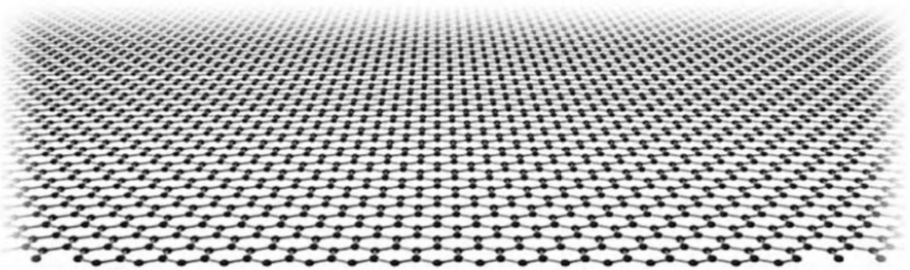
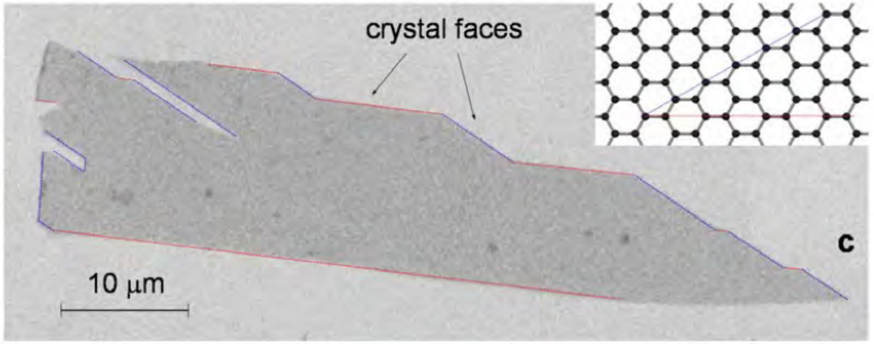
2D CARBON-GRAPHENE

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

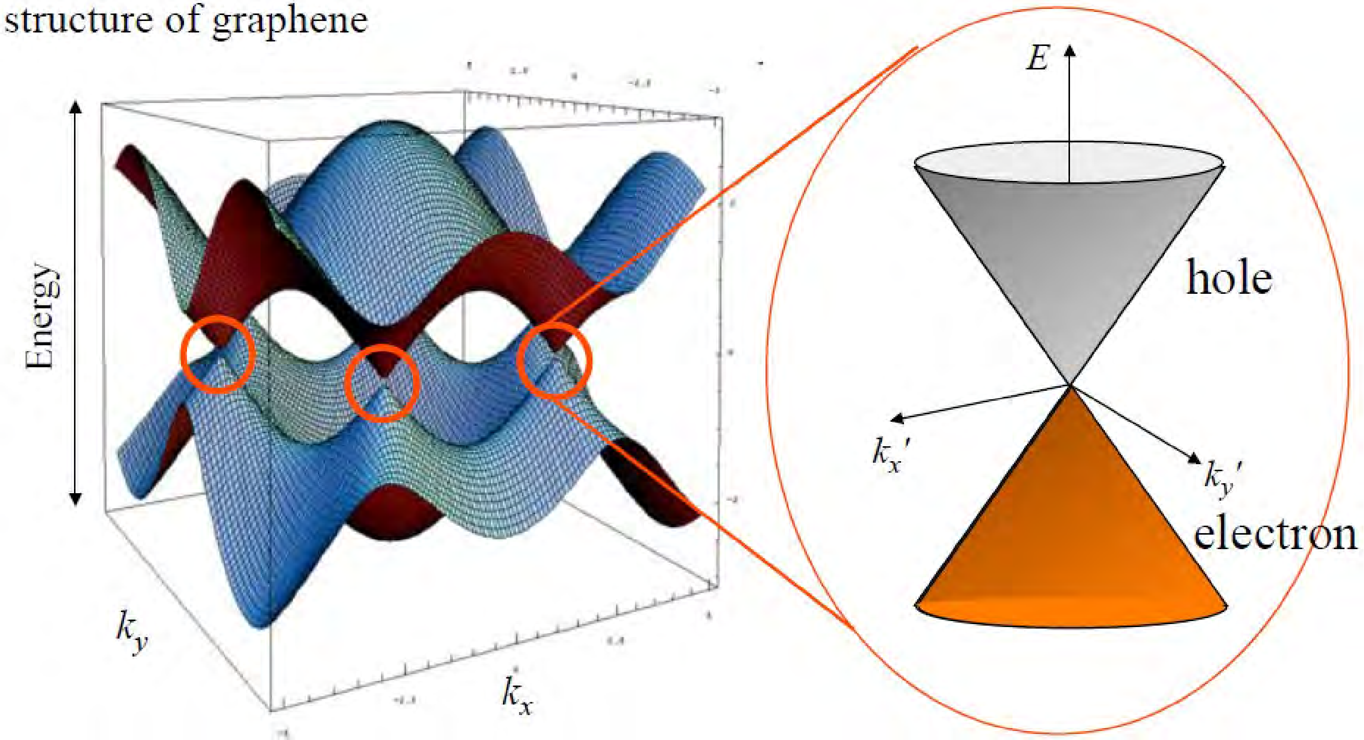
Graphene

Monolayer of carbon





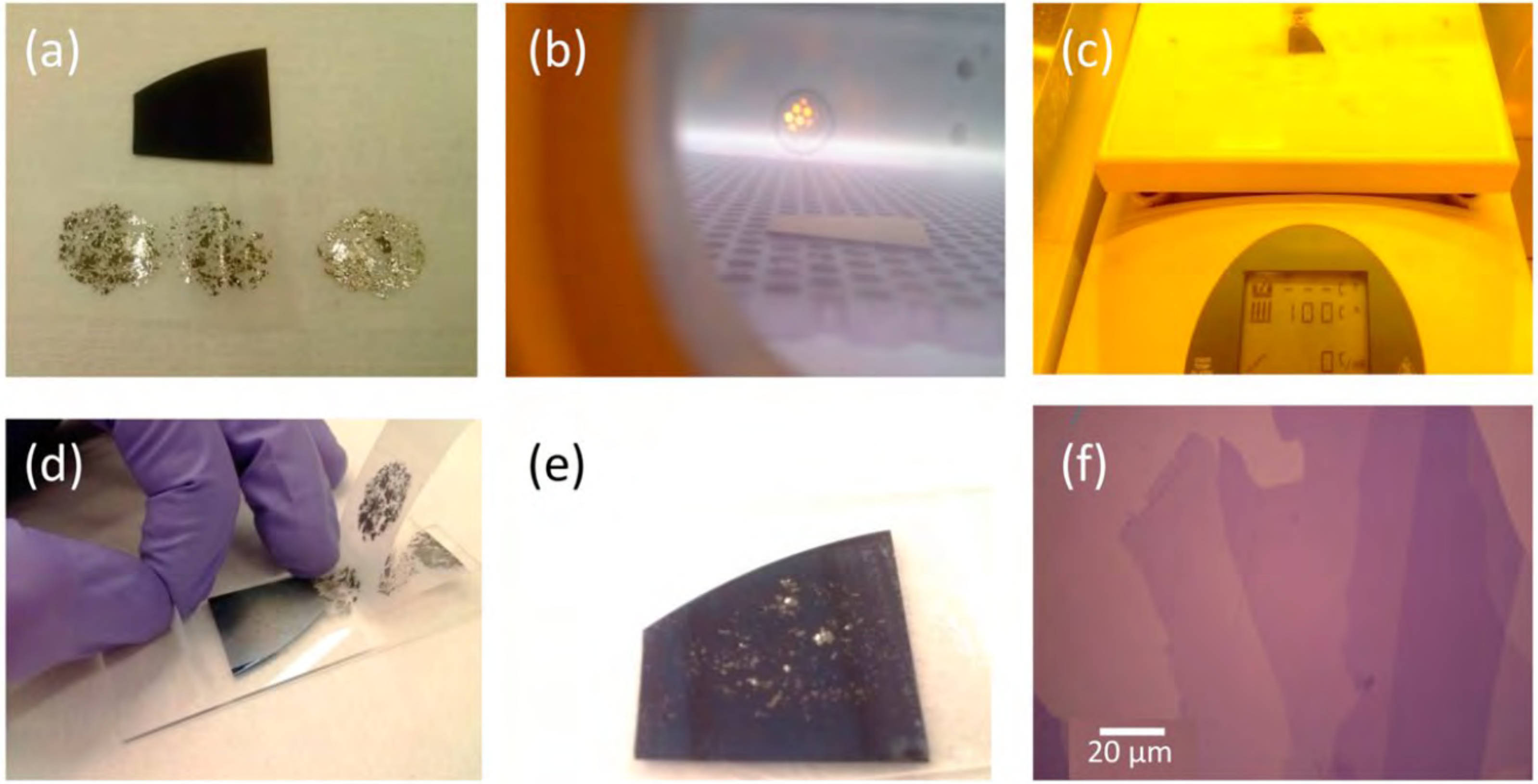
Band structure of graphene



- 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



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

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Andre Geim

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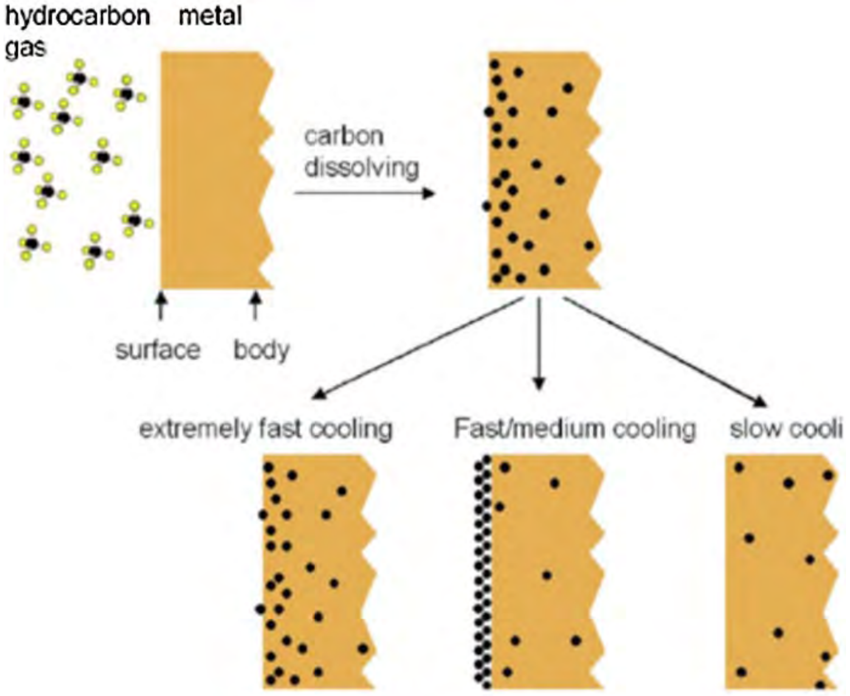
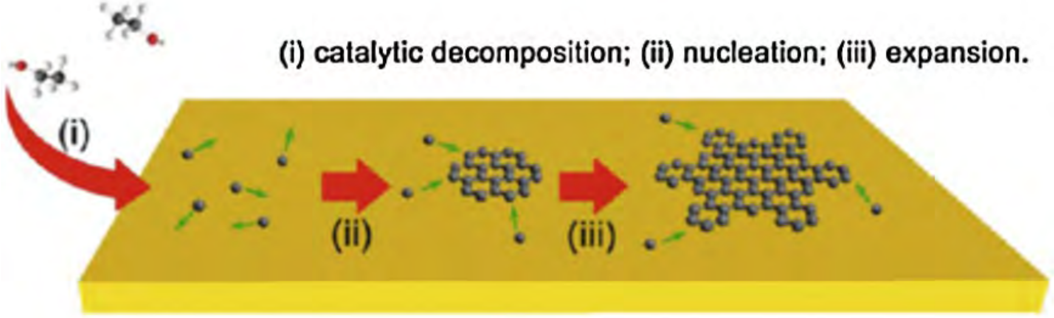
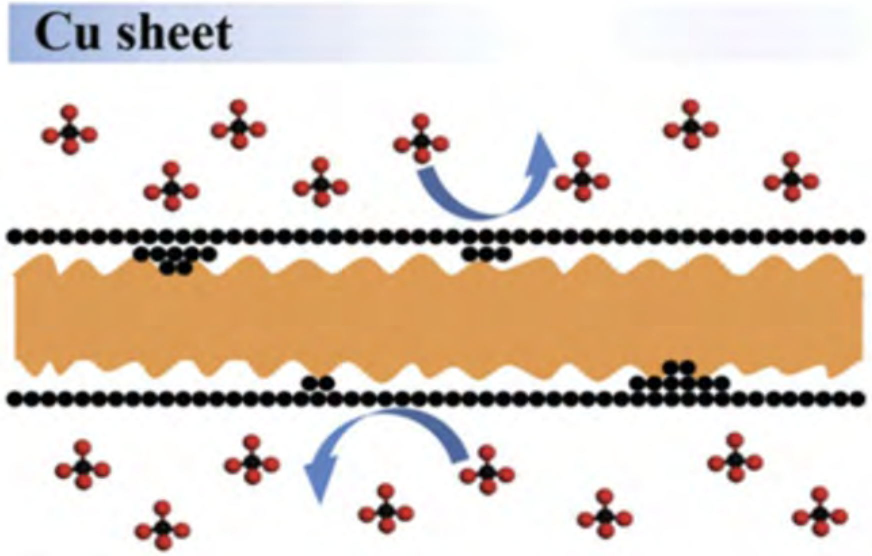
Konstantin Novoselov

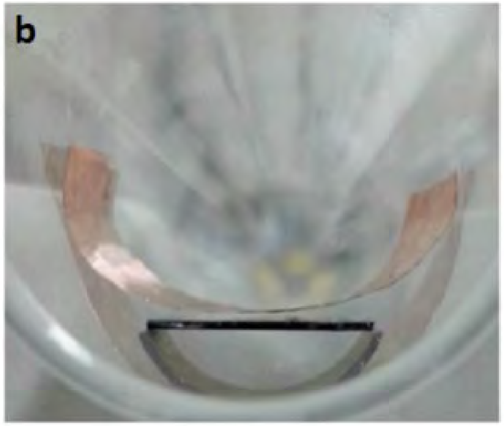
Making of graphene

- CVD



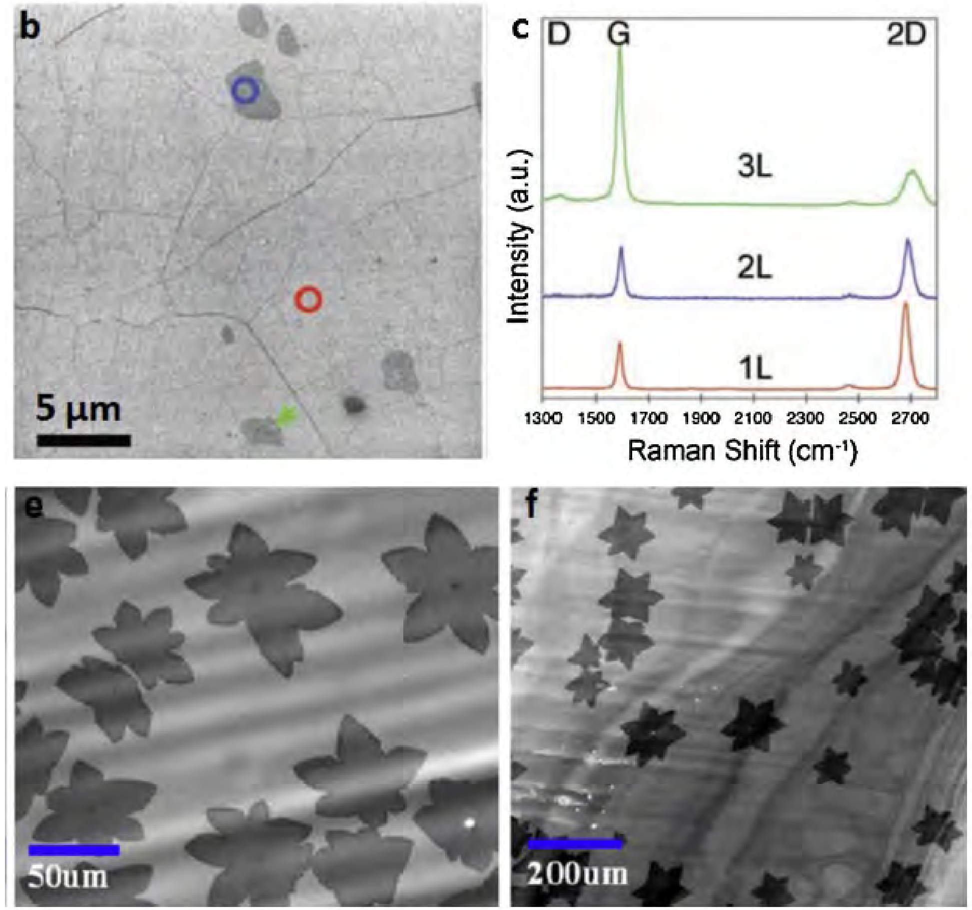


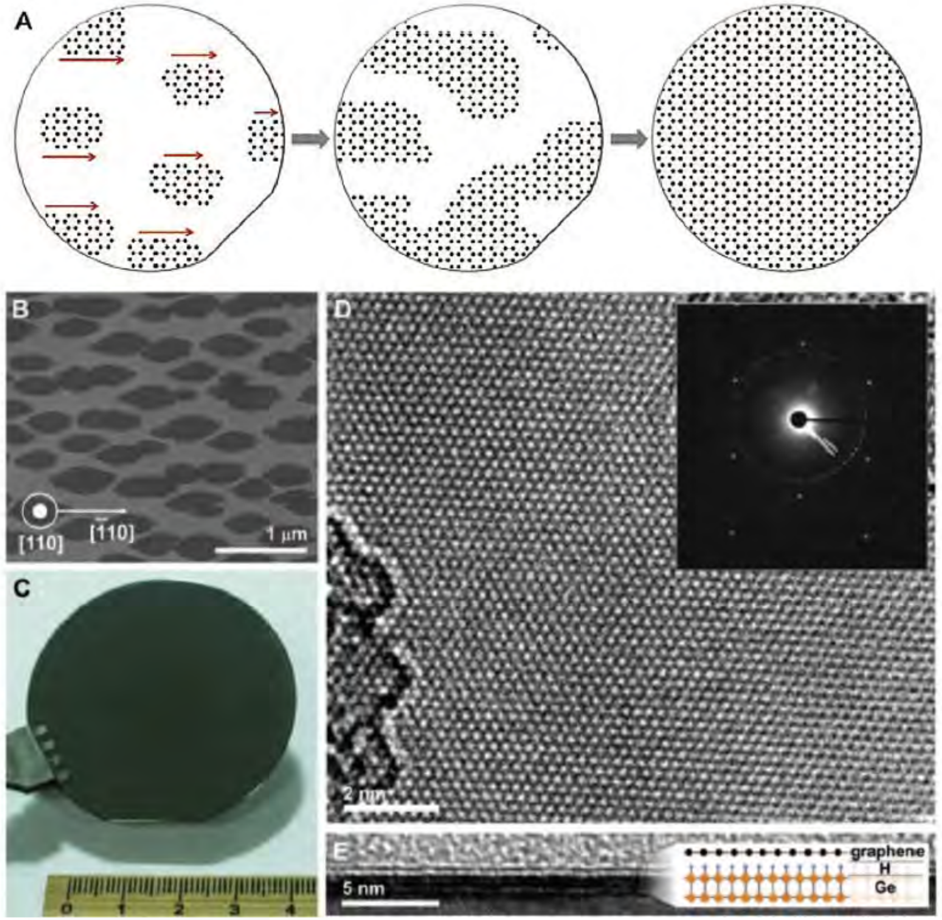




X. Chen et al. Synthetic Metals 210 (2015) 95–108

Making of graphene





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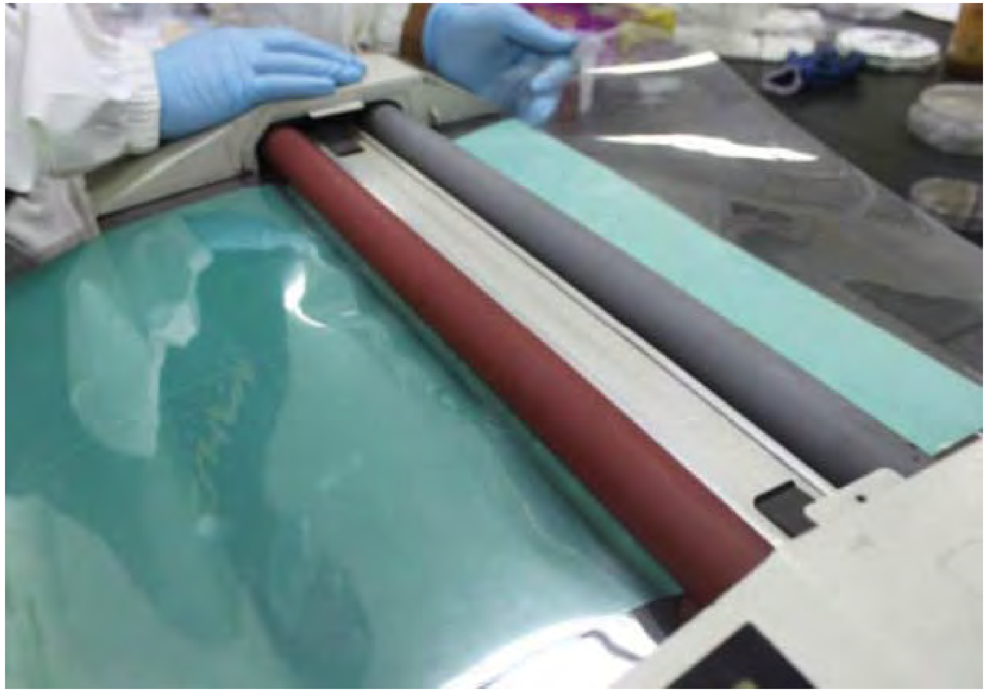
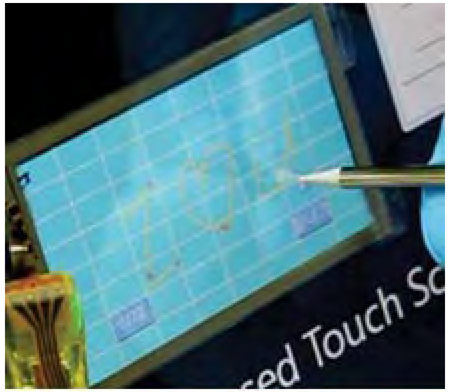
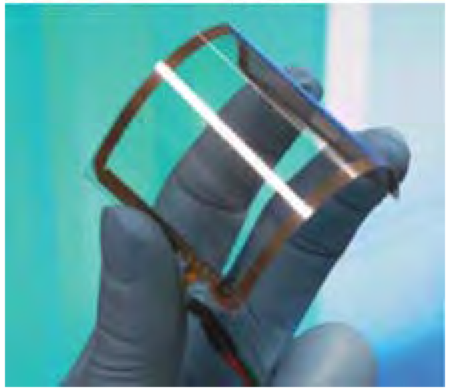
Large scale graphene

- "Printed" graphene for flexible device

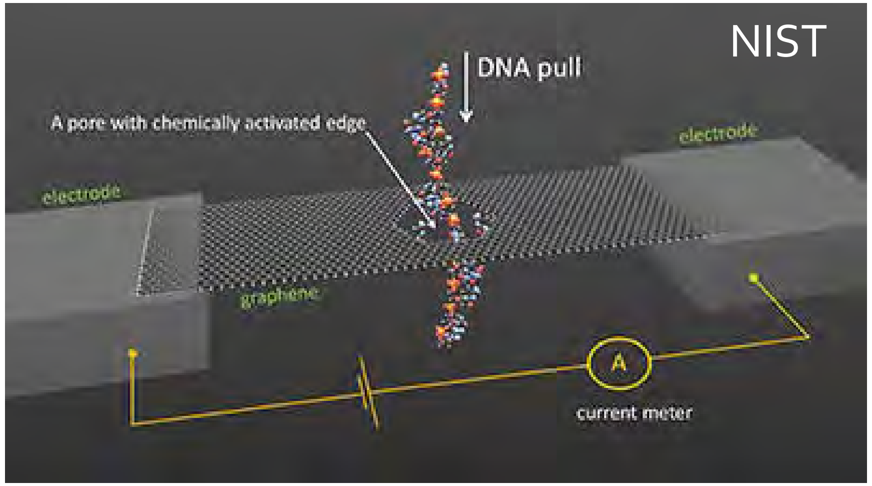




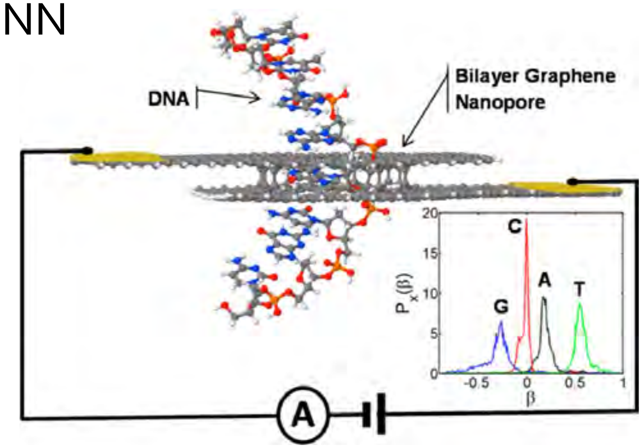


MIT technology review

- DNA sequencing



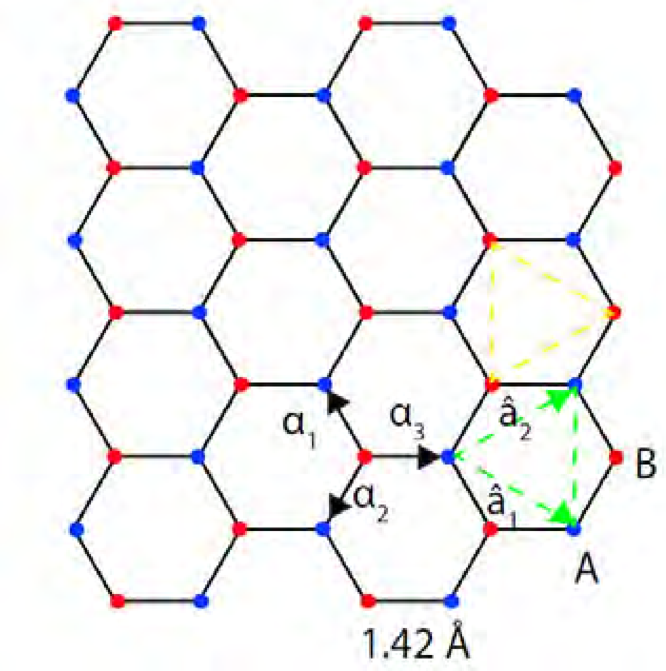
CINN



Electronic structure

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

- Honey cone lattice with two sublattice sites A and B



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

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

Using Bloch theory and considering two lattice sites, we have 4 by4 matrix elements, the wavefunction can be considered as the following :

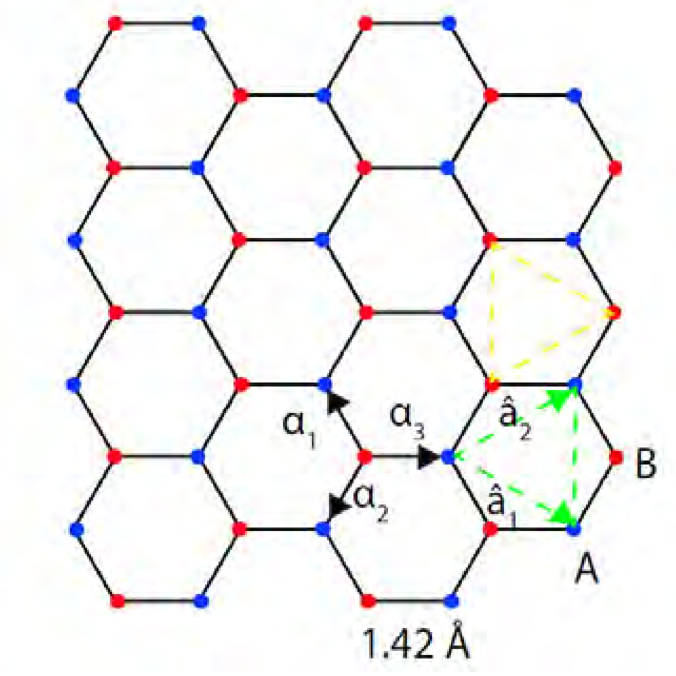
$$\Phi_j(k,r) = \frac{1}{\sqrt{N}}\sum_{i=1}^{N} e^{ikRj,i}\phi_j(r - R_{j,i})$$

