TEM Characterization of Graphene and Perspective

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U N I S T

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한국진공학회 Tutorial: Fundamentals and Applications of Graphene 2012/08/20

Introduction to The Transmission Electron Microscope (TEM)

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Microscope

A microscope (from the Greek: mikrós, "small" and skopeîn, "to look" or "see") is an instrument used to see objects that are too small for the naked eye. The science of investigating small objects using such an instrument is called microscopy. Microscopic means invisible to the eye unless aided by a microscope.

"What is seen was not made out of what was visible" (Hebrew 11:3)

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The Transmission Electron Microscope

A typical commercial transmission electron microscope (TEM) costs about $5 for each electron volt (eV) of energy in the beam and, if you add on all available options, it can easily cost up to $10 per eV. As you'll see, we use beam energies in the range from 100,000 to 400,000 eV, so a TEM is an extremely expensive piece of equipment. Consequently, there have to be very sound scientific reasons for investing such a large amount of money in one microscope.

Ex. Cost of a 200 keV modern TEM: 200,000 x $10 = 2M$

A TEM described by different acronyms: HRTEM, STEM, and AEM

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Why Use Electrons?

Why should we use an electron microscope?

Historically TEMs were developed because of the limited image resolution in light microscopes, which is imposed by the wavelength of visible light.

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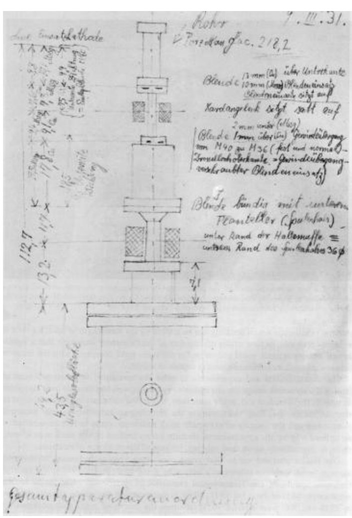
First Electron Microscopy



Sketch of first electron microscope, originally from Ruska's notebook in 1931.

The electron microscope built by Ruska (in the lab coat) and Knoll, in Berlin in the early 1930s.

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First Electron Microscopy

First Electron Microscope with Resolving Power Higher than that of a Light Microscope

Ernst Ruska, Berlin 1933 Replica by Ernst Ruska, 1980
For the first time the apparatus had a condensor in front of the specimen and two magnifying lenses. Magnification around 12,000

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Early TEM

JEOL DA1 (50kV, 5nm resolution), 1947년 제작

Electron microscope displayed
By Zonghoon Lee at JEOL, Japan, 2010

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Modern TEM

JEOL ARM200F

ARM200F TEM in JEOL demo room
By Zonghoon Lee at JEOL, Japan, 2010

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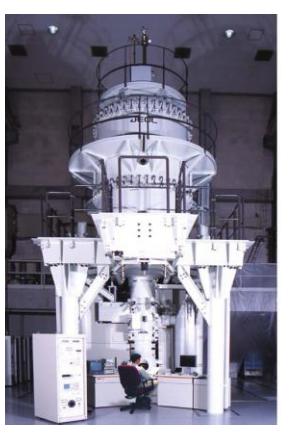
Modern TEMs

JEOL HVEM



Zeiss Libra

Modern TEMs

Hitachi 200kV STEM

JEOL 200kV TEM/STEM

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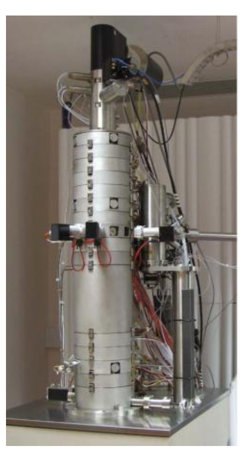
Modern TEMs

Nion 200kV SuperSTEM



FEI Titan

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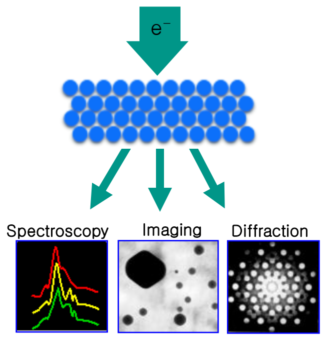
Role of Modern TEMs



At high spatial resolution…

Moderns electron microscopy plays a critical role in materials research.

By imaging inner structure at atomic resolution,
Significant role in the discovery, design and characterization of new materials.

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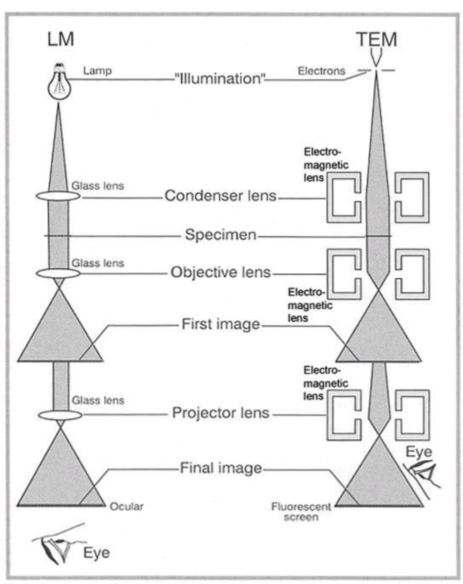
LM & TEM



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Microscopy and the Concept of Resolution

- Resolution limit of human eye = 0.1mm (100um)
  (smallest distance between two points the we can resolve by eyes
  =*resolution* or *resolving power* of eyes)
- Microscope must *magnify* detail to reach or exceed this dimension on the retina, and must *resolve* the detail in the first place.
- Resolution of an optical system depends upon wavelength and numerical apertures.

$$d = \frac{0.61\,\lambda}{N.\,A.}$$

Rayleigh criterion for VLM

d: the smallest distance that can be resolved
λ: wavelength of radiation
N. A.: numerical aperture

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Microscopy and the Concept of Resolution

$$d = \frac{0.61\,\lambda}{N.\,A.}$$

Approximately, the resolution is equal to about half of the wavelength of light

Ex. The wavelength of green light = 550 nm
~ resolution = 300nm (about 1000 atom diameters)

In TEM, ~ 1.22λ/β (β: semi-angle of collection of the magnifying lens)

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Microscopy and the Concept of Resolution

Electron Microscope

- Electrons strongly scattered by matter, giving a useful probe of internal structure.
  - "suitable interaction" criterion.
- At 100 kV accelerating potential, relativistic correction ≈ 10%; electron with this energy has wavelength of 0.037 Å.
  - No limitation on the resolution of atomic structure
- Electrons can be focused by the action of a magnetic field or an electrostatic field.
  - An electron lens...
  - Electron microscopes should resolve atoms !?

