Unrevealed Aspects of Field Emission from Nano-Carbon Materials

Physics behind Field Emission from nano-C materials with no sharp shape

1. graphene
(Pencil Lead / Gr-*h*BN-Si emitter)
2. C_{60}

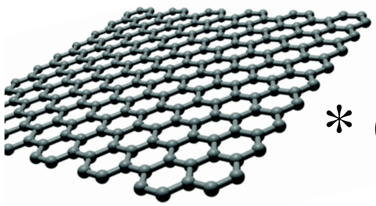
Masahiro Sasaki & Yoichi Yamada
University of Tsukuba

Multi-function of Carbon Materials

Allotrope

Diamond (sp^3): insulator/semiconductor,
wide band gap, extremely high thermal conductivity,
extremely mechanical hardness.

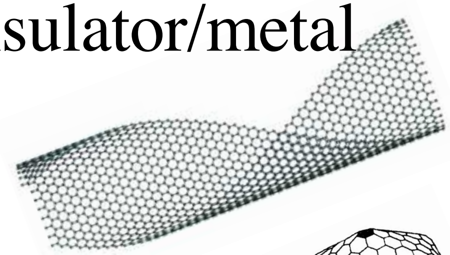
* Diamond-like Carbon: coating to lubricate and stabilize

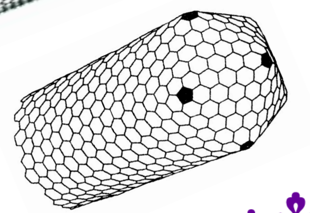


Graphite (sp^2): conductive, semi-metals, thermal conductivity

* Graphene: intrinsic 2D, superior electron transport,
high thermal conductivity.

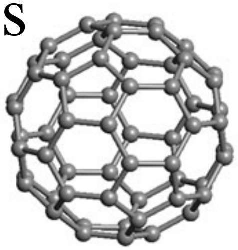
* Carbon Nanotube (CNT): intrinsic 1D, insulator/metal





Fullerene: isolated molecules

* C_{60}, C_{70}, C_{74}, C_{76}…



Their derivatives

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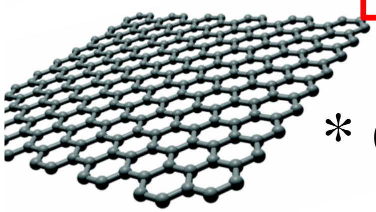

Graphite (sp^2): conductive, semi-metals, thermal conductivity

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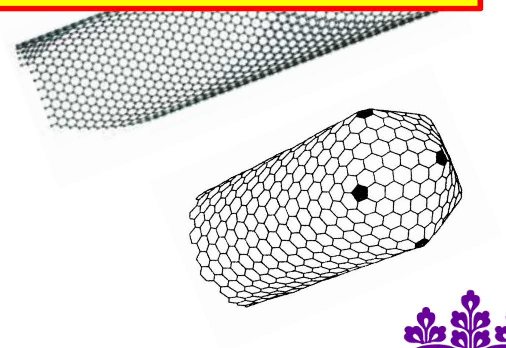
Unrevealed aspects in field emission will be discussed



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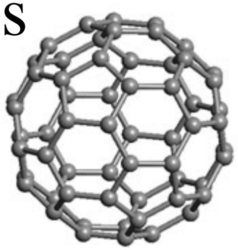
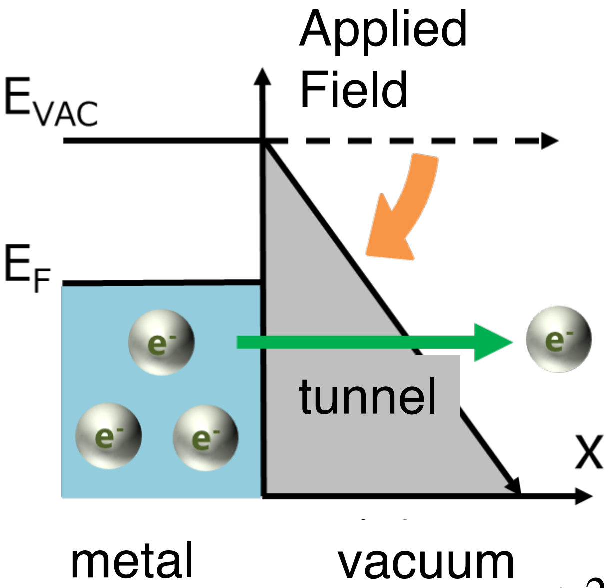
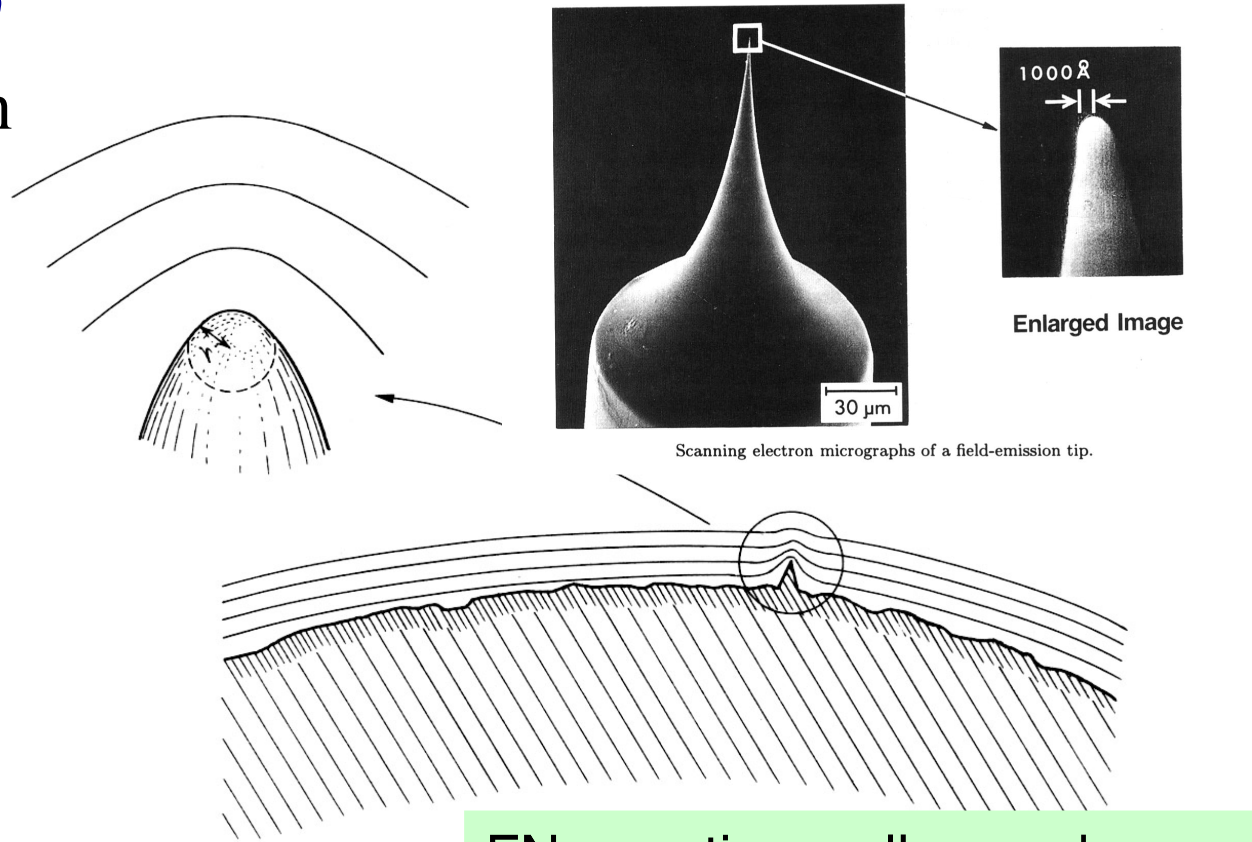


Their derivatives

Field Emission

low energy consumption
small energy spread
high brightness





Scanning electron micrographs of a field-emission tip.

FN equation well reproduces field emission currents.

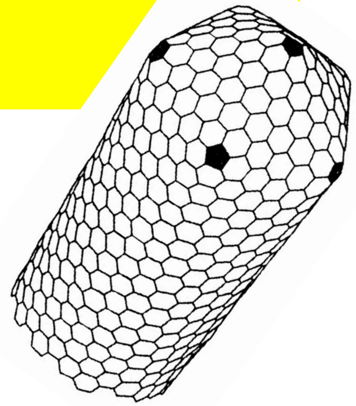
$$I = \frac{A(\gamma F_M)^2}{\phi} \exp\left[-B\frac{\phi^{3/2}}{\gamma F_M}\right]$$

ϕ: Effective work function
γ: Field enhancement factor

FE is determined by the work function and the sharpness of the tip

Nano-Carbon materials

Carbon nanotube (CNT), which is famous for its intrinsic shape with a extremely high aspect ratio, likely suitable for field emitter, has been well investigated so far.
CNT is not so ideal for field emitters.



Common merits of carbon-related materials besides their intrinsic sharp shape

1. High chemical stability
2. High mechanical strength
3. Low atom mobility
4. High electrical and thermal conductivity
5. Various electronic properties

Here, unrevealed aspects of field emission from nano-C materials except for their intrinsic sharp shapes will be discussed.

Outline

1. Introduction:
   Field Emission from Nano-Carbon materials

2. Graphene
   Graphitized Pencil Lead
   MIM (Graphene-*h*BN-Si) cathode

3. Fullerene (C_{60})

4. Summary

Graphene (1)

