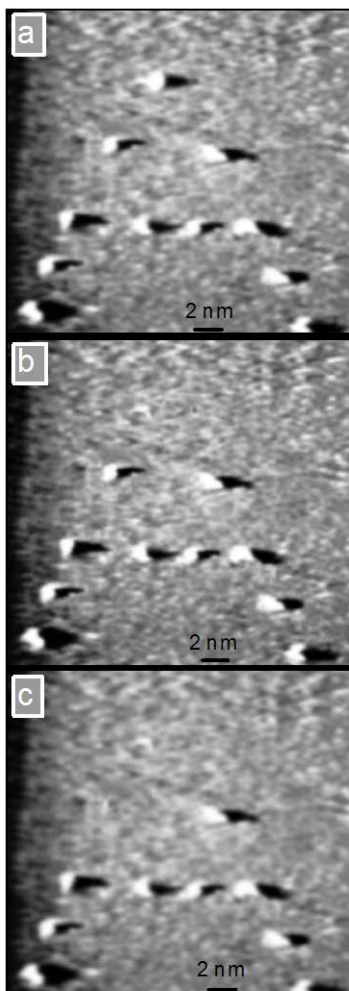
---



**On NBMN-pDA thin film, dot size,  $\sim 1.3$  nm;  
Shortest distance, 1.5 nm; Data Density,  $10^{13}$  bits/cm<sup>2</sup>.**

H.-J. Gao *et al.*, Phys. Rev. Lett. **84**, 1840(2000)

# Molecular Recording: Toward the Next Generation CD



Sunday, February 20, 2000 Page: 1

Toward the Next Generation CD

## Physical Review Focus

Reversible, Nanometer-Scale Conductance Transitions in an Organic Complex  
H. J. Gao, K. Sohlberg, Z. Q. Xue, H. Y. Chen, S. M. Hou, L. P. Ma, X. W. Fang, S. J. Pang, and S. J. Pennycook  
[Phys. Rev. Lett. 84, 1780](#) (21 February 2000)

### Toward the Next Generation CD

16 February 2000  
Andrew Gannon

From punch cards to floppy disks to CD-ROM's, data storage devices continue to evolve. Researchers at the Oak Ridge National Laboratory (ORNL) in Tennessee don't know what the next device will look like, but they believe they know what it will be made of: thin films of complex organic compounds. They report in the 21 February *PRL* that they have produced reversible changes in electrical resistance in molecule-sized regions of organic thin films. The results help pave the way for making thin-film storage devices because they mark the first time anyone has demonstrated reversibility—needed for "writing" and then "erasing" data—at a molecular level.

Other researchers have shown they could induce changes in conductance—the equivalent of "writing"—to a thin film, says Karl Sohlberg, a theoretician with the Oak Ridge group. But using only heat or laser pulses, they haven't been able to "erase," or reverse, the transition without clearing entire regions of the film, as if shaking clear a whole Etch-a-Sketch.

Sohlberg says organic compounds have peaked the interest of data-storage makers because of their incredible storage capacity. A typical CD-ROM, for example, has a storage density of perhaps  $10^8$  bits per  $\text{cm}^2$ . The thin films used by the ORNL group and their colleagues at the Chinese Academy of Sciences in Beijing and the University of Chicago can store  $10^{14}$  bits per  $\text{cm}^2$ —a million-fold increase. Sohlberg says that organic-based data storage will ultimately create headaches for the engineers who have to design the machines fast enough to read from and write to such materials, but "that's the engineering hurdle."

The team made films of a complex of two organic molecules on a graphite surface. By applying a range of voltages

© 2000 Photodisc, Inc.

Today's technology. Like punch cards and floppy disks, CD-ROM's may become obsolete if organic thin films live up to their potential for storing a million times more data.

<http://focus.aps.org/v5/i7.html>



## Manhandled molecules, midget memories

Gangsters break someone's arm to deliver a message, leaving a powerful impression that may never go away. Now, a team of Chinese and U.S. scientists finds that roughing up organic molecules also can leave an enduring, though small, memory. In this case, however, some reverse strong-arming can quickly wipe out that memory.

Today's CD-ROMs squeeze 100 million bits into each square centimeter of recording surface. In the Feb. 21 *PHYSICAL REVIEW LETTERS*, Hongjun Gao of the Chinese Academy of Sciences in Beijing and his colleagues report writing and erasing data in minute dots. These dots could potentially be crammed together to encode information a million times more densely than CD-ROMs do and top even hard disks by a factor of nearly 100,000. However, the lab accomplishment remains far from commercial realization, the experimenters caution.

"This is very attractive work. It probably has applications as an organic [chemical]-based memory," comments James M. Tour of Rice University in Houston.

Gao, currently a guest scientist at Oak Ridge (Tenn.) National Laboratory, and his coworkers in China have spent years investigating substances that have potential for high-density data storage and molecular-scale electronics. In particular,

the researchers have considered a class of carbon-based materials, called conjugated organic compounds, that show unusual electronic properties.

For many of the compounds, the molecules have positively and negatively charged ends. This polarization makes them pushovers for electric fields, which exert forces on the charged regions.

Testing two such compounds, 3-nitrobenzyl malononitrile and 1,4-phenylenediamine, the researchers found that a blend of the plasticity substances can form a thin, electrically resistive coating on graphite or glass plates. By applying positive voltage pulses with the probe of a scanning tunneling microscope, the Chinese team created tiny spots in the film with only a ten-thousandth the electrical resistivity of the rest of the film. Each spot was a nanometer or less in diameter.

The researchers found that the spots hold their low resistivity until subjected to negative voltage pulses, which restore them to the high-resistivity state.

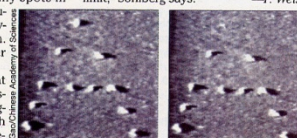
Not knowing what characteristic of the material allows the resistivity to change, the Chinese researchers teamed

with scientists at the Oak Ridge lab and the University of Chicago. In a series of experiments, the collaborators discovered that the applied positive voltage transforms a patch of organic material into a disorderly, or amorphous, arrangement, which is much less resistive than the ordered crystalline film.

The voltage pulse wrestles the polarized molecules into their new configuration. "They get torqued, twisted, and all disoriented," says Karl W. Sohlberg of Oak Ridge. A pulse of opposite polarity realigns the molecules with the lattice.

The number of molecules affected must be very small, the researchers argue, since each spot roughly covers one unit of the crystal structure. "If you're talking about reorienting individual molecules, we are certainly very close to that limit," Sohlberg says.

—P. Weiss



Nanometer-size bright spots, indicating low resistivity, form an A shape (left) on a novel chemical coating. After researchers zap the A's with a negative voltage pulse, the spot there vanishes (right), indicating restored high resistivity.

## Power plants: Algae chum out hydrogen

Could the green scum that grows on the walls of a fish tank produce the fuel of the future? Some scientists think so. They've found a way to coax green algae into producing significant amounts of hydrogen gas. In these researchers' view, large pools of algae could generate clean-burning hydrogen fuel for cars and other applications.

As microscopic plants, algae use photosynthesis to create sugar from water, carbon dioxide, and sunlight. Algae also have the biochemical machinery to produce hydrogen, notes Tasios Melis of the University of California, Berkeley. Under some conditions—in the absence of oxygen, for example—algae strip hydrogen

sensitivity to oxygen to protect against that danger, he says.

Melis and his coworkers discovered a way around this dilemma. By depriving the algae of sulfur, which the cells need to make several important proteins, the researchers can turn off normal photosynthesis. This shuts down the algae's oxygen production and forces the cells to make hydrogen instead. Melis presented his group's findings this week in Washington, D.C., at the annual meeting of the American Association for the Advancement of Science.

To prevent the algae from dying during the hydrogen production, the researchers must permit them every few



Hydrogen bubbles rise to the surface in a flask containing green algae.

gineer at the National Renewable Energy Laboratory in Golden, Colo.

On NBMN/pDA thin films, "A" pattern, voltage pulse: 3.5 V, 12 $\mu$ S.  
Erasing voltage: -4.5 V, 50  $\mu$ S.

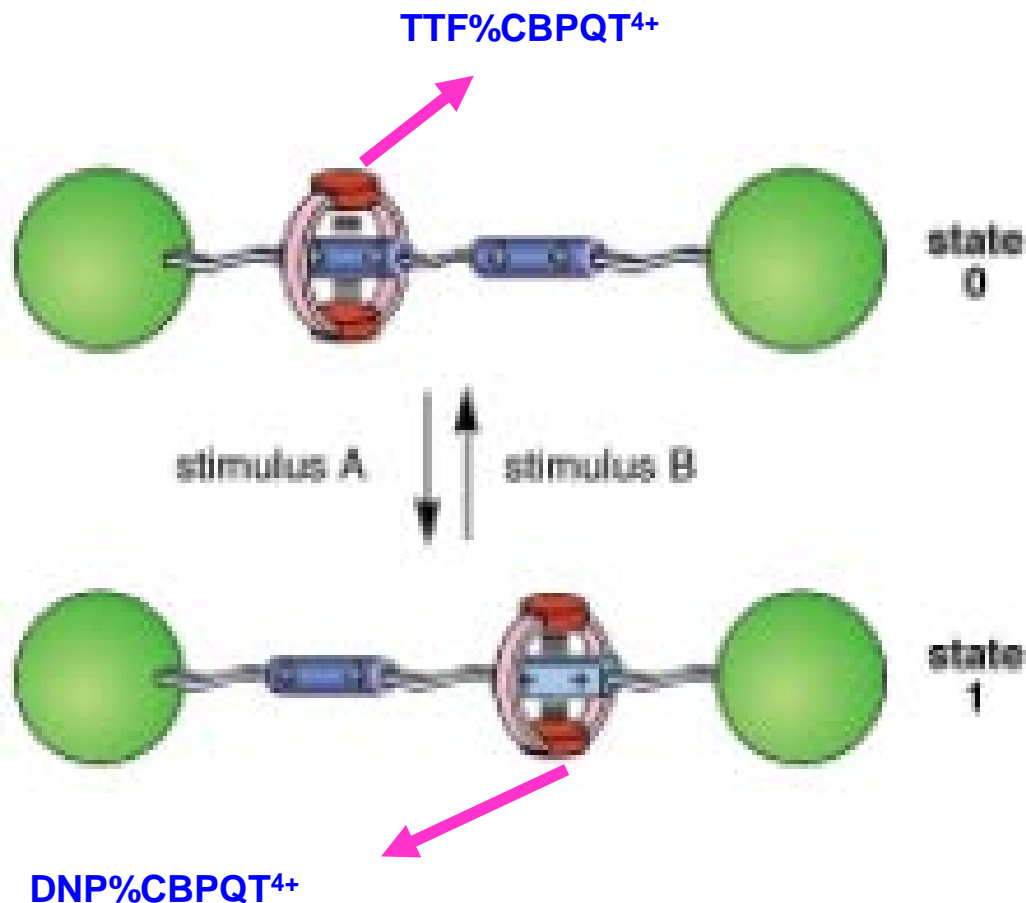
– **Program Contact:** Iran L. Thomas, SC-10 (301) 903-3081

– **The Library of Congress on a Single Disk:** Disordering and re-ordering tiny regions of a thin film shows promise for storing a million times more information than with today's computer disks and CD's, and with no increase in space. This is the conclusion from work performed in a collaboration between H. J. Gao, K. Sohlberg, and S. J. Pennycook of Oak Ridge National Laboratory and the Beijing Laboratory for Vacuum Physics [Phys. Rev. Lett., Vol. 84, p 1780 (2000)]. The film is made of organic material and supported by graphite. It is so thin that 40,000 layers would be only as thick as a sheet of paper. Exposing the film to voltage pulses with a scanning tunneling microscope (STM), nano-meter sized regions were switched from crystalline to disordered, changing their electrical conductivity by 10,000 times. Each tiny spot is one bit of information, not much bigger than a single molecule of the film. This is the first demonstration that information can be written and erased in a film at or near the single molecule limit. Drs. Gao, Sohlberg, and Pennycook are supported by the Office of Basic Energy Sciences/Division of Materials Sciences and Engineering.

– **Program Contact:** Iran L. [REDACTED] 3081

(2000)

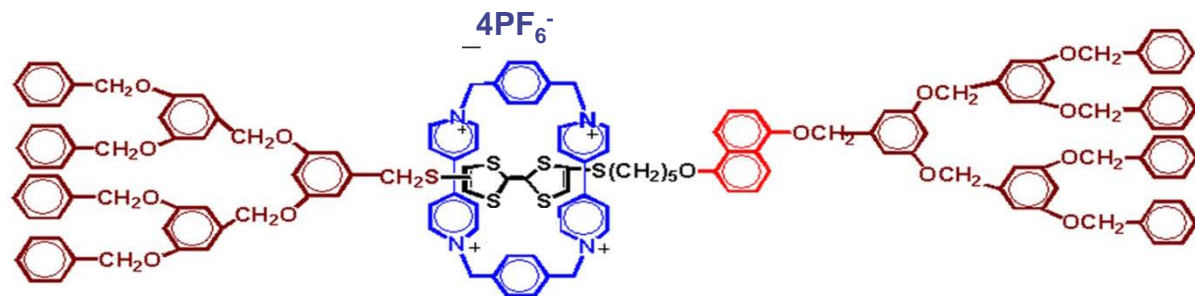
# "0" "1" Bistability of Rotaxane Molecule



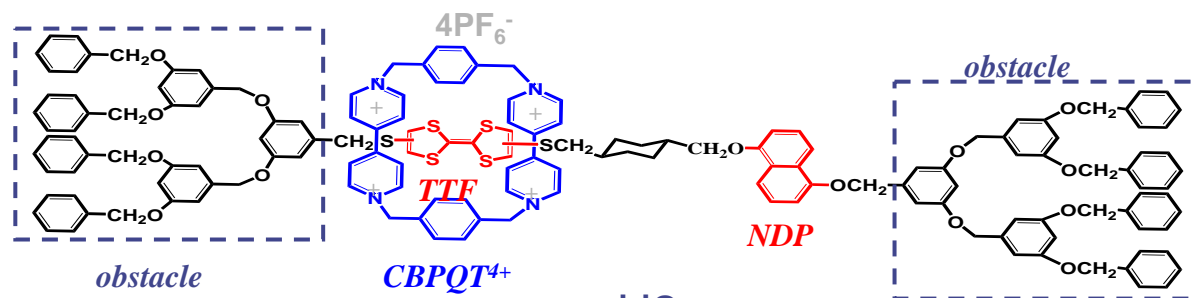
when the TTF unit be oxidized or reduced, the CBPQT<sup>4+</sup> ring will move along the axe and stay on different position



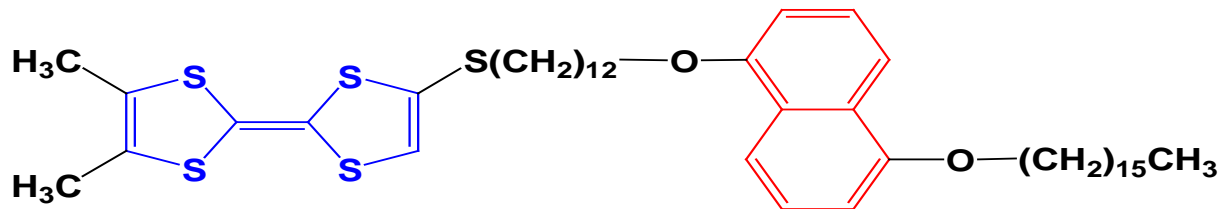
# H1, H2, and W2 Molecules



H1

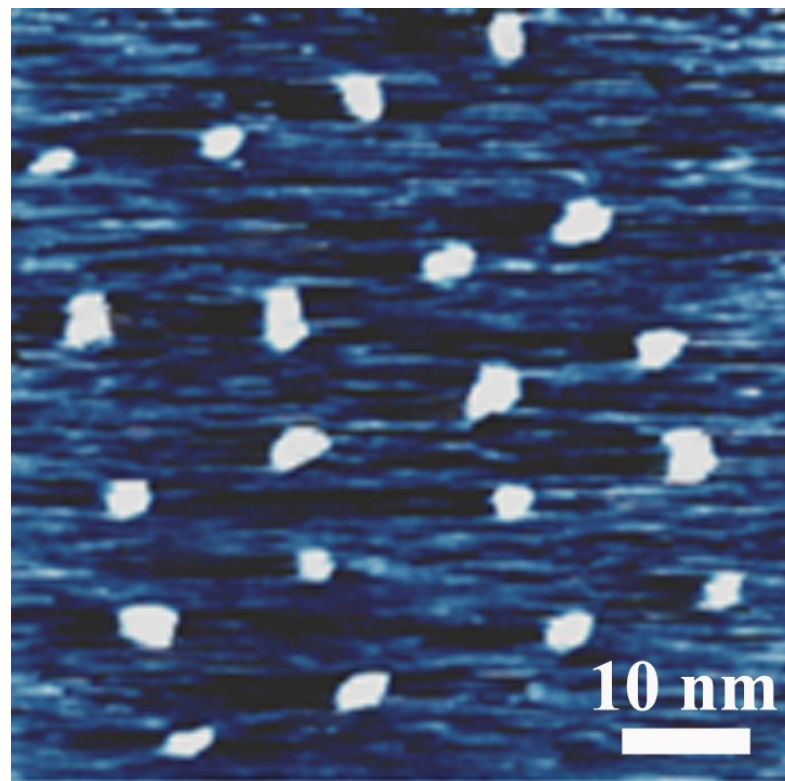
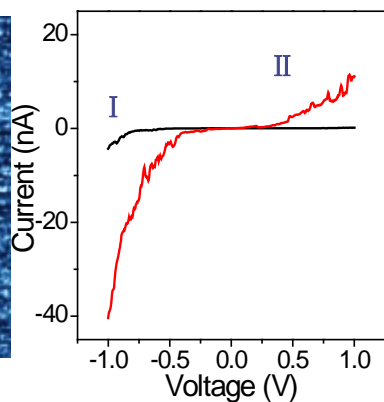
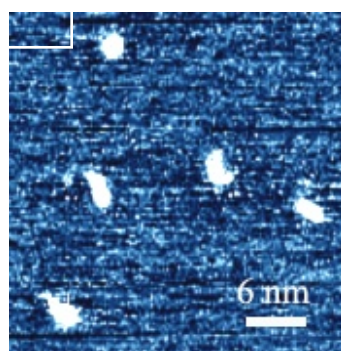
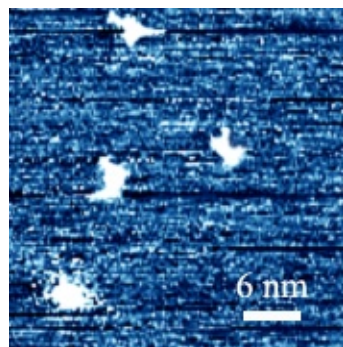
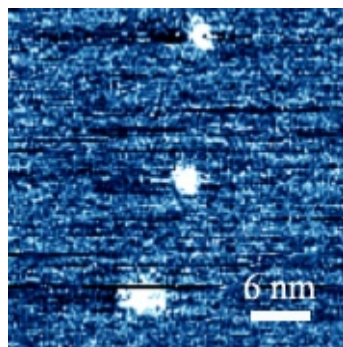


H2



W2

# Stable, Reproducible Conductance Transition and Ultrahigh Density Data Storage

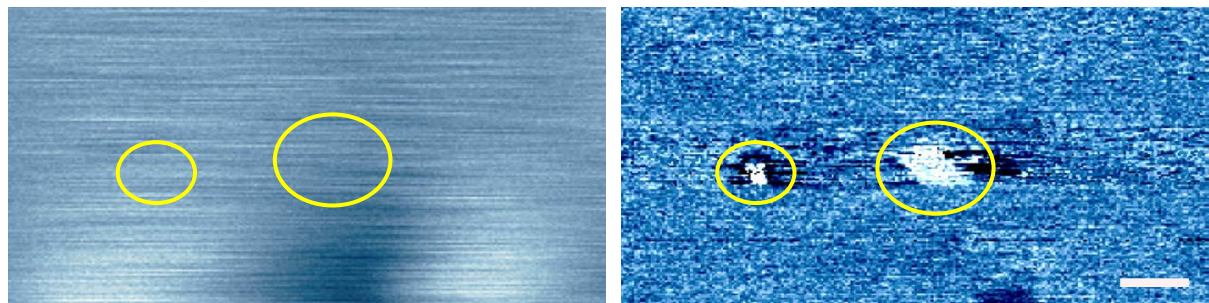
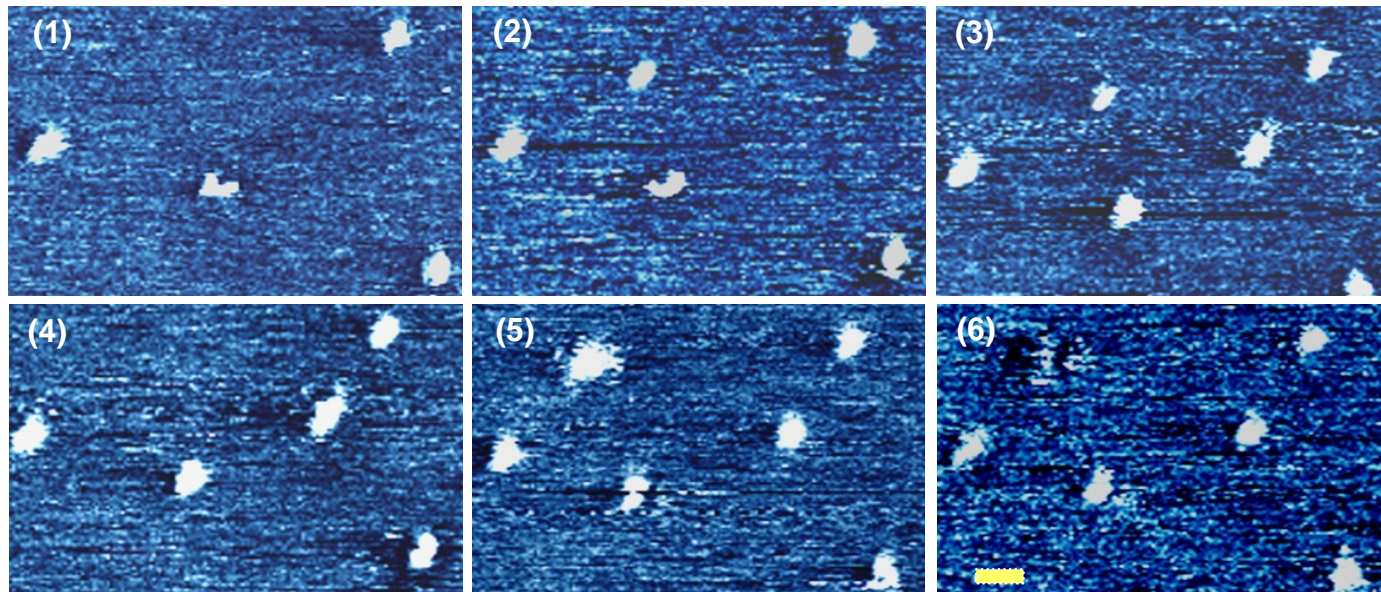


**Reproducible nano-recording on H1 thin films: writing one by one**

**Stable reproducible nano-recording**

M. Feng, H.-J. Gao *et al.*, JACS 127, 15338 (2005)

# *Erasable, Re-writable, Re-erasable Nanorecording*



**Reproducible and reversible erasing and writing of recording marks of about 3 nm in diameter on H<sub>2</sub> thin films**

M. Feng, H.-J. Gao *et al.*, JACS 127, 15338 (2007)

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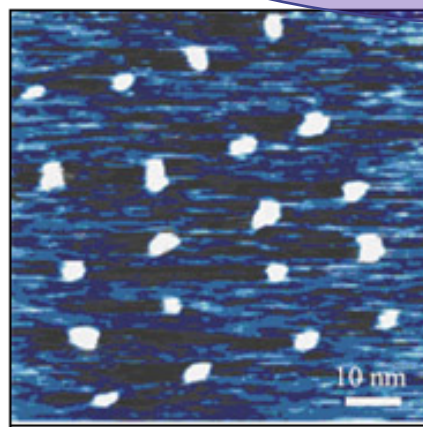
## nanozone news

17 November 2005

### Joining the dots for molecular memories

Data can be written reversibly into mechanically switchable molecules at the nanoscale.

PHILIP BALL



Chinese researchers have demonstrated the recording of information at the nanoscale using molecular switches<sup>1</sup>.

Hongjun Gao and colleagues at the Chinese Academy of Sciences' Institutes of Physics and Chemistry in Beijing have used the scanning tunnelling microscope (STM) to draw erasable dots just a few nanometres across in thin films of organic molecules that can be switched between two stable states.

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*Nature Nanotechnology* Published online: 16 February 2007 | doi:10.1038/nnano.2007.58Subject Category: [Surface patterning and imaging](#)

## Nanorecording: Rewriting history

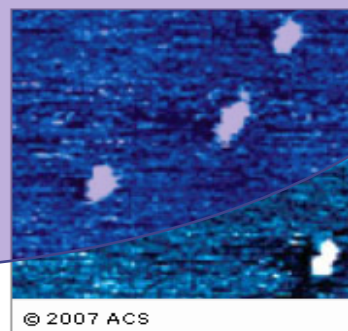
Samia Mantoura

## Using a scanning tunnelling microscope, researchers can write, erase and rewrite nanoscale information on an organic thin film

Recording nanoscale information on organic thin films may be a route to ultrahigh-density information storage. However, even the best writers could use an easy way to correct their mistakes.

Now, Hongjun Gao and co-workers<sup>1</sup> at the Chinese Academy of Science in Beijing have synthesized a new molecule (which they called 'H2 rotaxane') for making erasable and rewritable organic thin films. By applying positive and then negative voltage pulses to the films with a scanning tunnelling microscope tip, the conductivity of the film below the tip can be changed from high (write) to low (erase). The appearance and erasure of 'written' dots can be seen in atomic force microscope images, which are sensitive to the surface conductivity. However, topographic images show that there is no change in the height of the surface, suggesting that the changes are purely electronic.

The rotaxane in this study has a dumbbell-shaped axle component encircled by an electron-deficient ring-shaped molecule. The ring can move between two different electron-rich recognition sites, which correspond to distinct conductance states of the molecule. It is suggested that, because of its structure, this molecule is able to move back to its ground state more readily than a similar compound previously studied by Gao and co-workers, which makes it easier to 'erase' old information and 'rewrite' something new.



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## REFERENCES

1. Feng, M. *et al.* Reversible, erasable, and rewritable nanorecording on an H2 rotaxane thin film. *J. Am. Chem.* doi: 10.1021/ja067037p (2007).

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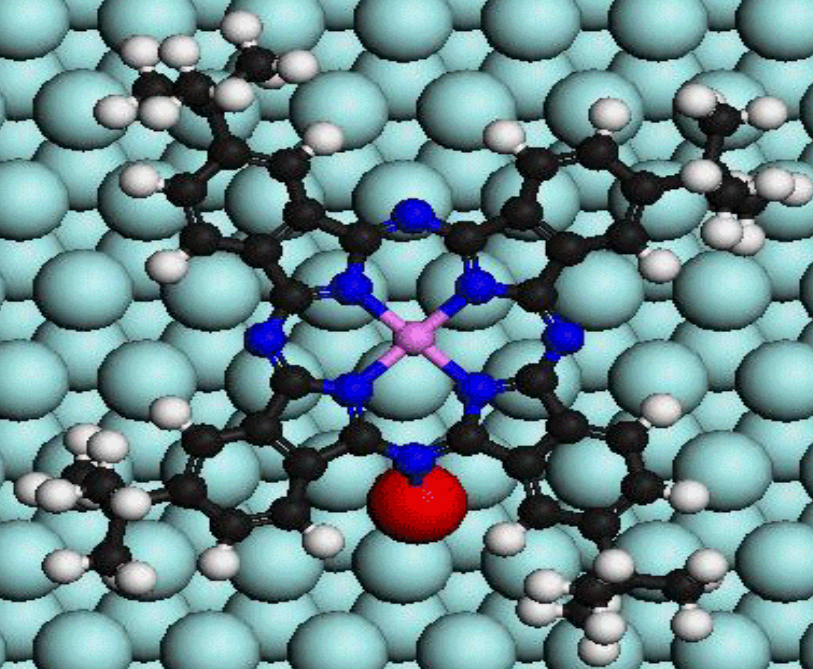
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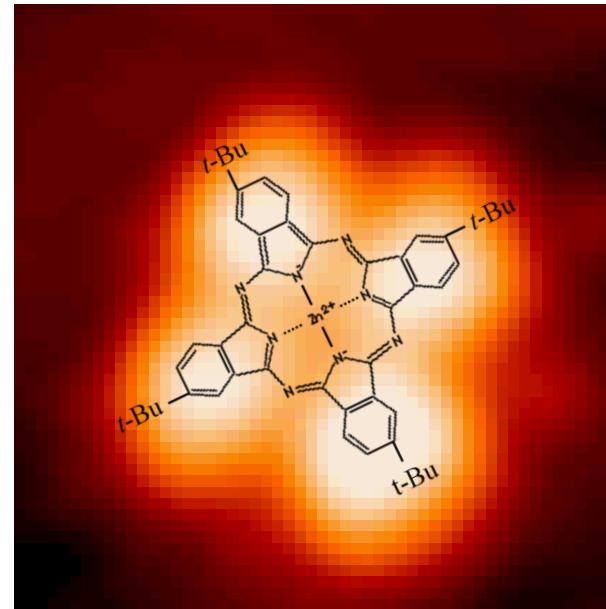
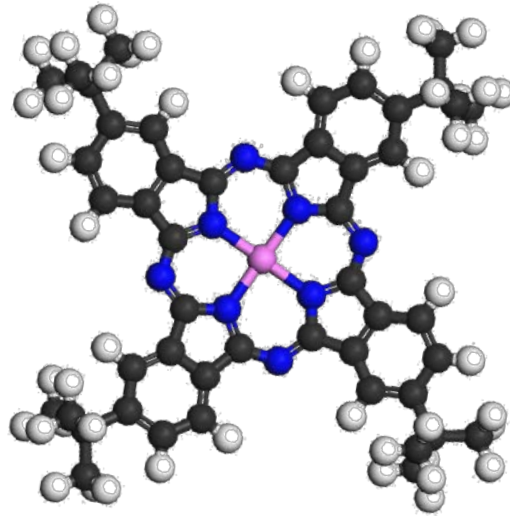


H.-J. Gao Group, IOP-CAS, China



# $(t\text{-Bu})_4\text{-ZnPc}$ Molecule

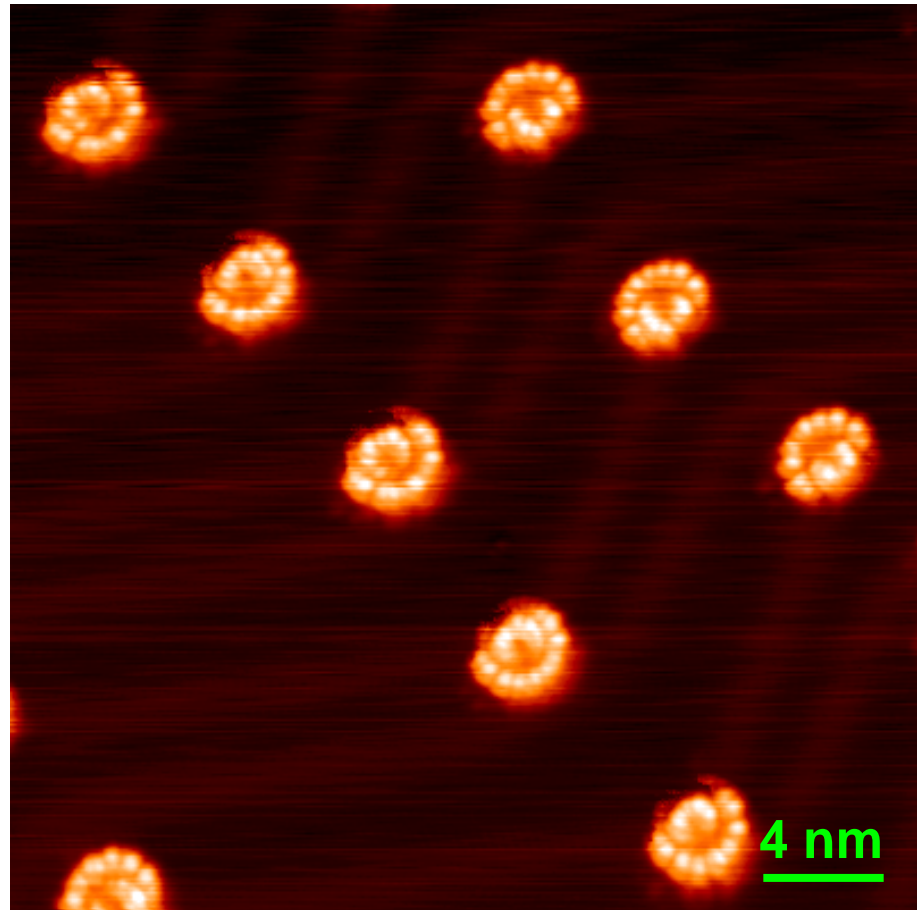
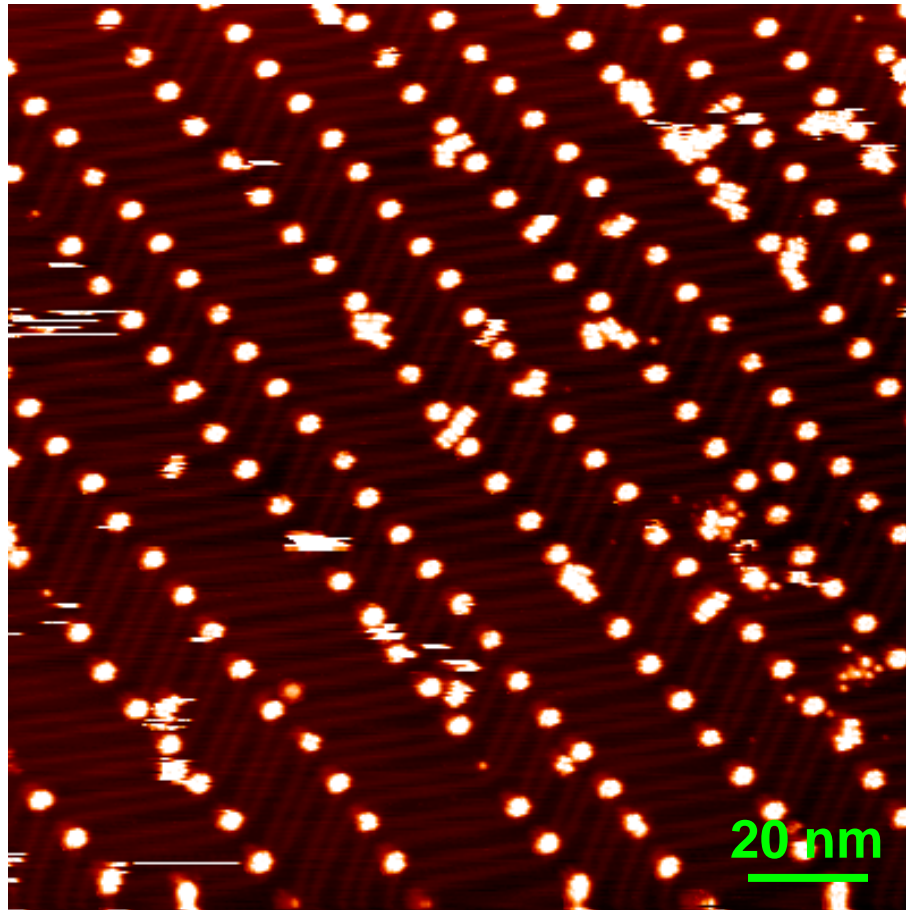
- Carbon
- Nitrogen
- Zinc
- Hydrogen



- Full name: tetra-*tert*-butyl zinc phthalocyanine ( $\text{C}_{48}\text{H}_{48}\text{N}_8\text{Zn}$ )
- STM image of single stationary molecule: four bright lobes

# *Array of Single Molecular Rotors*

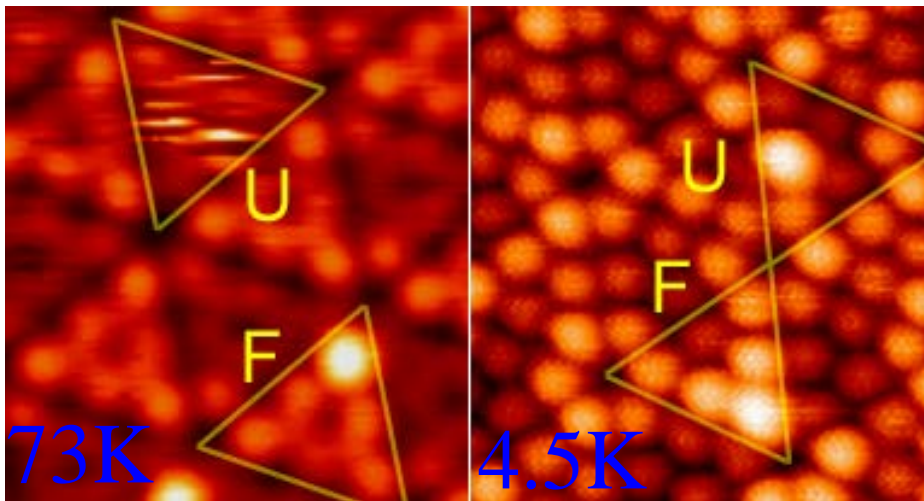
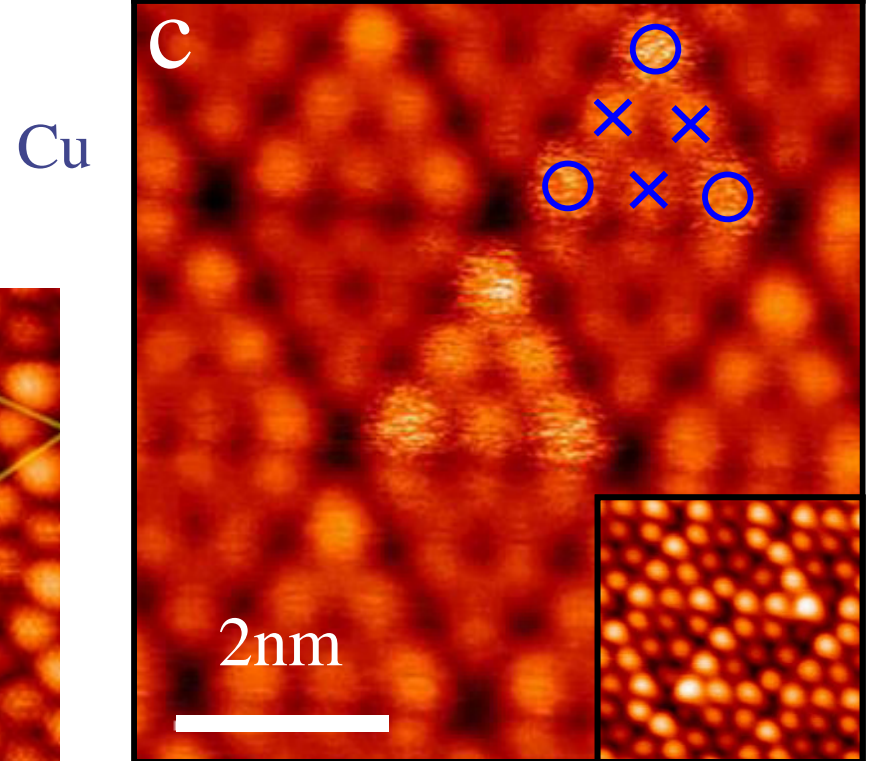
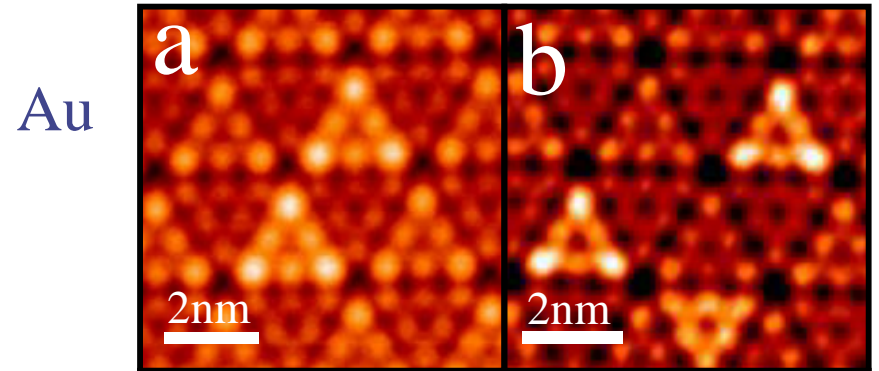
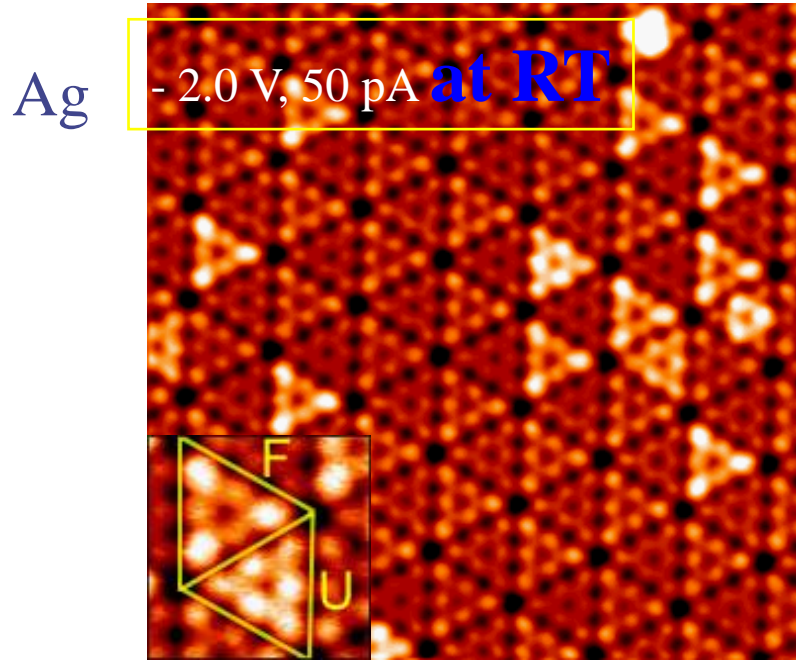
$(t\text{-Bu})_4\text{-ZnPc}$  on Au(111), 78 K



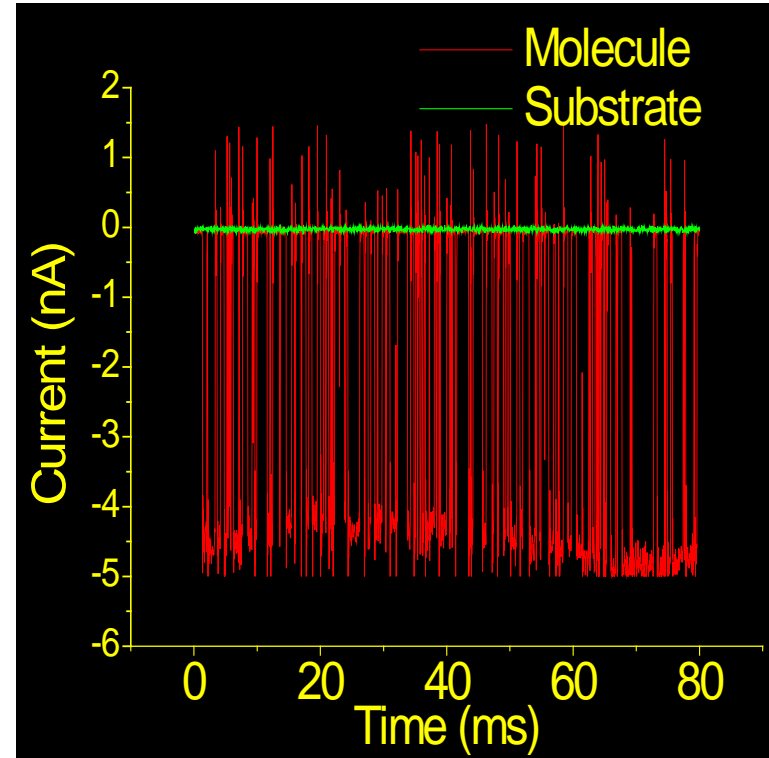
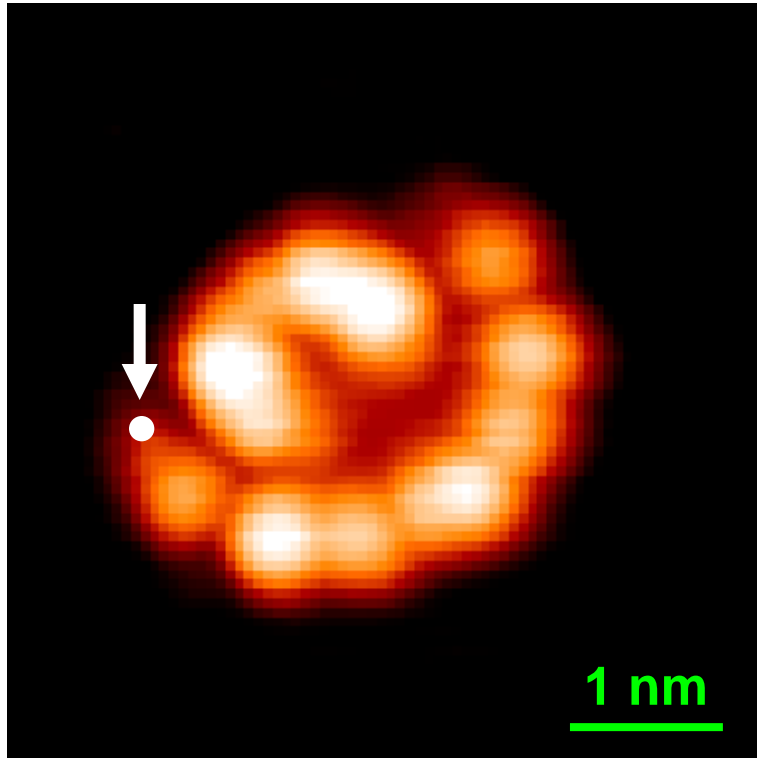
L. Gao *et al.* Phys. Rev. Lett. **101**, 197209 (2008).



# Diffusion Induced STM Images



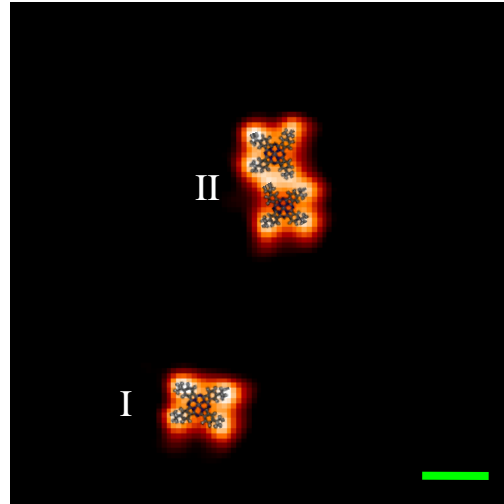
# Tunneling Current Oscillation



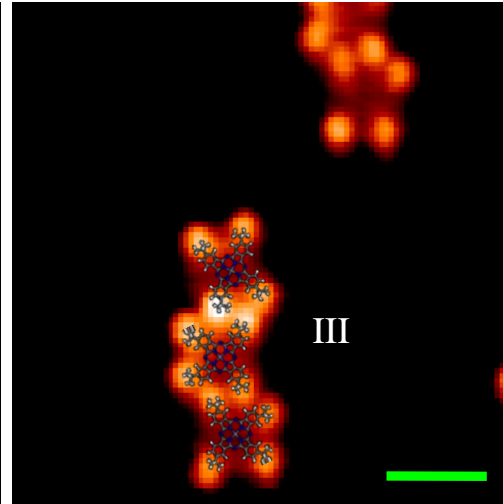
- Single Site  $I-t$  Measurement (-1.8 V)
- Current Oscillation  $0 \leftrightarrow 5$  nA ( $f > 350$  Hz)
- Molecular Motion

# *STM Imaging of Molecular Aggregates at Surfaces*

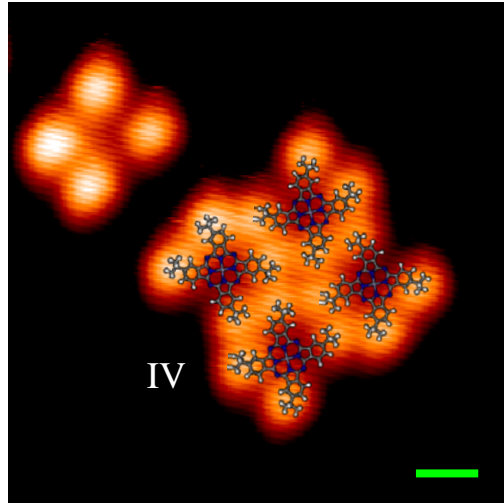
**A**



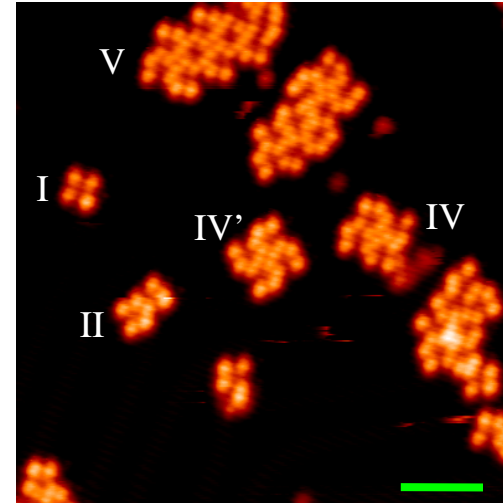
**B**



**C**

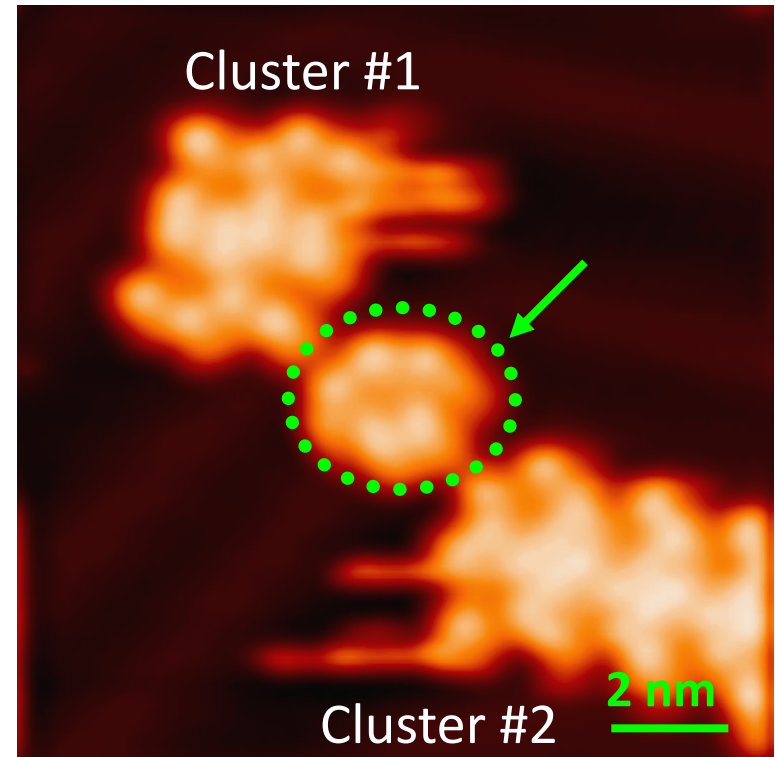
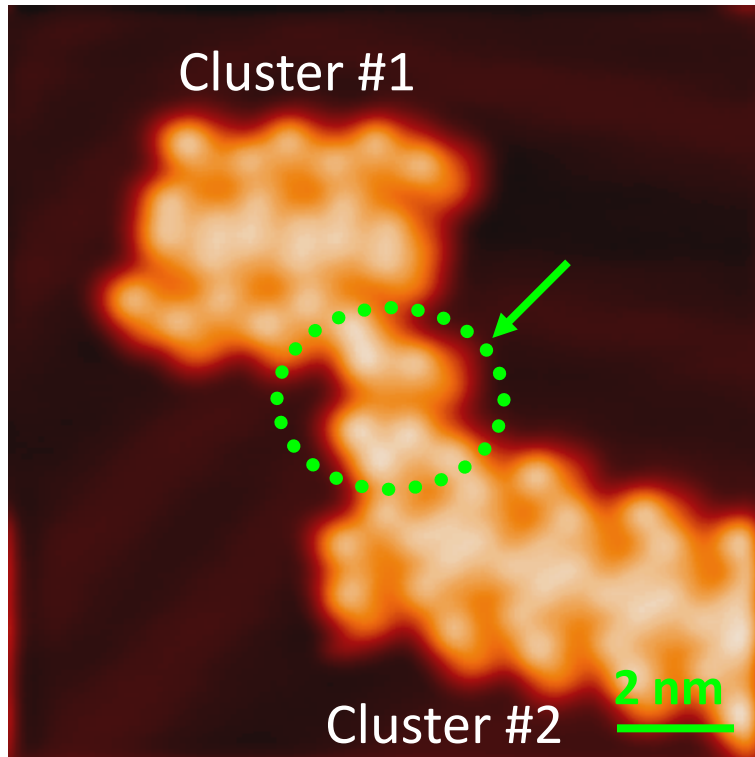


**D**



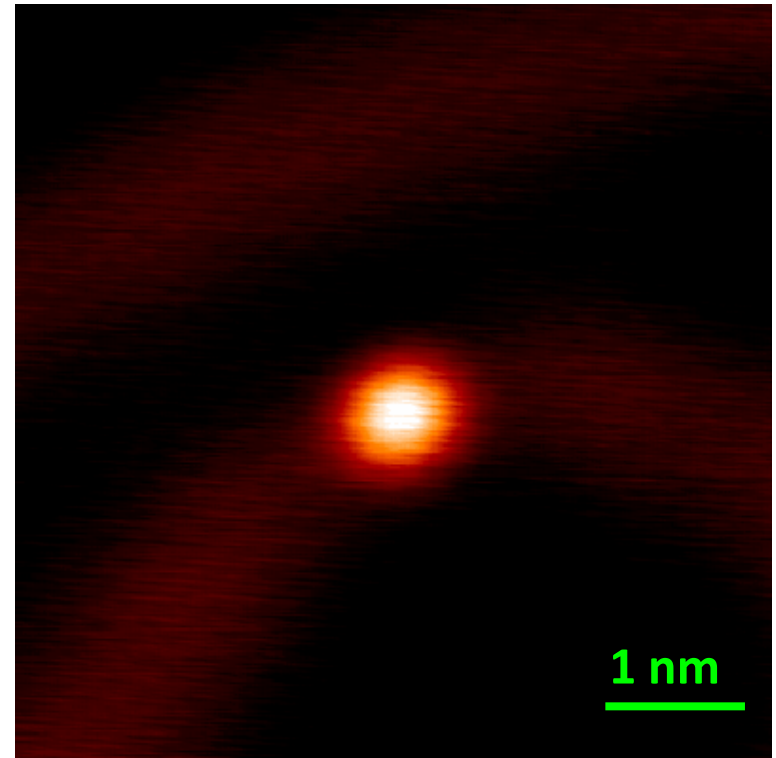
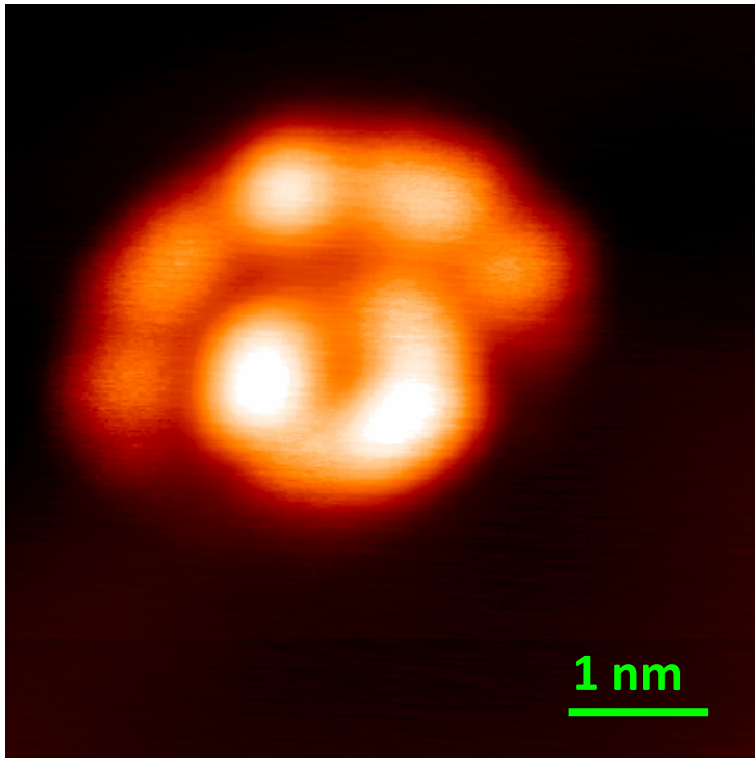
A, B, C, D: at 4.5K

# Real Physical Process



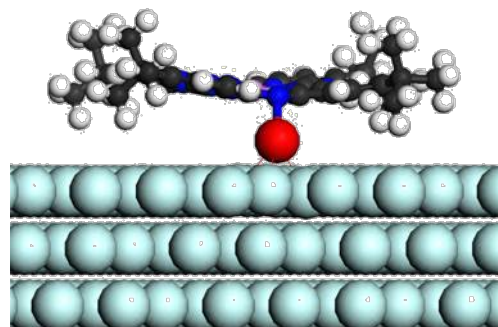
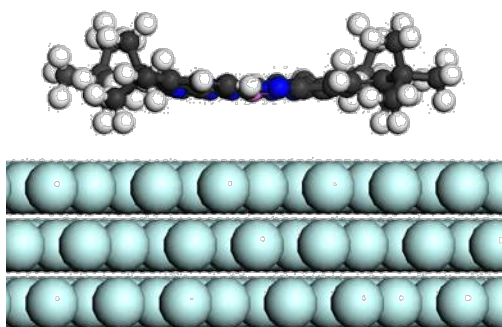
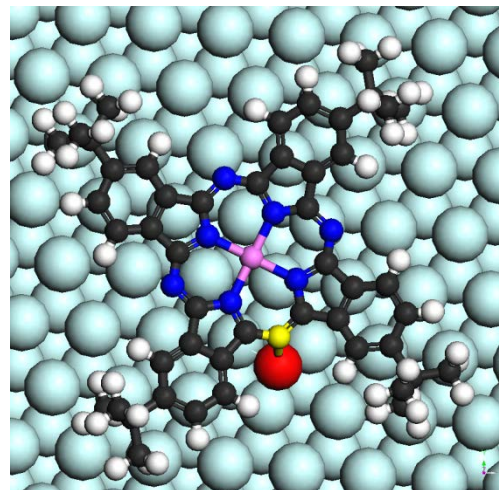
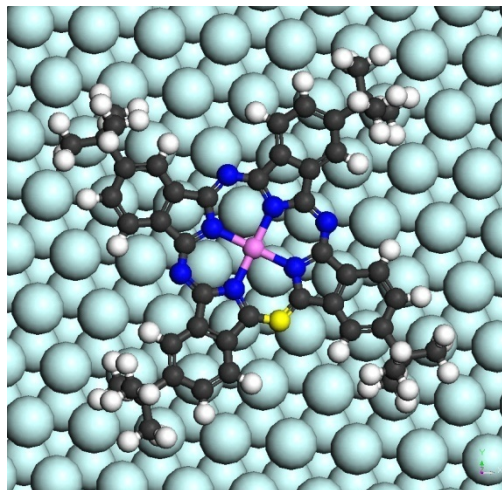
- Stationary single molecule attached to molecular clusters.
- Instable single molecule isolated from molecular clusters.
- Single molecule involved

# *Underlying Au Adatom*

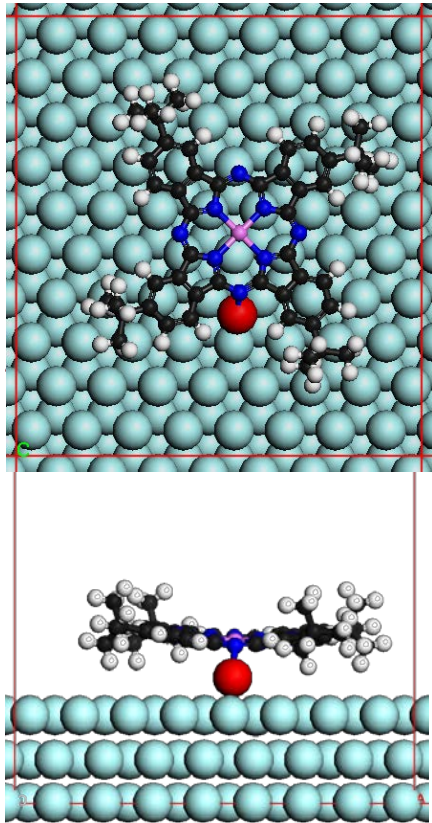


- Bright Spots Left After Removing Molecules
- Center Position of Molecular Rotor
- Gold Adatoms\*

