Graphene – intercalation and chemical functionalization

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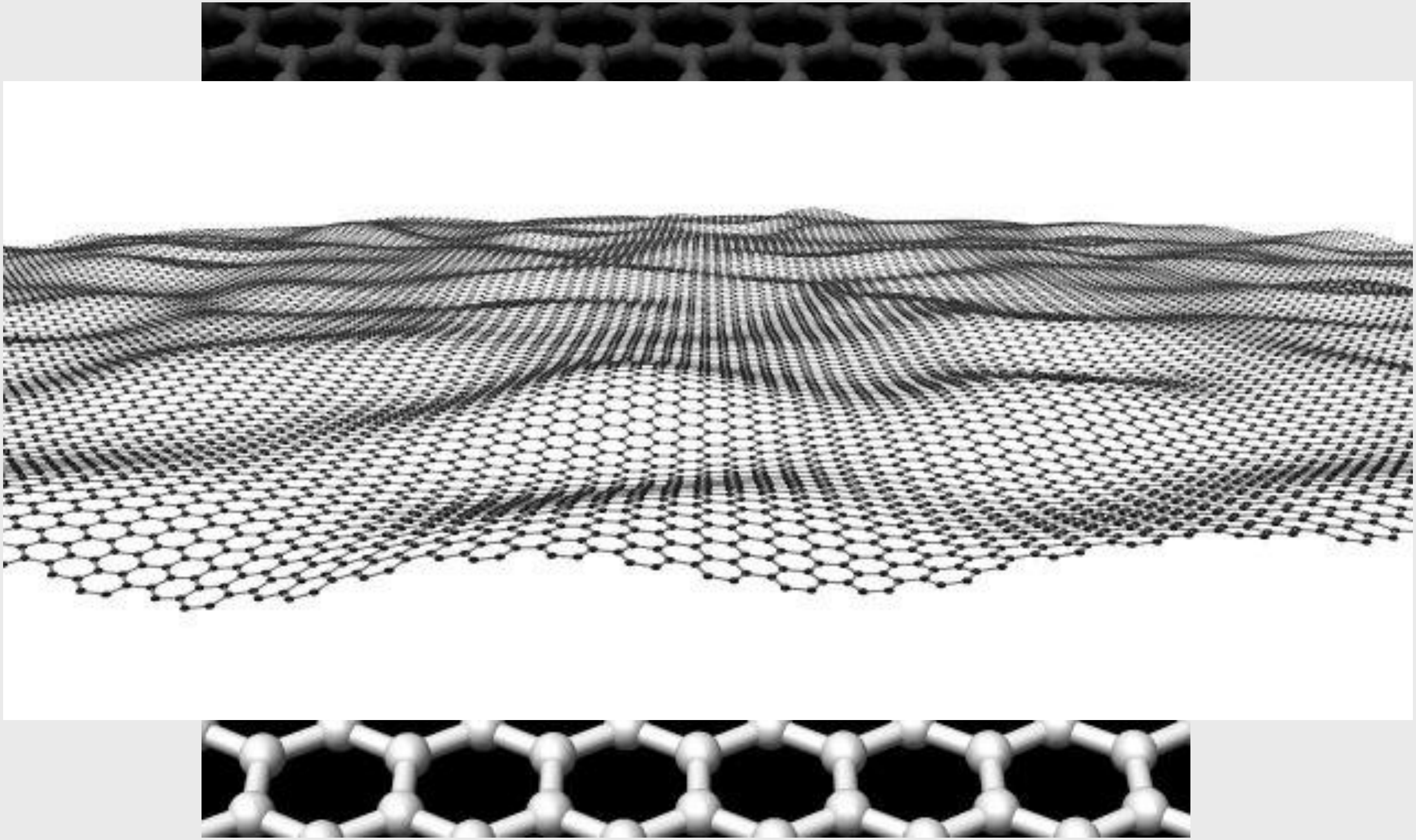
iNANO

Graphene



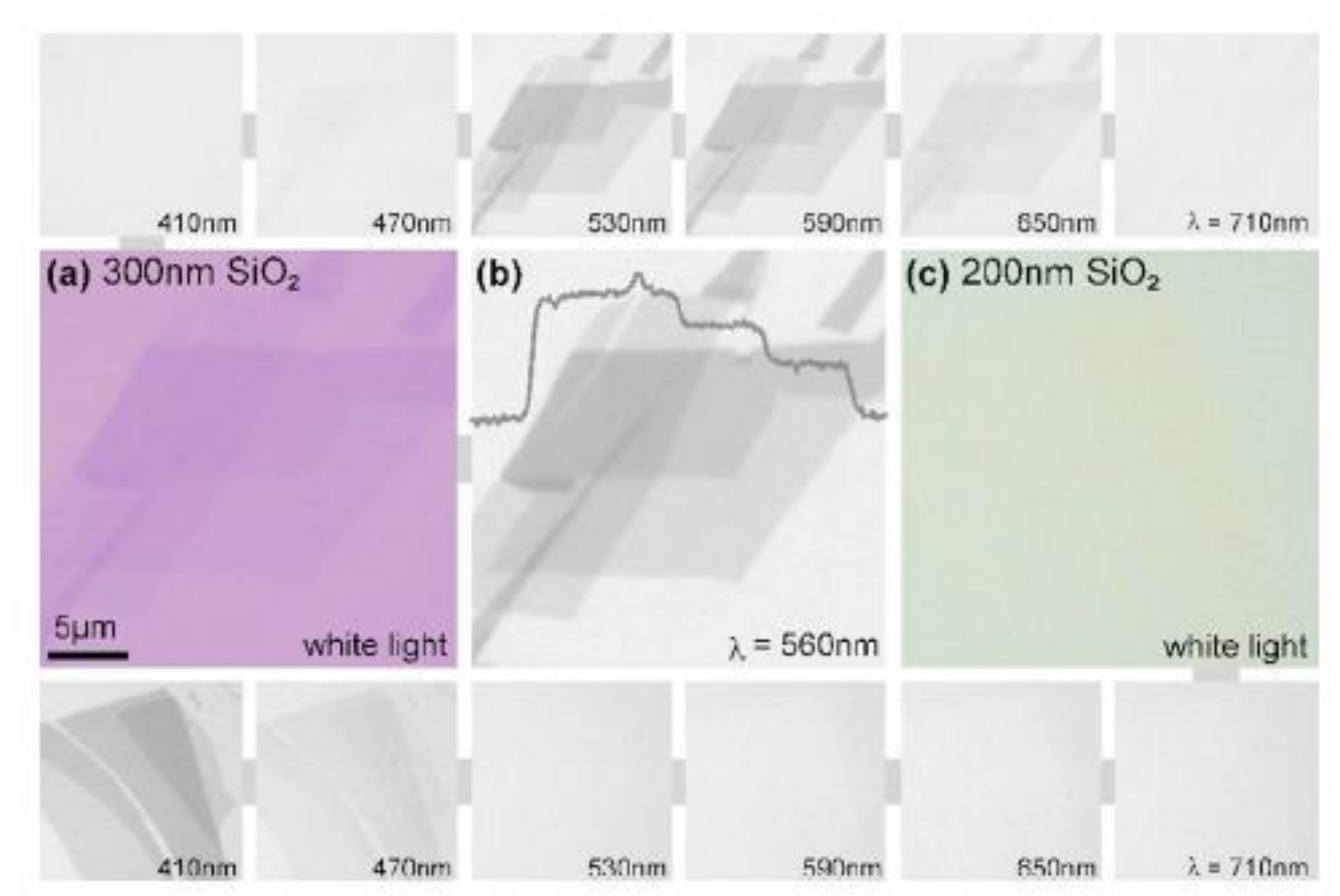
Graphene - properties

- *1 Atom layer thin*
- *Very strong*
- *High thermal conductivity*
- *Optical absorption:* $\pi\alpha$
- *Thermally and chemically stable*
- *Unique electronic properties*

Graphene - applications

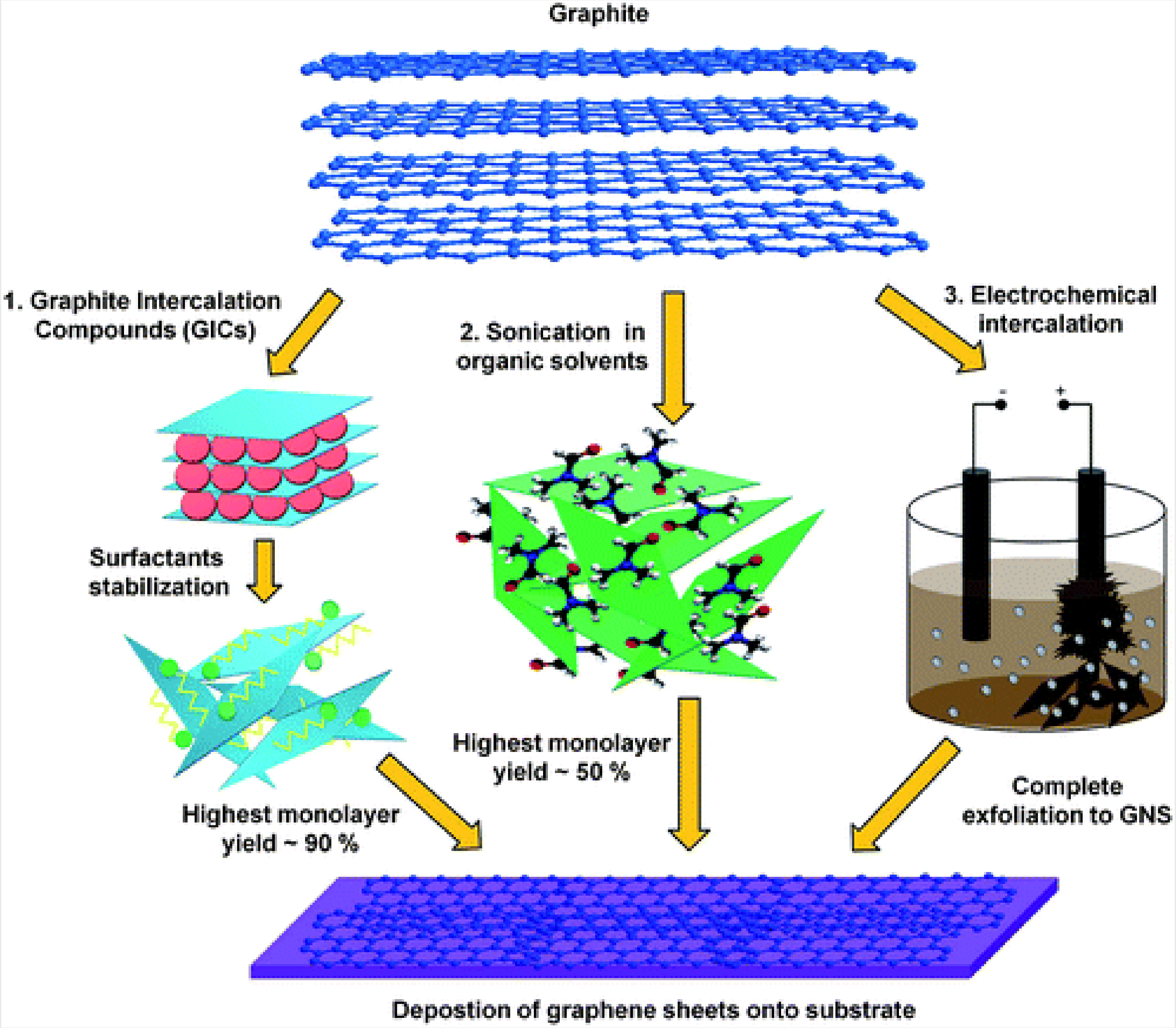
- *Ultra fast electronics*
- *Touch screen devices*
- *OLEDs*
- *Flexible, transparent batteries and superkapacitors*
- *Coatings*
- *Composites*

Making graphene micromechanical cleavage



Blake et al. App. Phys. Lett. **91**, 063124 2007

Chemical approaches



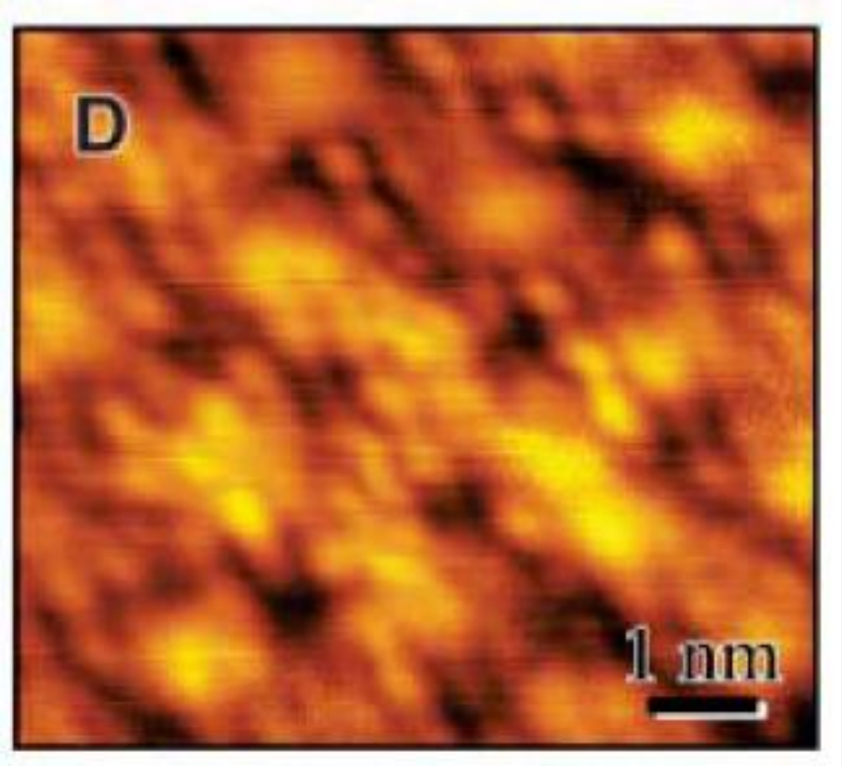
Growing graphene on SiC

Recipe:

6H-SiC(001) wafers (Si side)
H-etching (smooth surface)
Si flux at 900°C
(removal of surface oxides)
gradual annealing to 1250°C
(graphene growth)

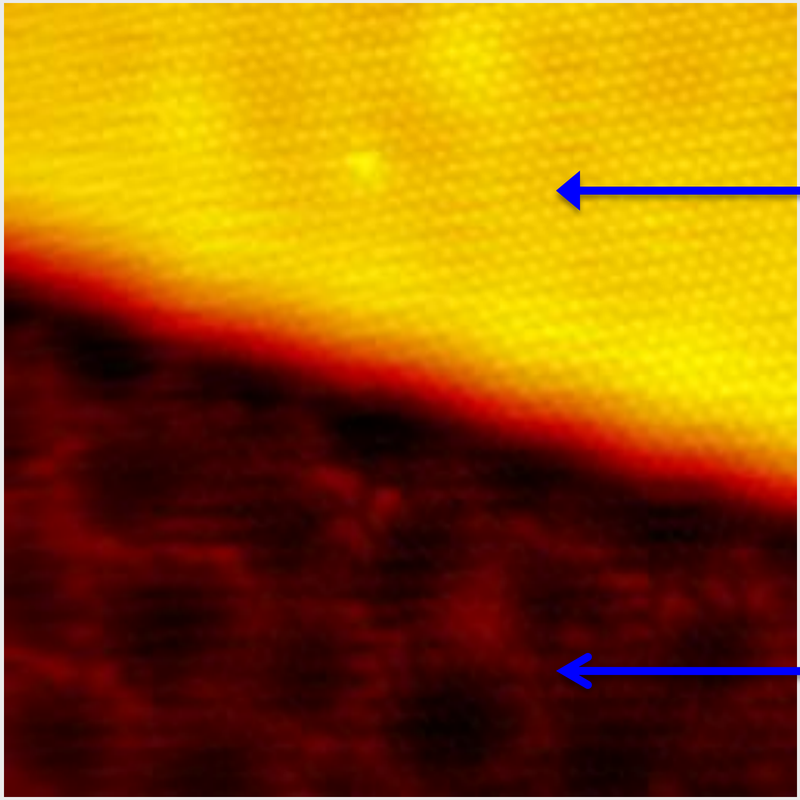
High temperature/pressure route
Exercise this afternoon

Buffer layer

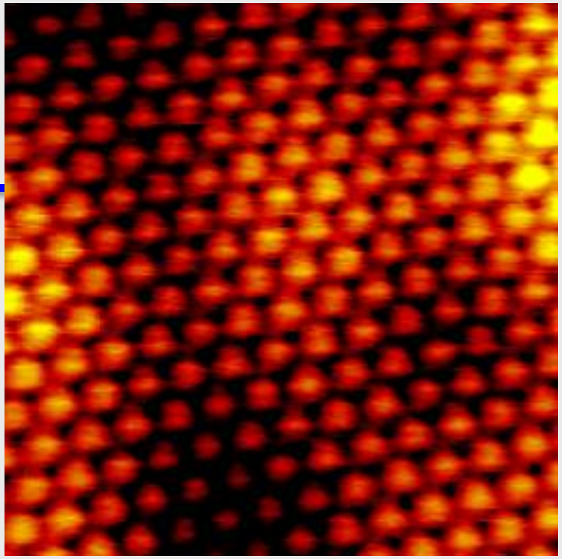


Berger et al., Science **312**, 1191 (2006)

Graphene on SiC

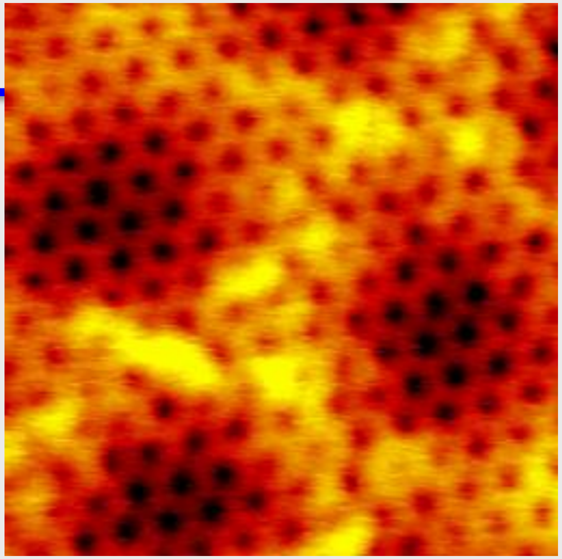


100x100Å, V= -0.41V, I= -0.36nA
step edge height 3.1Å



30x30Å,
V= -0.41V,
I= -0.39nA

Bi-layer graphene
showing
triangular pattern



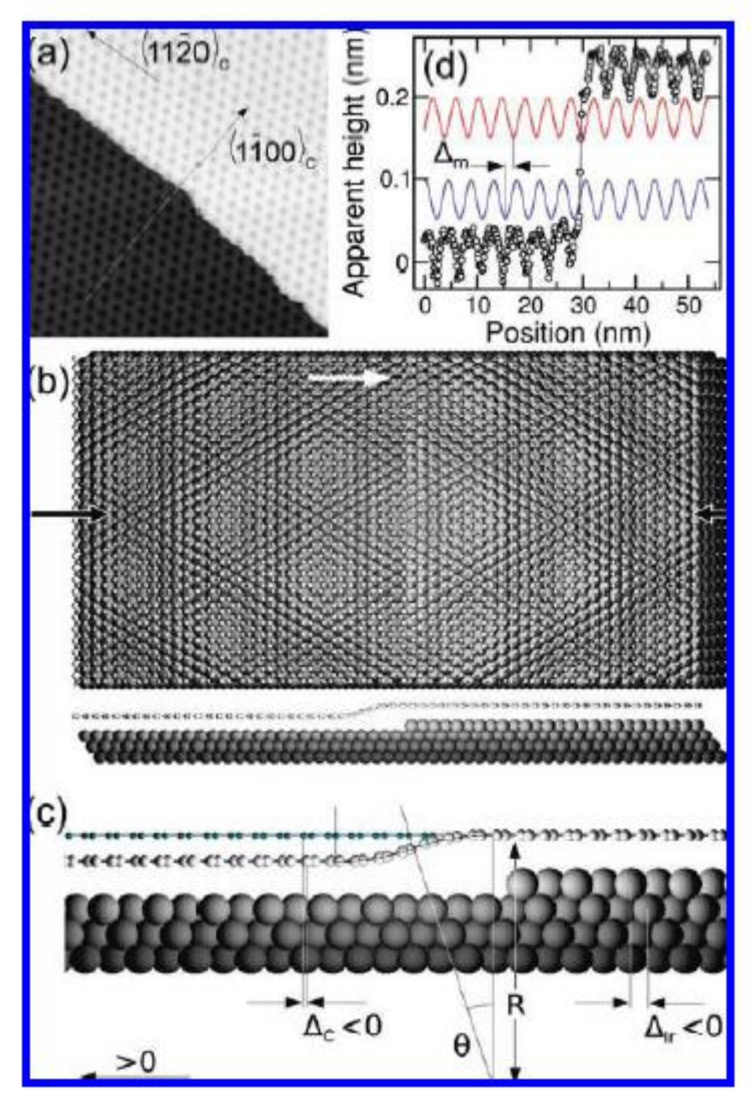
30x30Å,
V= -0.41V,
I= -0.38nA

Mono-layer graphene
showing
honeycomb structure

Metals – CVD

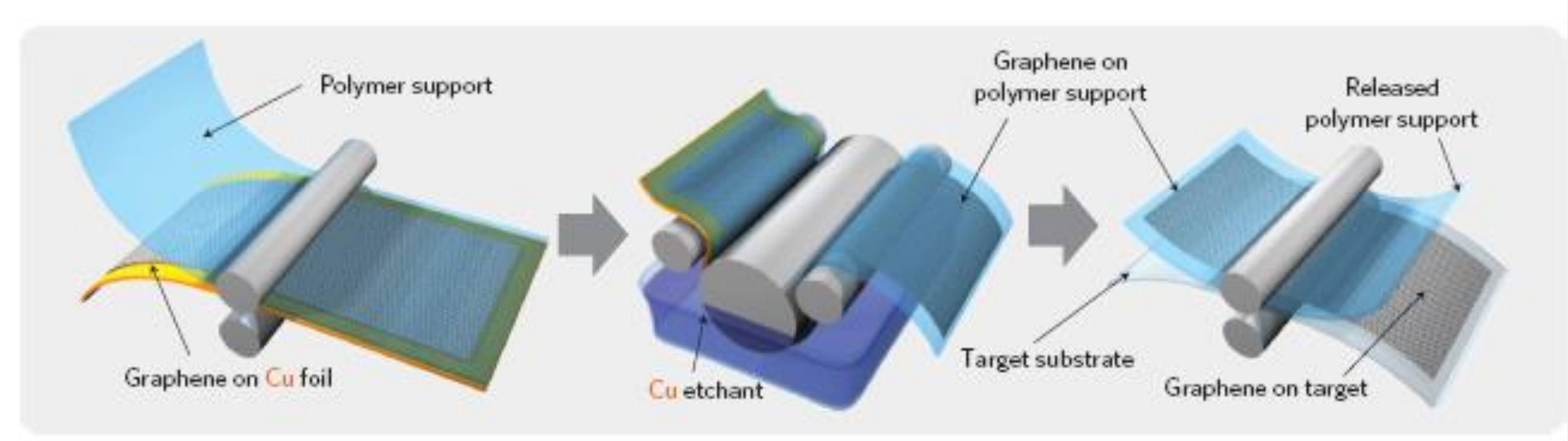
Decomposition of:
Ethylene, propene
Methane, acetylene, CO
Cyclohexane, n-heptane
Benzene, toluene

Here: graphene on Ir(111)
- Ethylene (2 x 10-5 Pa)
  @ 550 K for 100 s
- flash anneal to 1420 K.
- Repeat many times



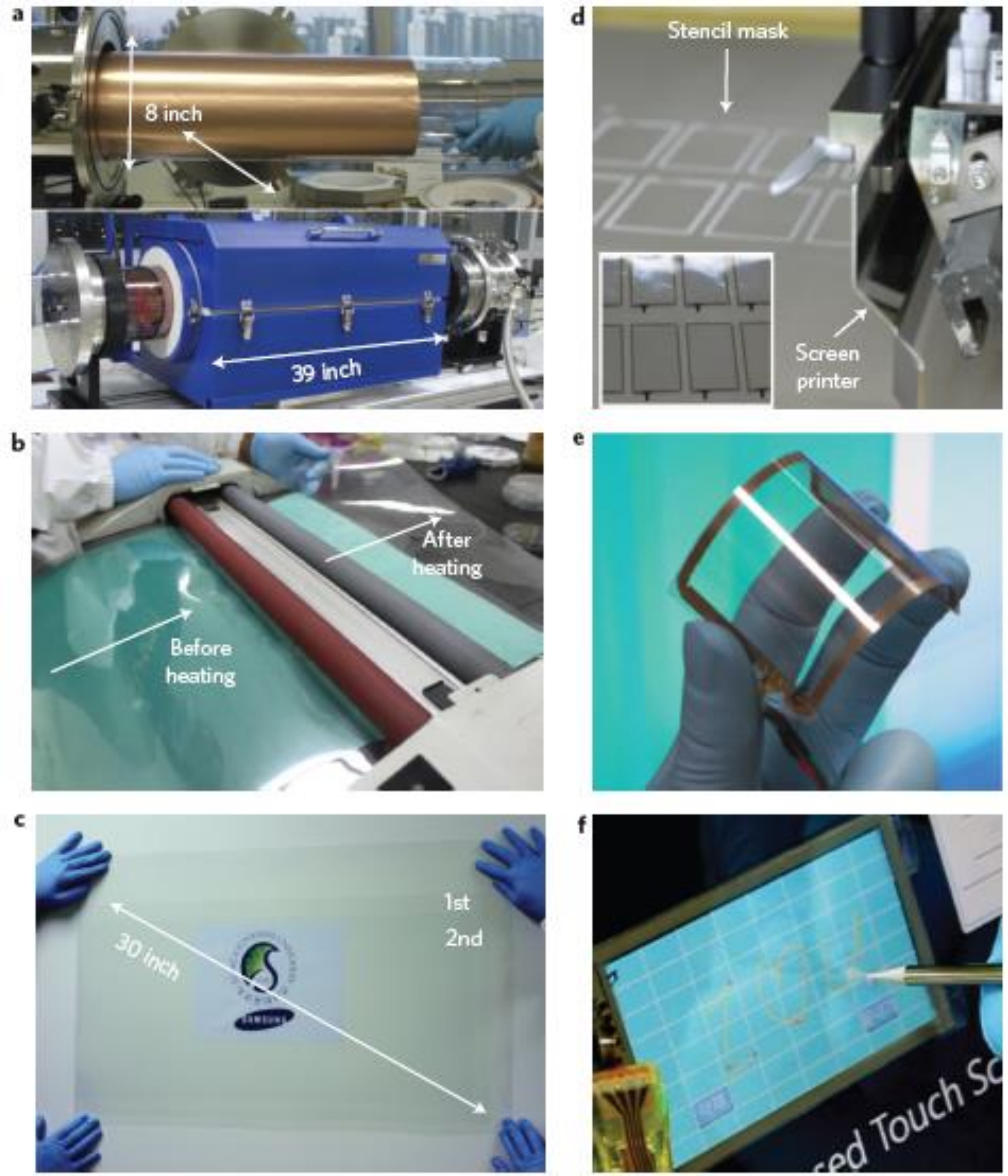
Coraux et al. PRL 103, 166101 (2009)

Mass production



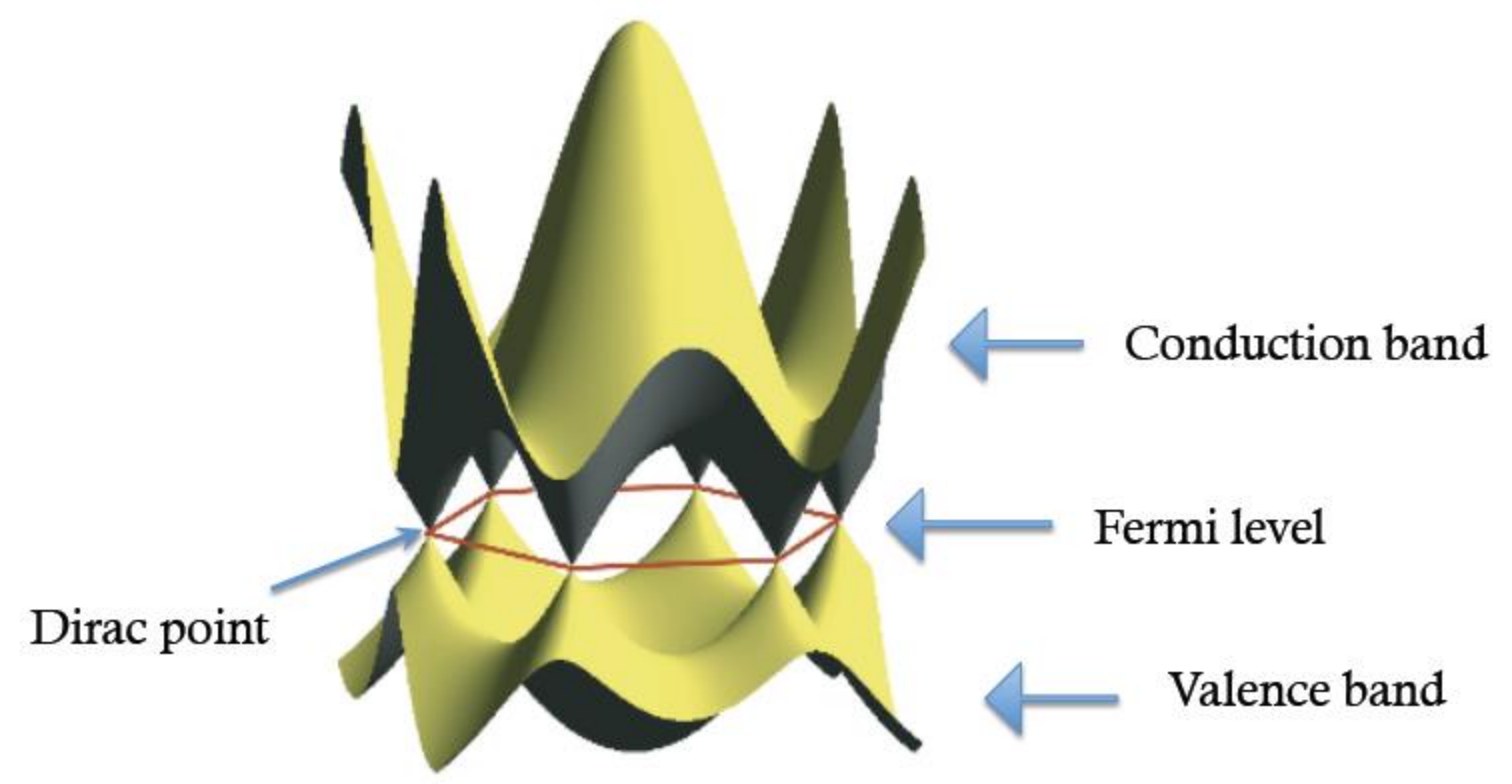
Bae et al., ONLINE: 20 JUNE 2010 | DOI: 10.1038/NNANO.2010.132