Based on the Bloch theory:

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

Jean-No¨el FUCHS and Mark Oliver GOERBIG

Electronic structure



Hamiltonian will meet the conditions:

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

Work out the matrix elements:

$$H_{BB} = H_{AA} \approx \epsilon_{2p}$$

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

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

For the diagonal terms

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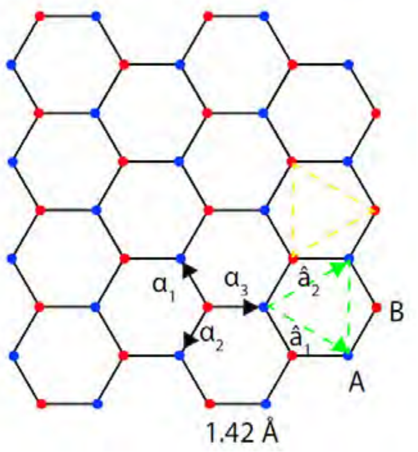
Electronic structure



$$H_{AB} \approx -\frac{1}{N}\sum_{i=1}^{N}\sum_{l=1}^{3} e^{i\mathbf{k}.(\mathbf{R}_{B,l}-\mathbf{R}_{A,i})}\gamma_0 ,$$

$$= -\frac{\gamma_0}{N}\sum_{i=1}^{N}\sum_{l=1}^{3} e^{i\mathbf{k}.\boldsymbol{\delta}_l} \equiv -\gamma_0 f(\mathbf{k})$$

$$f(\mathbf{k}) = \sum_{l=1}^{3} e^{i\mathbf{k}.\boldsymbol{\delta}_l} ,$$

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

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

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

$$f(\mathbf{k}) = \sum_{l=1}^{3} e^{i\mathbf{k}.\boldsymbol{\delta}_l}$$

$$= e^{ik_y a/\sqrt{3}} + 2e^{-ik_y a/2\sqrt{3}}\cos(k_x a/2) .$$

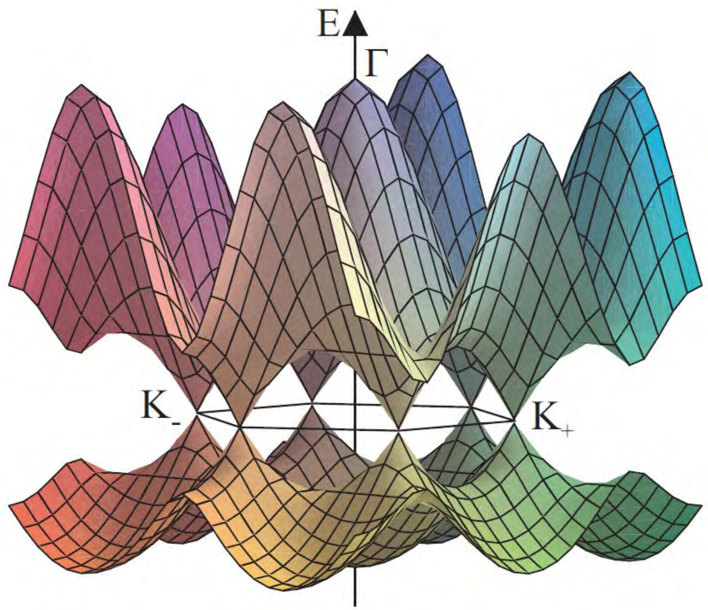
Off diagonal elements for H

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

Electronic structure

The same for the other matrix

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



The matrixes for low energy band:

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

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

$s_0 = 3.033\ eV$ and $\gamma_0 = 0.129\ eV$

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, $f(k) \approx -\frac{\sqrt{3}a}{2\hbar}(\xi p_x - ip_y)$ ξ =+ for K and – for K’

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

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

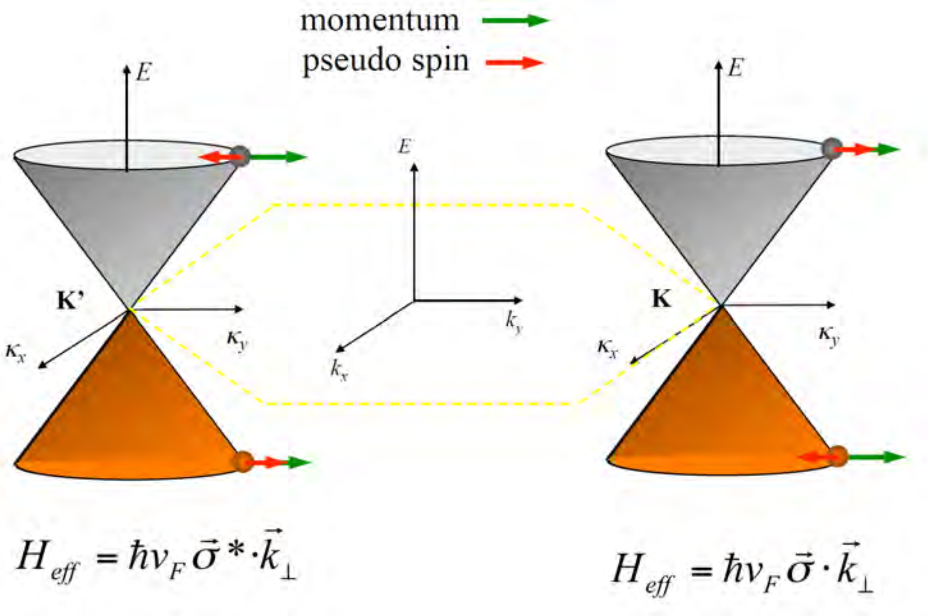
The basis now can be written: $\hat{H}_K = -i\nu\sigma\nabla$ with σ the Pauli matrices

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

The AB (Valleys) sites act as a pseudospin

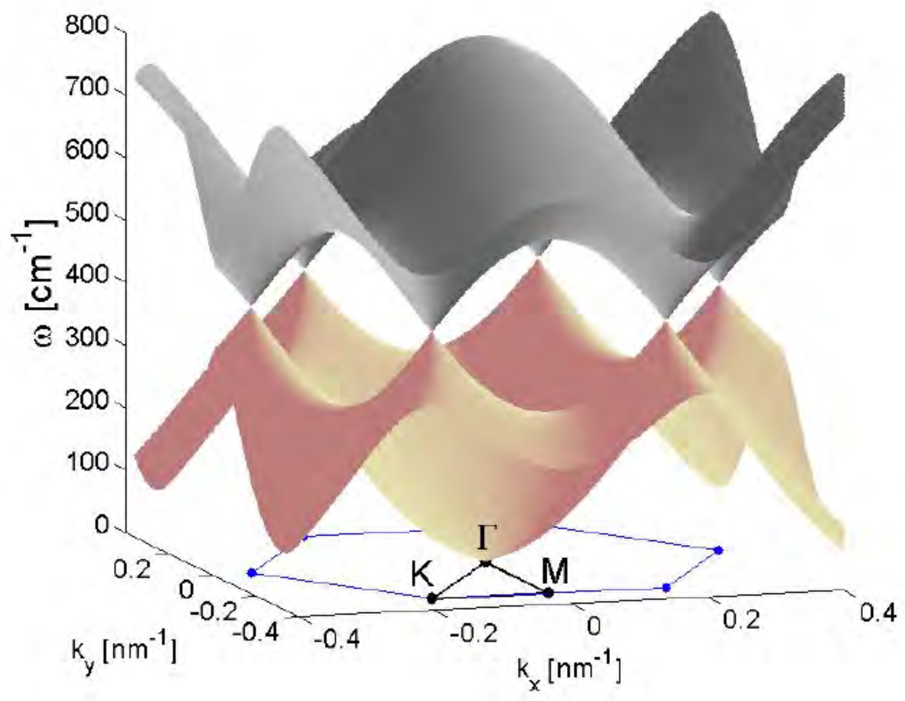
One important property: chiral behavior

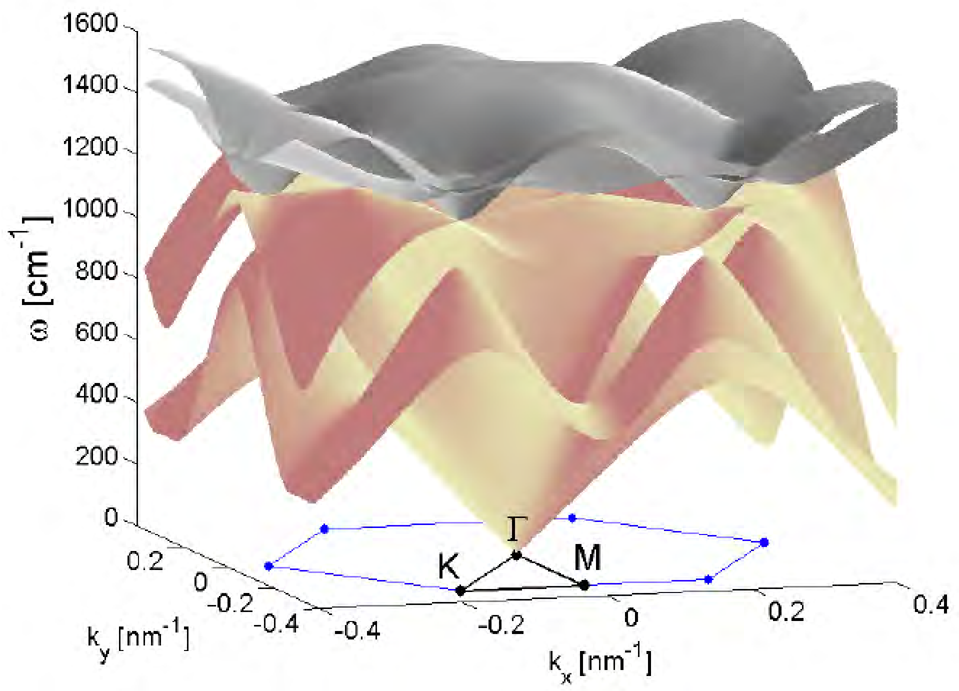
$$\frac{\vec{k}\,\vec{\sigma}}{k}\psi_\pm = \pm\psi_\pm .$$



Phonon dispersion

The out of plane and in-plane phonon mode

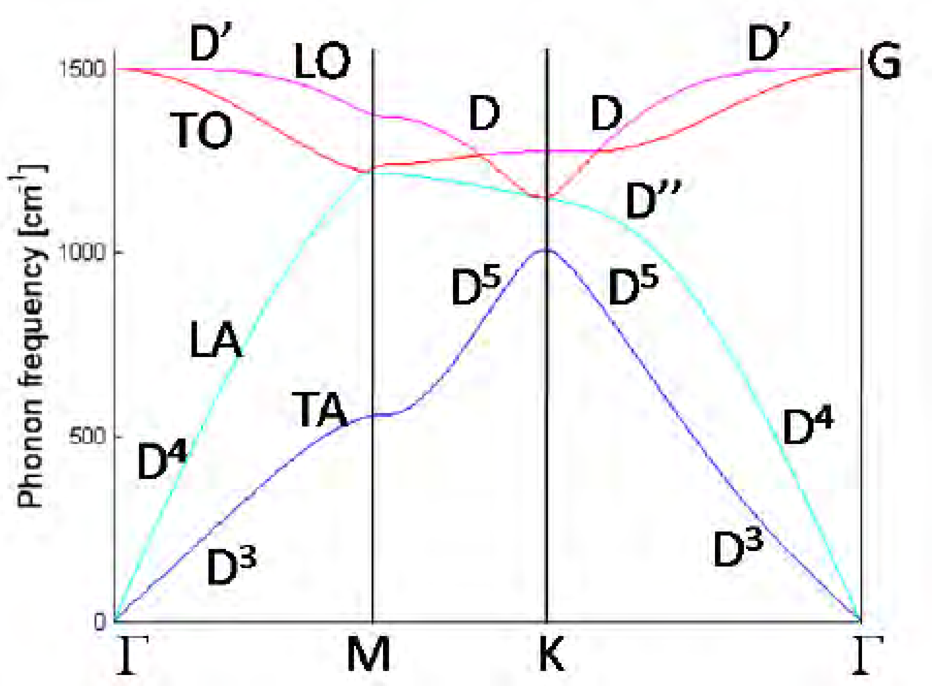


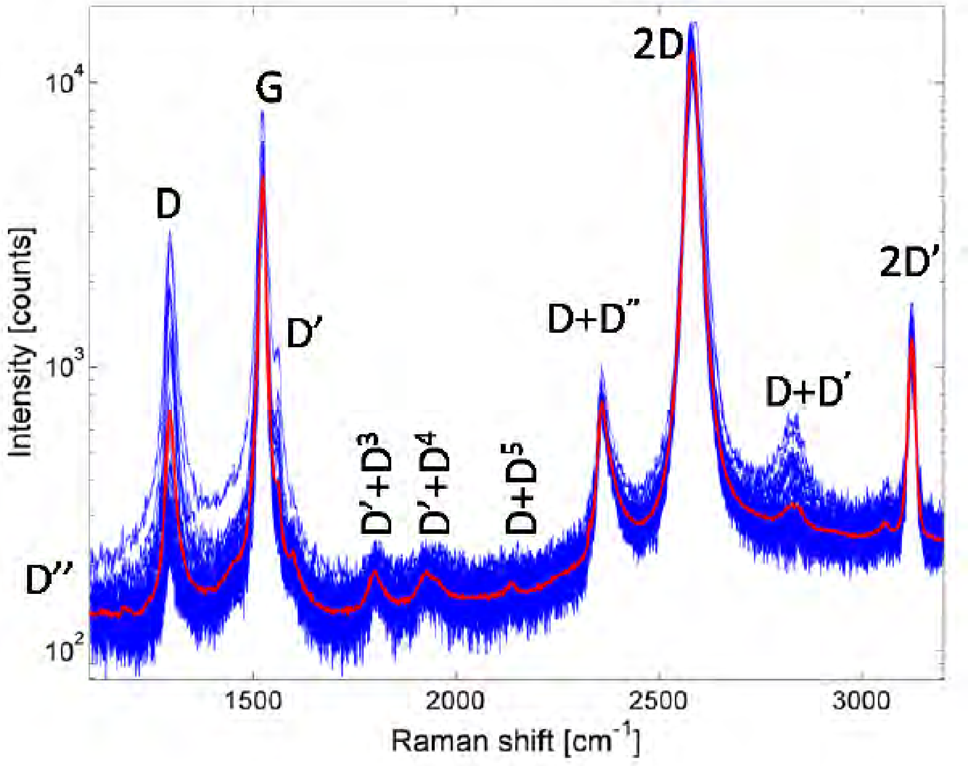


D. R. Cooper et al, arXiv:1110.6557 (2011)

Phonon dispersion

Theoretical calculation of in-plane modes

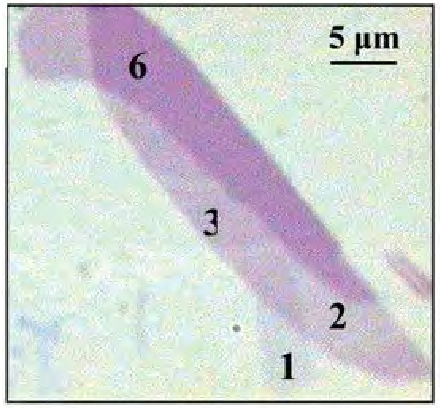




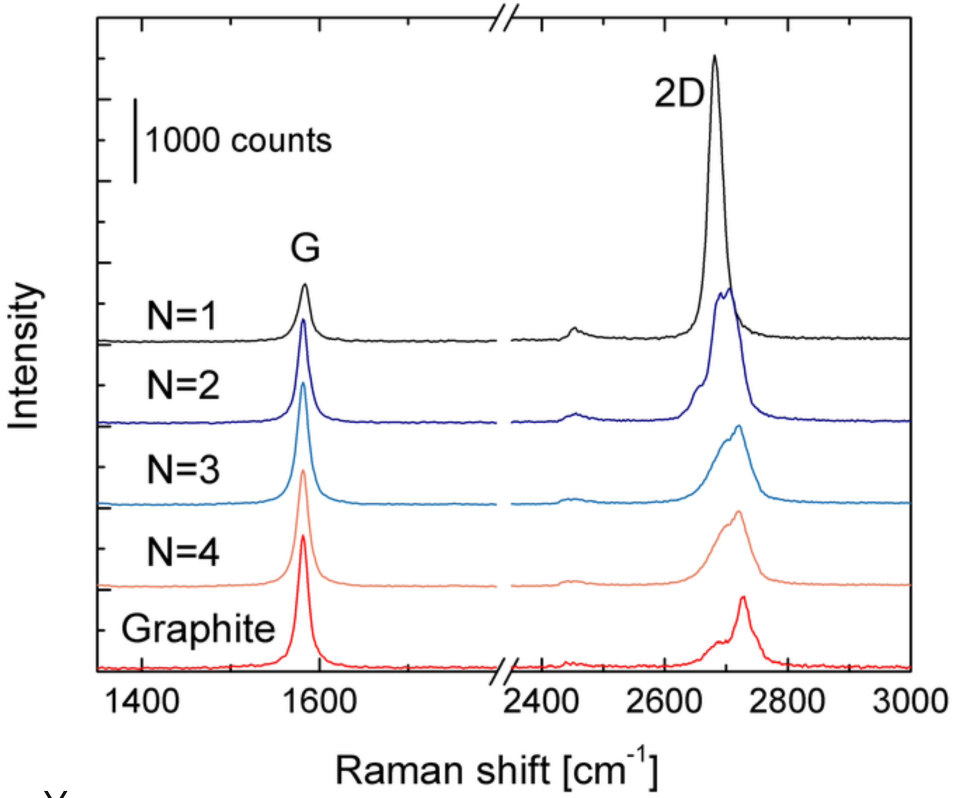
D. R. Cooper et al, arXiv:1110.6557 (2011)

Layer dependence

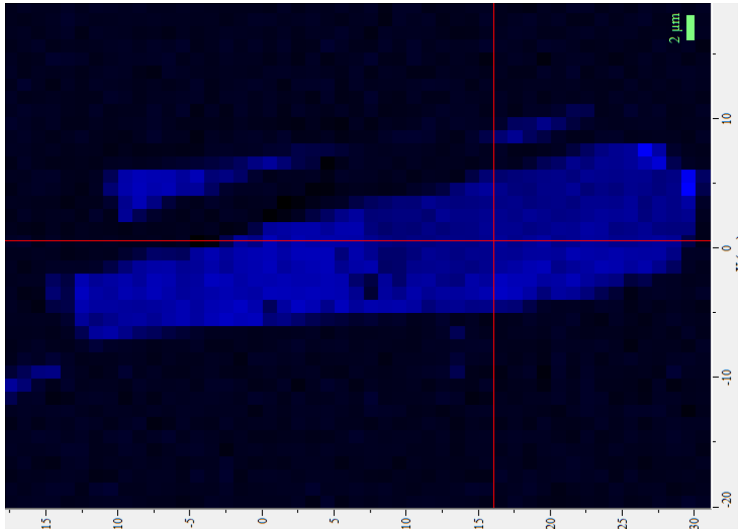
- Raman spectra

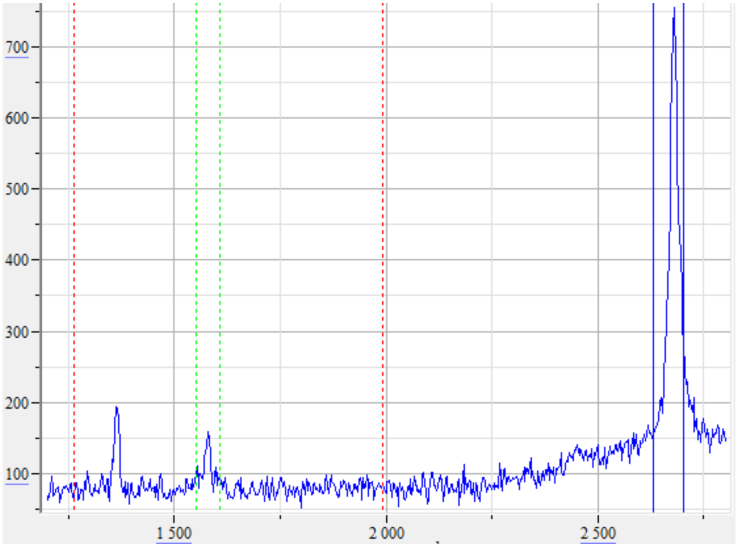


Y Lan et al.
Crystal 2018



Yu, 2010





Other important properties

- Berry phase

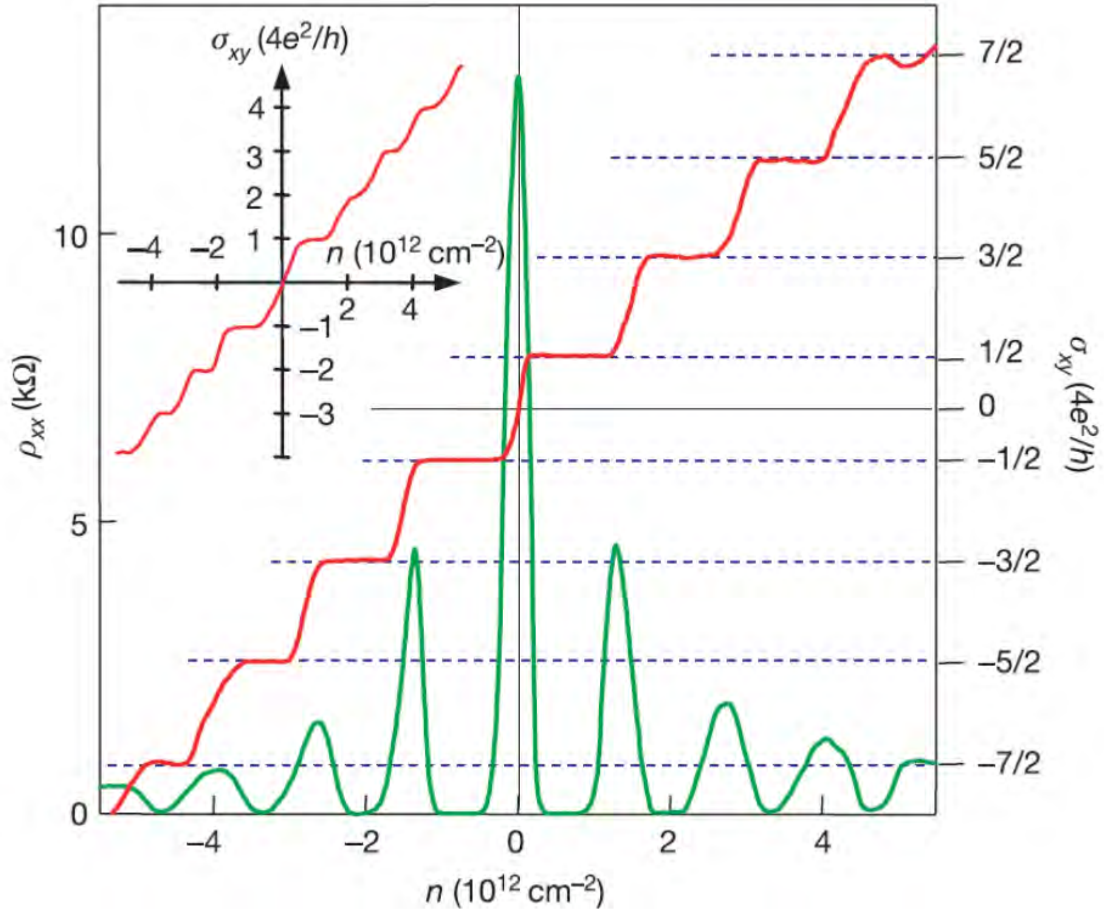
One can consider the Berry phase as a geometrical phase under the pseudospin rotation.

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

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.

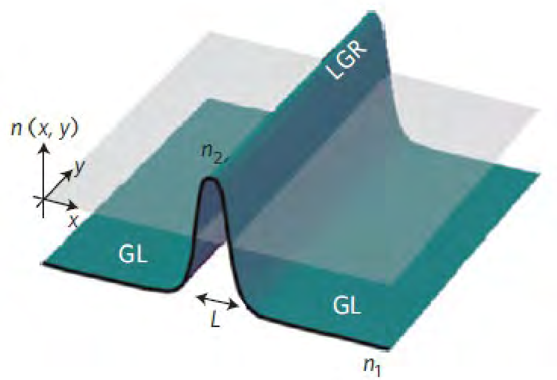
$$\sigma_{xy} = (N + \frac{1}{2})(\frac{4e^2}{h})$$

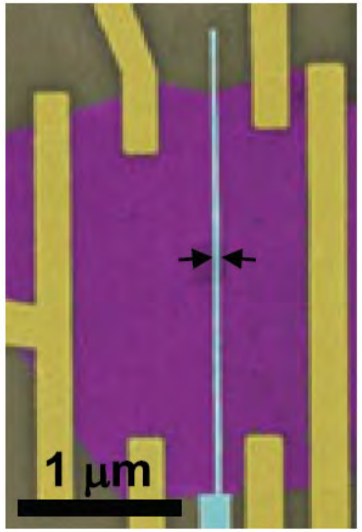


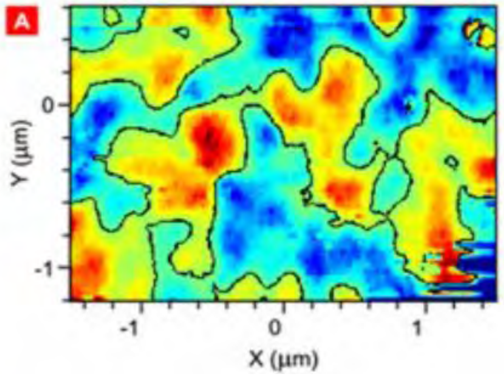
Other important properties

- Klein paradox

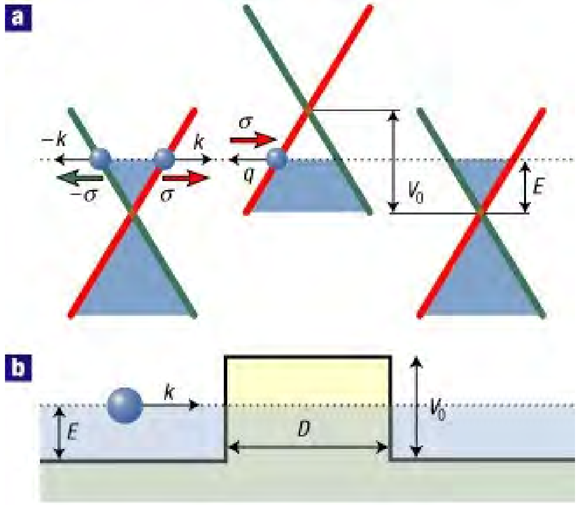
When electrons or holes encounter a barrier at DP, electron or hole backscattering is forbidden because of charity. Therefore, the only path is to convert to another type of particle which maintains the momentum conservation.



