Apport de la microscopie à effet tunnel pour l'ingénierie de défauts dans les matériaux bidimensionnels

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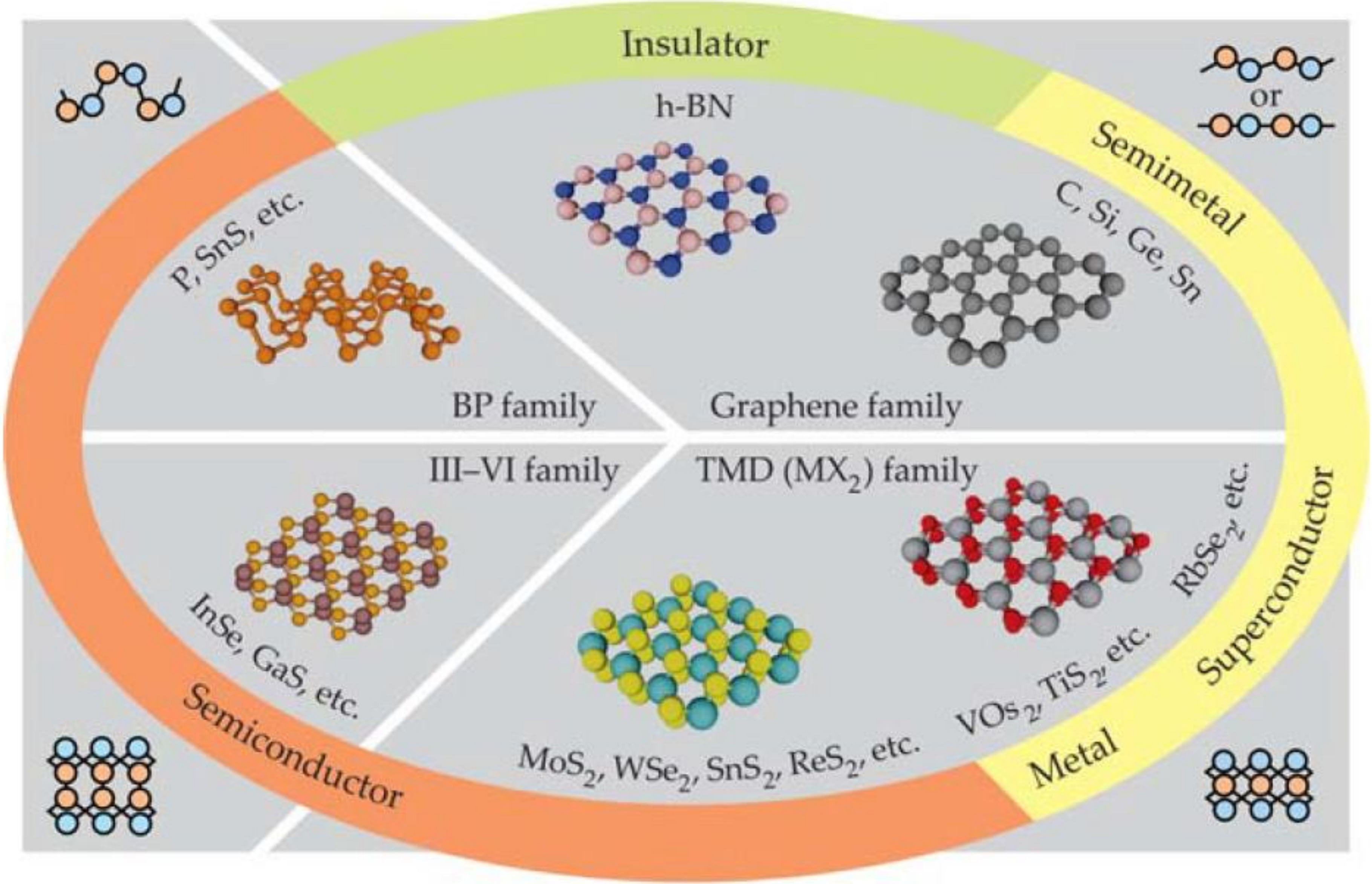
Université Paris Cité

Outline

- Introduction
- Nitrogen doping of graphene
- Charge density waves in Transition Metal Dichalcogenides

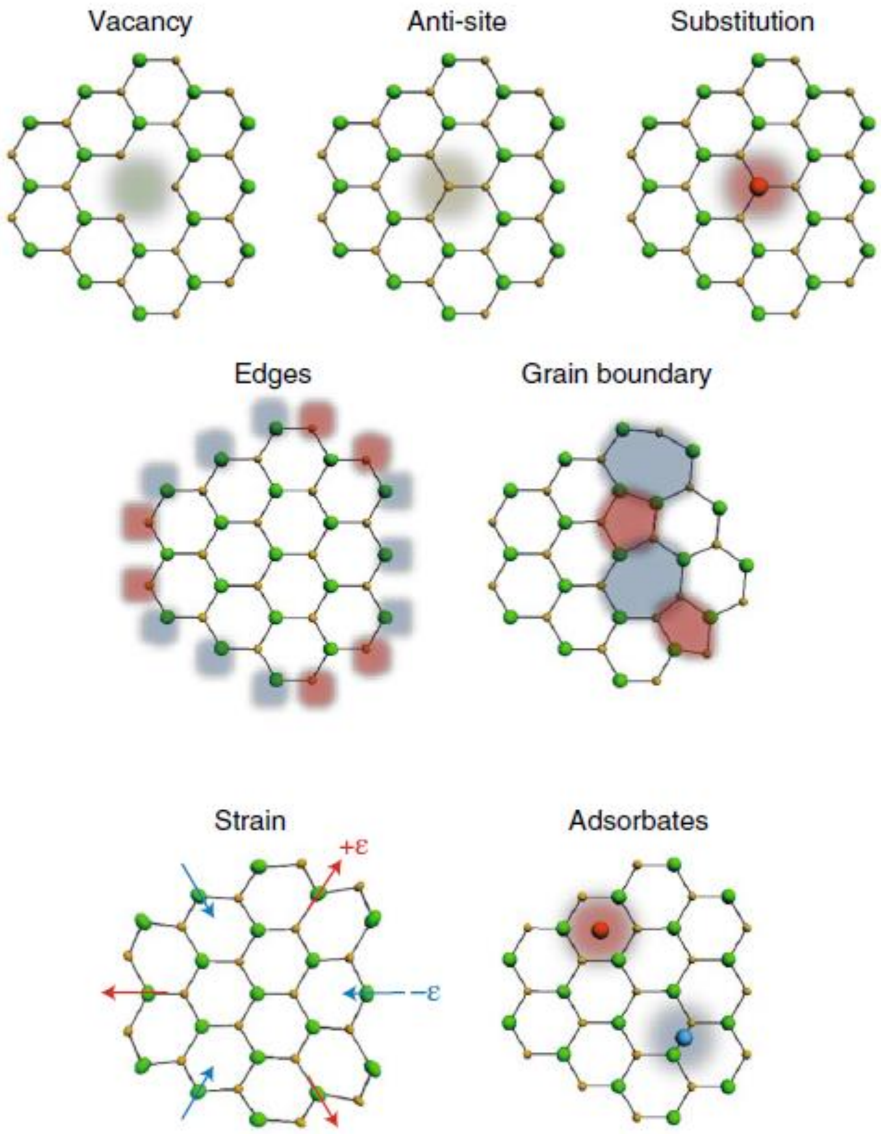
2D materials familly



P. Ajayan, P. Kim, and K. Banerjee, Phys. Today 69, 38, (2016)

Defects in 2D materials

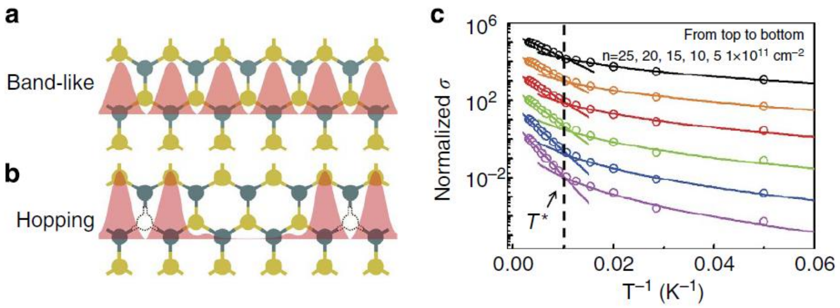
- Native defects are unavoidable
- Defects can alter the performances of materials
- Defect engineering: an approach to modulate the properties on demand and achieve dedicated functionalities



Nat. Materials 18, 541 (2019)

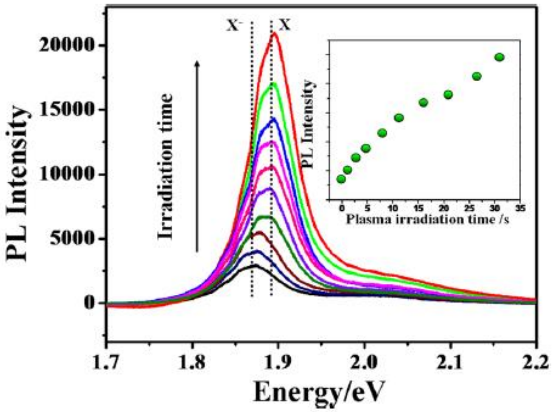
Defect engineering in 2D materials

Vacancies in MoS_2: Hopping transport



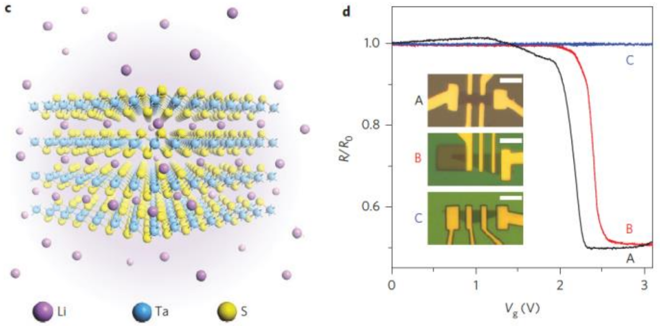
Nat. commun., 4, 2642 (2013)

Enhanced Photoluminescence
in MoS_2 due to O_2 bonding on vacancies



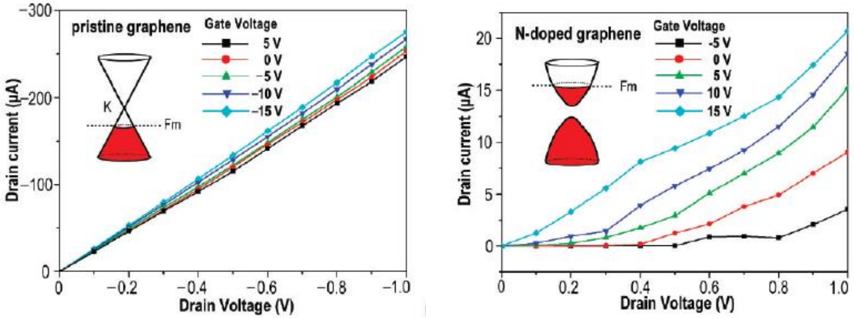
ACS Nano 8, 5738 (2014)

Intercalation induced CDW transition
in TMDs



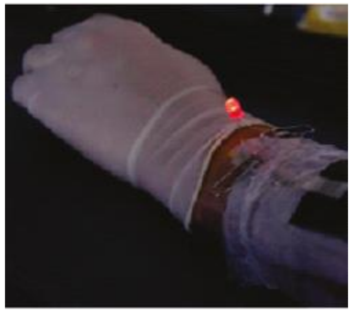
Nat. Nanotechnol. 10, 270 (2015)

Nitrogen doped graphene:
Transistors: high ratio I_{ON}/I_{OFF}



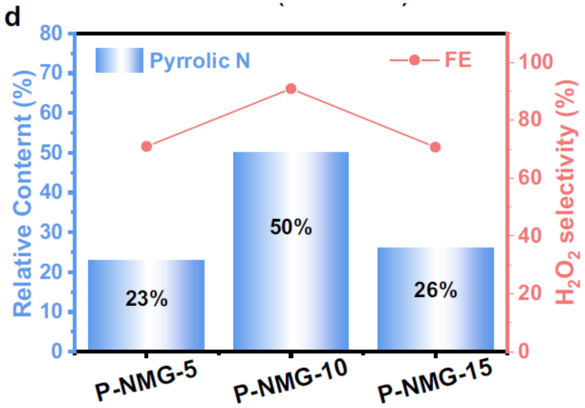
D. Wei et al., Nano Lett., 9, 1752 (2009)

Supercapacitor



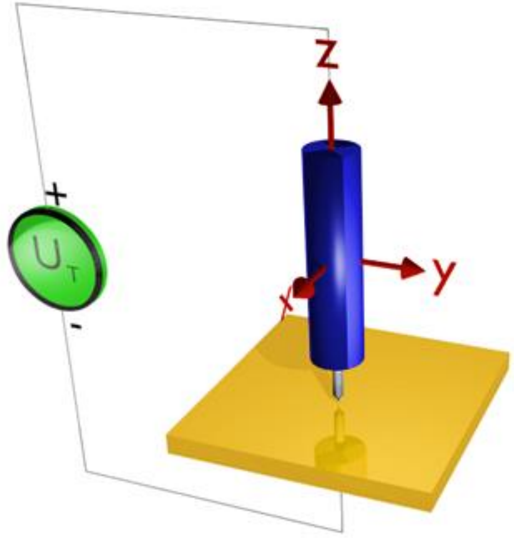
H. M. Jeong et al., Nano Lett 11, 2472 (2011)

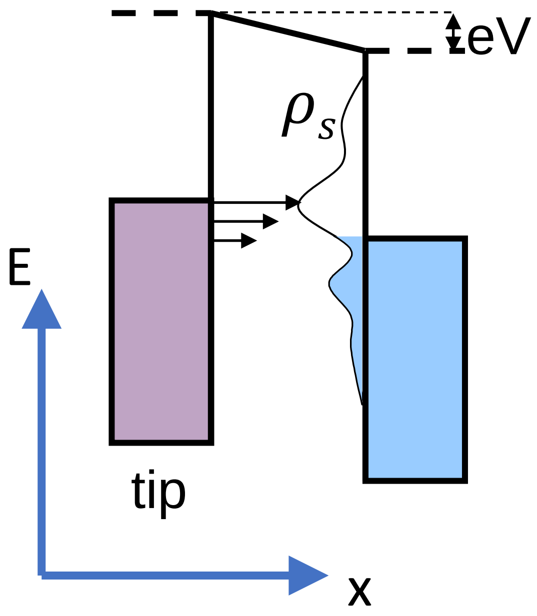
Nitrogen doped graphene:
enhanced oxygen reduction



Nat Commun 14, 4430 (2023)

Scanning tunneling microscopy





Tersoff and Hamann approximation:

$$I_t \propto \int_{E_F}^{E_F+eV} \rho_t(E-eV)\,\rho_s(E,\vec{r_0})dE$$

assuming a metallic tip with ρ_t=cte

$$I_t \propto \rho_t \int_{E_F}^{E_F+eV} \rho_s(E,\vec{r_0})dE$$

$$\frac{dI}{dV} \propto \rho_t\rho_s(eV,\vec{r_0})$$

dI/dV(V) is proportional to the local density of states (LDOS) of the sample at the energy eV

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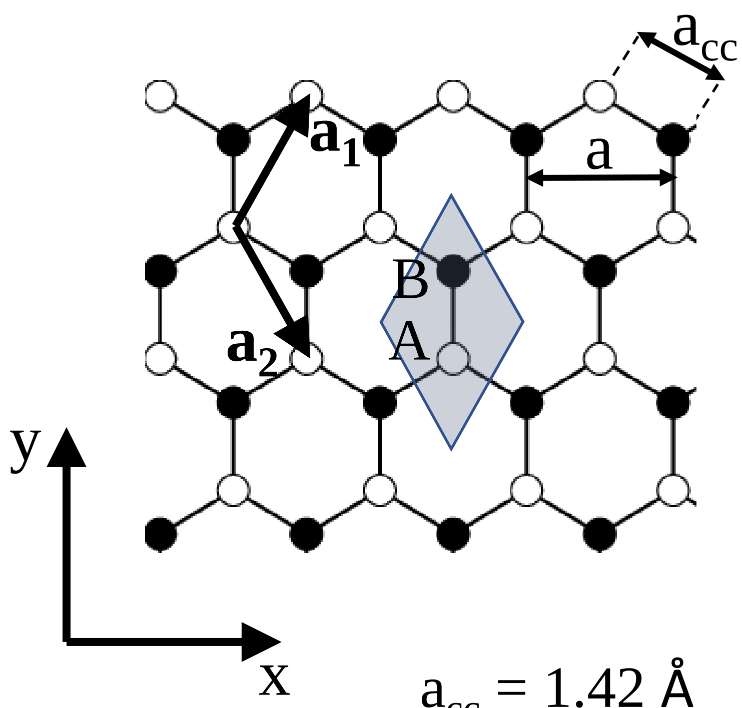
Electronic properties of graphene

Real space: crystal structure



a_{cc} = 1.42 Å

a = $\sqrt{3}a_{cc}$ = 2.46 Å

Bloch functions on the two sublattices

$$\Phi_A(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{i=1}^{N} e^{i\vec{k}.\overrightarrow{R_{A,i}}}\,\Phi(\vec{r} - \overrightarrow{R_{A,i}})$$

$$\Phi_B(\vec{r}) = \frac{1}{\sqrt{N}}\sum_{i=1}^{N} e^{i\vec{k}.\overrightarrow{R_{B,i}}}\,\Phi(\vec{r} - \overrightarrow{R_{B,i}})$$

$$H = \begin{pmatrix} E_0 & \gamma_0 f(\vec{k}) \\ \gamma_0 f^*(\vec{k}) & E_0 \end{pmatrix}$$

