

CARBON-BASED NANOMATERIALS

Chung-Ting Ke

04/29/26

TiGP@AS

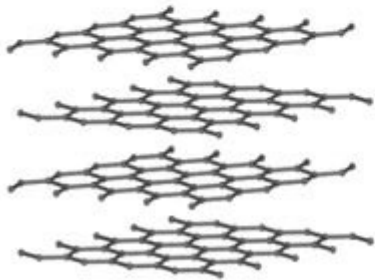
Carbon

Graphite vs Diamond

Graphite



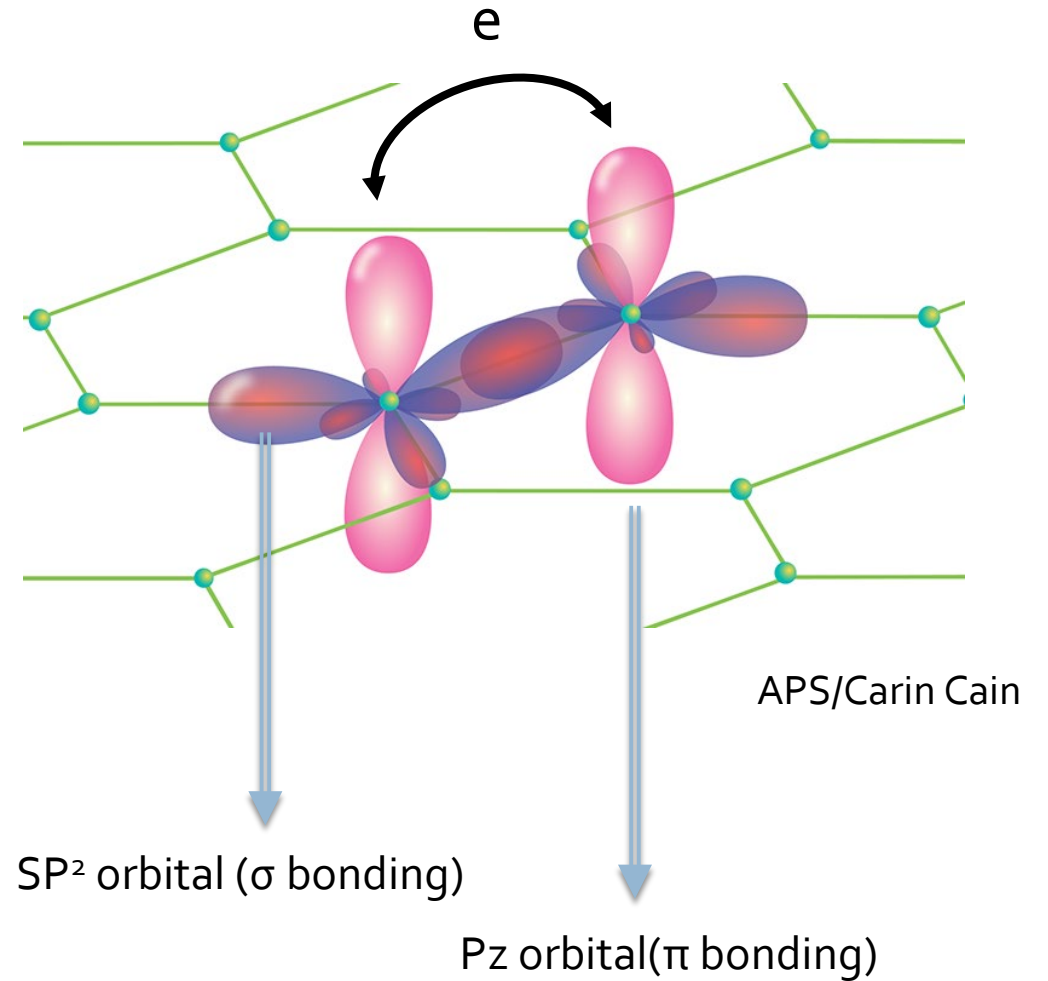
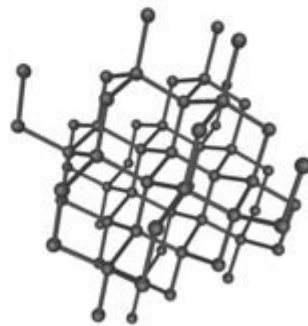
Dull, opaque, soft, common



Diamond



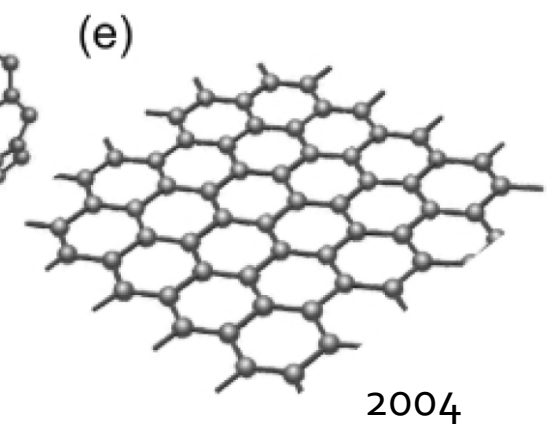
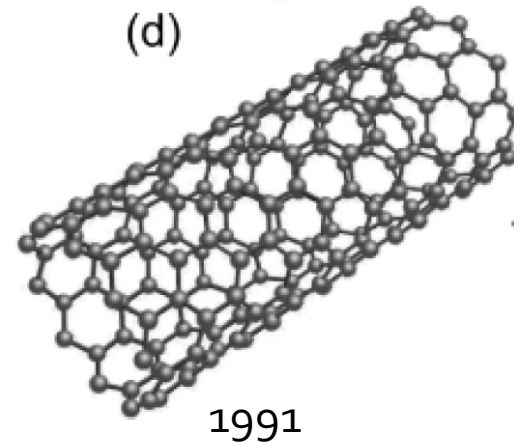
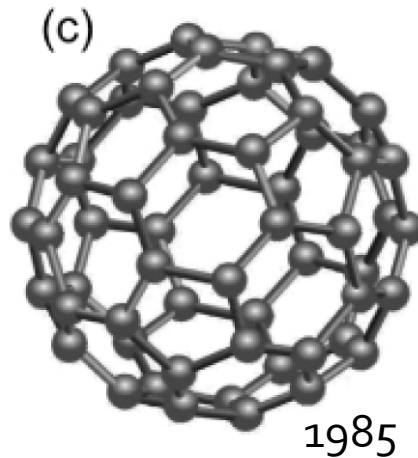
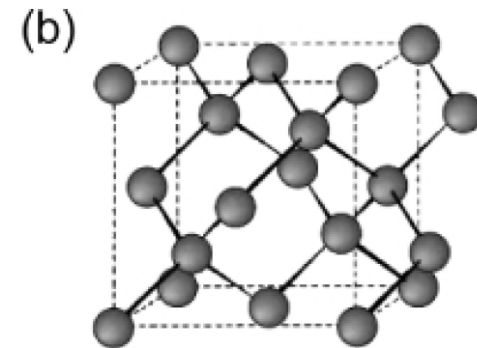
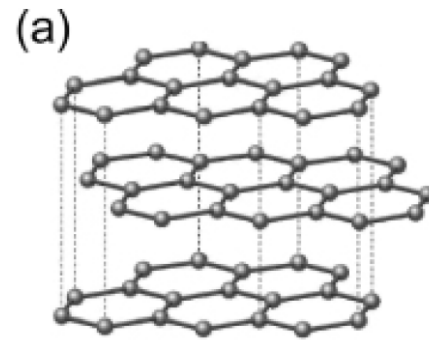
Brilliant, transparent, hard, rare



Carbon materials

Simply arrange carbon differently, you will obtain very different outcomes:

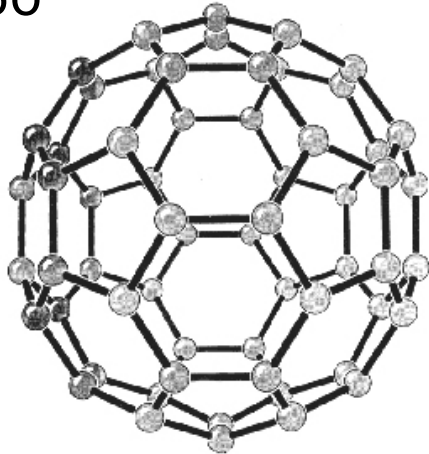
- (a) Graphite
- (b) Diamond
- (c) Buckminster C_{60}
- (d) Carbon nanotube
- (e) Graphene



Fullerene

Nobel prize 1996

C₆₀



Models of the structures of C₆₀. (Acc. Chem. Res., Vol. 25, No. 3, 1992)

20 hexagons and 12 pentagons

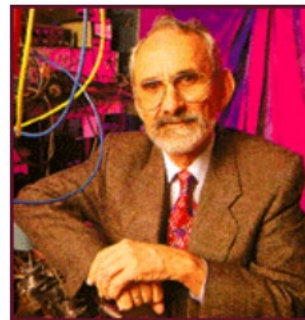


Photo: P. S. Howell, Rice University

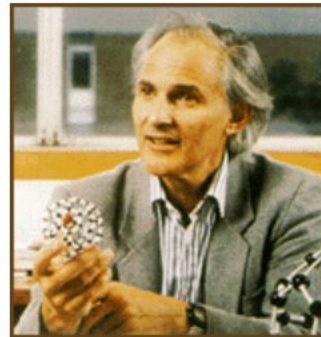
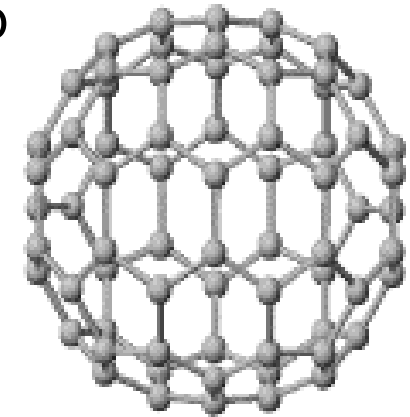


Photo: Prudence Cummings Associates

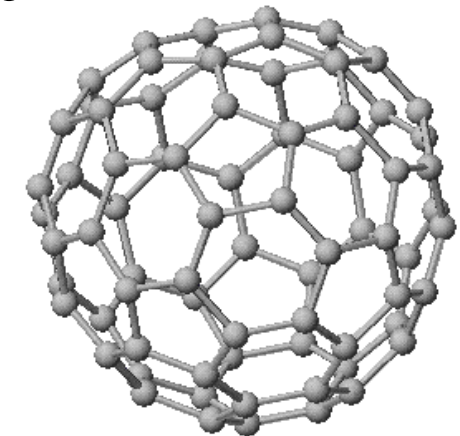


Photo: P. S. Howell, Rice University

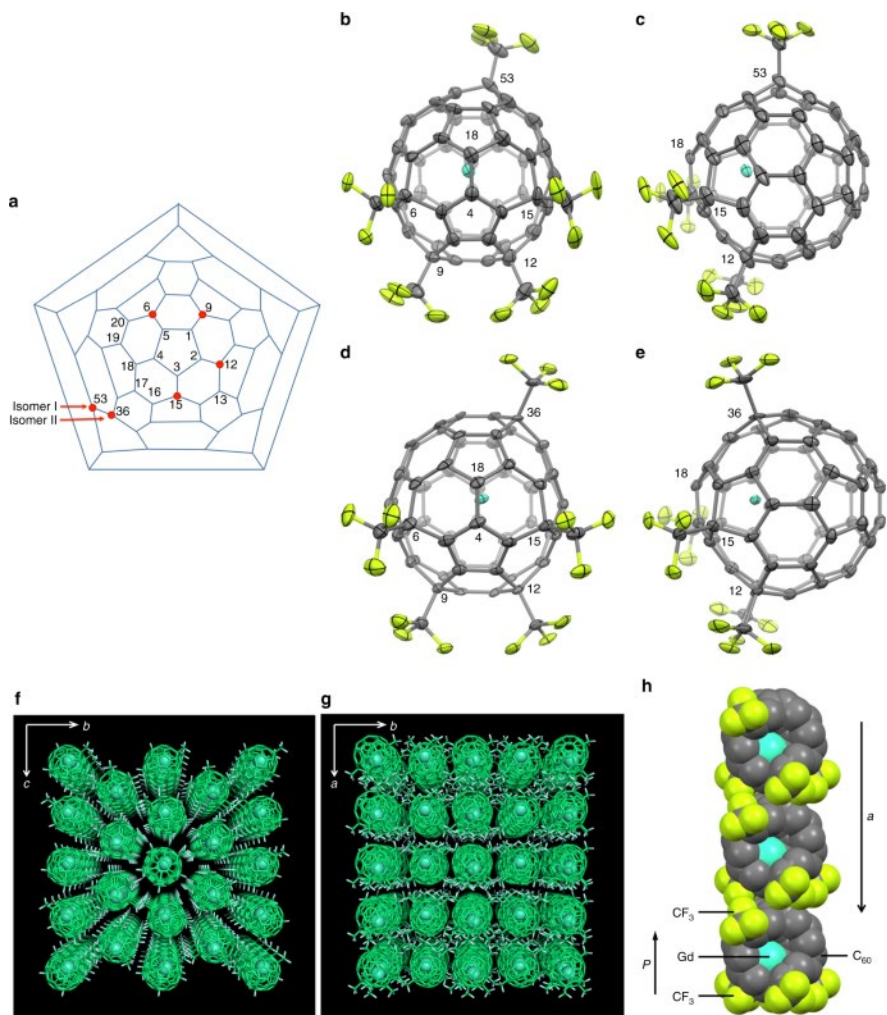
C₇₀



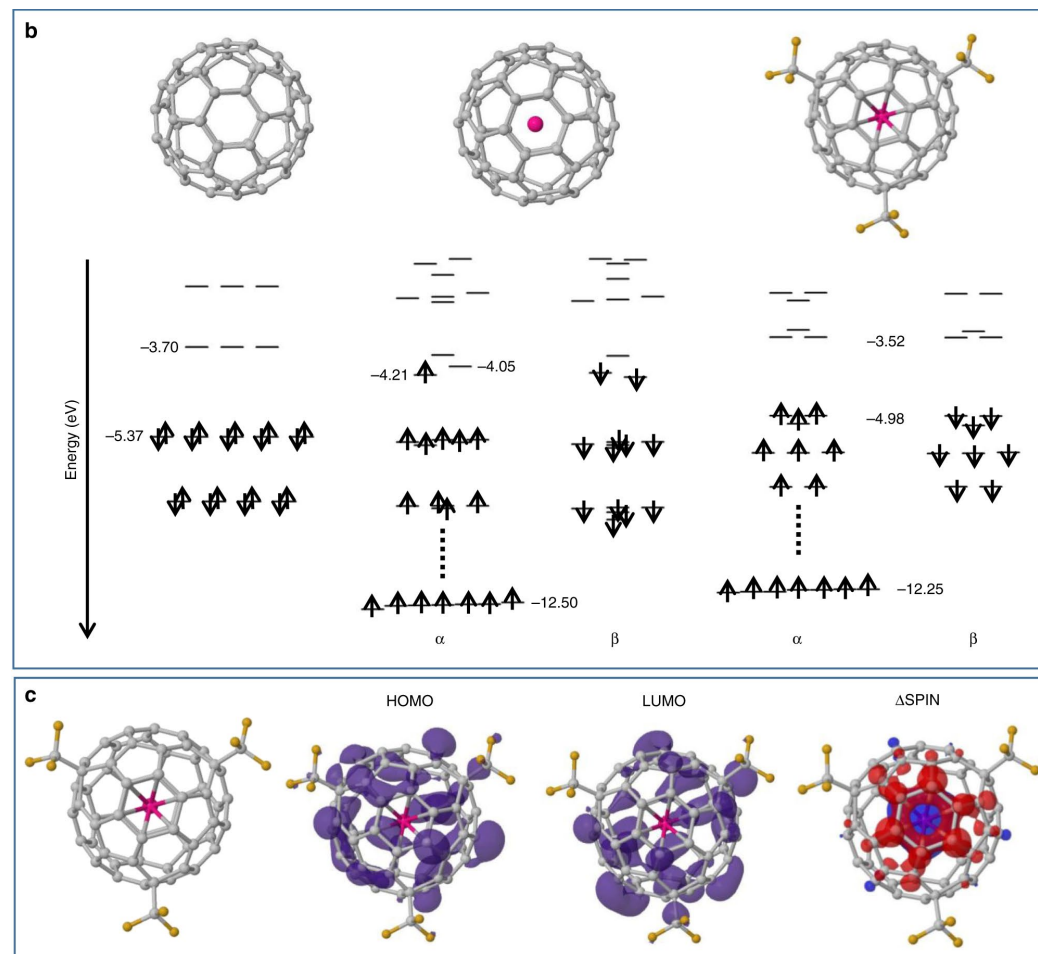
C₇₆



Fullerene



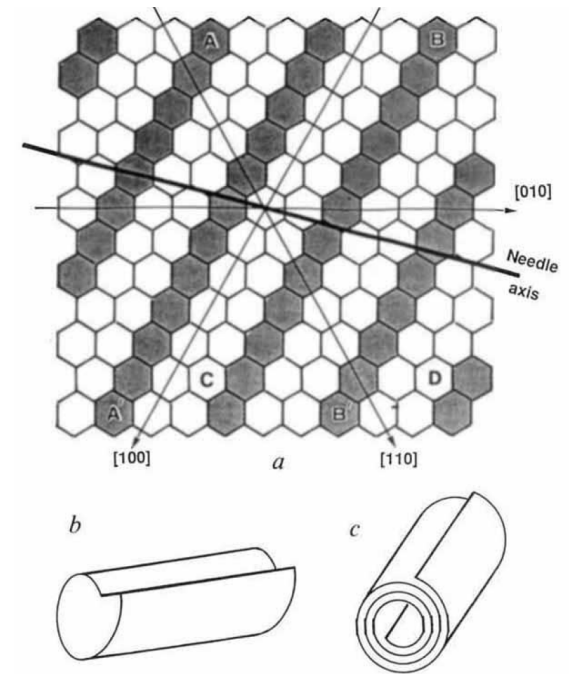
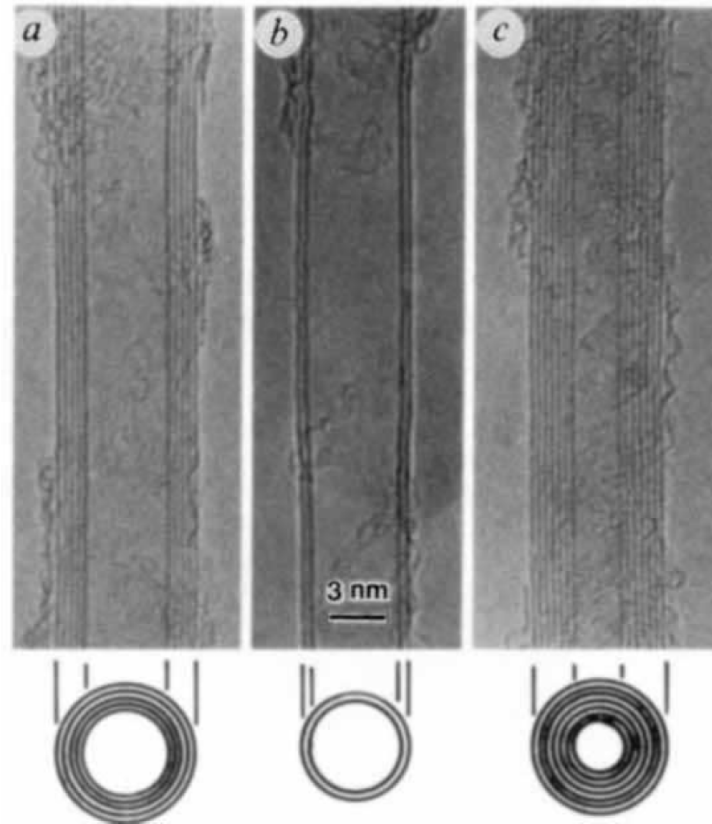
A. Nakagawa et al. Nat. Commun. 2018



- One can use C₆₀ to form various compounds.
- Even control the band structure
- Many applications in chemistry, biology, and solar cells

Carbon nanotubes

- First discovered by Sumio Iijima at 1991.
- Grown by DC arc-discharge evaporation of carbon which is used to produce the C₆₀



Carbon nanotubes

The 1D nanostructure with very unique electrical and mechanical properties. It is widely used in many fields.

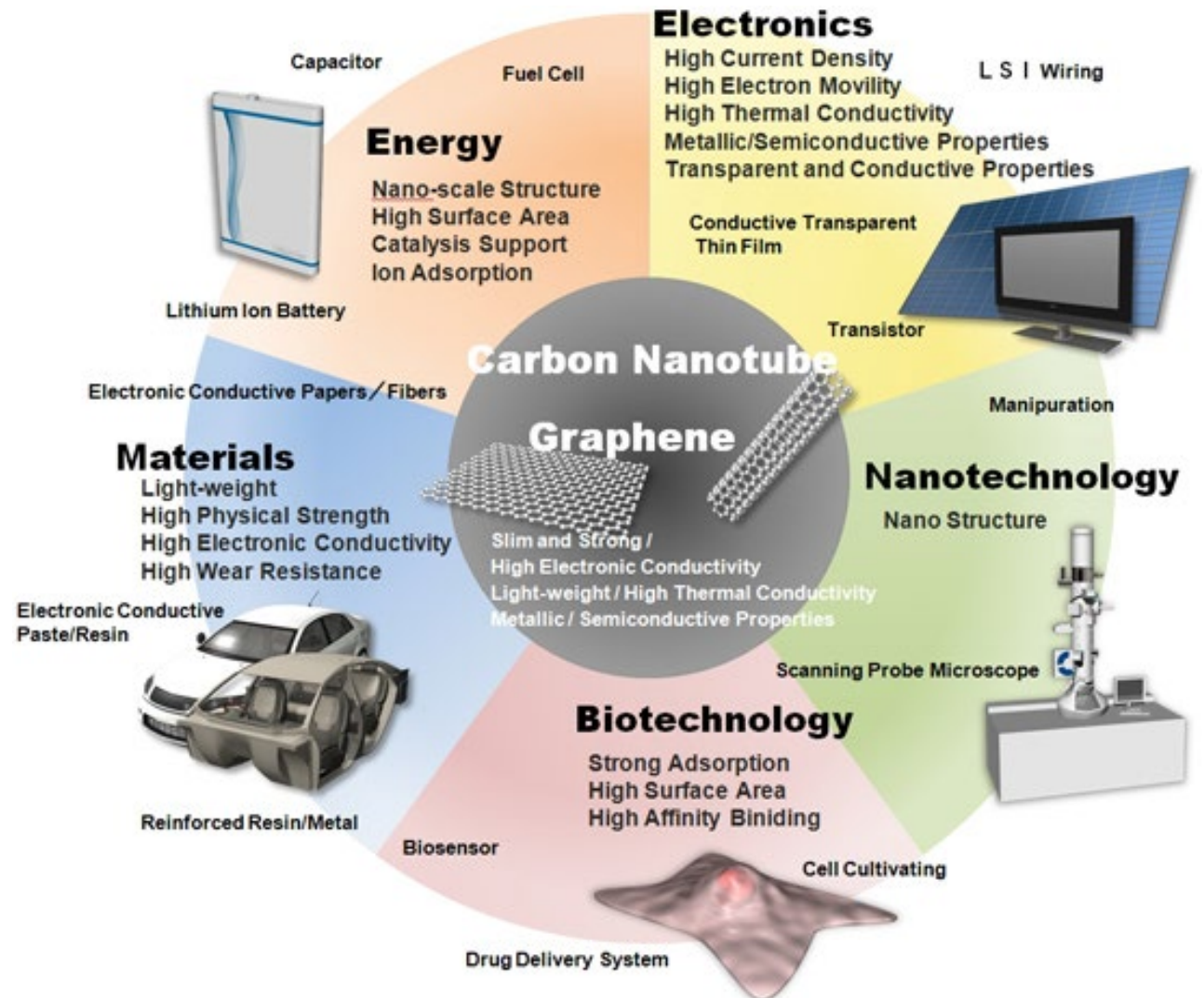
Energy storage and applications

Electronic devices

Material applications

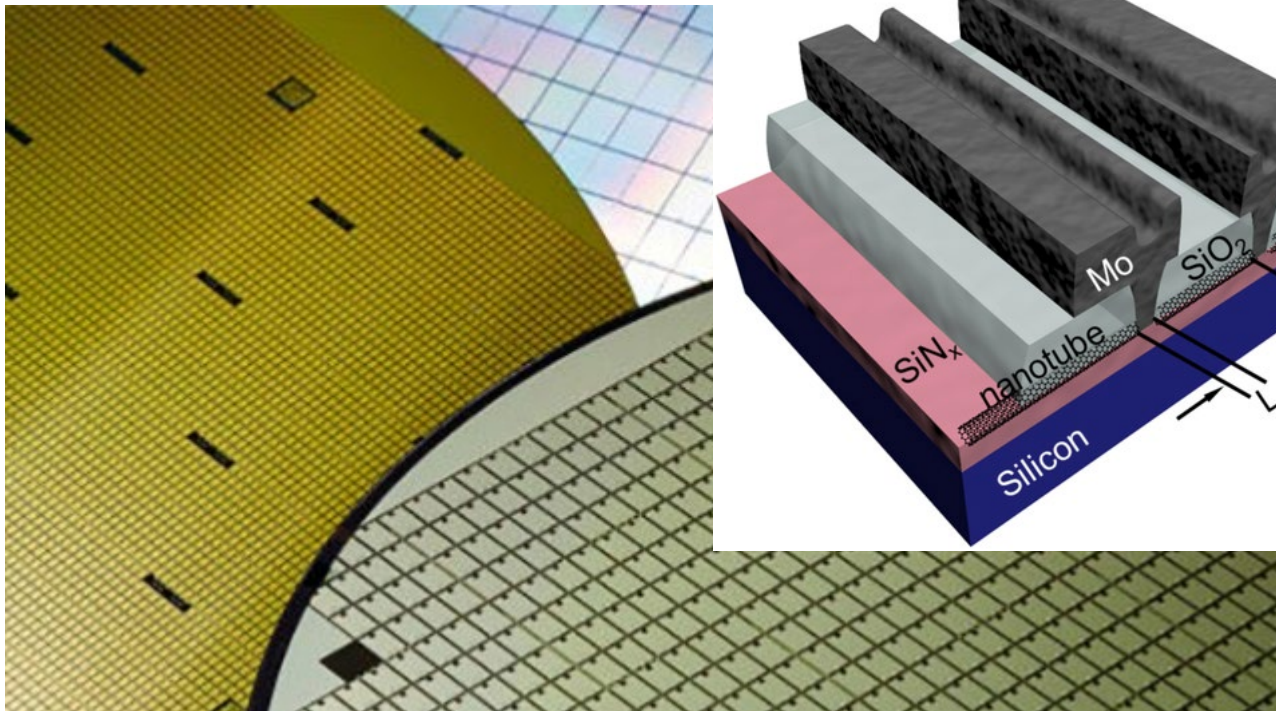
Bio-related applications

Nanostructure for research

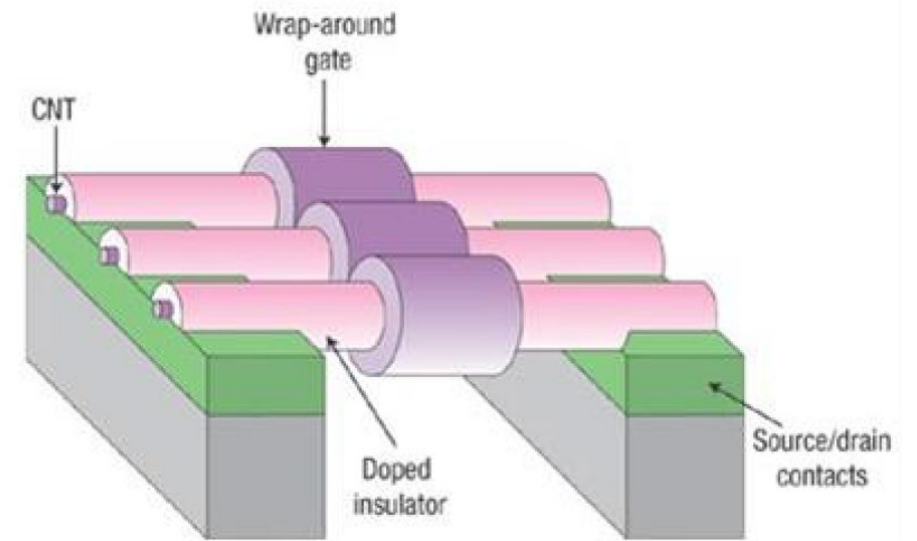


Carbon nanotubes

- Use the size of tube to scale down the size of transistors



IBM research



P. Avouris et al. Nat. Nanotech. (2007)

Quote to quote about nanotubes

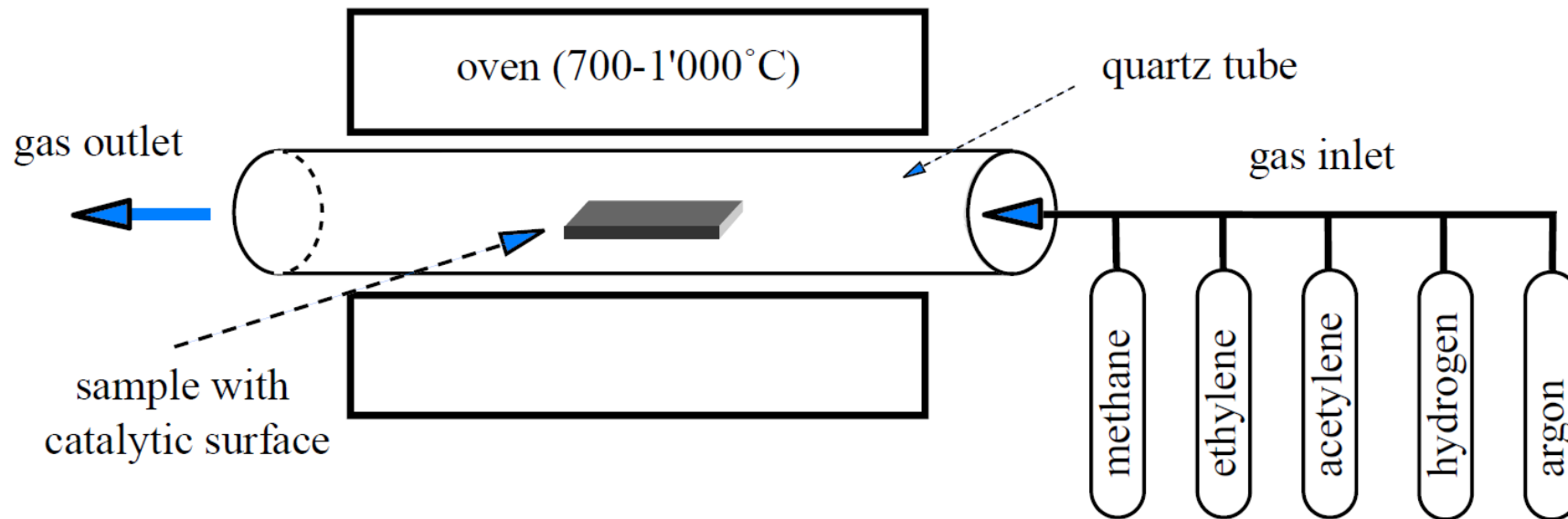
listening to exciting quotations about CNT:

- - "CNT is 100 times stronger than stainless steel and six times lighter..."
- - "CNT is as hard as diamond and its thermal capacity is twice that of pure diamond..."
- - "CNT's current-carrying capacity is 1000 times higher than that of copper..."
- - "CNT is thermally stable up to 4000K..."
- - "CNT can be metallic or semiconducting, depending on their diameter and chirality..."

That all make CNT a very compelling system to work on.....

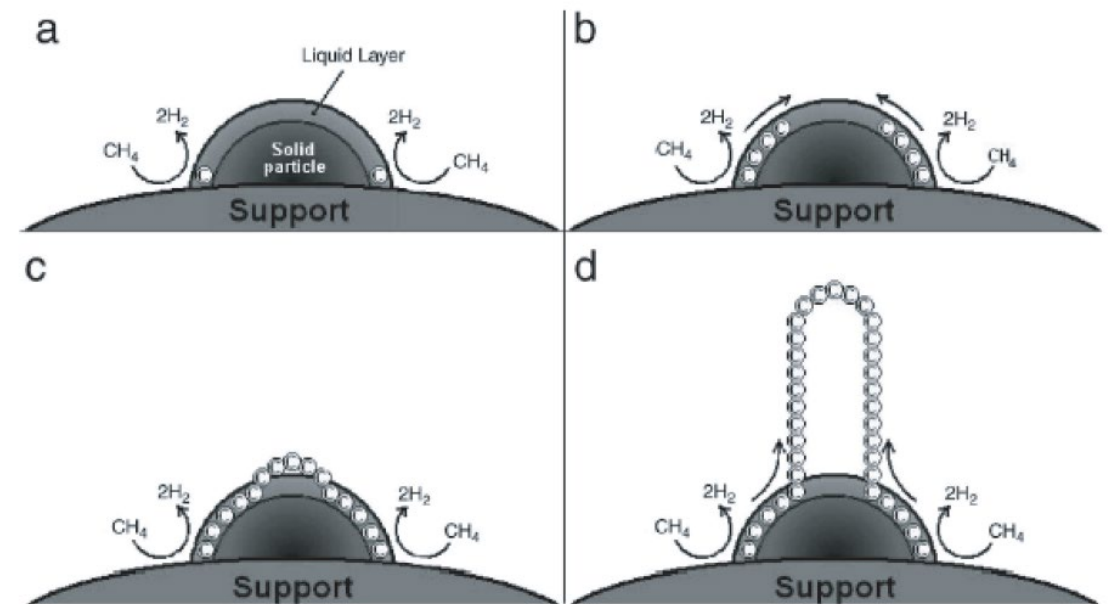
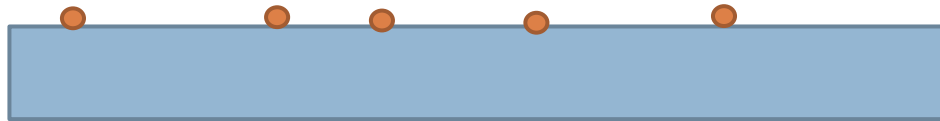
Growth of SWNTs

Typical method: chemical vapor deposition



Growth of SWNTs

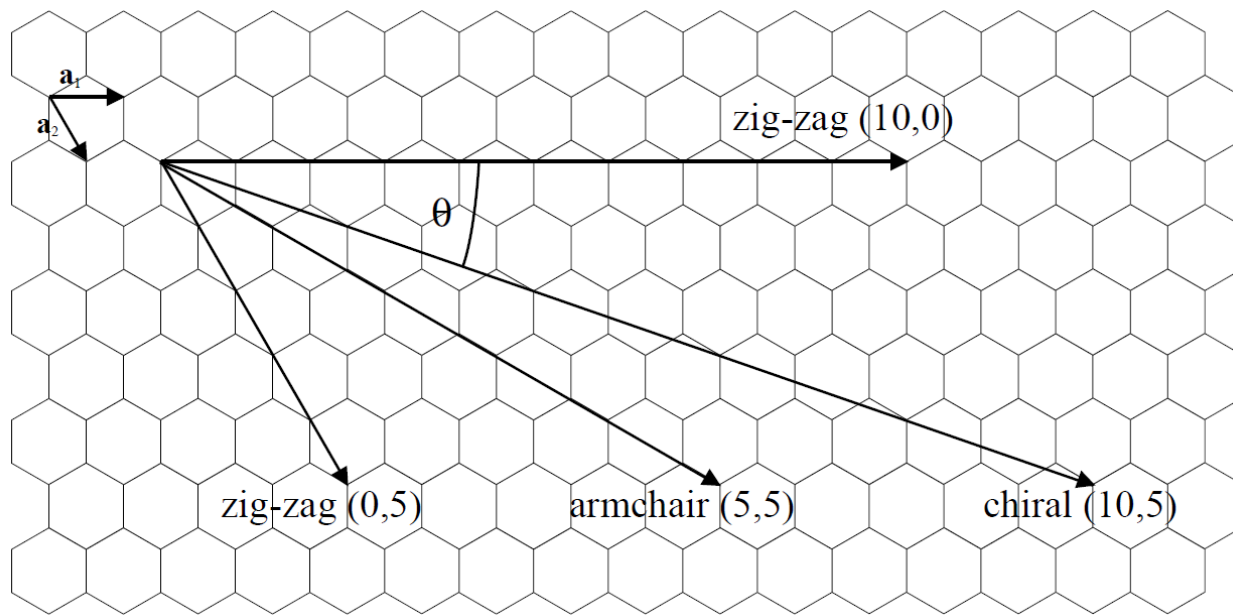
- The carbon needs to attach to something like dirt or debris.
- This usually can be done purposely, it is called catalysts.
- The typical catalyst: Fe, W, Ni Au, etc. based nanoparticles.
- Very high growth rate $60 \mu\text{m}/\text{min}$



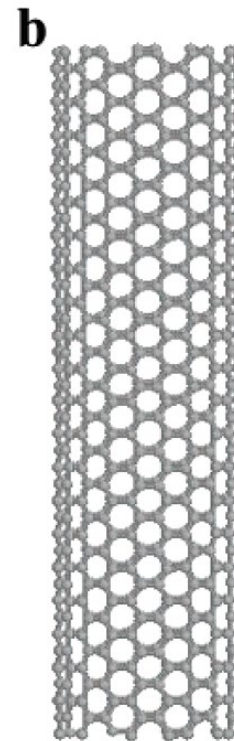
Type of CNTs

One can fold a graphene sheet in different directions:

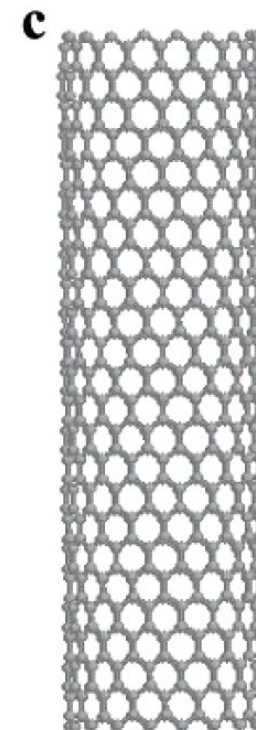
The folded direction can be decided by the coordinate (n,m)



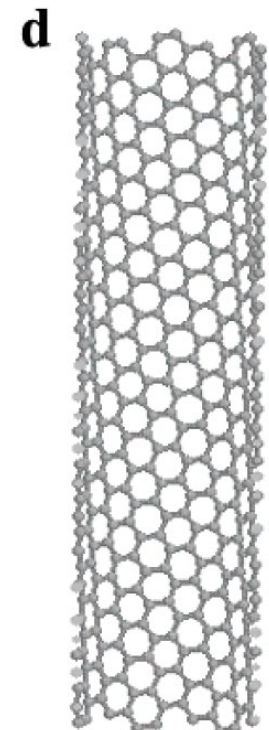
HongJie, Dai, Acc. Chem. Res. 35 (2002)
Jürg Furer thesis, (2006)



Armchair(n,n)

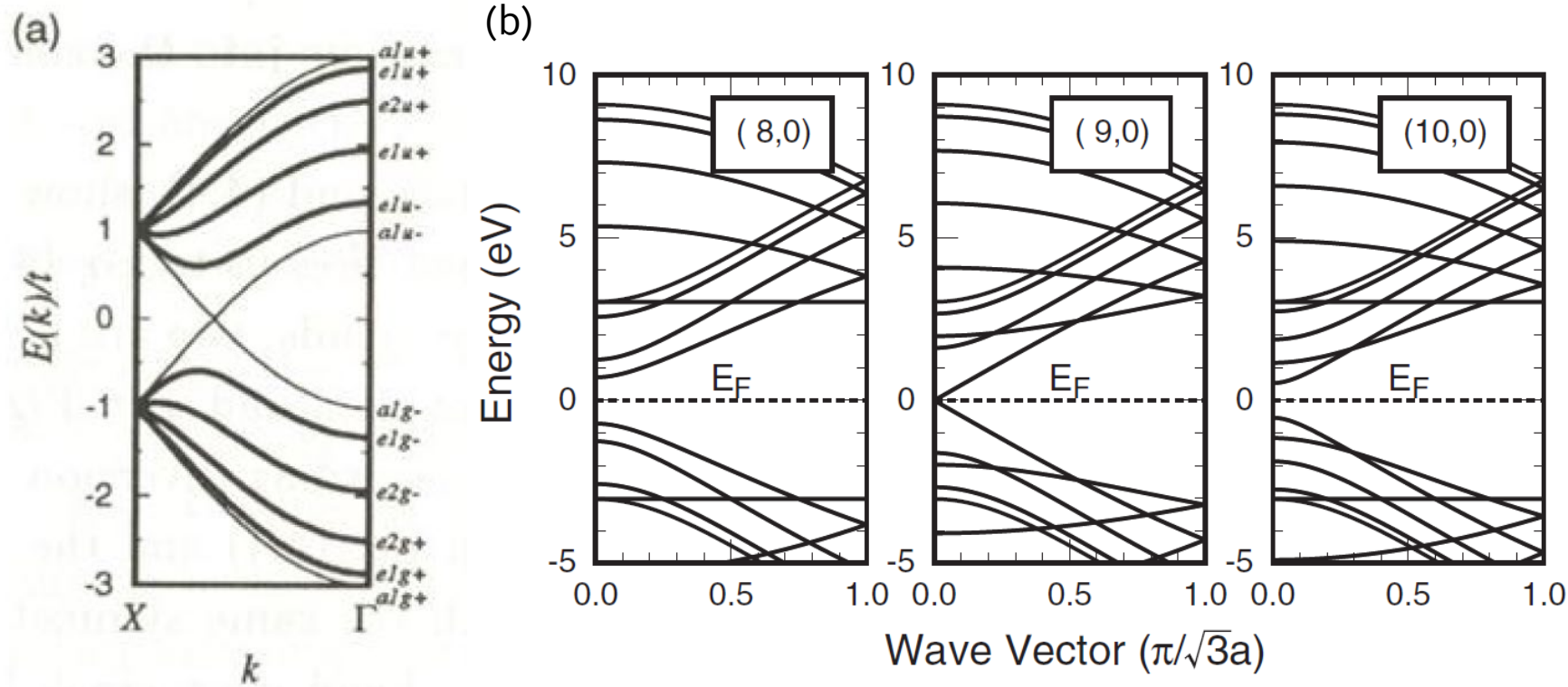


Zigzag ($n,0$)



Chiral ($10,5$)

Band structure



For SWNT,
The (n,m) can determine
the diameter d and chiral
angle θ .

$$d = \frac{a}{\pi} \sqrt{n^2 + m^2 + nm}$$

$$\sin\theta = \frac{\sqrt{3}ma}{2d\pi}$$

General rule: $n-m=3l$,
metallic $n-m=3l\pm 1$,
semiconductor.