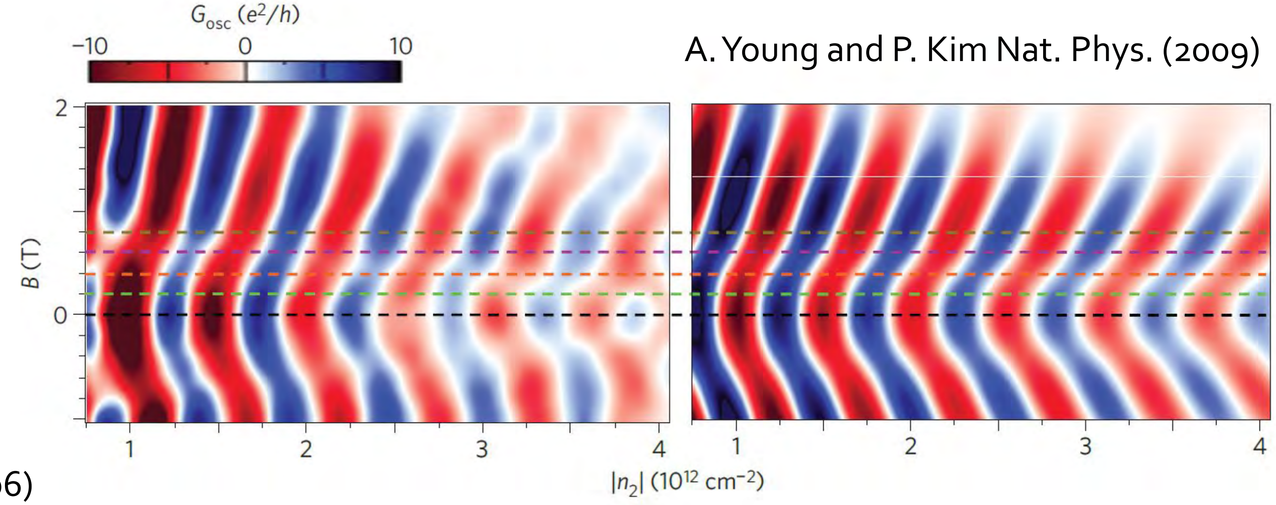




Martin *et al.* Nature Phys. (2008)



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

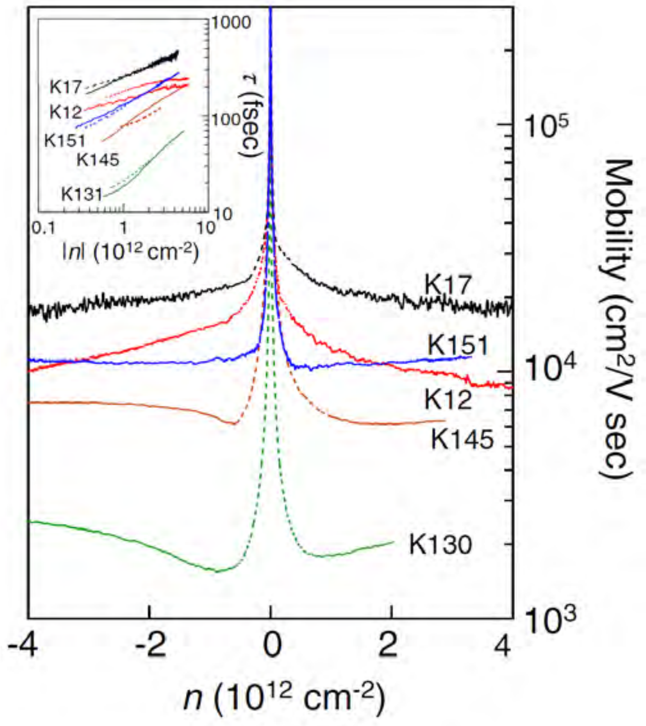


A. Young and P. Kim Nat. Phys. (2009)

Graphene research

Classical mobility

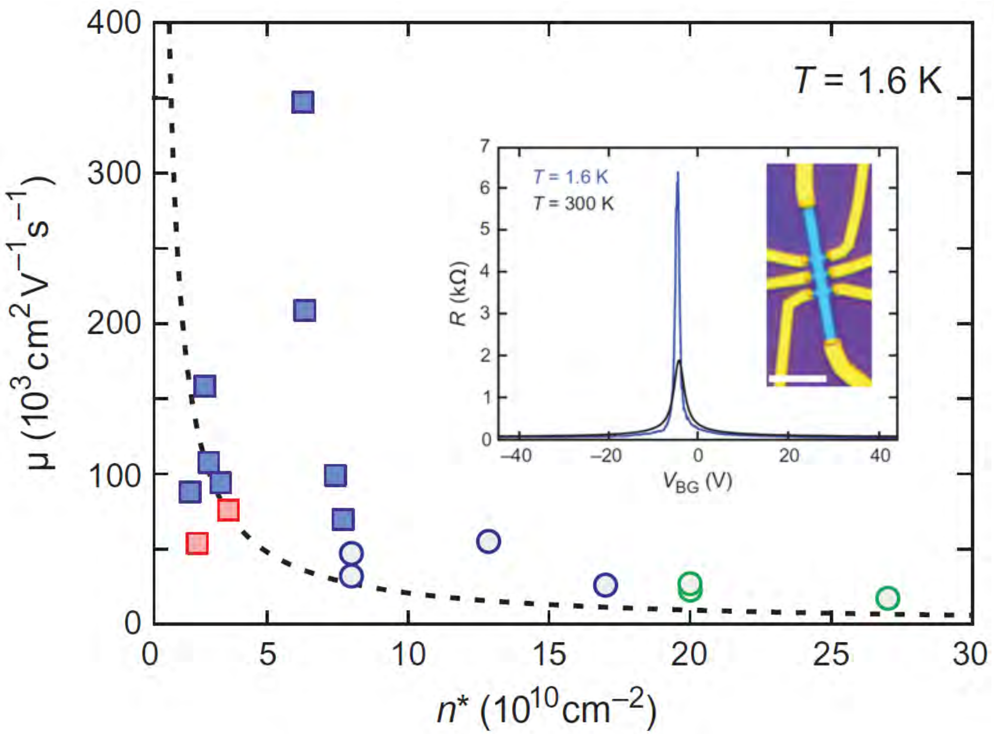
Exfoliated graphene



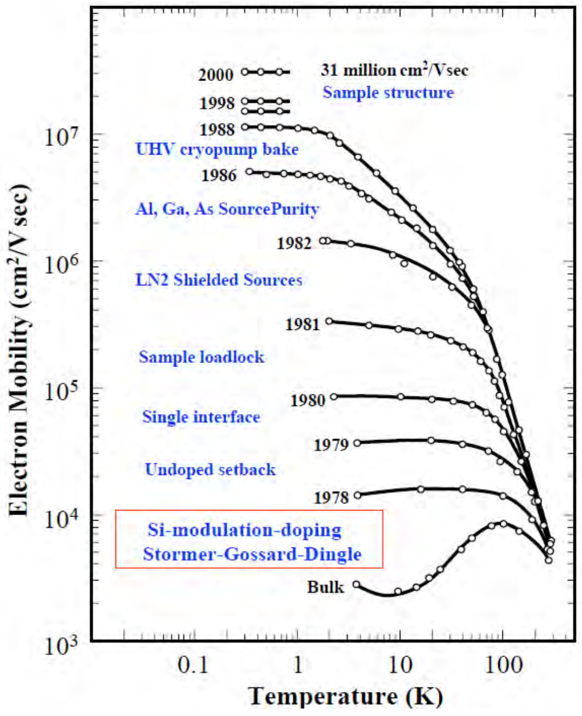
Y.-W. Tan et al. PRL (2007)

Quantum mobility

CVD graphene

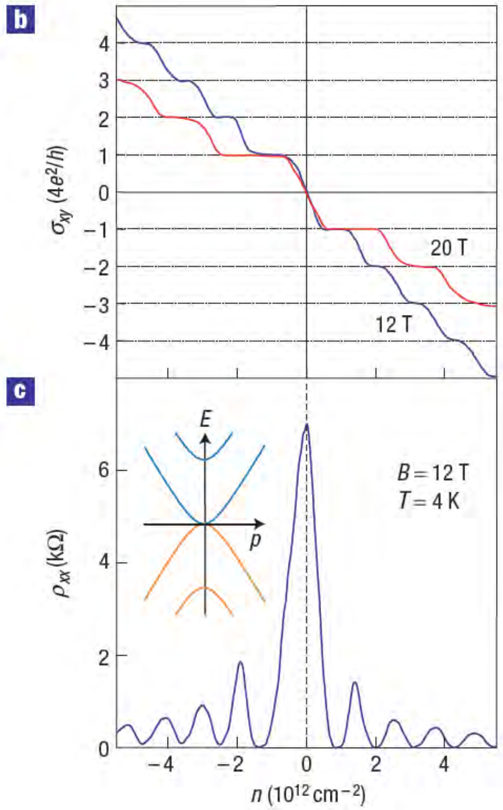


L. Banszerus et al. Science Advances (2015)



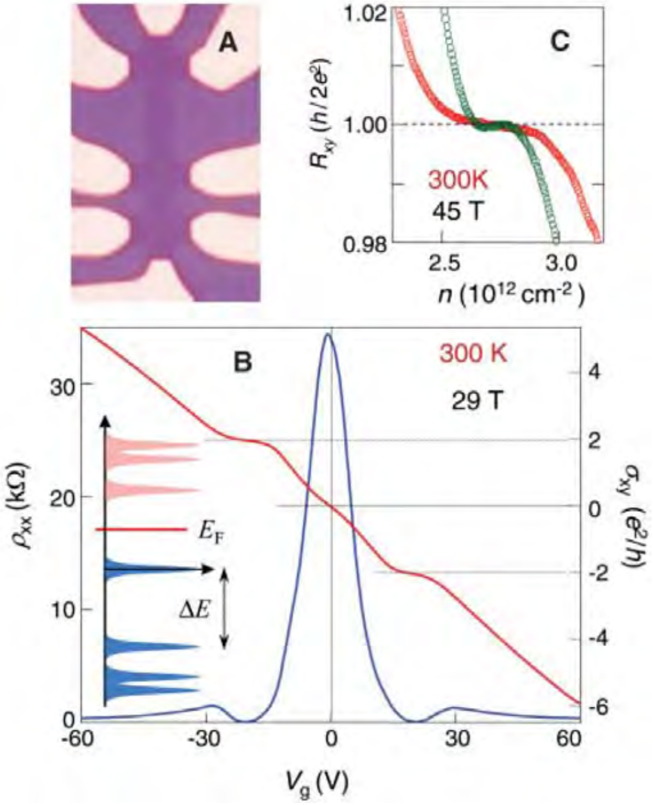
Graphene research

Quantum Hall effect



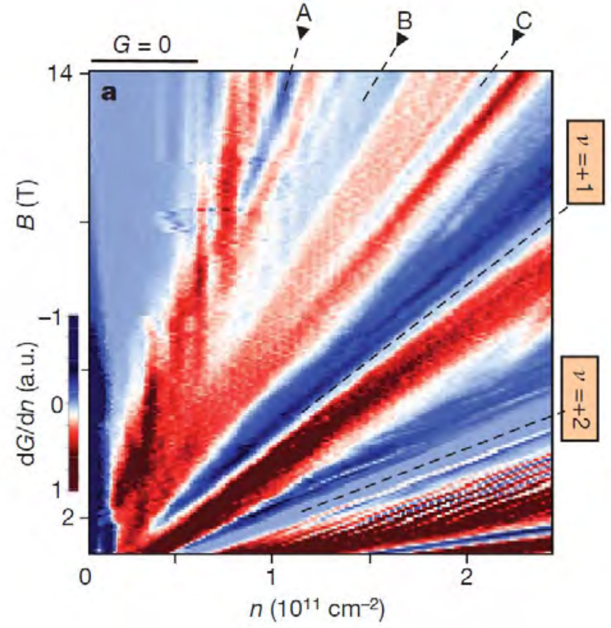
K. S. Novoselov et al. Nat. Phys. (2006)

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

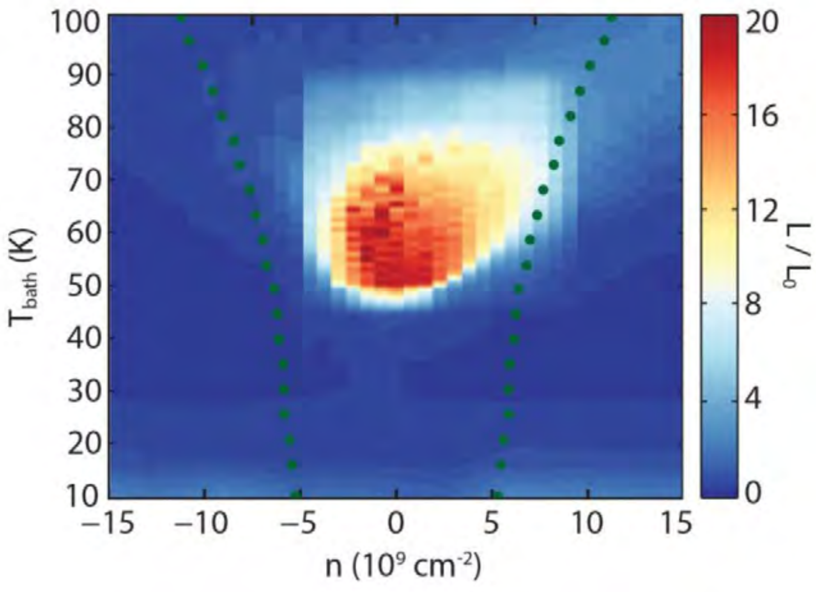
Kirill I. Bolotin, et al. Nature (2009)

Graphene research

- Thermal behavior

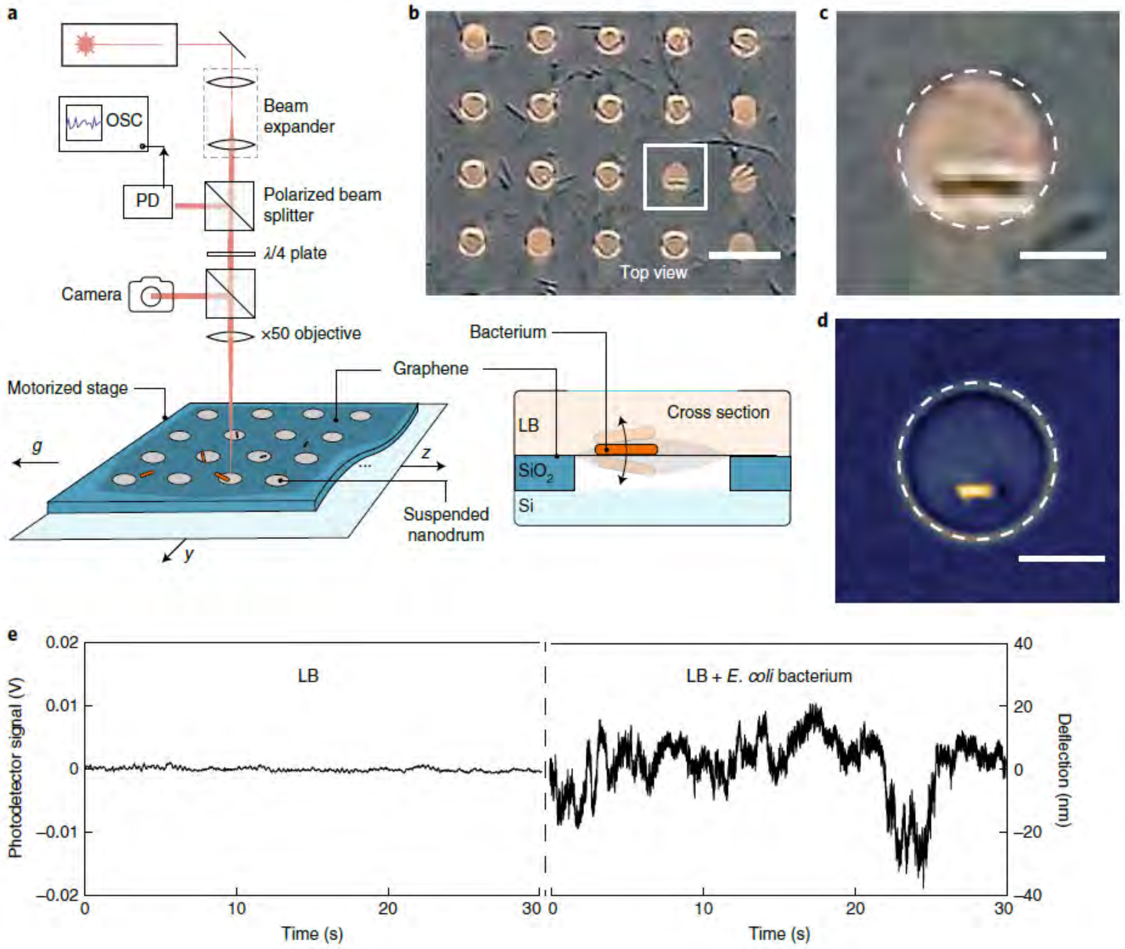
$$\mathcal{L} \equiv \frac{\kappa_e}{\sigma T} = \frac{\pi^2}{3}\left(\frac{k_B}{e}\right)^2 \equiv \mathcal{L}_0$$

Breakdown of Weidman-Franz law



J. Crossno et al. Science(2016)

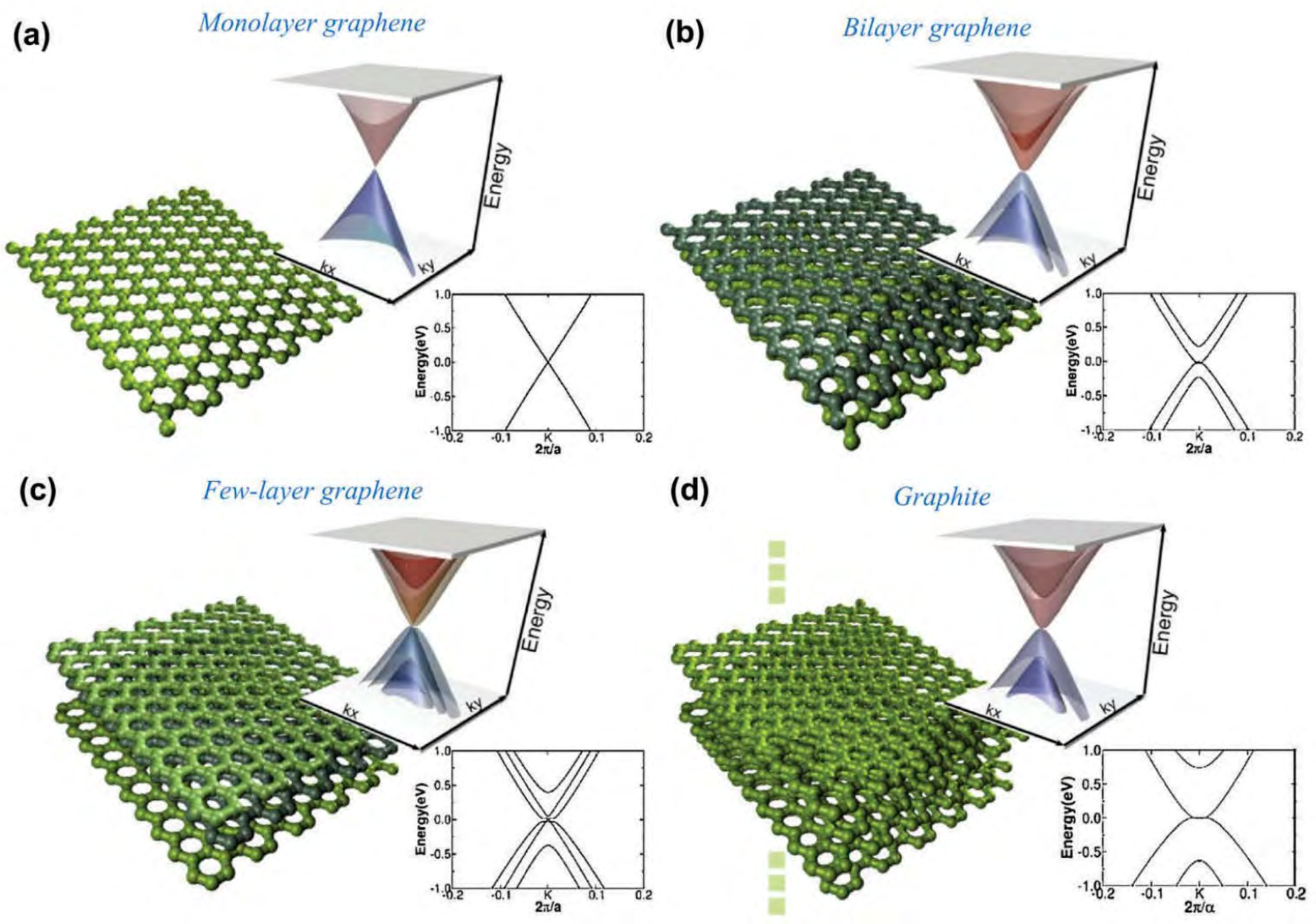
- Bio-nanotechnology



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

More layers of graphene

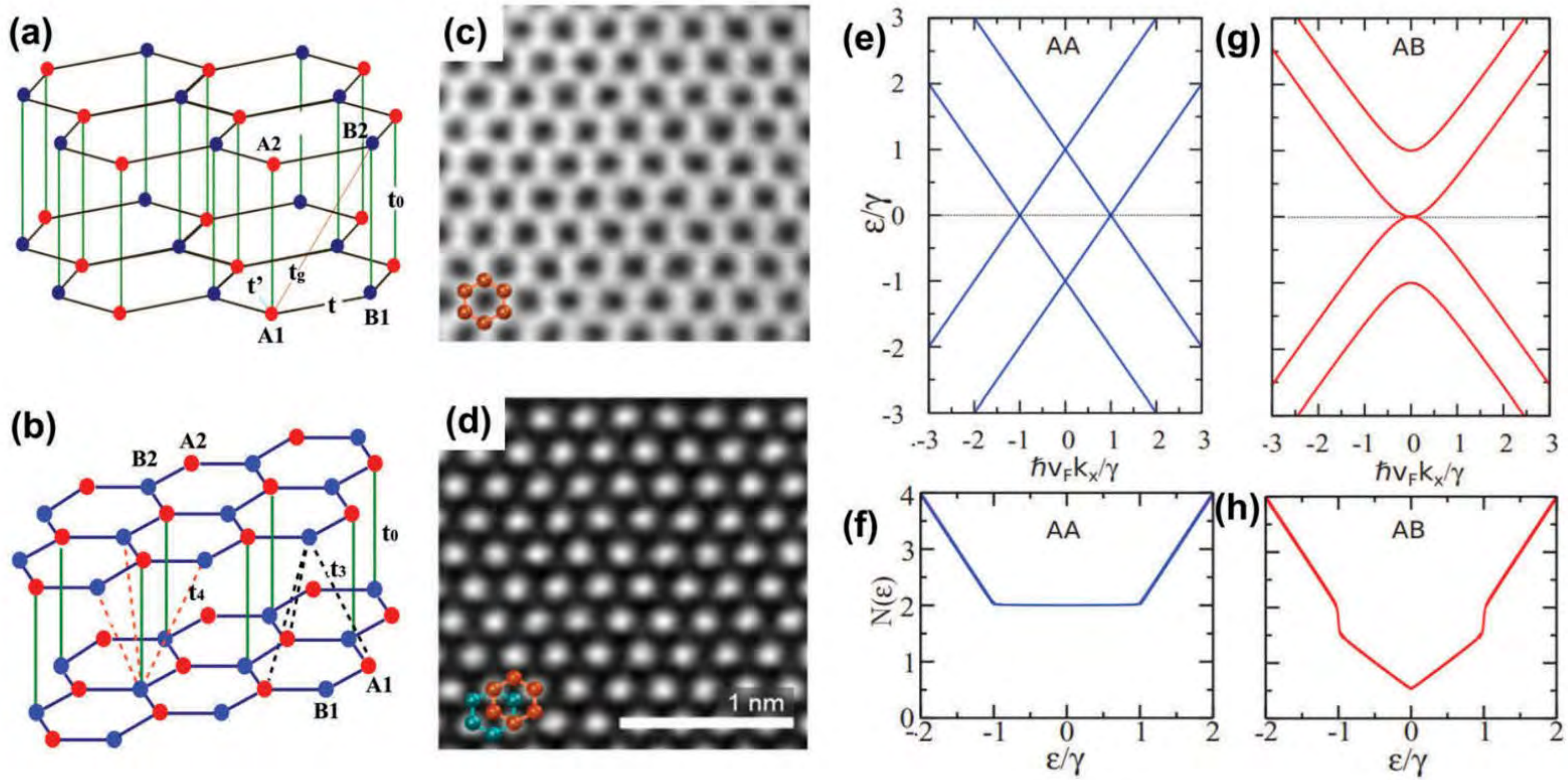
- Number of layers will influence the band and dispersion.
- From massless particles to a massive particle case.
- For two or few layers, there is also a difference in the way graphene sits on top of each other