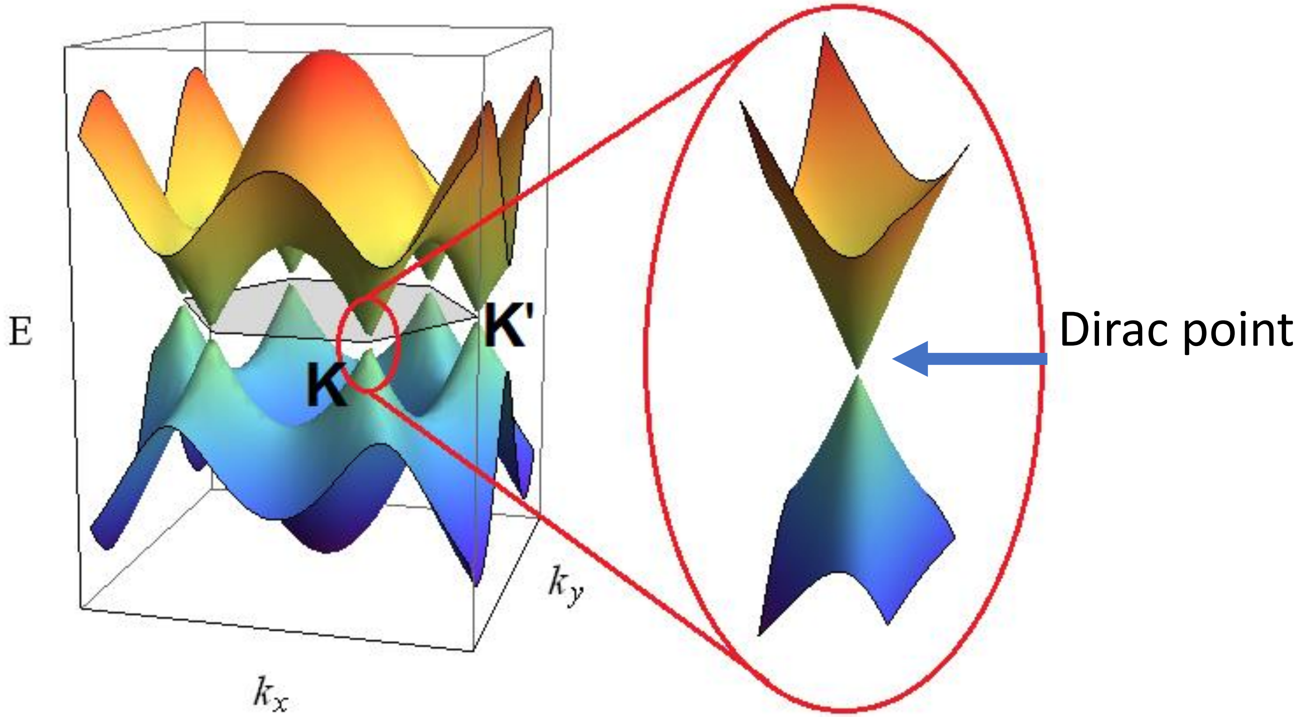
$$f(\vec{k}) = e^{ik_y a/\sqrt{3}} + 2e^{-ik_y a/2\sqrt{3}}\cos(k_x a/2)$$

Electronic properties of graphene

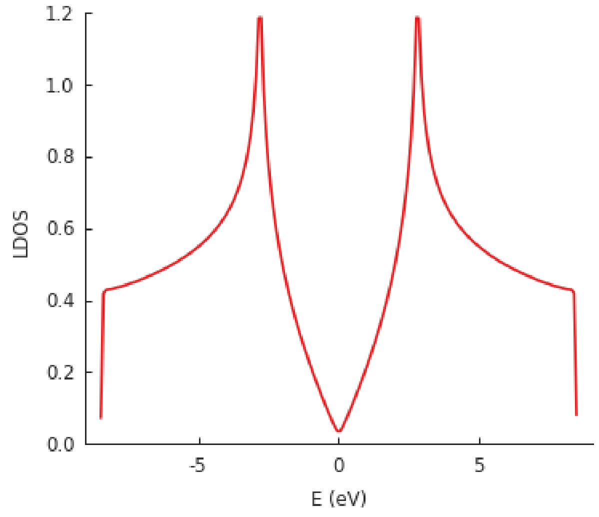
$$E = E_0 \pm \gamma_0 \left| f(\vec{k}) \right|$$

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

Electronic bandstructure

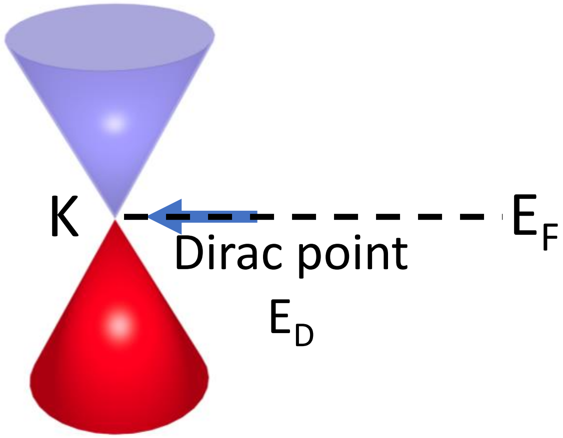


Density of states

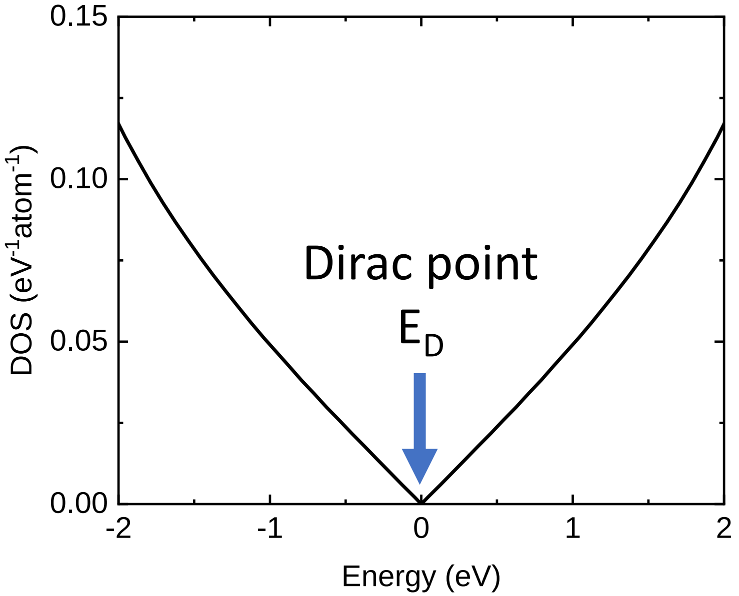


Electronic properties near the Dirac point

Bandstructure around K point



Density of states



Linear dispersion

$$\mathrm{E} = \pm \hbar k v$$

v : Fermi velocity

k measured from the K point

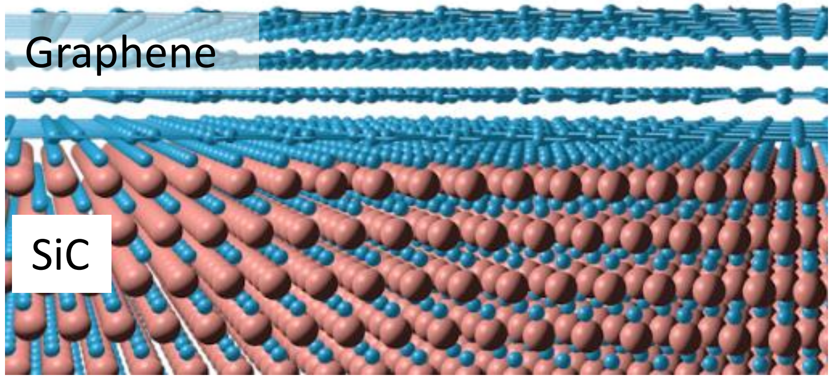
Linear density of states

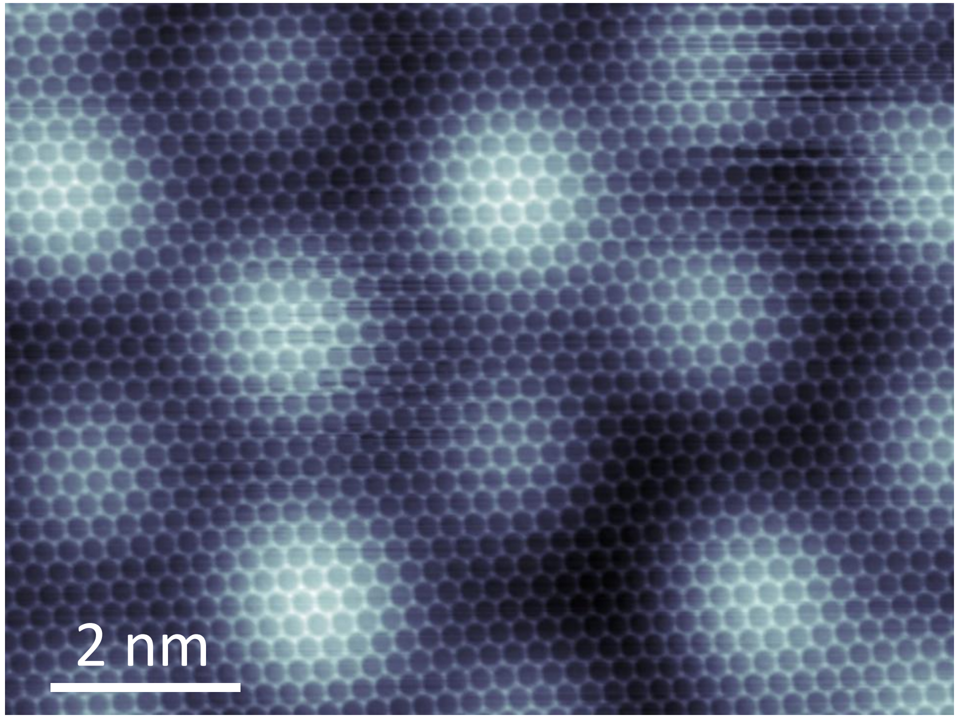
$$\frac{dN}{dE} = \frac{dN}{dk}\frac{dk}{dE} = \frac{k}{2\pi}\ \frac{1}{\hbar v} = \frac{|E|}{2\pi(\hbar v)^2}$$

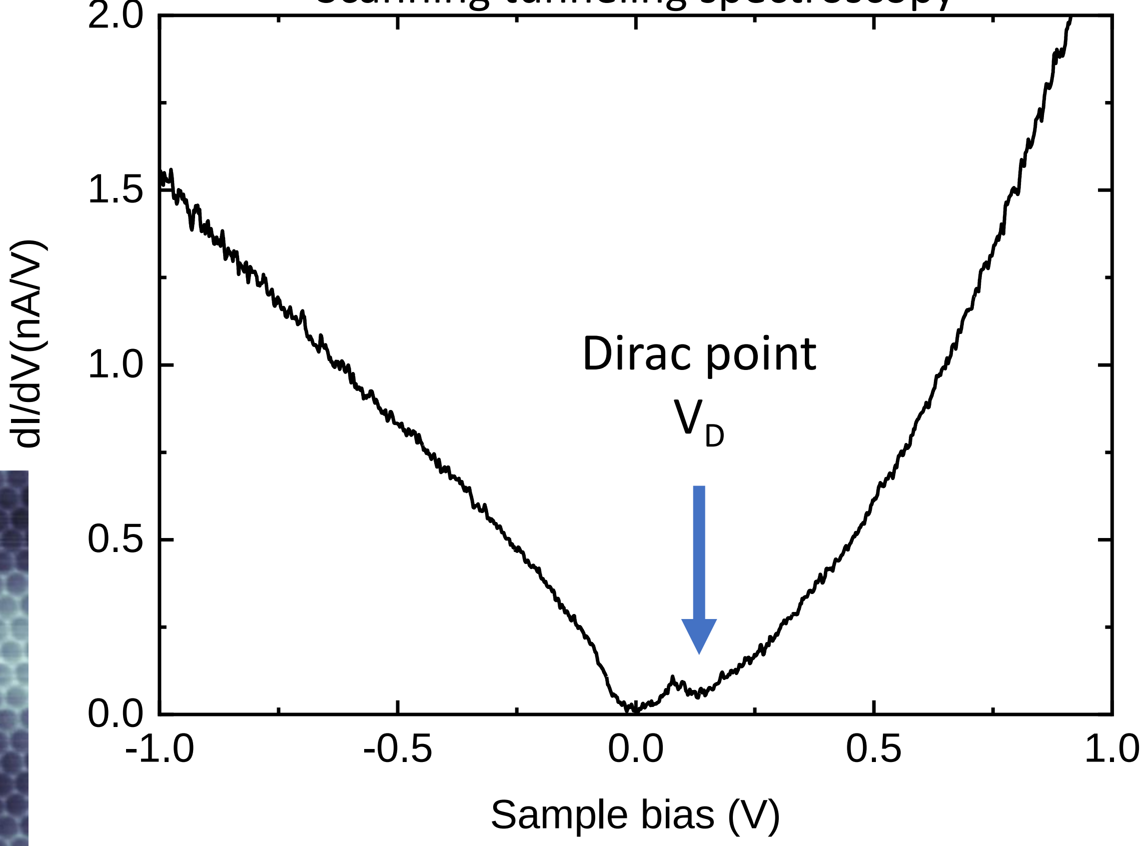
$$N(E) = \frac{2|E|}{\pi(\hbar v)^2}$$

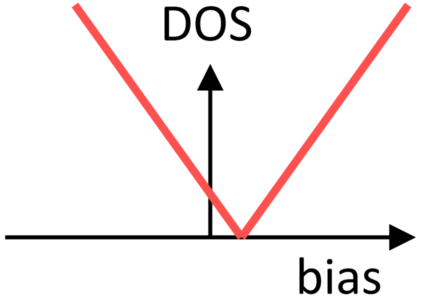
Scanning tunneling spectroscopy on graphene on SiC(000$\bar{1}$)

Multilayer graphene on SiC(000-1)

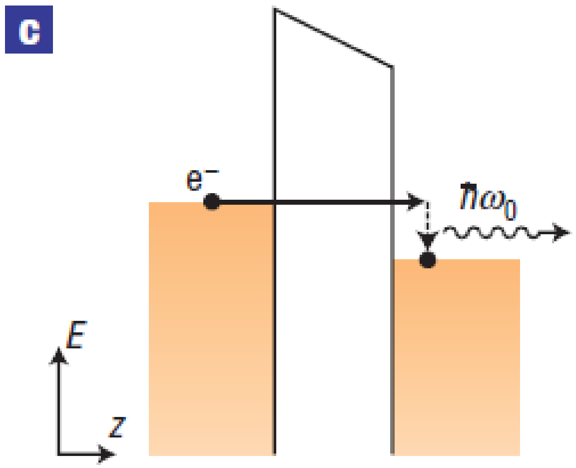


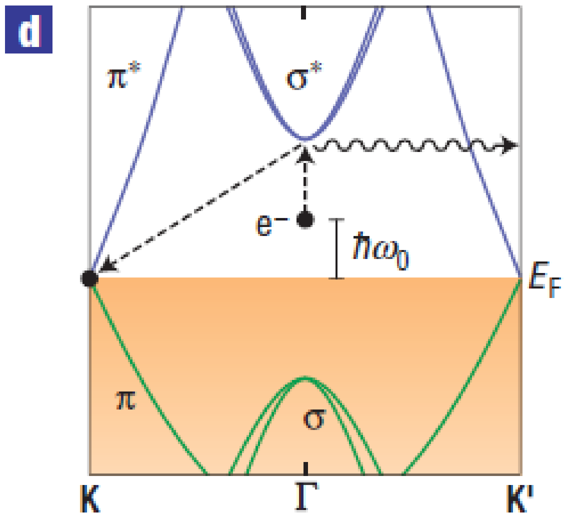






Inelastic process in STM measurement on graphene





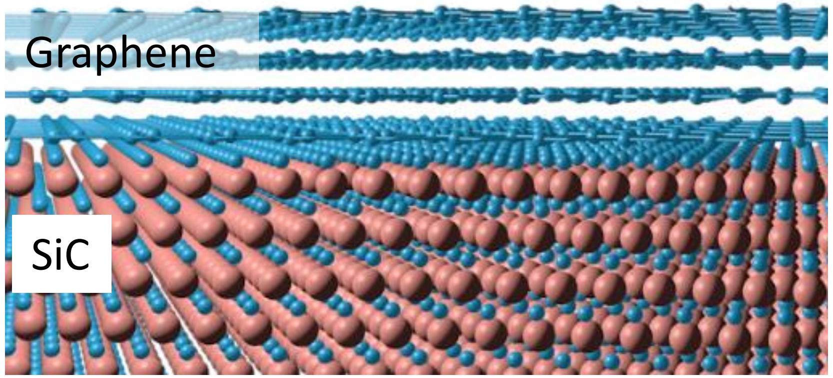
$$\mathrm{LDOS}(z, k_{\parallel}) \propto \mathrm{e}^{-z/\lambda} \qquad \lambda^{-1} = 2\sqrt{2m\phi/\hbar^2 + k_{\parallel}^2},$$

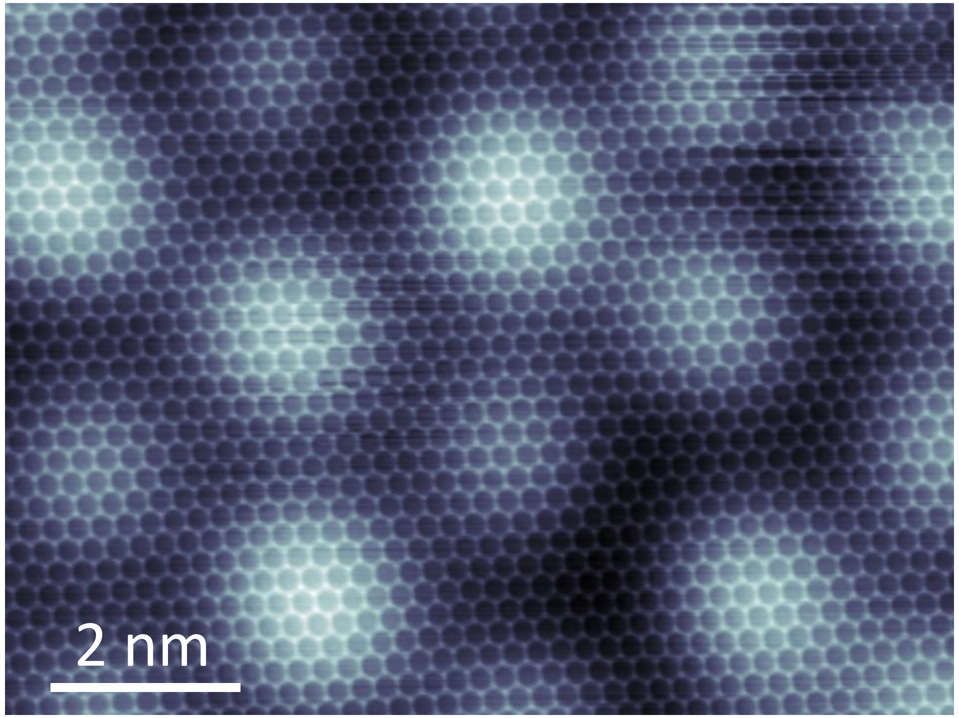
STM current dominated by states around Γ point
No state at Γ point in graphene
=> need phonon excitation at K point to tunnel through the K point of graphene