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Microscopy and the Concept of Resolution

Intermediate voltage electron microscopes (IVEMs) were introduced in the 1980s. These TEMs operate at 200–400 kV, but still offer very high resolution, close to that achieved at 1 MV. In fact, progress is such that most IVEMs purchased these days are, effectively, HRTEMs with atomic resolution.

Recent breakthroughs in spherical- and chromatic-aberration corrections are revolutionizing the TEM field.
Among many advantages, corrections of spherical aberration (Cs) and chromatic aberration (Cc) allow us to produce sharper atomic-resolution images. By filtering out electrons of different wavelengths we can also better image thicker specimens.
The combination of IVEMs and Cs correction has pushed TEM image resolution to well below the 0.1 nm (1 Å) barrier.

***Sub-angstrom resolution, LVEM??**

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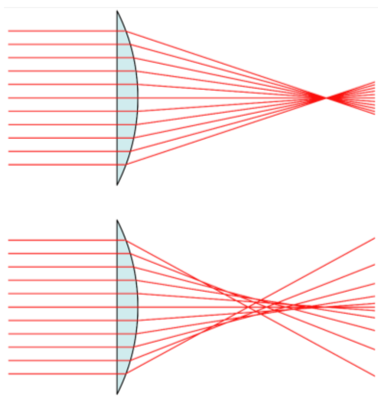
Aberrations



A perfect lens (top) focuses all incoming rays to a point on the optic axis.

Spherical aberration:

A real lens with spherical surfaces (bottom, positive spherical aberration) suffers from spherical aberration: it focuses rays more tightly if they enter it far from the optic axis than if they enter closer to the axis.

It therefore does not produce a perfect focal point.

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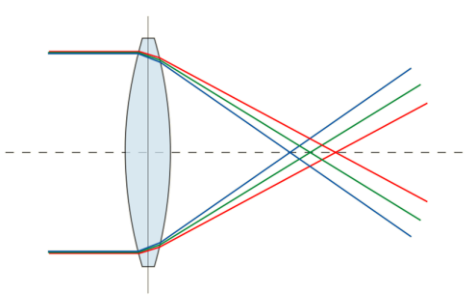
Aberrations



Chromatic aberration:

Chromatic aberration of a single lens causes different wavelengths of light to have differing focal lengths

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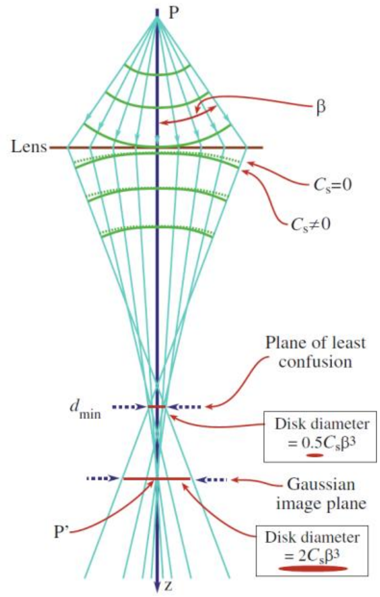
Aberrations

Spherical Aberration

FIGURE Spherical aberration in the lens causes wavefronts from a point object P to be spherically distorted by bending the rays at the outside of the lens more than those close to the axis.

The point is thus imaged as a disk with a minimum radius in the plane of least confusion and a larger disk at P' in the Gaussian-image plane. The plane of least confusion is where the smallest image of the object is formed. Schematic intensity distributions at these two important planes are shown beside the ray diagram.

The units of *r* and *Cs* have to be the same and since *Cs* is typically a few mm, then we can measure *r* in (very small fractions of) mm.



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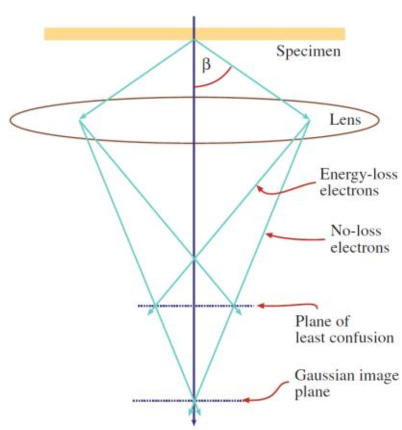
Aberrations

Chromatic Aberration

This term is related to the 'color' (i.e., frequency, wavelength, or energy) of the electrons.

$$r_{chr} = C_c \frac{\Delta E}{E_0} \beta \qquad (6.16)$$

FIGURE Chromatic aberration results in electrons with a range of energies being focused in different planes. Electrons emerging from the specimen with no loss of energy are less strongly focused than those that suffered energy loss within the specimen. A point in the object is imaged as a disk in the Gaussian image plane and there is a plane of least confusion.



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Aberrations

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Aberrations

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***Sub-angstrom resolution**
***Low voltage TEM??**

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TEM: two principle modes

You can operate the illumination system in two principal modes:

parallel beam: used primarily for TEM imaging and selected-area diffraction (SAD)

convergent beam: used mainly for scanning (STEM) imaging, analysis via X-ray and electron spectrometry, and convergent beam electron diffraction (CBED)

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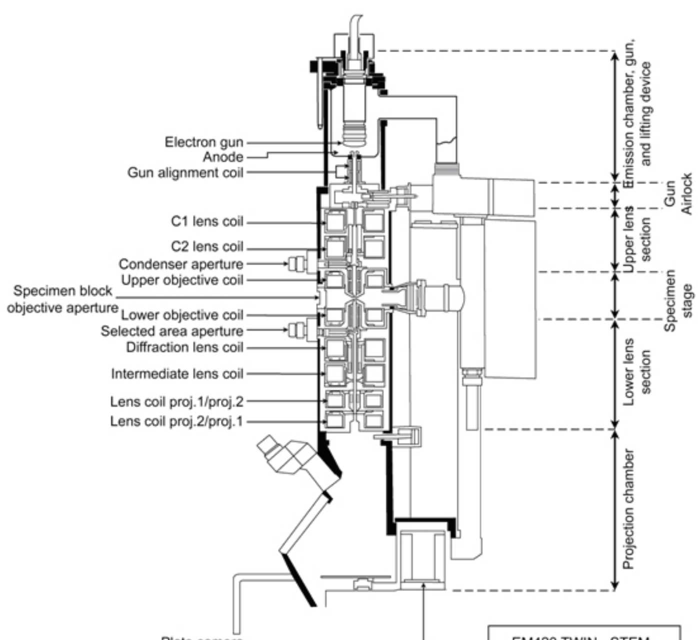

EM420 TWIN - STEM,
Ghent University,
Courtesy L.SAMEK [2005]

Improving Spatial Resolution

- Improve resolution? Reduce λ...
  - Visible spectrum?
    - Red light, λ= 6,300 Å
    - Green light, λ = 5,600 Å
    - Using green light & oil immersion, spatial resolution = 2,400 Å.
    - UV, λ = 1,000 Å
  - X-rays? (λ = 1 Å): Needs focusing (LBL)...
  - Electrons? (λ << 1Å): The Electron Microscope!