G. Yang et al. Sci. Technol. Adv. Mater. (2018)

More layers of graphene

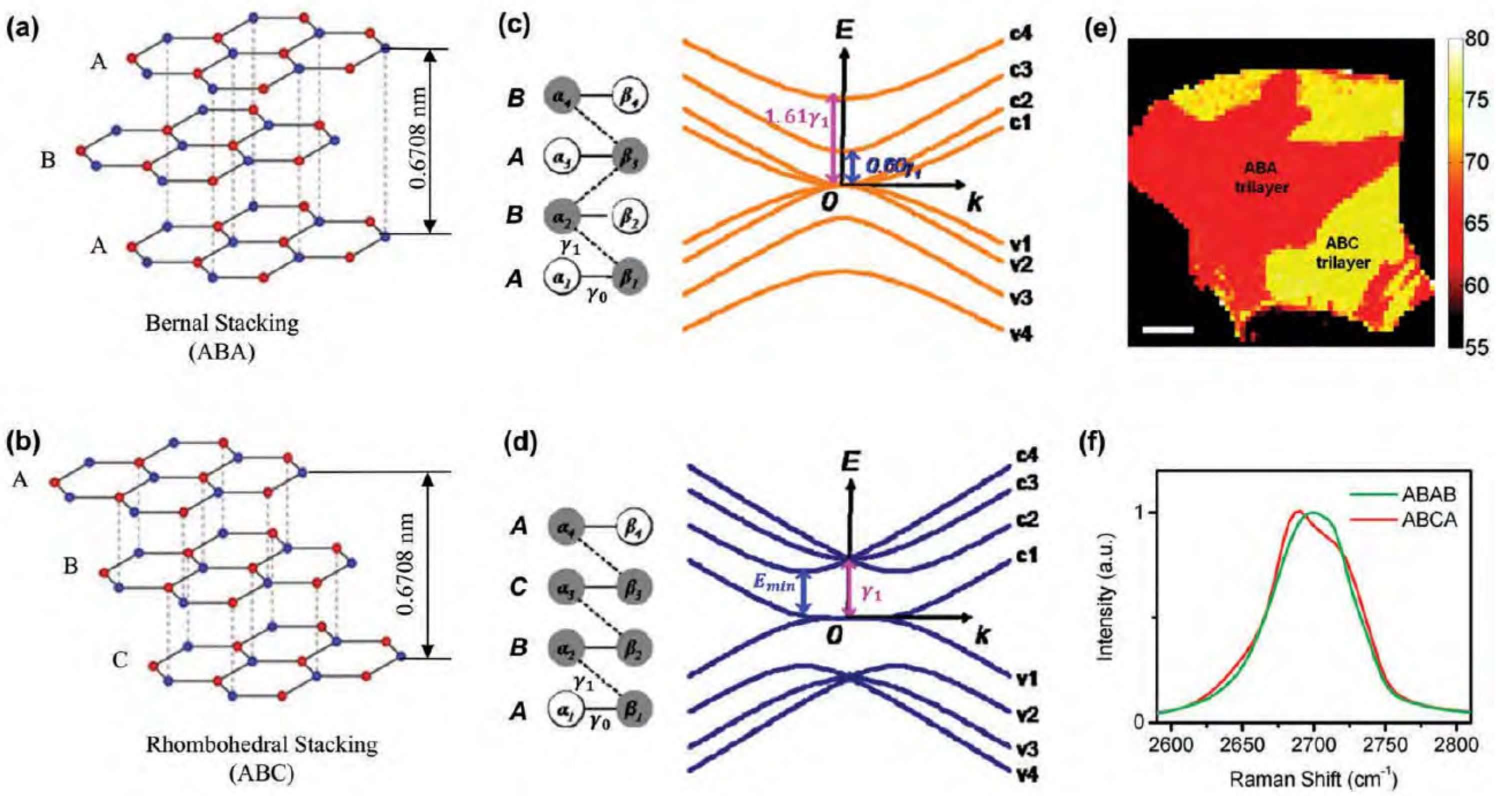
- For example bilayer graphene



G. Yang et al. Sci. Technol. Adv. Mater. (2018)

More layers of graphene

- Another example trilayer graphene

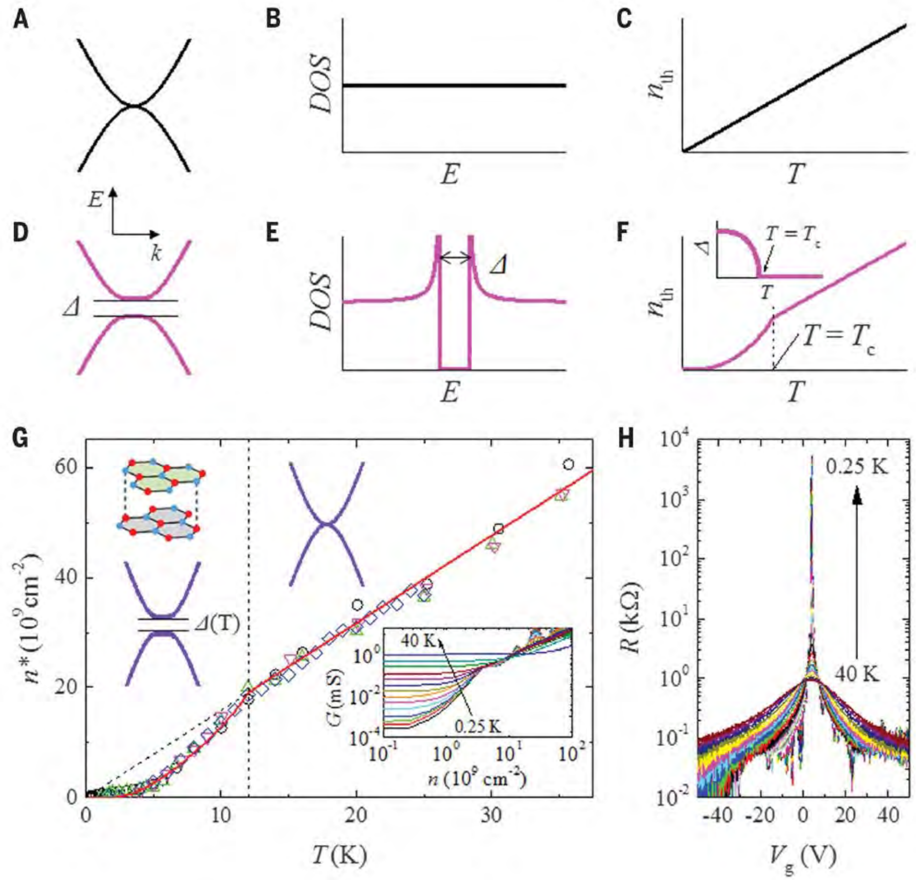


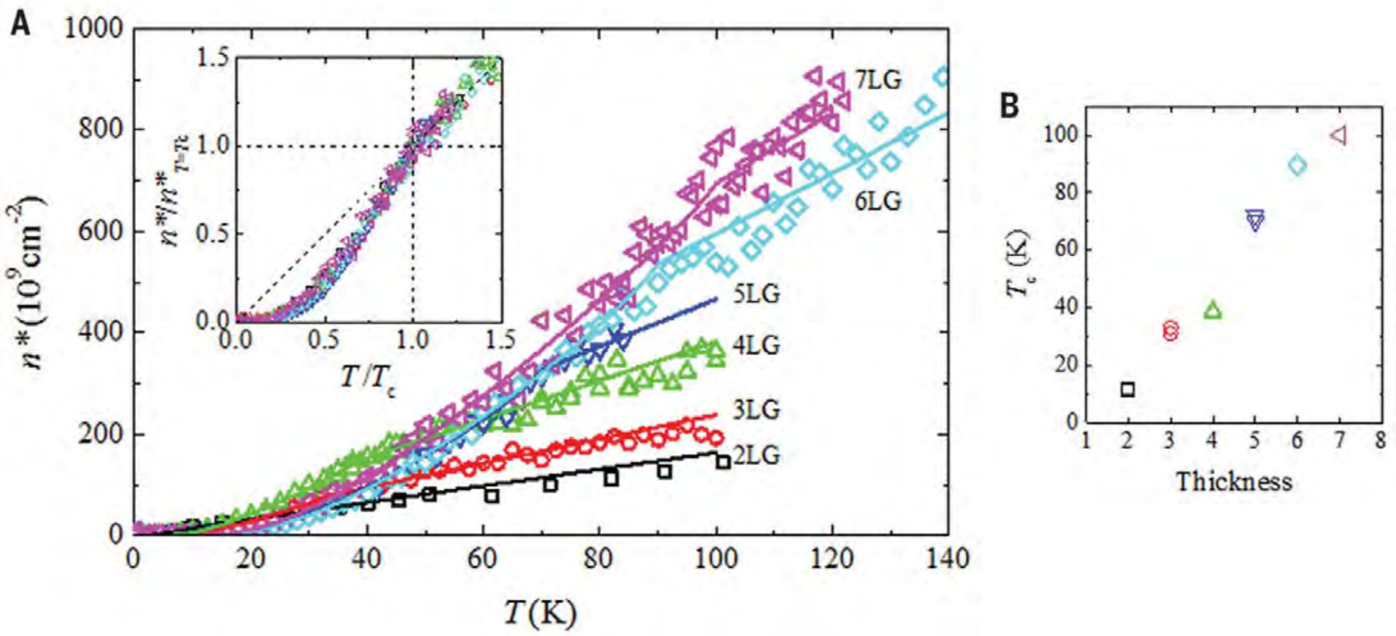
G. Yang et al. Sci. Technol. Adv. Mater. (2018)

More layers of graphene

- Phase transition for multiple layers

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

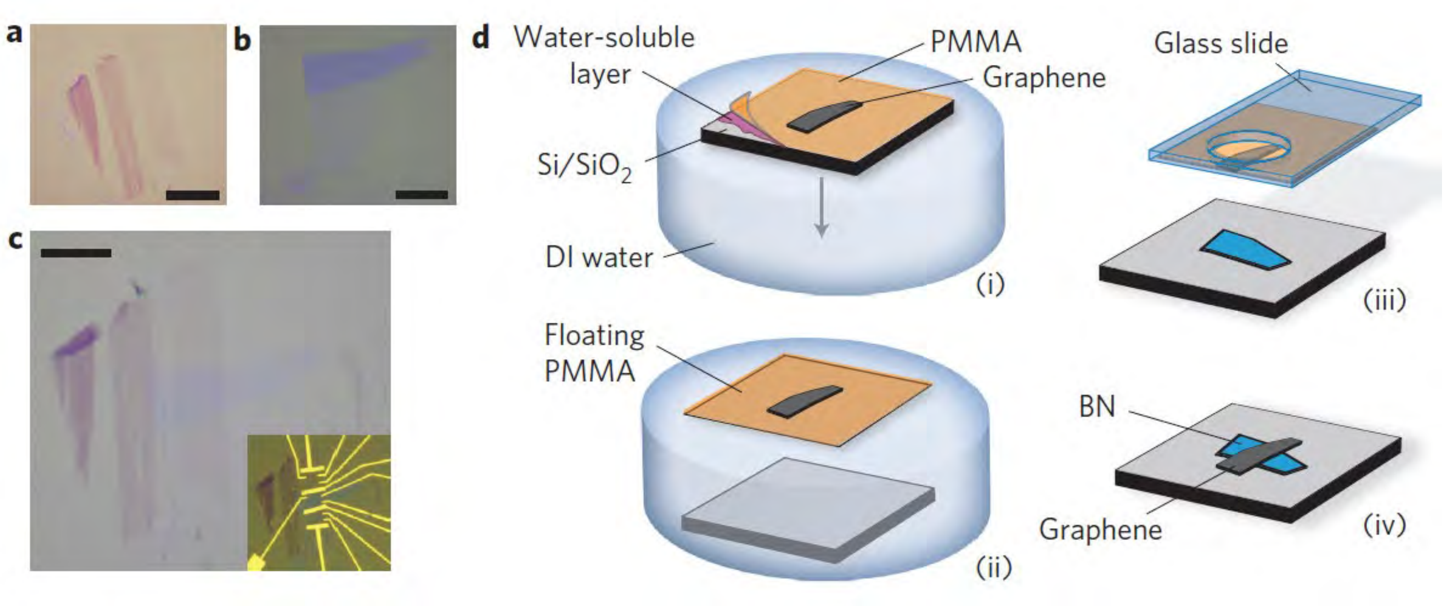


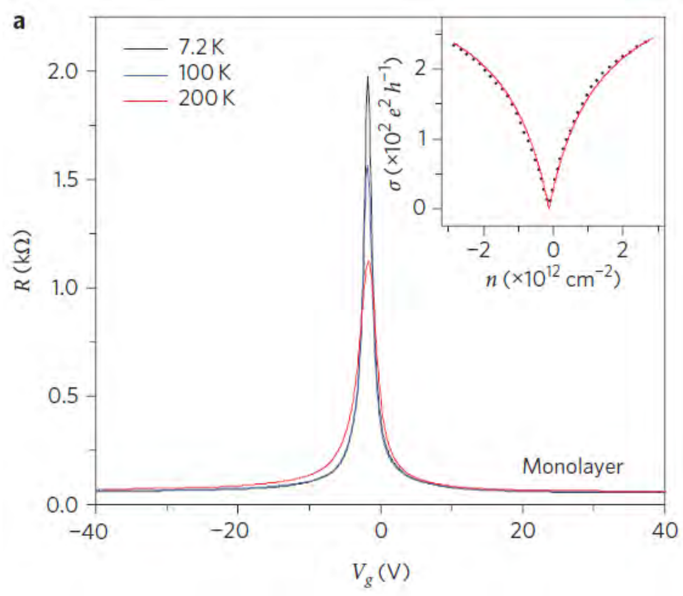


- The gap opening is due to the interaction picture.
- Transition is associated with spin and valley dependent staggered potential with a sign change in layers

Further improvement in quality

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

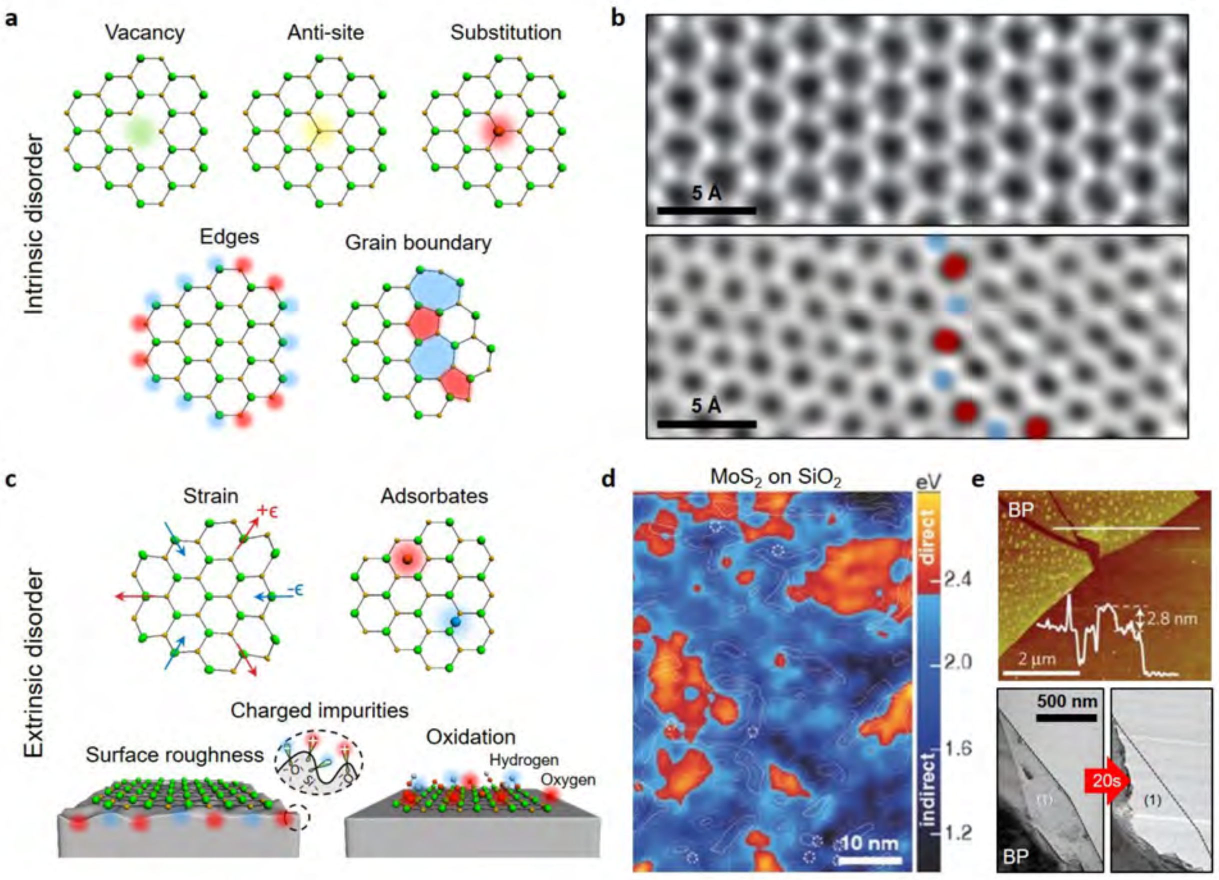




C. Dean et al. Nat. Nanotech. (2010)

Further improvement in quality

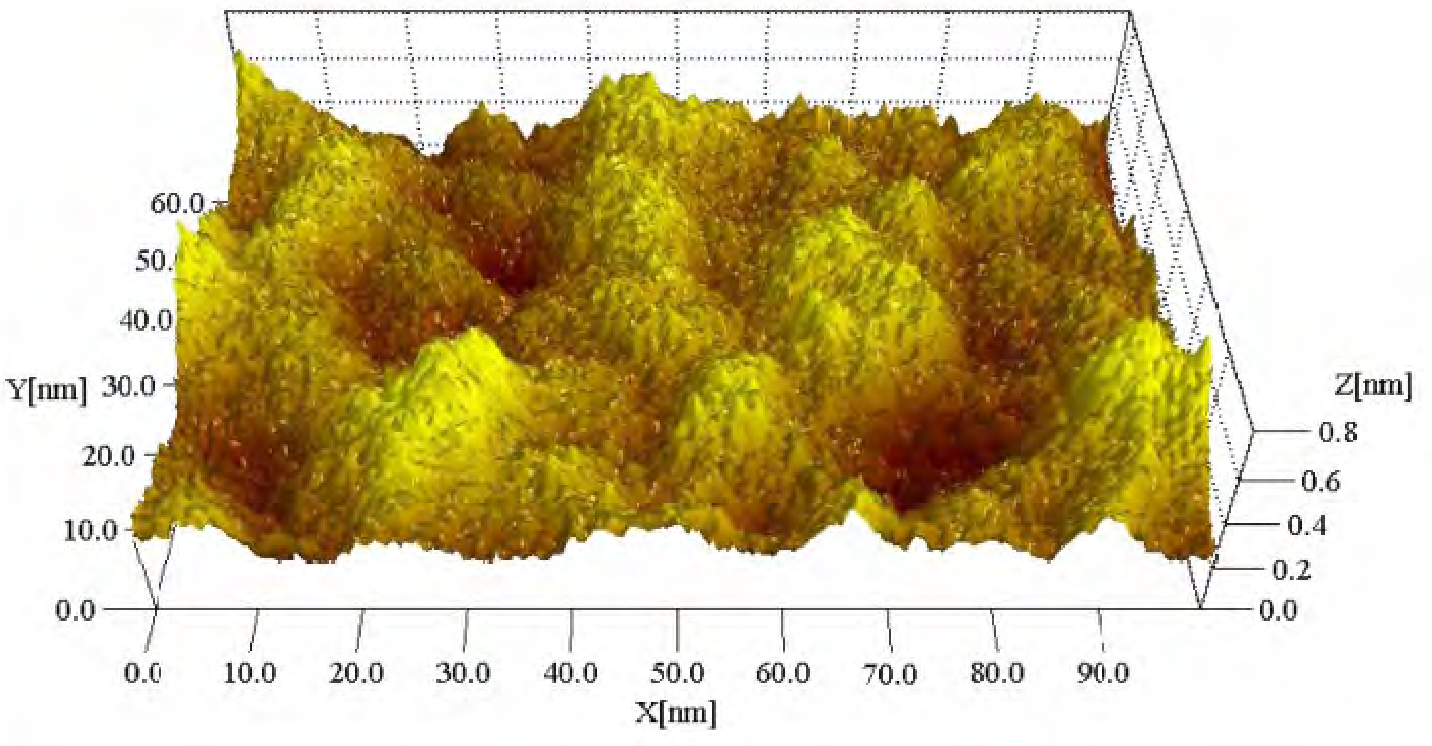
- Disorders from internal and external largely degraded graphene quality
- To obtain a better quality of graphene can lead more intrinsic graphene properties
- Around the DP, density fluctuation creates electron-hole puddles



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

Detailed structure of graphene on SiO2

STM image of graphene on SiO2



Elena Stolyarova et al. PNAS (2007)

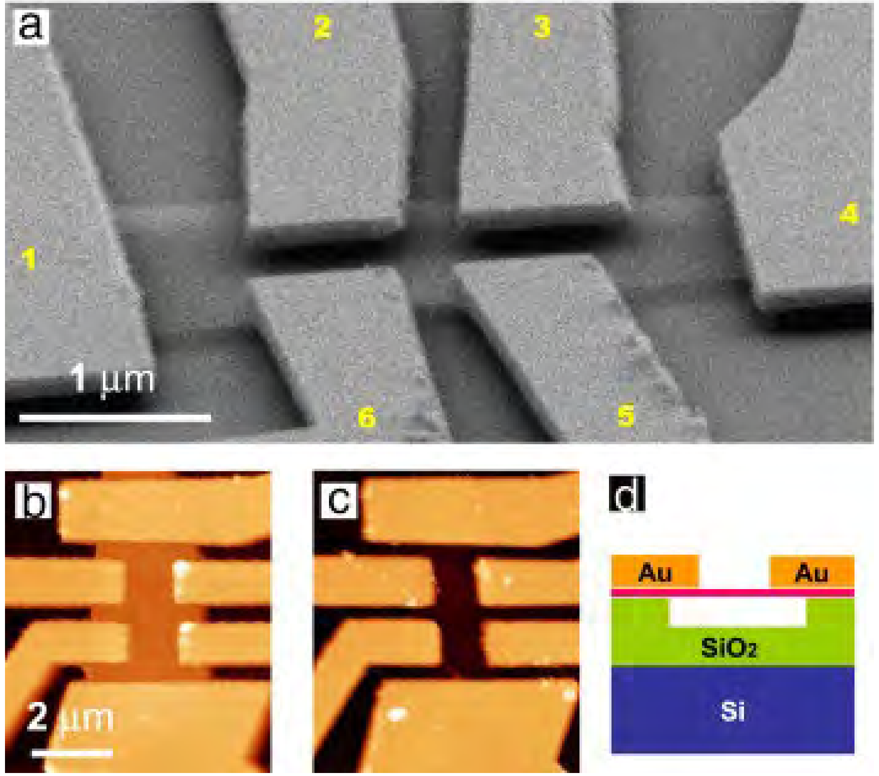
- The ripples create local fluctuations----leading to e-h puddles.
- The causes could come from

1. Substrate
2. Structure defects
3. Absorption

- This greatly degraded graphene quality

Putting graphene in the air

- Suspending graphene improved the mobility

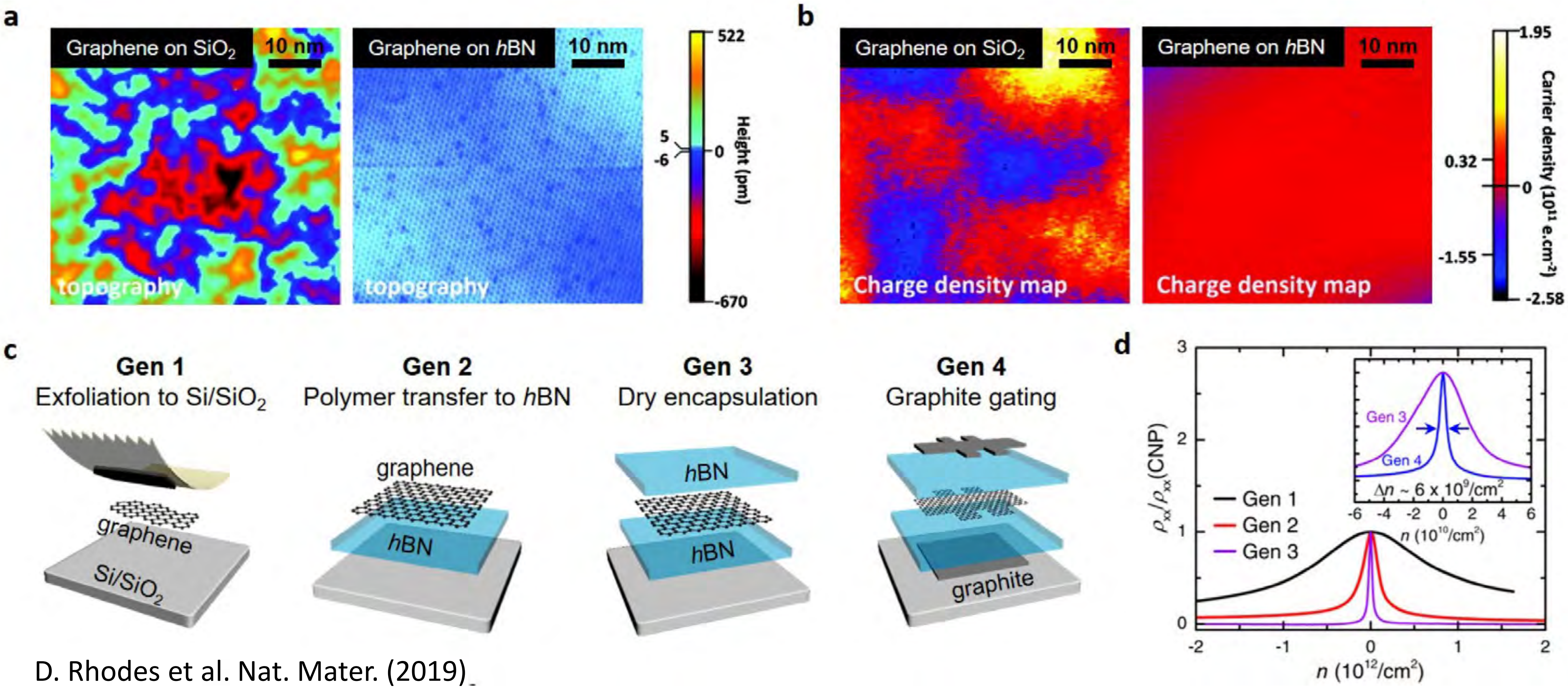


Electron mobility up to 200,000 $cm^2V^{-2}s^{-1}$

A factor of 10 higher than the non-suspended graphene

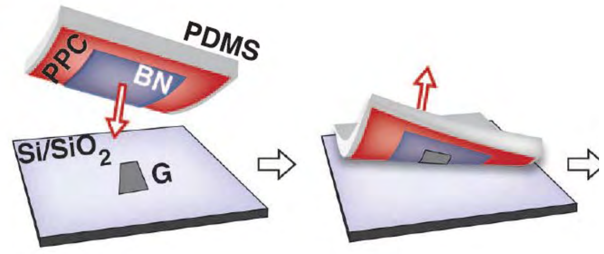
K. I. Bolotin et al. Solid State Communication (2008)

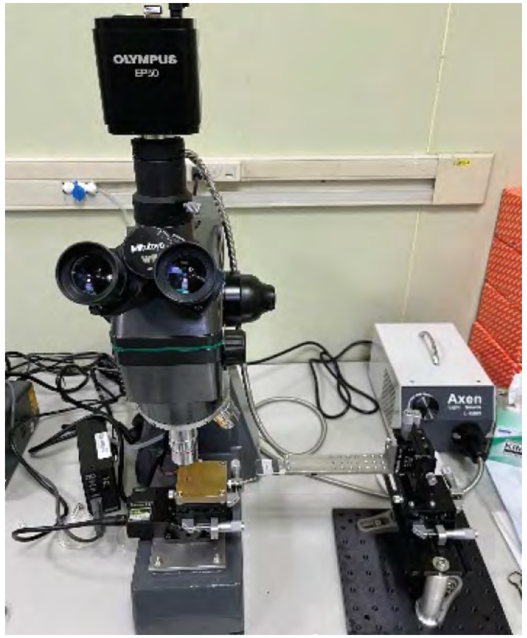
Further improvement in quality



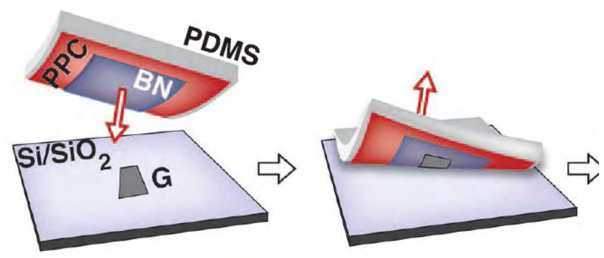
D. Rhodes et al. Nat. Mater. (2019)