(a) Armchair (metallic) (b) Zigzag (semiconductor or semimetal)

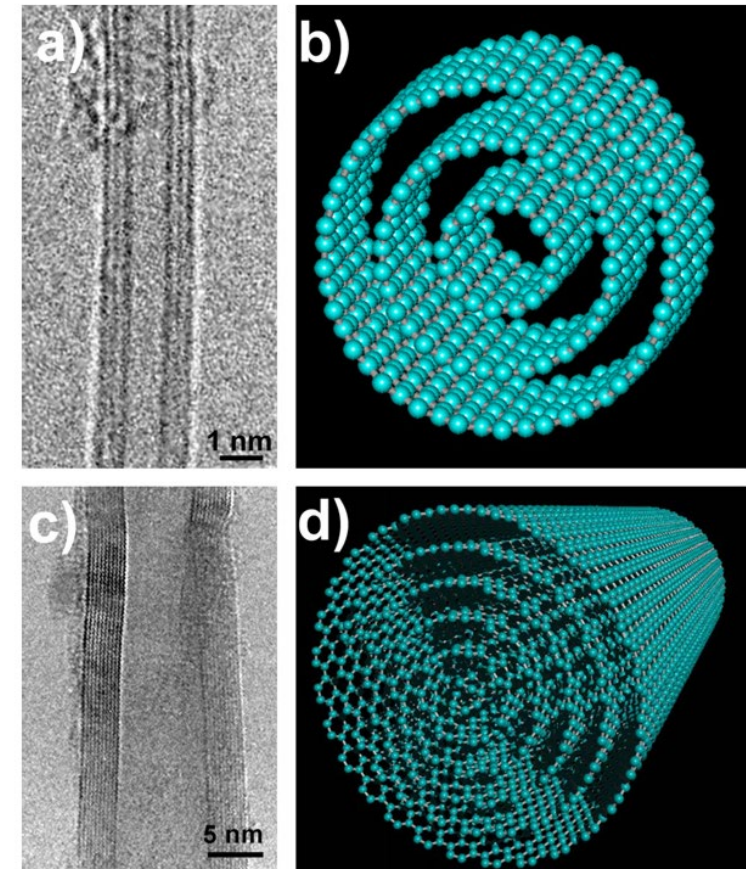
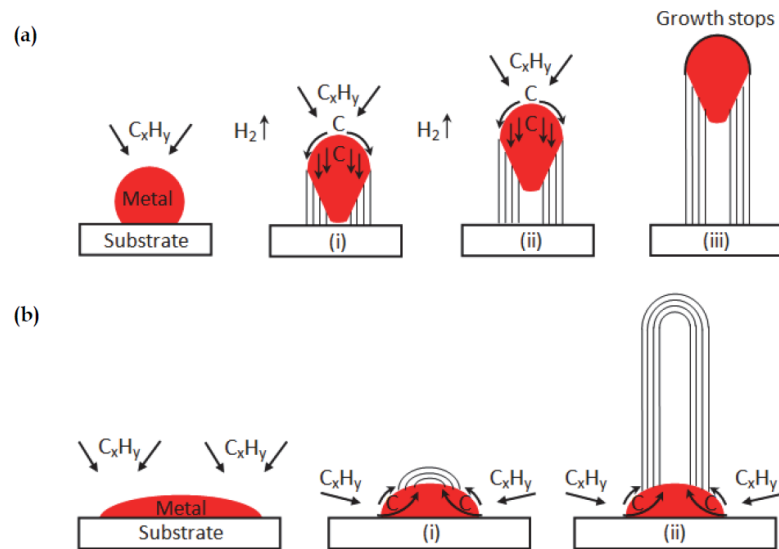
Two types of tubes are semiconductor and metallic.

R. Saito et al. Physical properties of carbon nanotubes. (1998)

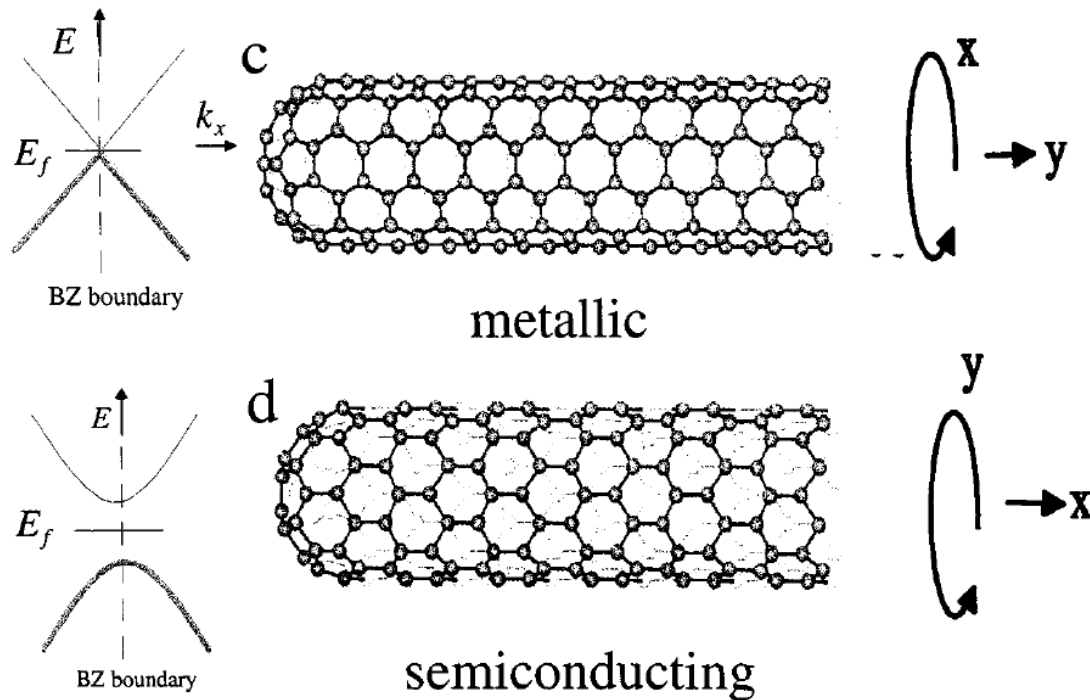
Tsuneya ANDO 0.1143/JPSJ.74.777 (2005)

Multi-wall nanotubes

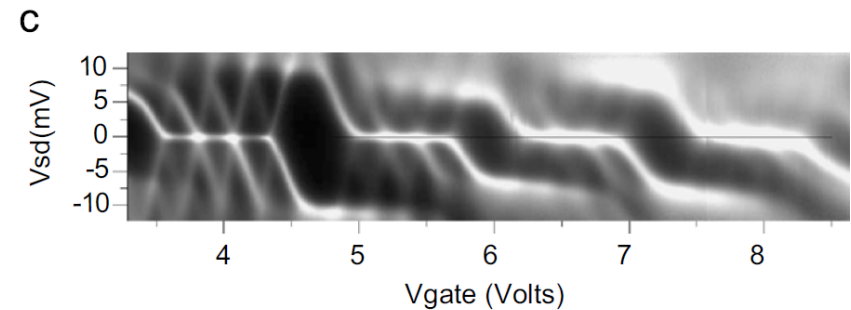
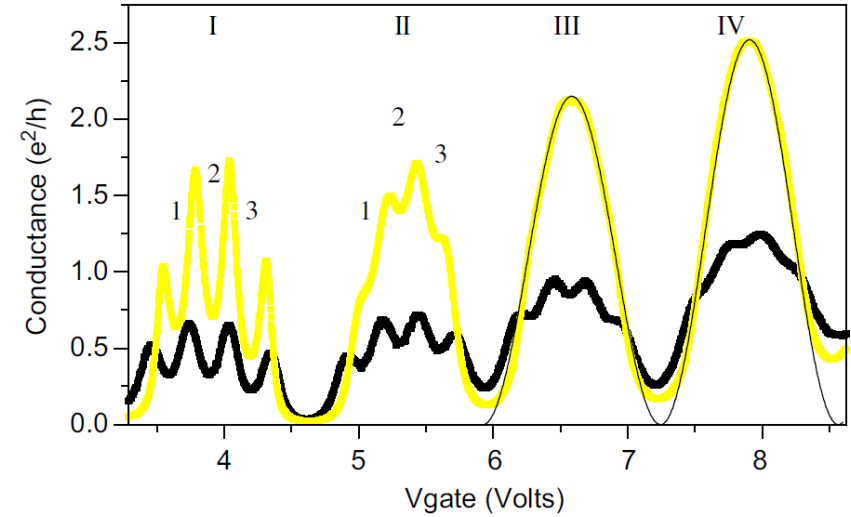
- Usually grown at a lower temperature, 750 C
- Still possessing very good properties, high tensile strength, good hardness, conductivity, thermal properties etc.



Symmetry of the tubes



Paul L. McEuen, et al. IEEE trans. on nano. (2002)

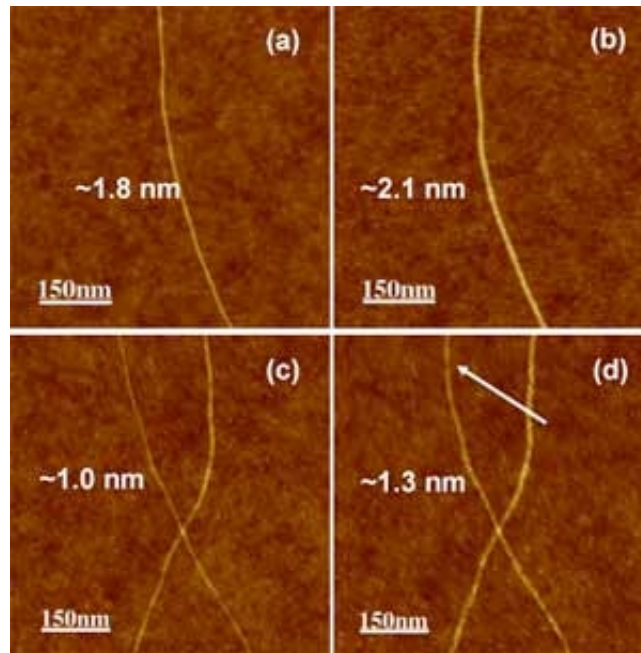


A. Makarovski, G. Finkelstein, Physica B(2008)

- Chiral + Spin leads to a four-fold degeneracy of SNT

Tube characterization

- AFM/SEM/TEM



Credit: Anton Nikitin, SSRL

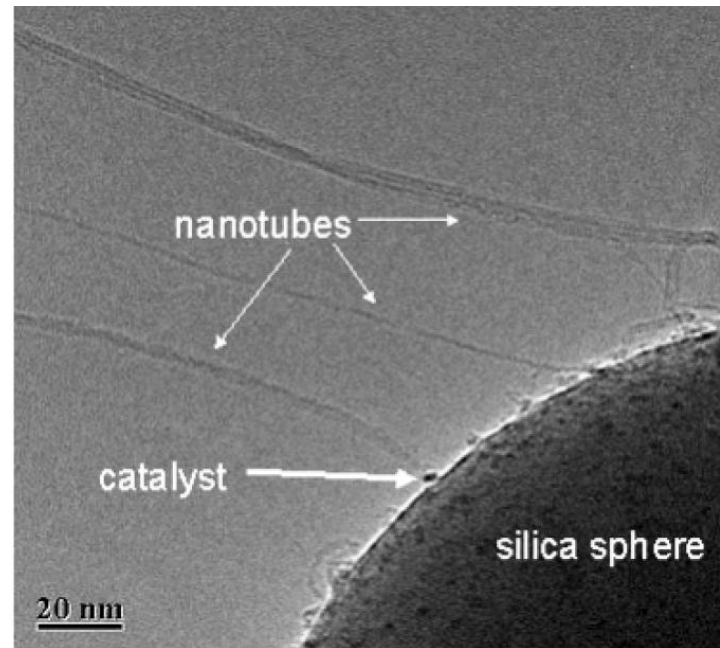
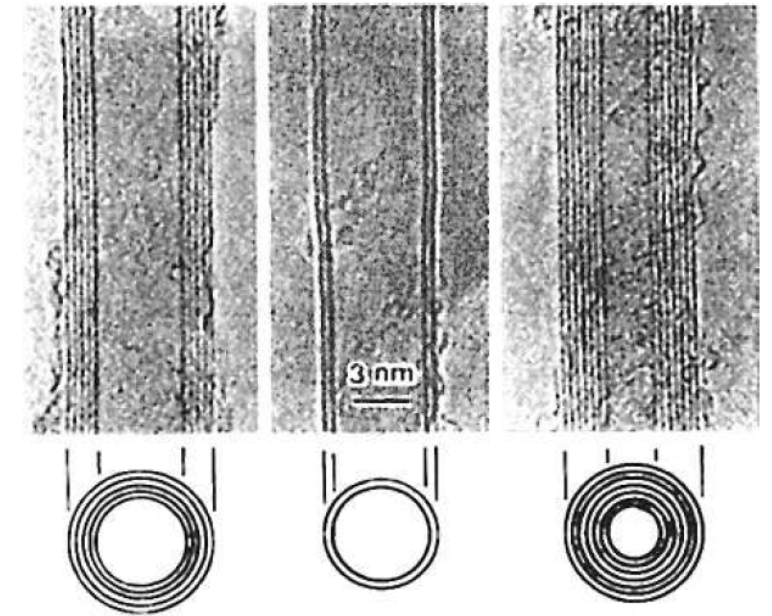


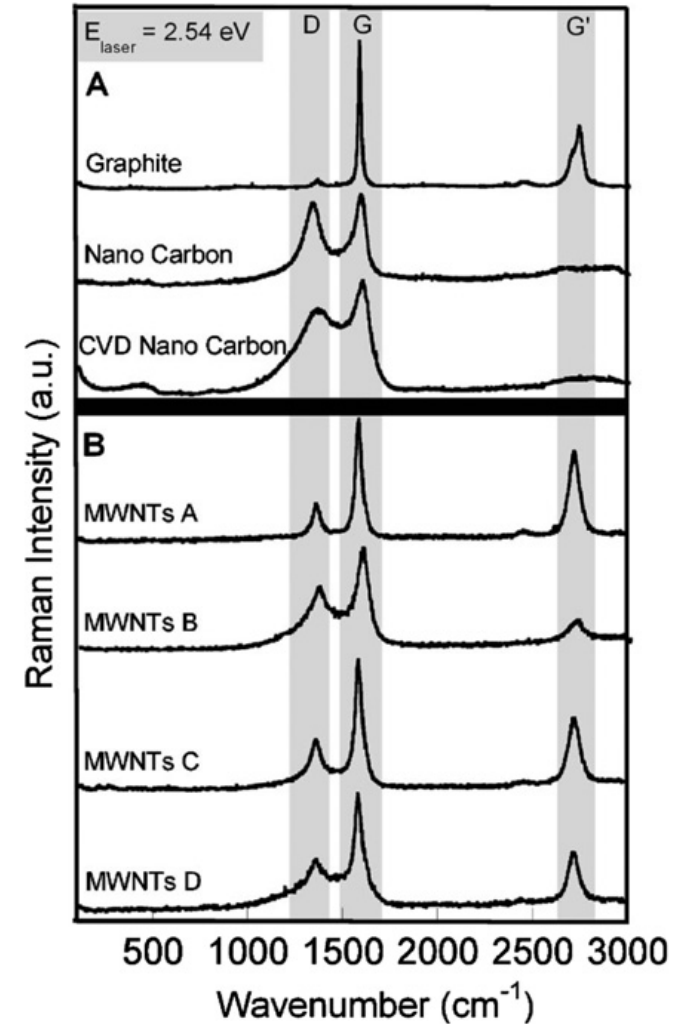
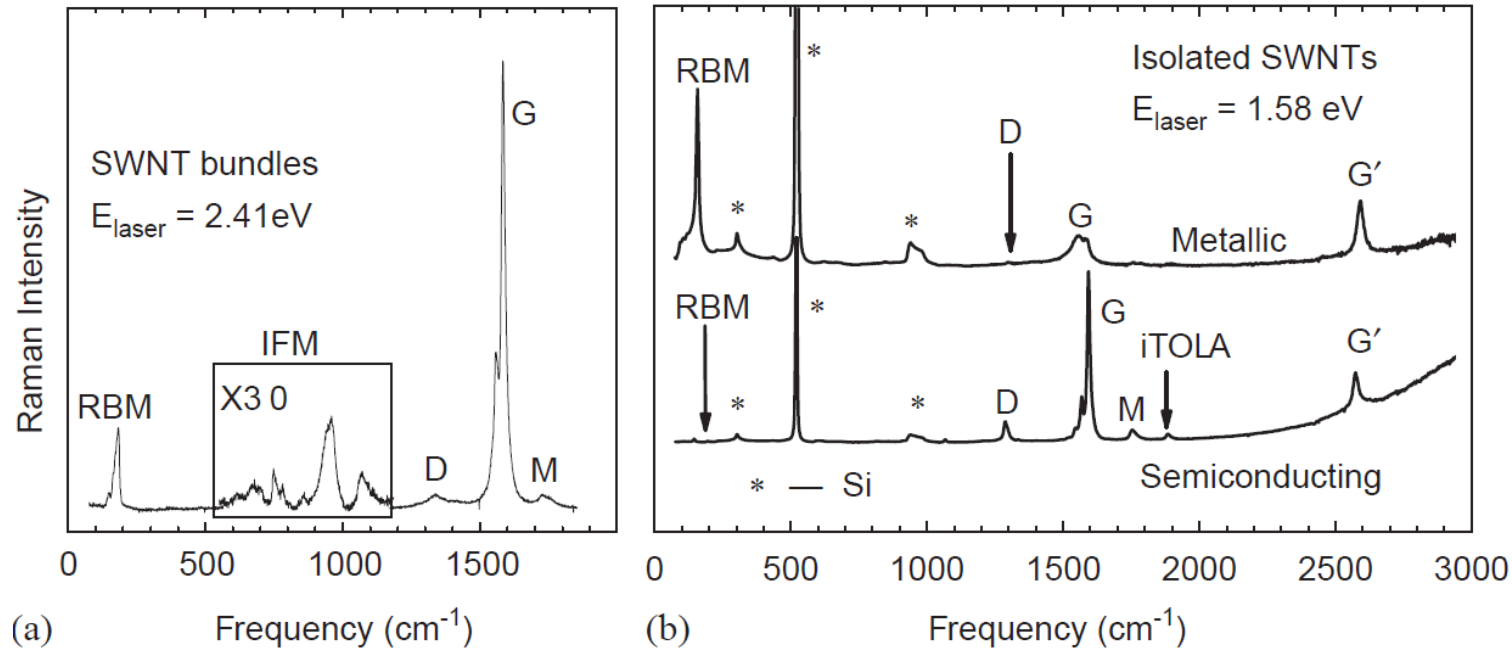
Image: NJIT SEM



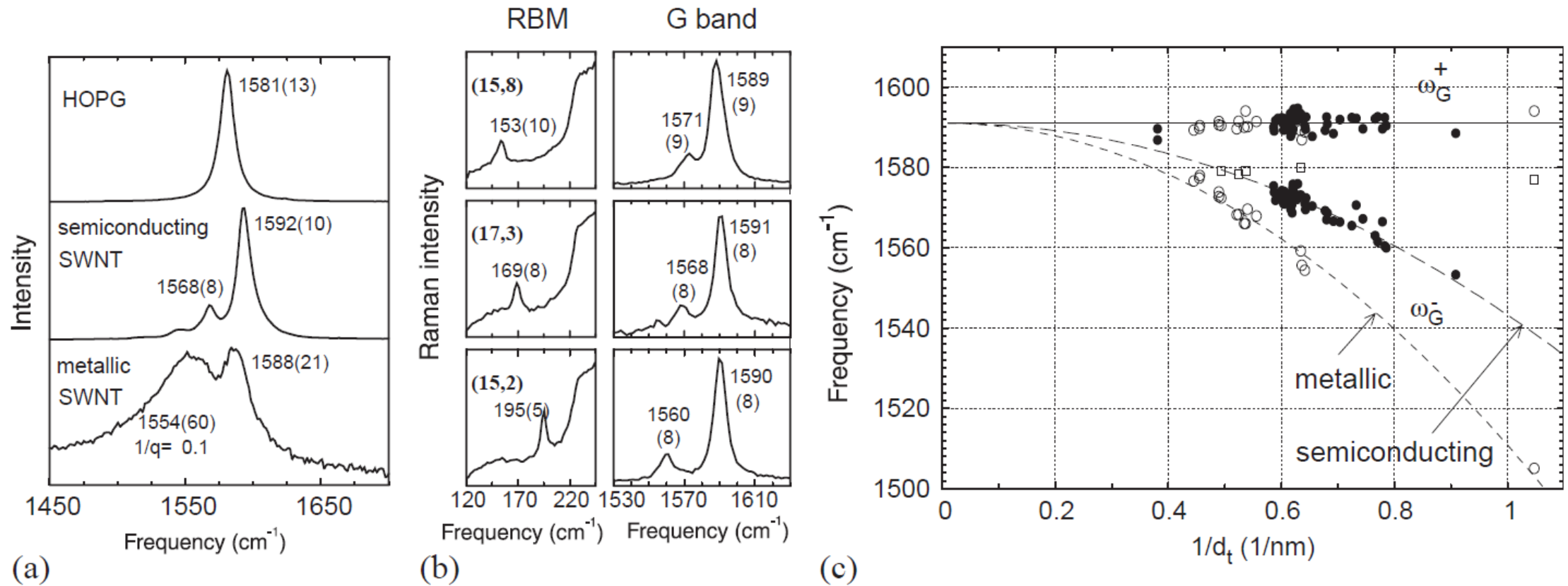
JÄurg Furer thesis, (2006)

Tube characterization

- Raman spectroscopy

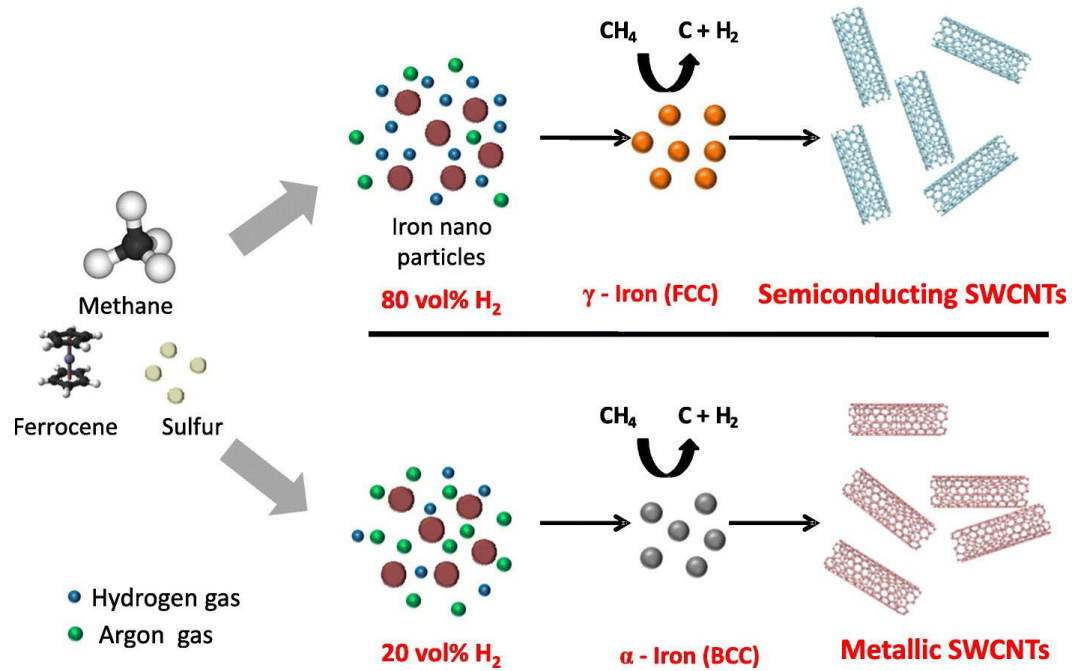


Selective growth or filtering

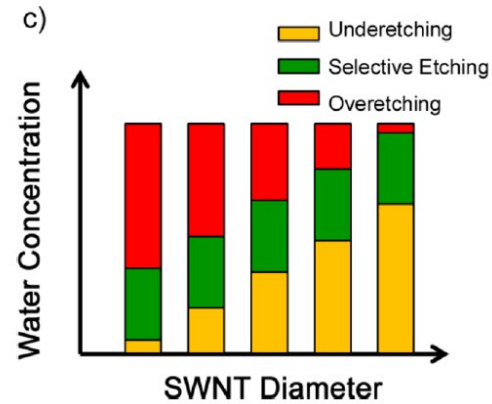


- Selected by Raman spectra

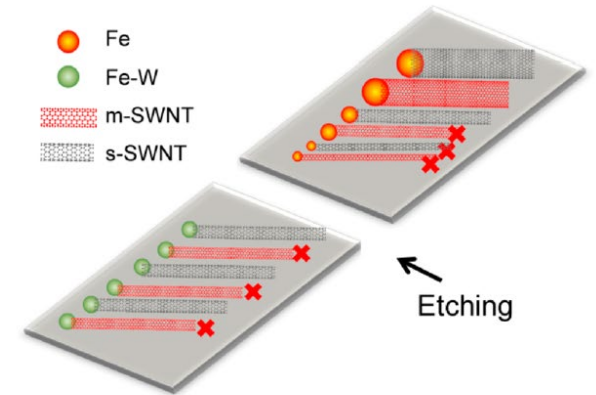
Selective growth or filtering



M. D. Yadav, et al. (2019)

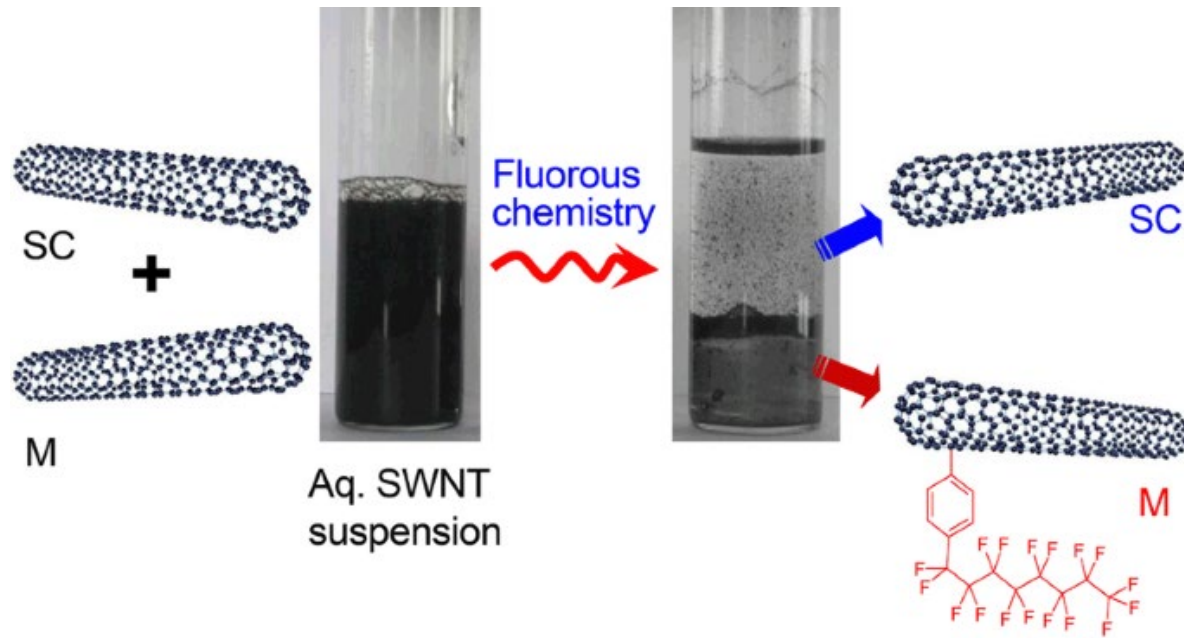


J. Li, et al. ACS nano (2014)



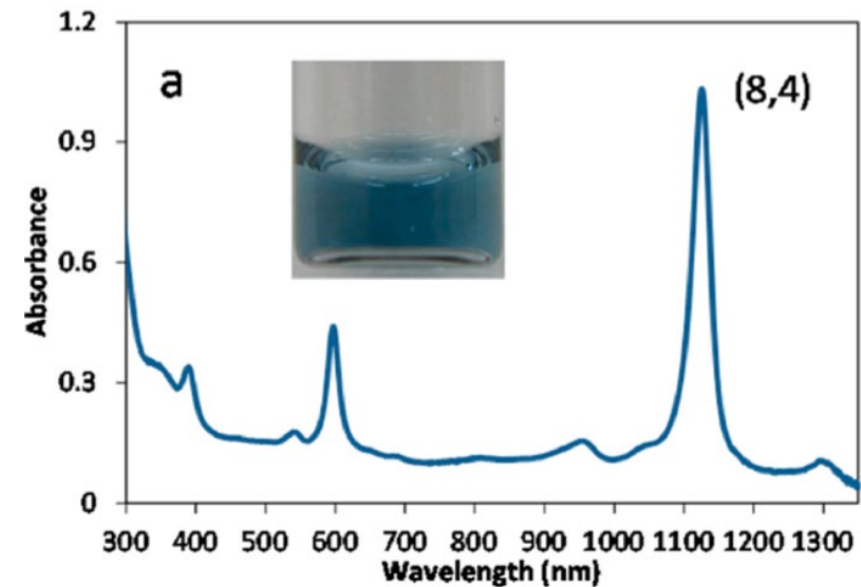
- Control of catalyst is the key to selectively growth CNTs

Selective growth or filtering



S. Ghosh & C. N. R. Rao, Nano Research (2009)

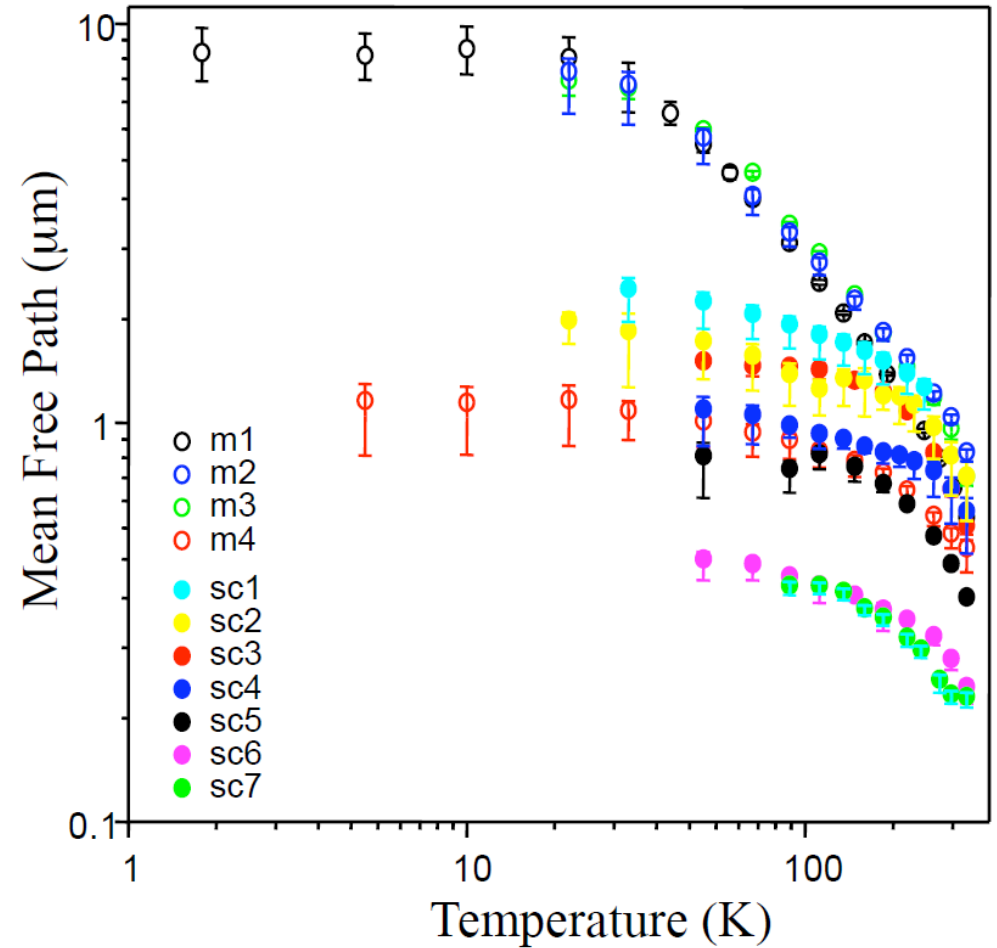
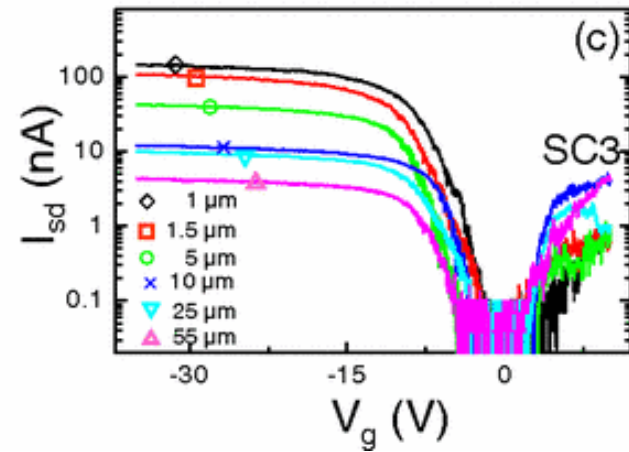
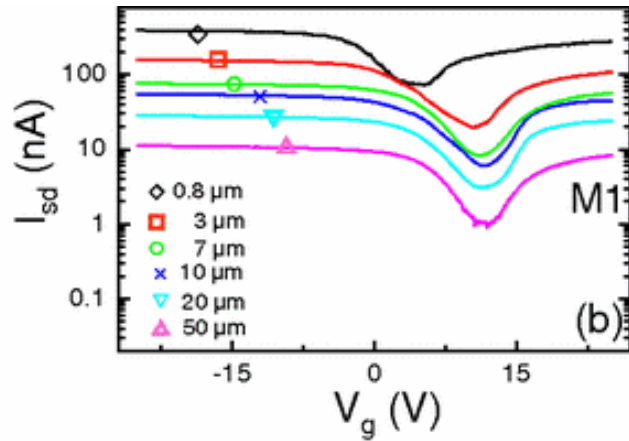
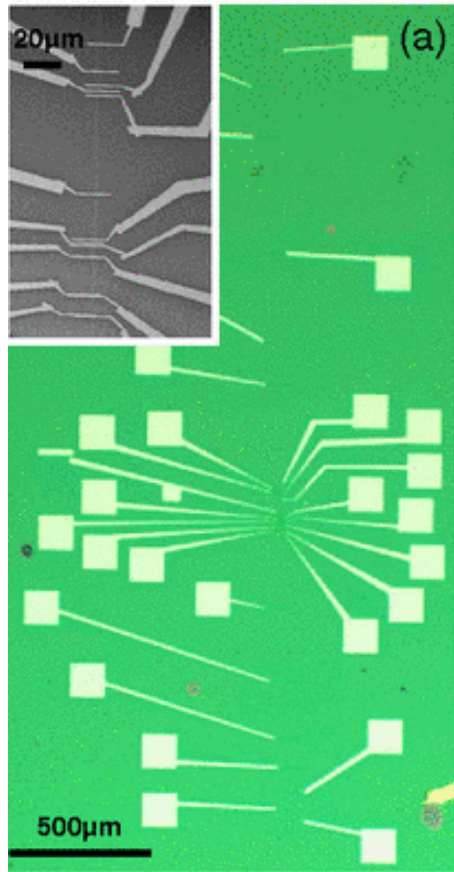
- Purification with chemistry methods



M. S Y Tang, et al. Nanotechnology (2016)

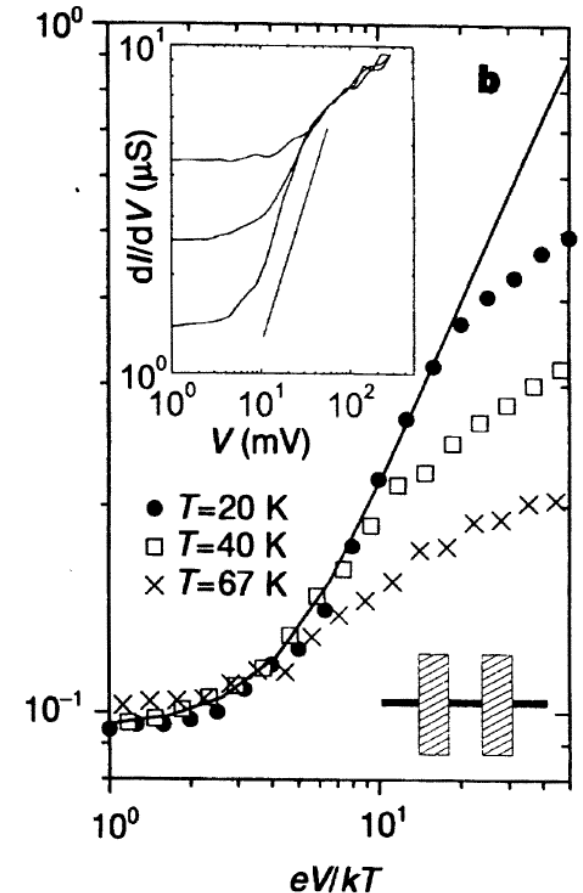
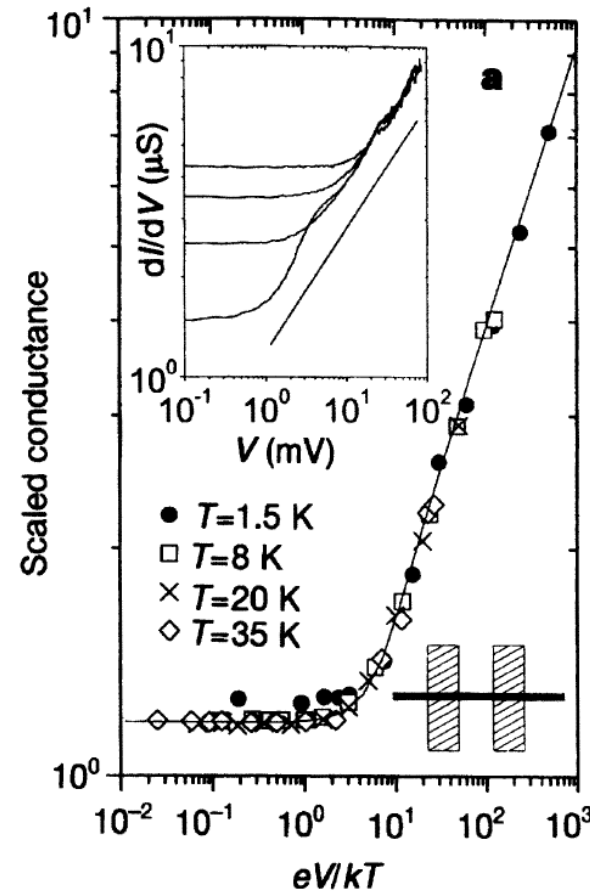
High quality 1D wire

$$R(L) = \left(\frac{h}{4e^2}\right) \left(\frac{L}{L_m} + 1\right) + R_c$$



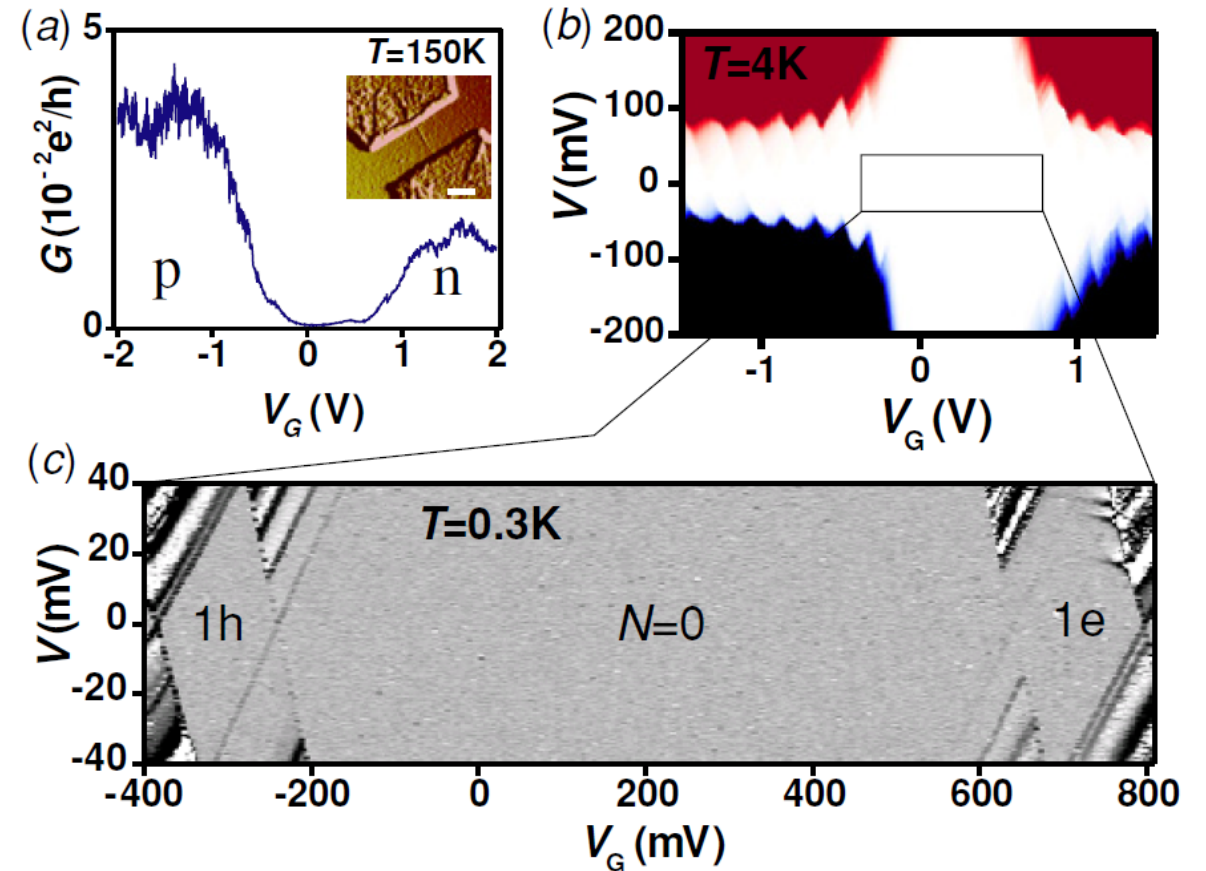
Temperature dependence: Luttinger liquid

- An interaction picture for a 1D conductive system when Fermi liquid breakdown.
- The low energy excitation electron can be described by Boson instead of Fermion.
- Power law dependence in temperature was observed in the 1D carbon nanotubes.

