GRAPHENE MEMBRANE FOR IMAGING MOLECULAR ASSEMBLY AND DYNAMICS

Kwanpyo Kim

Department of Physics, UNIST

Korea University

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ENPL

Experimental Nanoscale Physics Laboratory

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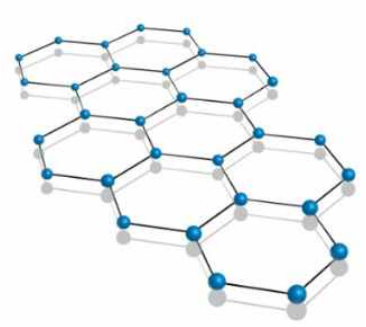
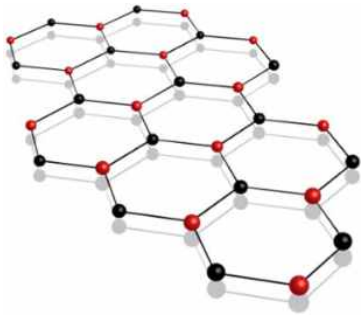
2009

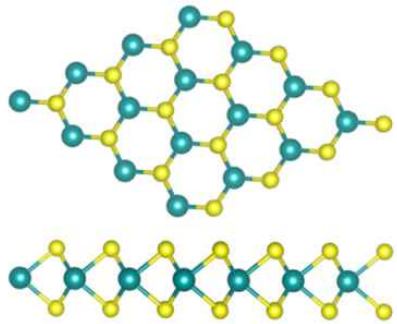
VARIOUS 2D MATERIALS



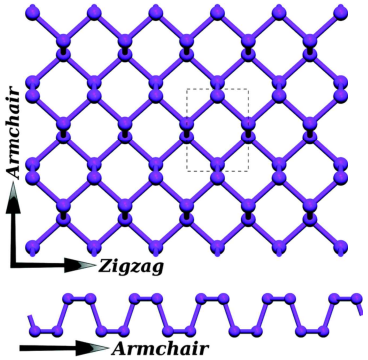
Graphene



Hexagonal Boron Nitride (h-BN)



Transition Metal Dichalcogenides (TMDCs)

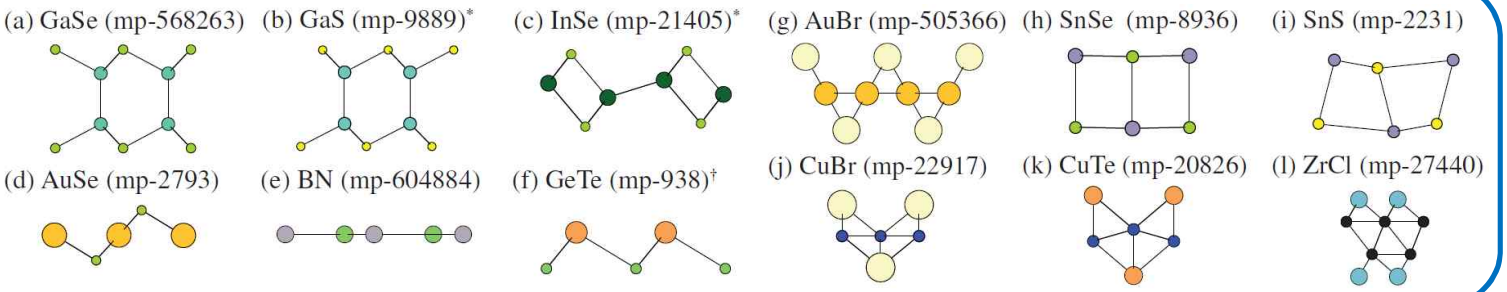


Phosphorene (Black Phosphorus)

- Isolation in atomically-thin forms

  => Emergence of new properties (different from bulk)

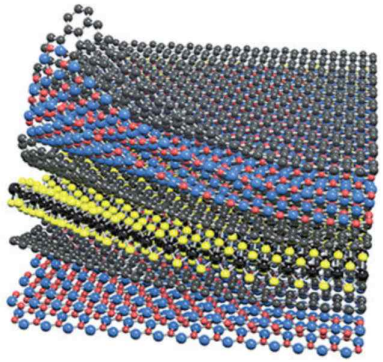
- Various accessible tuning knobs for controlling material properties by doping (electrical gating), mechanical stimuli (strain) and defect manipulations, etc.



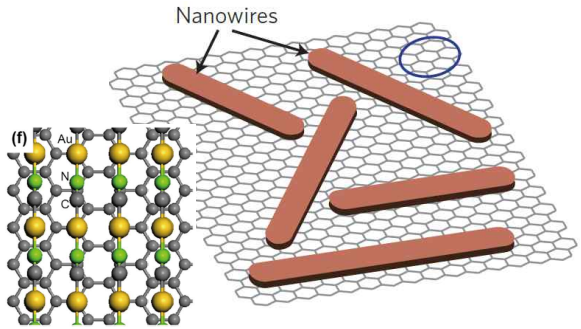
# of available 2D materials > 820

M. Ashton *et al.* *PRL* 118, 106101 (2017)

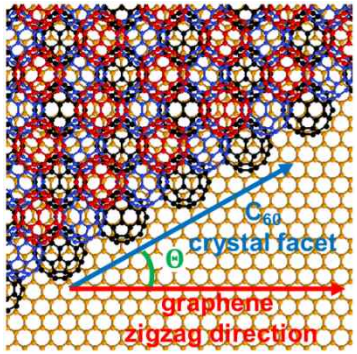
2D Material-Based Heterostructures



2D-2D van der Waals Heterostructure



1D-2D van der Waals Heterostructure



0D-2D van der Waals Heterostructure

Simply putting different materials together is not what we want!

High-quality 2D crystals
(Large-scale synthesis for real applications)

Coherent interaction between components
- Clean interfaces
- Well-defined inter-component lattice relations

New phenomena and applications
from 2D materials and heterostructures

Intrinsically weak van der Waals interaction may result in misaligned inter-component packing.

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WHY ATOMIC RESOLUTION IMAGING?

1. High-quality 2D crystals
(Large-scale synthesis for real applications)

2. Coherent interaction between components
- Clean interfaces
- Well-defined inter-component lattice relations

3. New phenomena and applications
from 2D materials and heterostructures

Atomic Resolution Imaging & Spectroscopy

Atomic-Scale Defects?
Stacking Relation?
Grain Size?
Crystal Edge?
Flatness?
Surface Residues?

Interlayer Rotation?
Stacking Sequence?
Interface Quality?
In-Plane Strain?
→ **2D/2D**

Assembly Behavior? → **1D/2D**
Interface Quality? → **0D/2D**

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MICROSCOPES USING ELECTRONS: TEM AND STM

The Nobel Prize in Physics 1986

Ernst Ruska
Prize share: 1/2

Gerd Binnig
Prize share: 1/4

Heinrich Rohrer
Prize share: 1/4

The Nobel Prize in Physics 1986 was divided, one half awarded to Ernst Ruska *"for his fundamental work in electron optics, and for the design of the first electron microscope"*, the other half jointly to Gerd Binnig and Heinrich Rohrer *"for their design of the scanning tunneling microscope"*.

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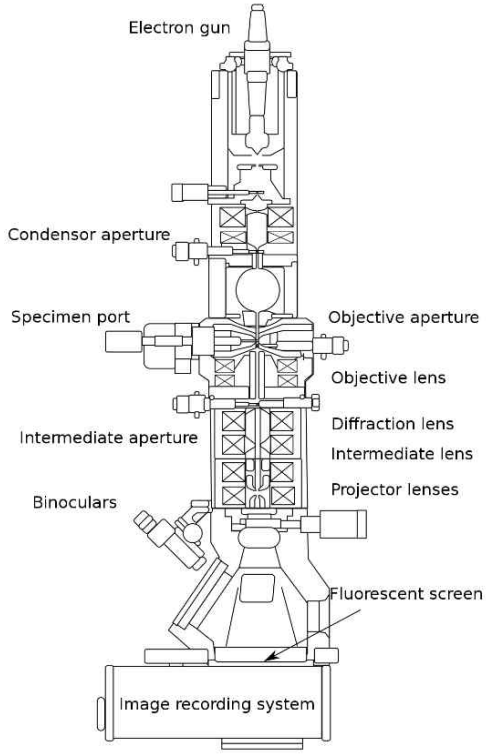
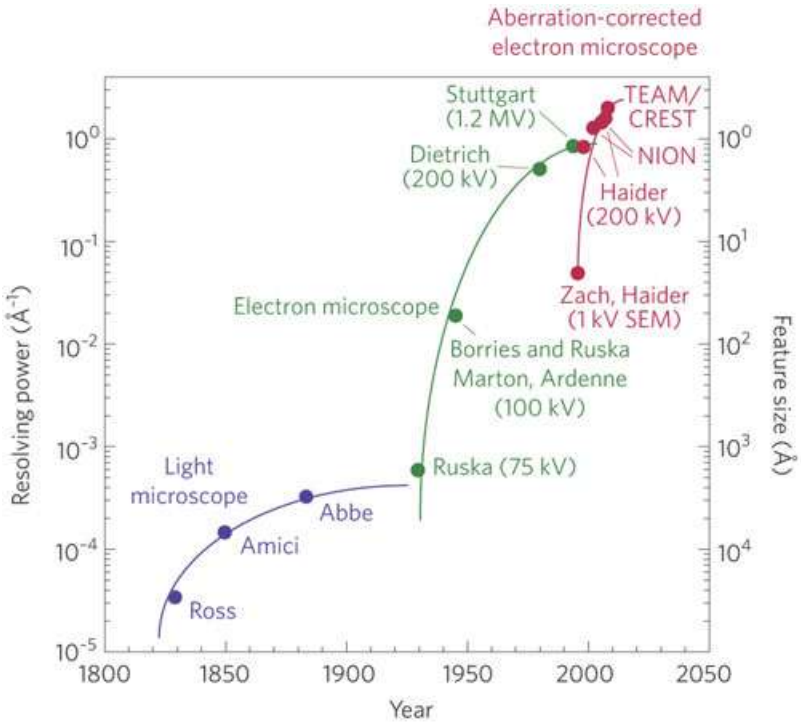
Transmission Electron Microscopy



http://en.wikipedia.org/wiki/Transmission_electron_microscopy



D. A. Muller, *Nature Materials* 8, 263 (2009)

- Imaging and spectroscopy using high energy electrons (20 ~ 300 keV) on a very thin sample
- Study of atomic-scale structure, chemistry, and atomic dynamic

- Development of aberration correctors in the late 1990s
- Sub Å resolution imaging and spectroscopy with low acceleration voltages

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CONTENTS

- Atomic Resolution TEM Imaging of Graphene and Other 2D Materials

- Nanostructure Assembly on Graphene

  - Organic Molecular Assembly (Pentacene and Fullerene)