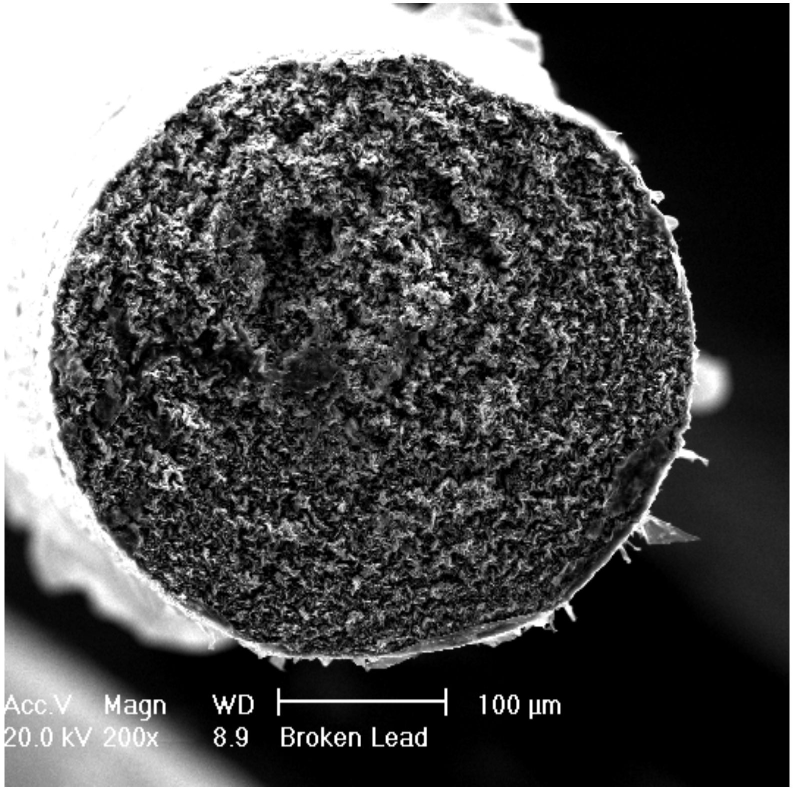
Cheapest but Superior Field Emitter

Graphitized Pencil Lead

Mechanical pencil lead as an emitter

PILOT Corp., Japan
NEOX-ENO B
0.3 mm * 60 mm

~$ 1.00 / 10 rods



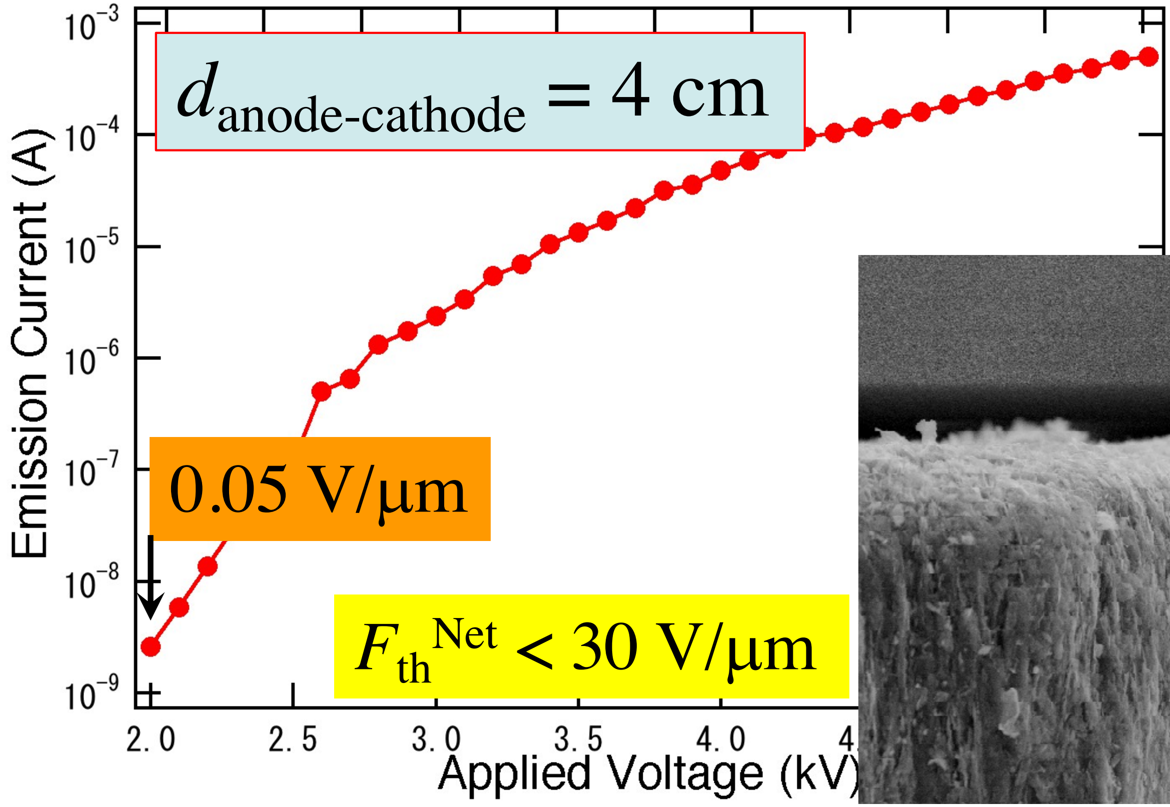
1. scribed around side of the lead rod
2. broken perpendicularly
3. put into vacuum and evacuated
4. carbonized completely at > 2000°
5. in-situ measured FE

Not sharpened

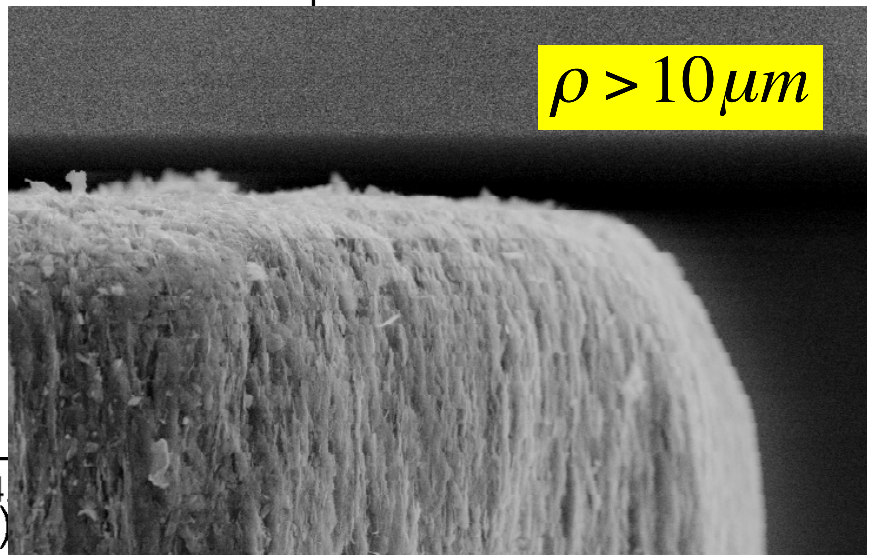
FE current vs. voltage (pencil lead)

as cut and carbonized

$\gamma_{geo} = 600$



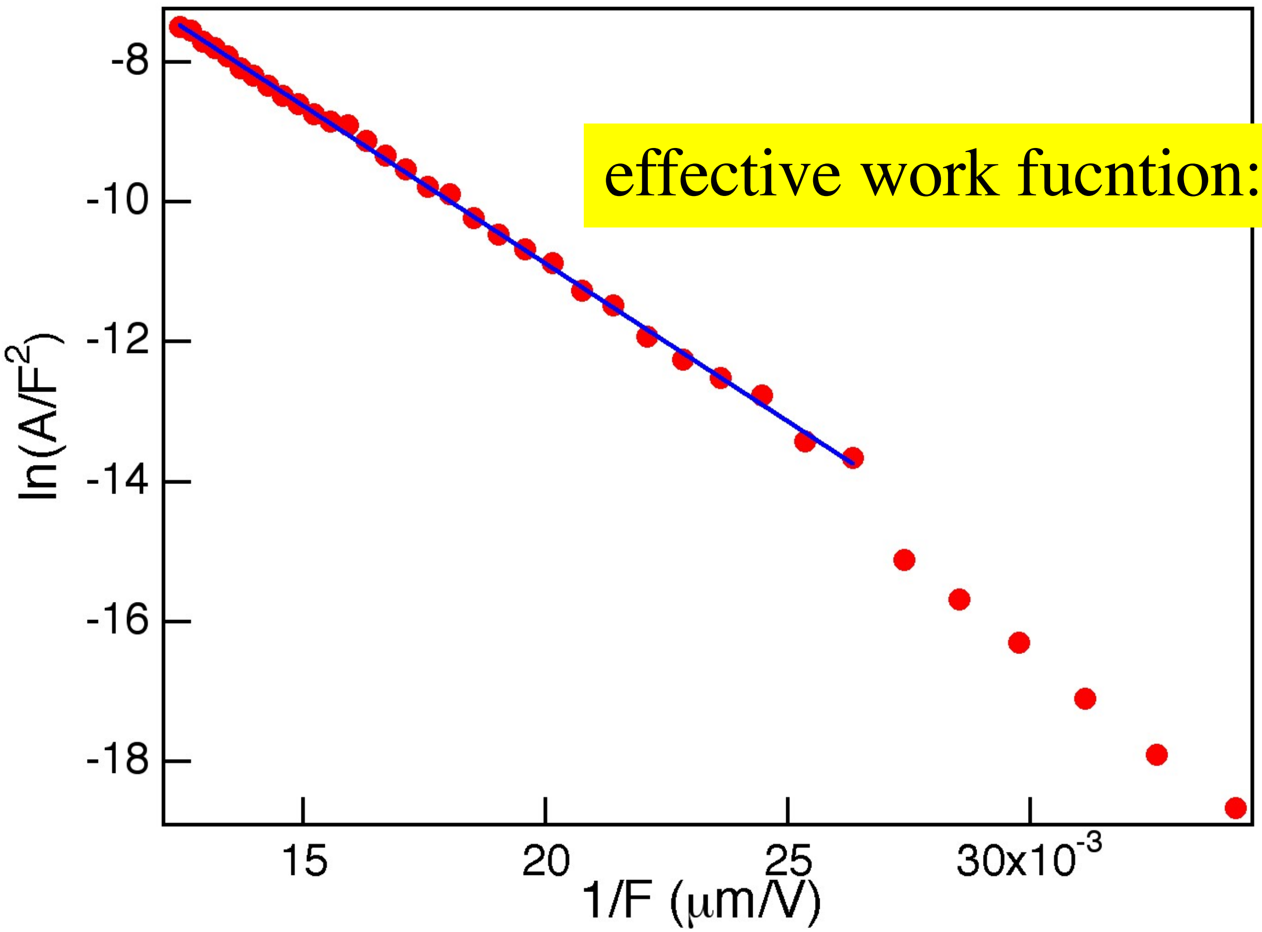
$j_{max} > 1$ A/cm^2



Net field is estimated from the finite element method.
Poisson/Superfish (Los Alamos NL) when ρ = 10 μm

Fowler-Nordheim plot (pencil lead)

