

Interesting Properties of Strained or Defective Graphene

ACS NANO 2013 7(10), 8350

Kian Ping LOH

Department of Chemistry, National U of Singapore
Graphene Research Centre

Acknowledgement to
National Research Foundation, Andrew Wee TS, Antonio Castro Neto, O. Barbaros

Contributions by
Lu Jiong (NUS), Su chenliang (NUS)
Candy Lim Yixuan (NUS)



NUS

Loh KP's Group

The Graphene Lab

Graphene (dry)

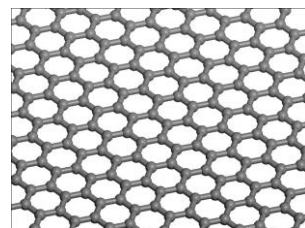
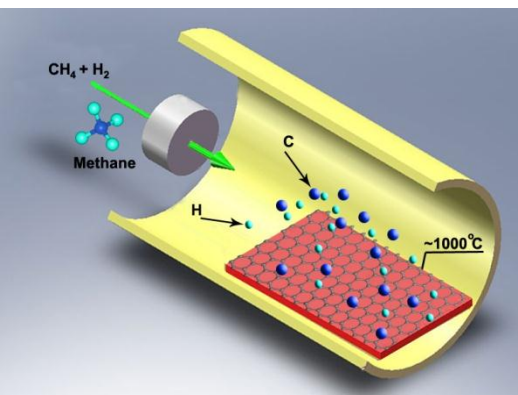
Grown by dry CVD process

Planar structure

High π electron density

bonding interactions

Governed by π - π interactions

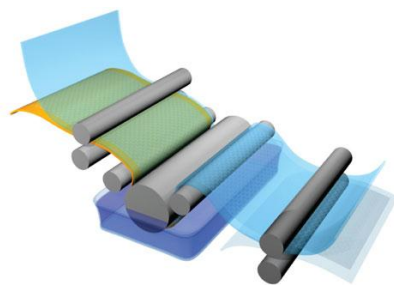


Pioneers: Rodney Ruoff, (U Texas)

Byung Hee Hung (SKKU)

Science 324, **2009**, 1312

Nature Nanotechnology 5, **2010**, 574



Graphene-oxide (wet)

Wet chemistry, from graphite

Non-stoichiometric CO_x

Complex interplay of ionic and non-ionic intercalations

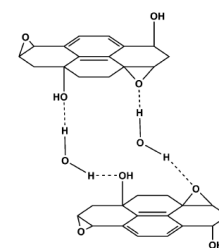
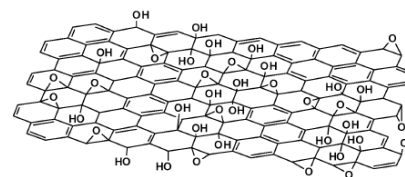
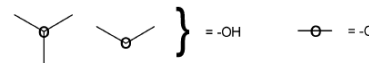
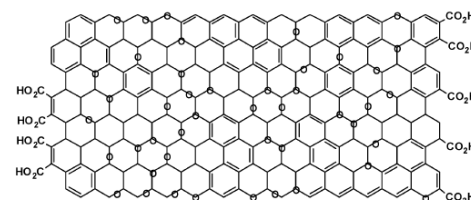
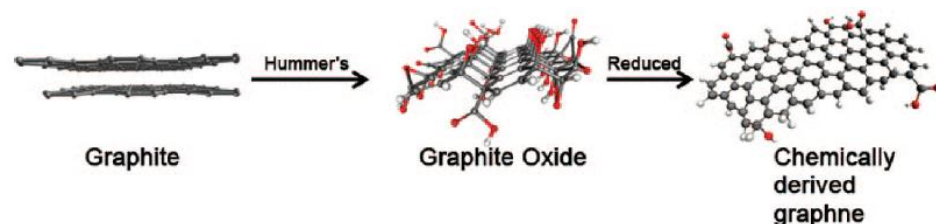
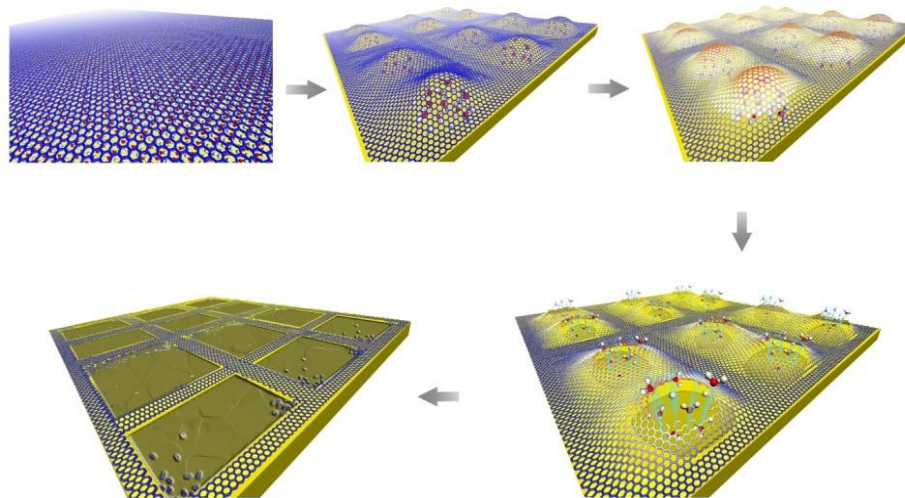