Mass production



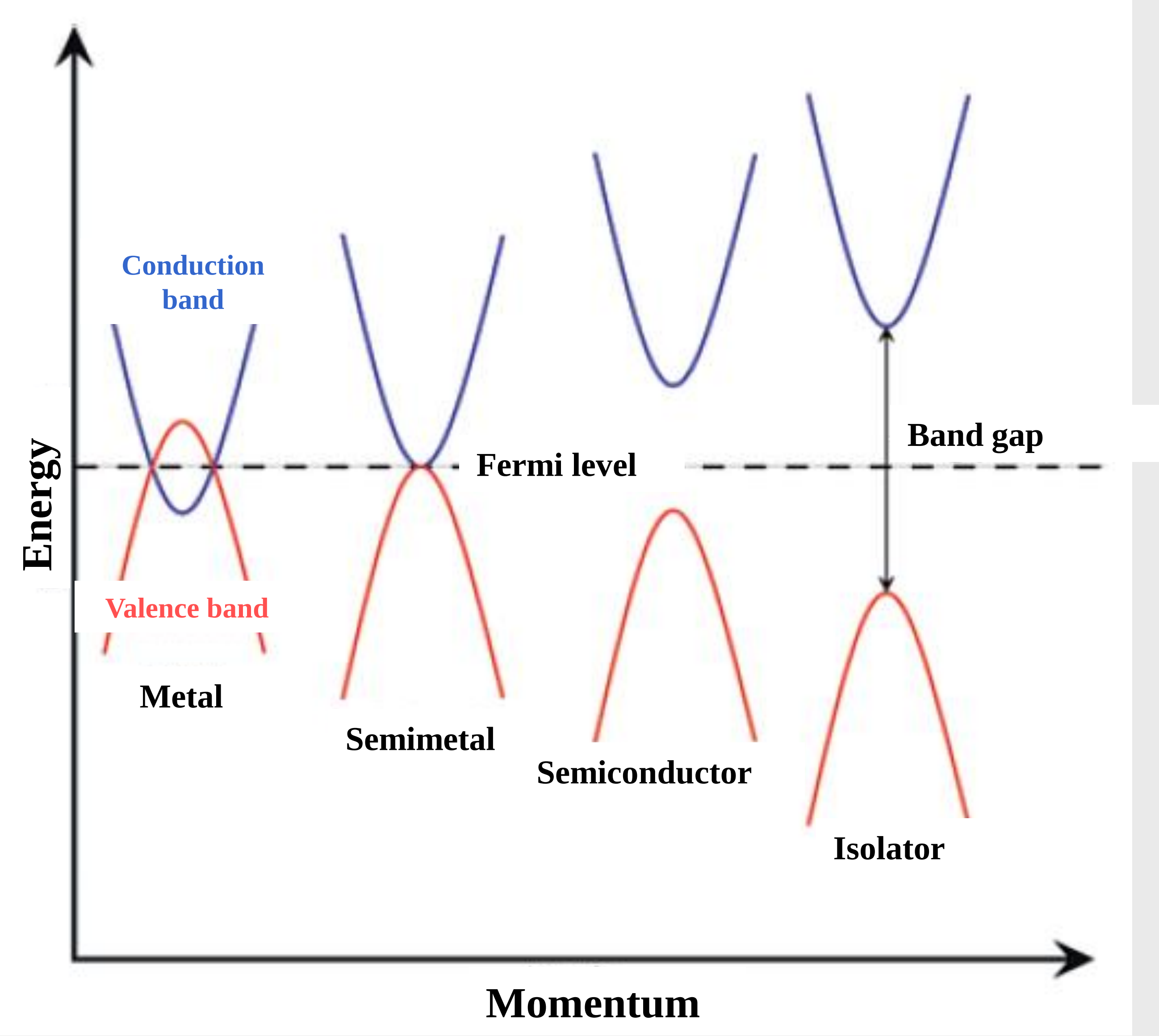
Bae et al., 2010

Graphene – electronic properties

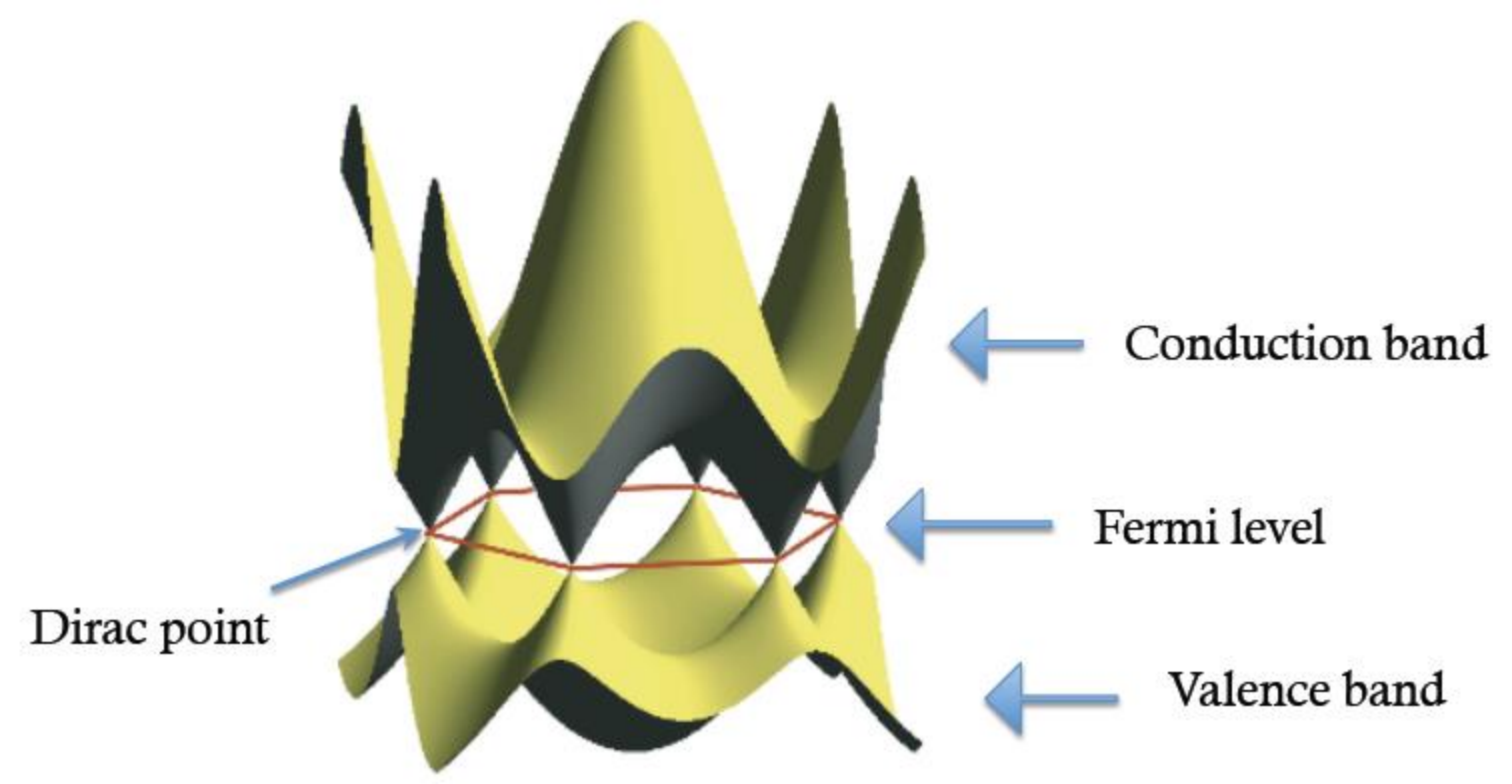


- Semi-metal
- Mass less Dirac fermions
- Ballistic charge transport

Band gap


Conduction band
Valence band
Fermi level
Band gap
Energy
Momentum
Metal
Semimetal
Semiconductor
Isolator

Graphene – electronic properties



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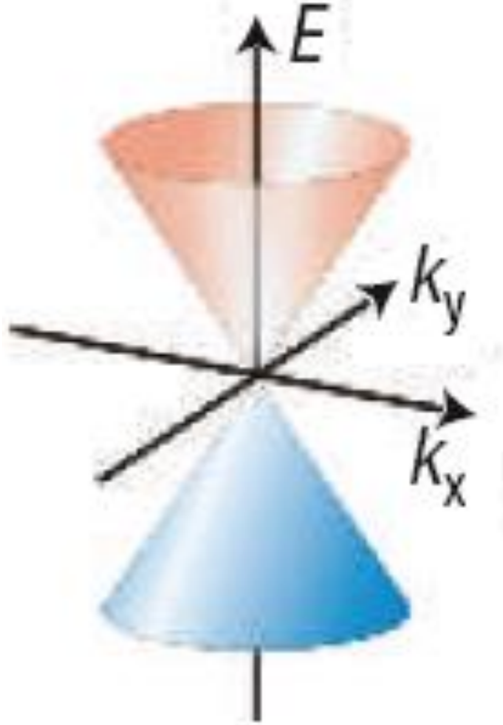

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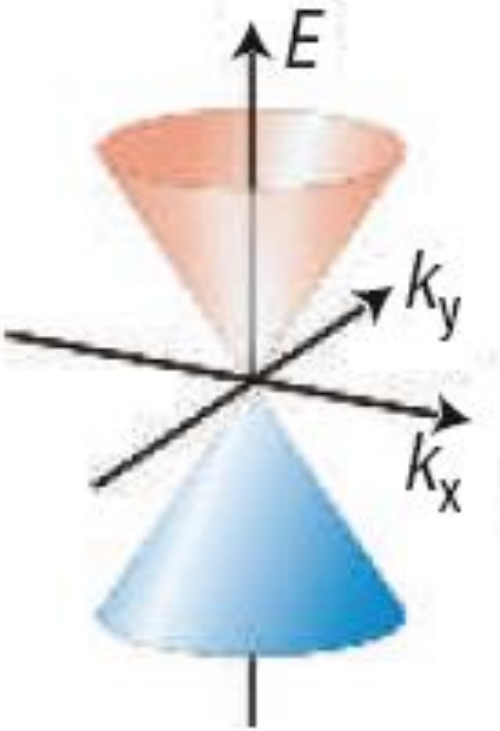
Graphene – electronic properties

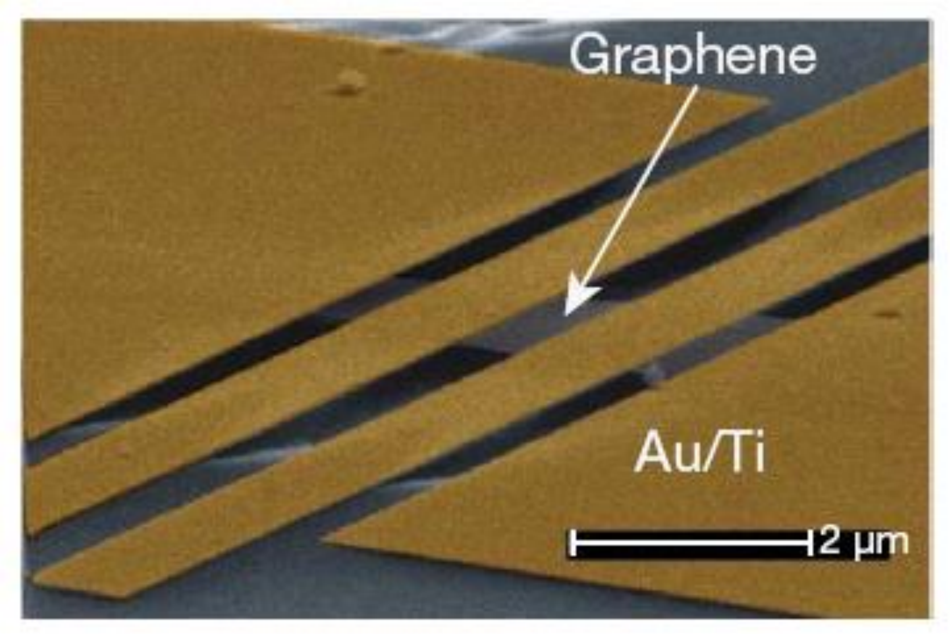


$$E = \hbar \nu_F k$$

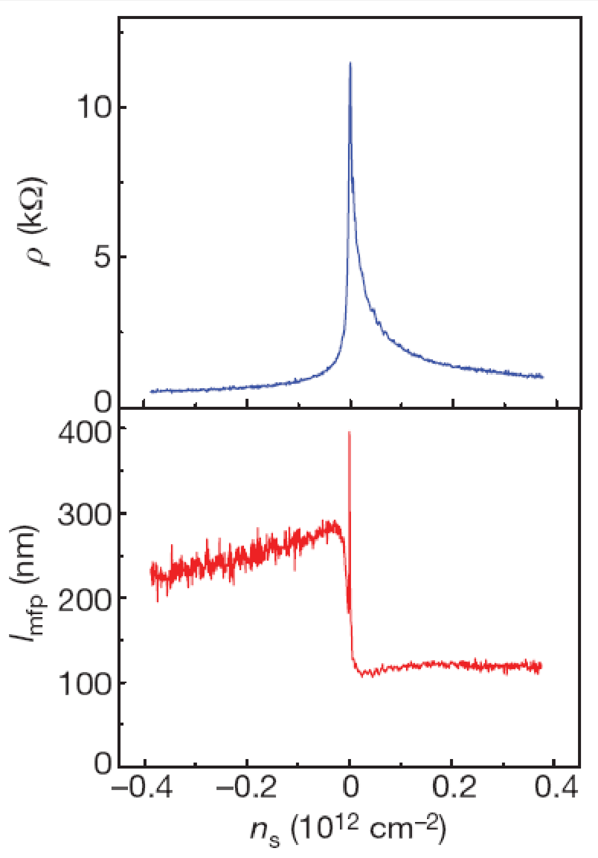
$$\nu_F \approx 10^6 \text{ m/s}$$

- Semi-metal
- Mass less Dirac fermions
- Ballistic charge transport

Ballistic charge transport in graphene



$\mu = 200{,}000\ \mathrm{cm^2/Vs}$

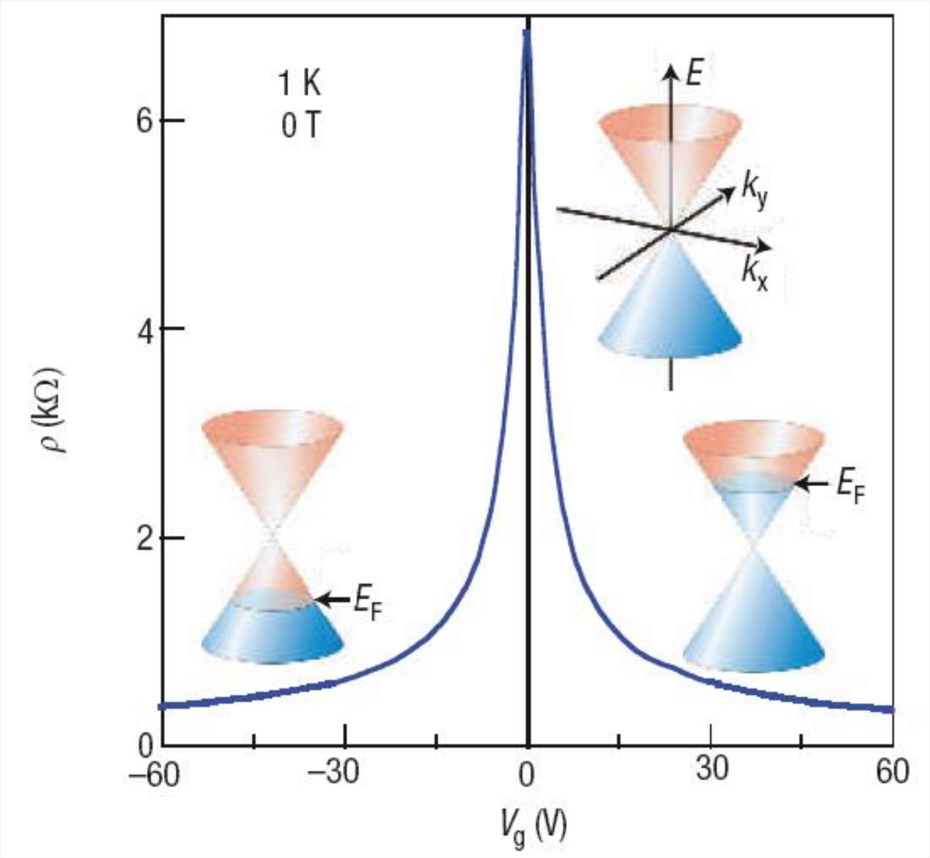


Du et al. Nature ***462,*** *192 (2009)*

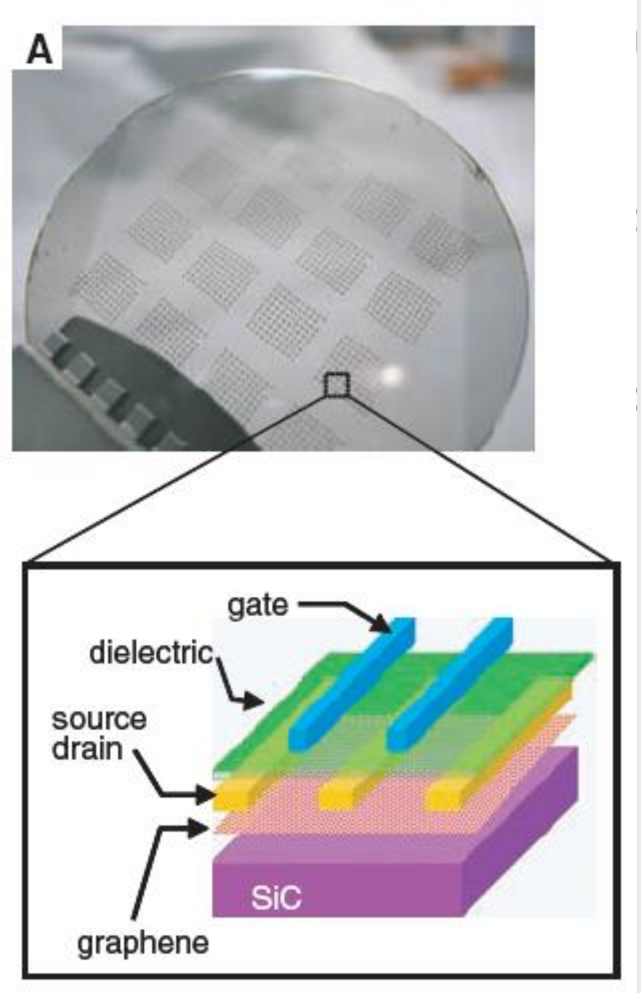
LT: Reported for suspended graphene: $\mu = 10^6\ \mathrm{cm^2/Vs}$ (Geim et al.)
RT: Standard: 10,000-15,000 $\mathrm{cm^2/Vs}$ (Si: 1400 $\mathrm{cm^2/Vs}$)
Suggested max: 70,000 $\mathrm{cm^2/Vs}$

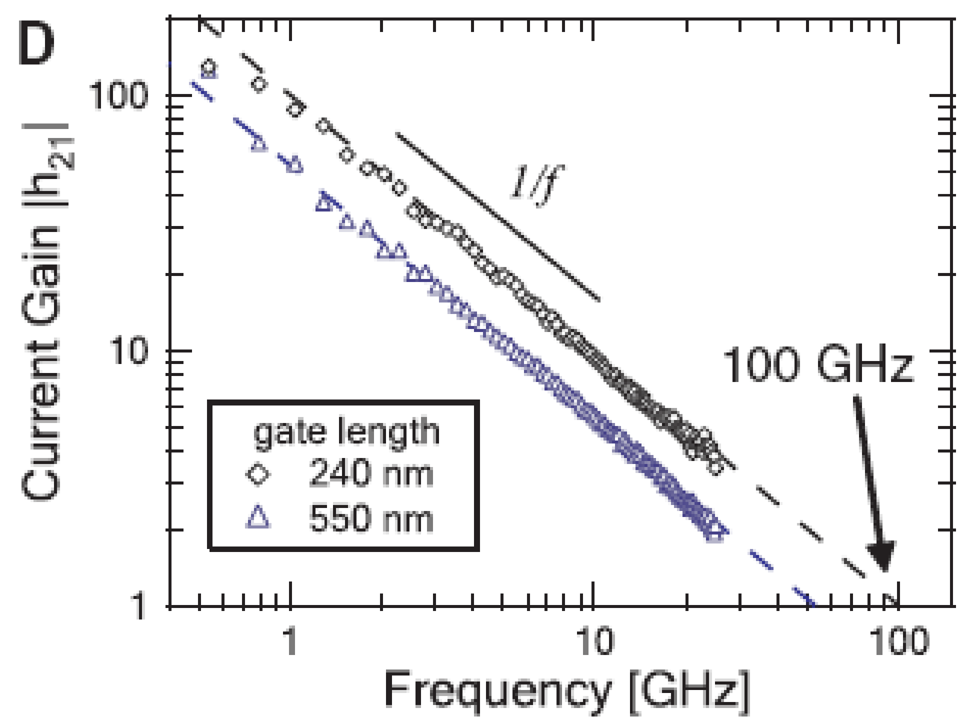
Charge neutrality point - conduction

$\sigma_{\mathrm{min}} = 4e^2/h\pi$



Graphene FET



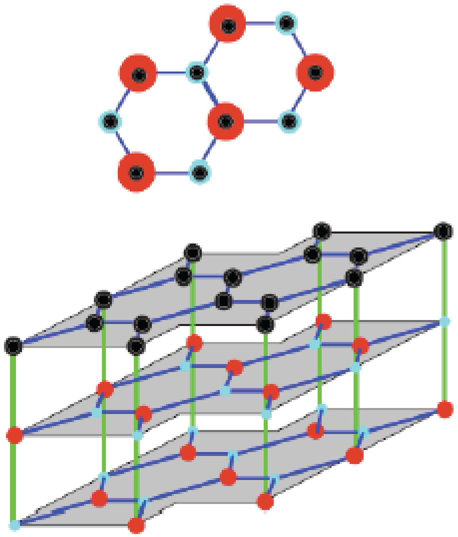


*Lin et al., Science **327**, 662 (2010)*

Bad on/off ratio due to lack of a band gap (~0.4 eV or more)

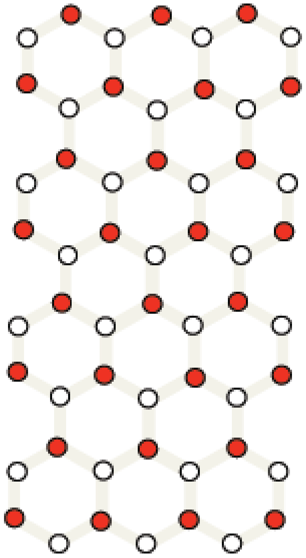
Opening a band gap in graphene

induced by interaction with the underlying substrate



Giovannetti et al. Phys. Rev. B (2007) vol. 76 (7) pp. 073103

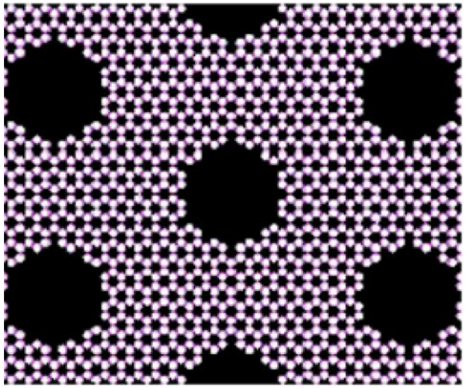
production of nanoribbons



Han et al. Phys Rev Lett (2007) 98 (20) pp. 206805

chemical modification

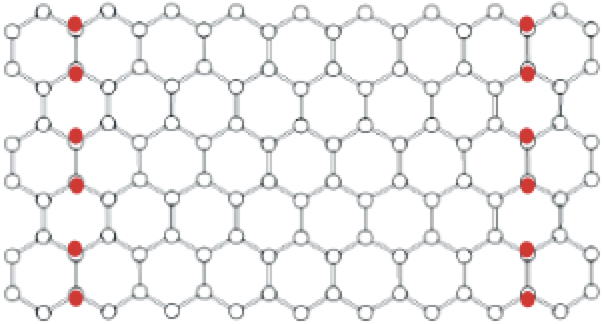
(Antidot-lattice)



Pedersen et al. Phys Rev Lett (2008) 100 pp. 136804

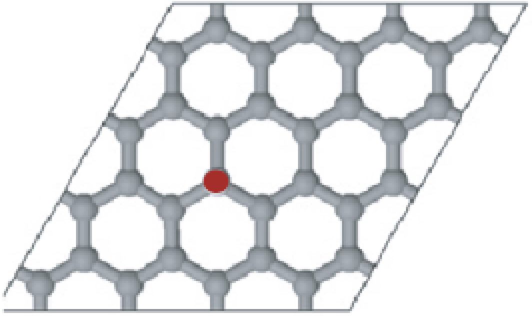
Hydrogen induced band gap opening

a) Hydrogen atoms arranged in lines



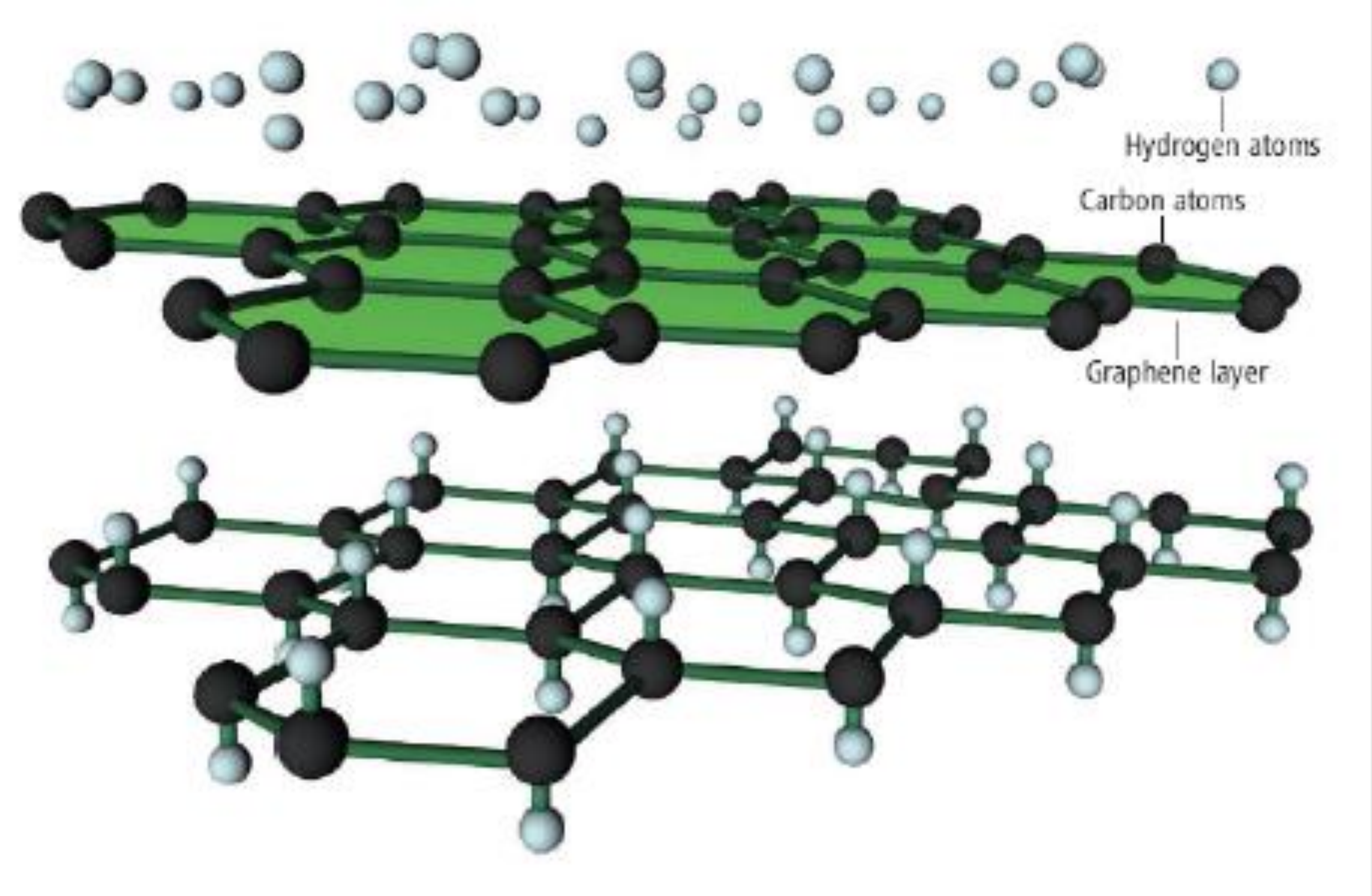
Chernozatonskiĭ et al., *Jetp Lett,* **85** (1), 77-81 (2007).

b) periodic arrangement



Duplock, E.J.et al. *Phys Rev Lett*, **92**, 225502 (2004).

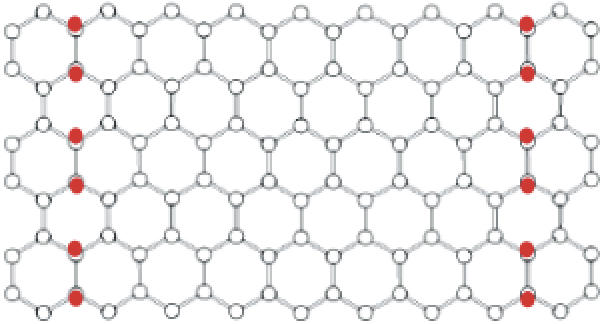
Chemical modification by H



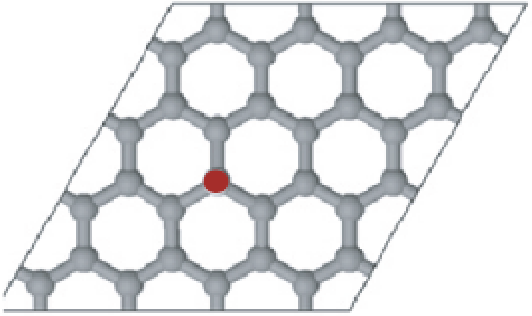
Sofo et al. *Phys. Rev. B* (2007) vol. 75 (15) pp. 153401
Savchenko. *Mat. Science* (2009) vol. 323 (5914) pp. 589-590

Hydrogen induced confinement

a) Hydrogen atoms arranged in lines



b) periodic arrangement



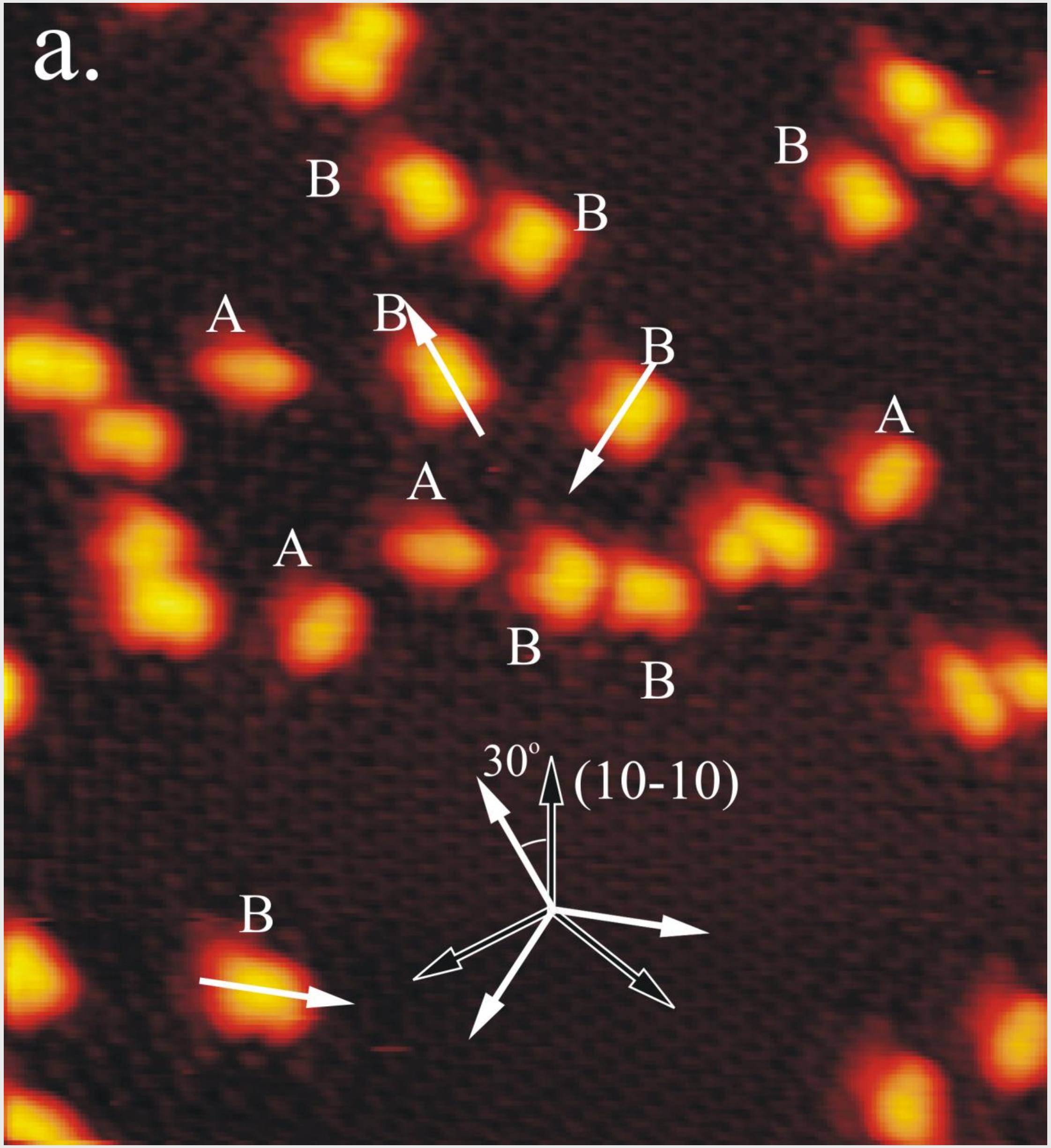
Chernozatonskiĭ et al., *Jetp Lett,* **85** (1), 77-81 (2007).

Duplock, E.J.et al. *Phys Rev Lett*, **92**, 225502 (2004).

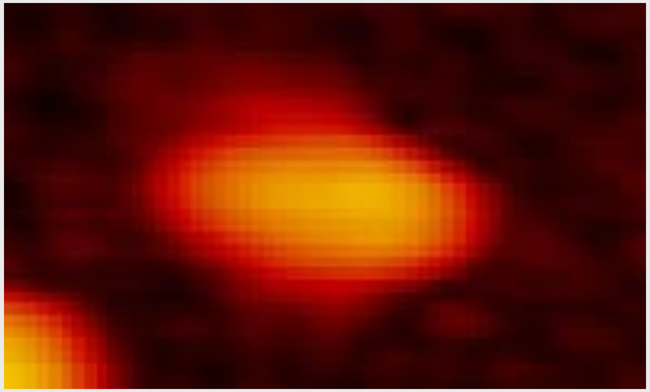
Can atomic hydrogen be arranged in ordered structures on graphene and thereby facilitate gand gap engineering?