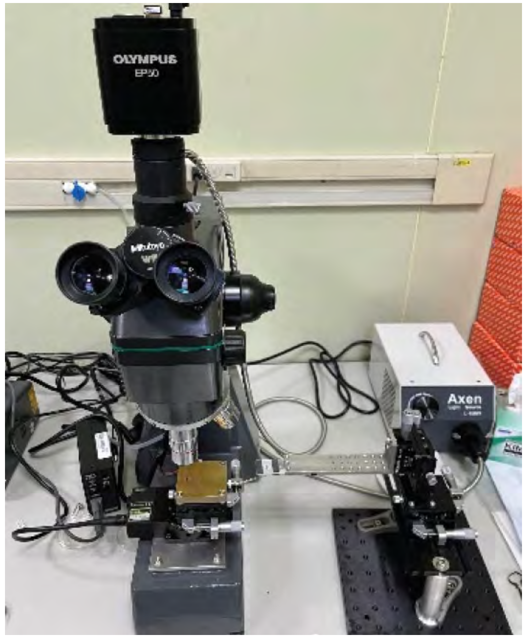
Dry pick up method

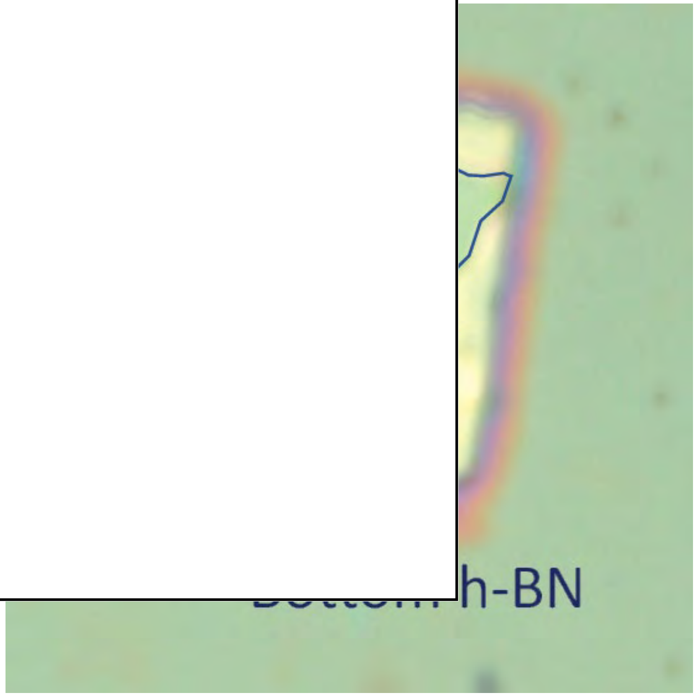




Dry pick up method

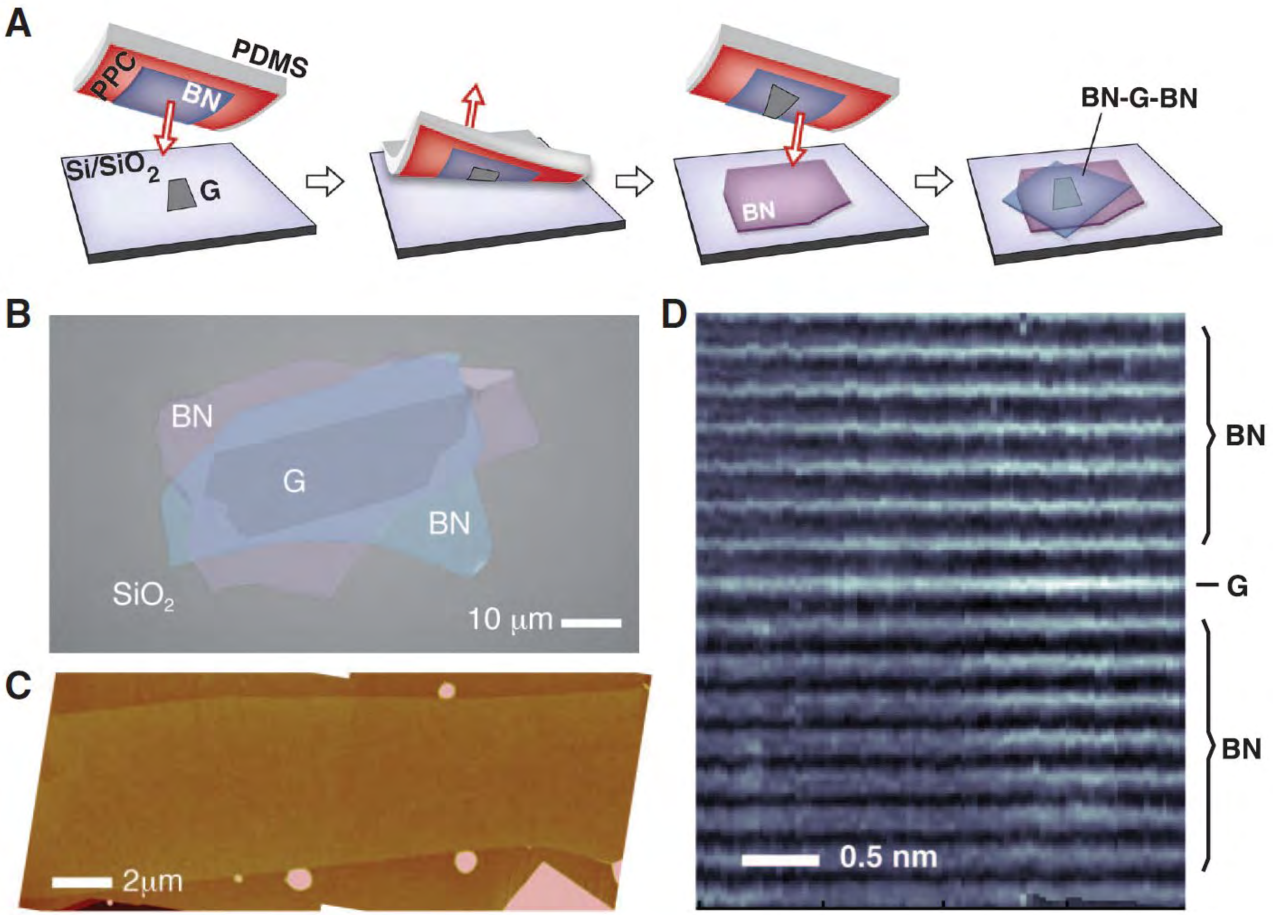


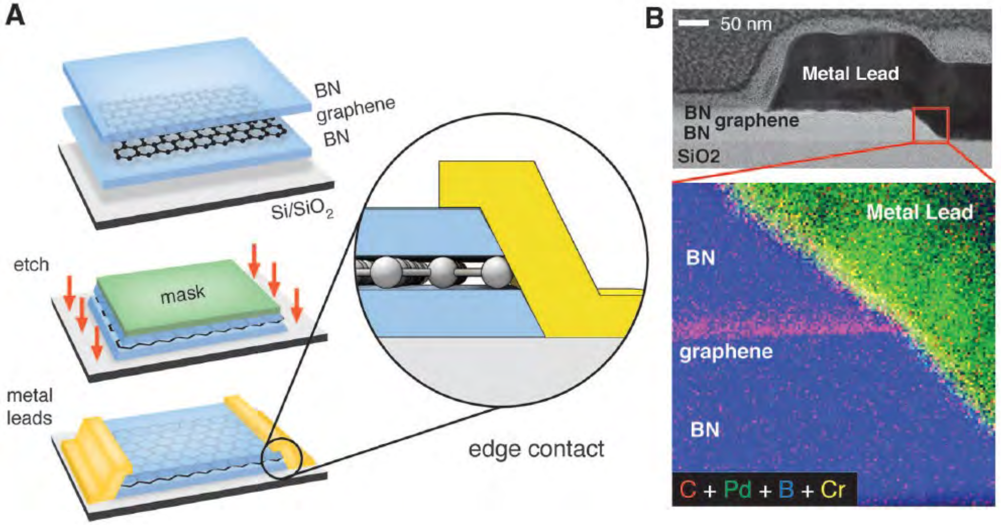




Further improvement in quality

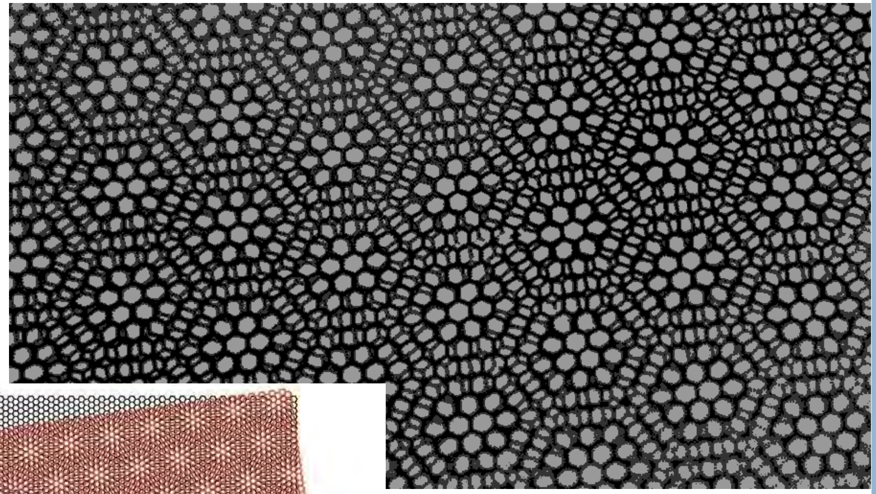
- Encapsulated graphene with h-BN



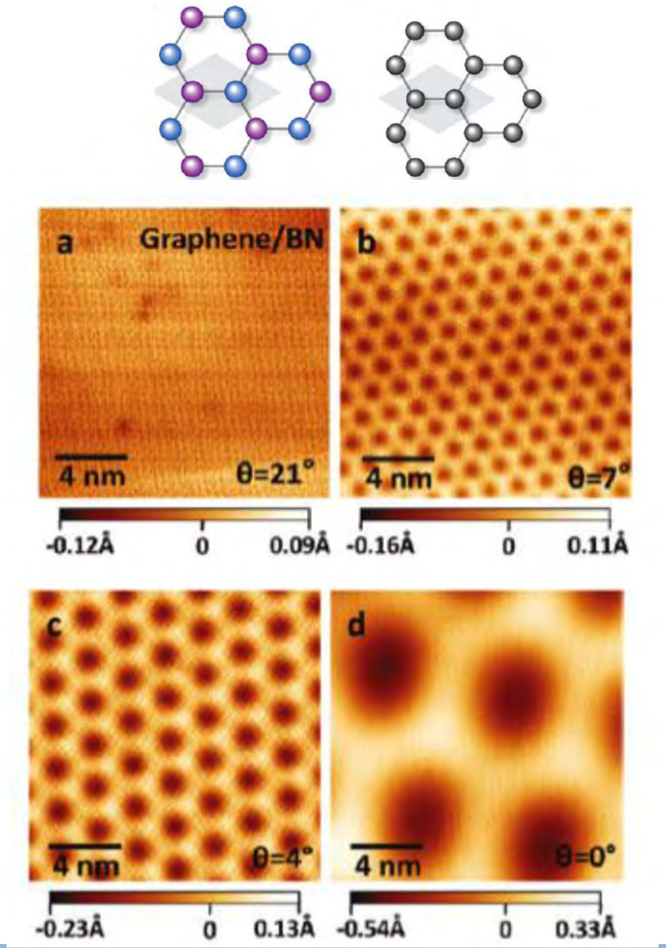


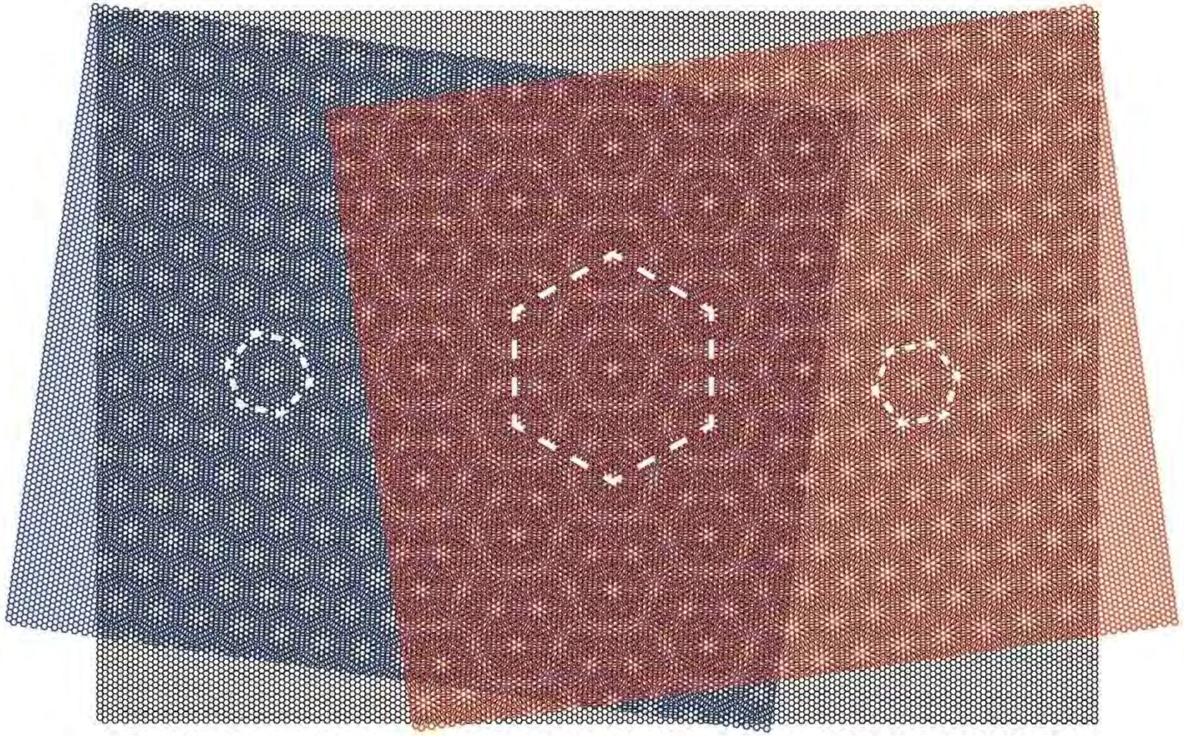
L. Wang et al. Science (2013)

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.

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

Hofstadter's butterfly

By choosing the Landau gauge

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

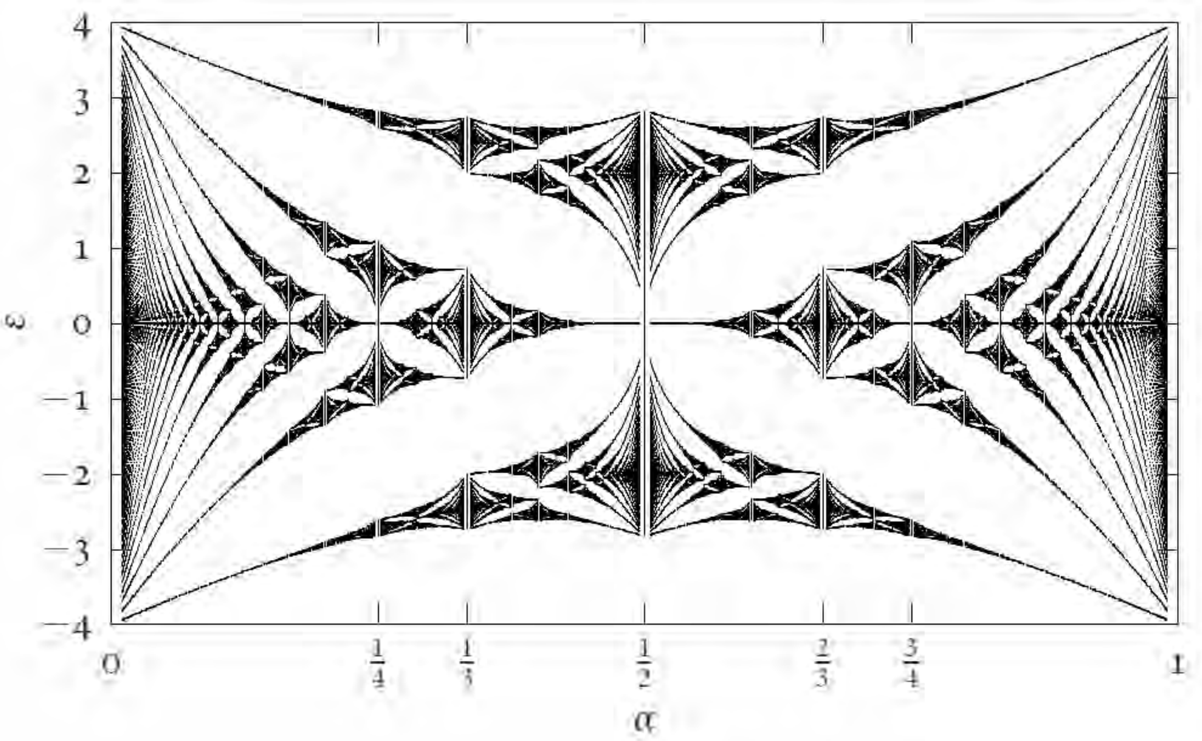
Making several definitions:

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

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

a dimensionless parameter

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



Put everything in one obtains Harper's equation:

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

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

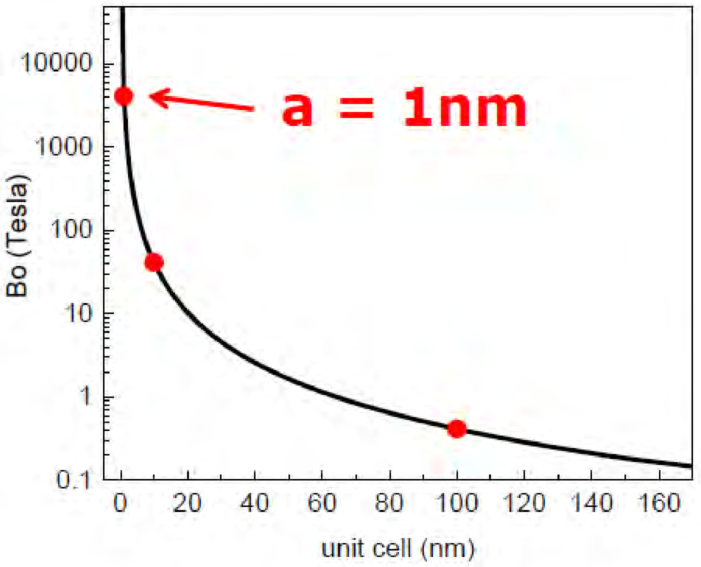
The magnetic flux per unit cell

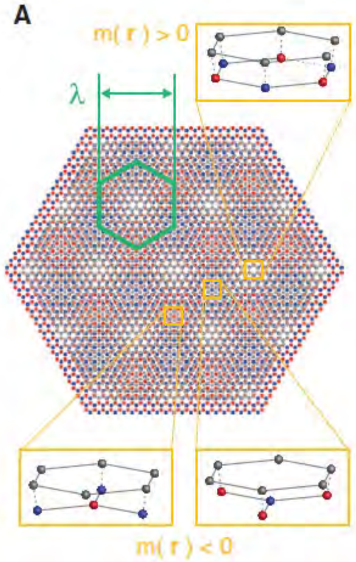
Dirac flux quantum

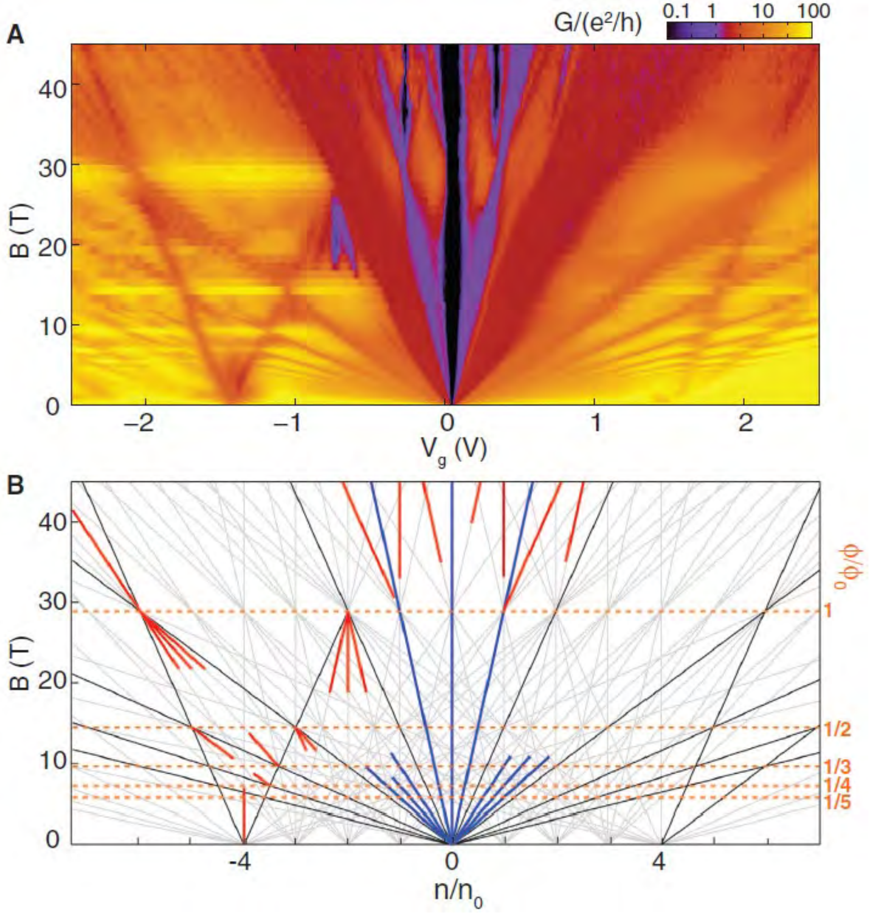
Realistic situation

Obvious technical challenge:

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



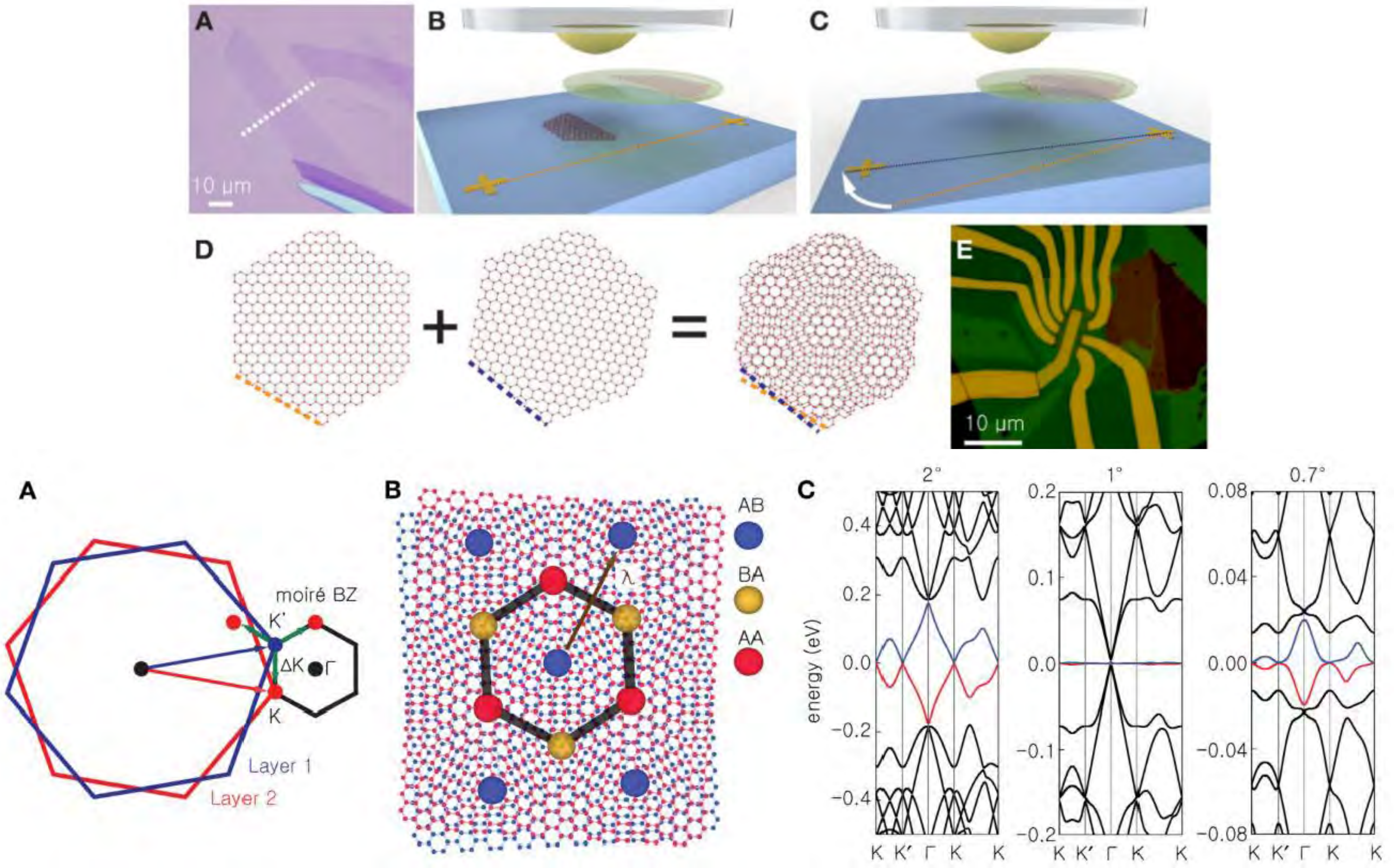




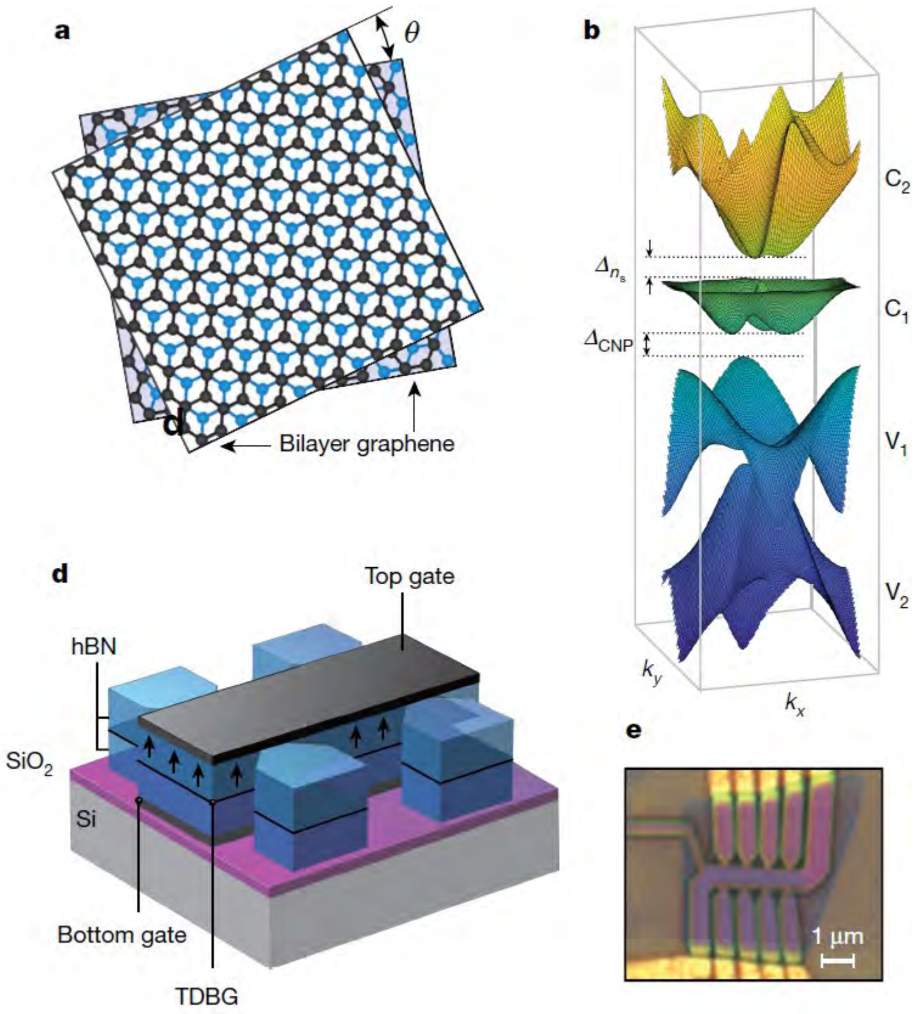
- Early works are limited to a field and accessible density range.
- No fully quantized minigap in the fractional spectrum.
- But now, by twisting the angle, we can control the superlattice size.