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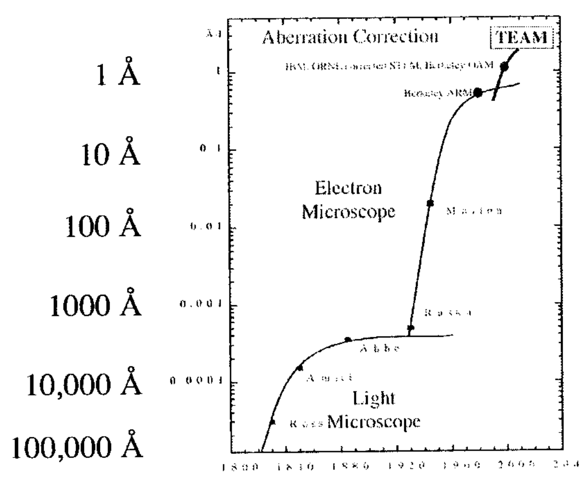
Evolution of Spatial Resolution



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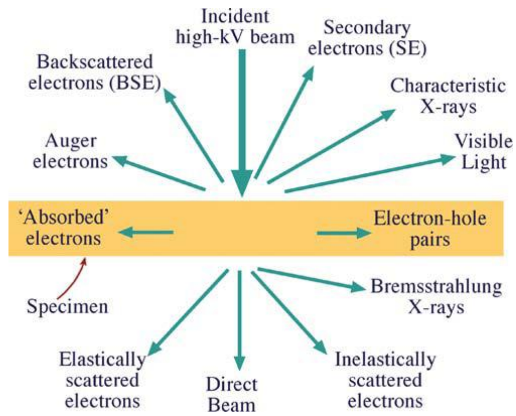
WHY WE ARE INTERESTED IN ELECTRON SCATTERING



In the TEM, we are most interested in those electrons that do not deviate far from the incident-electron direction.
→ the information of the internal structure and chemistry of the specimen.

Modern TEMs

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Aberration-corrected TEMs

JEOL 2100F probe C_s corrected
d-STEM

FEI Titan G2 Cube- Image C_s corrected
monochromated
d- Low kV TEM Imaging

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Can we see individual carbon atoms?

In a Single Raw Image Clearly?

?

Resolution, Sensitivity and More…

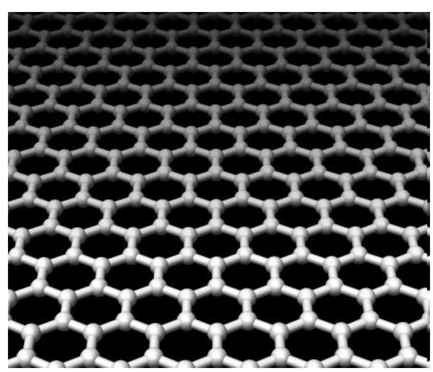
Characterization of Synthesized Free Standing Graphene

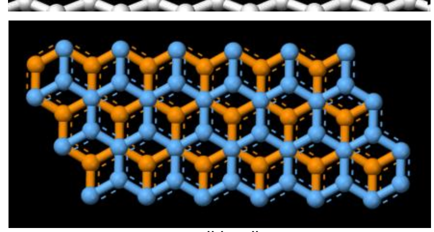
What is Graphene?

Graphene can be described as …

- single atomic sheet of carbon
- one-atom-thick planar sheet of sp^2-bonded carbon atoms that are densely packed in a honeycomb crystal lattice
- 2-D (dimensional) crystal of carbon
- the basic structural element of all other graphitic materials including graphite, carbon nanotubes and fullerenes

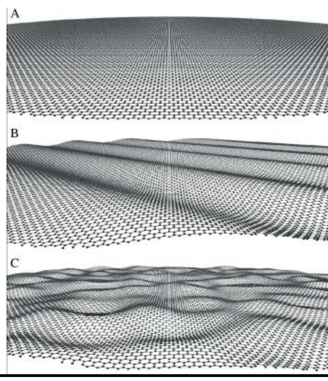
- ***graphite*** itself consists of many graphene sheets stacked together
- *two layer graphite is not graphene until it is separated*





wikipedia.org

Nearly perfect 2D graphene can exist in 3D space



Theoretically, strict 2D can not exist because thermal fluctuation should destroy long range order, resulting in melting of a 2D lattice at any finite temperature. (70 years ago, based on standard harmonic approximation)

first isolated and studied graphene in 2004, and defined it in Science
Novoselov, K.S. et al. Science 306, 666 (2004)

Suspended graphene sheet obtained and observed in TEM
Meyer J. et al. Nature 446, 60 (2007)

- **Showed free standing graphene can exist while random elastic deformation occurs in 3D**
- **"rippling" of the flat sheet, with amplitude of about one nanometer.**

Crumpled Graphene Models

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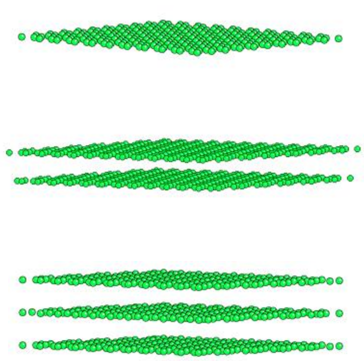
How to prepare graphene

Obtaining graphene sheets is a challenge!



Micromechanical cleavage from 3D graphite followed by microfabrication (so called tape method)
-graphene flakes prepared on top of an oxidized silicon wafer (300 nm of SiO_2)

Chemical reduction of exfoliated graphite oxide

Vacuum graphitization of silicon carbide substrates

PECVD for carbon nanostructures required low-pressure and substrate

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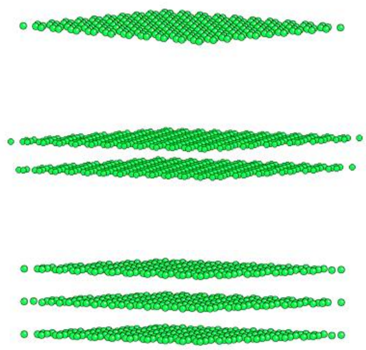
How to identify single or double layers?

Characterization of graphene sheets is a challenge, too!

TEM would be easier and more reliable way to identify graphene,
if free standing graphene can be prepared.