Y. Zhang et al., Nature Physics, 4, 627 (2008)

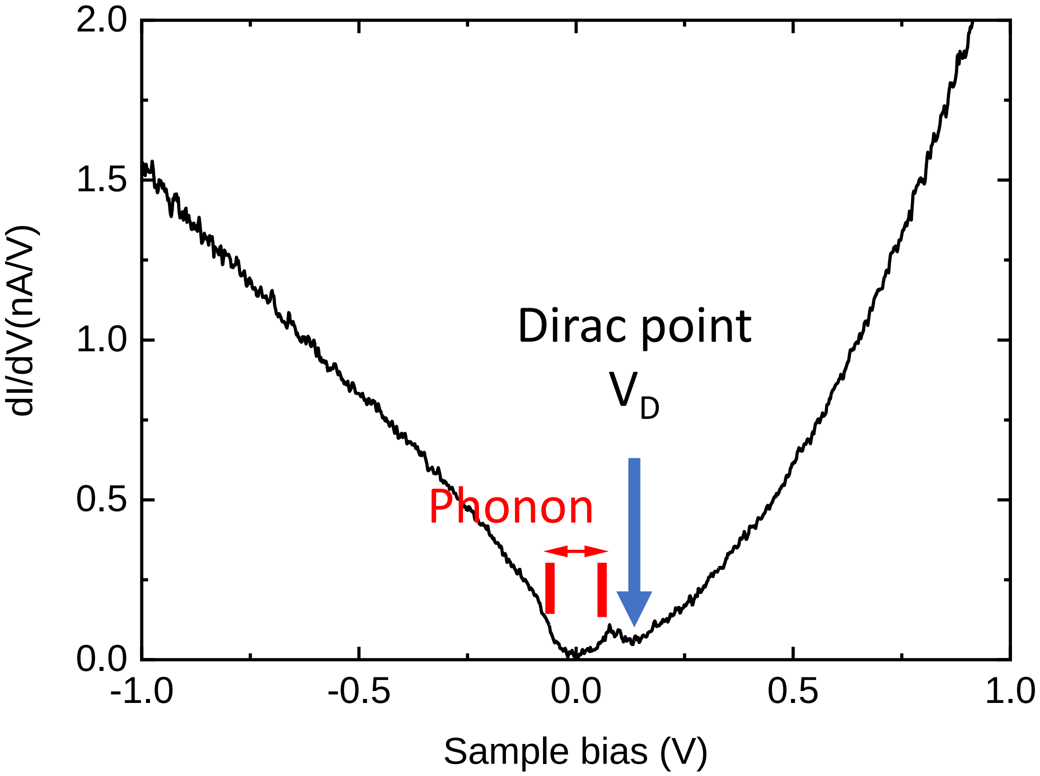
Scanning tunneling spectroscopy on graphene on SiC(000$\bar{1}$)

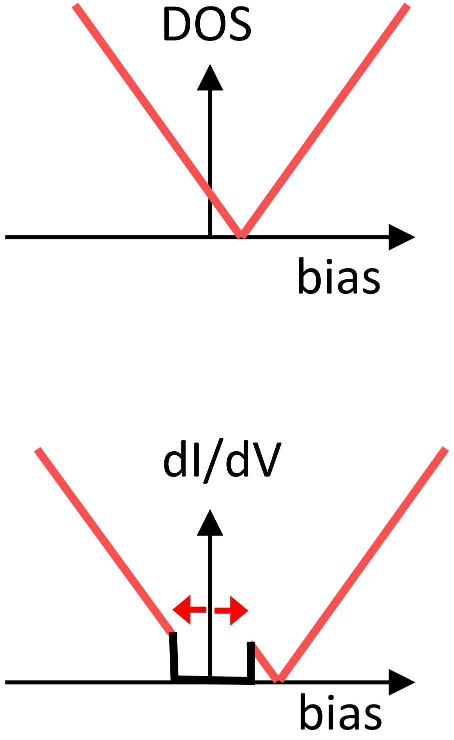
Multilayer graphene on SiC(000-1)





Scanning tunneling spectroscopy



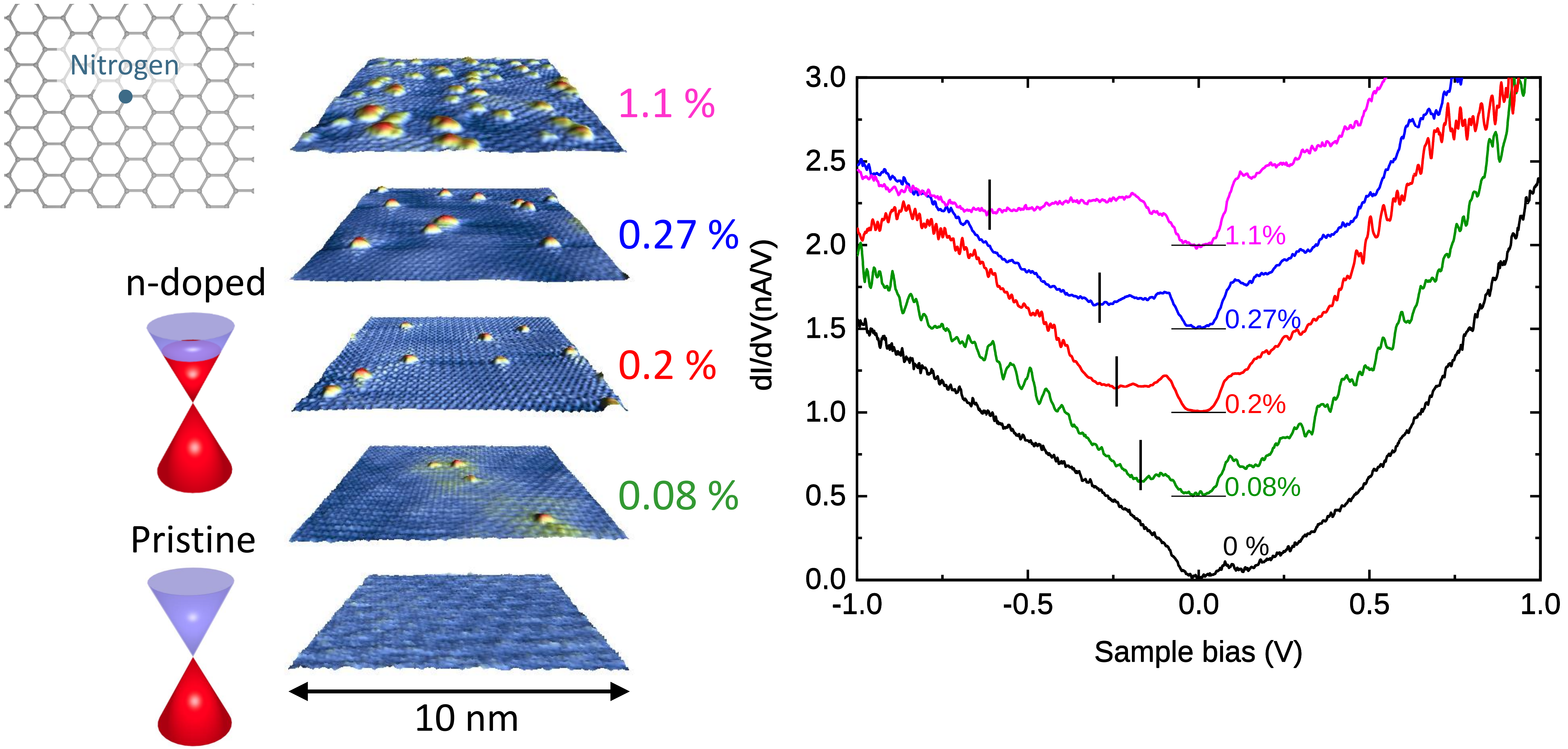


Phonon inelastic excitation at ±60 mV

V_D = 140 mV => E_D = 80 mV

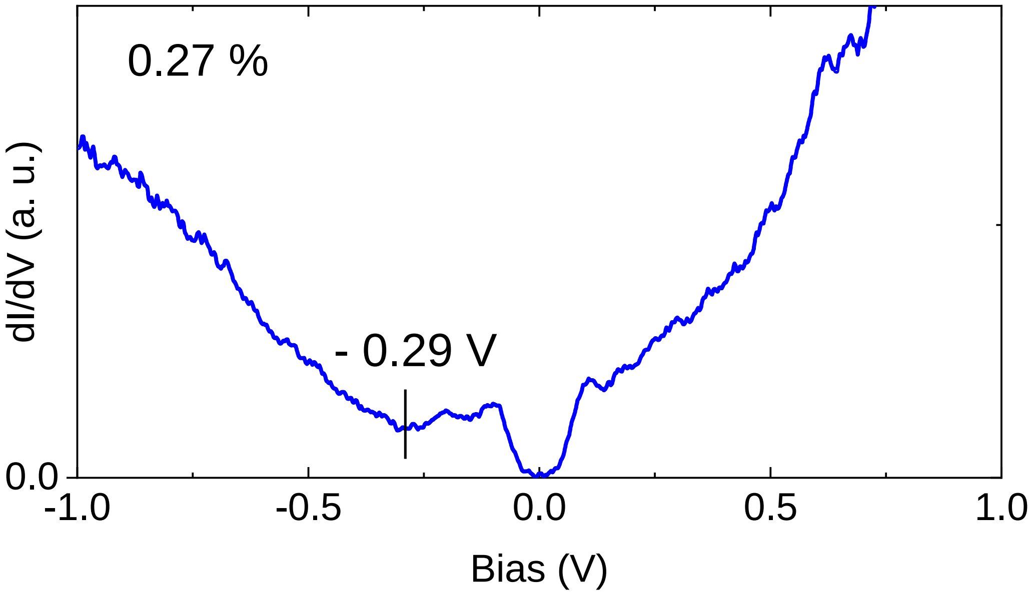
Slight natural p-doping in pristine graphene on SiC carbon side

Nitrogen doped graphene



F. Joucken et al., *Scientific Report* 5, 14564 (2015)
Review article:
Joucken, L. Henrard and J. Lagoute, *Phys. Rev. Materials* 3, 110301 (2019)

Nitrogen doped graphene



Charge density

$$n = \int_{E_F}^{E_D} N(E)dE = \int_{0}^{E_D} \frac{2E}{\pi(\hbar v_F)^2} dE = \frac{E_D^2}{\pi(\hbar v_F)^2} = 3.7 \times 10^{16} m^{-2}$$

Nitrogen concentration

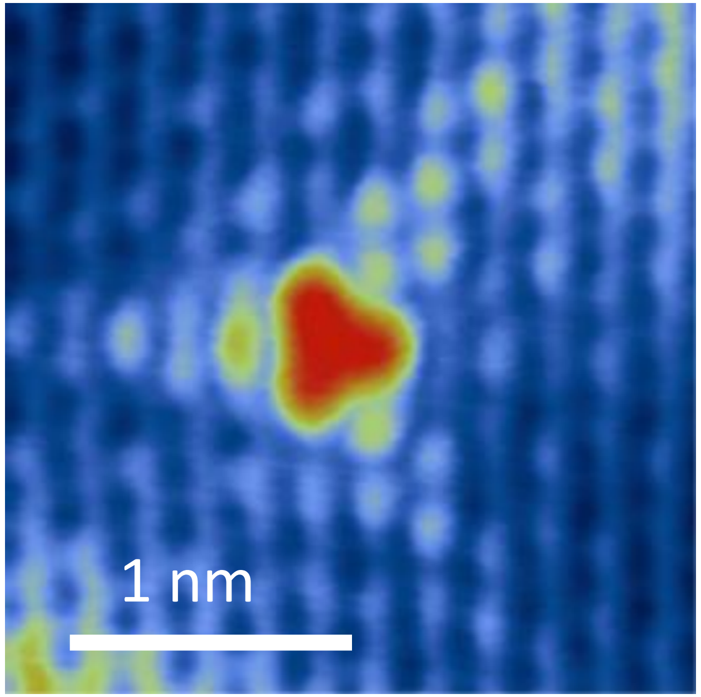
$$n_N = n_C \times 0.27\% = 10.4 \times 10^{16} m^{-2}$$

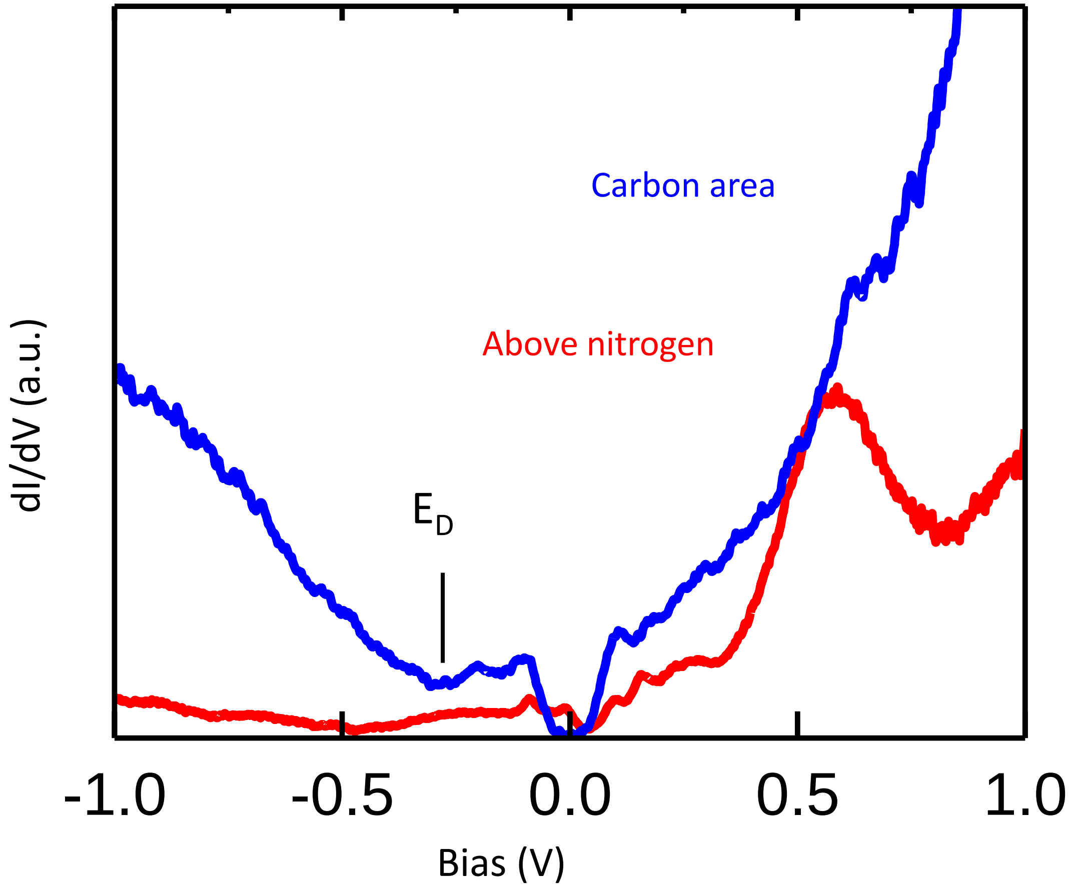
Charge given by each nitrogen atom:

$\frac{n}{n_N} = 0.36$ electron per nitrogen

Less than 1 !