  - Epitaxial Growth of Inorganic Nanowires on Pristine Graphene

- Imaging Liquid-Phase Dynamics Using Graphene Liquid Cells

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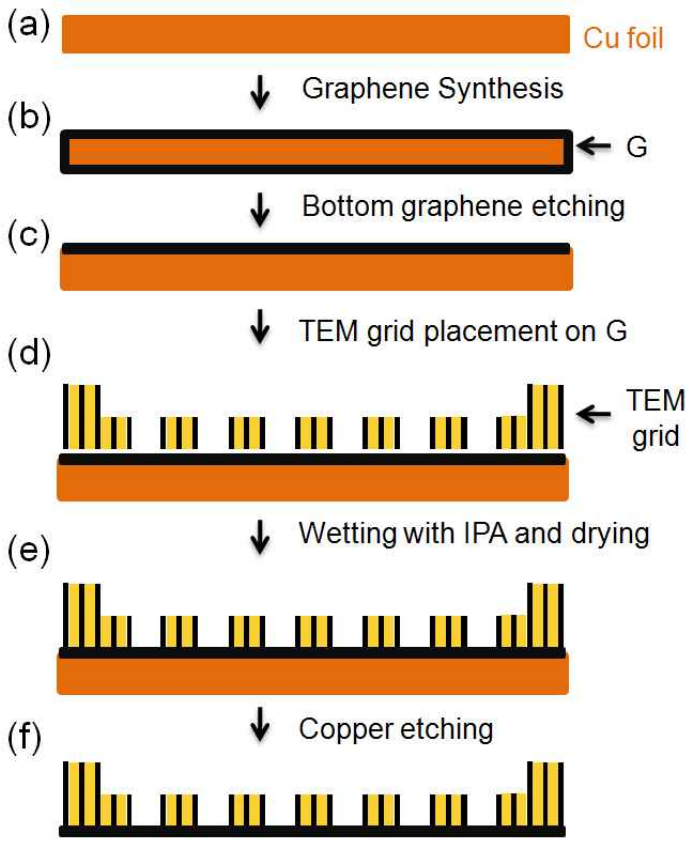
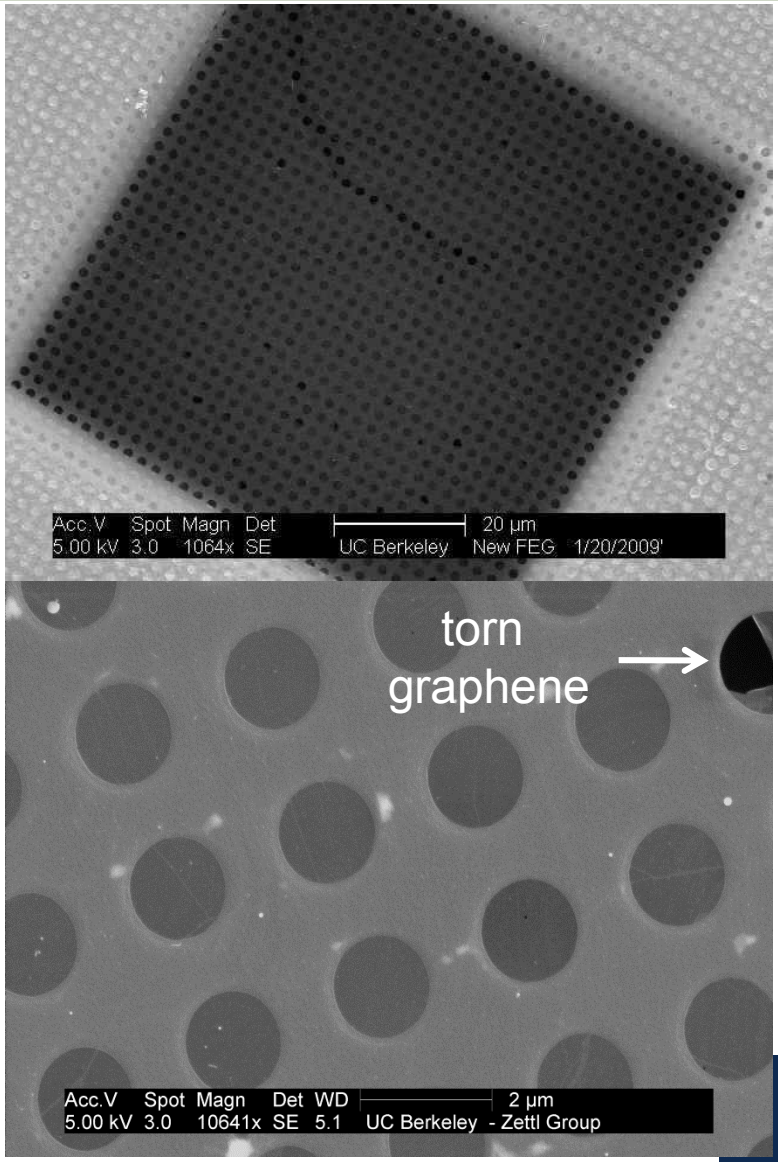
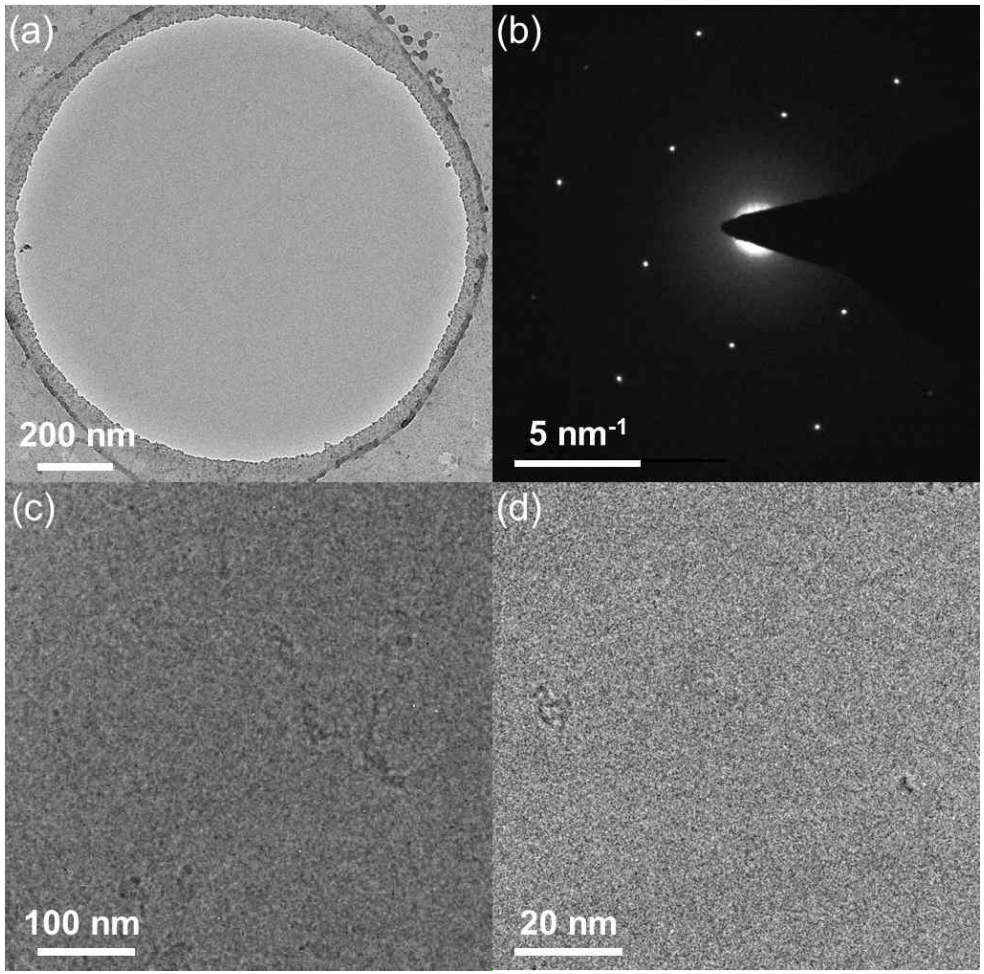
CLEAN TRANSFER OF LARGE-SCALE GRAPHENE

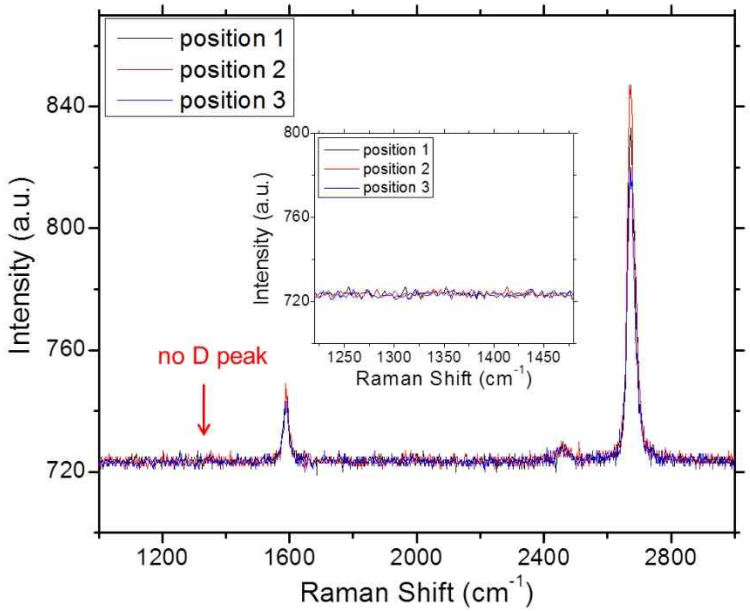


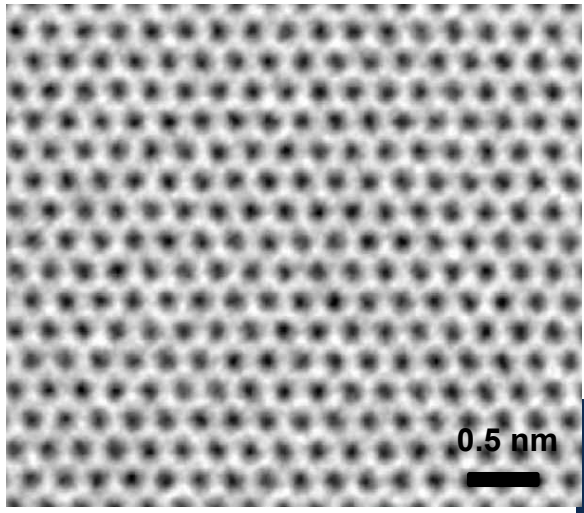
W. Regan *et al.*, *Appl. Phys. Lett.* 96, 113101 (2010)



GRAPHENE MEMBRANE







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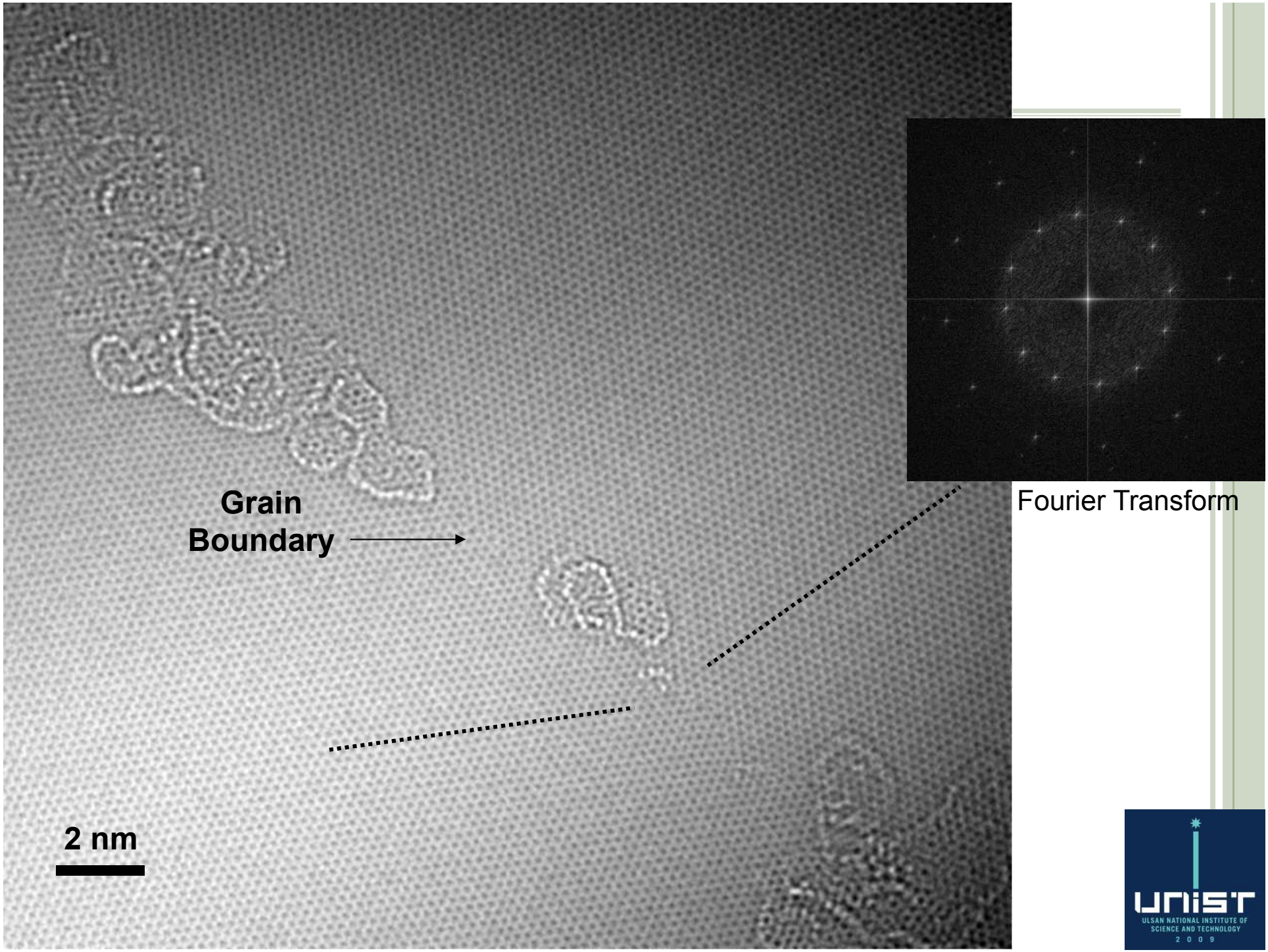

Fourier Transform

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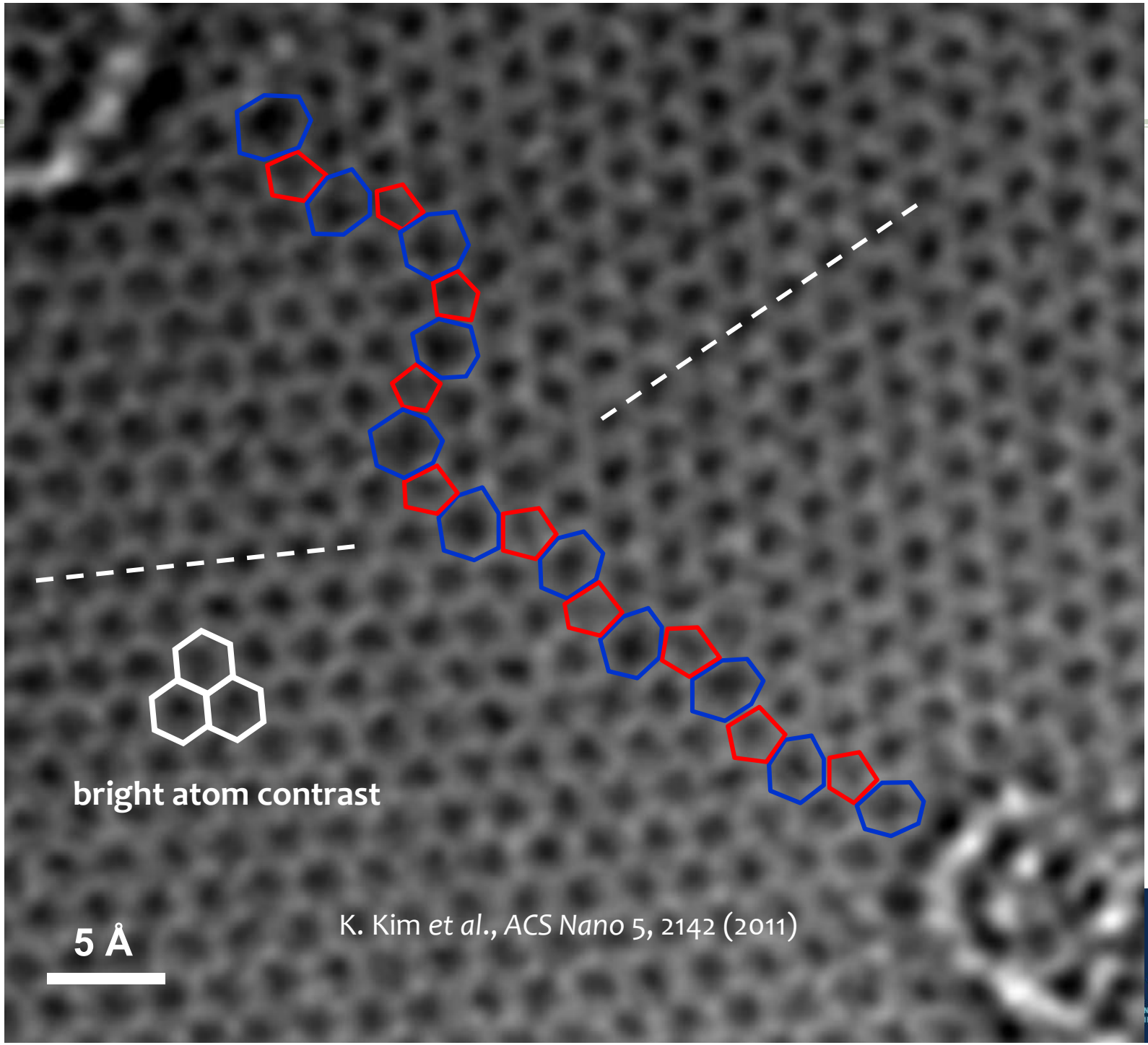
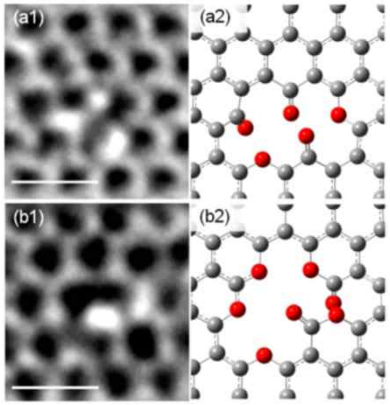

bright atom contrast
5 Å
K. Kim *et al.*, *ACS Nano* 5, 2142 (2011)