H-Dimers on graphite

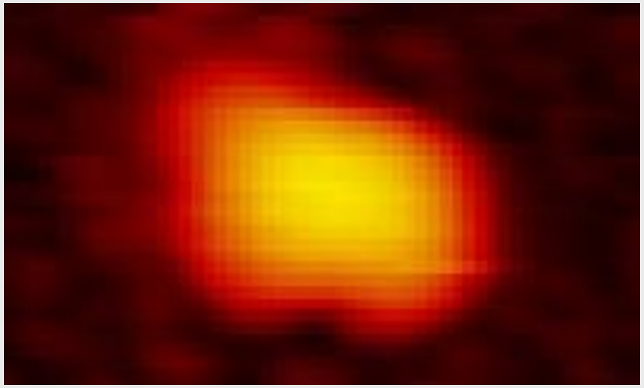
103 x 114 Å²



Dimer A



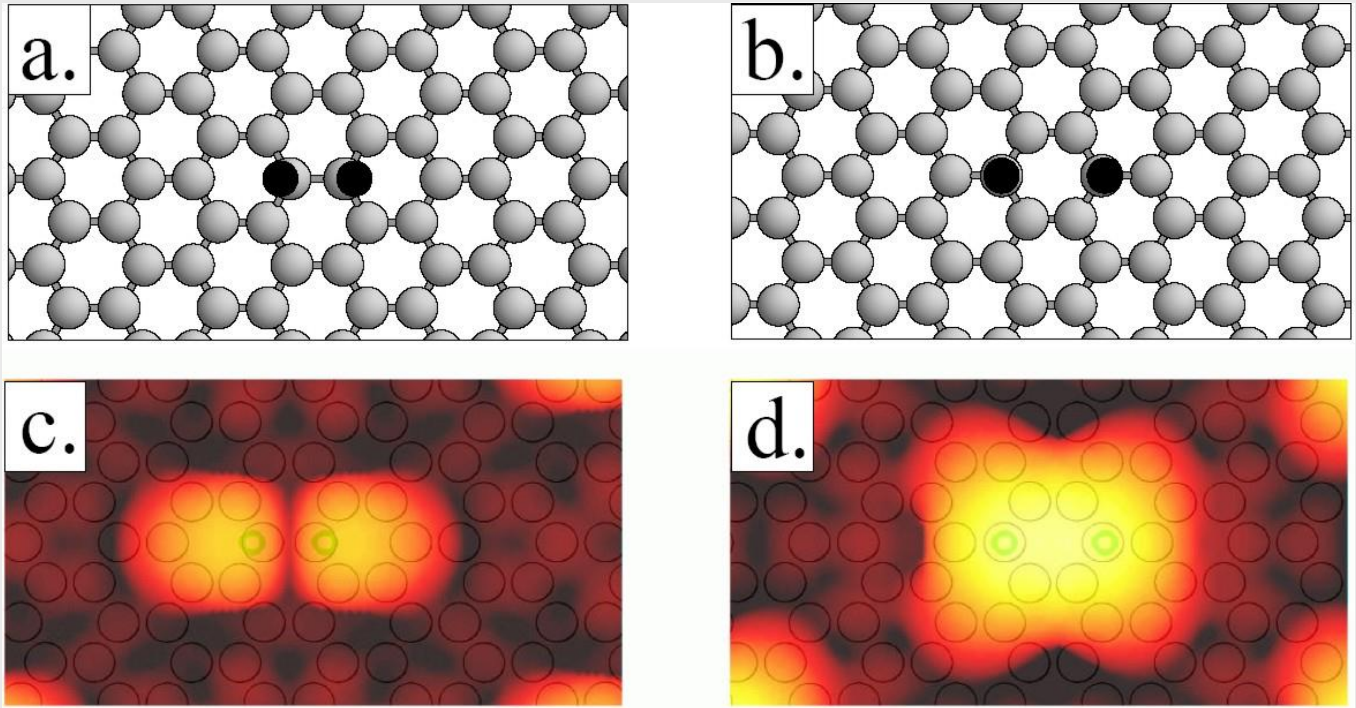
Dimer B



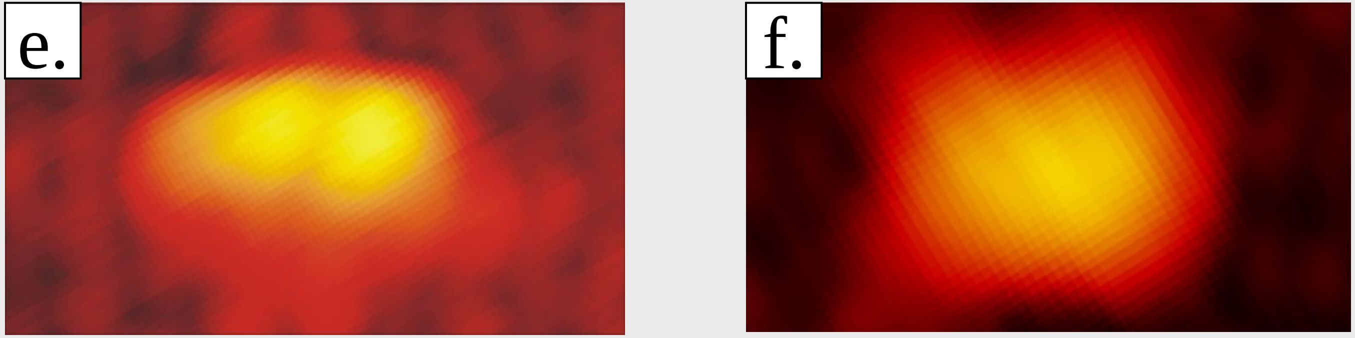
V_t = 884 mV, I_t = 0.16 n

Dimers: Theory vs. Experiment

Ortho dimer - Dimer A Para dimer - Dimer B



V_t=0.9 V, LDOS=1x10^{-6} (eV)$^{-1}$ Å^{-3}



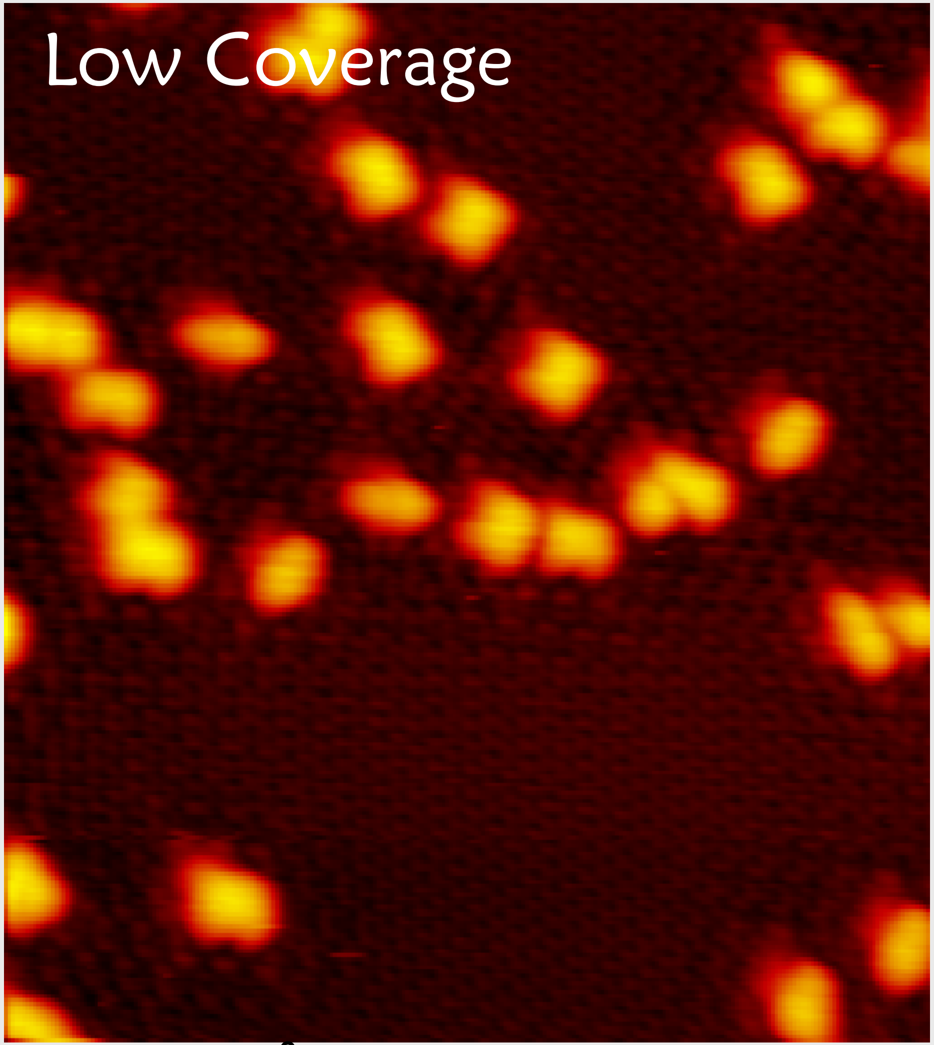
V_t = 884 mV, I_t = 0.16 nA

*Hornekær et al. Phys. Rev. Lett. **96**, 156104 (2006)*

Similar results for ortho dimer:

*Ferro et al. Chem. Phys. Lett. **368**, 609 (2003).*
*Y. Miura et al. J. Appl. Phys. **93**, 3395 (2003).*

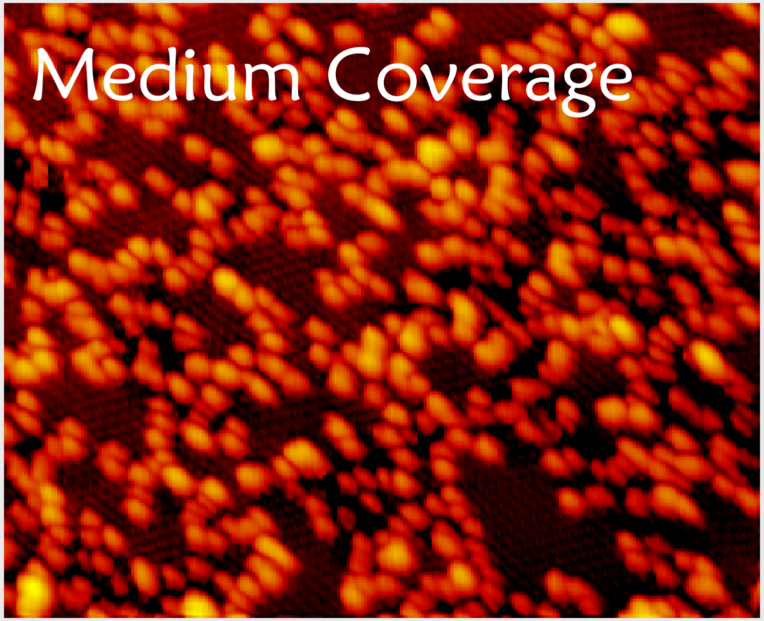
H on HOPG

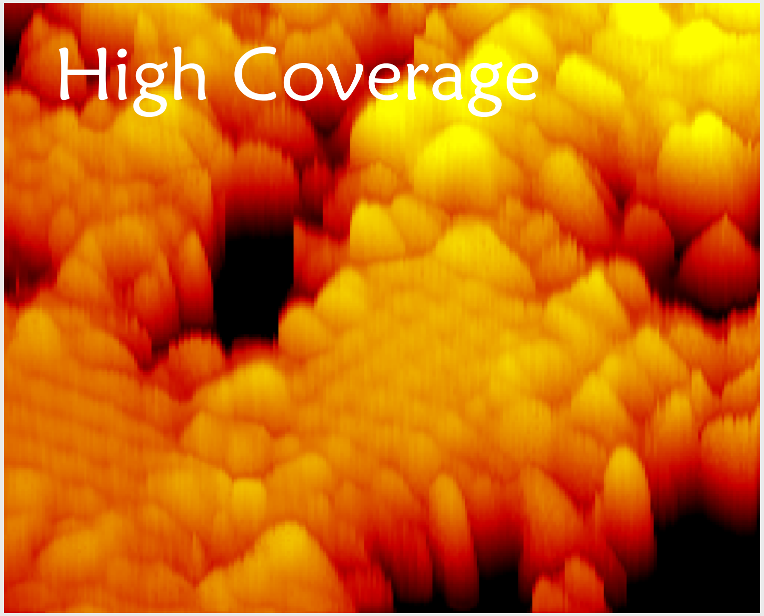


103 x 114 Å^2

V_t~800mV, I_t~0.15-0.2nA

171 x 155 Å^2

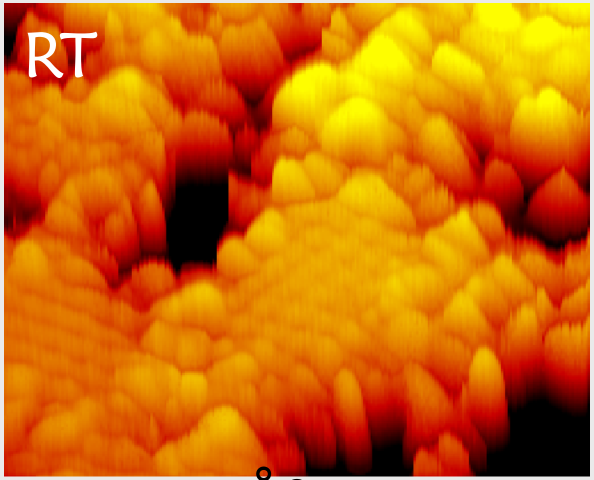




80 x 72 Å^2

High Coverage

V_t = -1.05 V, I_t = -0.55 nA



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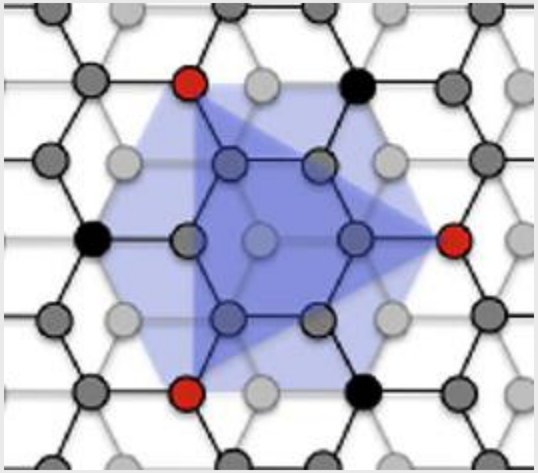
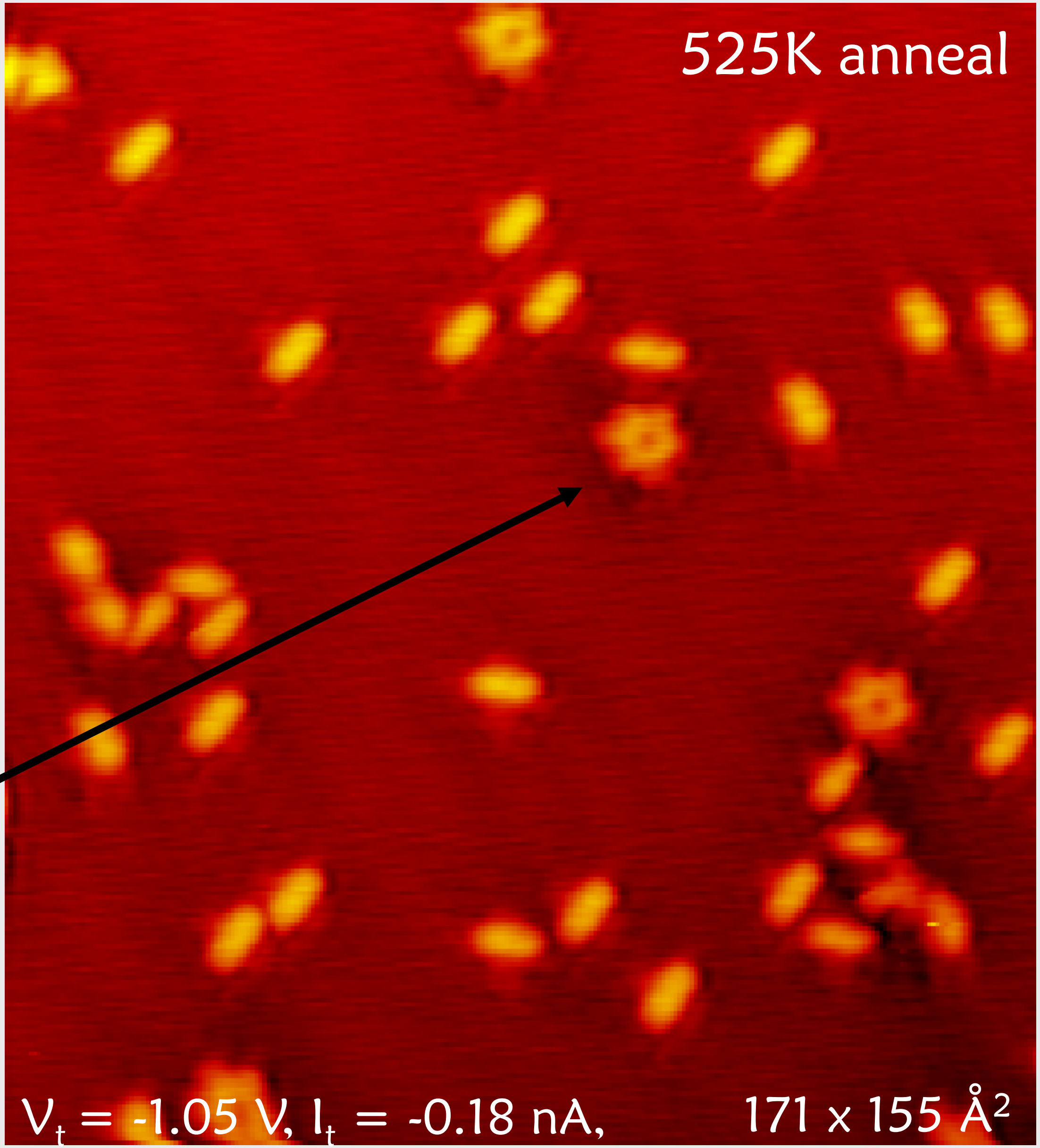


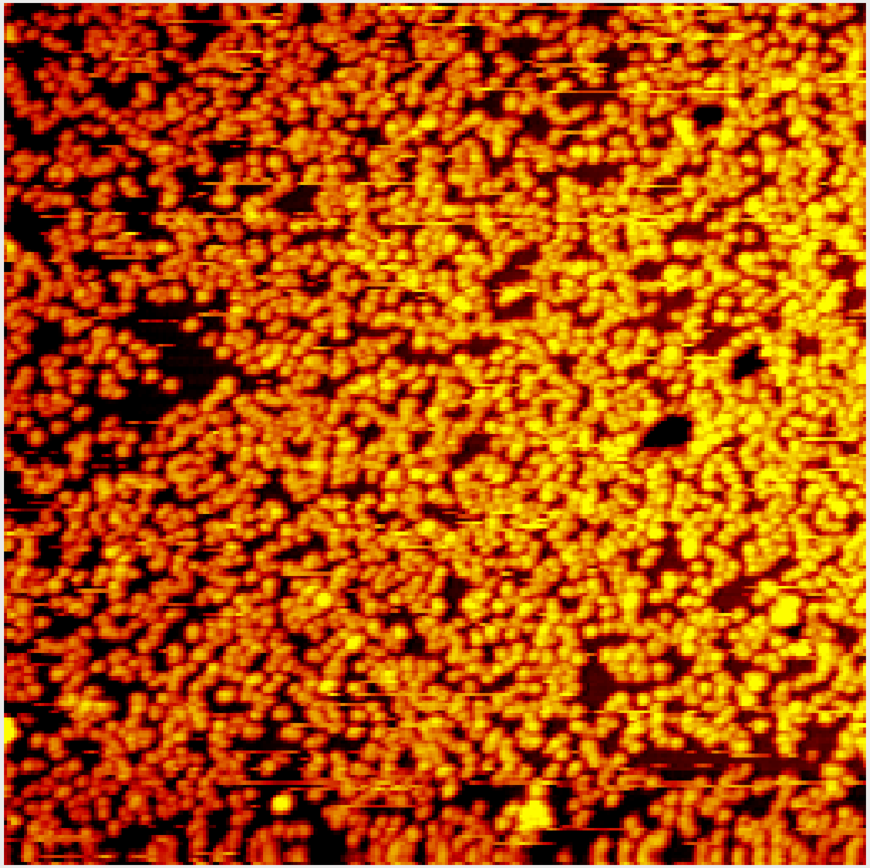
Ferro et al., Chem. Phys. Lett. ***478****, 42 (2009)*

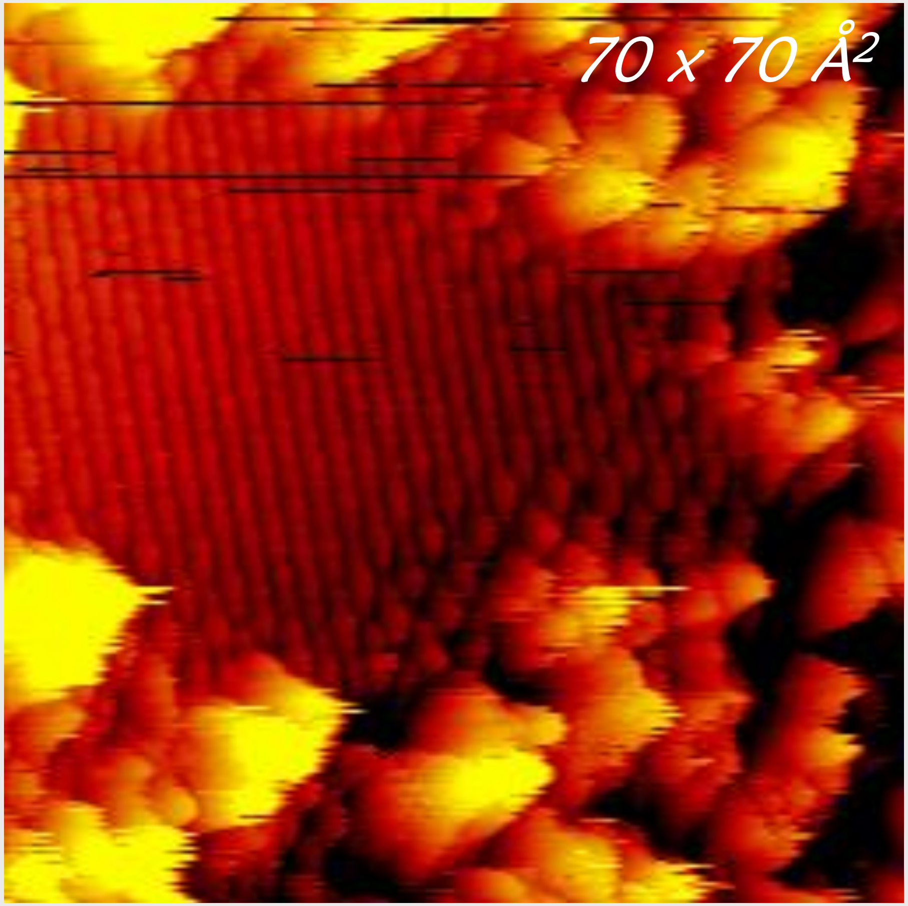


Hornekær et al., Chem. Phys. Lett. ***446****, 237 (2007)*

No periodic H adsorbate structures on ”graphene on graphite”

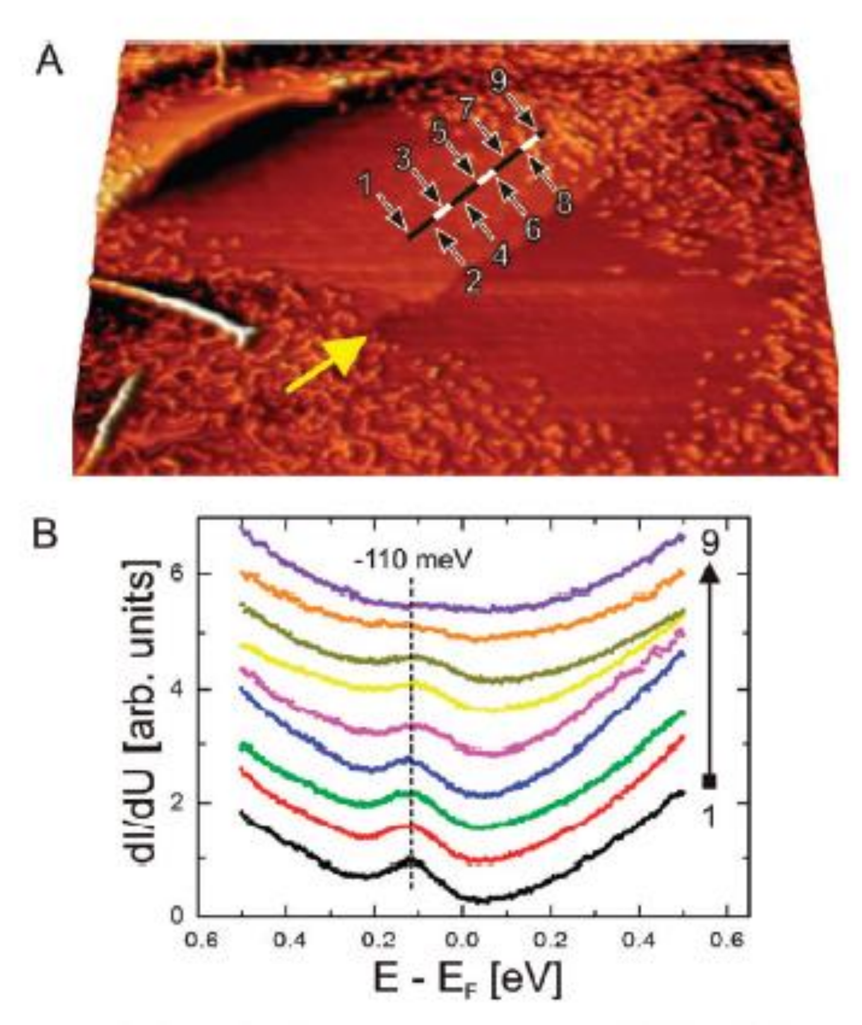
STM desorption of H





$V_t = -1.25$ V, $I_t = -0.37$ nA,

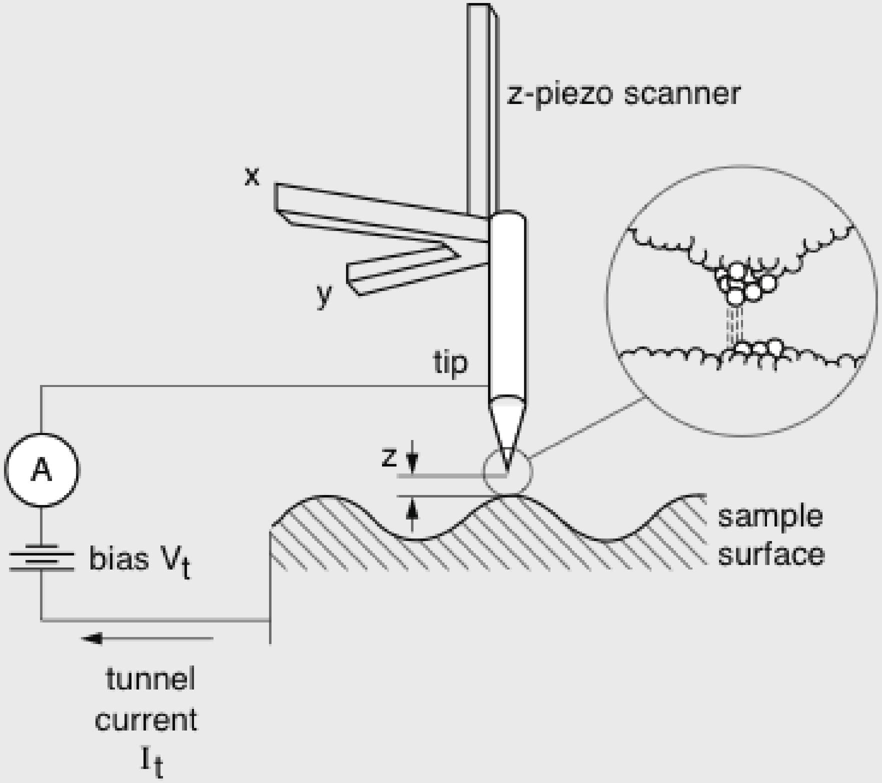
H patterning – bilayer graphene



Sessi et al. Nano Lett. 9, 4343 (2009)

scanning tunneling spectroscopy (STS)

- “park” tip above a certain sample position and measure I(V) curves
- stability problem: no feedback, thermal drift, vibrations, tip-changes
- tip problem: tip electronic structure not known and not easily reproducible



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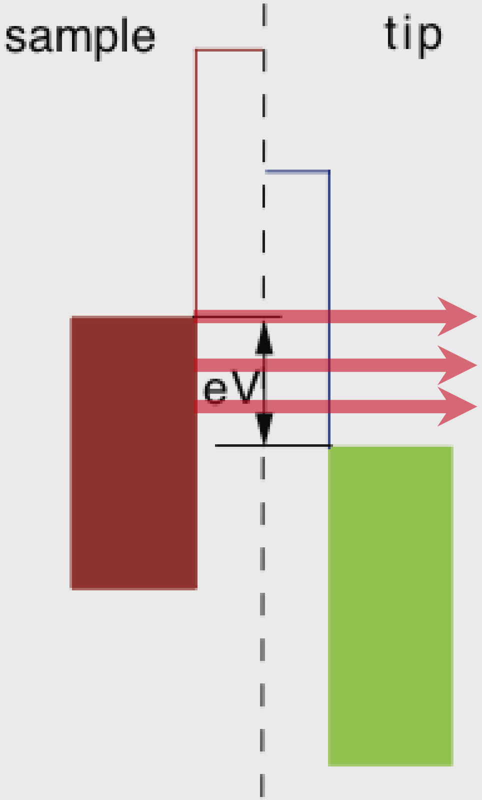


Tersoff-Haman model

$$I = \int_0^{eV} \rho_s(\vec{r}, E)\rho_t(\vec{r}, E - eV)T(E, eV, \vec{r})dE$$

assume

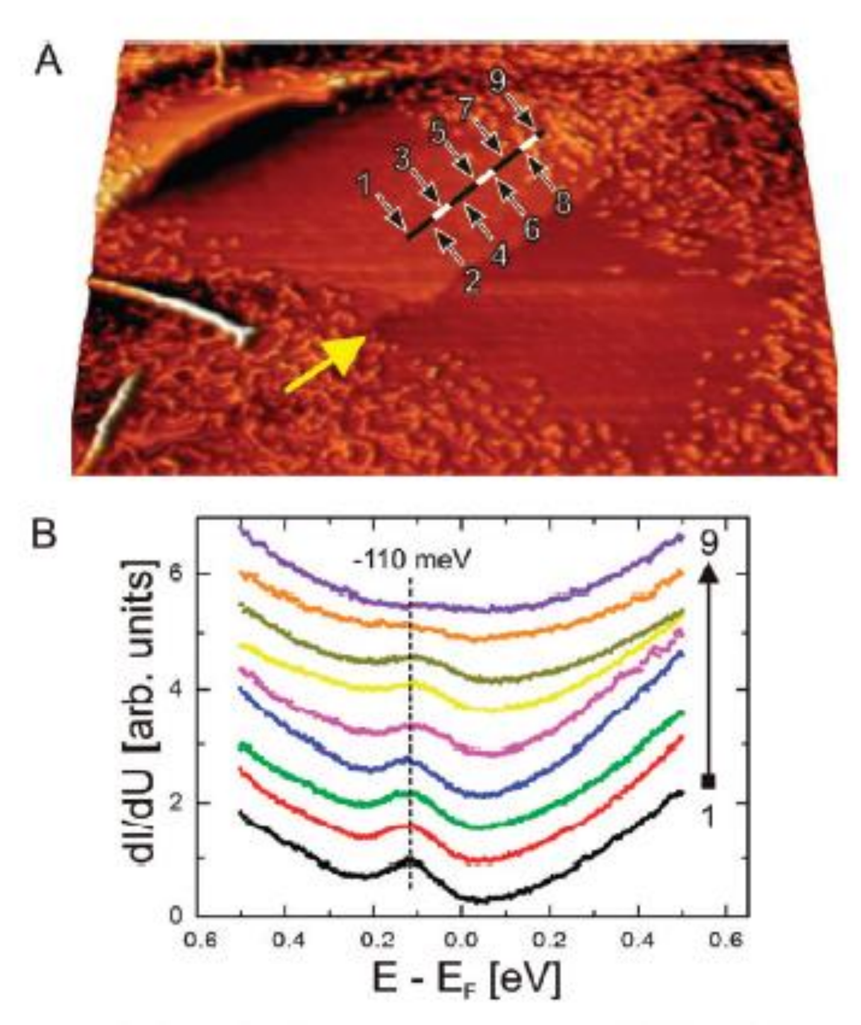
$\rho_t(E) = const.$ *(quite unjustified for atomic tips)*

$T(E, eV) = const.$ *(unjustified)*

then:

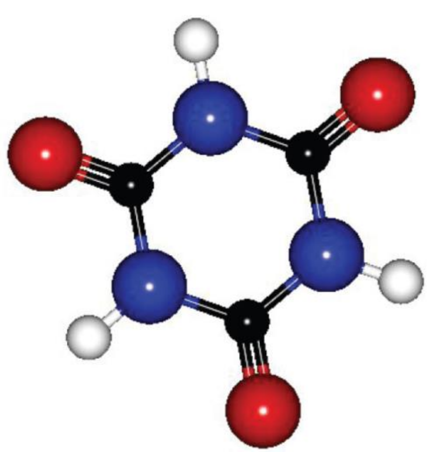
$$\rho_s(\vec{r}, E) \propto dI/dV$$

H patterning – bilayer graphene



Sessi et al. Nano Lett. 9, 4343 (2009)