Fig. 3 Proposed hydrogen bonding network formed between oxygen functionality on GO and water. For alternatives to this model see ref. 26 and 28.

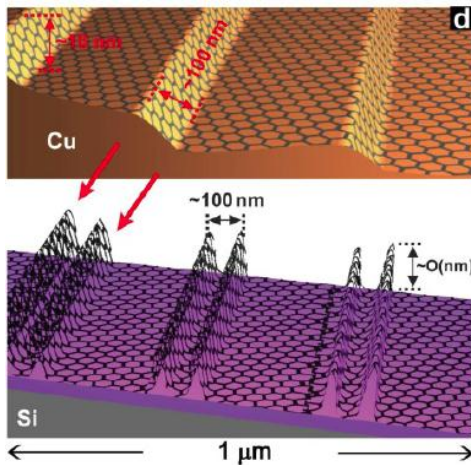
A giant polyaromatic framework that can mediate multiple interactions

A consequence of graphene being a soft membrane is that it can be strain-engineered to become highly corrugated by modifying its adhesion to the substrate.



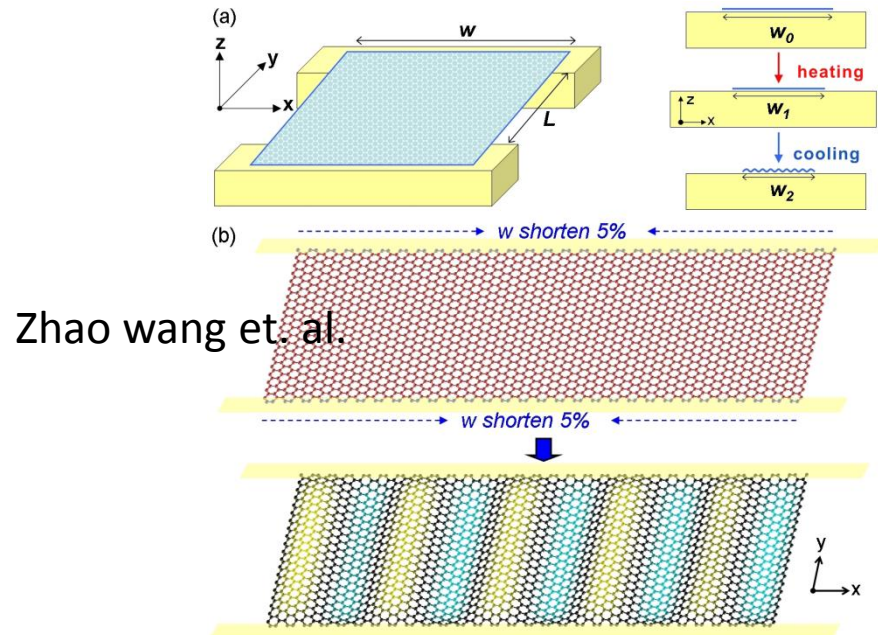
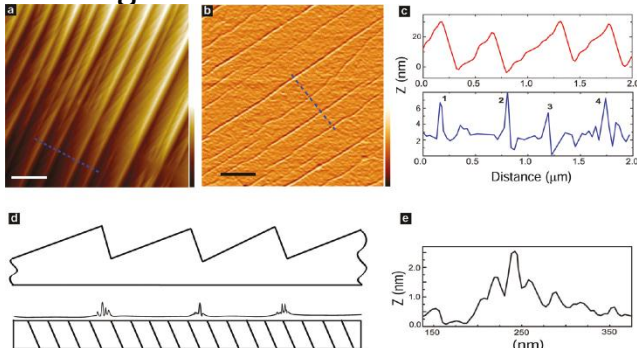
As a soft membrane – Graphene is easily rippled