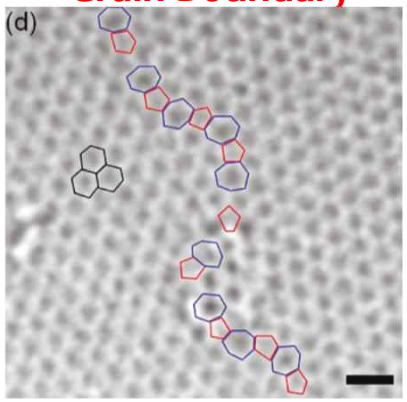
Atomic Scale Imaging of Graphene Defects

Point Defects



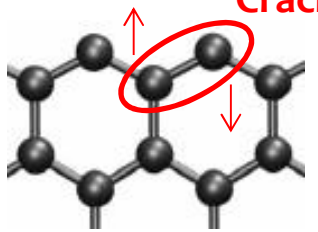
Y. Yamada et al. JACS (2014)

Grain Boundary

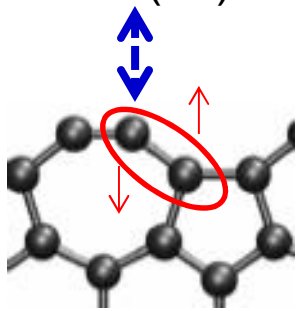


K. Kim et al. ACS Nano (2011)

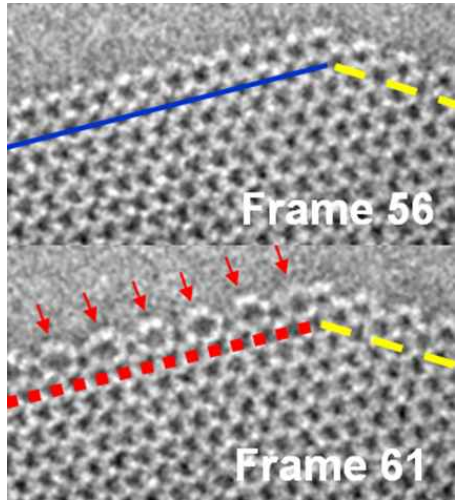
Crack and Crack Edges



ZZ (66)

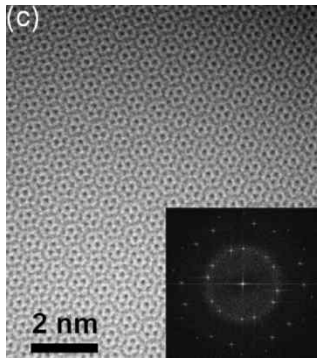


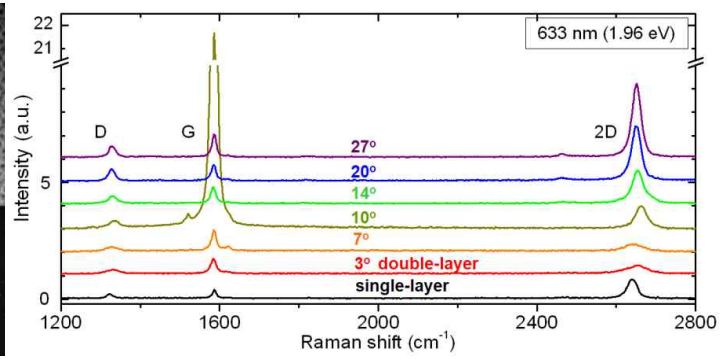
ZZ(57)



K. Kim et al. Nano Lett (2012)
K. Kim et al. Nature Commun (2013)

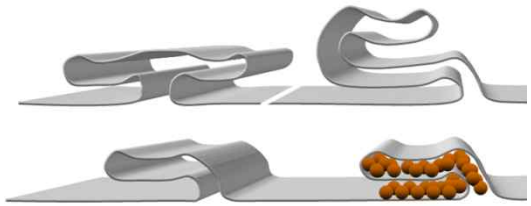
Moiré Patterns from Twisted Double-Layer





K. Kim et al. Phys Rev Lett (2012)
J. Kim et al. Sci Rep (2015)

Graphene Fold



K. Kim et al. Phys Rev B (2011)

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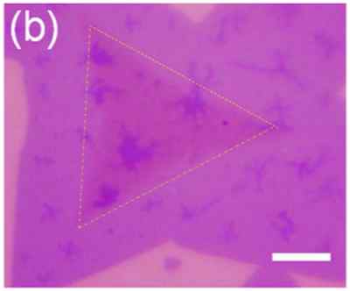
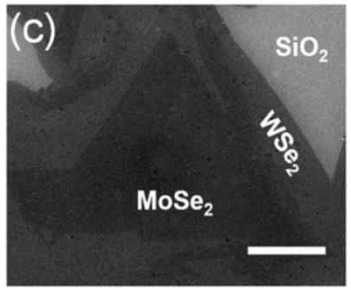
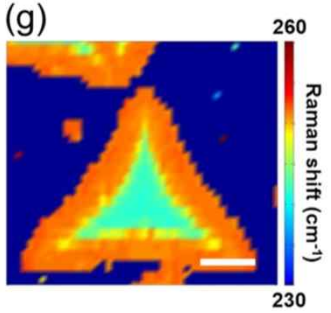
IMAGING OF 2D LATERAL HETEROSTRUCTURES

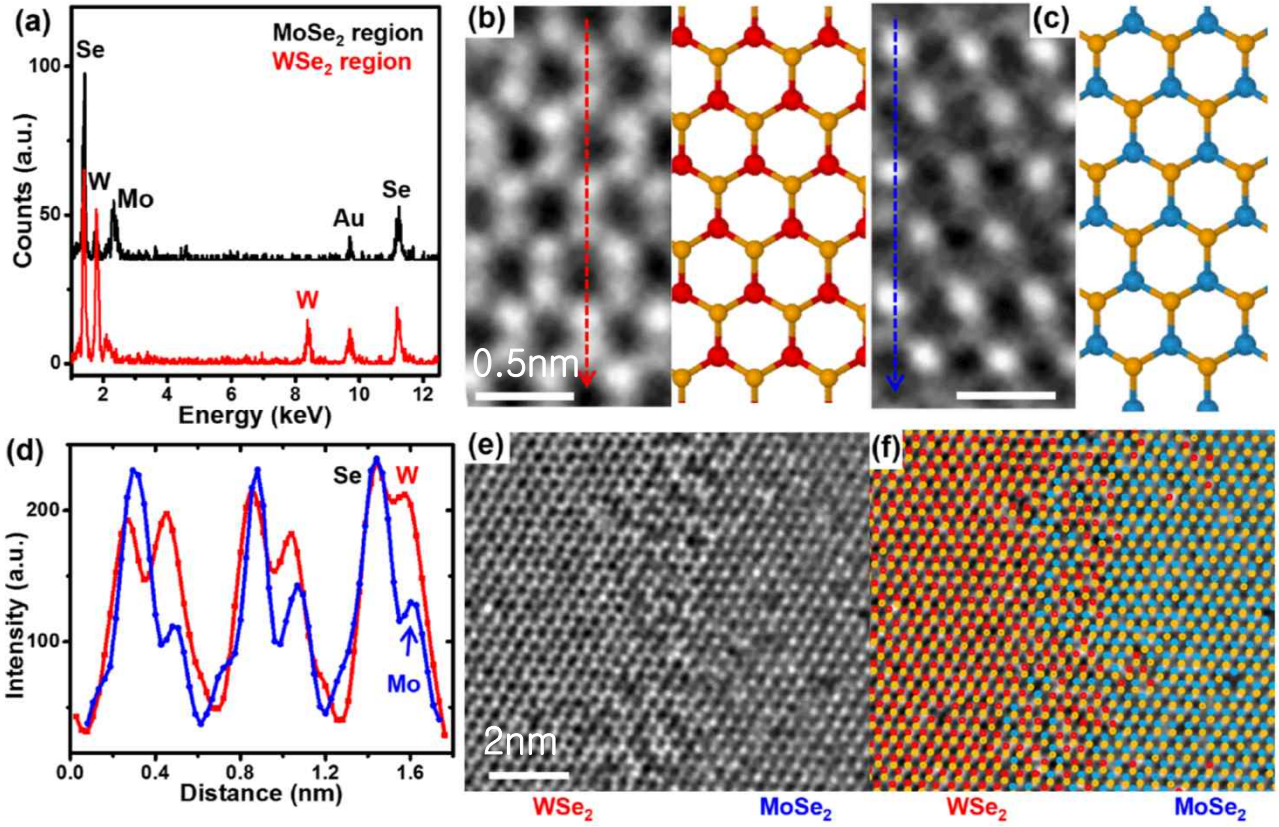






Samples provided by Univ. of Ulsan

Atomic Scale Imaging of $MoSe_2$-WSe_2 Lateral Heterostructures



F. Ullah *et al.* *ACS Nano* Advanced publication (2017)

CONTENTS

WHY GRAPHENE FOR TEM IMAGING?

Electrical properties

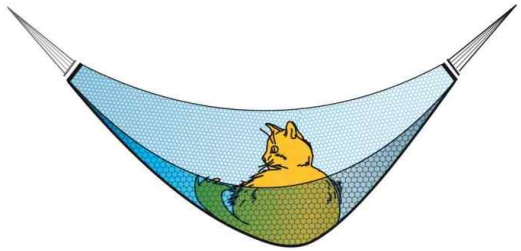
$$E^{\pm}(\kappa) = \pm\hbar v_F|\kappa| \quad m^* = 0$$

$$H = v_F\vec{\sigma}\cdot\vec{p}$$

$$v_F \approx 1\times10^6\,\mathrm{m/s} = c/300$$

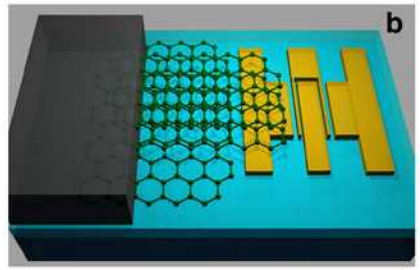
ultrahigh charge carrier mobility
μ > 200,000 cm²/Vs

Superior mechanical properties
(Y ~ 1 TPa)



http://nobelprize.org

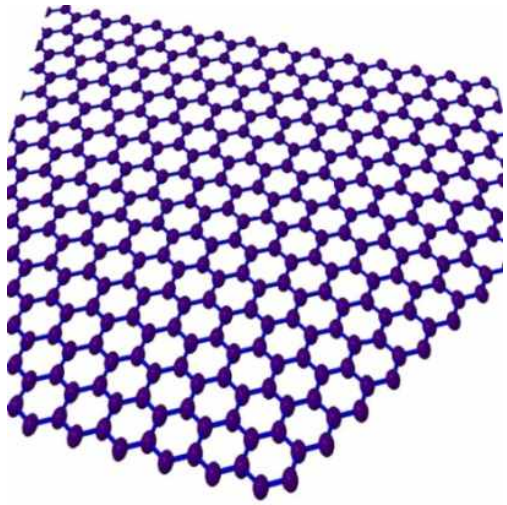
Excellent thermal properties
(K ~ 4000 W/mK)



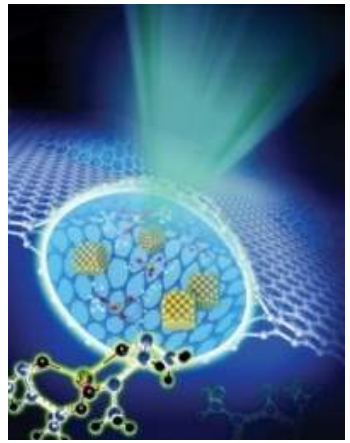
Z. Yan *et al.*, *Nature Commun.* **3**, 827 (2012)

- ☑ **Low background signals** (Thinnest membrane)
- ☑ **Mechanical & chemical stability**
- ☑ **Low damages from electron-beam** with high electrical & thermal conductivity

Ideal imaging template



Novel Imaging Platform



J. Yuk *et al.*, *Science* (2012)
J. Park *et al.*, *Science* (2015)

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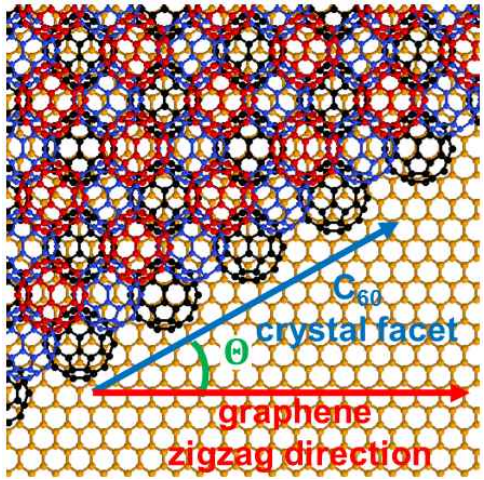
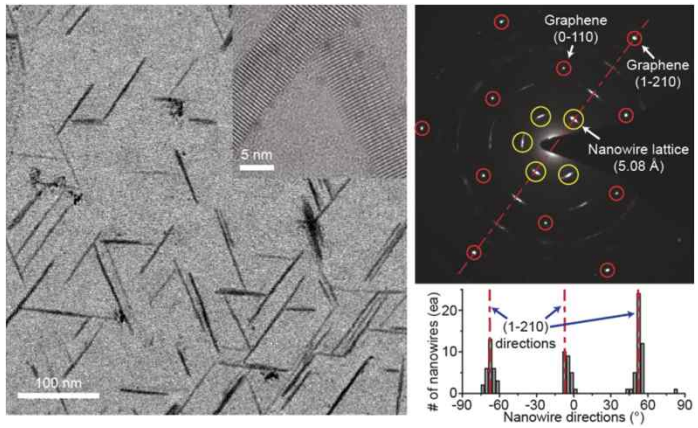
NANOSTRUCTURE ASSEMBLY ON GRAPHENE