Localized resonant state





Graphene with a point defect

Density of state $D(E)$

$$D(E) = -\frac{1}{\pi}Tr\left[Im\left(G(E)\right)\right]$$

Green function $G(E)$

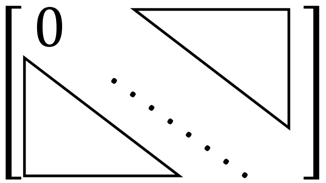
$$G(E) = \frac{1}{\mathcal{E} - H}$$

Where $\mathcal{E} = \lim_{\eta \to 0^+} (E + i\eta)I$

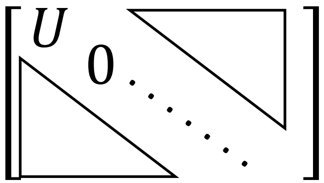
$$H = H^0 + U$$

H	Total Hamiltonian
H^0	Hamiltonian Wwthout defect
U	Defect potential

$H^0 =$



$U =$



Graphene with a point defect

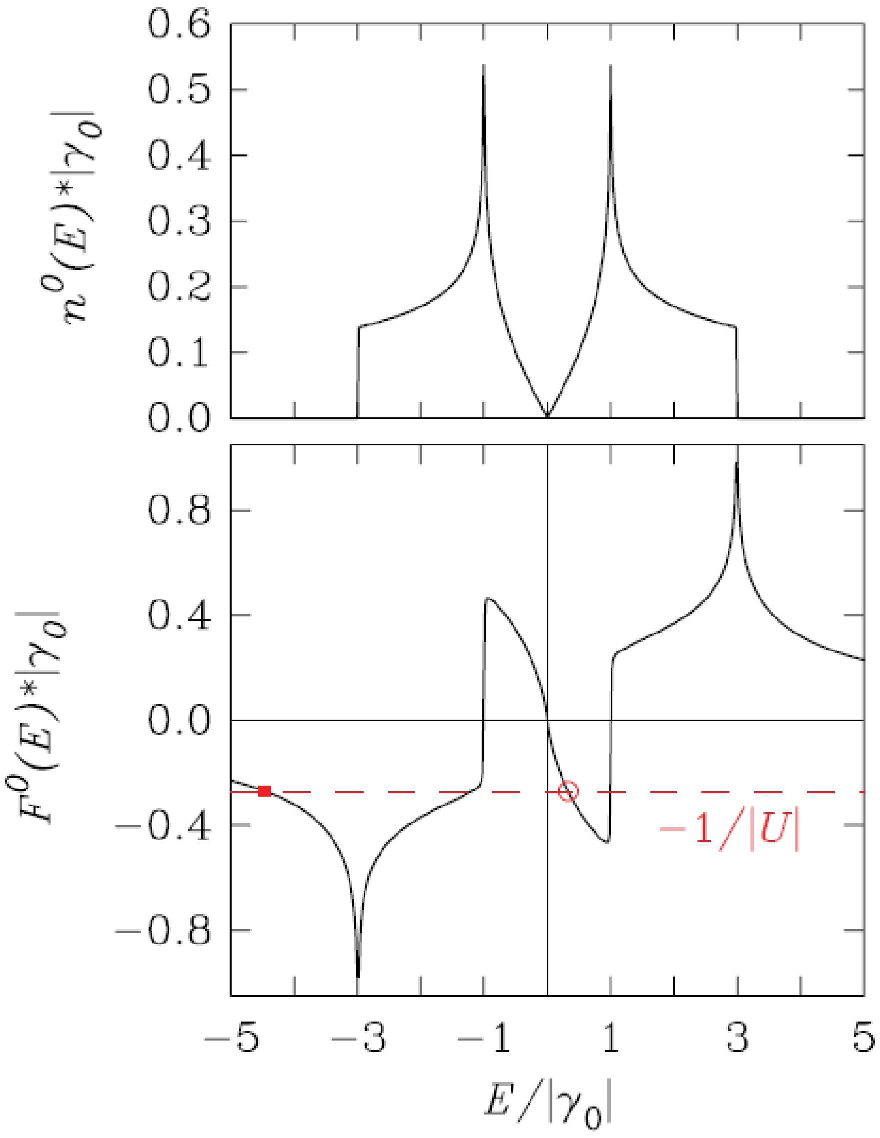
Density of state projected on the defect site

$$n_{00}(E) = -\frac{1}{\pi} Im(G_{00})$$

Green's function without defect $G_{00}^0 = F^0 + in^0$

$$n_{00}(E) = -\frac{1}{\pi} \frac{n^0}{(1 - UF^0)^2 + U^2 {n^0}^2}$$

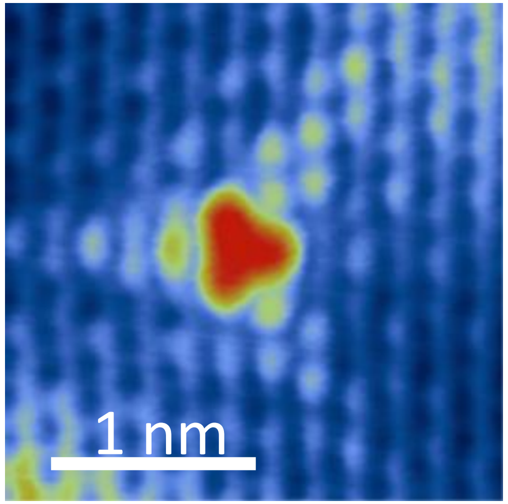
For small n^0 peak for $F^0 = \frac{1}{U}$



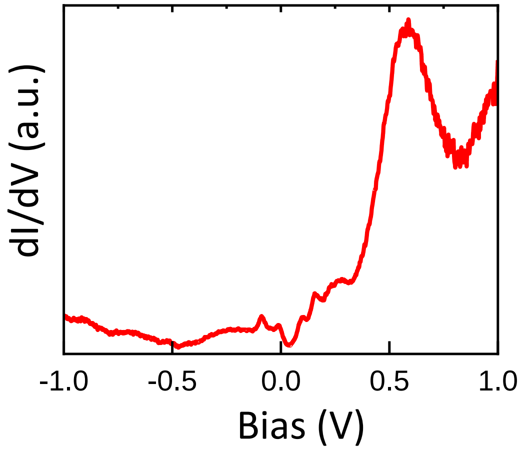
Ph. Lambin et al. Phys. Rev. B **86**, 045448 (2012)

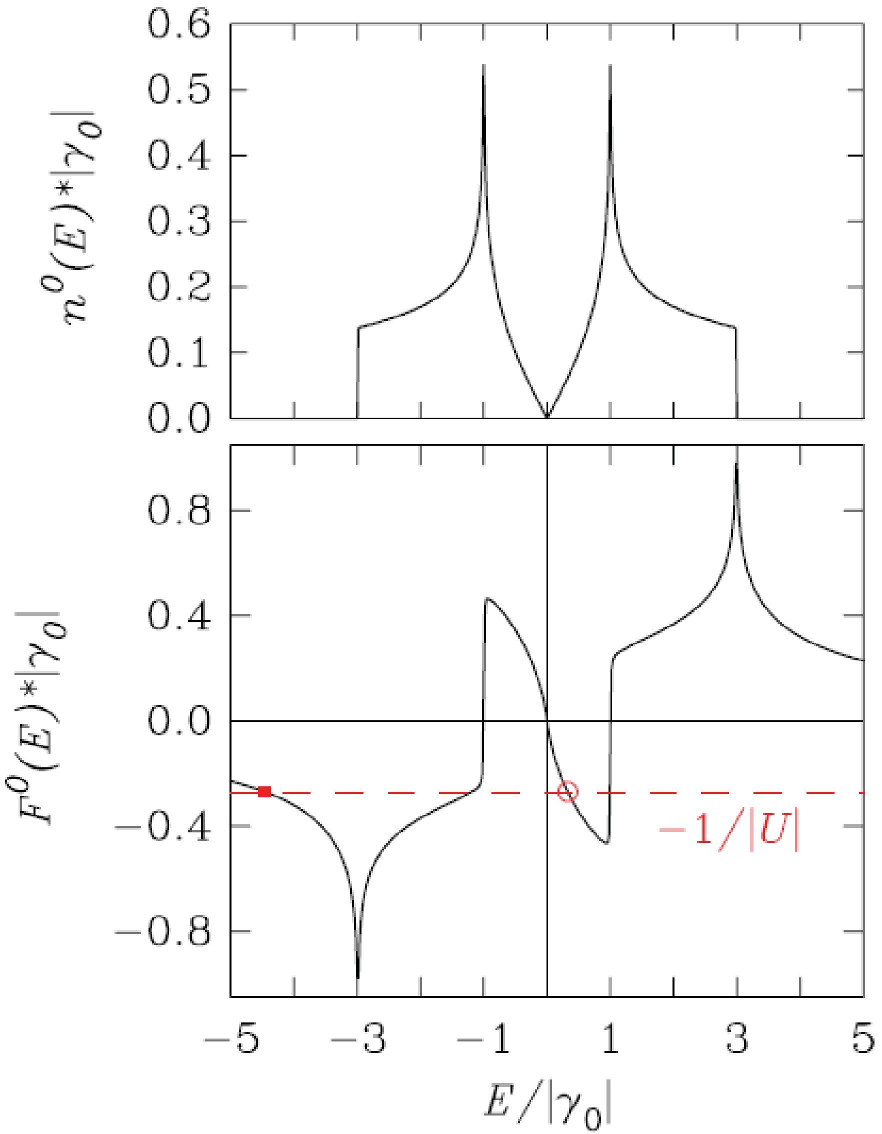
Nitrogen in graphene

STM on nitrogen in graphite



STS on nitrogen in graphite

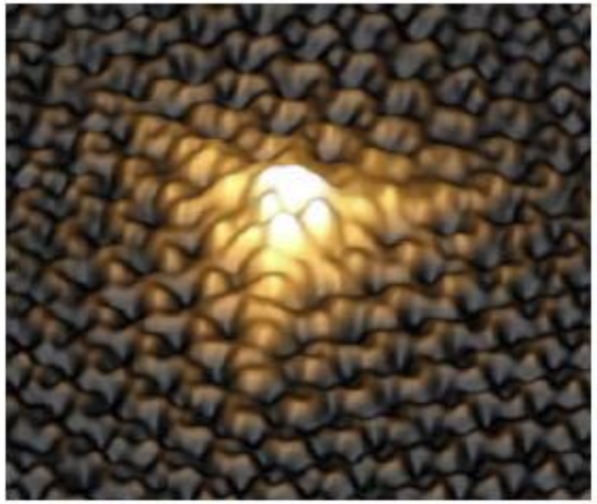




Ph. Lambin et al. Phys. Rev. B **86**, 045448 (2012)

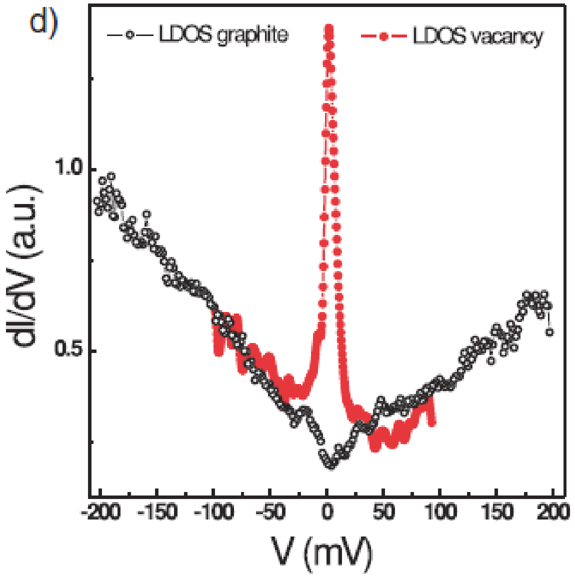
Vacancy in graphene

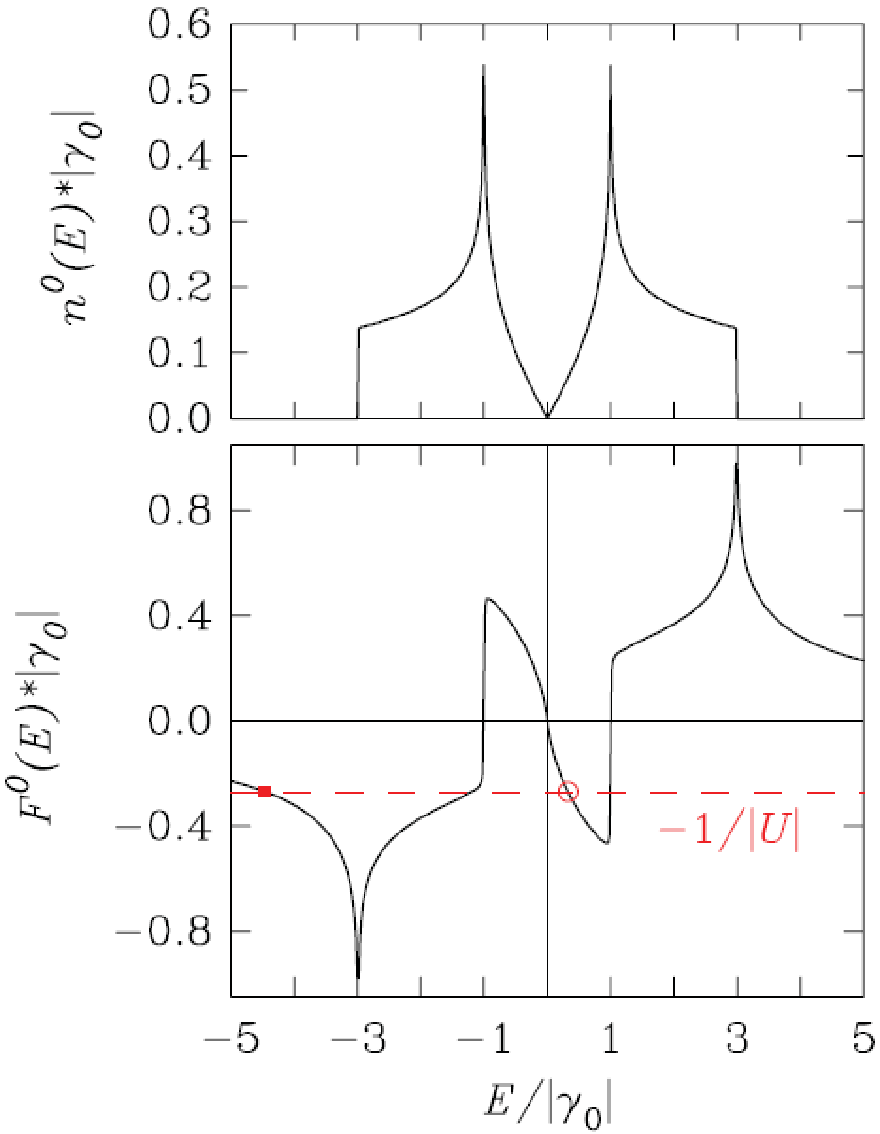
STM on vacancy in graphite



M. M. Ugeda et al. PRL **104**, 096804 (2010)

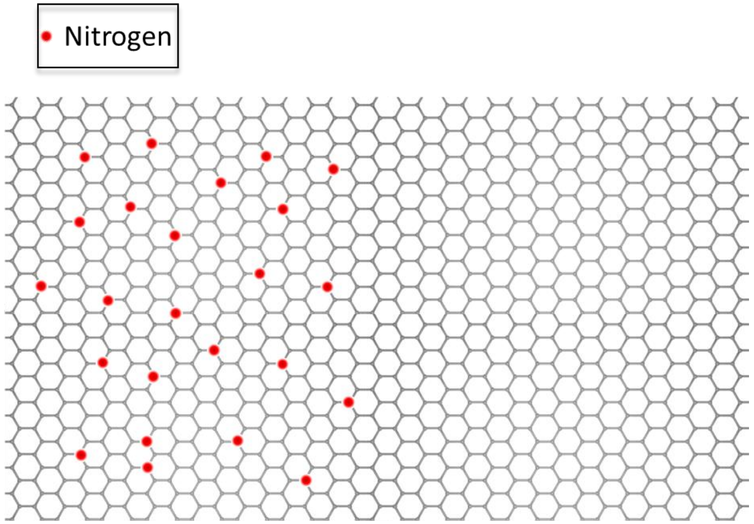
STS on vacancy in graphite

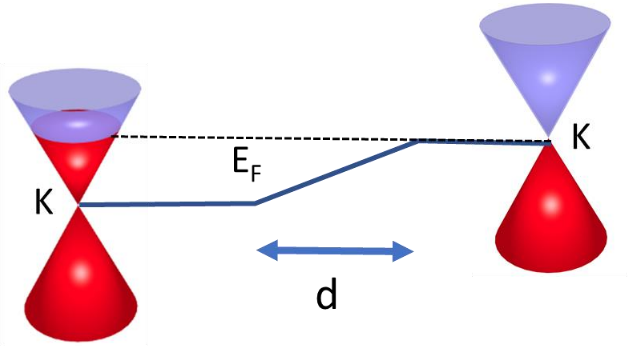




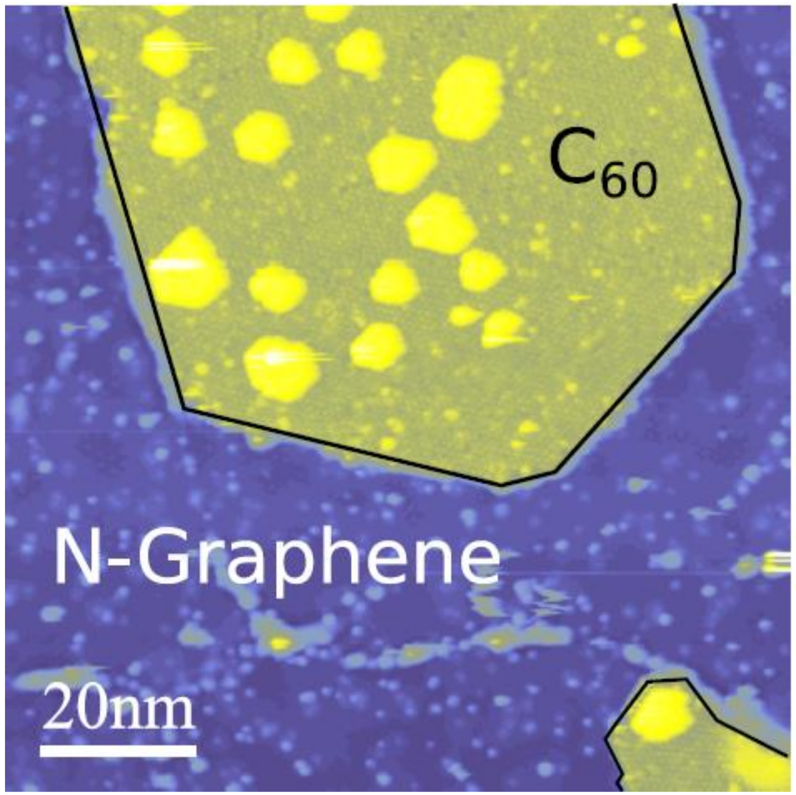
Ph. Lambin et al. Phys. Rev. B **86**, 045448 (2012)