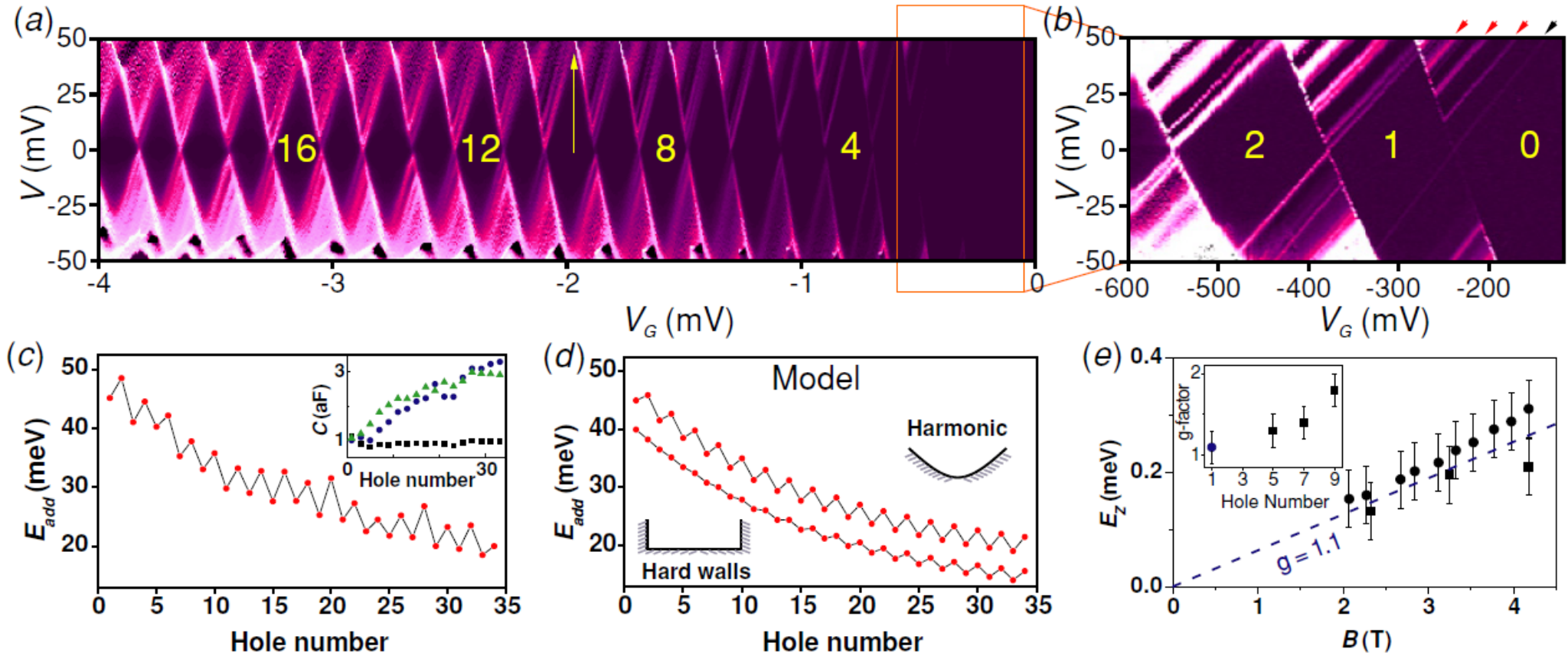


CNT quantum dot

- The clean 1d quantum wires make an easy route to create the zero-dimensional quantum dots.
- The quantum dot can be defined by adding metal contact to CNT with a designed distance.
- At a low enough temperature, quantization can be revealed. Therefore, one can count electrons one by one which knows as a single-electron transistor.

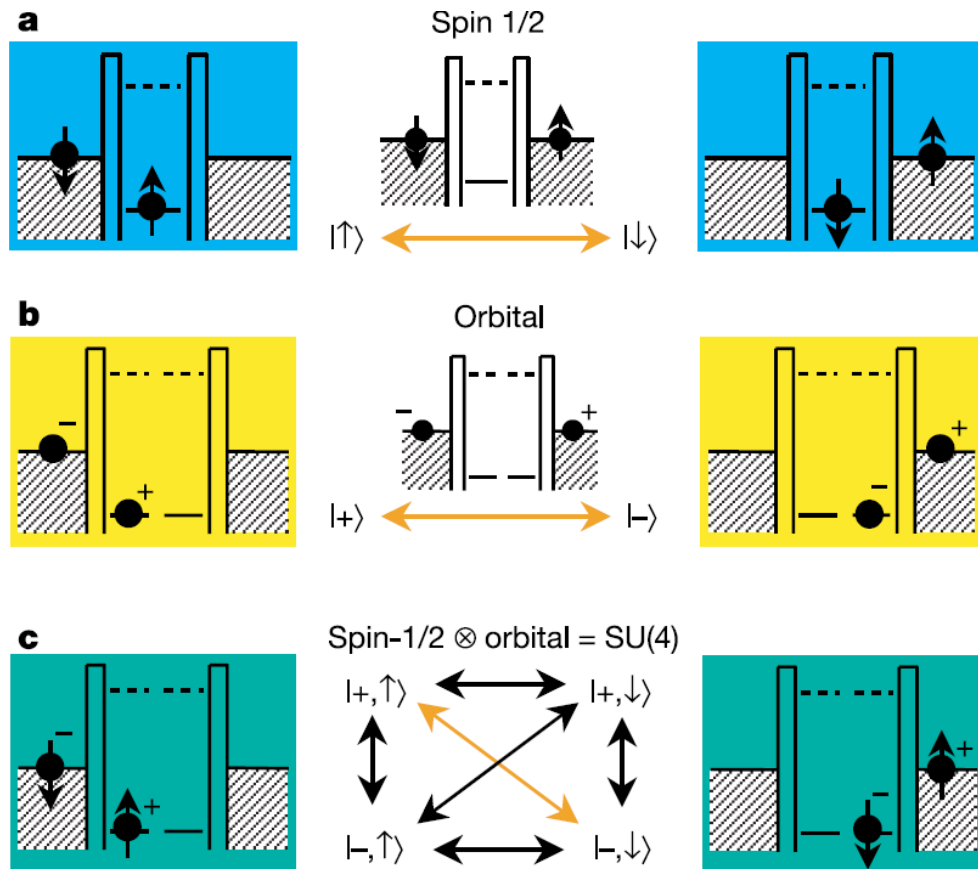


CNT quantum dot



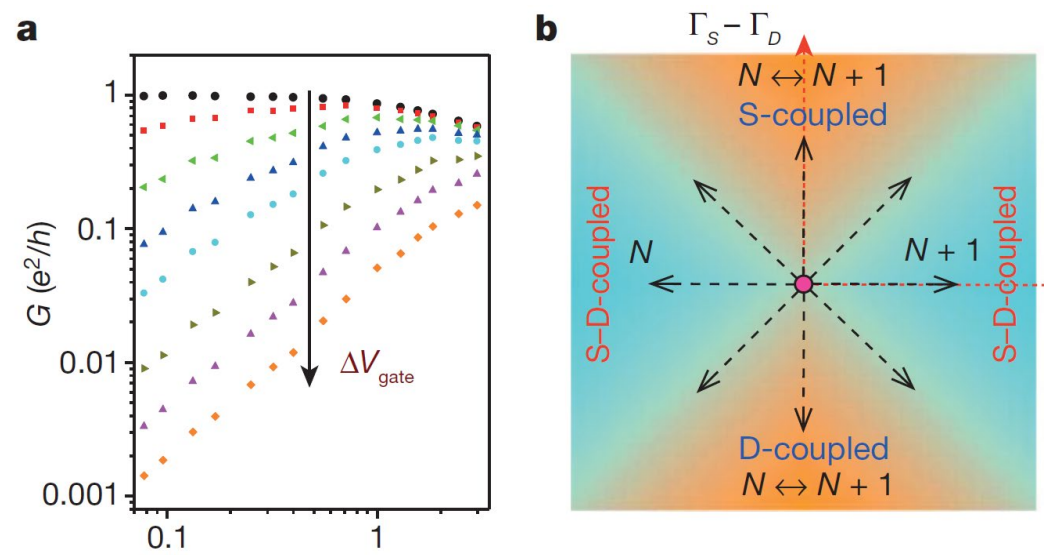
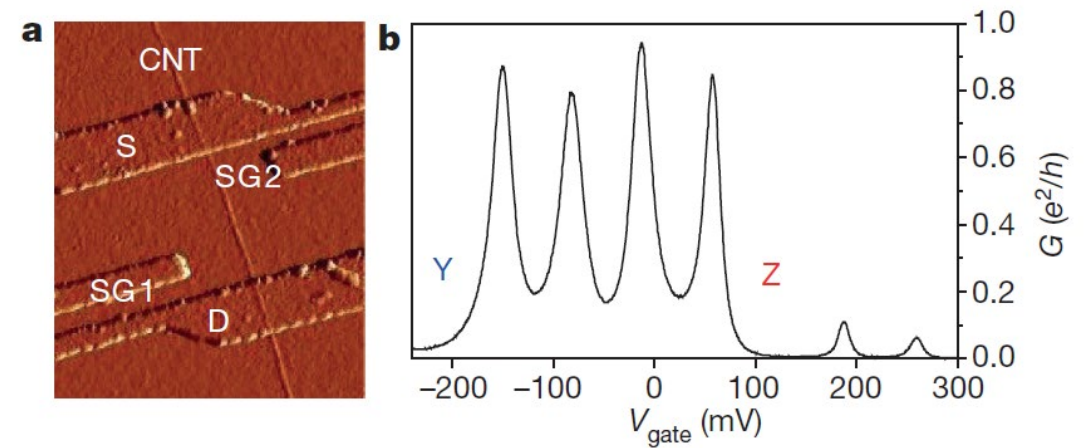
CNT quantum dot

Kondo effect



P. Jarillo-Herrero et al. Nature (2005)

Quantum phase transition



H. T. Mebrahtu et al. Nature (2012)

Quiz

- 1. which one is the 1D carbon materials

A graphene

B carbon nanotube

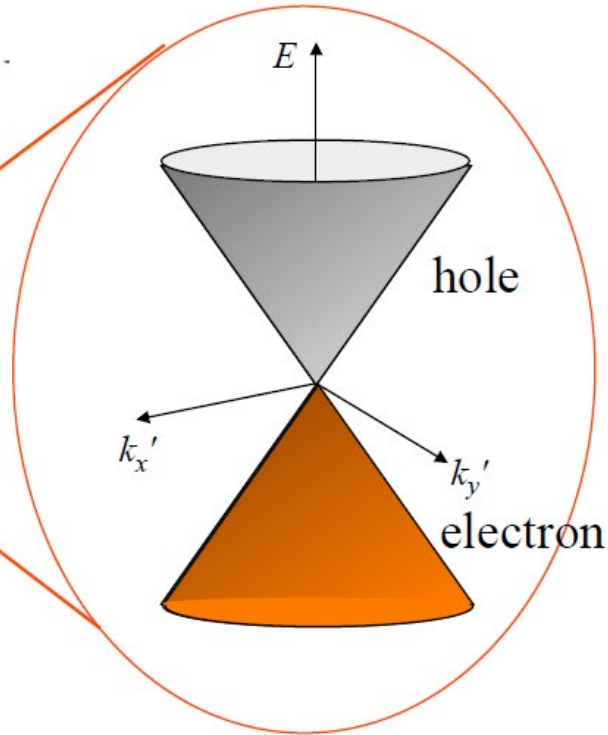
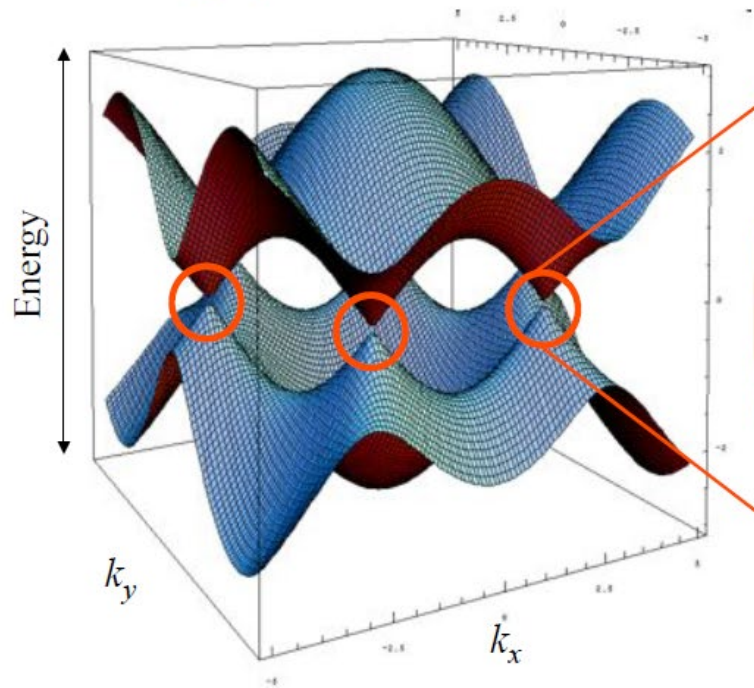
- 2. what is the difference between ebeam lithography and photo lithography(EUV)

2D CARBON-GRAPHENE

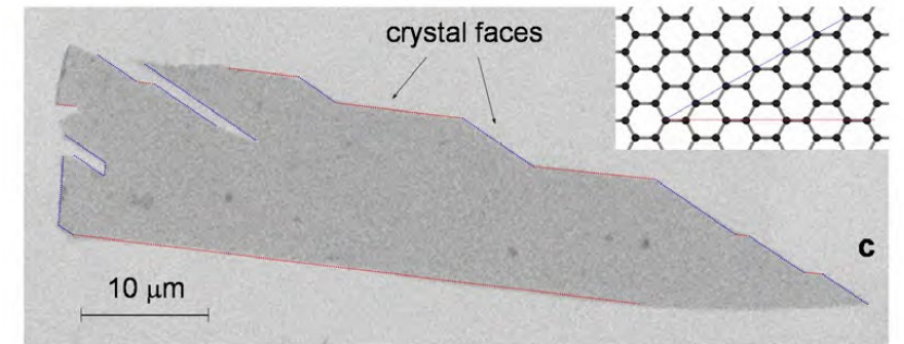
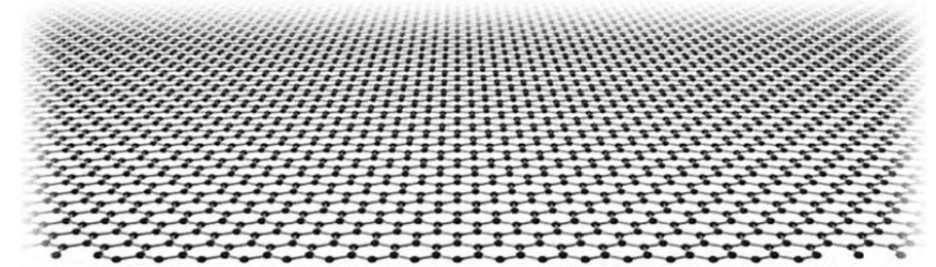
Graphene

Monolayer of carbon

Band structure of graphene



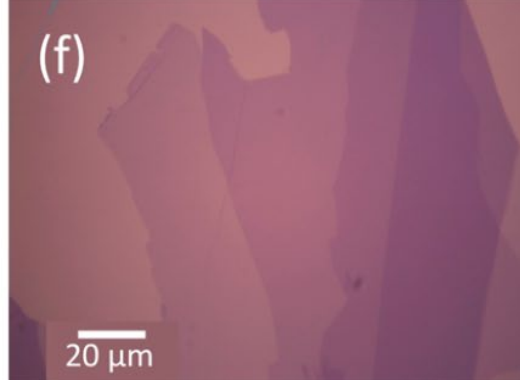
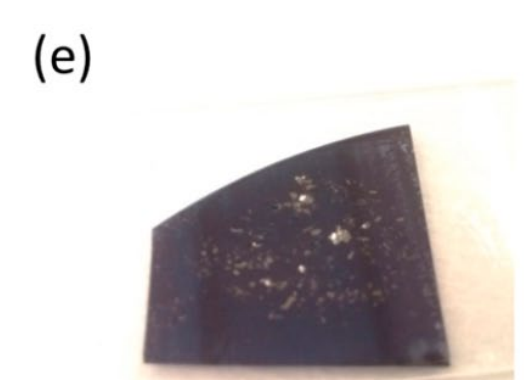
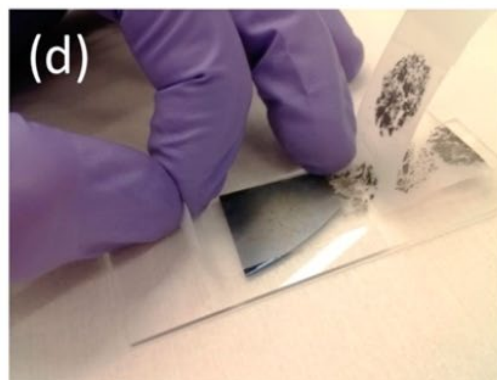
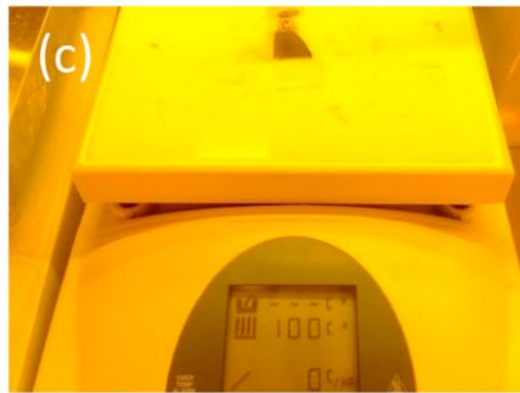
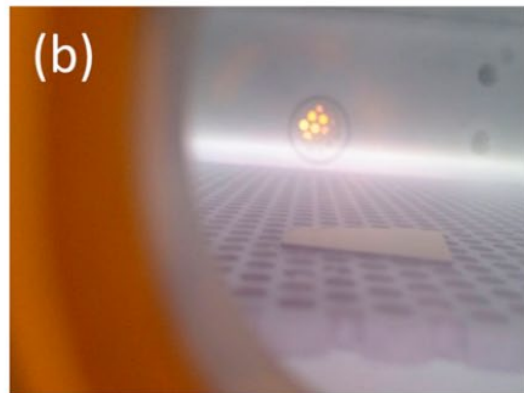
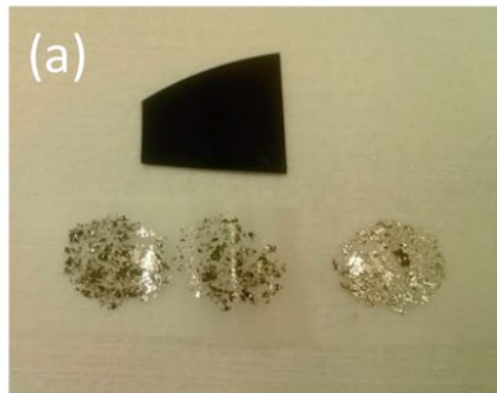
A. K. Geim and K.S. Novoselov Nat. Mat. (2007)



- Unique band structure, Dirac cone
- Relativistic particle, particle velocity close to the speed of light. Therefore, Dirac Hamiltonian is needed.
- K-K' point symmetry, Valley degeneracy

Making of graphene

- Exfoliation



© The Nobel Foundation. Photo: U. Montan
Andre Geim

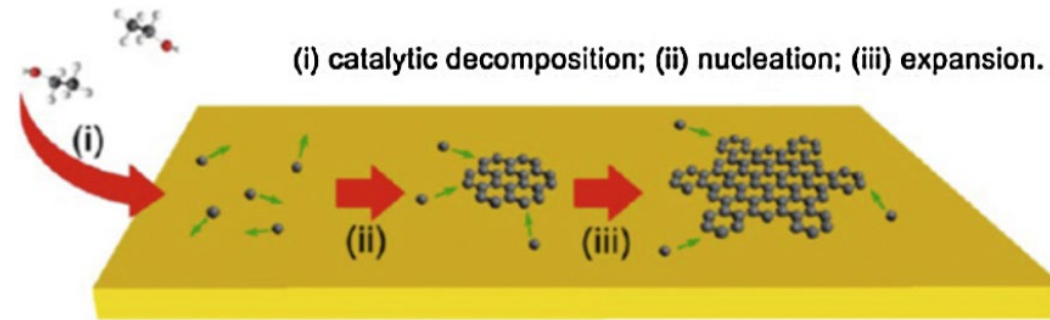
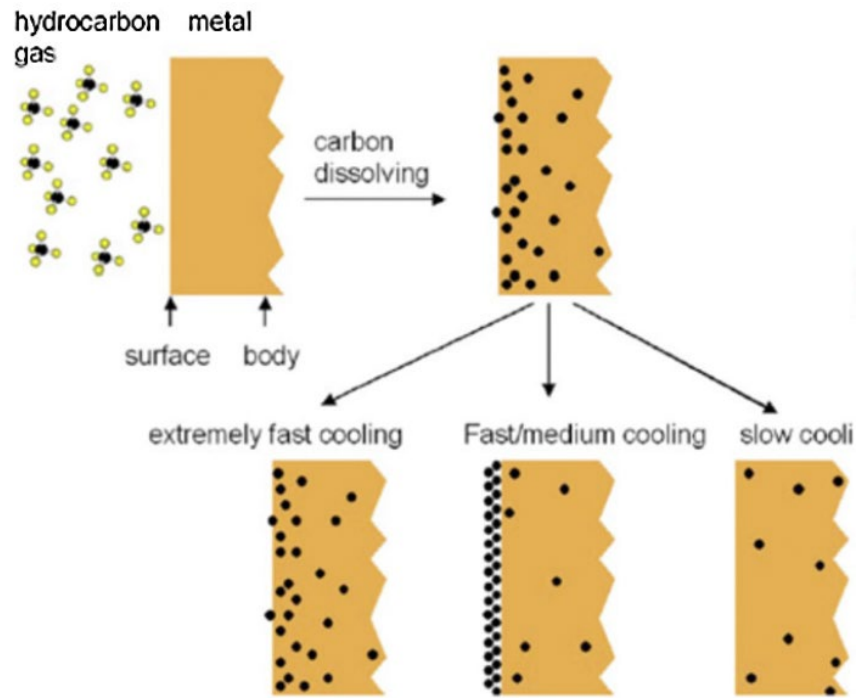


© The Nobel Foundation. Photo: U. Montan
Konstantin Novoselov

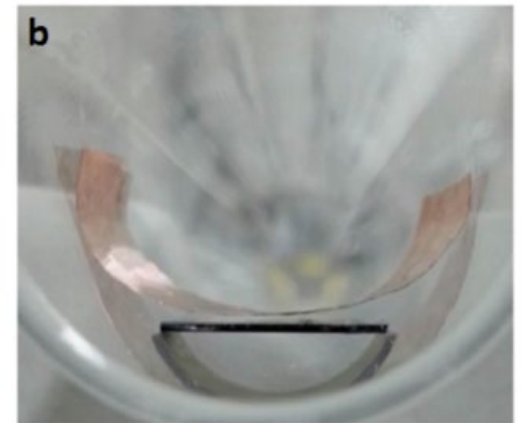
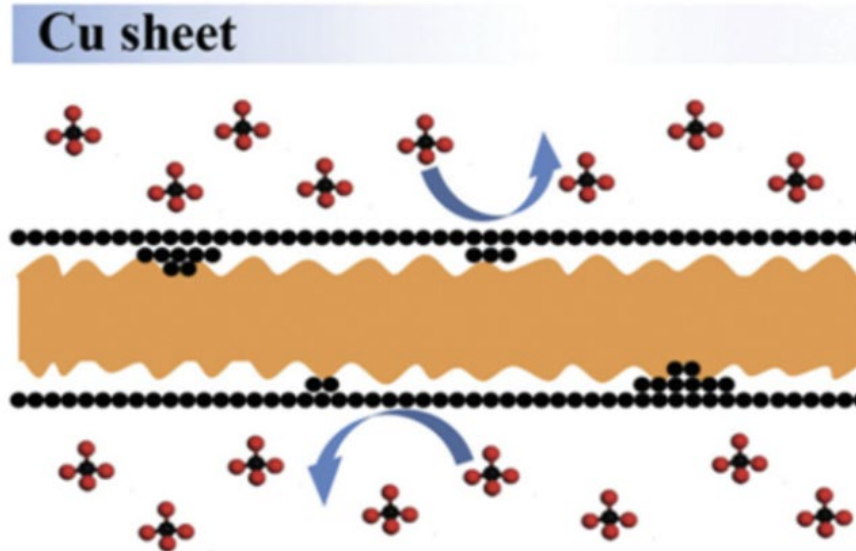
Yuan Huang et al. ACS. Nano. (2015)

Making of graphene

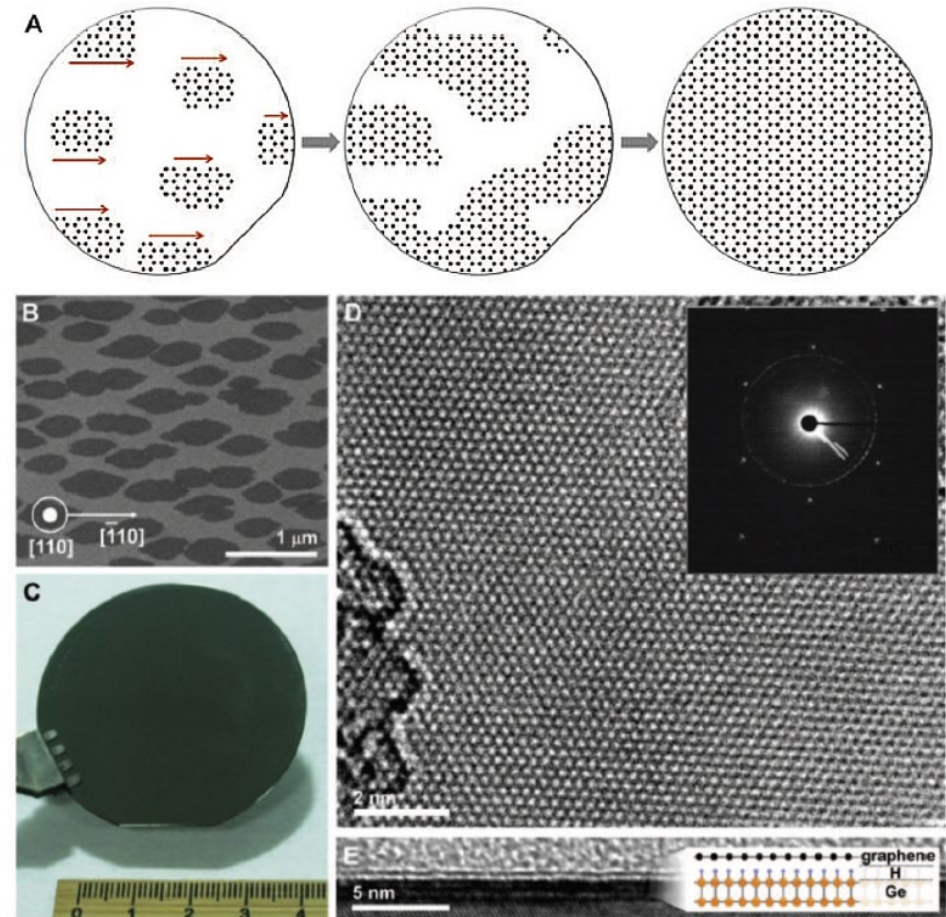
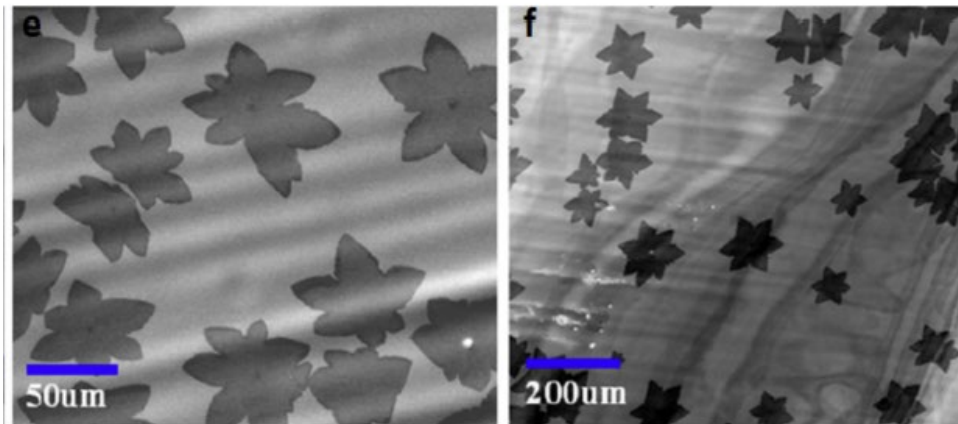
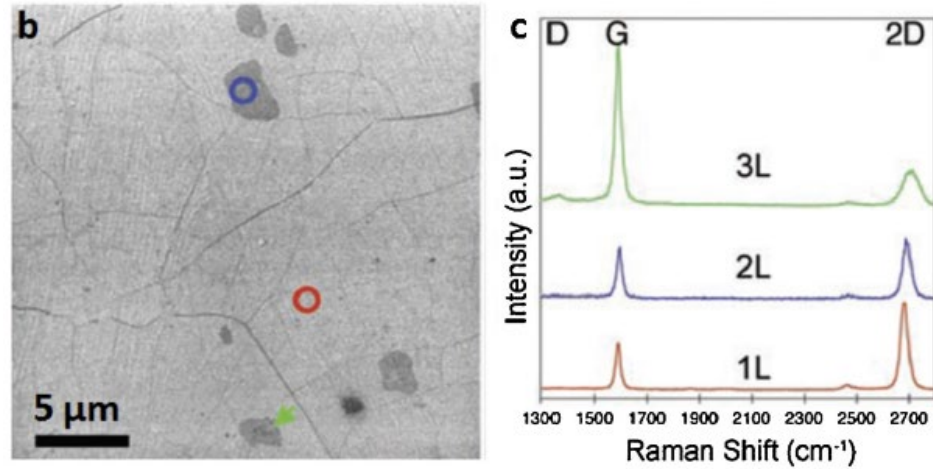
- CVD



(i) catalytic decomposition; (ii) nucleation; (iii) expansion.

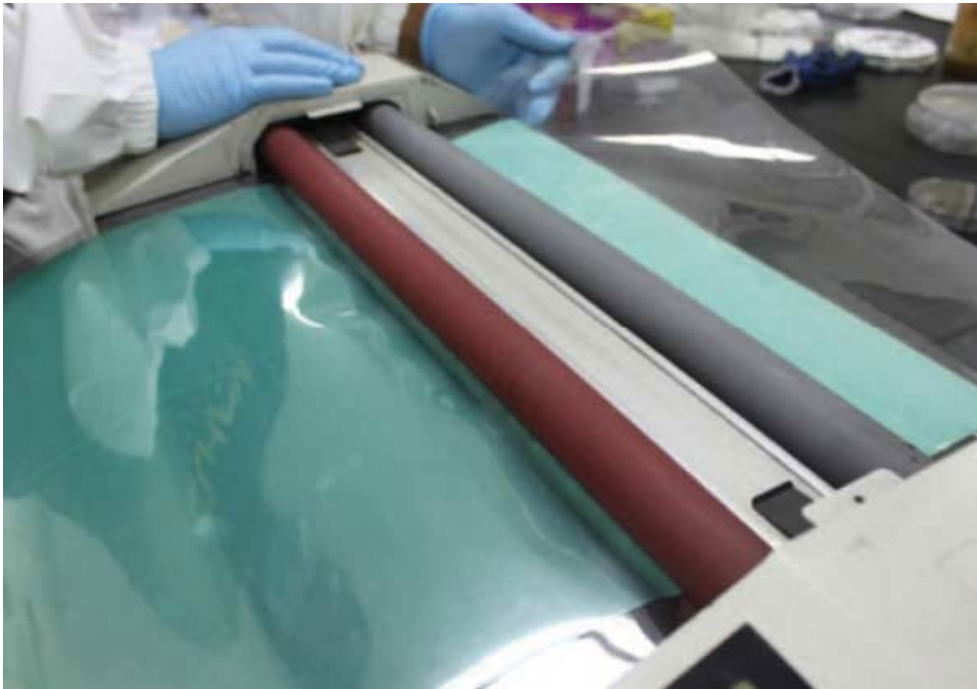


Making of graphene



Large scale graphene

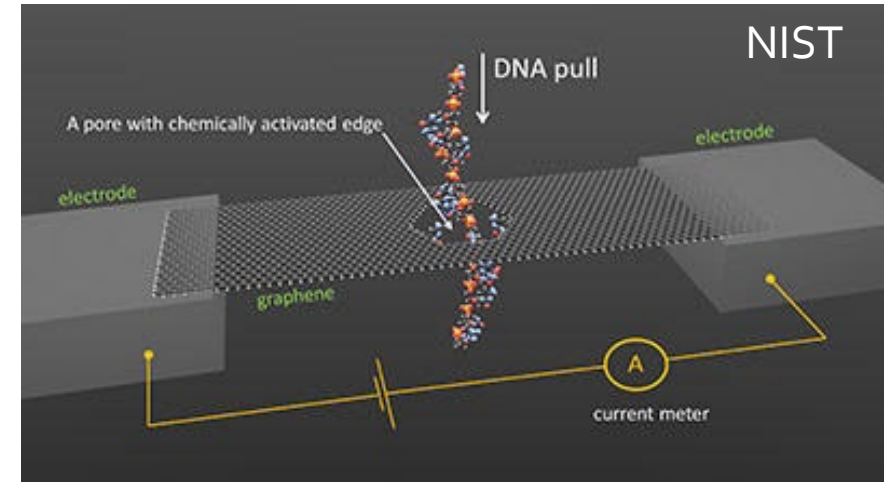
- “Printed” graphene for flexible device



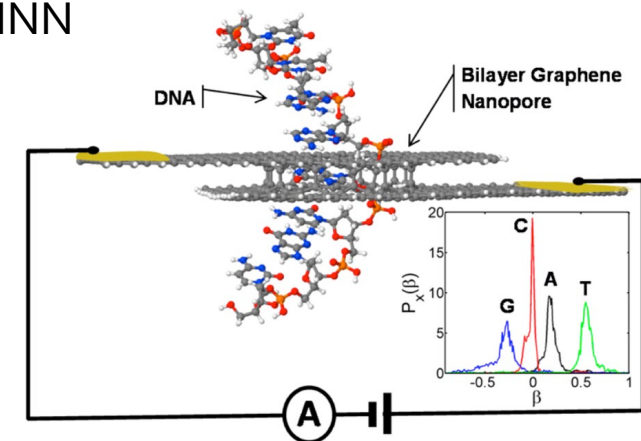
MIT technology review



- DNA sequencing

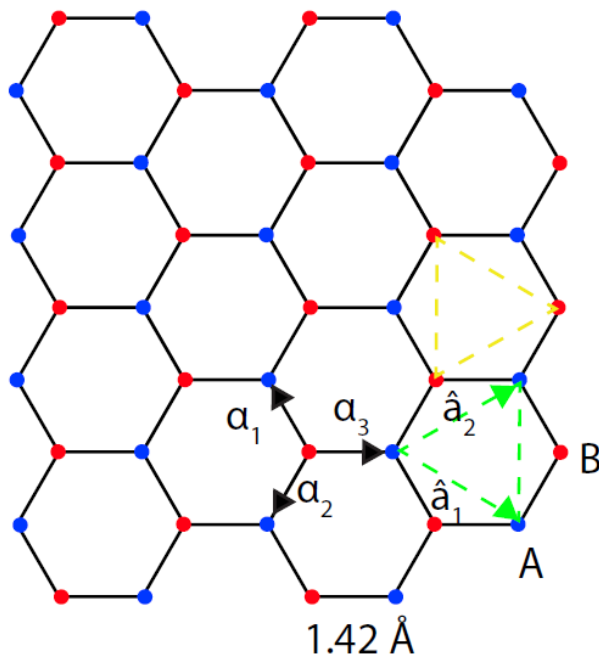


CINN



Electronic structure

- Honey cone lattice with two sublattice sites A and B



$$H_l^a = -\frac{\hbar^2}{2m}\Delta_l + V(\mathbf{r}_l - \mathbf{R}_l)$$

Use the tight-binding model, consider only nearest-neighbor hopping :

$$H_l = -\frac{\hbar^2}{2m}\Delta_l + \sum_{j=1}^N V(\mathbf{r}_l - \mathbf{R}_j) \quad \mathbf{R}_j = m_j\mathbf{a}_1 + n_j\mathbf{a}_2$$

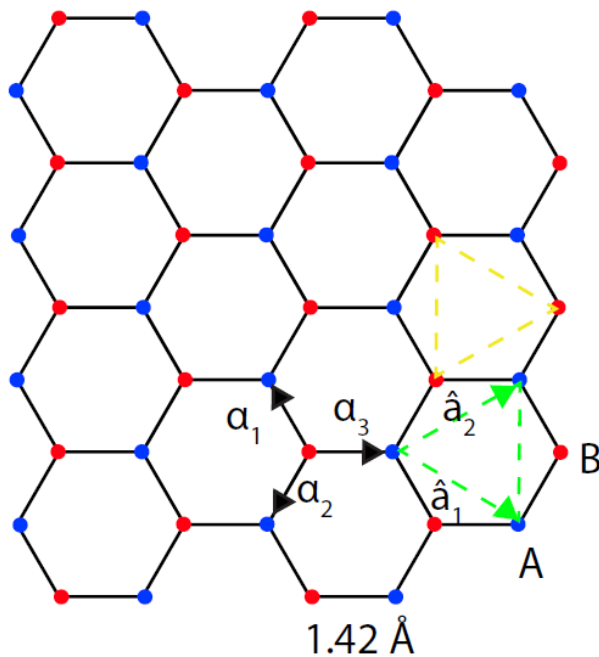
Using Bloch theory and considering two lattice sites, we have 4 by 4 matrix elements, the wavefunction can be considered as the following :

$$\Phi_j(k, r) = \frac{1}{\sqrt{N}} \sum_{i=1}^N e^{ikR_{j,i}} \phi_j(r - R_{j,i})$$

Based on the Bloch theory:

$$\begin{aligned} \mathcal{T}_{\mathbf{R}_i} \psi_{\mathbf{k}}(\mathbf{r}) &= \psi_{\mathbf{k}}(\mathbf{r} + \mathbf{R}_i) \\ &= \sum_{\mathbf{R}_j} e^{i\mathbf{k}\cdot\mathbf{R}_j} \phi^{(a)}[\mathbf{r} - (\mathbf{R}_j - \mathbf{R}_i)] \\ &= e^{i\mathbf{k}\cdot\mathbf{R}_i} \sum_{\mathbf{R}_m} e^{i\mathbf{k}\cdot\mathbf{R}_m} \phi^{(a)}(\mathbf{r} - \mathbf{R}_m) = e^{i\mathbf{k}\cdot\mathbf{R}_i} \psi_{\mathbf{k}}(\mathbf{r}), \end{aligned}$$