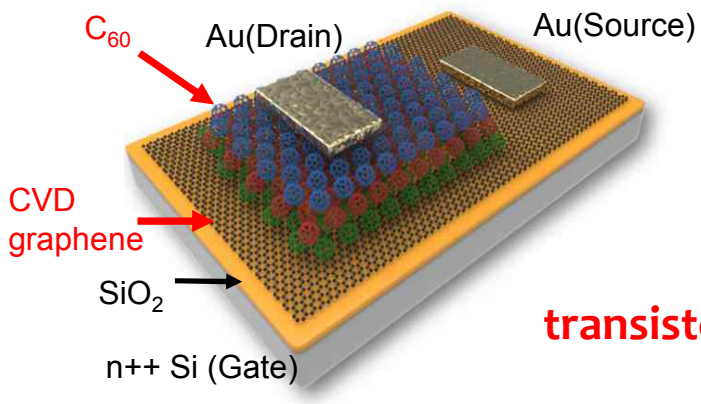
Excellent Assembly Template



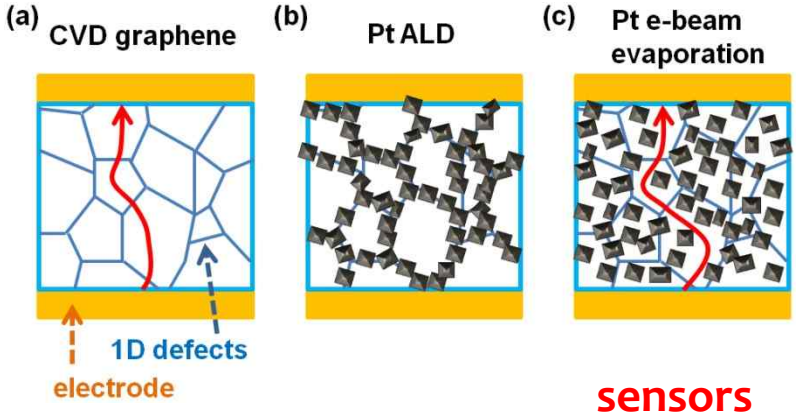


Molecule-Molecule Interactions vs. Molecule-Substrate Interactions

Added Functionality



transistors



sensors

Selective Functionalization for Various Applications

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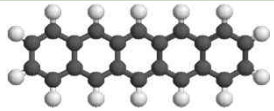
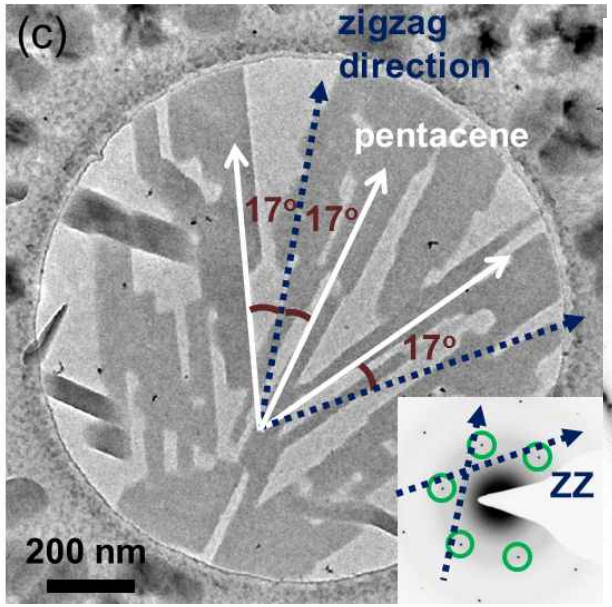
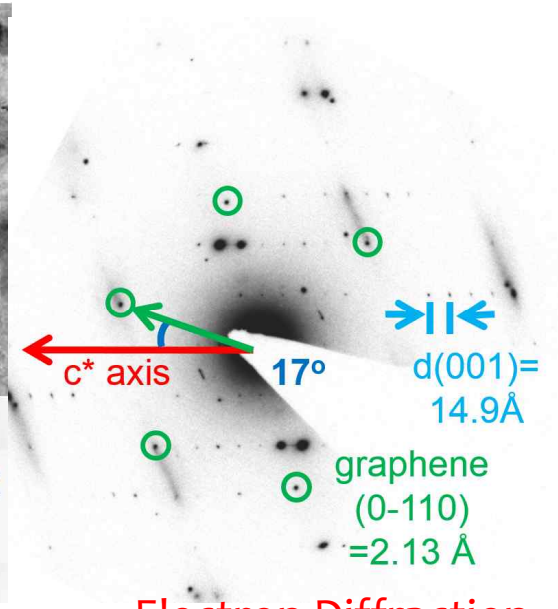
PENTACENE ASSEMBLY ON GRAPHENE

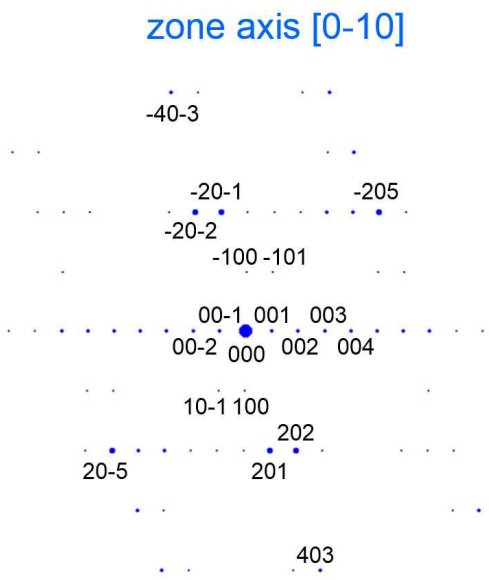
Molecular crystals of pentacene on graphene



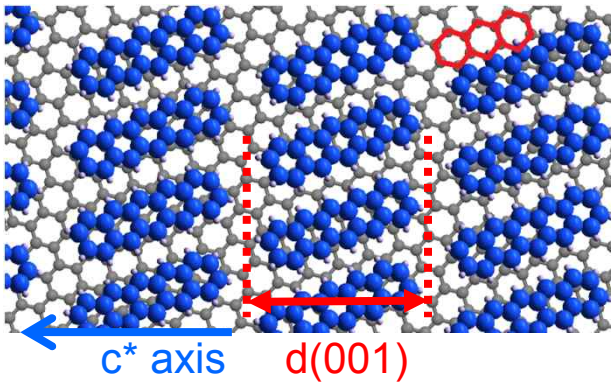




Electron Diffraction



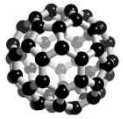
Simulation



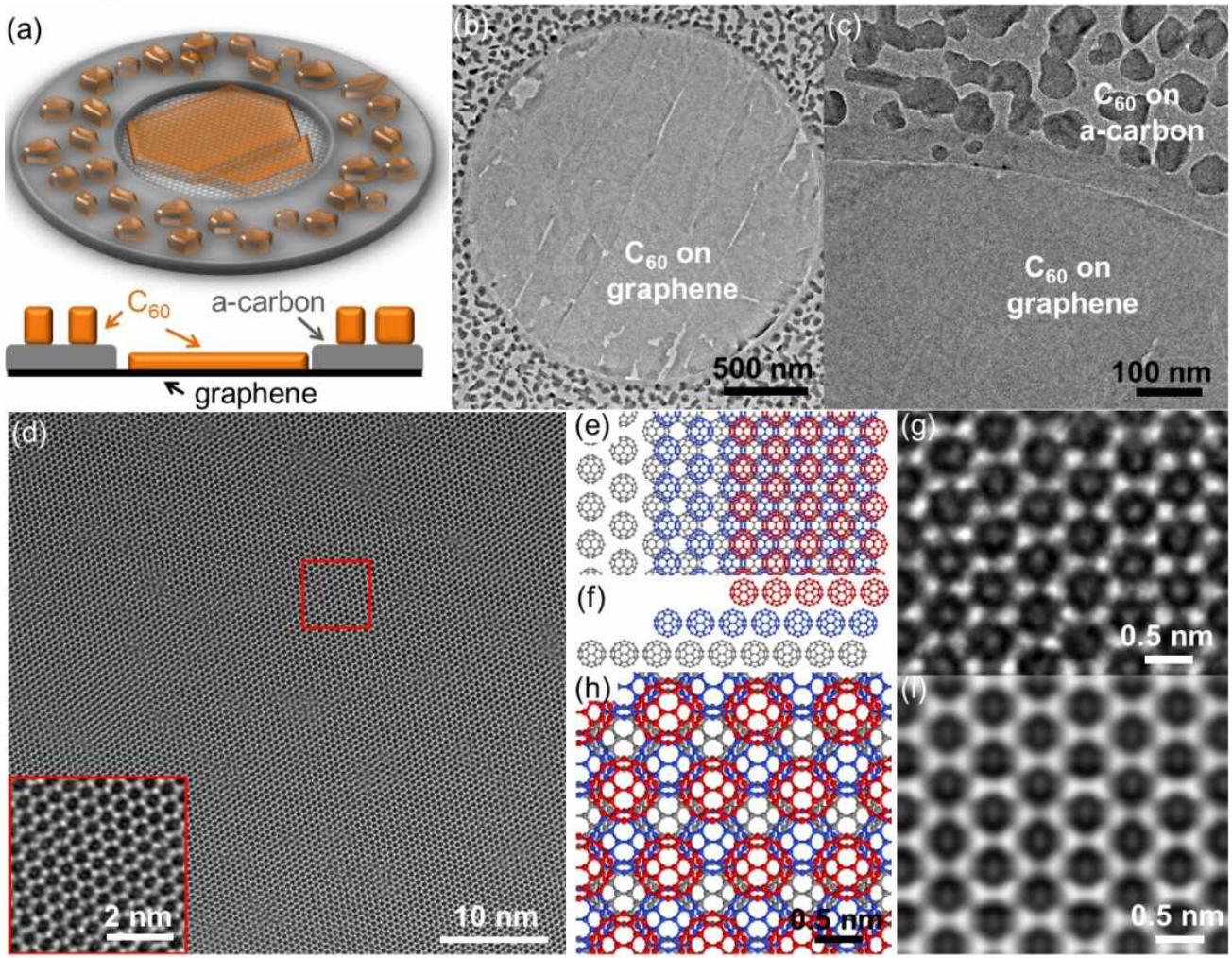
- **Strong azimuthal correlation with underlying graphene**
- **Unusual pentacene polymorph**

K. Kim *et al.*, *Small* 11, 2037 (2015)

C_{60} Assembly on Graphene



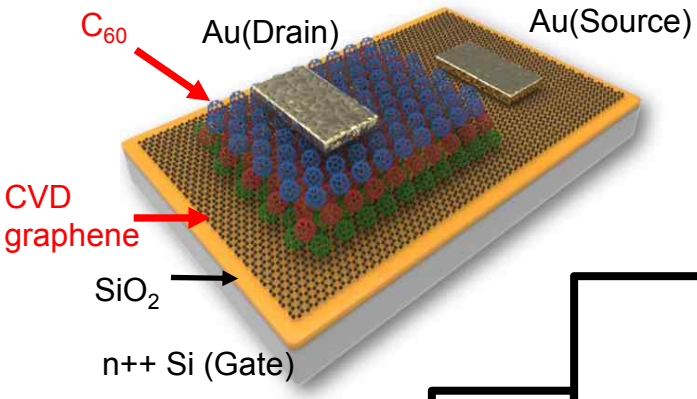
Molecular crystals of C_{60} on graphene