Band engineering: realization of in-plane junction



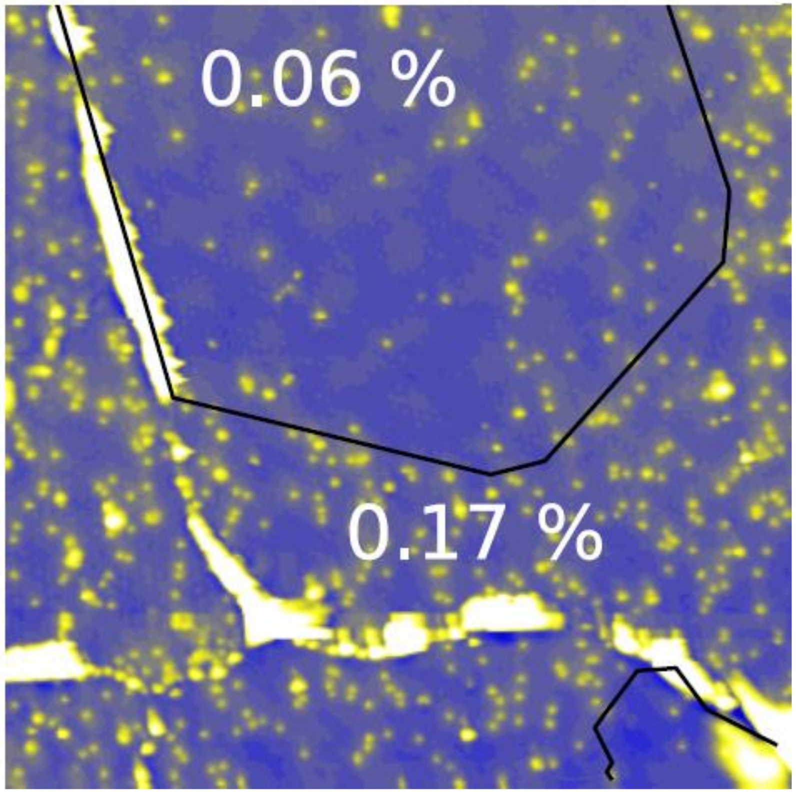


C_{60}/graphene after nitrogen plasma



2V, 10 pA

Nitrogen doping of graphene reduced below the C_{60} island

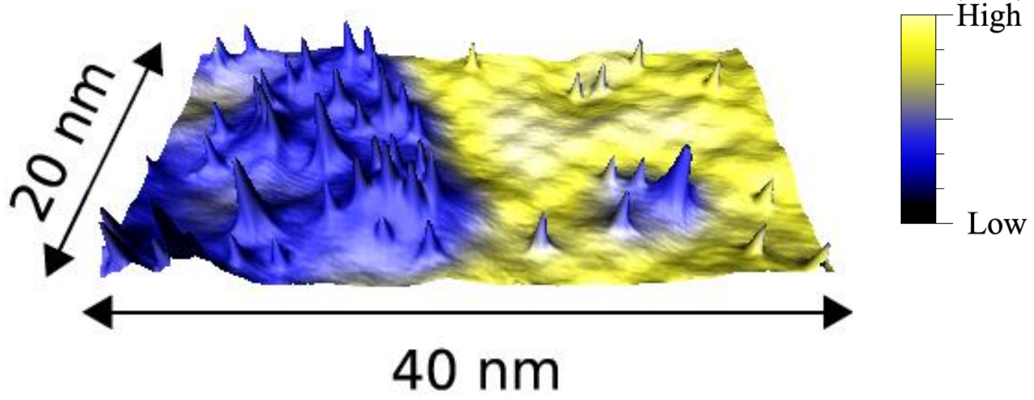


2V, 50 pA

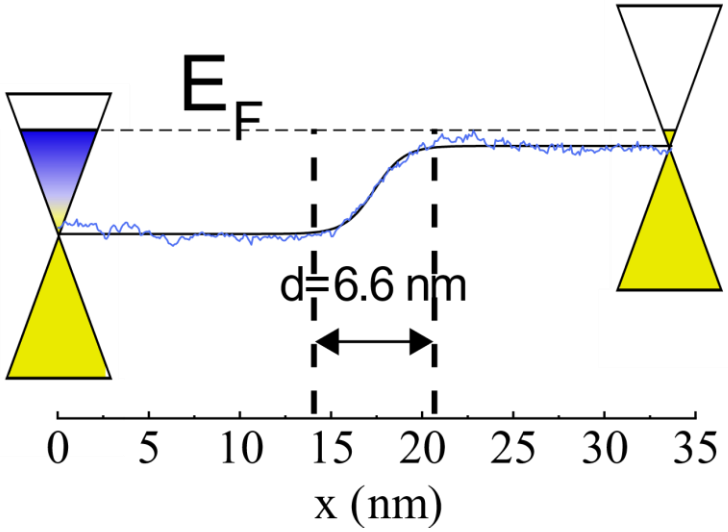
65% of incoming nitrogen species are stopped by the C_{60} monolayer

Sharp junctions (width<Fermi wavelength)

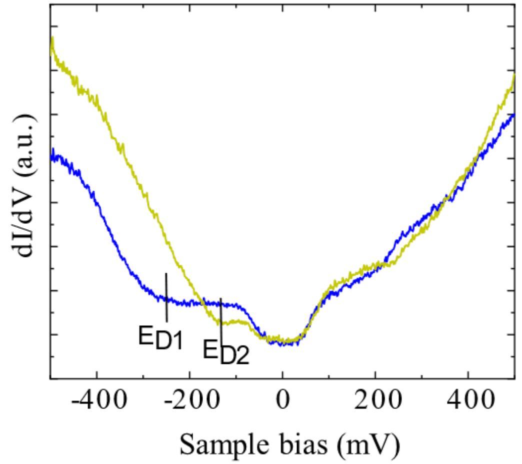
3D STM topography,
color map: dI/dV at -0.3 V



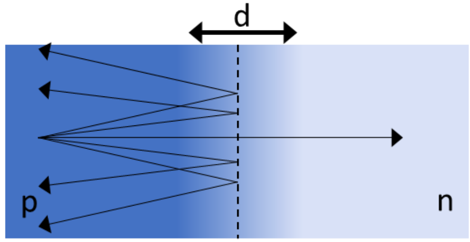
Linescan of dI/dV map through the junction



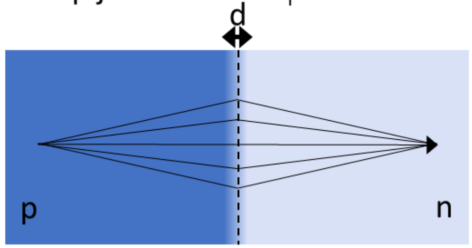
Spectroscopy on both sides of the junction



Smooth junction d > λ_F



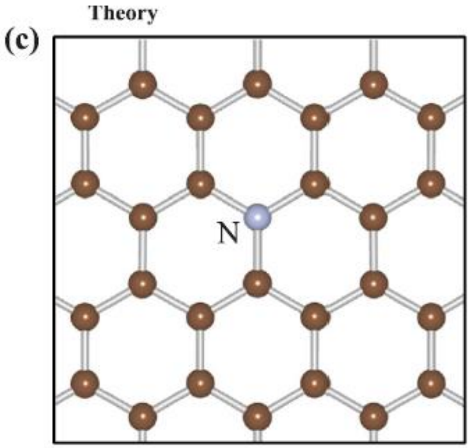
Sharp junction d < λ_F



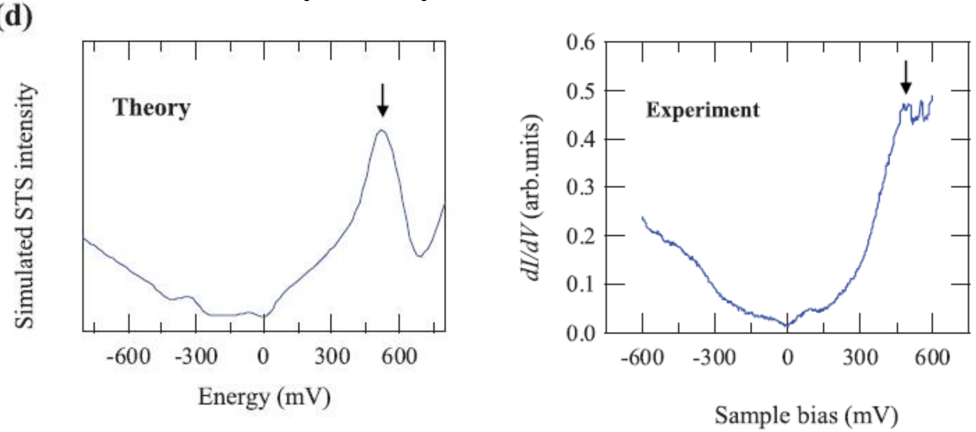
Sharp junction,
for d<20 nm

M. Bouatou et al., *Adv. Funct. Mater.*, **32**, 2208048 (2022)

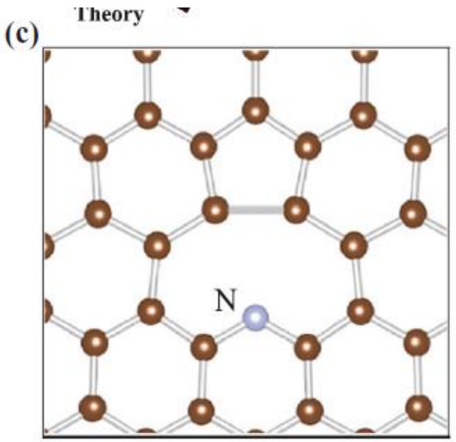
Localized state for chemical activity



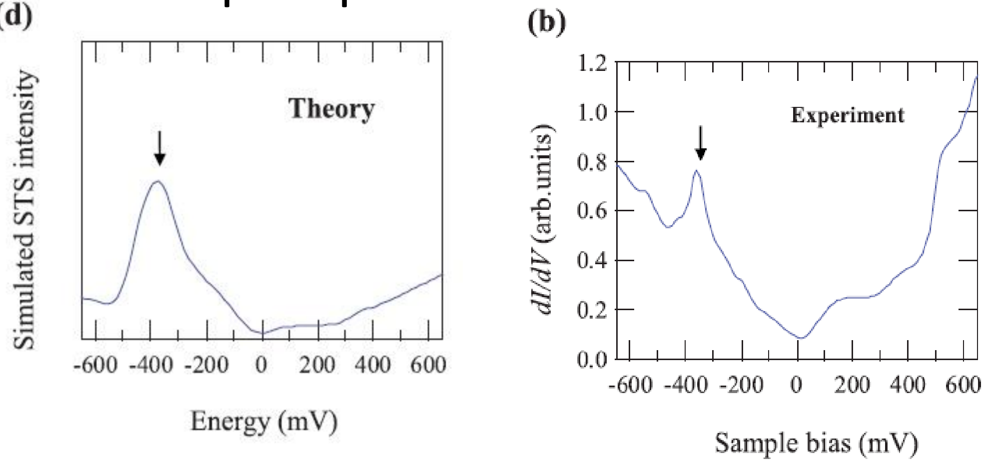
Graphitic N:
unoccupied peak **Lewis acid**

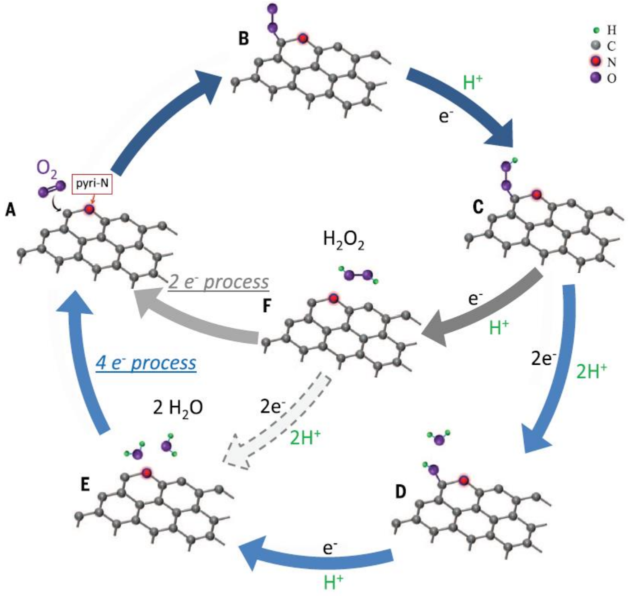


Occupied state on pyridine
⇒ Lewis base
⇒ active site for
oxygen reduction reaction



Pyridinic N:
occupied peak **Lewis base**

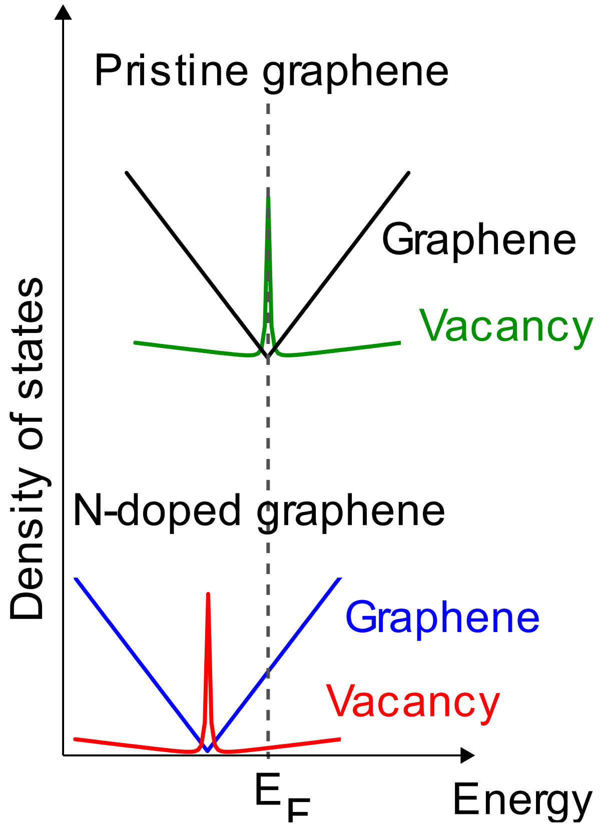




D. Guo et al., Science 351, 361 (2016)

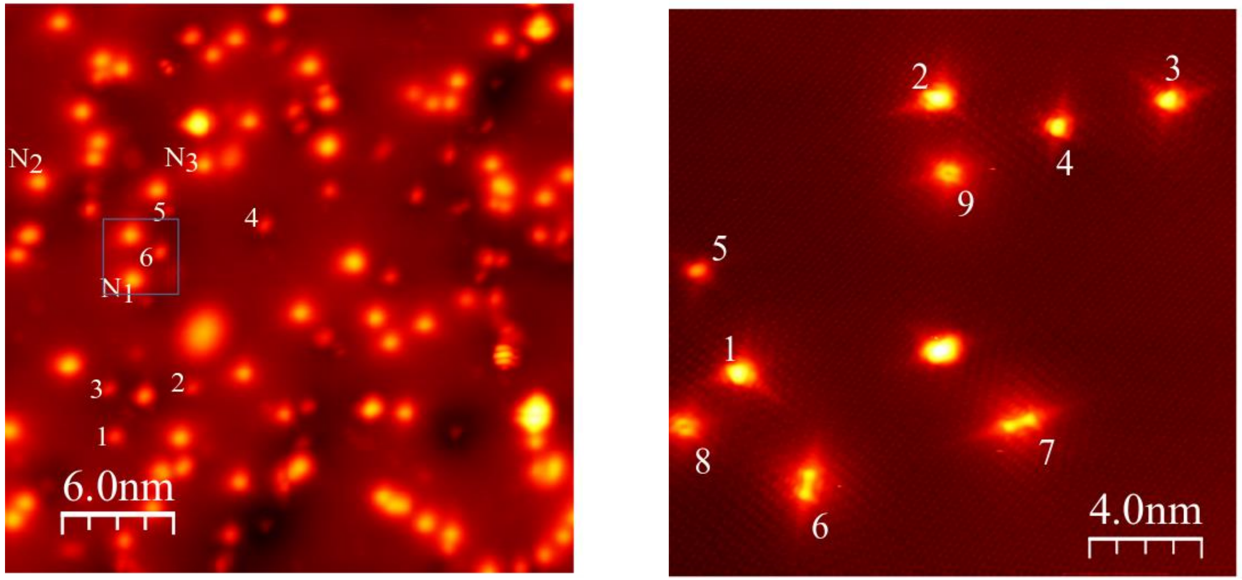
T. Kondo et al., PRB **86**, 035436 (2012)

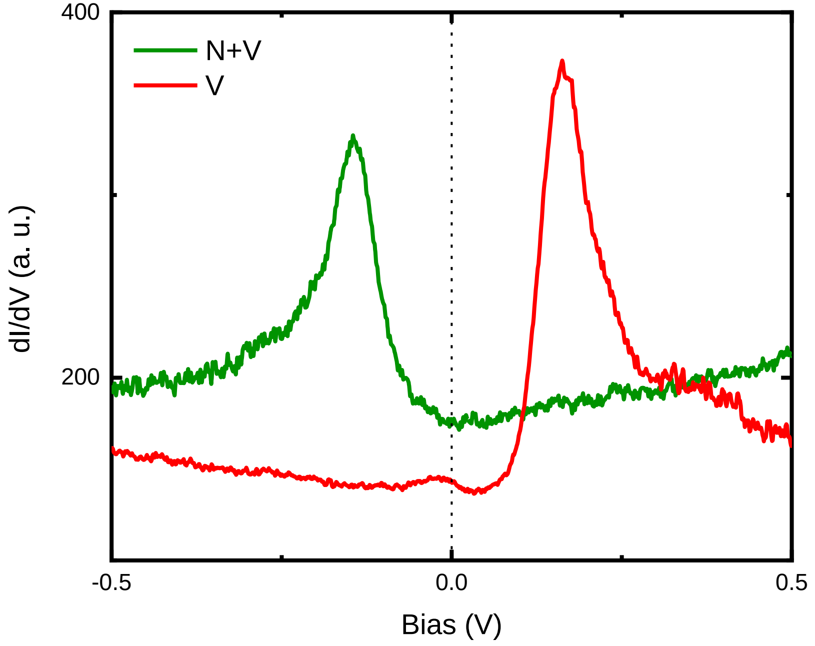
Defect engineering: combining vacancies and nitrogen