Another degree of freedom

- Twisted angle for graphene or bilayer graphene



K. Kim et al. PNAS(2017)

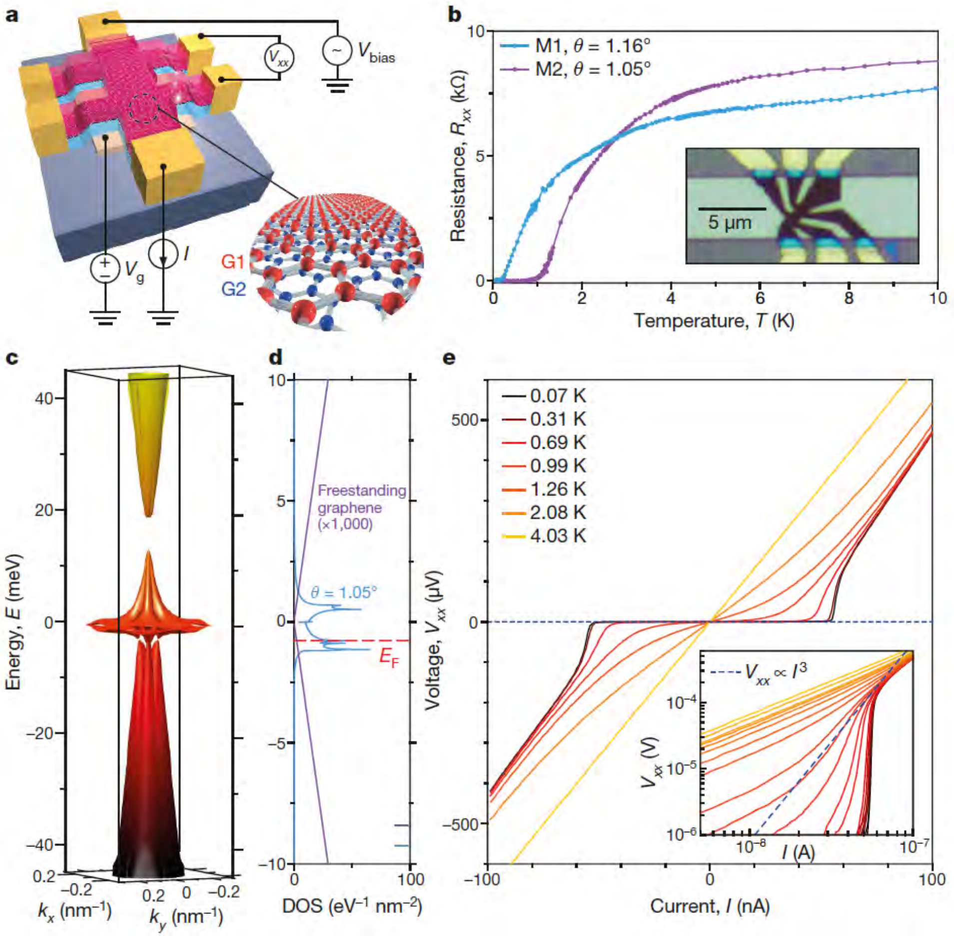


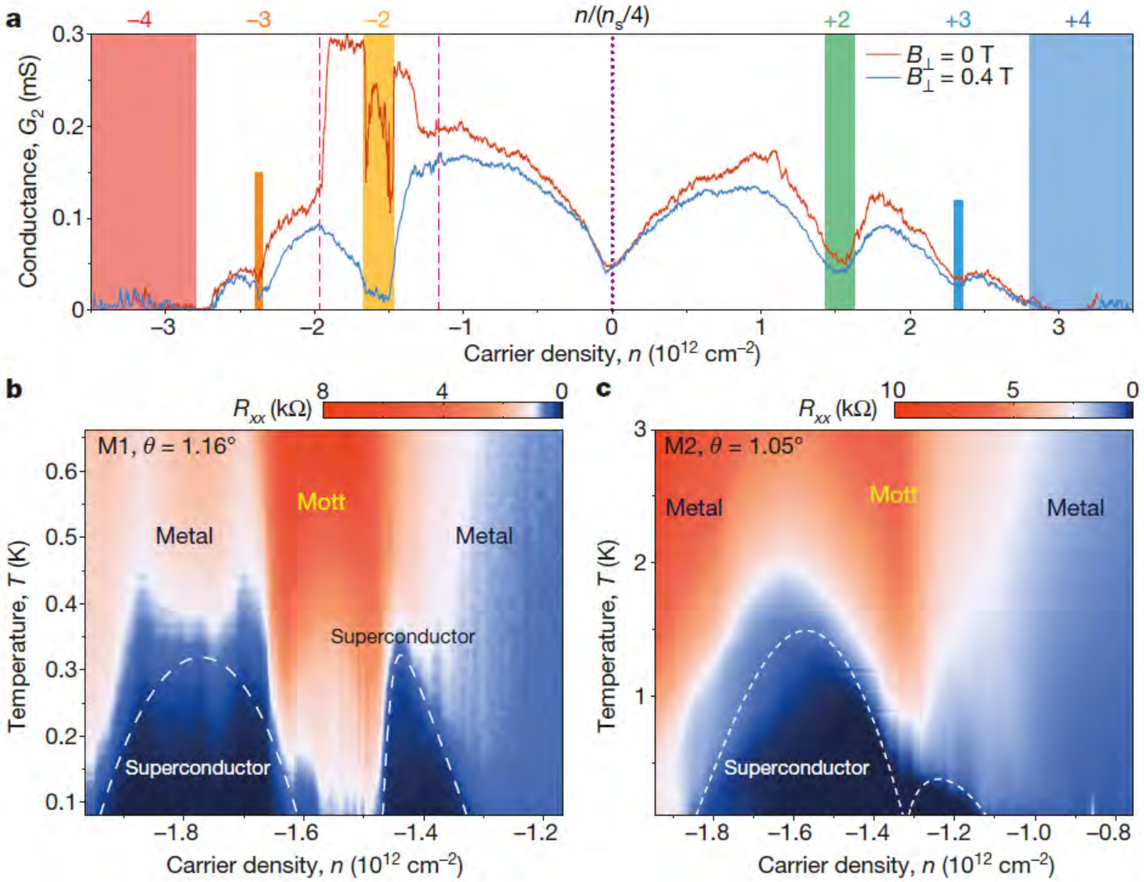
X. Liu et al. Nature (2020)

Another degree of freedom

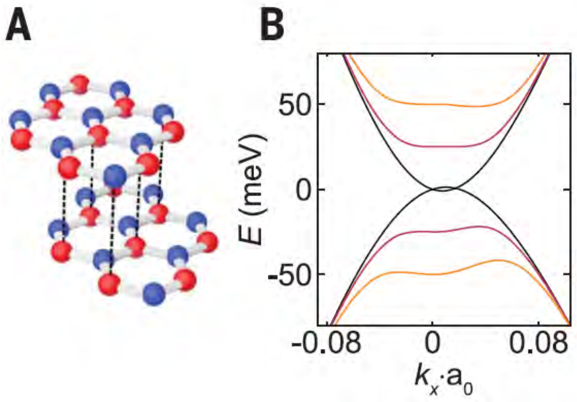
- Magic twisted angle bilayer graphene

Y. Cao et al. Nature (2018)



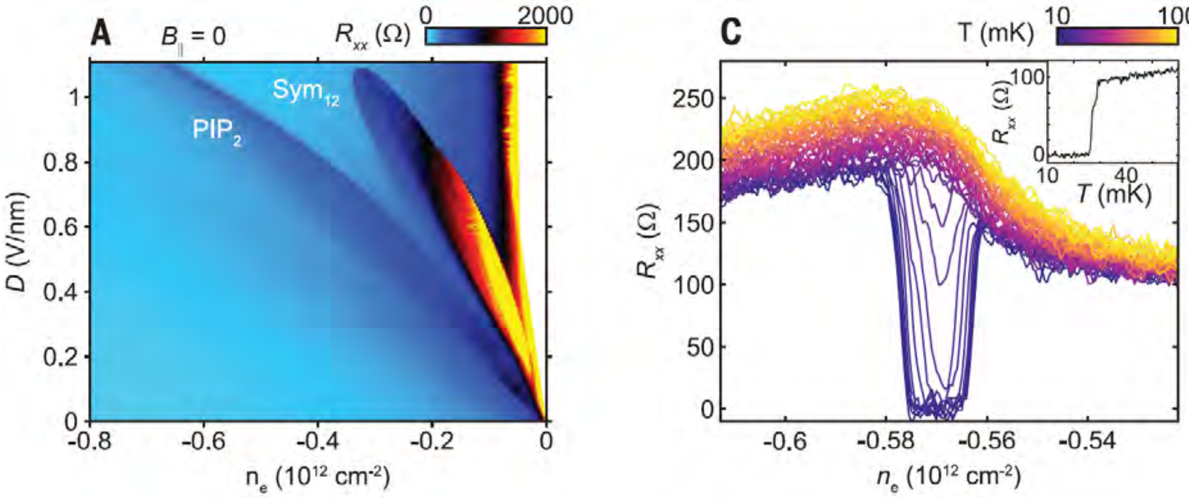


Superconductivity in graphene

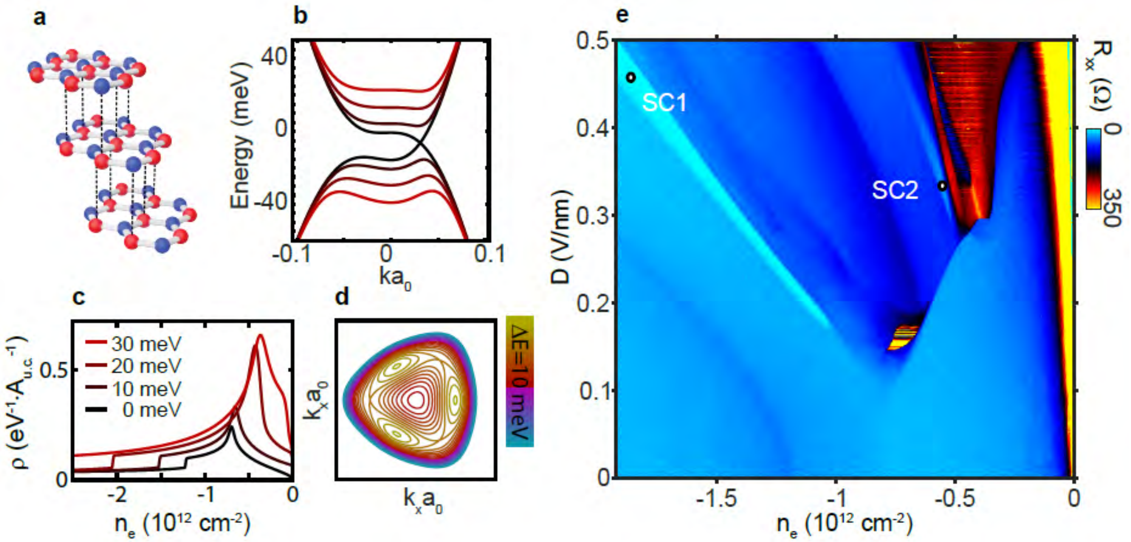


- In Bernal stack graphene, superconductivity can be found with a spin-polarized pairing under a large electrical field.

- Another experiment also demonstrated SC under a high magnetic field

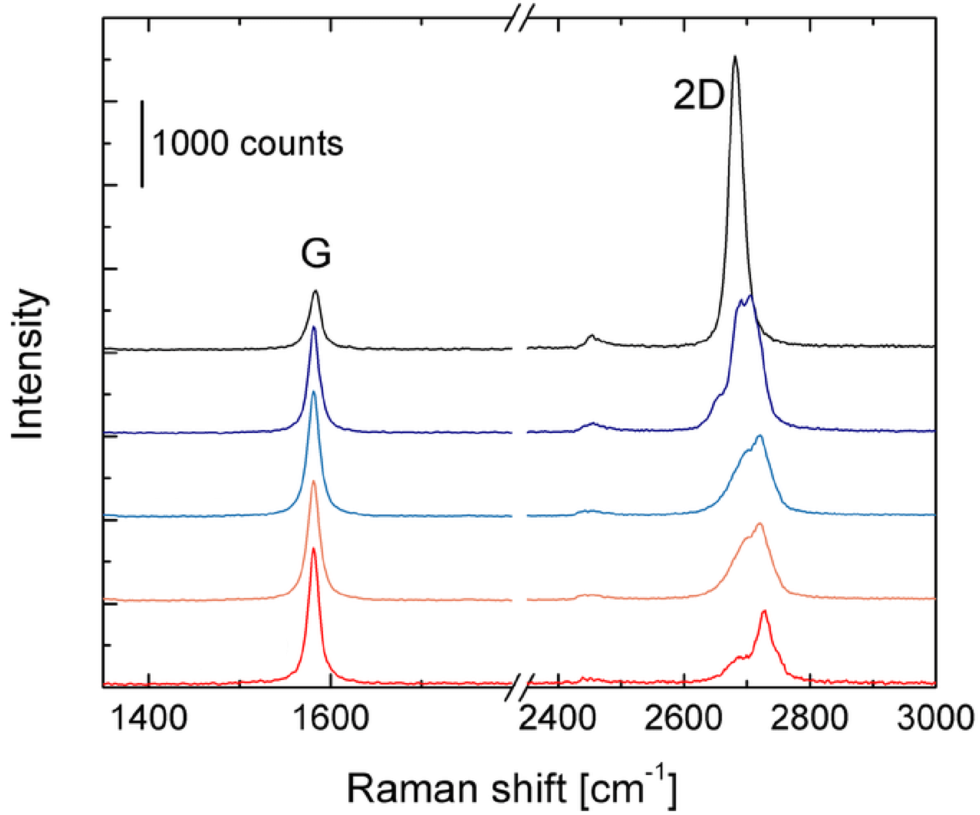


H. Zhou et al. Science (2022)



H. Zhou et al. Nature (2021)

Quiz

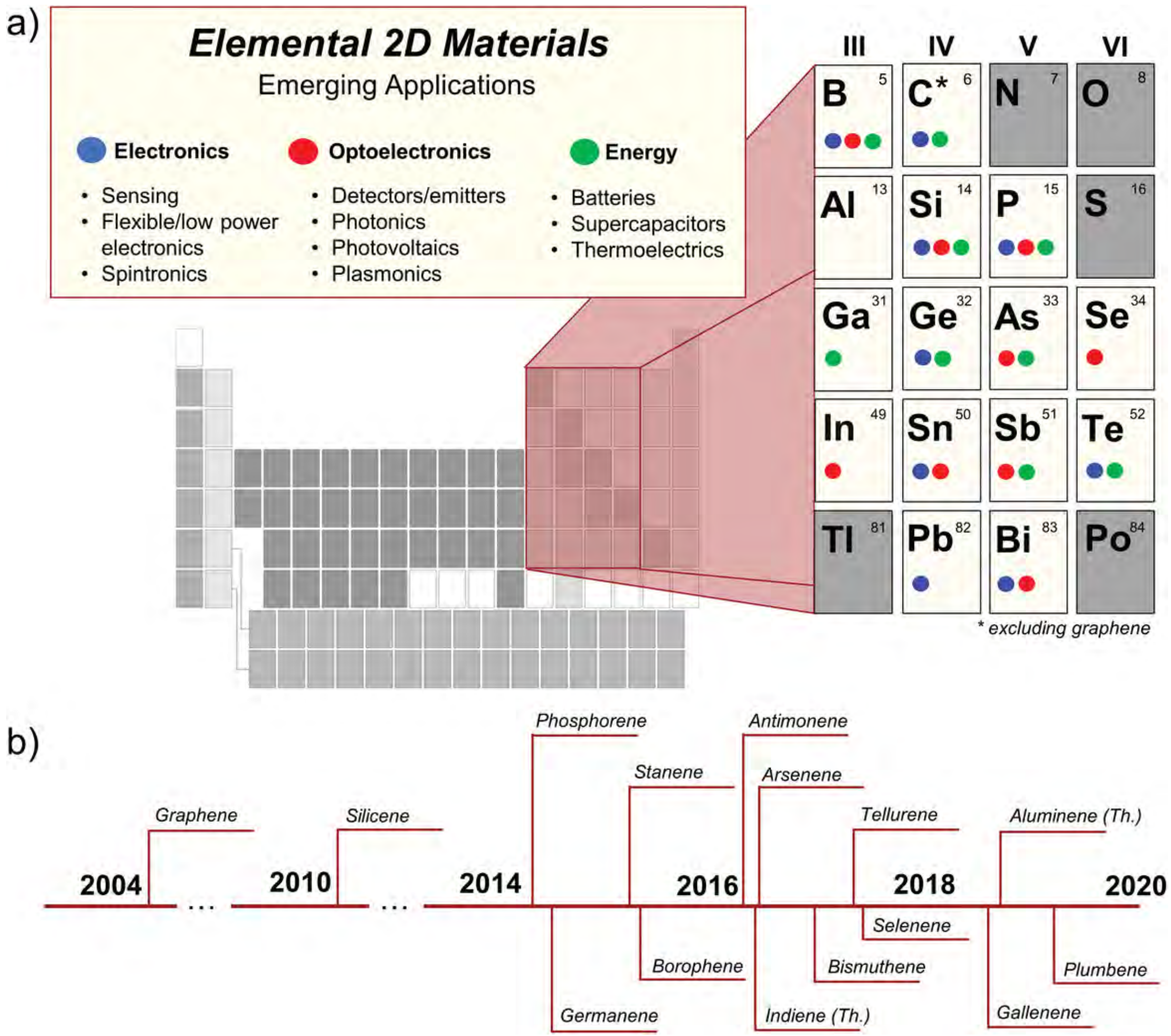


Which color of the spectrum is the monolayer graphene?

2D MATERIALS

Chung-Ting Ke

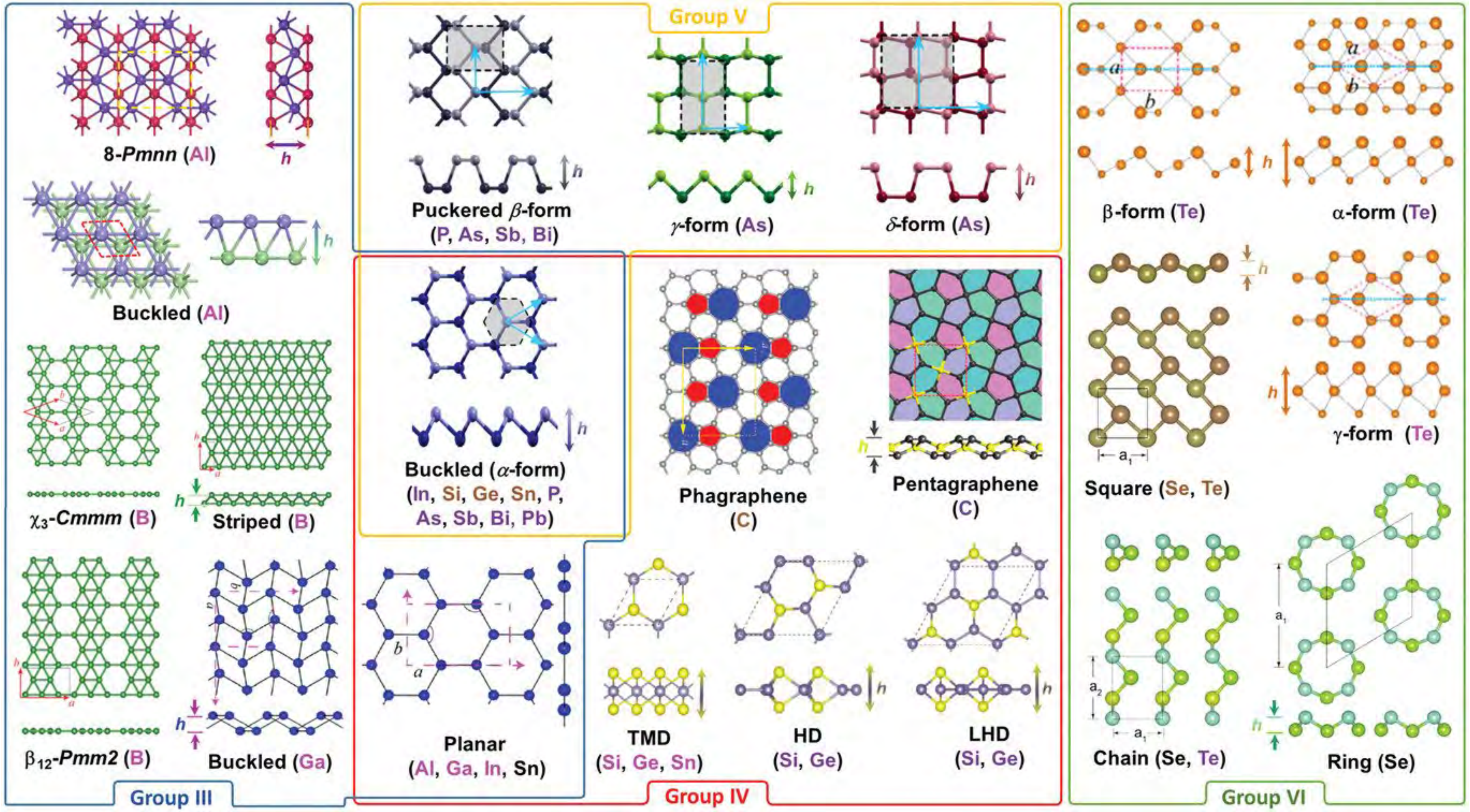
Graphene is the first but not only



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

N. C. Glavin et al. *Adv. Mater.* **2020**, *32*, 1904302

Allotropes are also rich

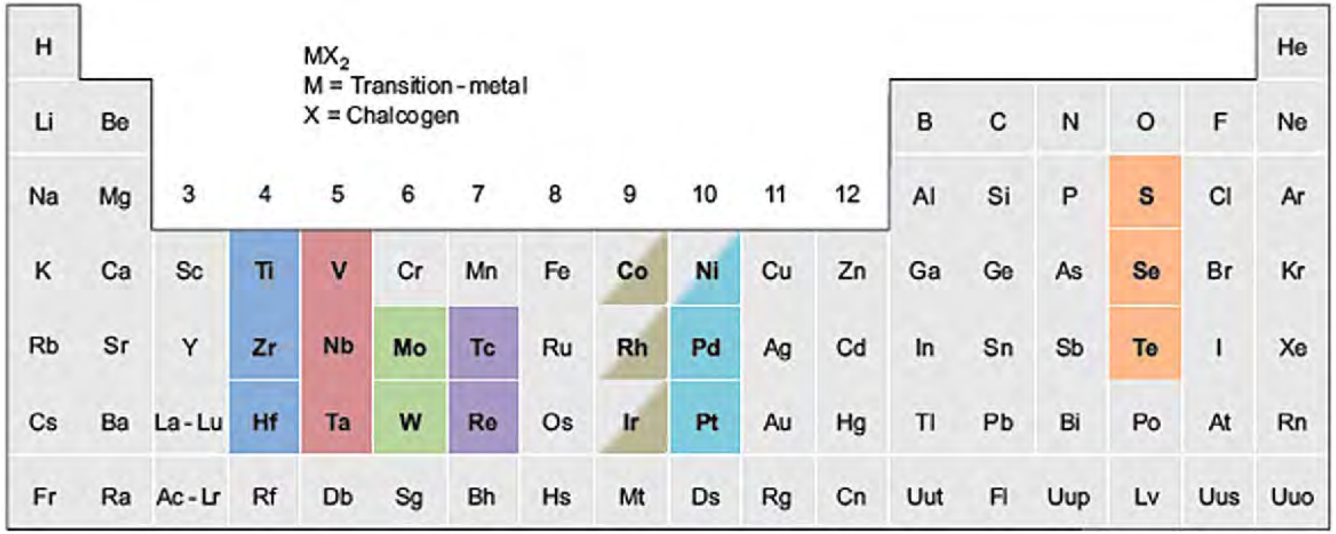


Similar to graphene, the allotrope of element 2D materials will determine the properties.

N. C. Glavin et al. *Adv. Mater.* **2020**, *32*, 1904302

More 2D materials

Transition Metal Dichalcogenides



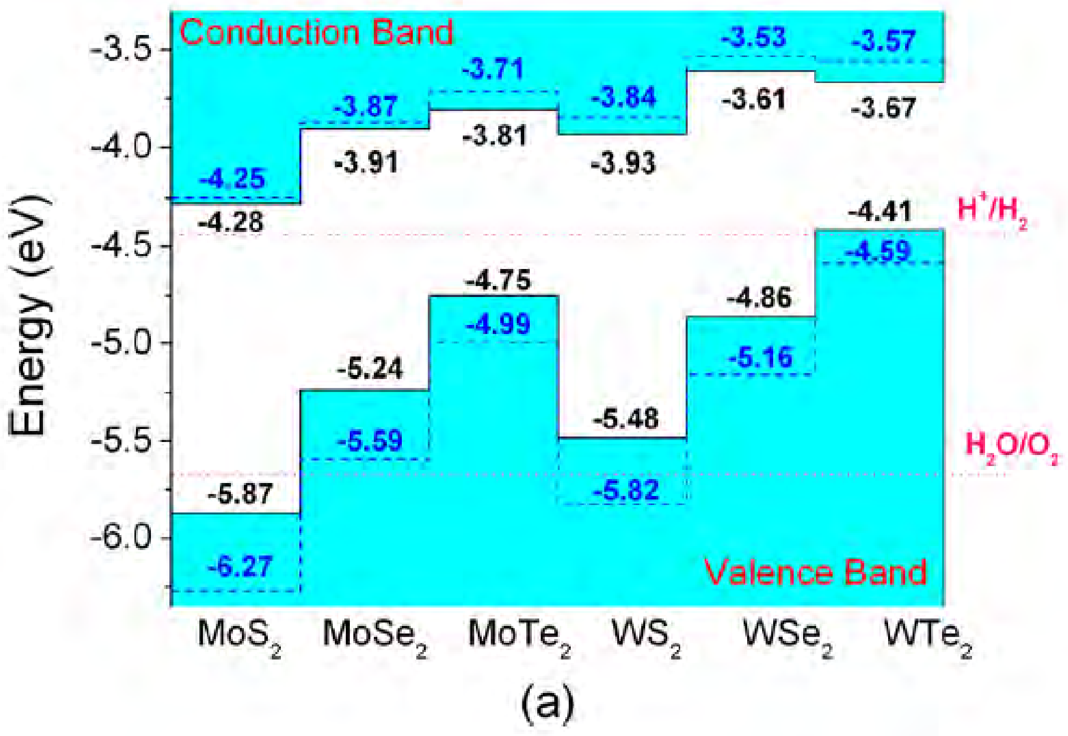
M. Pumera et al. DOI: 10.1016/J.TRAC.2014.05.009

WSe_2, WTe_2, $NbSe_2$ etc..

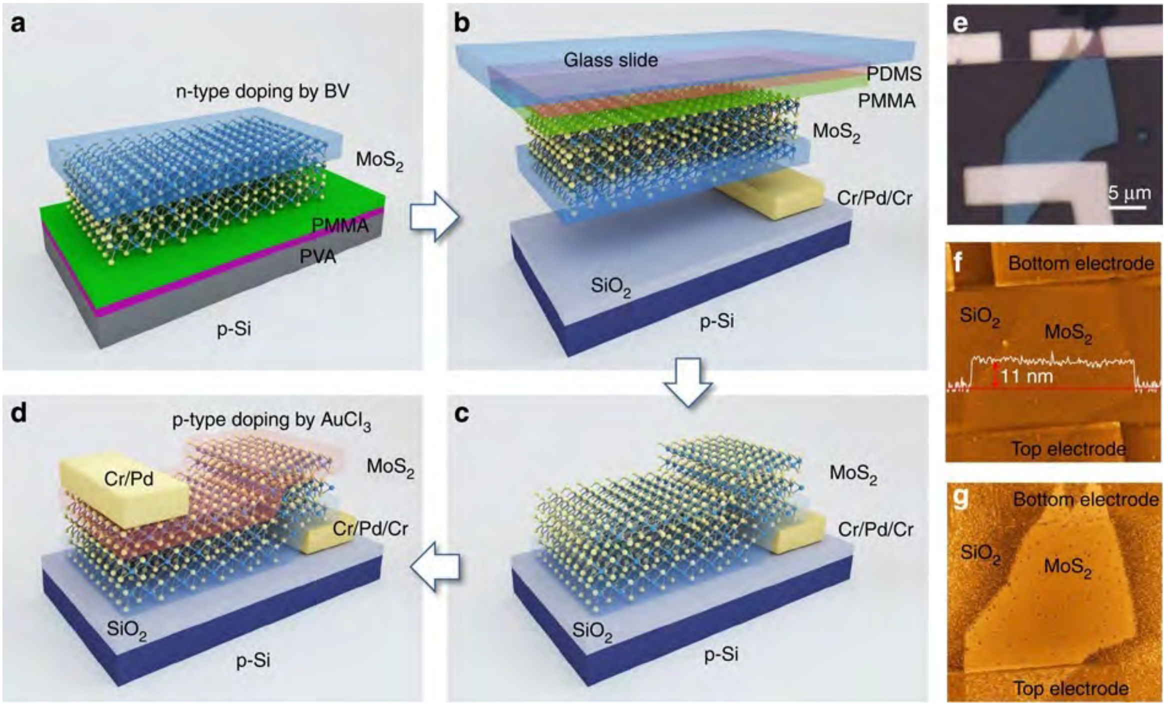
- Combining two different elements can enrich the phase space of the 2D materials
- One of the most famous groups of compound 2D material is Transition-metal dichalcogenide (TMDs).
- This new group of 2D materials provides a great platform for various research and applications

Rich band structures

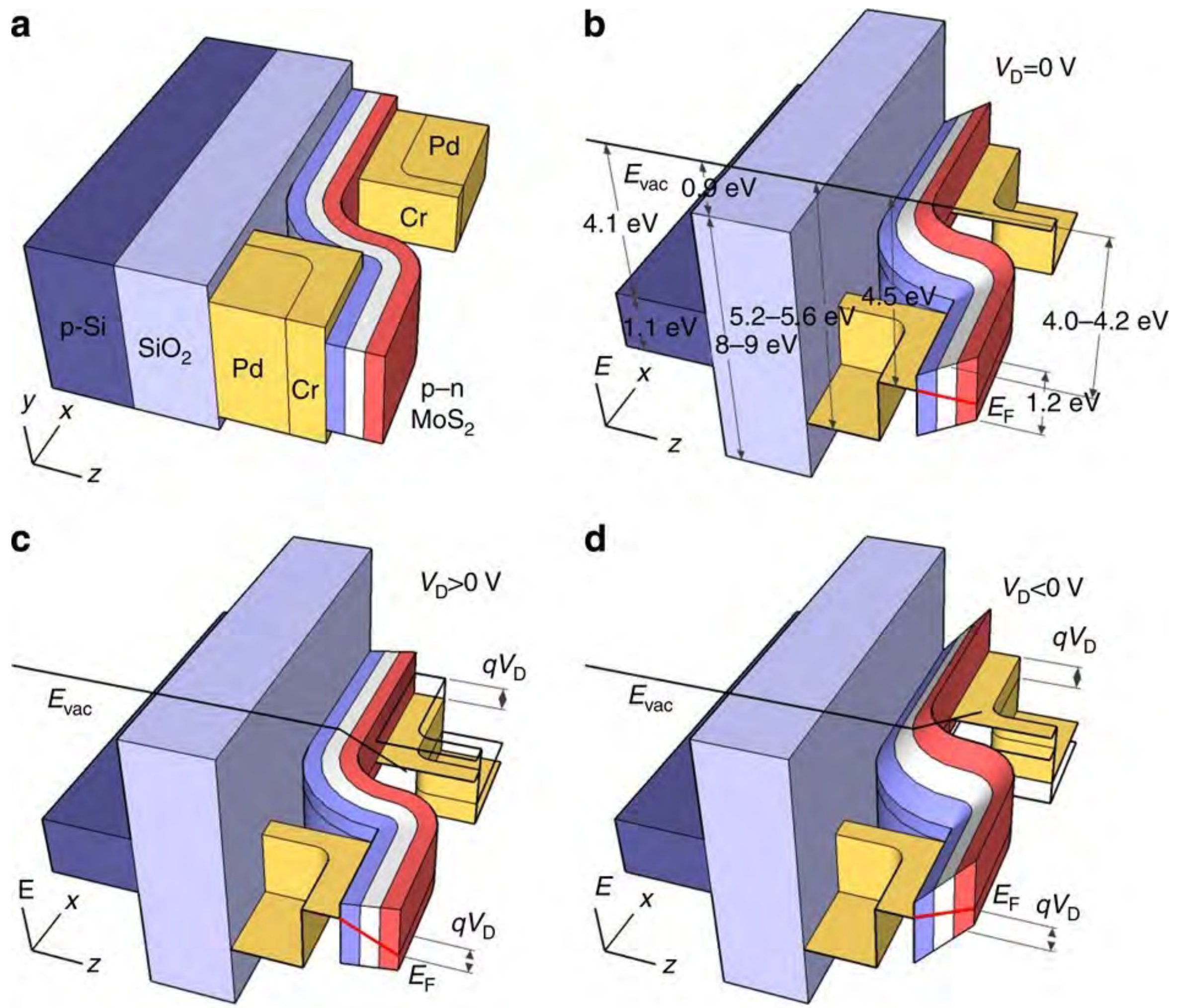
- The different gaps and direct-indirect bands allow us to conduct various research and applications in electronics, optics, sensing, etc.