pencil lead as cut and completely carbonized

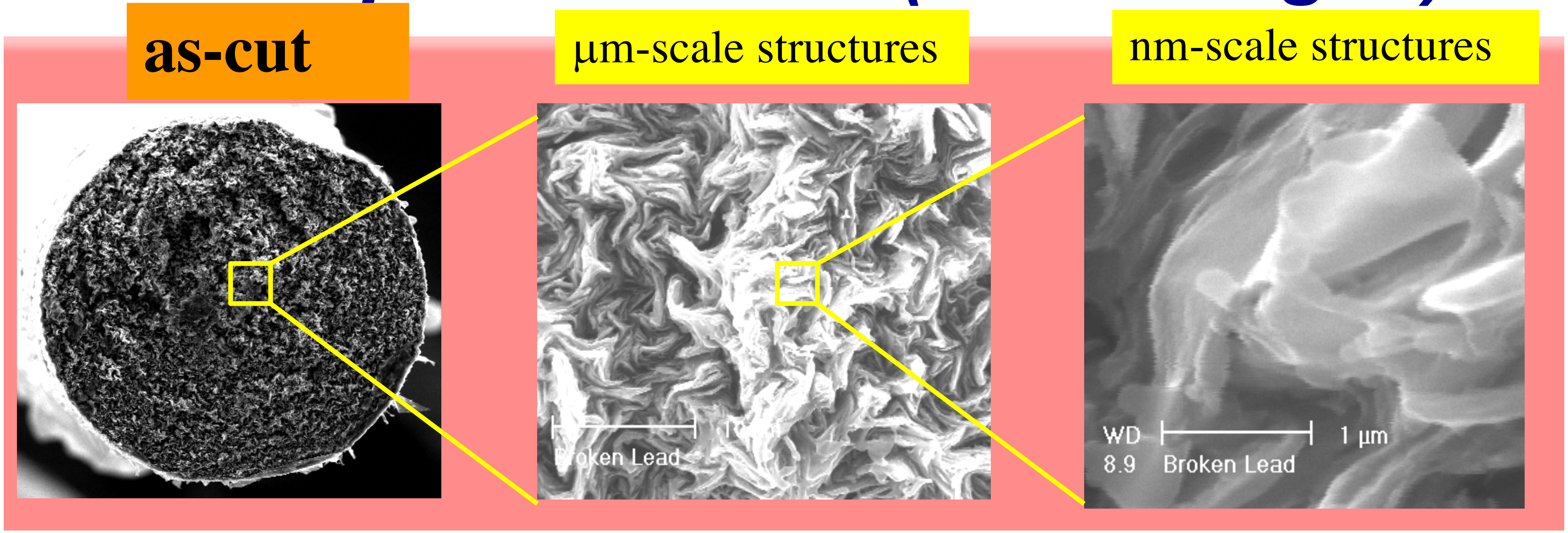


effective work fucntion: 0.16 eV

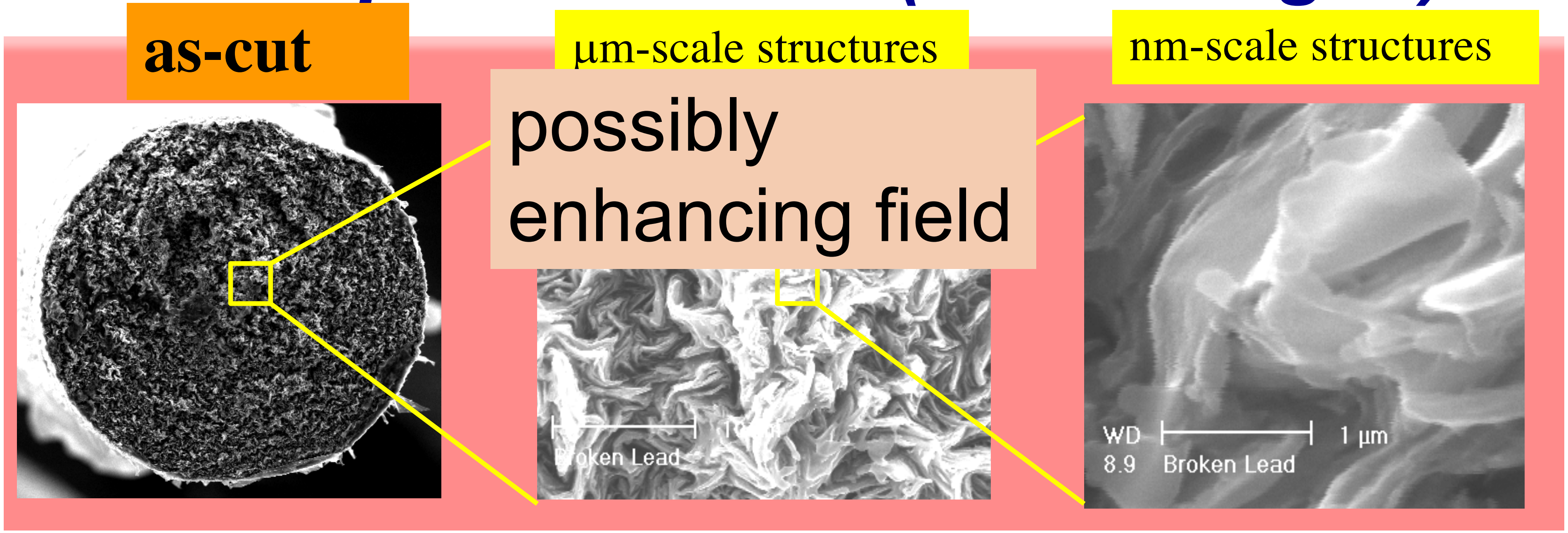
$\gamma_{ele} = 160$

$\gamma = \gamma_{geo} \text{ x } \gamma_{ele}$
$= 96{,}000$

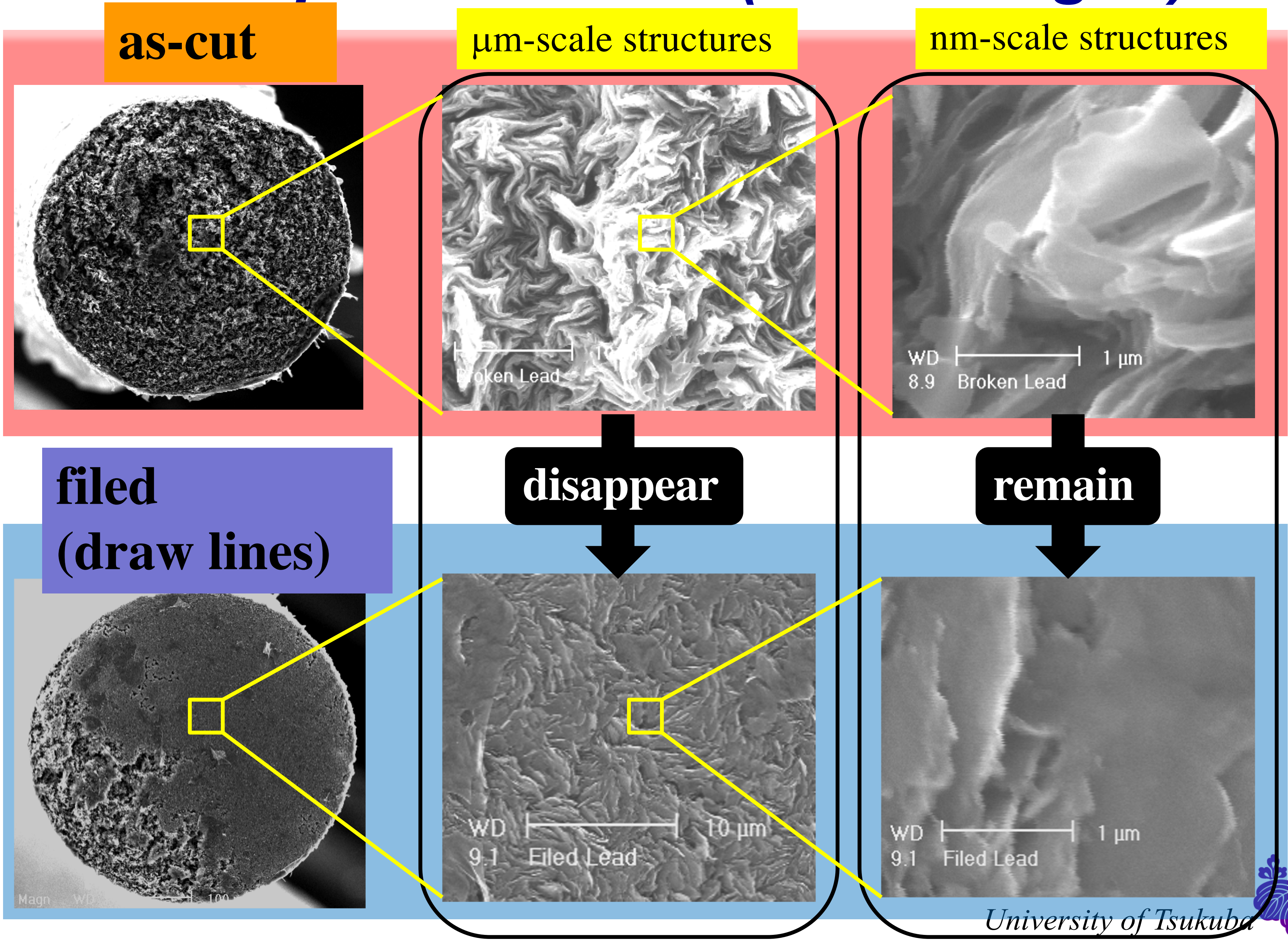
Microscopic structure (SEM images)



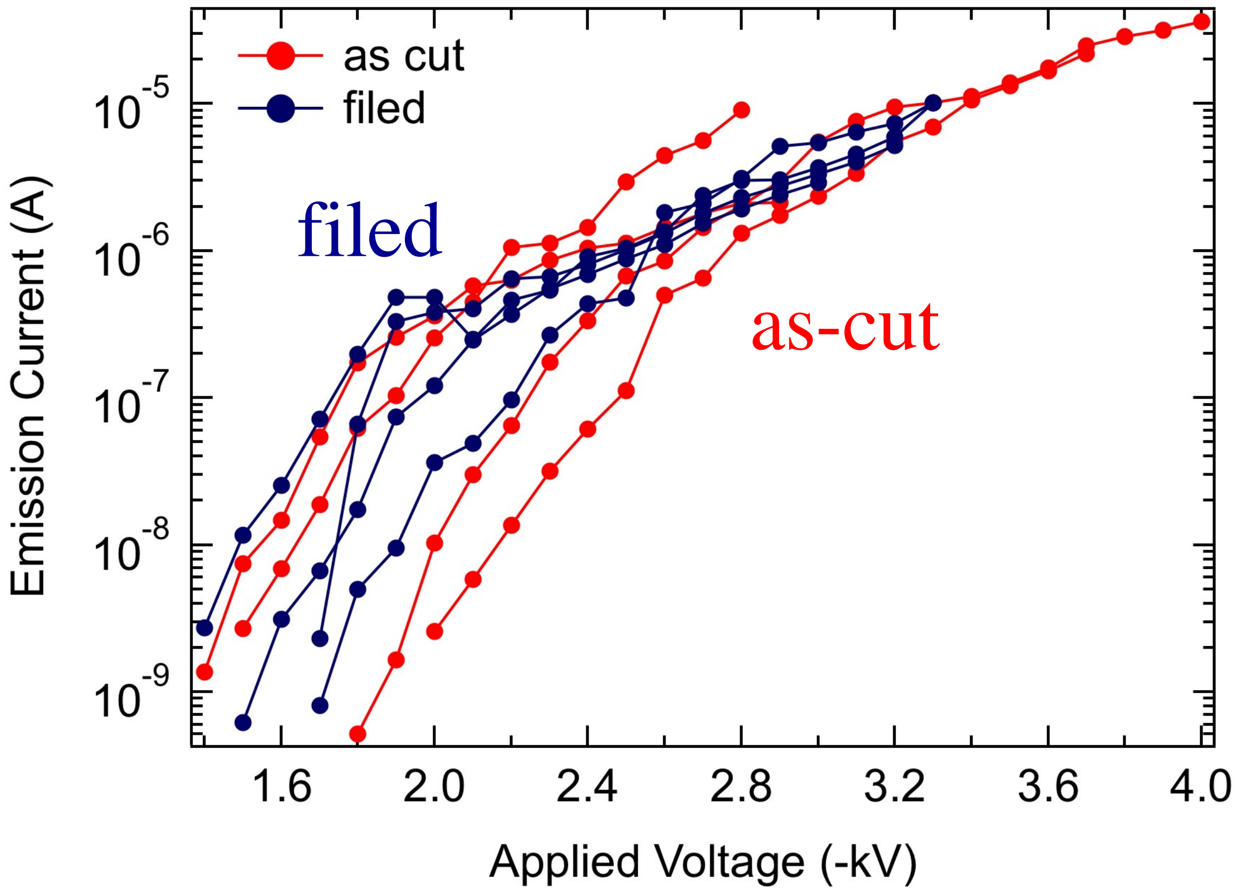
Microscopic structure (SEM images)



Microscopic structure (SEM images)