I. Nanoripples



Typical Cu surface after growth

Step edges (terrace) density ~ 2.5 per μm



Zhao wang et. al.

Electron-flexural phonon scattering in such partially suspended graphene devices introduces anisotropic charge transport and limits charge mobility. Influence of Flexural phonon is reduced under tension. Applying weak strain may be enough

CVDG/SiO₂ with high density nanoripples

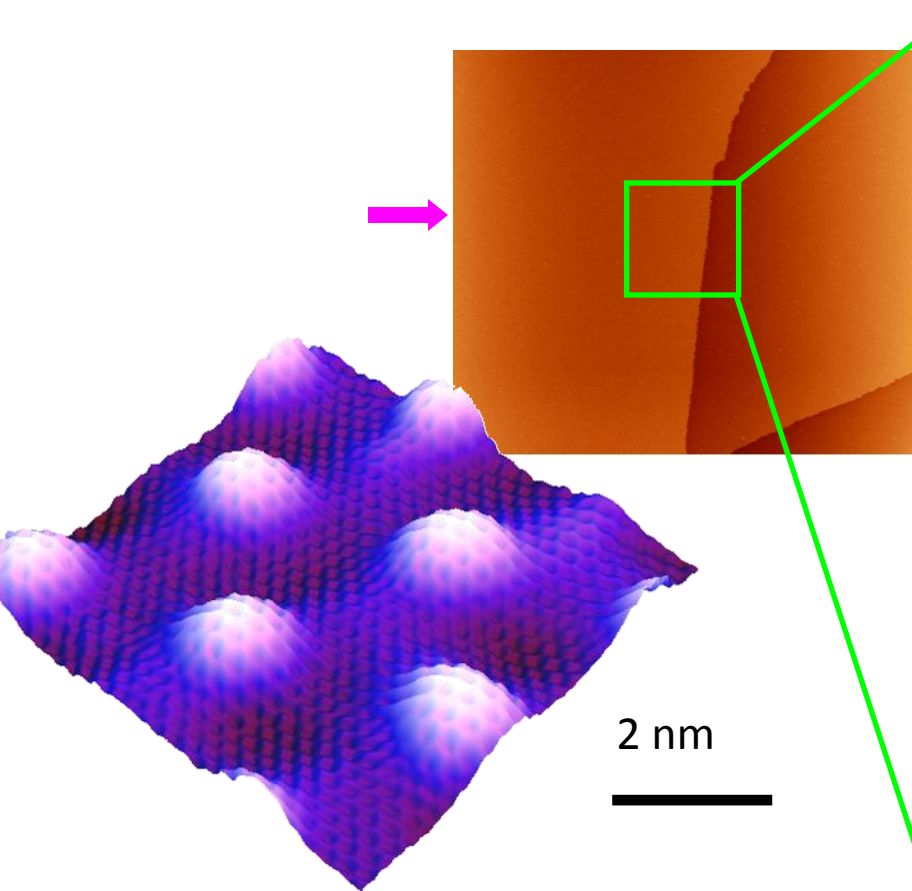
Nanoripple density ~ 1.5 per μm

Guangxin Ni, O. Barbaros, ACS NANO, 6(2012) 1158

1. Periodically Strained Graphene as a Reaction Breadboard

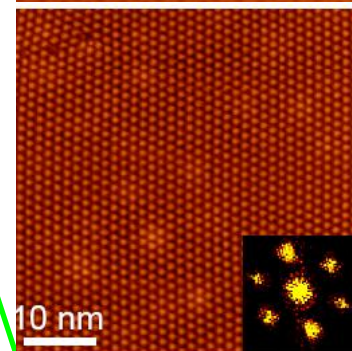
Graphene Moire Superstructure on Ruthenium: A Strained Reaction Breadboard

1300 K for 3-5 mins



- $\Theta > 1\text{ML C}_{60}$
- $T > 1000\text{ }^{\circ}\text{C}$
- Annealing 3 mins

Single crystal graphene
buckling instability
due to the compressive strain between lattice-
mismatched Ru and G
produces moire pattern