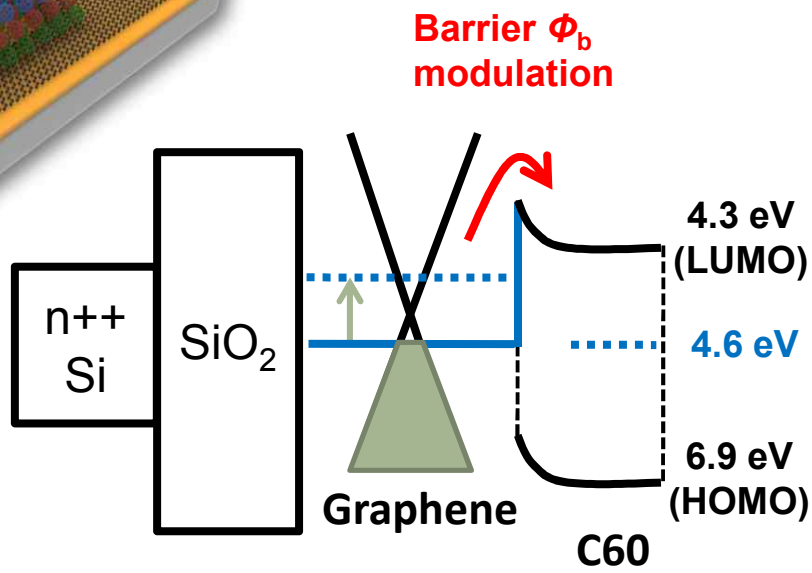


K. Kim *et al.*, *ACS Nano* 9, 5922 (2015)

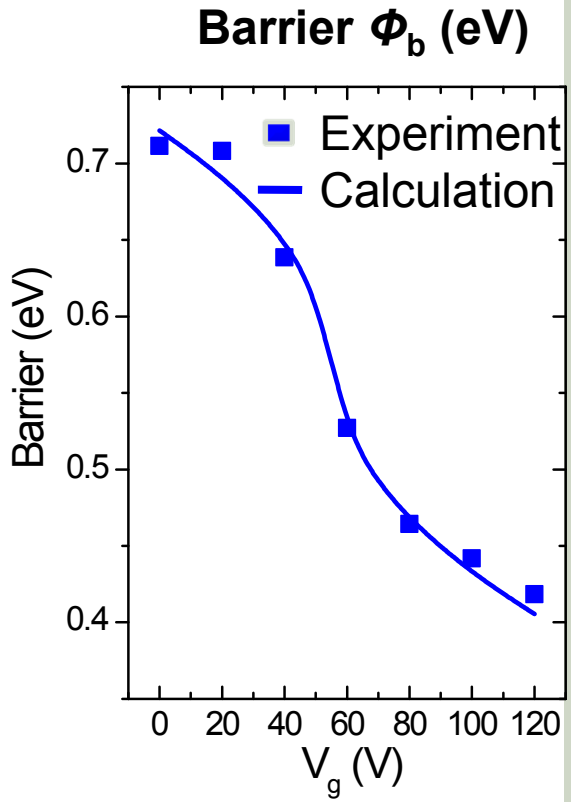
C_{60}/Graphene Vertical Transistors

C60/graphene Vertical Transistors





< Graphene/C60 Schottky Junction >



C_{60} on graphene
- Large grains
- Epitaxial growth

Low grain boundary trap density & Low interface trap density

Minimal traps

Schottky barrier modulation ~ 0.3 eV

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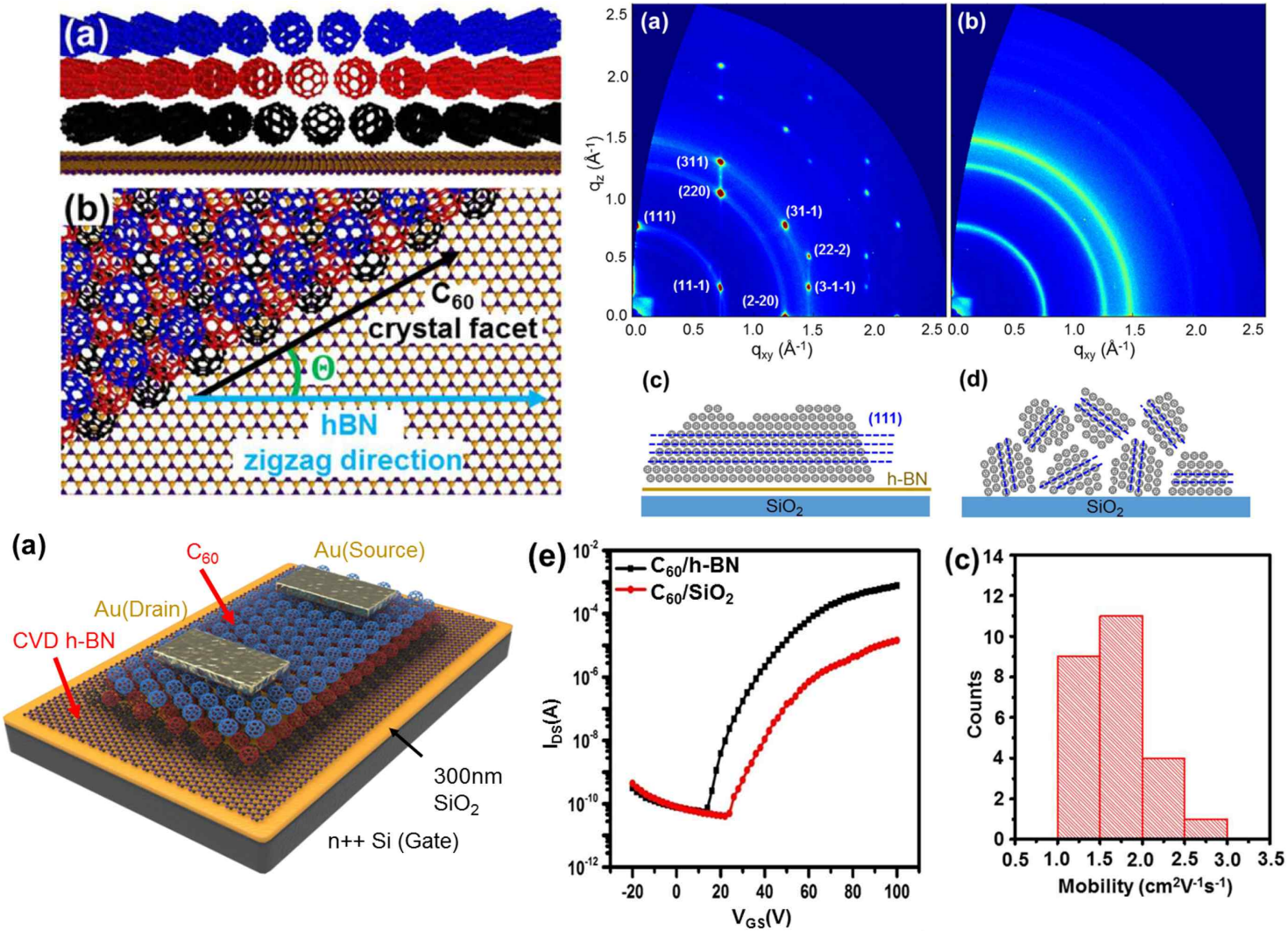
2009

C_{60}/h-BN Lateral Transistors

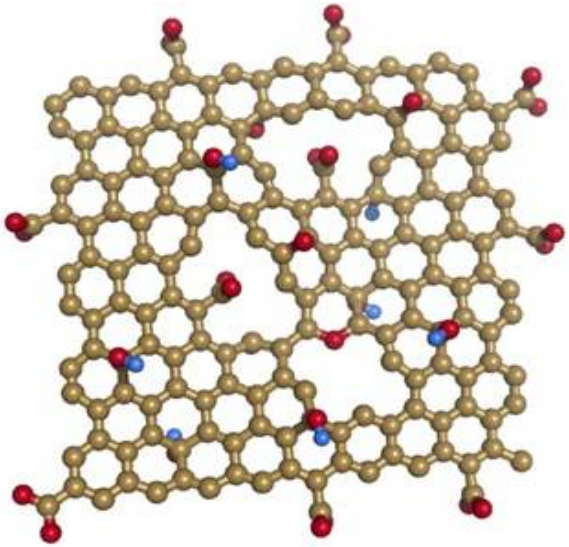
C60/h-BN Lateral Transistors



T. H. Lee *et al. Chem. Mater.* 29, 2341 (2017)

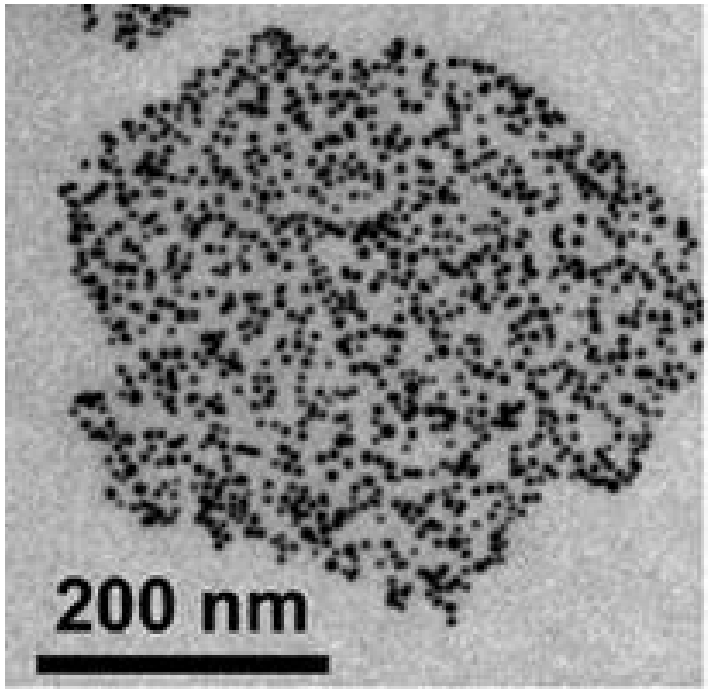
Previous Work: Graphene + Inorganic Materials

Graphene derivatives



+

Inorganic materials
(at graphene defects)



[J Phys Chem C, 2008]
[J Phys Chem C, 2009]
[JACS, 2010]
[Adv Mat, 2009]
……

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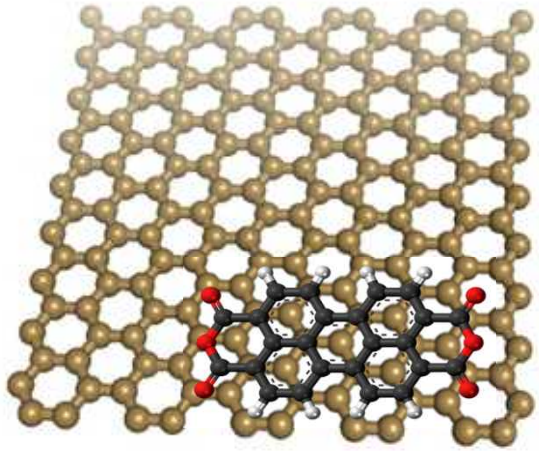
2009

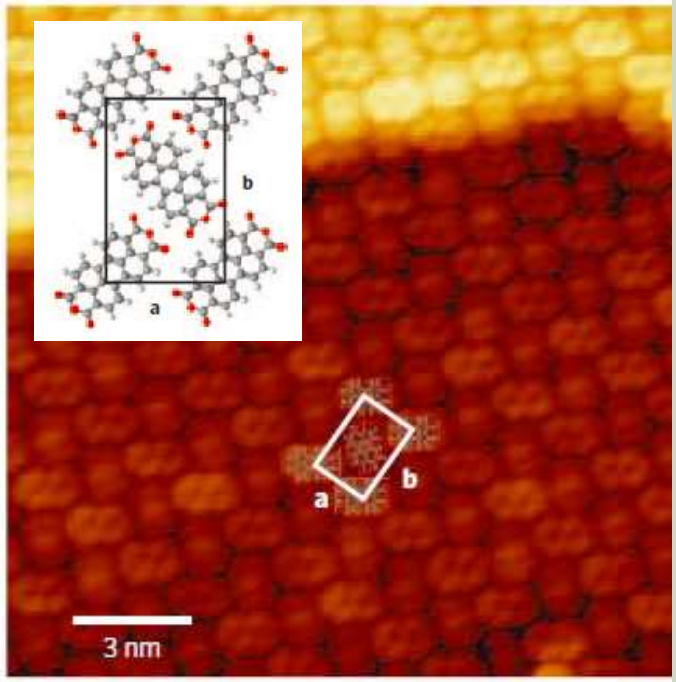
Previous Work: Graphene + Inorganic Materials

Linker molecules



+

Inorganic materials
(using organic linkers)



[Nat Chem, 2009]

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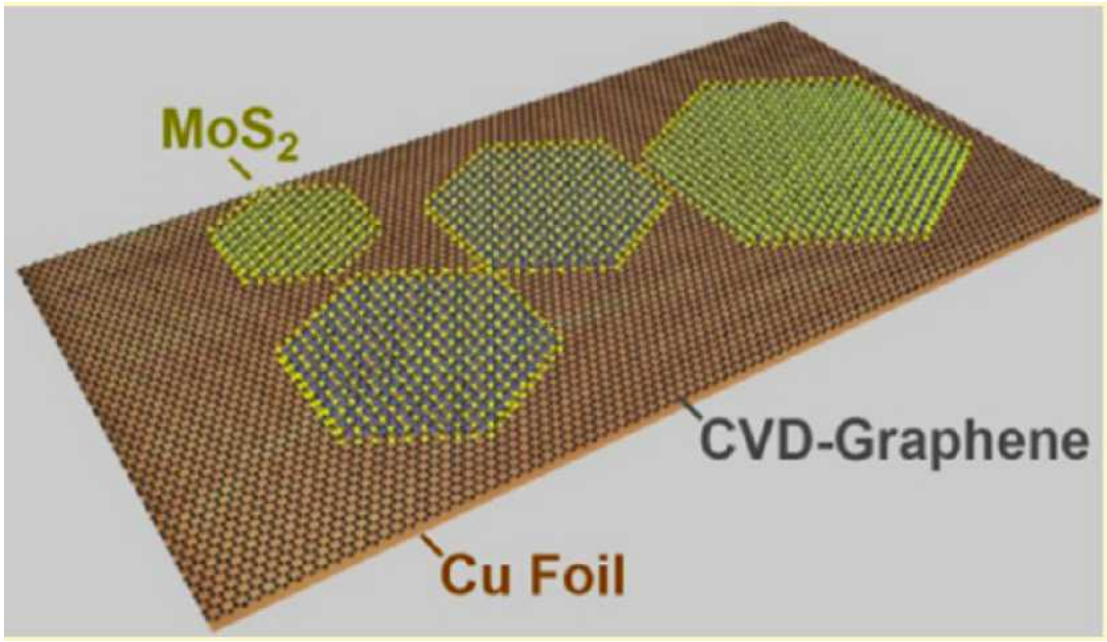
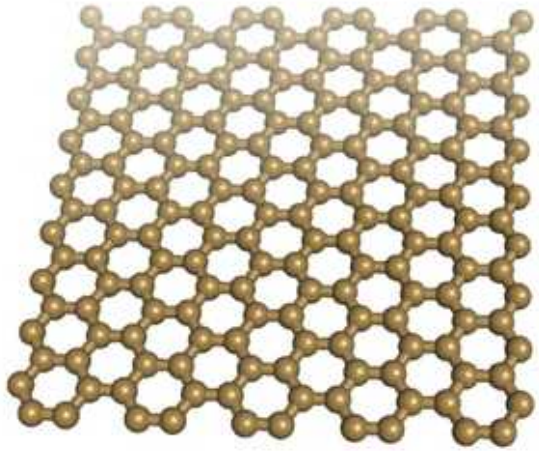
Previous Work: Graphene + Inorganic Materials



[Nano Lett, 2012]

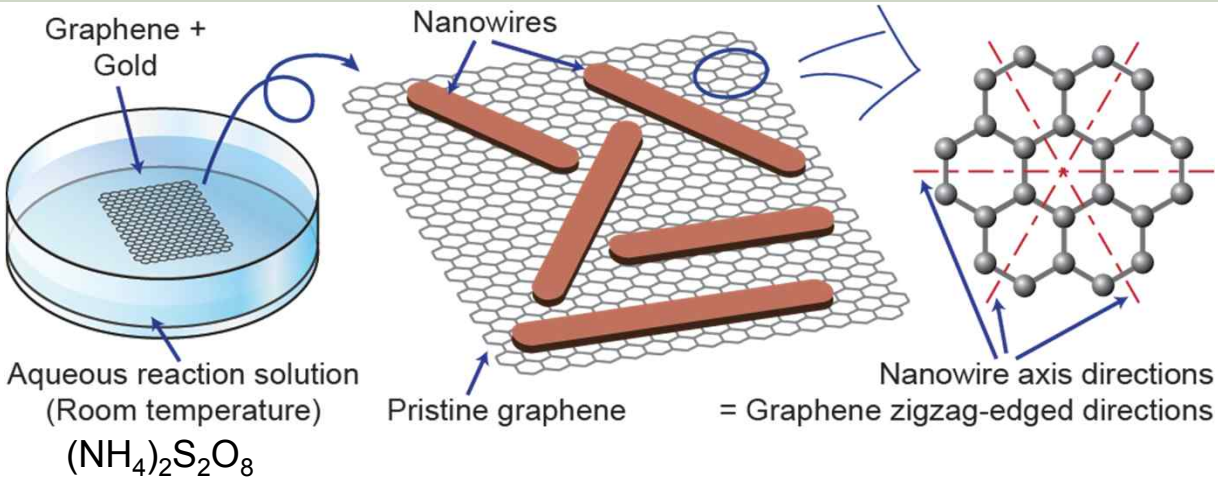
Vapor-phase deposition

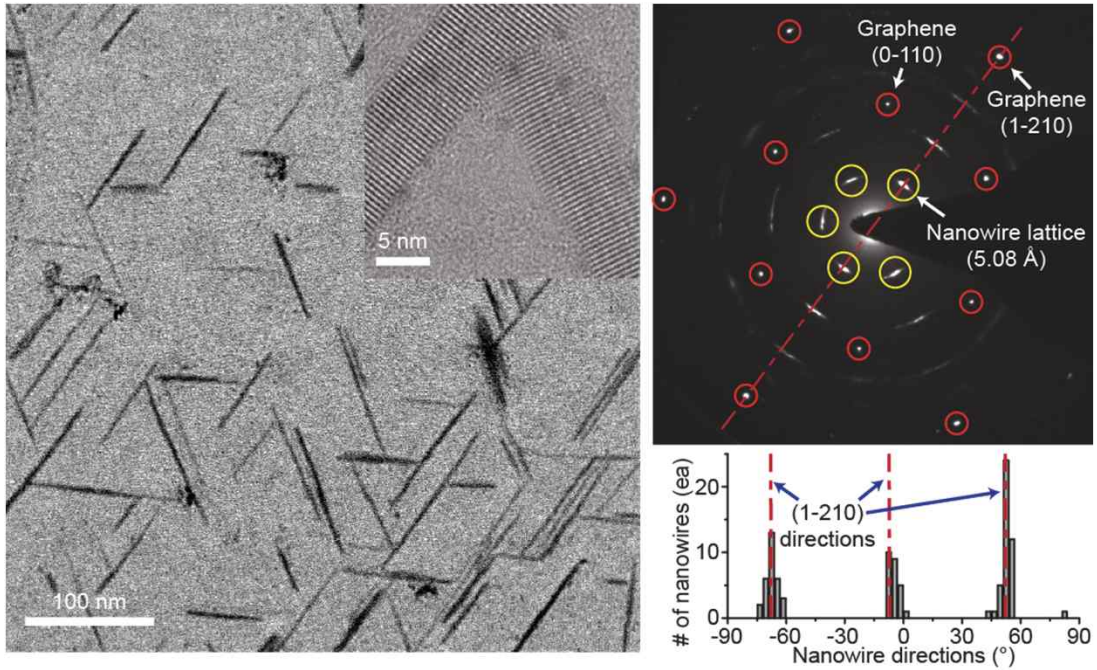


+

Inorganic materials
(at high temperature)