FE from as-cut and filed lead edges



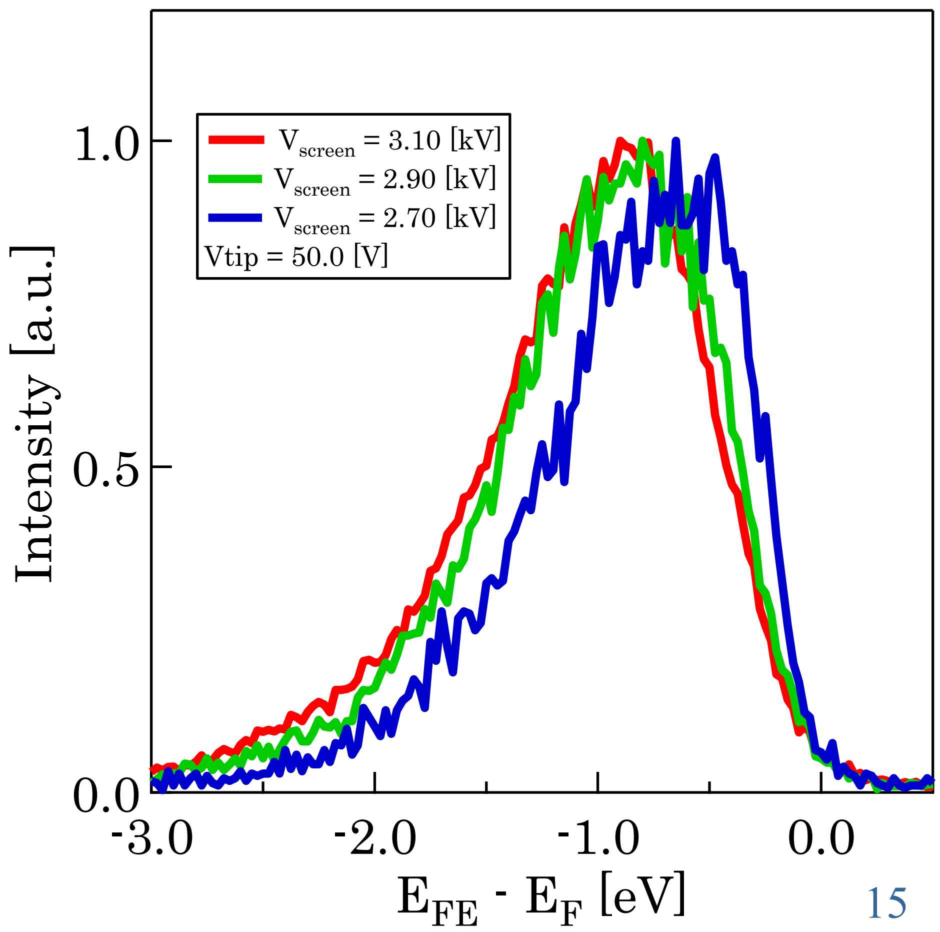
FE characteristics remain similar
even after μm-scale structures are removed by filing.

Effective low work function is not due to a geometrical factor,
but due to an intrinsic property.

Energy spectrum

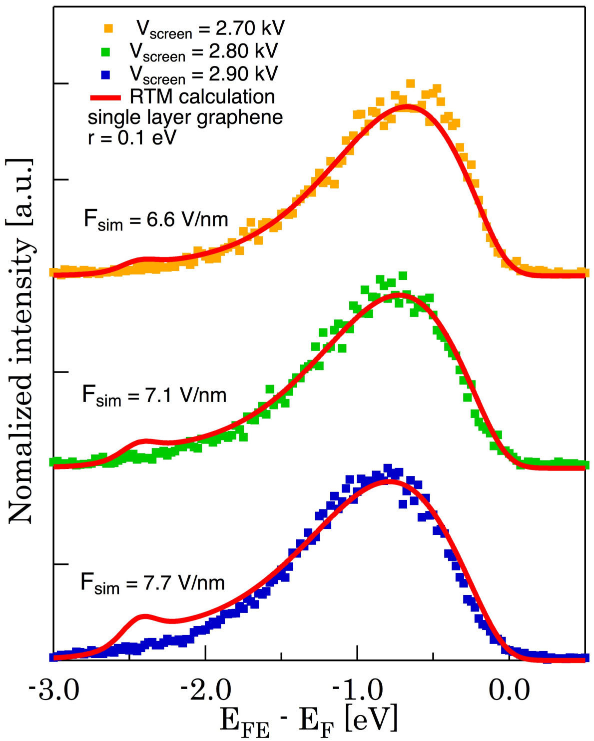
To clarify the origin of superior FE

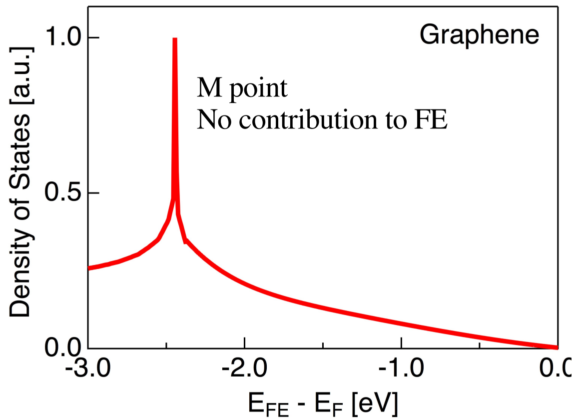
Peak shifts upon changing field.



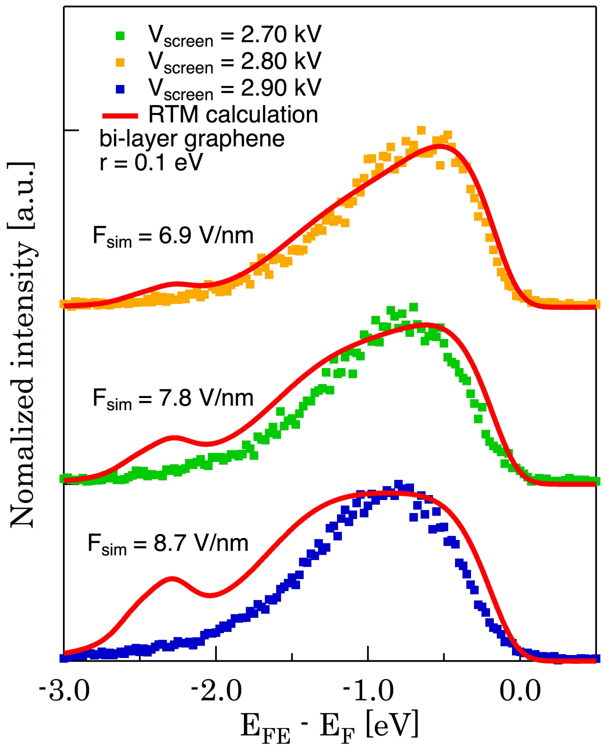
Compared with Simulations

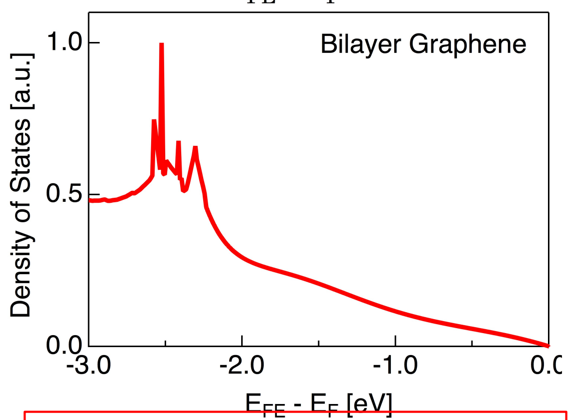
Graphene





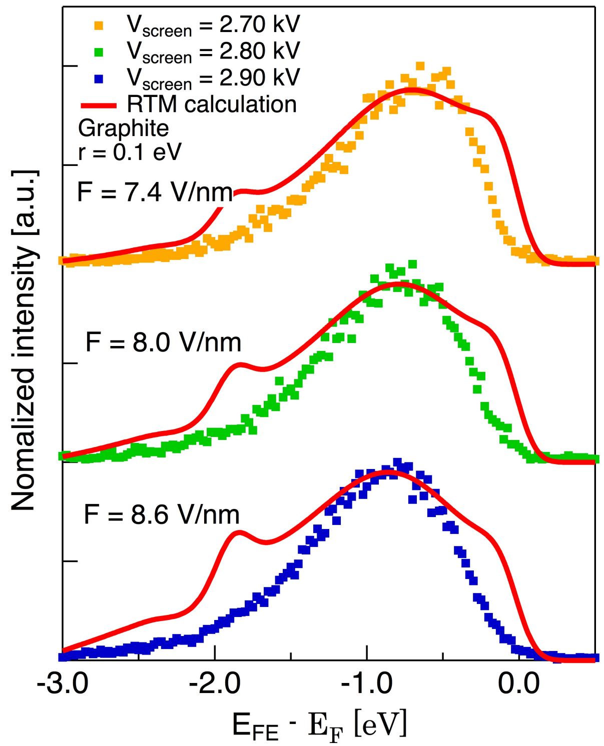
Bi-layer Graphene

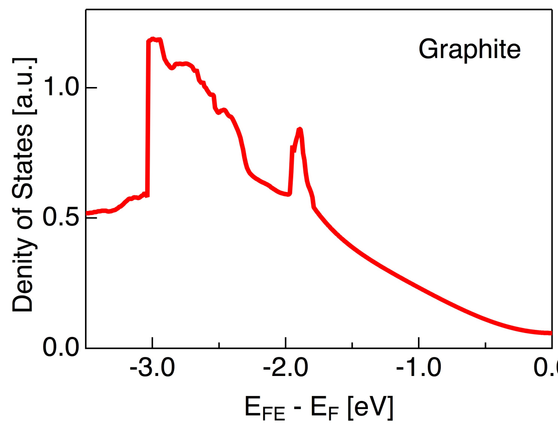




Based on DFT calculations

Graphite





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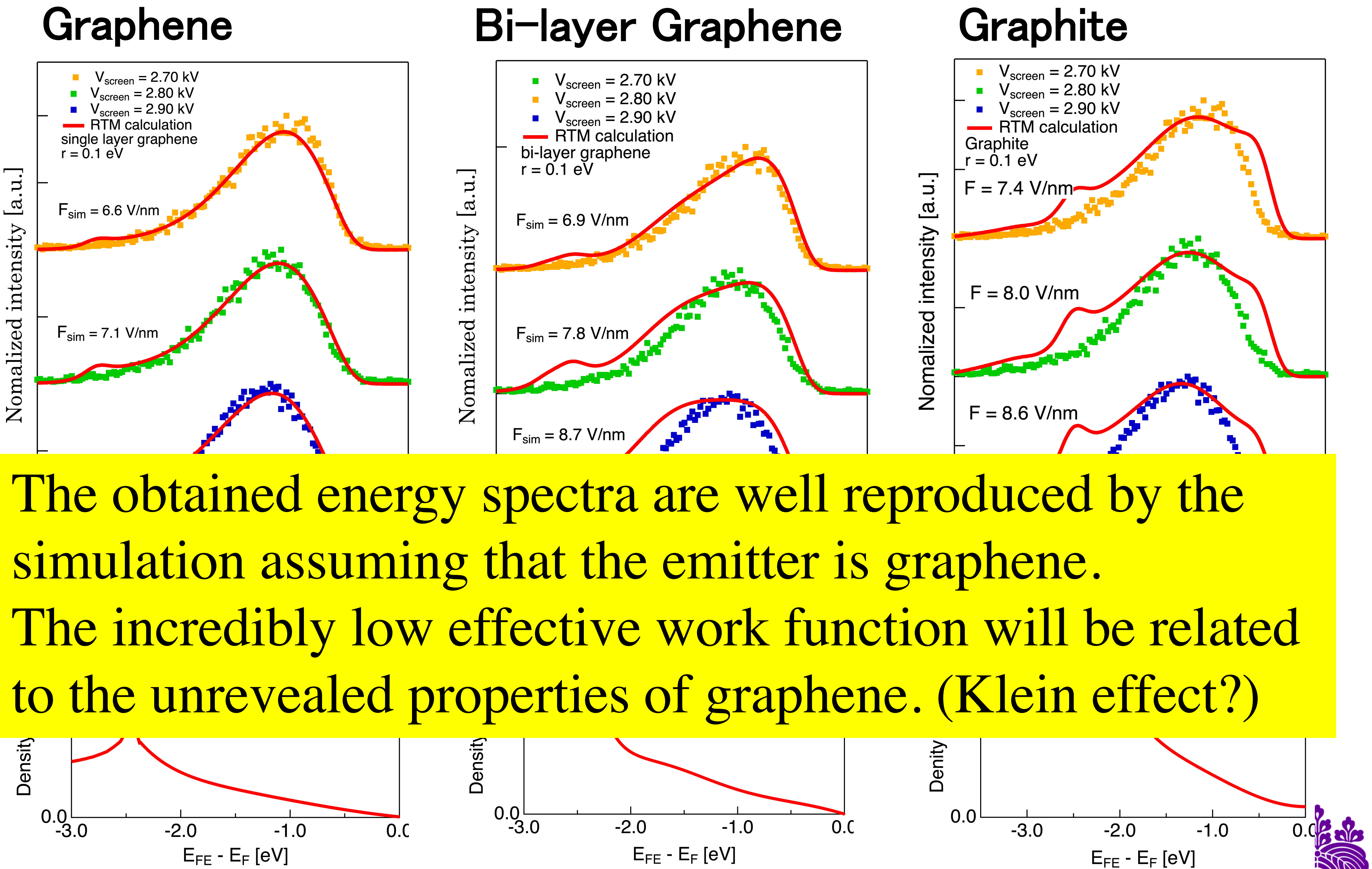