# *Molecular Configurations on a Au Adatom of Au(111)*

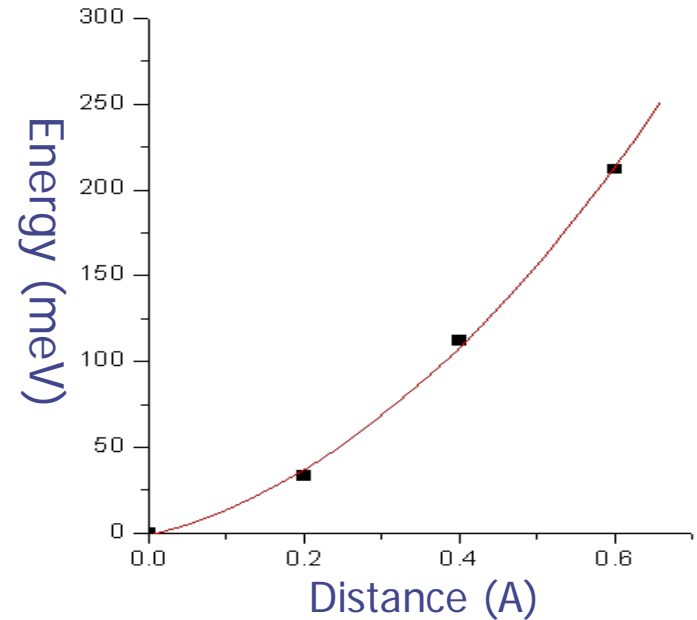


# *Lateral Translation Energy of the Molecule: Adsorption and Rotation around Au Adatom*



$$E_{\text{ad}}=804\text{meV}$$

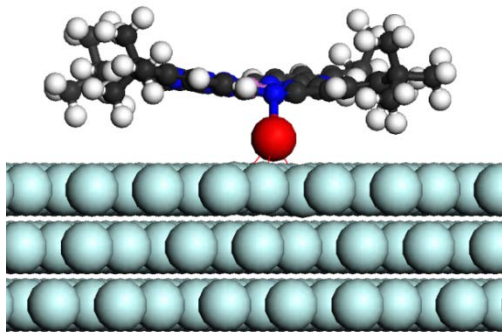
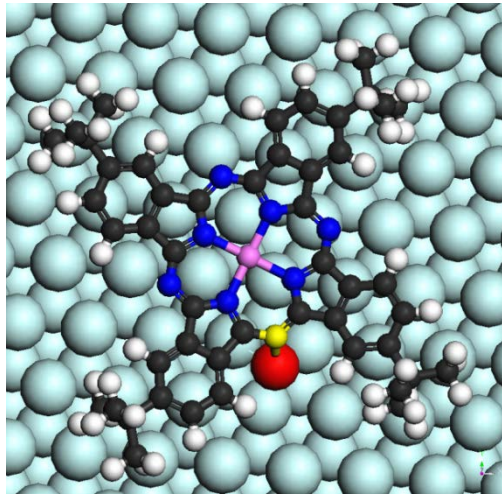
Lateral  
Translation



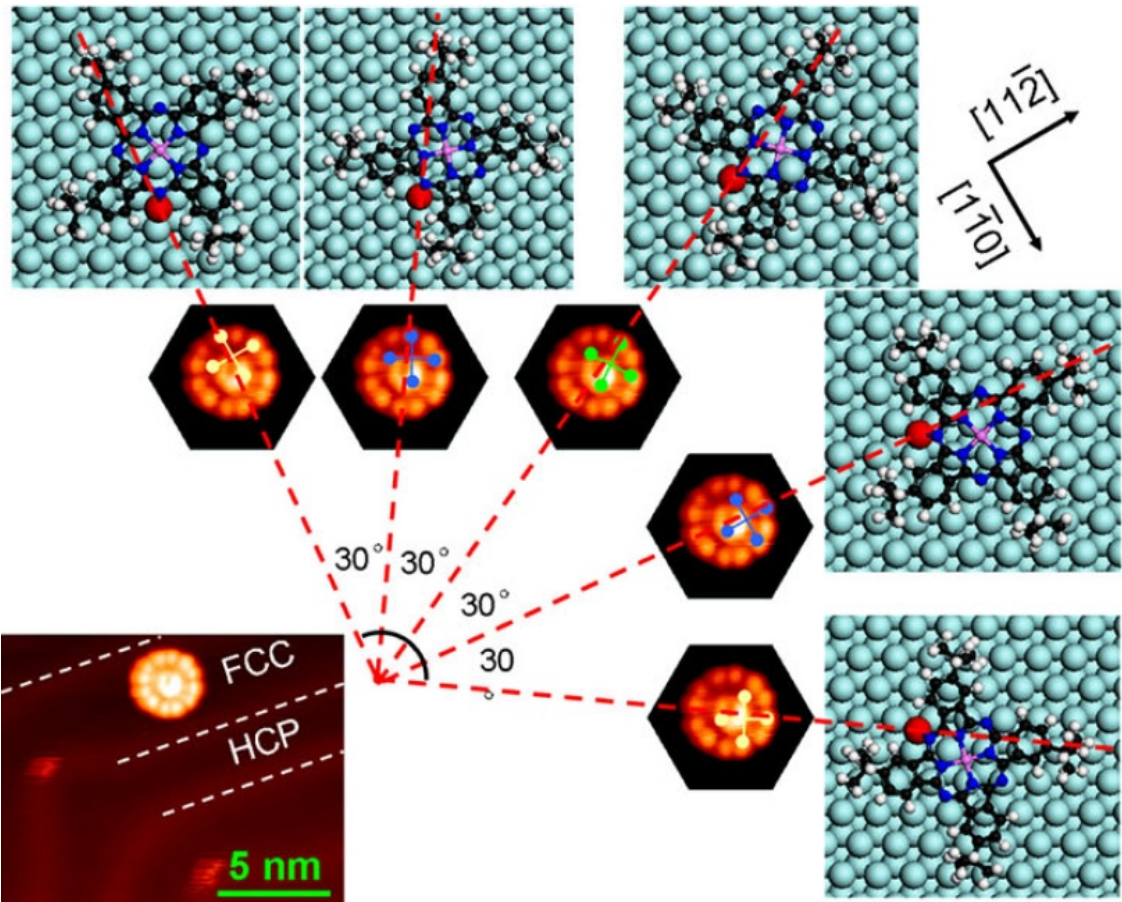
The diffusion barrier along different directions is still high ( $30^\circ$ )

# *Ab Initio Calculations of Meta-stable Configurations and Comparison with Experimental Observations*

$$E_{ad} = 804 \text{ meV}$$

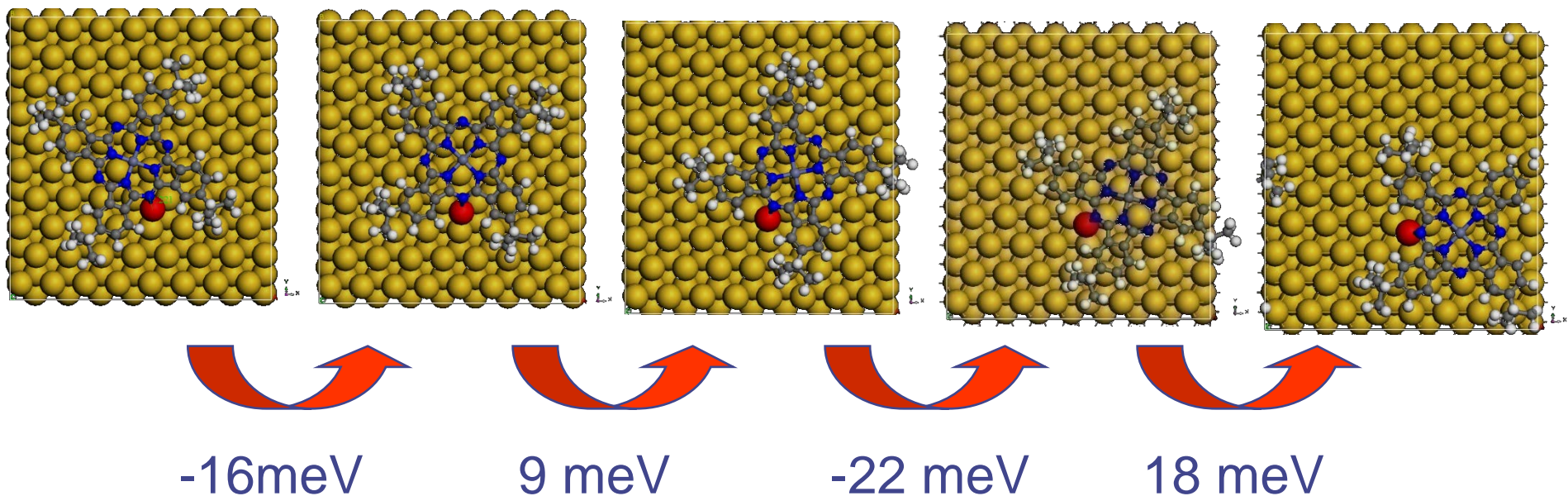


$$\text{Barrier} \sim 20 \text{ meV}$$

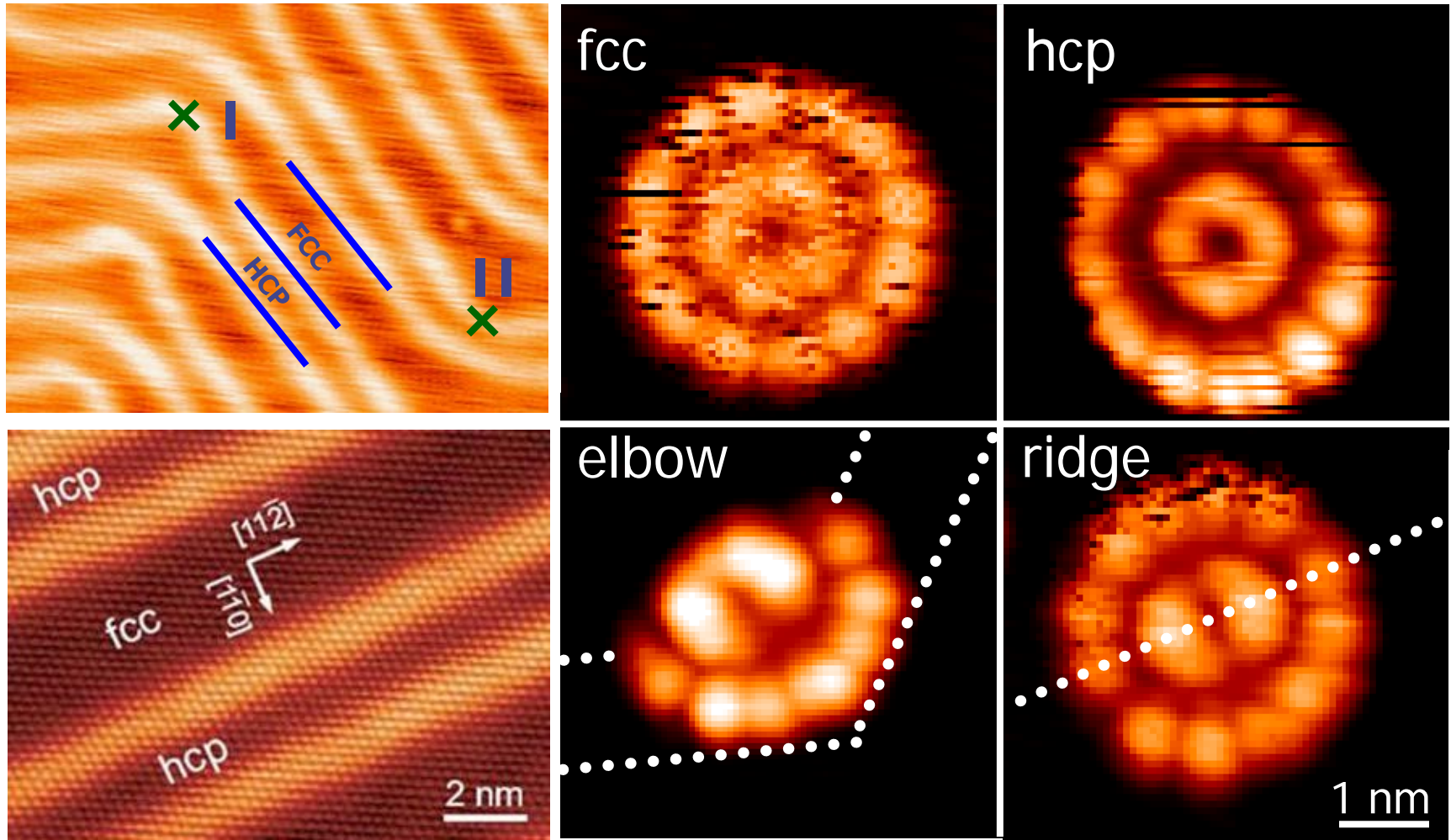




# *Energy Barriers between Molecular Configurations of Rotation around Au Adatom*

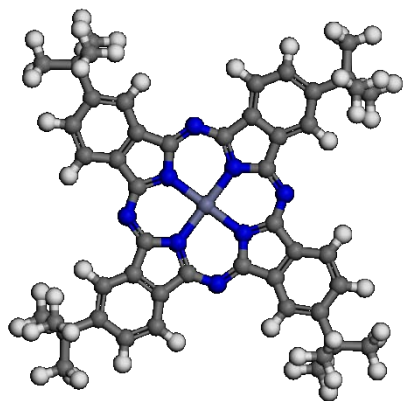


# Manipulating Single Molecular Rotors using Different Locations

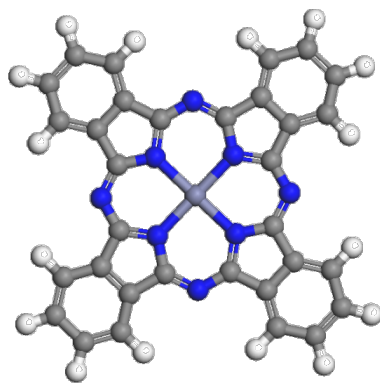


H.-J. Gao *et al.*, Phys. Rev. Lett. **101**, 197206(2008)

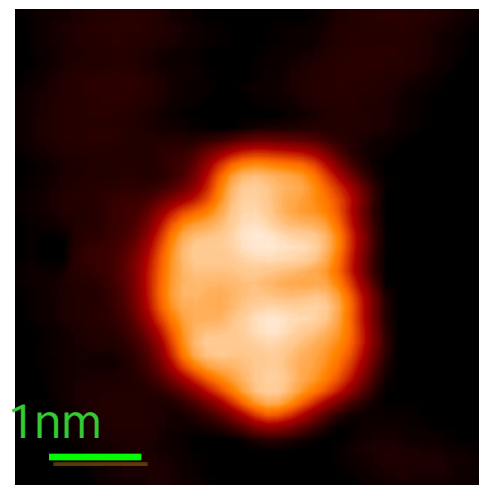
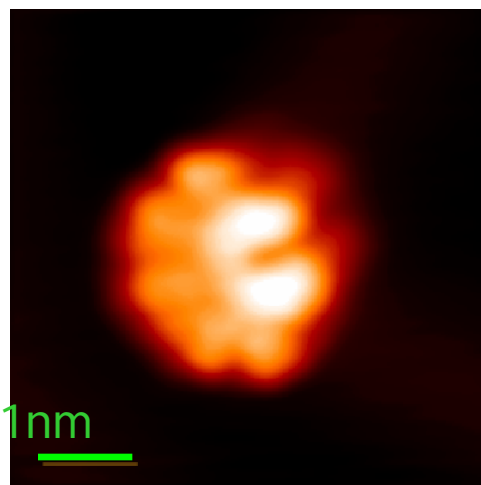
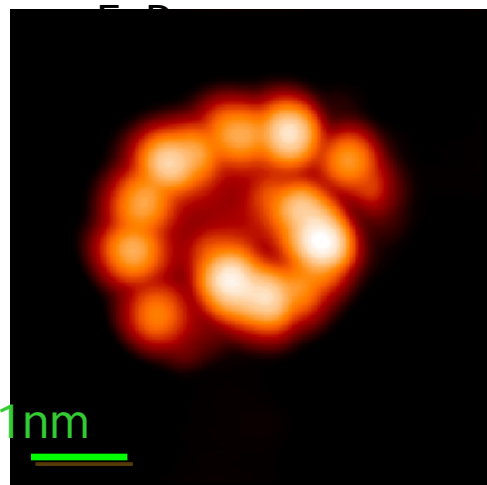
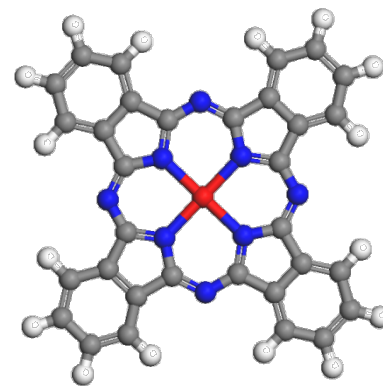
# *Change Structure of Molecule*



(t-Bu)<sub>4</sub>-ZnPc

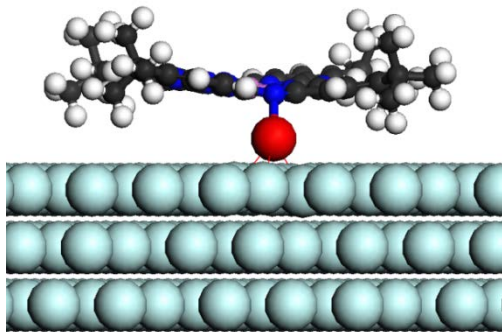
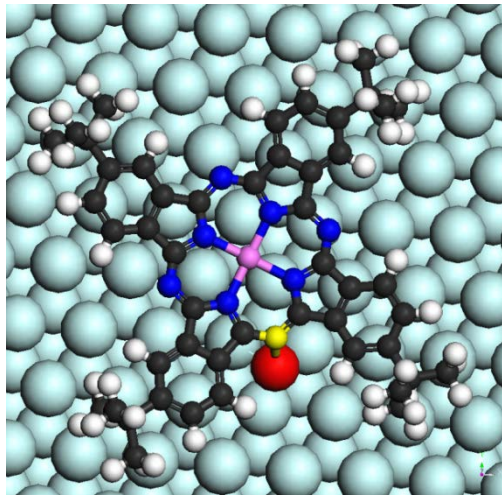


ZnPc

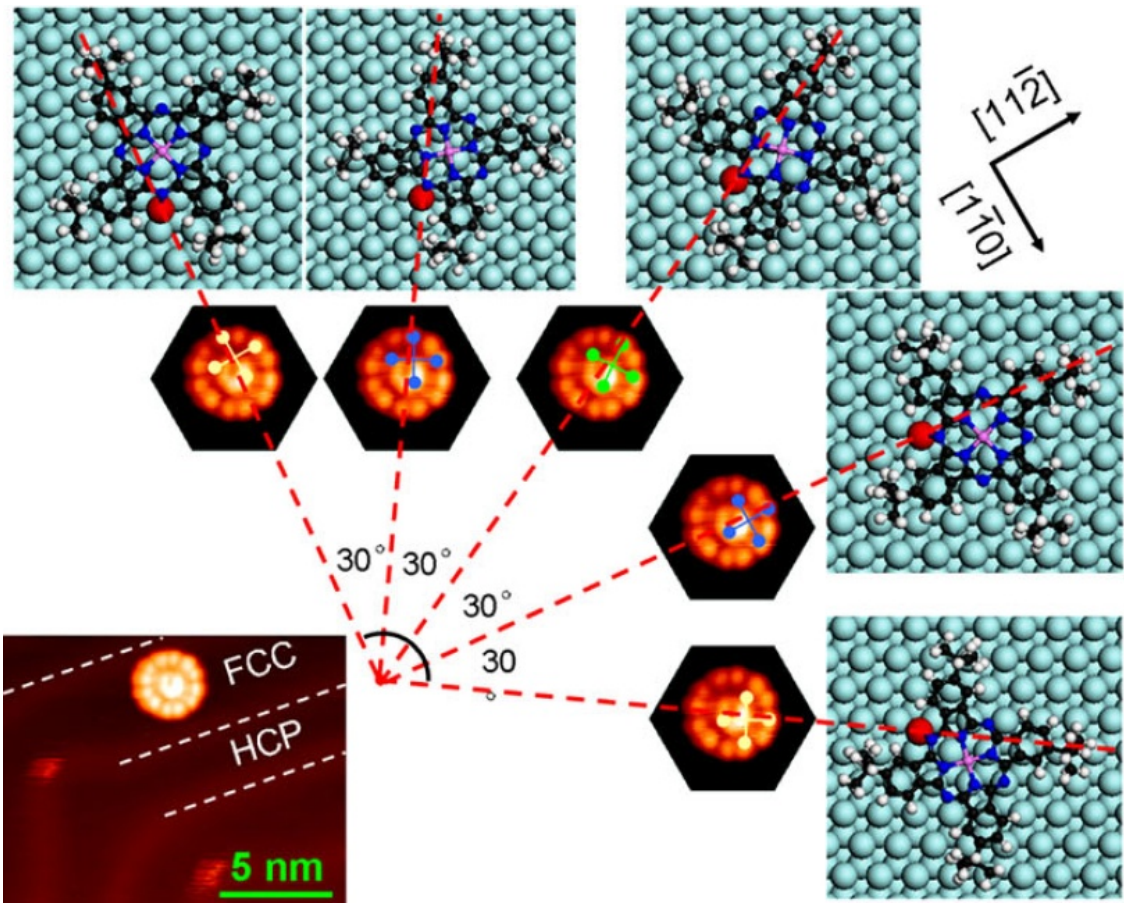


# *Ab Initio Calculations of Meta-stable Configurations and Comparison with Experimental Observations*

$$E_{ad} = 804 \text{ meV}$$



$$\text{Barrier} \sim 20 \text{ meV}$$



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Molecular rotors with a fixed off-center rotation axis have been observed for single tetra-*tert*-butyl zinc phthalocyanine molecules on an Au(111) surface by a scanning tunneling microscope at  $LN_2$  temperature. Experiments and first-principles calculations reveal that we introduce gold adatoms at the ...

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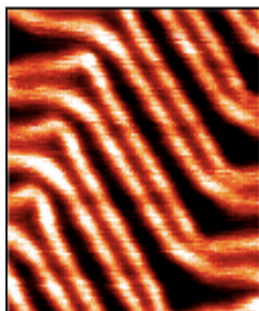
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## Spinning on a gold atom



### Constructing an Array of Anchored Single-Molecule Rotors on Gold Surfaces

L. Gao, Q. Liu, Y. Y. Zhang, N. Jiang, H. G. Zhang, Z. H. Cheng, W. F. Qiu, S. X. Du, Y. Q. Liu, W. A. Hofer, and H.-J. Gao

Phys. Rev. Lett. 101, 197209 (Published November 7, 2008)

• [Nanophysics](#)

In biological systems, molecules convert chemical energy into mechanical motion—the source of movement in living organisms. Such molecular motors could be assembled into nanoscale machines, provided we can control their motion and harness them into large-scale arrays on surfaces.

Li Gao and scientists at the Institute of Physics and the Institute of Chemistry in Beijing, in collaboration with the University of Liverpool, have constructed an array of anchored single-molecule rotors on a gold surface. In a paper appearing in *Physical Review Letters*, they have found that single  $(t\text{-Bu})_4\text{-ZnPc}$  (tetra-*tert*-butyl zinc phthalocyanin) molecules on a reconstructed gold surface possess a well-defined axis of rotation, and that these molecules also form large-scale ordered arrays.

50  
years  
PRL  
moving physics forward

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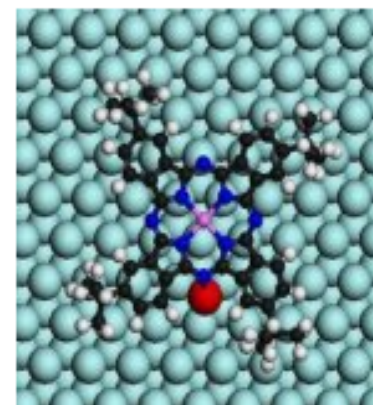
**NEWS**

Nov 18, 2008

**Nanorotors move together**

Researchers in China and the UK have made a new type of nanometre-sized rotor with an off-centre axis of rotation. The researchers have also made arrays of the devices that spread over distances as large as micrometres.

The individual rotors in the arrays work in concert, something that the team believes will be crucial for making molecular machines. Such machines could be used as tiny autonomous "nanorobots" in the future that would perform a wide range of tasks, such as assembling electronic circuits or delivering drugs to specific parts of the body.



Nanorotor

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## research highlight

### Molecular machines: Rows of rotors

Published online 0000-00-00 00:00:00

The ability to move individual atoms with the tip of a scanning tunneling microscope is a powerful first step towards building complex molecular machines at the atomic scale. But for practical applications of such molecular machinery, it must be possible to construct it easily and at low cost, on a large-scale. The key satisfying these requires is finding systems of molecules that assemble themselves into the desired shapes and functions on tailor-made surfaces.

To this end, Hong-Jun Gao and colleagues<sup>1</sup> from the Institute of Physics of the Chinese Academy of Sciences and Institute of Chemistry of the Chinese Academy of Sciences in Beijing, in collaboration with Werner Hofer of the University of Liverpool, demonstrate the self-

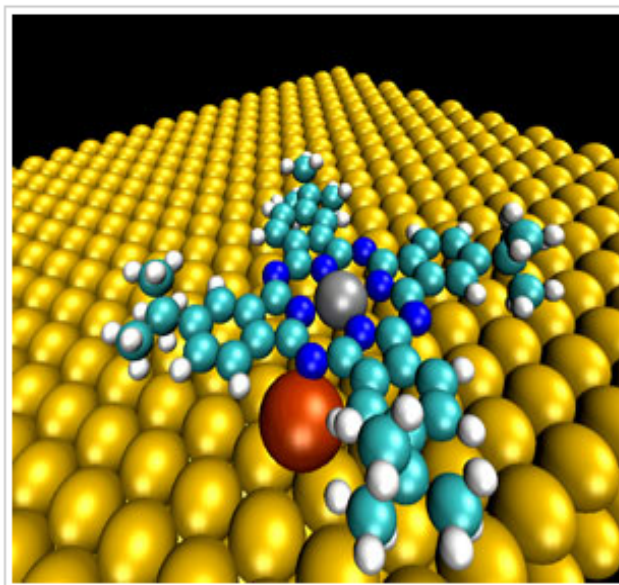


Fig. 1: Simulated image of the authors rotor attached to a gold surface. Red atom denote an absorbed gold atom that spontaneously becomes attached to the rotor at one of its





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The ability to move individual atoms with the tip of a scanning tunneling microscope is a powerful first step towards building complex molecular machines at the atomic scale. But for practical applications of such molecular machinery, it must be possible to construct it easily and at low cost, on a large-scale. The key satisfying these requires is finding systems of molecules that assemble themselves into the desired shapes and functions on tailor-made surfaces.

To this end, Hong-Jun Gao and colleagues<sup>1</sup> from the Institute of Physics of the Chinese Academy of Sciences and Institute of Chemistry of the Chinese Academy of Sciences in Beijing, in collaboration with Werner Hofer of the University of Liverpool, demonstrate the self-assembled construction of a well-ordered array of single molecule rotors on a gold surface, each of which is anchored to a fixed point on the surface and free to rotate around a well-defined axis on the molecule. These results represent a potential step forward in the large-scale construction of arrays of molecular motors and larger molecular machines.

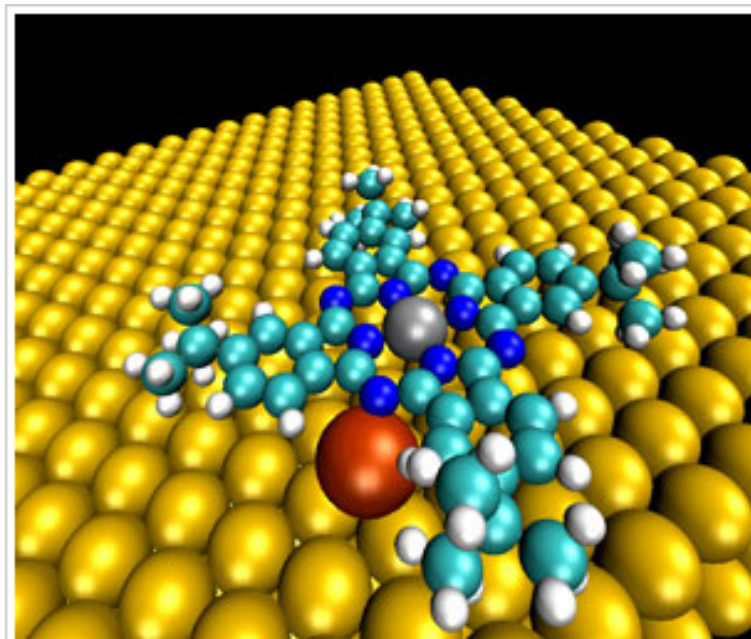
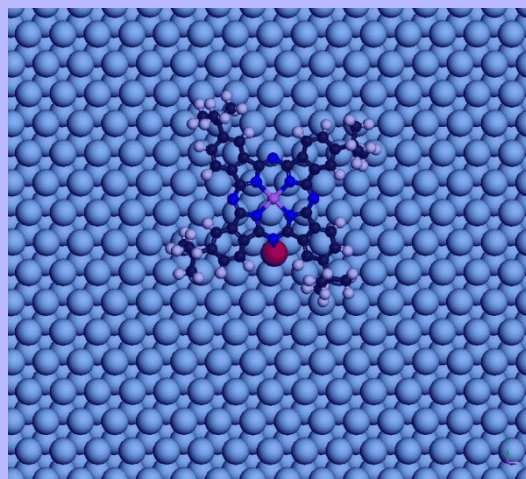
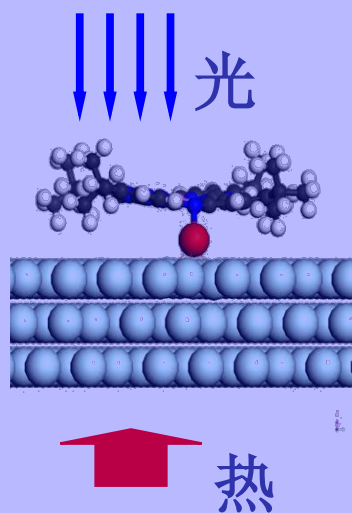


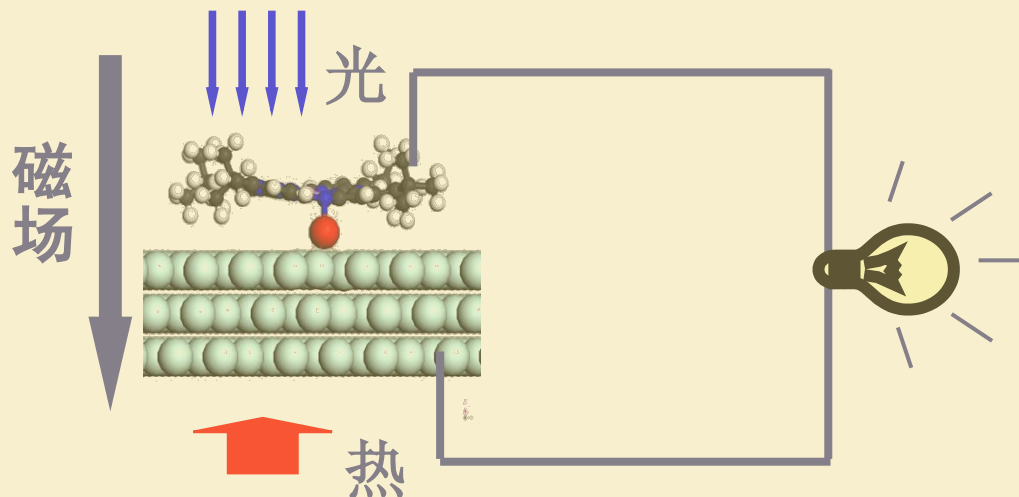
Fig. 1: Simulated image of the authors rotor attached to a gold surface. Red atom denote an absorbed gold atom that spontaneously becomes attached to the rotor at one of its off-centre nitrogen atoms (blue).

# 单分子发动机



表面上的某些分子，可以在热，电或者光的激发下在不同结构之间发生跳跃，当分子持续受到激发，而发生持续的跳跃时，就形成了持续的转动，就可能向外输出功。在本工作中， $(t\text{-Bu})_4\text{-ZnPc}$ 分子以金的顶原子和氮原子成的键为轴，在热激发下（78K）转动，是热动机。如果选用特定分子，可能用光进行激发，且可能转动方向保持不变，形成光动机。

# 单分子发电机



类比普通发电机，我们认为如果在垂直表面方向加上磁场，同时保持热激发或者光激发分子持续转动，则由于分子中心和转轴分离，使得分子切割磁力线，在分子内部，会构建起电动势；采用特殊的方法，可能将这个电动势输出。

# Reversible **Single Spin Control** of **Magnetic Molecule by H Atom Adsorption**

L.W. Liu/H.J. Gao *et al.*, Scientific Report **3**, 1210(2013)

# 单个磁性分子的Kondo效应及其调控

- Molecular structure of the magnetic impurities.
  - cut off ligands from impurities.
  - attach ligands to impurities.
- Changing the substrate properties.
  - different materials.
  - film thickness, Pb/Si(111).

## Nondestructive and Reversible Control

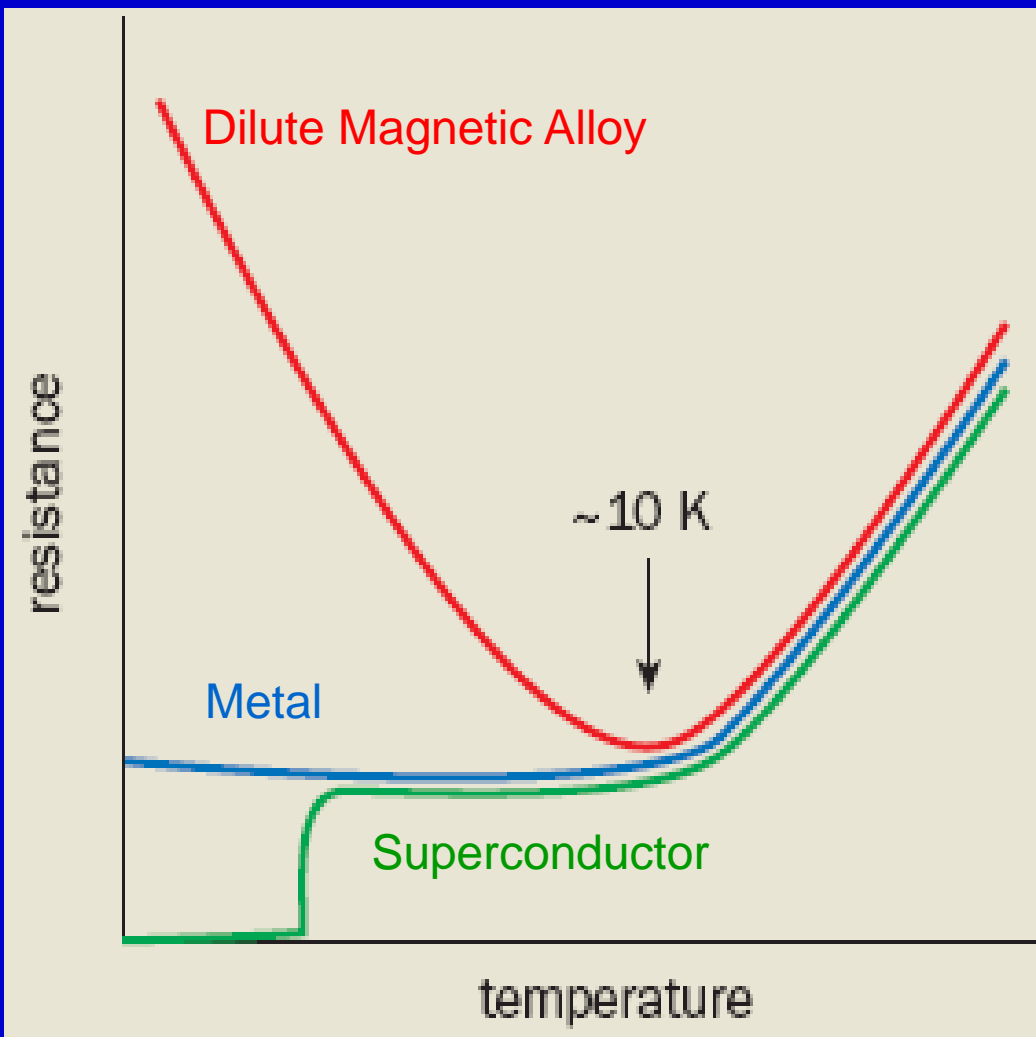
A. Zhao *et al.*, *Science* **309**, 1542 (2005).

P. Wahl *et al.*, *Phys. Rev. Lett.* **95**, 166601 (2005).

V. Iancu *et al.*, *Nano Lett.* **6**, 820 (2006).

P. Wahl *et al.*, *Phys. Rev. Lett.* **98**, 056601 (2007).

# Kondo Effect



- Discovered in 1930s.
- Dilute magnetic alloys:  
Metals: Au, Ag, Cu, Mg, Zn.  
Magnetic Impurities: Cr, Mn, Fe, Co, Ni, V, Ti.  
No inter-impurity interaction.
- Electrical resistance minimum at low temperatures for dilute magnetic alloys.

# Magnetism of Nanostructures

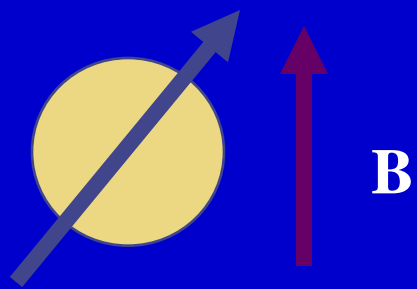
„Single Spin Objects“

Atoms, Molecules

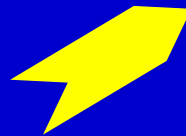


$4F_{9/2}$

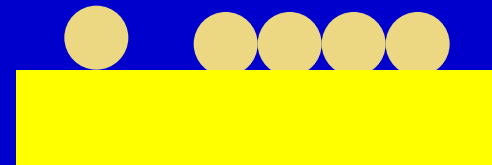
$S=3/2$   $L=3$   $J=9/2$



???



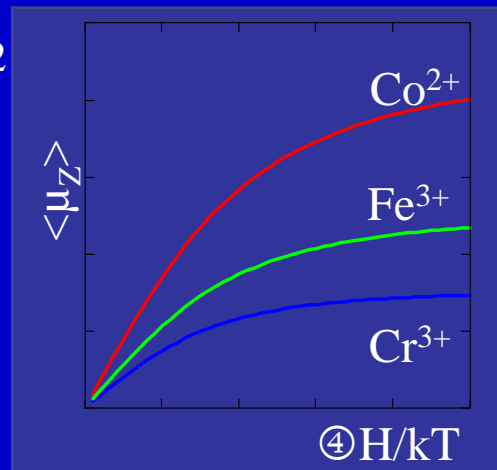
Nanostructures  
**at surfaces !**



magnetic moment ?

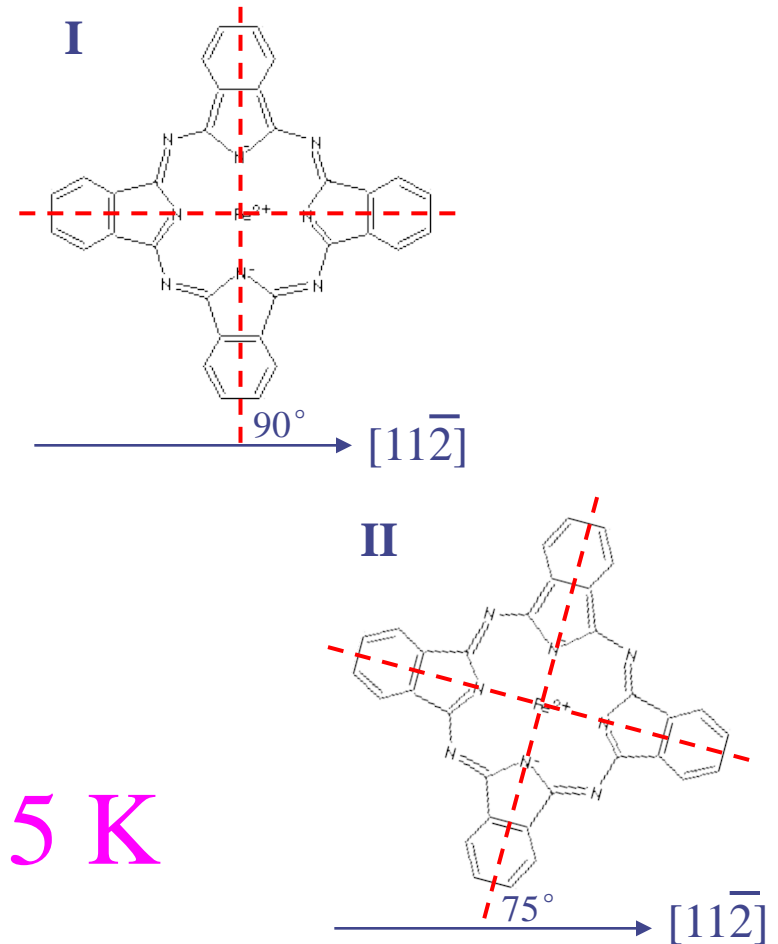
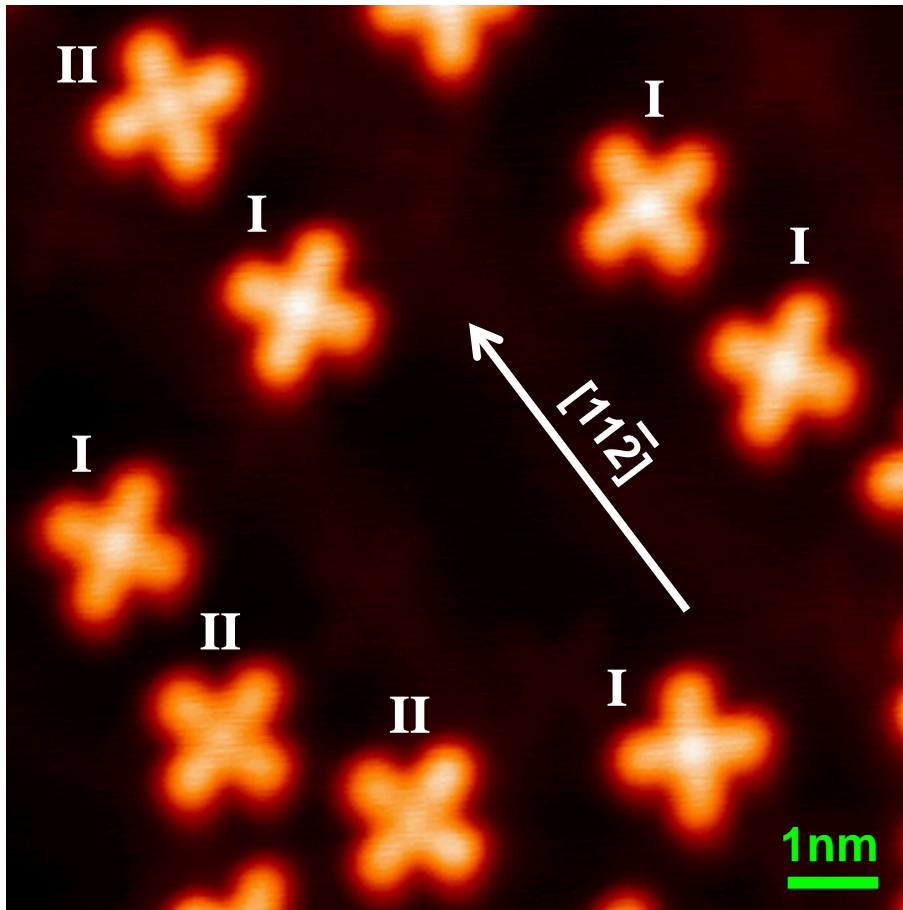
anisotropy ?

magnetic order ?



# 单个磁性分子的Kondo效应及其调控

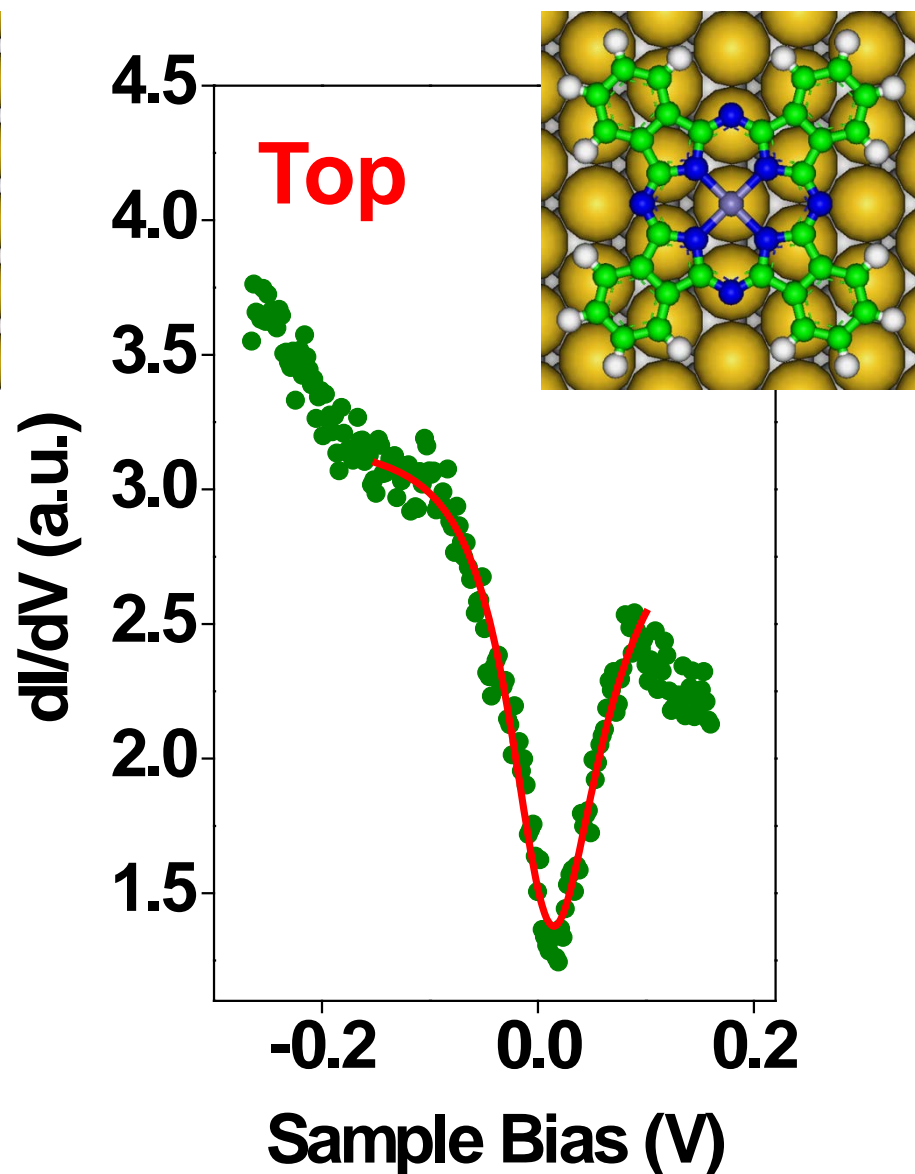
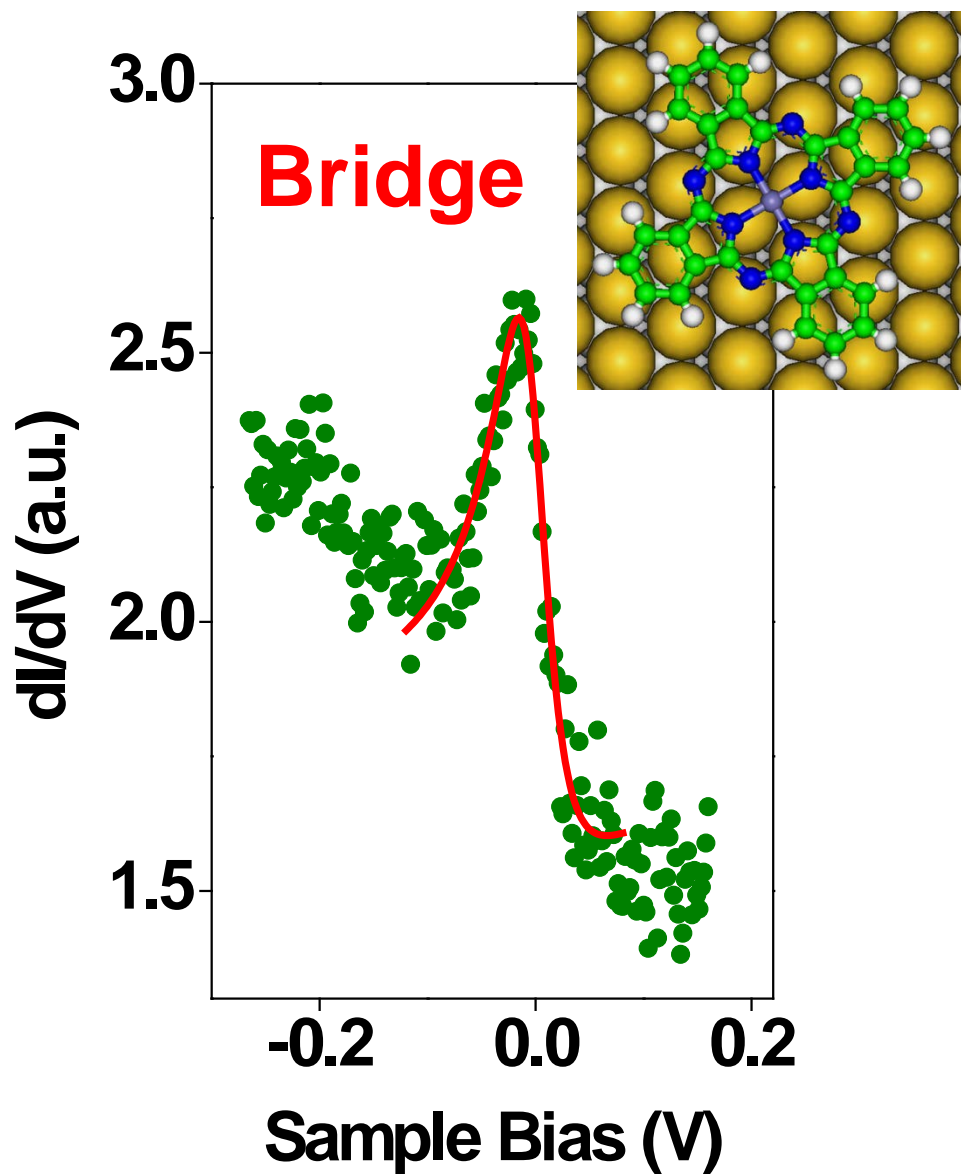
## Two Molecular Orientations



5 K

L. Gao *et al.* *Phys. Rev. Lett.* **99**, 106402 (2007).

# *$dI/dV$ Spectra at Molecular Center*





# Fano Function Fit

$$\frac{dI}{dV}(V) = A \times \frac{(e\phi + q)^2}{1 + e\phi^2} + B$$

$$k_B T_K = G$$

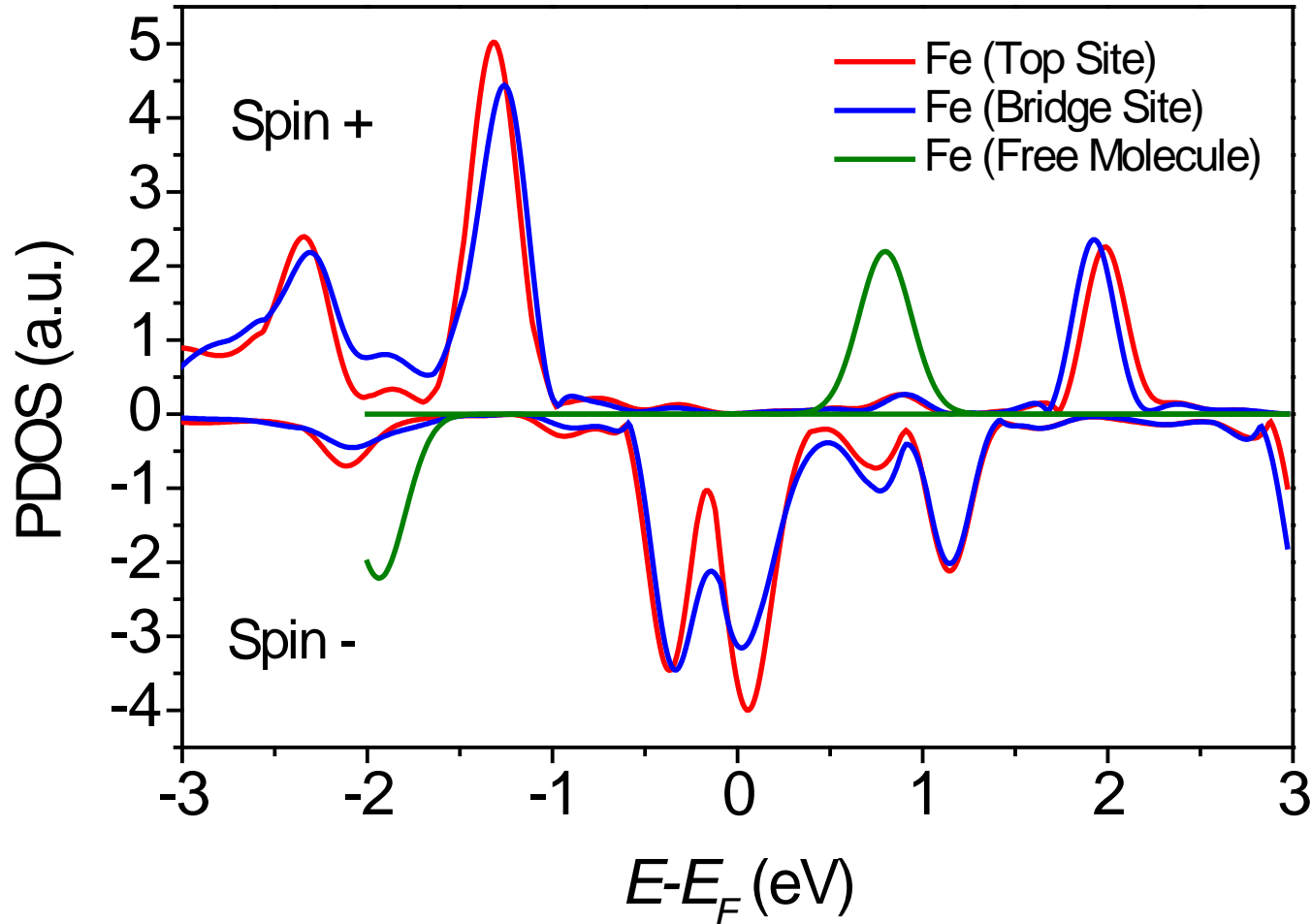
$$e\phi = (eV - e_0) / G$$

$$k_B T_K = D \exp\left(\frac{1}{2|J|g_F}\right)$$

	Bridge Site	Top Site
$q$	<b>2.20</b> $\pm$ 0.19	<b>0.12</b> $\pm$ 0.03
$e_0$	1.58 $\pm$ 0.82 meV	-8.39 $\pm$ 0.63 meV
$\Gamma$	<b>30.73</b> $\pm$ 1.77 meV	<b>51.52</b> $\pm$ 1.60 meV

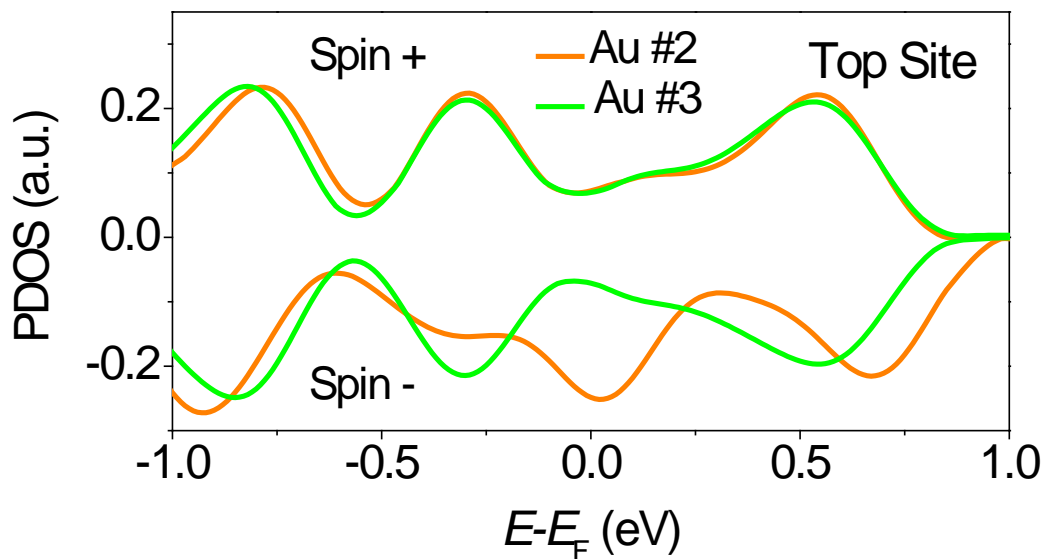
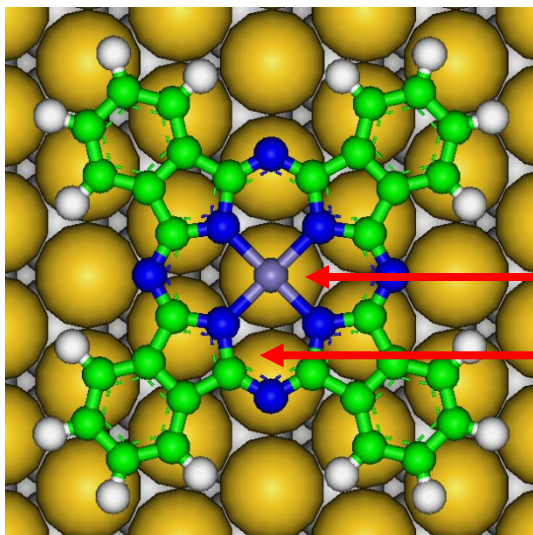
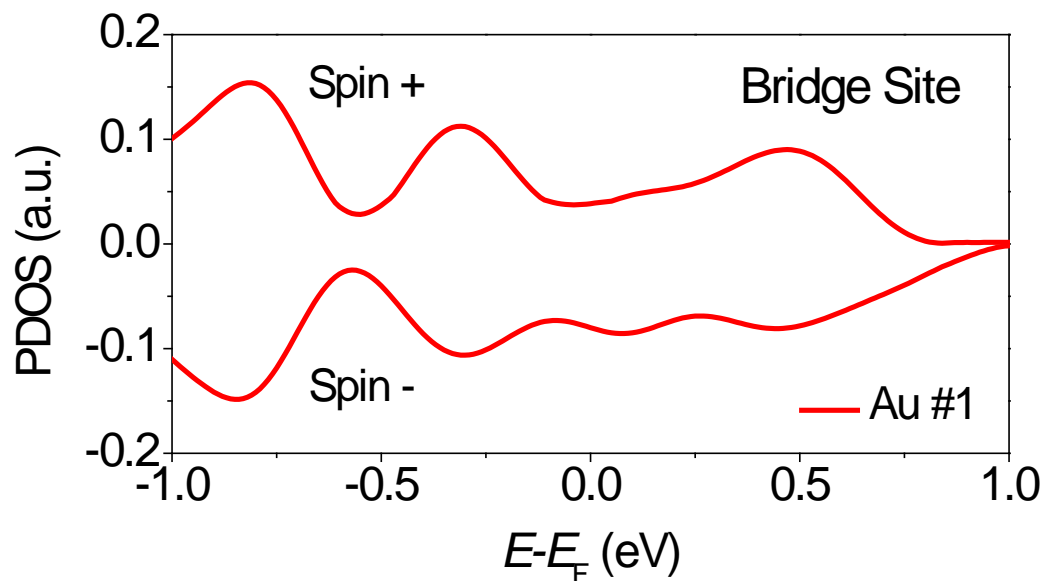
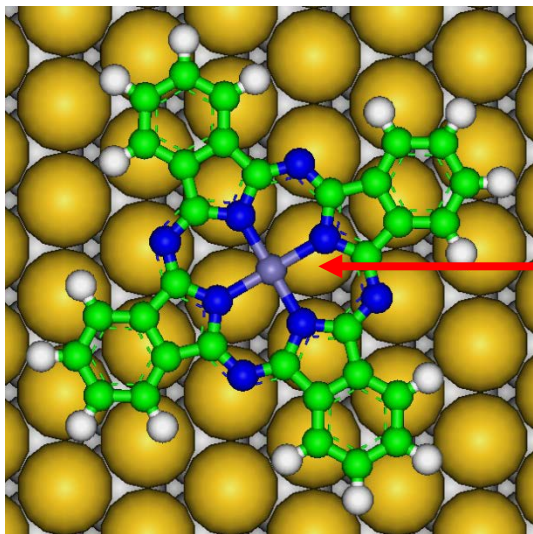
U. Fano, *Phys. Rev.* **124**, 1866 (1961).