Methods in TEM

- **dark fringes of folded edge – like nanotube**
- **nano-area parallel beam diffraction**
- **high resolution imaging**
- **plasmon of EELS**

Non-TEM method

- **Optical microscope (# of layers)**
- **Raman (graphene/graphite, defect)**
- **IR (clearness, absorbates)**
- **STM**
- **AFM**

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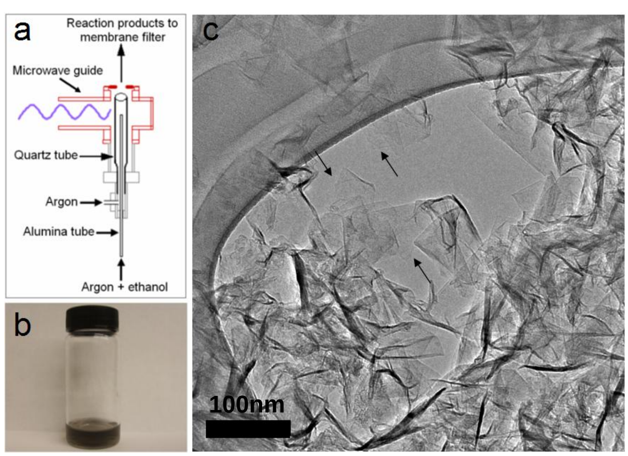
High Quality Synthesized Graphene

Free standing and substrate-free graphene synthesized from ethanol in a microwave plasma reactor. Applicable to large scale production.
(*A. Dato et al, Nano Lett., 8, 7, 2012, 2008*)



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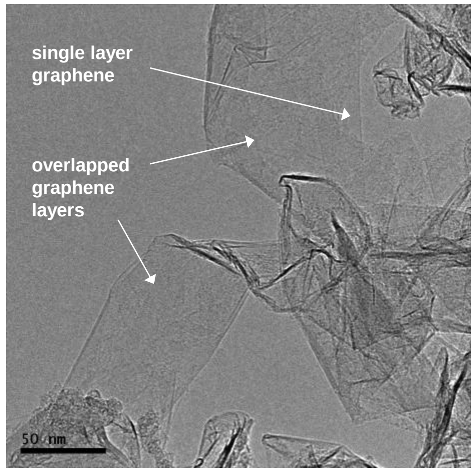
Graphene in a low magnification

Crumpled and overlapped free-standing graphene sheets.
Homogeneous and featureless regions may indicate monolayer graphene.

Conventional TEM at 200kV



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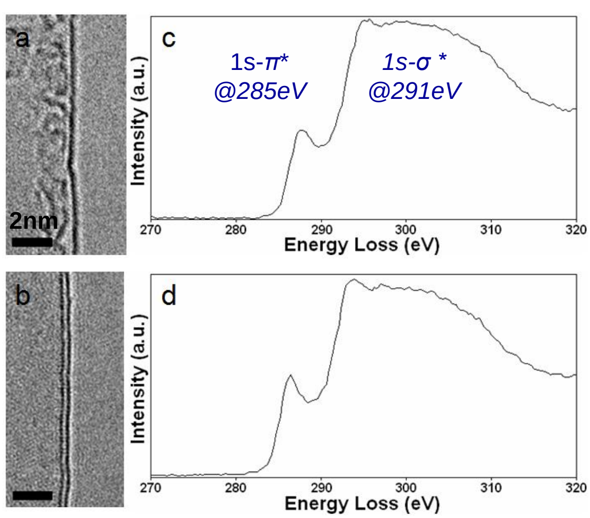
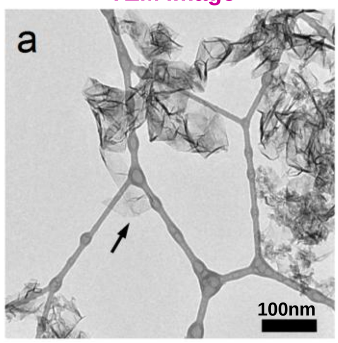
EELS of carbon K-edge



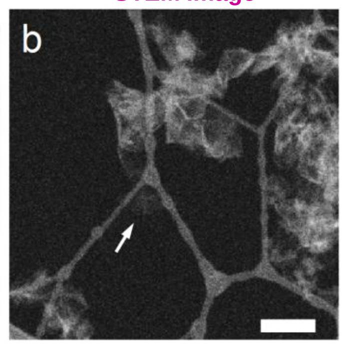
TEM & STEM

nano-area diffraction in STEM mode.

TEM image



STEM image



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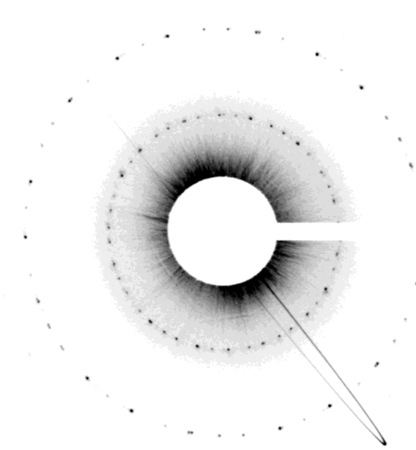
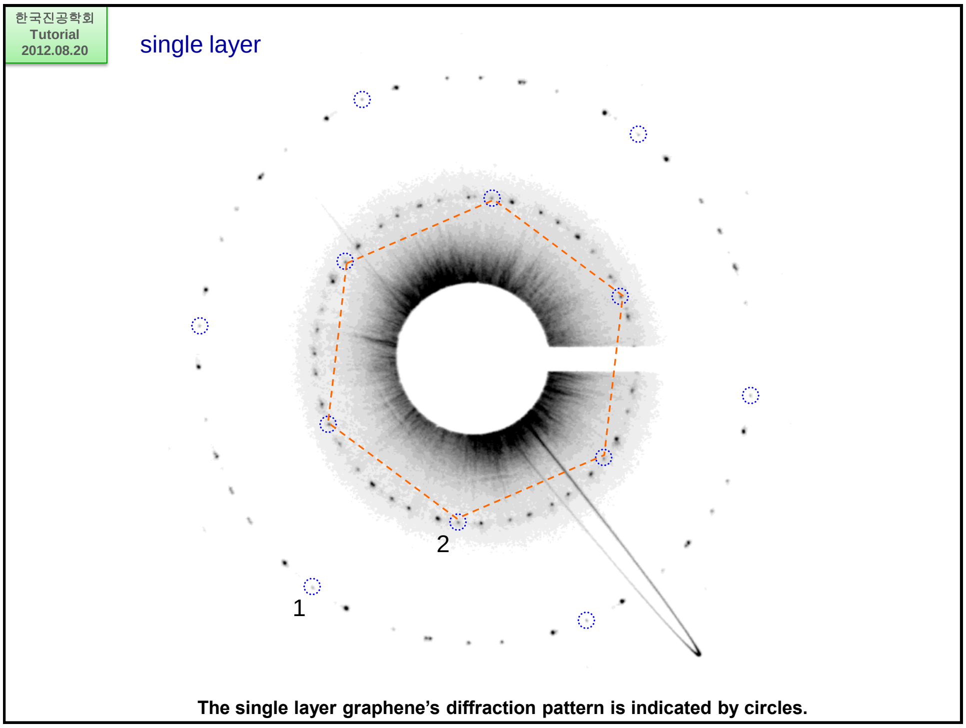
Nano-area Parallel Beam Diffraction