Vacancies + N in HOPG

Vacancies in HOPG





D. Demba et al., (2024) submitted

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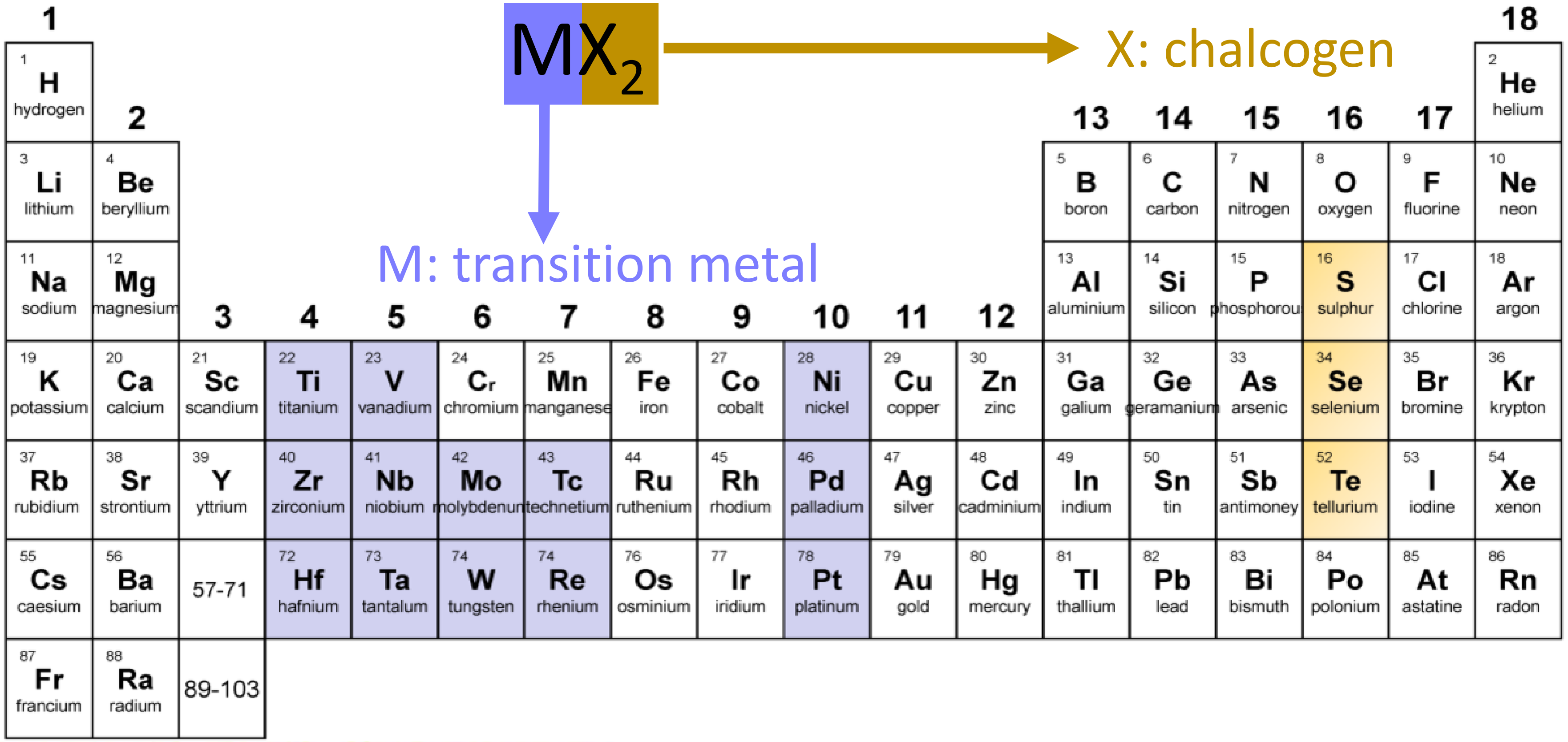
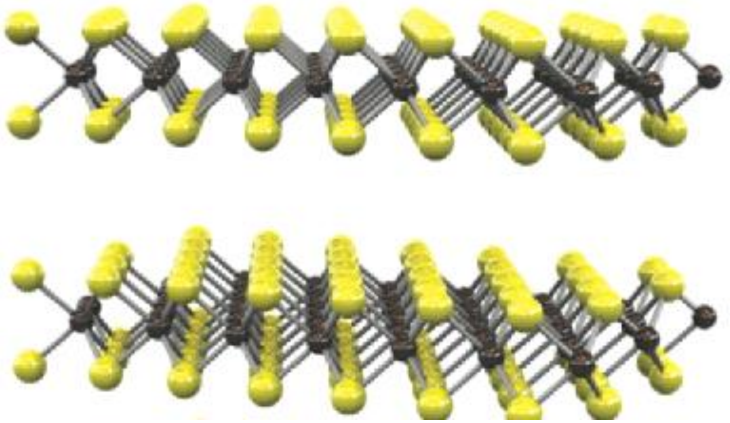
- Charge density waves in Transition Metal Dichalcogenides

Transition Metal Dichalcogenides (TMD)





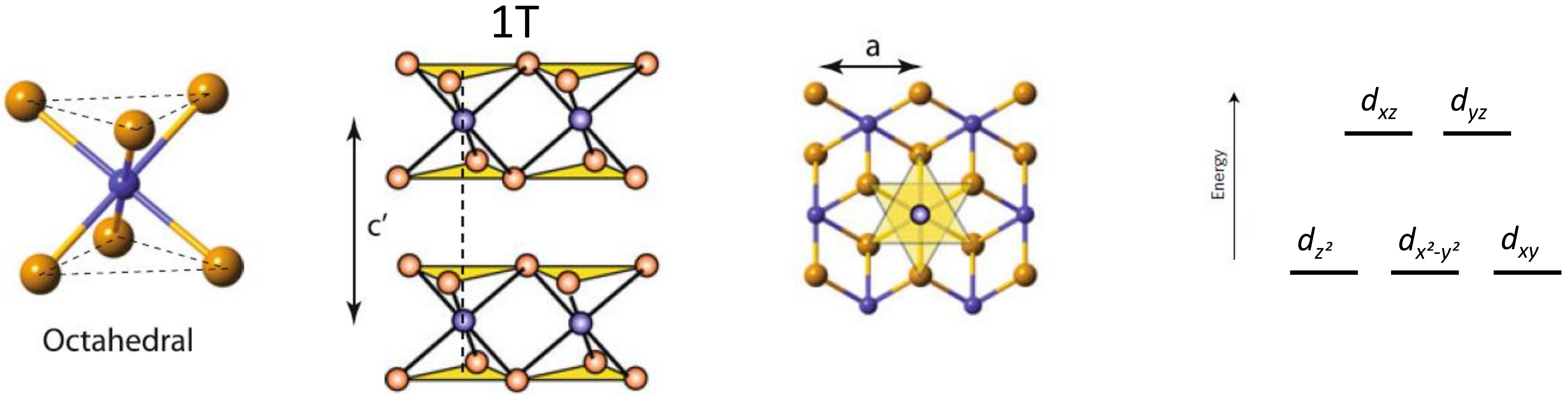
Formal charge: M^{4+}, X^{2-}

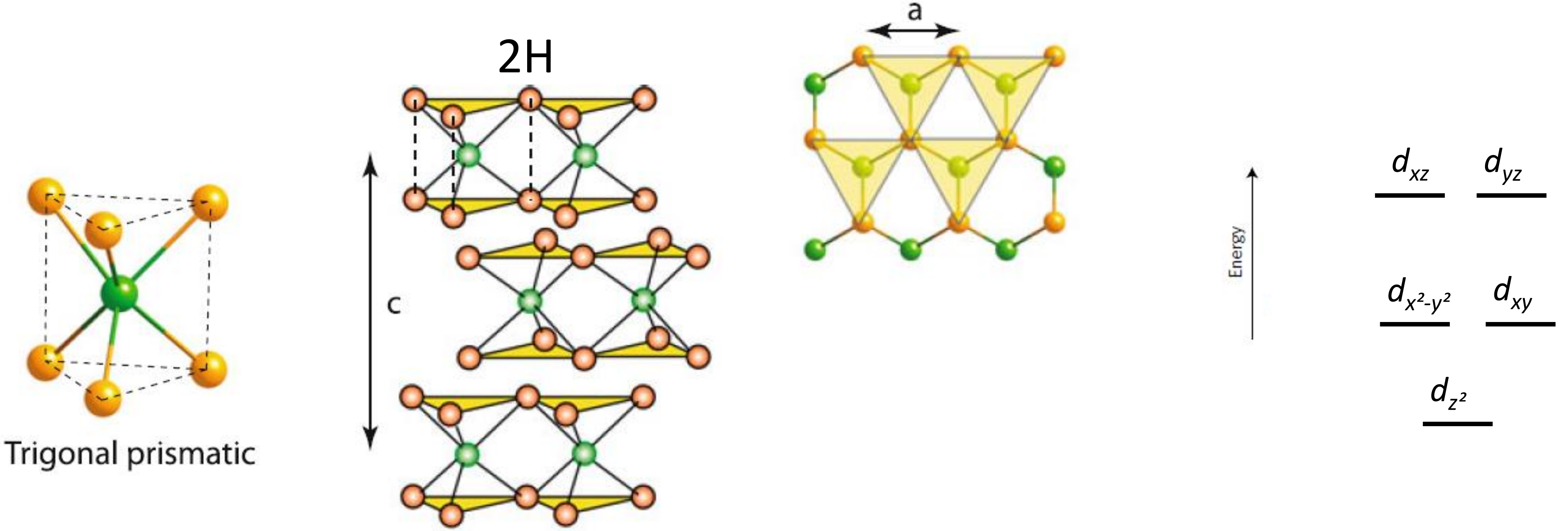
Electronic configuration:

Chalcogen: ns^2, np^6 (n=3,4,5 for X=S, Se, Te)

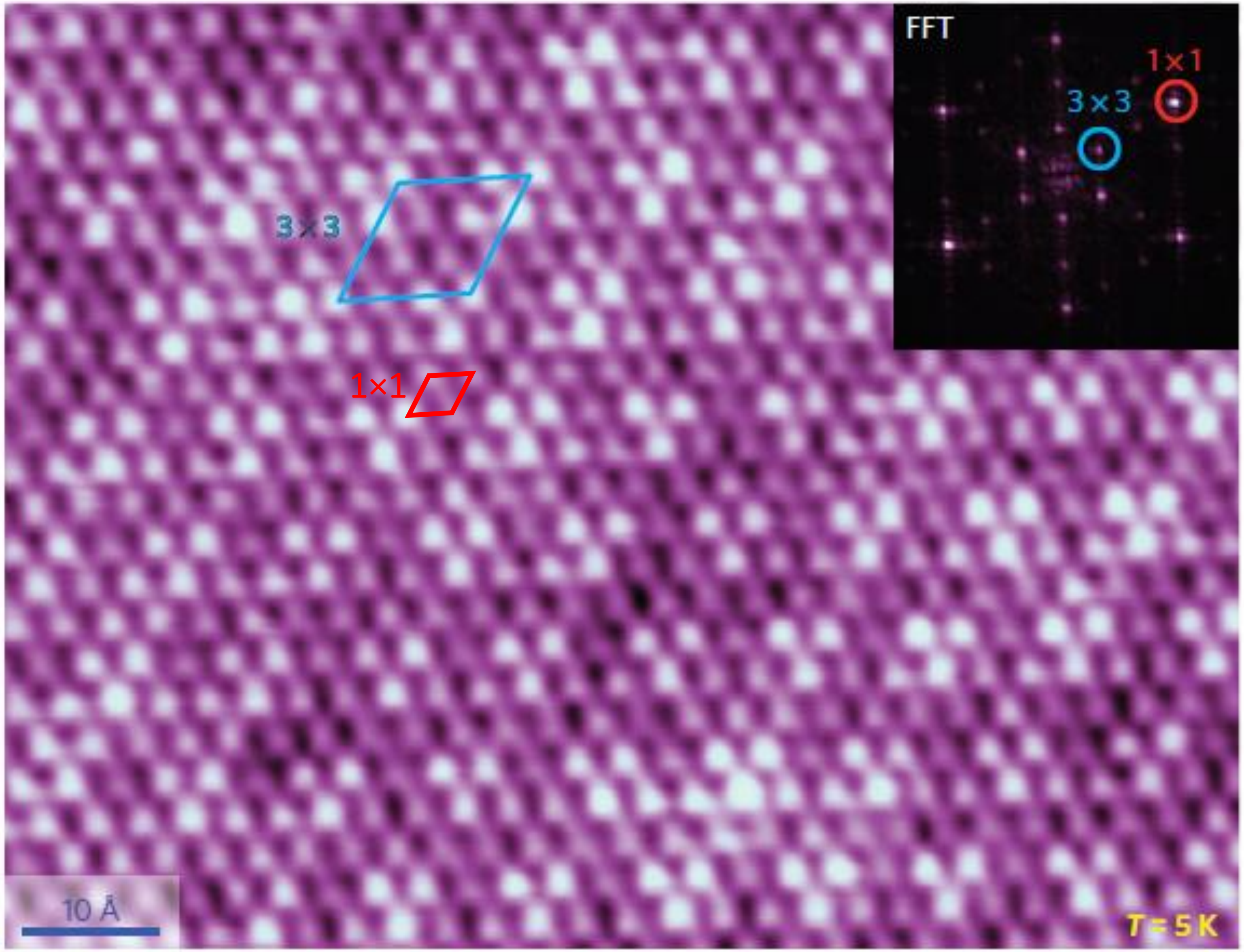
Transition metal: d^n, with n=0, 1, 2 , 3 for group 4, 5, 6 7

T and H polymorphs of TMDs



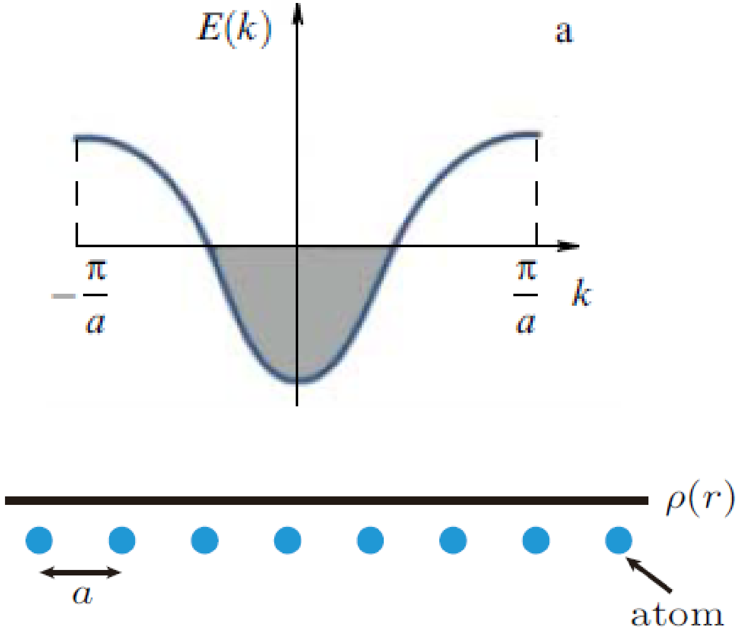


Charge density waves in metallic TMDs

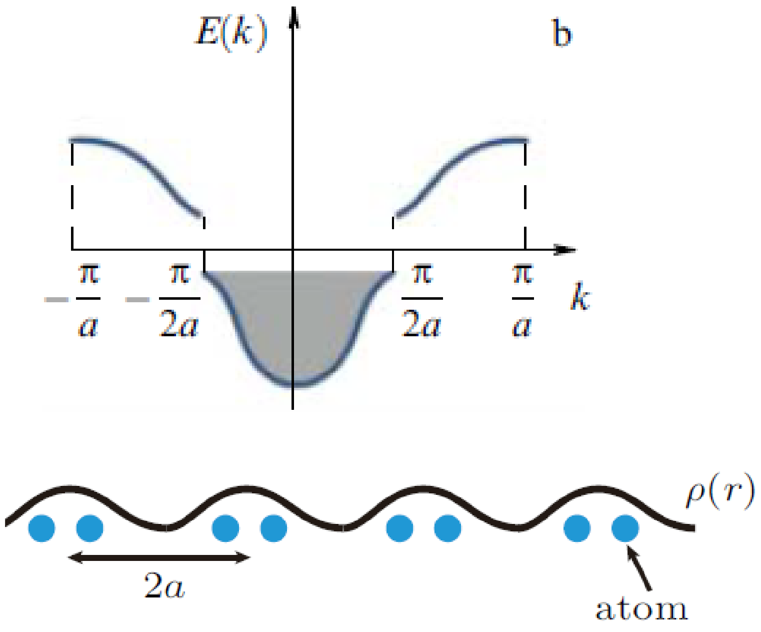


M. M. Ugeda et al., Nat. Phys. **12**, 92 (2016)

Charge density waves, Peierls transition



$$\rho(\boldsymbol{r}) = \rho_0$$



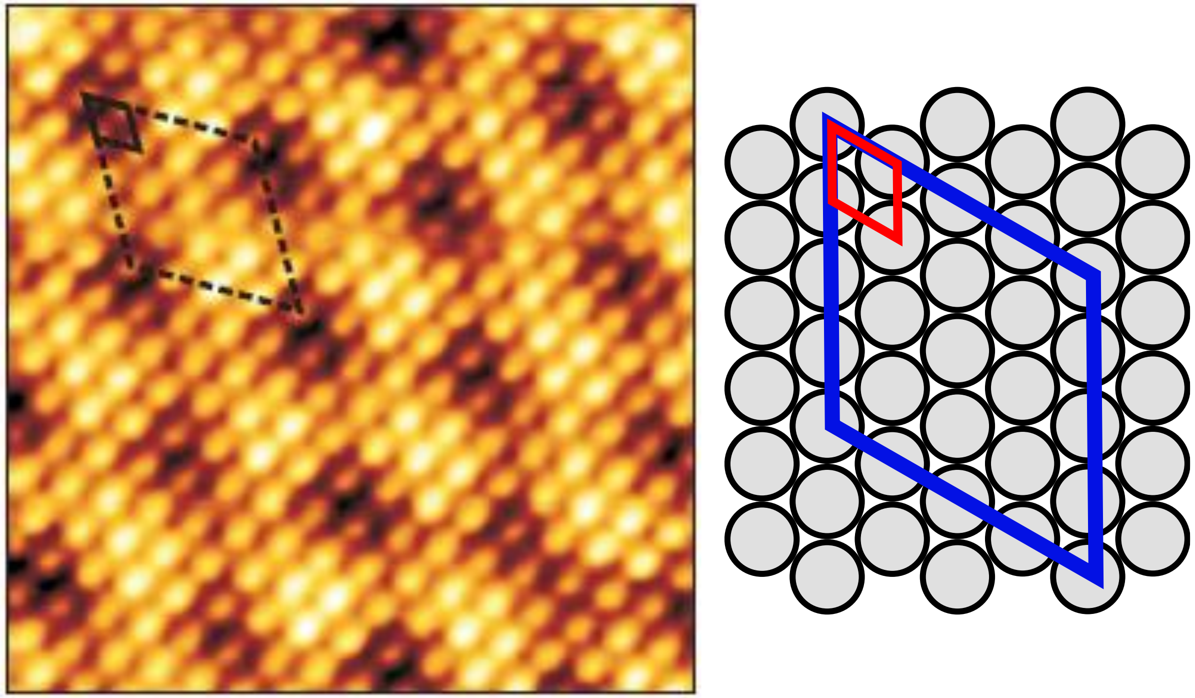
$$\rho(\boldsymbol{r}) = \rho_0 + \rho_1 \cos(2\boldsymbol{k}_F \cdot \boldsymbol{r} + \varphi)$$