Templated H adsorption by a SAM of CyA on graphite

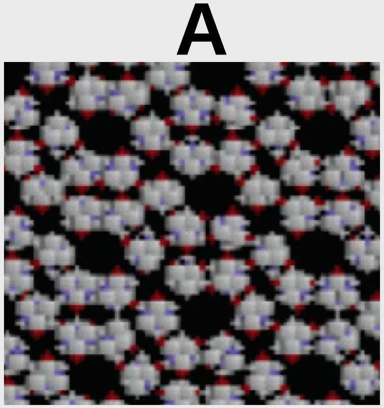


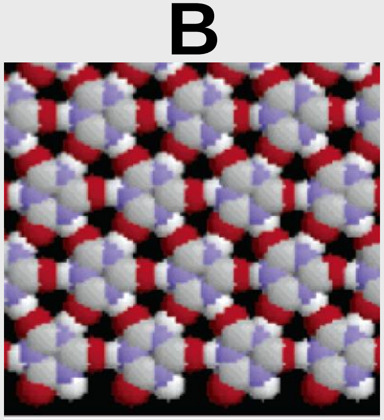
Red = Oxygen

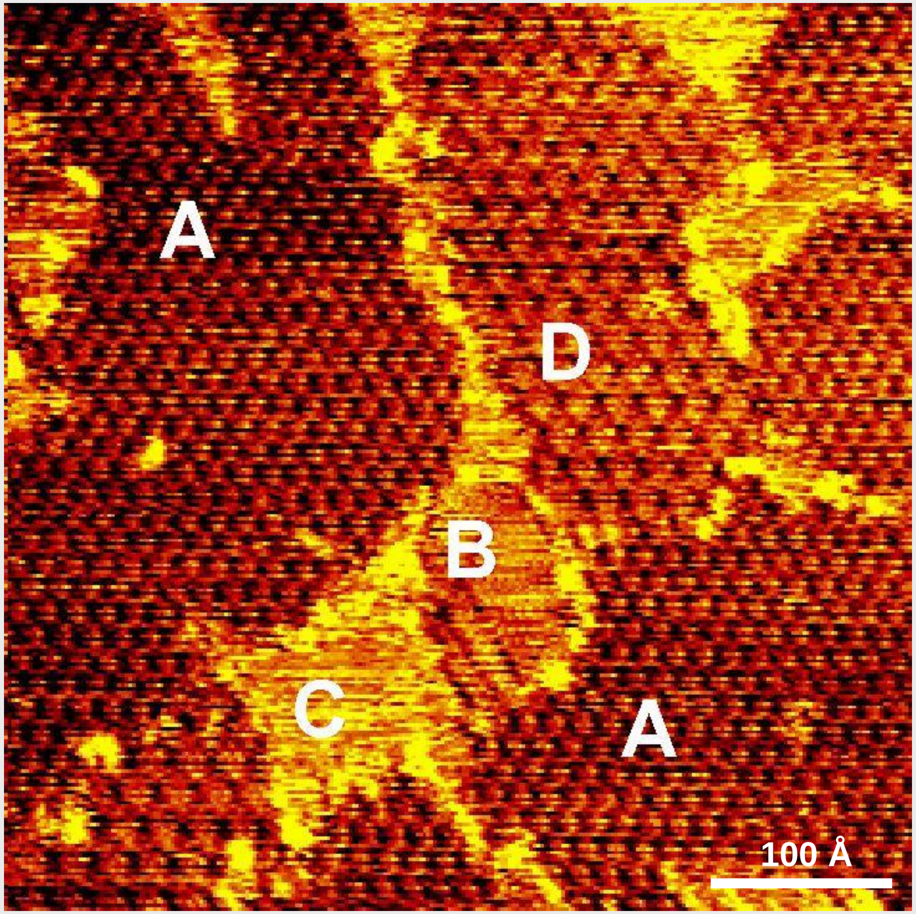
Blue = Nitrogen

Black = Carbon

White = Hydrogen



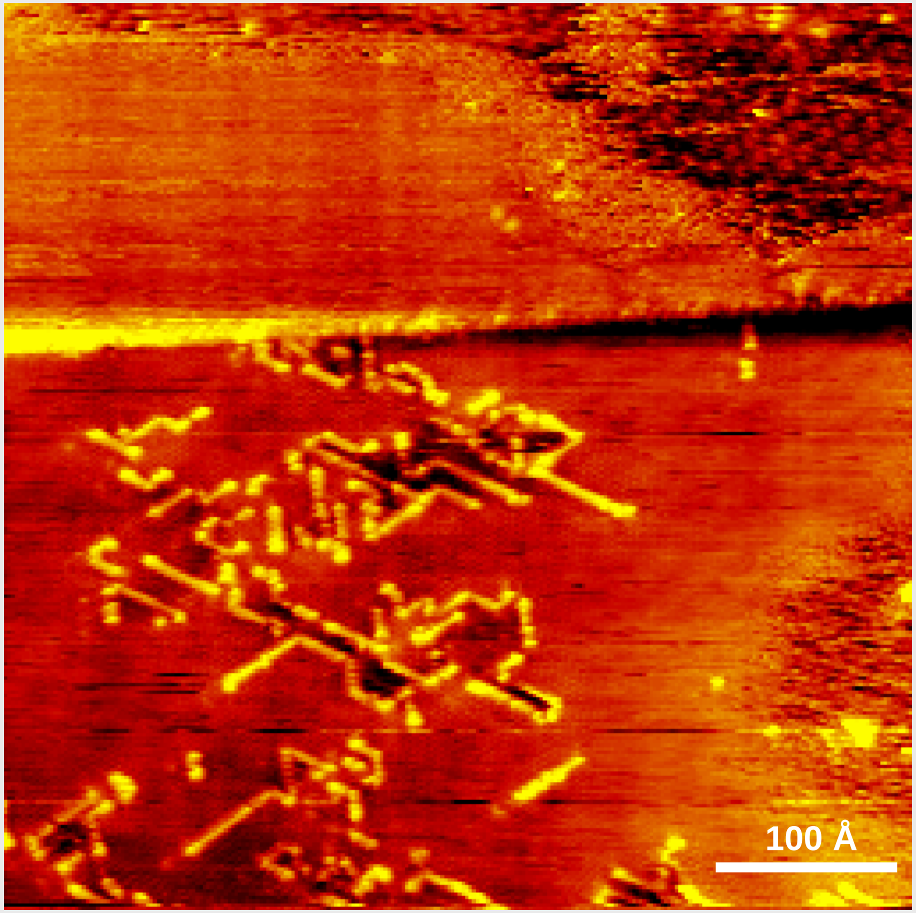




V_t = -1.25 V, I_t = -0.39 nA,

*Nilsson et al. CARBON **50**, 2052 (2012)*

Formation of linear H adsorbate structures



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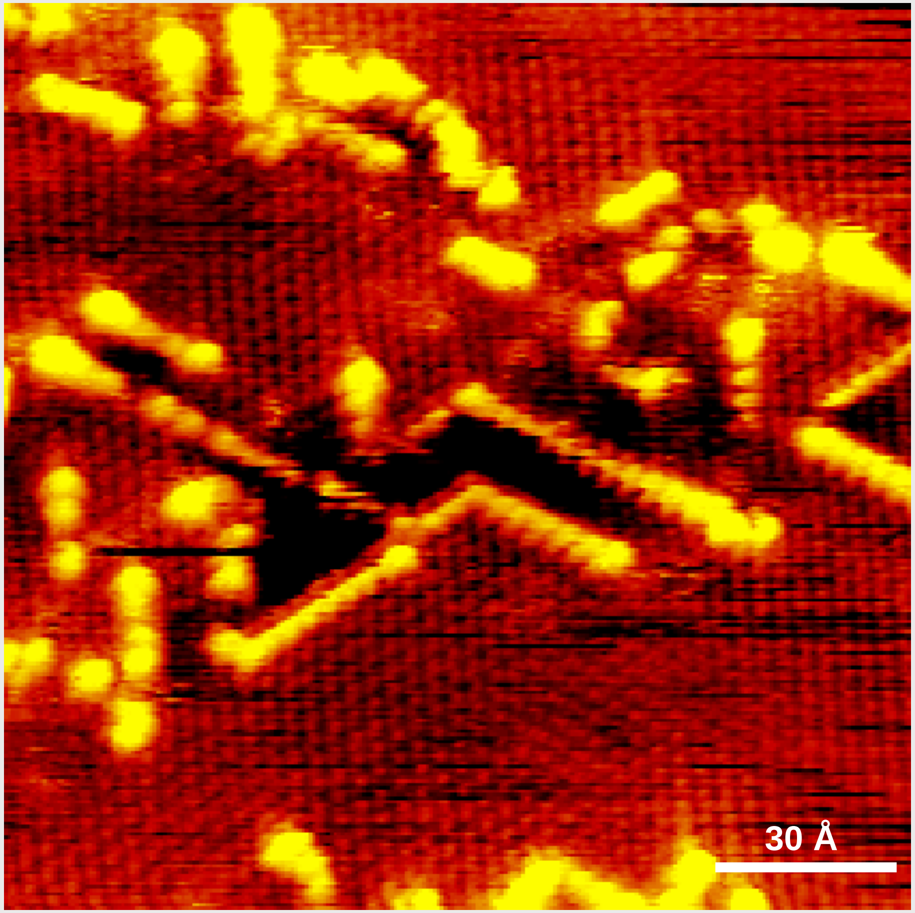
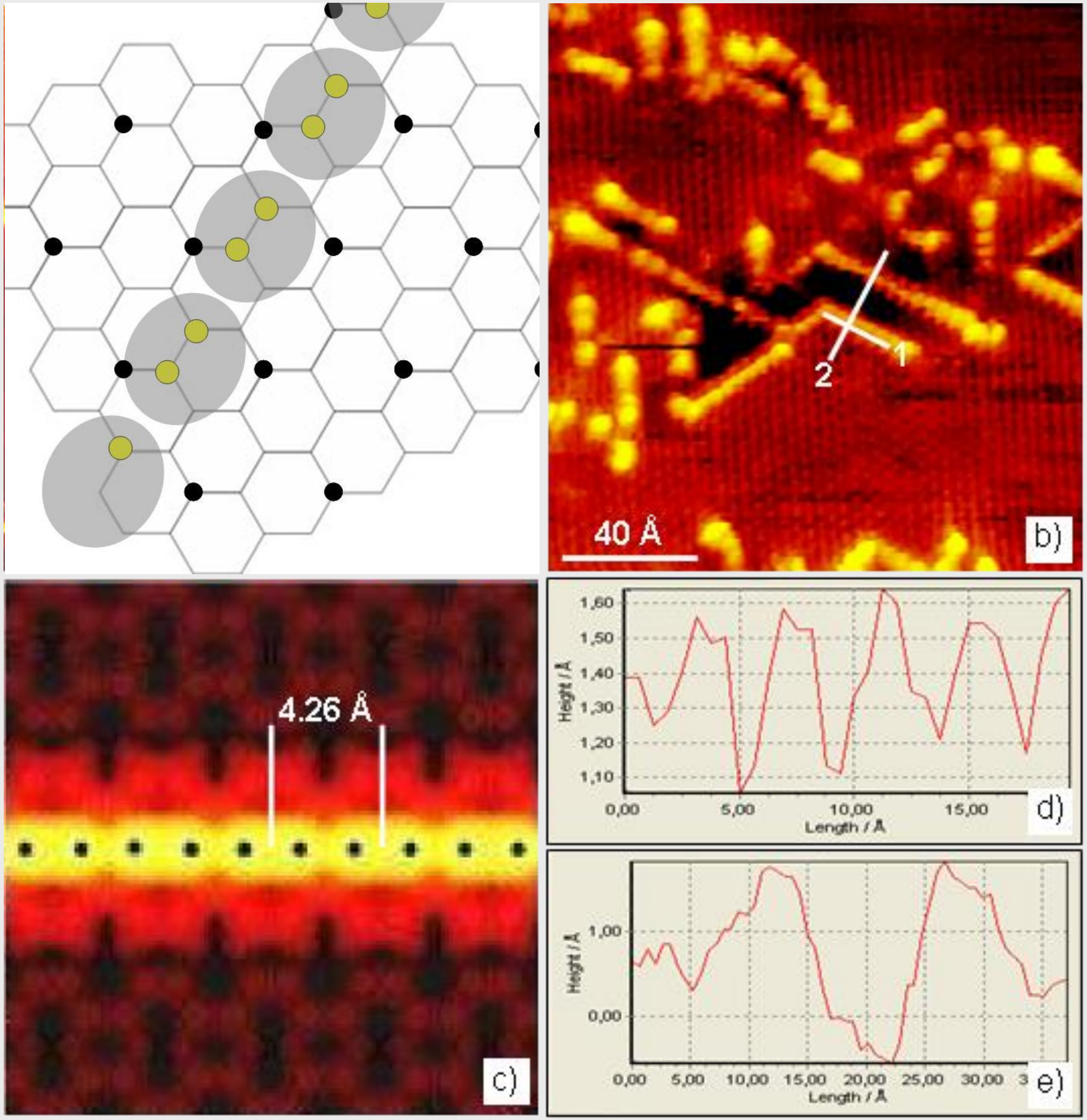


V_t = -1.25 V, I_t = -0.37 nA,

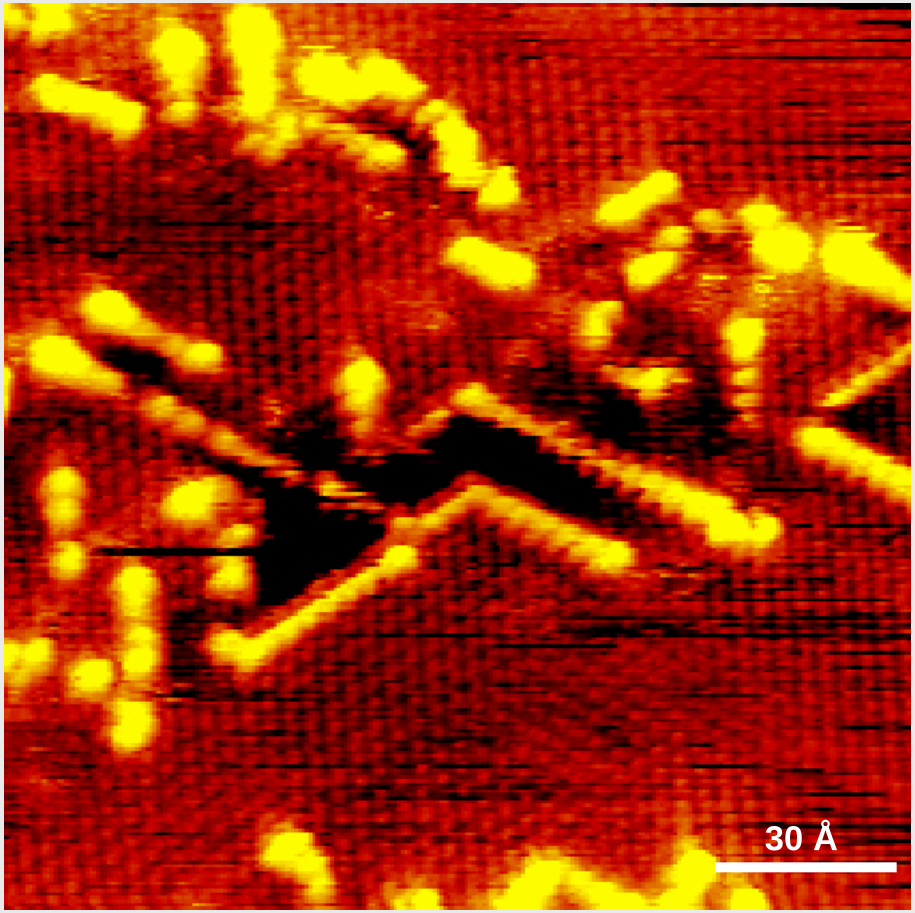
Nilsson et al. CARBON ***50****, 2052 (2012)*

Model structure



*Nilsson et al. CARBON **50**, 2052 (2012)*

Dark areas between lines – local band gap opening?



V_t = -1.25 V, I_t = -0.37 nA,

*Nilsson et al. CARBON **50**, 2052 (2012)*

Would this work on graphene?

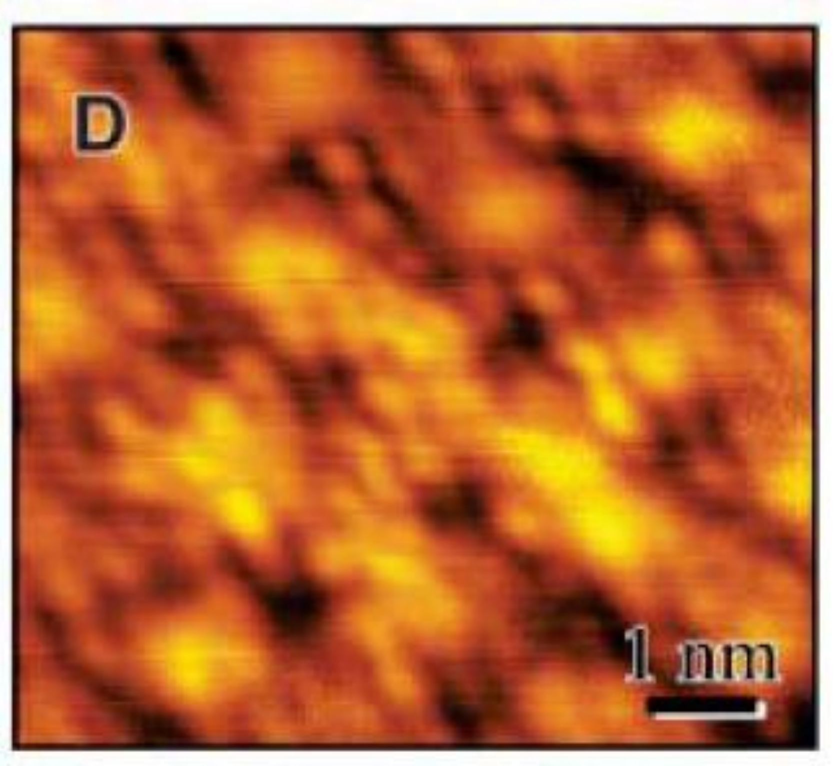
Growing graphene on SiC

Recipe:

6H-SiC(001) wafers (Si side)
H-etching (smooth surface)
Si flux at 900°C
(removal of surface oxides)
gradual annealing to 1250°C
(graphene growth)

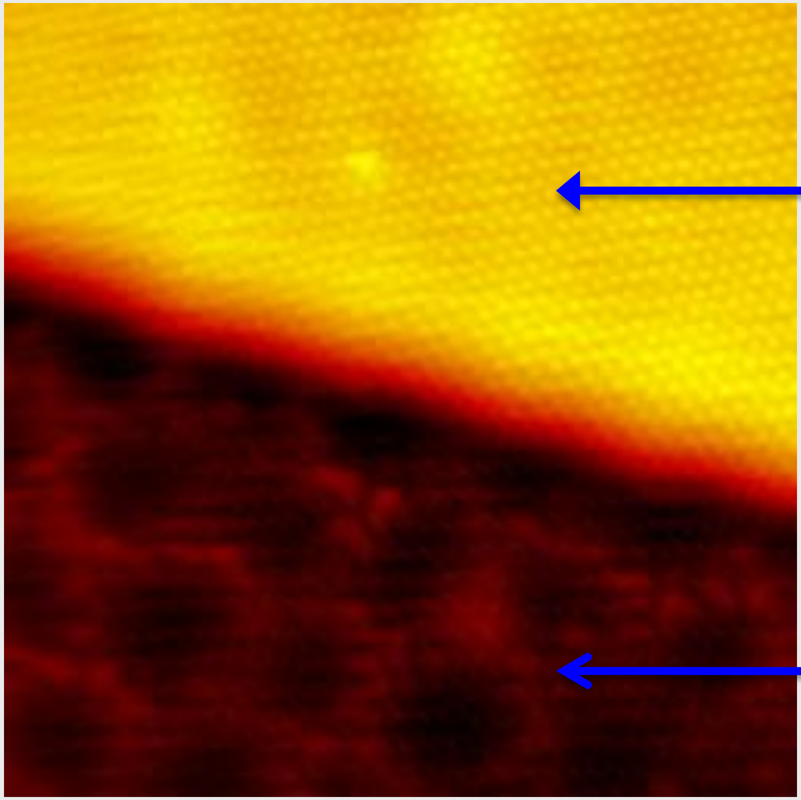
High temperature/pressure route
Exercise this afternoon

Buffer layer

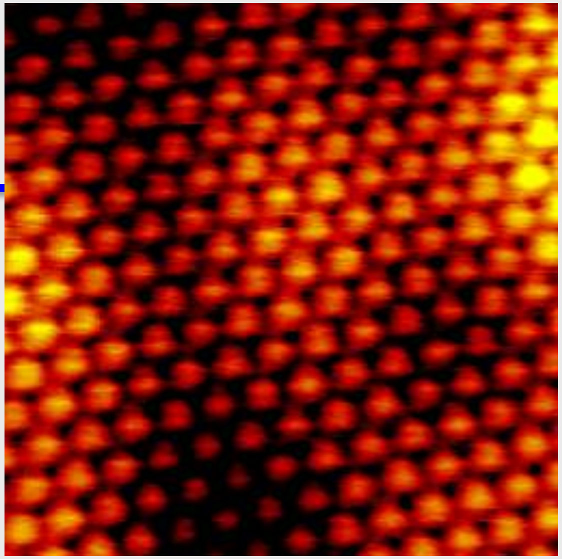


Berger et al., Science **312**, 1191 (2006)

Graphene on SiC

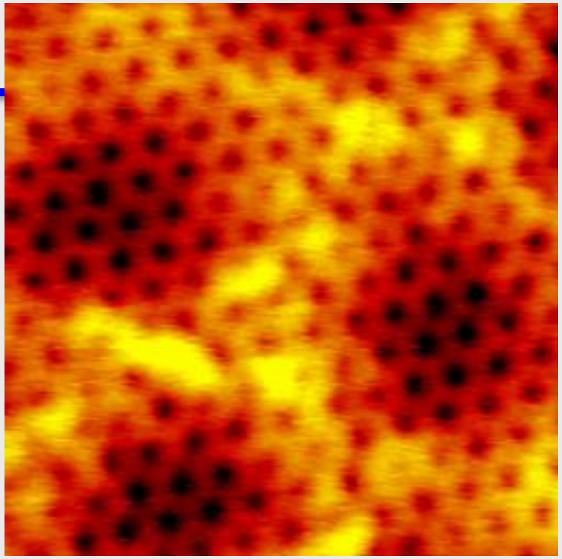


100x100Å, V= -0.41V, I= -0.36nA
step edge height 3.1Å



30x30Å,
V= -0.41V,
I= -0.39nA

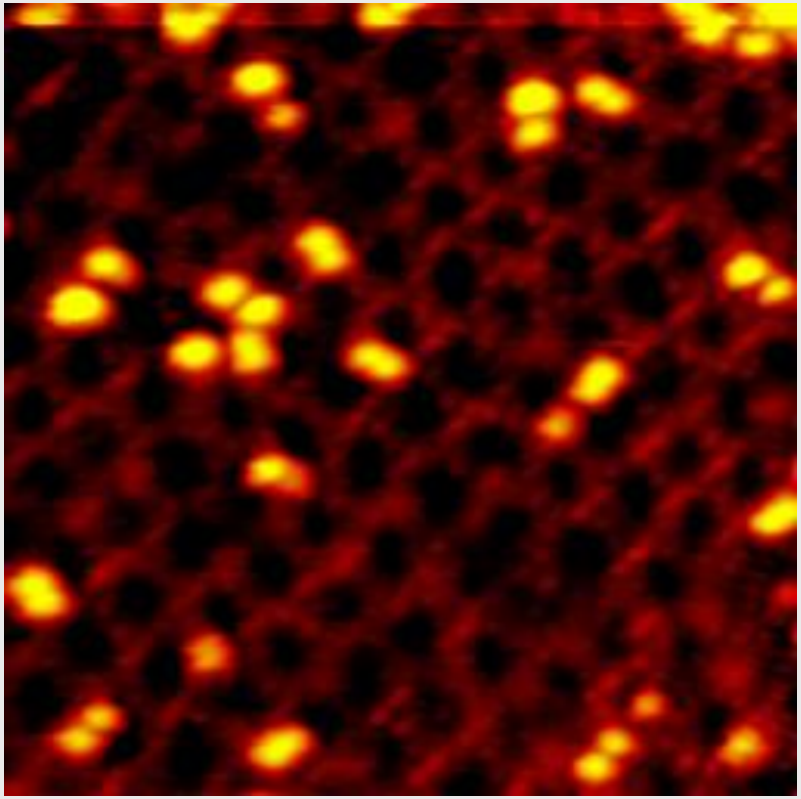
Bi-layer graphene
showing
triangular pattern



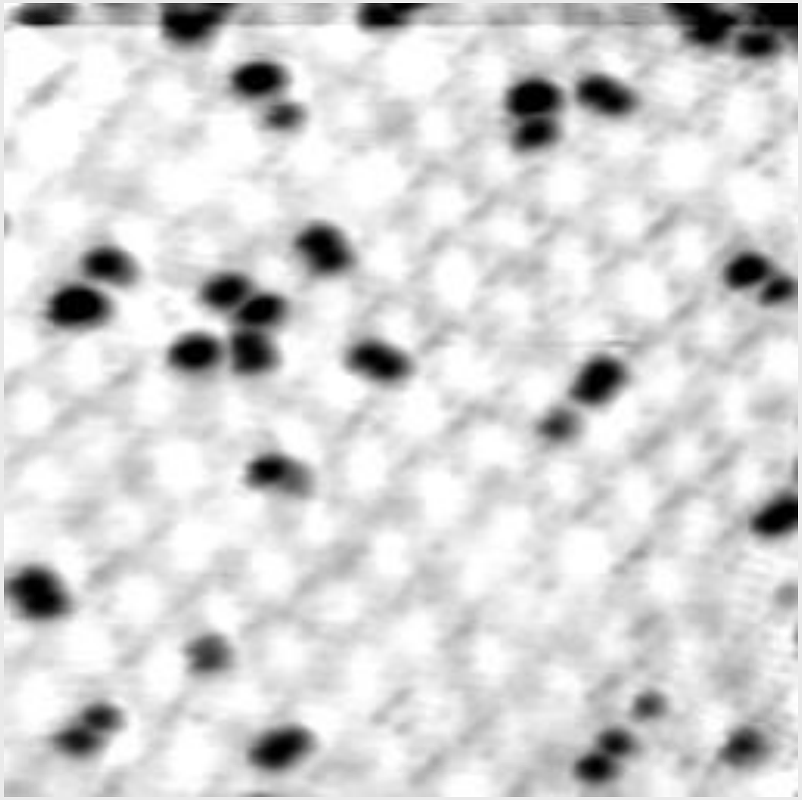
30x30Å,
V= -0.41V,
I= -0.38nA

Mono-layer graphene
showing
honeycomb structure

H on graphene/SiC



200x200Å, V= -0.245V, I= -0.26nA

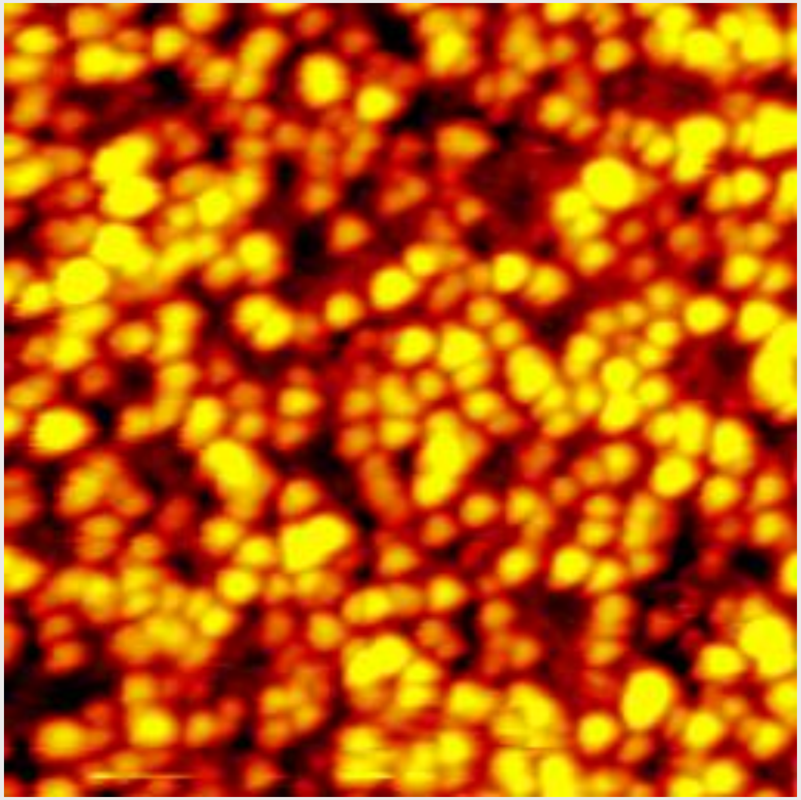


Balog et al. JACS ***131****, 8741 (2009)*

Hydrogen dose at 1600K, F=3x10^{12} atoms/cm^{2} s, **t=5s**

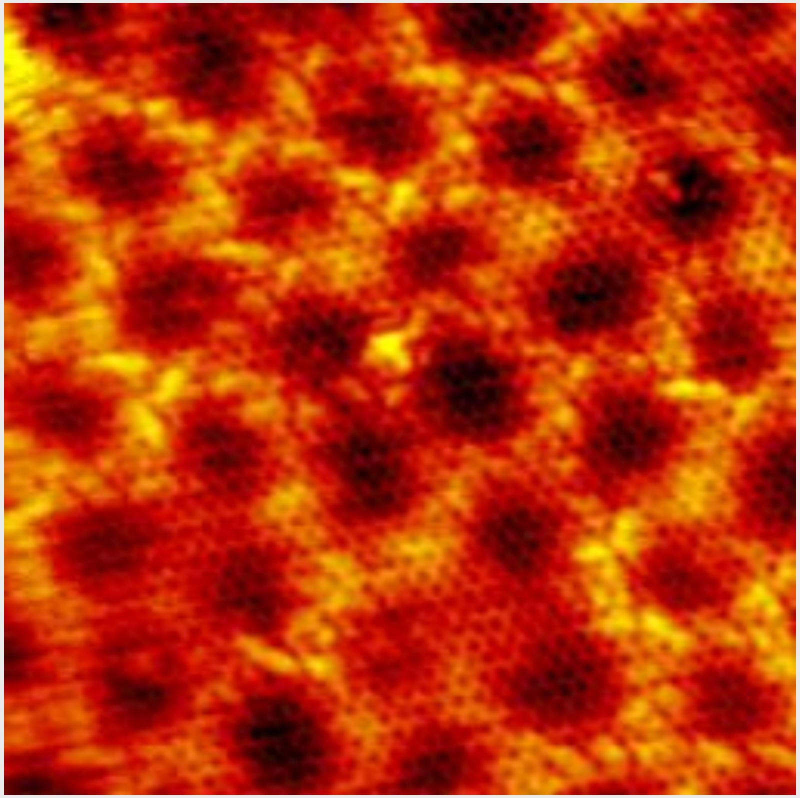
H on graphene/SiC

Hydrogenation: T=1600K, F=3x10^{12} atoms/cm^2 s, t=90s



200x200Å, V= -0.36V, I= -0.32nA

De-hydrogenation: Anneal to 800° C

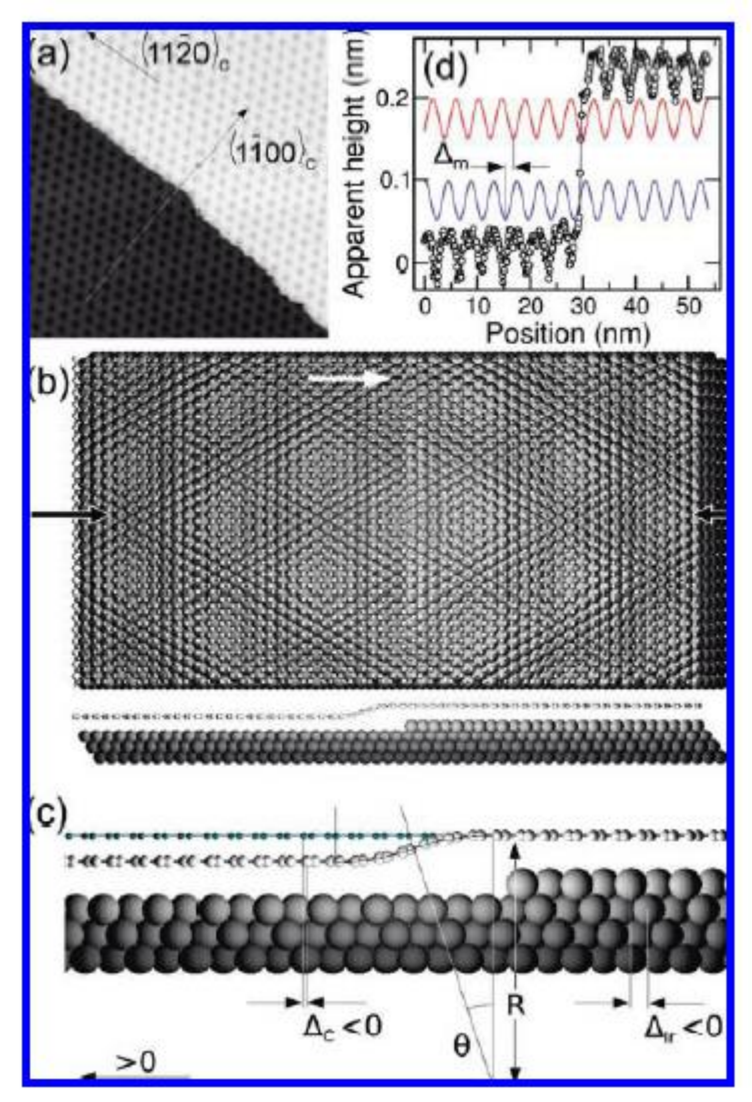


*Balog et al. JACS **131**, 8741 (2009)*

Metals – CVD

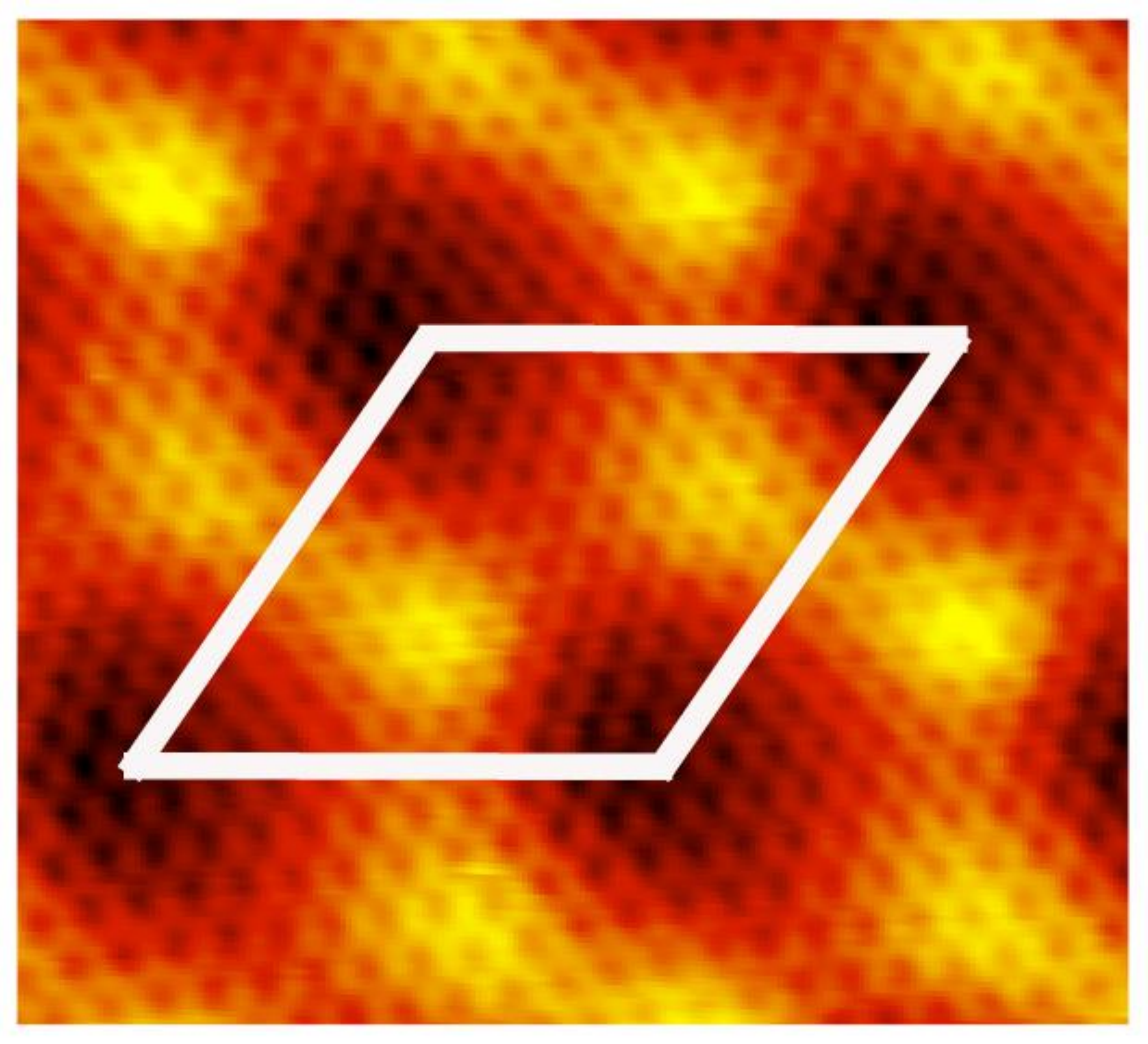
Decomposition of:
Ethylene, propene
Methane, acetylene, CO
Cyclohexane, n-heptane
Benzene, toluene

Here: graphene on Ir(111)
- Ethylene (2 x 10-5 Pa)
  @ 550 K for 100 s
- flash anneal to 1420 K.
- Repeat many times