J. Kang et al. APL (2013)



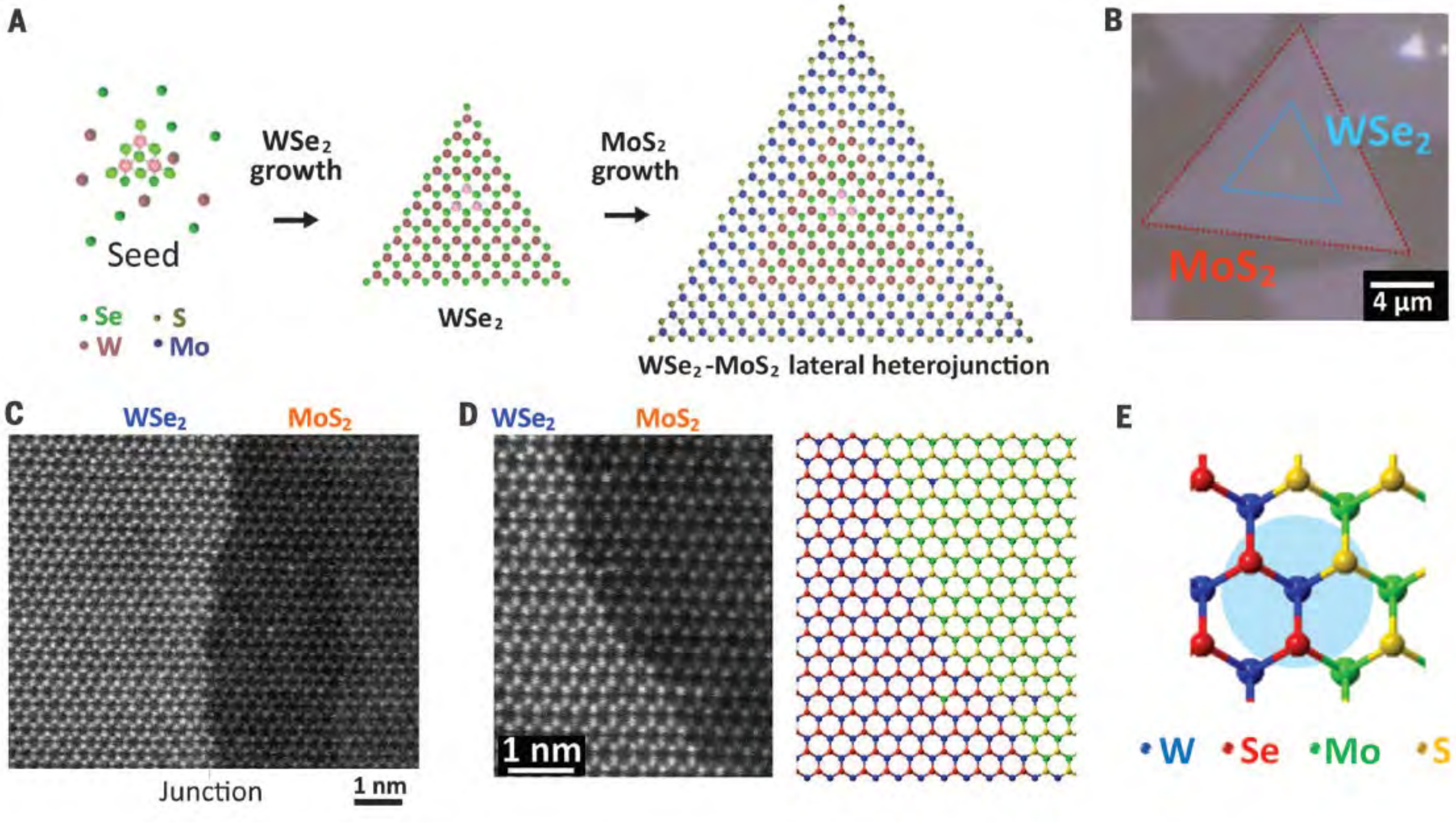
A 2D PN junction



- 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.

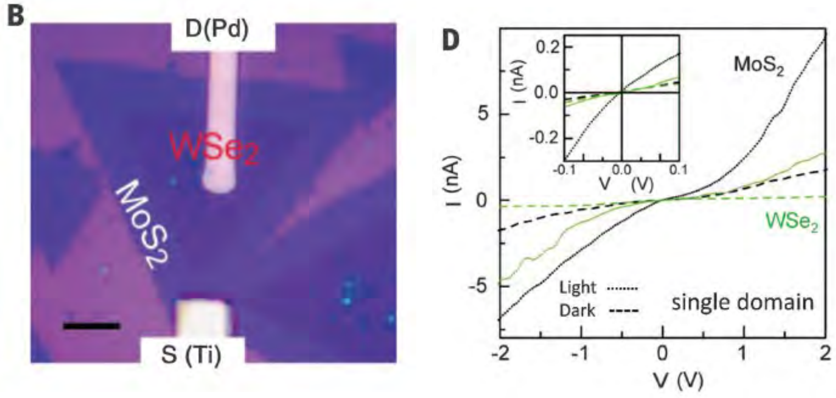
H.-M. Li et al. Nat. Commun. 2015

Another way to create a PN interface



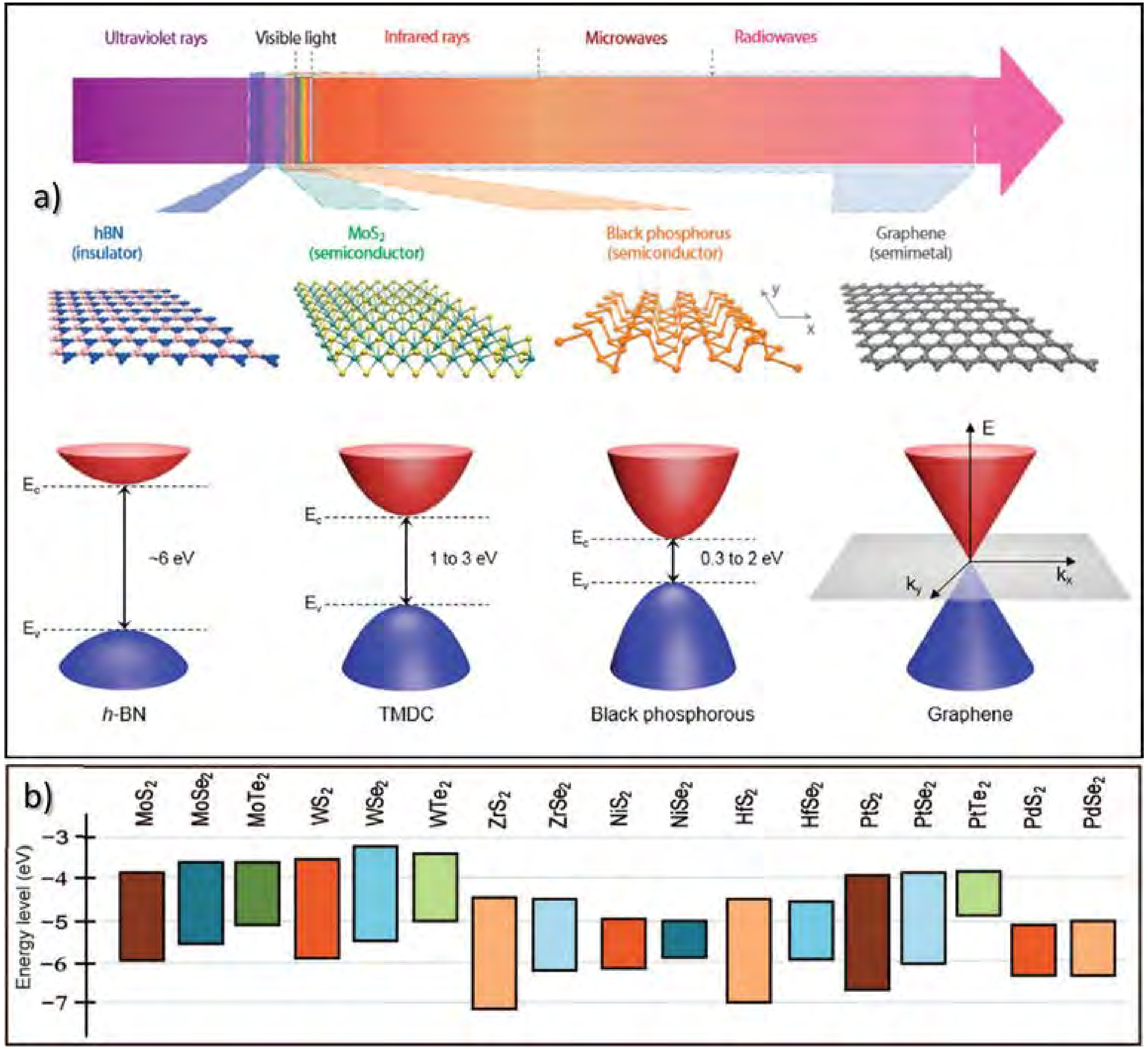
M.-Y. Li et al. Science (2015)

- Growth control to combine two 2D semiconductors
- A hetero junction forms a PN junction that can respond to the photon emissions.



Wild range spectrum

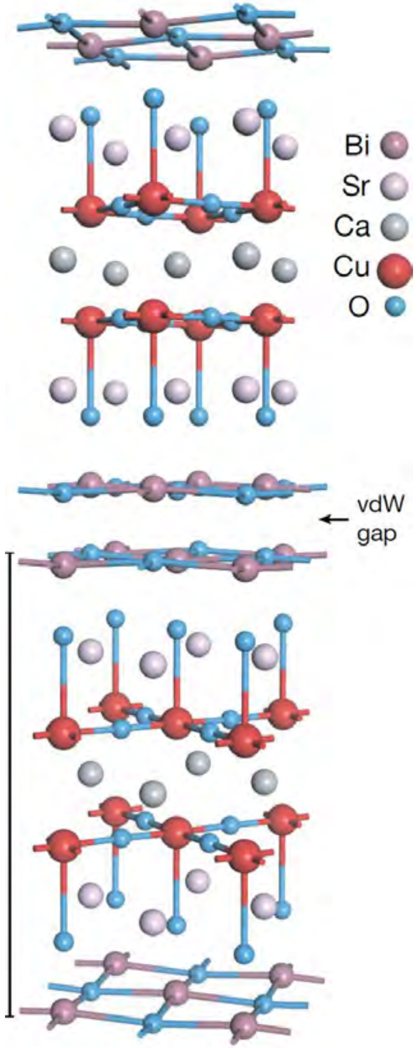
- The gap ranges from 6 eV to 0 eV.
- That creates a wild range of the spectrum.
- Therefore, 2D materials cover from insulator all to way to metal.



Inturu Omkaram et al. DOI: 10.5772/intechopen.72295

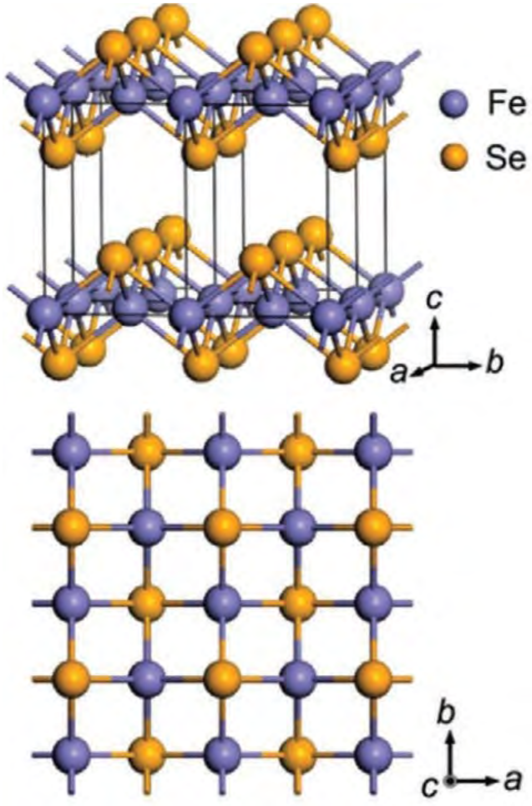
High Tc superconductor

BSCCO



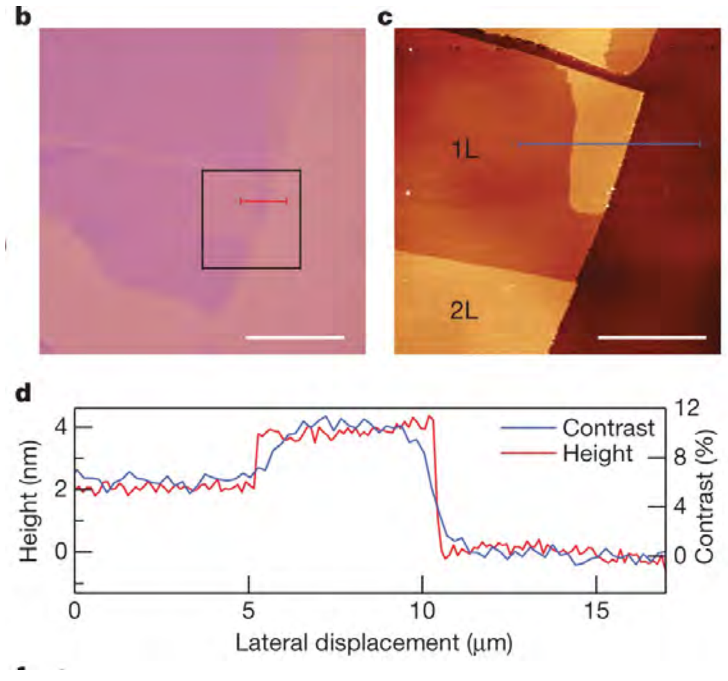
Y. Yu, et al Nature (2019)

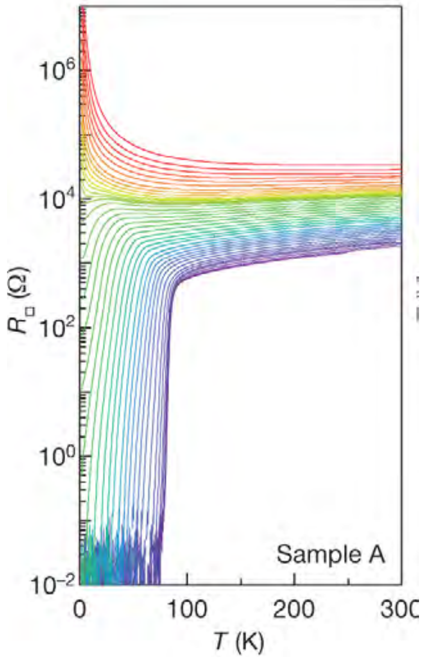
FeSe



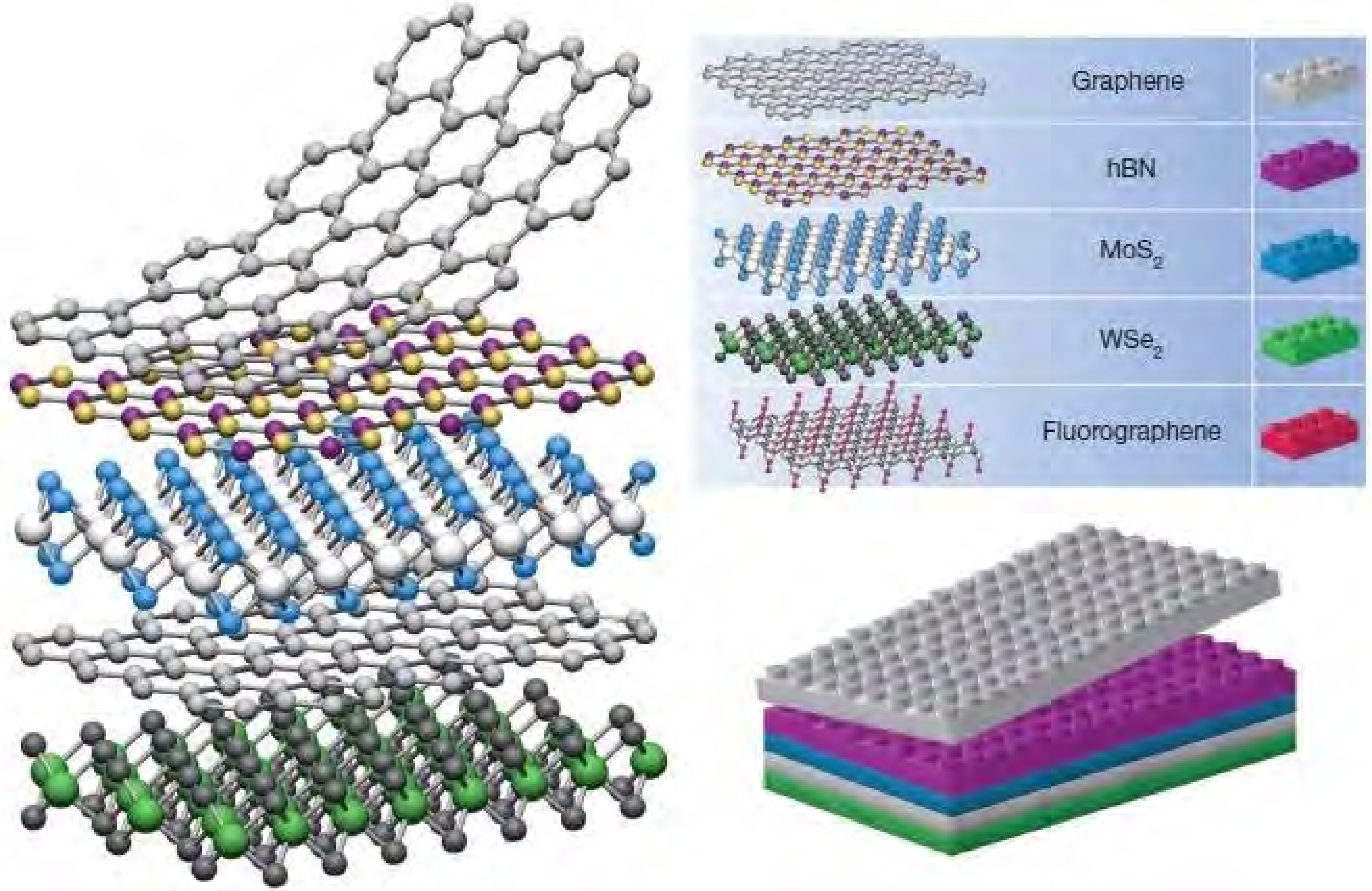
F.-C. Hsu, et al PNAS(2008)