Electronic structure



Hamiltonian will meet the conditions:

$$\det(H - E_j S) = 0, \text{ where } H_{ij} = \langle \phi_i | \mathbf{H} | \phi_j \rangle \quad S = \Phi_{ij} = \langle \phi_i | \phi_j \rangle$$

Work out the matrix elements:

$$H_{BB} = H_{AA} \approx \epsilon_{2p} \quad \text{with} \quad \epsilon_{2p} = \langle \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) | \mathcal{H} | \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) \rangle$$

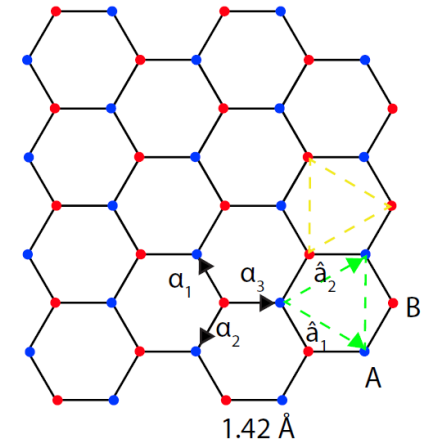
$$S_{BB} = S_{AA} = 1$$

For the diagonal terms

Electronic structure

$$\begin{aligned}
 H_{AB} &\approx -\frac{1}{N} \sum_{i=1}^N \sum_{l=1}^3 e^{i\mathbf{k} \cdot (\mathbf{R}_{B,l} - \mathbf{R}_{A,i})} \gamma_0, \\
 &= -\frac{\gamma_0}{N} \sum_{i=1}^N \sum_{l=1}^3 e^{i\mathbf{k} \cdot \boldsymbol{\delta}_l} \equiv -\gamma_0 f(\mathbf{k}) \\
 f(\mathbf{k}) &= \sum_{l=1}^3 e^{i\mathbf{k} \cdot \boldsymbol{\delta}_l},
 \end{aligned}$$

$$\gamma_0 = -\langle \phi_A(r - R_{A,i}) | \mathbf{H} | \phi_B(r - R_{B,i}) \rangle$$



Three possible B sites

$$\boldsymbol{\delta}_l = \mathbf{R}_{B,l} - \mathbf{R}_{A,i}$$

$$\boldsymbol{\delta}_1 = \left(0, \frac{a}{\sqrt{3}} \right), \quad \boldsymbol{\delta}_2 = \left(\frac{a}{2}, -\frac{a}{2\sqrt{3}} \right), \quad \boldsymbol{\delta}_3 = \left(-\frac{a}{2}, -\frac{a}{2\sqrt{3}} \right)$$

$$\begin{aligned}
 f(\mathbf{k}) &= \sum_{l=1}^3 e^{i\mathbf{k} \cdot \boldsymbol{\delta}_l} \\
 &= e^{ik_y a / \sqrt{3}} + 2e^{-ik_y a / 2\sqrt{3}} \cos(k_x a / 2).
 \end{aligned}$$

Off diagonal elements for H

$$H_{AB} \approx -\gamma_0 f(\mathbf{k}), \quad H_{BA} \approx -\gamma_0 f^*(\mathbf{k})$$

Electronic structure

The same for the other matrix

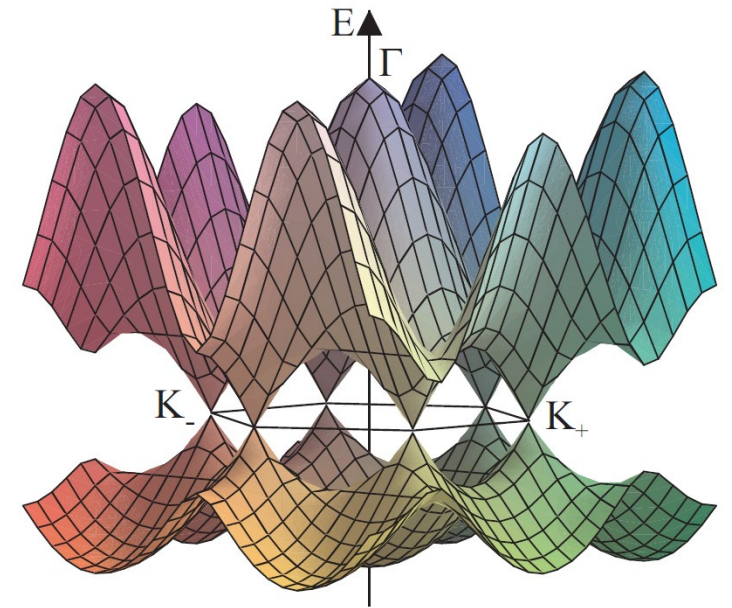
$$\begin{aligned}
 S_{AB} &= \frac{1}{N} \sum_{i=1}^N \sum_{j=1}^N e^{i\mathbf{k} \cdot (\mathbf{R}_{B,j} - \mathbf{R}_{A,i})} \langle \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) | \phi_B(\mathbf{r} - \mathbf{R}_{B,j}) \rangle, \\
 &\approx \frac{1}{N} \sum_{i=1}^N \sum_{l=1}^3 e^{i\mathbf{k} \cdot (\mathbf{R}_{B,l} - \mathbf{R}_{A,i})} \langle \phi_A(\mathbf{r} - \mathbf{R}_{A,i}) | \phi_B(\mathbf{r} - \mathbf{R}_{B,l}) \rangle, \\
 &= s_0 f(\mathbf{k}),
 \end{aligned}$$

The matrixes for low energy band:

$$H_1 = \begin{pmatrix} \epsilon_{2p} & -\gamma_0 f(\mathbf{k}) \\ -\gamma_0 f^*(\mathbf{k}) & \epsilon_{2p} \end{pmatrix}, \quad S_1 = \begin{pmatrix} 1 & s_0 f(\mathbf{k}) \\ s_0 f^*(\mathbf{k}) & 1 \end{pmatrix}$$

$$\longrightarrow E_{\pm} = \frac{\epsilon_{2p} \pm \gamma_0 |f(\mathbf{k})|}{1 \mp s_0 |f(\mathbf{k})|}$$

$$s_0 = 3.033 \text{ eV} \text{ and } \gamma_0 = 0.129 \text{ eV}$$



Dirac Fermion and chirality

Now we focus on the linear dispersion region where Dirac points(K, K') are and we should use the Dirac Fermion equation.

One thing to notice is that K and K' both yield $f(k) = 0$, which means, K and K' points degenerate.

Now, we take the linear dispersion, $f(k) \approx -\frac{\sqrt{3}a}{2\hbar} (\xi p_x - ip_y)$ $\xi = +$ for K and $-$ for K'

$$H_{1,\xi} = v \begin{bmatrix} 0 & \xi p_x - ip_y \\ \xi p_x + ip_y & 0 \end{bmatrix} \quad v = \frac{\sqrt{3}a\gamma_0}{2\hbar}$$

Shorten the Hamiltonian by replace momentum with $p_x \rightarrow i \frac{\partial}{\partial x}$ and $p_y \rightarrow i \frac{\partial}{\partial y}$, corresponding to perturbative $k \cdot p$ theory

Then we end up with Dirac equation $\hat{H}_K = -i\nu\sigma\nabla$ with σ the Pauli matrices

Dirac Fermion and chirality

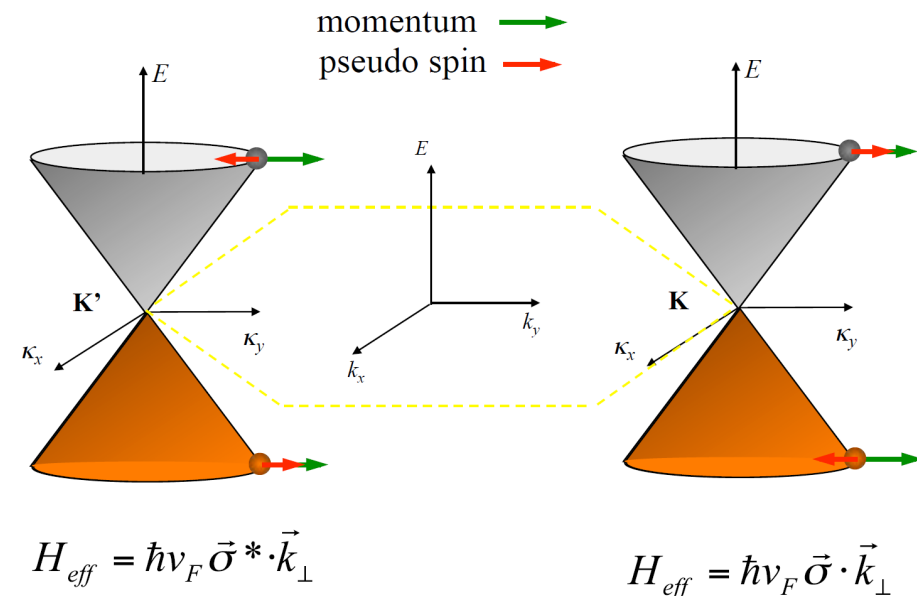
The basis now can be written: $\hat{H}_K = -i\nu\sigma\nabla$ with σ the Pauli matrices

$$\Psi = \begin{bmatrix} \psi_{K,A} \\ \psi_{K,B} \\ \psi_{K',B} \\ \psi_{K',A} \end{bmatrix} \quad E_{\pm} = \pm p\nu \quad \text{and} \quad \psi_{\pm}^{(K)} = \frac{1}{\sqrt{2}} \begin{pmatrix} \exp(-i\phi_{\mathbf{k}}/2) \\ \pm \exp(i\phi_{\mathbf{k}}/2) \end{pmatrix}$$

The AB (Valleys) sites act as a pseudospin

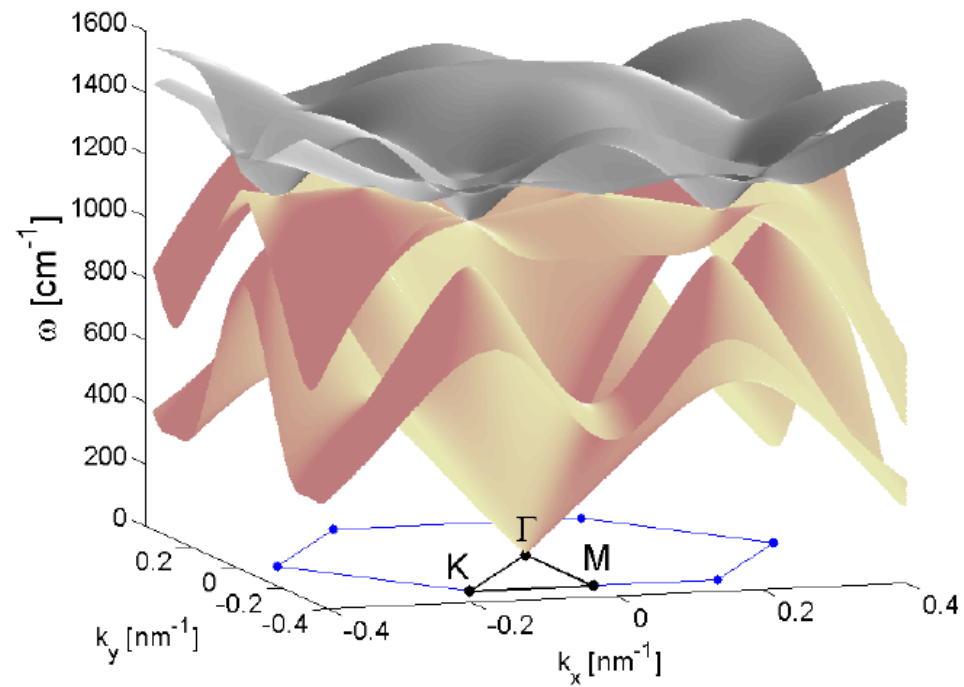
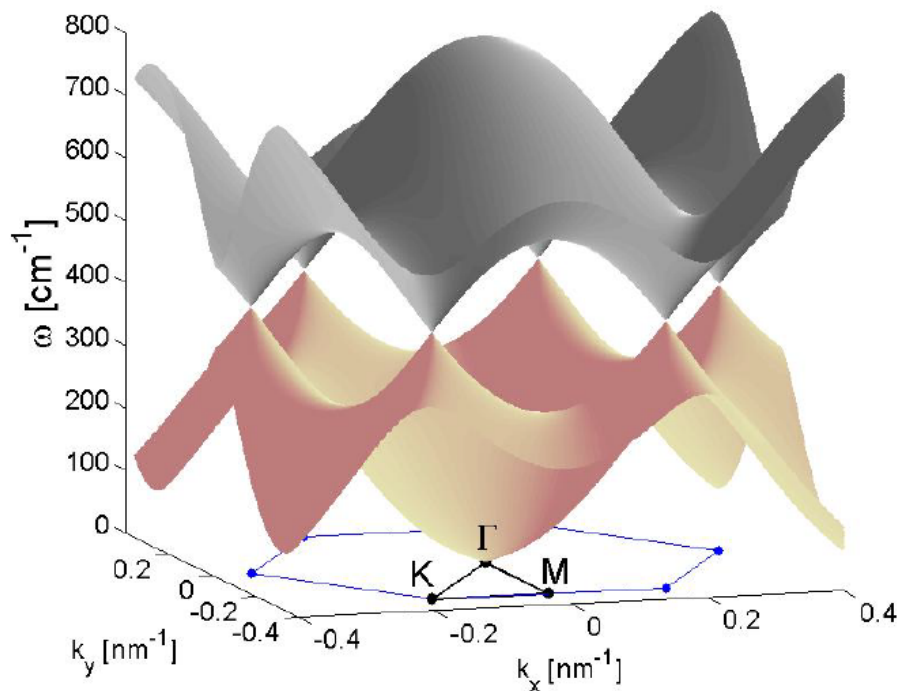
One important property: chiral behavior

$$\frac{\vec{k} \cdot \vec{\sigma}}{k} \psi_{\pm} = \pm \psi_{\pm}$$



Phonon dispersion

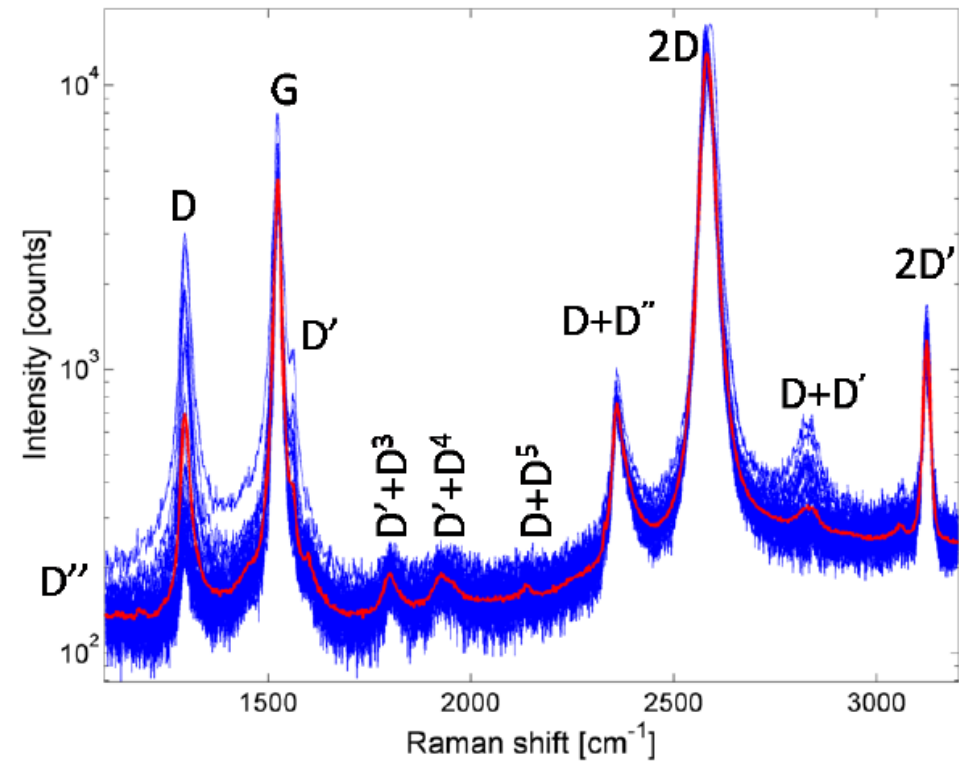
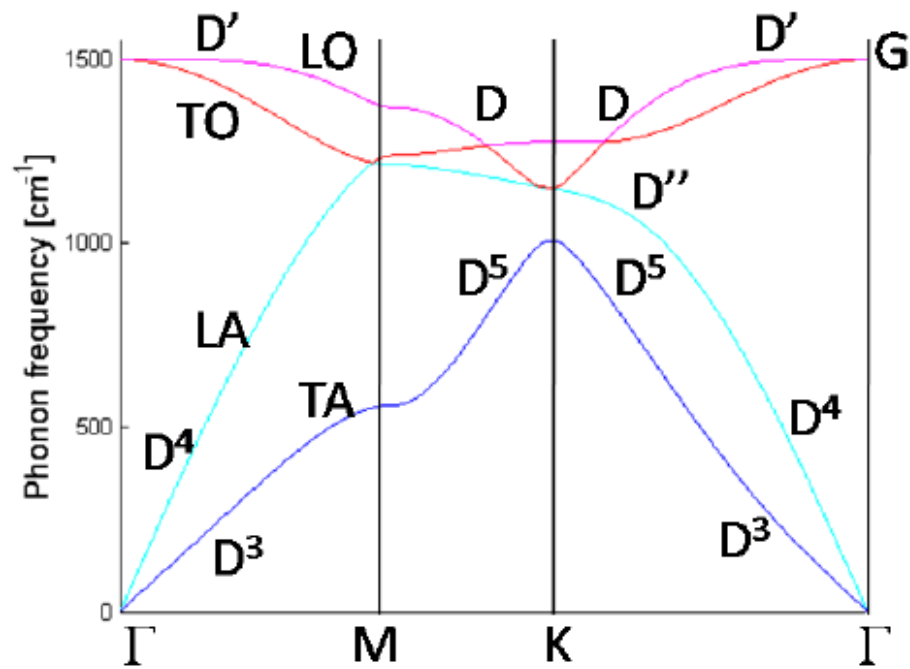
The out of plane and in-plane phonon mode



D. R. Cooper et al, arXiv:1110.6557 (2011)

Phonon dispersion

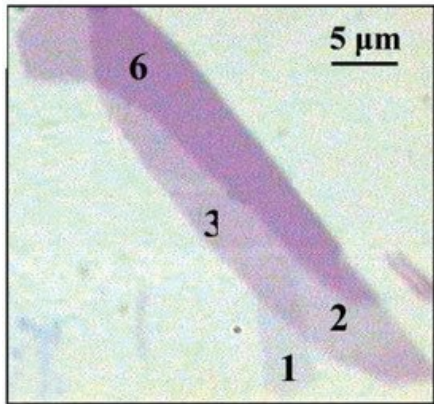
Theoretical calculation of in-plane modes



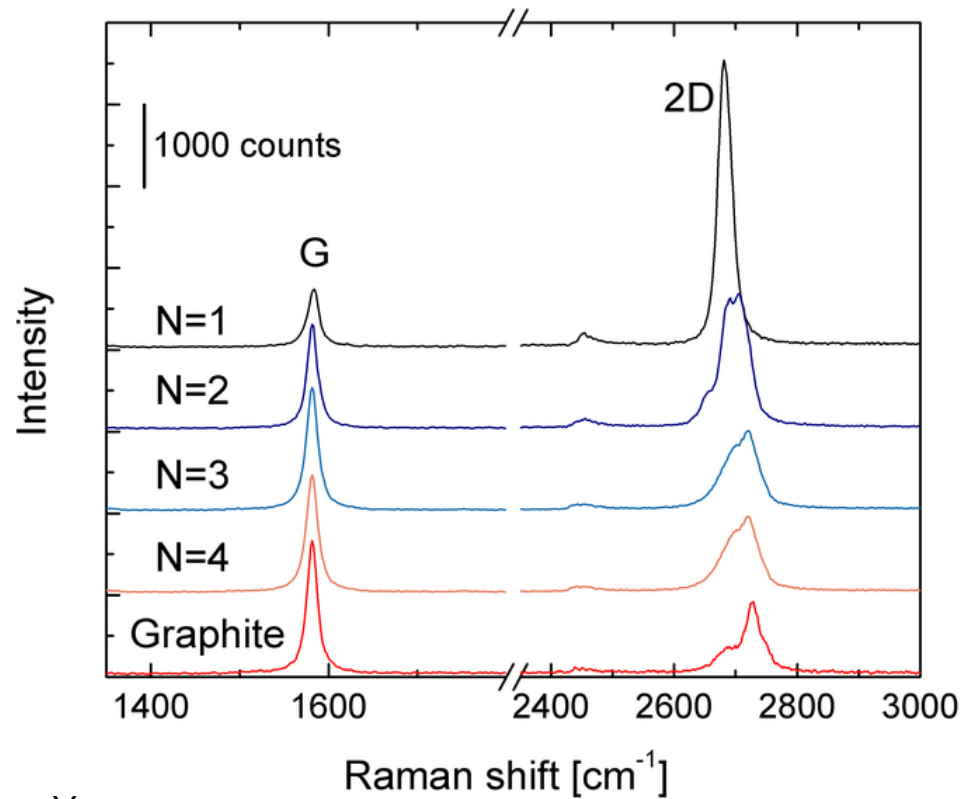
D. R. Cooper et al, arXiv:1110.6557 (2011)

Layer dependence

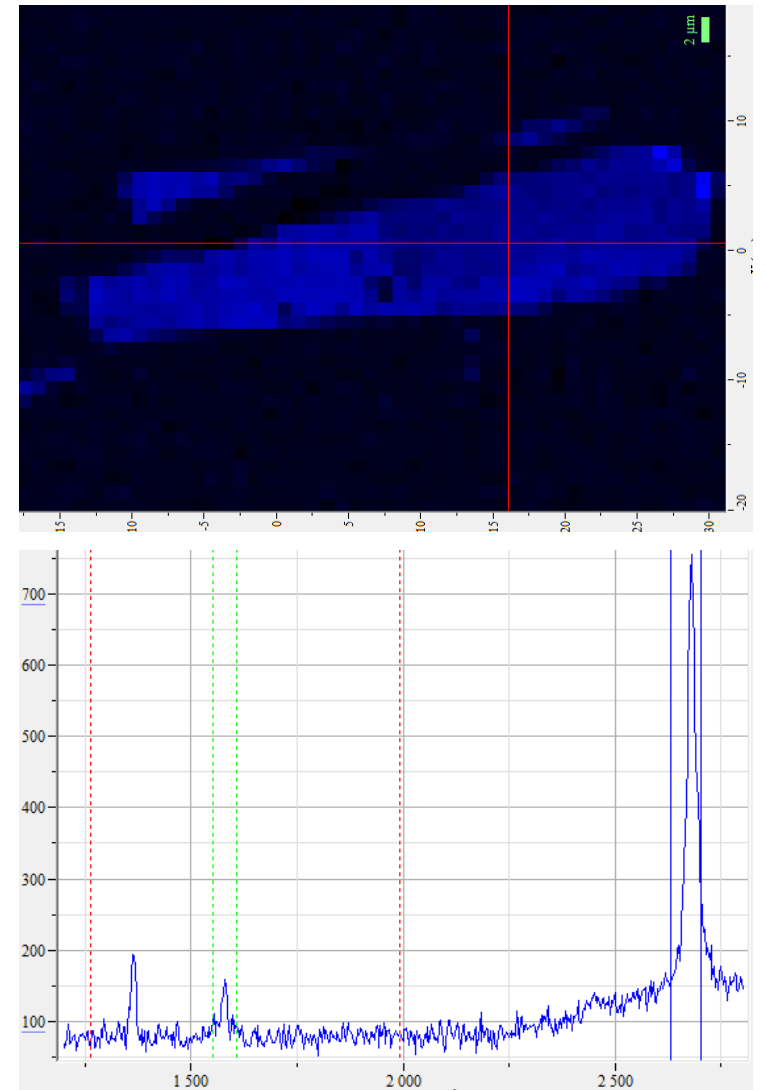
- Raman spectra



Y Lan et al.
Crystal 2018



Yu, 2010



Other important properties

- Berry phase

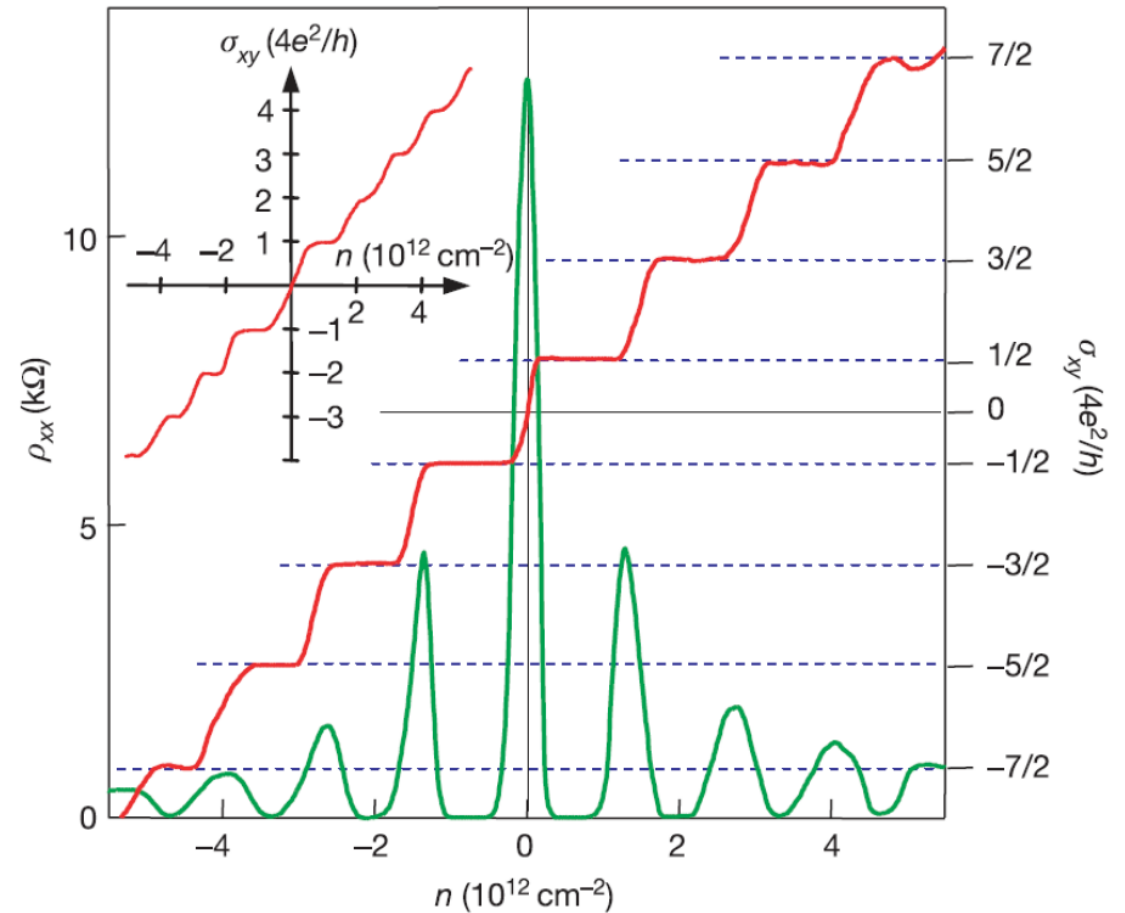
One can consider the Berry phase as a geometrical phase under the pseudospin rotation.

$$\psi_{\pm}(\phi_{\mathbf{k}} = 2\pi) = -\psi_{\pm}(\phi_{\mathbf{k}} = 0)$$

We end up with a π phase difference under a 2π pseudospin rotation.

Another result that comes from the berry phase is the offset of the QH levels at zero filling.

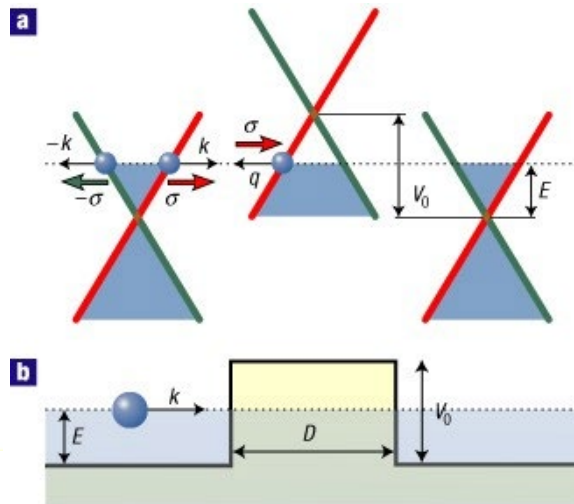
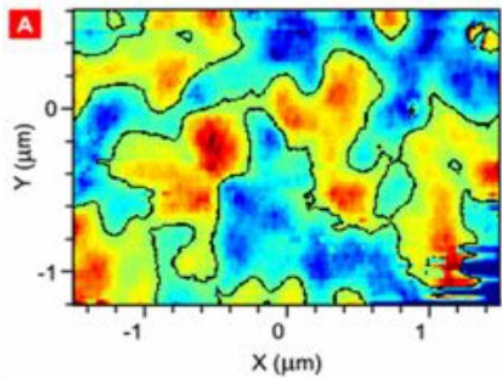
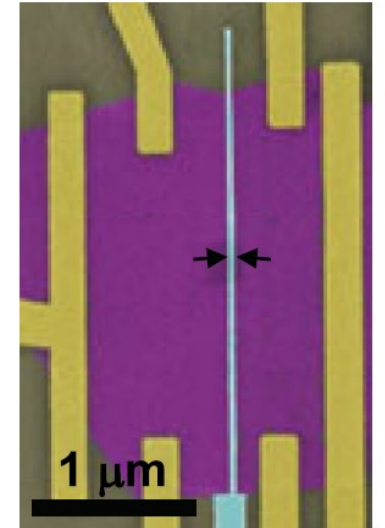
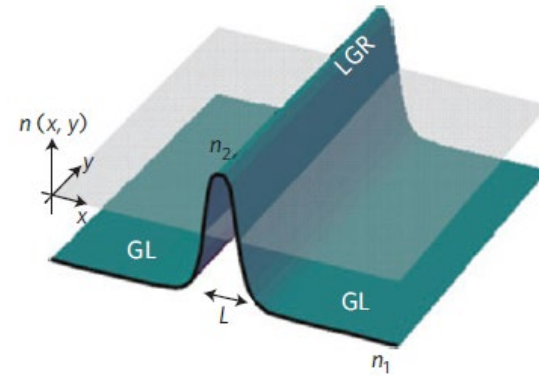
$$\sigma_{xy} = \left(N + \frac{1}{2}\right)\left(\frac{4e^2}{h}\right)$$



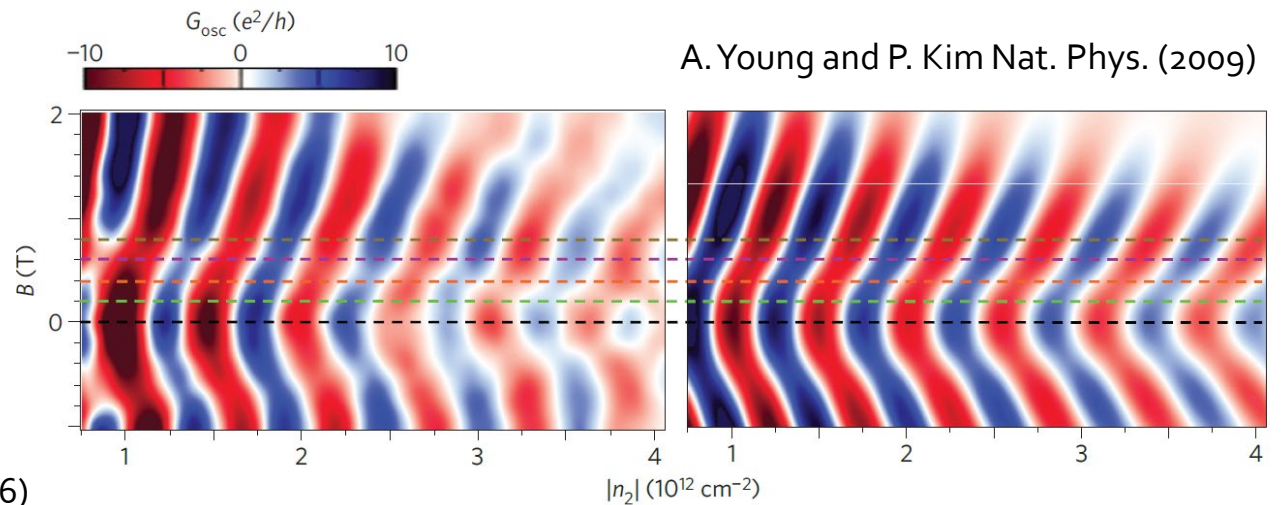
Other important properties

- Klein paradox

When electrons or holes encounter a barrier at DP, electron or hole backscattering is forbidden because of chirality. Therefore, the only path is to convert to another type of particle which maintains the momentum conservation.



M. I. Katsnelson et al. Nat. Phys. (2006)



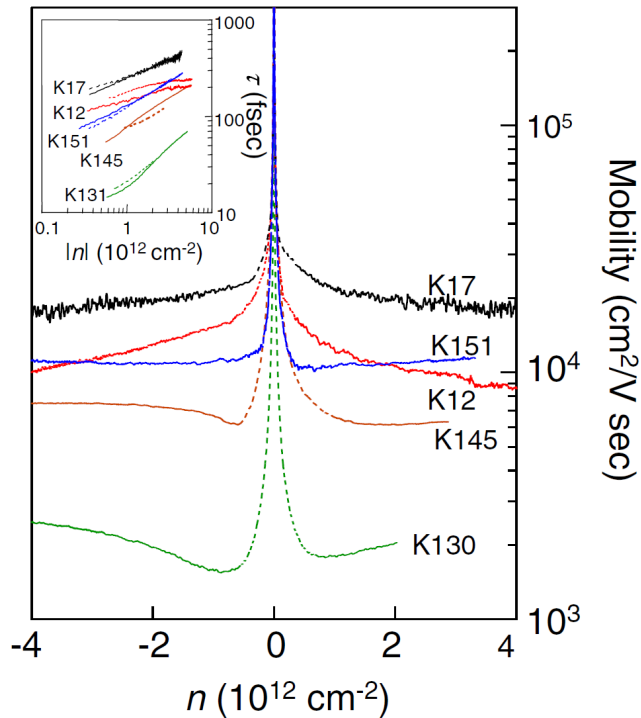
A. Young and P. Kim Nat. Phys. (2009)

Martin *et al.* Nature Phys. (2008)

Graphene research

Classical mobility

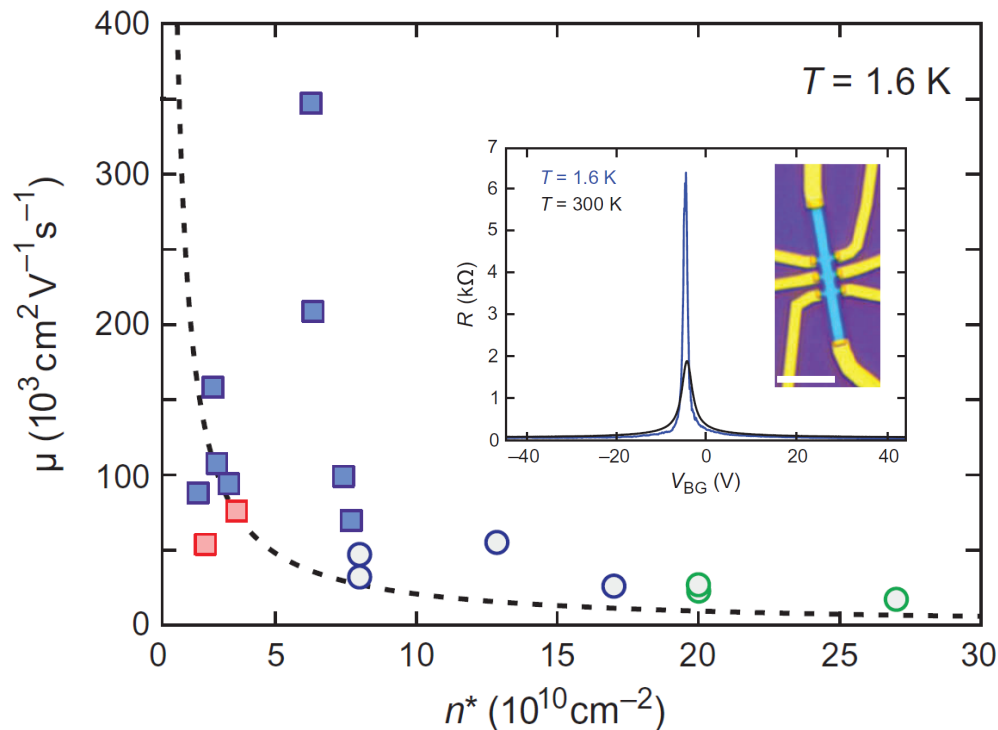
Exfoliated graphene



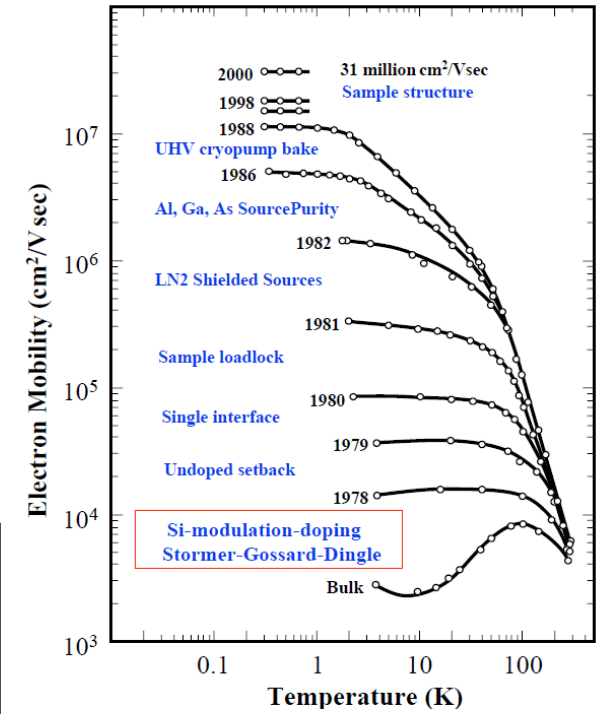
Y.-W. Tan et al. PRL (2007)

Quantum mobility

CVD graphene

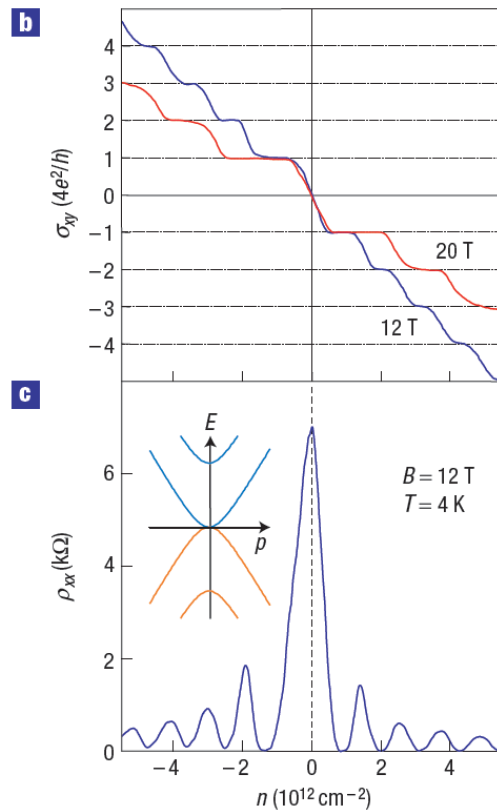


L. Banszerus et al. Science Advances (2015)



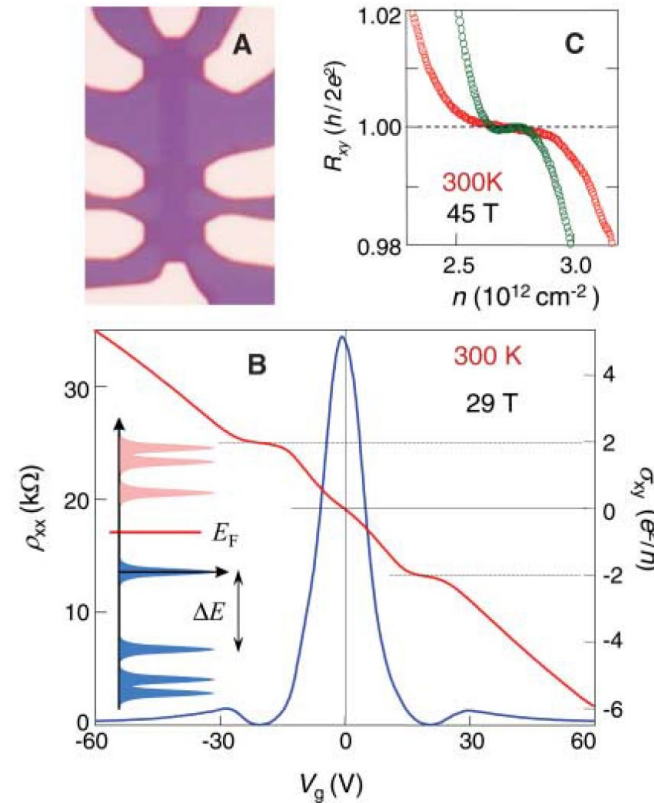
Graphene research

Quantum Hall effect



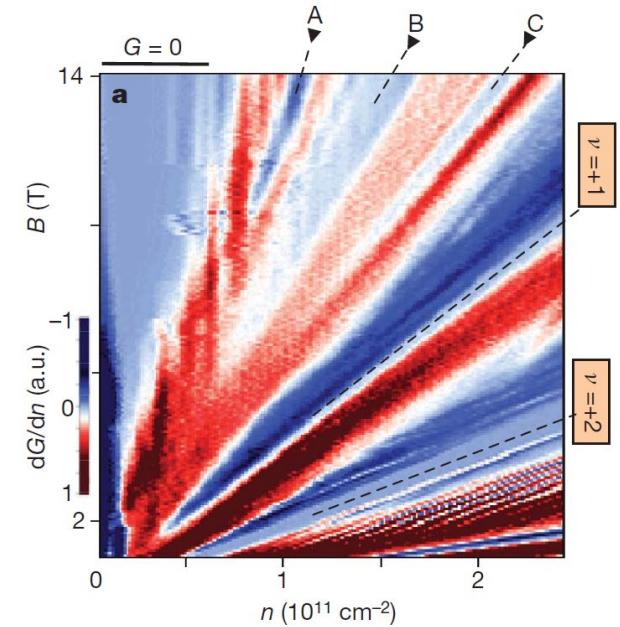
K. S. Novoselov et al. Nat. Phys. (2006)