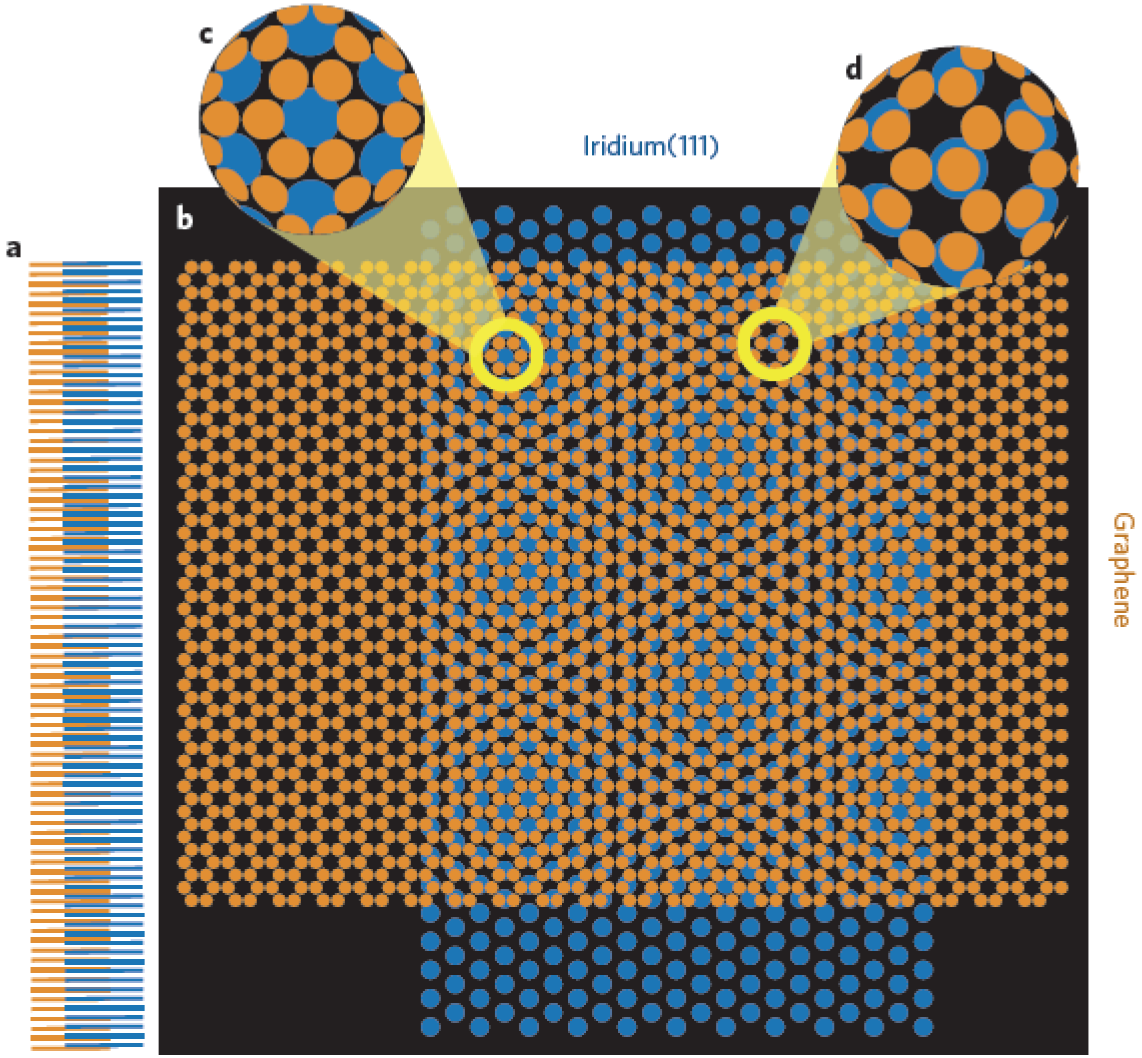


Coraux et al. PRL 103, 166101 (2009)

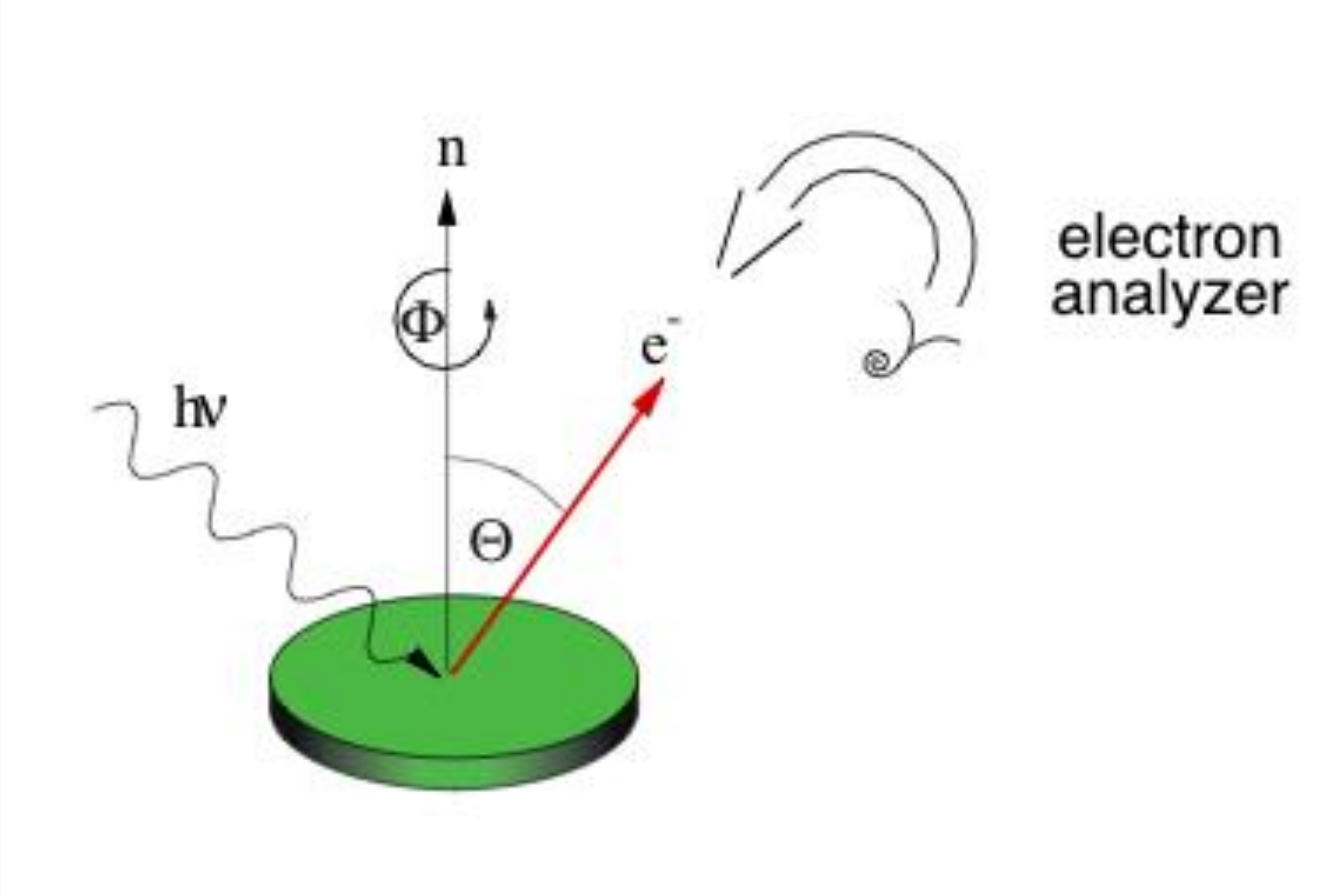
Graphene/Ir



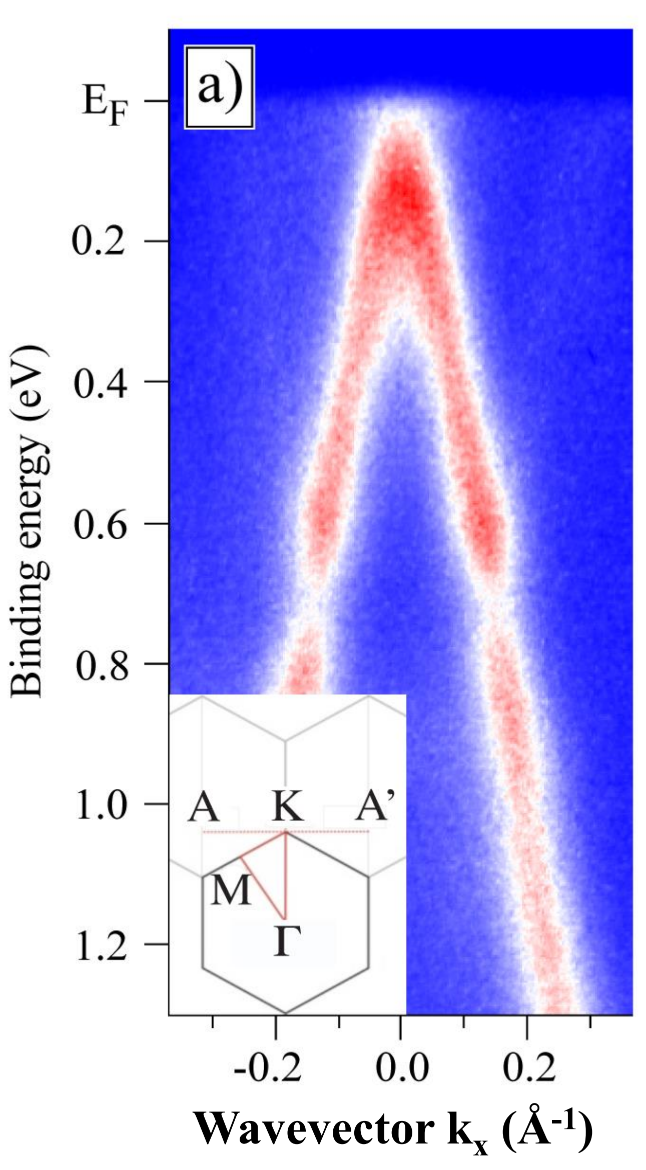
Moire Pattern

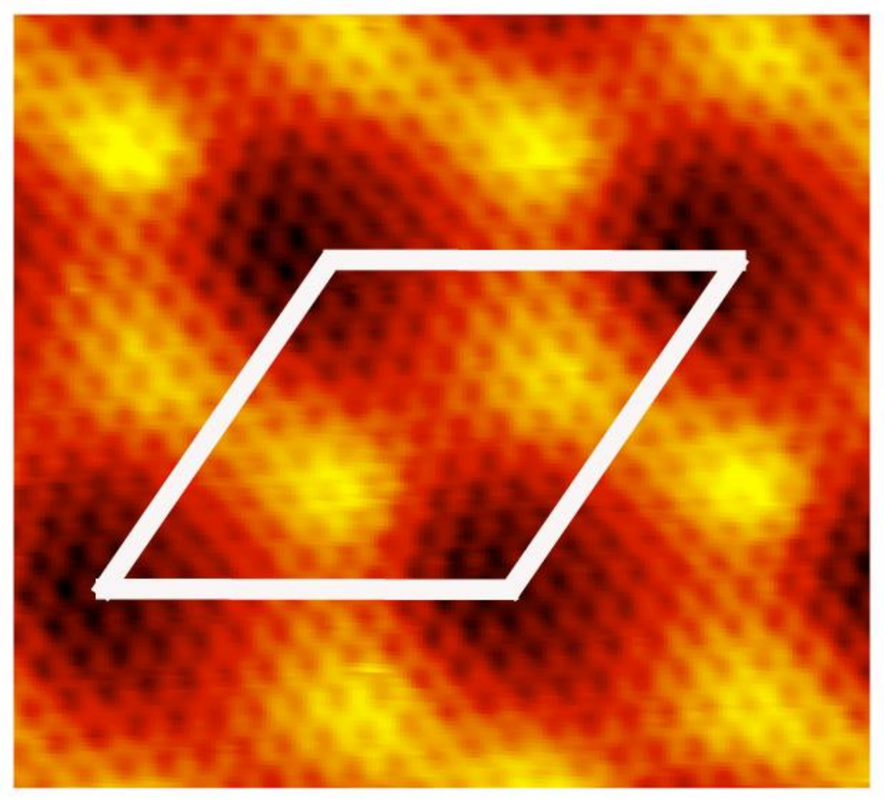


UPS

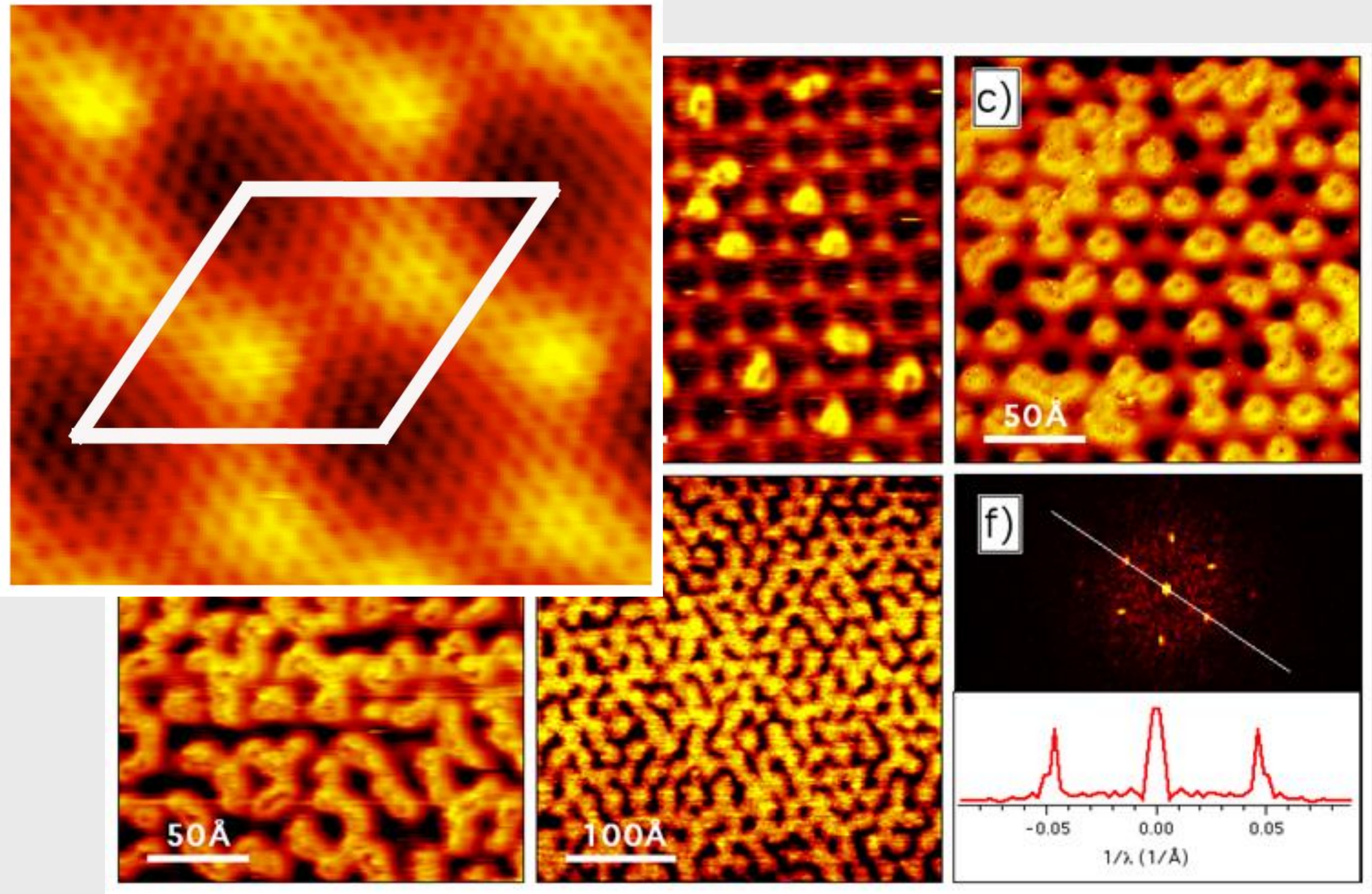


Graphene/Ir


a)
E_F
0.2
0.4
0.6
0.8
1.0
1.2
Binding energy (eV)
-0.2
0.0
0.2
Wavevector k_x (Å^-1)
A
K
A'
M
Γ

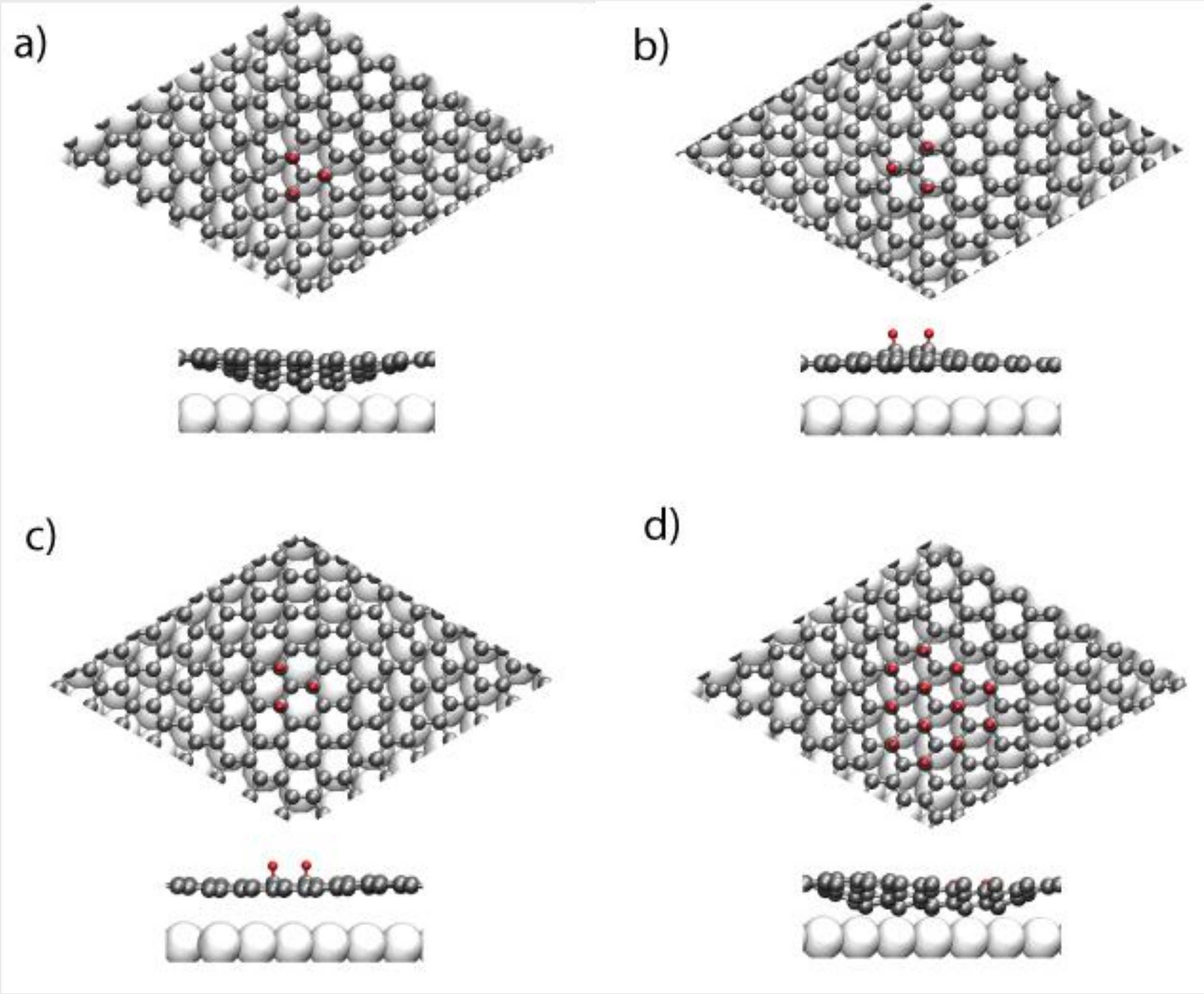


STM of H/Graphene/Ir



Balog et al., Nat. Mat. ***9****, 315 (2010)*

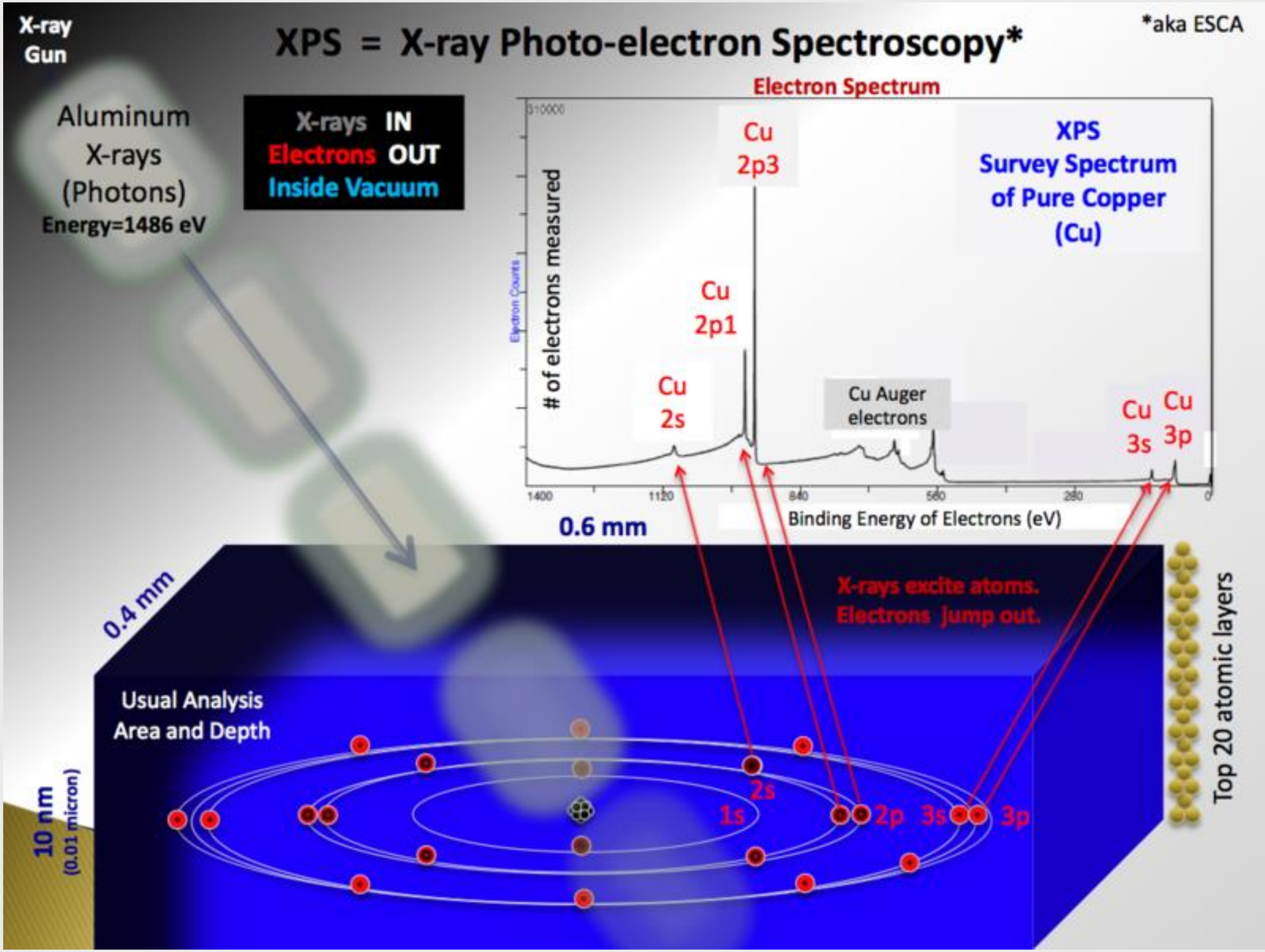
Adsorbate structures



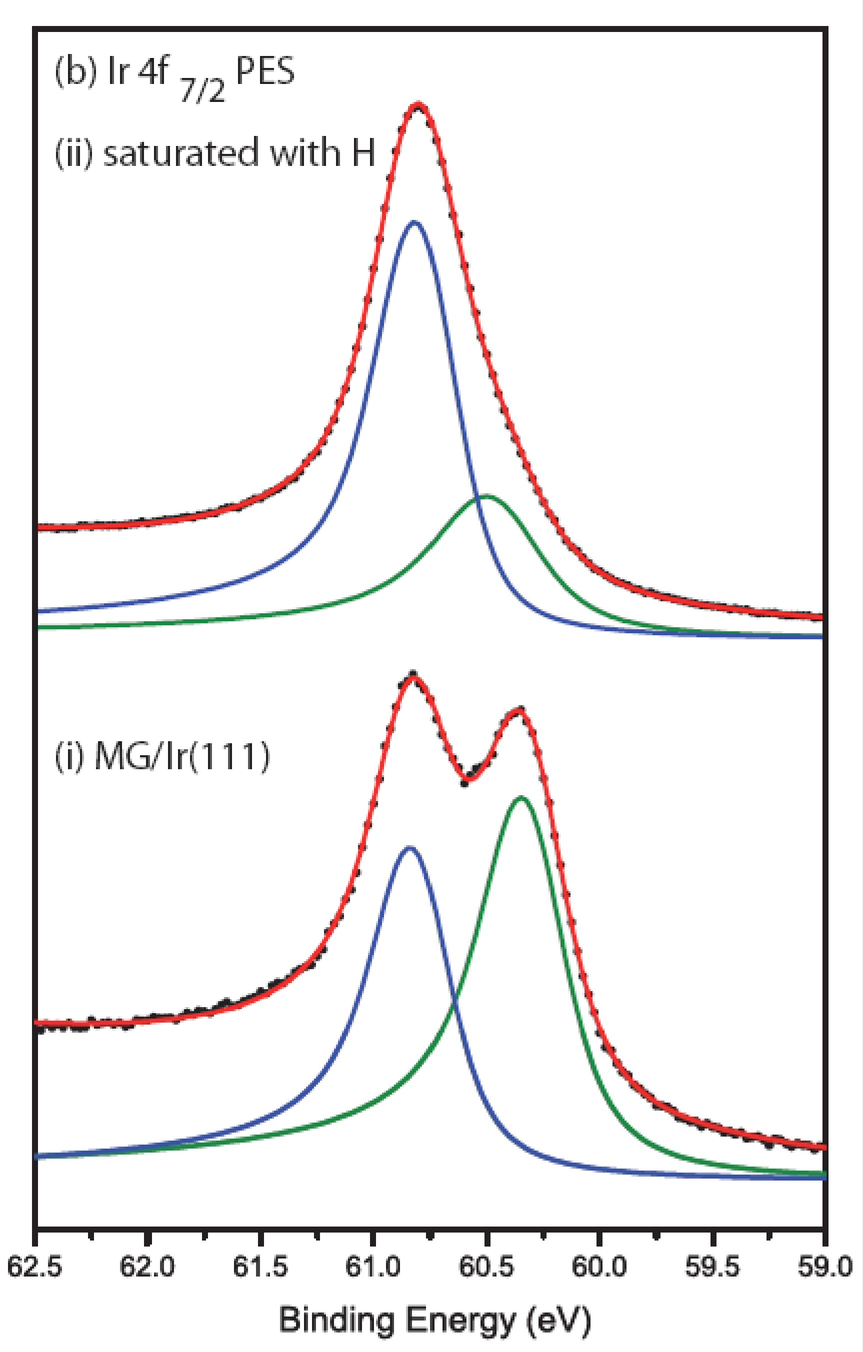
Balog et al., Nat. Mat. ***9****, 315 (2010)*

XPS = X-ray Photo-electron Spectroscopy*

*aka ESCA

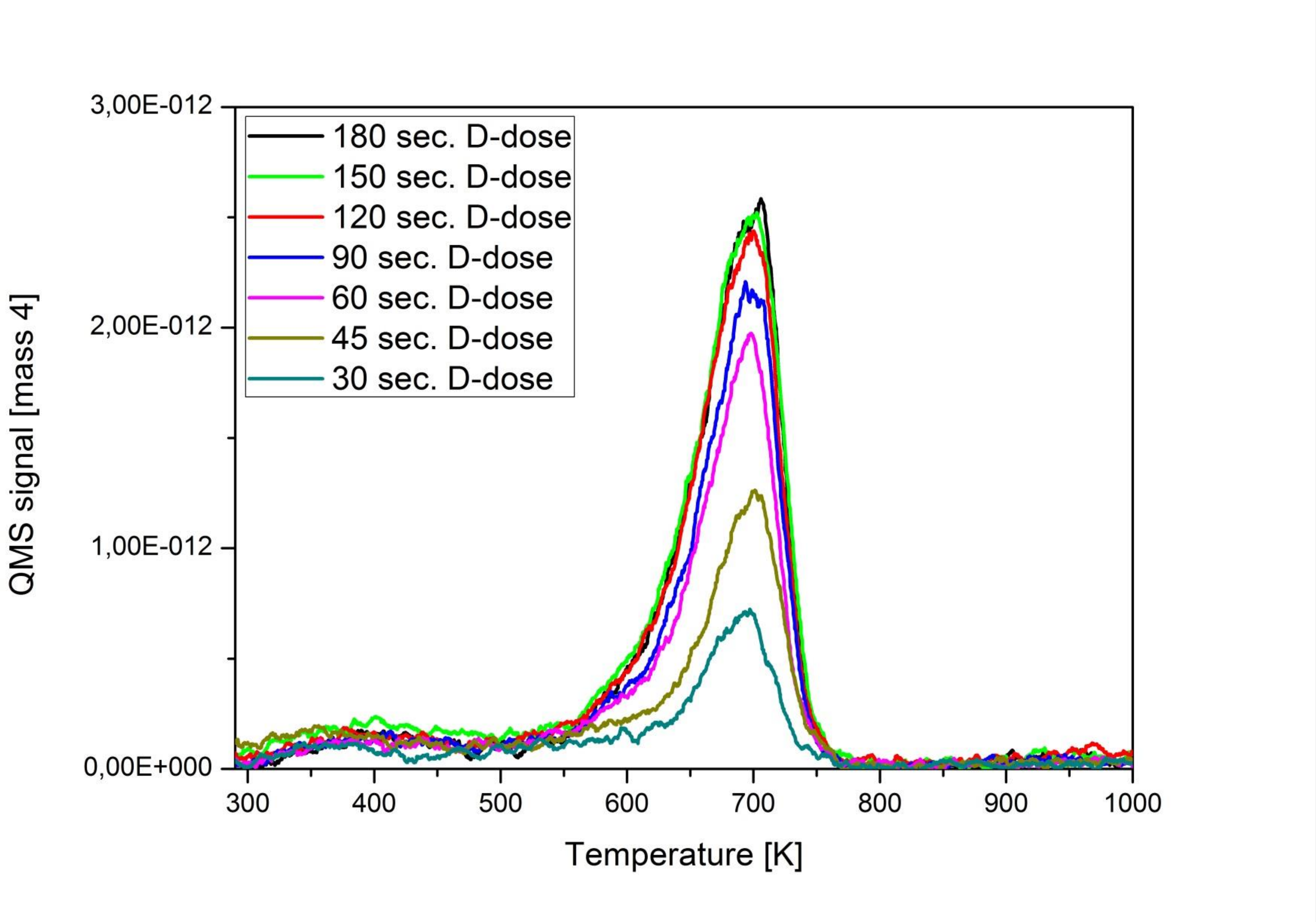


XPS:



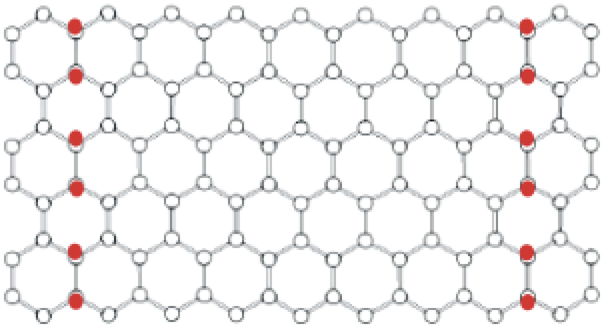
M. L. Ng, R. Balog, L. Hornekær, B. Preobrajenski, K. Schulte, N. A. Vinogradov, and N. Mårtensson.

Thermal stability - TDS



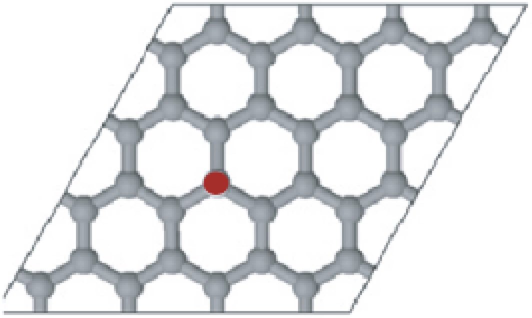
Global bandgap opening

a) Hydrogen atoms arranged in lines

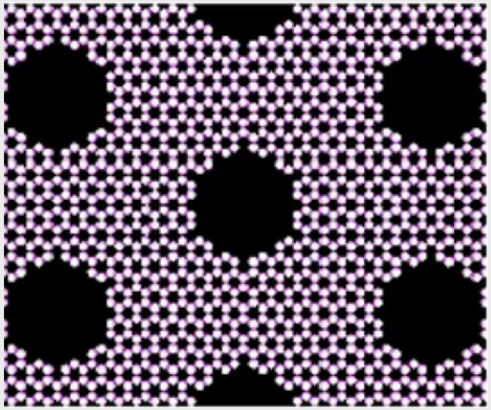


Chernozatonskiĭ et al., *Jetp Lett,* **85** (1), 77-81 (2007).

b) periodic arrangement

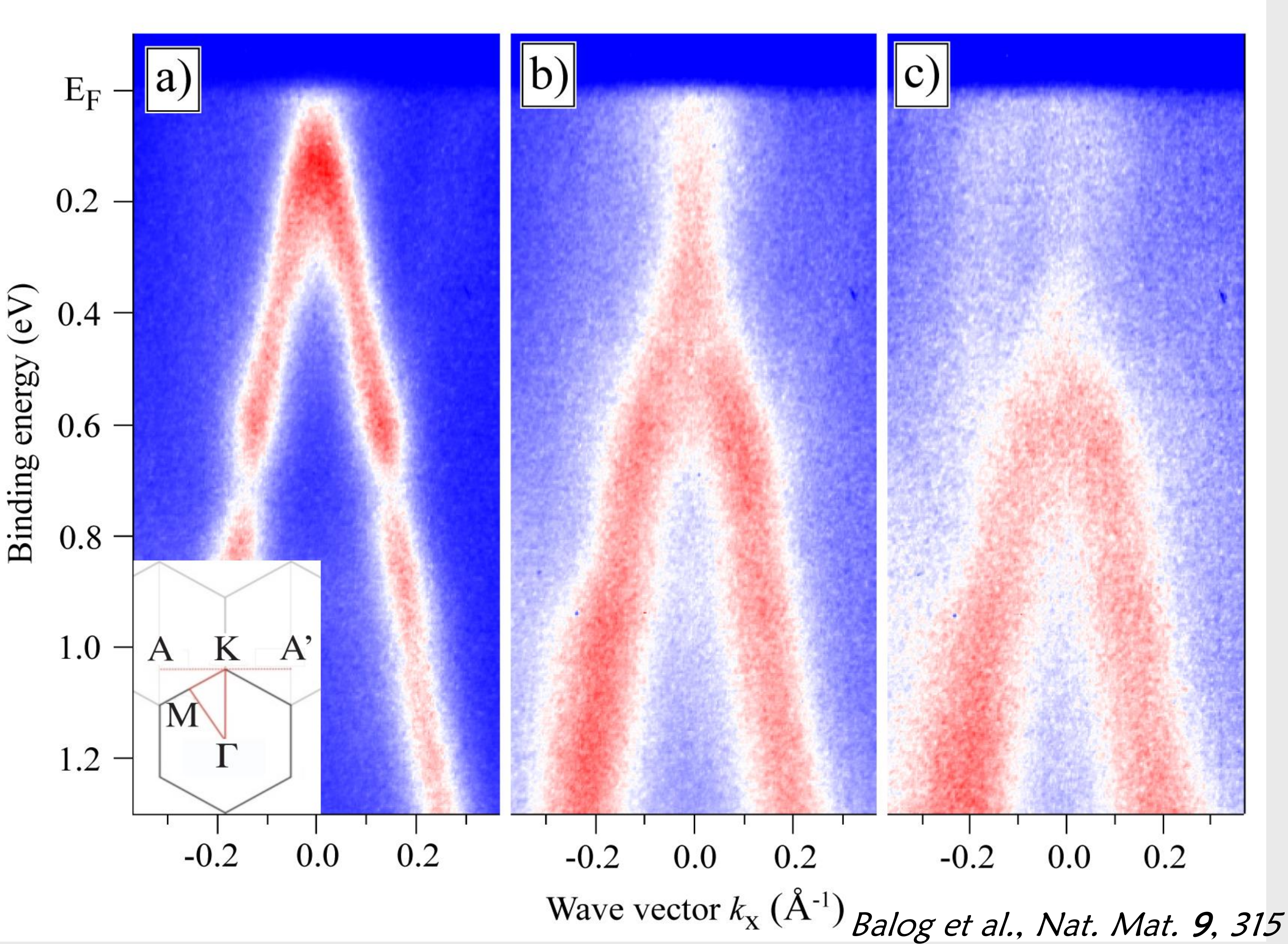


Duplock, E.J.et al. *Phys Rev Lett*, **92**, 225502 (2004).