Diffraction pattern from a region containing several overlapping single layer graphene and some bilayer sheets.



inner hexagon corresponding to indices (1-110) (2.13 Å spacing) and
outer hexagon corresponding to indices (1-210) (1.23Å spacing)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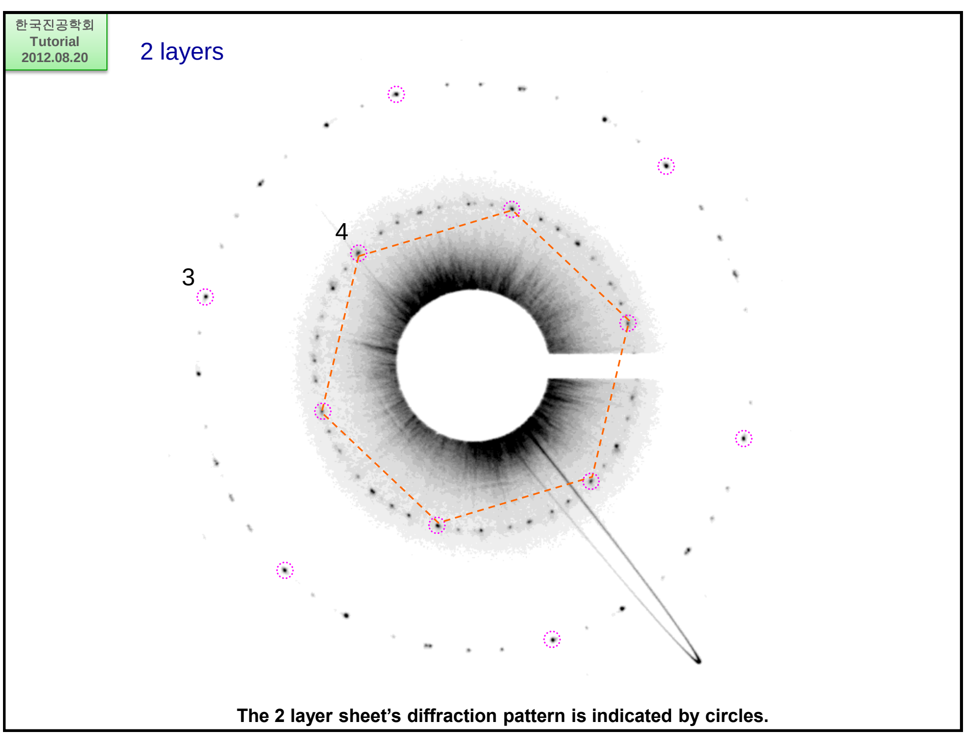
single layer
1
2
The single layer graphene's diffraction pattern is indicated by circles.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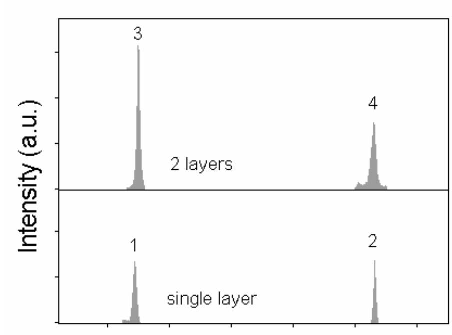
2 layers
3
4
The 2 layer sheet's diffraction pattern is indicated by circles.

Nano Parallel Beam Diffraction

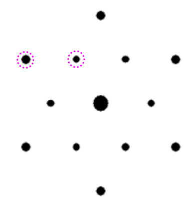
The uniform intensity profile between the inner and outer spots proves that the graphene sheet consists of a single layer.



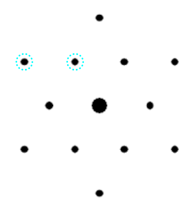
background subtracted

Intensity profiles of diffraction spots

2 layers sheet (graphitic)



single layer graphene



Simulated diffraction patterns

Characterization of a Bilayer

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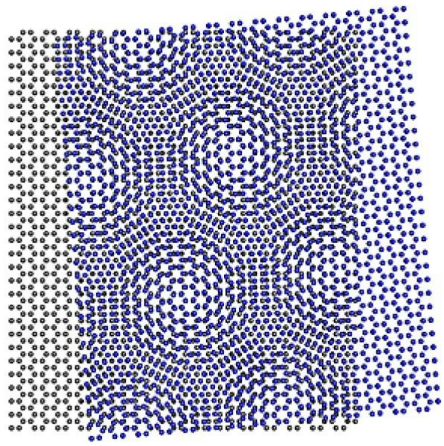
Bilayer Graphene (Moiré Fringes)



a moiré pattern is an interference pattern created, for example, when two grids are overlaid at an angle, or when they have slightly different mesh sizes.

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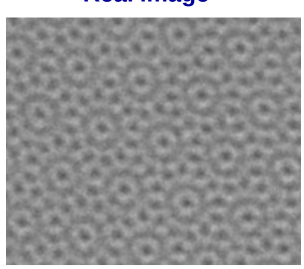
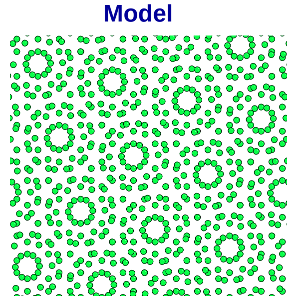
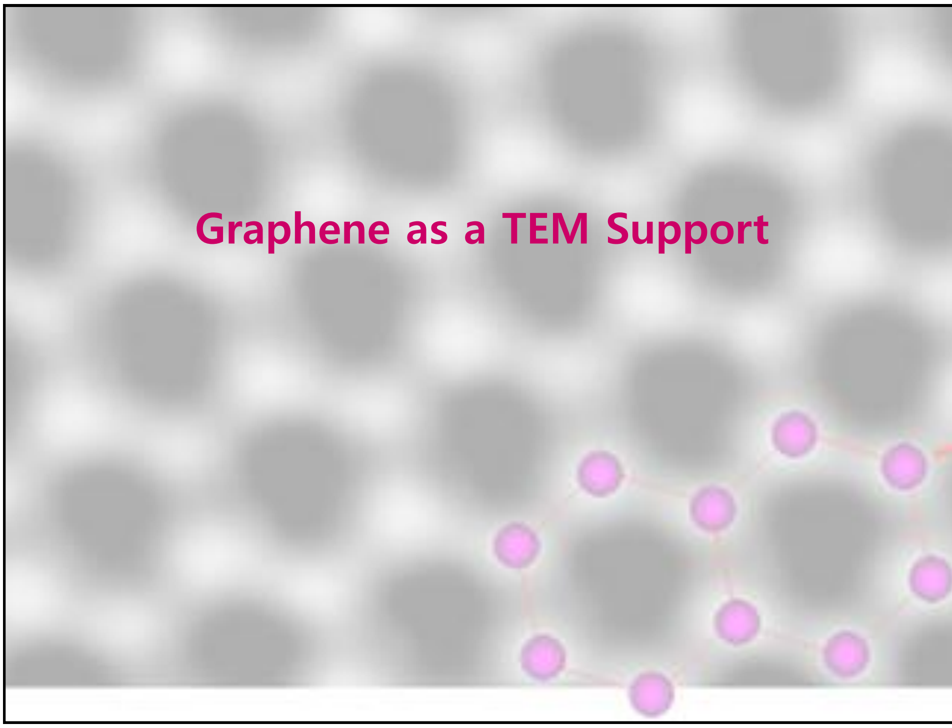
Bilayer Graphene (Moiré Fringes)