The obtained energy spectra are well reproduced by the simulation assuming that the emitter is graphene.
The incredibly low effective work function will be related to the unrevealed properties of graphene. (Klein effect?)

Graphene (2)

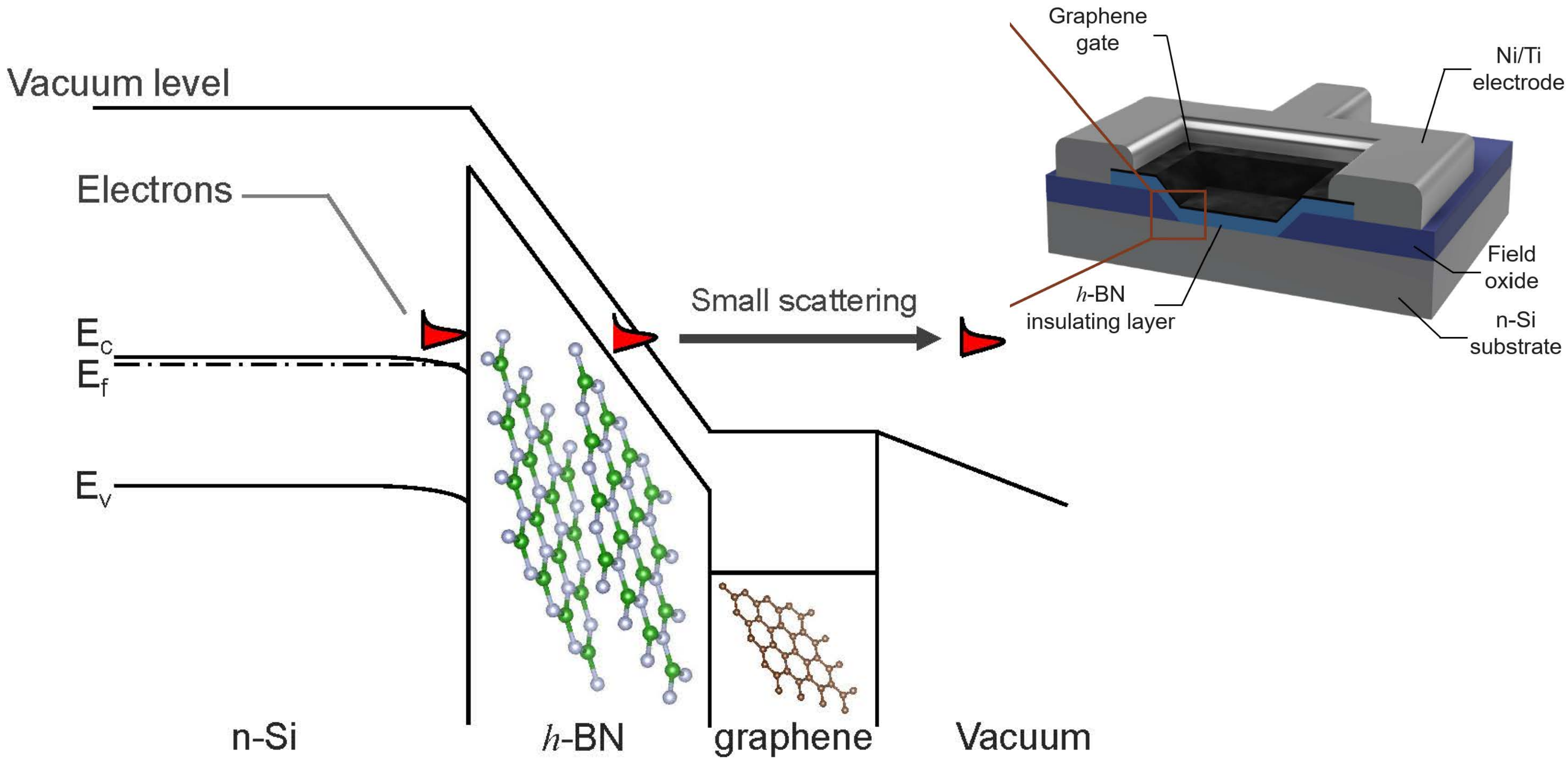
Ultimate Flat Emitter

Graphene/h-BN/Semicond. Emitter

K. Murakami, T. Igari, K. Mitsuishi, M. Nagao, M. Sasaki, Y. Yamada, ACS Applied Materials & Interfaces 12(3), 4061-67 (2020).

Tomoya Igari, Masayoshi Nagao, Yoichi Yamada, Masashiro Sasaki, Katsuhisa Murakami, IVNC-IVESC2019, Cincinnati, USA, 22-26, July, 2019.