# *Spin Polarized PDOS of Fe(2+)*

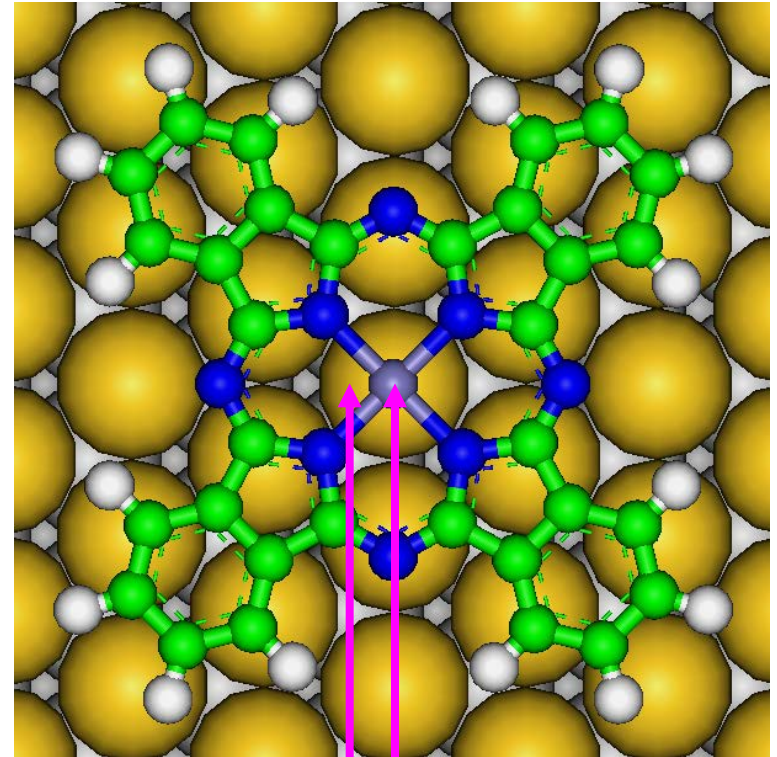
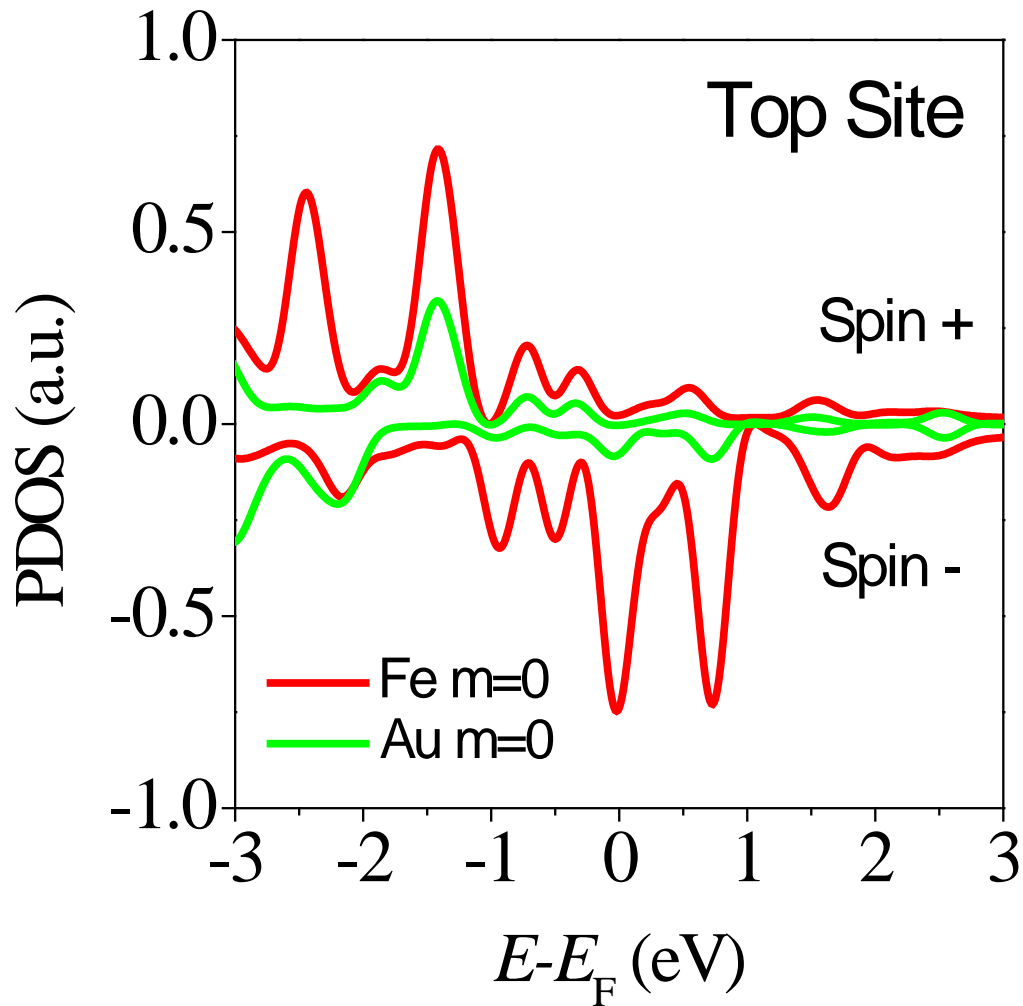


- ◆ Spin-polarized electronic structures lead to a local magnetic moment

# PDOS of Neighboring Au Atoms



# Top Site: *d*-level Hybridization



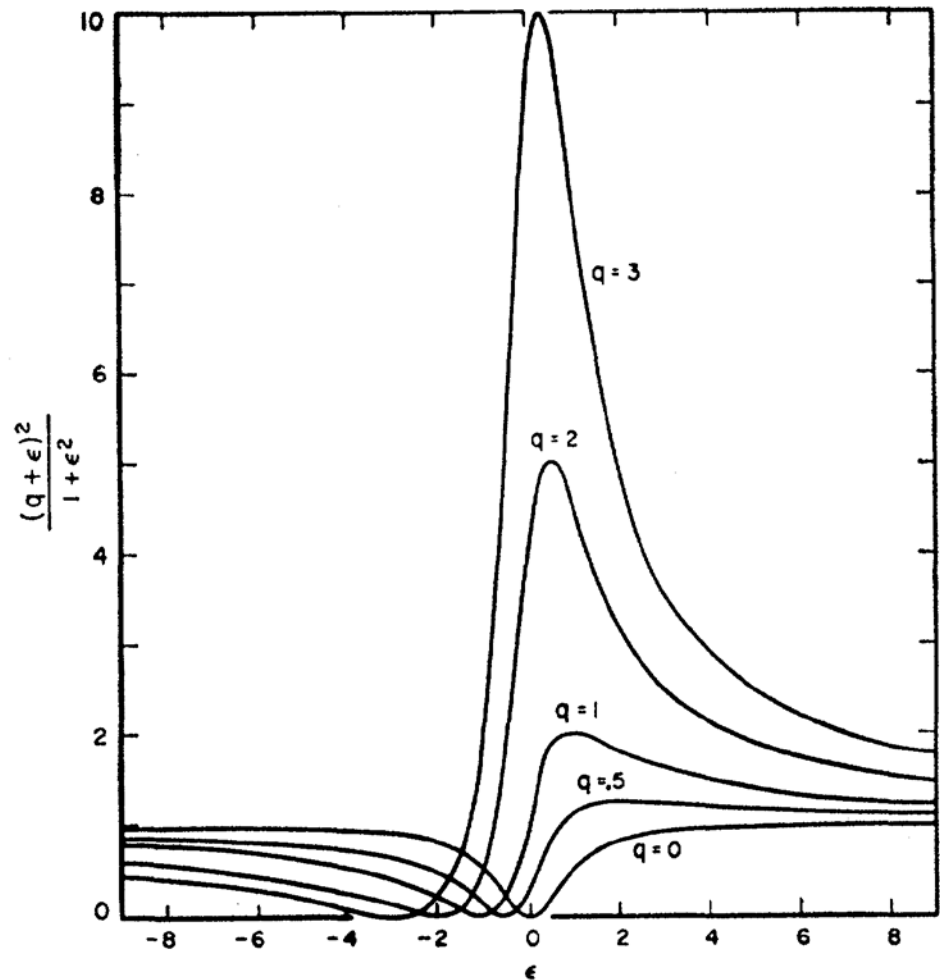
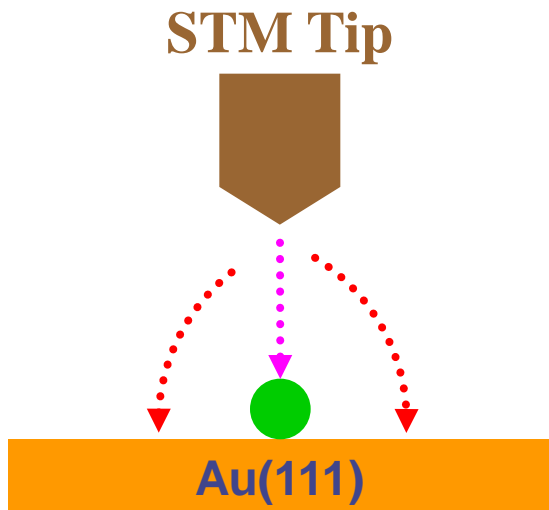
Au Fe

$d_z^2$  orbital contribution

# Line Shape of Kondo Resonance

- Bridge site:  $q = 2.20 \pm 0.19$
- Top site:  $q = 0.12 \pm 0.03$

$$\frac{1}{2} \rho q^2 = \frac{|\langle \Phi | T | i \rangle|^2}{|\langle \psi_E | T | i \rangle|^2} G$$

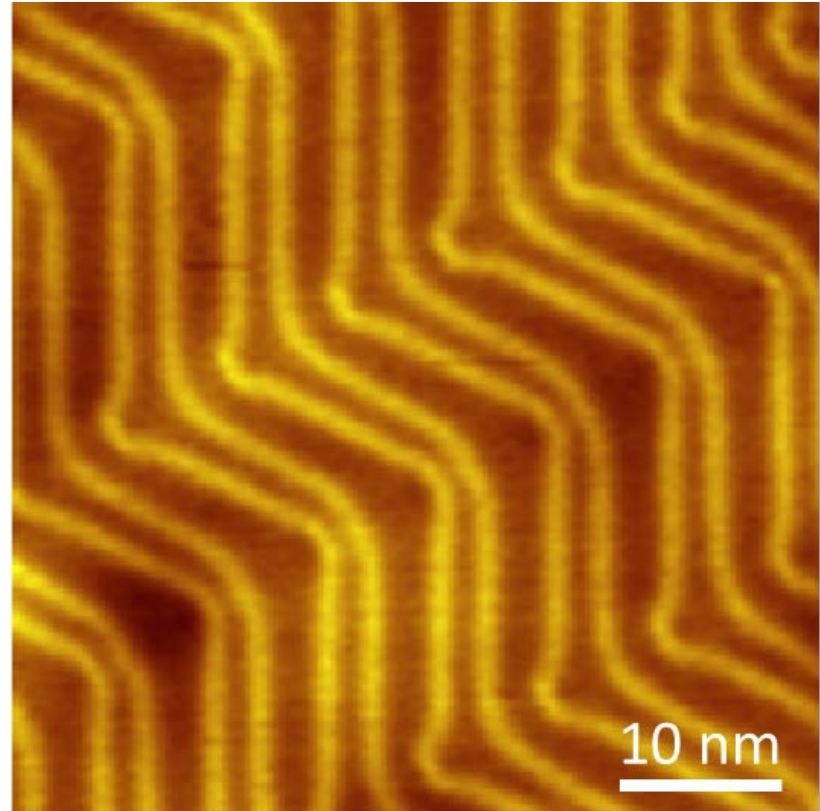
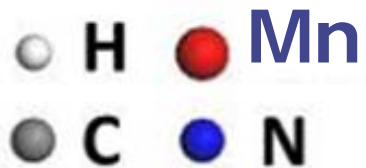
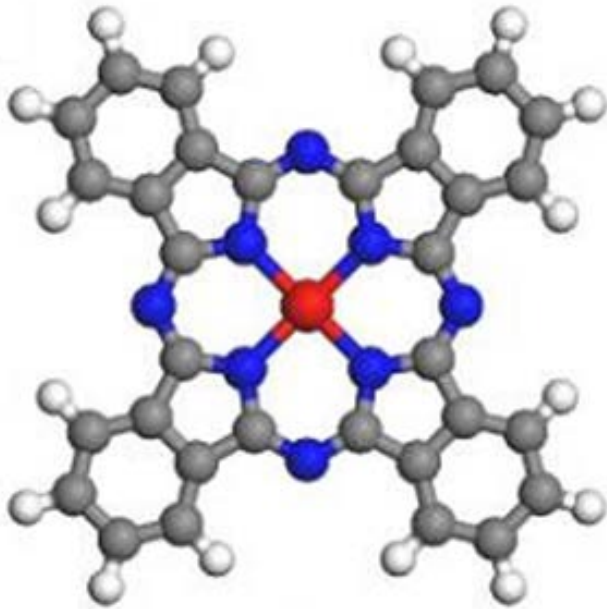


U. Fano, *Phys. Rev.* **124**, 1866 (1961).

# Studied Systems: MnPc+Au(111)

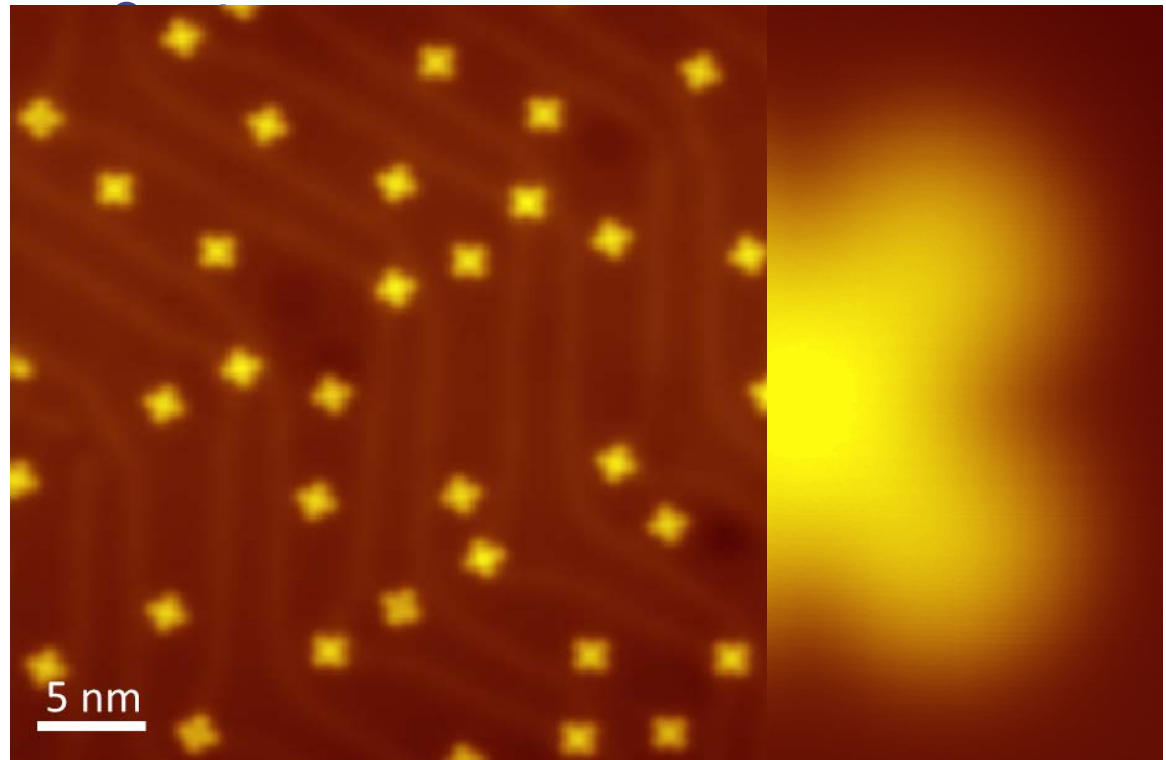
MnPc:  $S=3/2$

Au(111)



# STM Image of the MnPc/Au(111)

“Protrusion ” at the Molecular



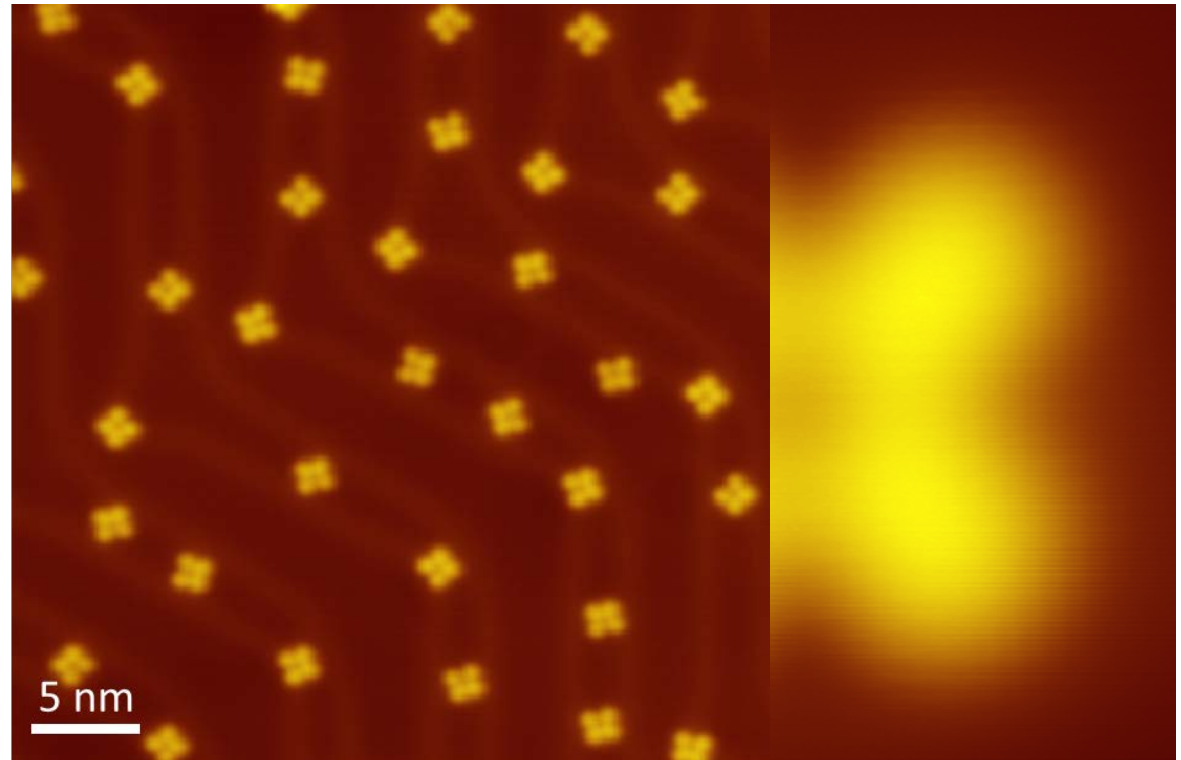
MnPc/Au(111)

H induced at room  
Temperature in the UHV



# STM Image of the MnPc/Au(111) after H adsorption

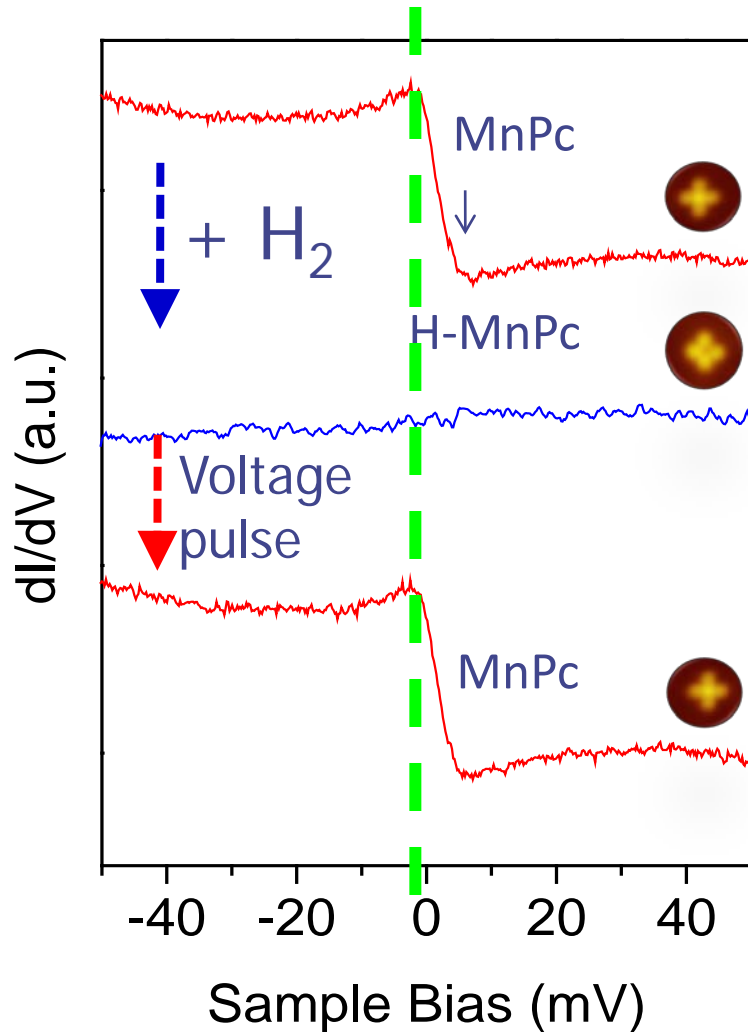
“Depression” at the Molecular



H-MnPc/Au(111)



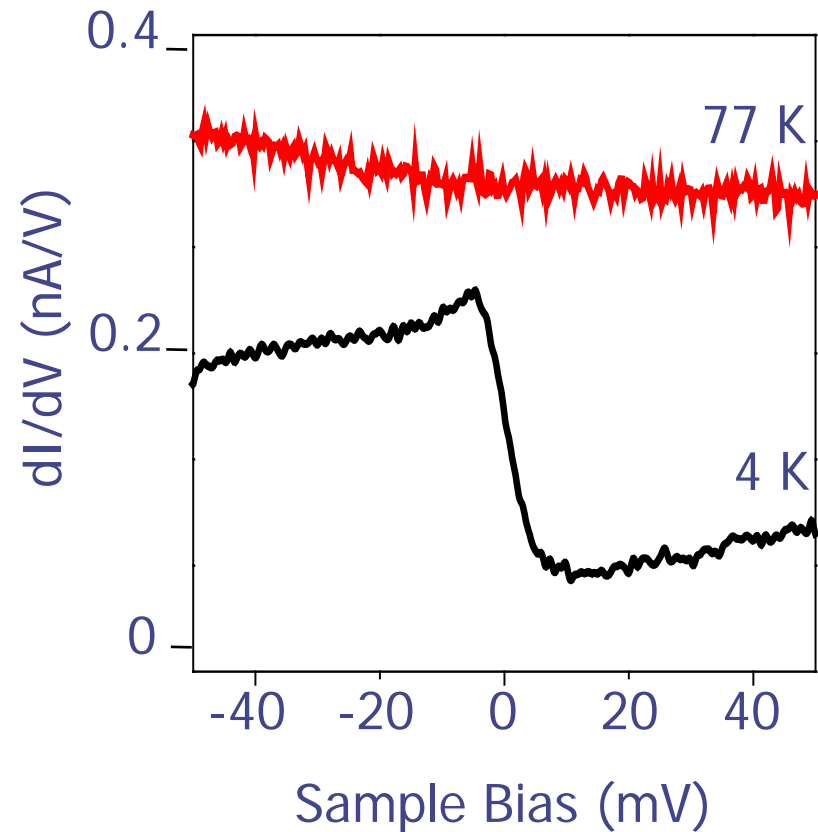
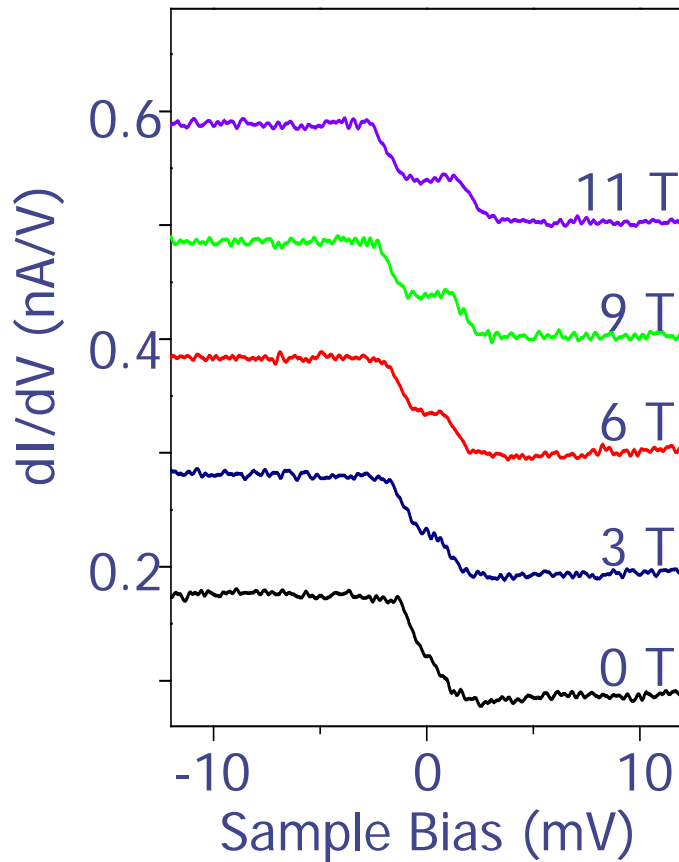
# Reversible Peak Feature at the Fermi Level



- MnPc/Au(111): A pronounced step shaped feature at zero bias---- which can be attributed to Kondo effect
- H-MnPc/Au(111): are featureless in this energy range
- once the H-MnPc state was switched back to the MnPc state, its electronic structure including the Kondo resonance can be fully recovered in addition to the recovery of the topographic feature.

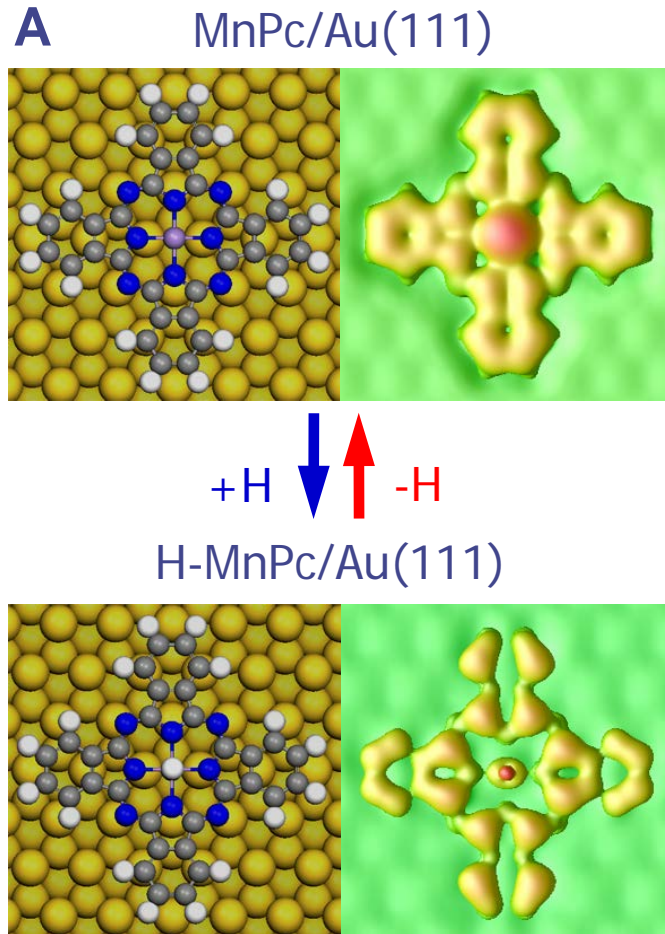
# Kondo Effect ???

## Magnetic Field and Temperature Dependence

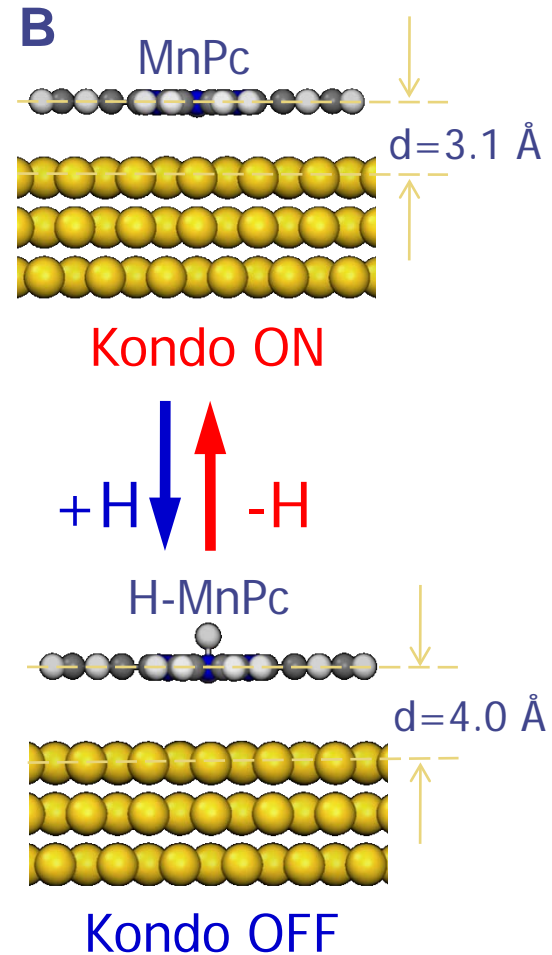


These **two hallmarks** confirmed the Kondo effect

# DFT Calculation: Larger Spacing with H

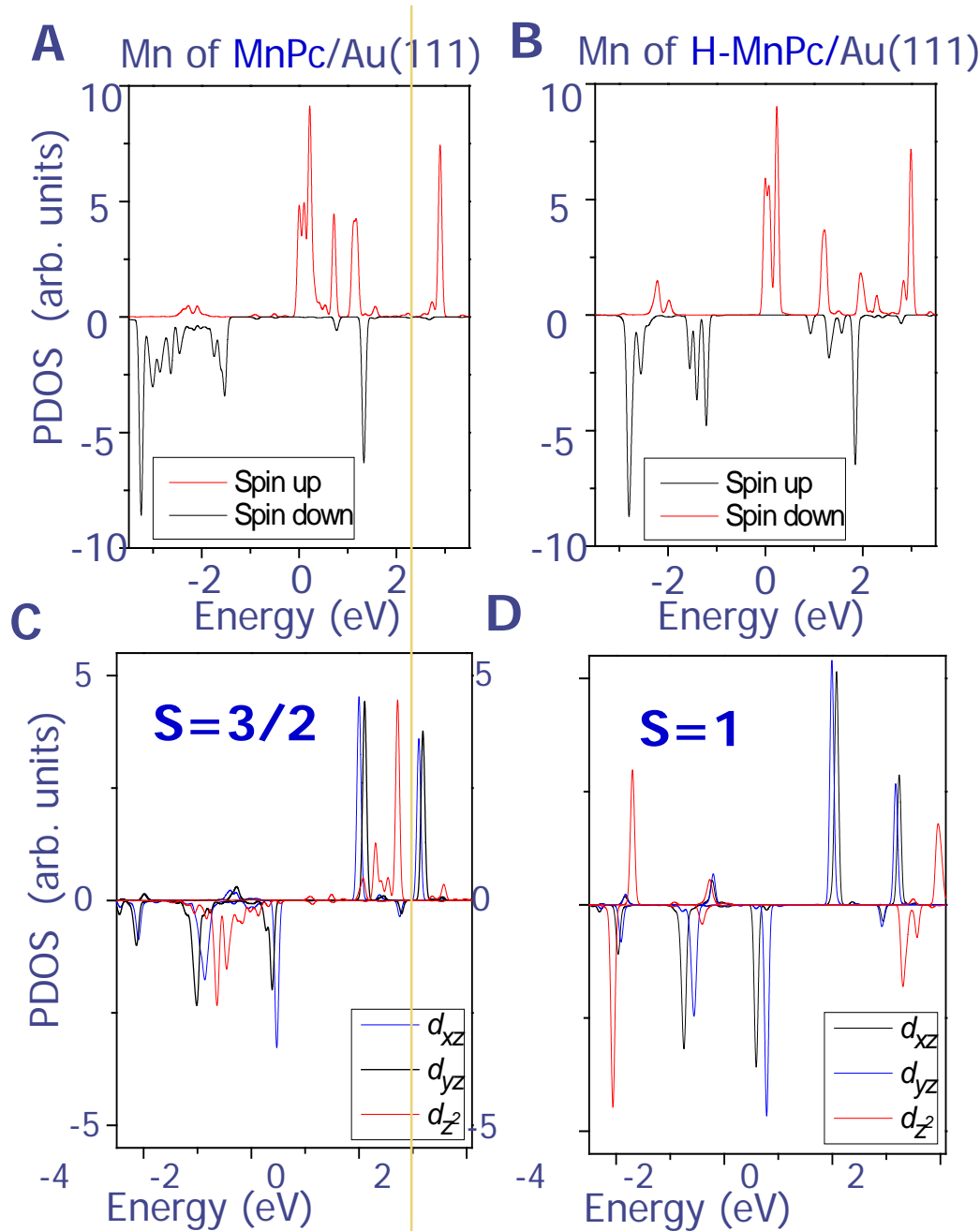


Topographic features of both the MnPc and H-MnPc states can be well reproduced by STM simulations



The separation between the molecular plane of the MnPc and the Au(111) surface increases after the H decoration

# DFT Calculation: Reduction of Molecular Spin



Gaining one single hydrogen atom:

➤ even though the **total number of electrons** of the Mn ion **remains** almost the same in the process

➤ redistribution of charges within 3d orbitals (mainly in  $d_{z^2}$ ) with a **reduction** of the molecular spin state **from S = 3/2 to S = 1**

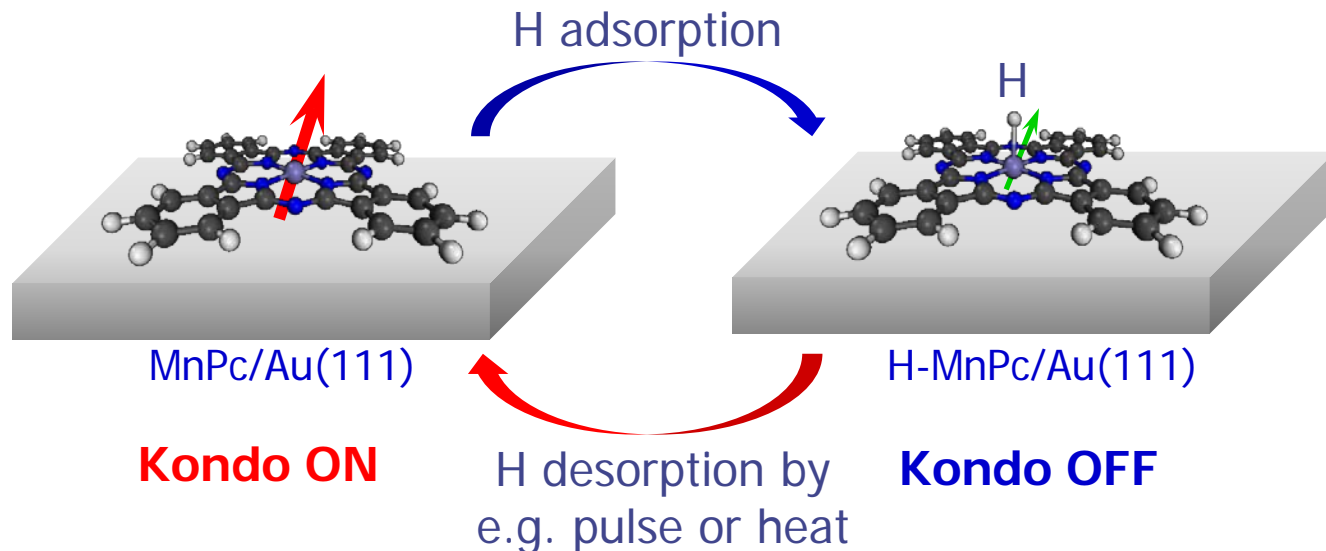
# Quench of Kondo Effect---Switching

## What Can be Done Using the Kondo Switching ?

1. Reduction of spin
  2. Larger distance between Mn and Au
- Both of the two factors lead to a lower interaction  $J$  and a lower Kondo temperature ( $T_K$ ) below our measurement temperature.

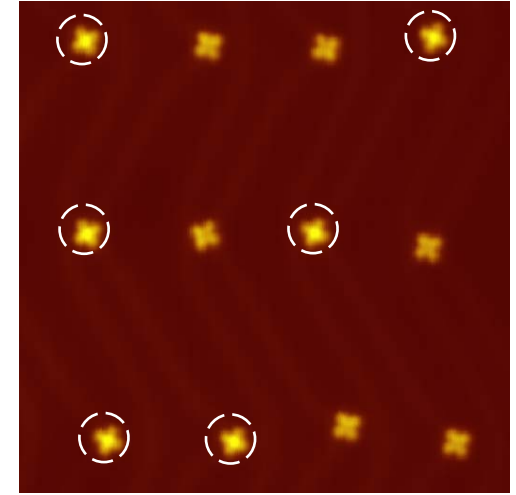
$$T_K \sim e^{-1/\rho J}$$

where  $\rho$  and  $J$  are the density of states at the Fermi energy and the exchange coupling between the spin of the adsorbed molecule and that of the host, respectively

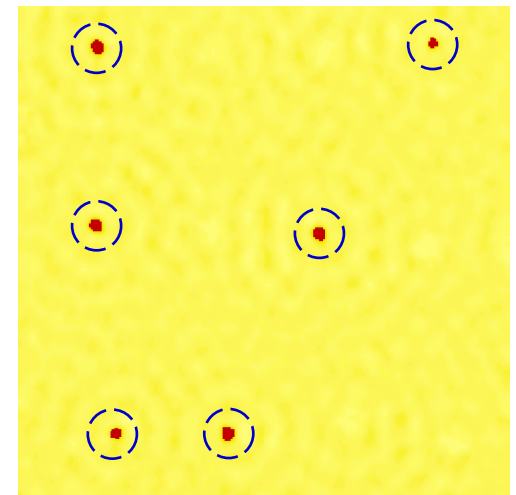
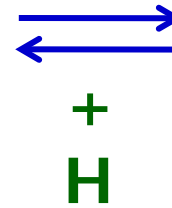
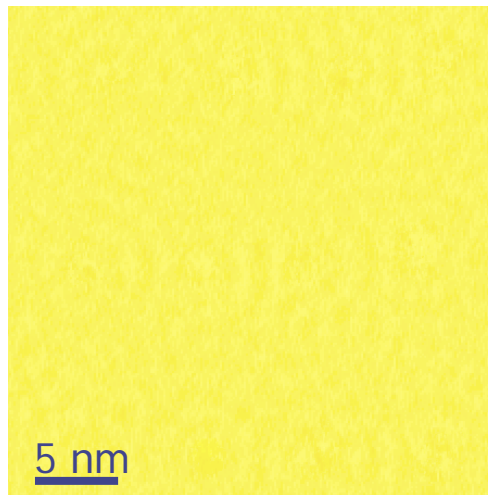


# Implication: Quantum Recording and Processing?

Topography



$dI/dV$  mapping



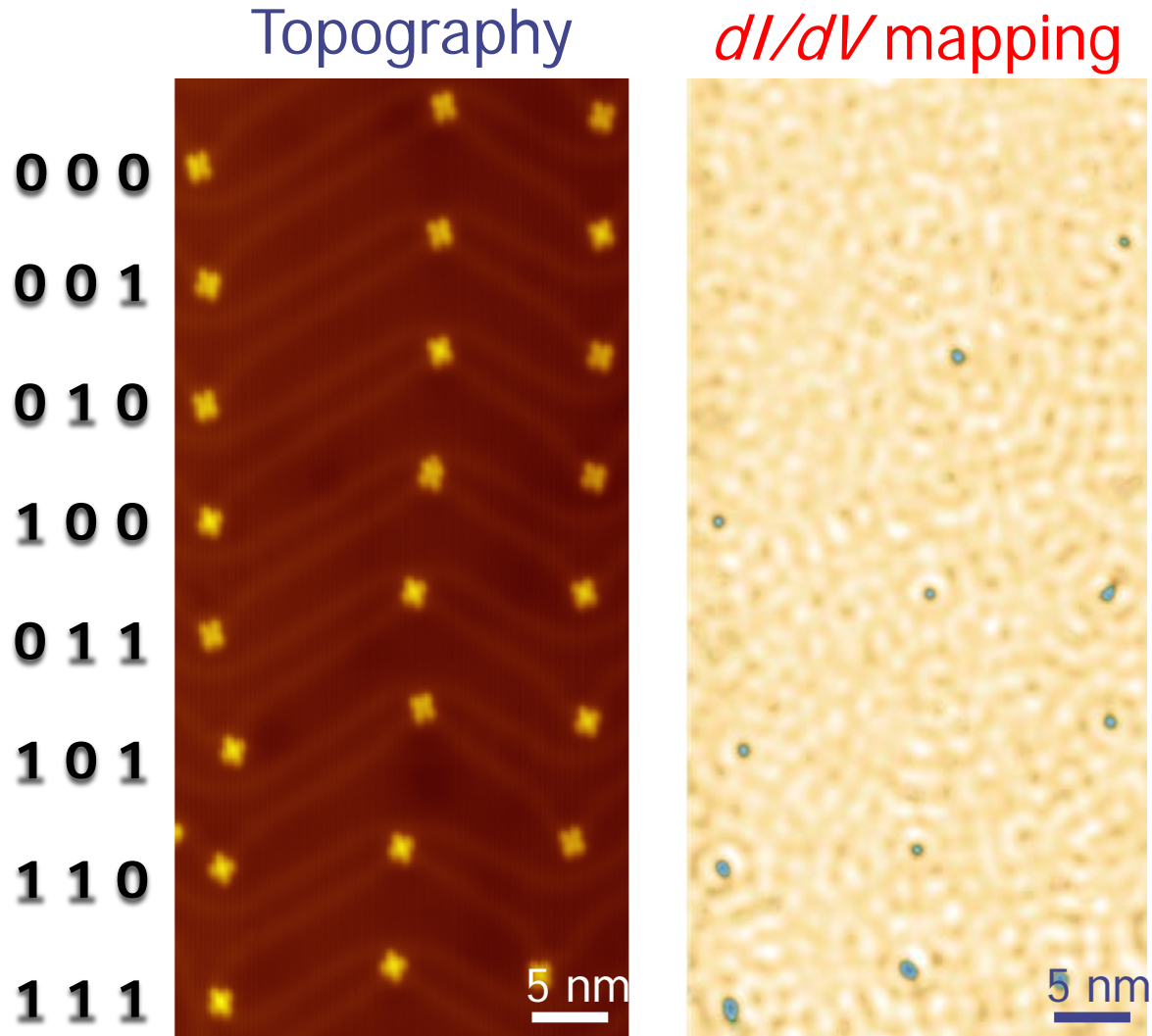
+  
H

Data Density: 6Tb/inch<sup>2</sup>

5 nm

- Kondo On/OFF on this magnetic molecule: a single bit of information recording and storage at the ultimate molecular limit!
- This process can be realized in an ordered molecular array, patterns

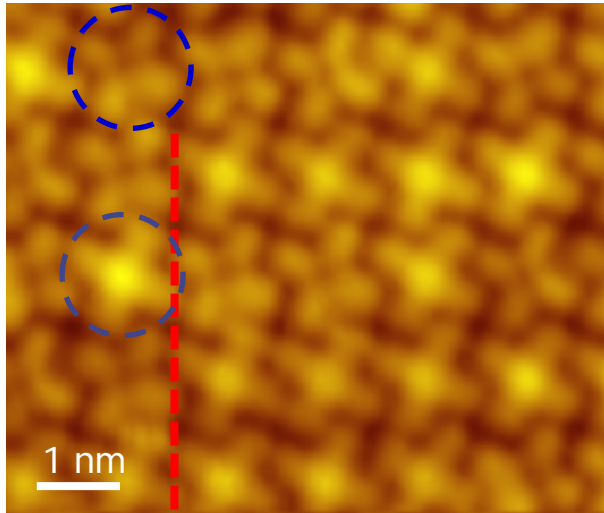
# Reversible Spin OFF-ON Switching in $3 \times 8$ Molecular Arrays by Kondo Effect and Data Recording



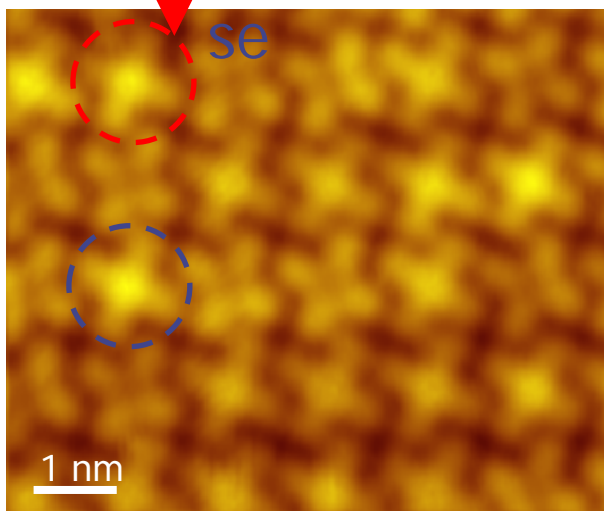
# In Closely-packed Molecular Arrays

## Reversible Spin OFF-ON Switching by Kondo Effect

A

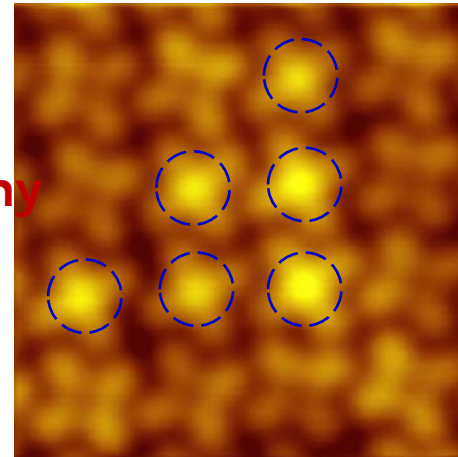


B

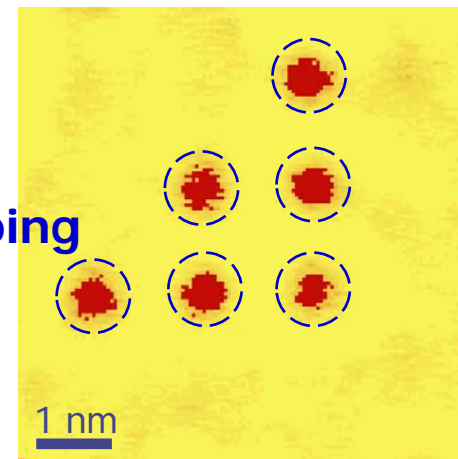


C

Topography



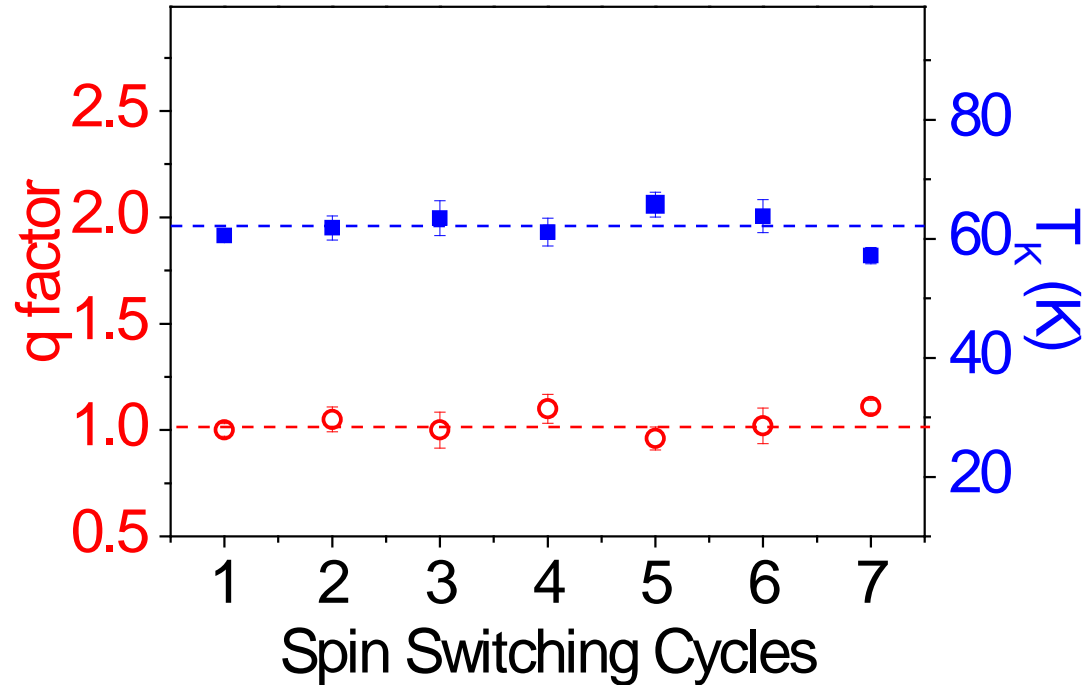
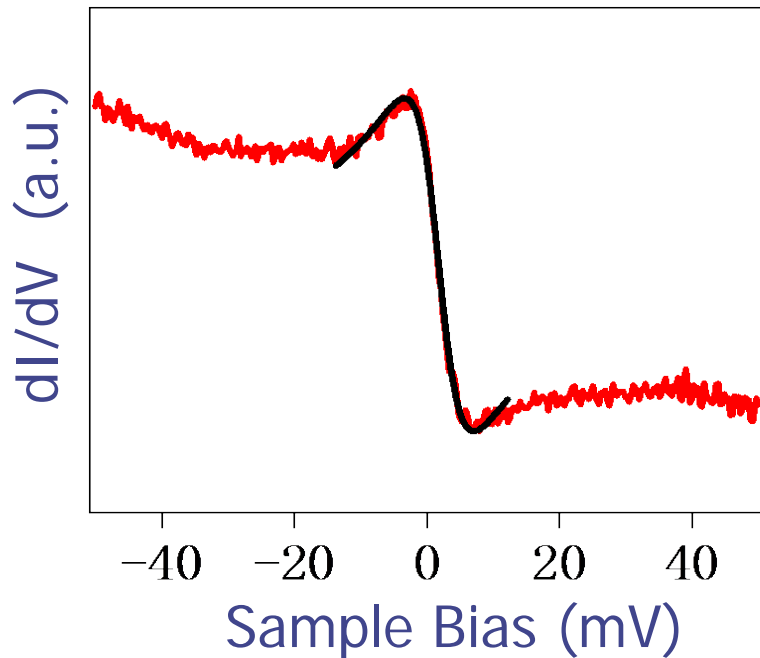
$dI/dV$  mapping



Spacing:  $\sim 1.5$  nm  
Density: 280 Tb/inch<sup>2</sup>



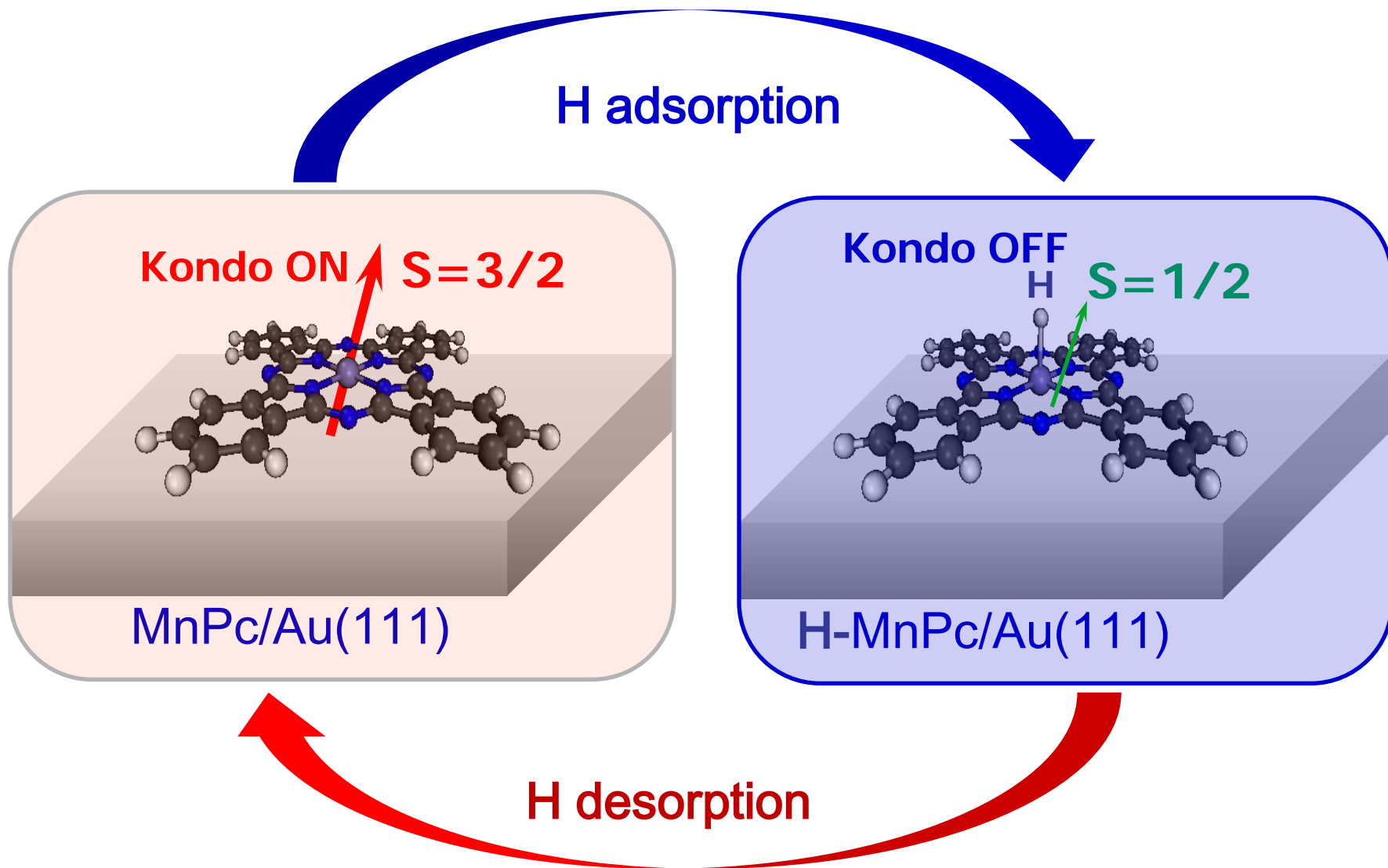
# Robustness of the Spin Switching Process



Fano fitting:  $T_K \sim 61.9 \pm 2.7$  K,  $q \sim -1.03 \pm 0.05$

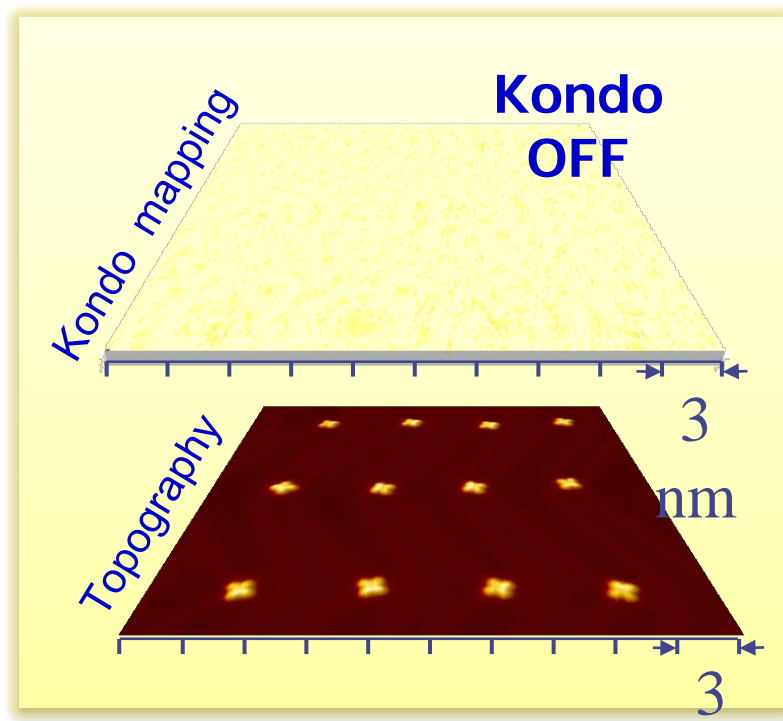
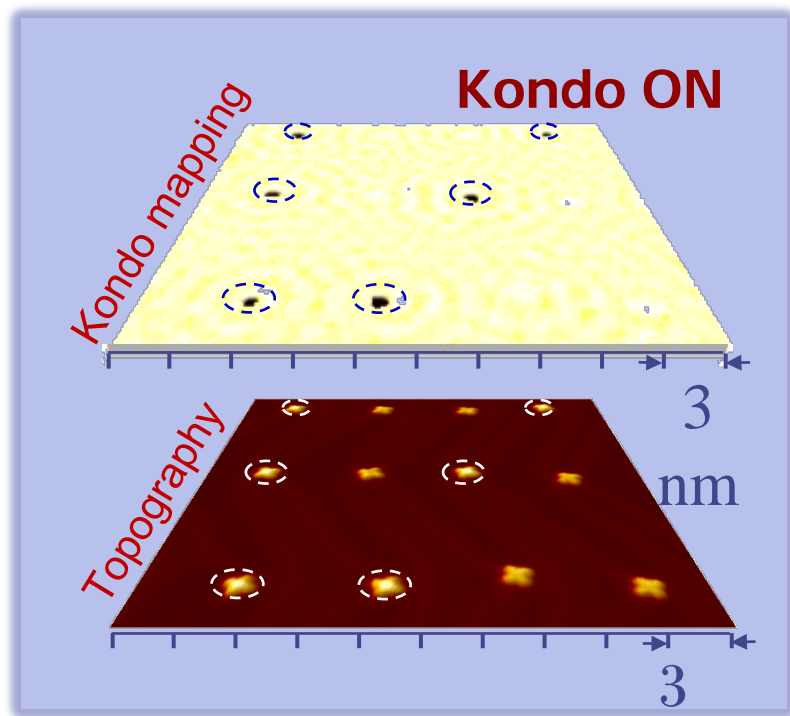
Such molecular spin switching can be consistently achieved **back-and-forth for many times** with no observable change of the Kondo features-

# Reversible Spin Control of Individual Magnetic Molecule by Hydrogen Atom Adsorption



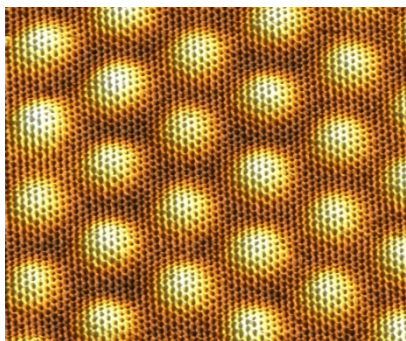
# Reversible Spin Control of Individual Magnetic Molecule by Hydrogen Atom Adsorption