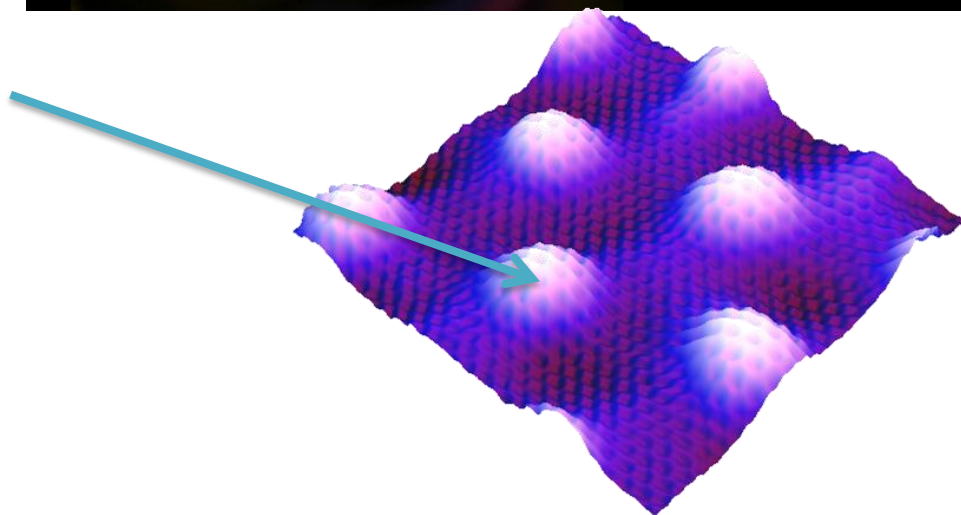
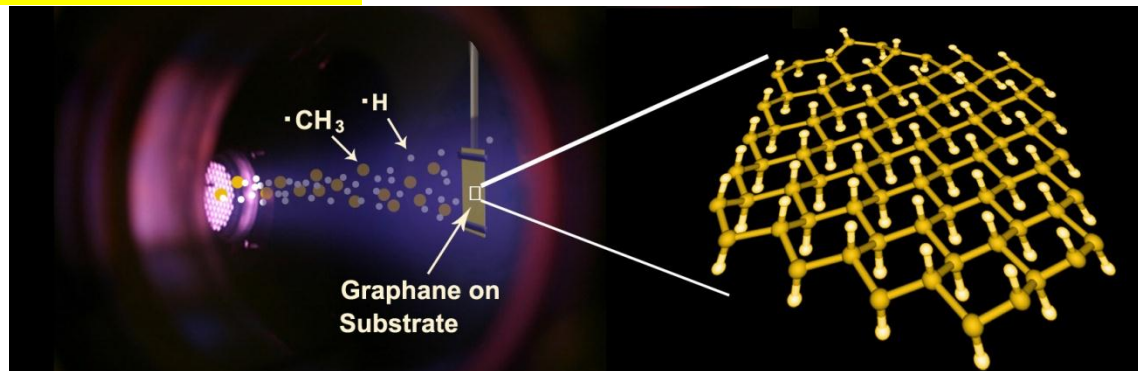
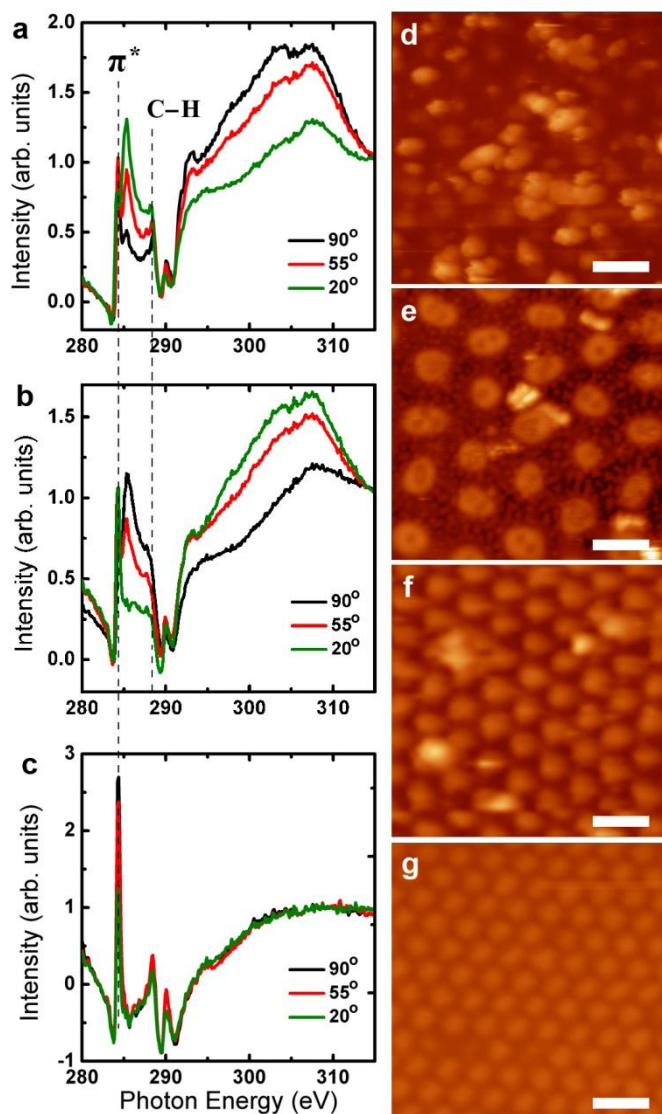
40 nm

One inspiration from looking at the periodic blisters on the Moiré superlattice is the remarkable resemblance of these blisters to an ordered array of nano-bubbles !!

Moire Superlattice as Reaction Breadboard:

Example 1: Selective Hydrogenation Occurs on the Hump Region of the Moire Superlattice

Yu Wang and K. P. Loh, ACS NANO, 4, 6146 (2010)