Real image



Model





Graphene as a TEM Support

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Graphene: an Ideal TEM Support for soft and hard nanomaterials

Problem: ultra-thin a-carbon grids ~2-3 nm thick, contribute the overall electron scattering for imaging, which diminishes the contrast of low-atomic-number atoms

A Practical Application of Free-standing Graphene

Why graphene would be good for TEM support:

- ✓ Atomically thin (and flat)
- ✓ Chemically inert
- ✓ Consisting of light atoms
- ✓ Structurally stable
- ✓ Good electrical and thermal conductor
- ✓ Large thin area

Prerequisite of graphene support:

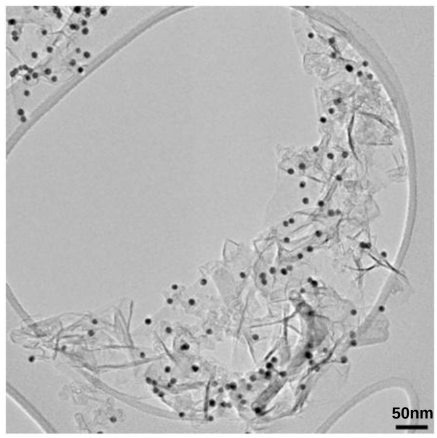
- ✓ Single layer or few layers
- ✓ Clean
- ✓ Highly ordered (low defect density)

Challenge:

- ➢ Synthesis
- ➢ Transfer
- ➢ Cleaning
- ➢ Dispersion
- ➢ Irradiation damage

Dispersion of Au Nanoparticles on Graphene

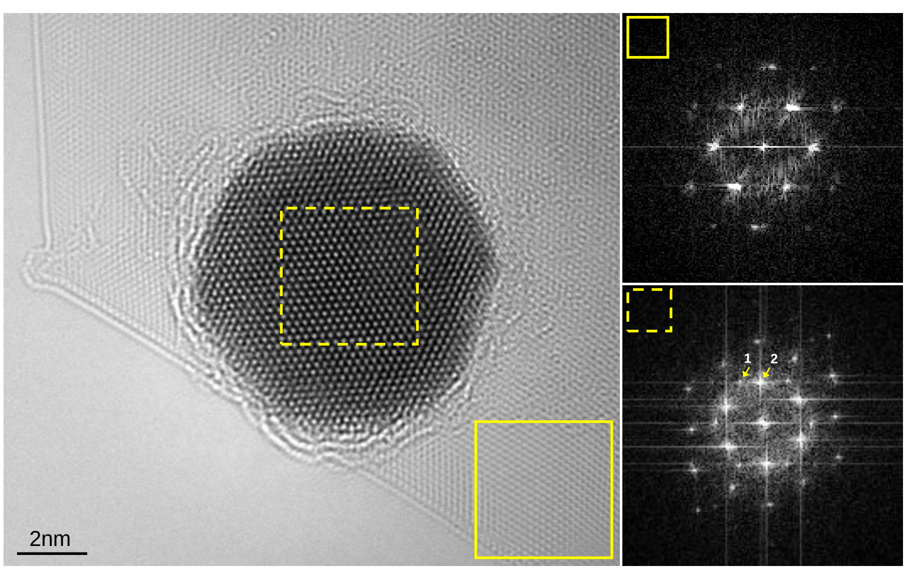
Citrate-capped Au NPs (~10nm) exceptionally well-dispersed on free-standing graphene sheets



Au NPs sitting on near the edges or planar areas - for TEM observation

Direct Imaging of Au NPs & Surrounding Citrate Capping Layers in Atomic Resolution

Citrate-capped cuboctahedral Au NP [111] sitting on graphene edge



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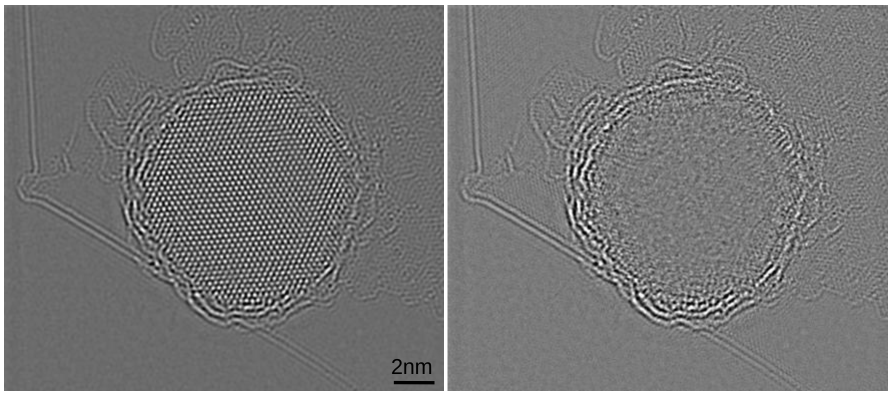
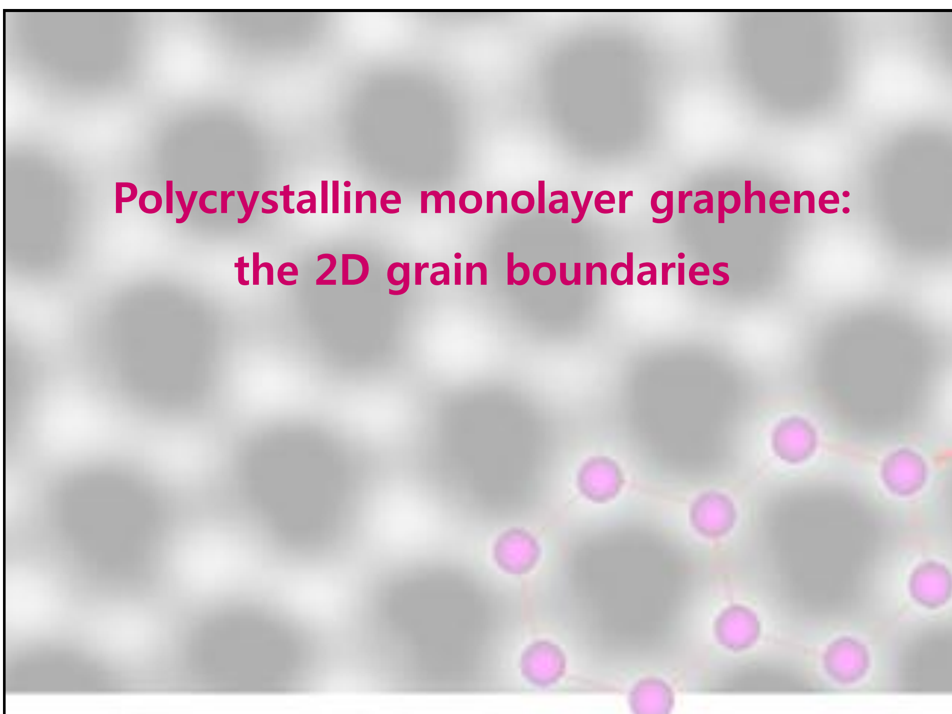
Can Graphene Support be Invisible in TEAM, too?