H adsorption

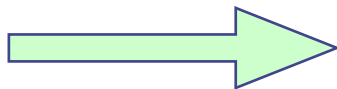


H desorption

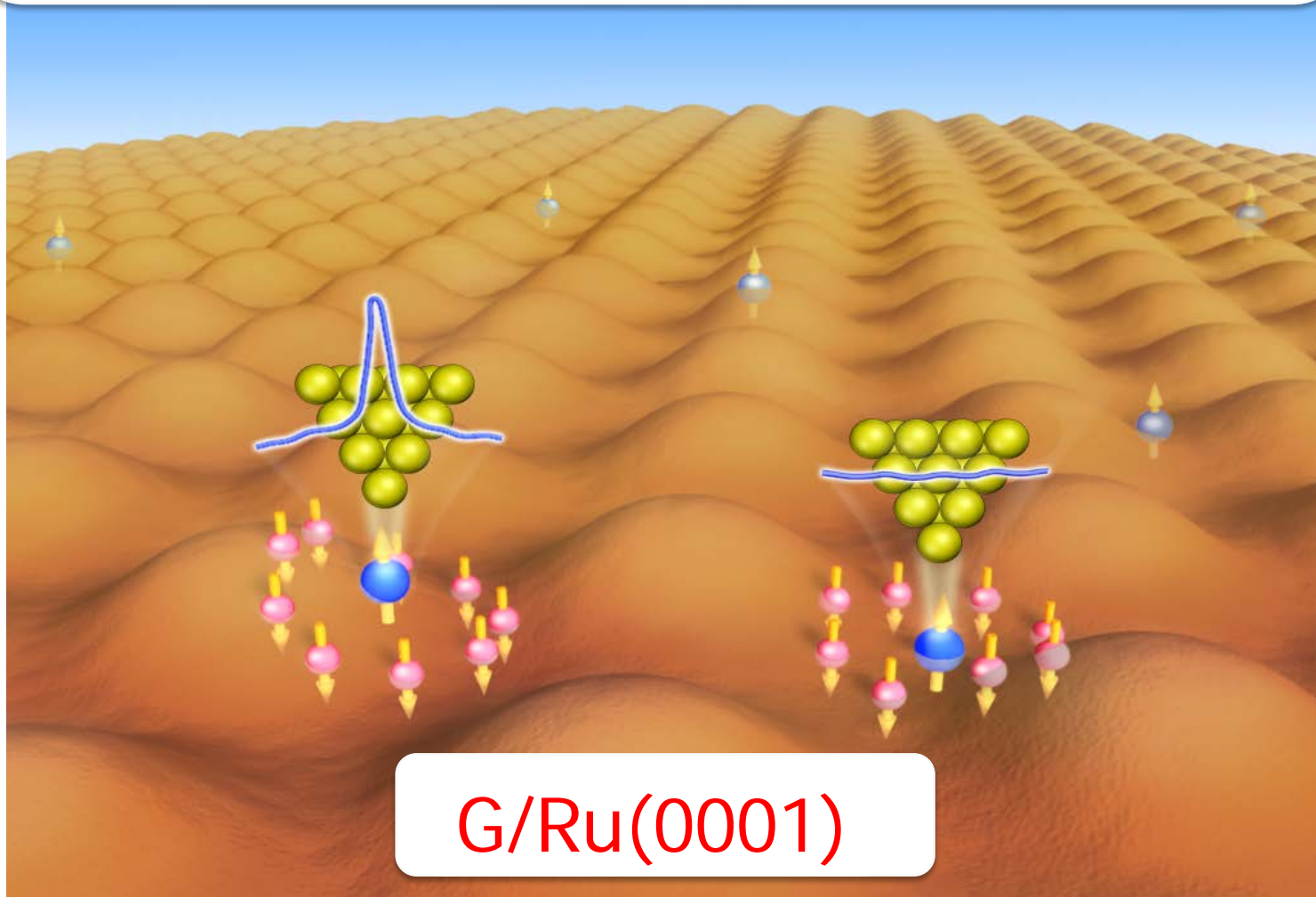
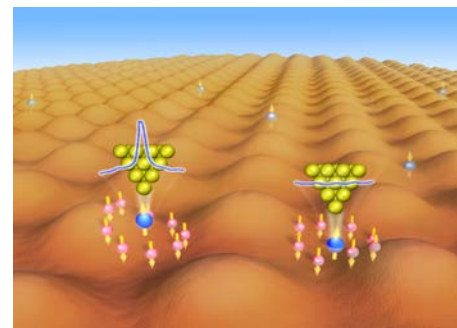




Co 原子低温沉积



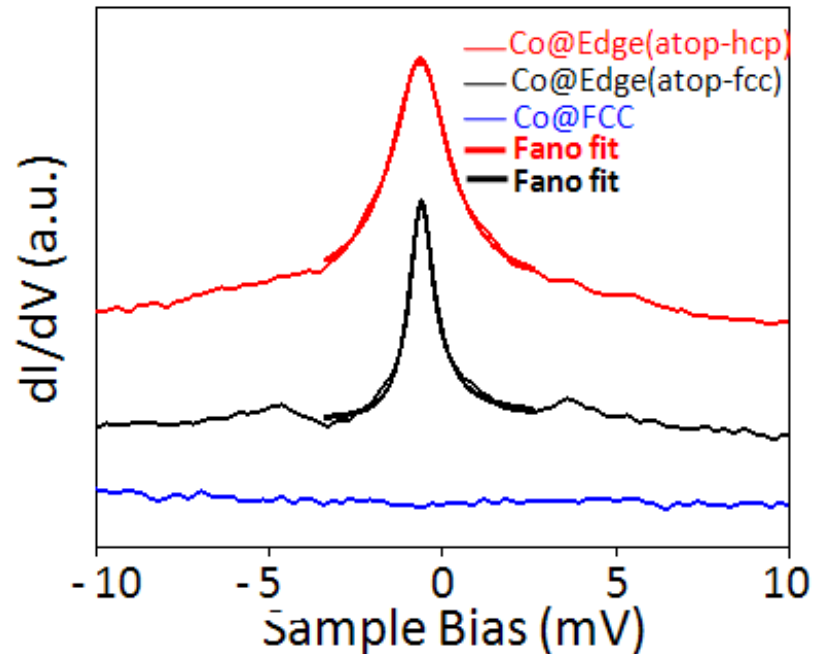
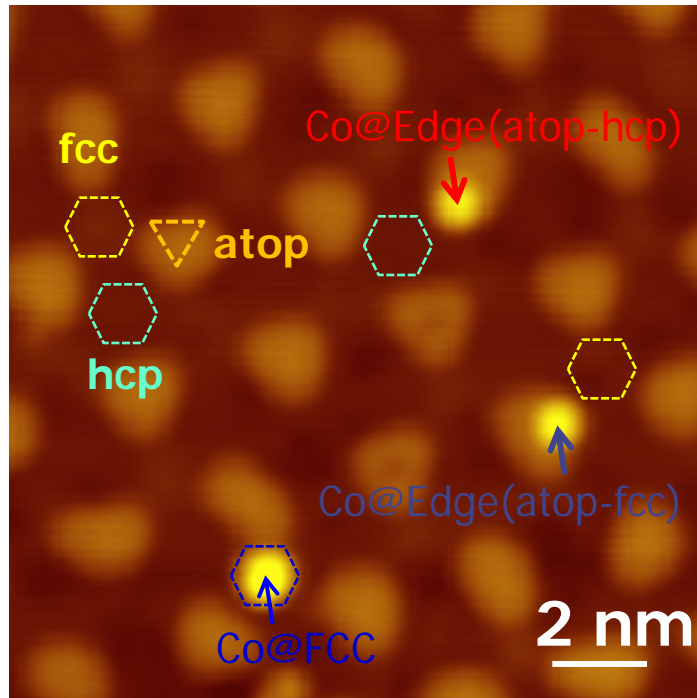
mK-矢量磁场 STM



G/Ru(0001)

# Co Atoms at Different Sites of G/Ru: STM & STS

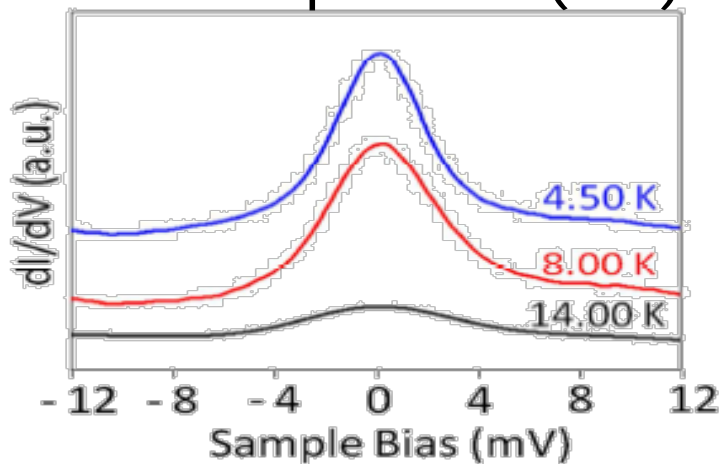
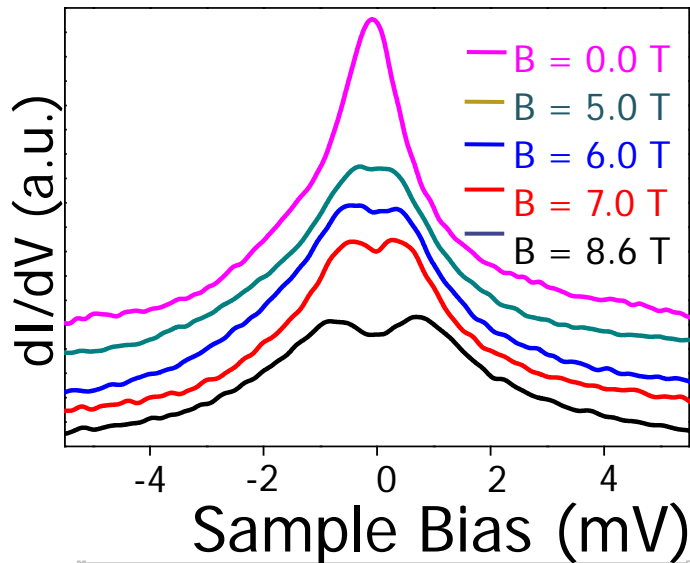
Co atoms are deposited onto G/Ru(0001) at  $\sim 20$  K.



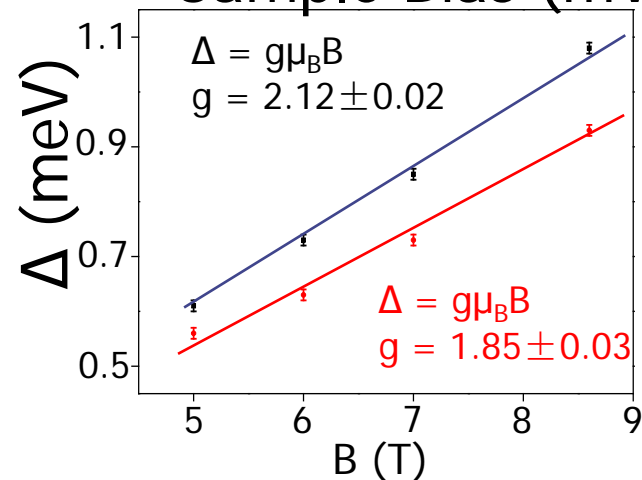
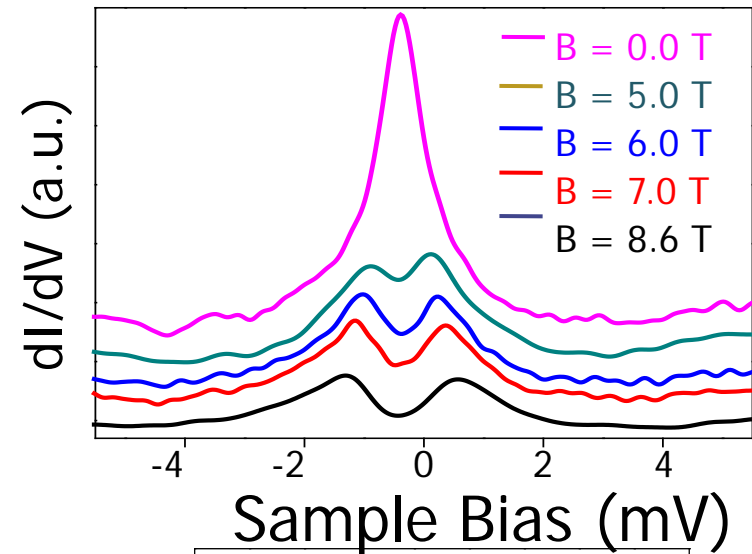
- Three Co adsorption regions: hcp, fcc, and edge of atop regions (>50%)
- Co@edge can be divided into two different kinds of species: facing to the fcc side (Co@edge(atop-fcc)) or to the hcp side (Co@edge(atop-hcp)).
- Only Co adatoms at edge sites show Kondo peaks around  $E_F$ ;
- $T_K$  of Co@edge(atop-hcp) and Co@edge(atop-fcc) is  $12.10 \pm 0.10$  K and  $5.39 \pm 0.06$  K by fitting the Fano formula, respectively.

# Kondo Resonance at Different Magnetic Fields & T

## Co@Edge(atop-hcp)



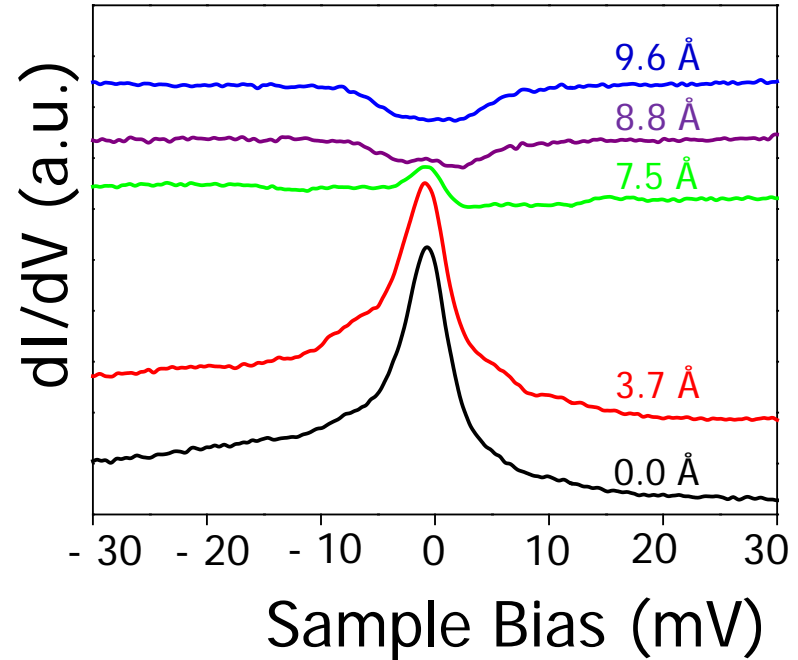
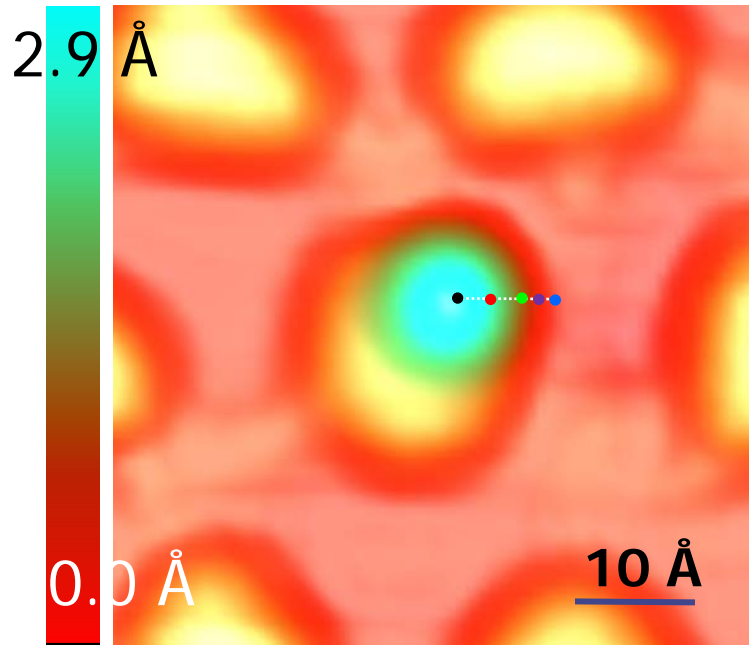
## Co@Edge(atop-fcc)



- The peaks around Fermi level start to split under external magnetic field, further confirm that the peaks are Kondo resonance.

# Spatial Distribution of Kondo Resonance

Co@edge(atop-hcp)

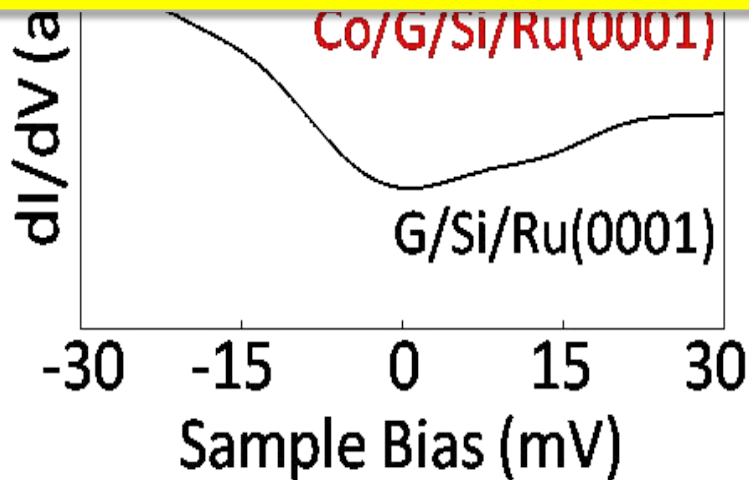


- ◆ The resonance peak disappears up to a distance of  $\sim 10$  Å away from the center of Co atom.

# dl/dV Spectra of Co Adatom on G/Si/Ru(0001)



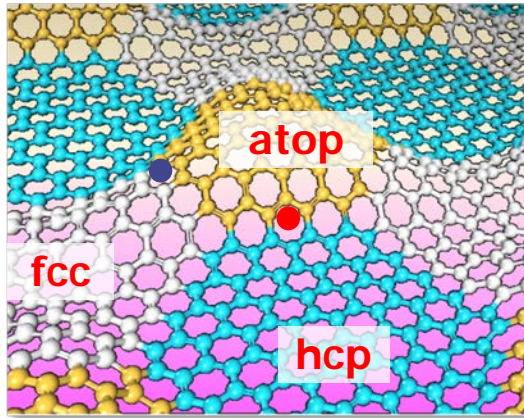
- ◆ Si插层削弱了石墨烯与Ru的相互作用，单层Si插层后的石墨烯接近于自由石墨烯；
- ◆ 磁性原子Co的Kondo效应消失。



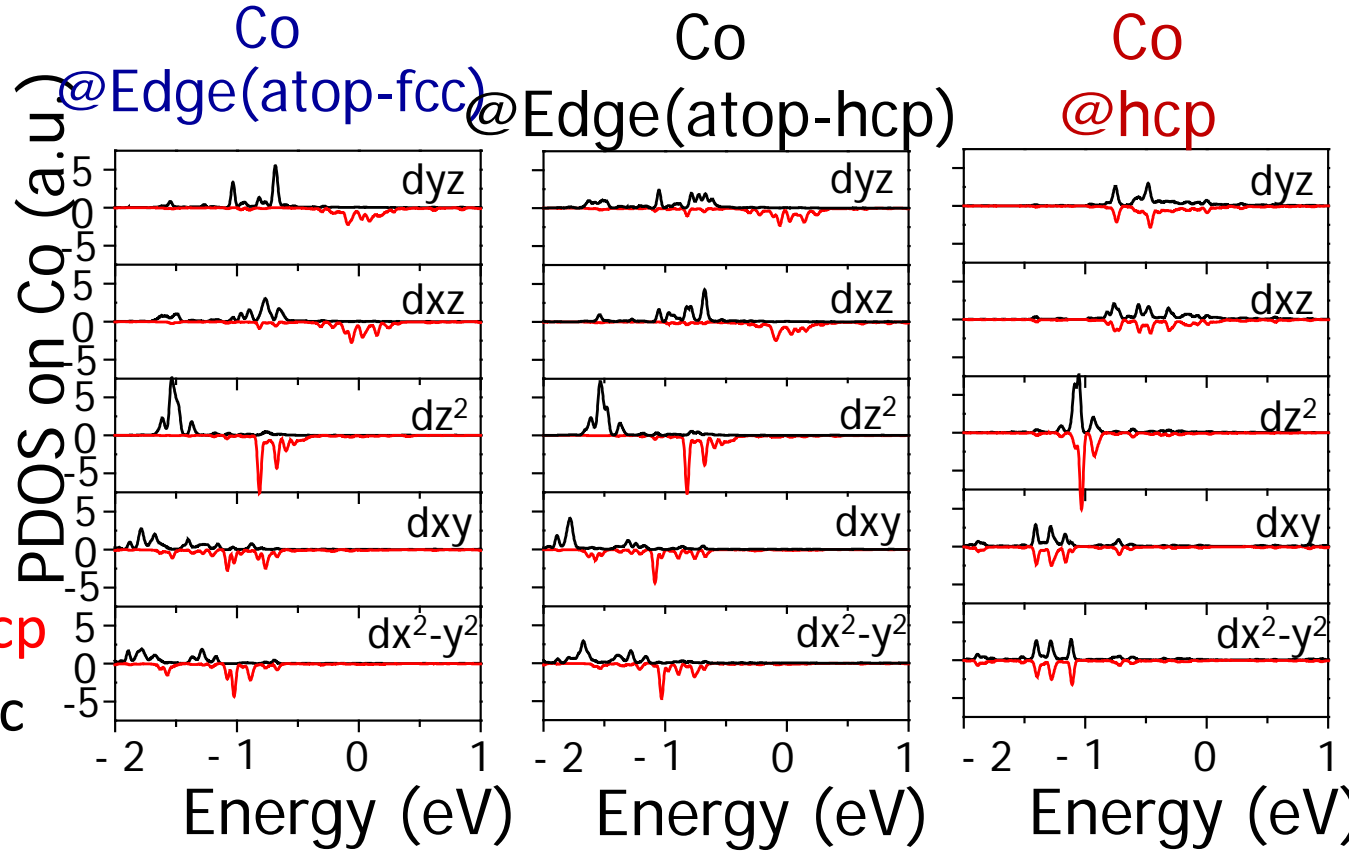
- The intercalation of Si weakens the interaction between graphene and substrate.
- It makes the DOS at the  $E_F$  vanish as in freestanding graphene, thus quenching the Kondo effect.



# Electronic Structures of Co Adatoms



- Co@edge-atop/hcp
- Co@edge-atop/fcc



➤ Co@Edge(atop-fcc):  $1.0 \mu_B$ ;

Co@Edge(atop-hcp):  $1.0 \mu_B$ ;

➤ Co@fcc:  $0.6 \mu_B$ ;

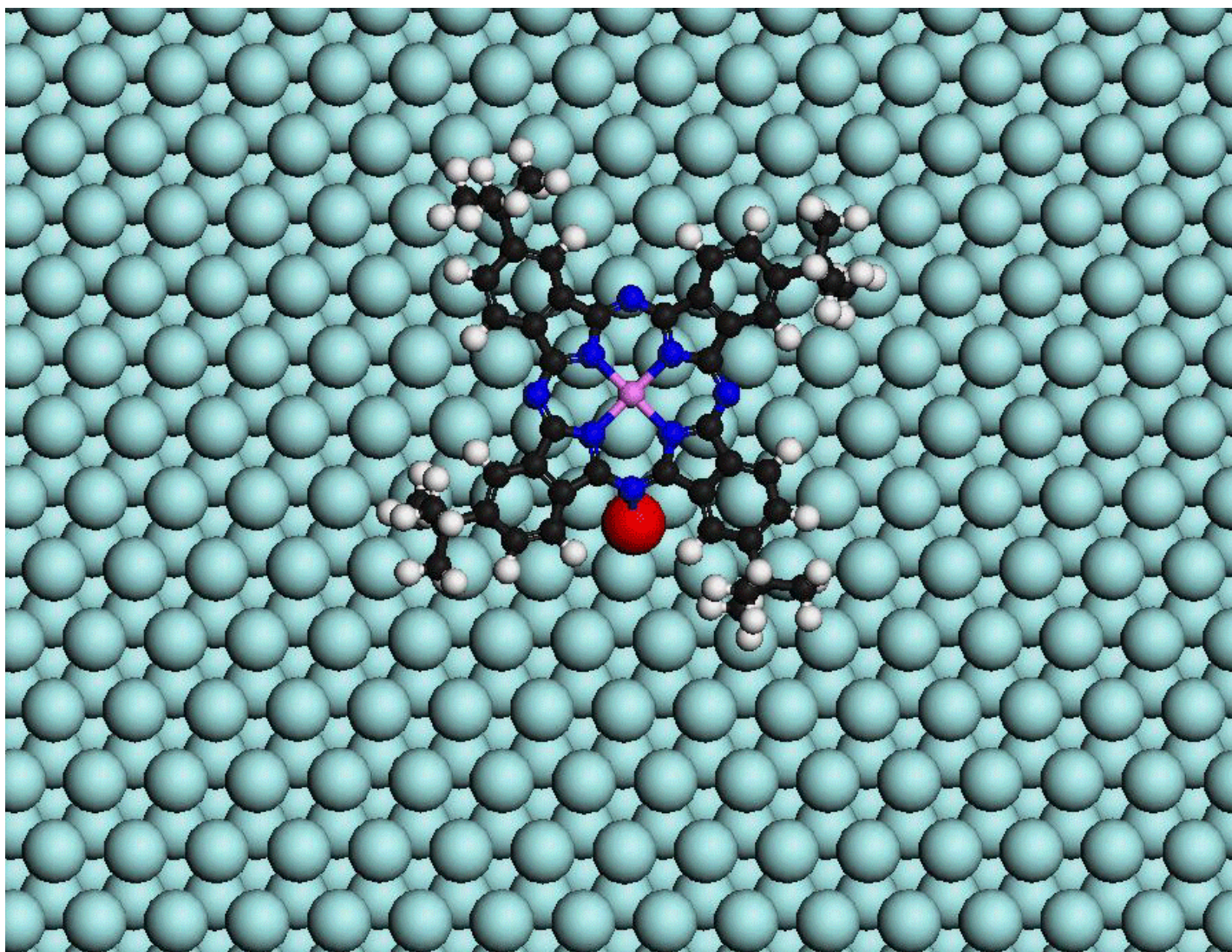
Co@hcp:  $0.0 \mu_B$ .

# 单层石墨烯上钴磁性原子近藤效应的调制

	atop	edges-atop	
		/hcp	/fcc
d/nm	0.51	0.46	0.47
$E_b$ /eV	4.20	4.30	4.28
$\mu/\mu_B$	1.0	1.0	1.0
LDOS/a.u.	0.1	0.8	0.7
Tc/K	no	$12.10 \pm 0.10$	$5.39 \pm 0.06$

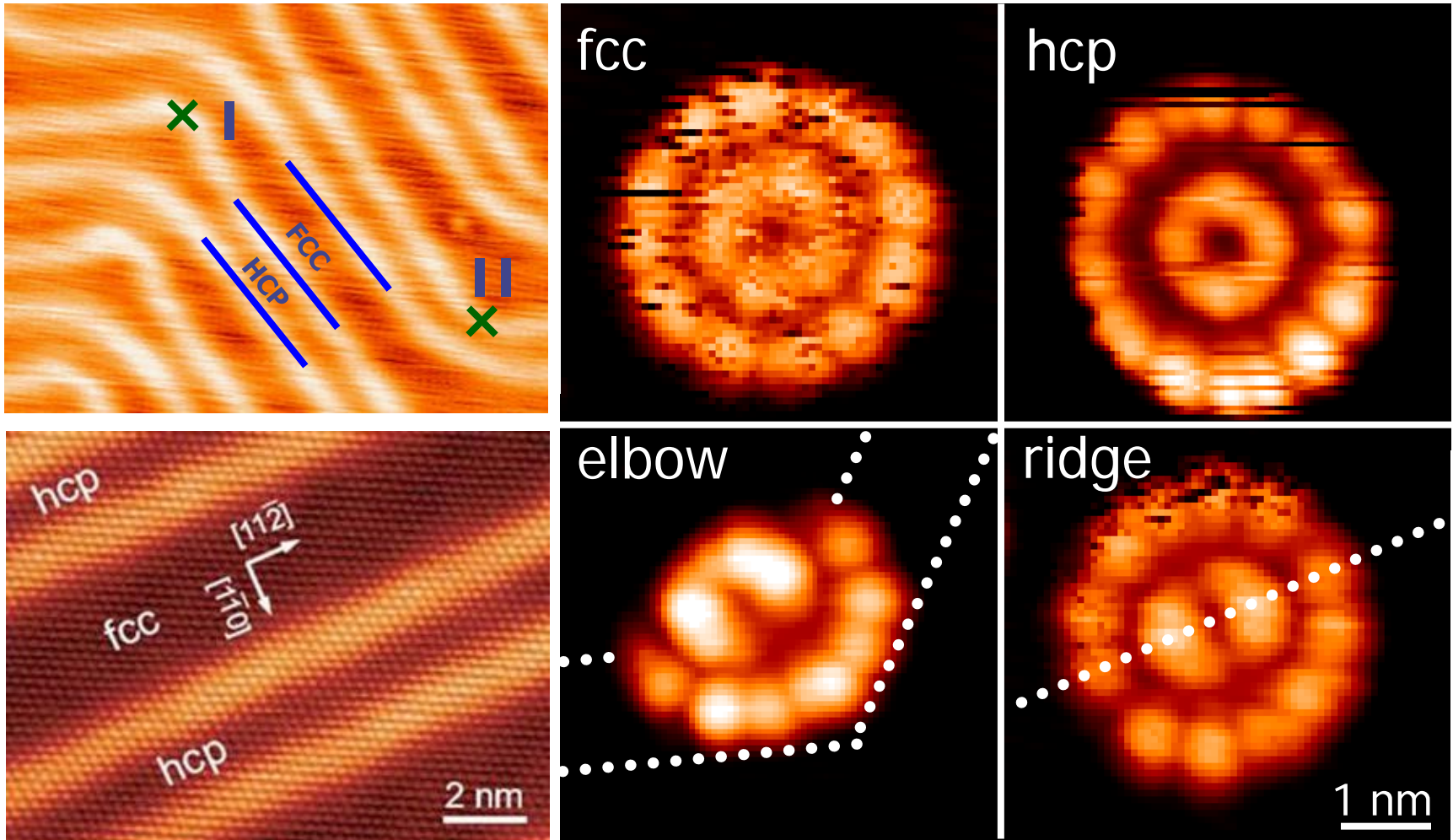
- 通过 G/Ru(0001) 的周期性 moiré 结构来调制石墨烯电子态密度、单个 Co 磁性原子的自旋、以及与钴原子的交换耦合作用能等。atop 边界位置上吸附的 Co 原子具有较大磁矩和适合的态密度，在低温下 (4.2 K) 观测到近藤效应。
- 这是在石墨烯上观察到磁性原子近藤效应的第一个实验结果，并通过基底对其近藤温度实现了调控。

# Conclusions and Outlook



◆ *Construction of an Anchored and Off-centered Single Molecular Rotor Array*

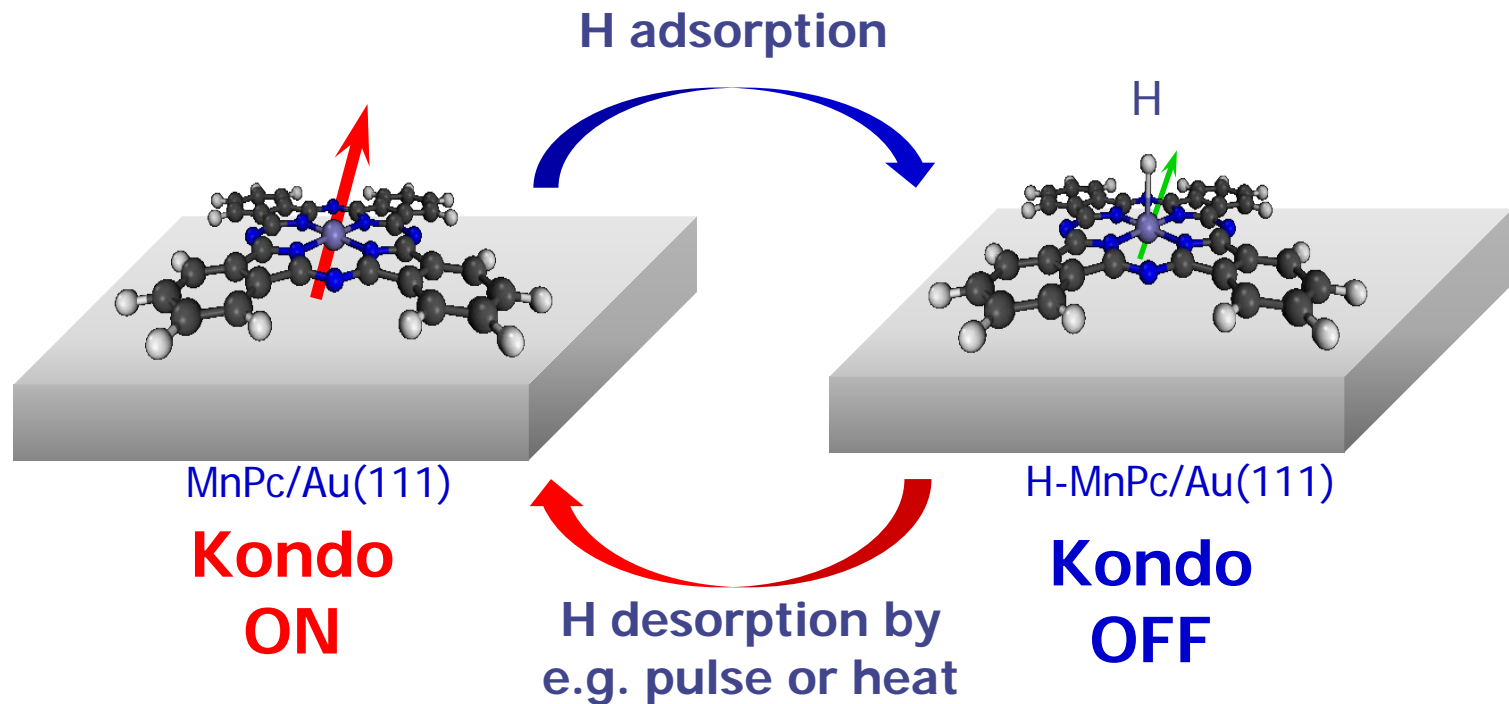
# Conclusions and Outlook



◆ *Manipulating Single Molecular Rotors using Different Locations*

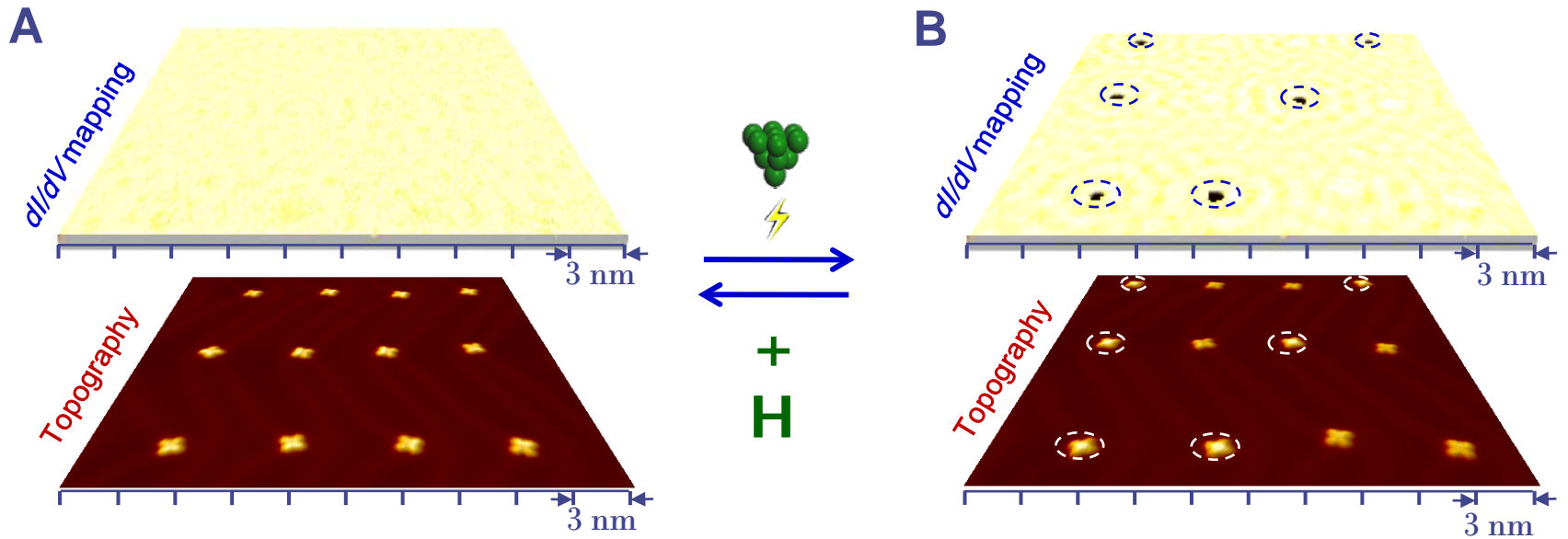
# Conclusion and Outlook

- ◆ Reversible single spin control has been demonstrated on individual molecules



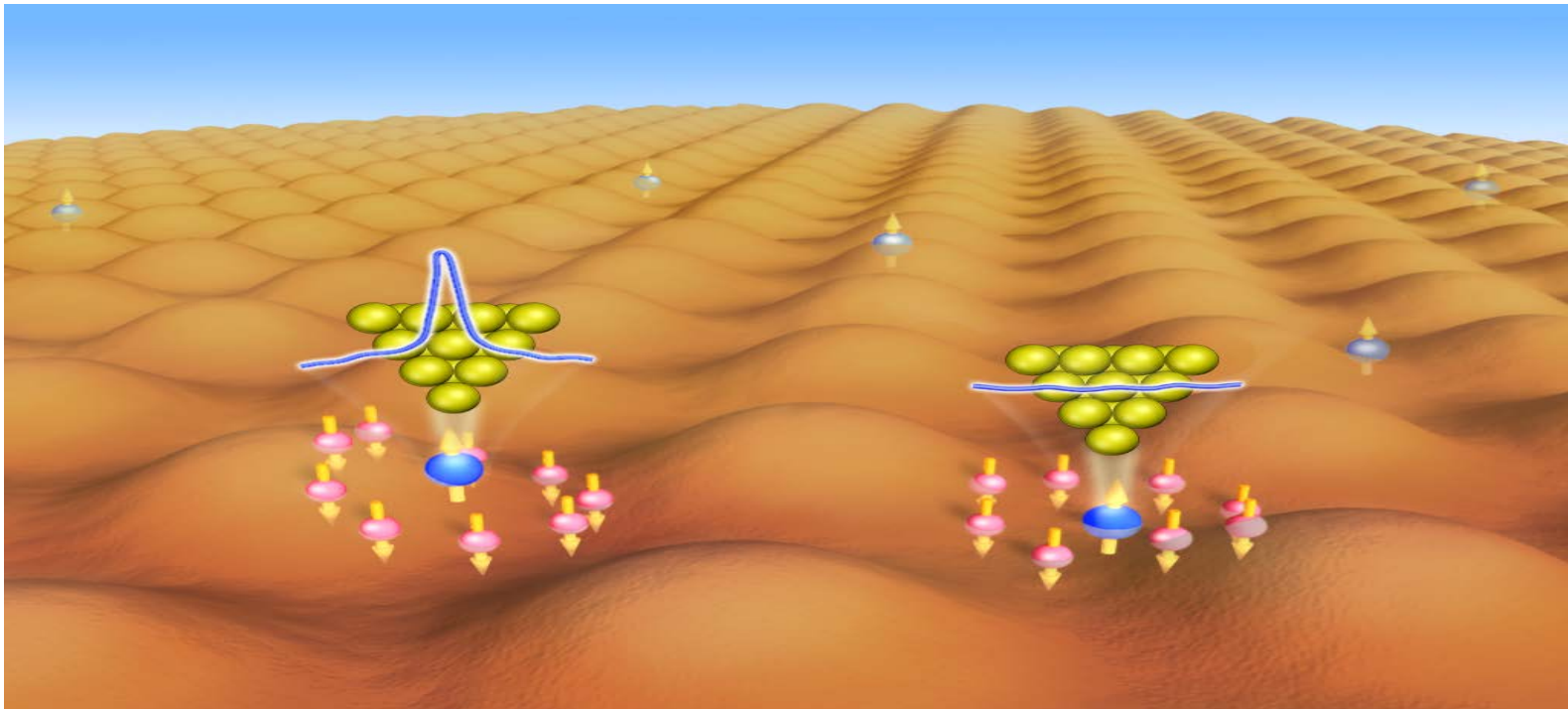
# Conclusion and Outlook

- ◆ Potential application in quantum data recording or processing.



# Conclusions and Outlook

- ◆ We observed the **site-specific Kondo effect** of Co adatoms on a rippled graphene at a Ru(0001) surface.
- ◆ DFT calculations show that **the delicate balance among the local spin, the LDOS at the Fermi energy, and their coupling** are crucial factors in generating the Kondo effect for magnetic impurities on graphene.



# Exploration of Novel 2D Atomic Crystals

◆ **Graphene**

◆ **Silicene**

◆ **Hafnene**

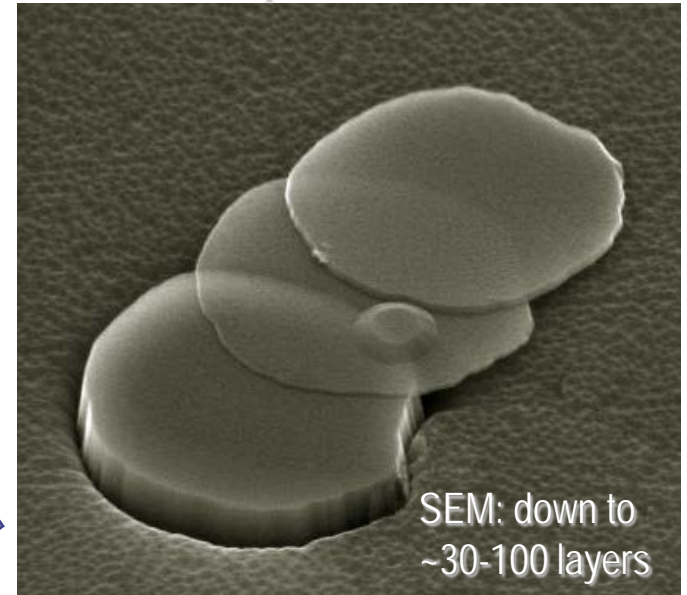
◆ **...??? and beyond**



# Starting with graphite



Split into increasingly thinner “pancakes”



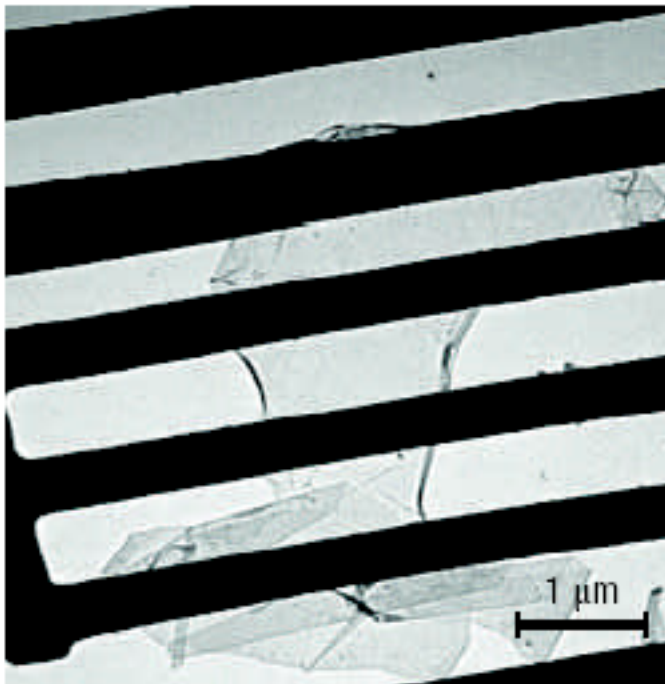
one atomic plane deposited on Si wafer



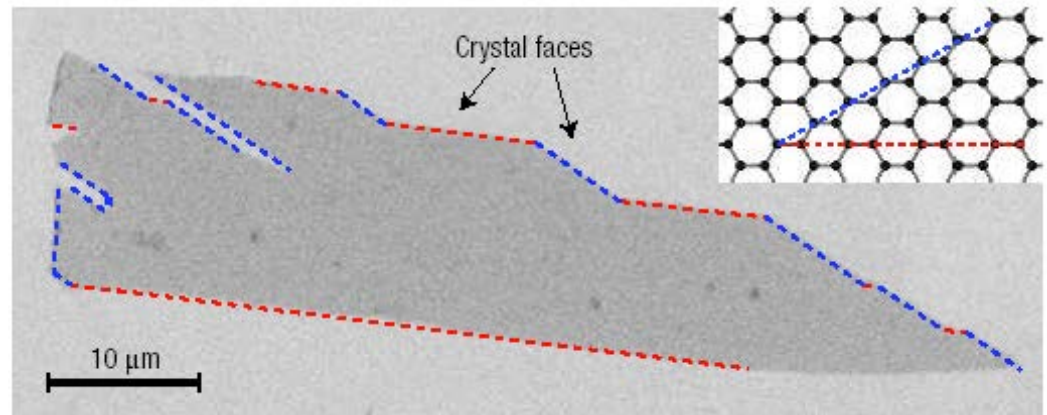
Split off  
a single layer  
called GRAPHENE

Geim *et al.*, Manchester, *Science* 2004

# *Fabrication Techniques: Peel Off* (Geim's Group)



A TEM image of a graphene sheet suspended on a micrometer-size metallic scaffold



Scanning electron microscopy of a relatively large graphene

*Science* **36**, 666 (2004).

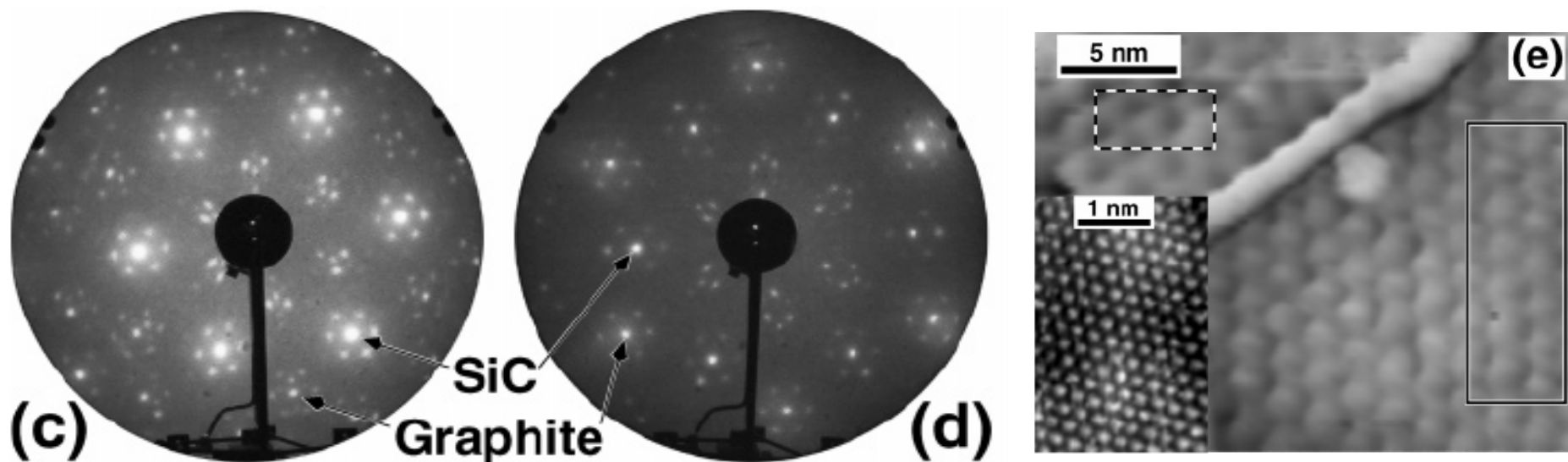
*PNAS* **102**, 10451 (2005).

*Nature Materials*, **6**, 183 (2007)

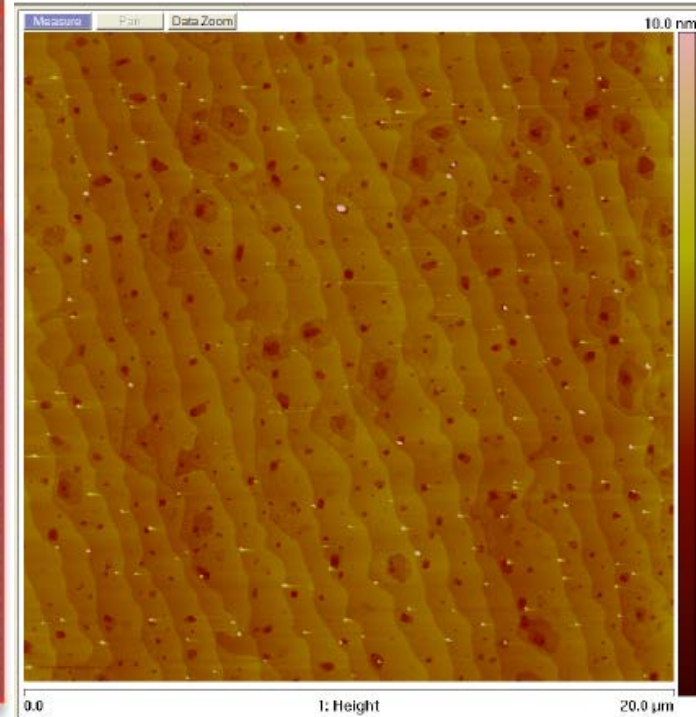
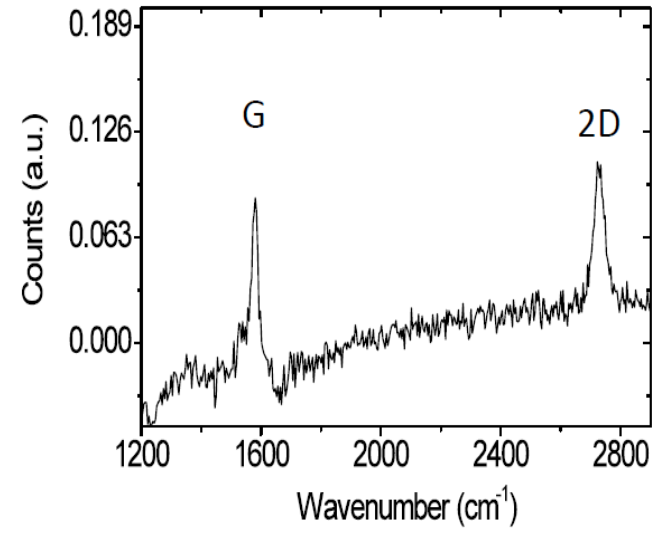
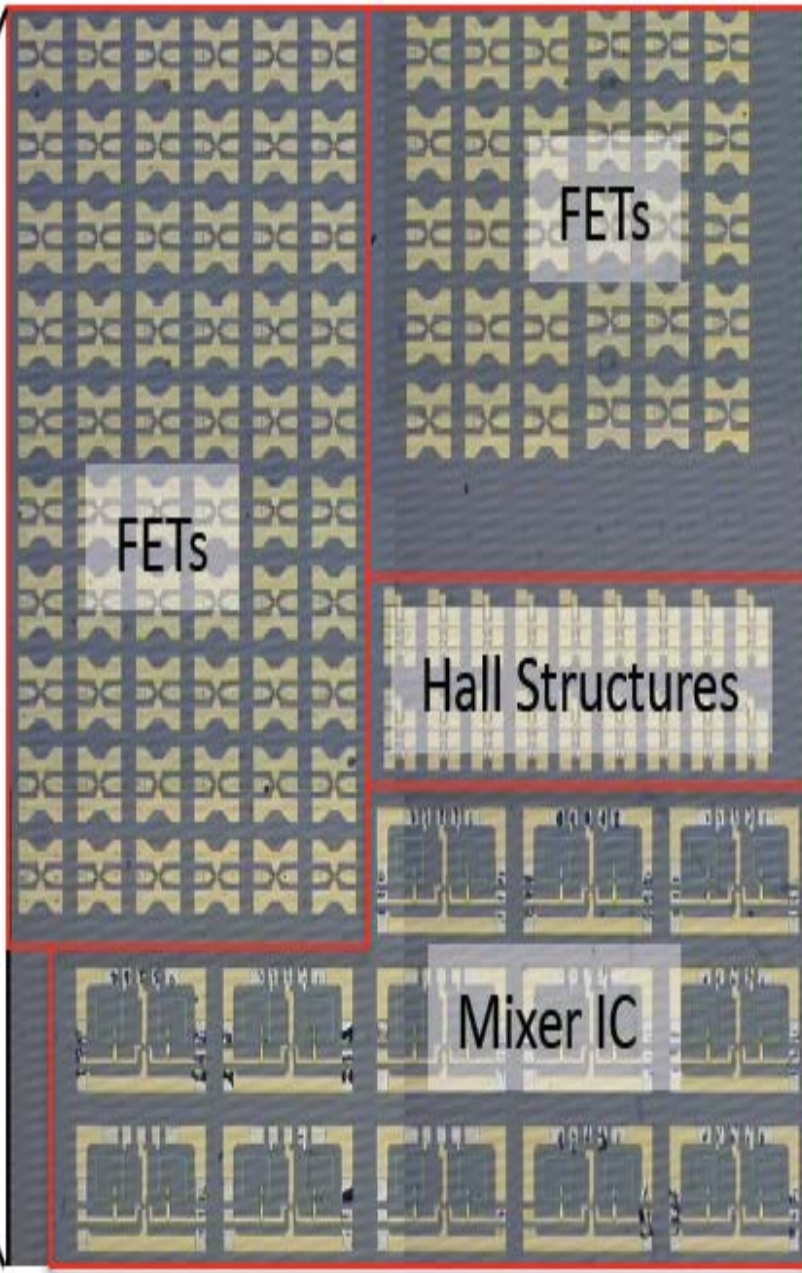
*Nature*, **446**, 60 (2007)

## *Fabrication Technique: SiC*

Georgia Institute of Technology, de Heer Group



J. Phys. Chem. B, **108**,19912(2004); *Science* **312**, 1191 (2006)



# Operation of Graphene Transistors at Gigahertz Frequencies

Yu-Ming Lin,\* Keith A. Jenkins, Alberto Valdes-Garcia, Joshua P. Small, Damon B. Farmer, and Phaedon Avouris

IBM T.J. Watson Research Center, Yorktown Heights, New York 10598

Received November 3, 2008; Revised Manuscript Received December 9, 2008

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2009  
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422-426

# 100-GHz Transistors from Wafer-Scale Epitaxial Graphene

Y.-M. Lin,\* C. Dimitrakopoulos, K. A. Jenkins, D. B. Farmer, H.-Y. Chiu, A. Grill, Ph. Avouris\*

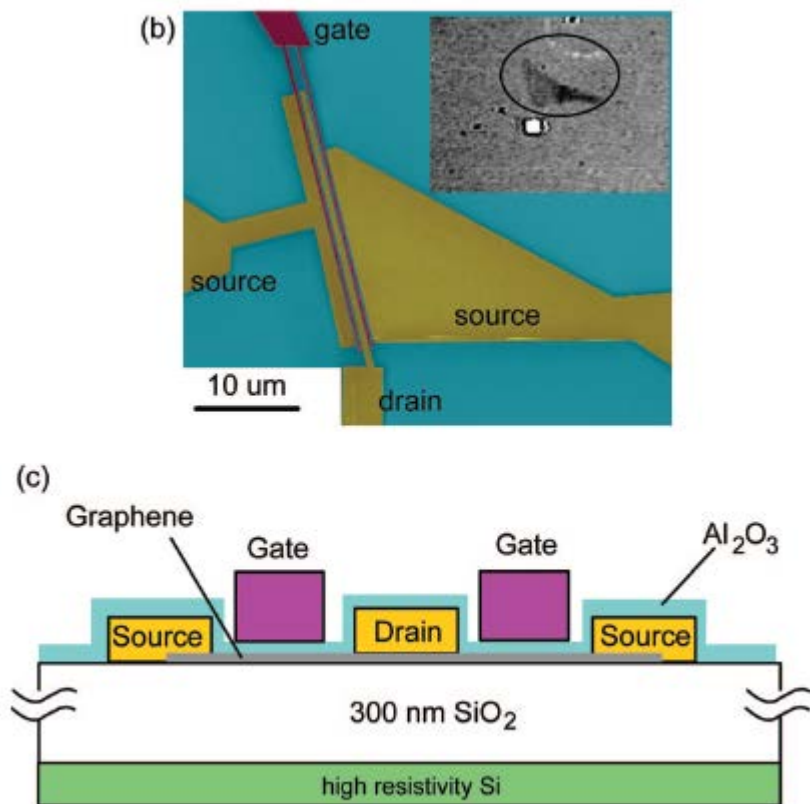


Figure 1. (a) Optical image of the device layout with ground-

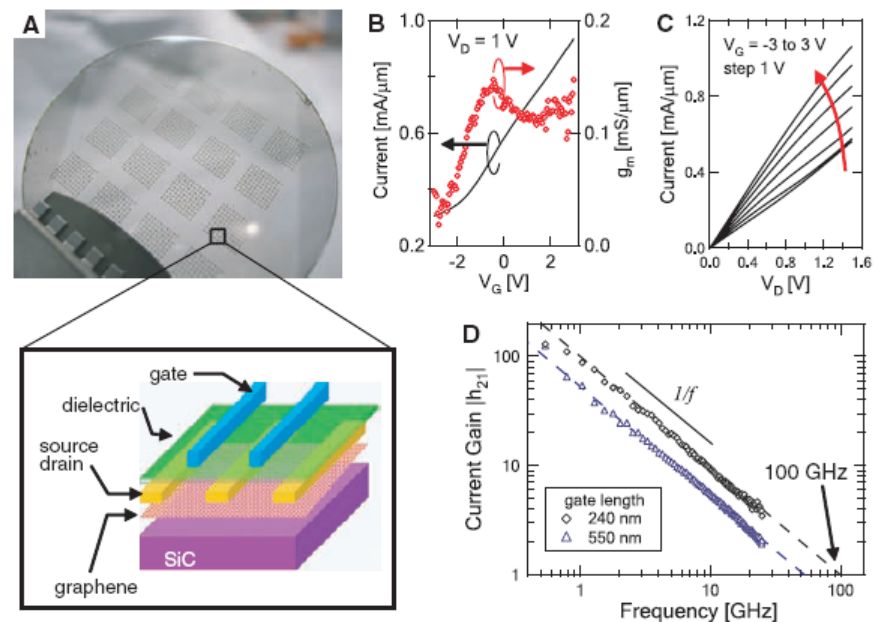
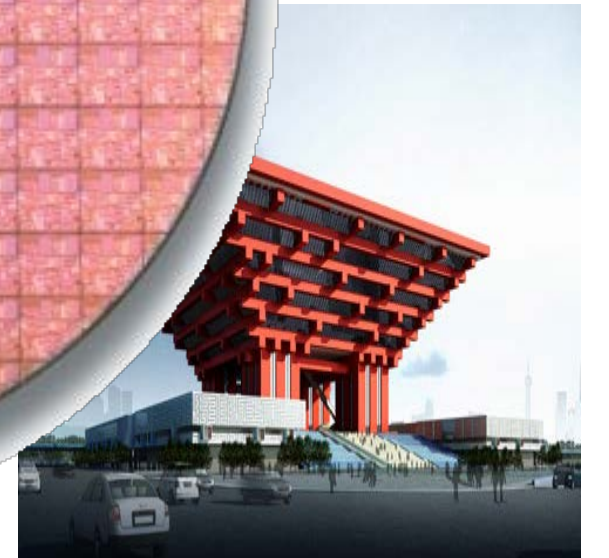
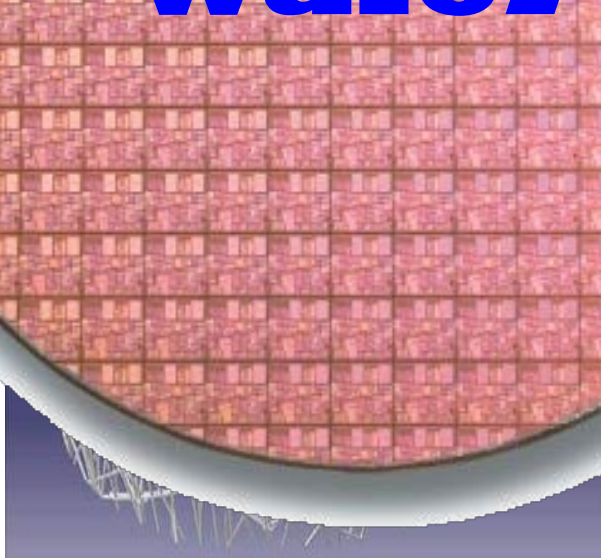
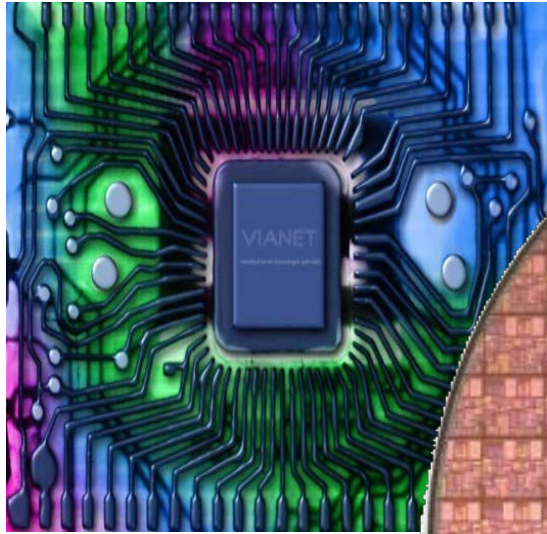


Fig. 1. (A) Image of devices fabricated on a 2-inch graphene wafer and schematic cross-sectional view of a top-gated graphene FET. (B) The drain current,  $I_D$ , of a graphene FET (gate length  $L_G = 240$  nm) as a function of gate voltage at drain bias of 1 V with the source electrode grounded. The device transconductance,  $g_m$ , is shown on the right axis. (C) The drain current as a function of  $V_D$  of a graphene FET ( $L_G = 240$  nm) for various gate voltages. (D) Measured small-signal current gain  $|h_{21}|$  as a function of frequency  $f$  for a 240-nm-gate (◇) and a 550-nm-gate (△) graphene FET at  $V_D = 2.5$  V. Cutoff frequencies,  $f_c$ , were 53 and 100 GHz for the 550-nm and 240-nm devices, respectively.