Self-Organized Nanowires on Graphene





W. C. Lee *et al.*, *Nature Nanotech.* 10, 423 (2015)

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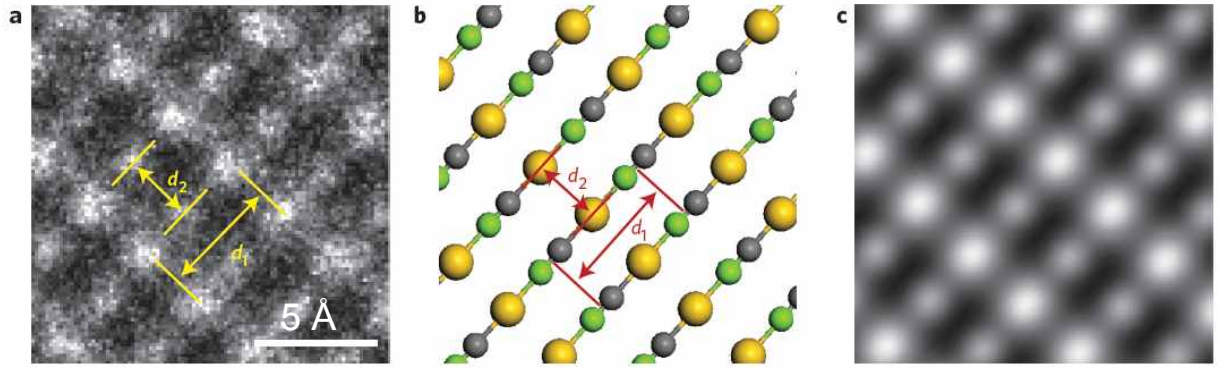
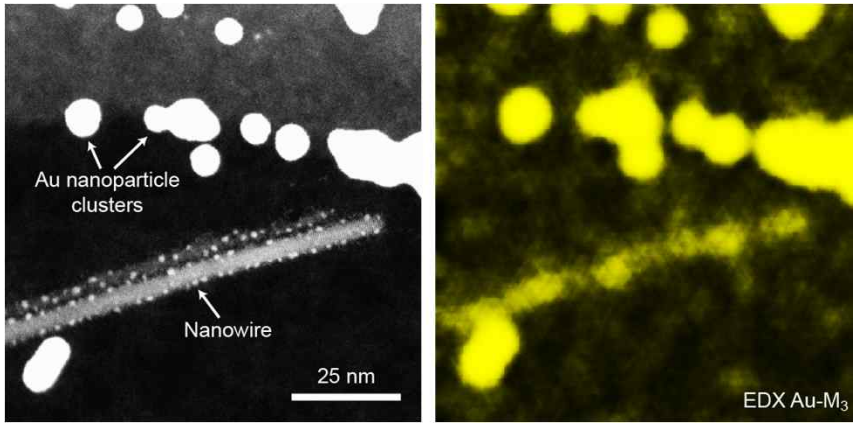
2009

Nanowire Identification: AuCN

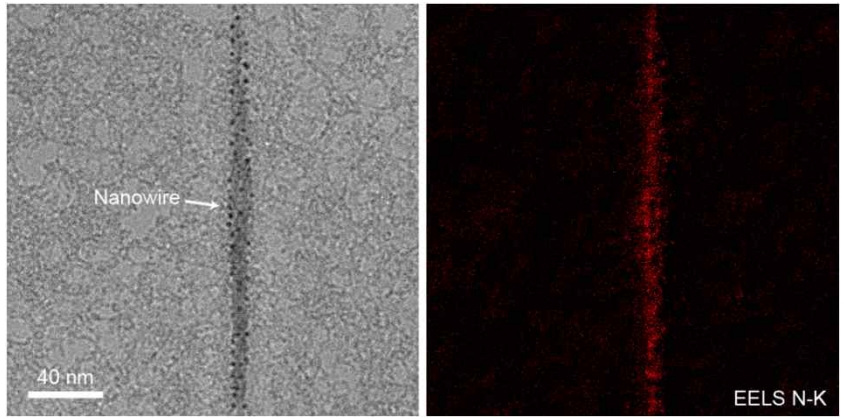
<TEM imaging>



<Au EDX Mapping>



<EFTEM image at the N K-edge>

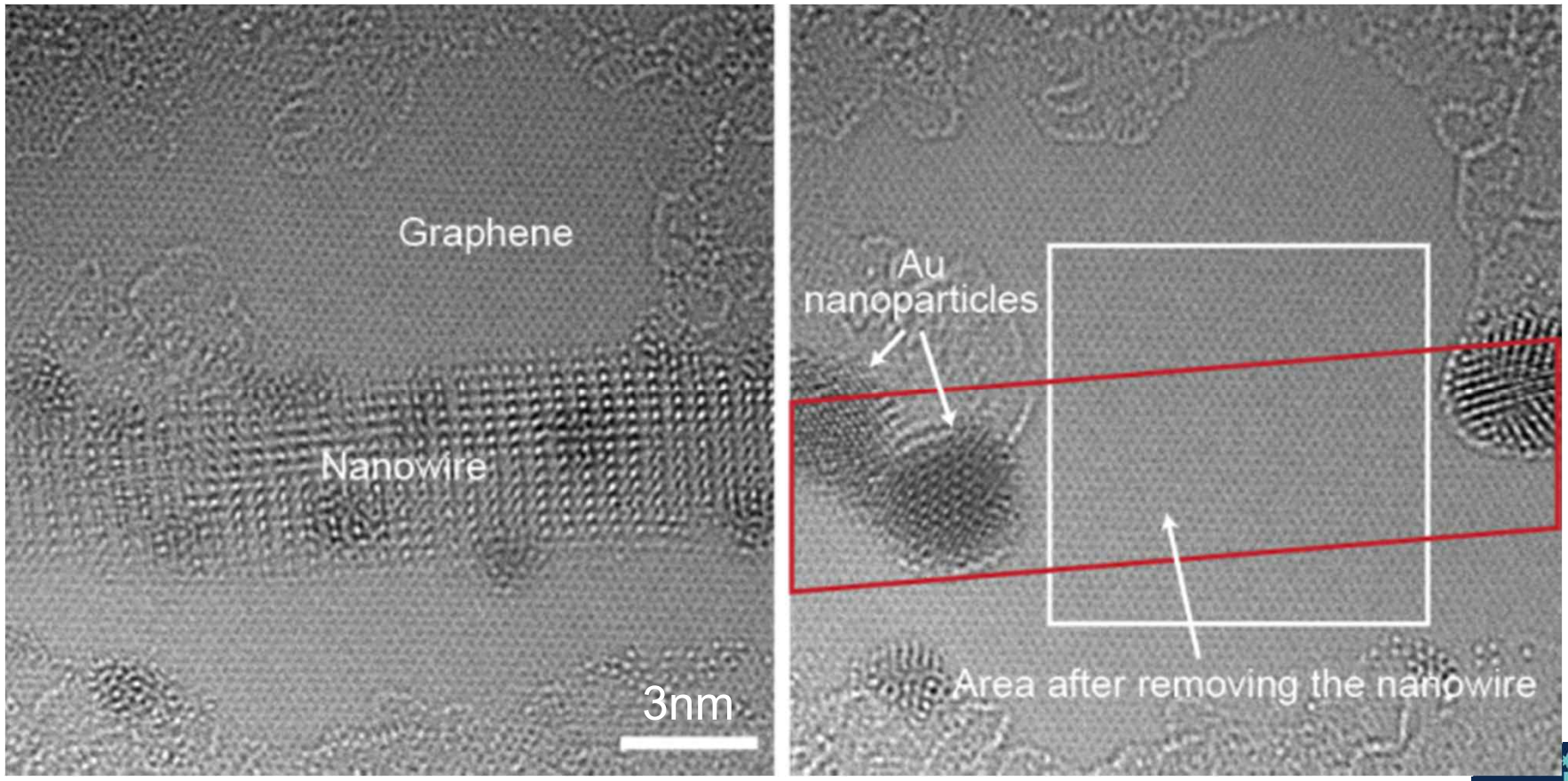


W. C. Lee *et al.*, *Nature Nanotech.* 10, 423 (2015)

Pristine Graphene Underneath the Nanowires

<Initial state>

<After removing the nanowire>



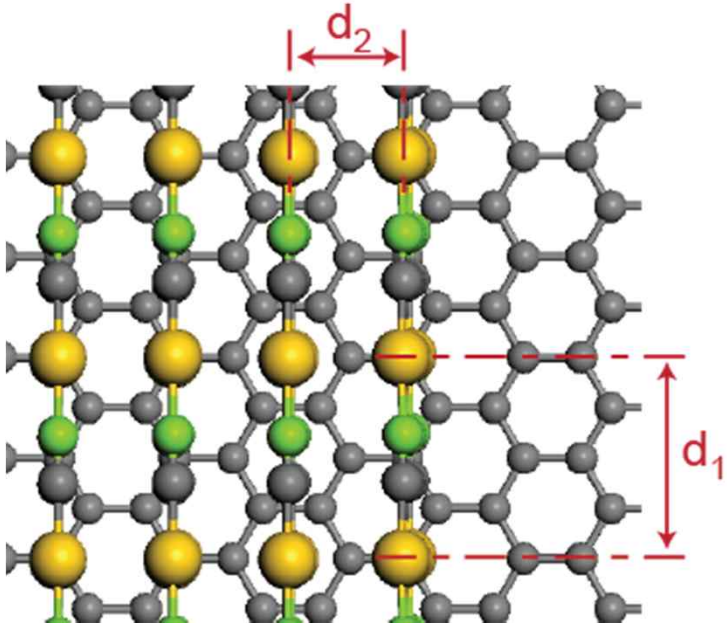
W. C. Lee *et al.*, *Nature Nanotech.* 10, 423 (2015)

Alignment Mechanism

- Known information

  Lattice matching induces epitaxial alignments.

- AuCN vs. Graphene



	d_1	d_2
AuCN	5.08 ± 0.01 Å	3.00 ± 0.12 Å
Graphene	4.92 Å	3.19 Å
Lattice mismatching	3.3 ± 0.2 %	- 6.1 ± 3.8 %

<Previous examples: epitaxial alignments>

- Bi_2Se_3 on graphene: ~2.9 %
- MoS_2 on graphene: ~28 %

Calculations by Prof. H. Lee (Kunkuk Univ.)