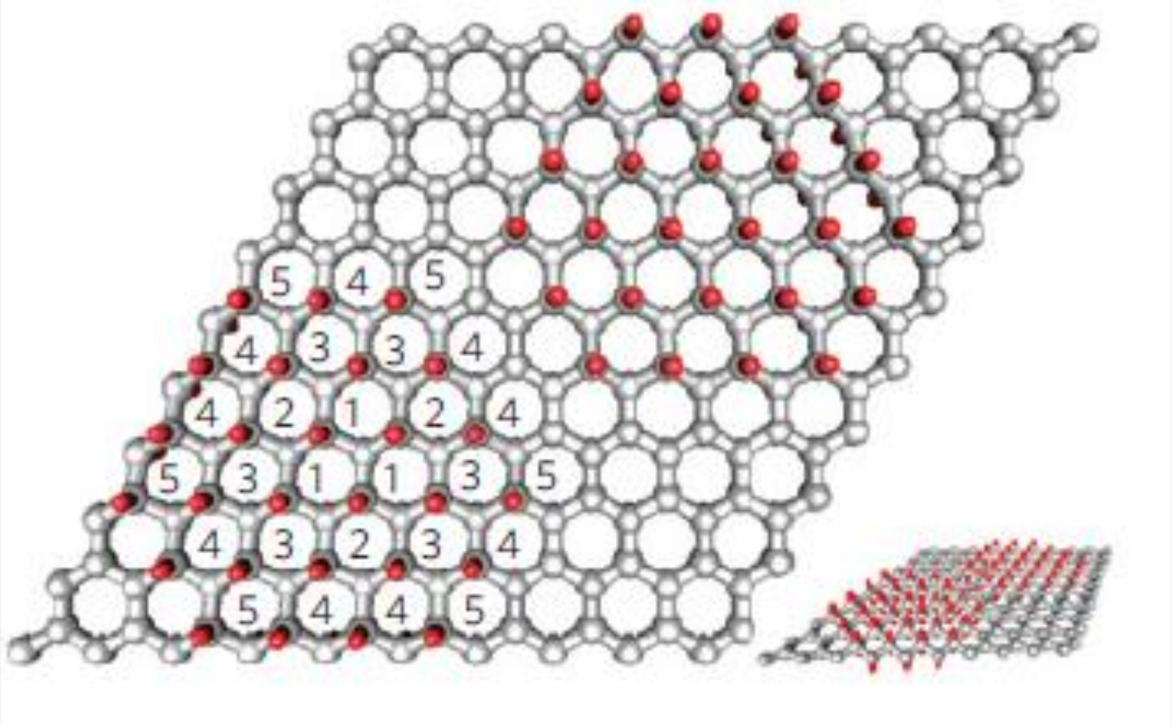
Pedersen et al. PRL 100, (2008)

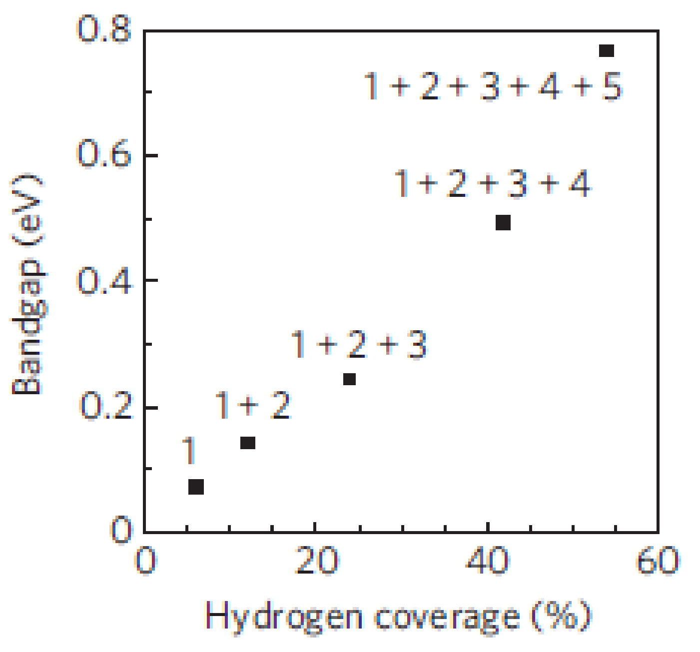
ARUPS of H/Graphene/Ir – bandgap opening



Balog et al., Nat. Mat. ***9****, 315 (2010)*

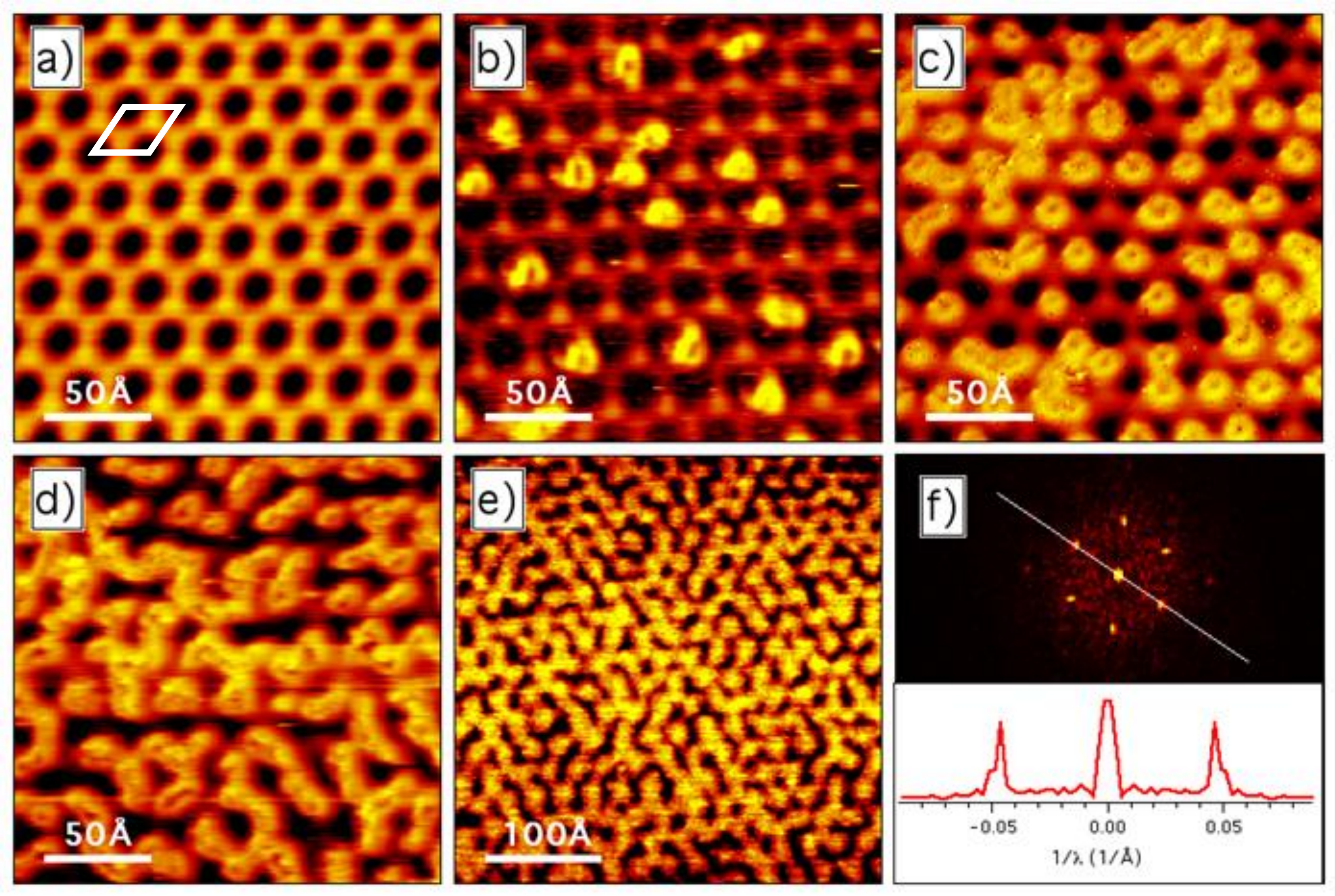
Size of bandgap





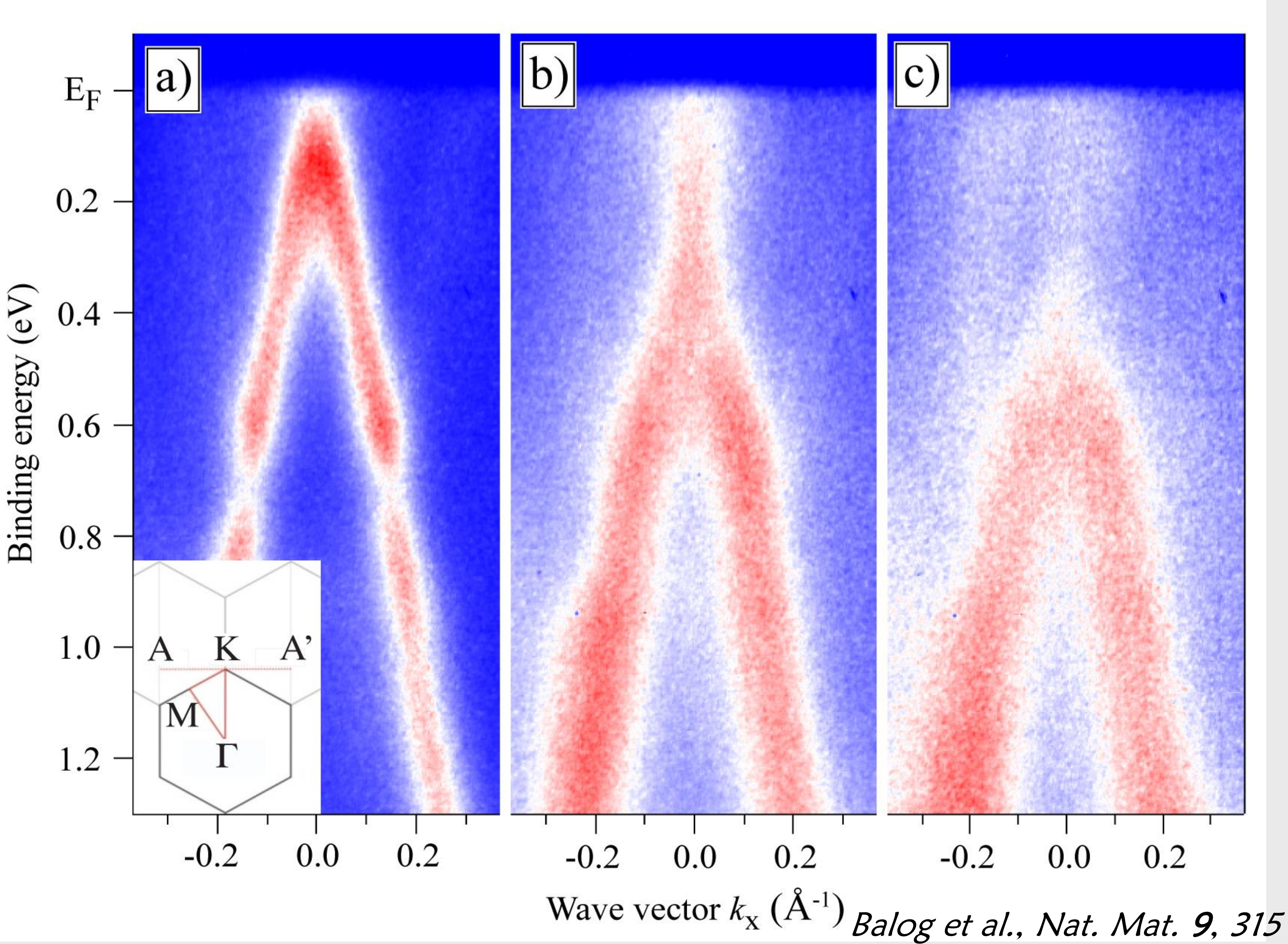
Balog et al., Nat. Mat. ***9****, 315 (2010)*

STM of H/Graphene/Ir



Balog et al., Nat. Mat. ***9****, 315 (2010)*

ARUPS of H/Graphene/Ir – bandgap opening



*Balog et al., Nat. Mat. **9**, 315 (2010)*

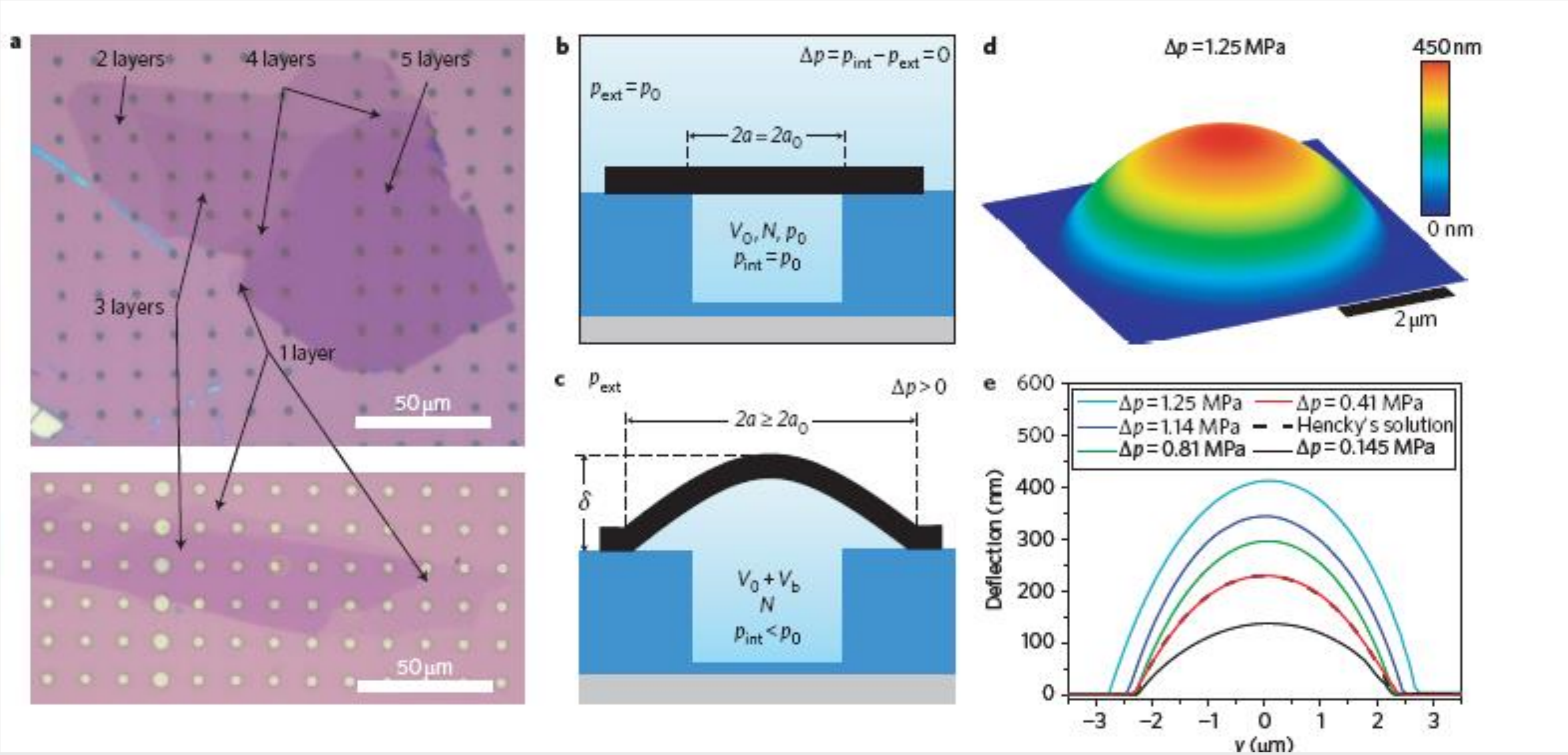
Origin of band gap opening

Confinement ?

Periodic structures ?

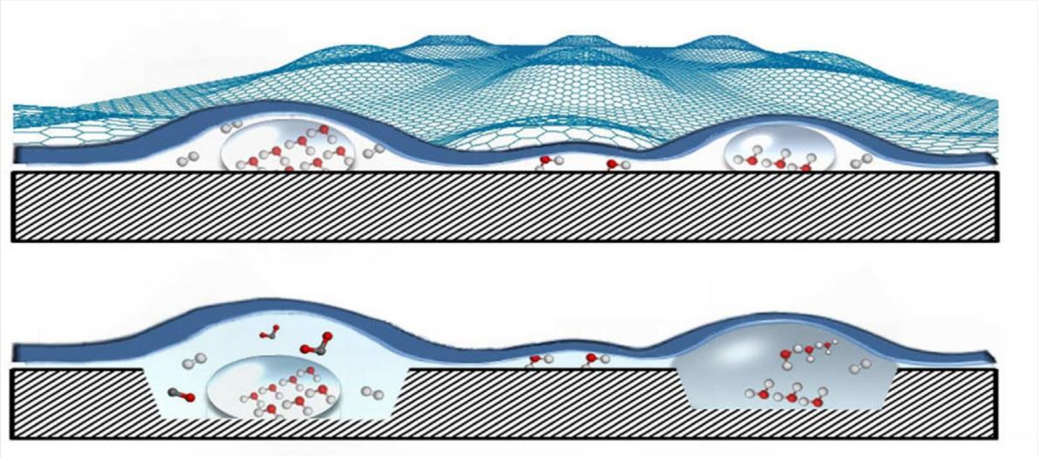
Scattering ?

Graphene coatings

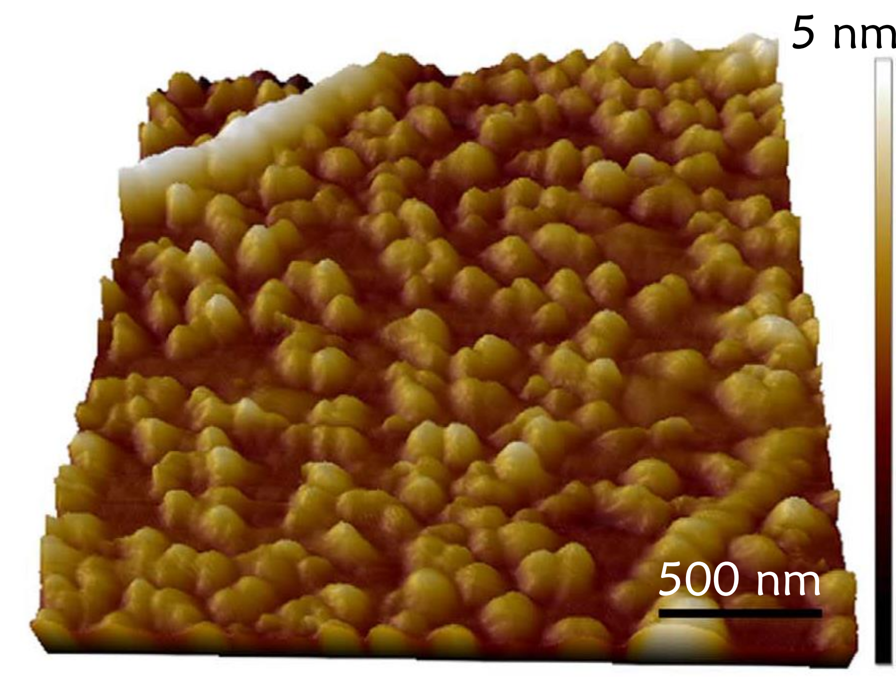


From J. S. Bunch et al. Nano Letters 8, 2458 (2008).

Graphene-diamond anvil

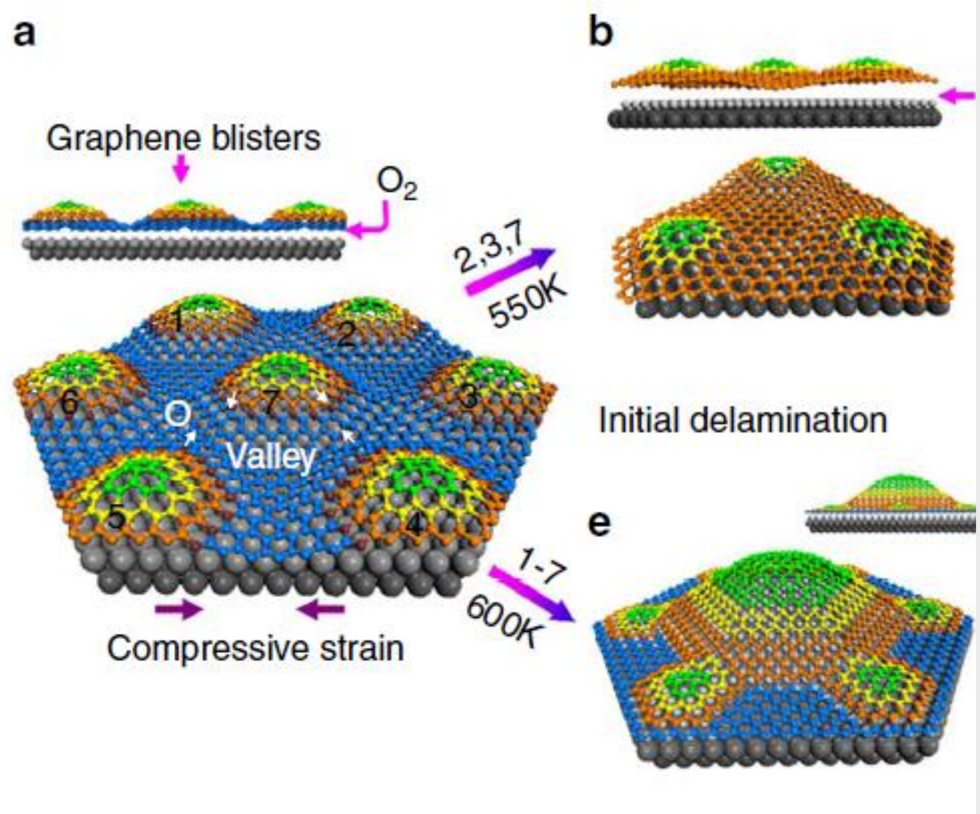


1GPa water /H_2 at 1500 K

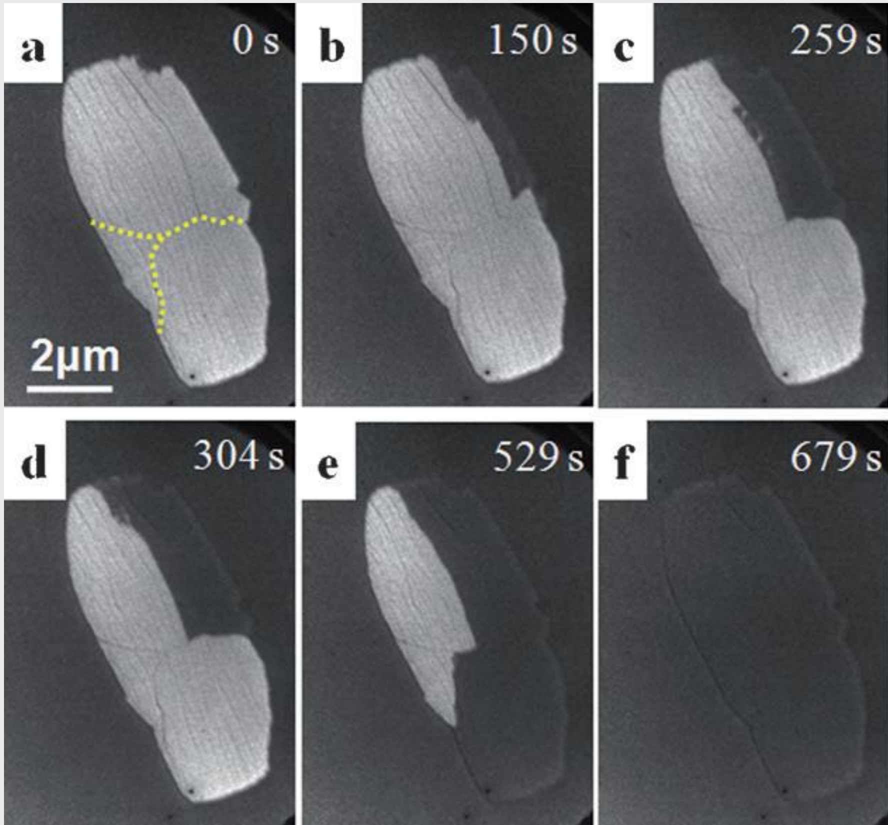


Lim et al., Nature Comm. 4:1556 (2013)

Oxygen and CO intercalation



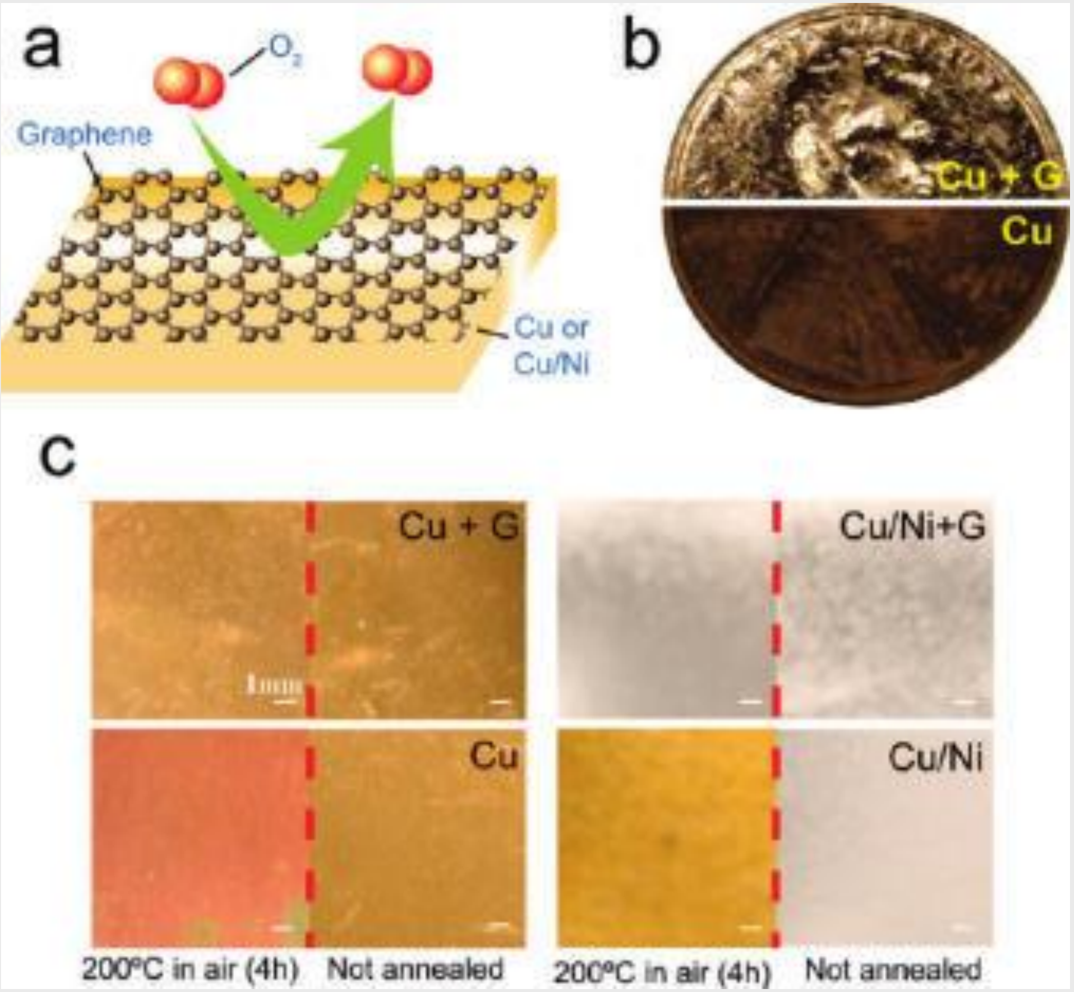
CO on Gr/Pt(111)
Mu et al, Angew. Chem.
***124**, 4940 (2012)*



O on Gr/Ru(0001):
*Lu et al. Nat. Com. **3**, 823 (2012)*
Zhang et al., *J. Phys. Chem. C **113***, 8296 (2009
*Sutter et al., JACS **132***, 8175 (2010)

O on Gr/Ir(111):
*Laciprete et al., ACS NANO **6**, 9551 (2012)*
*Grånäs et al., ACS NANO **6**, 9951 (2012)*

Graphene Coatings

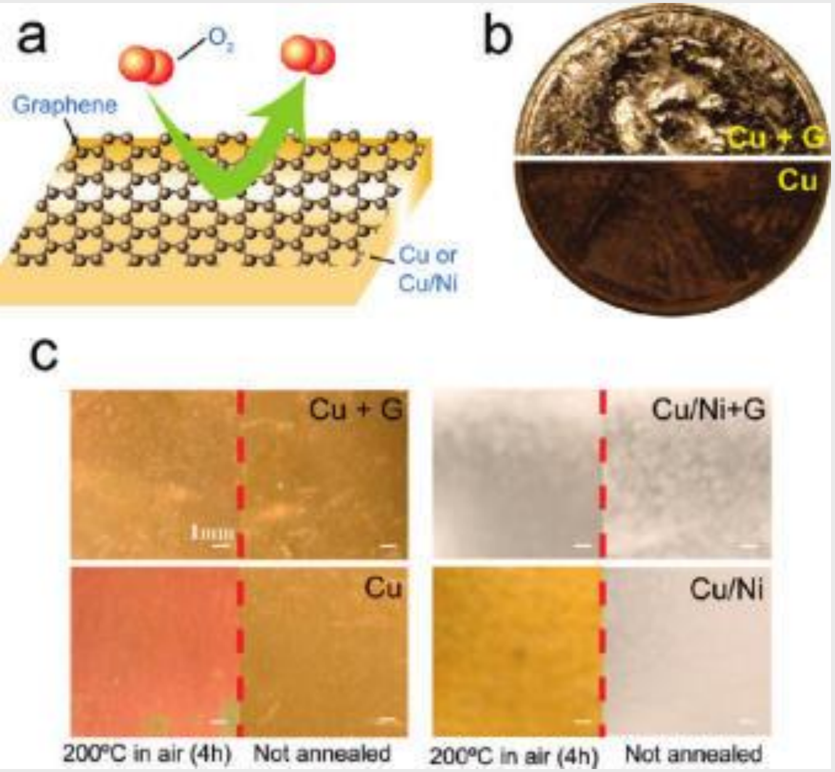


Hydrogen peroxide

Air

Chen et al., ACS NANO **5**, 1321 (2011)

Graphene Coatings



Hydrogen peroxide

Air

Chen et al., ACS NANO **5**, 1321 (2011)

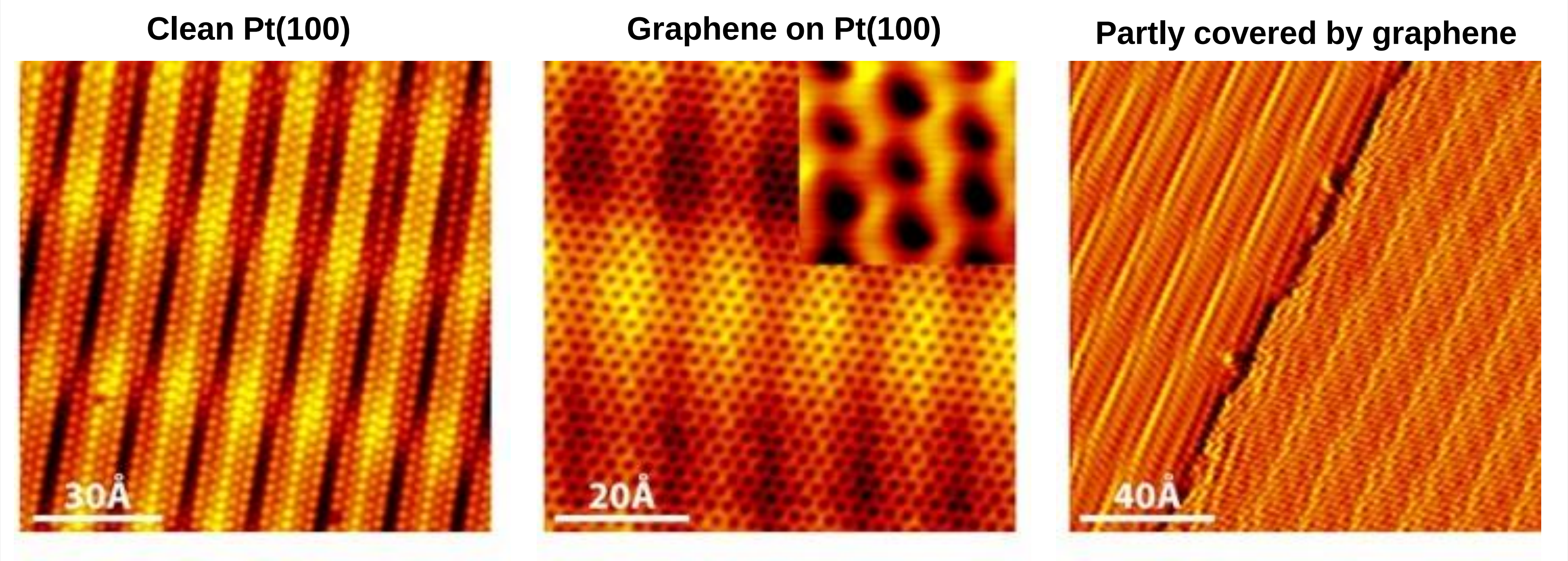
Prasai et al., ACS NANO 6, 1102 (2012):