# **Main Challenges about Graphene Applications in Future Electronics**

- **Fabrication of large-scale, highly-ordered, single crystalline graphene layers of “High Quality”.**
- **Compatible to Si Processing Technology.**
- **Without Transfer Technique.**

# Similar to the Single Crystal Si Based Science, and Industrial Applications

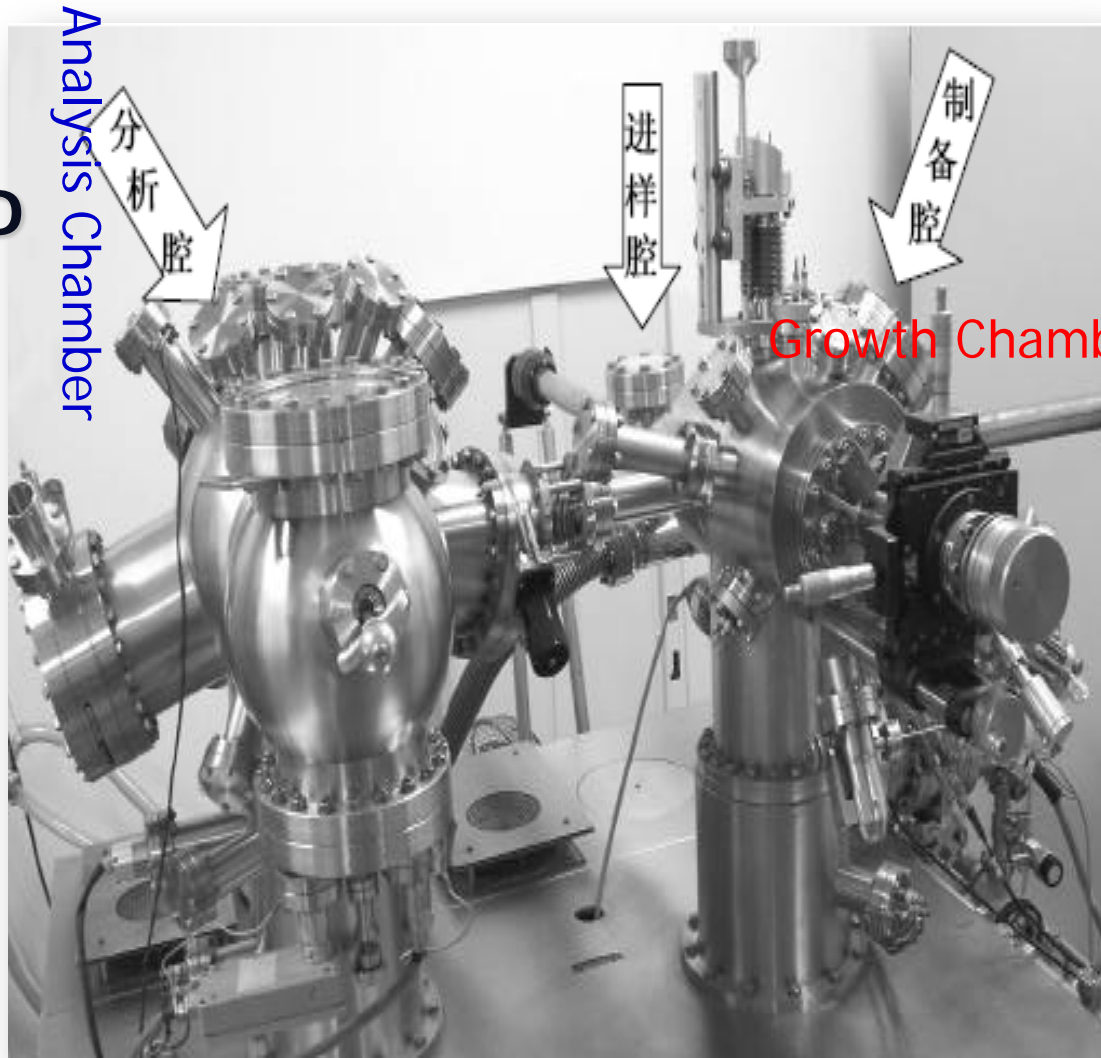


*Highly Ordered, Millimeter-scale,  
Single Crystalline Graphene Monolayer Epitaxially Grown  
on Ru (0001)*

Y. Pan/H.J. Gao *et al.*, Adv. Mater. 21, 2777(2009)



# *Growth System with In situ Analysis Techniques*



- LEED
- AES
- STM

Analysis Chamber

分析腔

进样腔

制备腔

Growth Chamber

- Carbon Source
- Ar+ Ion gun
- Sample Heater
- Evaporator

**Ru, Pt, Ni, Cu, Ir metal crystals have been used**

# Formation of graphene on Ru(0001) surface\*

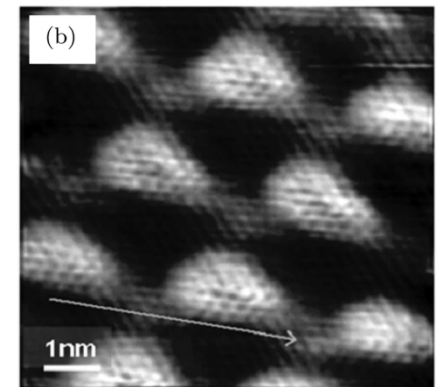
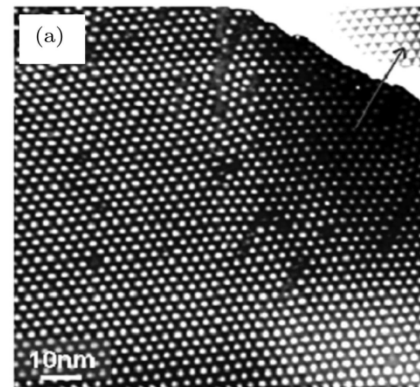
Pan Yi(潘毅), Shi Dong-Xia(时东霞), and Gao Hong-Jun(高鸿钧)<sup>†</sup>

*Nanoscale Physics and Devices Laboratory, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China*

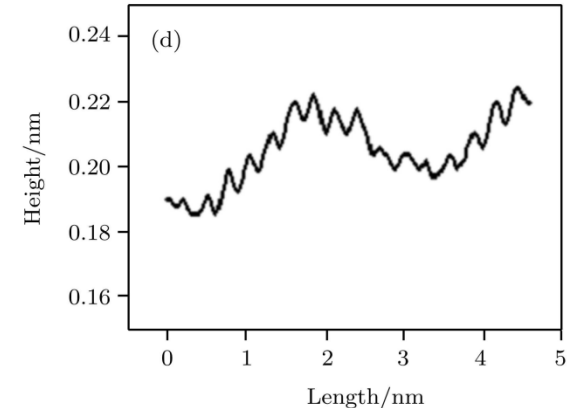
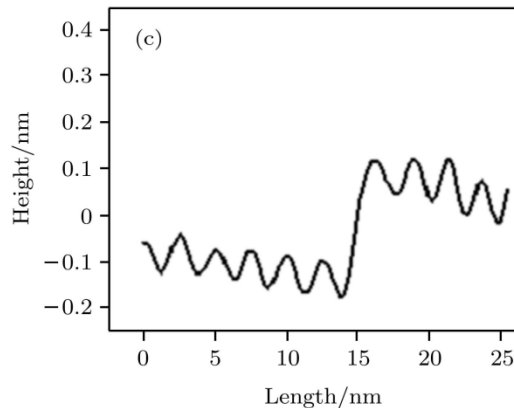
(Received 17 May 2007; revised manuscript received 1 July 2007)

We report on the formation of a graph  
The samples are characterized by scanning  
images show that the Moiré pattern is caus  
and has an  $N \times N$  superlattice. It is furth  
at high temperatures. Our results provide  
Ru(0001) surface, which is used as a templ  
and catalysis.

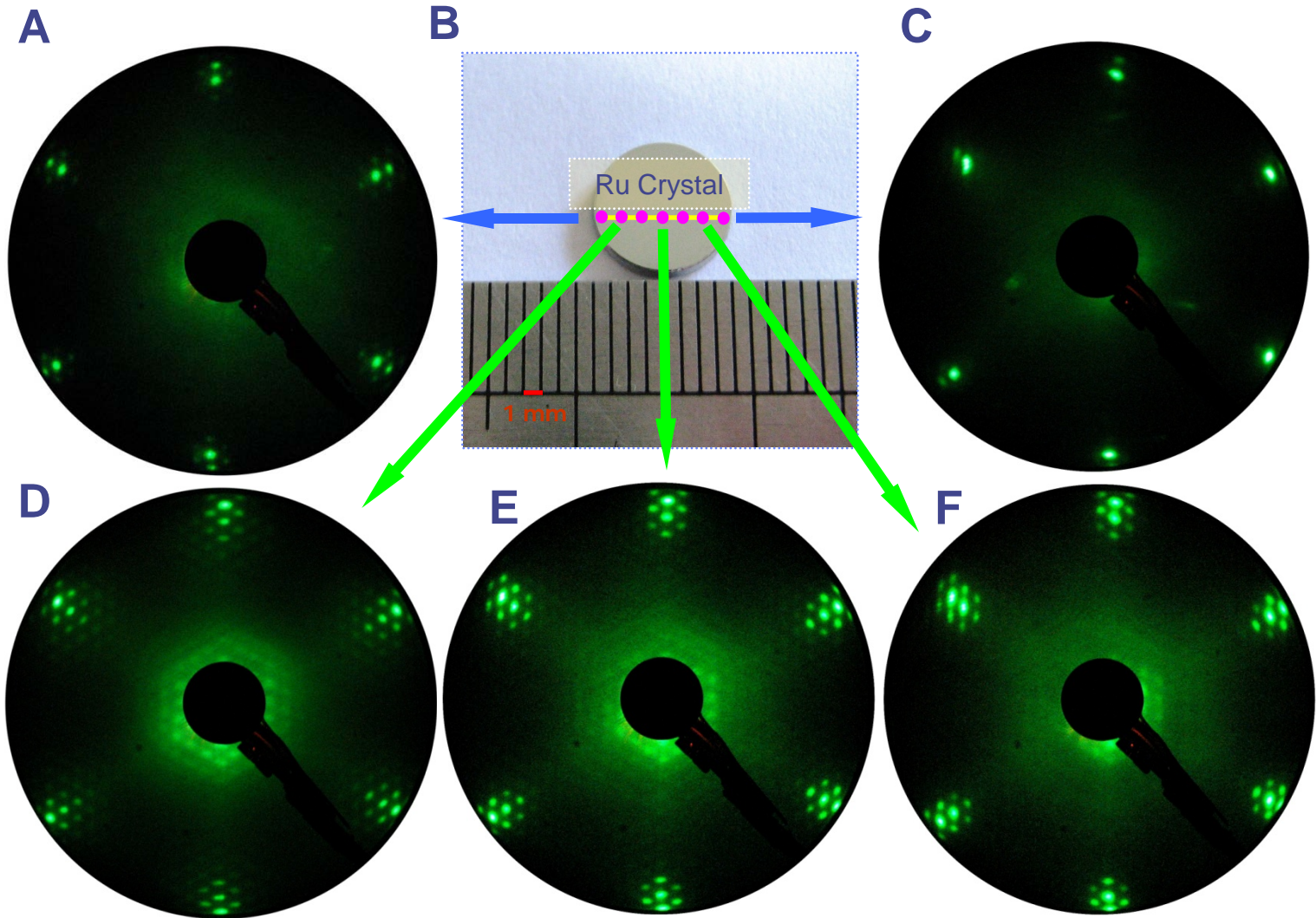
**Keywords:** graphene, Ru (0001), M  
**PACC:** 8120V, 0779, 6820



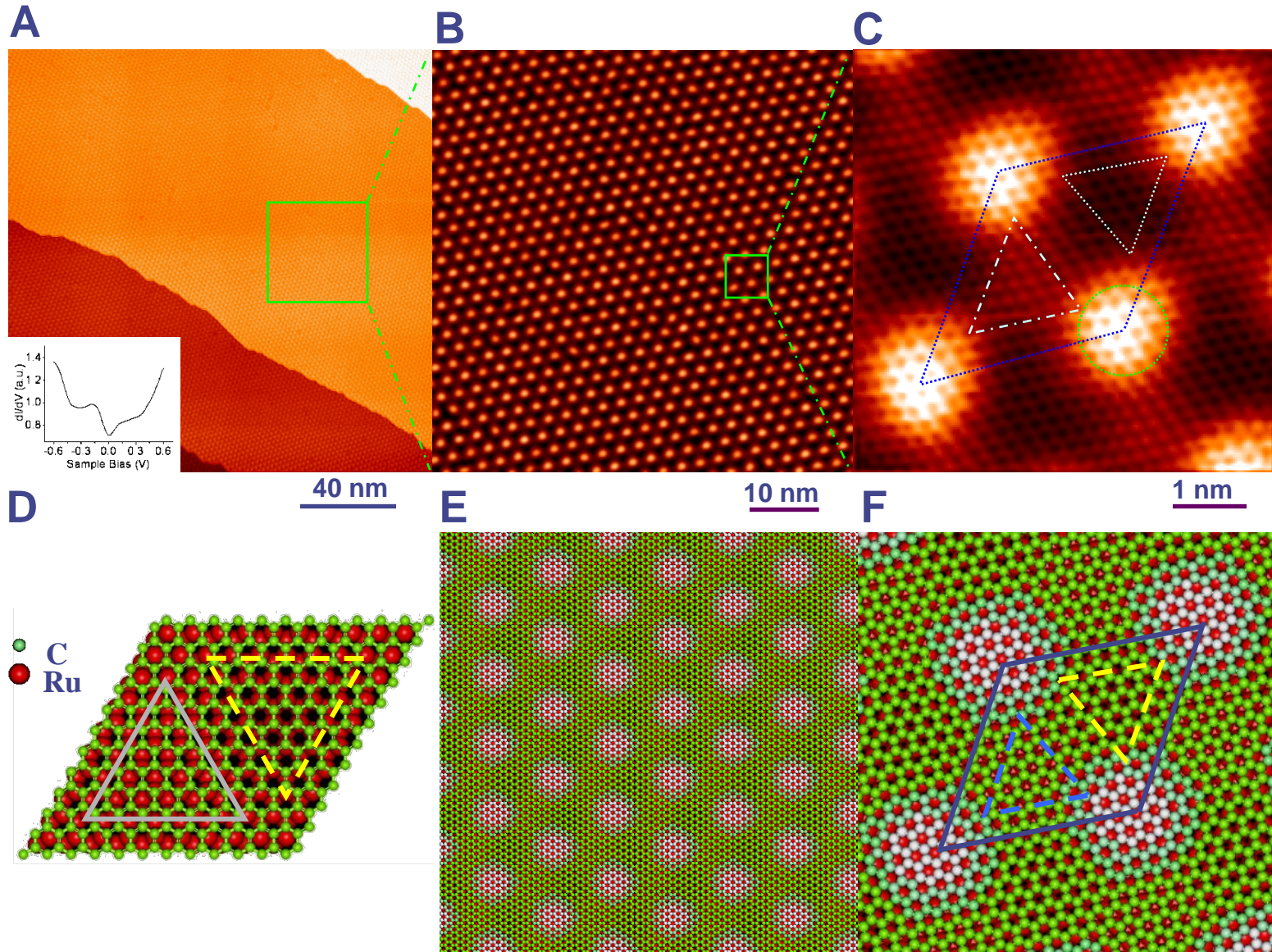
Graphene has aroused a great i  
cause of its novel properties<sup>[1-3]</sup> an  
applications.<sup>[4-8]</sup> All the existing method  
been utilized up to now are the micr  
cleavage or chemical exfoliation of high



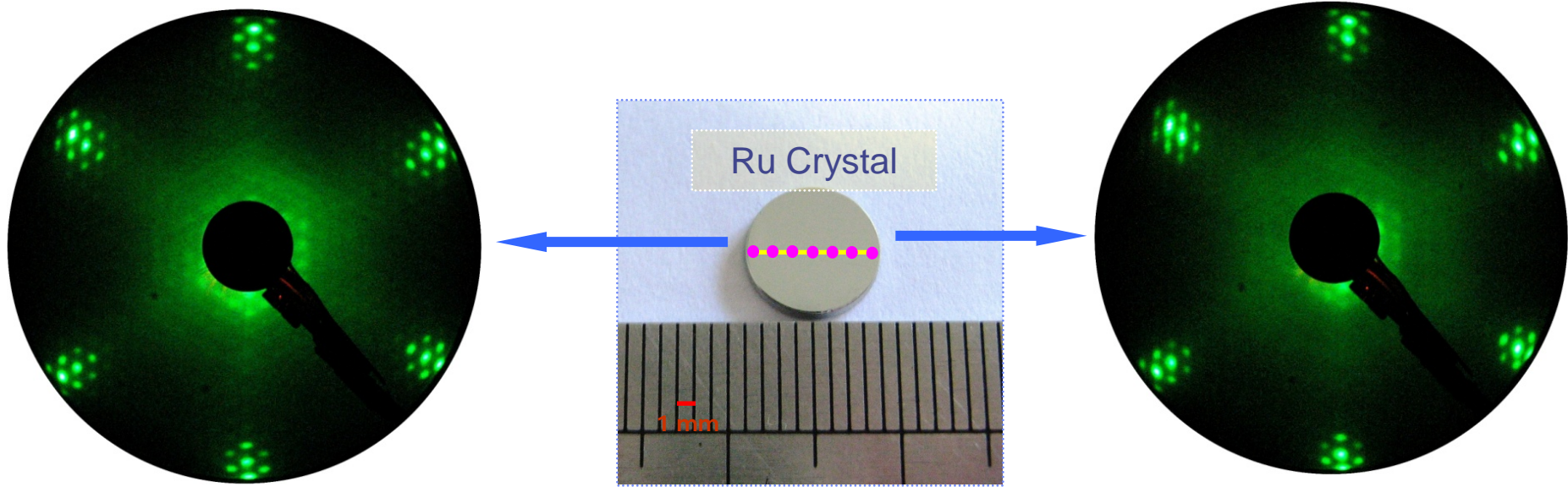
# *LEED Patterns of the Graphene/Ru(0001)*



# STM Images of Graphene/Ru(0001) and DFT Theoretical Calculations



# Challenges



## Large-scale Single Crystalline Graphene Monolayer

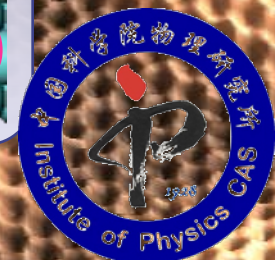
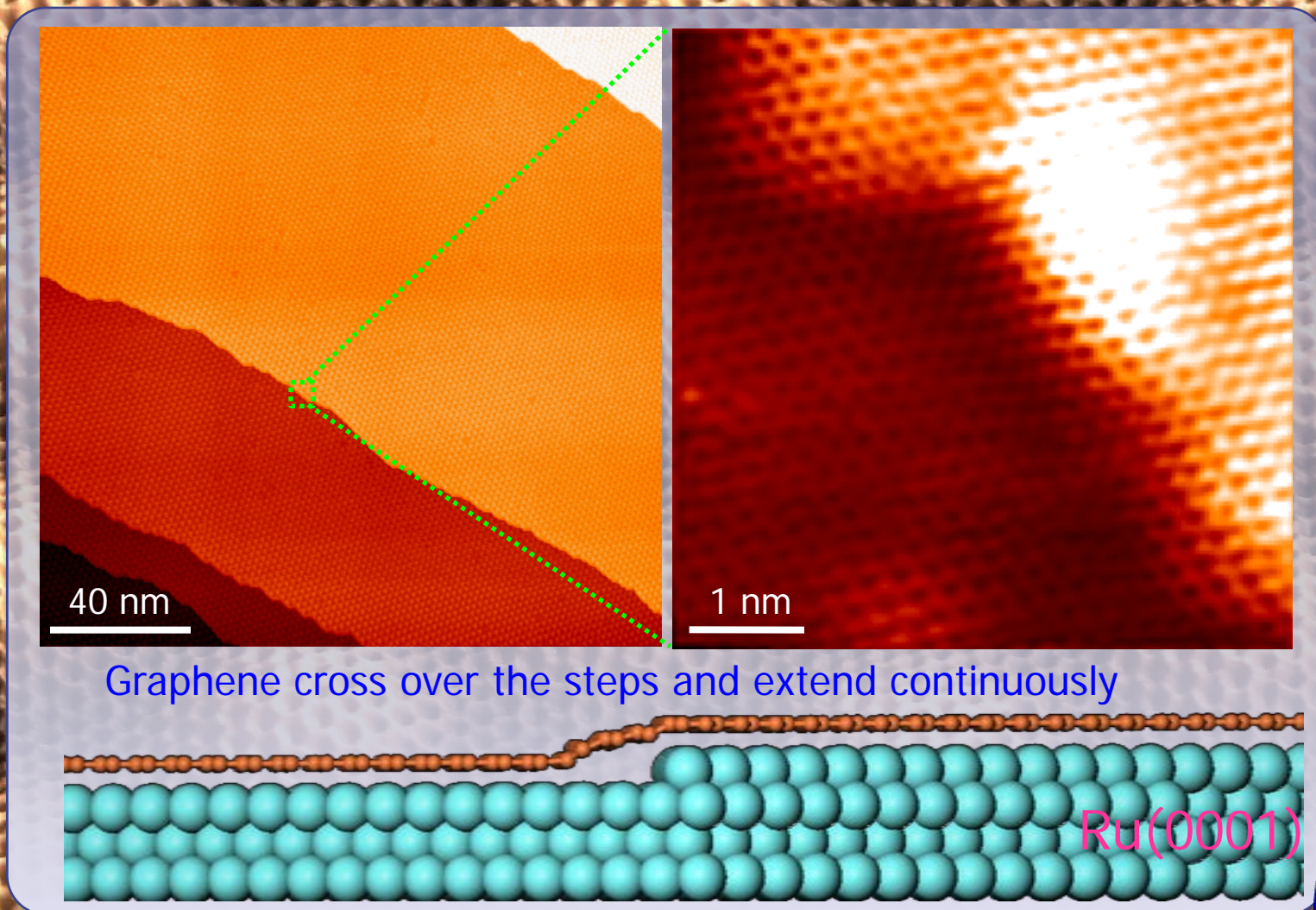
**High Quality !  
However,**

...

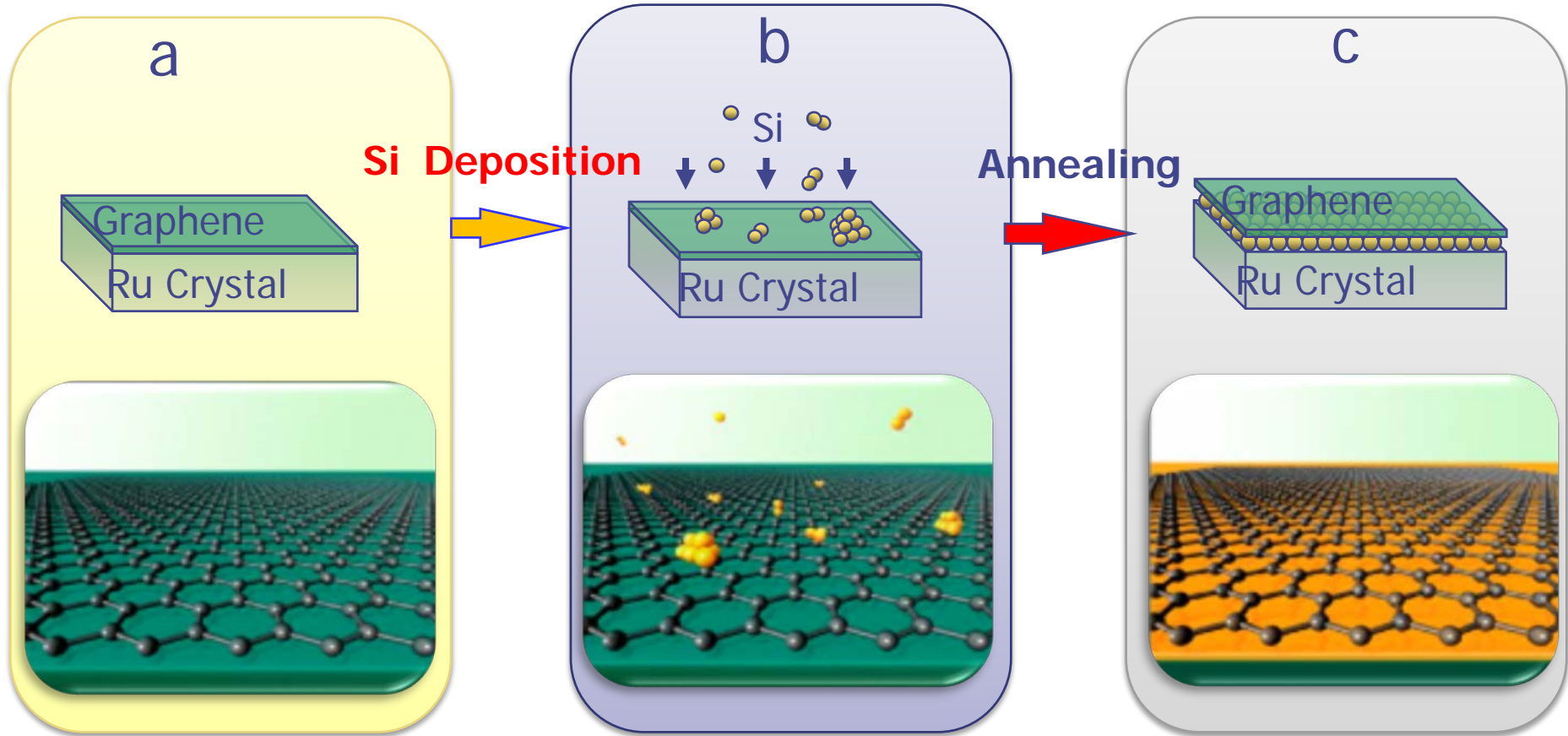
**&**

- 1) On insulator or semiconductor**
- 2) Without Transfer ???**

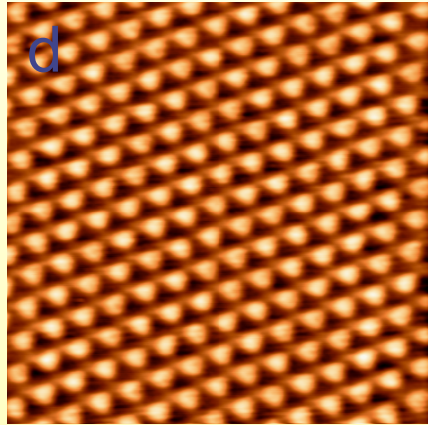
# STM image of graphene/Ru(0001)



# *Procedure of Silicon-layer Intercalation Approach*

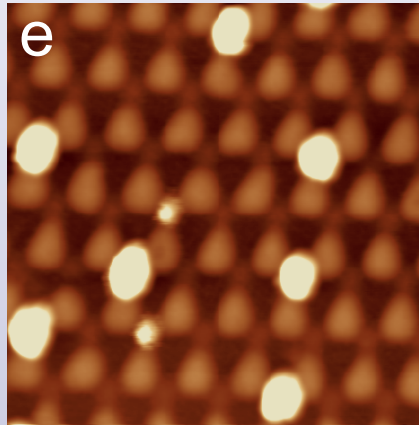
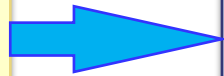


# *Procedure of Silicon-layer Intercalation Approach*



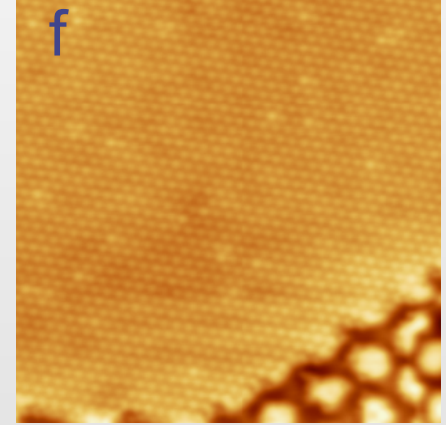
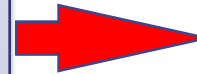
Moiré pattern of  
Gr./Ru(0001)

Si  
Deposition



Si clusters at RT

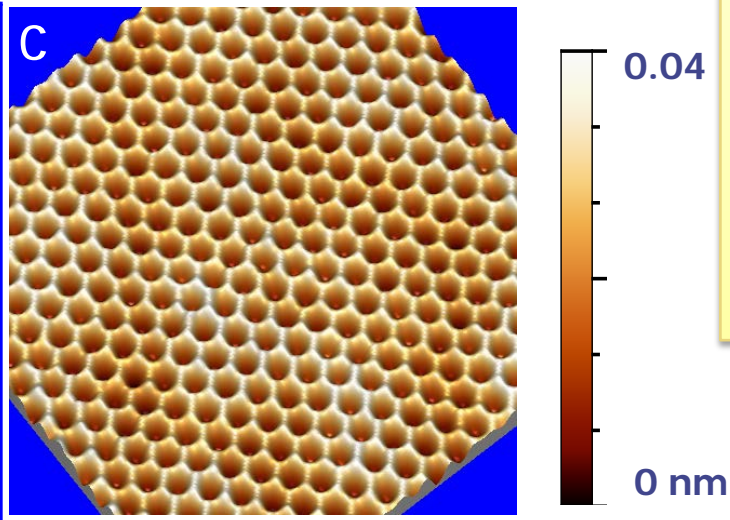
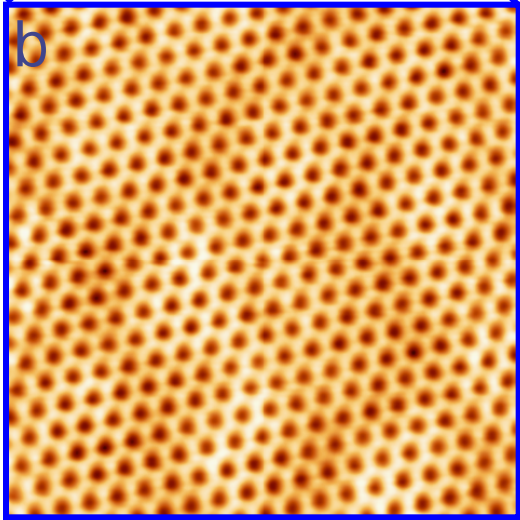
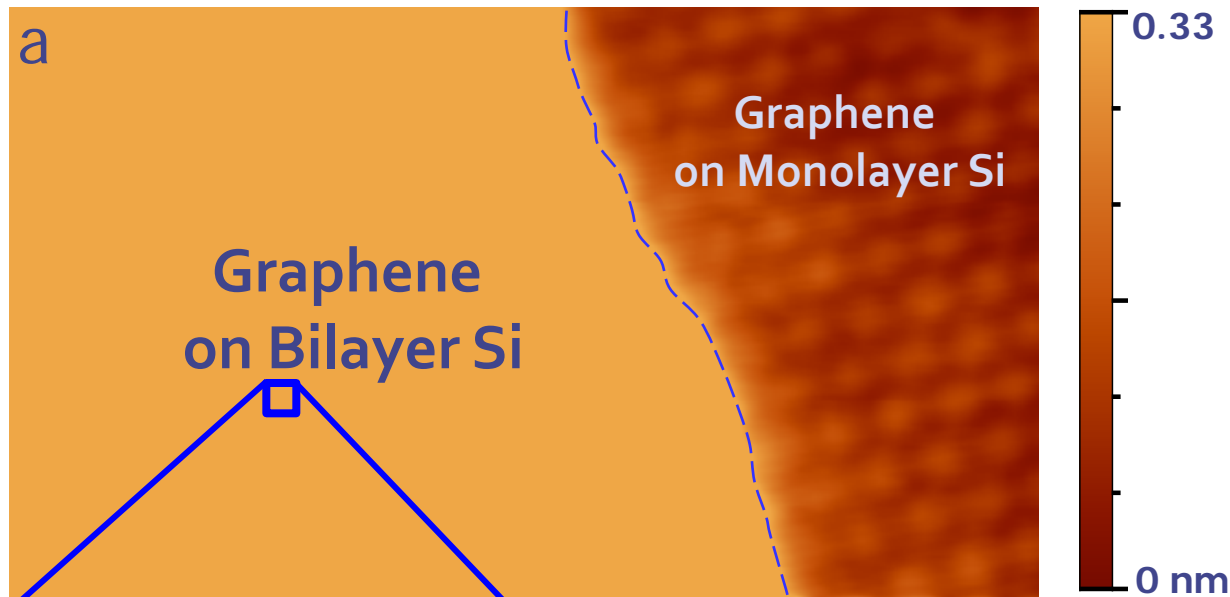
Annealing



Uniform  
and flat

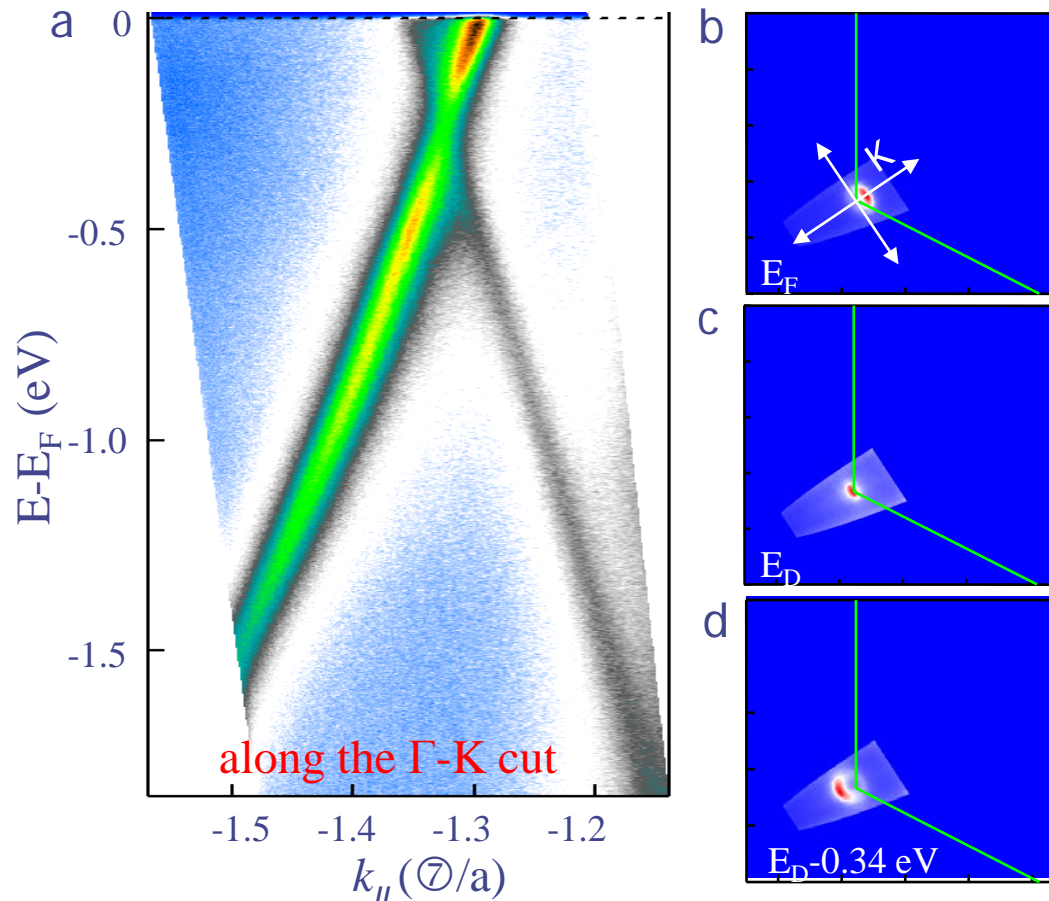


# *Thick Silicon-layer Intercalation*



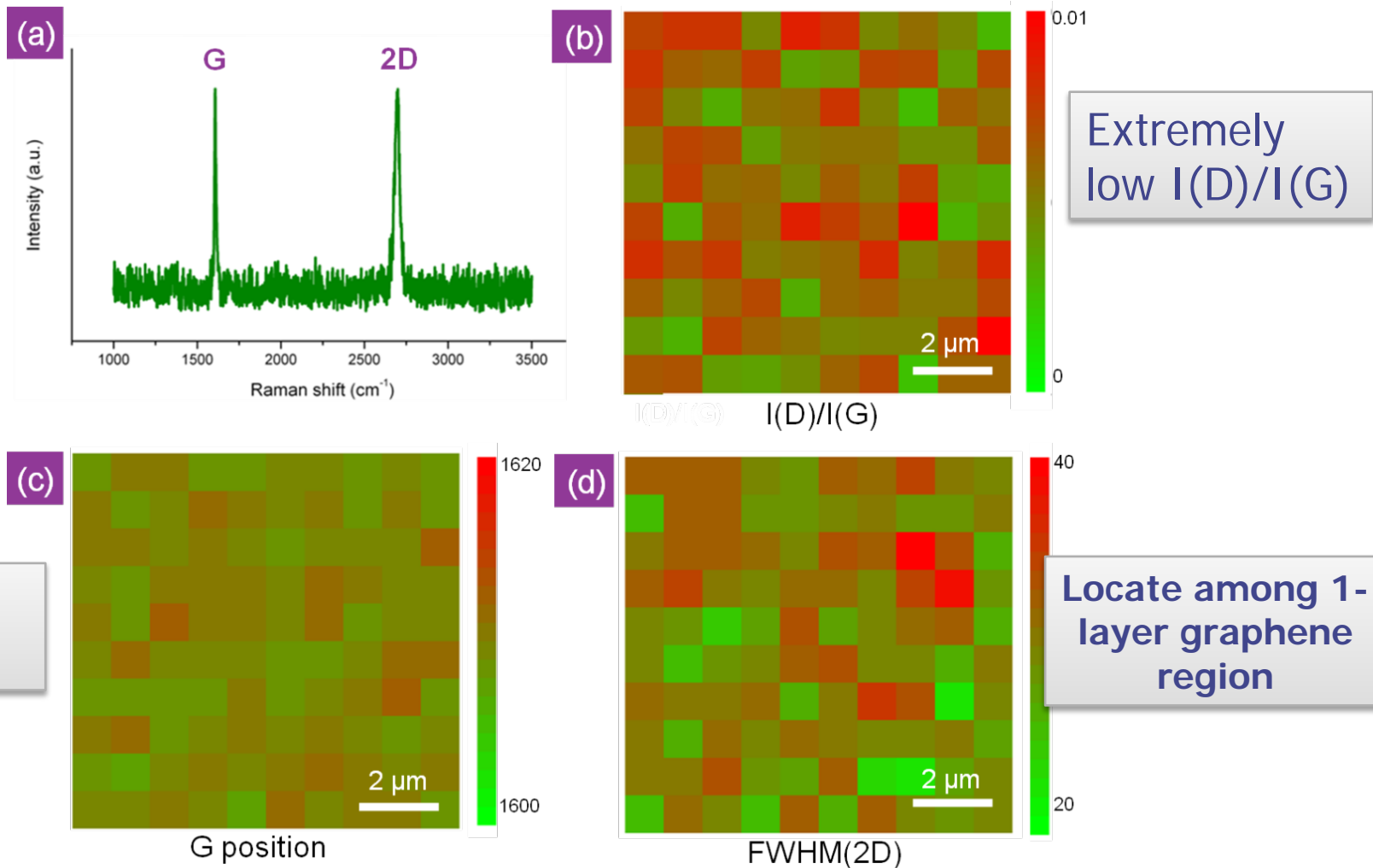
- Graphene becomes uniform and atomic flat.
- Atomic control of the distance between graphene and metal.

# Band Structure by ARPES



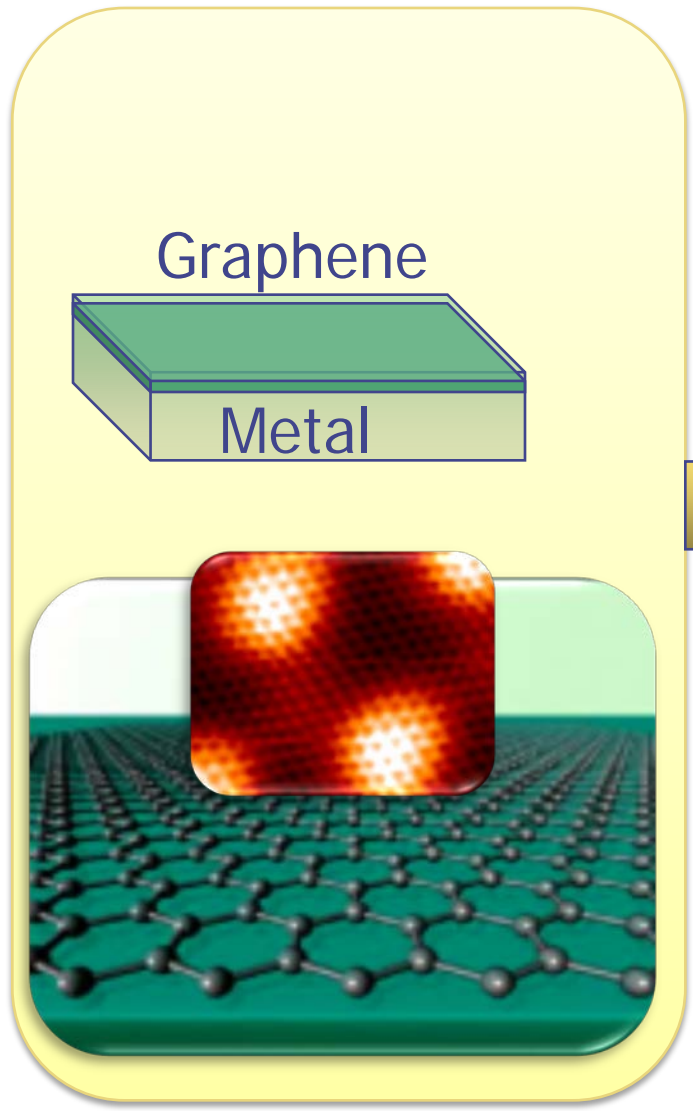
- ◆ The band is clear and sharp, like a free-standing graphene → **the intercalated**
- ◆ Silicon layer blocked the interactions from the Ru(0001) substrate.

# Raman data of G/Si/Ru



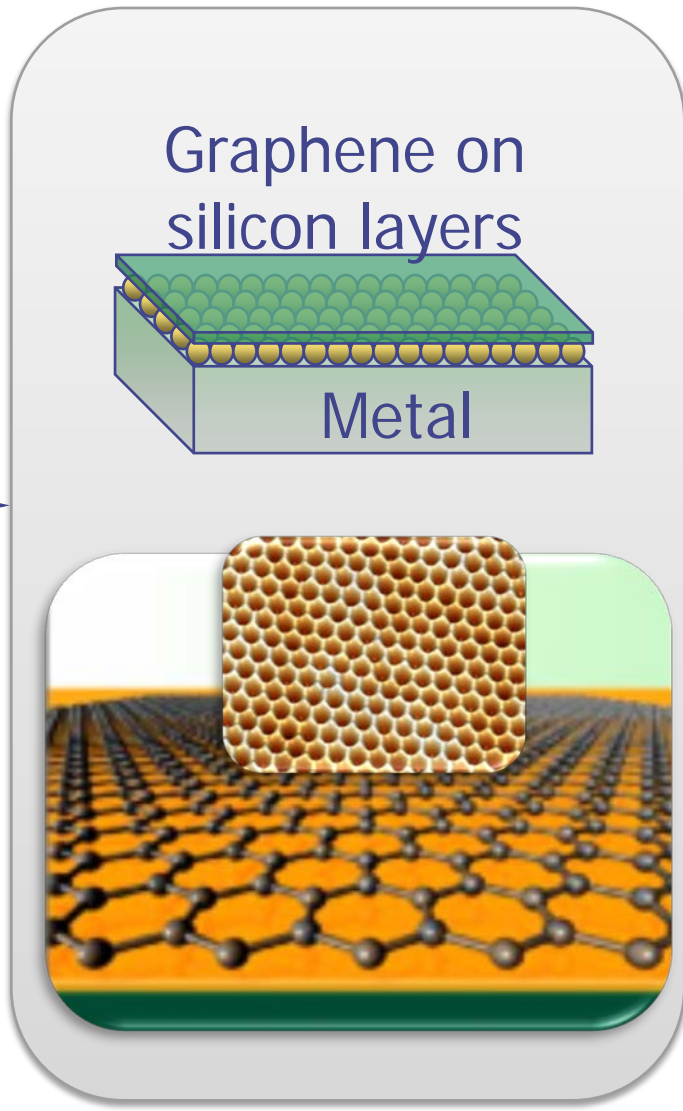
**After thick silicon-layer intercalation:**

- G and 2D peaks are visible and sharp, no D peak.



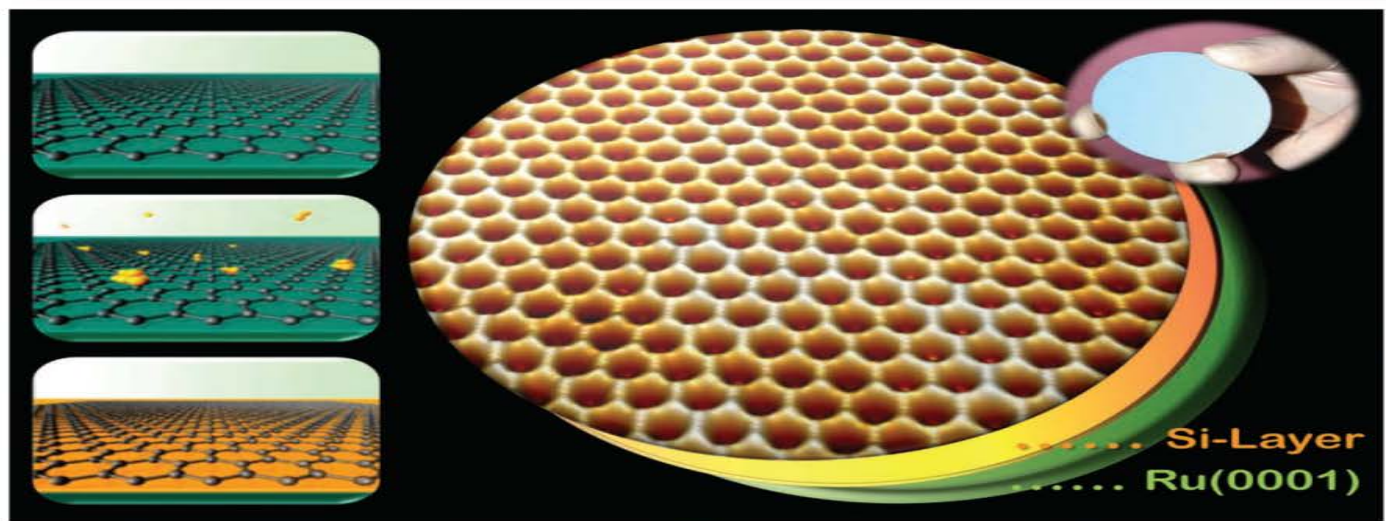
Silicon layers intercalation

A large yellow arrow points from the left panel to the right panel, indicating the direction of the process.



**Graphene's high quality is preserved, decoupled from metals.**

# AIP | Applied Physics Letters



## Silicon-Layer Intercalation of Epitaxially-grown Graphene on Metal Crystals

50<sup>th</sup>  
Anniversary

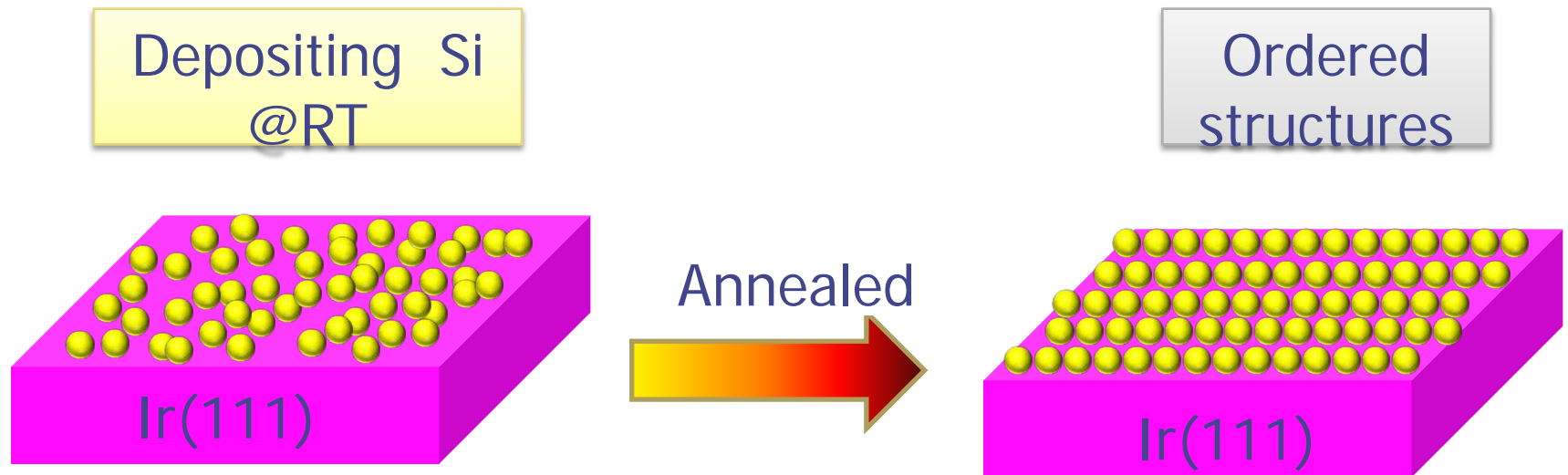
# Two-dimensional Materials Based on d-block Elements

The image shows a periodic table of elements. A red box highlights the d-block elements, which are the transition metals in groups 3 through 10. A large red question mark is placed over the d-block elements, specifically over the elements from Scandium (Sc) to Zinc (Zn) in the first row of the d-block, and from Yttrium (Y) to Cadmium (Cd) in the second row. The periodic table is color-coded by groups: Group 1 (pink), Group 2 (purple), Groups 3-10 (blue), Groups 11-12 (light blue), Group 13 (orange), Group 14 (green), Group 15 (light green), Group 16 (yellow-green), Group 17 (yellow), and Group 18 (orange).

1A 11A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8 VIII 8	9 VIII 9	10 VIII 10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 H Hydrogen 1.0079	2 He Helium 4.00260																
3 Li Lithium 6.941	4 Be Beryllium 9.01218											5 B Boron 10.811	6 C Carbon 12.011	7 N Nitrogen 14.00674	8 O Oxygen 15.9994	9 F Fluorine 18.998403	10 Ne Neon 20.1797
11 Na Sodium 22.989768	12 Mg Magnesium 24.305											13 Al Aluminum 26.981539	14 Si Silicon 28.0855	15 P Phosphorus 30.973762	16 S Sulfur 32.066	17 Cl Chlorine 35.4527	18 Ar Argon 39.948
19 K Potassium 39.0983	20 Ca Calcium 40.078	21 Sc Scandium 44.95591	22 Ti Titanium 47.88	23 V Vanadium 50.9415	24 Cr Chromium 51.9961	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.9332	28 Ni Nickel 58.6934	29 Cu Copper 63.546	30 Zn Zinc 65.39	31 Ga Gallium 69.723	32 Ge Germanium 72.64	33 As Arsenic 74.92159	34 Se Selenium 78.96	35 Br Bromine 79.904	36 Kr Krypton 83.80
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.90585	40 Zr Zirconium 91.224	41 Nb Niobium 92.90638	42 Mo Molybdenum 95.94	43 Tc Technetium 98.9072	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.9055	46 Pd Palladium 106.42	47 Ag Silver 107.8682	48 Cd Cadmium 112.411	49 In Indium 114.818	50 Sn Tin 118.71	51 Sb Antimony 121.760	52 Te Tellurium 127.6	53 I Iodine 126.90447	54 Xe Xenon 131.29
55 Cs Cesium 132.90543	56 Ba Barium 137.327	57-71 Lanthanides	72 Hf Hafnium 178.49	73 Ta Tantalum 180.9479	74 W Tungsten 183.85	75 Re Rhenium 186.207	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.9665	80 Hg Mercury 200.59	81 Tl Thallium 204.3833	82 Pb Lead 207.2	83 Bi Bismuth 208.98037	84 Po Polonium [209, 8824]	85 At Astatine 209, 8871	86 Rn Radon 222.0176
87 Fr Francium 223, 8187	88 Ra Radium 226, 0254	89-103 Actinides	104 Rf Rutherfordium [261]	105 Db Dubnium [262]	106 Sg Seaborgium [266]	107 Bh Bohrium [264]	108 Hs Hassium [269]	109 Mt Meitnerium [268]	110 Ds Darmstadtium [269]	111 Rg Roentgenium [272]	112 Cn Copernicium [277]	113 Uut Ununtrium unknown	114 Uuq Ununquadium [289]	115 Uup Ununpentium unknown	116 Uuh Ununhexium [288]	117 Uus Ununseptium unknown	118 Uuo Ununoctium unknown

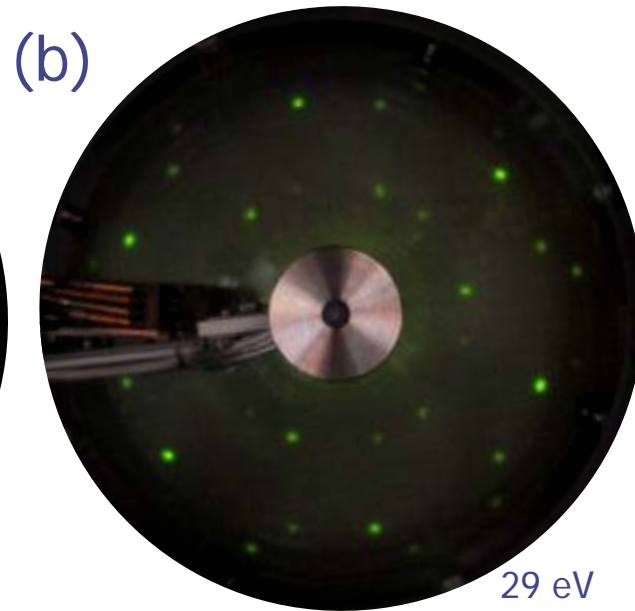
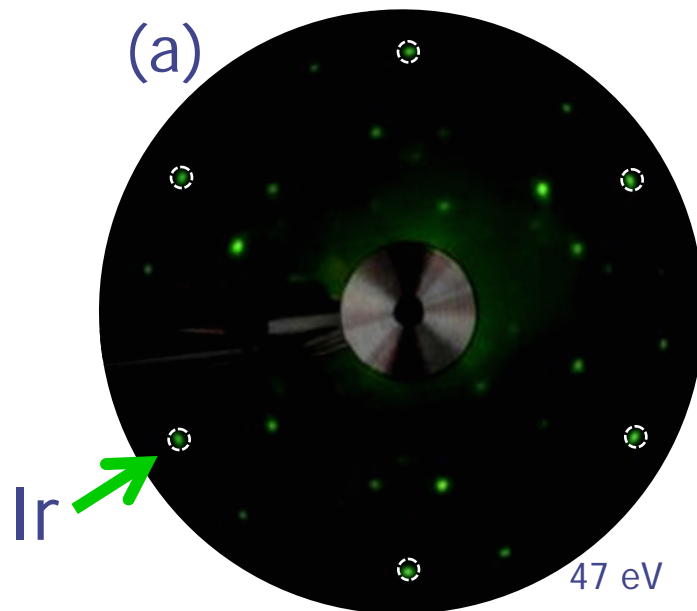
- ◆ The reported 2D honeycomb materials are made of elements with p-orbital electronic structure
- ◆ with d electrons have not been reported before

# Silicene on Ir(111)

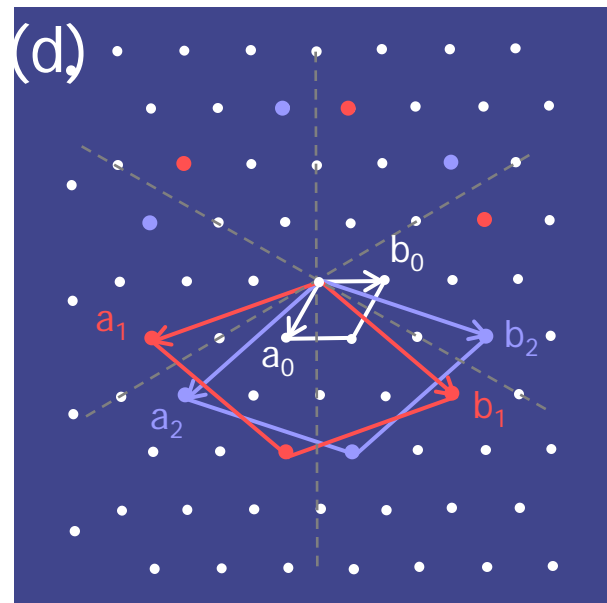
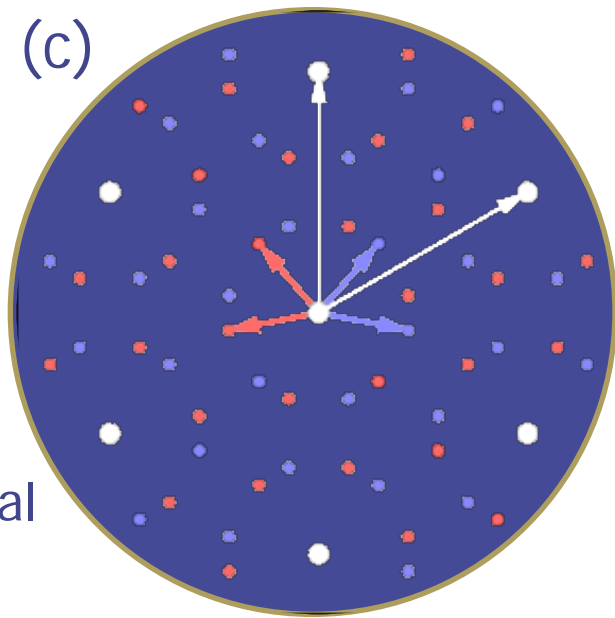


L. Meng *et al.*, Nano Letters **13**, 685 (2013).

# LEED Patterns of Si Adlayer on Ir(111)

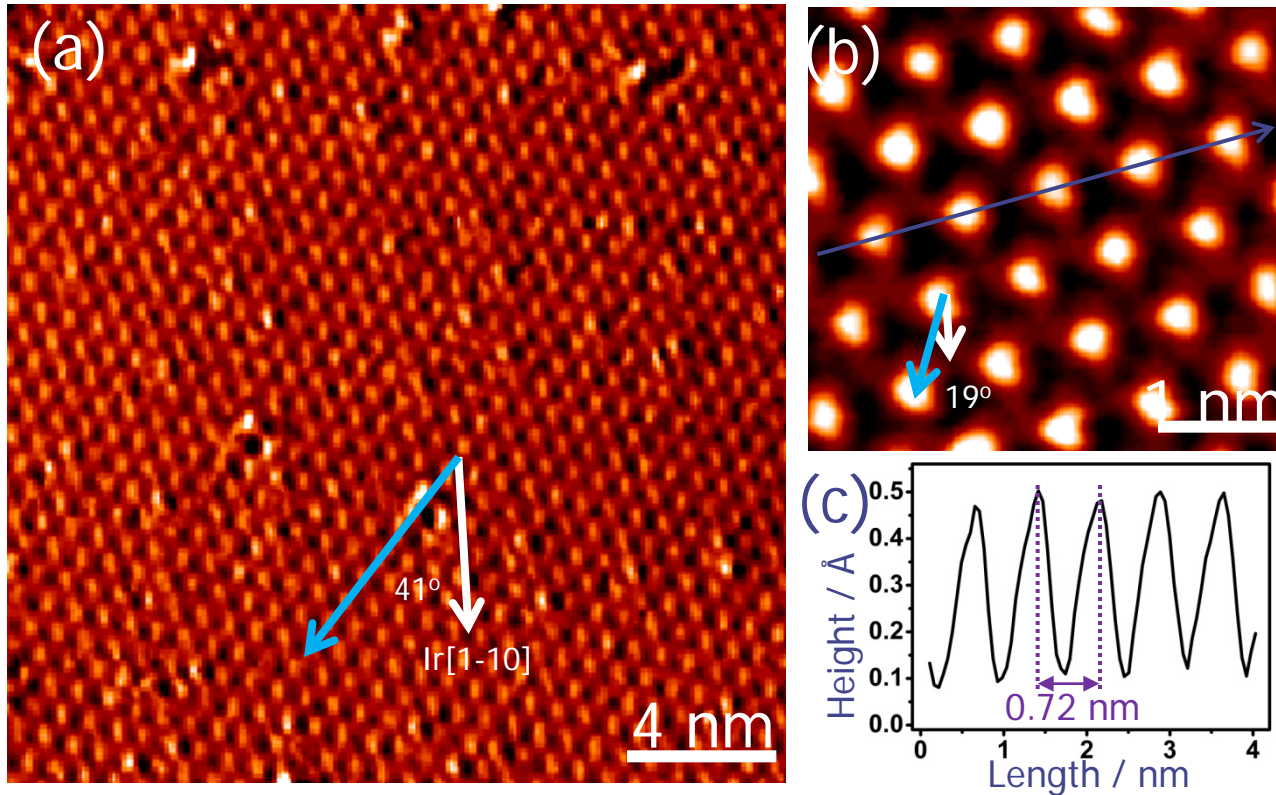


$(\sqrt{7} \times \sqrt{7})$   
superstructure





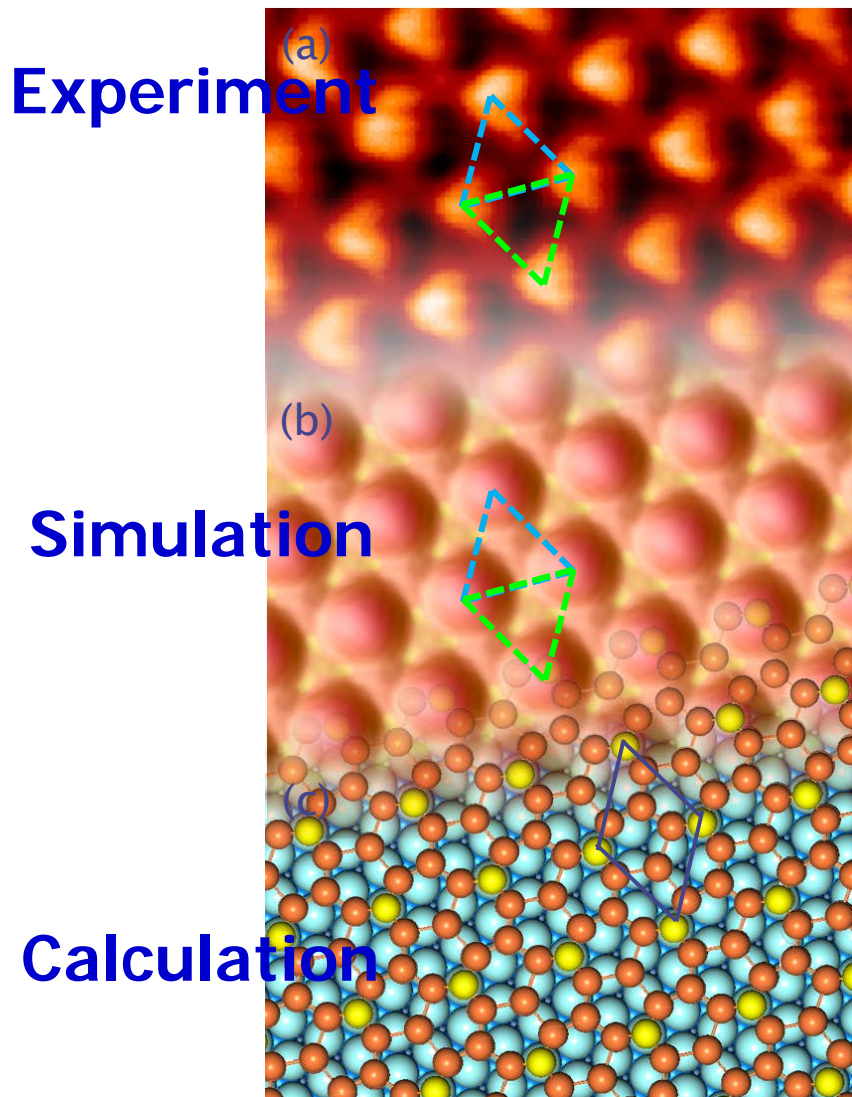
# STM Characterization: Buckled Si Adlayer



$$\sqrt{7} \times a_{\text{Ir}} (0.271 \text{ nm}) = 0.717 \approx 0.72 \text{ nm}$$

- $\sqrt{7} \times \sqrt{7}$  superstructure accords with LEED observations.