W. C. Lee *et al.*, *Nature Nanotech.* 10, 423 (2015)

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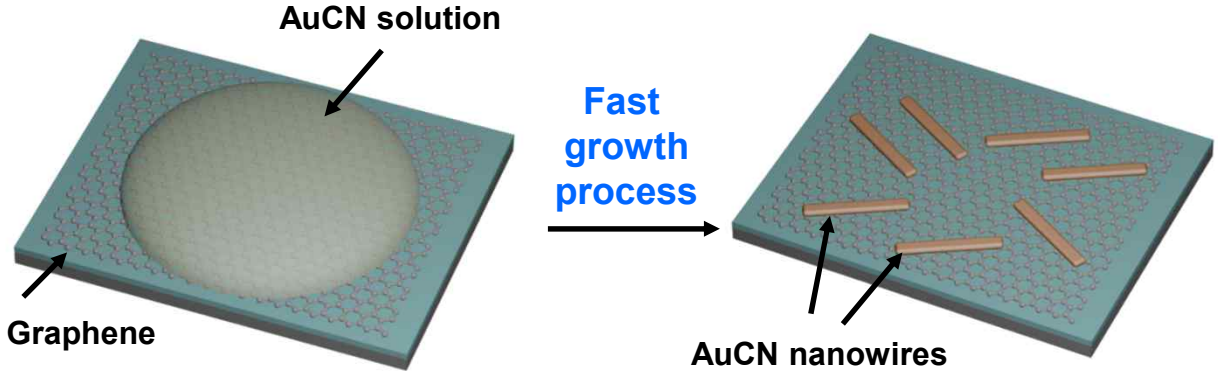
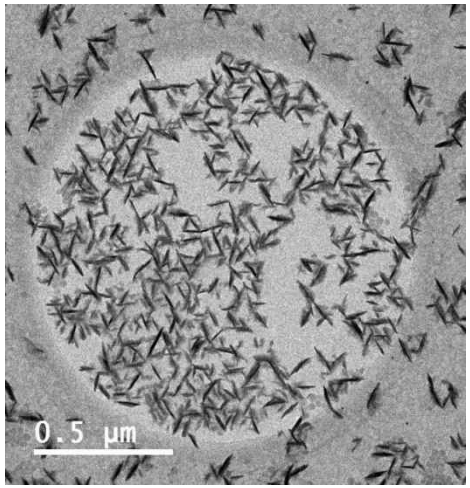
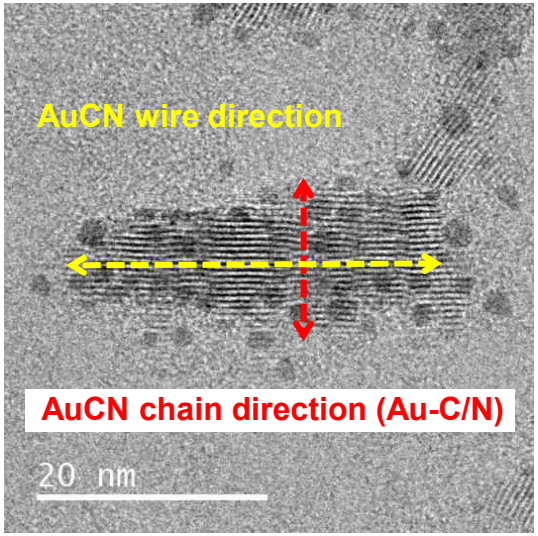
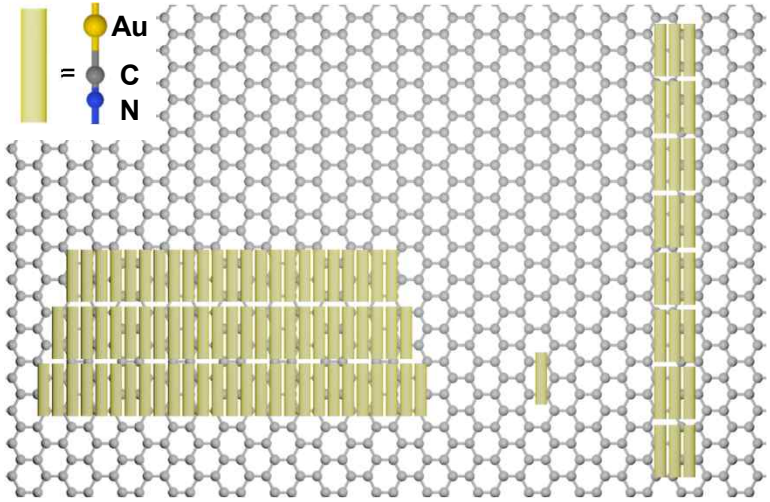
THERMODYNAMICS VS. KINETIC FACTORS





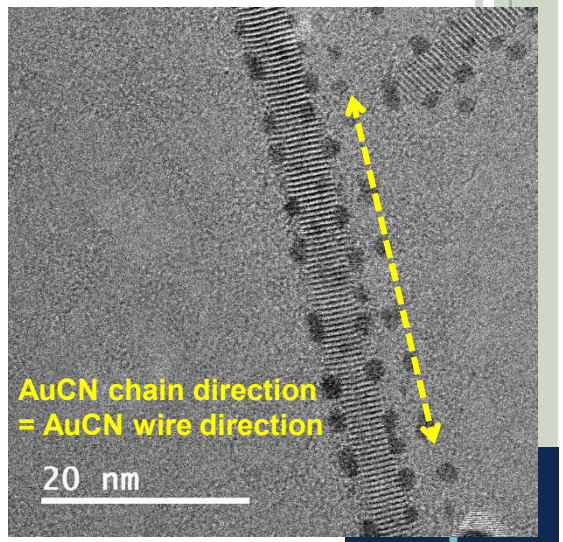
Kinetics





Fast growth → Slow growth

Thermodynamics



J. Jang *et al.*, to be submitted

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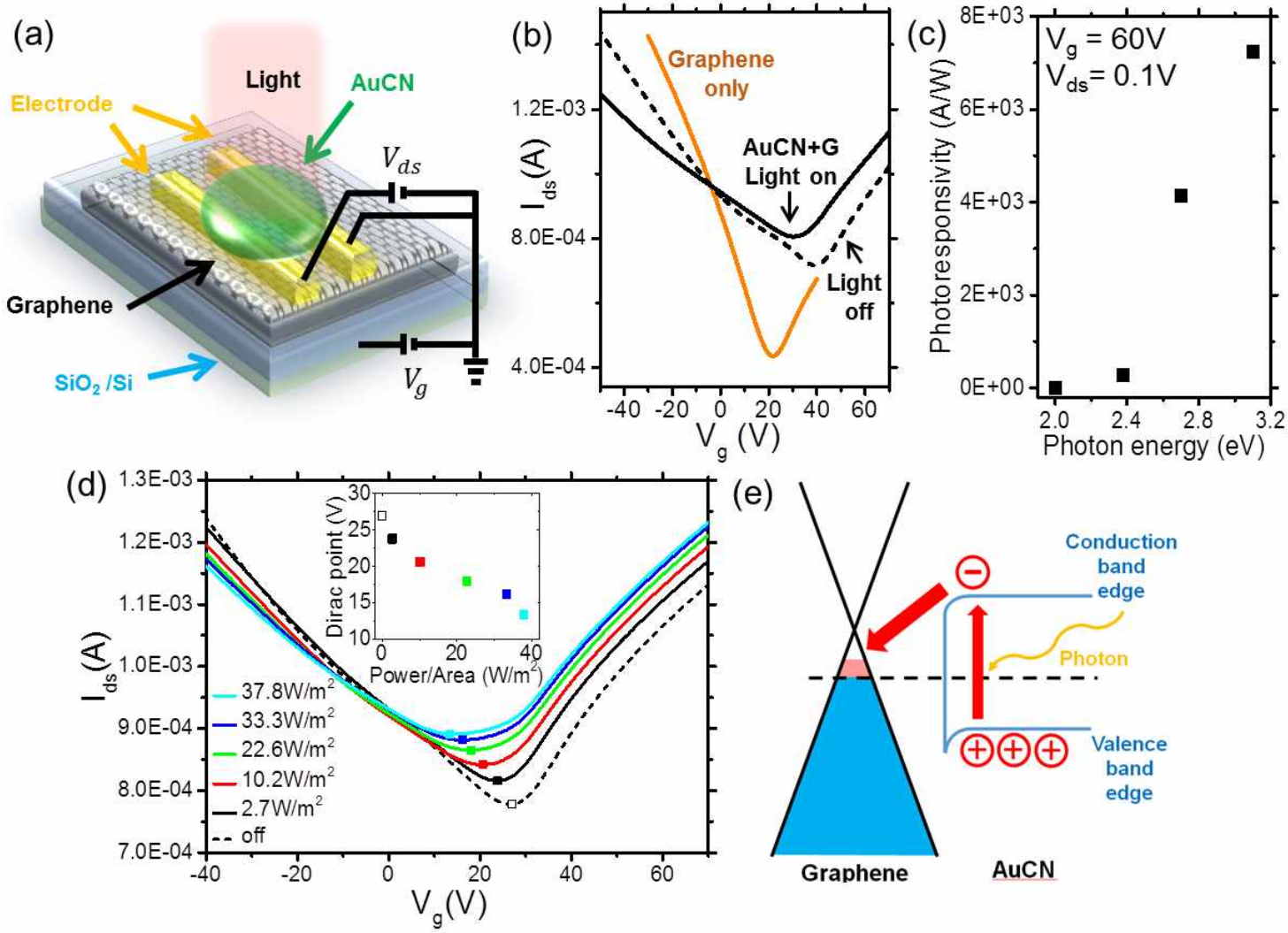
2009

AuCN/Graphene Hybrid Photodetector



J. Jang *et al.*, to be submitted

CONTENTS

- Atomic Resolution TEM Imaging of Graphene and Other 2D Materials

- Nanostructure Assembly on Graphene

  - Organic Molecular Assembly (Pentacene and Fullerene)

  - Epitaxial Growth of Inorganic Nanowires on Pristine Graphene

- Imaging Liquid-Phase Dynamics Using Graphene Liquid Cells

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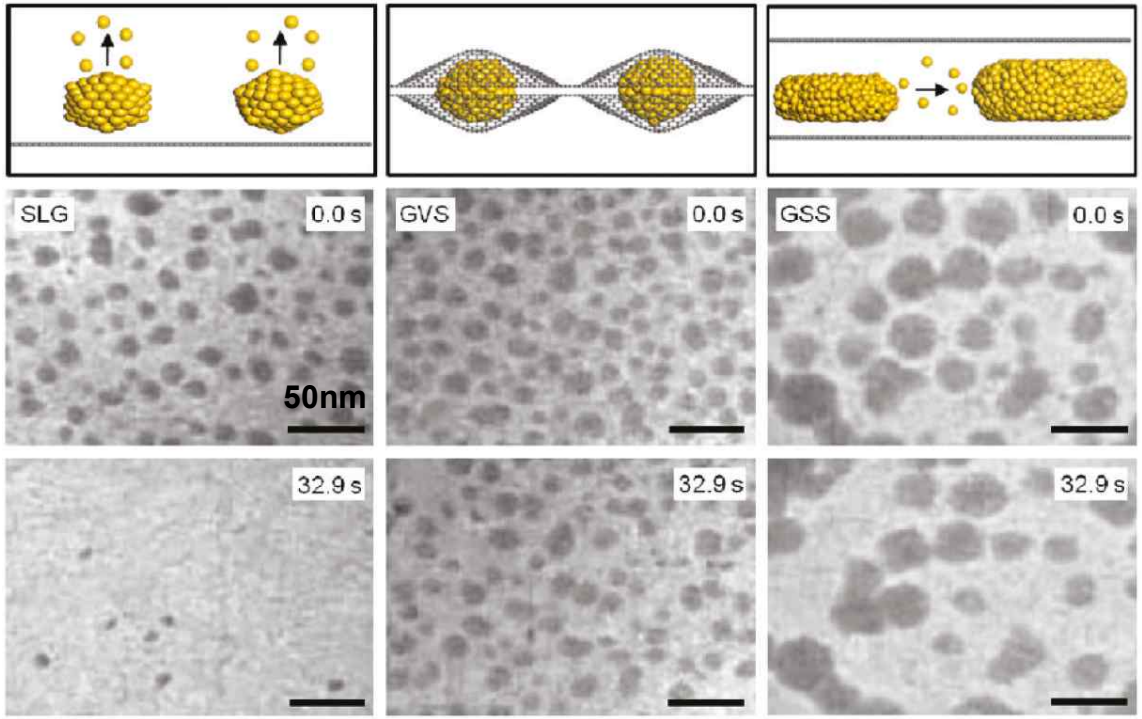
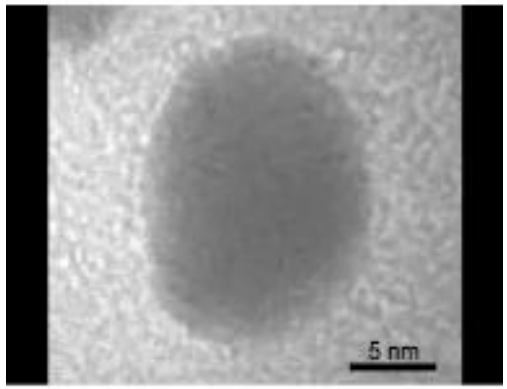
HIGH-TEMPERATURE IMAGING WITH GRAPHENE SANDWICH

Observation of high-temperature reactions and dynamics



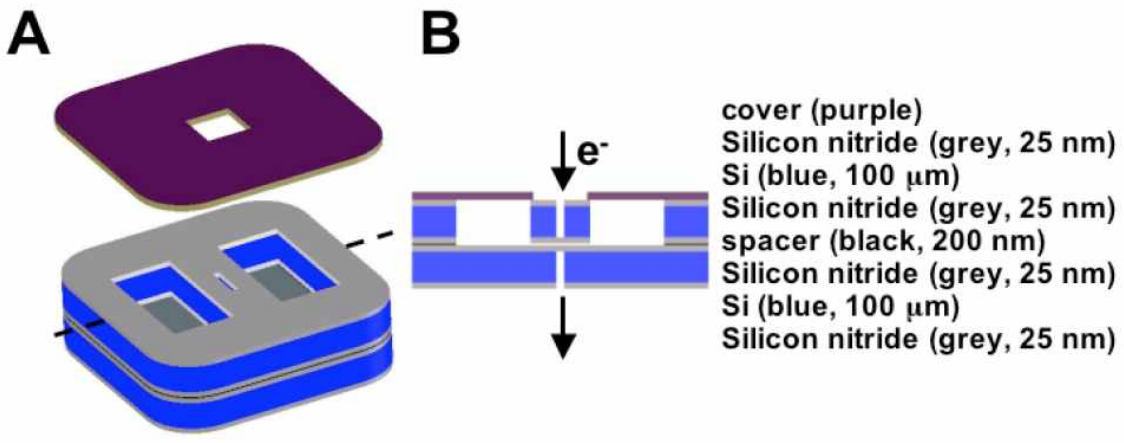
***T* ~ 1400K**

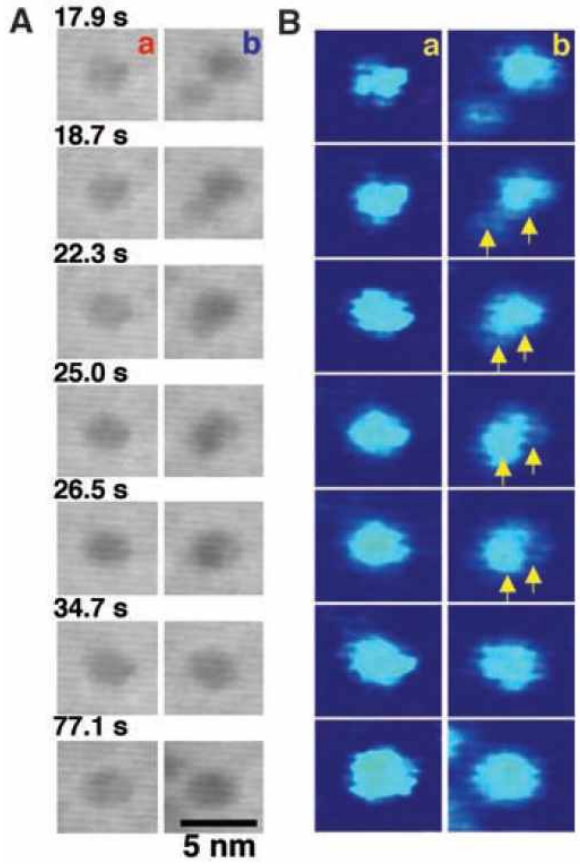


Liquid Au

J. Yuk *et al. Nano Lett.* 11, 3290 (2011)

Previous Imaging in Liquid Environments





Thick specimen (including membrane) prevents atomic resolution imaging in liquid environments