Room temperature QH effect



K. S. Novoselov, et al. Science (2007)

fractional Hall effect



	ν	G (e^2/h)
A	0.30 ± 0.02	0.32 ± 0.02
B	0.46 ± 0.02	0.54 ± 0.02
C	0.68 ± 0.05	0.94 ± 0.02

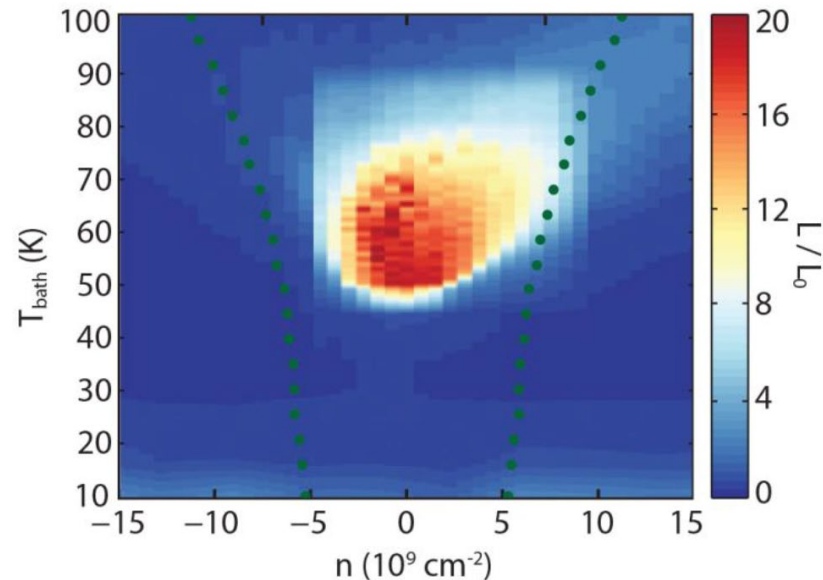
Kirill I. Bolotin, et al. Nature (2009)

Graphene research

- Thermal behavior

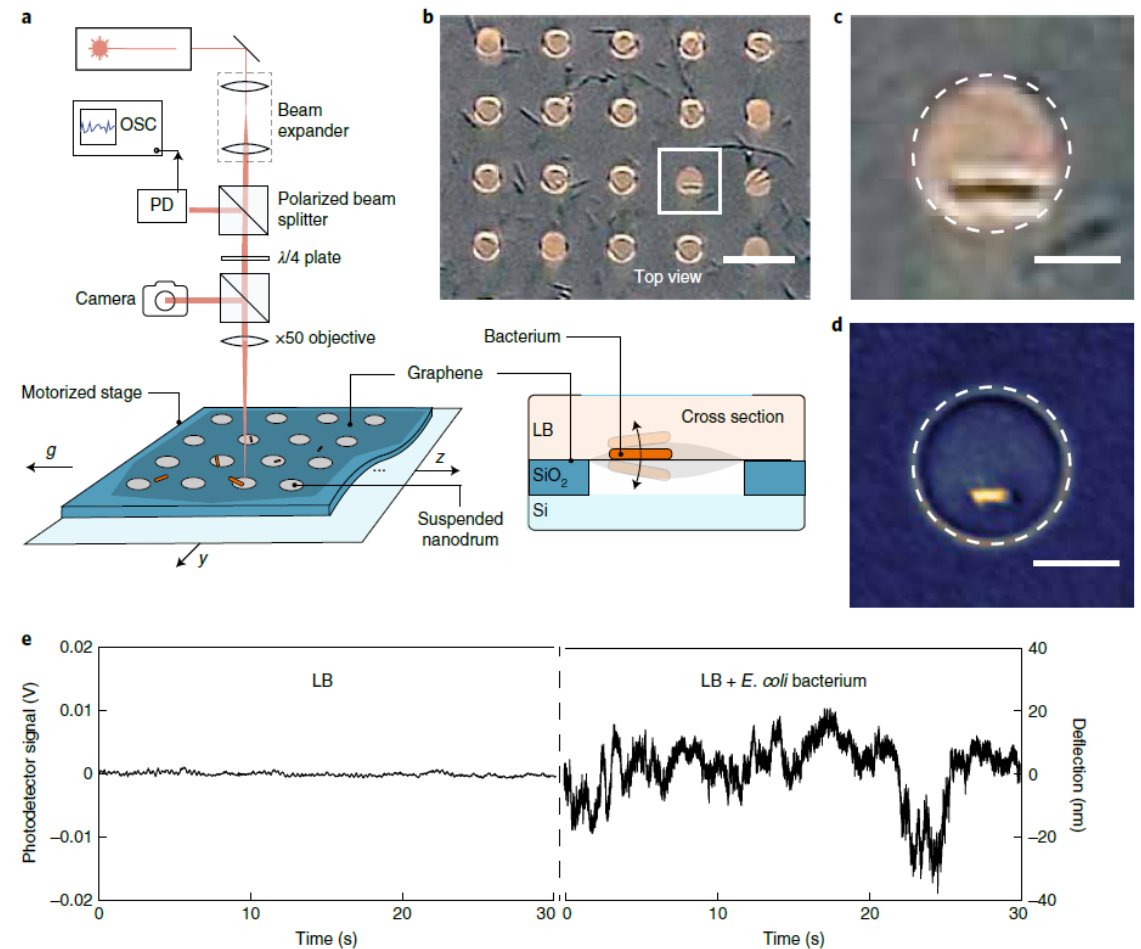
$$\mathcal{L} \equiv \frac{\kappa_e}{\sigma T} = \frac{\pi^2}{3} \left(\frac{k_B}{e} \right)^2 \equiv \mathcal{L}_0$$

Breakdown of Weidman-Franz law



J. Crossno et al. Science(2016)

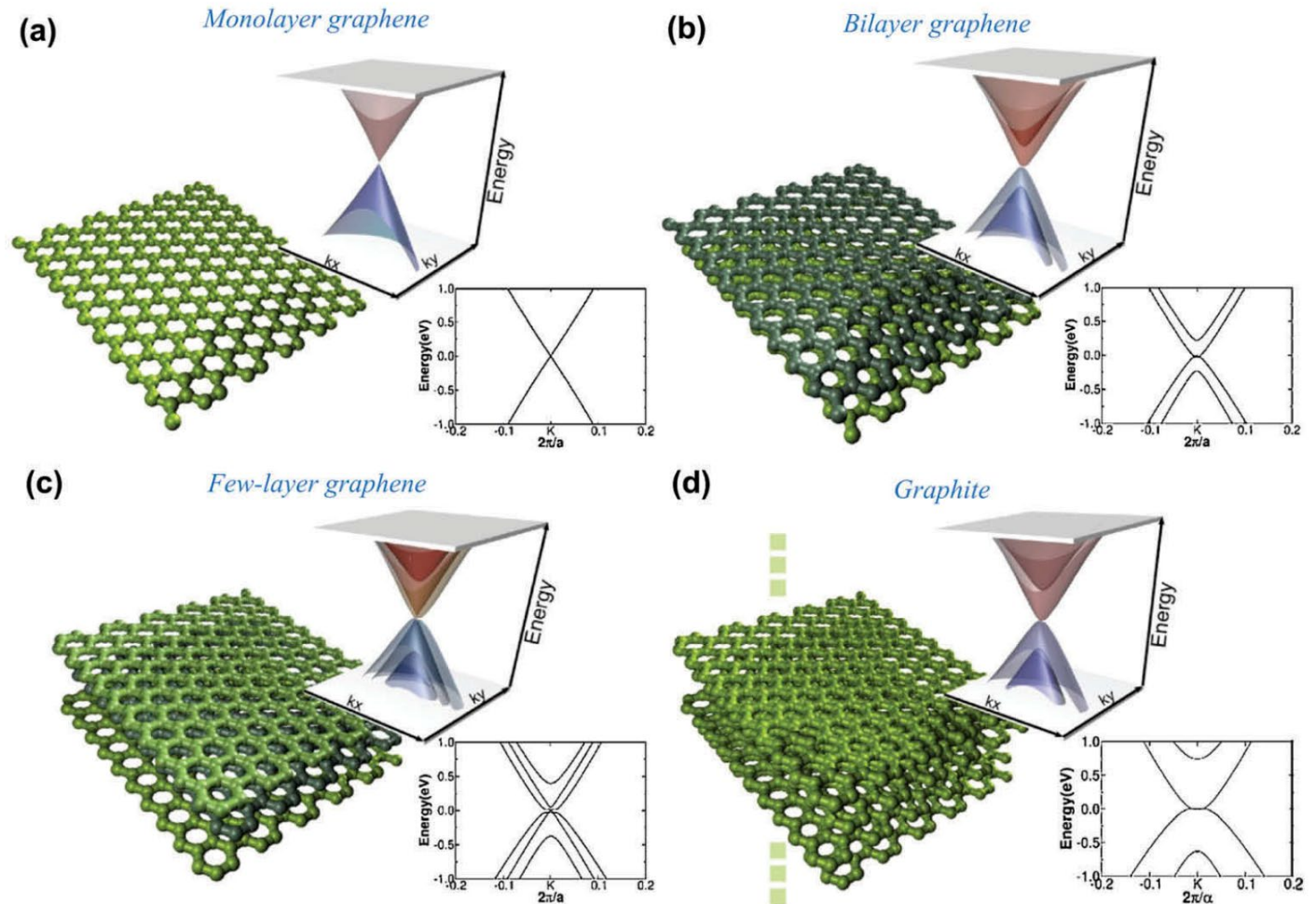
- Bio-nanotechnology



Irek E. Rostań et al, Nat. Nanotech. (2022)

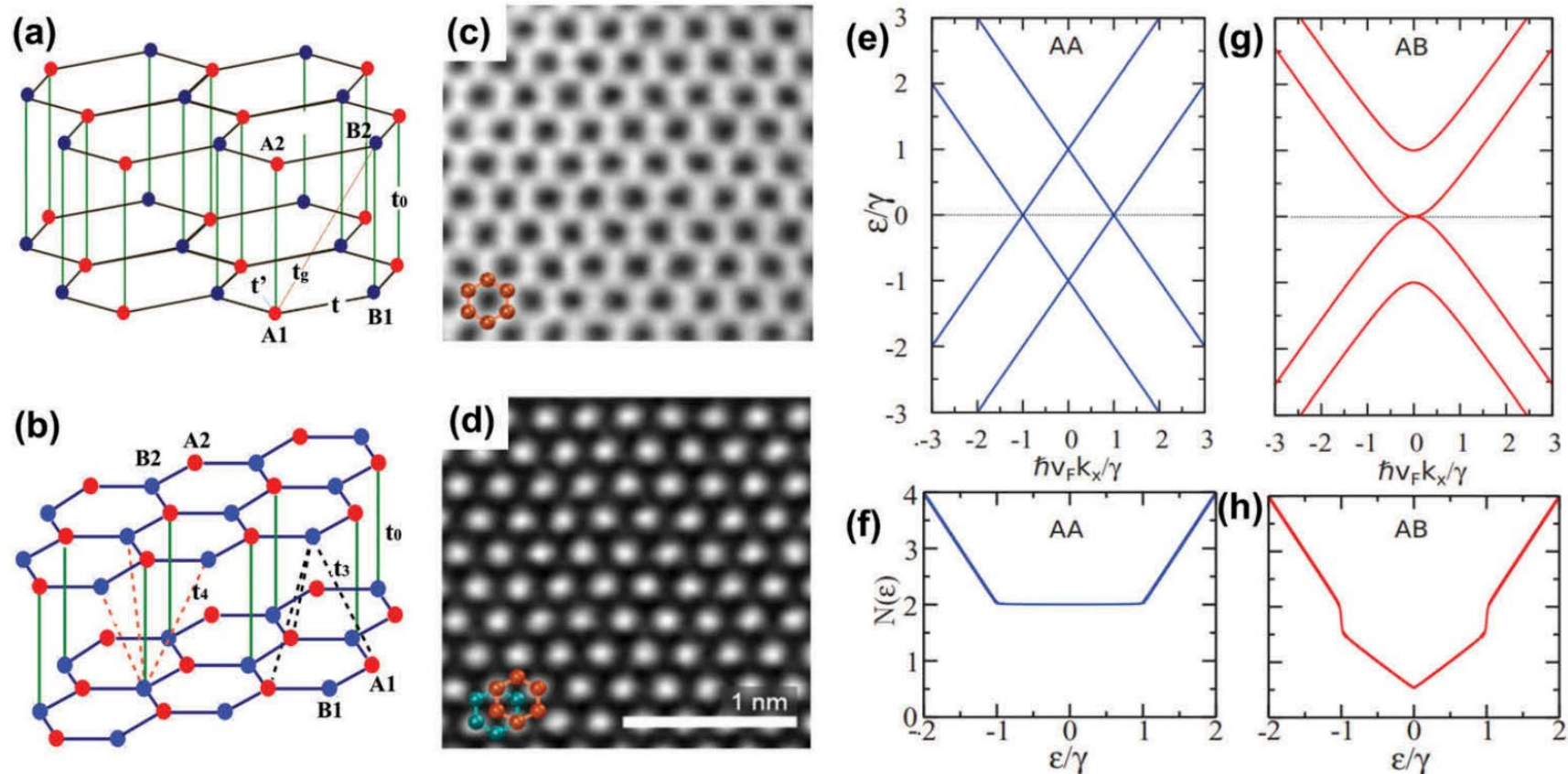
More layers of graphene

- Number of layers will influence the band and dispersion.
- From massless particles to a massive particle case.
- For two or few layers, there is also a difference in the way graphene sits on top of each other



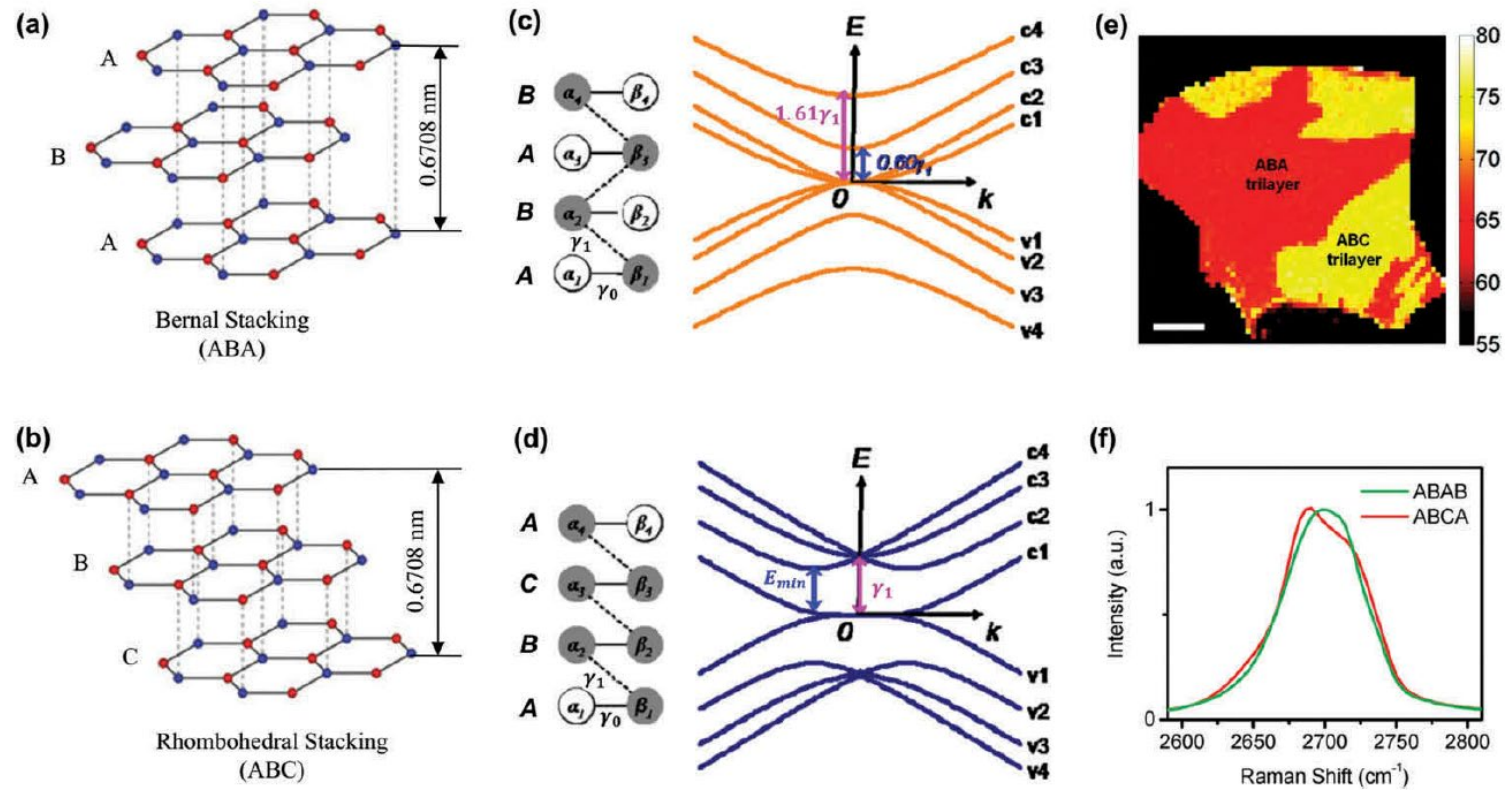
More layers of graphene

- For example bilayer graphene



More layers of graphene

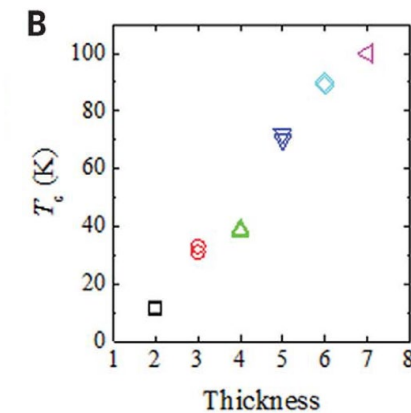
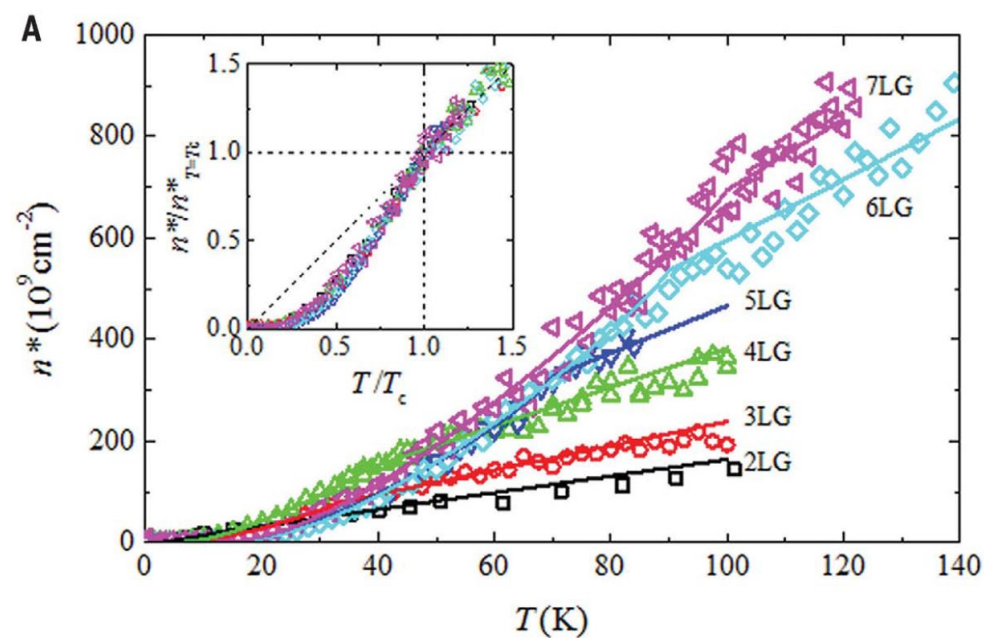
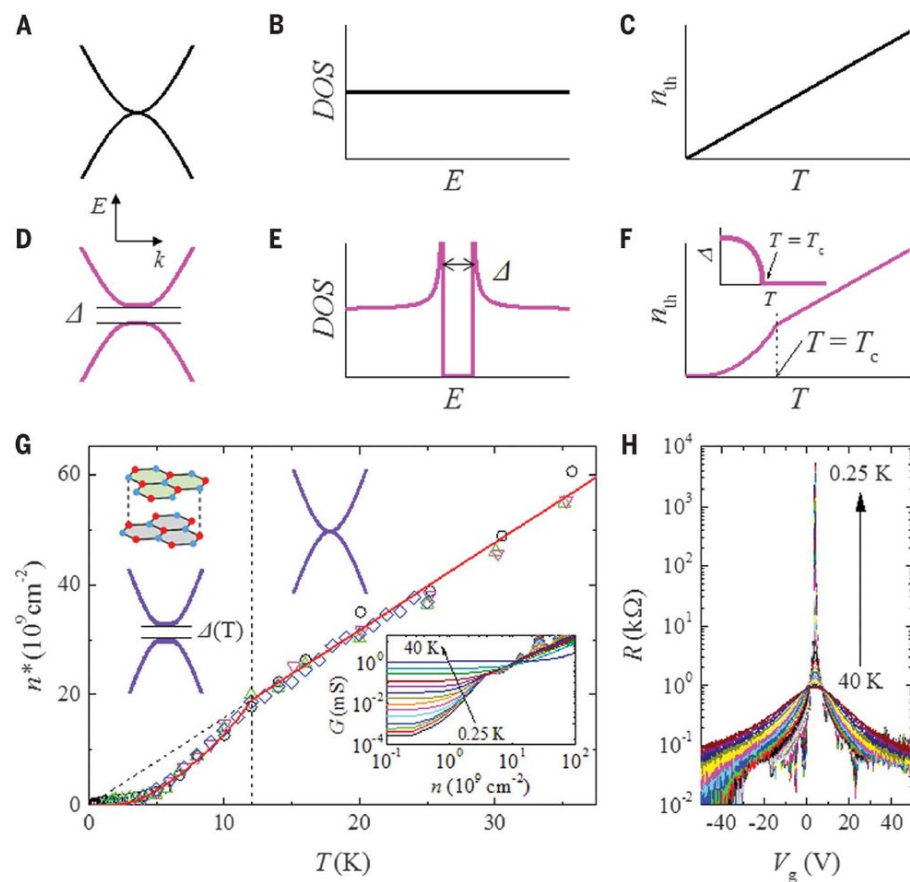
- Another example trilayer graphene



More layers of graphene

- Phase transition for multiple layers

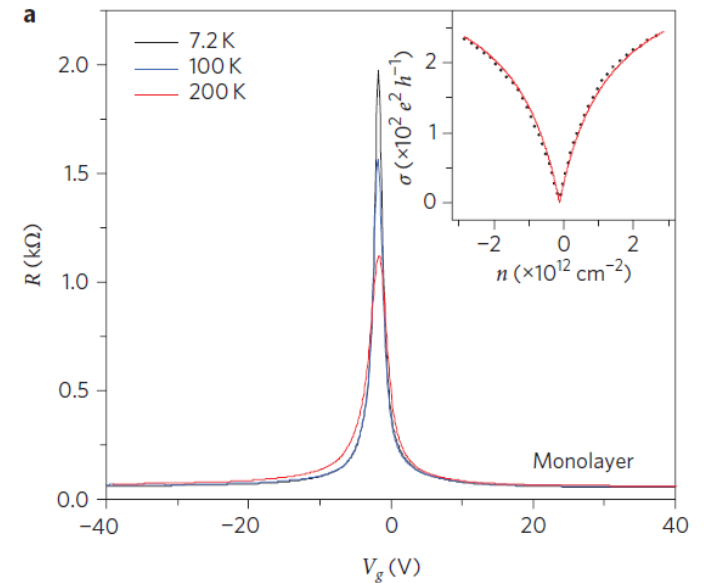
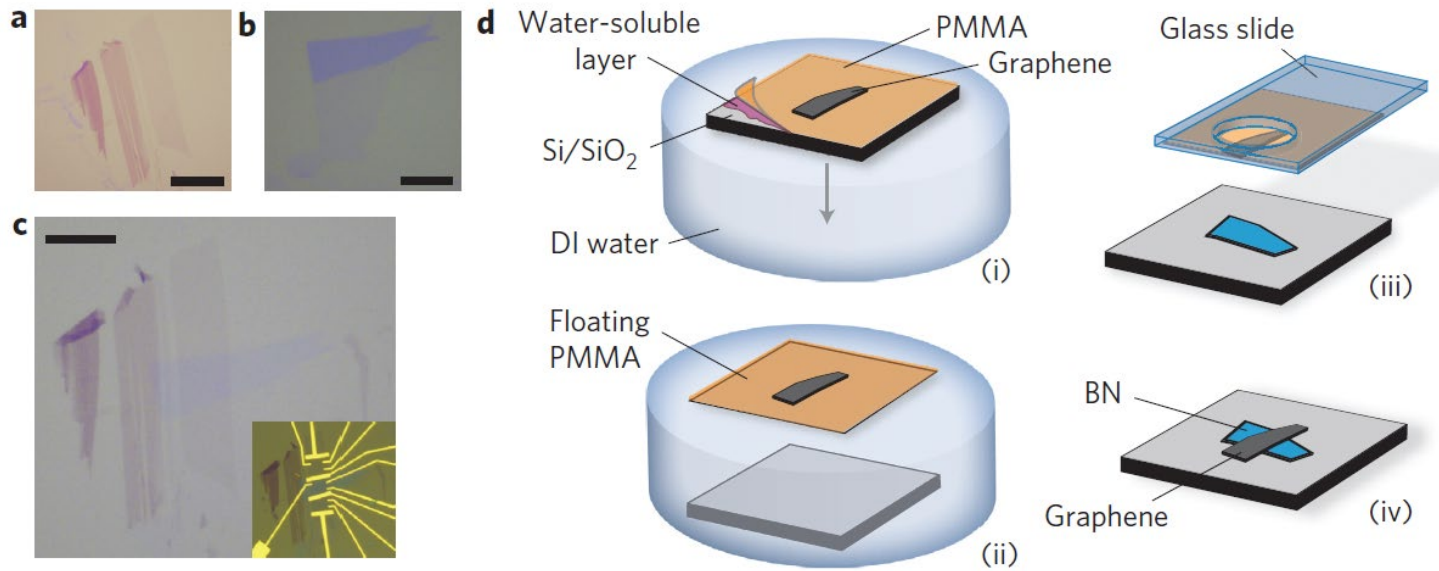
Nam, Y., et al. *Science*, 362(2018)



- The gap opening is due to the interaction picture.
- Transition is associated with spin and valley dependent staggered potential with a sign change in layers

Further improvement in quality

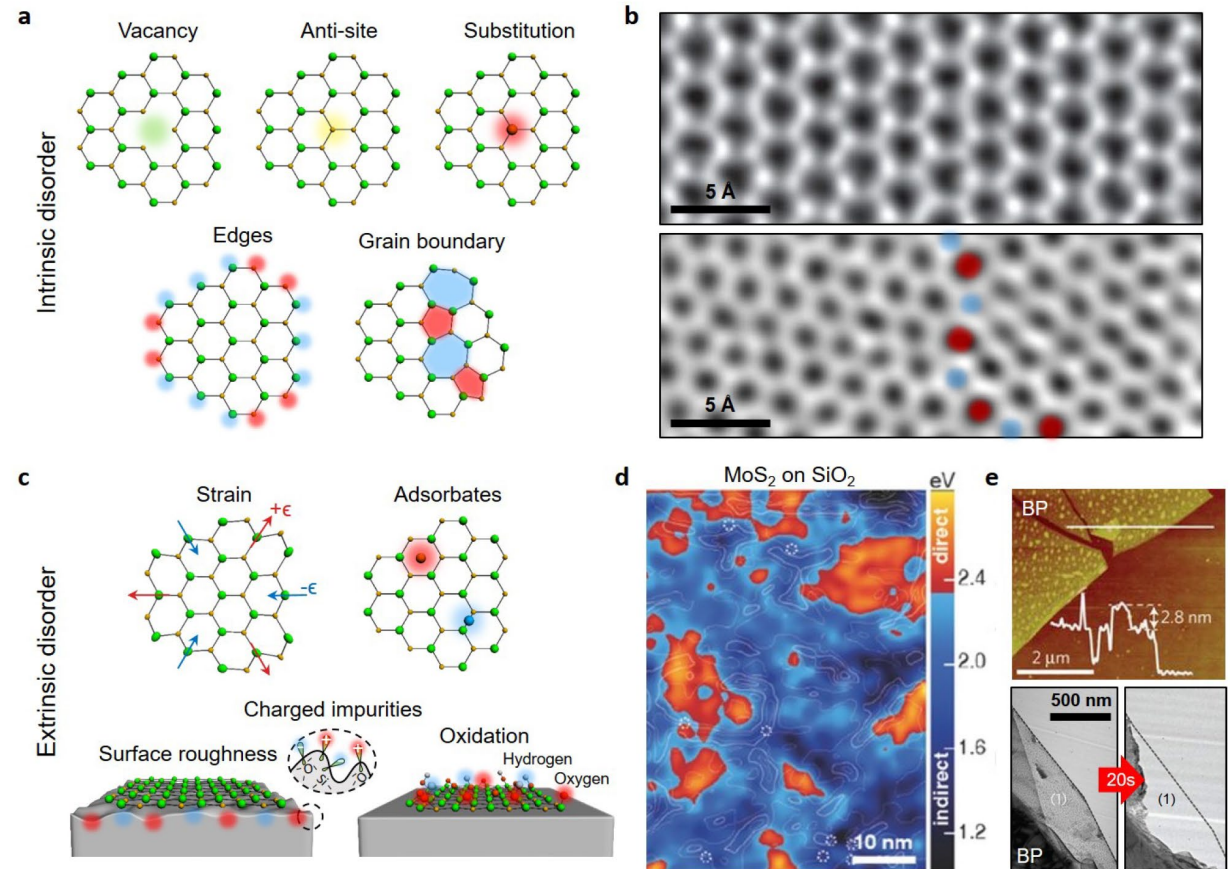
- Use lattice match hexagonal Boron-Nitride as a buffer layer



C. Dean et al. Nat. Nanotech. (2010)

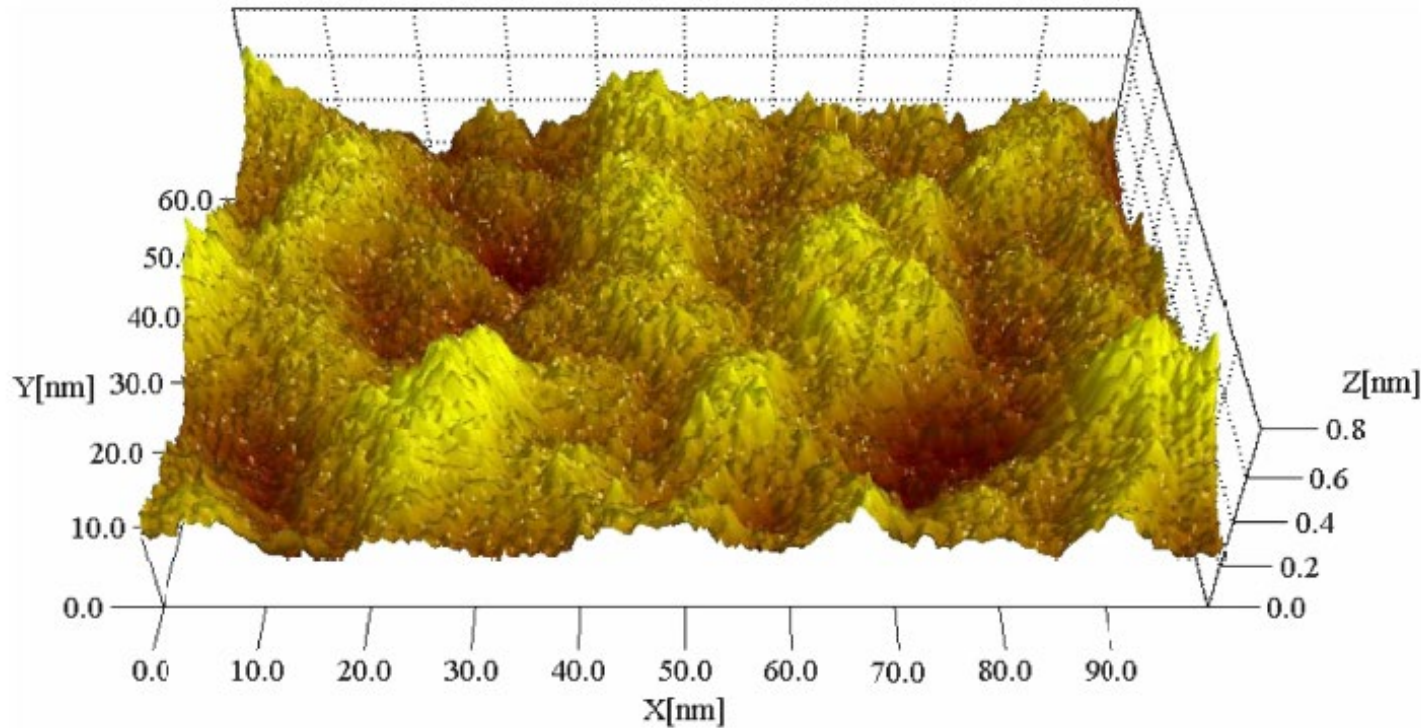
Further improvement in quality

- Disorders from internal and external largely degraded graphene quality
- To obtain a better quality of graphene can lead more intrinsic graphene properties
- Around the DP, density fluctuation creates electron-hole puddles



Detailed structure of graphene on SiO₂

STM image of graphene on SiO₂

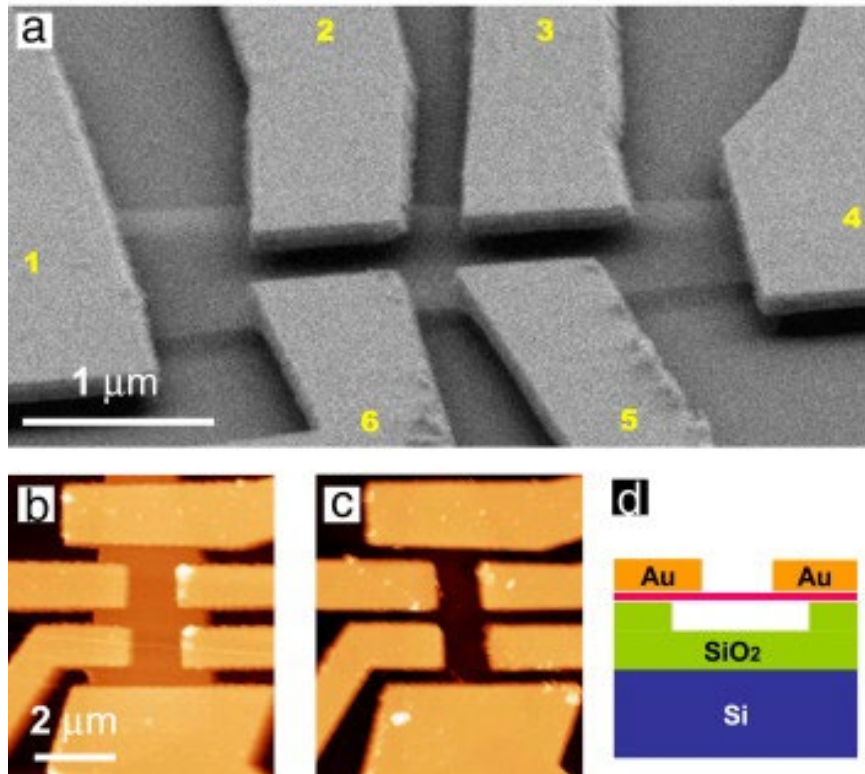


Elena Stolyarova et al. PNAS (2007)

- The ripples create local fluctuations----leading to e-h puddles.
- The causes could come from
 1. Substrate
 2. Structure defects
 3. Absorption
- This greatly degraded graphene quality

Putting graphene in the air

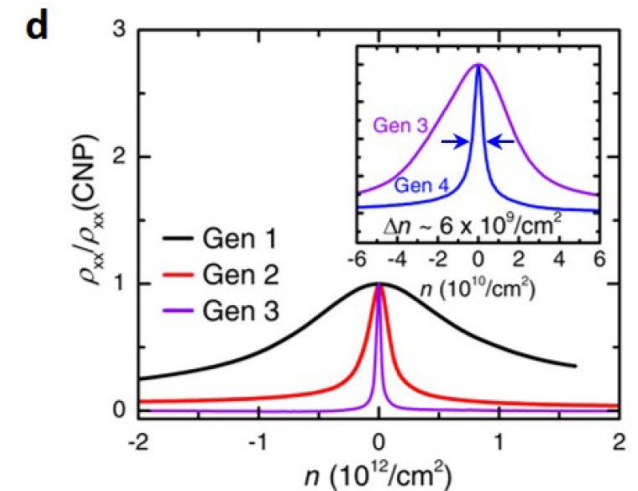
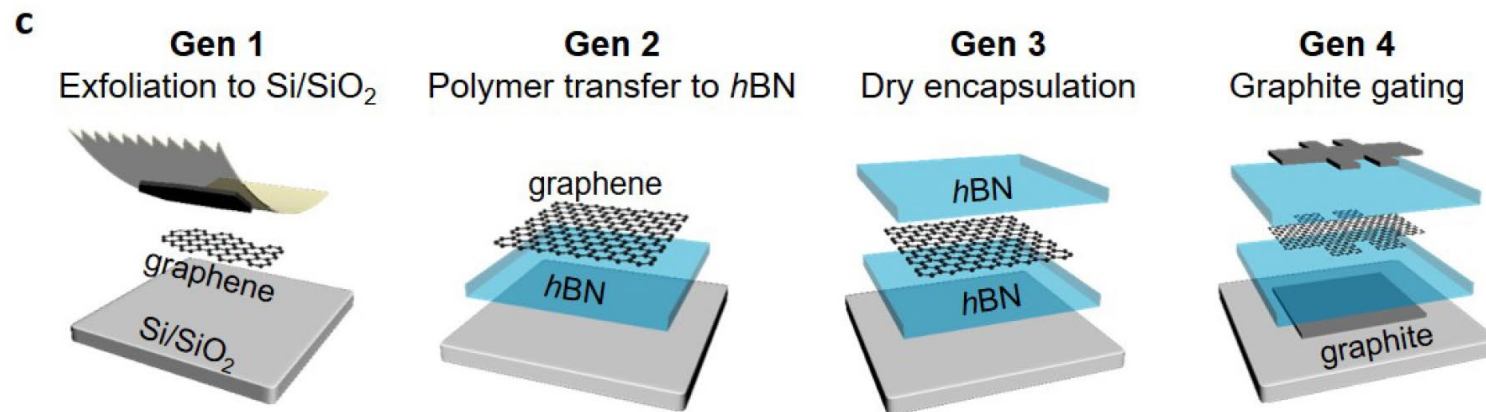
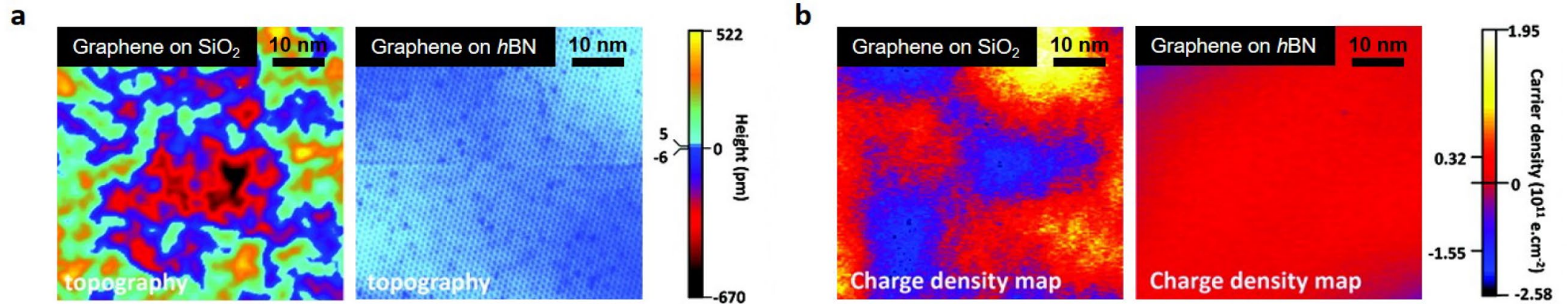
- Suspending graphene improved the mobility