# Atomic Configuration of Si Adlayer on Ir(111)

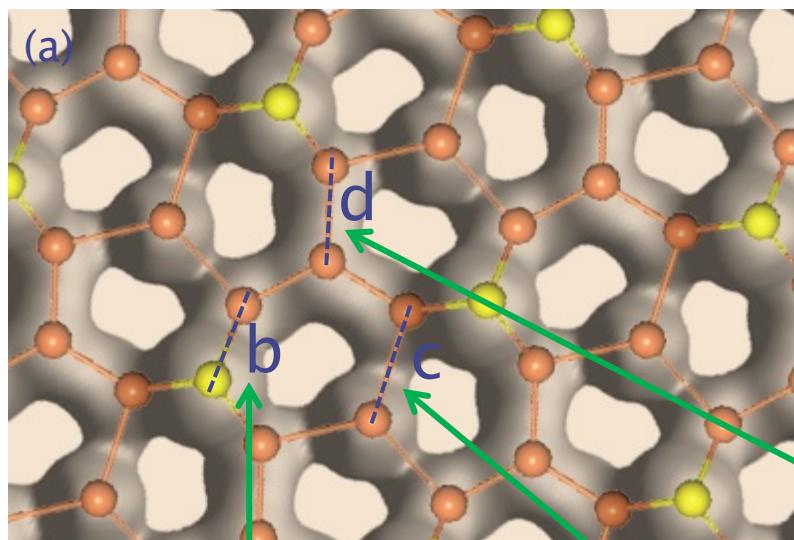


➤  $\sqrt{3}\times\sqrt{3}$  silicene /  $\sqrt{7}\times\sqrt{7}$  Ir(111)

➤ The simulated STM image is in excellent agreement with the STM observations.

Calculated by Prof. Shixuan Du

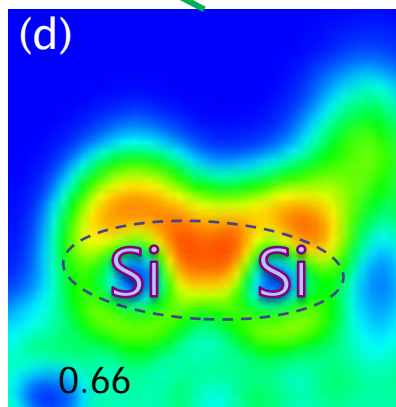
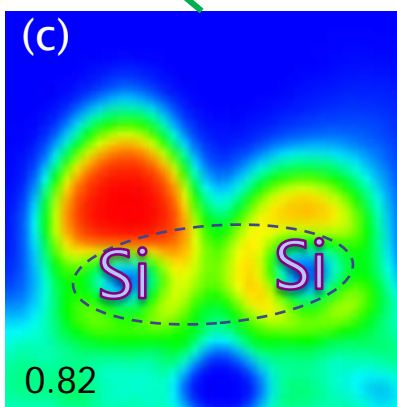
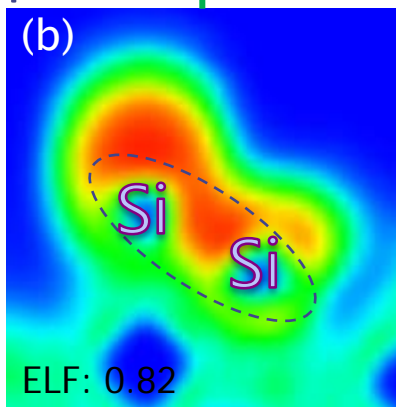
# Evidence of Covalent Interaction between Silicon Atom Pairs



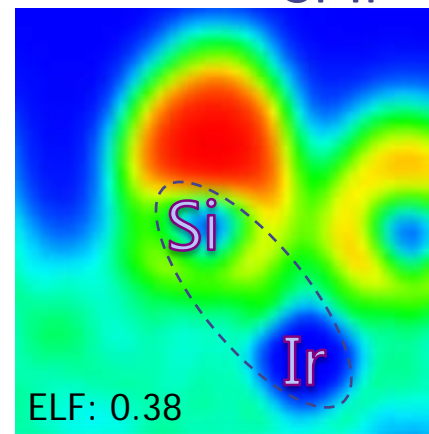
(a) Top view of overall ELF (electron localization function) of 0.6, showing a continuity of the Si layer.

(b-d) Cross section of ELFs along each Si pair: covalent interaction existing between Si-Si atoms.

Si-Si



Si-Ir



A 2D continuous silicon layer, silicene, was successfully fabricated on Ir(111).

## - References

1. Vogt, P. *et al. Phys. Rev. Lett.* **108**, 155501 (2012).  
[+ Show context](#)
2. Fleurence, A. *et al. Phys. Rev. Lett.* **108**, 245501 (2012).  
[+ Show context](#)
3. Meng, L. *et al. Nano Lett.* **13**, 685–690 (2013).  
[+ Show context](#)

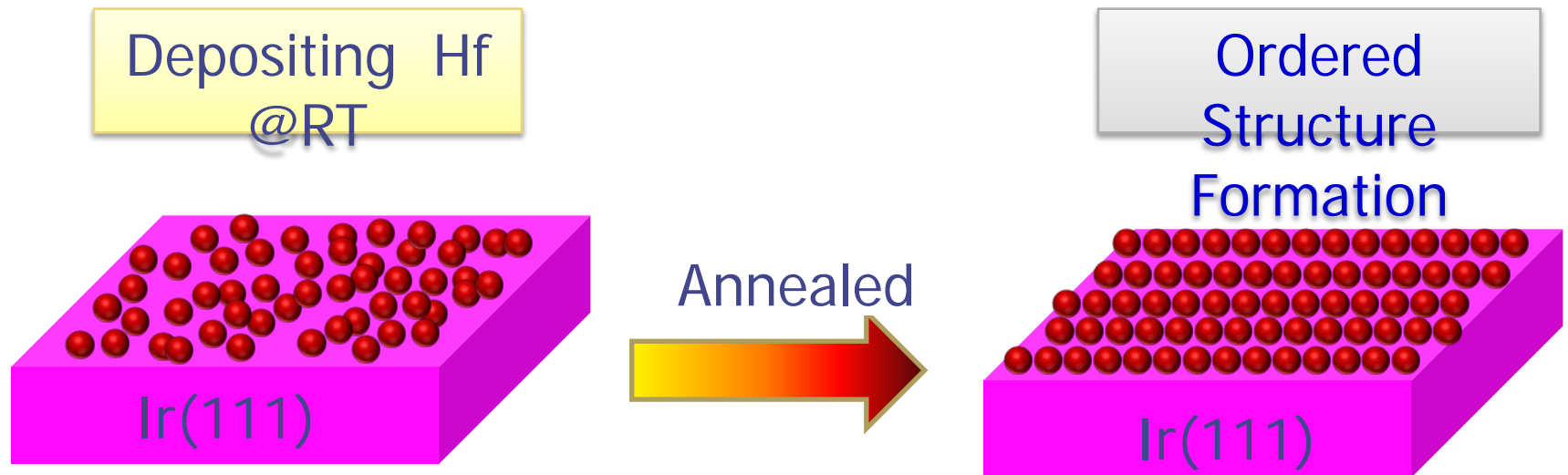
Only two other materials have been found to support silicene up to now. One, zirconium diboride, has the advantage of naturally sucking silicene onto its surface from a block of silicon positioned below<sup>2</sup>. The other, crystalline iridium, was reported as a possibility only in January this year<sup>3</sup>.

12 March 2013 | Corrected: 14 March 2013

In 2011, physicist Guy Le Lay stood before a half-filled room on the last day of the American Physical Society's March meeting in Dallas,

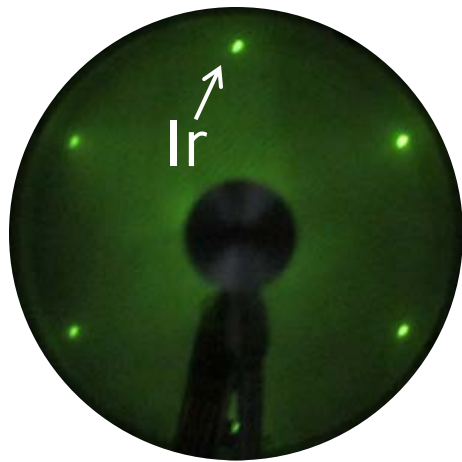


# Hafnene on Ir(111)

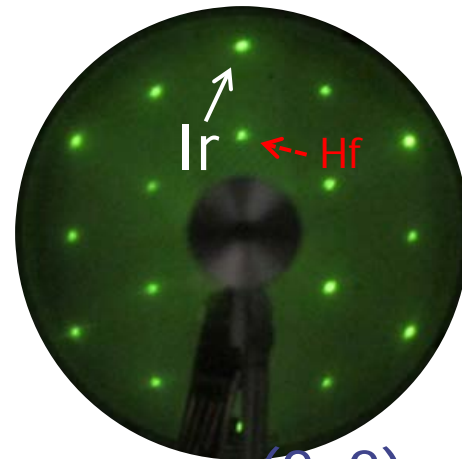


L. F. Li *et al.*, Nano Letters 13, 4671 (2013).

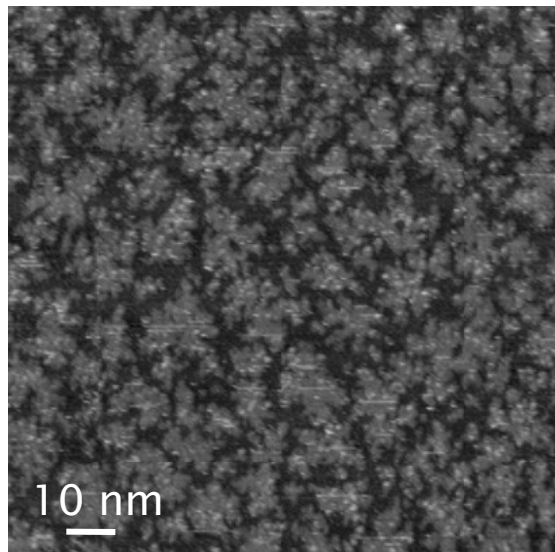
# LEED and STM Observations of Hf/Ir(111)



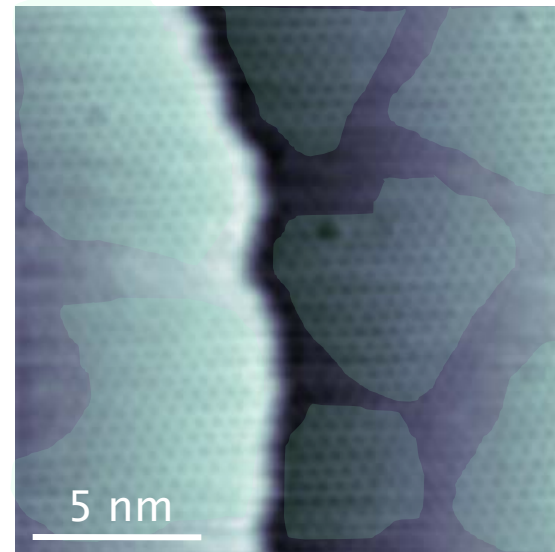
annealing



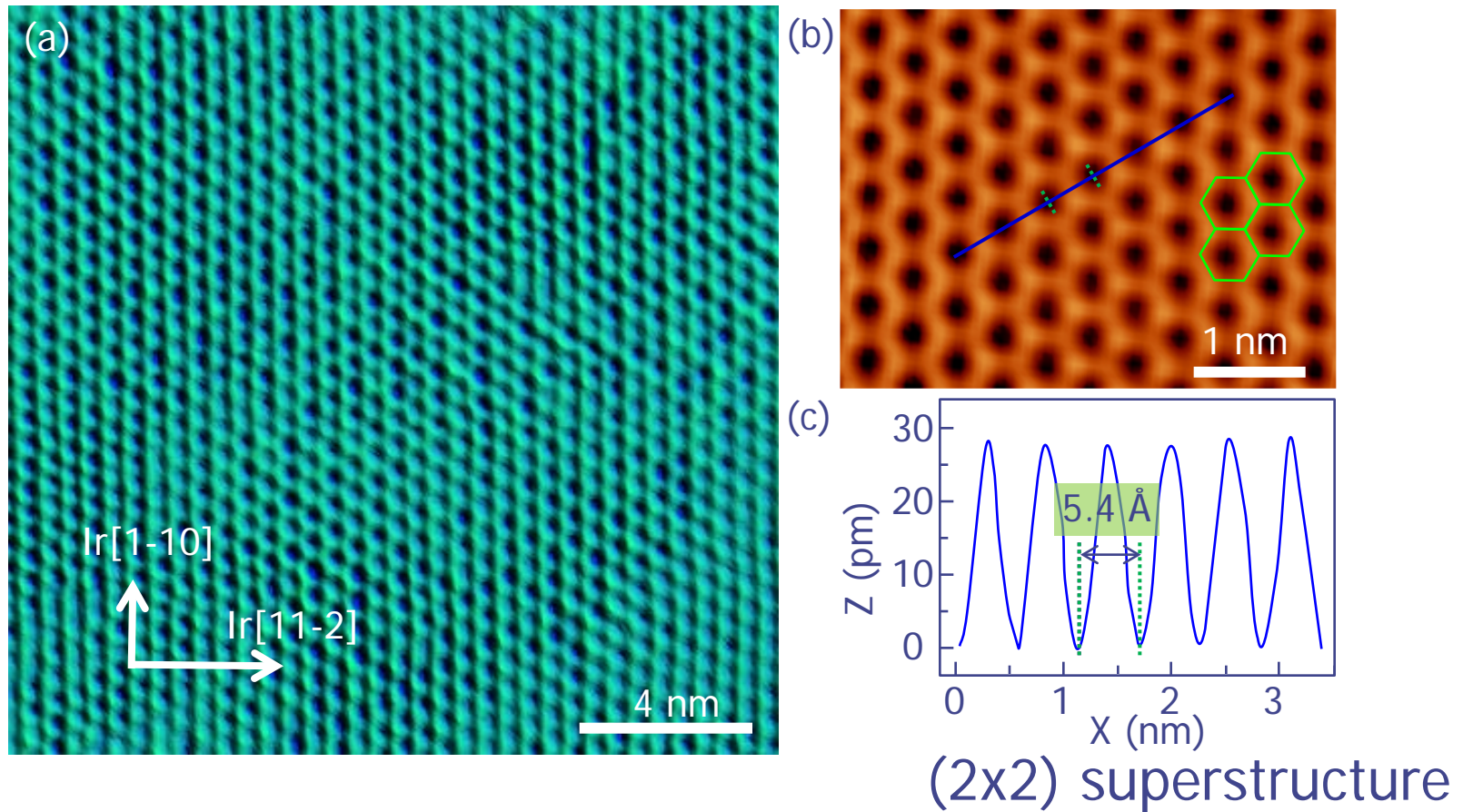
$(2 \times 2)$  superstructure



annealing



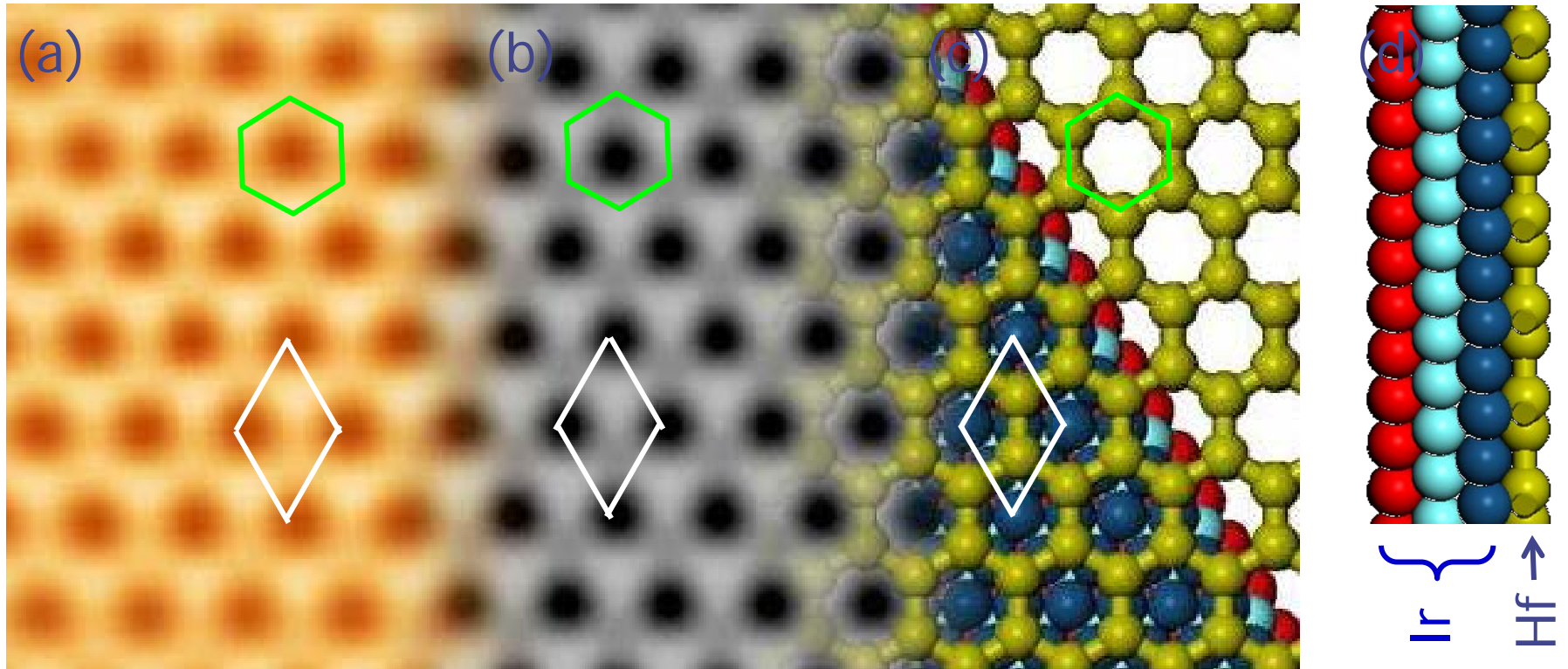
# STM Images of Hf Layer on Ir(111)



- Continuous 2D lattice of honeycomb structure.
- Periodicity of  $5.40 \text{ \AA} \approx 2 \times 2.71 \text{ \AA}$  [surface lattice constant of Ir(111)].
- Hf-Hf distance of  $3.12 \text{ \AA} \approx 3.19 \text{ \AA}$  in the (0001) facet of bulk Hf.

# Atomic Configuration of Hf Honeycomb Lattice on Ir(111)

In collaboration with Prof. S.B. Zhang



Experimental

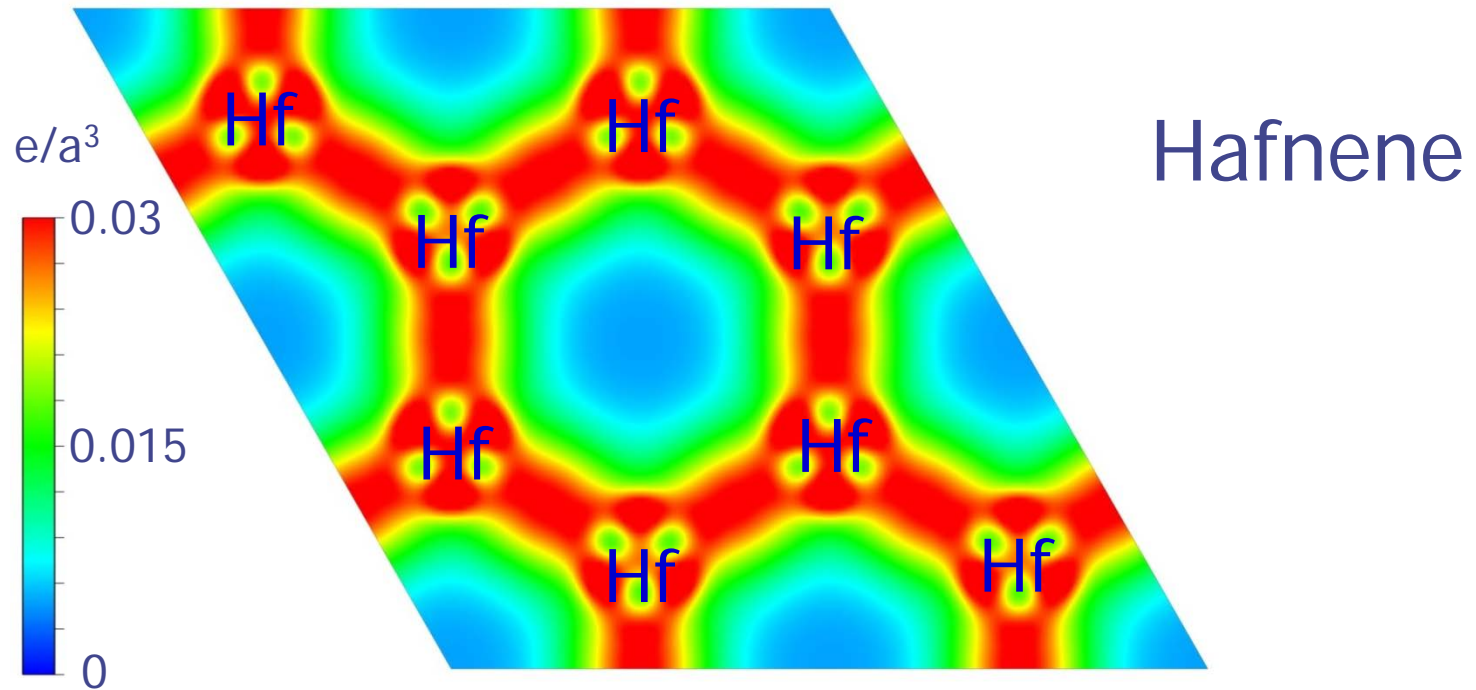
DFT-simulated

Relaxed structure

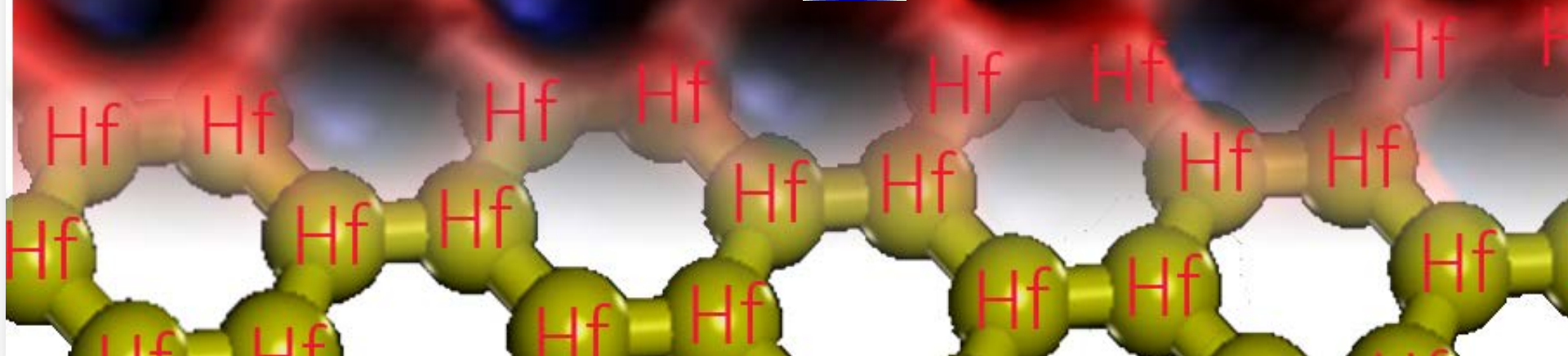
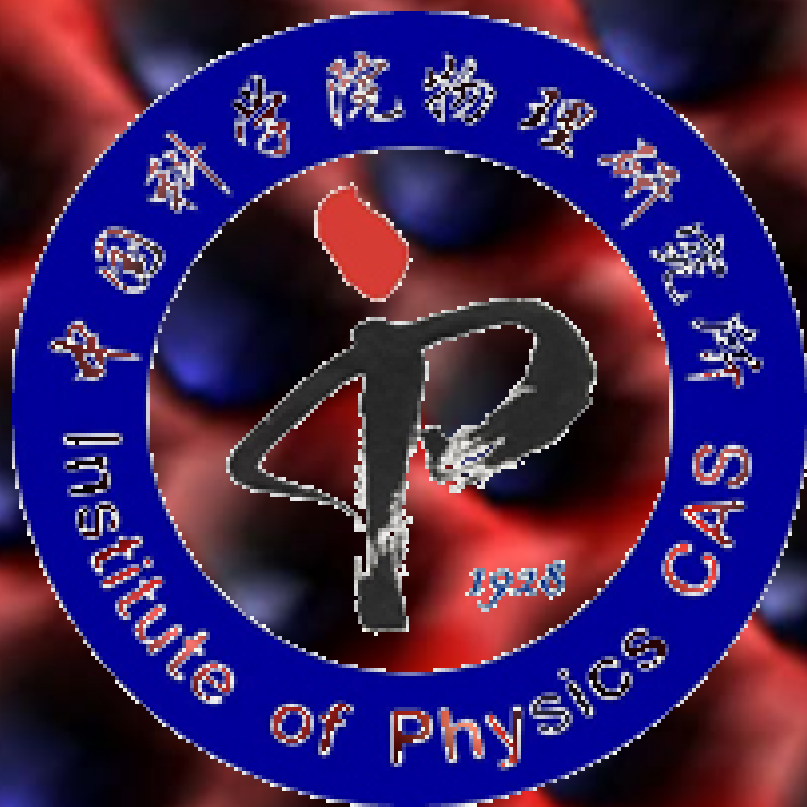
- The honeycomb is clearly seen.
- The simulated results are in remarkable agreement with exp. data.



# Calculated 2D Charge Density in Hf Plane on Ir(111)



- Directional bonding between adjacent Hf atoms.
- Hf-Hf bonds are responsible for the honeycomb structure.



Journal h

### ELECTROPORATION

#### Tips for cleaning water

*Nano Lett.* **13**, 4288–4293 (2013)

Journal

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+ Adva  
publi

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+ Curre

+ Archi

+ Focu

+ Press

Current methods of disinfecting water, such as membrane filtration and ultraviolet disinfection, have high financial and energy costs; cheaper methods, such as adding chlorine, have been found to produce carcinogenic by-products. Electroporation, a technique often used in molecular biology, is an alternative method that works by applying a strong electric field, damaging the cell membranes of bacteria and viruses and causing death. However, the high external voltage required has implications in terms of cost, energy consumption and safety.

Yi Cui and colleagues at Stanford University have now developed a nanosponge filtration device, which incorporates nanomaterials into a commercial polyurethane sponge to achieve efficient disinfection by electroporation.

Carbon nanotubes are added to the sponge to make it conductive and silver nanowires are added to create a large number of nanoscale tips. The tips increase the strength of the electric field that can be generated by several orders of magnitude compared with an electric field generated by flat surfaces.

The researchers evaluated the performance of the nanosponge using water sources containing various model bacteria and a model virus. Inactivation of the microorganisms increased with rising external voltage, with over 99% of bacteria and viruses inactivated at 10 V and 20 V, respectively. Additionally, no harmful by-products were formed during the

process and the energy consumption at 10 V was  $100 \text{ J l}^{-1}$  compared with more than  $500 \text{ J l}^{-1}$  for membrane filtration. SB

### TWO-DIMENSIONAL MATERIALS

#### Hafnium honeycombs

*Nano Lett.* <http://doi.org/nvr> (2013)



Graphene has a variety of intriguing properties because of its honeycomb lattice. Other materials with such two-dimensional structures are known including hexagonal boron nitride and silicene. However, these materials, like graphene, are typically made of *p*-block elements. Yeliang Wang, Shengbai Zhang, Hong-Jun Gao and colleagues have now shown that two-dimensional honeycomb lattice structures can also be created using transition metal atoms.

The researchers — who are based at Beijing National Laboratory of Condensed Matter Physics, Jilin University and Rensselaer Polytechnic Institute — created a crystalline layer of hafnium on an iridium(111) surface.

To prepare the layer, hafnium atoms were deposited on the surface under ultrahigh-vacuum conditions using an electron-beam evaporator. The hafnium initially forms nanoclusters on the surface, but after annealing a well-ordered honeycomb structure was observed using low-energy electron diffraction and scanning tunnelling microscopy.

The experimental results, together with charge-density calculations, suggest that the hafnium forms its own honeycomb lattice with direct hafnium–hafnium bonds. A second hafnium layer can also be formed on top of the first by increasing the hafnium coverage on the surface. Furthermore, calculations suggest that freestanding layers of the material would be ferromagnetic. OV

### ORGANIC SOLAR CELLS

#### Overcoming attraction

*Nature Commun.* **4**, 2334 (2013)

Solar cells convert solar energy into electrical signals. Alongside silicon-based photovoltaic devices, solar cells made from blends of conjugated polymer and fullerenes are being developed because of their inherently lower production costs. In these devices, the absorption of photons generates bound hole–electron pairs, which have to overcome Coulomb attraction to be separated into free electrons and holes. These charge carriers can subsequently be collected at electrodes to generate a photocurrent. The mechanism for charge separation is, however, not well understood, hindering optimization of material parameters. Vidmantas Gulbinas of Vilnius University and colleagues have now

# Neighbors of Carbon

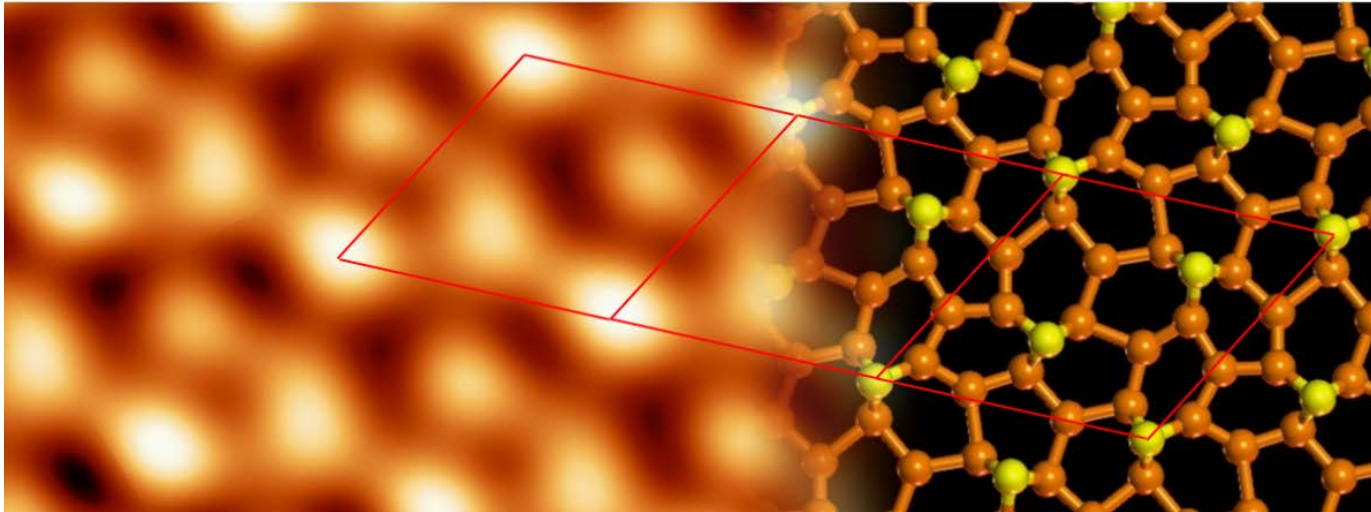
1																		18	
1	<b>H</b> 1.008																	2	<b>He</b> 4.003
2	<b>Li</b> 6.941	<b>Be</b> 9.012											5	<b>B</b> 10.81	<b>C</b> 12.01	<b>N</b> 14.01	<b>O</b> 16.00	<b>F</b> 19	<b>Ne</b> 20.18
3	<b>Na</b> 22.99	<b>Mg</b> 24.31									13	<b>Al</b> 26.98	<b>Si</b> 28.09	<b>P</b> 30.97	<b>S</b> 32.07	<b>Cl</b> 35.45	<b>Ar</b> 39.95		
4	<b>K</b> 39.10	<b>Ca</b> 40.08	<b>Sc</b> 44.96	<b>Ti</b> 47.88	<b>V</b> 50.94	<b>Cr</b> 52.00	<b>Mn</b> 54.94	<b>Fe</b> 55.85	<b>Co</b> 58.93	<b>Ni</b> 58.69	<b>Cu</b> 63.55	<b>Zn</b> 65.39	<b>Ga</b> 69.72	<b>Ge</b> 72.59	<b>As</b> 74.92	<b>Se</b> 78.96	<b>Br</b> 79.90	<b>Kr</b> 83.80	
5	<b>Rb</b> 85.47	<b>Sr</b> 87.62	<b>Y</b> 88.91	<b>Zr</b> 91.22	<b>Nb</b> 92.91	<b>Mo</b> 95.94	(98)	<b>Tc</b> 101.1	<b>Ru</b> 102.9	<b>Rh</b> 106.4	<b>Pd</b> 107.9	<b>Cd</b> 112.4	<b>In</b> 114.8	<b>Sn</b> 118.7	<b>Sb</b> 121.8	<b>Te</b> 127.6	<b>I</b> 126.9	<b>Xe</b> 131.3	
6	<b>Cs</b> 132.9	<b>Ba</b> 137.3	<b>La</b> 138.9	<b>Hf</b> 178.5	<b>Ta</b> 180.9	<b>W</b> 183.9	<b>Re</b> 186.2	<b>Os</b> 190.2	<b>Ir</b> 190.2	<b>Pt</b> 195.1	<b>Au</b> 197	<b>Hg</b> 200.5	<b>Tl</b> 204.4	<b>Pb</b> 207.2	<b>Bi</b> 209.0	<b>Po</b> (210)	<b>At</b> (210)	<b>Rn</b> (222)	

- ◆ 2D crystalline sheet materials by Si (Ge)?
- ◆ Honeycomb lattice like graphene?

# Silicene & Germanene

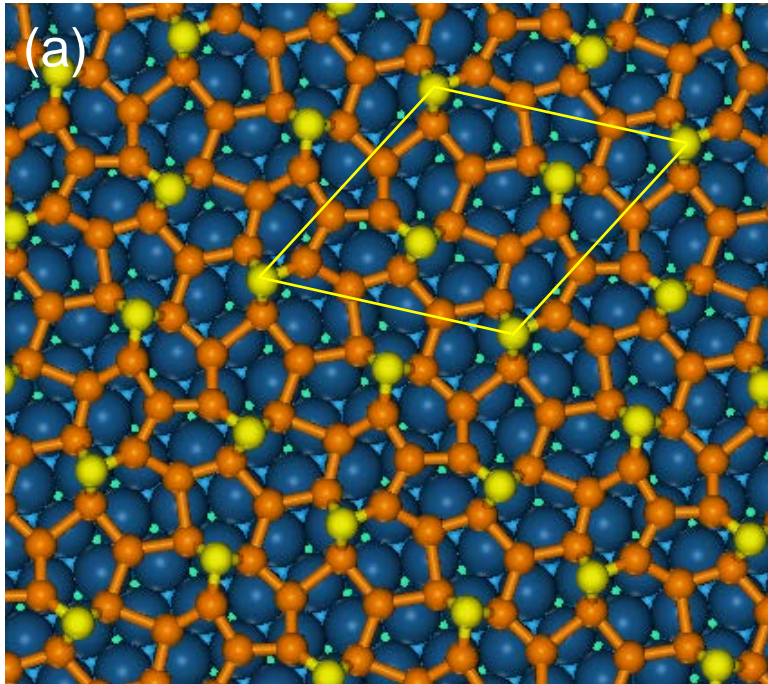
*(Theoretical → Experimental)*

# Germanene on Pt(111)

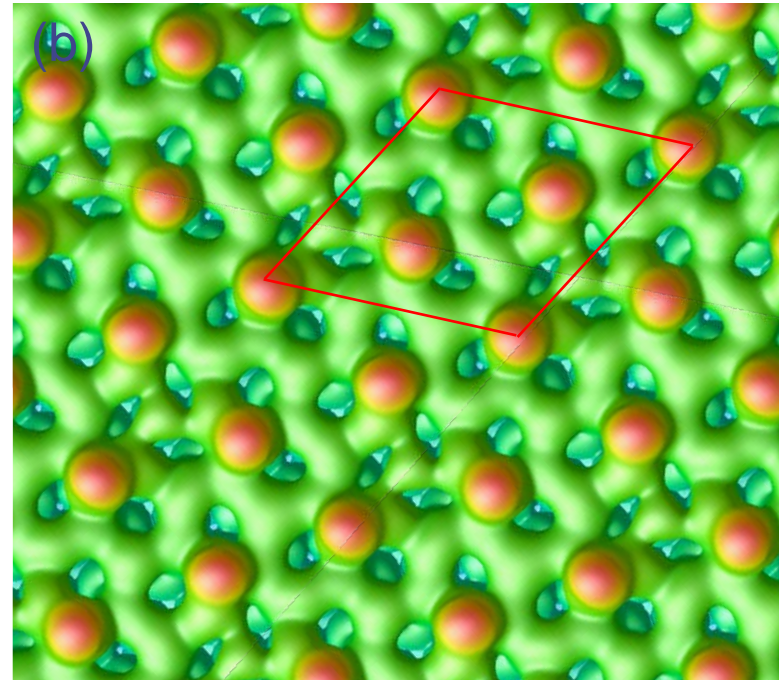


L.F. Li, Y.L. Wang/H.J.Gao *et al.*, *Adv. Mater.* **26**, 4820(2014)

# Atomic configuration of germanene lattice on Pt(111)



Relaxed structure



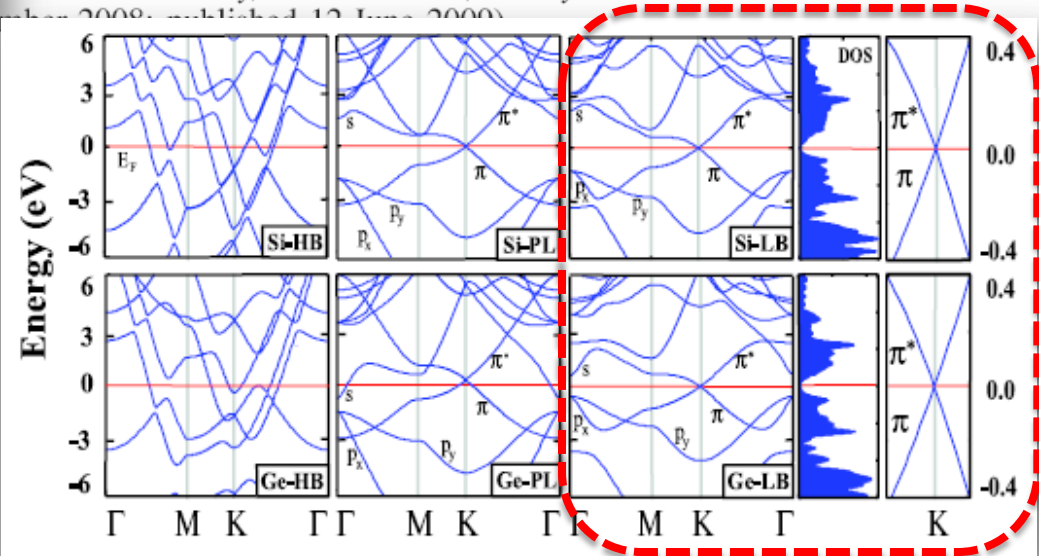
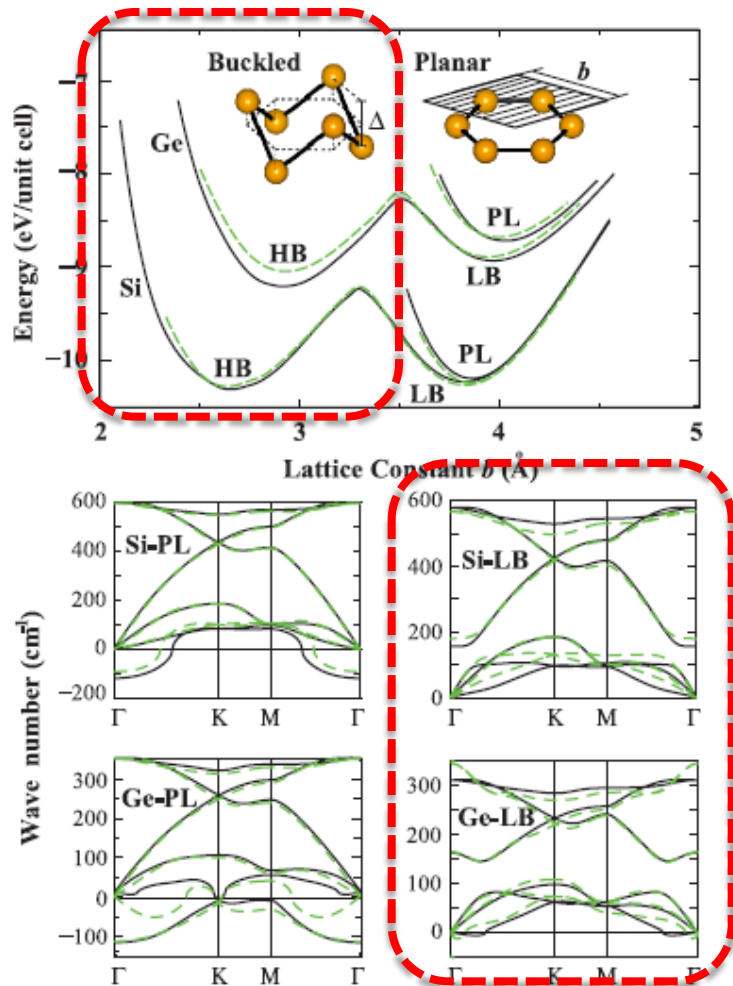
DFT-simulated

- $(3 \times 3)$  Germanene/ $(\sqrt{19} \times \sqrt{19})$  Pt(111) superstructure
- The simulated results are in remarkable agreement with exp. data

## Two- and One-Dimensional Honeycomb Structures of Silicon and Germanium

S. Cahangirov,<sup>1</sup> M. Topsakal,<sup>1</sup> E. Aktürk,<sup>1</sup> H. Şahin,<sup>1</sup> and S. Ciraci<sup>1,2,\*</sup>

<sup>1</sup>Department of Physics, Faculty of Sciences, Bilkent University, Ankara 06800, Turkey  
<sup>2</sup>Department of Physics, Faculty of Sciences, Bilkent University, Ankara 06800, Turkey  
 Received 2008; published 12 June 2009



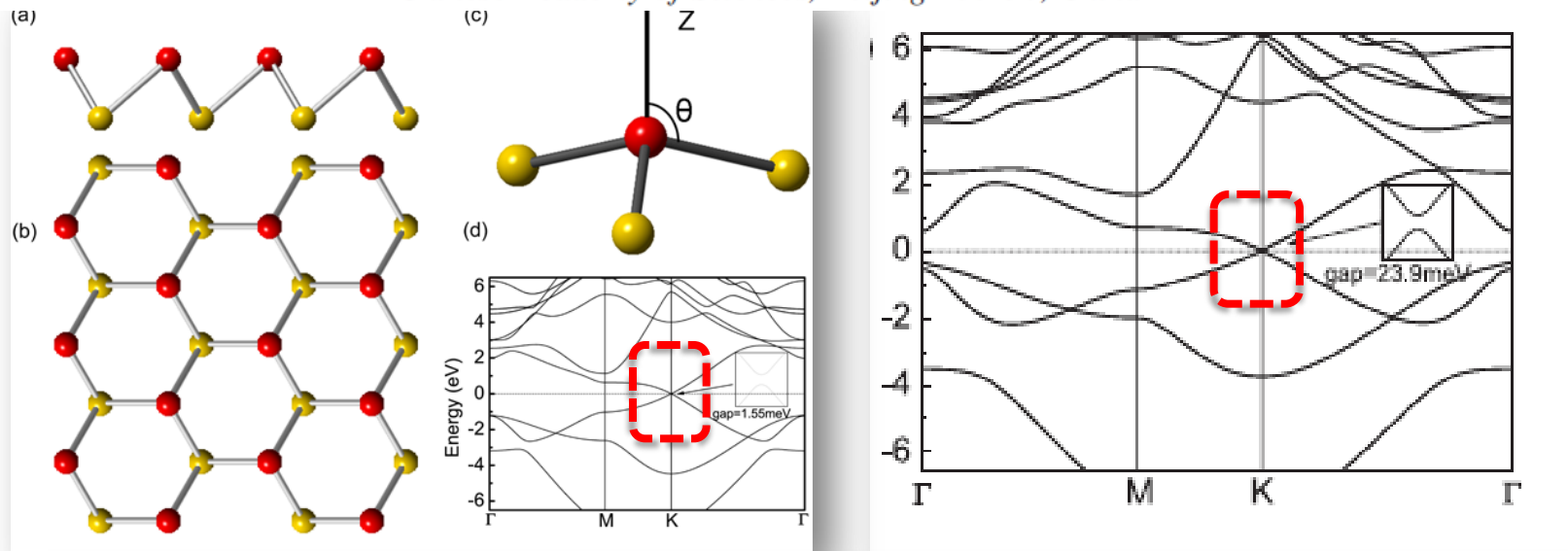
➤ ab initio studies revealed that a buckled honeycomb structure of Si & Ge can exist.



## Quantum Spin Hall Effect in Silicene and Two-Dimensional Germanium

Cheng-Cheng Liu, Wanxiang Feng, and Yugui Yao\*

*Beijing National Laboratory for Condensed Matter Physics and Institute of Physics,  
Chinese Academy of Sciences, Beijing 100190, China*



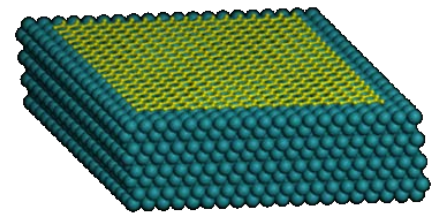
◆ QSHE can be observed in silicene and germanene.

◆ Spin-orbit band gap (1.55 meV in silicene, 23.9 meV in germanene), much higher than that of graphene ( $\mu\text{eV}$ ).

# Fabrication Methods: Graphene vs Silicene & Germanene

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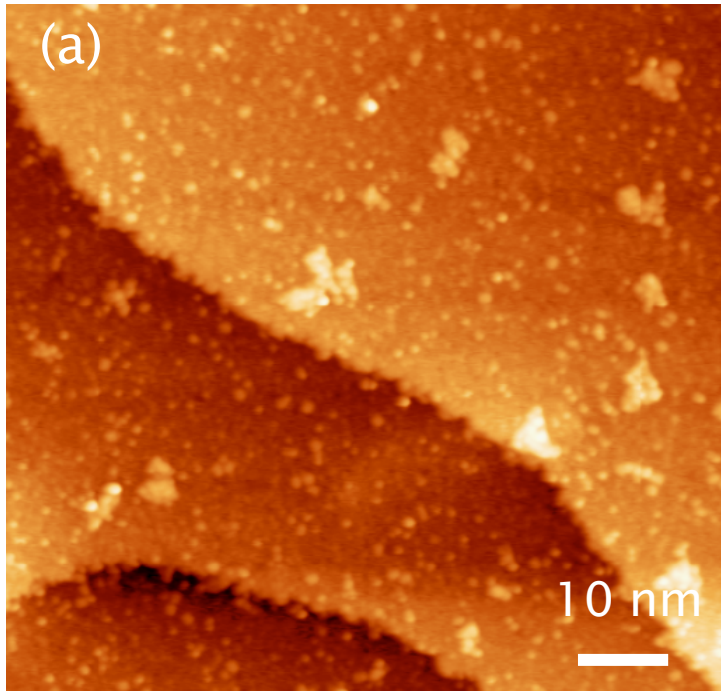
- Micromechanical cleavage of HOPG
  - Thermal decomposition of SiC
  - Chemical-based methods  
(chem-cleave HOPG, ...)
  - Upzip carbon nanotubes
  - Epitaxial growth on solid surfaces
- 



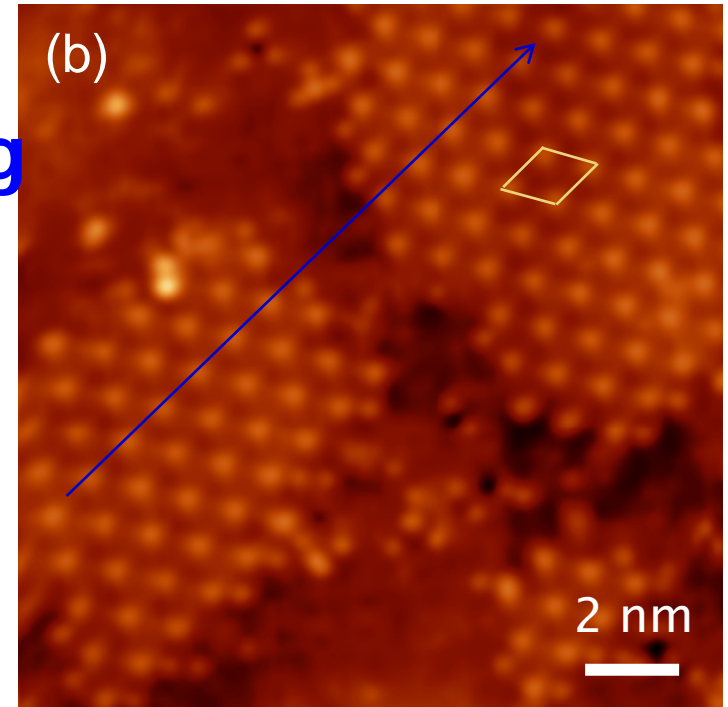
# Sample Preparation and STM Imaging

Depositing Ge @RT

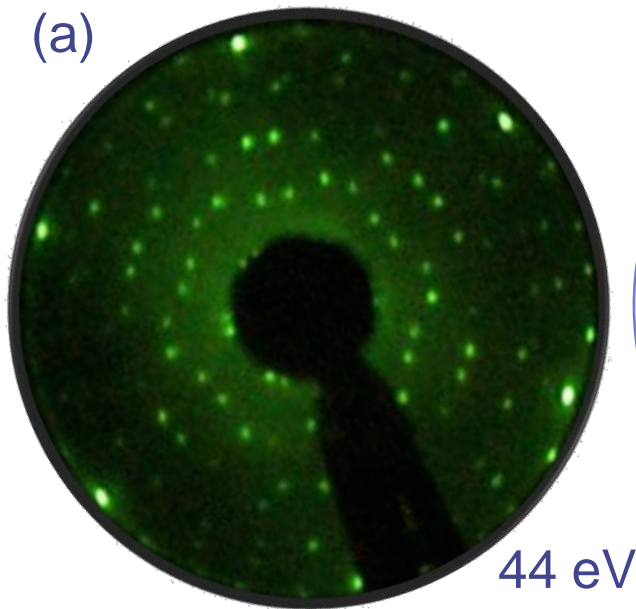
Ordered structures



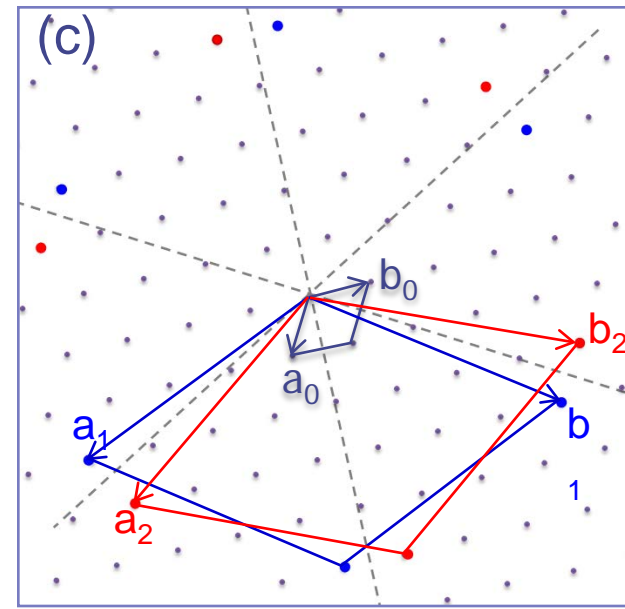
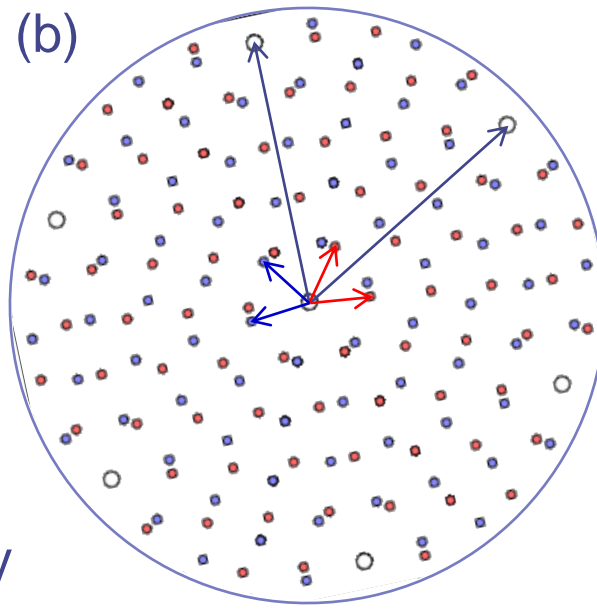
Annealing



# LEED Patterns of Ge Adlayer on Pt(111)



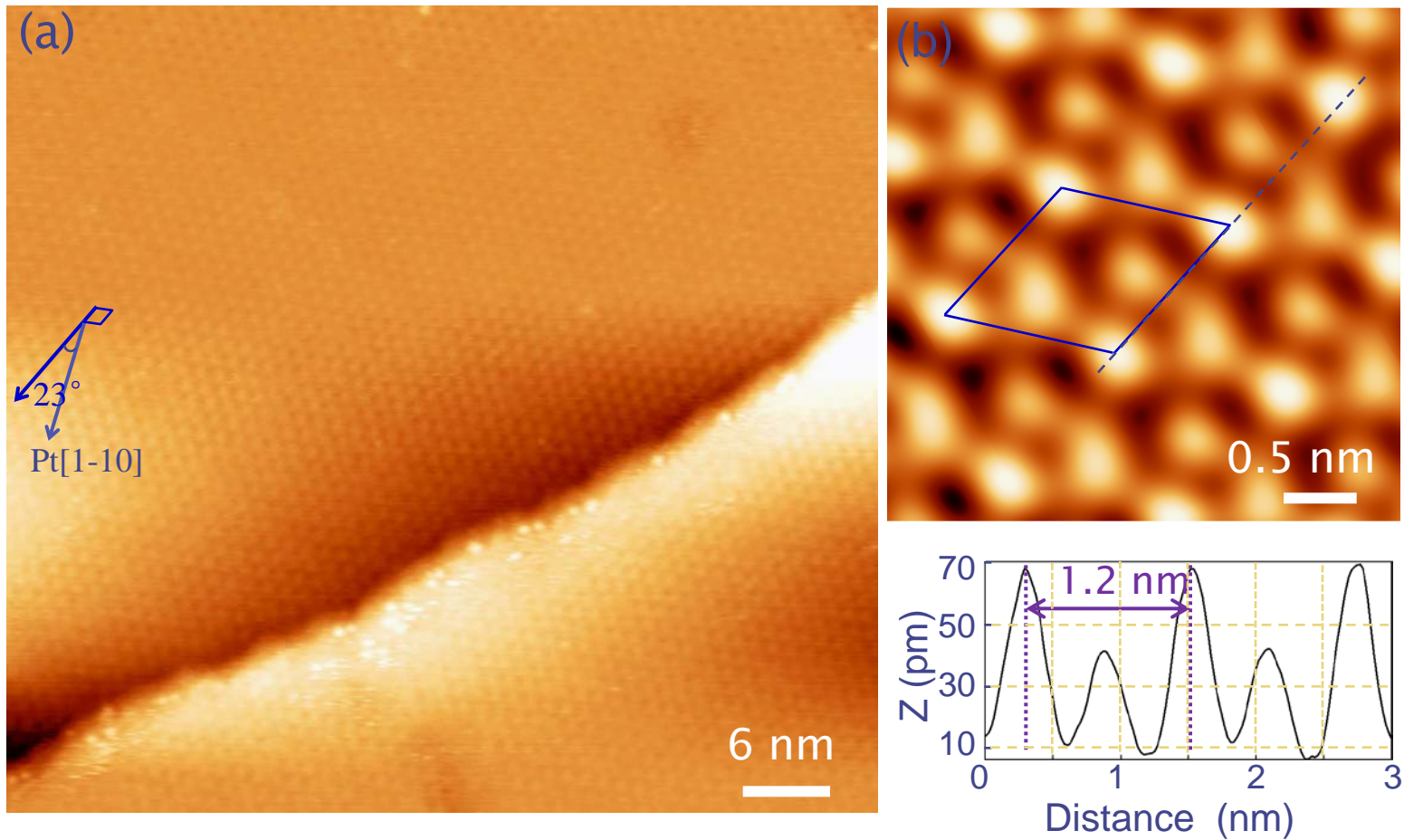
Reciprocal space



Real space

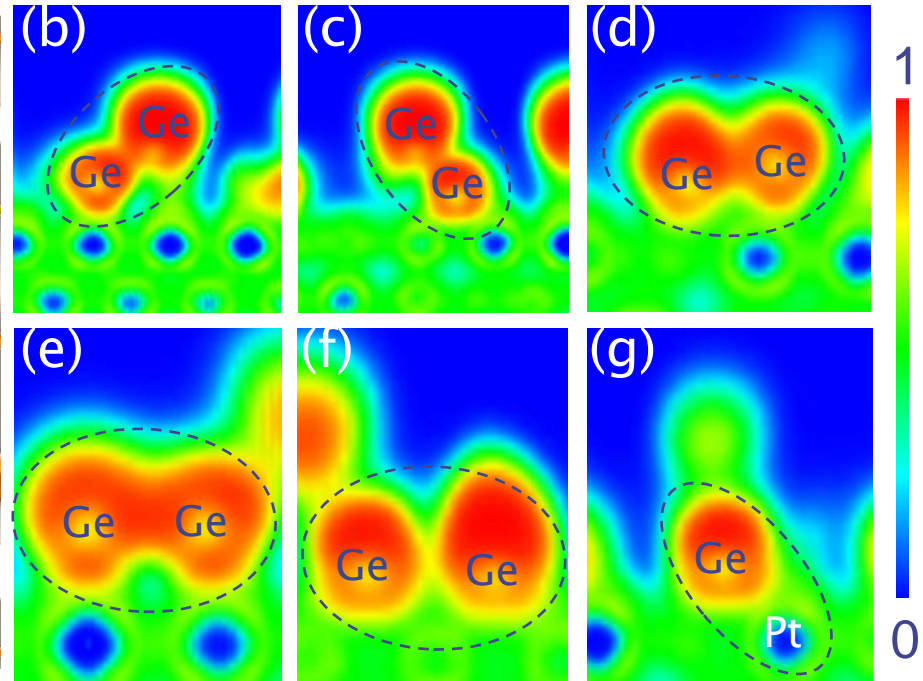
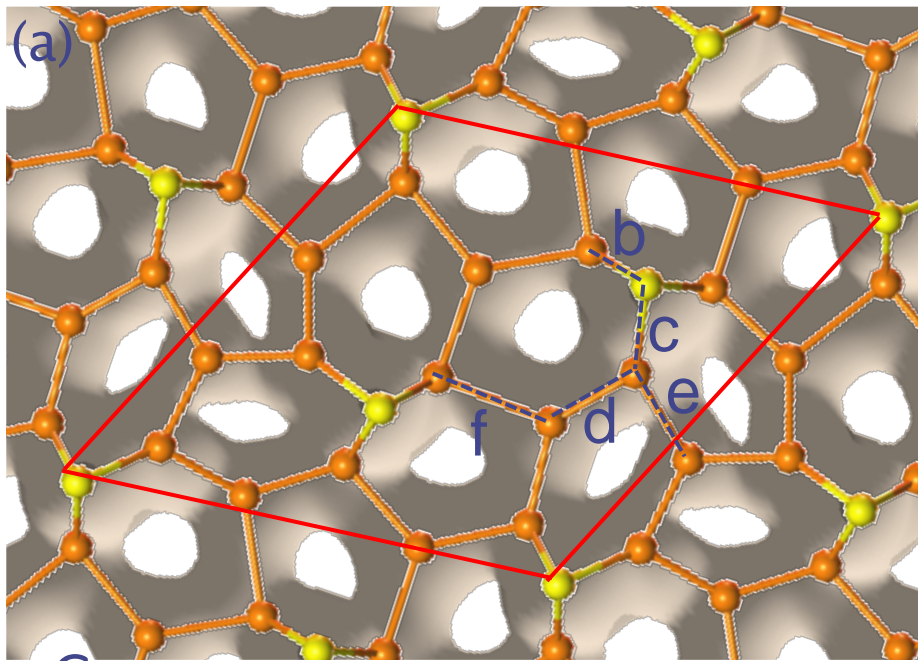
➤  $(\sqrt{19} \times \sqrt{19})$  superstructure with respect to the substrate lattice

# STM: buckled Ge adlayer on Pt(111)



- $\sqrt{19} \times \sqrt{19}$  superstructure accords with LEED observations

# Evidence of covalent interaction between Ge atom pairs



(a) Top view of overall ELF (electron localization function) of 0.5, showing a continuity of the Ge layer.