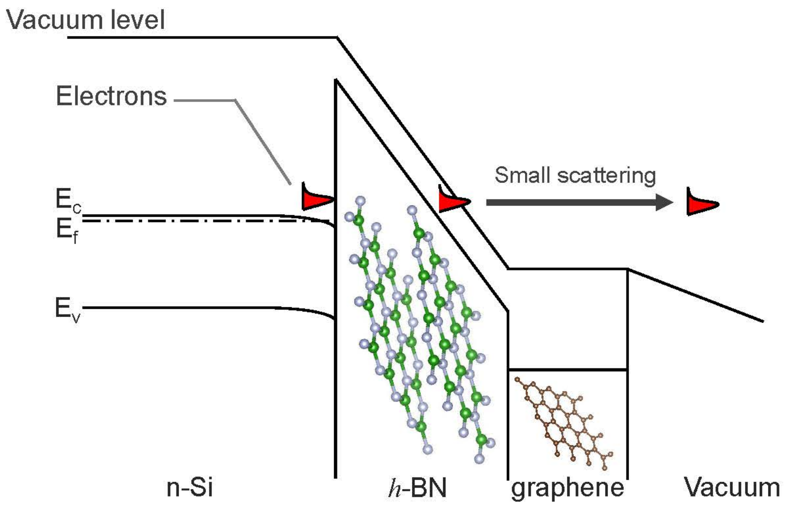
Graph./h-BN/Semicond. Emitter

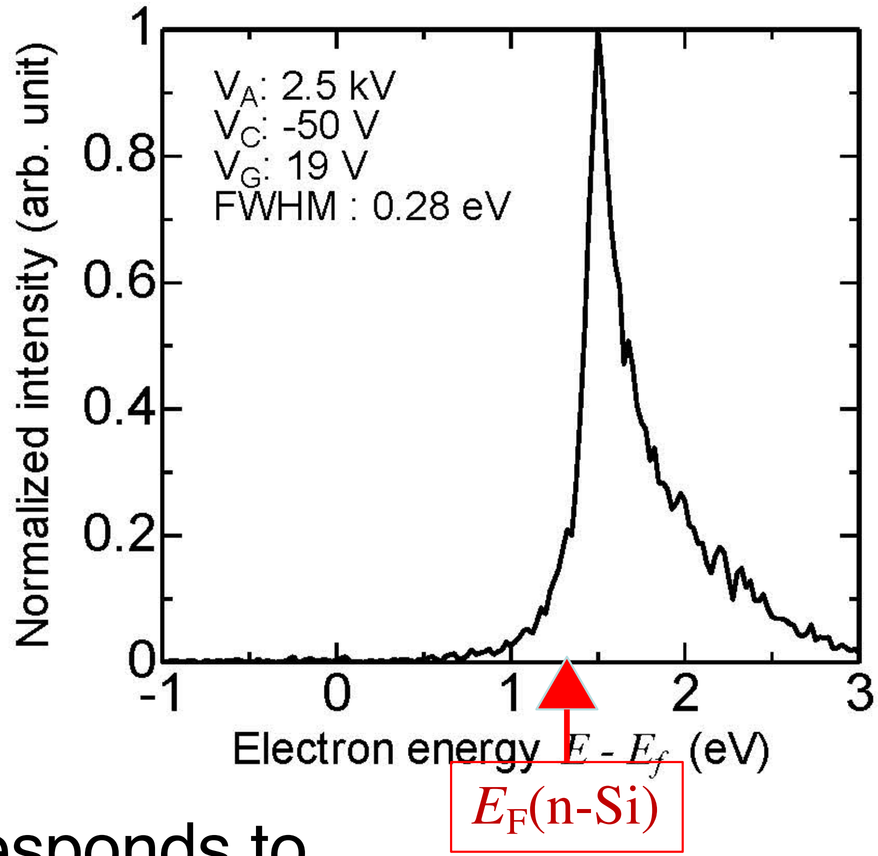


Semiconductor | Insulator | Metal

Lattices well-matched
Keep intrinsic properties each other

Graph./h-BN/Semicond. Emitter

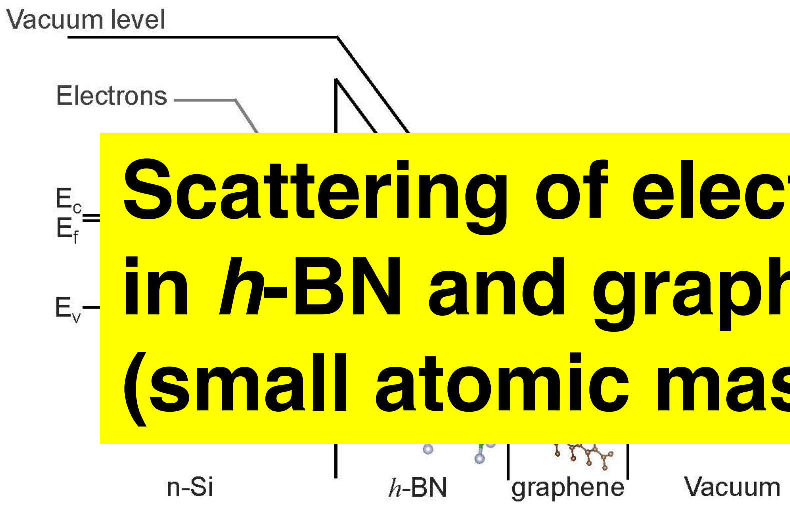


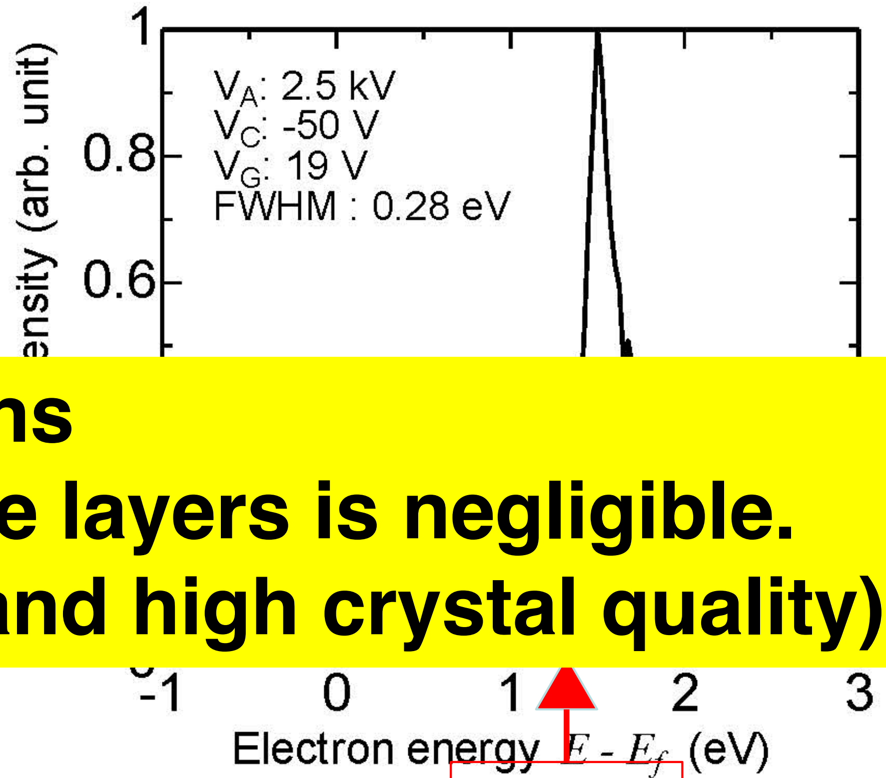


Energy spectrum well corresponds to the electron energy distribution in the Si substrate.

The spectrum shape changes, corresponding to the impurity concentration and the material.

Graph./h-BN/Semicond. Emitter





Scattering of electrons
in *h*-BN and graphene layers is negligible.
(small atomic mass and high crystal quality)

Energy spectrum well corresponds to
the electron energy distribution in the Si substrate.

The spectrum shape changes, corresponding to
the impurity concentration and the material.

Highly symmetric nano-carbon materials

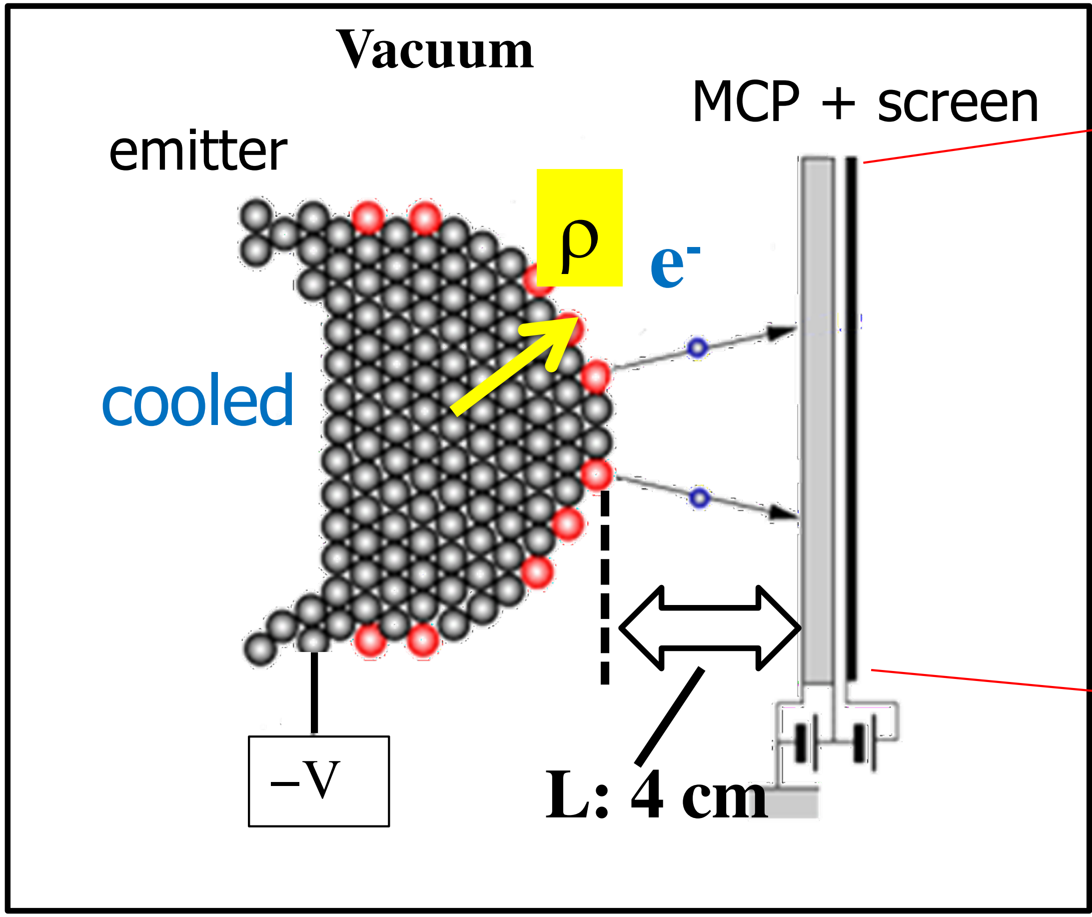
C_{60} / W emitter

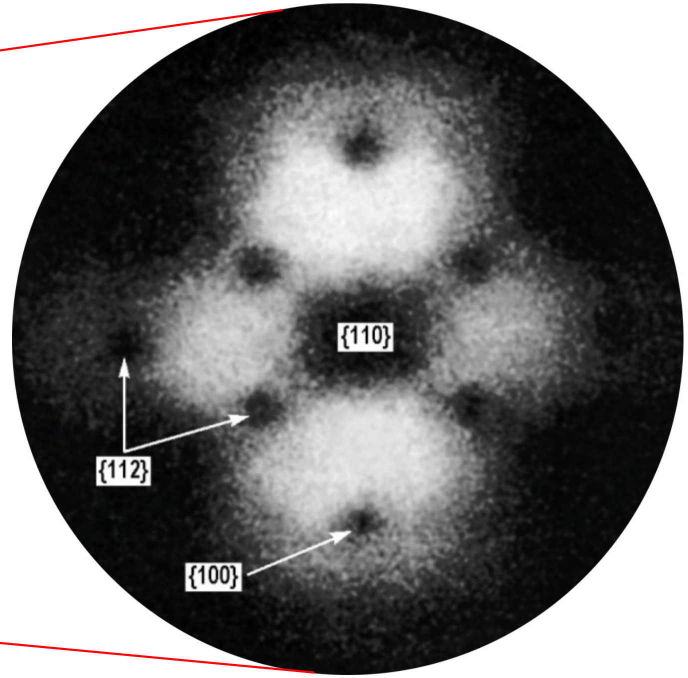
attract electrons

Field Electron Microscopy (FEM)

Field emission distribution

Magnification: L/ρ (10^6–10^8)



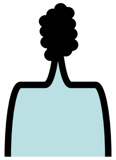


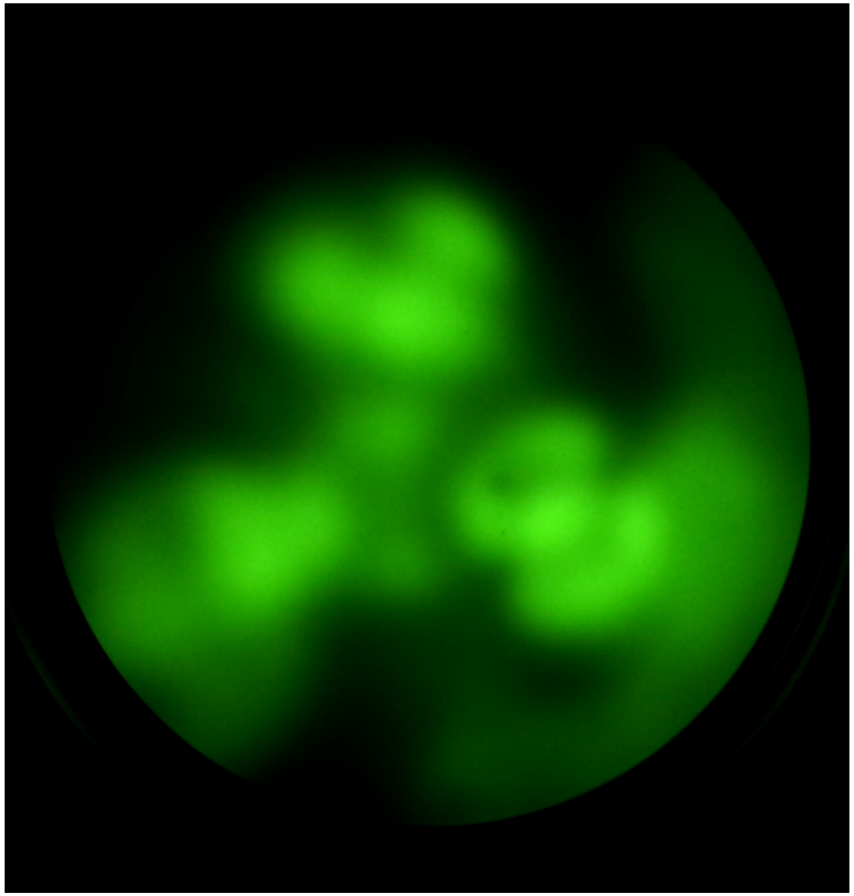
FEM image (W tip)