can be achieved by subtracting the periodic contrast of carbon atoms in graphene using Fourier filtering

Graphene-subtracted image by Fourier filtering | **Both graphene & gold NP-subtracted image by Fourier filtering**



Graphene enabled isolation and imaging of citrate molecules.



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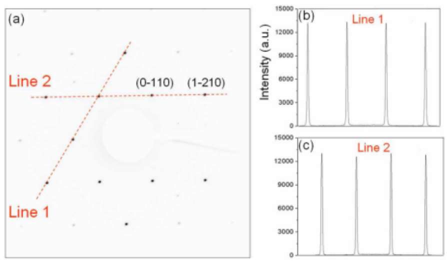
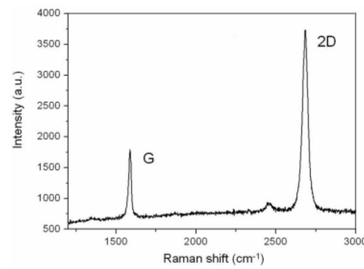
Is graphene single crystal?

Large Area Monolayer Graphene produced by CVD

Nanoparallel Electron Beam Diffraction



Raman Spectroscopy



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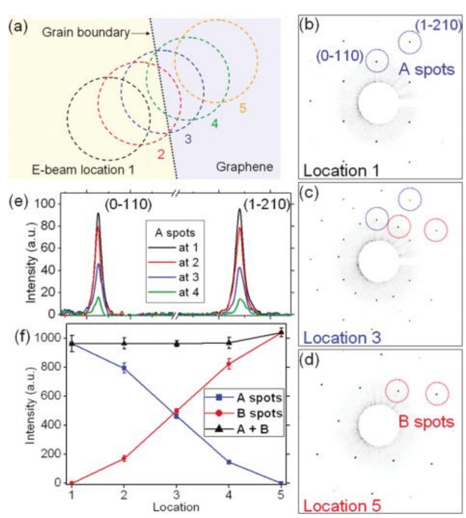
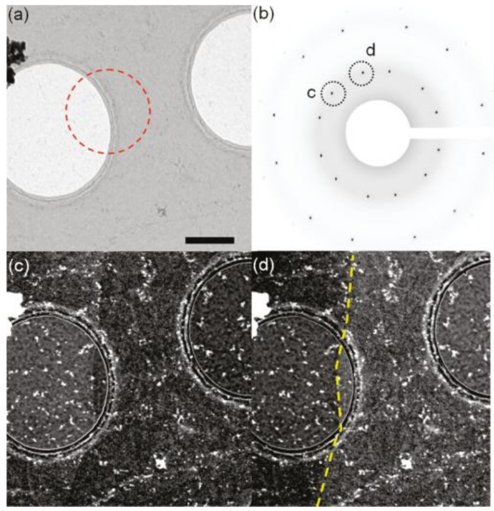
Can we find grain boundary with diffraction?

Nanoparallel Electron Beam Diffraction (STEM mode)



Can we find grain boundary with dark field imaging?

TEM Dark Field Imaging



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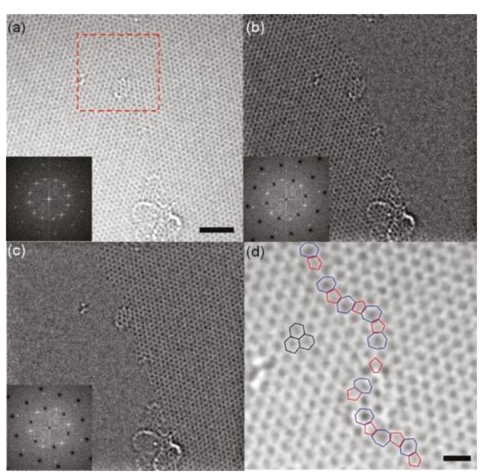
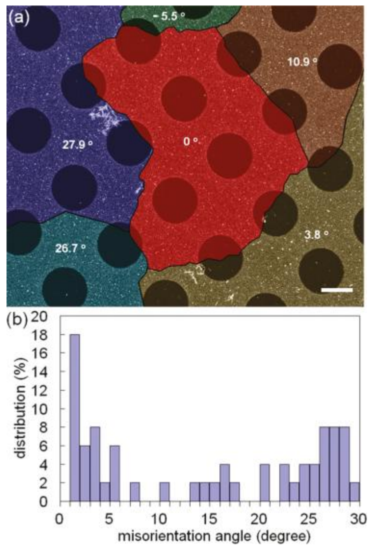
High Angle Grain Boundary in Atomic Resolution TEM

A single TEM image at 80kV



Title Angles of Graphene GBs

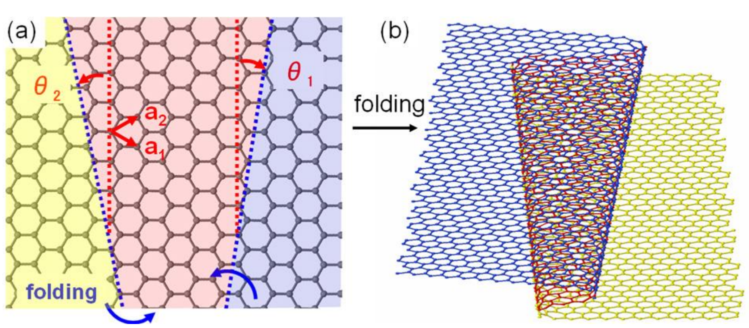
Reconstruction of grain boundaries in a low mag



It's polycrystalline graphene!