Gain in electronic energy from the lowering of occupied electronic states

But elastic energy cost

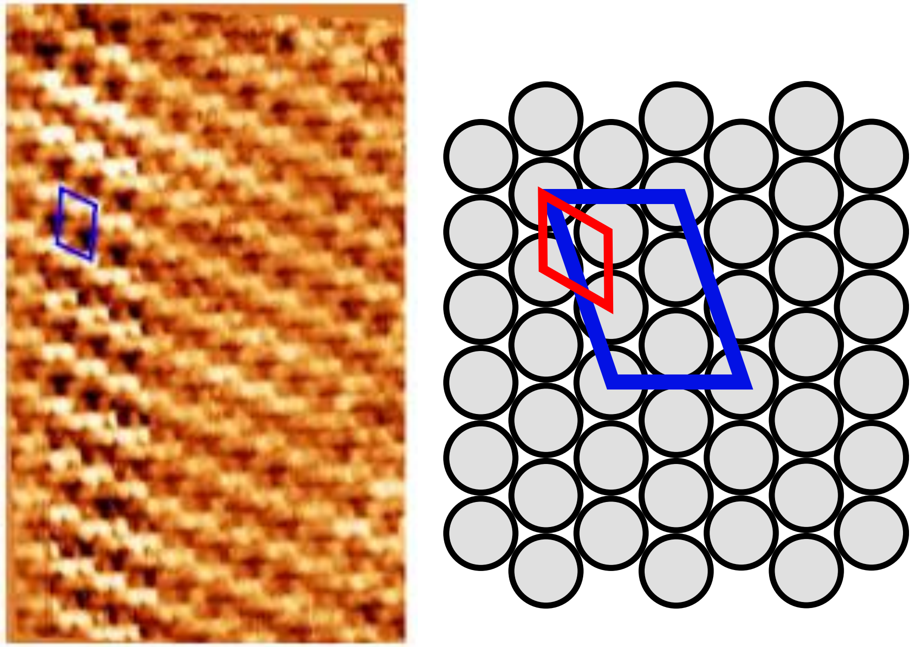
Bulk vs monolayer CDW in VSe_2

Bulk VSe_2 4x4 CDW



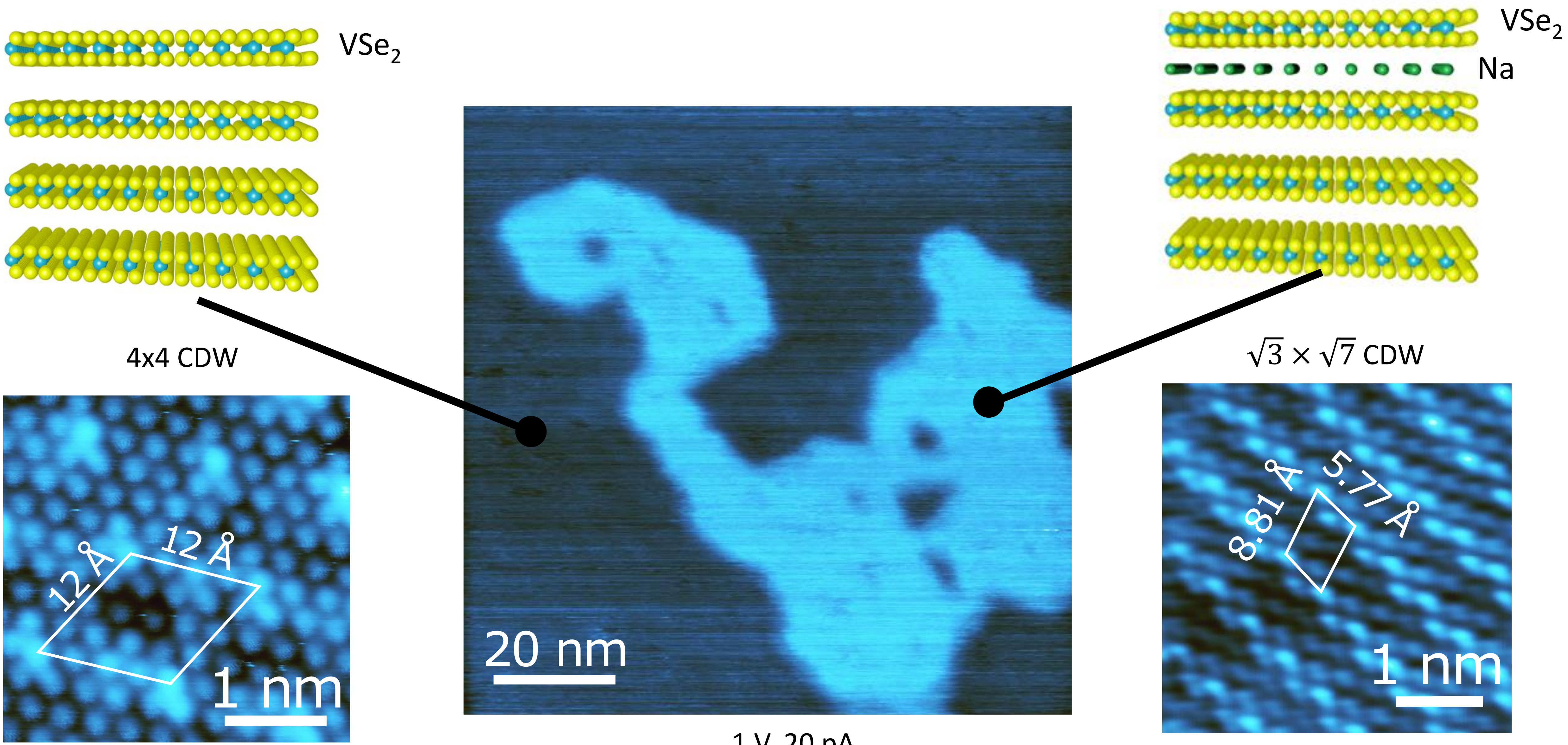
W. Jolie *et al.*, PRB **99**, 115417 (2019)