Field emission angular distribution

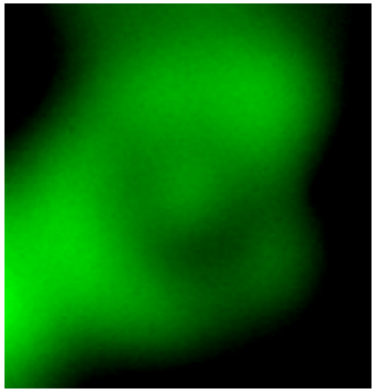
FEM from C_{60}/W emitter

C_{60}/W emitter

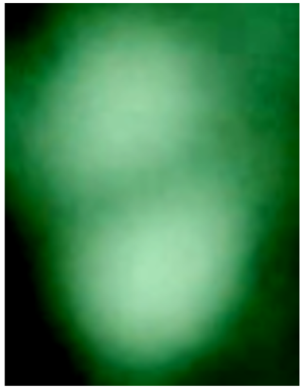




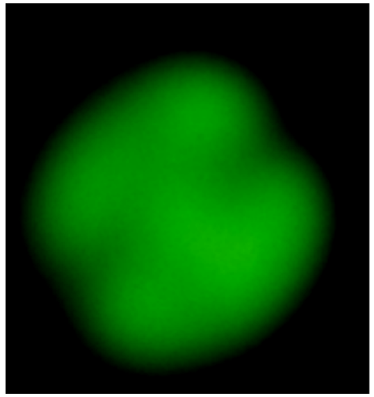
V_{tip} = -1.3 kV



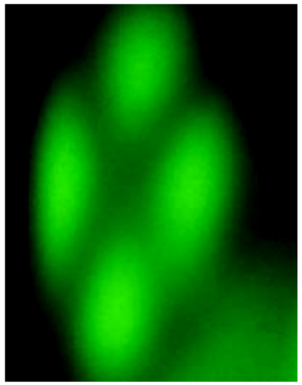
circle

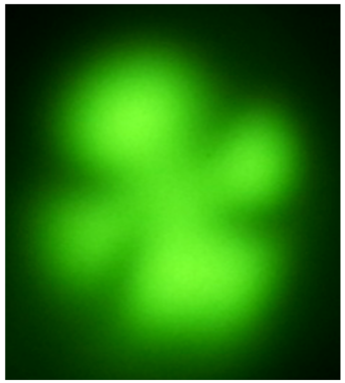


two lobes

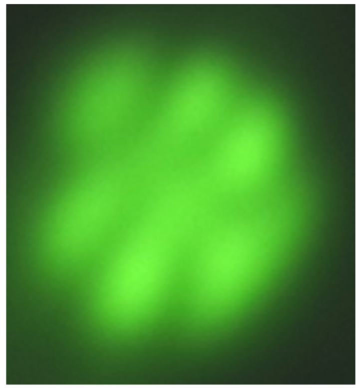


circle



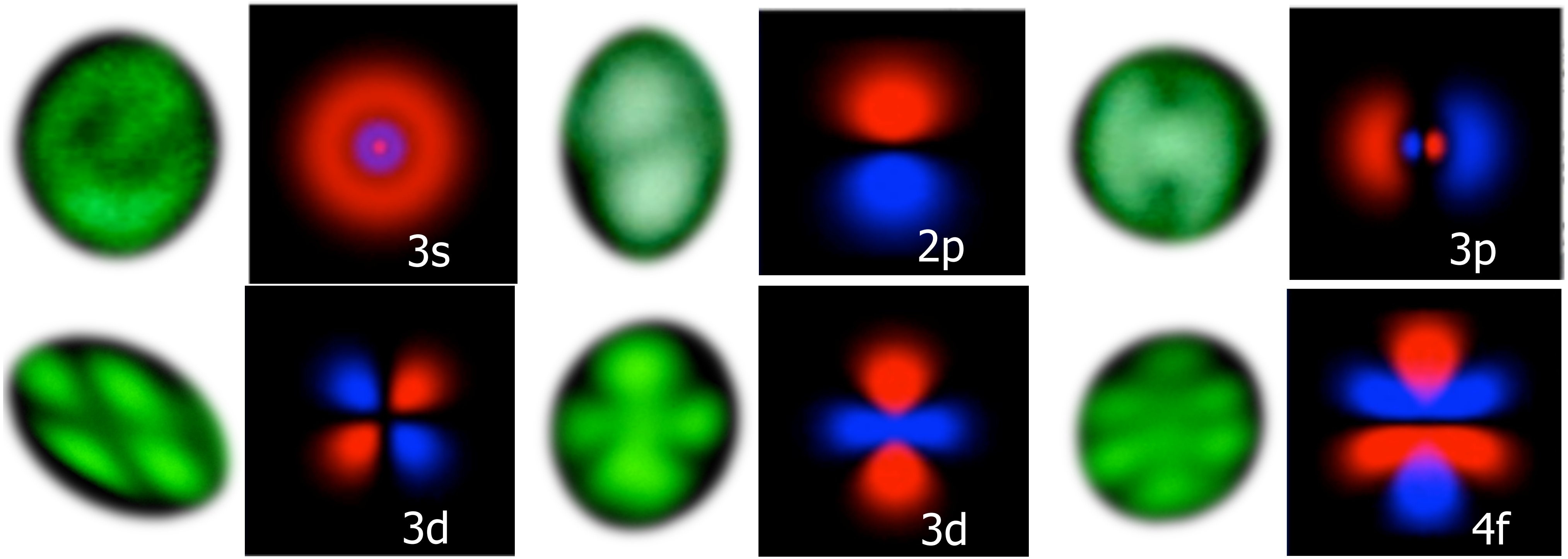


four lobes



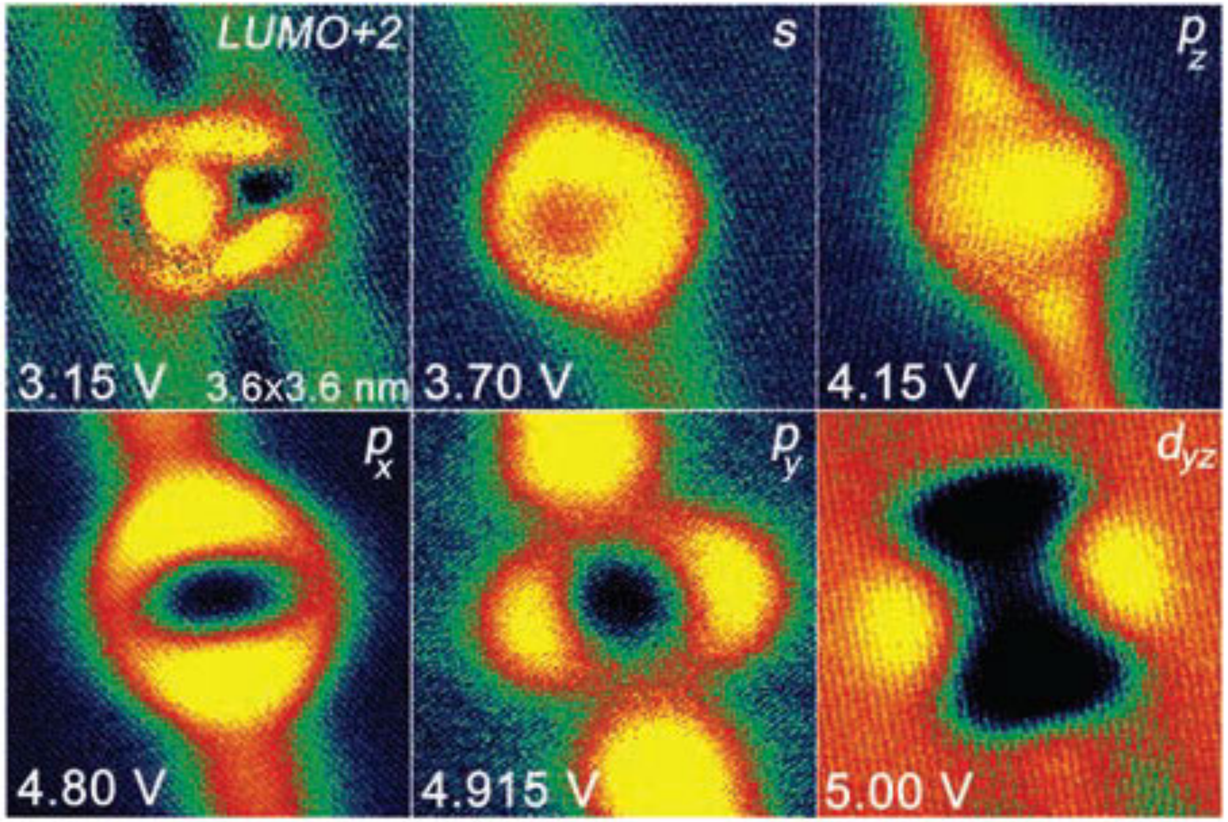
six lobes

Comparison between atomic states and FEM patterns



The obtained highly symmetric FEM pattern corresponds to the atomic orbitals.

Orbital shapes of C_{60} states by STM



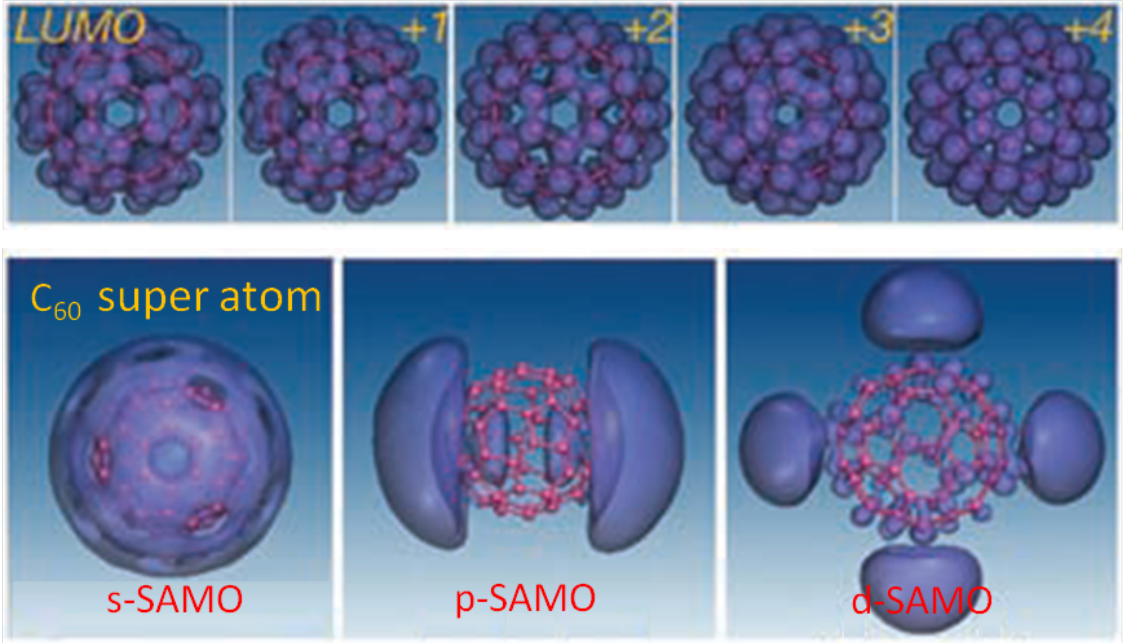
The existence of Super Atomic Molecular Orbitals (SAMOs) is experimentally observed by using STM.

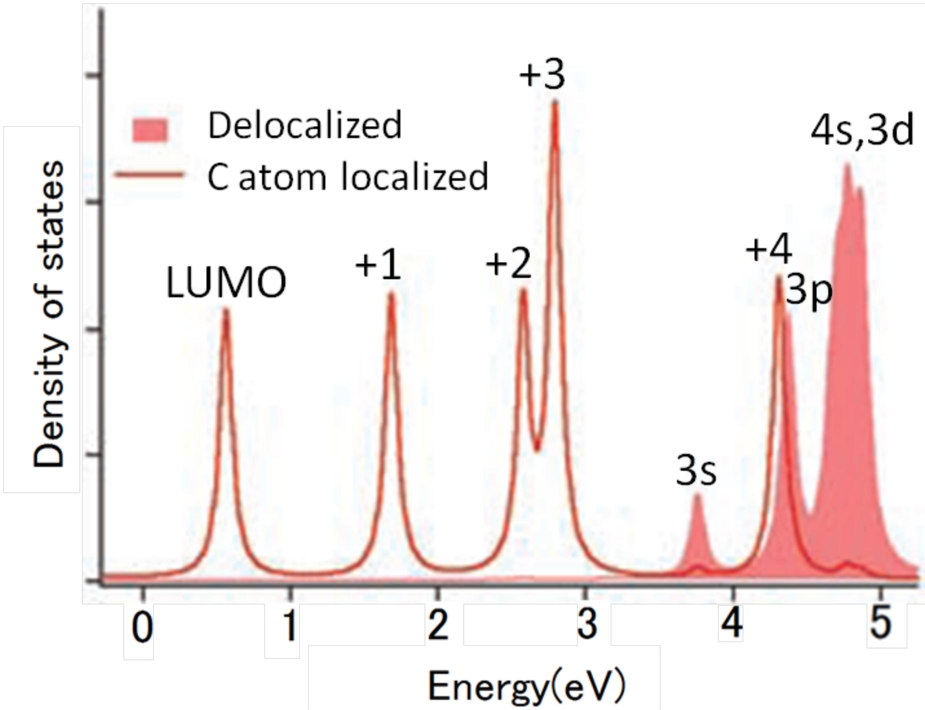
M. Feng, J. Zhao, H. Petek, *Science* **320**, 359 (2008).