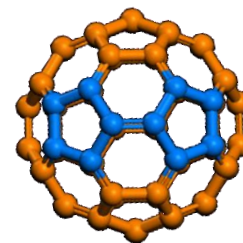
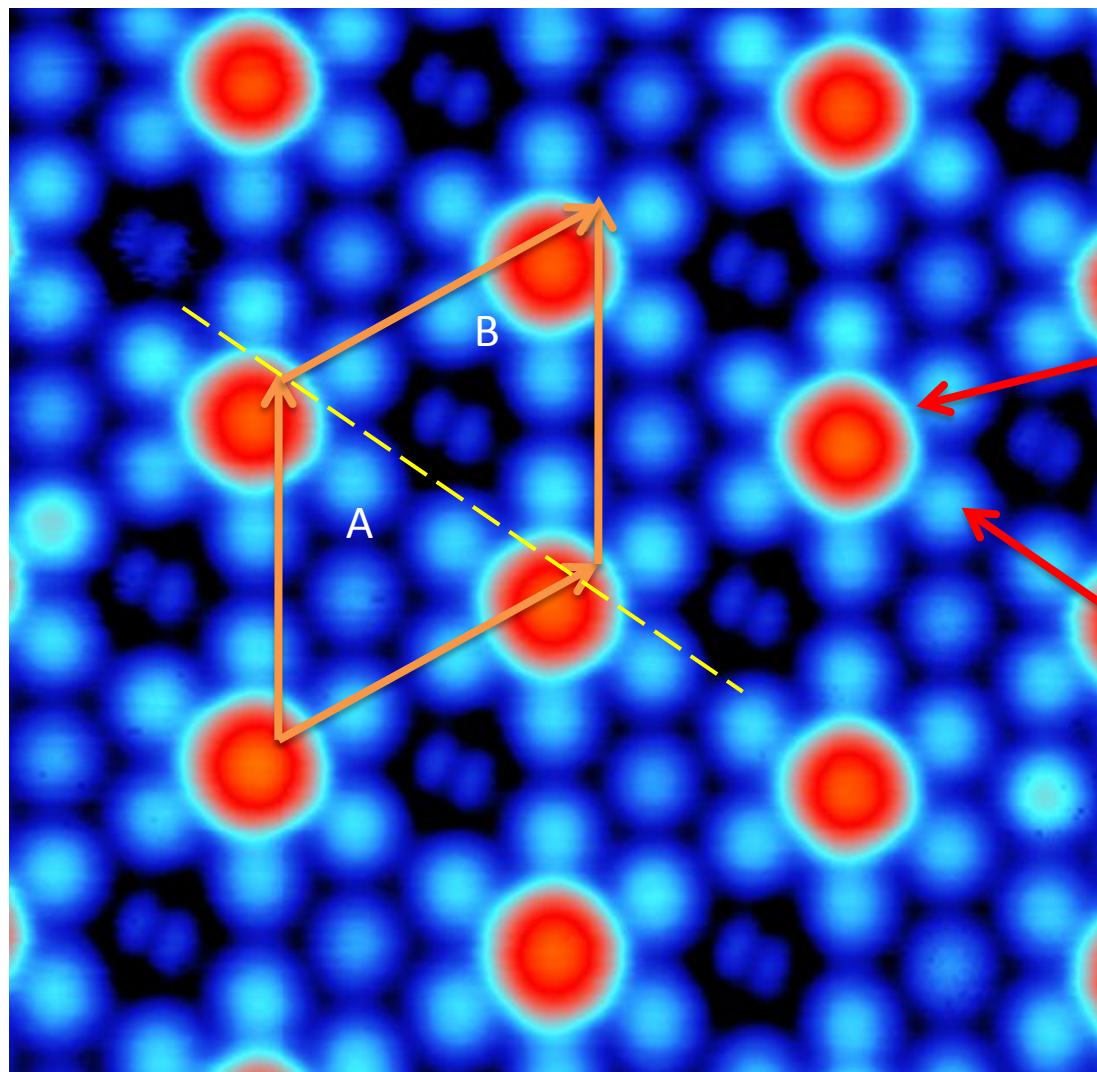
Hump region is a sink for diffusing H atoms
d. H adsorption at room temperature, random cluster
e. After annealing to 300 deg C, ordered cluster on bright regions of moire = hump.
f,g: after annealing to cause H desorption