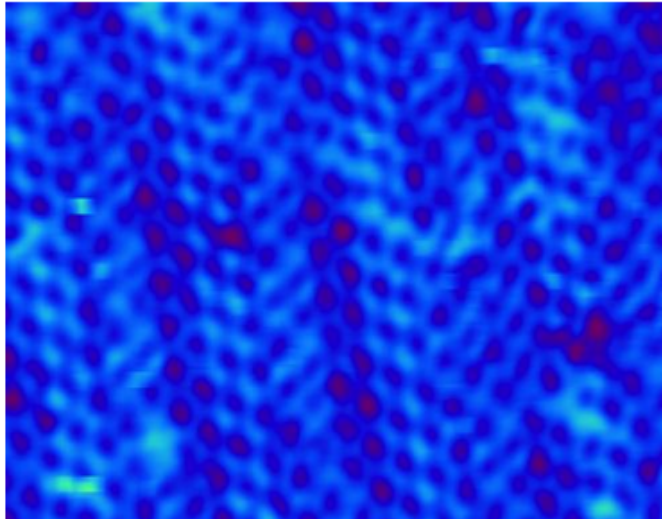
(b-f) Cross section of ELFs along each Ge pair: covalent interaction existing between Ge-Ge atoms.

A 2D continuous Ge layer, **Germanene**, was successfully fabricated on Pt(111).

## Meet Germanene, Graphene's Newest 2-D Competitor

It's a single-atom-thick array of germanium atoms that could make for super fast transistors.

By Francie Diep | Posted 09.10.2014 at 10:00 am



**Under the Microscope** A scanning tunneling microscope image of germanene *M. E. Dávila et al., New Journal of Physics, 2014*

Guy Le Lay says he's working his way down the periodic table. In 2011, he was the senior scientist on a research team that was the first to say it had created **silicene**, a one-atom-thick array of silicon atoms. Silicene is the silicon equivalent of graphene, which is a flat array of carbon atoms with a number of potential applications in super fast computing. Silicon also happens to be just below carbon on the periodic table. Le Lay and his colleagues are **publishing evidence** that they've made germanene, a material made of a single layer of atoms of germanium.

### Germanene on Au(111)

The report from Le Lay, a professor emeritus of nanotechnology at the Aix-Marseilles University in France, comes just a month after a Chinese

Meet Germanene, Graphene's Newest 2-D Competitor  
atoms of germanium, the next element down the list.

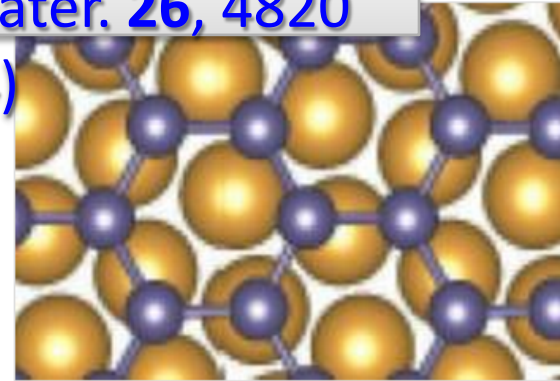
The report from Le Lay, a professor emeritus of nanotechnology at the Aix-Marseilles University in France, comes just a month after a Chinese team became the **first to create** germanene. The coincidental publishing highlights the work scientists have put into making two-dimensional materials.

.....comes just a month after a Chinese team became the **first to create** germanene.

to across graphene.

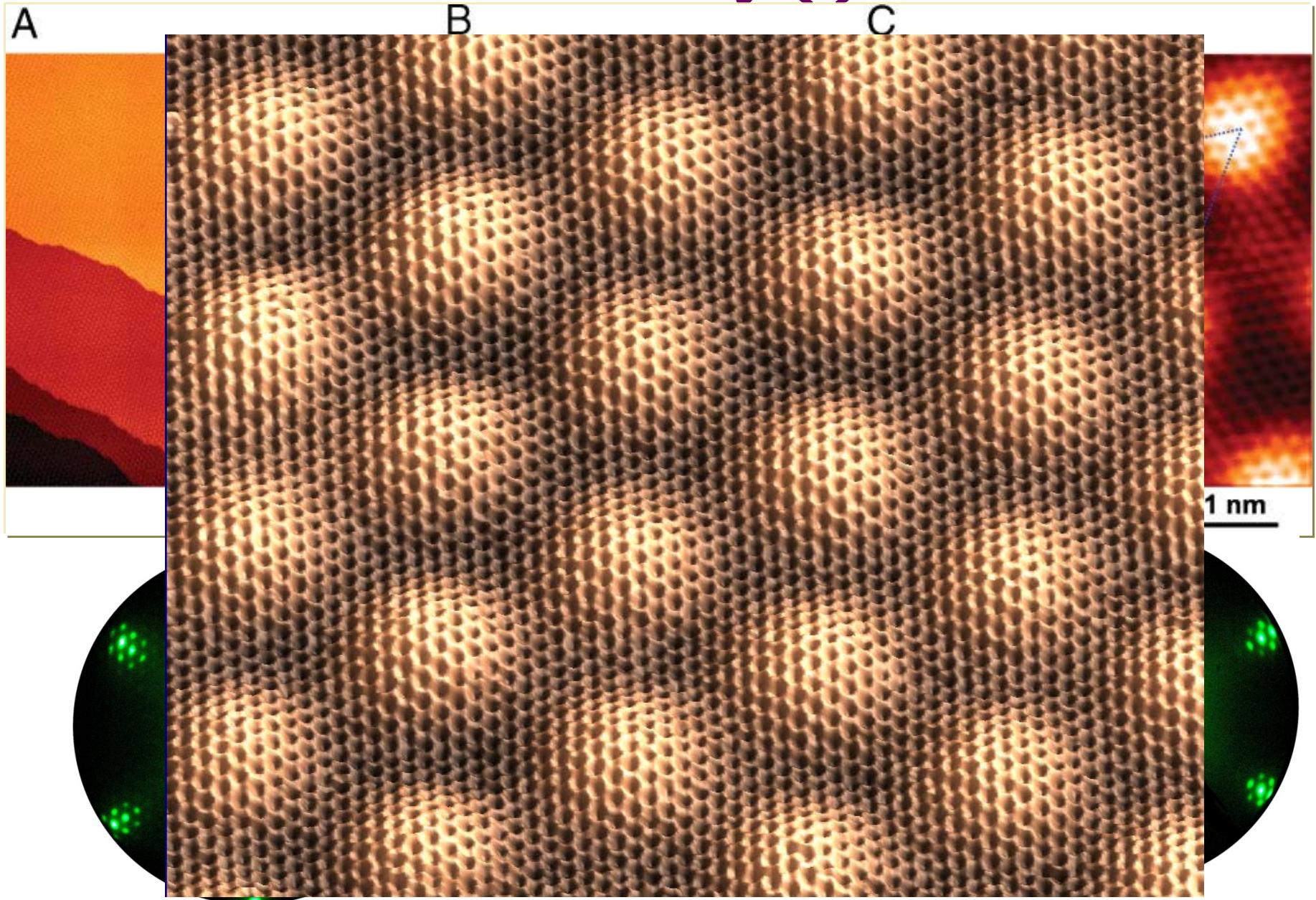
**L.F.Li et al., Adv. Mater. 26, 4820**

It's hard to say if it's the computers of our future. Graphene? Germanene? Tinene, a 2-D array of tin atoms, which Le Lay wants to make next? (Yes, tin is the next element underneath germanium.) Every 2-D material has its own strengths and weaknesses. Germanene and silicene have natural bandgaps, a quality necessary for transistors, while graphene does not. Graphene has been studied far longer, however, so engineers are better at manufacturing it. They've already tried making transistors with graphene, using workarounds to deal with its lack of bandgaps.



**Picture This** This illustration shows the arrangement of germanium atoms (purple) in germanene. The golden atoms in the background represent germanene's gold substrate. *M. E. Dávila et al., New Journal of Physics, 2014*

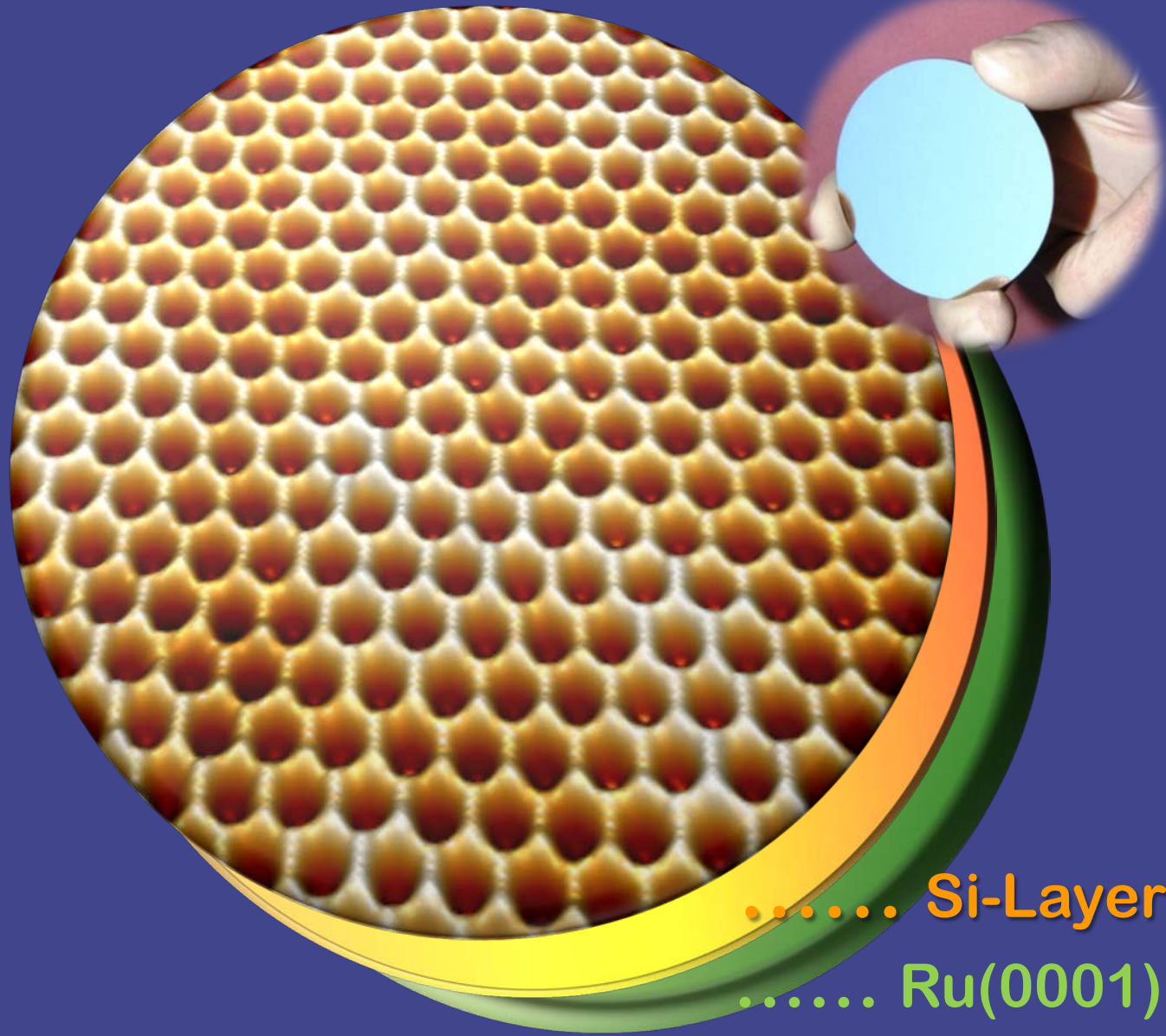
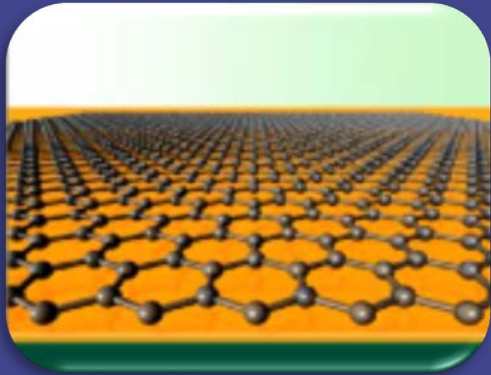
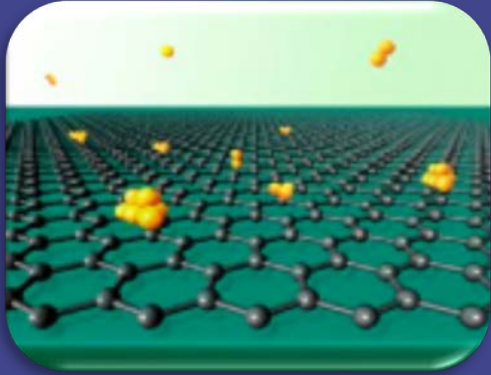
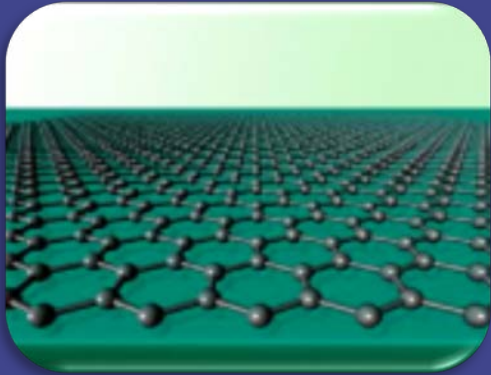
# Summary (I)



**Formation of Large-scale Single Crystalline Graphene Monolayer**



# Summary (II)

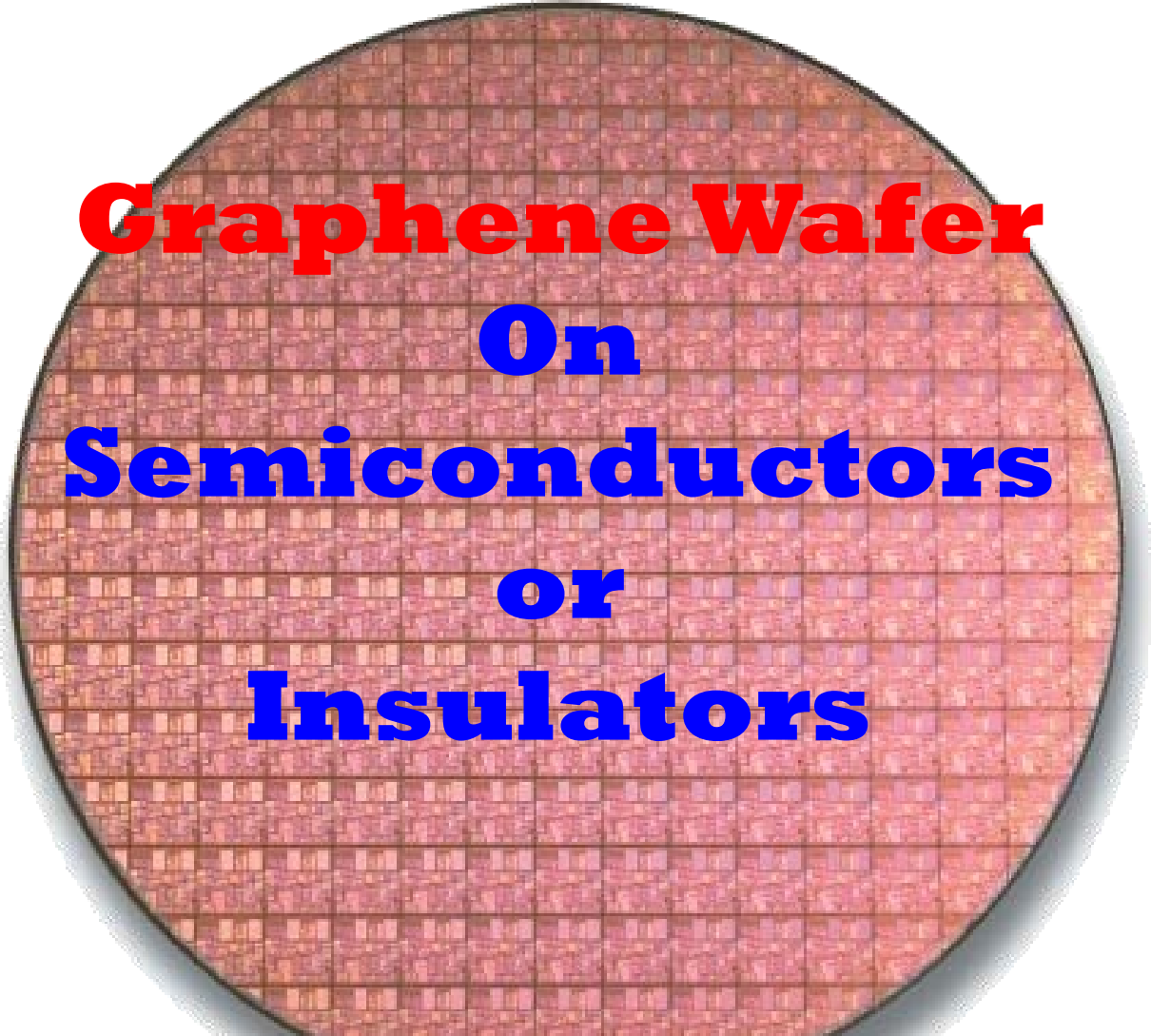


..... Si-Layer

..... Ru(0001)

# Outlooks

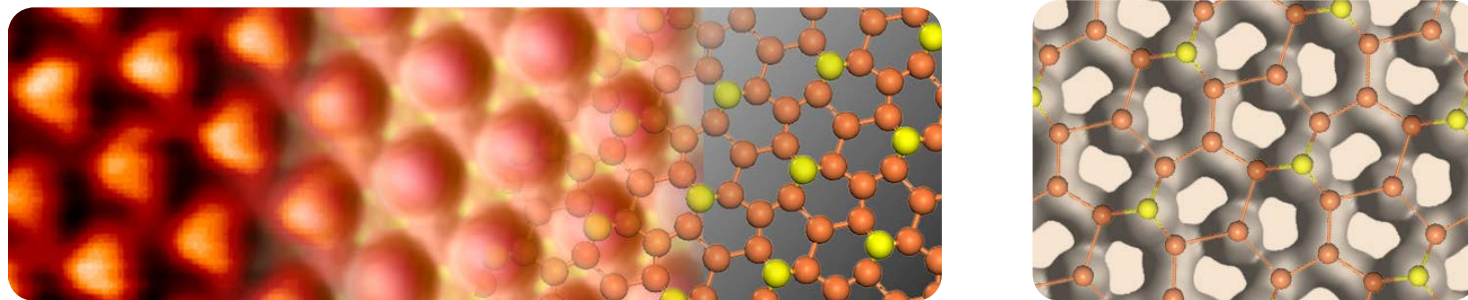
**Graphene Wafer and Graphene Complex Systems for the  
Future Nano-Electronics or Mol-tronics**

A circular graphic with a grid pattern, containing text about graphene wafers. The text is centered and reads: 

**Graphene Wafer  
On  
Semiconductors  
or  
Insulators**

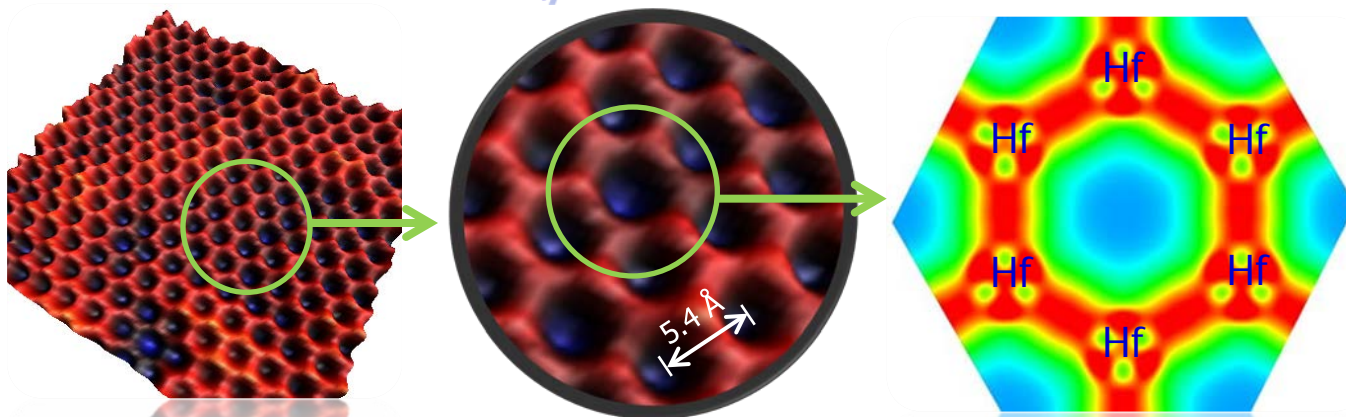
# Summary (III)

## Buckled Silicene Formation on Ir(111)

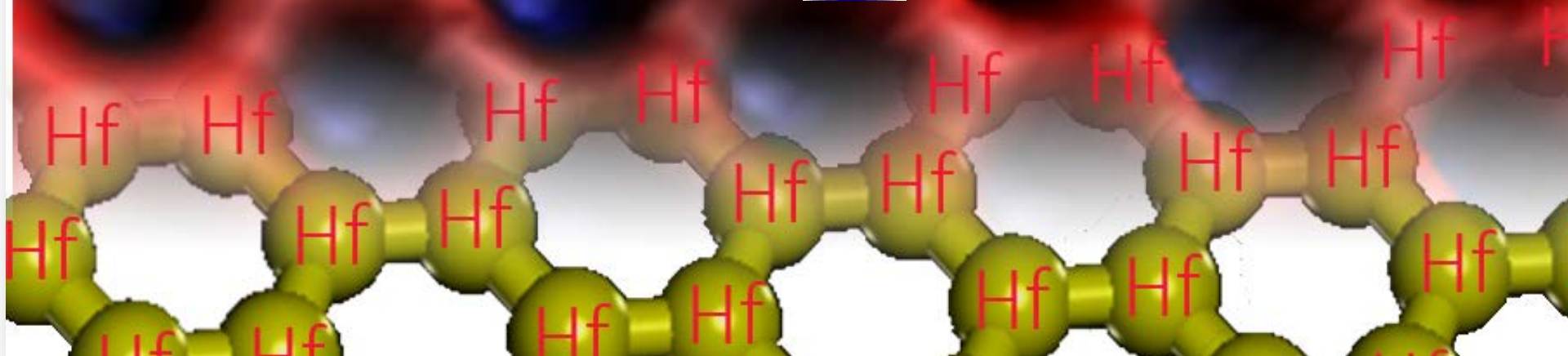
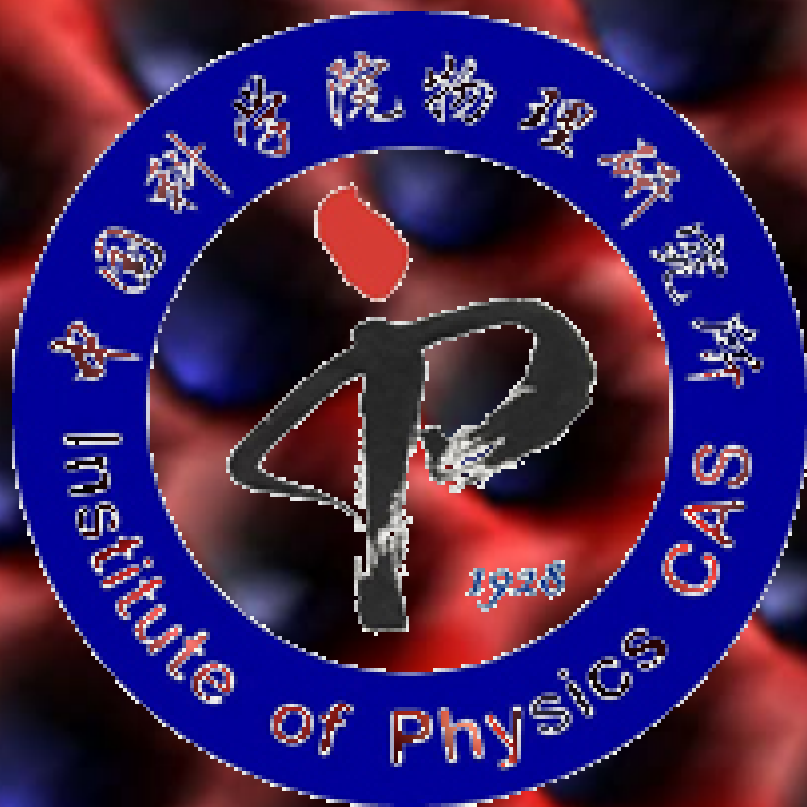


*Nano Lett.* **13**, 685 (2013)

## 2D Transition Metal Honeycomb Lattice: Hafnene on Ir(111)

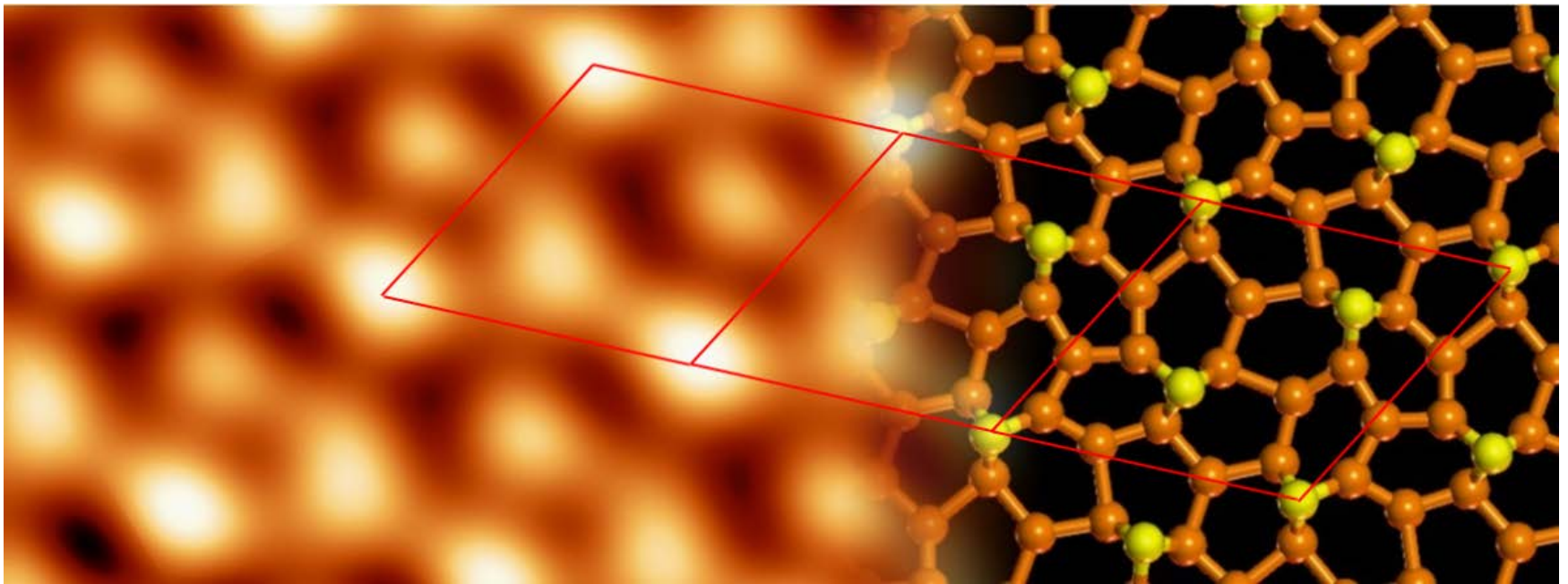


*Nano Lett.* **13**, 4671 (2013)



# Summary (IV)

## Germanene on Pt(111)



L.F. Li, Y.L. Wang/H.J.Gao *et al.*, Adv. Mater. 26, 4820(2014)

# Acknowledgements

L. Gao, Y.L. Wang, X. Lin, Y. Pan, Q. Liu, H.G. Zhang, Z.T. Deng, Z.H. Cheng, X.B. He, W. Ji, S.X. Du, C.M. Sheng, D.X. Shi, and .....

IOP CAS, China

**Werner Hofer**

*Liverpool Univ., UK*

**Hong Guo**

*Mcgill U., Canada*

**Feng LIU**

*Utah U., USA*

**X.C. Xie**

*IOP/ASU*

o o o o o o

The National Science Foundation of China,  
MOST "863" and "973" projects, and  
Chinese Academy of Sciences



谢谢大家!

## *What Else for Graphene/Ru(0001)?*

- *It can be as a Graphene-based Quantum Dots*
- *It can provide a way of Direct Imaging of Intrinsic Molecular Orbitals*
- *It can provide a way of Formation and Tuning of Kagome Lattices of Magnetic Molecules*
- *It can provide a way of Selective Adsorption of Monodispersive metal clusters and Magnetic Molecules*



## FAST TRACK COMMUNICATION

## Graphene based quantum dots

 H G Zhang<sup>1</sup>, H Hu<sup>1</sup>, Y Pan<sup>1</sup>, J H Mao<sup>1</sup>, M Gao<sup>1</sup>,  
 S X Du<sup>1</sup>, T Greber<sup>2</sup> and H-J Gao<sup>1</sup>
<sup>1</sup> Institute of Physics, Chinese Academy of Sciences, PO Box 603, Beijing 100049, People's Republic of China

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### Abstract

Laterally localized electronic states are identified on a corrugated graphene surface by low temperature scanning tunneling spectroscopy (STS). The corrugations are 3 nm and comprise regions of about 90 carbon atoms. This dot-array with molecular precision. It is evidenced by quantum dot-like energy levels and energies that relate to the corrugation of the graphene layer. The energy levels are modeled by a layer height dependent potential-well which describes the barrier for electron penetration into graphene. The energy levels are highest and lowest in energy on the isolated 'hill' regions which are decoupled from the surface.

(Some figures in this article are in colour only in the electronic version.)

J. Phys.: Condens. Matter 22 (2010) 302001

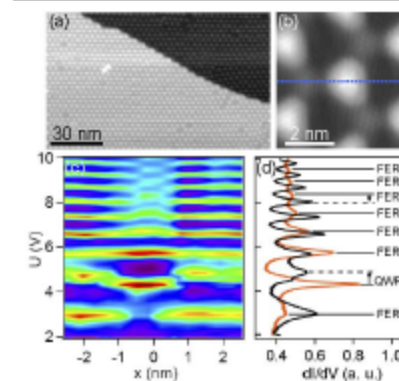
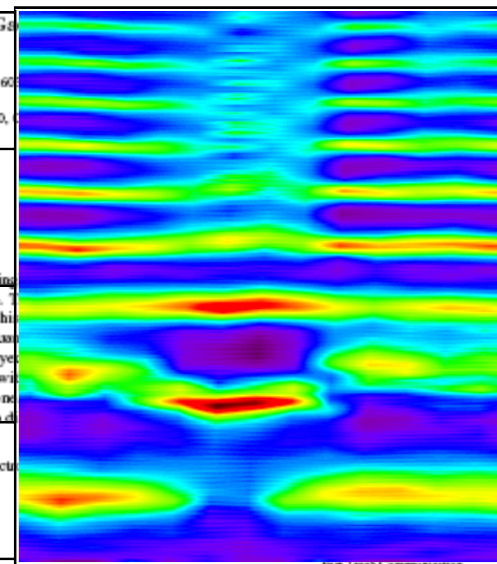


Figure 1. STM image and STS for monolayer graphene on Ru(0001). (a) Large-scale ( $U_t = -2.0$  V,  $I_t = 100$  pA) STM topographic image across two substrate terraces separated by a monoatomic step. (b) A high resolution image, the dotted line indicates the cut shown in (c). (c) Color-scale map of the conductance ( $dI/dV$ ) into the unoccupied substrate states as a function of tunneling voltage  $U$  and position along the dashed line marked in (b). The center of the hill is taken as the zero position. (d) Conductance  $dI/dV$  spectra on the hill  $x = -0.2$  nm (orange, grey) and the valley  $x = 2.0$  nm (black). The spectra are taken at constant current  $I_t = 100$  pA.


 related to the corrugation, where about one third has a 0.6 eV binding energy [21]. On the other hand, in the valleys no such splitting could be found. Only one dispersive  $\pi$  band with a relatively large gap was observed [14]. This seeming paradox of absence of quantum induced splitting in the valence band [22] may be resolved if we assign to the hills a molecule like behavior as isolated quantum dots, without dispersion. The isolation of these dots and the concomitant electronic states are related to the corrugation of the structure, where the lift off of the hills causes lateral localization. The vertical localization arises from the interface and is pronounced by the decoupling of the graphene layer from the substrate.

$dI/dV$  conductance spectra are shown as a  $U$  versus  $x$  map in figure 1(c), where  $U$  is the tunneling voltage and the  $x$  axis corresponds to the dotted line in figure 1(b). The color code represents the conductance from the tip into unoccupied states of g/Ru(0001). Clearly, a series of resonances at distinct tunneling voltages is observed. The energies and the sharpness of the resonances change within the 5 nm cut across the super-cell. One of these peaks, the second lowest one, shows a behavior that deviates from the others, which are the well known field emission resonances (FERs), sometimes called image potential states, ubiquitous at tip-surface junctions [23, 24]. The FER energies may be used to determine the local work function, whereby a decrease in energy indicates a decrease of the work function of the probed surface region [25, 26]. For the present case, g/Ru(0001), the FER energy increase on the hill confirms the local work function shift as found by photoemission from adsorbed xenon [14]. The peak that opposes the trend of

Volume 22 Number 30 4 August 2010

### Featured in this issue

Surface, Interface and Atomic-Scale Science

### Special section

Atom-surface scattering

Guest Editor: Salvador Miret-Artés


[iopscience.org/jpcmm](http://iopscience.org/jpcmm)

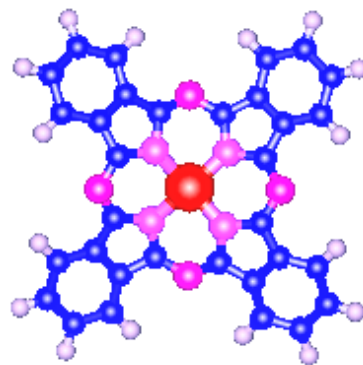
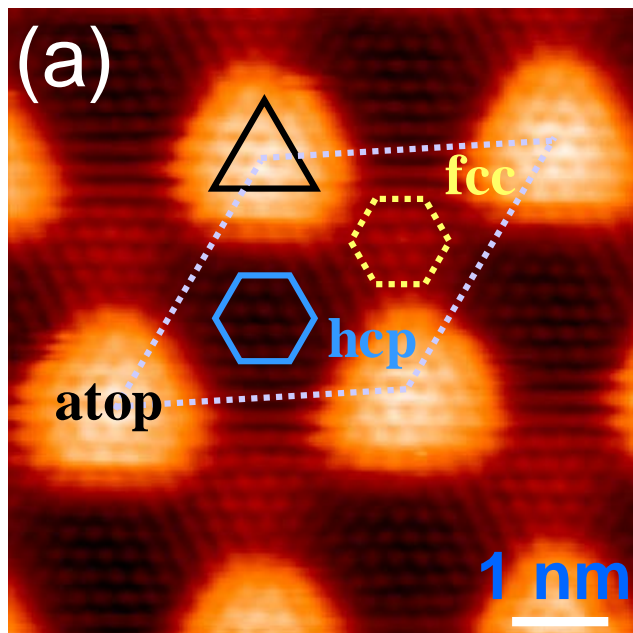
IOP Publishing

# Selective Molecular Adsorption at the Initial Stage

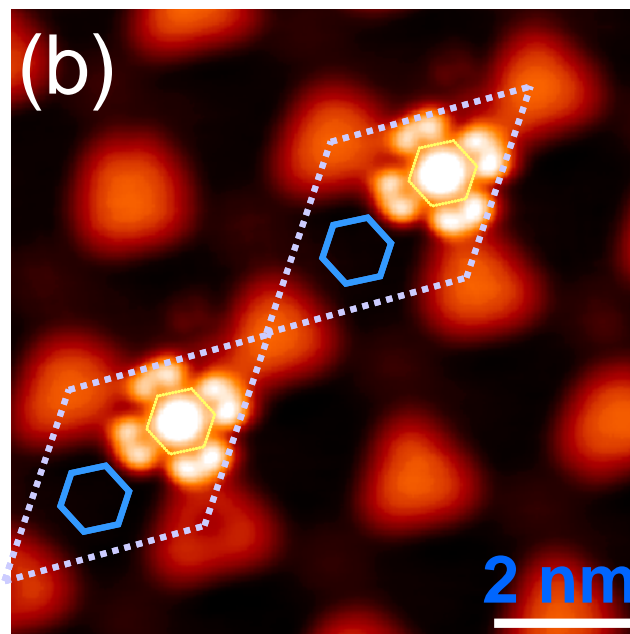
Graphene/Ru(0001)

FePc

FePc/Graphene/Ru(0001)

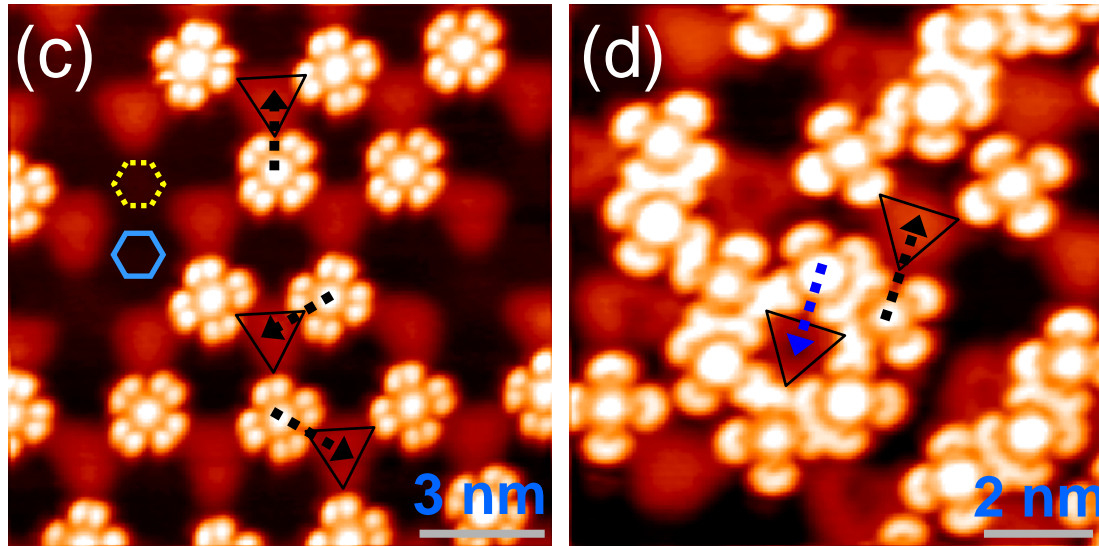


● Fe ● N ● C ● H



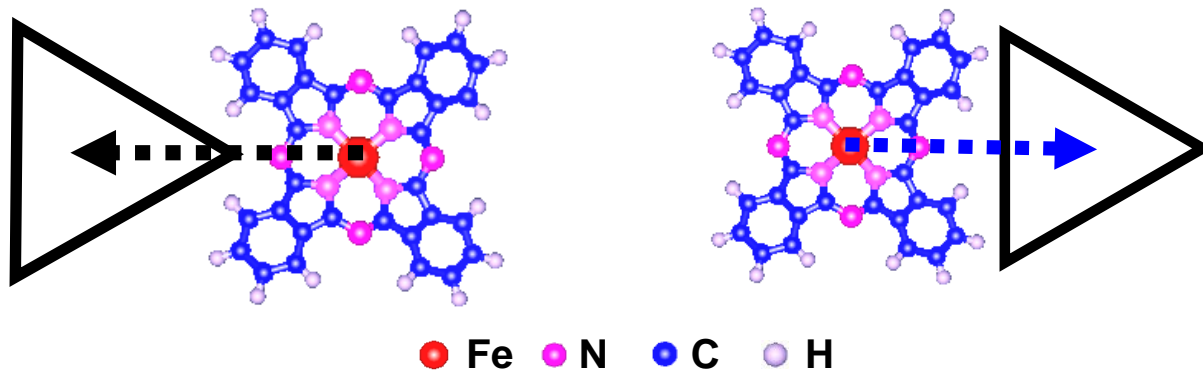
(H.G. Zhang/H.J. Gao *et al.*, PR B 84, 245436(2011))

# Adsorption Sites and Orientations with Increasing Coverage

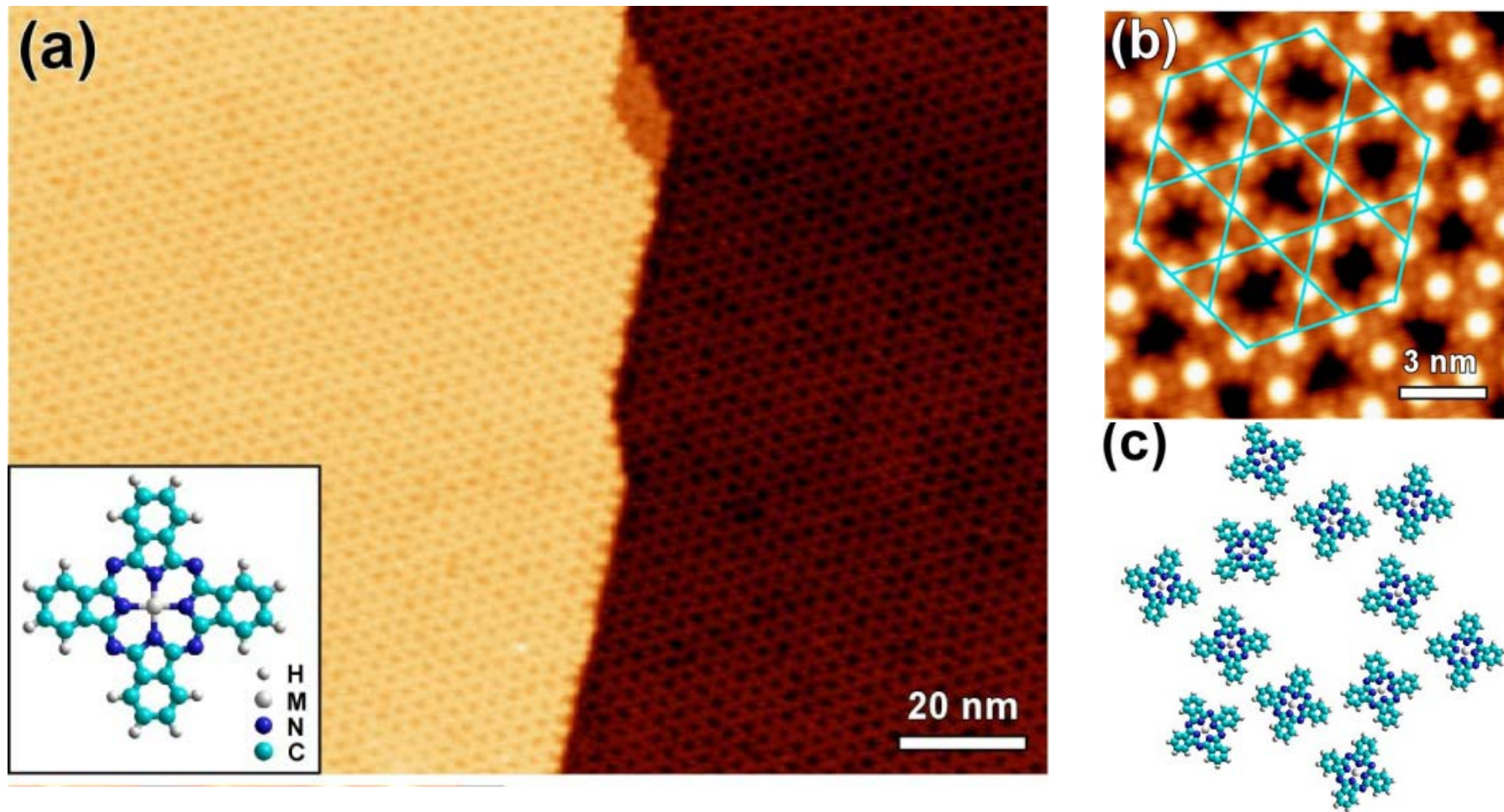


"A" type at fcc

"B" type at edge of atop



# Kagome Lattice: FePc/MG/Ru(0001)

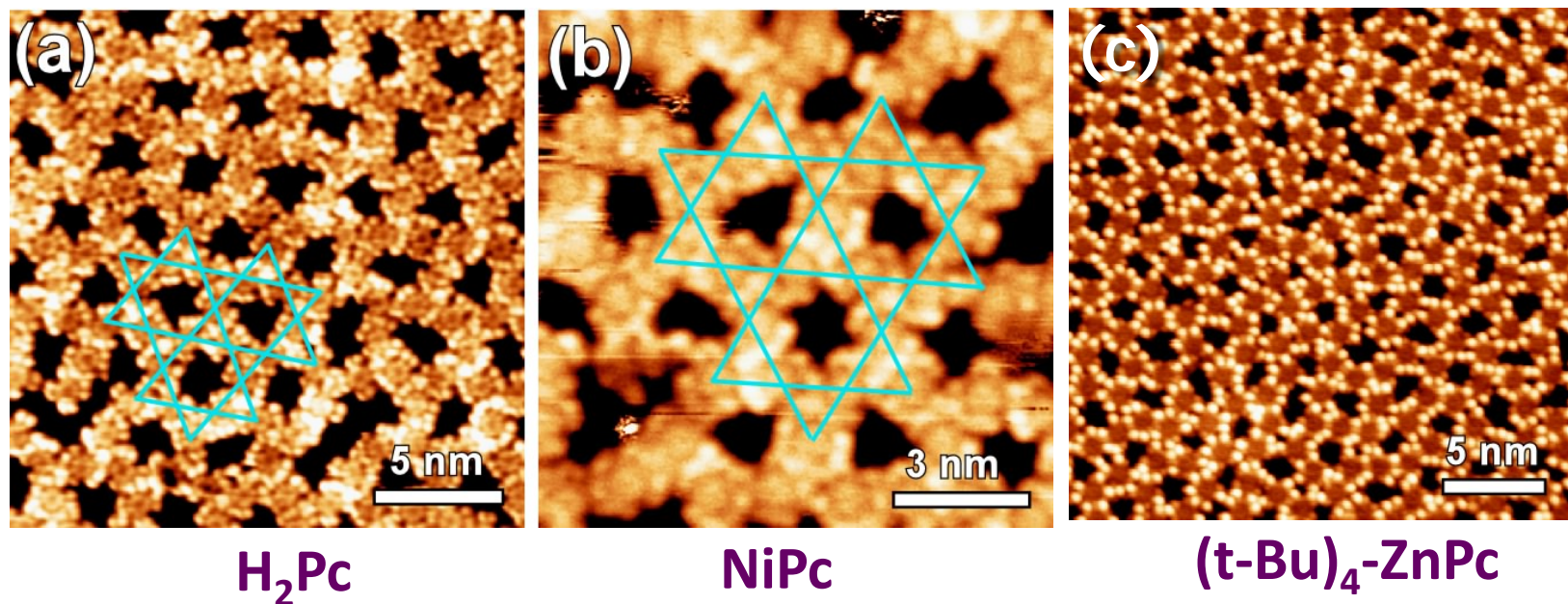


- (a) Kagome lattice of FePc across steps of the Ru(0001) substrate.  
(b) Details of the Kagome lattice of FePc.  
(c) Structural model of the Kagome lattice: molecular orientation disorder.