Electron mobility up to 200,000 $\text{cm}^2\text{V}^{-2}\text{s}^{-1}$

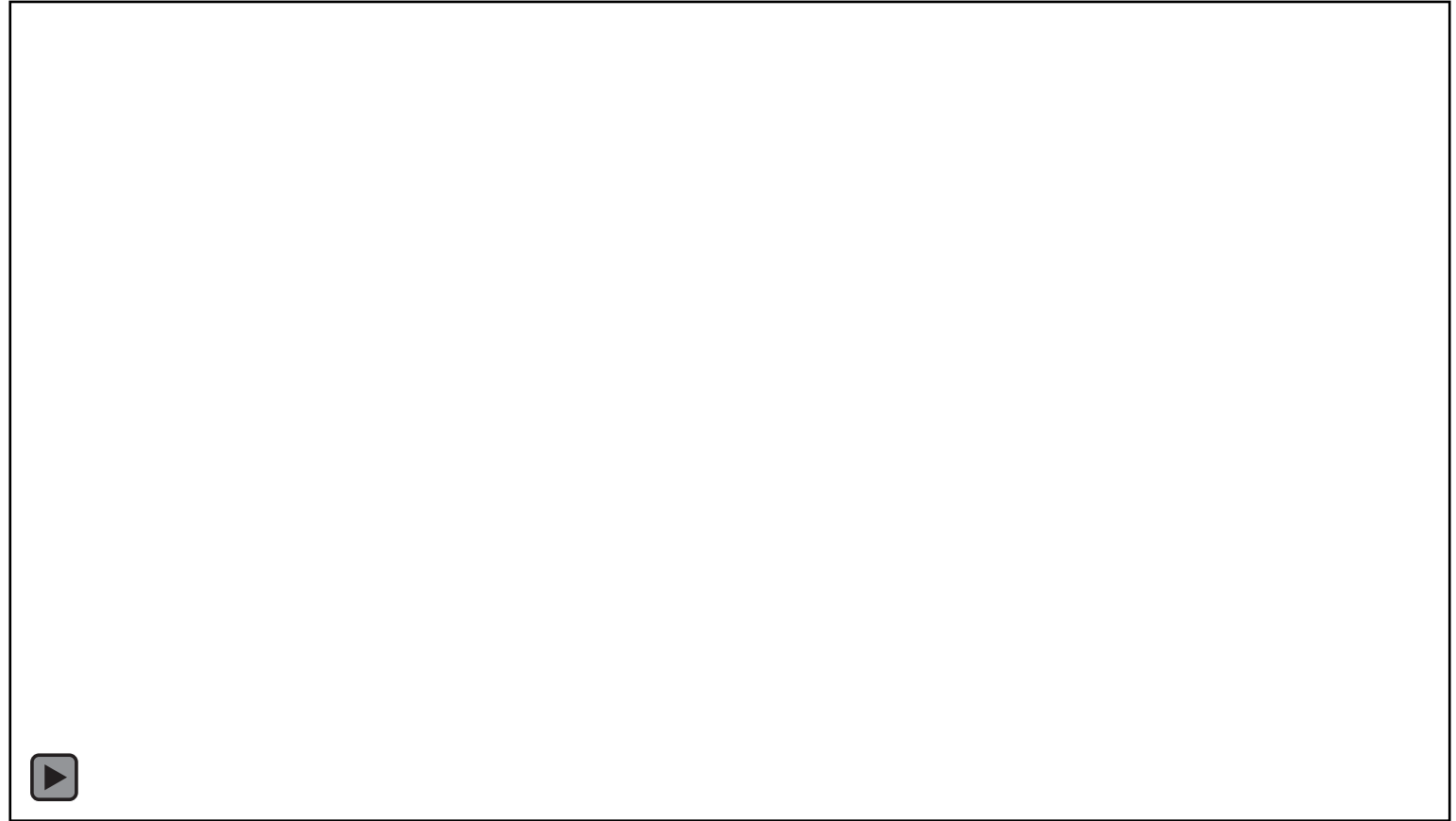
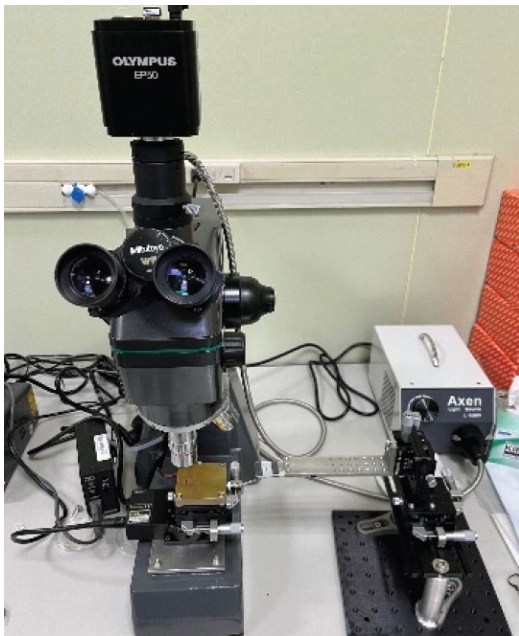
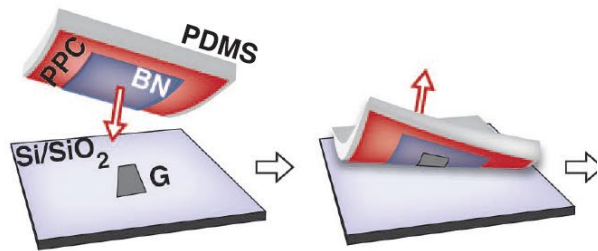
A factor of 10 higher than the non-suspended graphene

Further improvement in quality

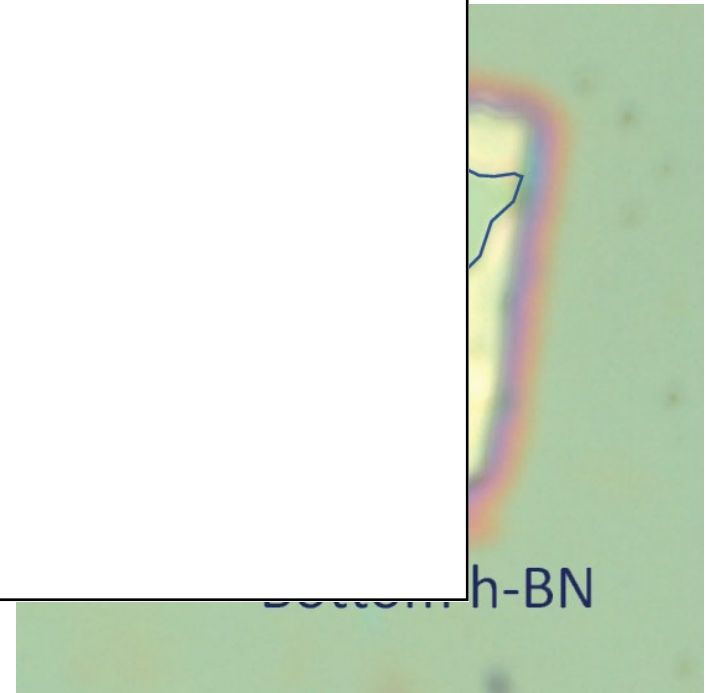
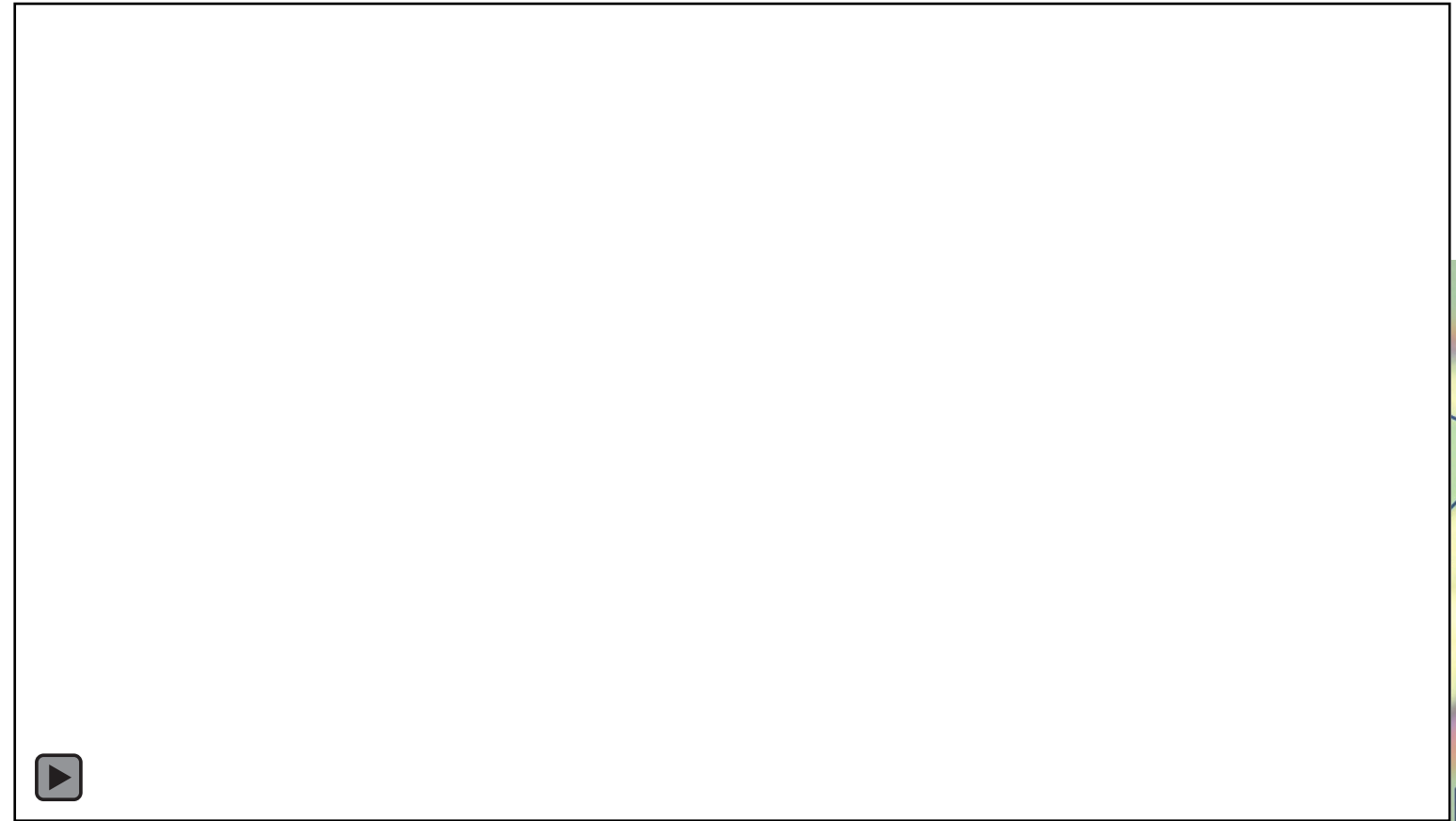
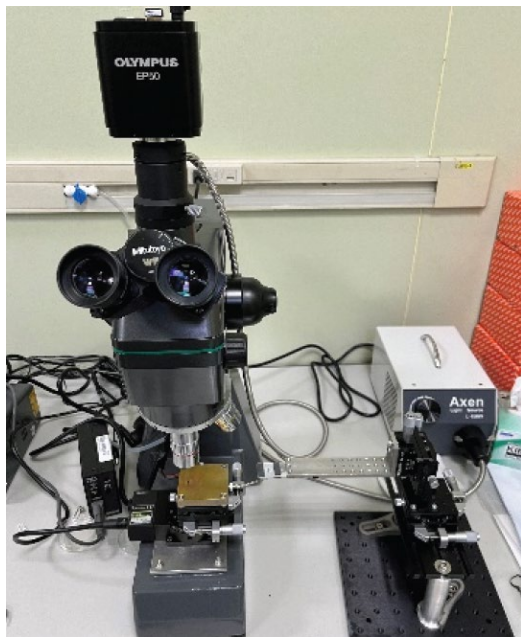
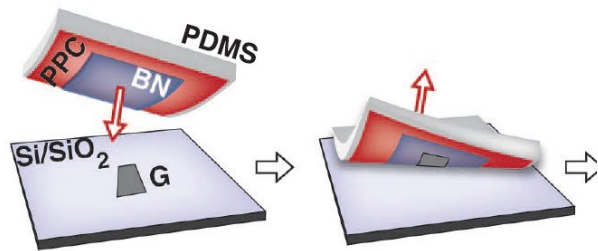


D. Rhodes et al. Nat. Mater. (2019)

Dry pick up method

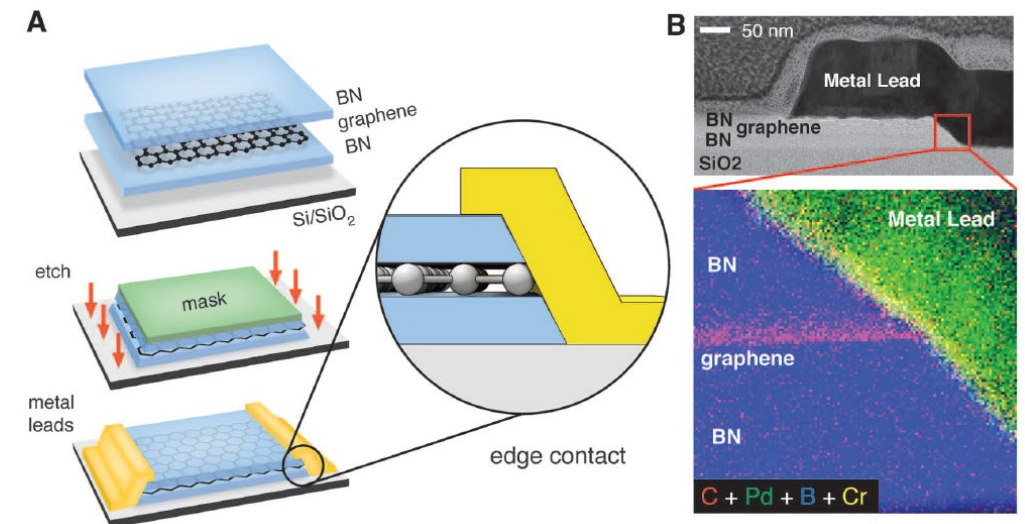
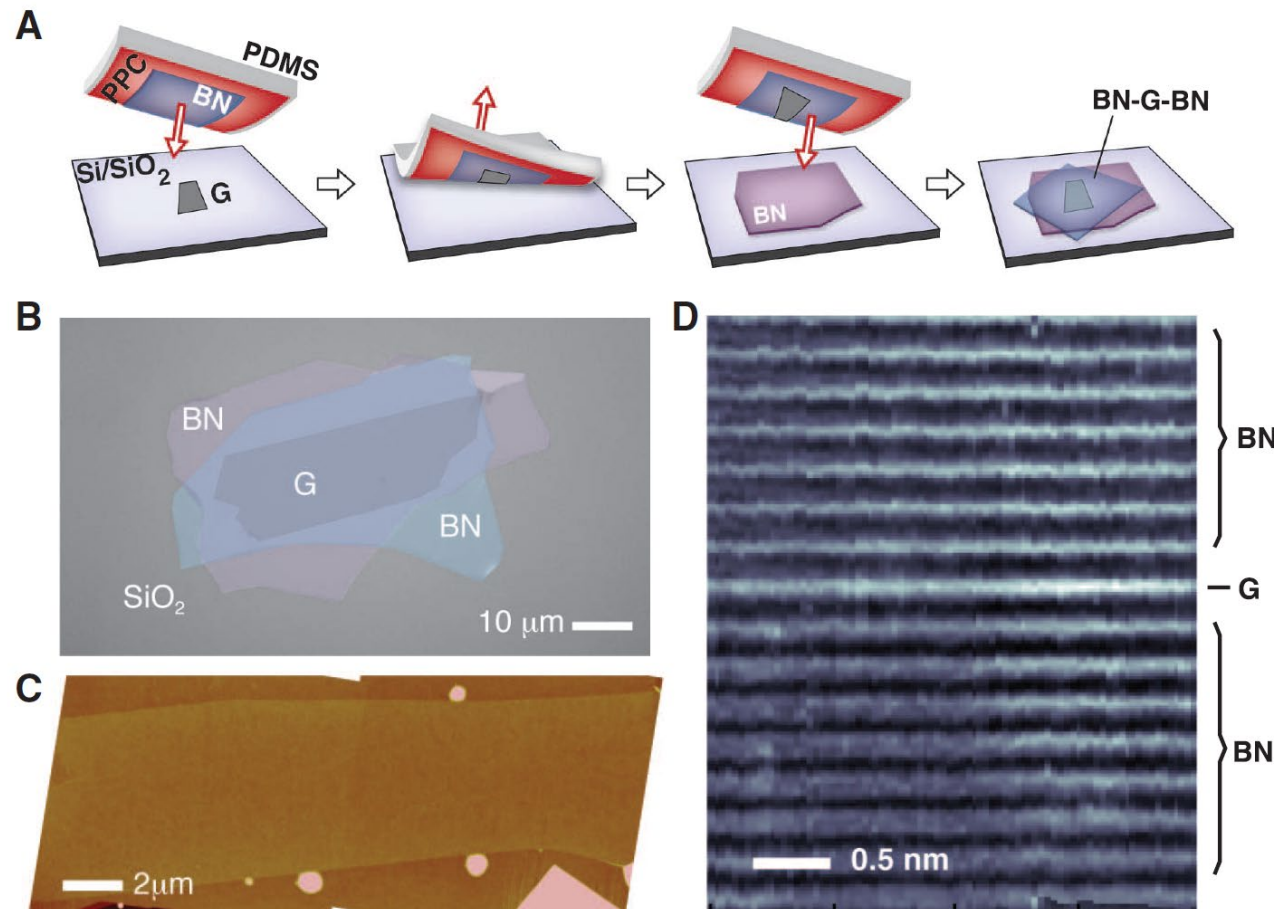


Dry pick up method



Further improvement in quality

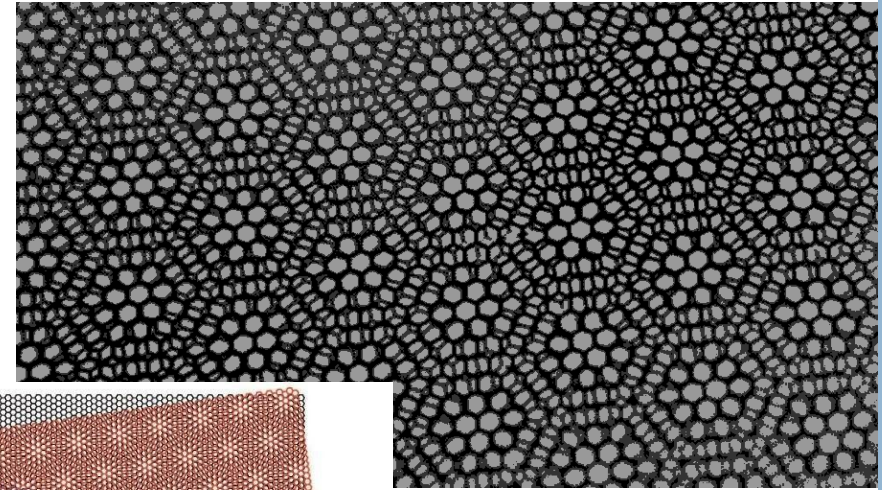
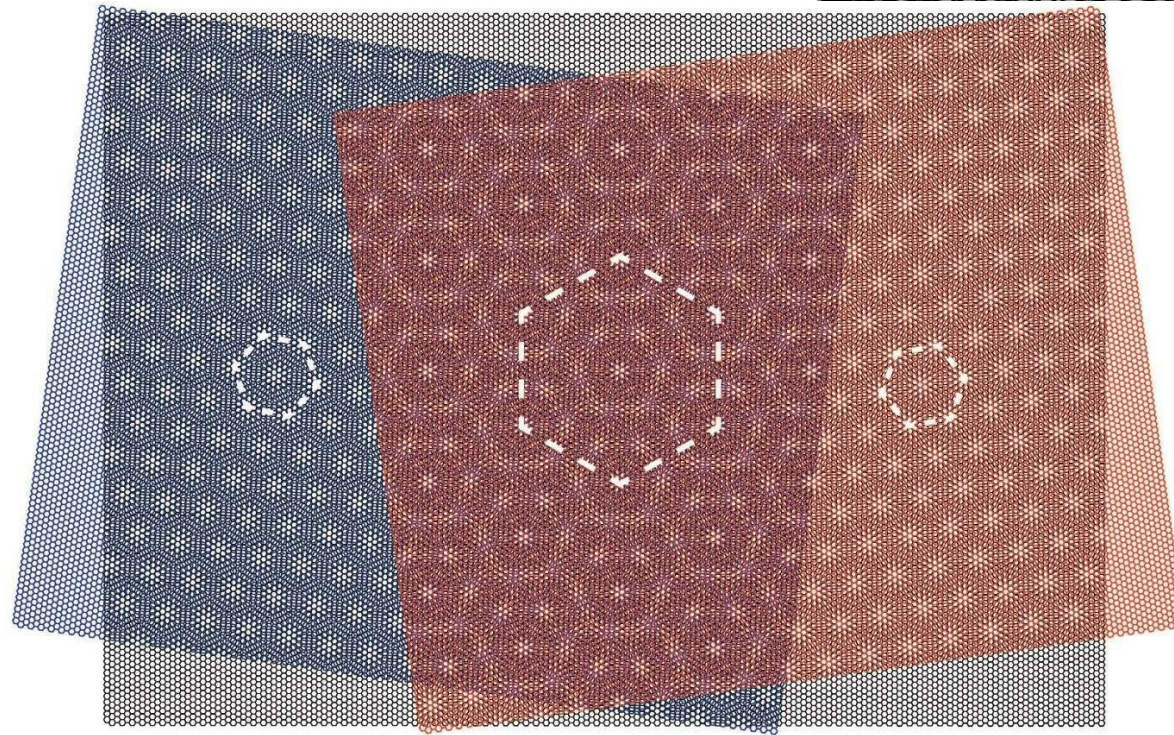
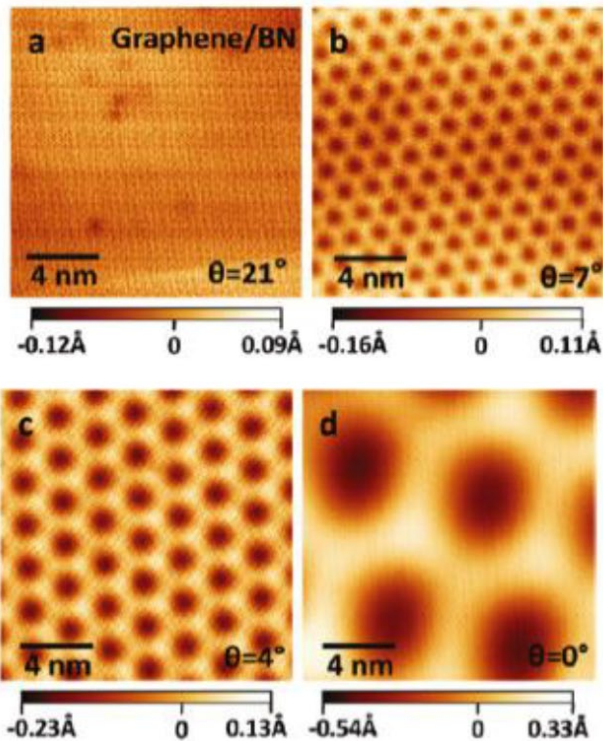
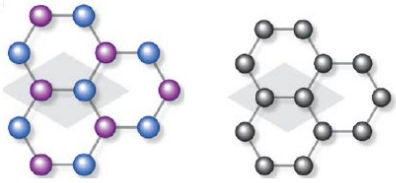
- Encapsulated graphene with h-BN



L. Wang et al. Science (2013)

Another degree of freedom

- Angle dependence between layers: Moiré pattern



Xue et al, Nature Mater (2011);
Decker et al Nano Lett (2011)

L. Wang et al. Nano Lett. (2019)

Hofstadter's butterfly

- Under a square lattice with a period potential and a magnetic field

$$\hat{H}\varphi(\mathbf{r}) = \frac{[\hat{\mathbf{p}} + e\mathbf{A}(\mathbf{r})]^2}{2m}\varphi(\mathbf{r}) + V(\mathbf{r})\varphi(\mathbf{r}) = E\varphi(\mathbf{r}),$$

- To the first order approx. in the field with a 2D system, the Bloch band represented by

$$E_n(k_x, k_y) = E_n^{(0)} + E_n^{(1)}(\cos k_x a + \cos k_y a)$$

- Solving the Schrodinger-like eq.

$$E_n^{(0)}\bar{\varphi}(x, y) + \frac{E_n^{(1)}}{2}\left[\bar{\varphi}(x + a, y) + \bar{\varphi}(x - a, y) + e^{-ieB_z x/\hbar}\bar{\varphi}(x, y + a) + e^{ieB_z x/\hbar}\bar{\varphi}(x, y - a)\right] = E\bar{\varphi}(x, y)$$

Hofstadter's butterfly

By choosing the Landau gauge

$$\nabla_{\mathbf{r}} \cdot \mathbf{A}(\mathbf{r}) = 0 \text{ with } \mathbf{A}(\mathbf{r}) = (0, B_z x, 0)$$

Making several definitions:

$$n \stackrel{\text{def}}{=} x/a, \quad v \stackrel{\text{def}}{=} k_y a, \quad \text{and } \varepsilon \stackrel{\text{def}}{=} 2(E - E_n^{(0)})/E_n^{(1)}$$

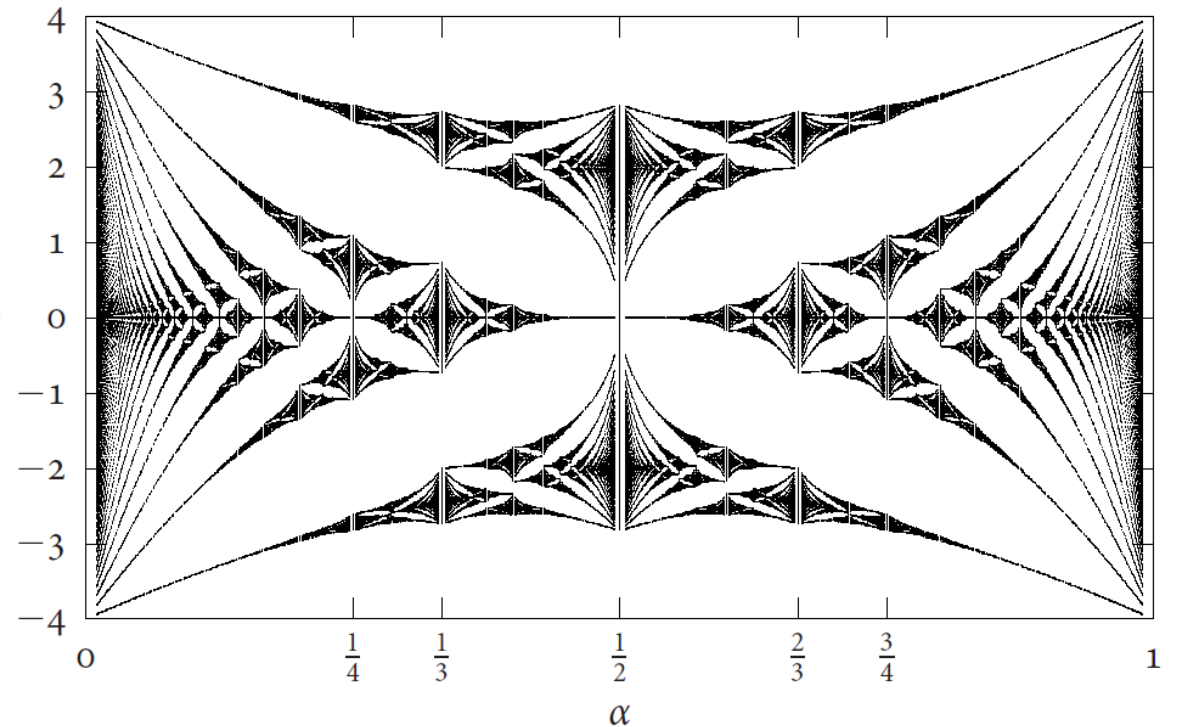
$$\bar{\varphi}(x, y) = \exp(ivy/a)g_n$$

a dimensionless parameter

$$\alpha \stackrel{\text{def}}{=} eB_z a^2 / (2\pi\hbar)$$

Put everything in one obtains Harper's equation:

$$g_{n+1} + g_{n-1} + 2 \cos(2\pi n\alpha - v)g_n = \varepsilon g_n$$



$$\alpha = (B_z a^2) / (h/e) = \Phi / \Phi_0^{(D)}$$

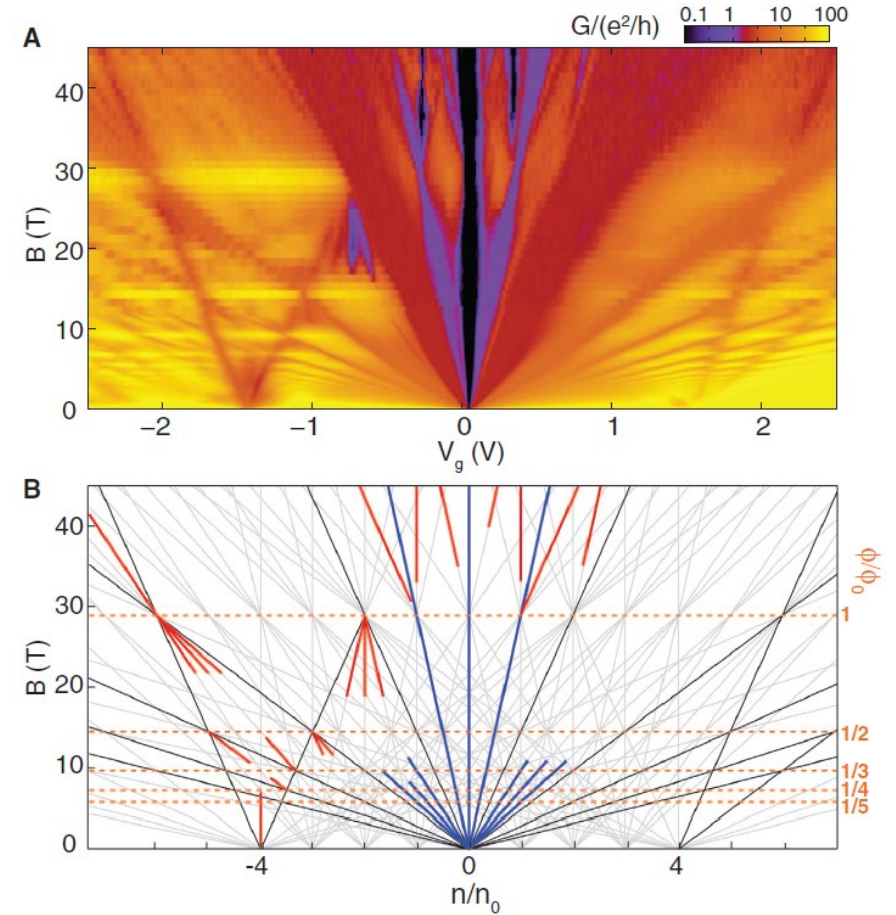
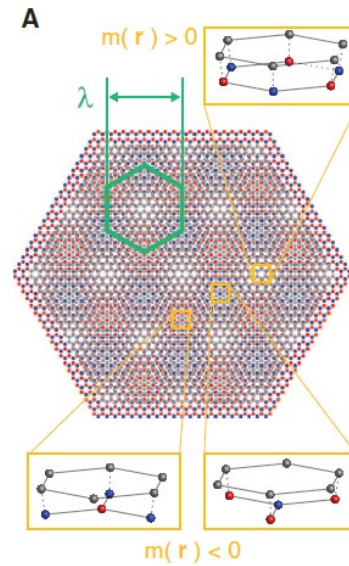
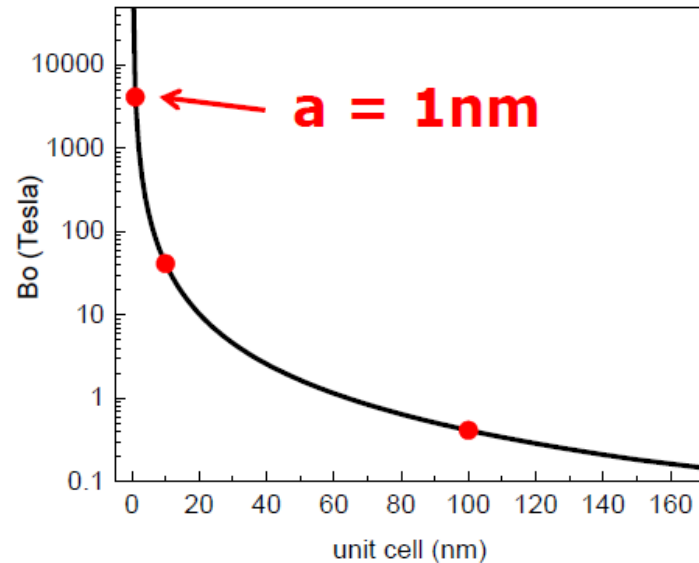
The magnetic flux per unit cell

Dirac flux quantum

Realistic situation

Obvious technical challenge:

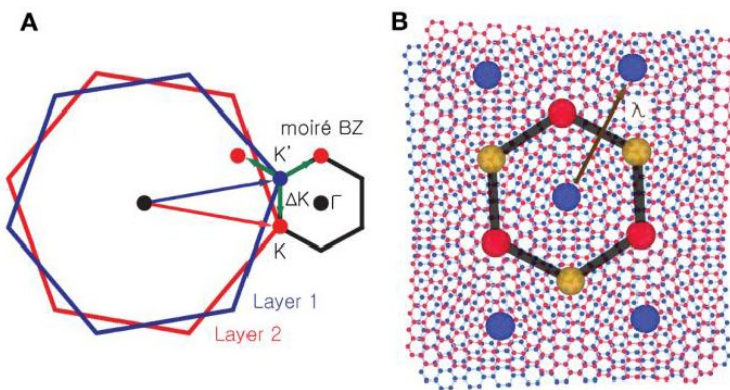
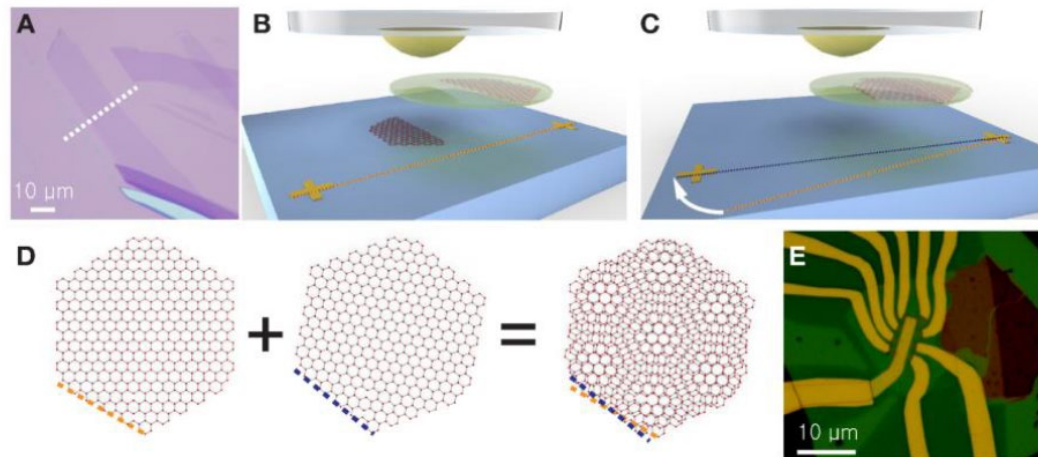
$$\frac{\phi}{\phi_0} = \frac{Ba^2}{h/e} \sim 1$$



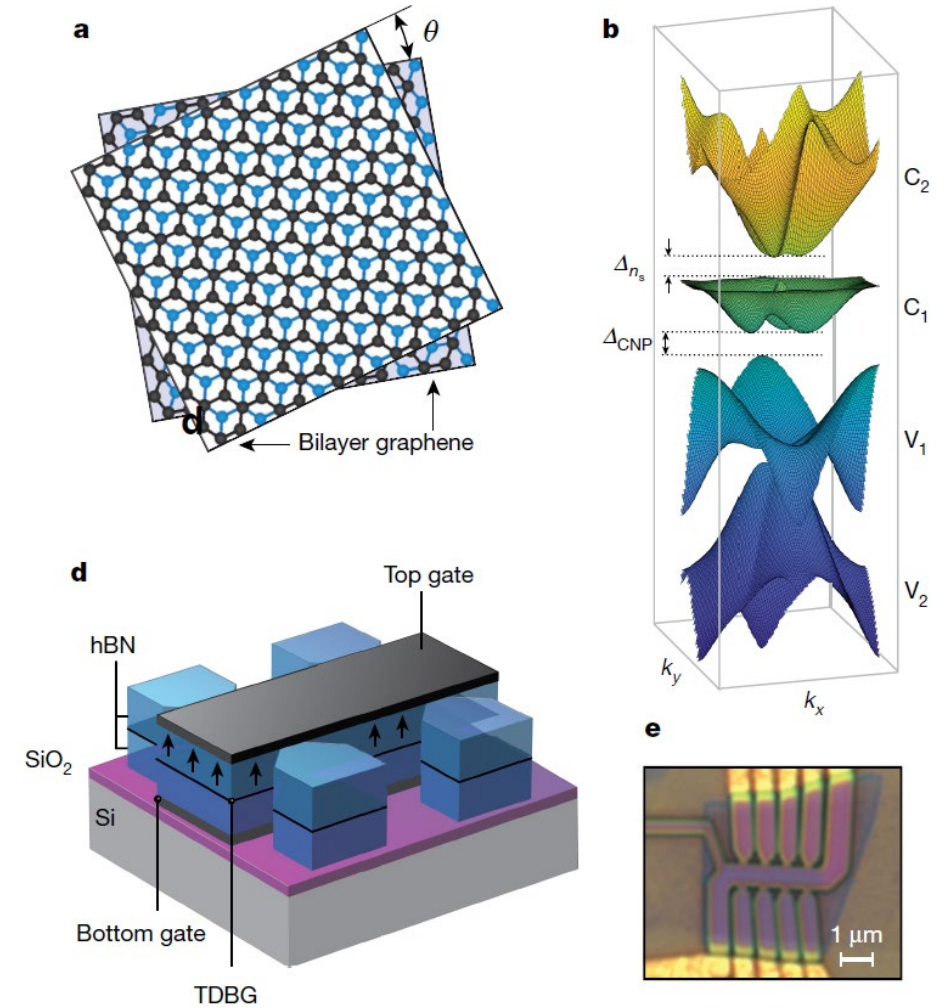
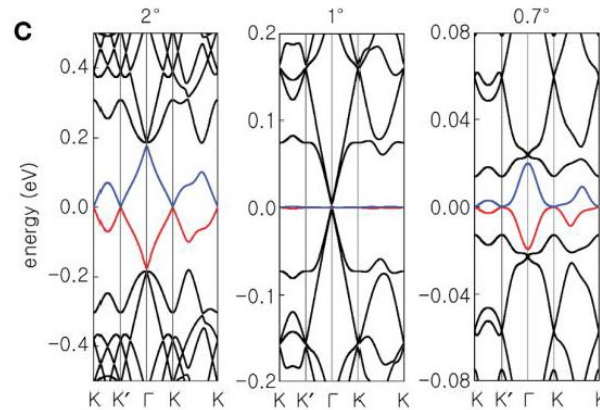
- Early works are limited to a field and accessible density range.
- No fully quantized minigap in the fractional spectrum.
- But now, by twisting the angle, we can control the superlattice size.