Multiply Folded Graphene: Grafold

Various multiple folding structures of graphene



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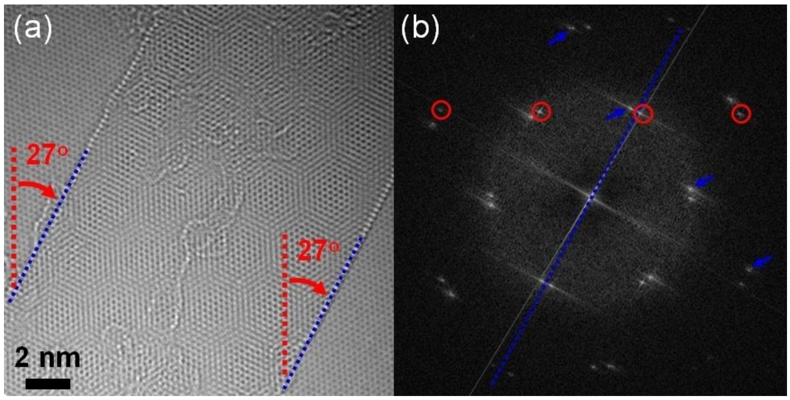
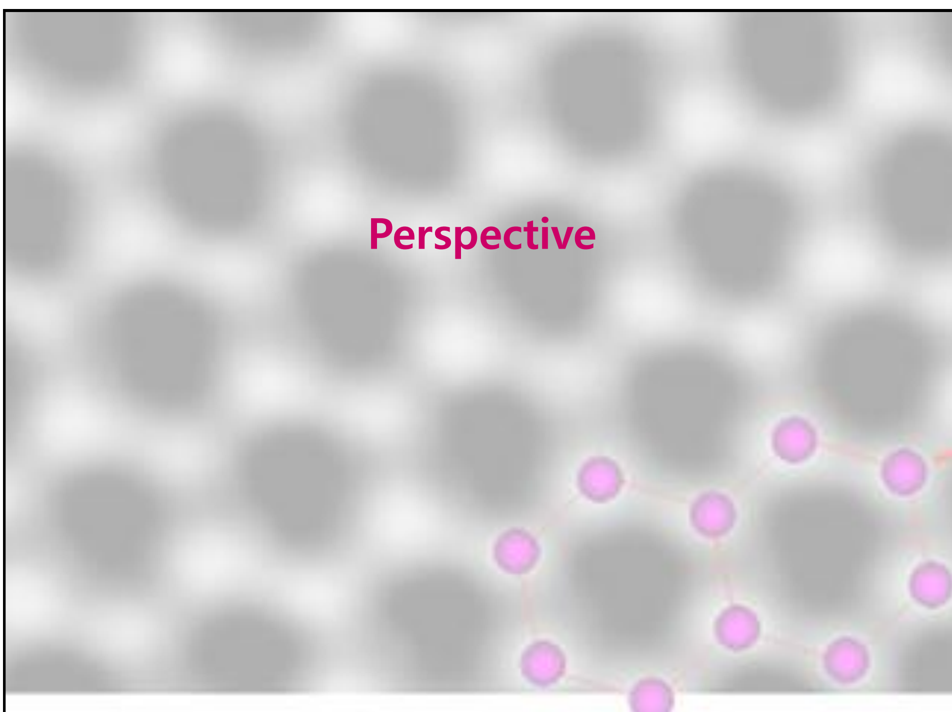
Multiply Folded Graphene



Atomic resolution TEM image of a pleat folding structure



Perspective

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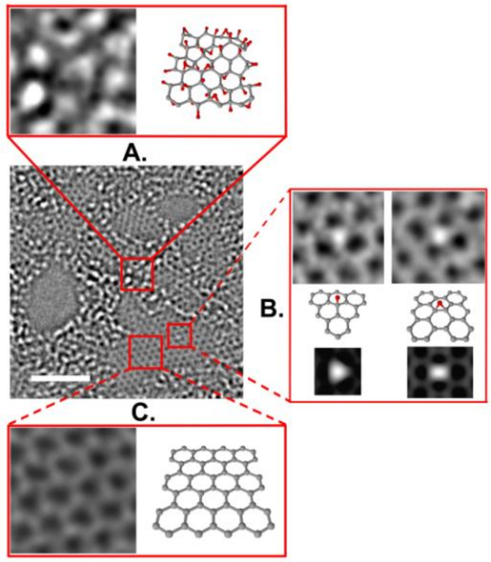
GO at Atomic Resolution



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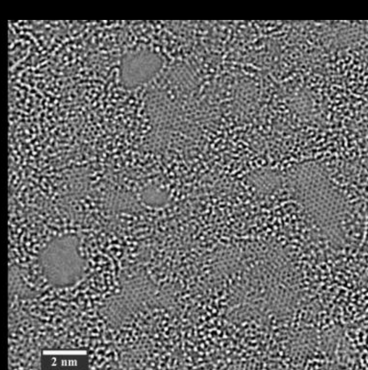
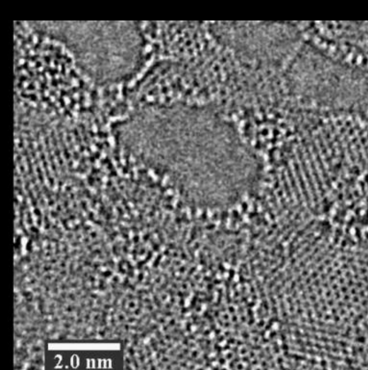
Real Time Observation at Atomic Resolution

Single sheet graphene oxide (GO) – Movie 1



Single sheet reduced and annealed graphene oxide (raGO) – Movie 2



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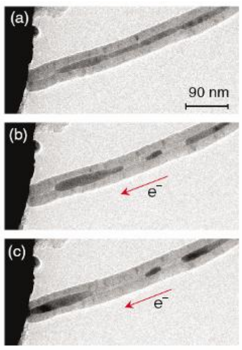
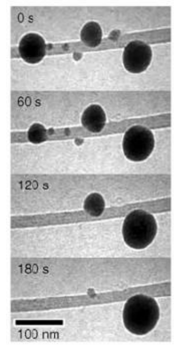
Real Time Observation

Thermal: cryo-, heating / **Electrical**: bias and STM
Mechanical: tension, compression / **Chemical**: gas phase, liquid phase



Sequential TEM images showing the induced movement of iron in the carbon nanotube.

***Phys. Rev. Lett.* 93, 145901-145904 (2004).**



Four TEM video images showing left-to-right indium transport on a single MWNT.

***Nature* 428, 924-927 (2004).**

Thank You