**(J.H. Mao/H.J. Gao et al., JACS, 131, 14136(2009))**

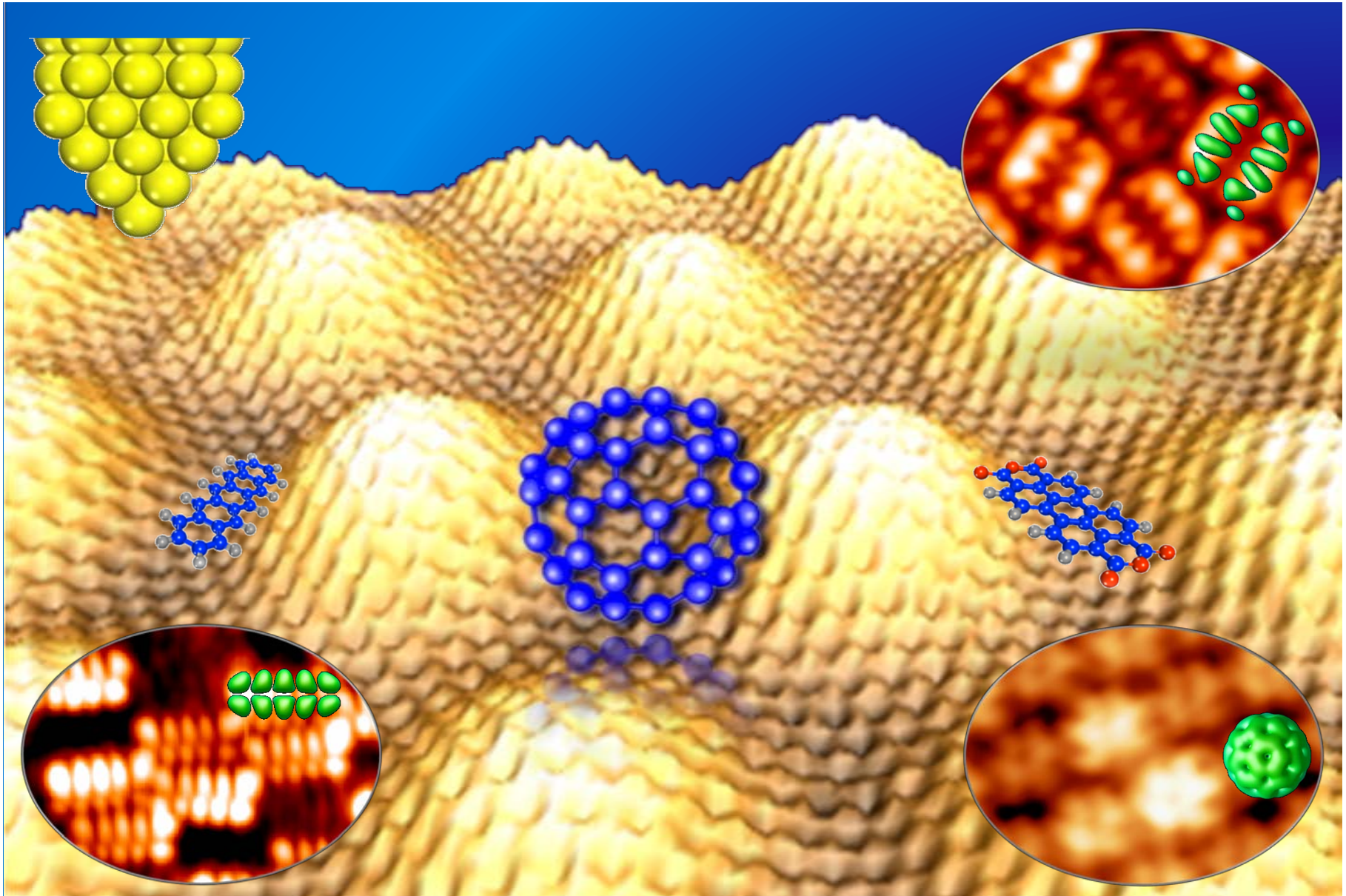
# Kagome Lattice:

$H_2Pc$ ,  $NiPc$ ,  $(t-Bu)_4-ZnPc/MG/Ru(0001)$



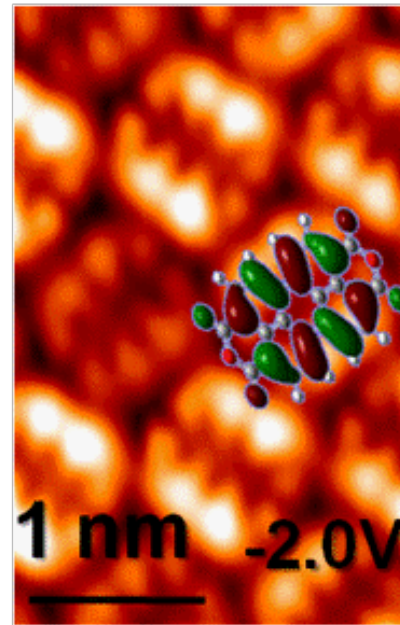
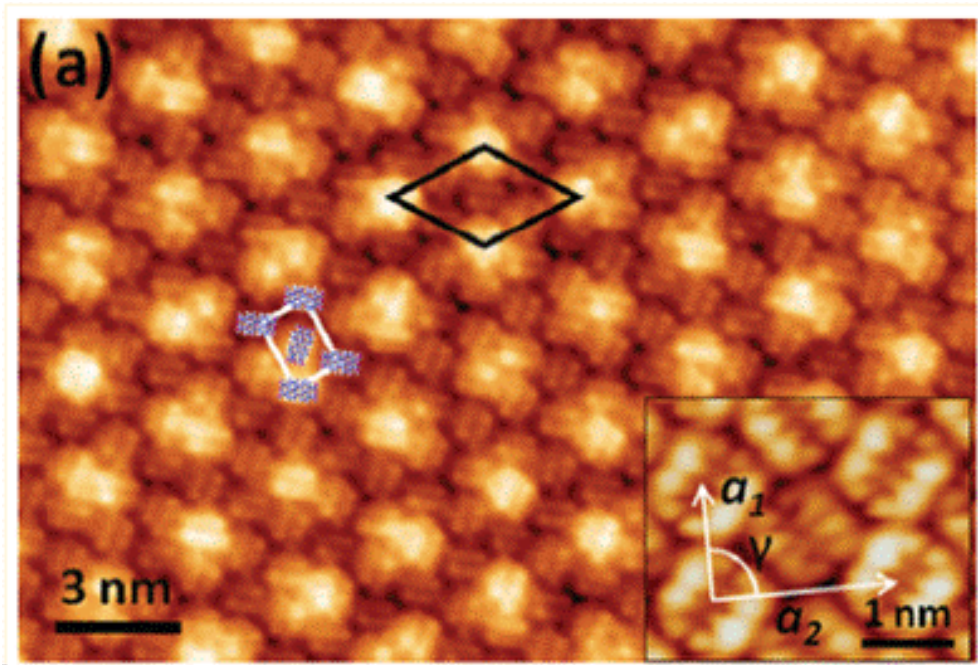
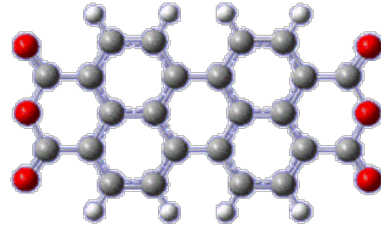
(J.H. Mao/H.J. Gao et al., JACS, 131, 14136(2009))

*Direct Imaging of Intrinsic Molecular Orbitals  
Using Epitaxially-grown Graphene  
For Study of Single Molecules*

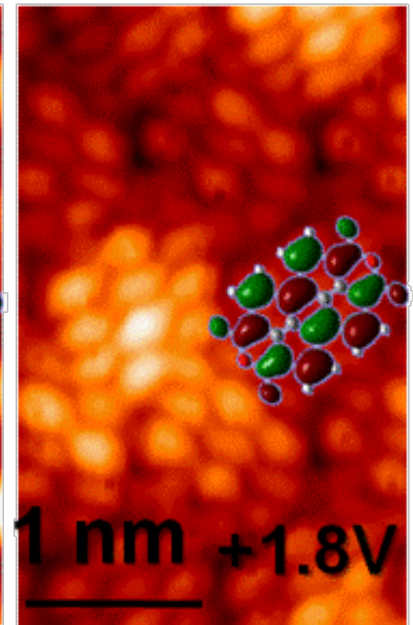


*Intrinsic Molecular Orbitals Observed after Graphene/Ru serves  
as a buffer-layer*

PTCDA



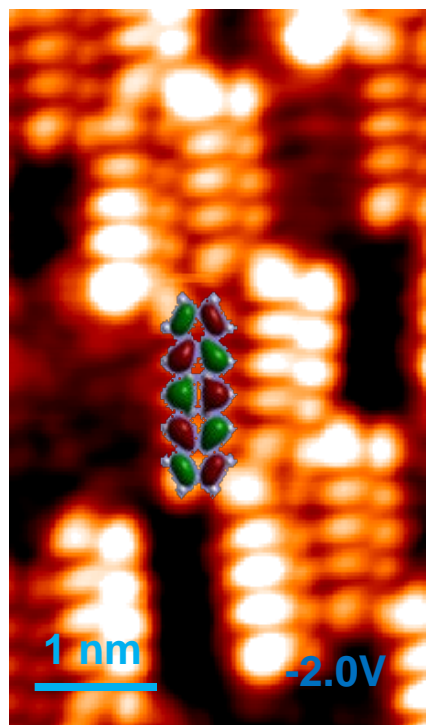
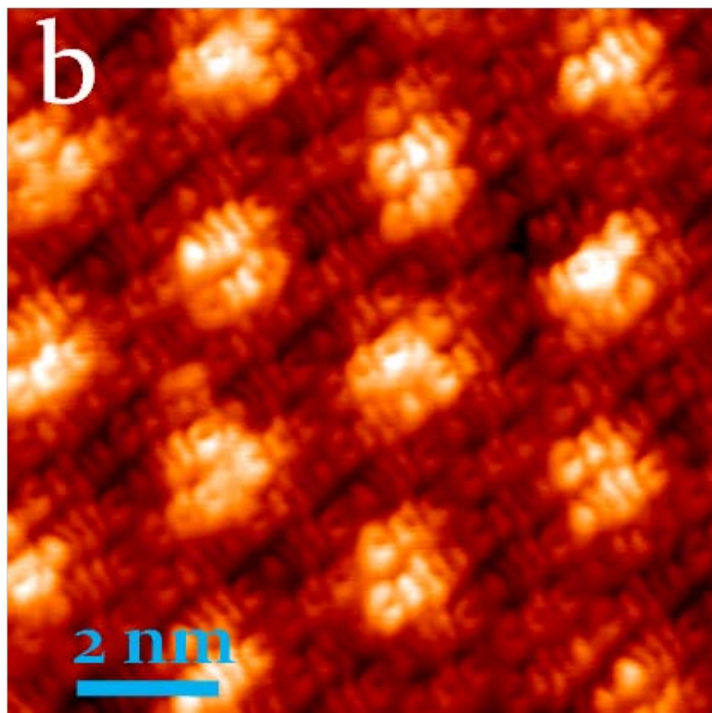
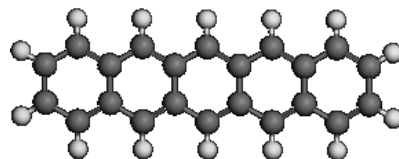
HOMO



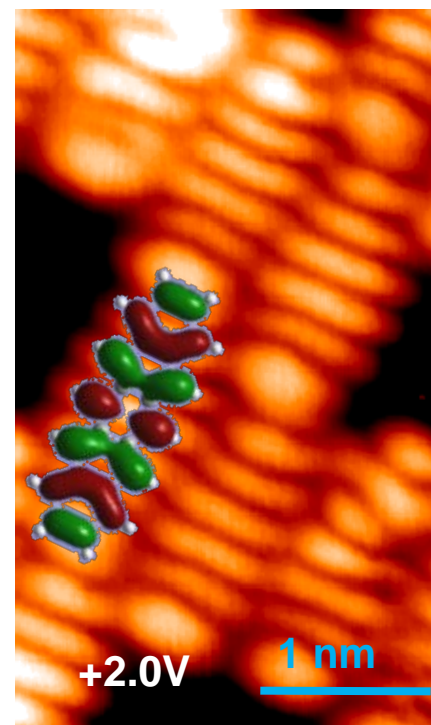
LUMO

# *Intrinsic Molecular Orbitals Observed after Graphene/Ru serves as a buffer-layer*

Pentacene



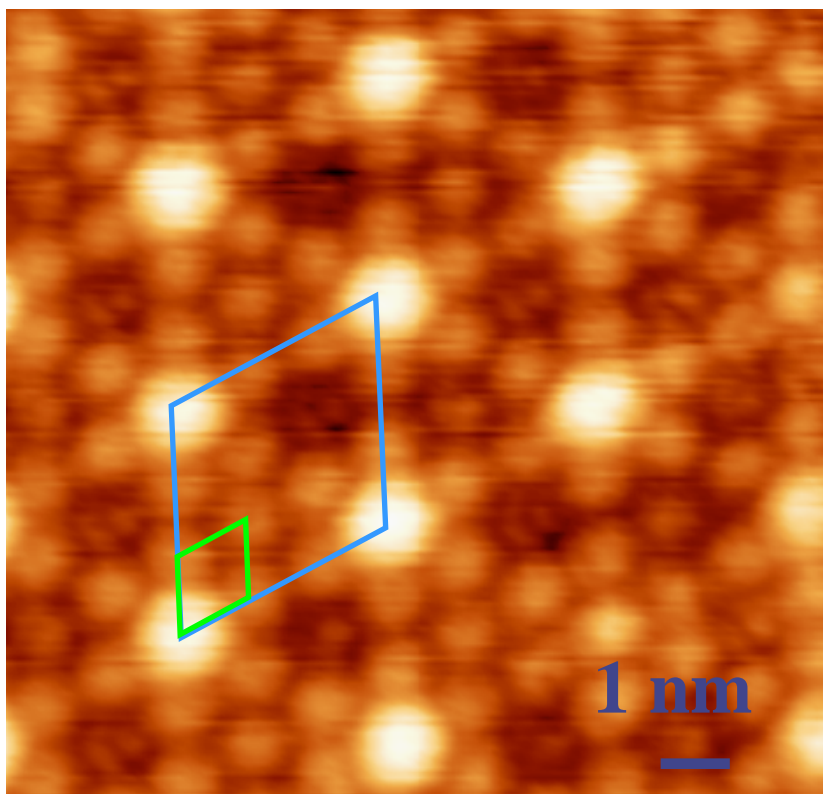
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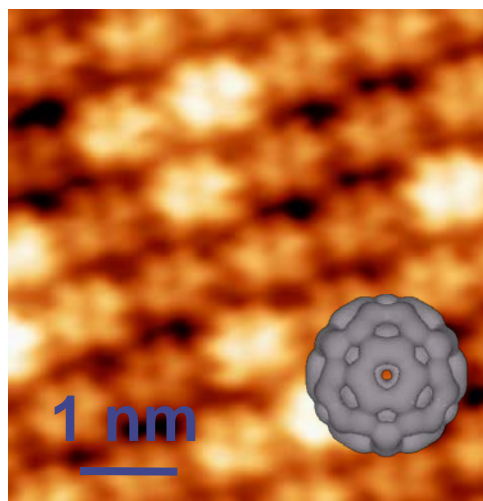
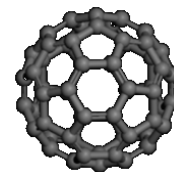
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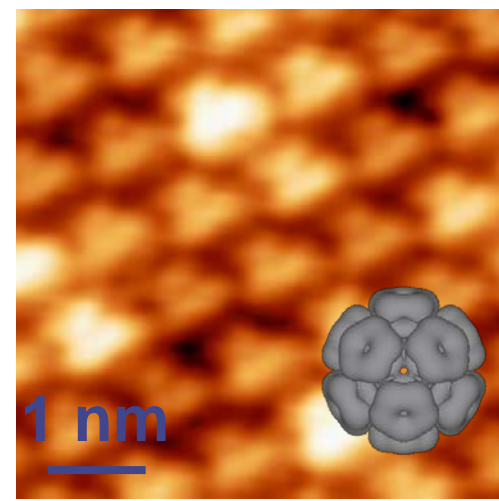
*Intrinsic Molecular Orbitals Observed after Graphene/Ru serves as a buffer-layer*



C<sub>60</sub>



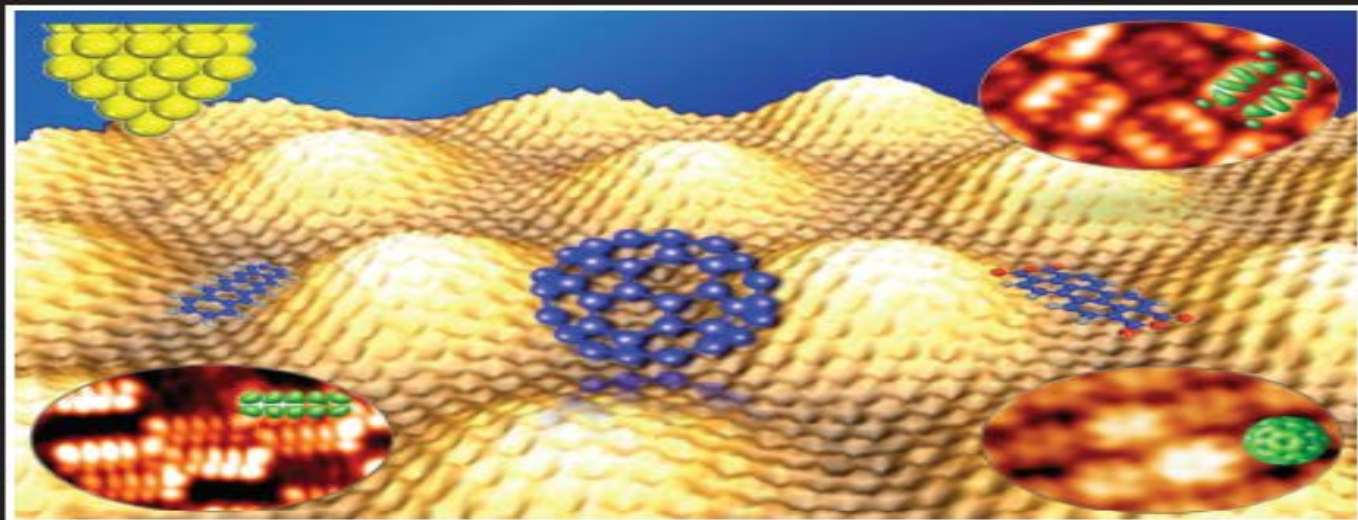
-2.0 V  
HOMO



+1.4 V  
LUMO

Articles published week of 10 OCTOBER 2011  
Volume 99 Number 15

# APPLIED PHYSICS LETTERS



AIP

## Research Highlights

*Nature Nanotechnology*

Published online: 18 September 2009 | doi:10.1038/nnano.2009.301

Subject Categories: [Nanoparticles](#) | [Surface patterning and imaging](#)

### Platinum nanoclusters: Made to order

Adarsh Sandhu

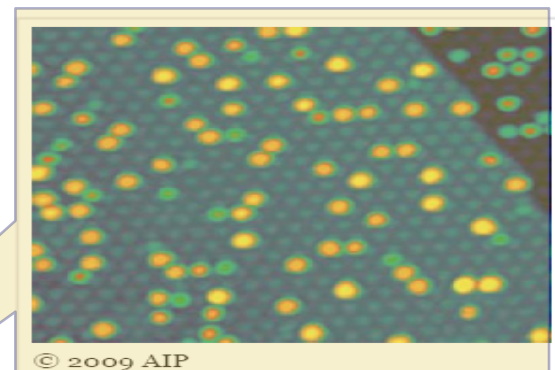
#### Growing mono-dispersed platinum nanoclusters using a graphene Moiré template.

Metallic nanoclusters dispersed across the surface of a support material are used as catalysts in many important chemical reactions. However, controlling the precise size and arrangement of metal nanoclusters is challenging, which hinders the quantitative understanding of their properties. Hong-Jun Gao and colleagues at the Institute of Physics of the Chinese Academy of Science in Beijing and the University of Utah have now developed a method for controlling the size of platinum nanoclusters by using the Moiré structure of graphene on a ruthenium(0001) surface as a template<sup>1</sup>.

The stable graphene Moiré pattern was formed by annealing the ruthenium single crystal to 1,000 K in a vacuum, which caused carbon impurity segregation from the bulk. Platinum was then deposited onto the template by thermal evaporation from a platinum rod placed inside the vacuum chamber.

Using a scanning tunnelling microscope, the researchers found that platinum nanoclusters with diameters of 2–3 nm could self-assemble, forming well-defined arrays on the graphene Moiré unit cells. Notably, the nanoclusters grew by a self-limited, layer-by-layer mechanism, without coalescing.

Hong-Jun Gao and colleagues also suggest that the graphene Moiré-patterned template could be used to grow nanoclusters of numerous other metallic and non-metallic materials.



## Reference

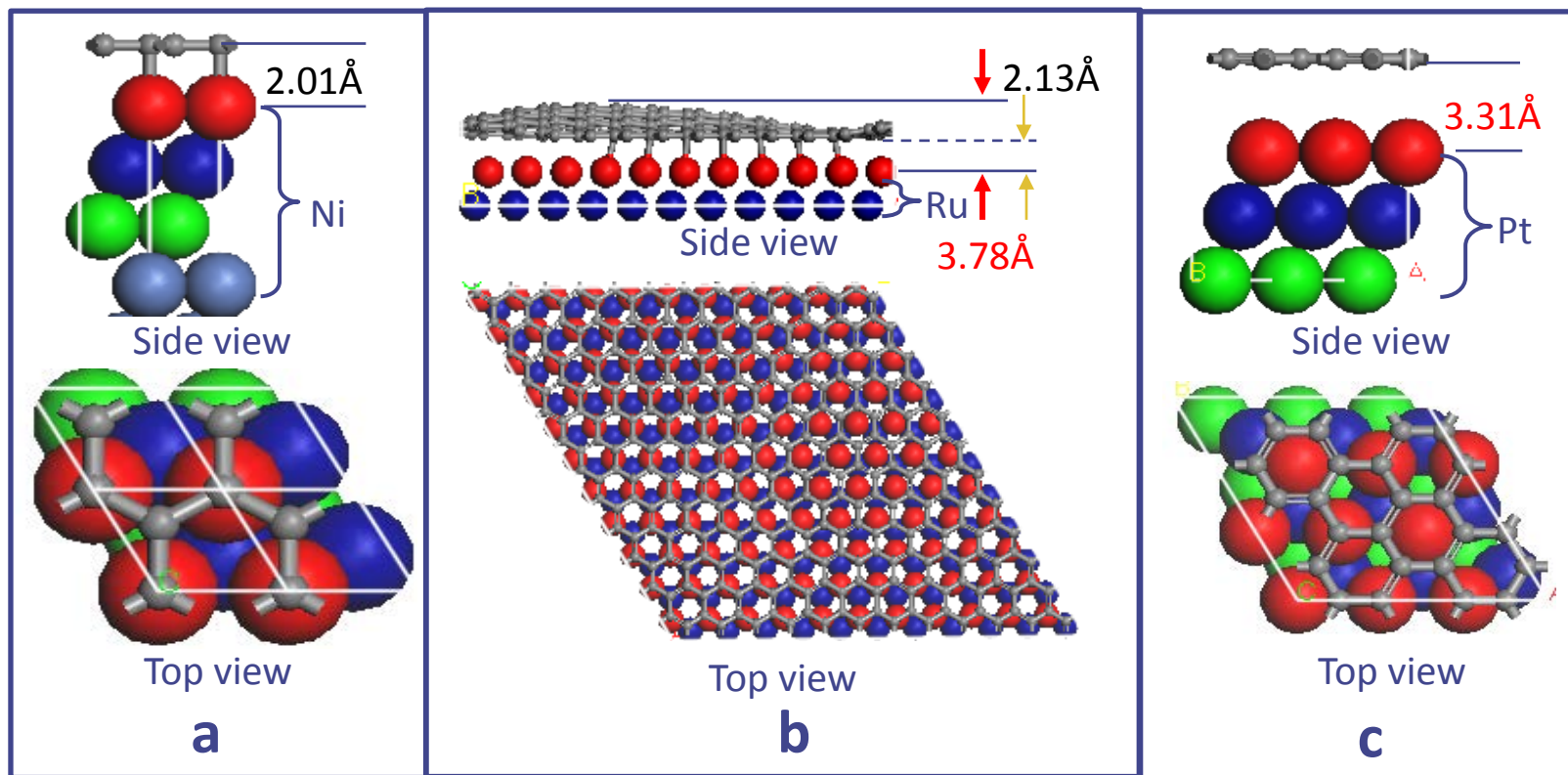
1. Pan, Y., Gao, M., Huang, L., Liu, F. & Gao, H.-J. Directed self-assembly of monodispersed platinum nanoclusters on graphene Moiré template. *Appl. Phys. Lett.* **95**, 093106 (2009). | [Article](#) | [ChemPort](#) |

# *Tunable Interfacial and Physical Properties of Epitaxial Graphene on Metal Substrates*

*M. Gao/H.J. Gao et al., APL, 2010*

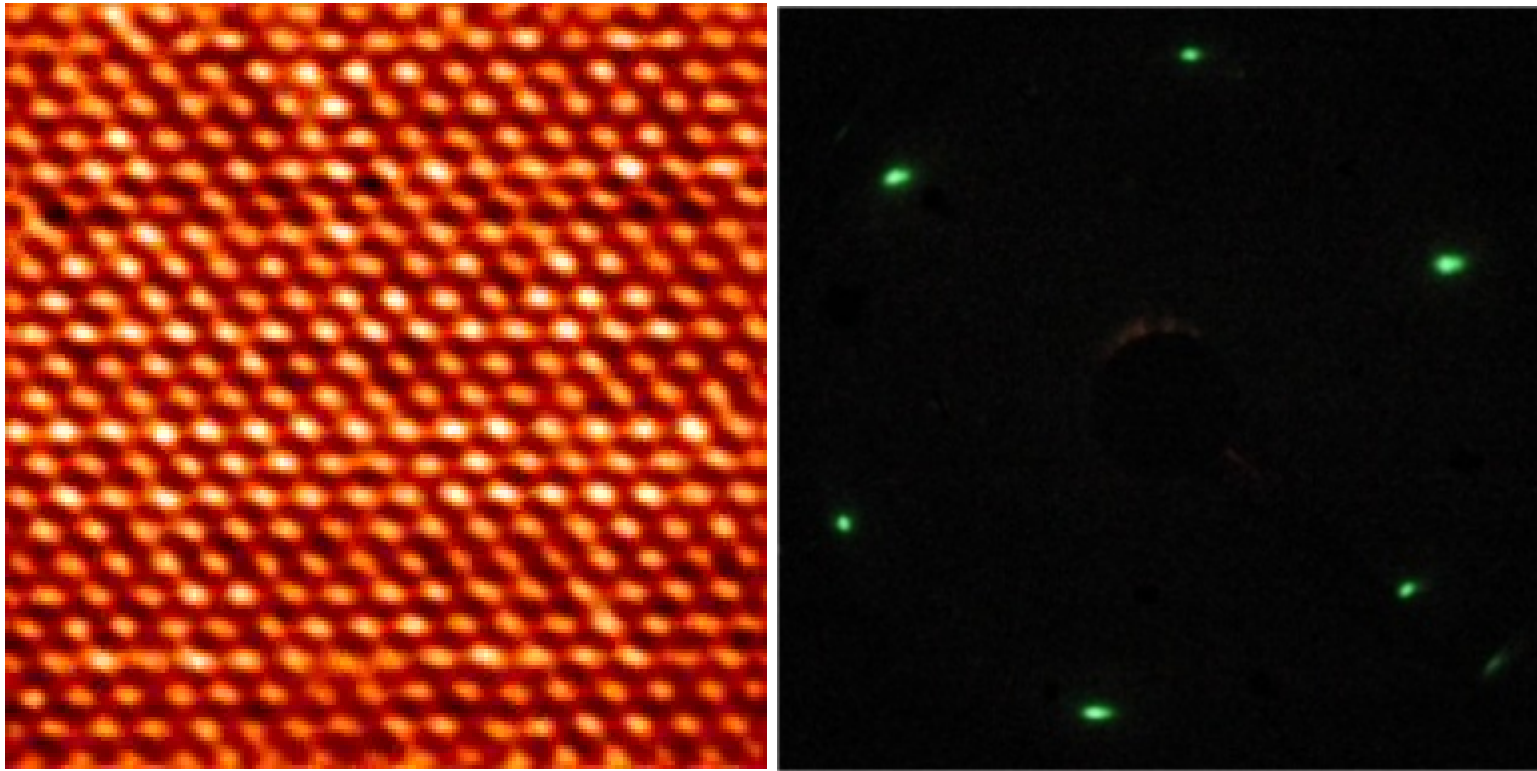
*M. Gao/H.J. Gao et al., APL, 2011*

# Idea and Calculation Results of Graphene Interfacial Structure on Ni(111), Ru(0001) and Pt(111)



- The atomic model of graphene on Ni(111), Ru(0001) and Pt(111).
- On Ni(111). The interfacial distance is 2.01 Å.
- On Ru(0001). The distance is 2.13 Å and 3.79 Å.
- On Pt(111). The distance is 3.31 Å.

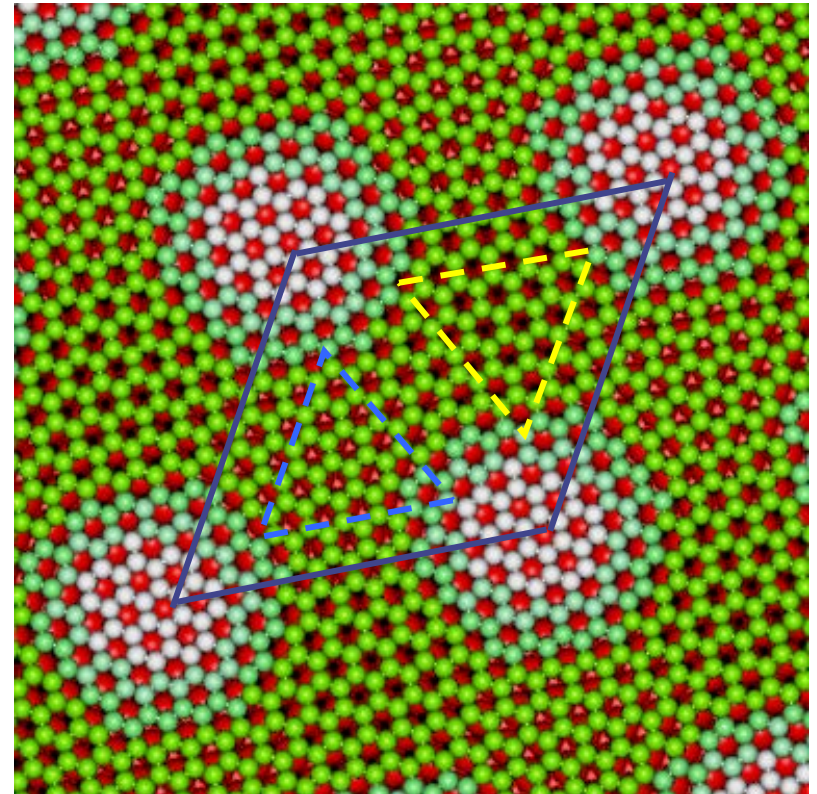
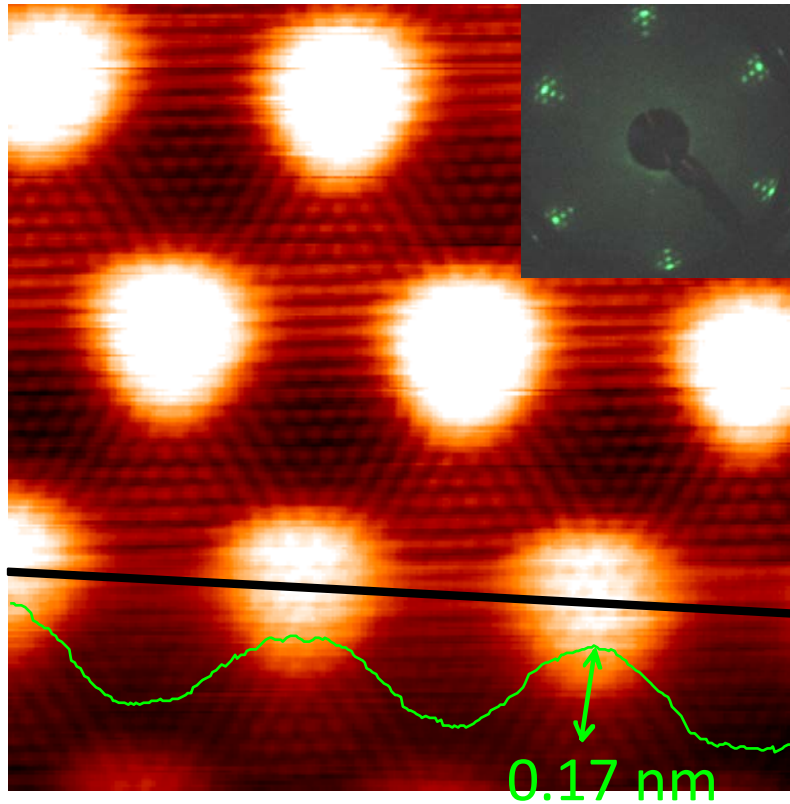
## *STM Image of Graphene on Ni(111)*



1 nm

- Atomic resolution STM image of graphene on Ni(111) grown at 700°C.
- The inset is the LEED pattern of the sample. The beam energy is 60 eV.
- The image was taken with a sample bias voltage of  $V_s = -40$  mV and a tunneling current of  $I = 1.5$  nA.

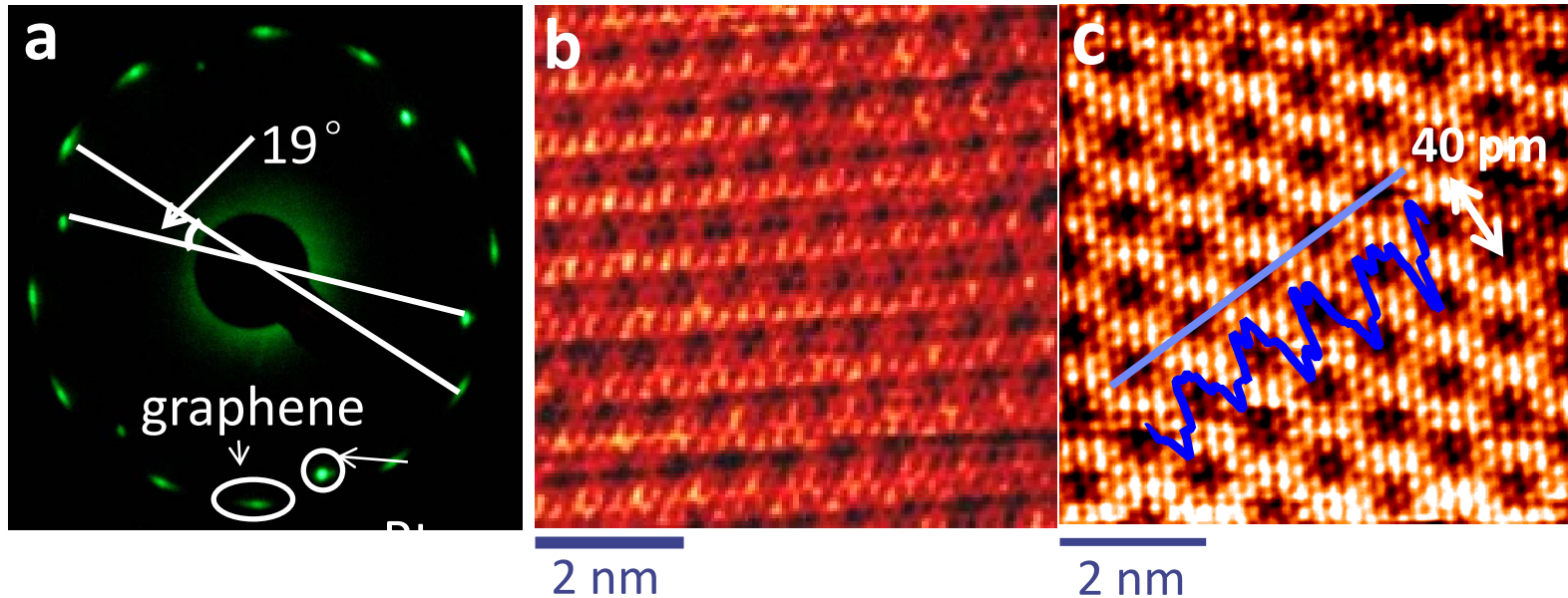
# STM Image of Graphene on Ru(0001)



2 nm

- Atomic resolution STM image of graphene on Ru(0001) grown at 800 °C. The image was taken with a sample bias voltage of  $V_s = -300$  mV and a tunneling current of  $I = 1.3$  nA.
- The height profile is taken along the black line in the STM image, showing the fluctuation of graphene on Ru(0001) is 0.17 nm.

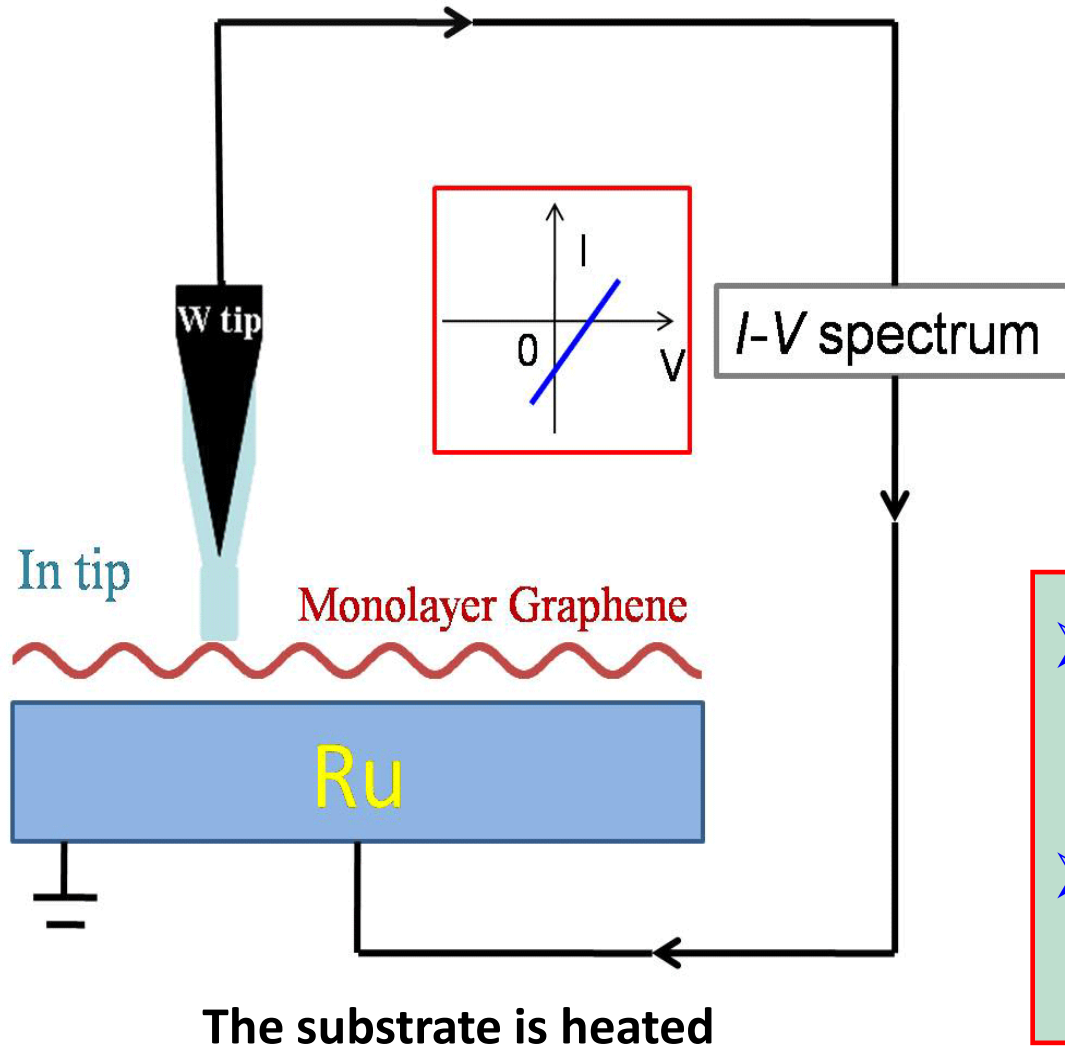
# LEED Pattern and STM images of Graphene on Pt(111)



- LEED pattern of graphene on Pt(111) grown at 600°C. The circular and the elliptical lines indicate the Pt and graphene pattern, respectively.
- Atomic resolution STM images show moiré patterns of two graphene domains of different rotational angles with respect to Pt(111) surface.
- All images were taken at  $V_s = -0.4$  V,  $I = 0.2$  nA.



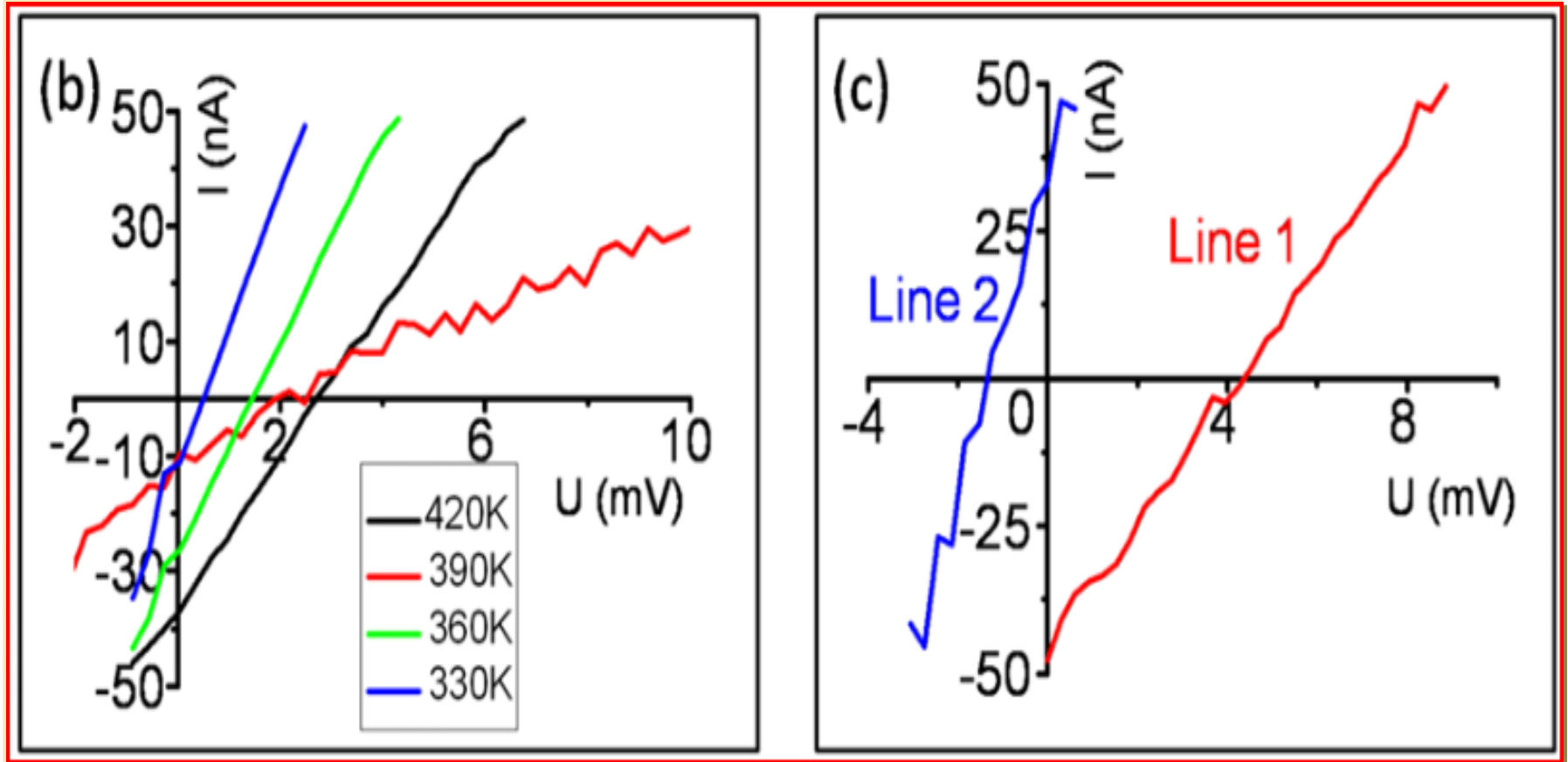
# The Schematic of Thermoelectric Voltage Measurement



- Sketch of thermoelectric measurement.
- The W tip is coated with indium.

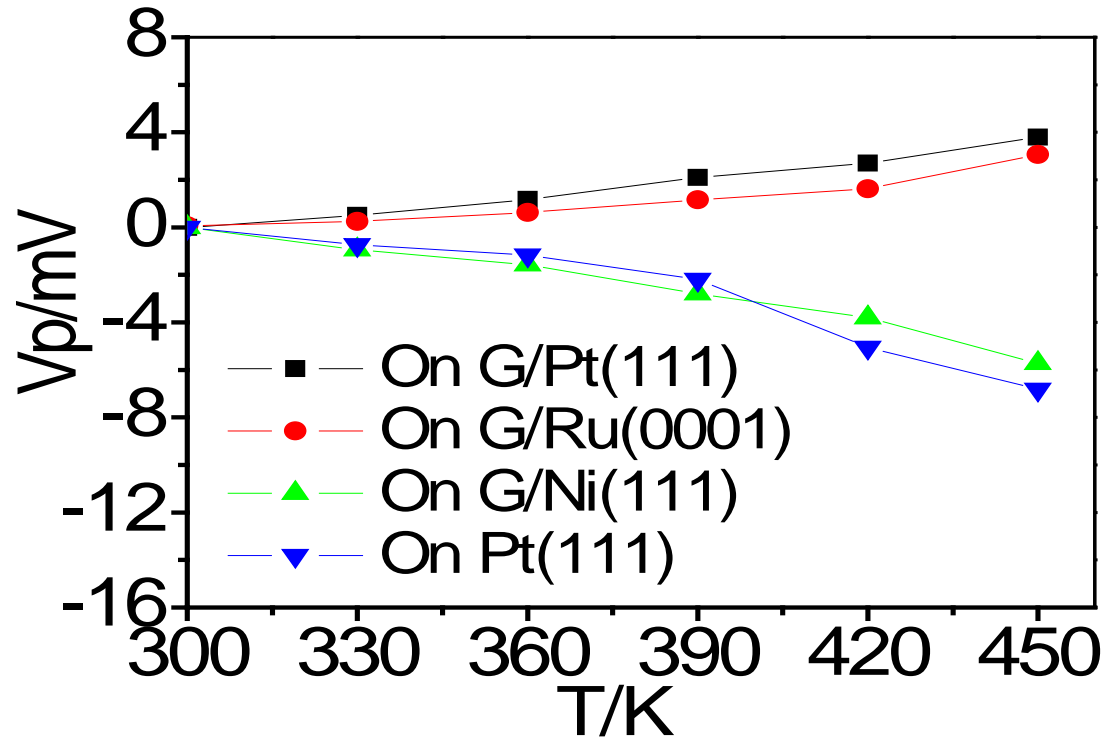
- The I-V curve shows  
 $V_{\text{bias}} \neq 0$
- Thermoelectric voltage:  
 $V = V_{\text{bias}}$

# The Measurement of Thermoelectric Voltage



- (b) The  $I$ - $V$  curve of graphene on Pt(111) at 330 K, 360 K, 390 K and 420 K.
- (c) The  $I$ - $V$  curve of graphene on Ru(0001) at 450 K: two typical states: **positive** thermoelectric potential and **negative** thermoelectric potential, showing the variation from **positive state (line 1)** to **negative state (line 2)** when the tip approaches by a step.

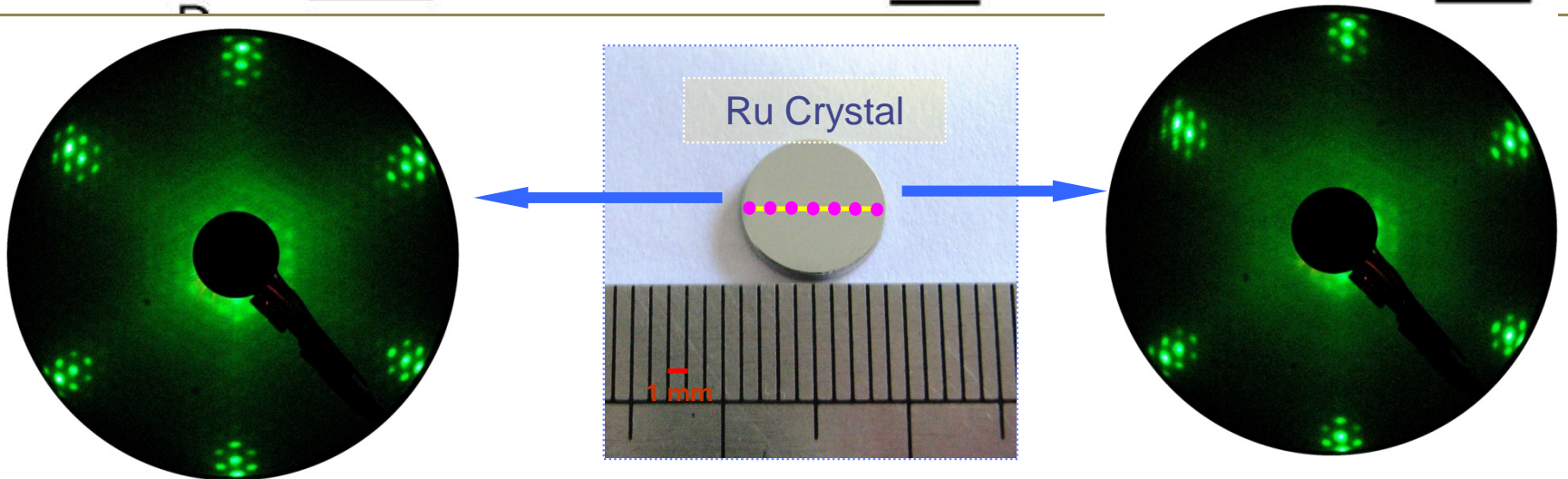
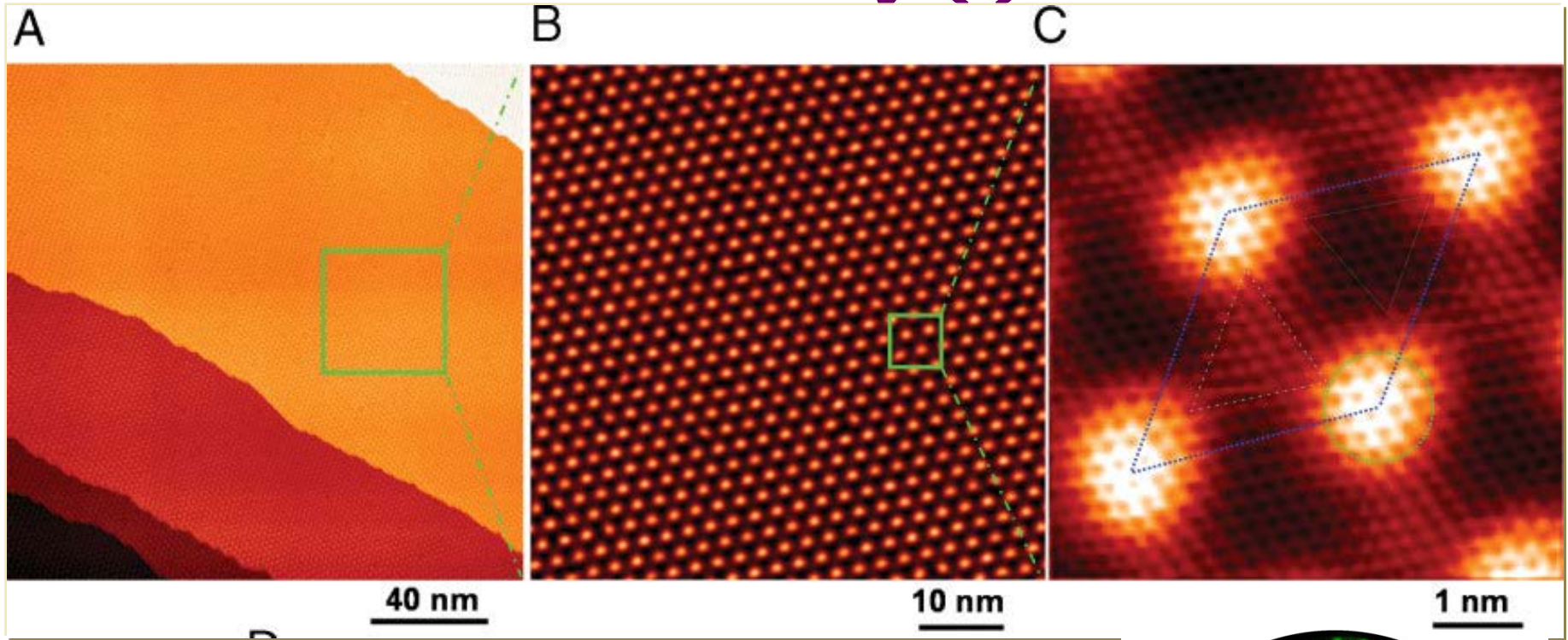
# Thermoelectric Properties of Graphene on Metals



➤ Theoretical consideration was collaborated with (Qian Niu, UT-Austin X.C. Xie, OSU/IOP)

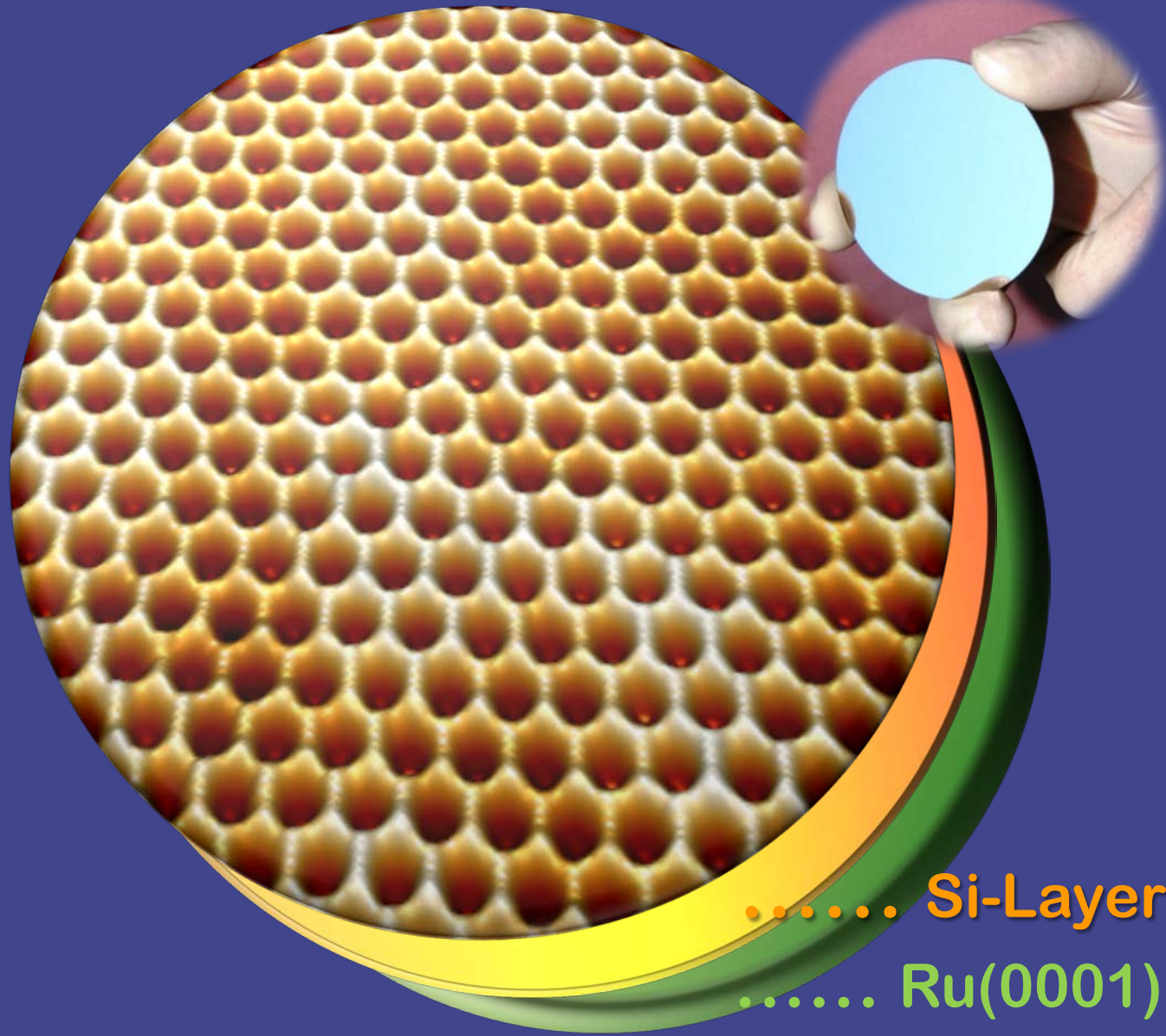
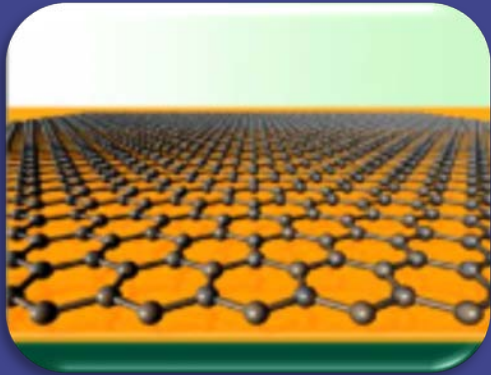
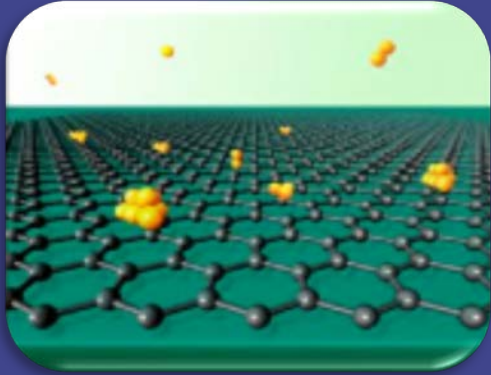
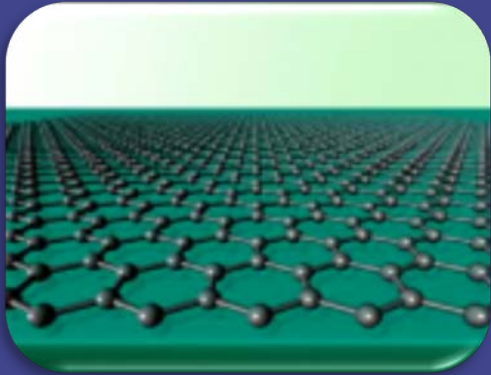
- The voltage-temperature (V-T) relationship of graphenes on different metal surfaces, in comparison with the V-T curve of bare Pt(111) surface.
- Voltage polarity gets changed.
- High Seebeck co-efficiency.

# Summary (I)



**Formation of Large-scale Single Crystalline Graphene Monolayer**

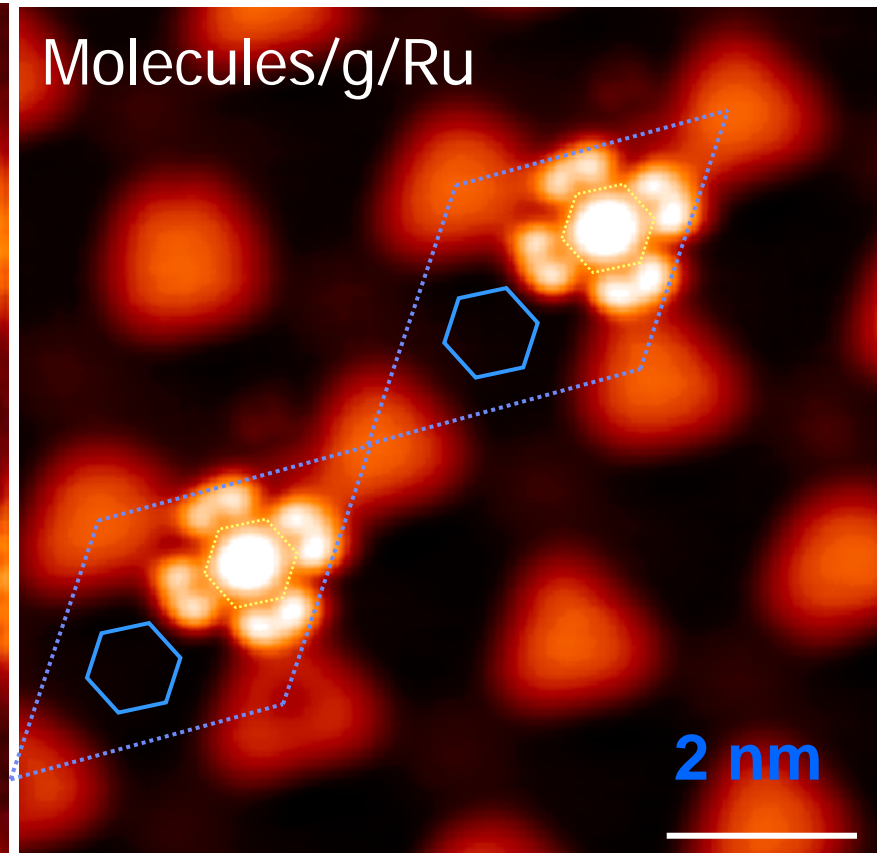
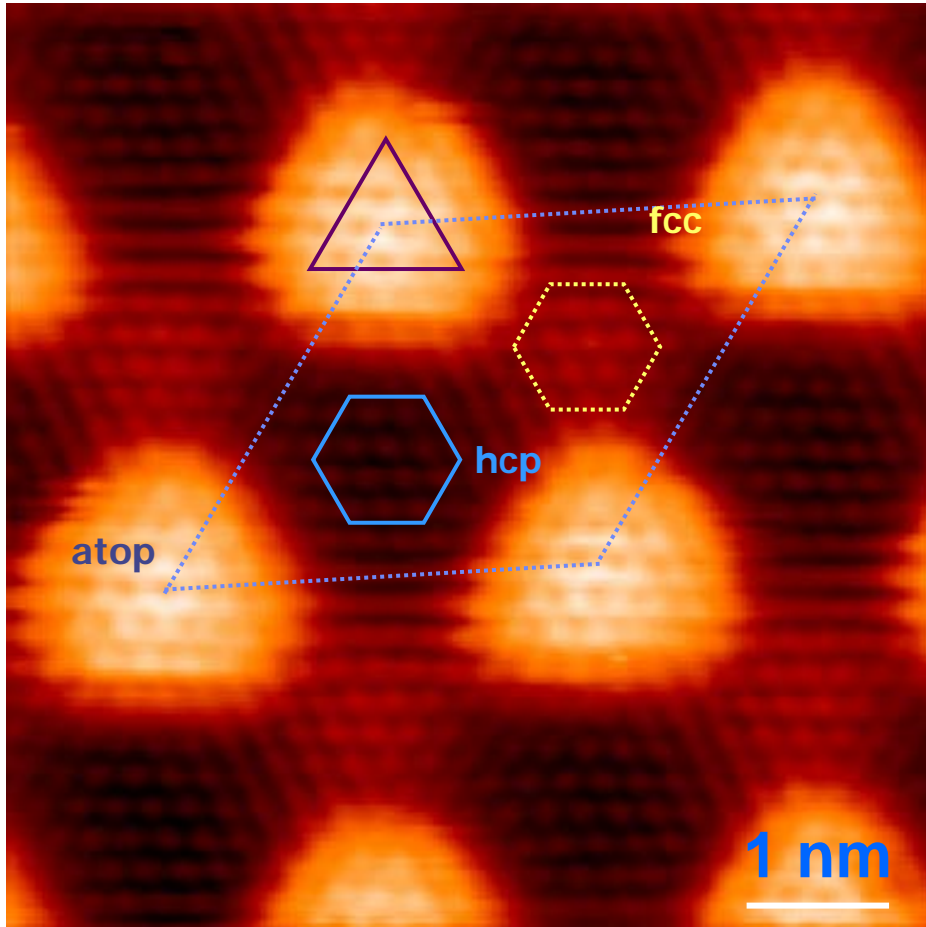
# Summary (II)



..... Si-Layer

..... Ru(0001)

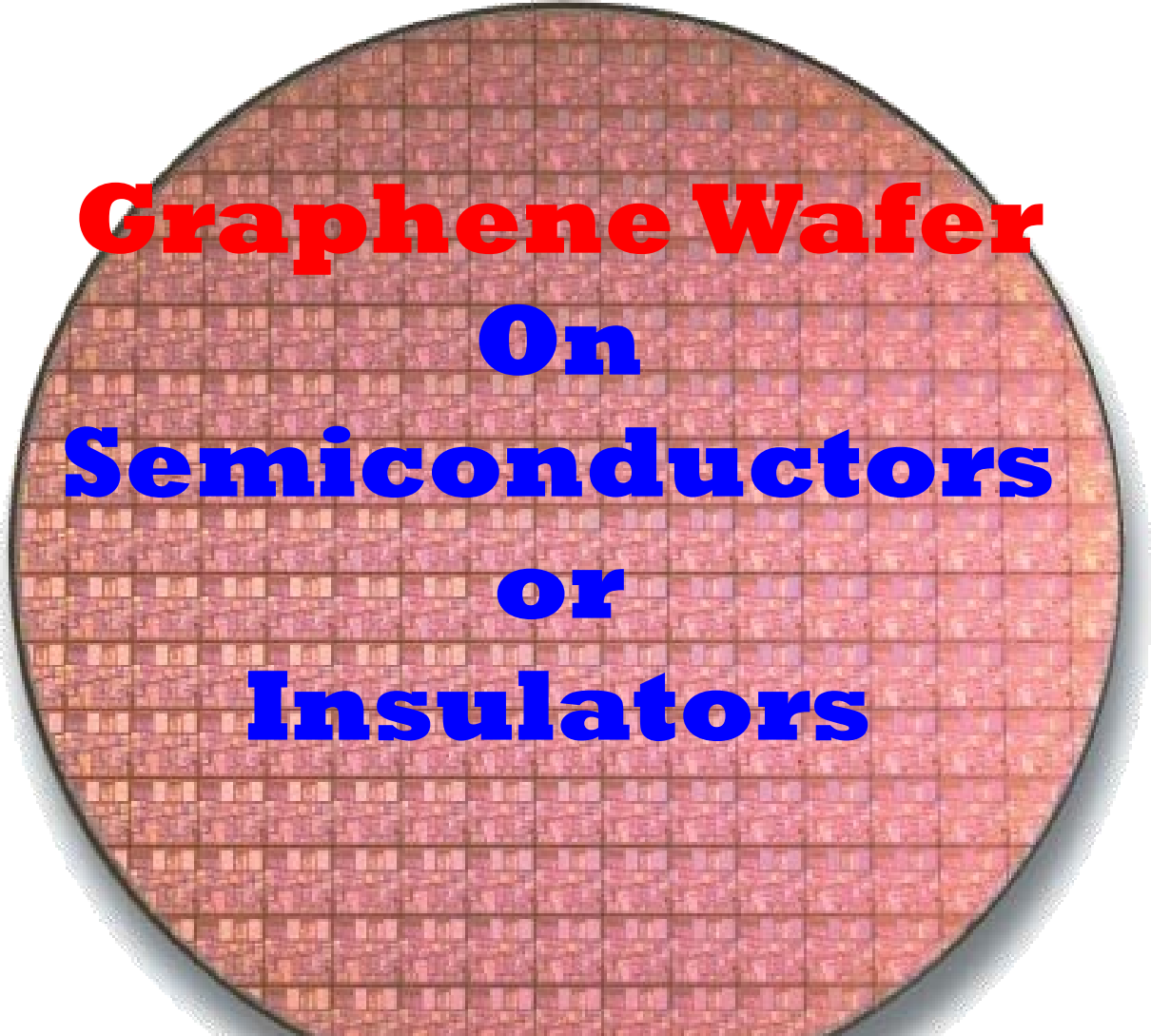
# Summary (III)



**Ordered Moiré Pattern Used for Ordered Molecular/cluster Array Formation and Tunability**

# Outlooks

**Graphene Wafer and Graphene Complex Systems for the  
Future Nano-Electronics or Mol-tronics**

A circular graphic with a grid pattern, containing text about graphene wafers. The text is centered and reads: 

**Graphene Wafer  
On  
Semiconductors  
or  
Insulators**