- 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



Dirac metal

Insulator

Semiconductor

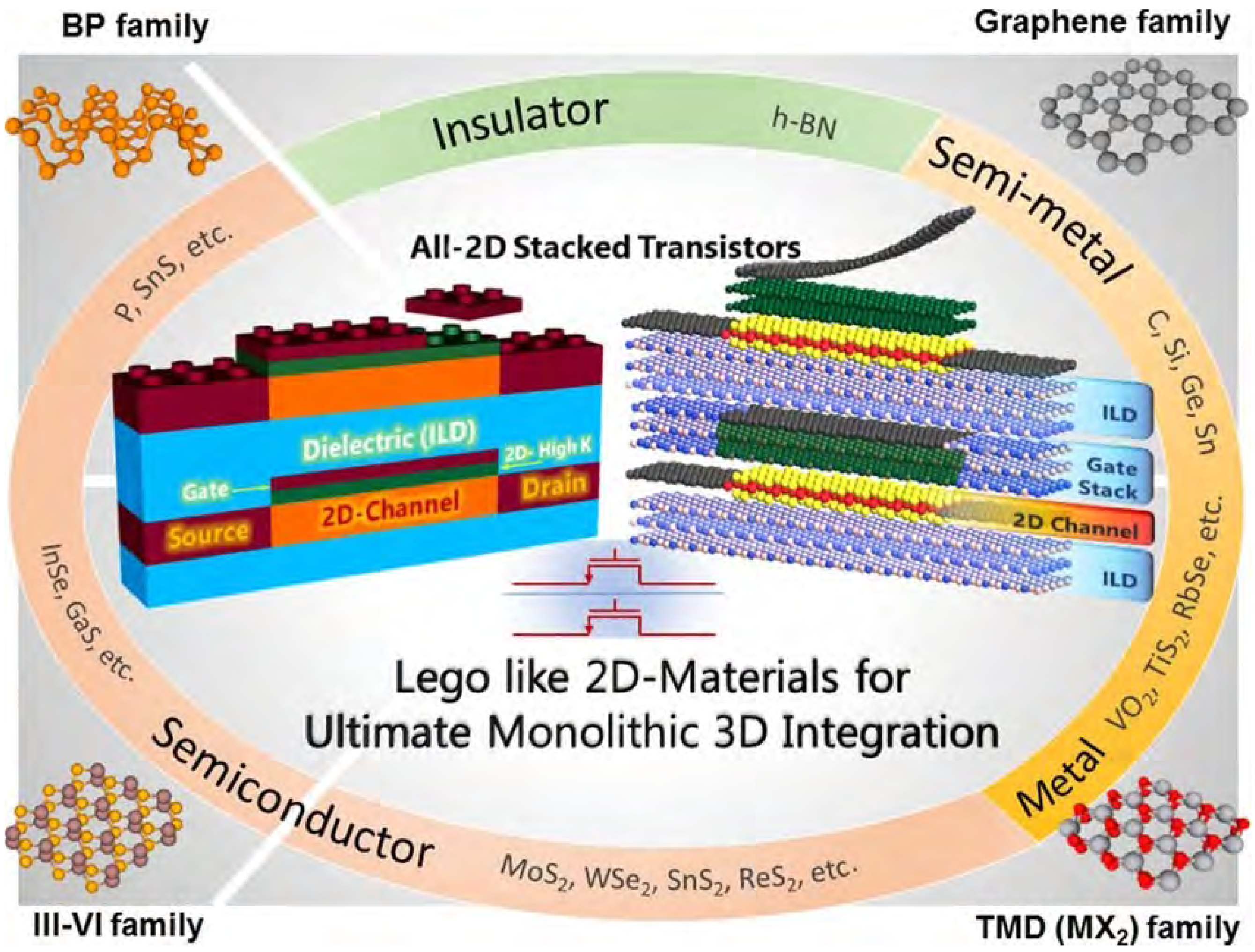
Semiconductor

Insulator

A. K. Geim and I. V. Grigorieva, *Nature* **499** *(2013)*

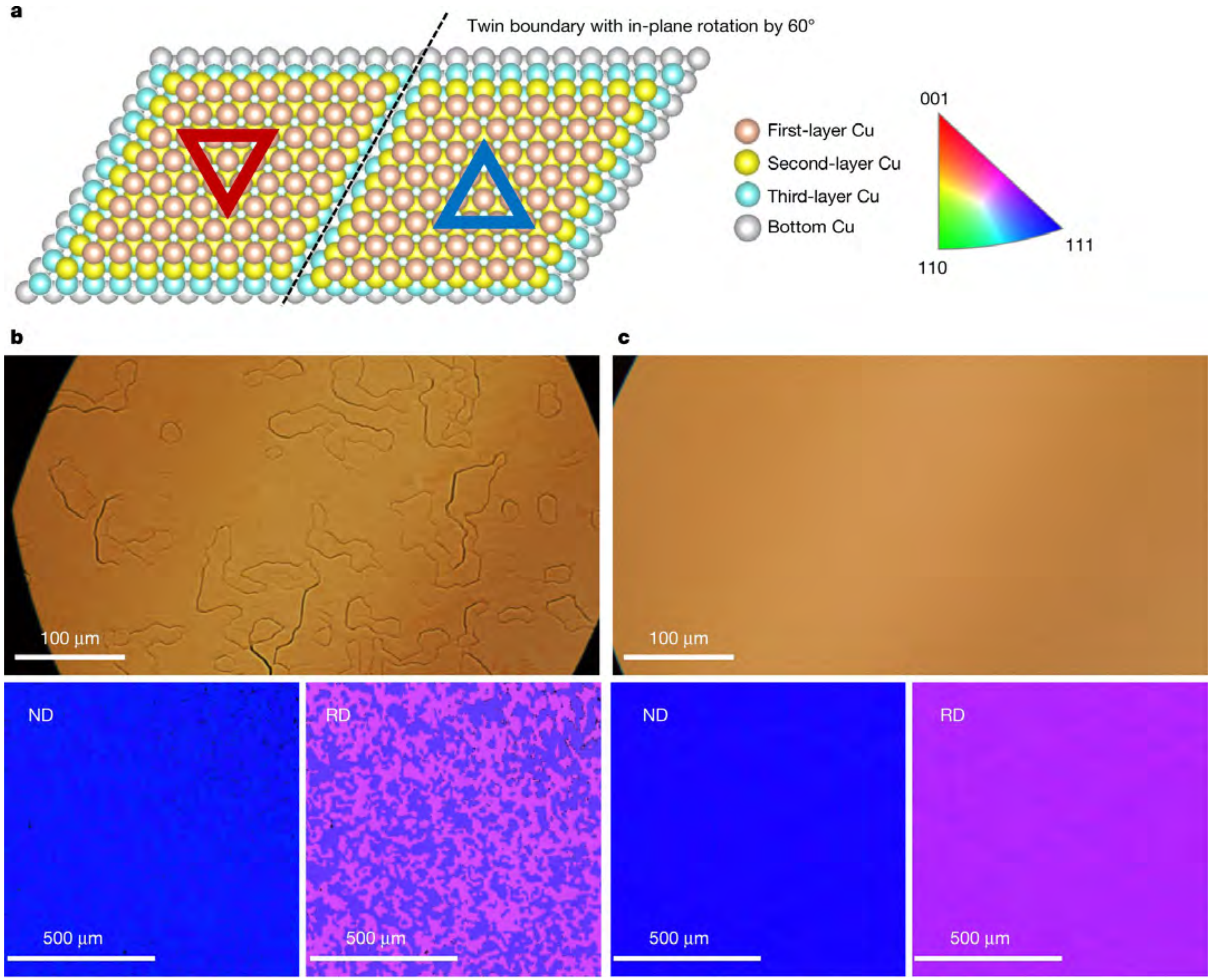
2D materials

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



J. Jiang et al. DOI:10.1109/JEDS.2019.2925150

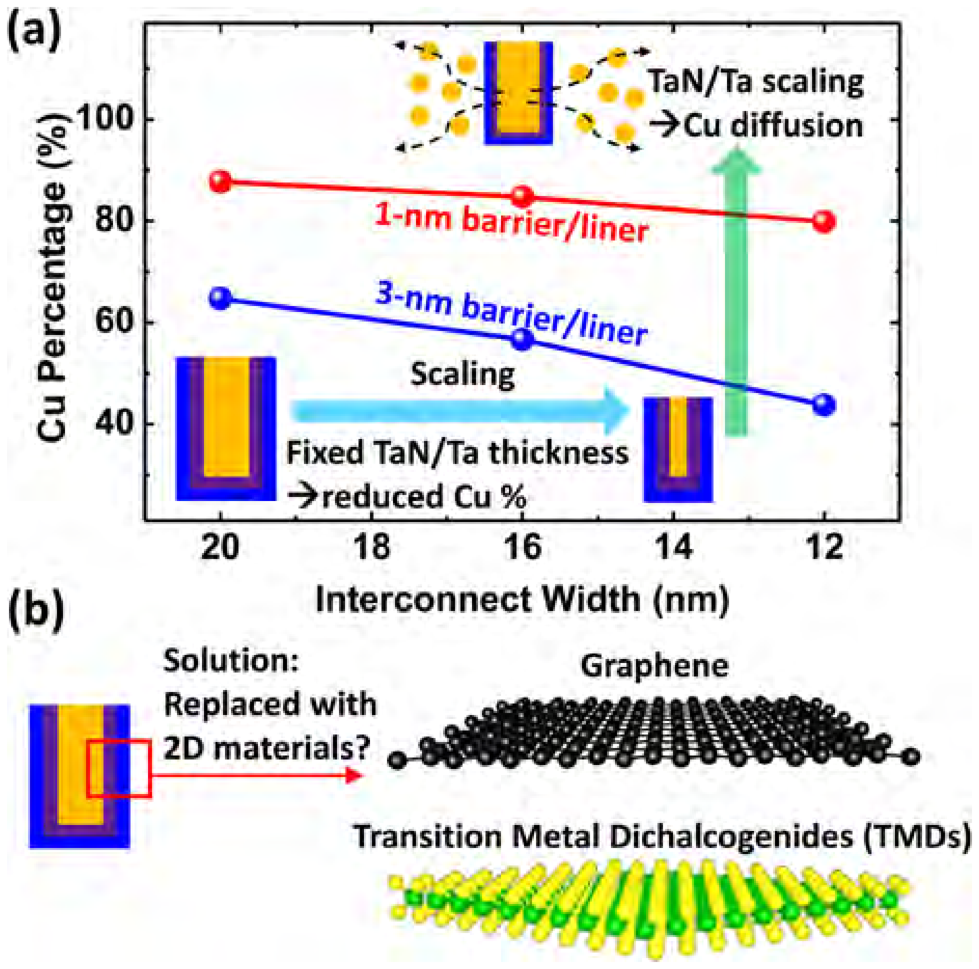
Wafer-scale materials



- 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

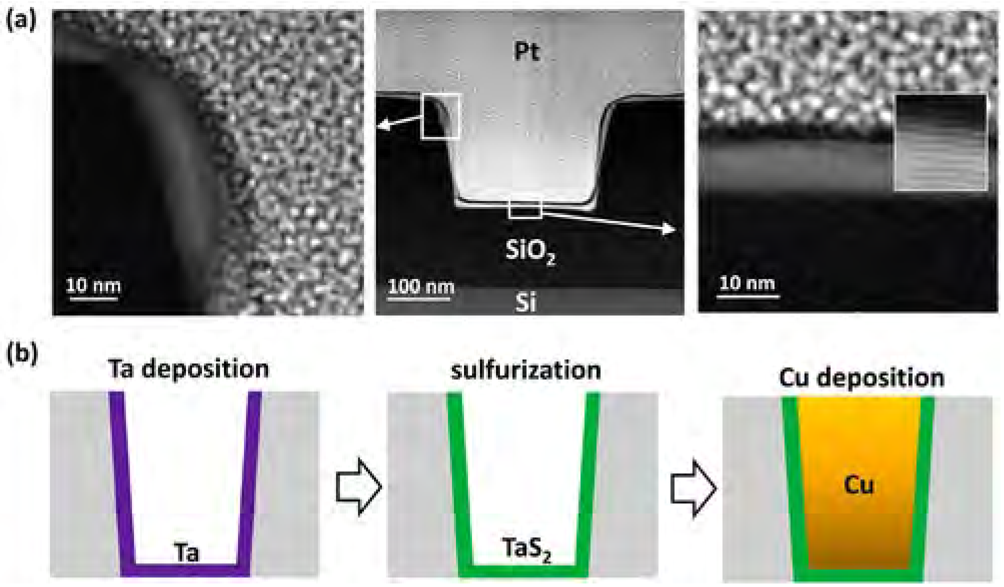
T. A. Chen, et al. Nature (2020)

Advancing the MOSFET fab

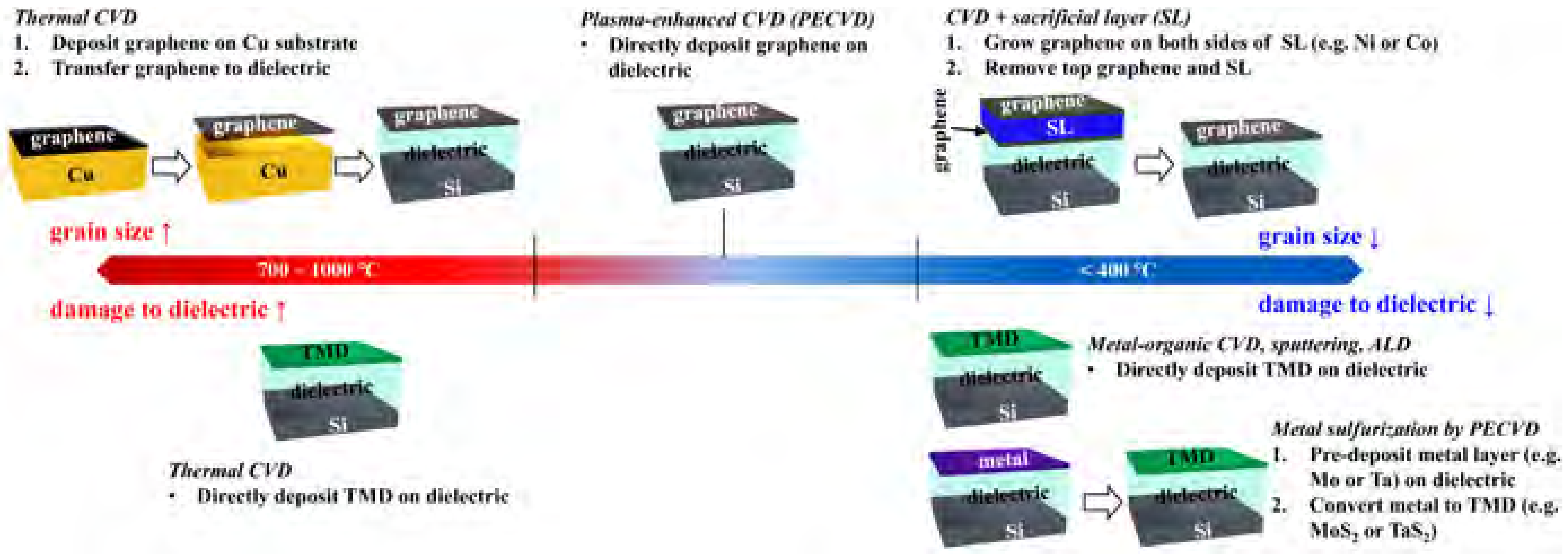


C.-L. Lo et al. JAP 2020

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

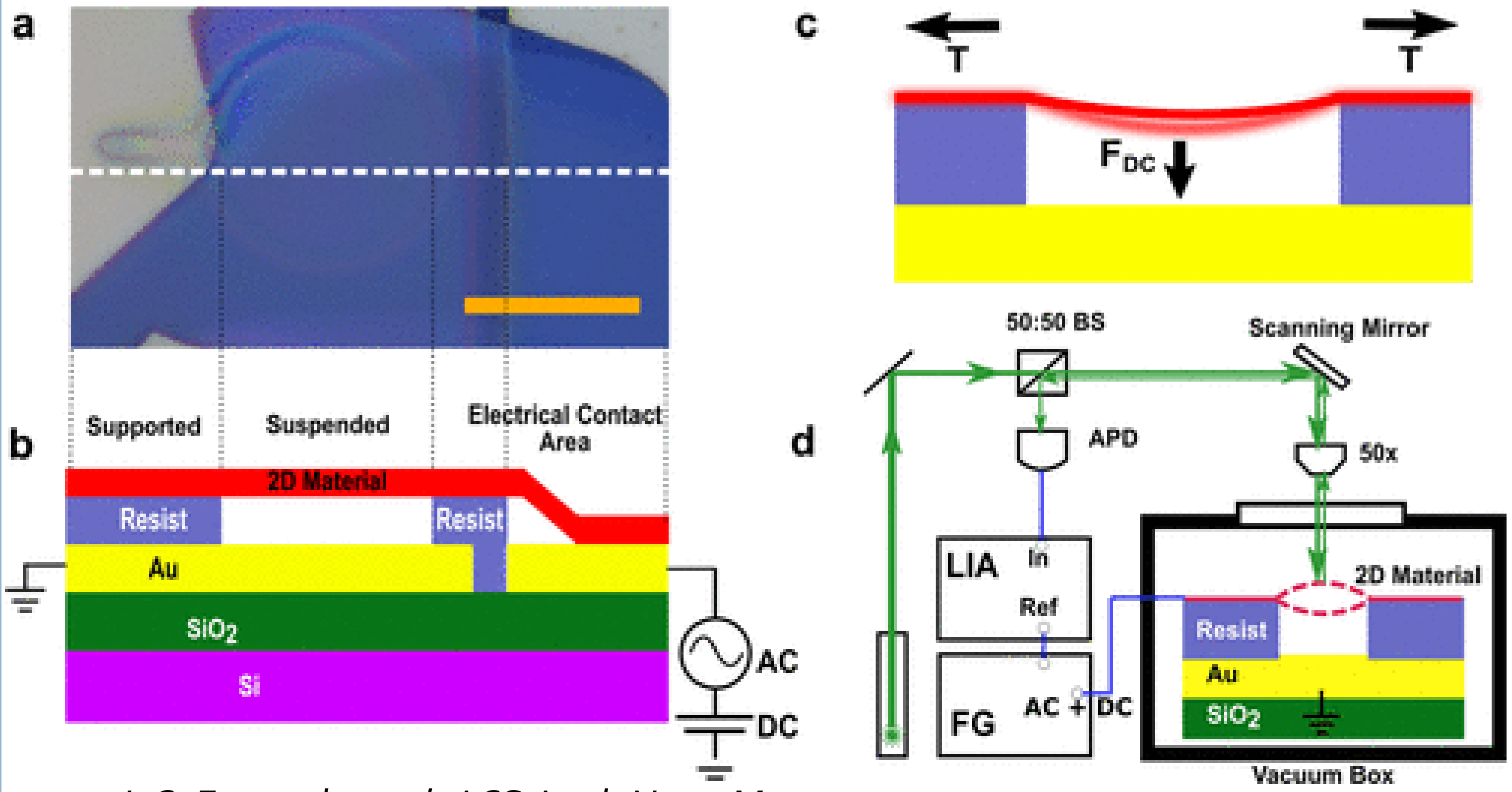


Growth of 2D materials



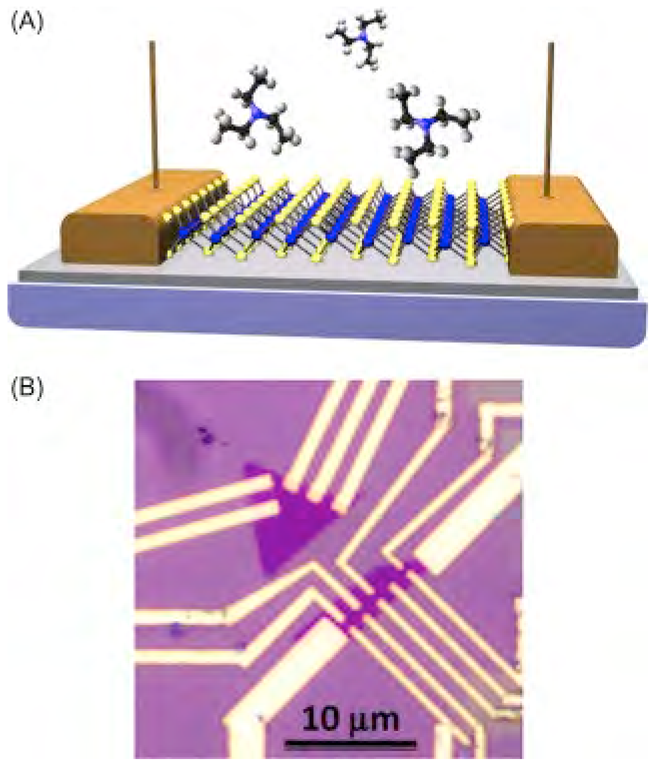
C.-L. Lo et al. JAP 2020

Sensor applications



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

Gas sensor



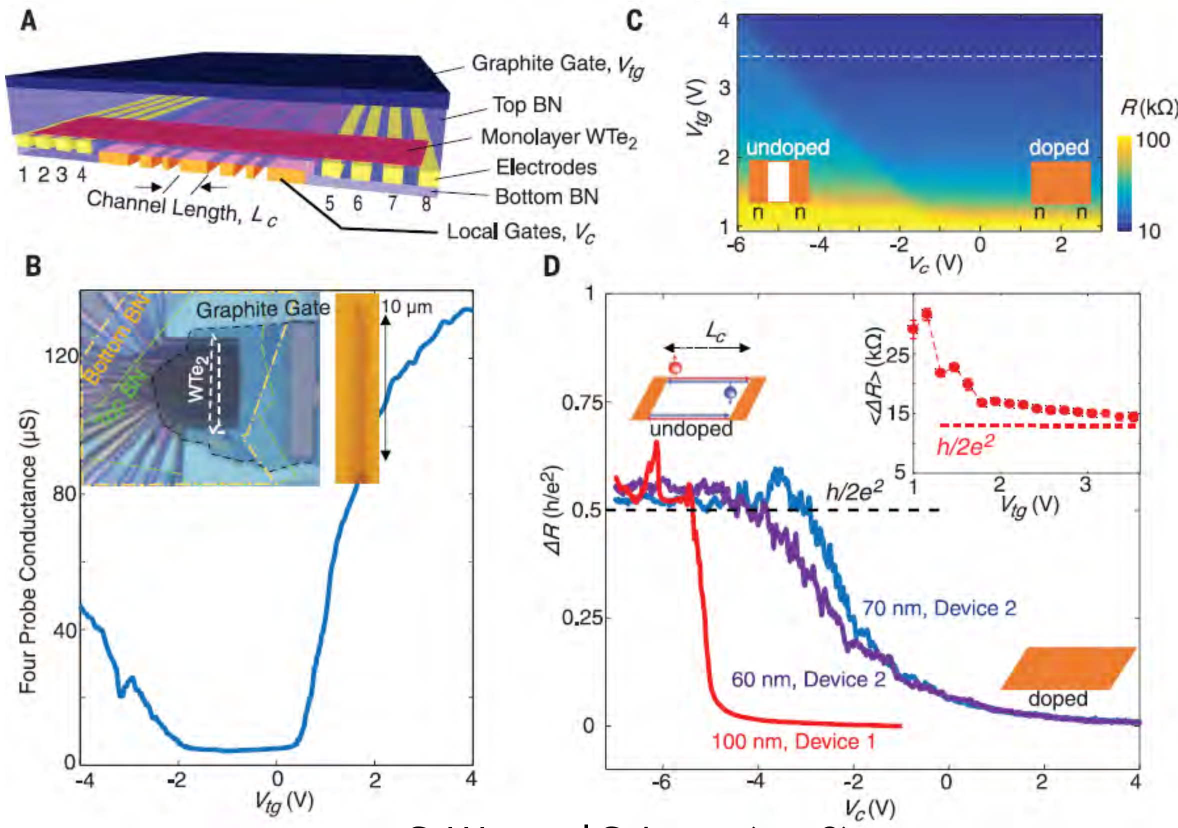
F. K. Perkins et al. Nano Letter (2013)

- 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

Transition Metal Dichalcogenides

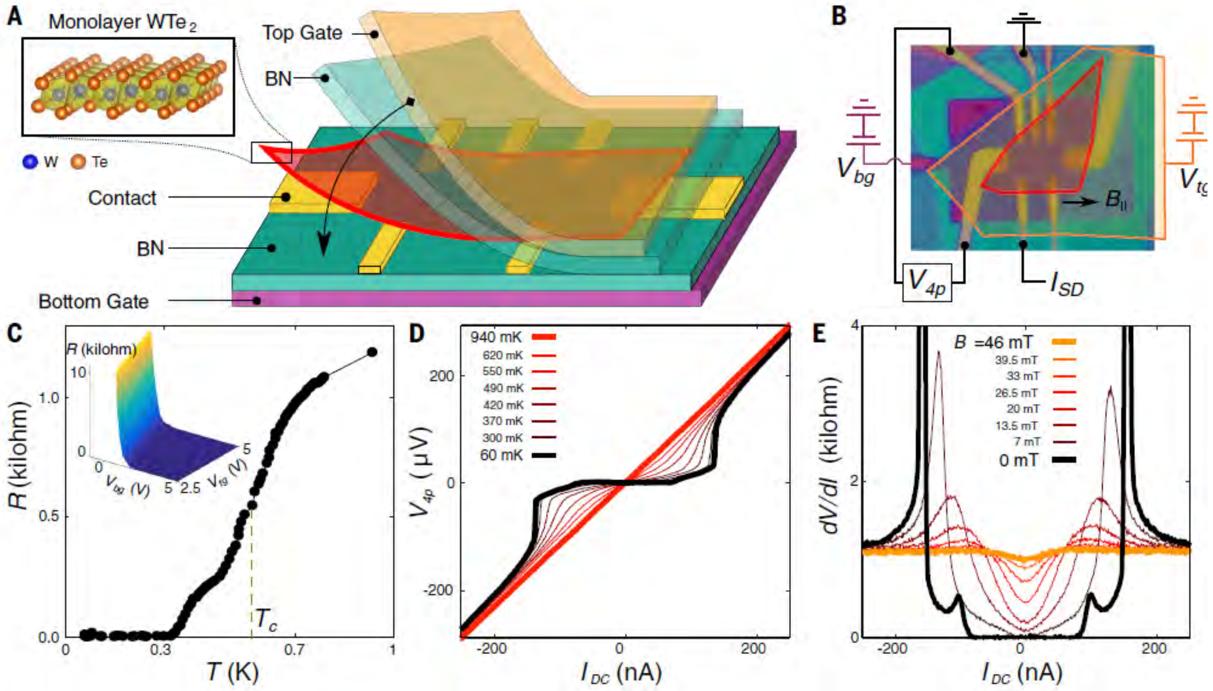
WTe_2

Quantum Spin Hall



S. Wu et al Science (2018)

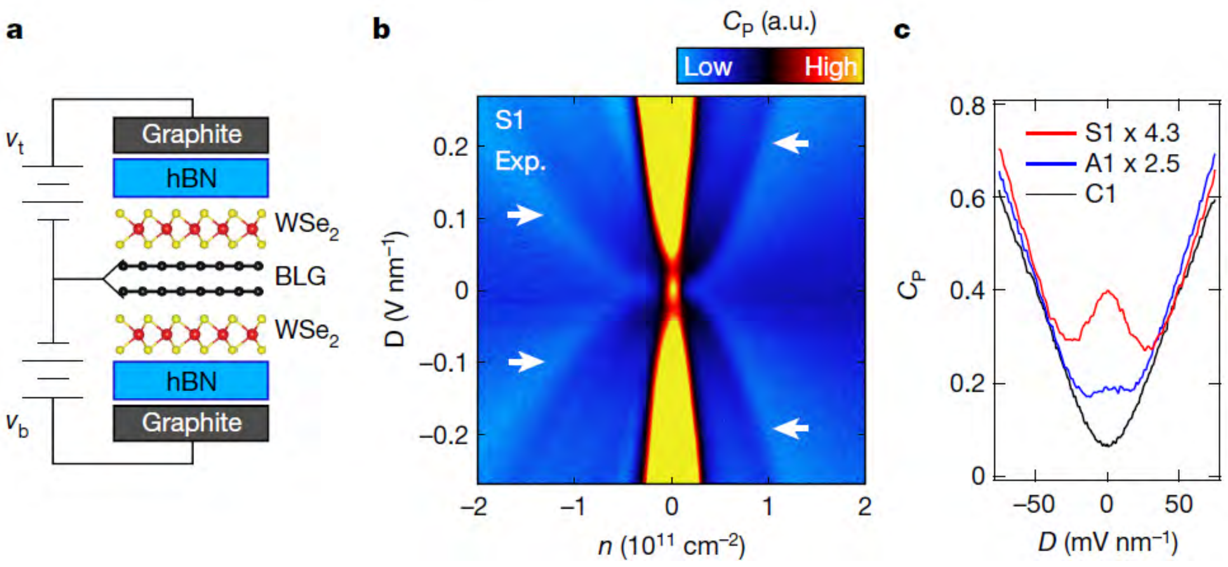
Superconductivity



V. Fatemil et al Science (2018)

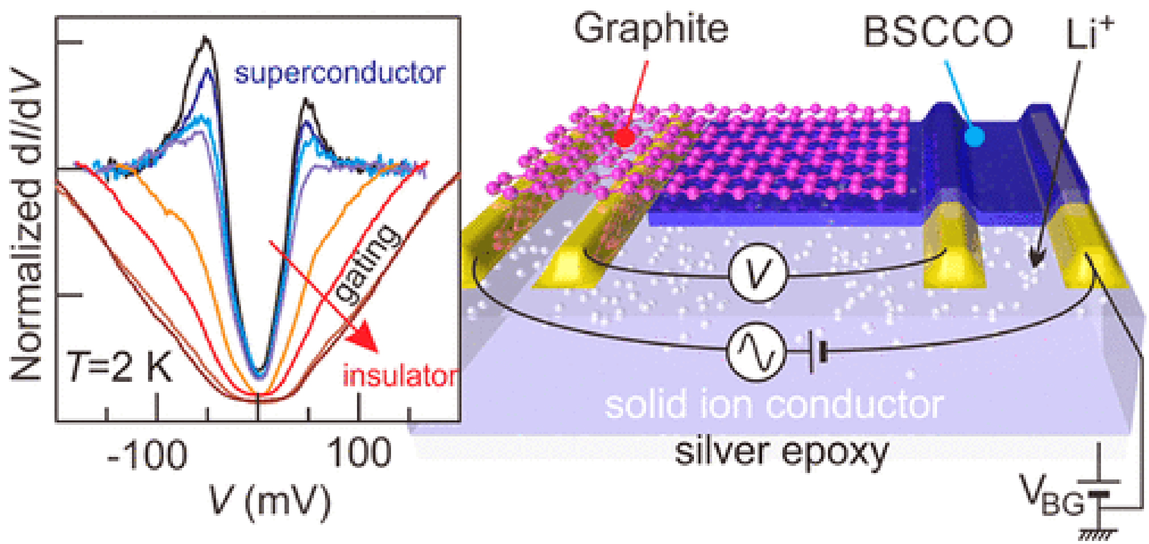
Hybrid material systems

Induce spin-orbital coupling in BLG



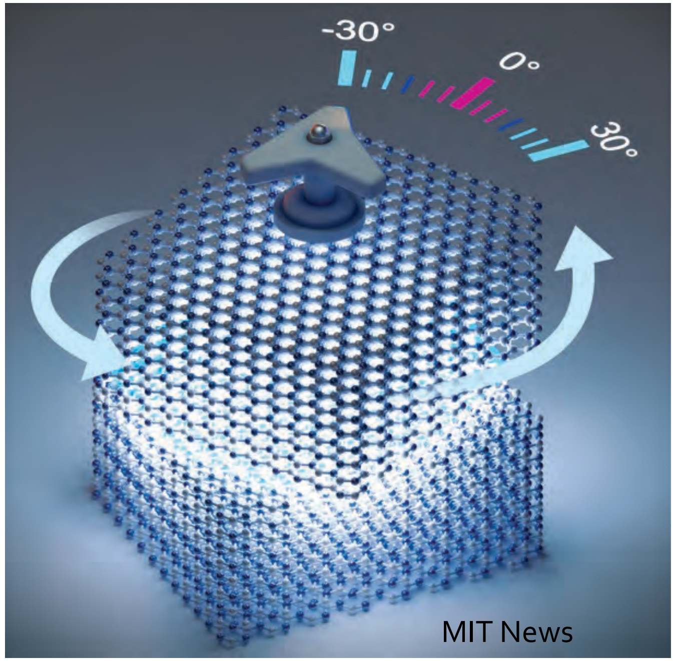
J. Island et al. Nature 2019

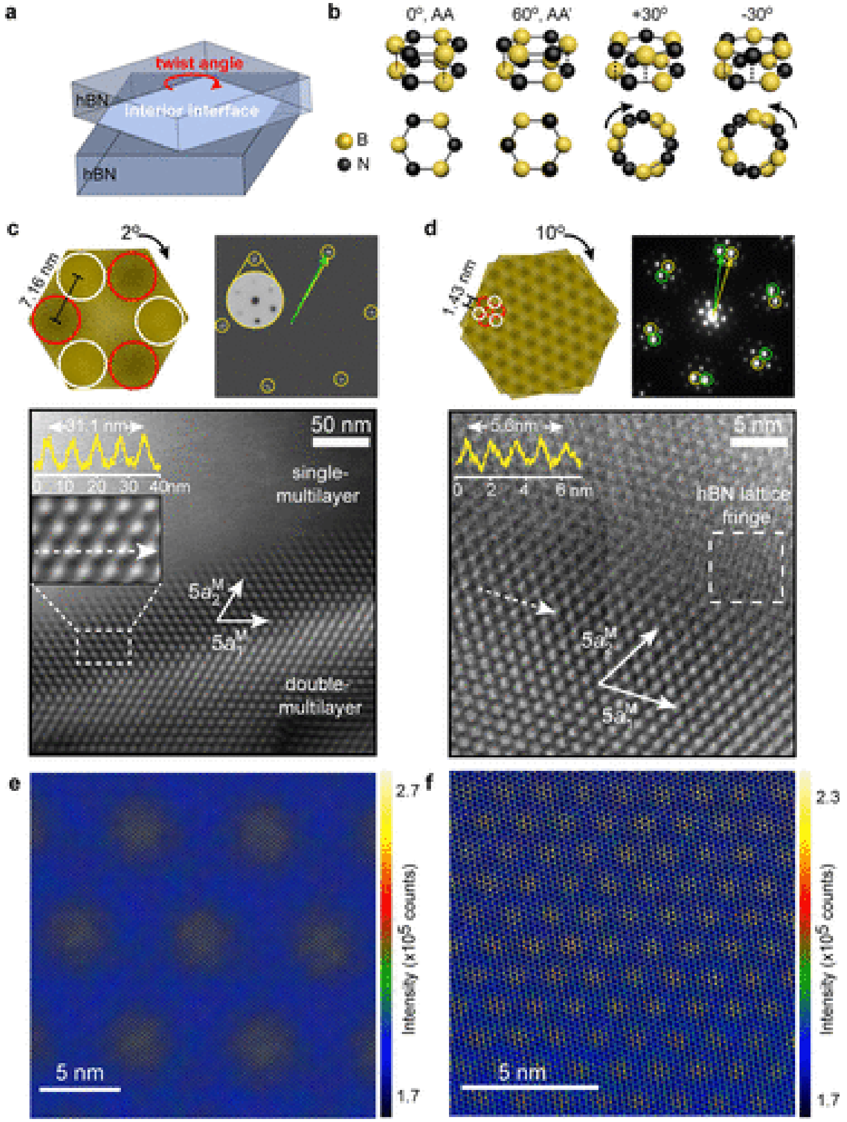
Coupling layered superconductor with graphite



M. Liao et al. Nano Letter 2018

Twist





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

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