Orbital shape of C_{60} states

Super Atomic molecular Orbitals (SAMOs) is theoretically confirmed.

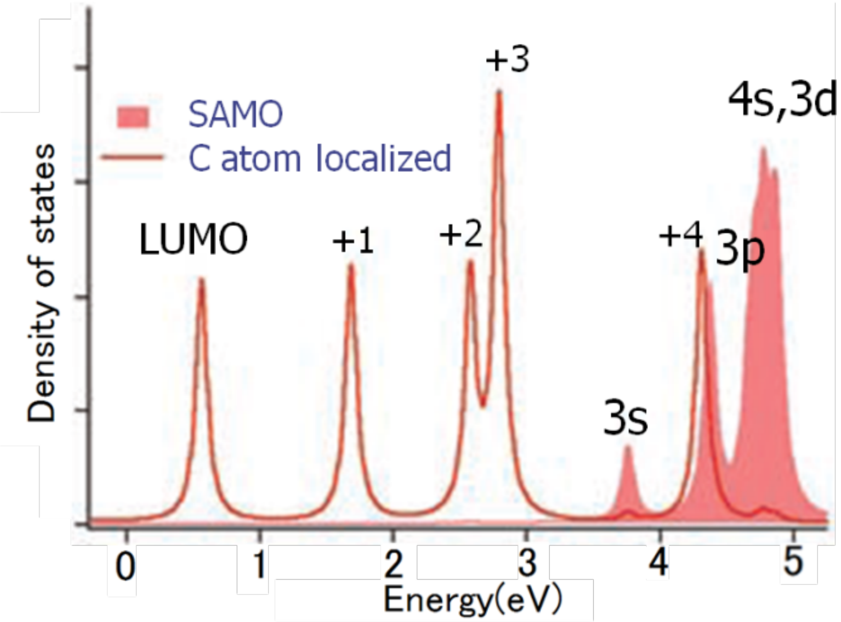
M. Feng, J. Zhao, H. Petek, Science 320, 359 (2008).

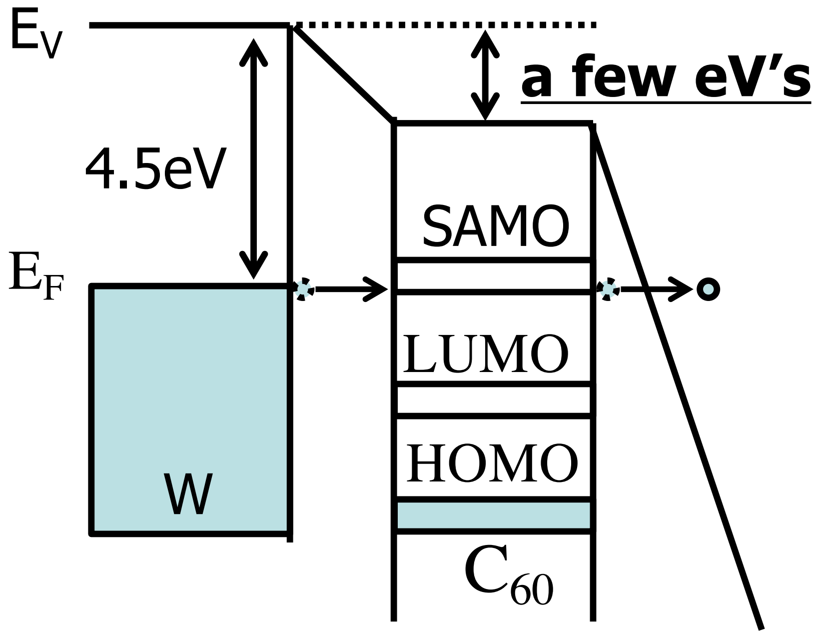




In FEM image,
SAMO states are visualized.

Energy Shift in C_{60} layer



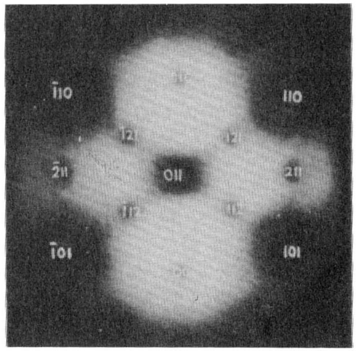


SAMO states are located at shallower positions.
Large shift of states should occur due to the field penetration in the C_{60} layer.
Then electrons are resonantly transmitted through SAMO states.

FEM can visualize the orbitals of weakly bound unoccupied states much more easily than STM or electron spectrometers.

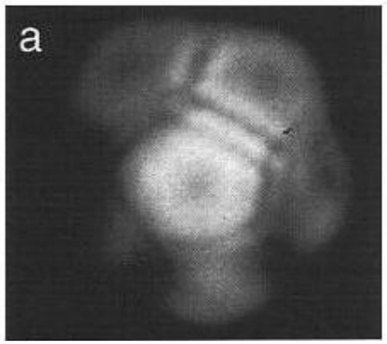
Origins of FEM Pattern in Literature

1. Local work function



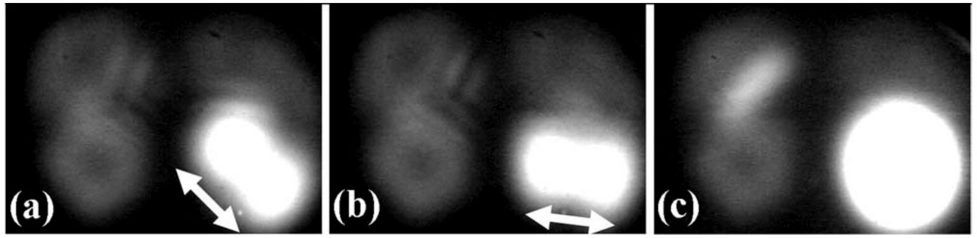
2. Local field enhancement
(geometrical field enhancement)

3. Interference

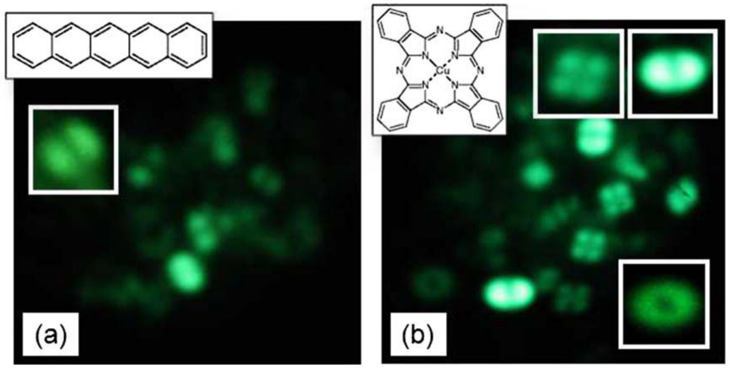


Y. Yahachi, K. Hata, T. Murata, JJAP 39, L271 (2000).

4. Molecular shape



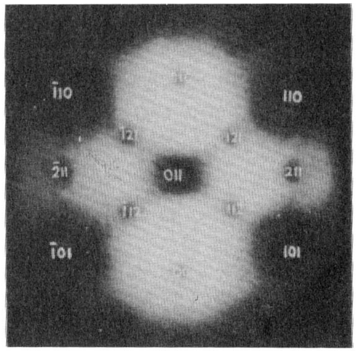
S. Waki, K. Hata, H. Sato, Y. Saito, JVST B25, 517 (2007).



Y. Neo, T. Matsumoto, M. Tomita, M. Sasaki, T. Aoki, H. Mimura, JVST B28, C2A1 (2010).

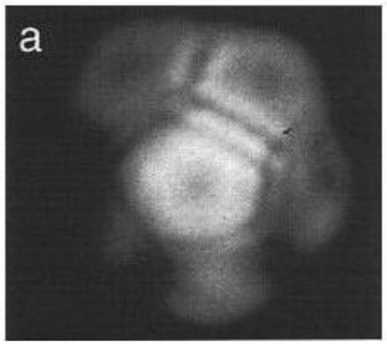
Origins of FEM Pattern in Atomic Scale

1. Local work function



2. Local field enhancement (geometrical field enhancement)

3. Interference



Y. Yahachi, K. Hata, T. Murata, JJAP 39, L271 (2000).

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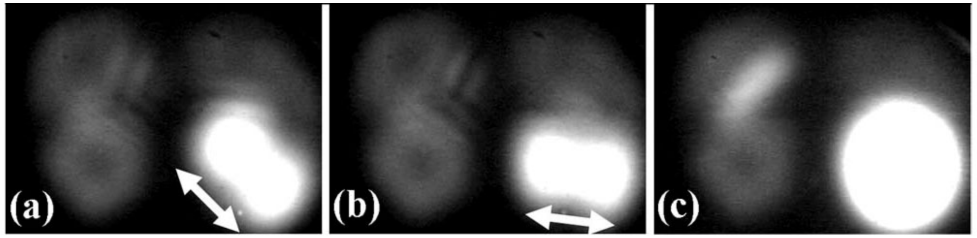

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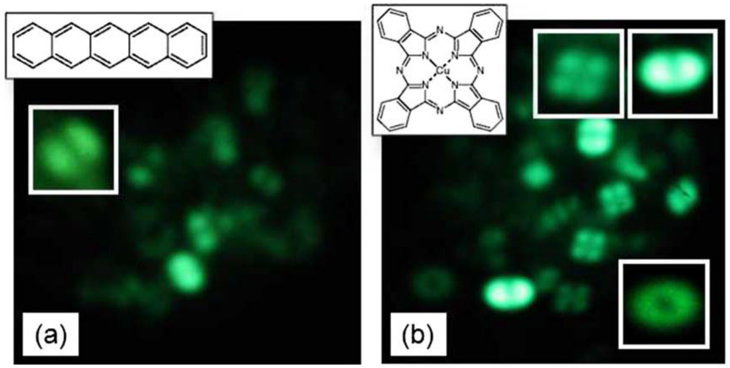

Y. Neo, T. Matsumoto, M. Tomita, M. Sasaki, T. Aoki, H. Mimura, JVST B28, C2A1 (2010).

5. Projection of the orbital from which electrons emit

Comprehensive Identification

Summary

We have presented here unusual and unrevealed features of FE from nano-carbon materials.

Effective work function of graphitized pencil lead was very low.

Spectra suggest that electrons emit from graphene edges.

Graphene should have special properties giving efficient FE.

The combination of graphene and h-BN gives superior FE.

It emits electrons efficiently to vacuum.

Electron scattering is negligible during the penetration.

Special FEM pattern corresponding to SAMO states appeared.

Highly symmetric shape of C_{60} make the identification easier.

FEM can be a new method to visualize electron orbitals.

Physics in nano-carbon in high field is attractive, but far from matured at present.

Thank you.