-reduction of Cu and Ni corrosion (factor 7 amd 20) in Na_2SO_4 solution

Raman et al., CARBON 50, 4040 (2012):

– increased resistance of Cu to electrochemical degradation

Graphene on Pt(100)



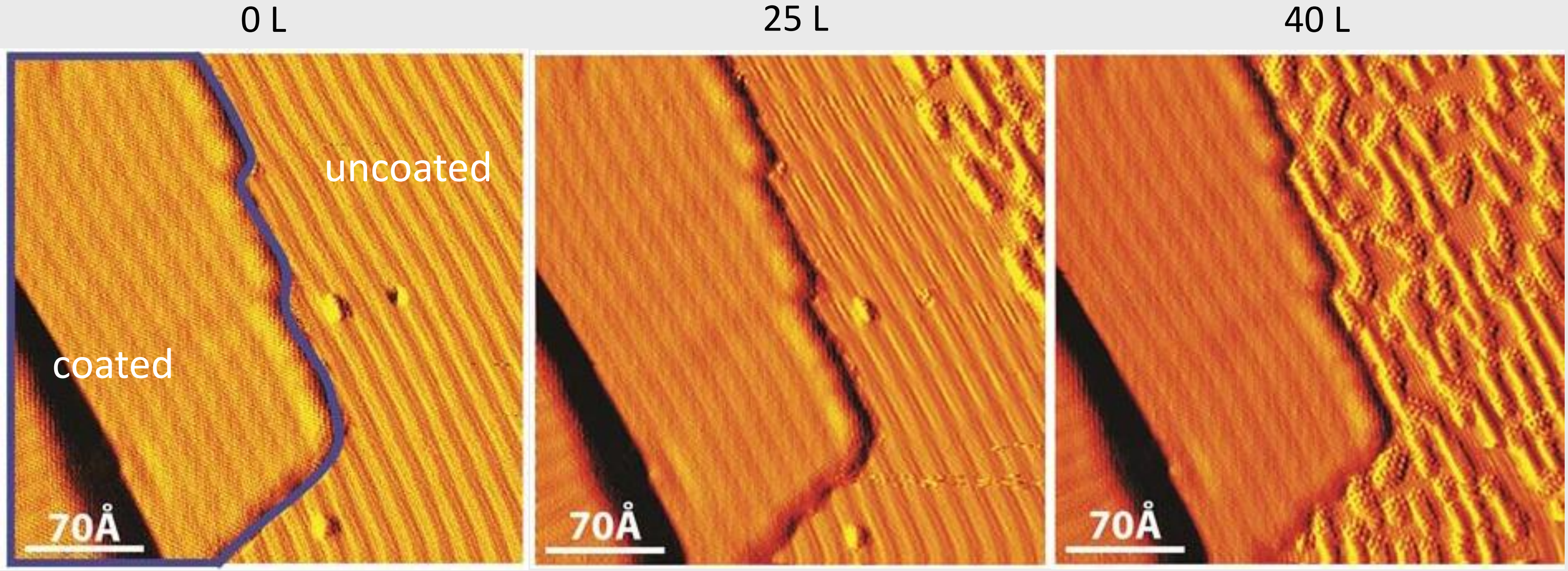
Clean Pt(100)

Graphene on Pt(100)

Partly covered by graphene

L. Nilsson *et al.* Surface Science **606**, 464 (2012)

O_2 Exposure


0 L

25 L

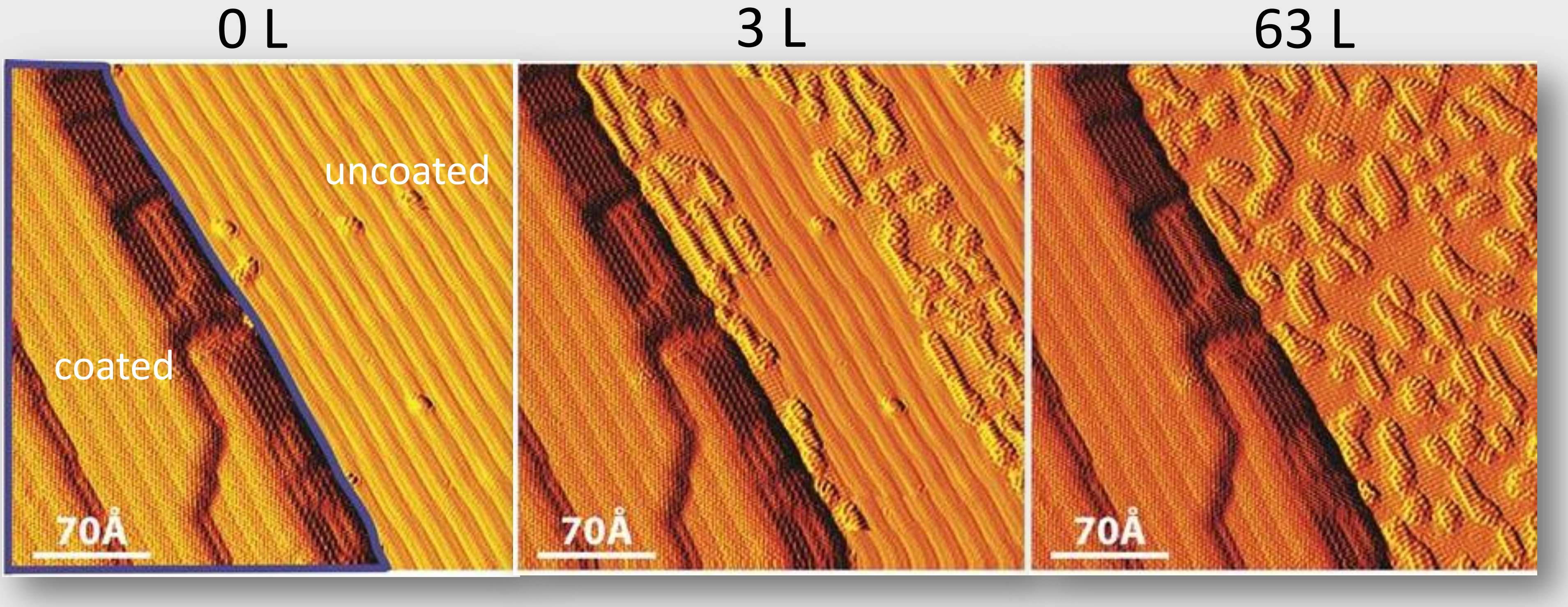
40 L

-4.3 mV, 0.480 nA

O_2 that reacts with the Pt surface lifts the reconstruction
Graphene protected regions are unaffected.

L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

CO Exposure



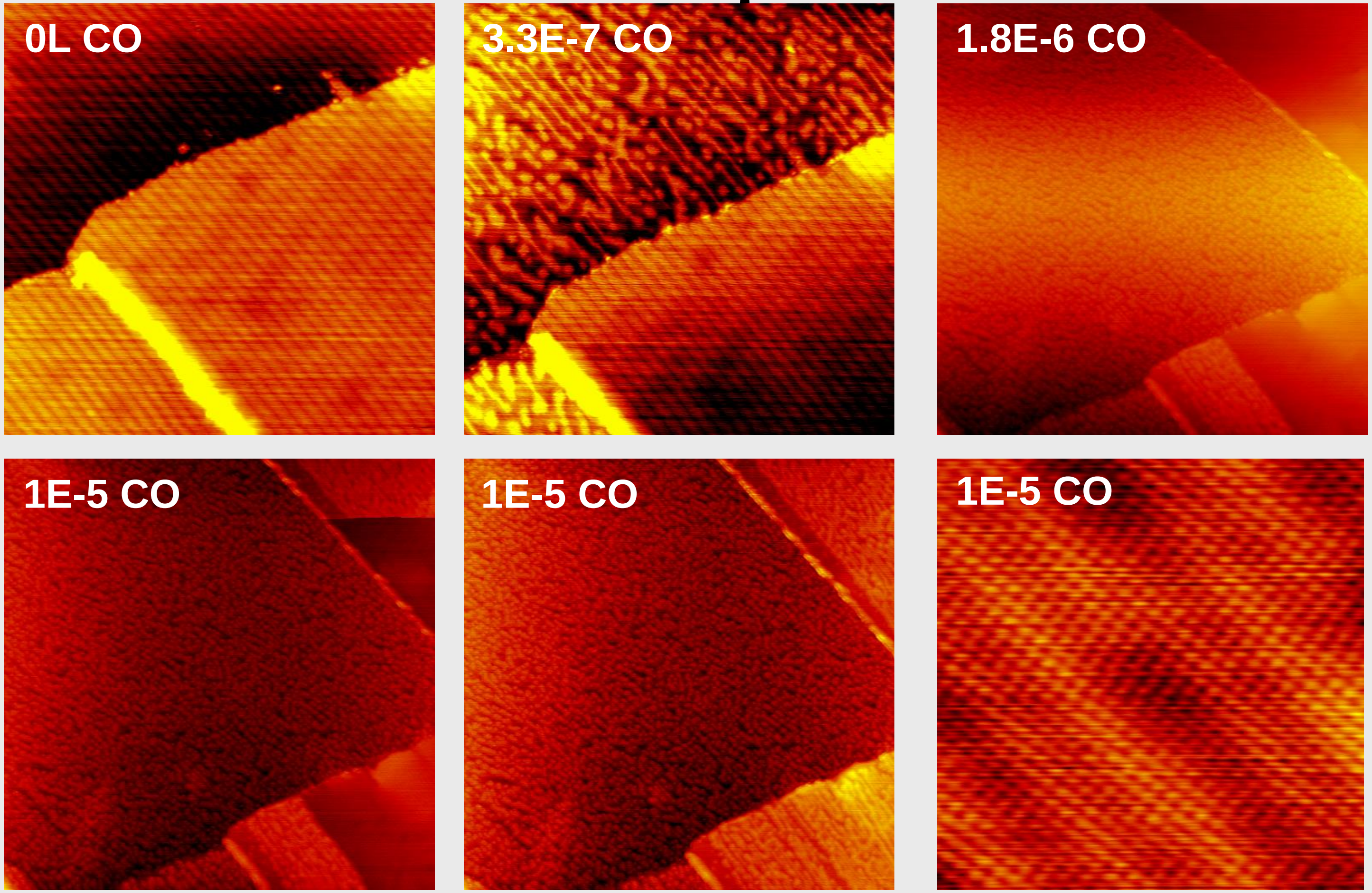
0 L

3 L

63 L

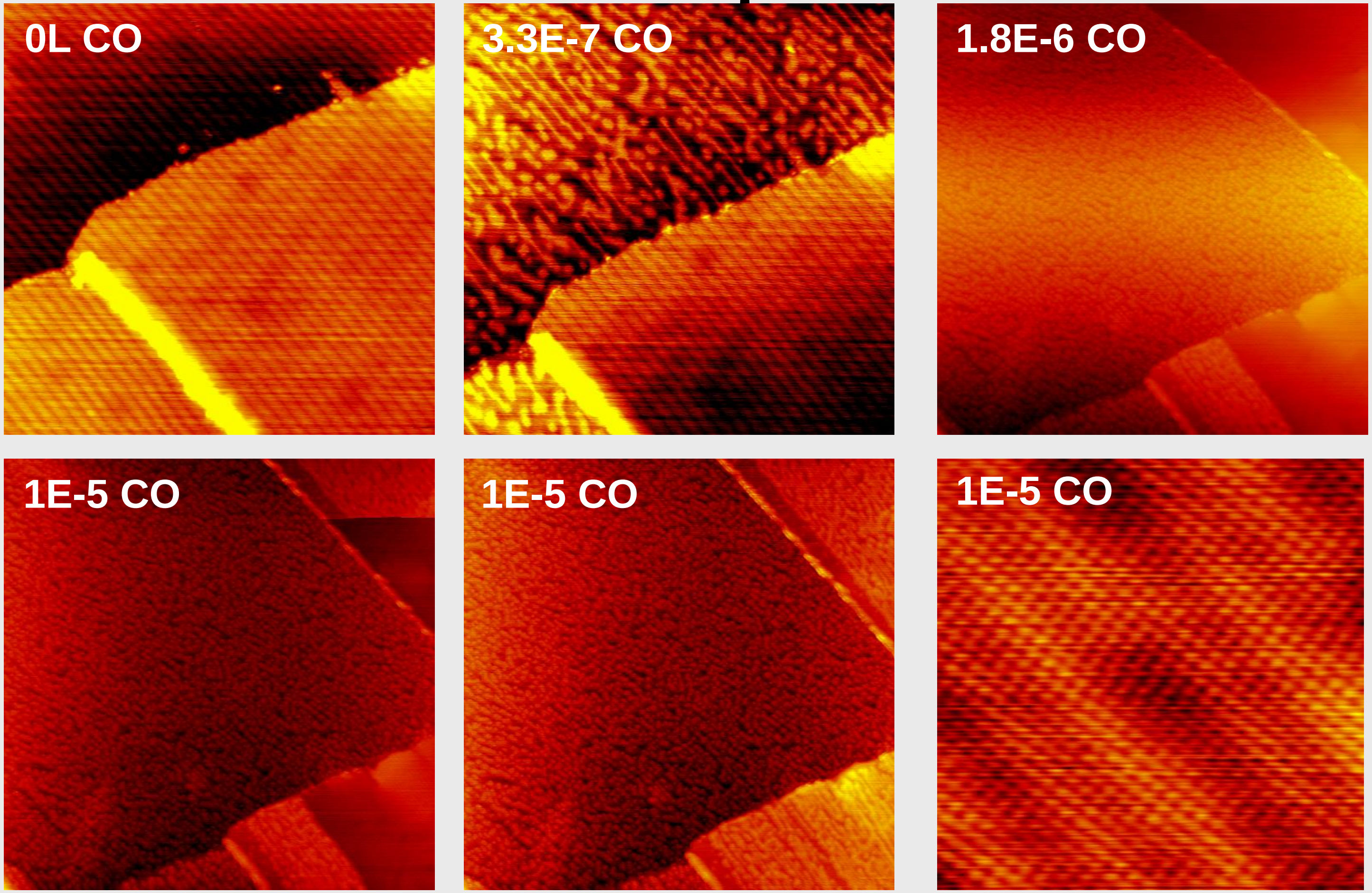
4.6 mV, 0.440 nA

CO Exposure



L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

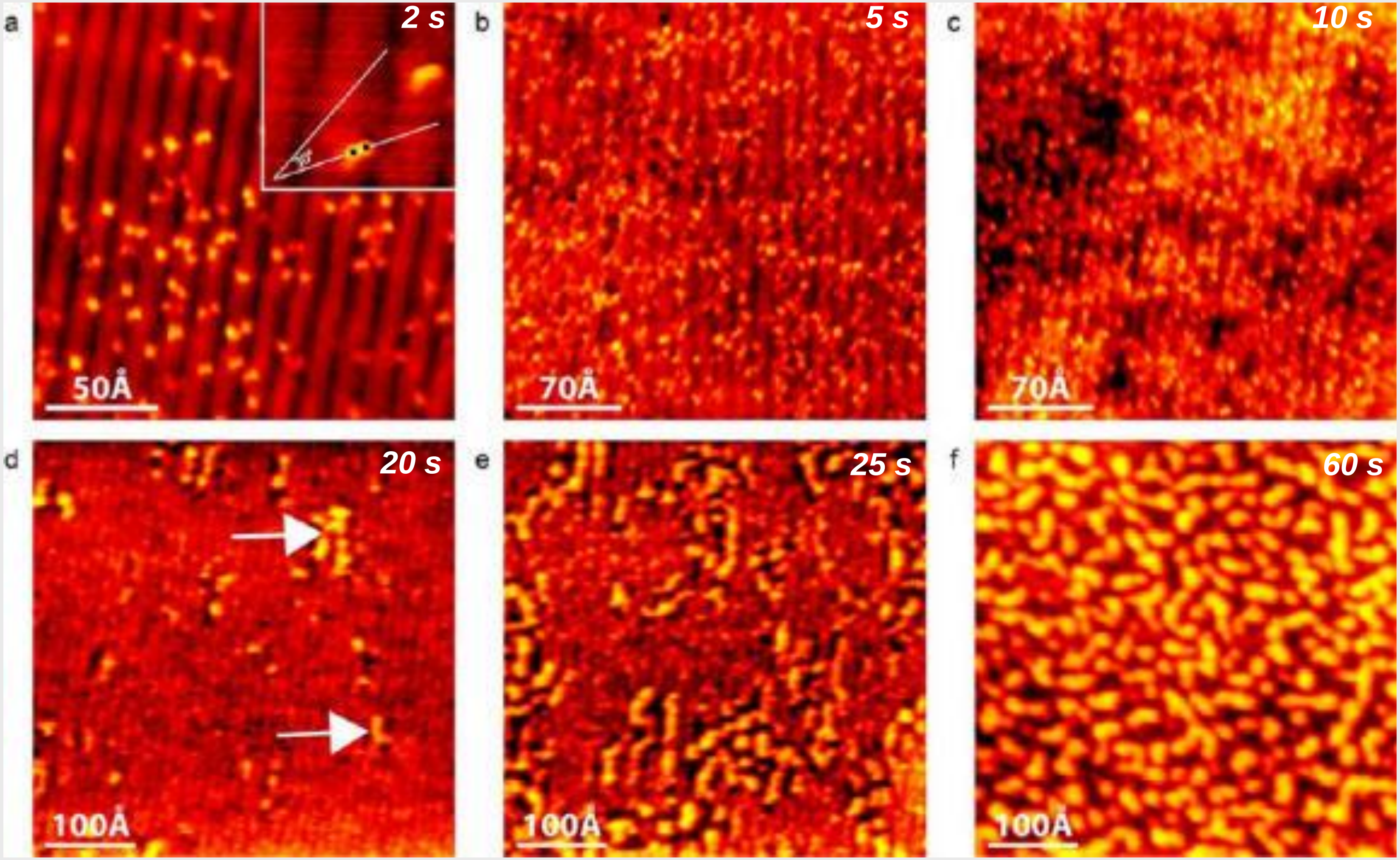
CO Exposure



Similar results on Pt(111): Mu et al., Angew. Chem., Int. Ed. **51**, 4856 (2012)

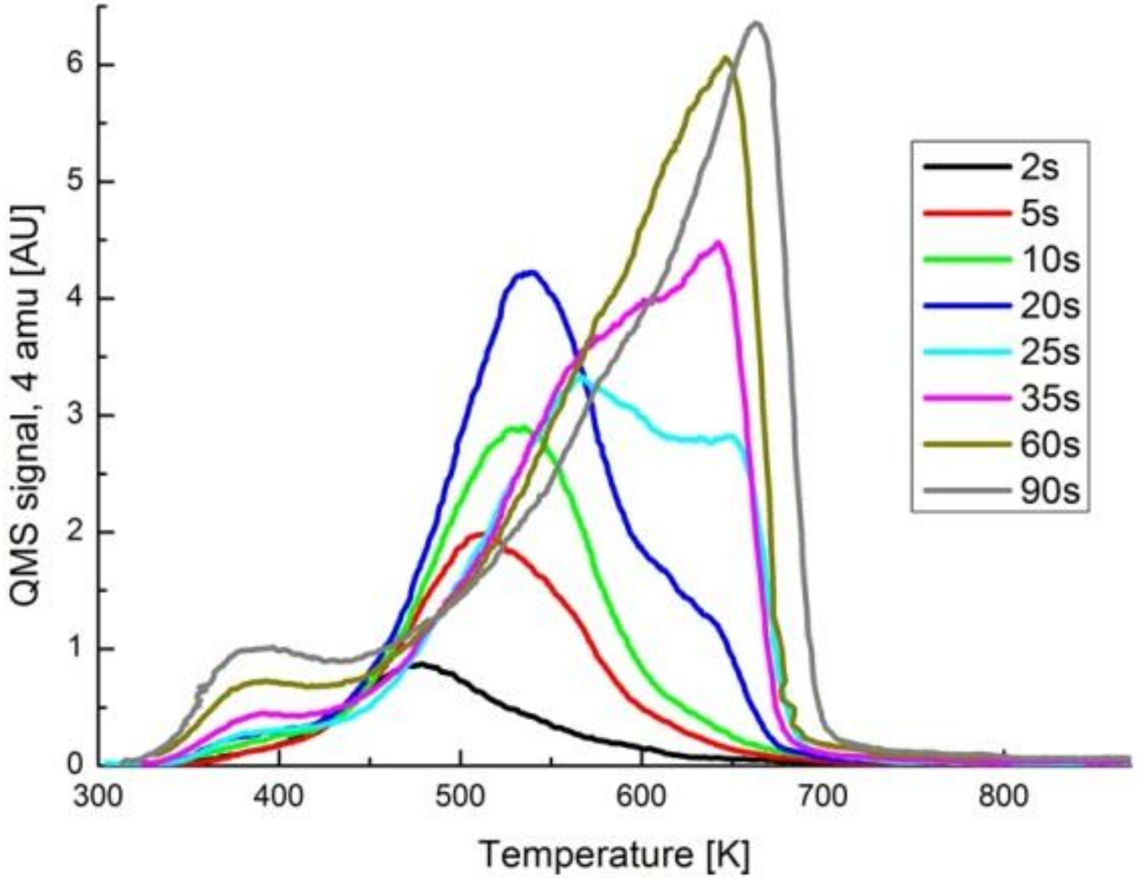
L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

Hydrogenation of graphene on Pt(100)



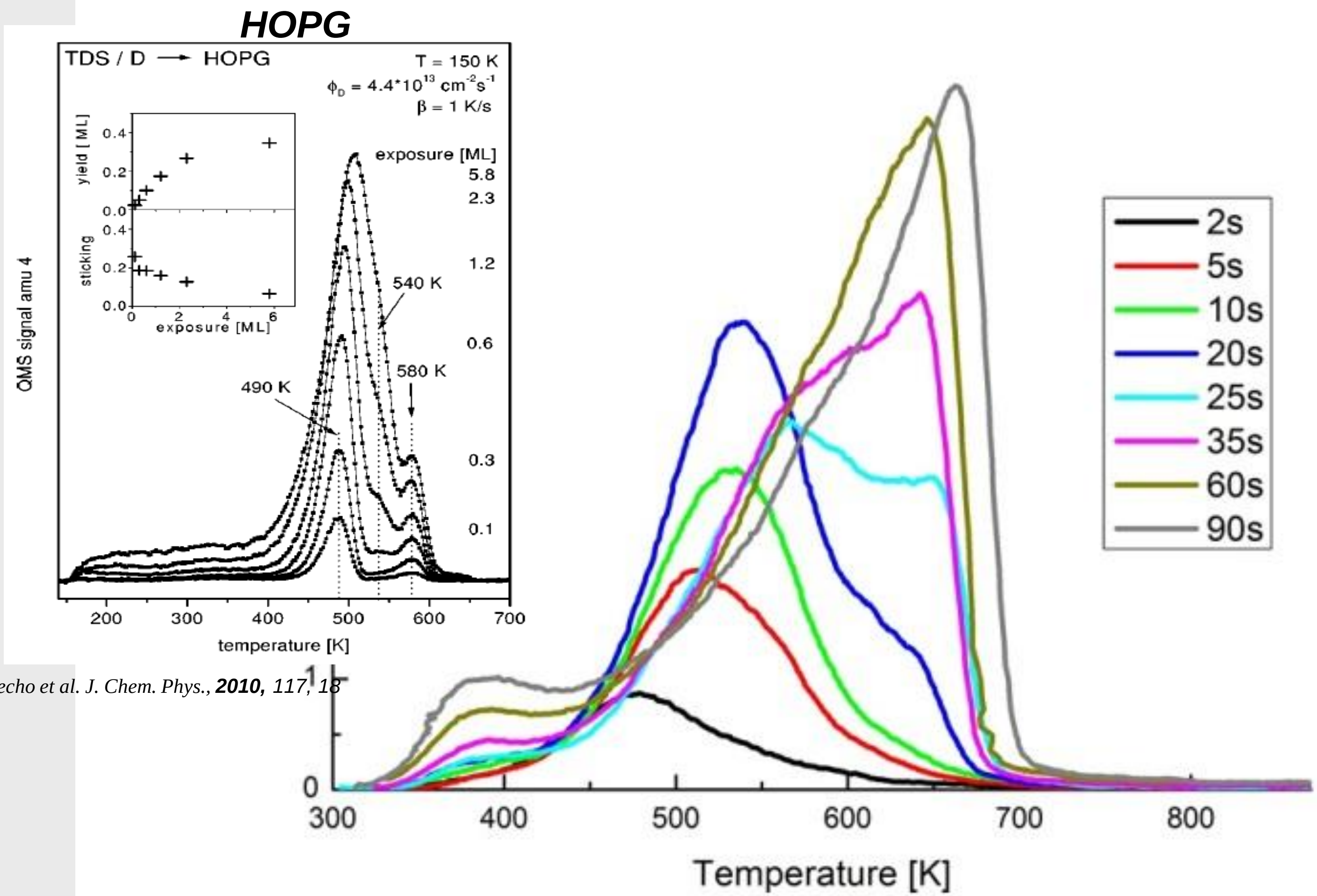
L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

D_2-TPD



L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

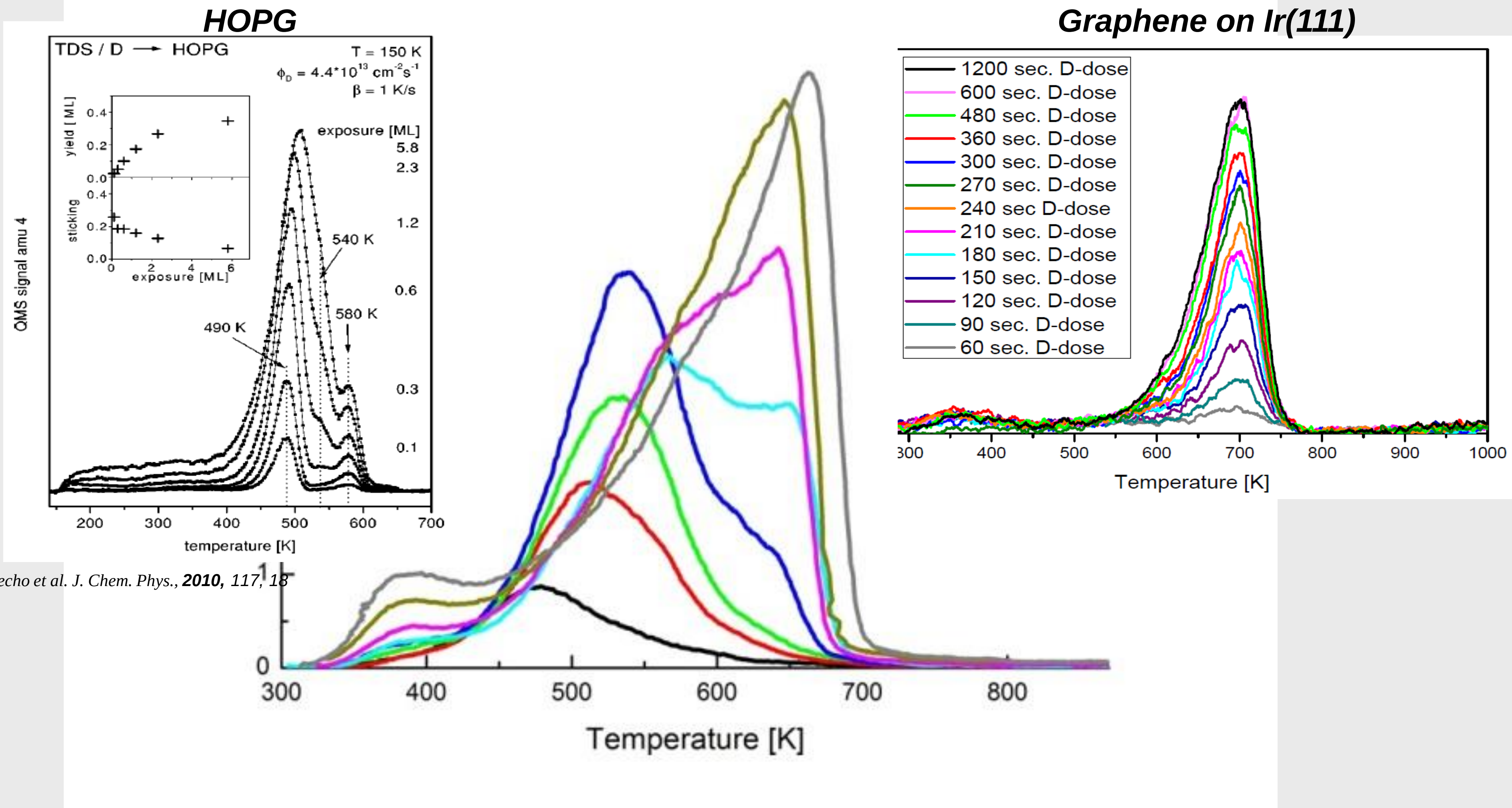
D_2-TPD



Zecho et al. J. Chem. Phys., ***2010,*** *117, 18*

L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

D_2-TPD



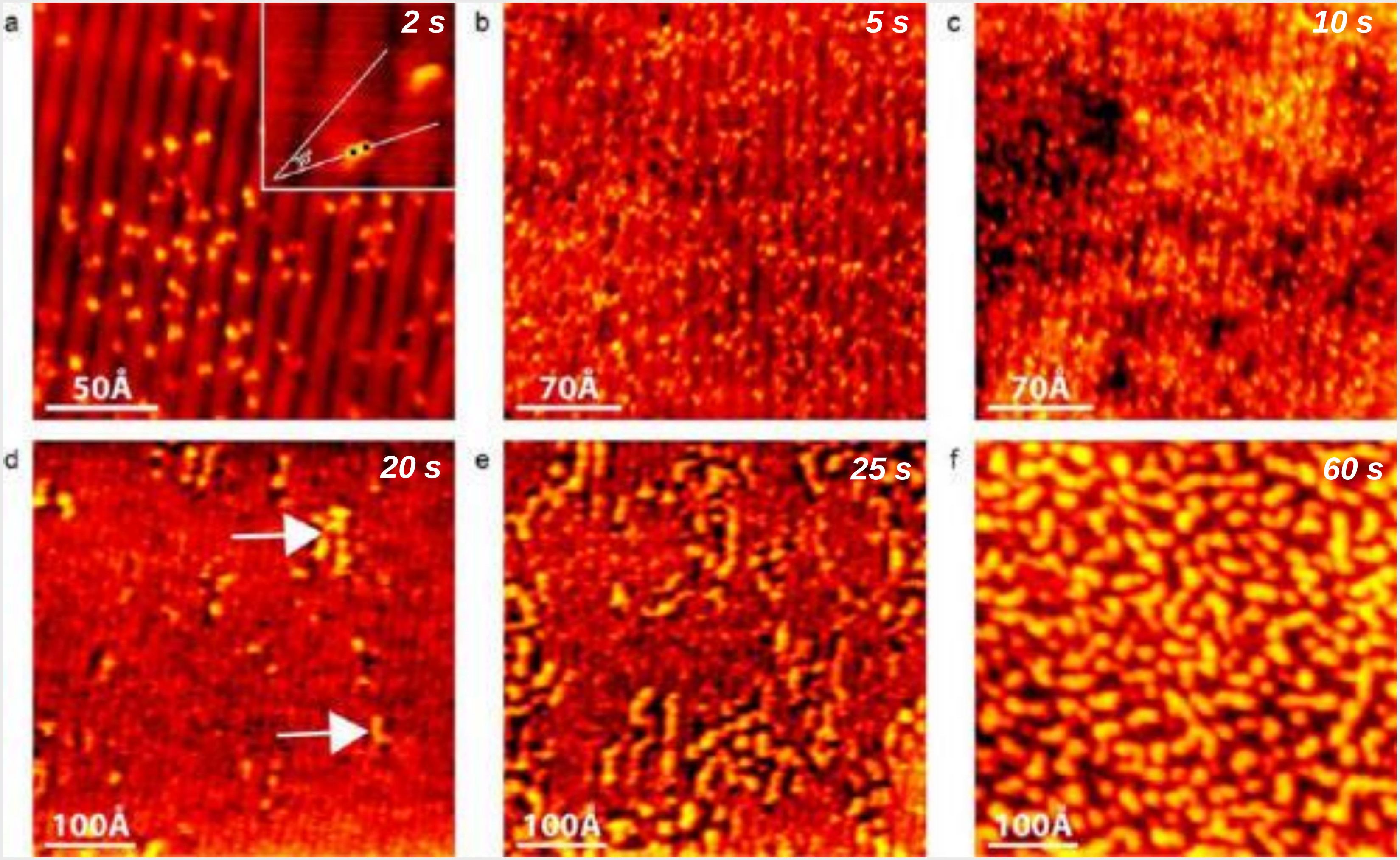
HOPG

Graphene on Ir(111)

Zecho et al. J. Chem. Phys., ***2010,*** *117, 18*

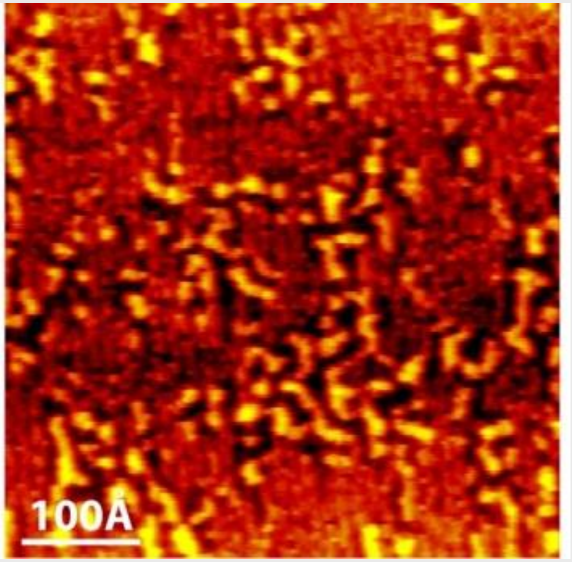
L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

Hydrogenation of graphene on Pt(100)



L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

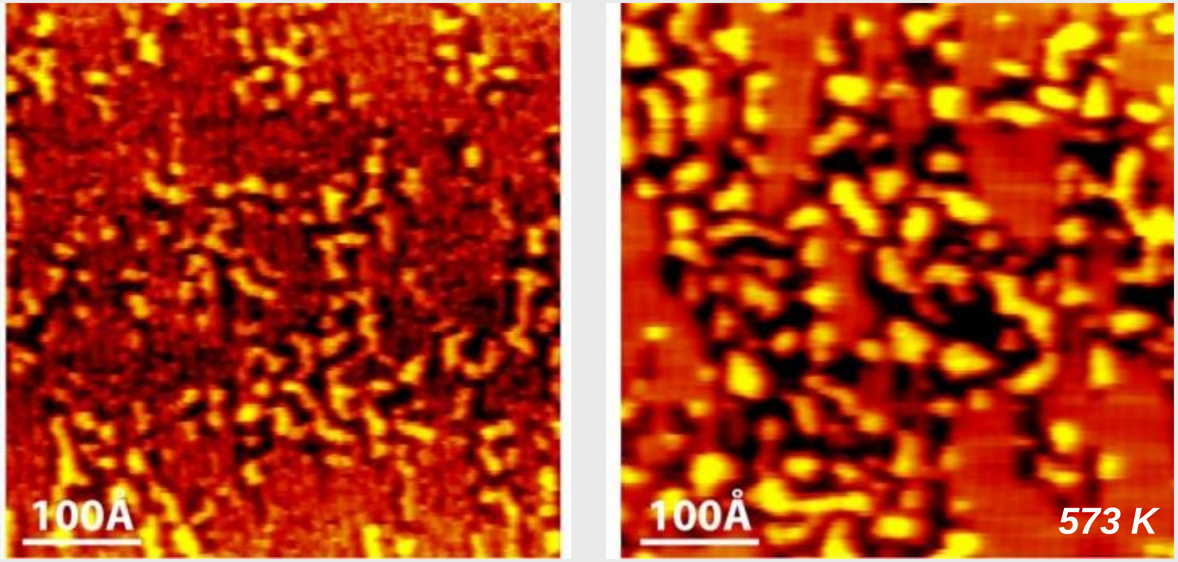
Anneal experiment



573 K

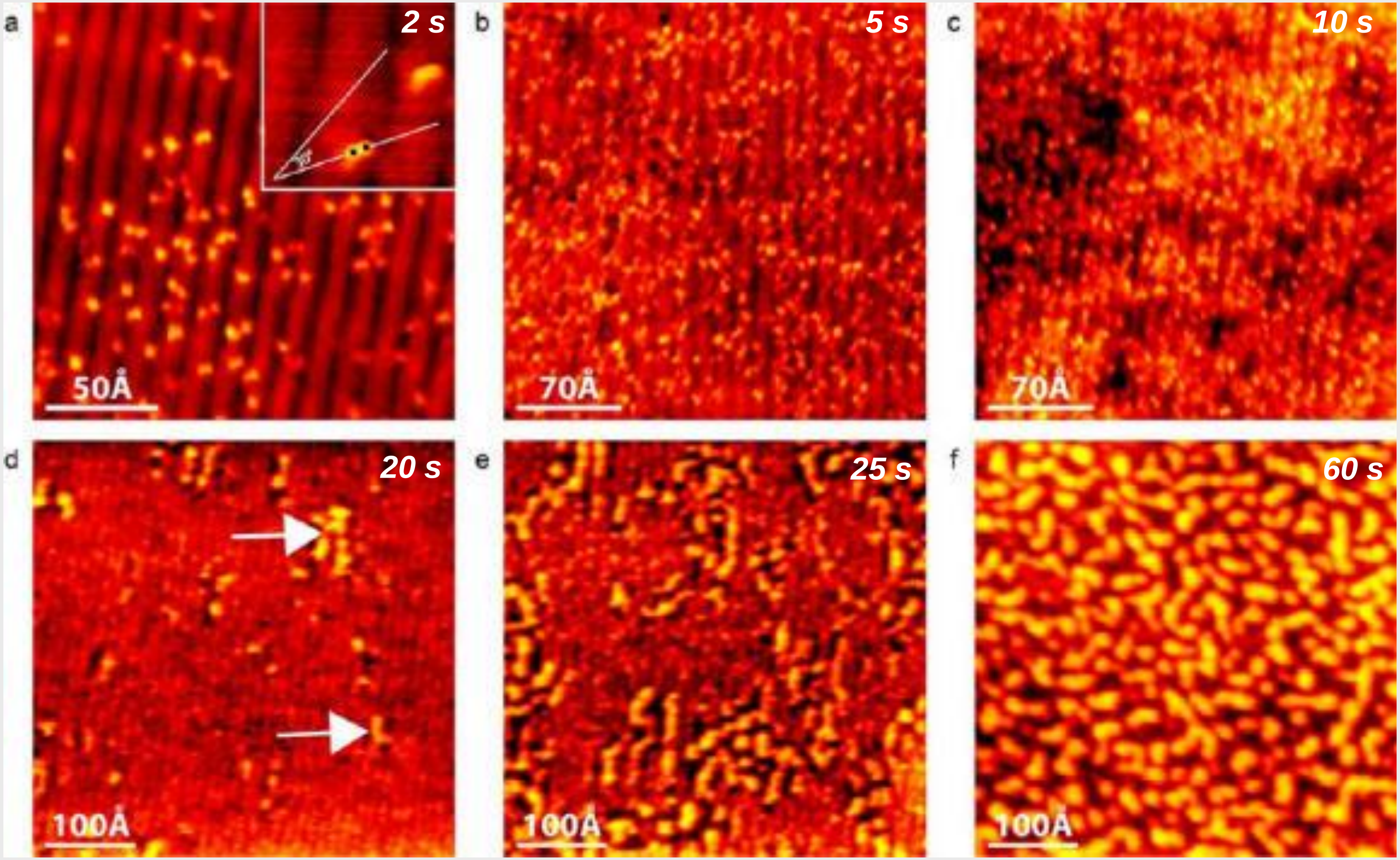
L. Nilsson et al. In preperation.