Another degree of freedom

- Twisted angle for graphene or bilayer graphene



K. Kim et al. PNAS(2017)

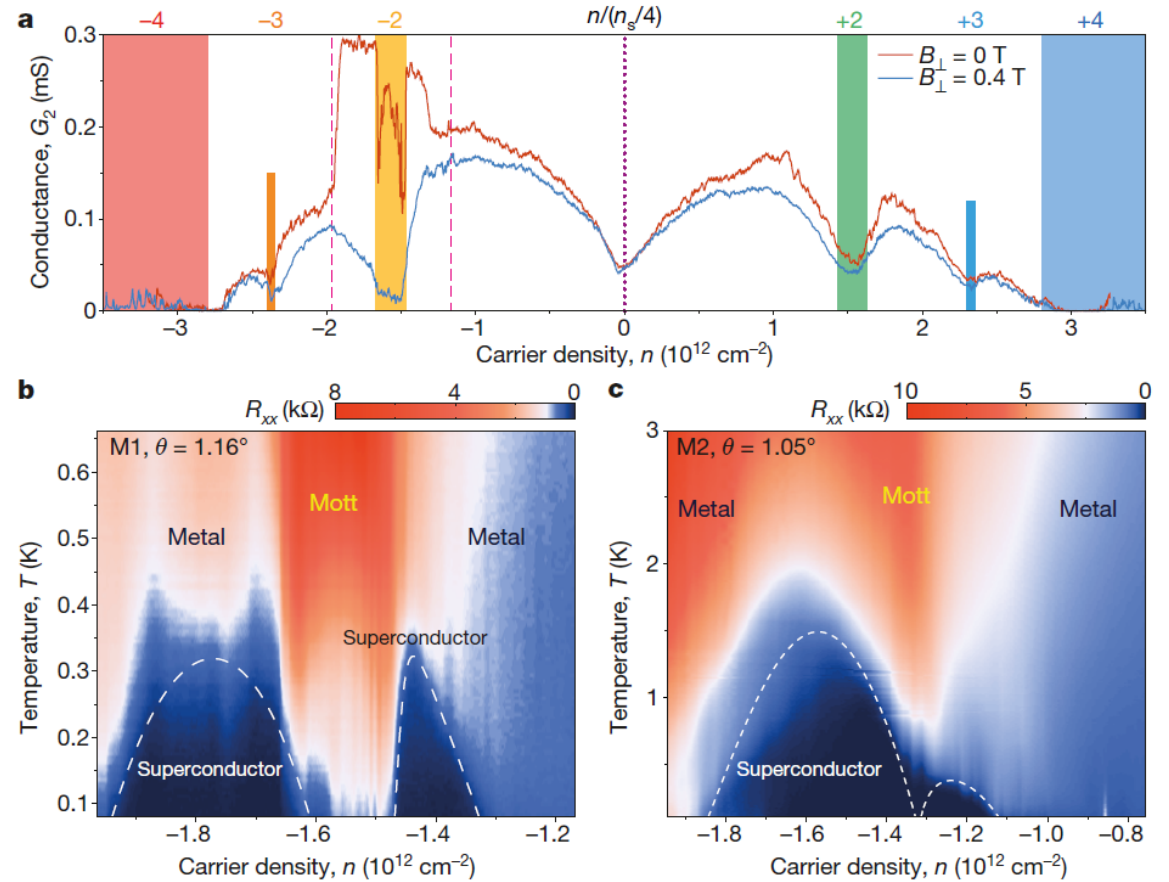
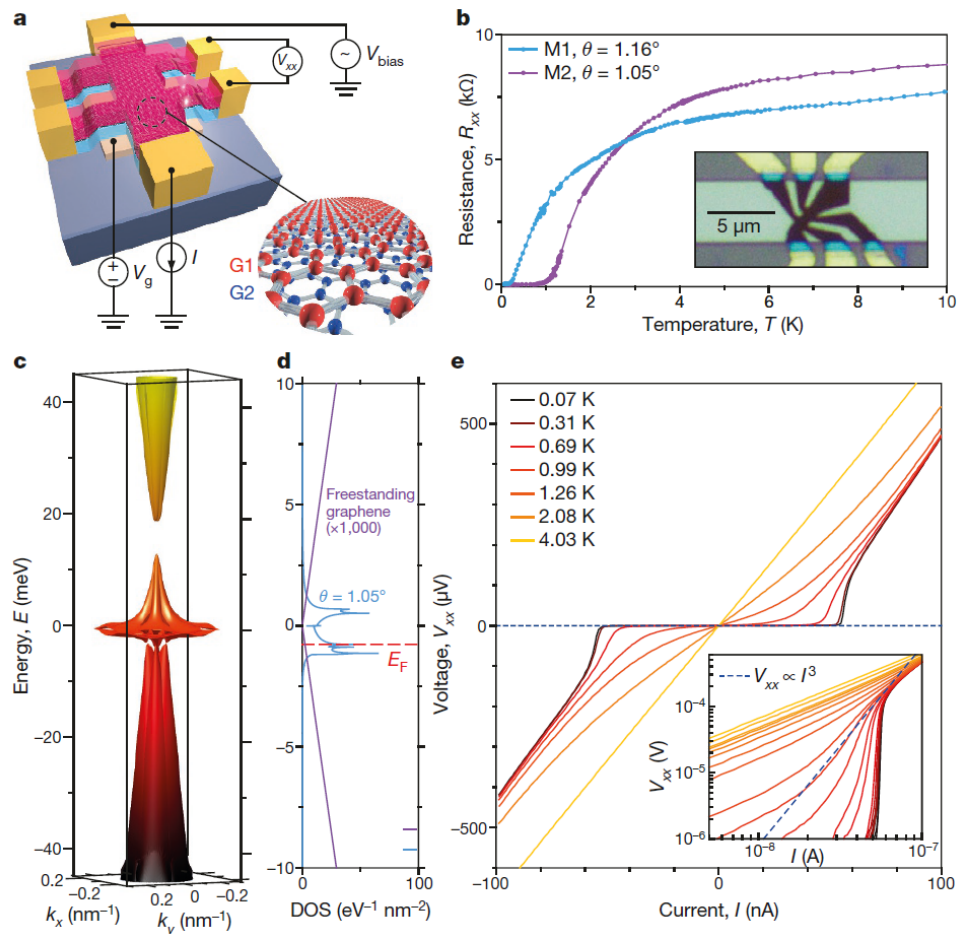


X. Liu et al. Nature (2020)

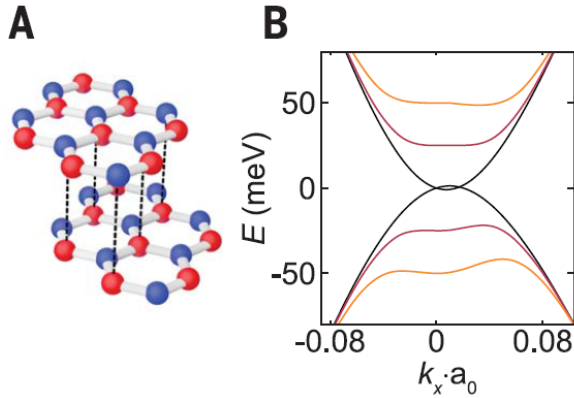
Another degree of freedom

- Magic twisted angle bilayer graphene

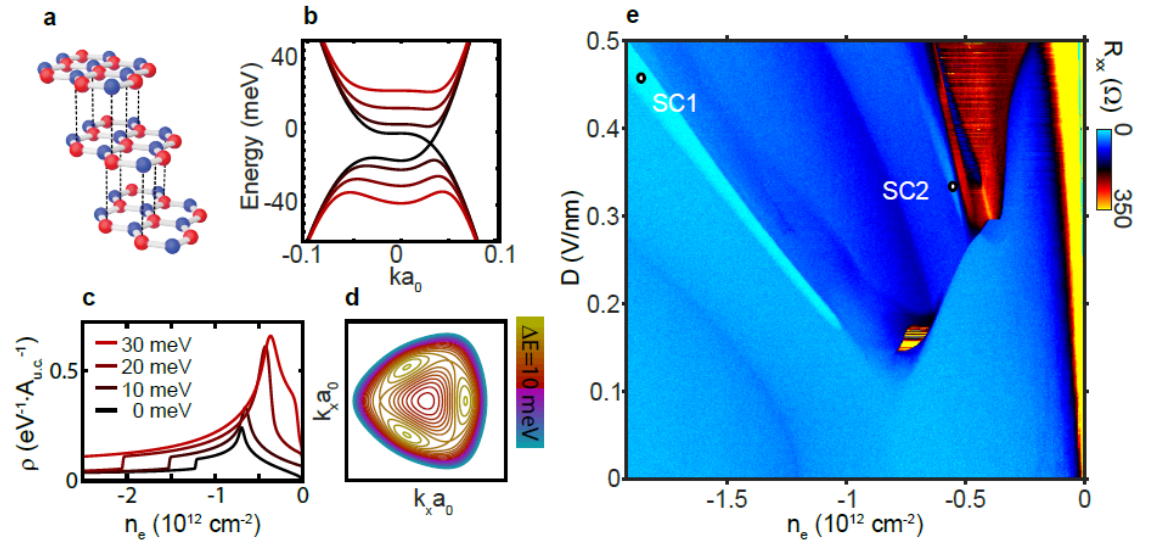
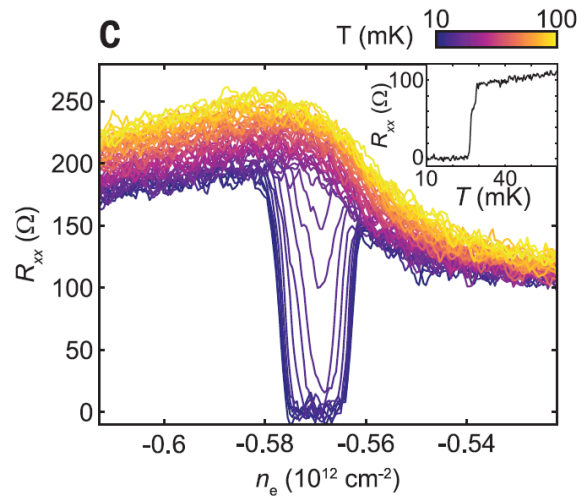
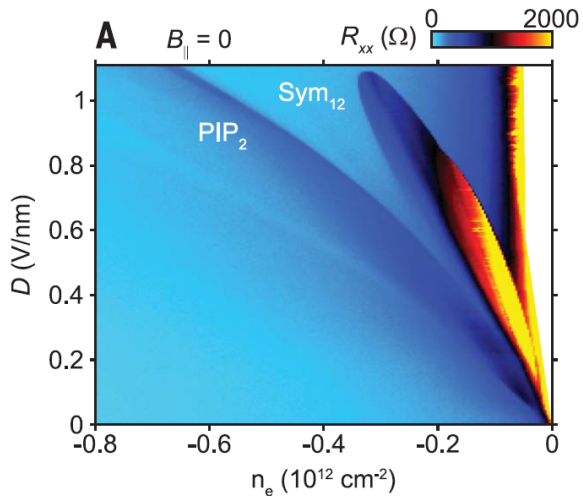
Y. Cao et al. Nature (2018)



Superconductivity in graphene



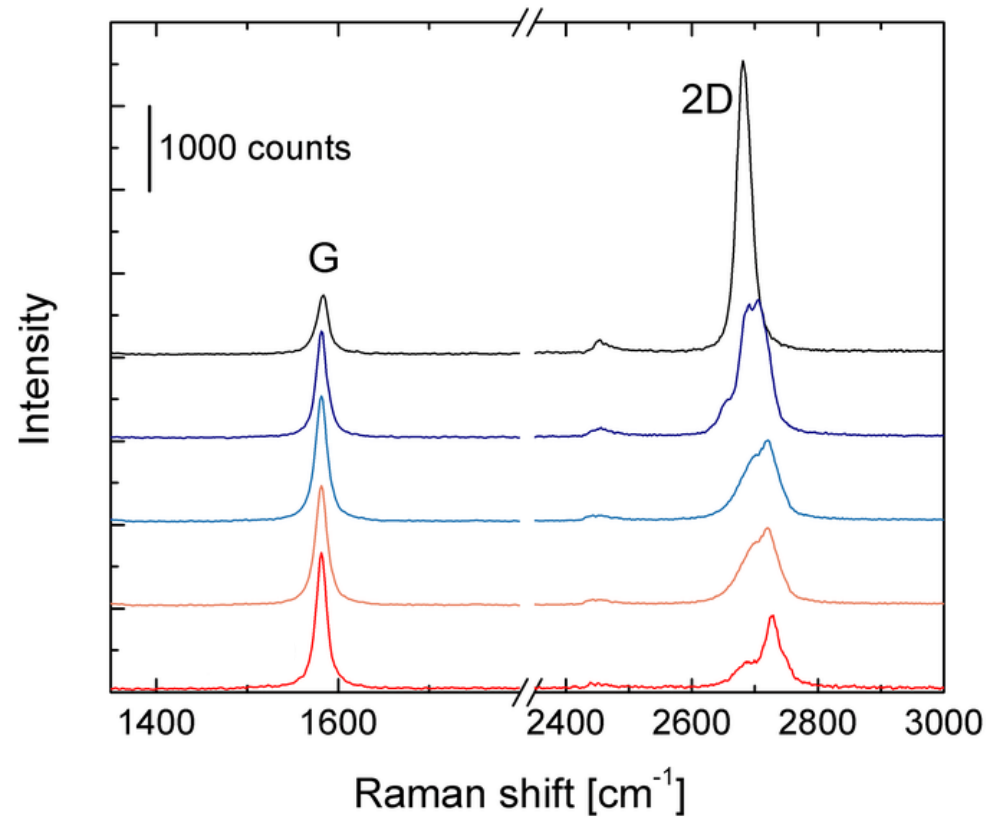
- In Bernal stack graphene, superconductivity can be found with a spin-polarized pairing under a large electrical field.
- Another experiment also demonstrated SC under a high magnetic field



H. Zhou et al. Science (2022)

H. Zhou et al. Nature (2021)

Quiz

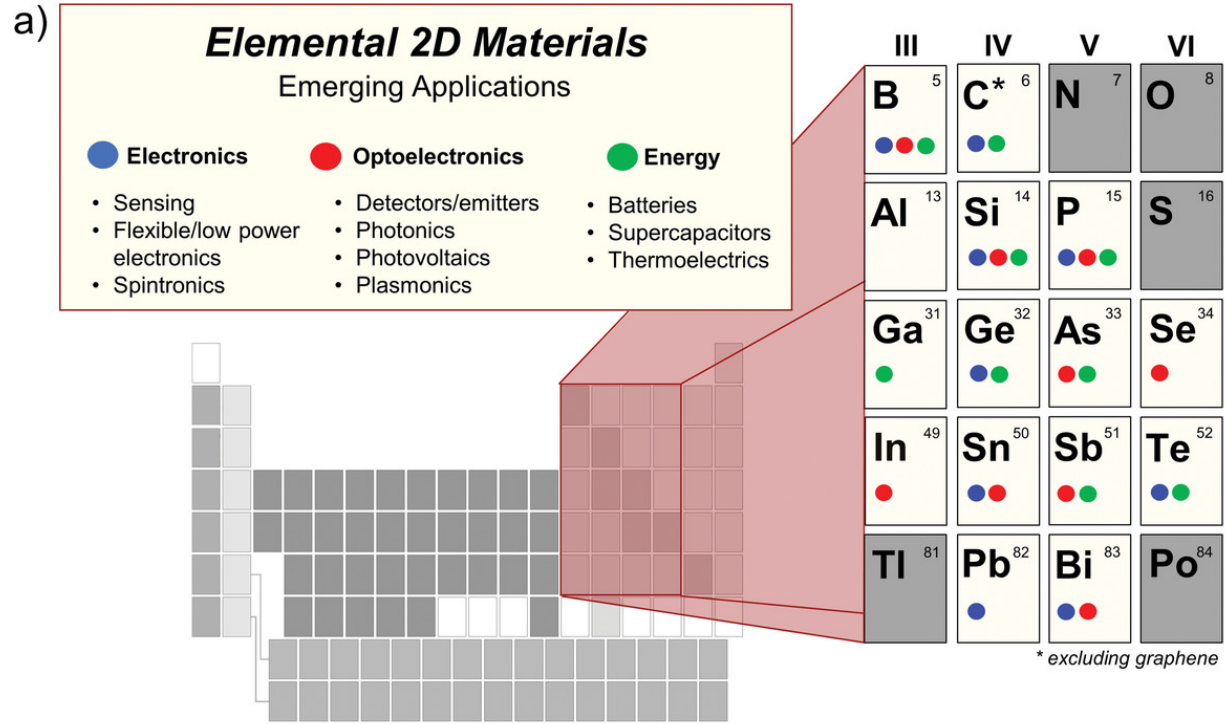


Which color of the spectrum is the monolayer graphene?

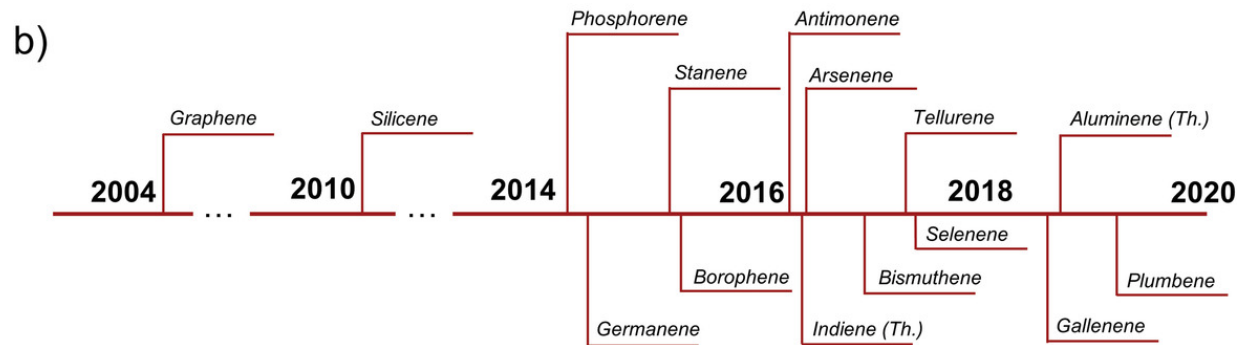
2D MATERIALS

Chung-Ting Ke

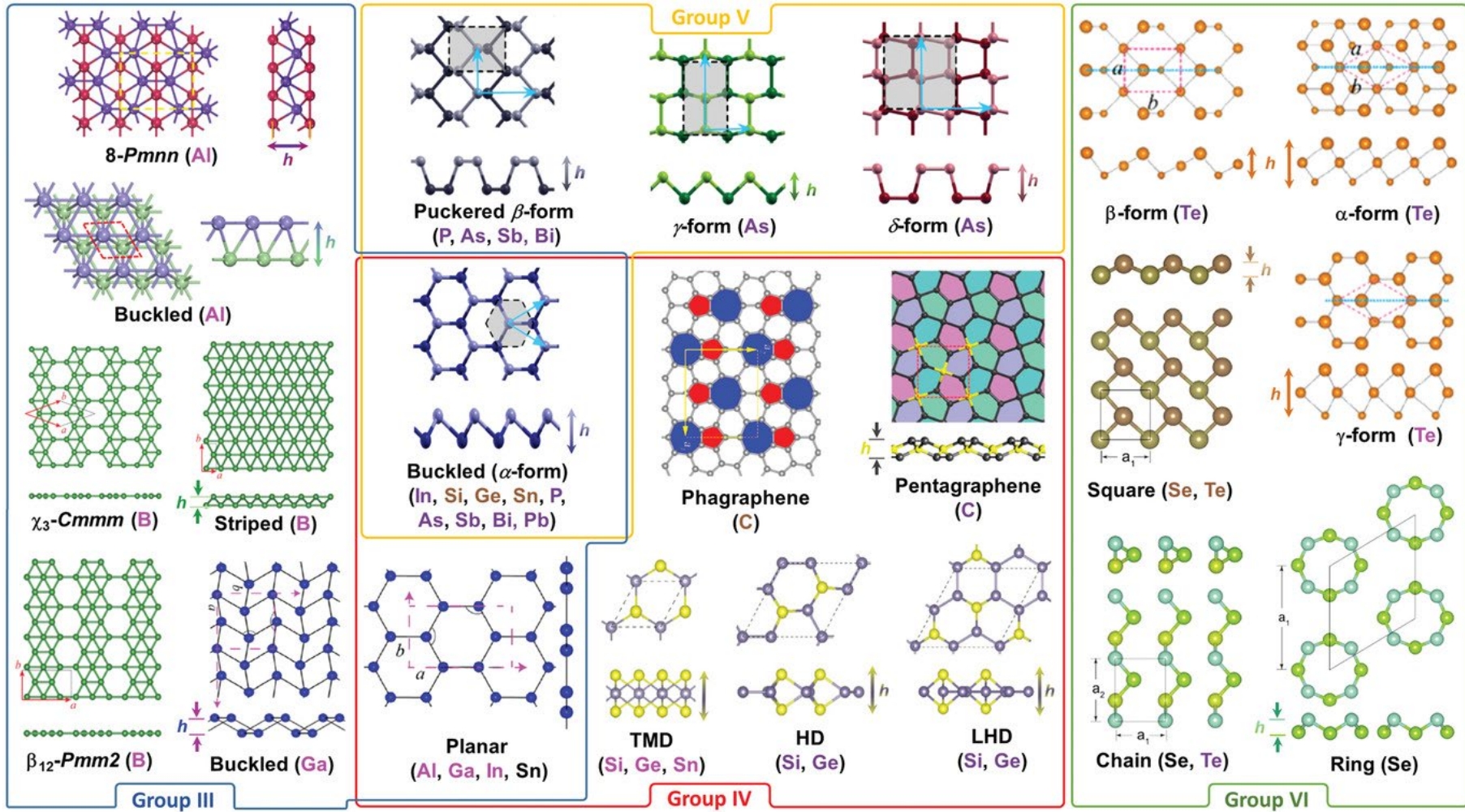
Graphene is the first but not only



- After graphene, a lot of different 2D materials are discovered.
- The applications immediately impact the industry.



Allotropes are also rich



Similar to graphene, the allotrope of element 2D materials will determine the properties.

More 2D materials

Transition Metal Dichalcogenides

H																	He
Li	Be	MX ₂ M = Transition-metal X = Chalcogen										B	C	N	O	F	Ne
Na	Mg	3	4	5	6	7	8	9	10	11	12	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

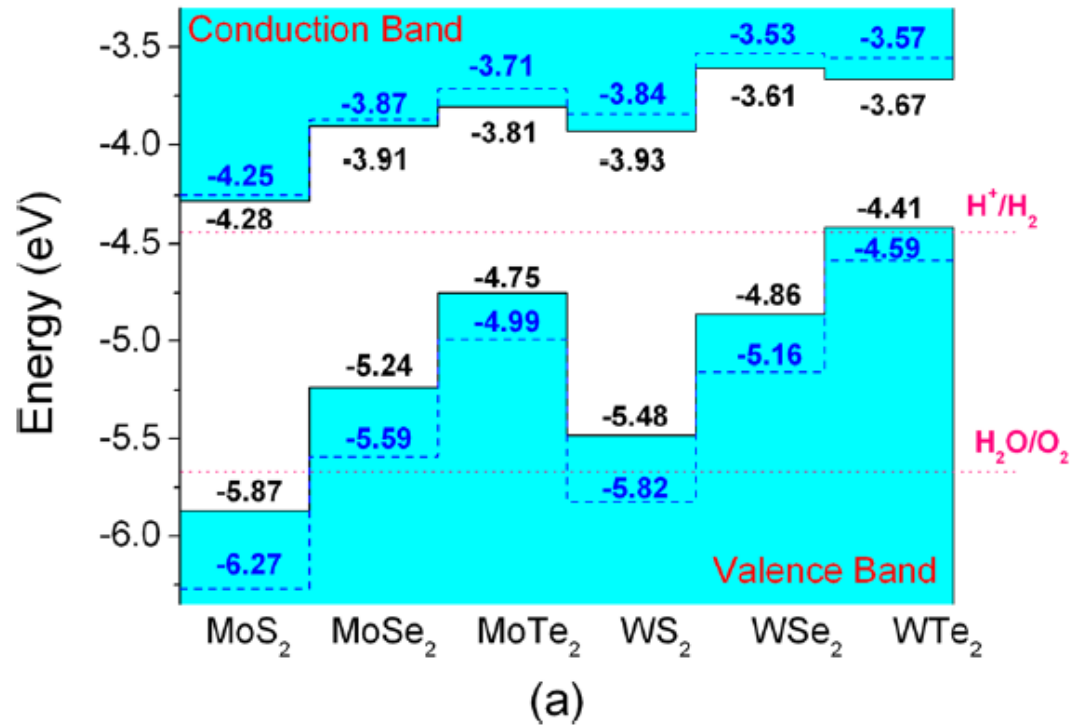
M. Pumera et al. DOI: 10.1016/J.TRAC.2014.05.009

WSe₂, WTe₂, NbSe₂ etc..

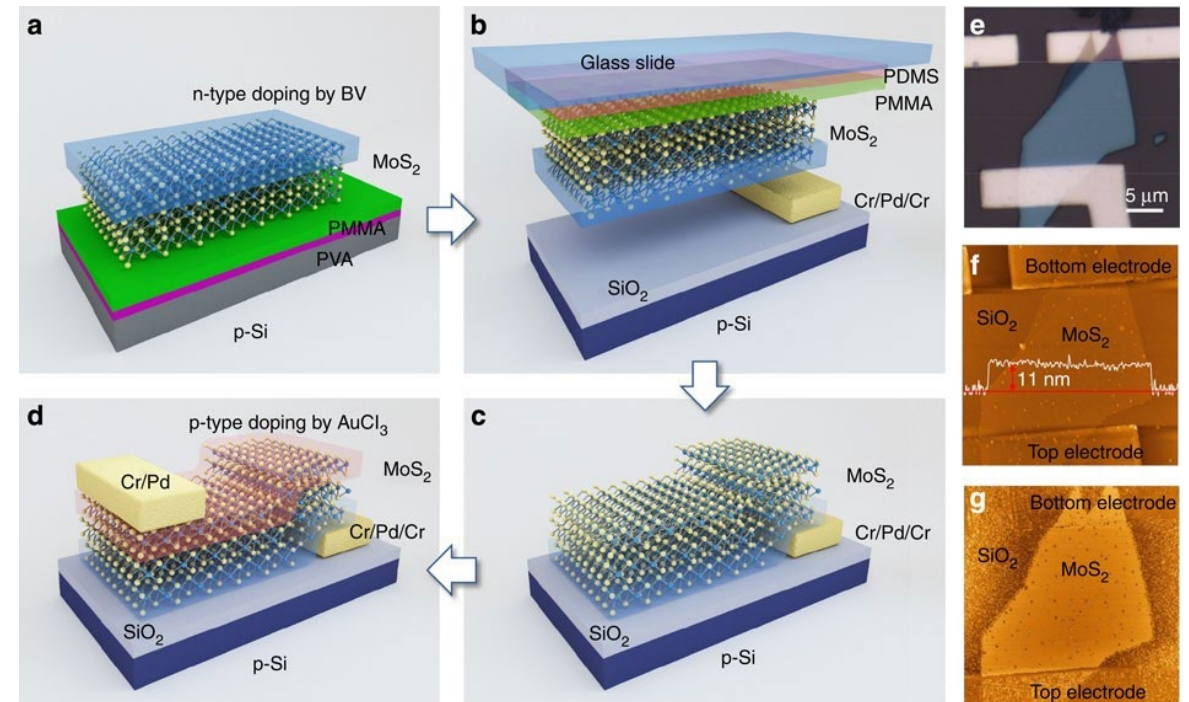
- Combining two different elements can enrich the phase space of the 2D materials
- One of the most famous groups of compound 2D material is Transition-metal dichalcogenide (TMDs).
- This new group of 2D materials provides a great platform for various research and applications

Rich band structures

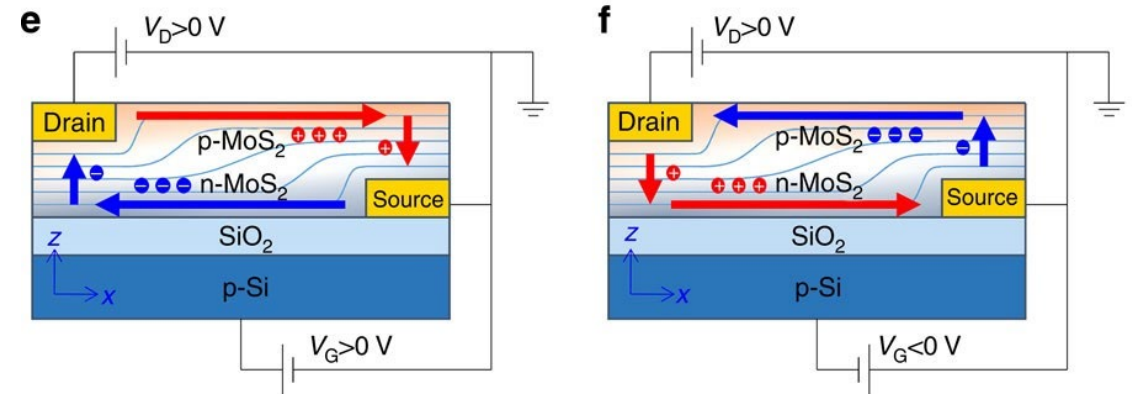
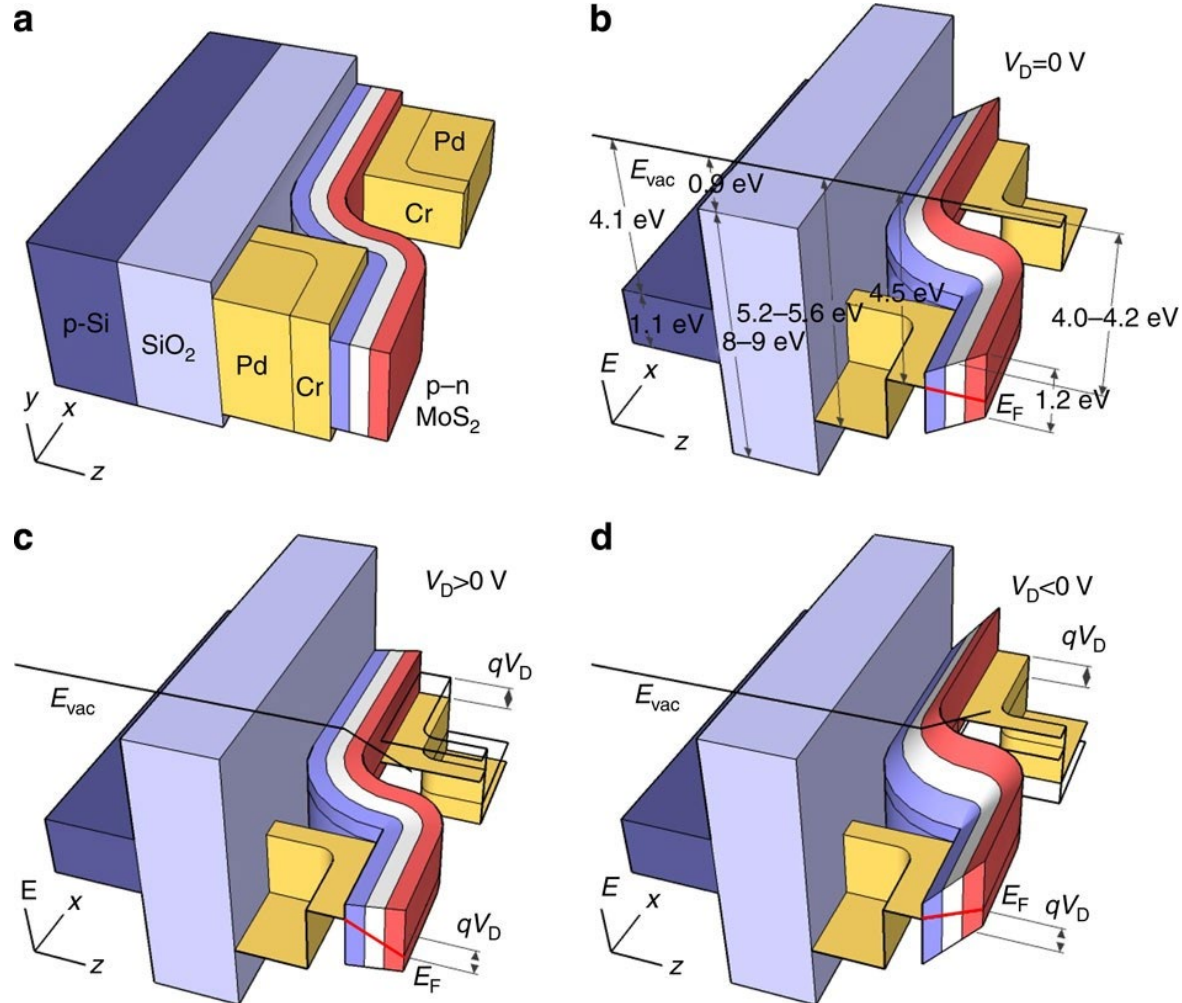
- The different gaps and direct-indirect bands allow us to conduct various research and applications in electronics, optics, sensing, etc.



J. Kang et al. APL (2013)

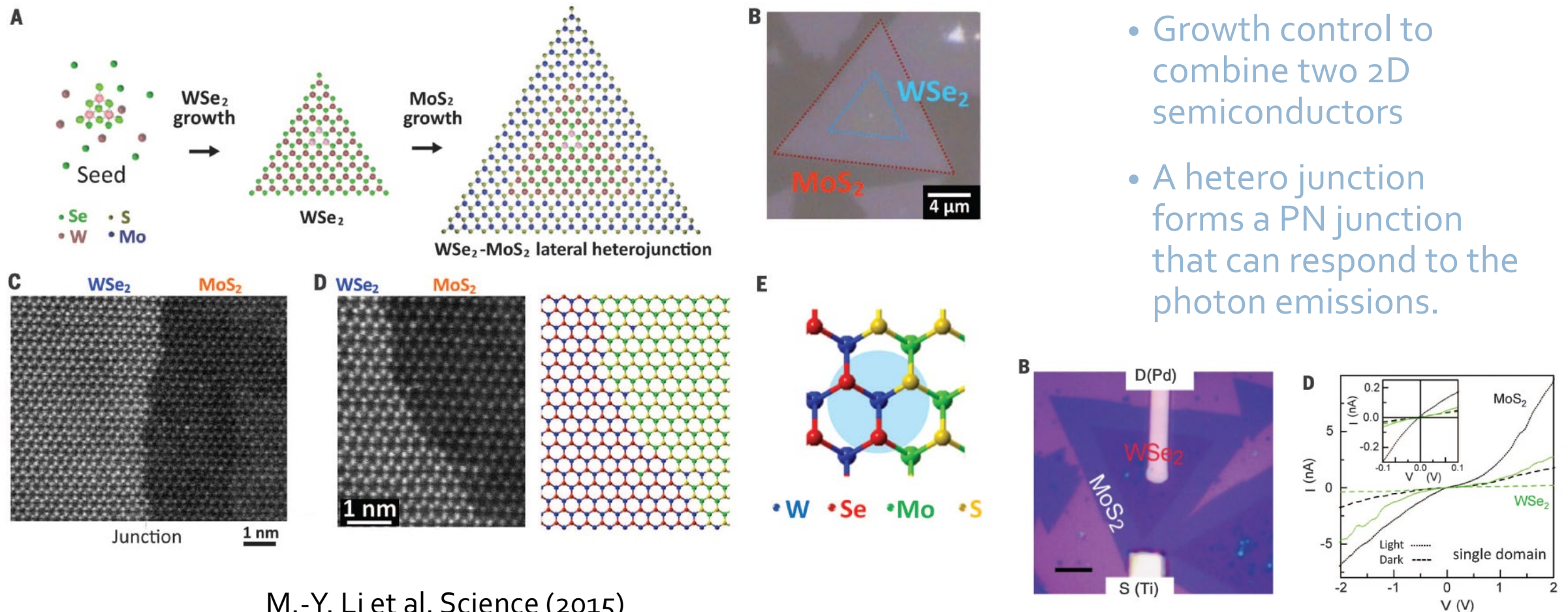


A 2D PN junction



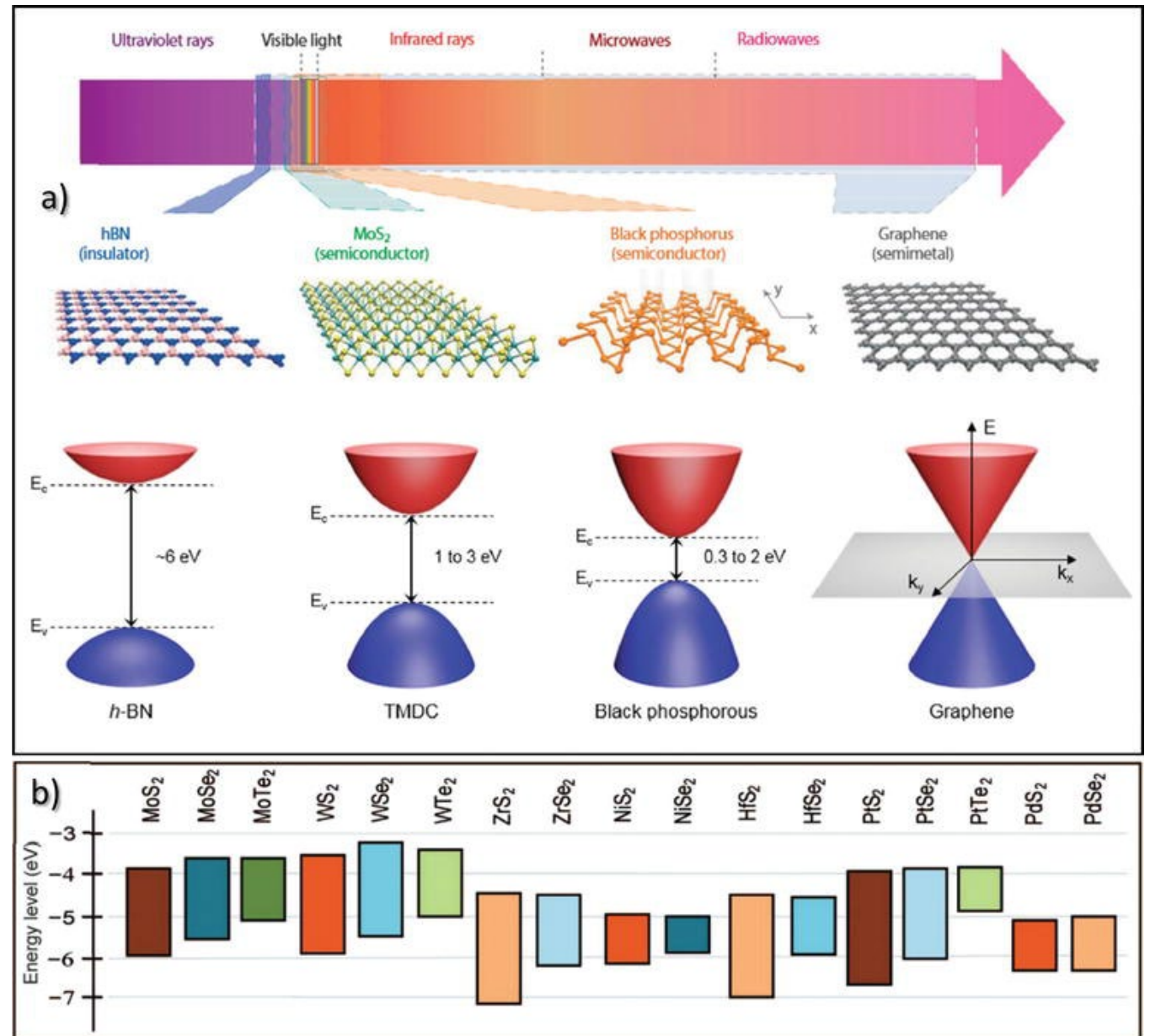
- By controlling the charge density, one can form a PN junction due to the strong gate effect for 2D material.
- Here MoS₂ is an example of realizing a 2D material-based PN junction.

Another way to create a PN interface



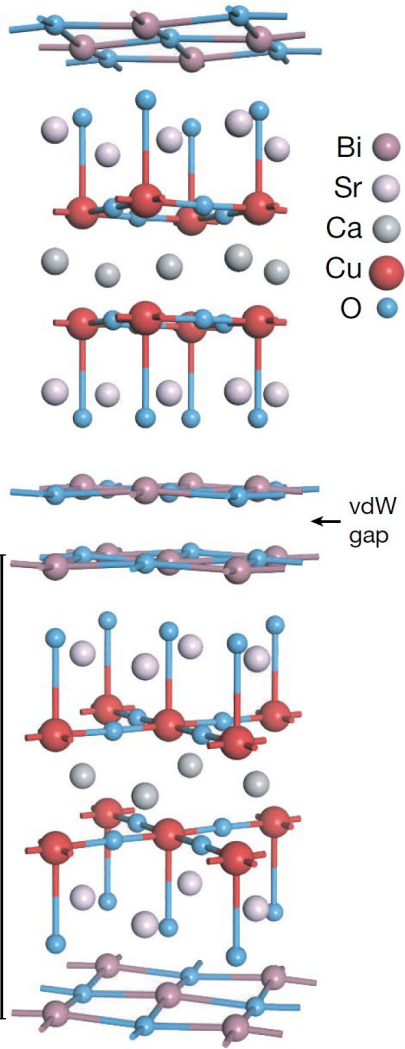
Wild range spectrum

- The gap ranges from 6 eV to 0 eV.
- That creates a wild range of the spectrum.
- Therefore, 2D materials cover from insulator all the way to metal.