H. Zheng *et al.*, *Science* 324, 1309 (2009)

Previous work from A. P. Alivisatos Group (Chem, UC Berkeley)

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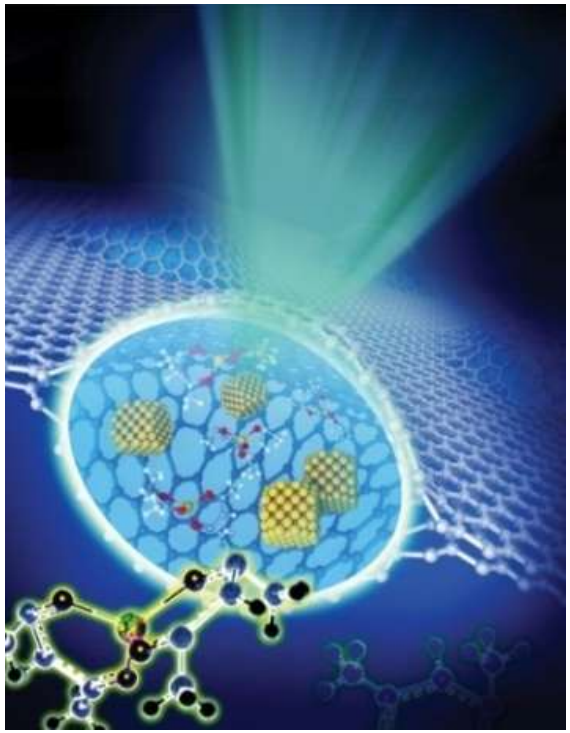
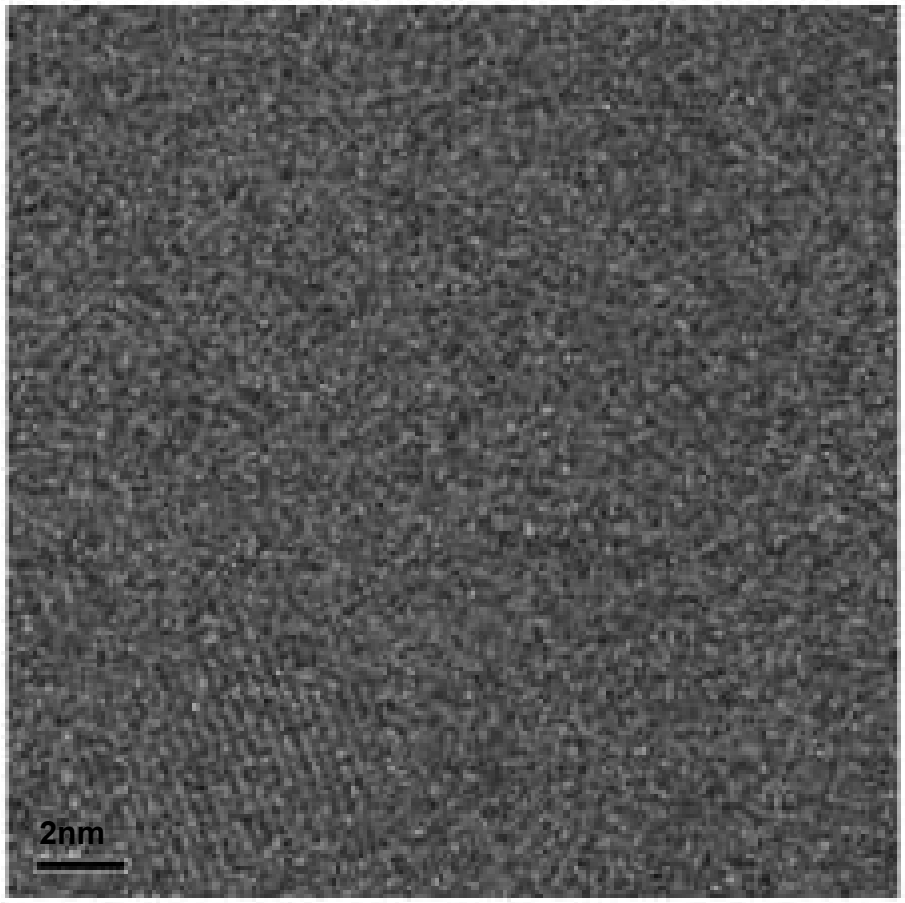
2009

In Situ TEM Imaging with Graphene Liquid Cell

Atomic resolution imaging enabled by graphene liquid cells



Pt nanoparticle growth and dynamics



J. Yuk *et al.*, *Science* 336, 61 (2012)

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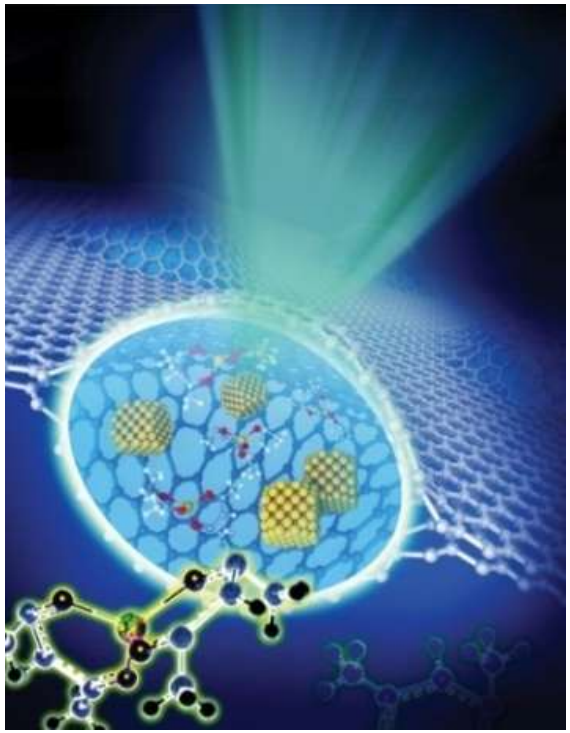
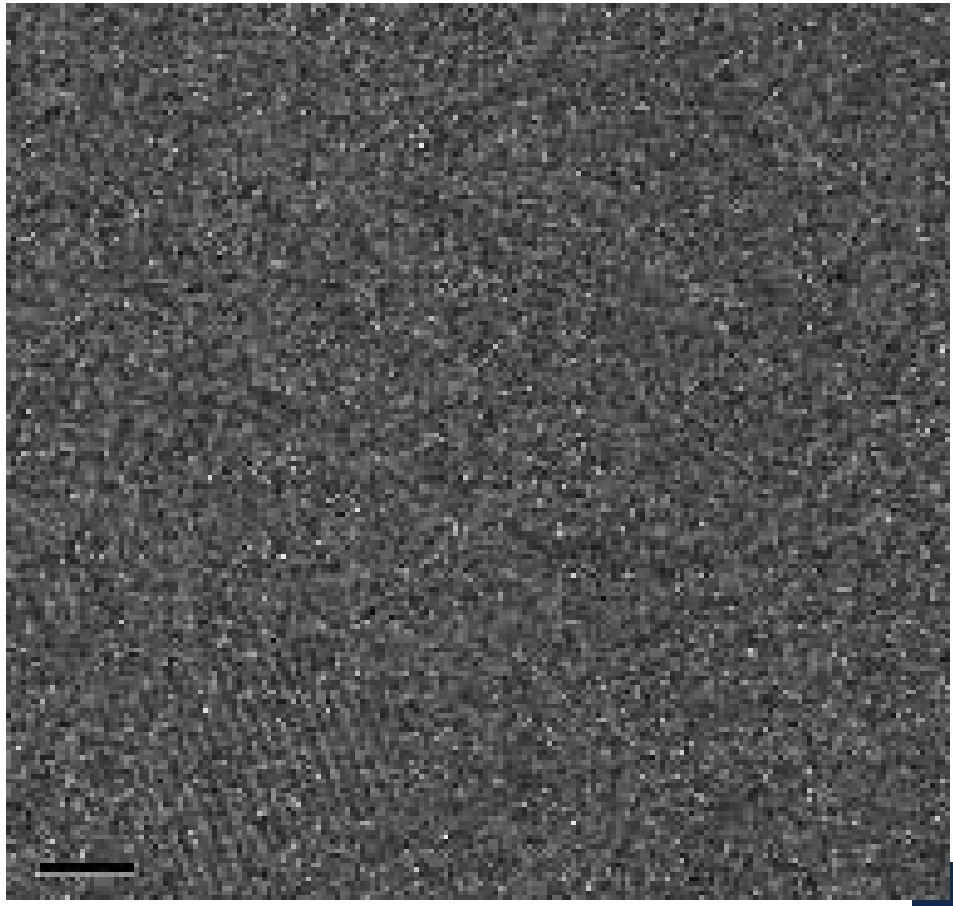
Atomic resolution imaging enabled by graphene liquid cells

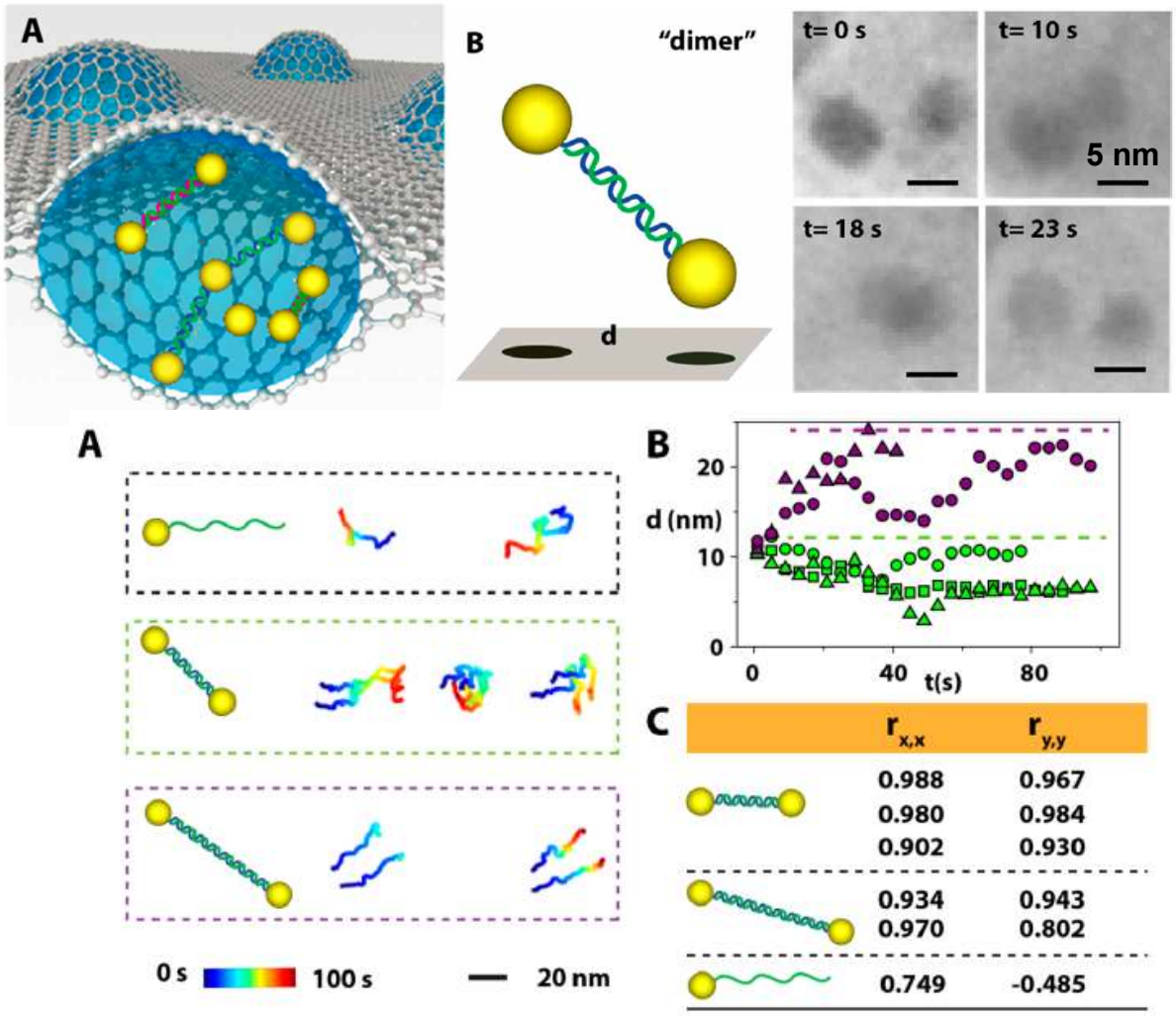


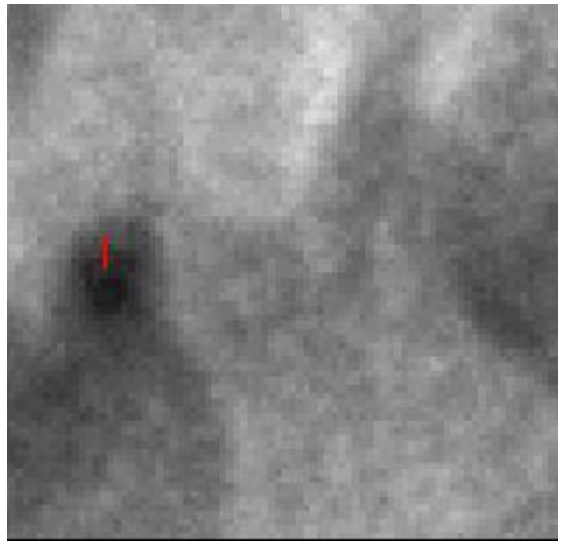
Pt nanoparticle growth and dynamics



J. Yuk *et al*., *Science* 336, 61 (2012)

DYNAMICS OF DNA-AU NANOCONJUGATES





Q. Chen *et al.*, *Nano Lett.* 13, 4556 (2013)

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  - Yangjin Lee
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  - Jeongheon Choe
  - Sol Lee

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  - Salizhan Kylychbekov

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  - Prof. Z. Bao (Stanford Univ.)
  - Prof. Z. Lee (UNIST)
  - Prof. W. C. Lee (Hanyang Univ.)
  - Prof. J. Park (Seoul Natl Univ.)
  - Prof. H. Lee (Konkuk Univ.)
  - Prof. Y. S. Kim (Univ. of Ulsan)
  - Prof. H. S. Shin (UNIST)
  - Prof. J. M. Yuk (KAIST)
  - Prof. K. Park (UNIST)
  - ...

NRF 한국연구재단 National Research Foundation of Korea

포스코청암재단 POSCO TJ Park Foundation

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Thank you!