Monolayer VSe_2 $\sqrt{3} \times \sqrt{7}$ CDW



P. Chen et al., PRL 121, 196402 (2018)

Alkali intercalation: Na intercalated bulk VSe_2

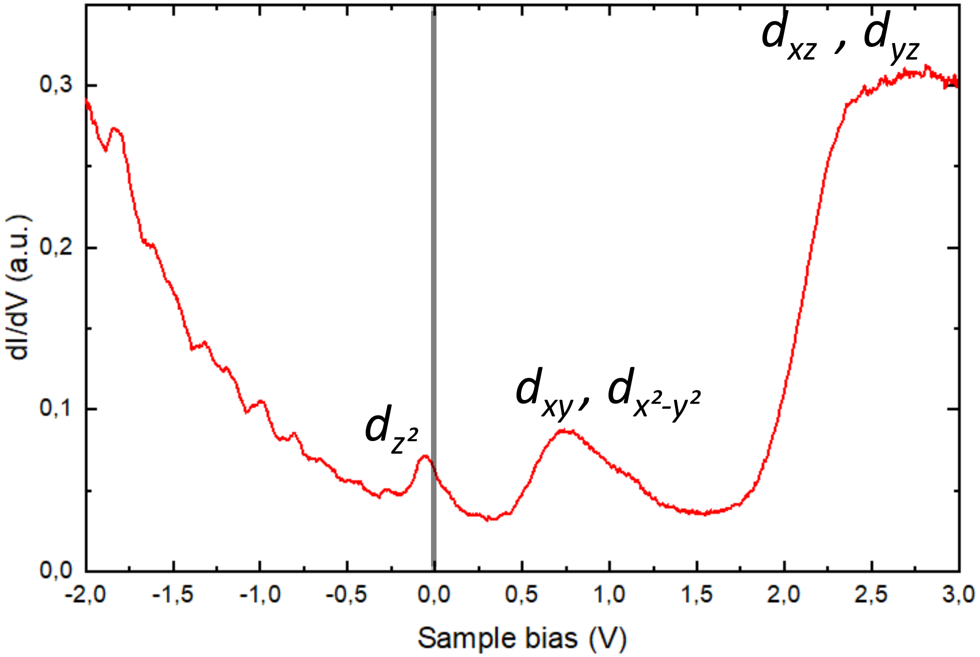


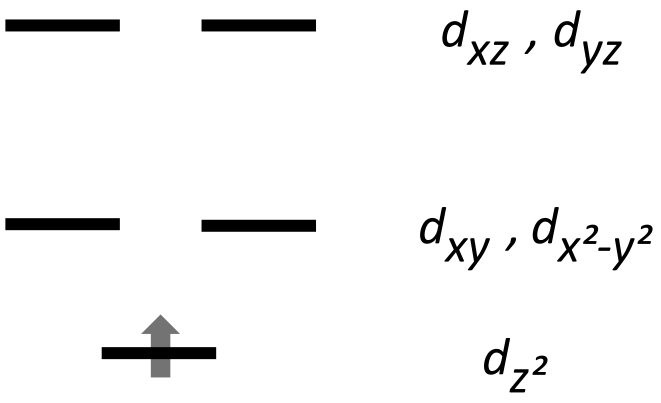
1 V, 20 pA

U. Chazarin et al., Adv. Mater. Interfaces 10, 2201680 (2023)

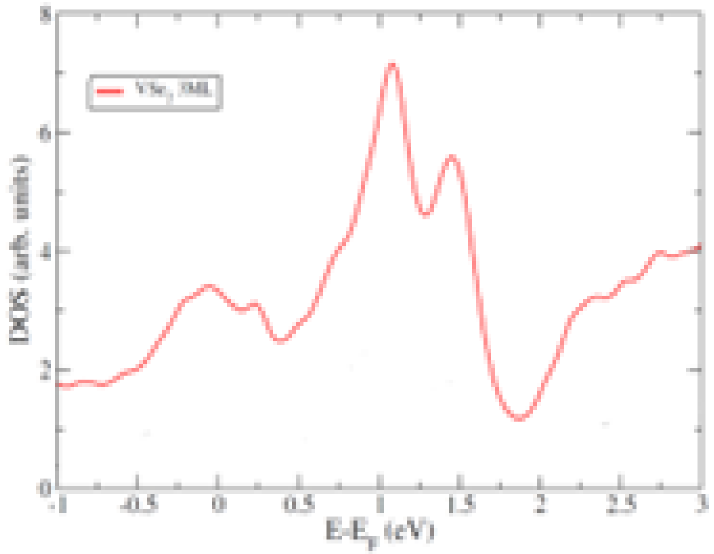
Spectroscopy of 1T- VSe_2

Experimental dI/dV spectrum

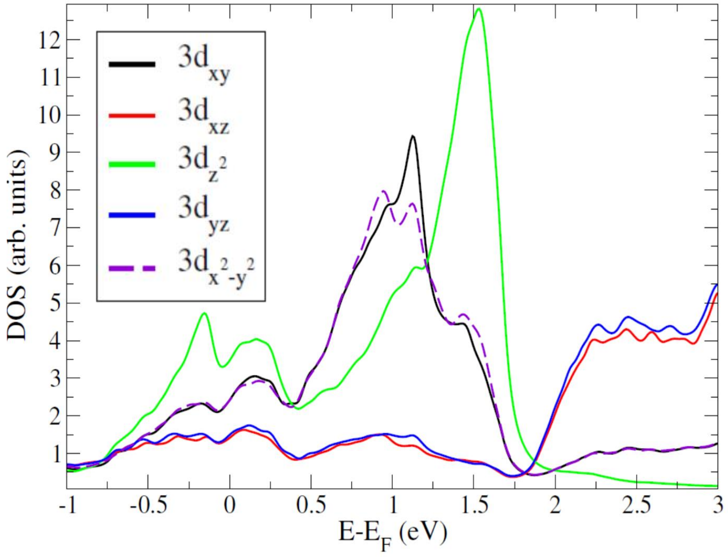




Calculated DOS

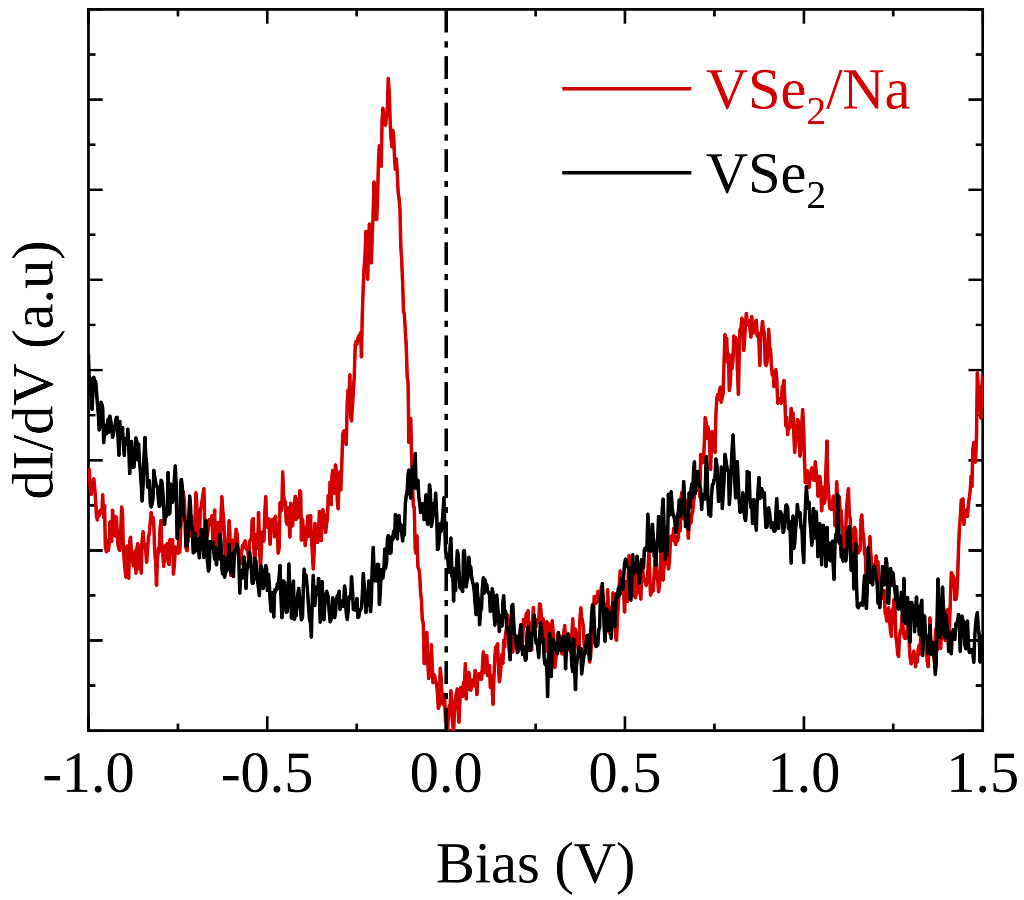


Calculated PDOS

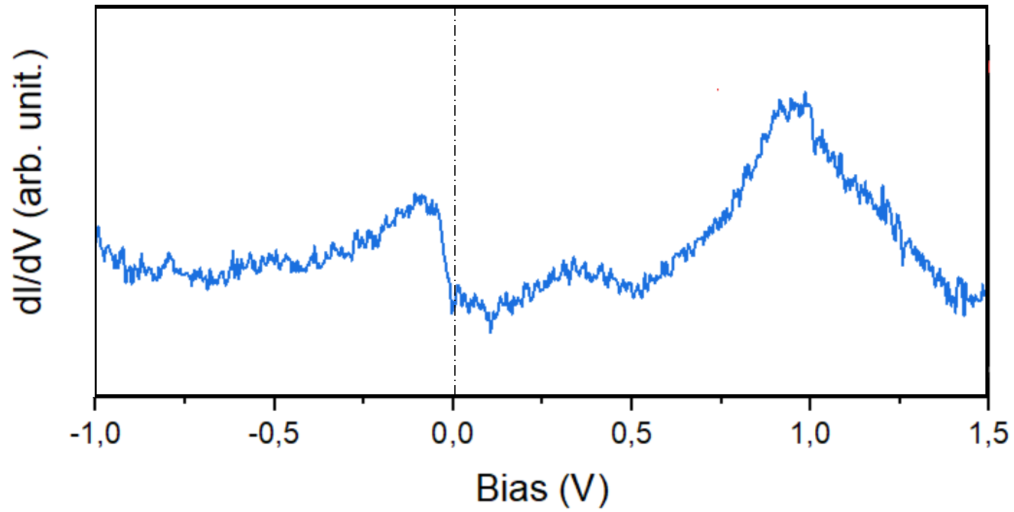


Alkali intercalation: Na intercalated bulk VSe_2

STS on Na intercalated and non-intercalated VSe_2

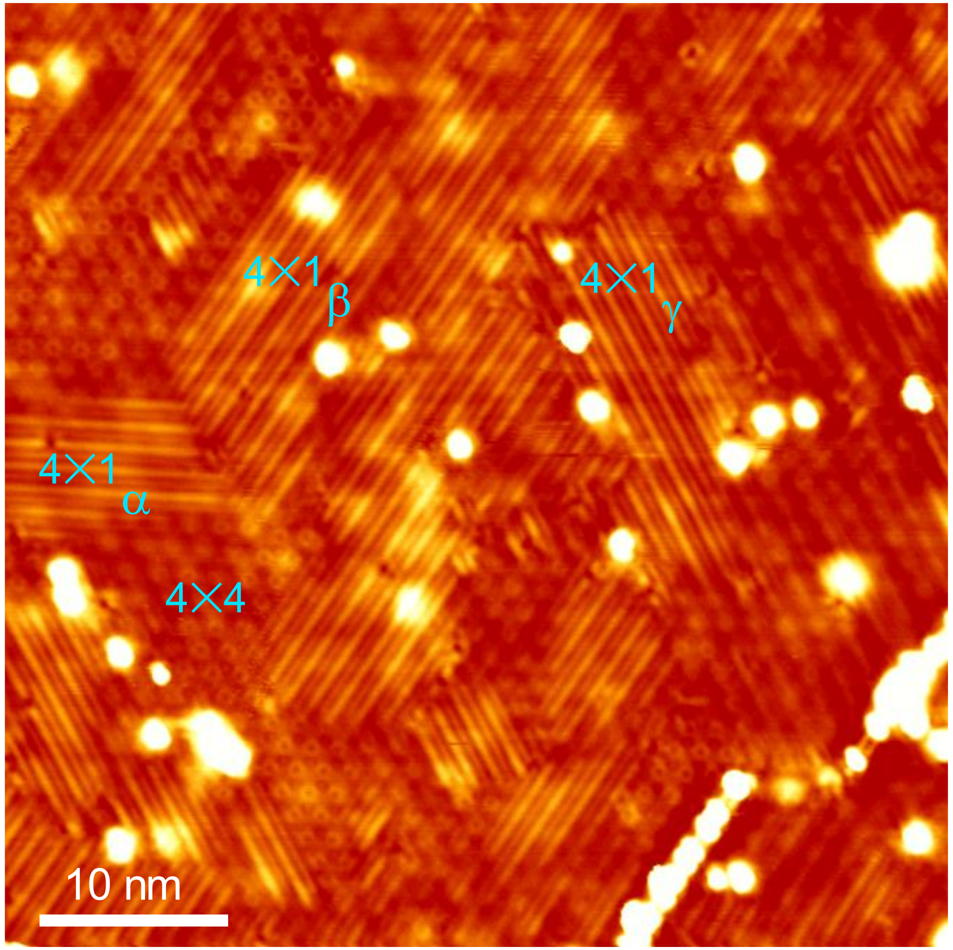


STS on VSe_2 monolayer

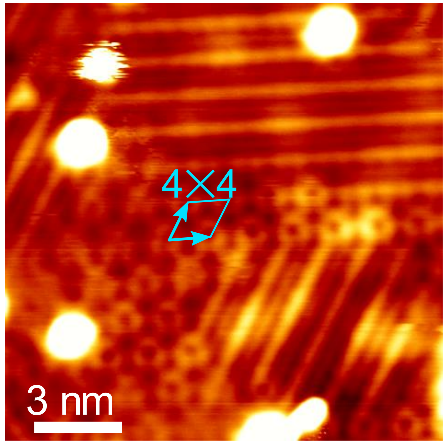


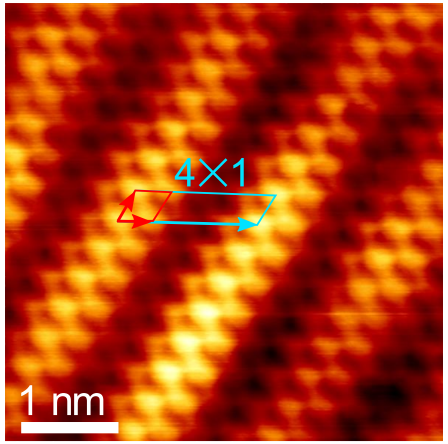
Coexisting multiple CDW in VTe2 monolayer

VTe_2 monolayer on graphene bilayer



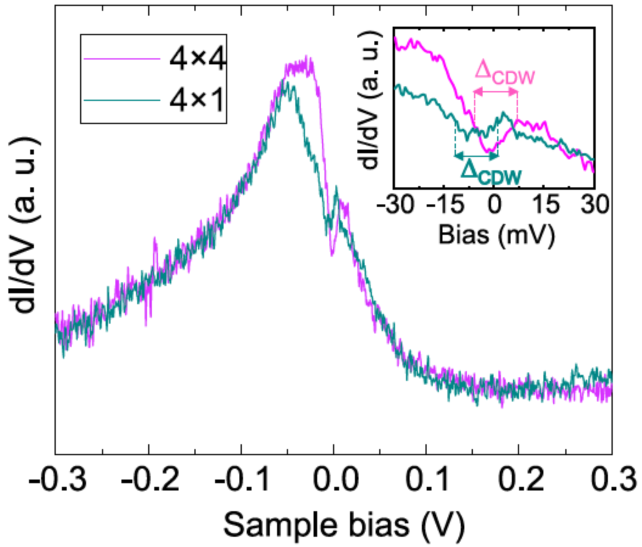
0.5 V, 100 pA



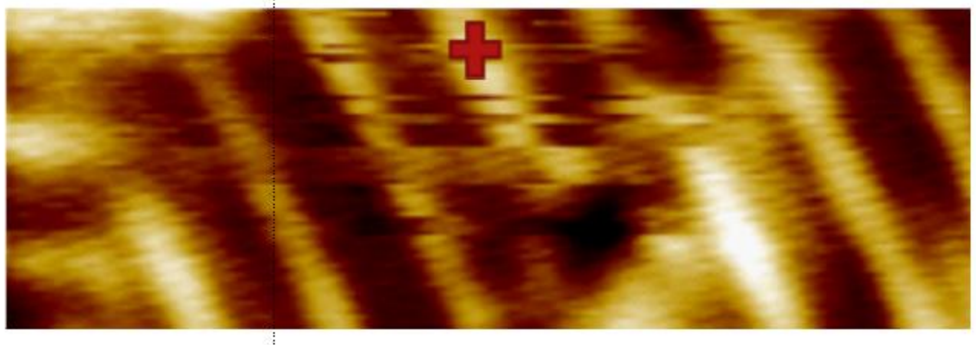


0.15 V, 20 pA

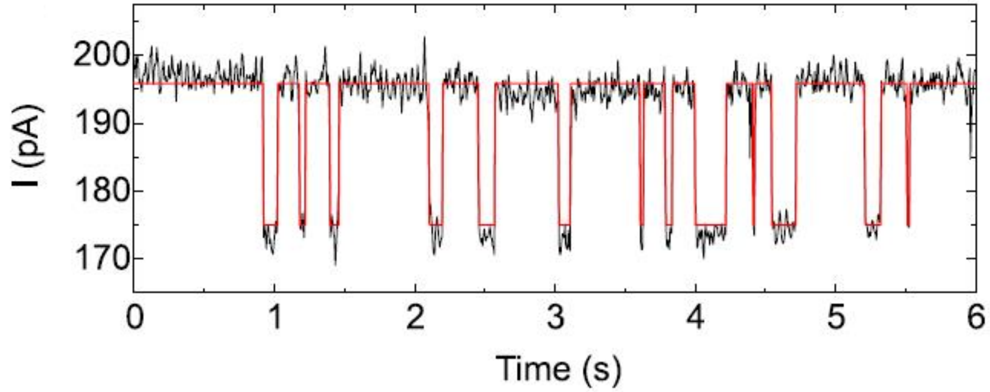
dI/dV spectroscopy

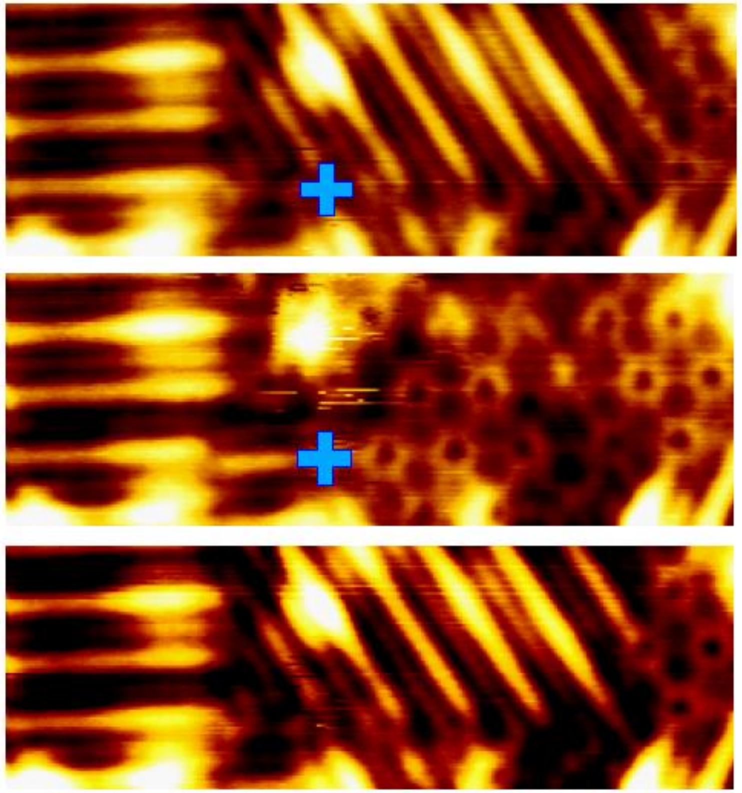


CDW phase switching induced by STM tip

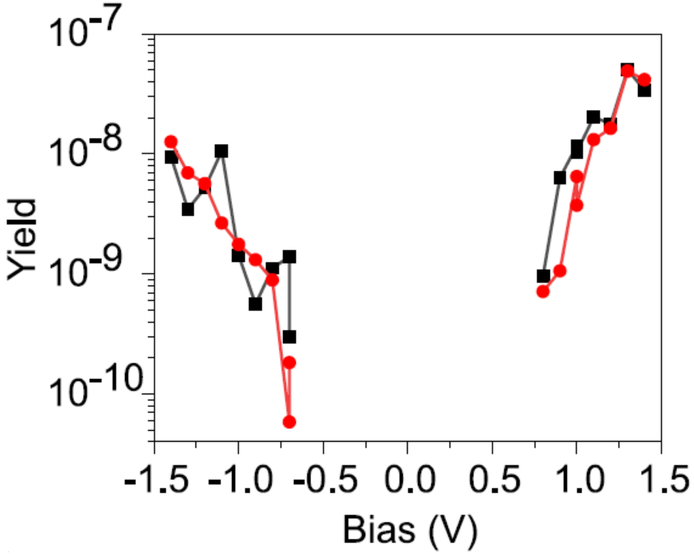


0.8 V, 200 pA





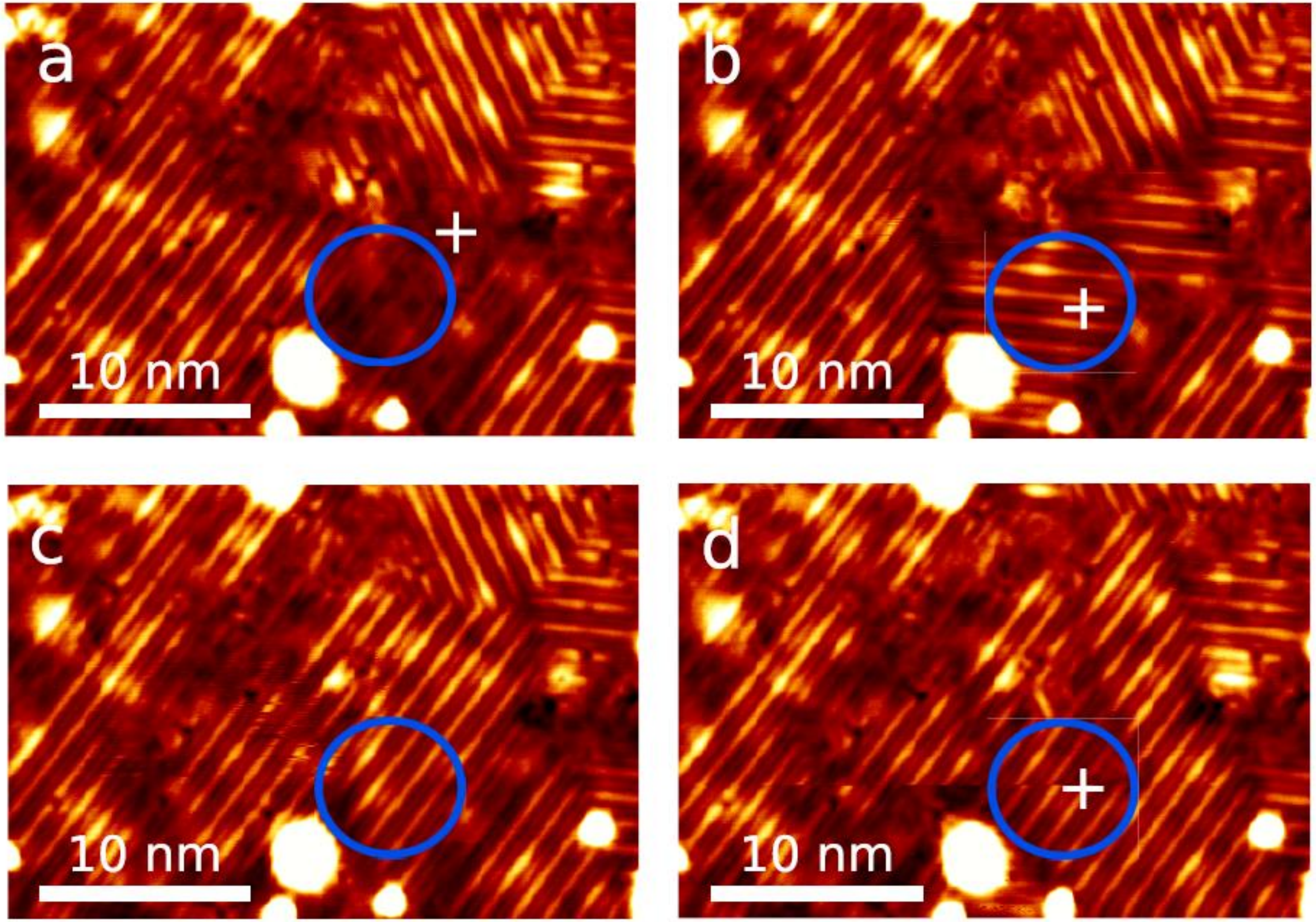
0.5 V, 100 pA



Visualisation of Elementary excitations: phase switch, rotation, sliding

4x4 -> 4x1

Rotation



Sliding

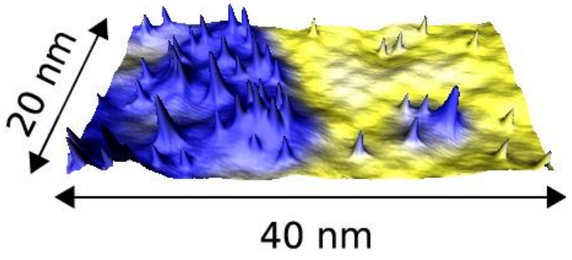
U. Chazarin et al., Nano Lett. 24, 3470 (2024)

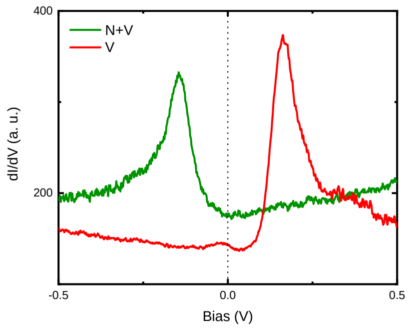
Conclusions

Point defects in graphene:

Dopants for band engineering

Localized states for chemical activity

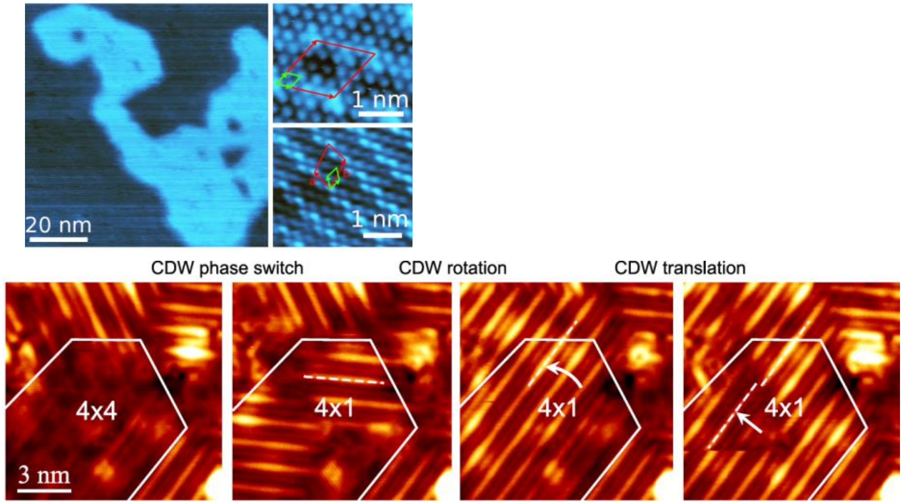




Charge density waves in TMDs:

Intercalants for doping, decoupling

Local excitation for extended CDW phase switching



Mastering defects opens fascinating routes toward applications of 2D materials in electronics, sensors, optics, catalysis…

Acknowledgements

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- la microscopie à effet tunnel (STM) et ses dérivées (STM-photon et STM sous champ magnétique)
- les différentes spectroscopies STS (I(V), I(Z), imagerie dI/dV, ...) qui y sont associées
- la microscopie à force atomique en mode non contact (nc-AFM)
- la nanosonde de Kelvin (KPFM) et les différentes spectroscopies de force (Δf(V), Δf(z), EFM,...) qui y sont associées