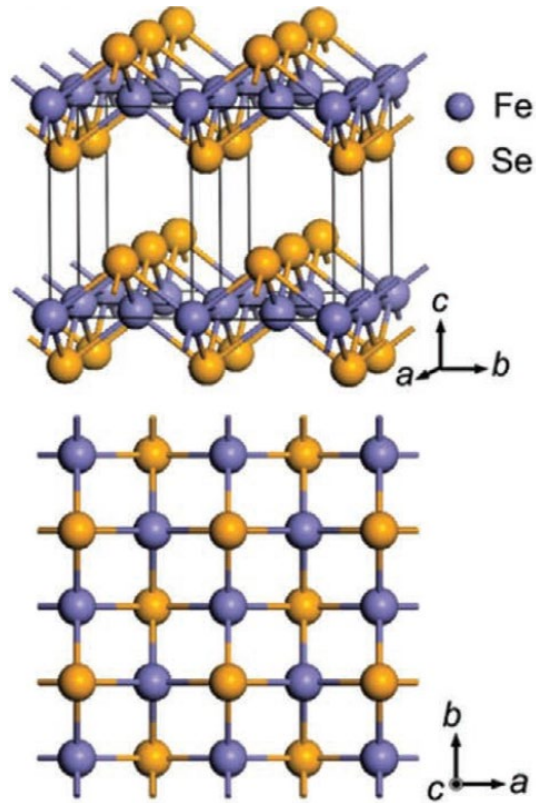
High Tc superconductor

BSCCO



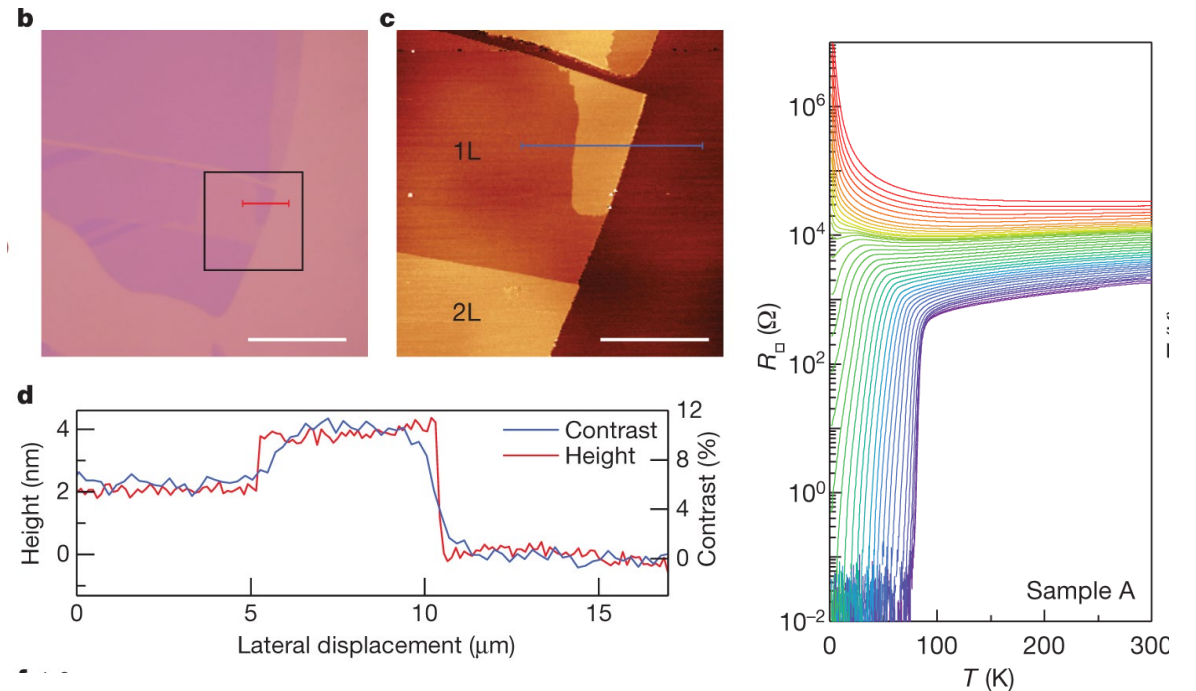
Y. Yu, et al Nature (2019)

FeSe

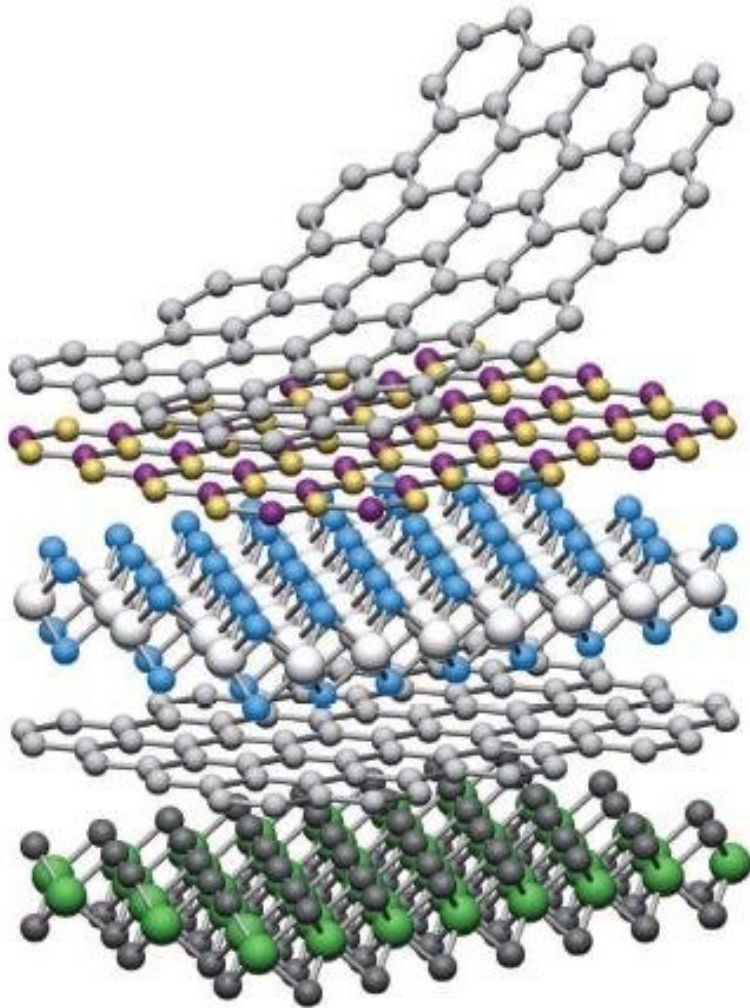




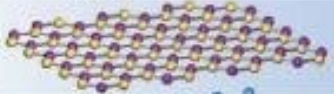





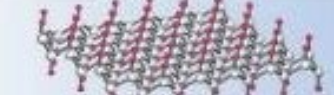

F.-C. Hsu, et al PNAS(2008)

- Layered high Tc superconductors can be turned into a 2D sheet.
- The superconductivity limit in the 2D system may be useful to understand the physics of high Tc superconductors



One can mix and match them



	Graphene	
	hBN	
	MoS ₂	
	WSe ₂	
	Fluorographene	

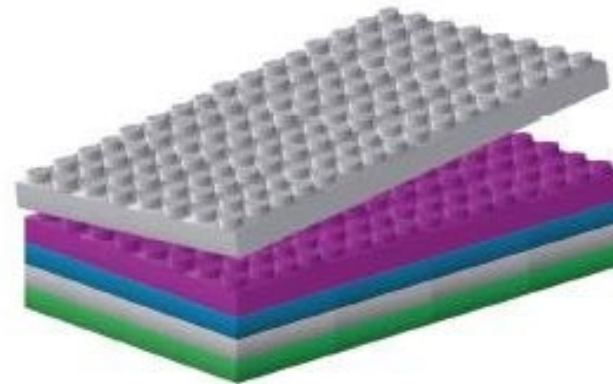
Dirac metal

Insulator

Semiconductor

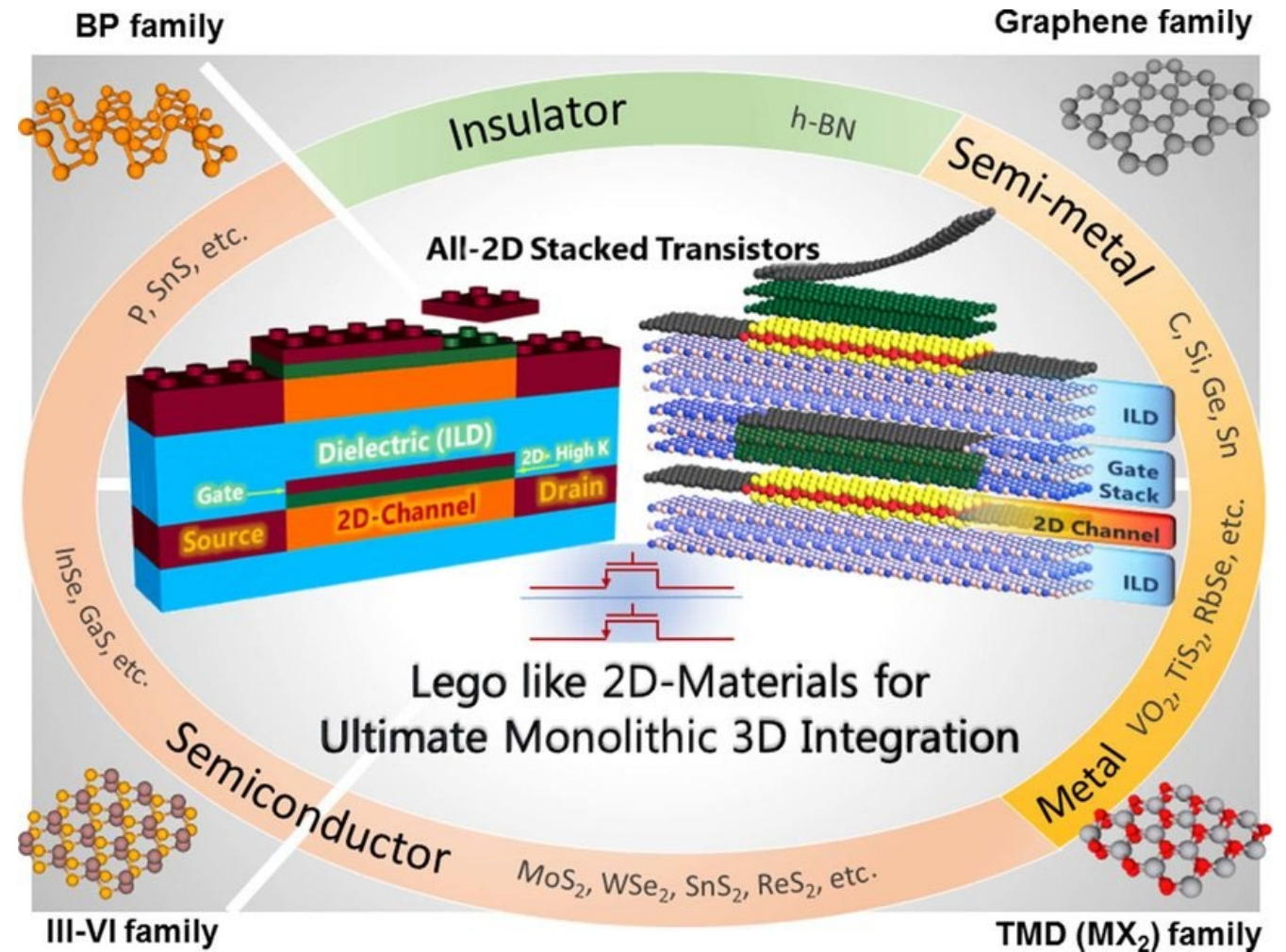
Semiconductor

Insulator

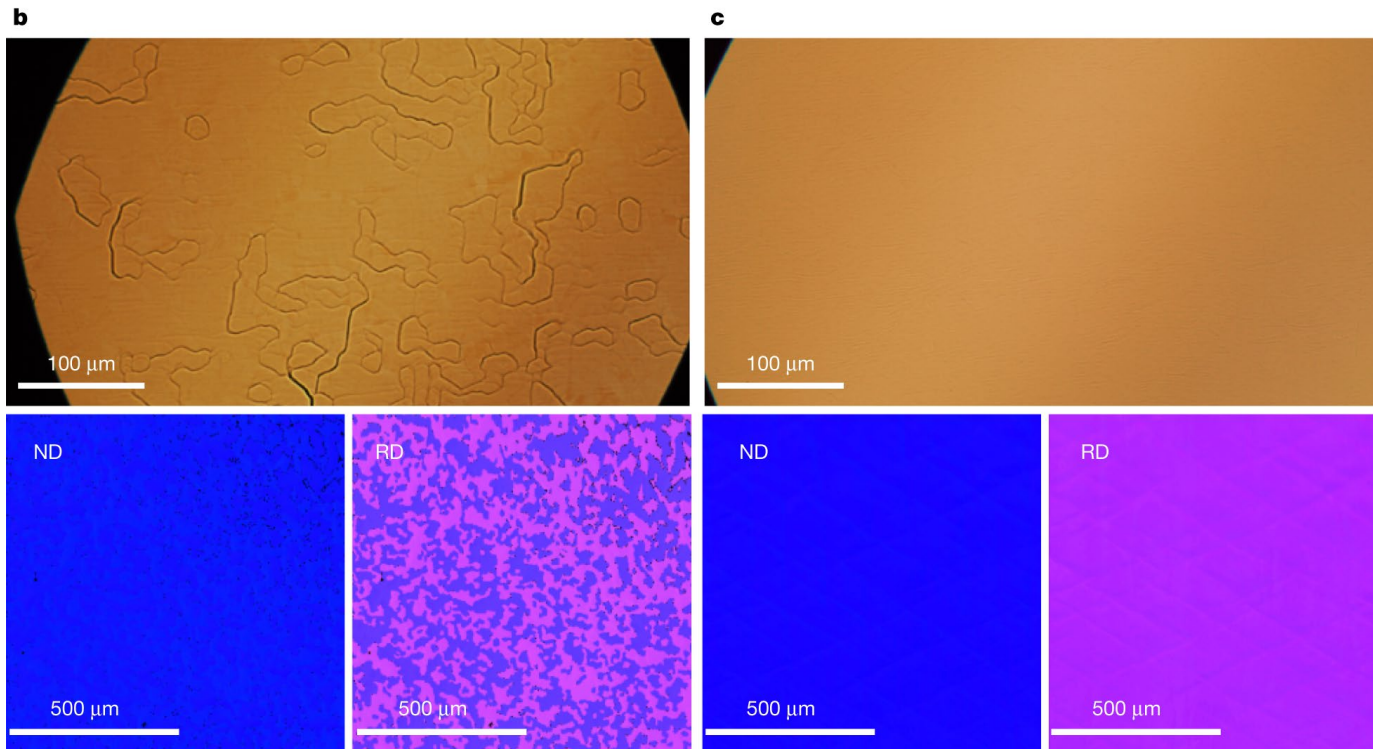
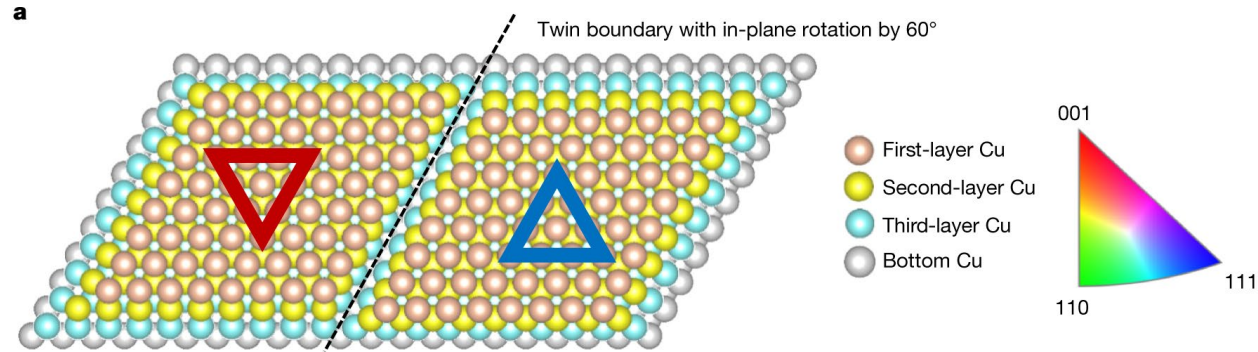


2D materials

- Many possibilities when one can combine different materials together
- The possible applications can be enlarged by engineering the hybrid materials



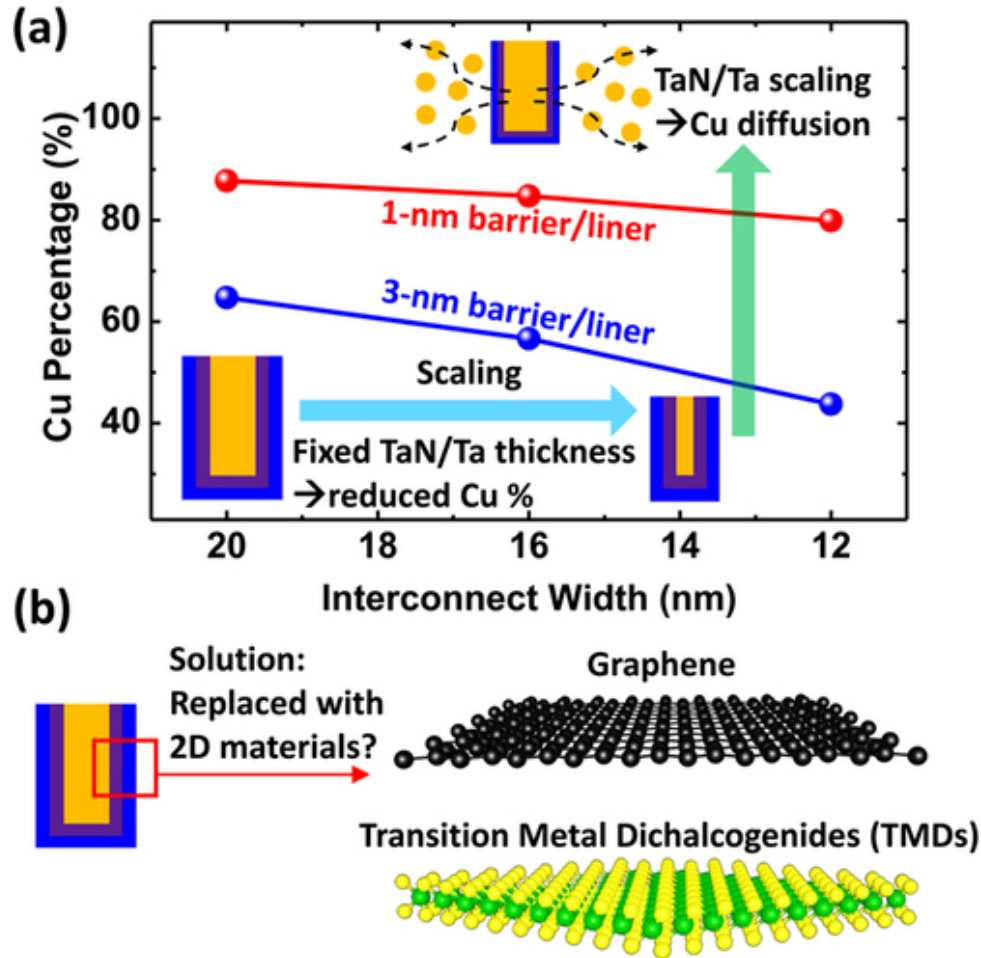
Wafer-scale materials



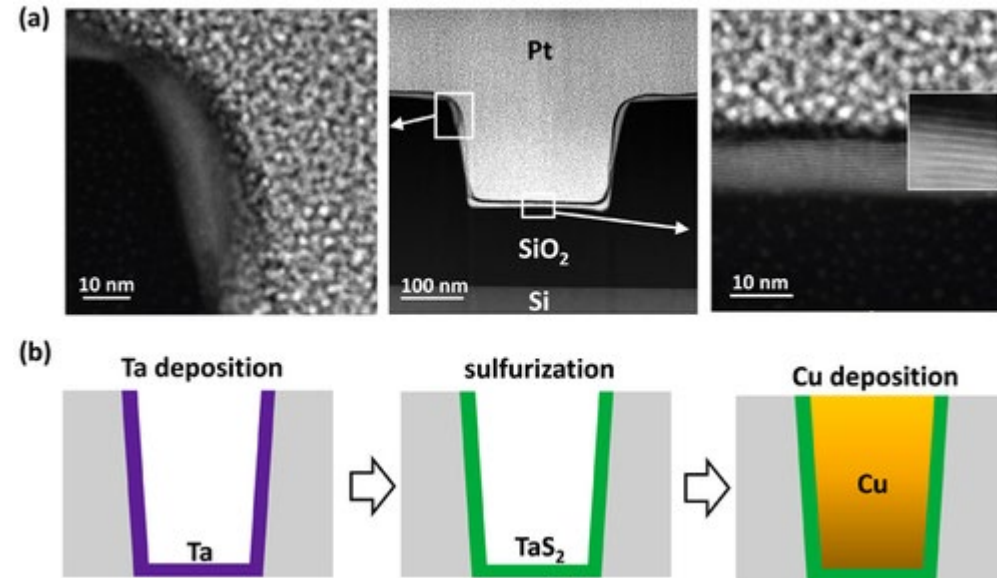
- Quote from TSMC “The benefits of using 2D and 1D materials include high mobility at atomic thickness, excellent gate control, and potential applications for low-power and high-performance devices. Thus, transistor scaling may be extended. ”
- This is one of the TSMC focused directions

T. A. Chen, et al. Nature (2020)

Advancing the MOSFET fab



- To resolve the metal diffusion issues.
- Provide good electrical and thermal conductivity
- Growth remains a key issue.



Growth of 2D materials

Thermal CVD

1. Deposit graphene on Cu substrate
2. Transfer graphene to dielectric



grain size ↑

700 – 1000 °C

damage to dielectric ↑



Thermal CVD

- Directly deposit TMD on dielectric

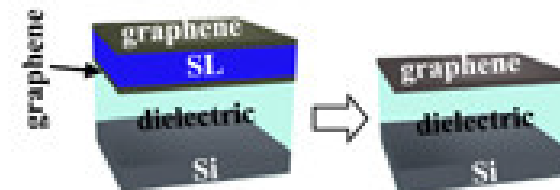
Plasma-enhanced CVD (PECVD)

- Directly deposit graphene on dielectric



CVD + sacrificial layer (SL)

1. Grow graphene on both sides of SL (e.g. Ni or Co)
2. Remove top graphene and SL



grain size ↓

< 400 °C

damage to dielectric ↓



Metal-organic CVD, sputtering, ALD

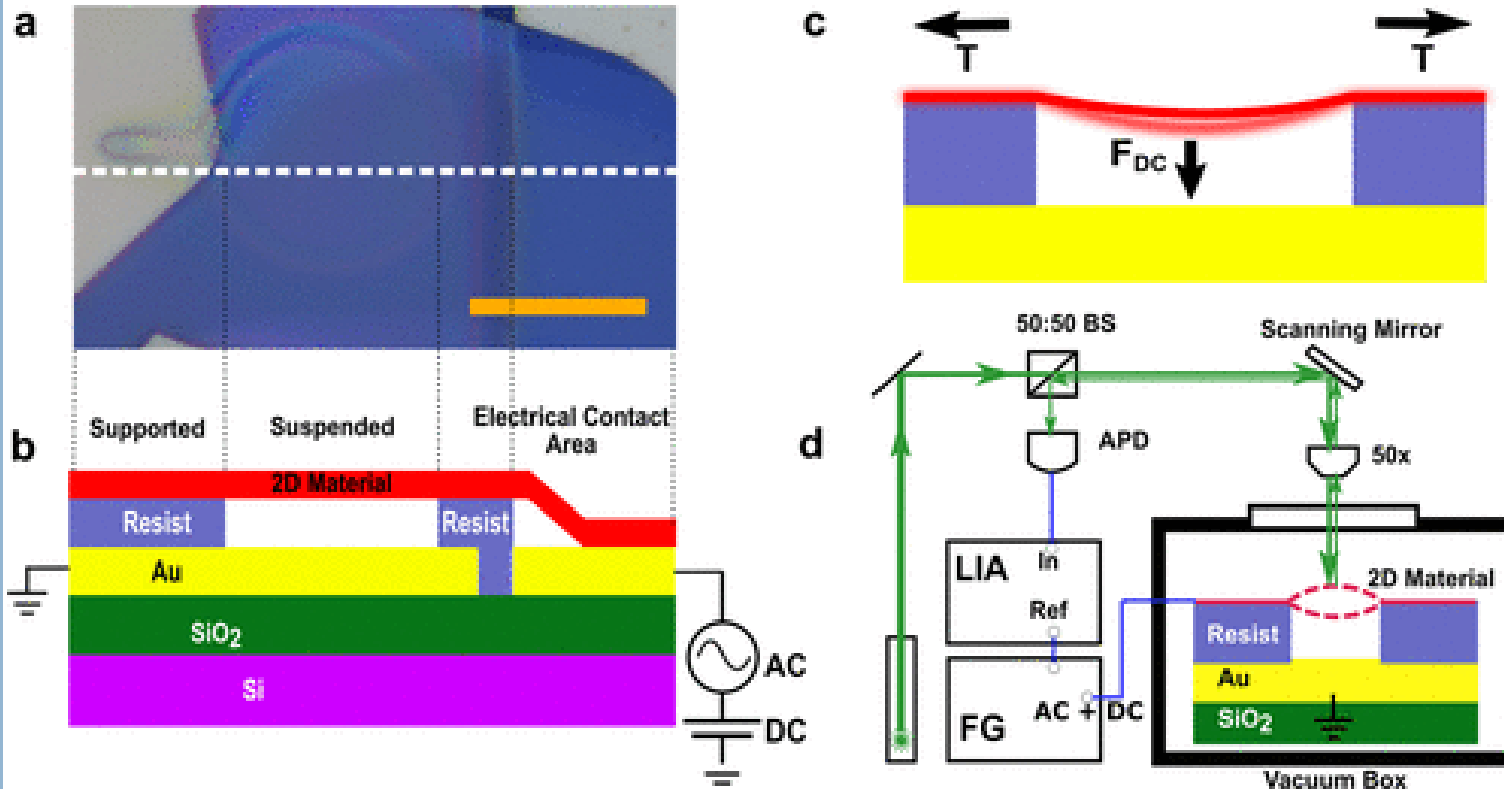
- Directly deposit TMD on dielectric



Metal sulfurization by PECVD

1. Pre-deposit metal layer (e.g. Mo or Ta) on dielectric
2. Convert metal to TMD (e.g. MoS₂ or TaS₂)

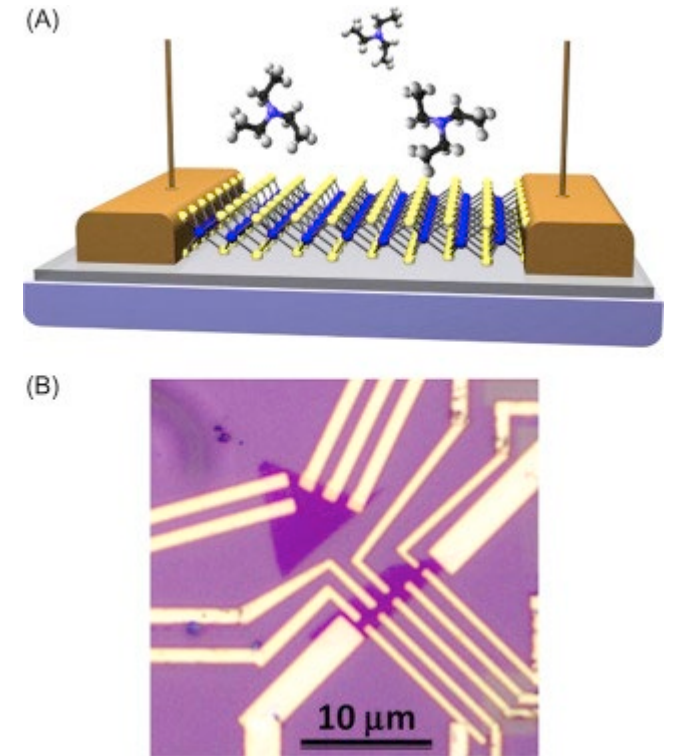
Sensor applications



J. C. Esmenda et al, ACS Appl. Nano Mater. 2022

- Utilize the mechanical properties of 2D materials to realize an optical-mechanical energy conversion.
- It can be used in photon detectors, gas or heat sensor

Gas sensor



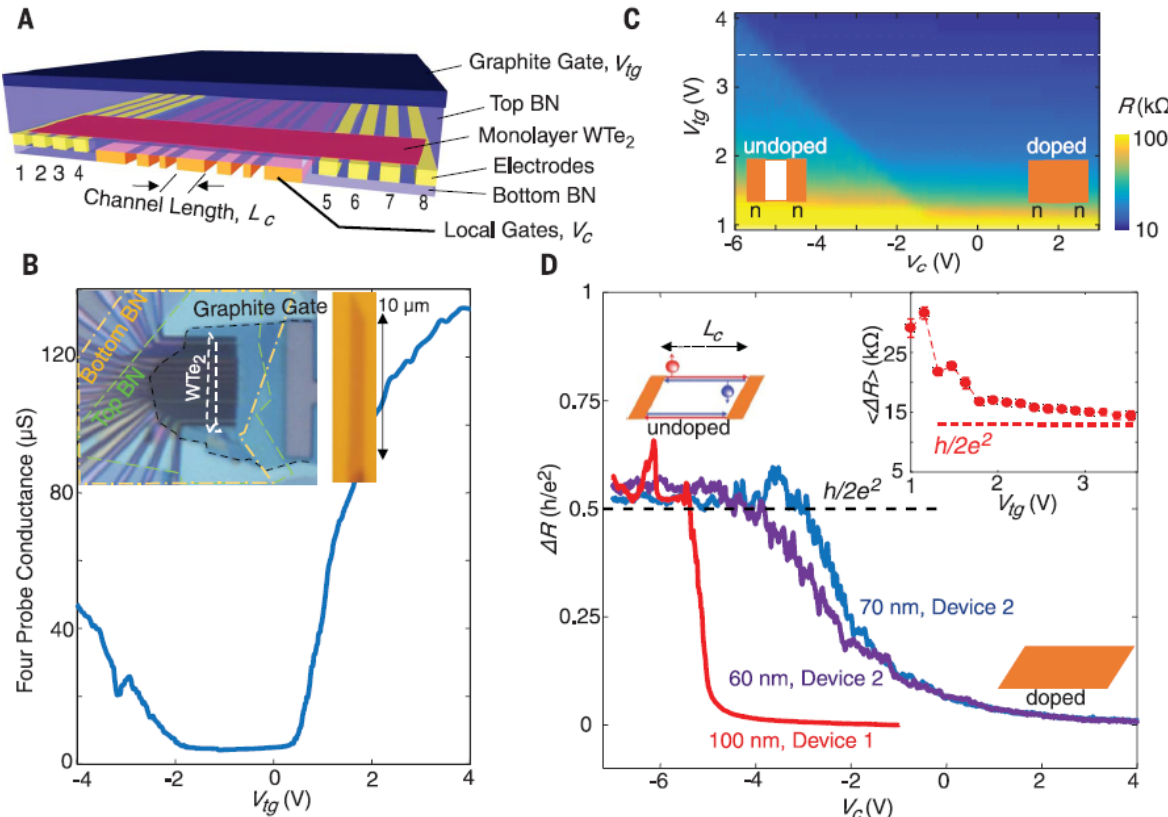
F. K. Perkins et al. Nano Letter (2013)

Transition Metal Dichalcogenides

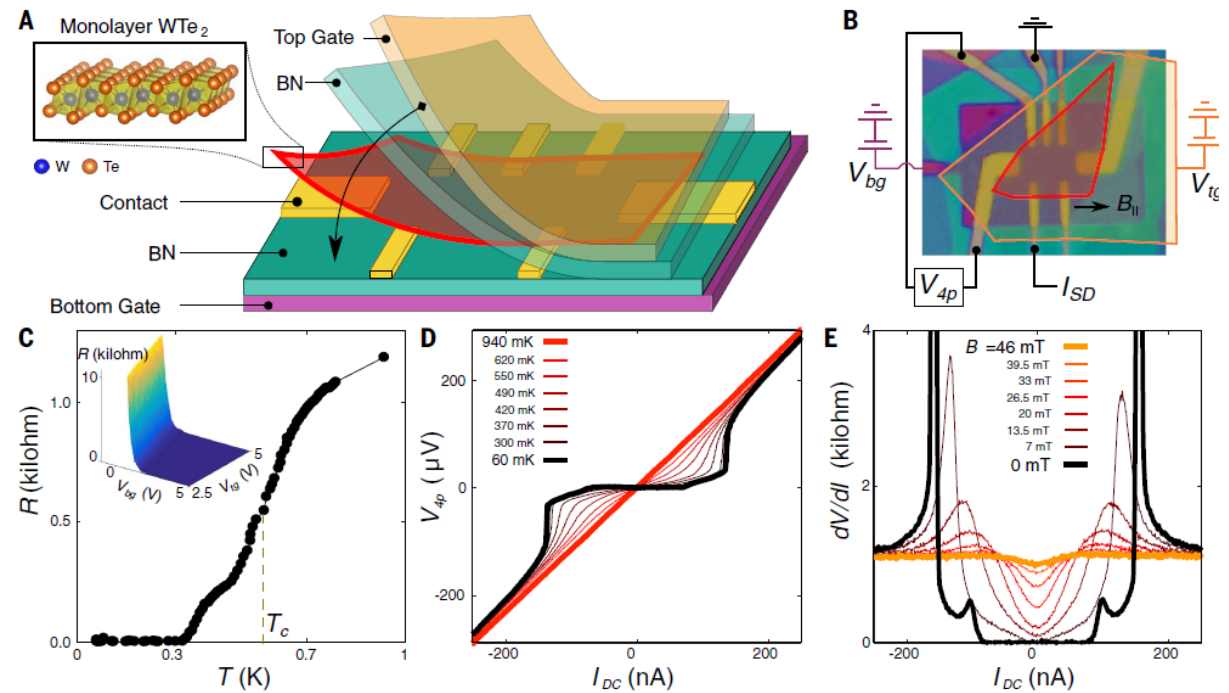
WTe₂

Quantum Spin Hall

Superconductivity



S. Wu et al Science (2018)

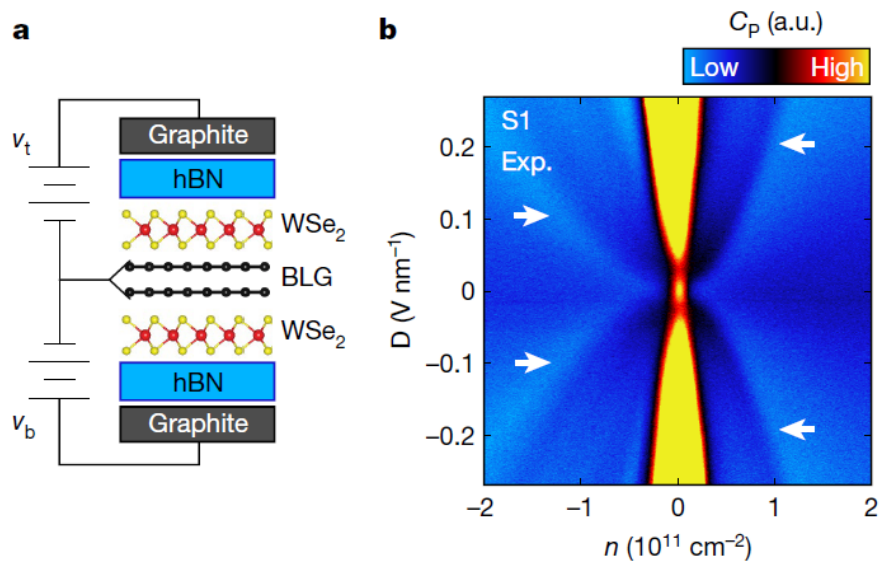


V. Fatemil et al Science (2018)

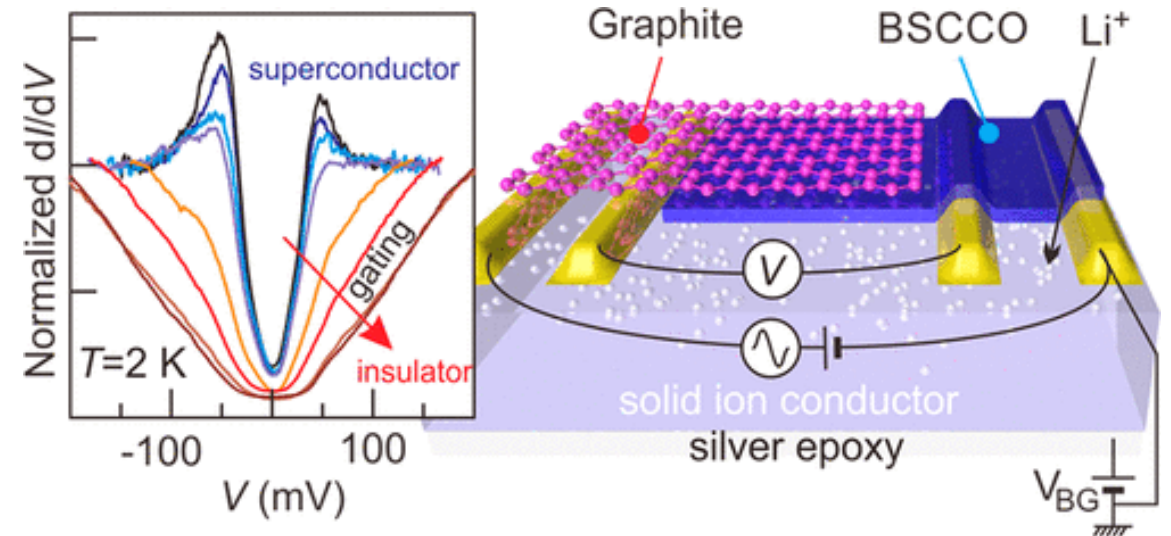
Hybrid material systems

Induce spin-orbital coupling in BLG

Coupling layered superconductor with graphite

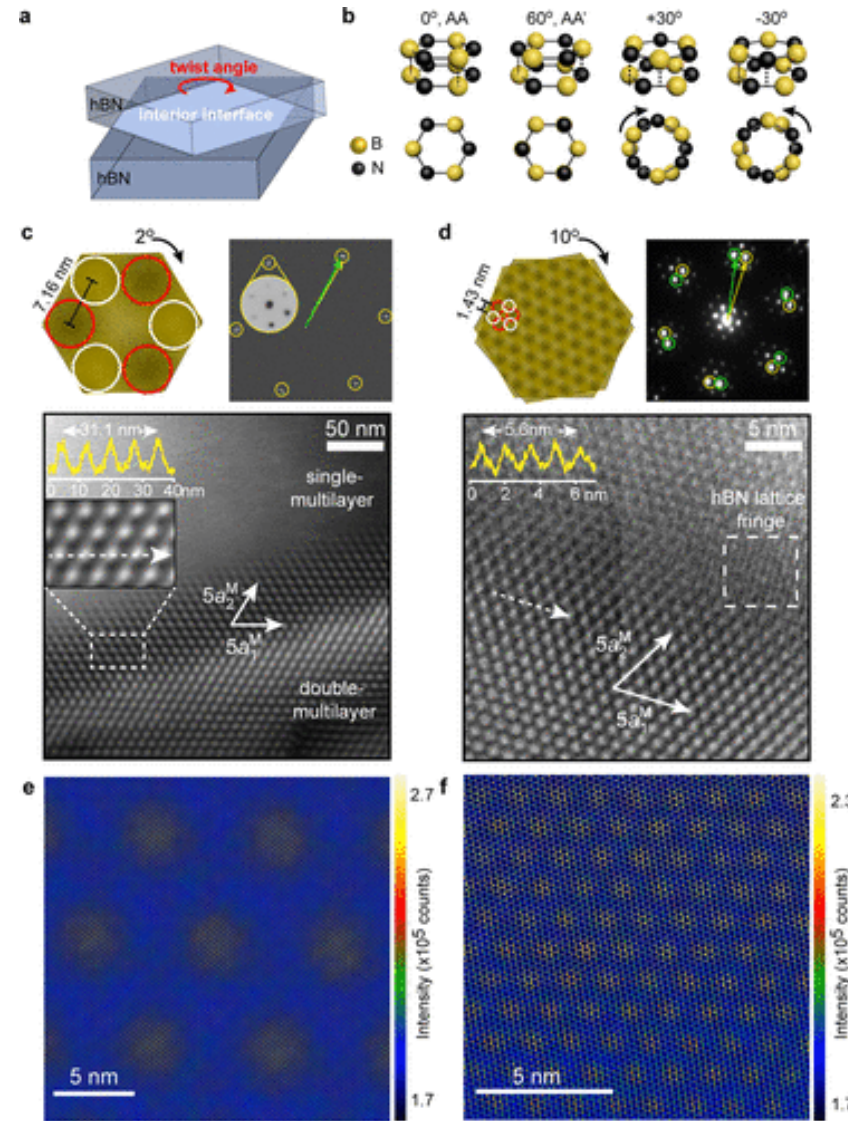
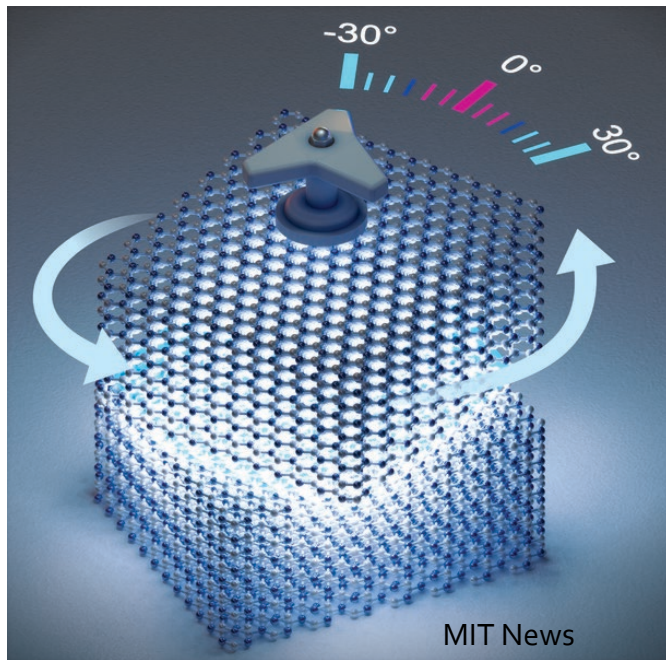


J. Island et al. Nature 2019



M. Liao et al. Nano Letter 2018

Twist



- Twisted hBN forming a superlattice structure. By controlling the twisted angle. One can design a particular twisted angle to have the wanted angle.

H.Y. Lee, et al, Nano Letter (2021)