Anneal experiment

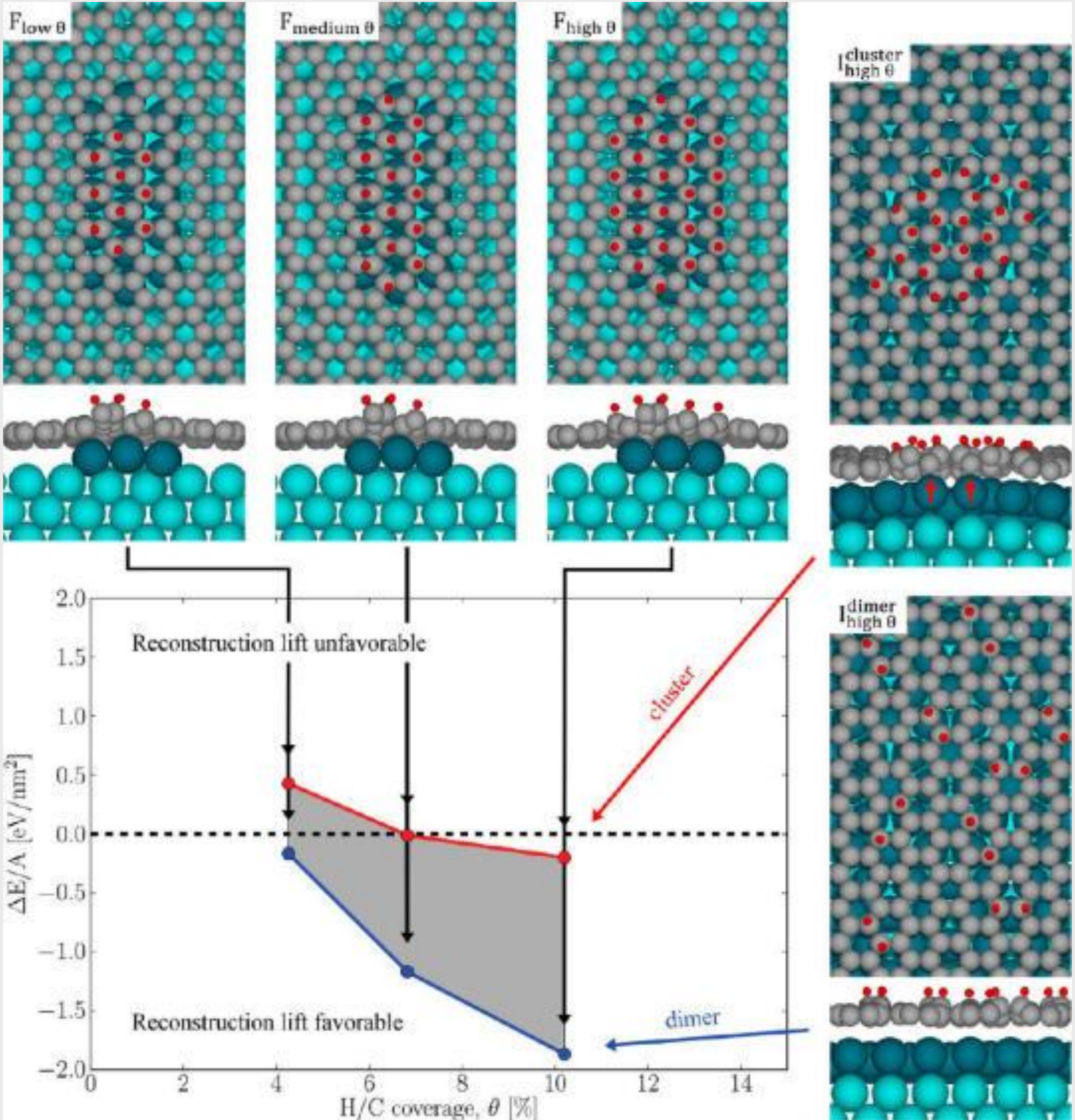


L. Nilsson et al. In preperation.

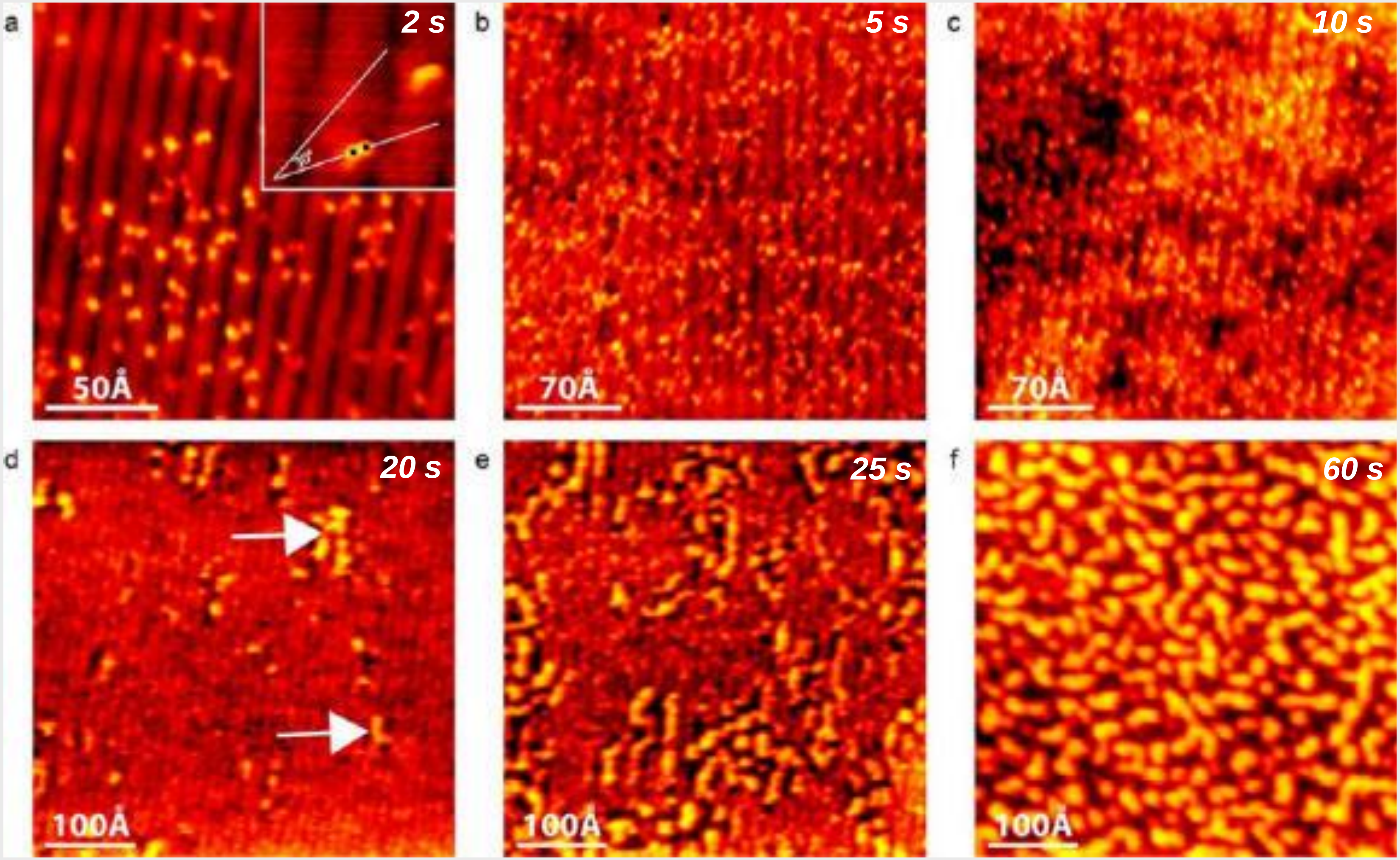
Hydrogenation of graphene on Pt(100)



L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

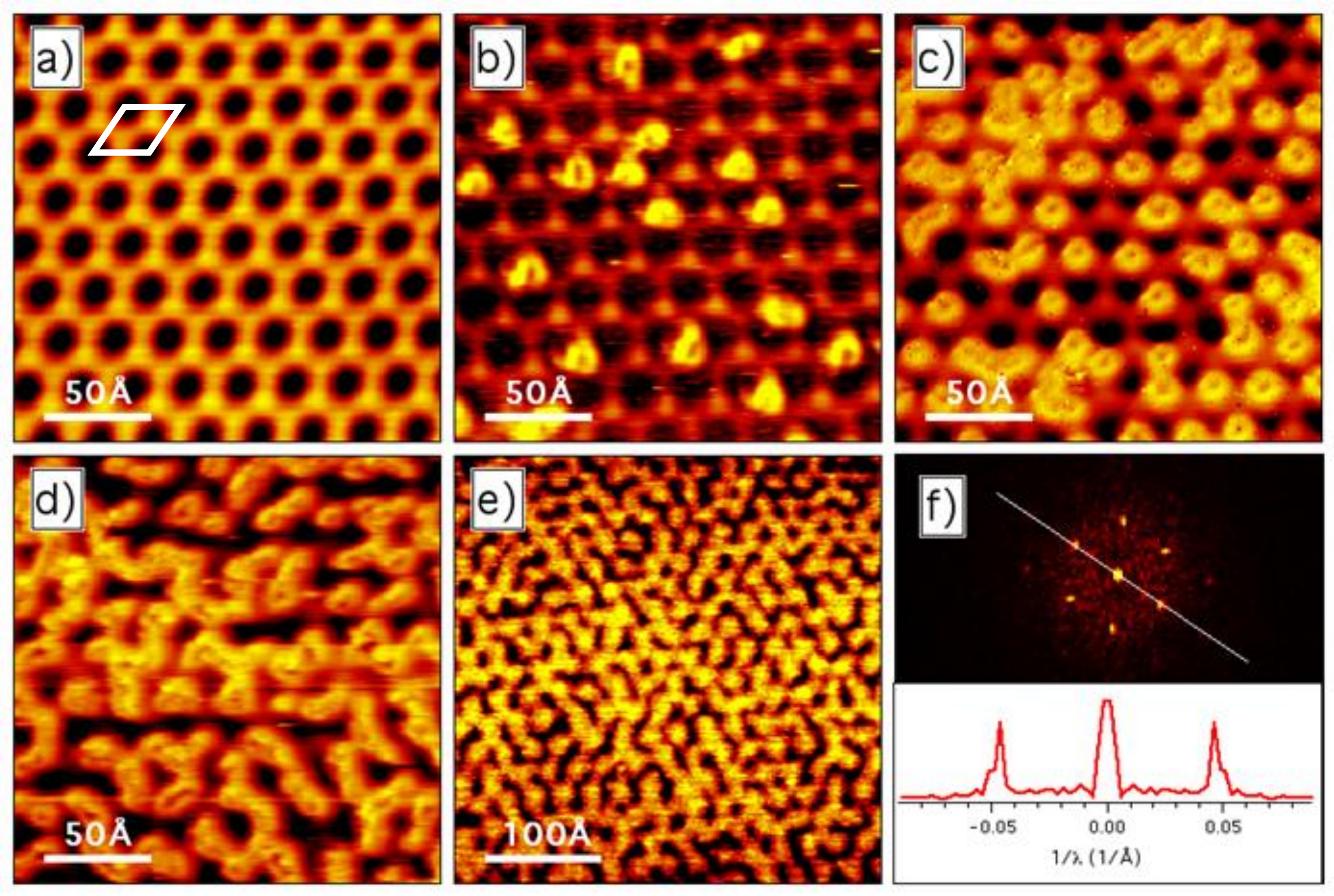

$F_{\text{low }\theta}$
$F_{\text{medium }\theta}$
$F_{\text{high }\theta}$
$I^{\text{cluster}}_{\text{high }\theta}$
$I^{\text{dimer}}_{\text{high }\theta}$
Reconstruction lift unfavorable
Reconstruction lift favorable
cluster
dimer
$\Delta E/A$ [eV/nm^2]
2.0
1.5
1.0
0.5
0.0
−0.5
−1.0
−1.5
−2.0
0
2
4
6
8
10
12
14
H/C coverage, θ [%]

Hydrogenation of graphene on Pt(100)



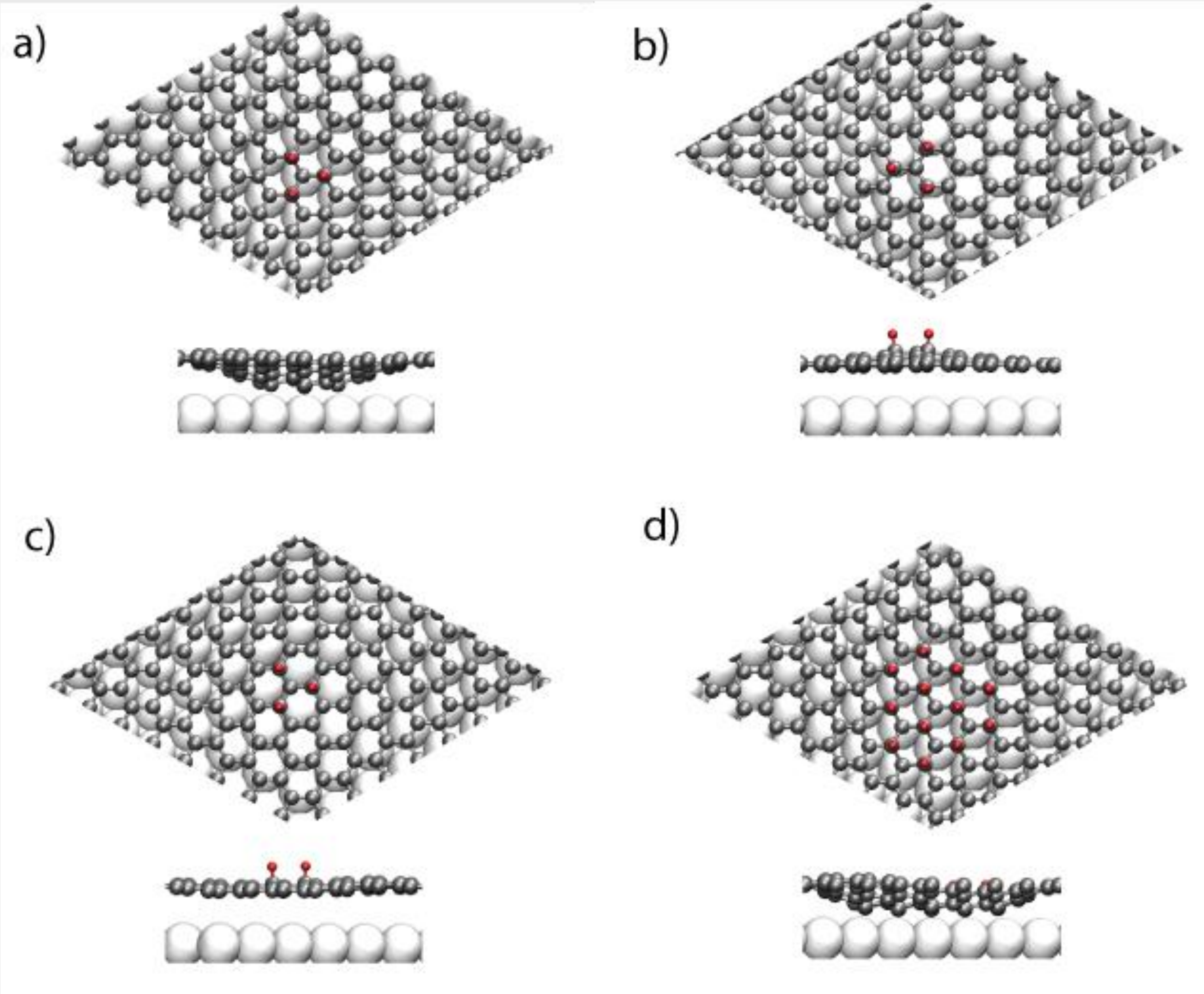
L. Nilsson *et al.* ACS NANO **6**, 10258 (2012)

STM of H/Graphene/Ir



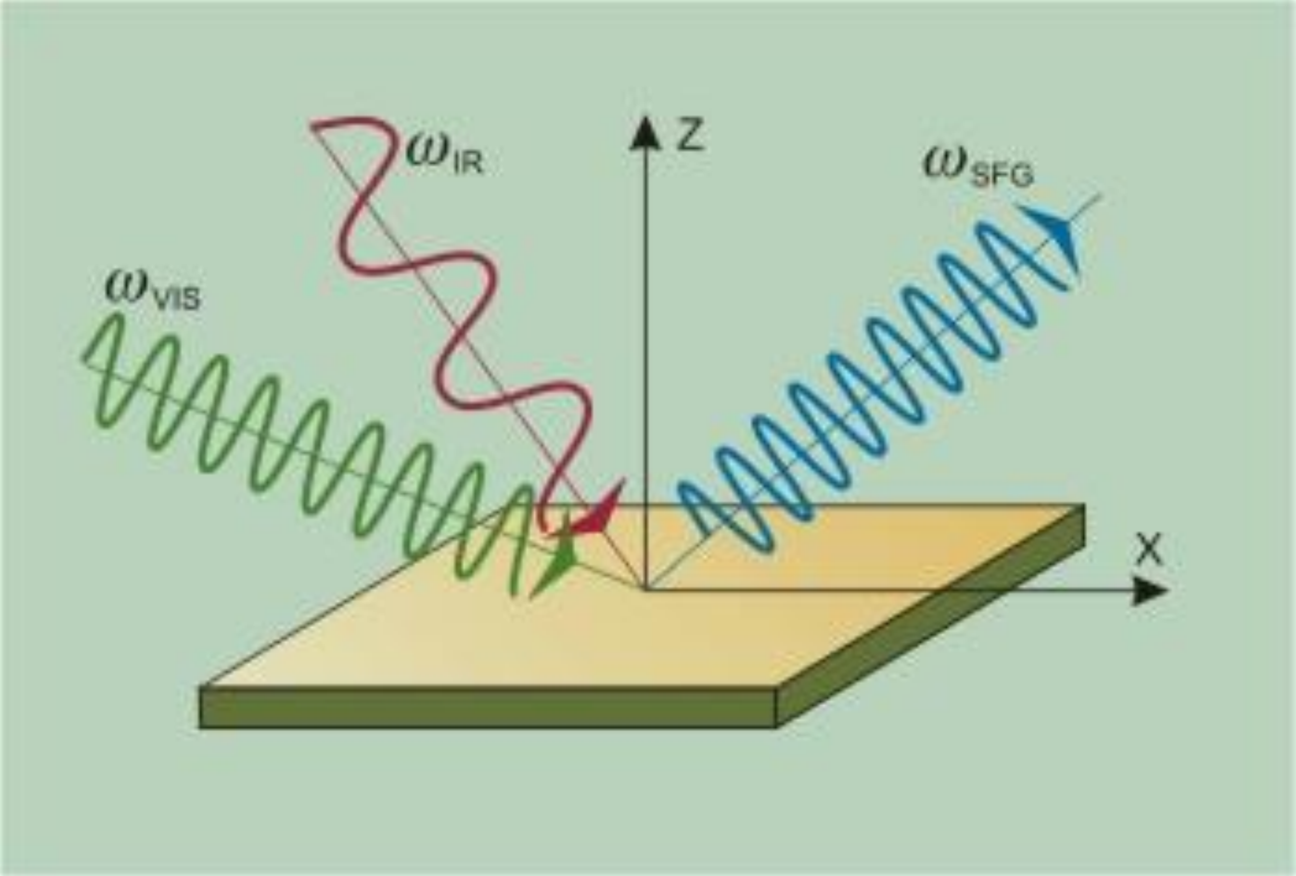
Balog et al., Nat. Mat. ***9****, 315 (2010)*

Adsorbate structures



*Balog et al., Nat. Mat. **9**, 315 (2010)*

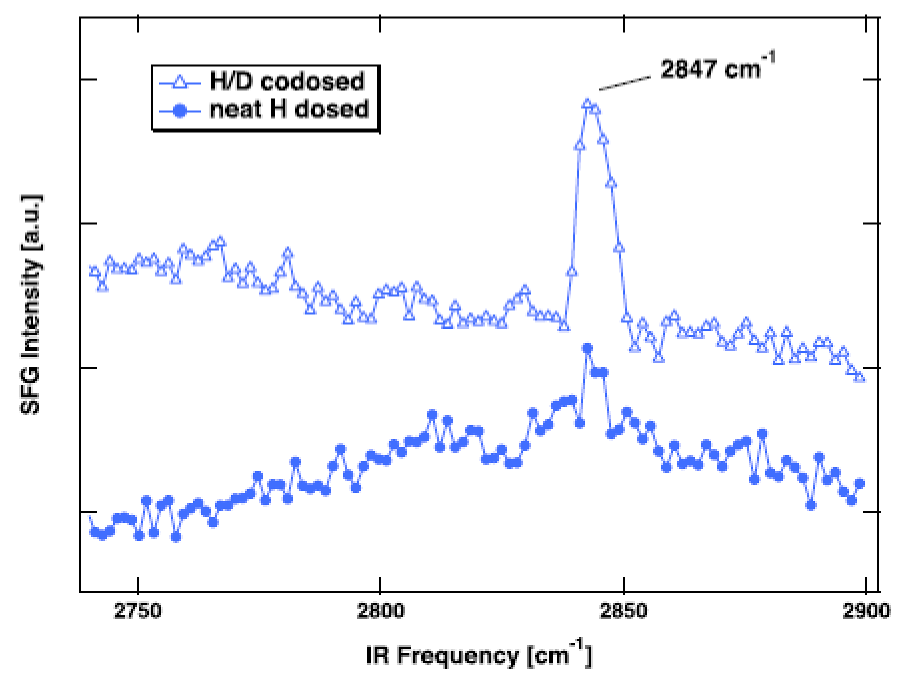
Sum frequency generation

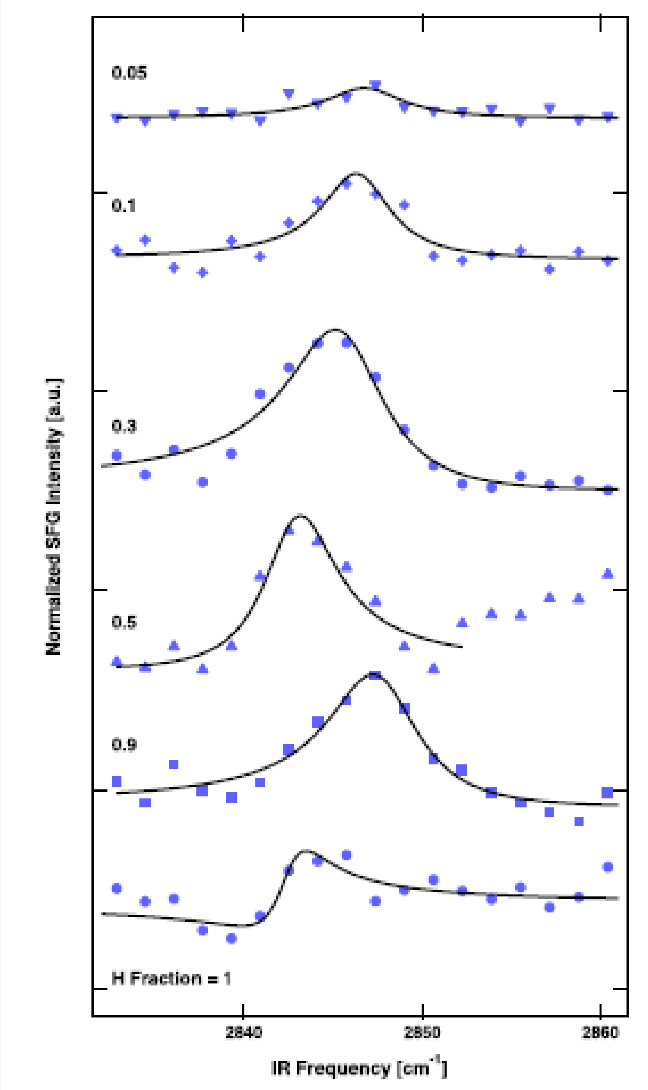


$$I(\omega) \propto |\chi^{(2)}|^2 I_1(\omega_1) I_2(\omega_2)$$

$$\chi = \chi_{nr} + \chi_r$$

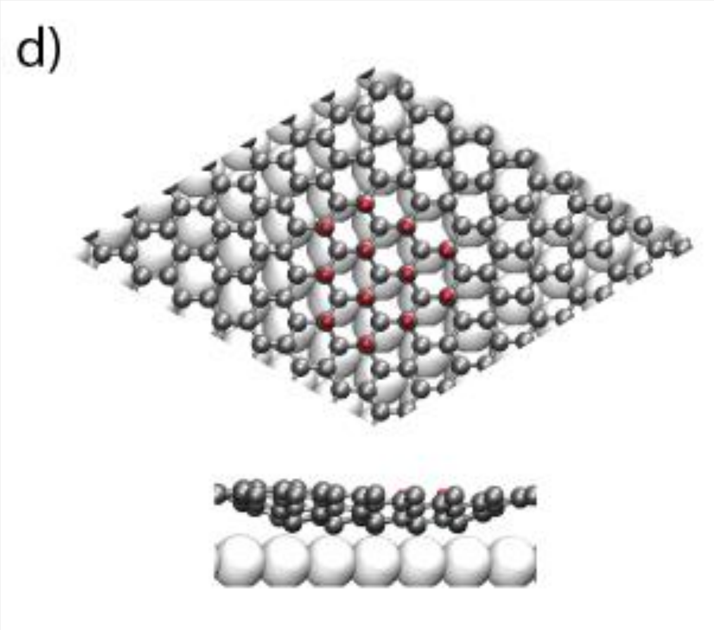
Real graphane ?

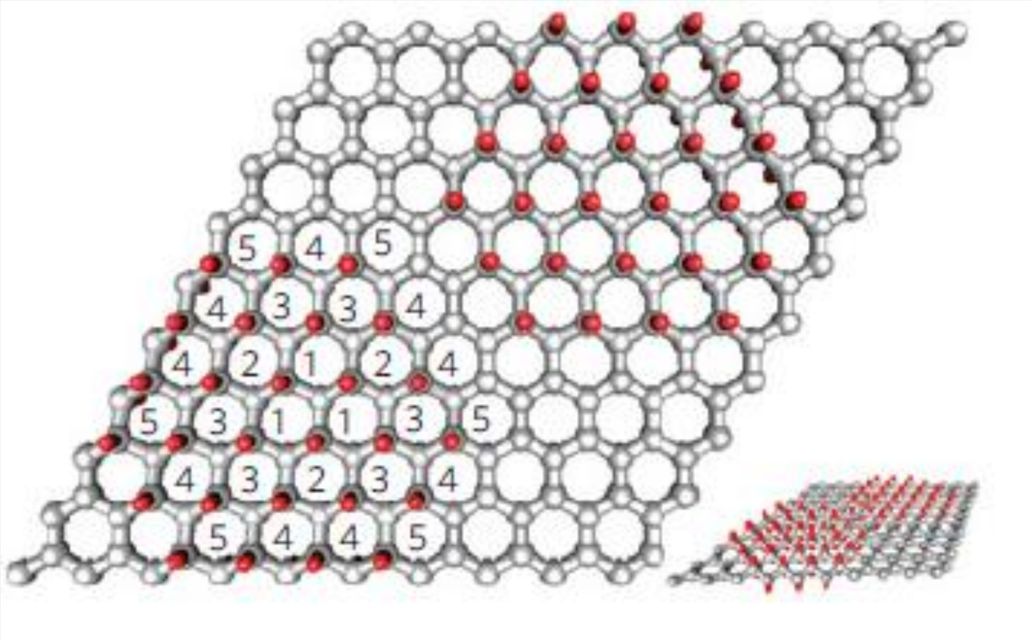




Kim et al. CPL 2012

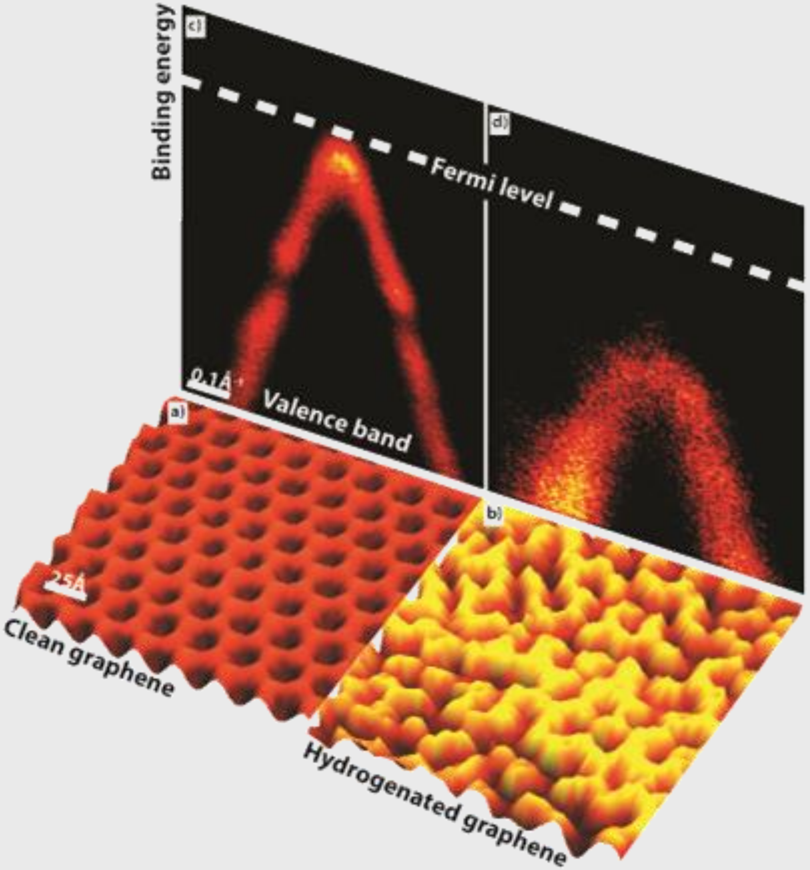
Real graphane ?





Balog et al., Nat. Mat. ***9****, 315 (2010)*

Conclusion



hydrogen nanoscale patterning =>
Graphene semiconductor
    Band gap origin?

Graphene coatings
    Mechanical limitations
    Edge effects
    Can we control the edges?

People involved

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