Reaction Breadboard

Example 2: Contrasting Potential Energy Landscape on the Moire Surface

Rotation of C60 frozen on Moire Valley BUT free Rotation of C60 on Moire Hump

Jiong Lu, K. P. Loh, ACS Nano, 2012, 6 (1), pp 944–950



C60 in the hump

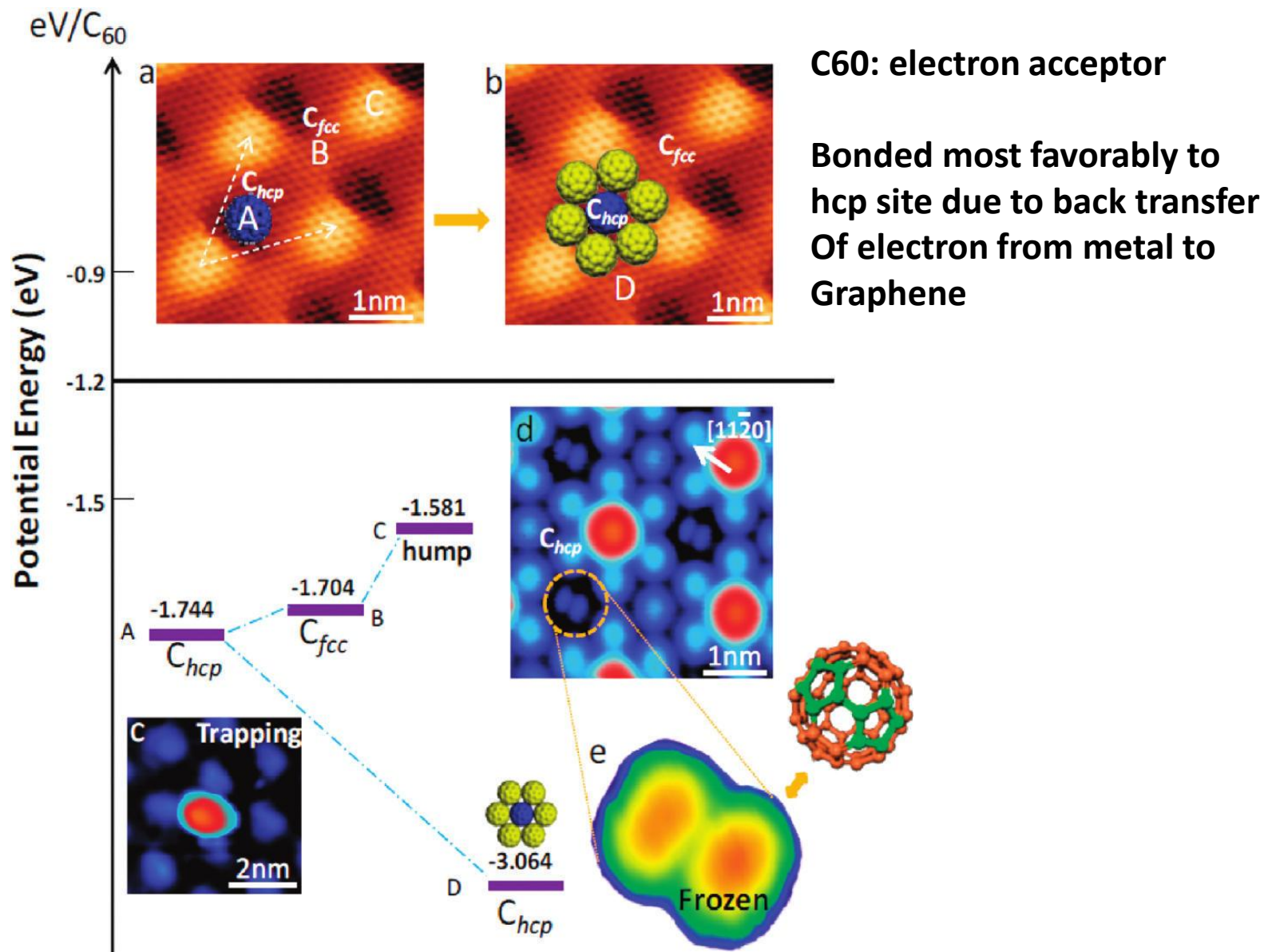
C60 in the valley

C60 in the rim

In one unit cell,

Rim: hump: valley = 6:1:1

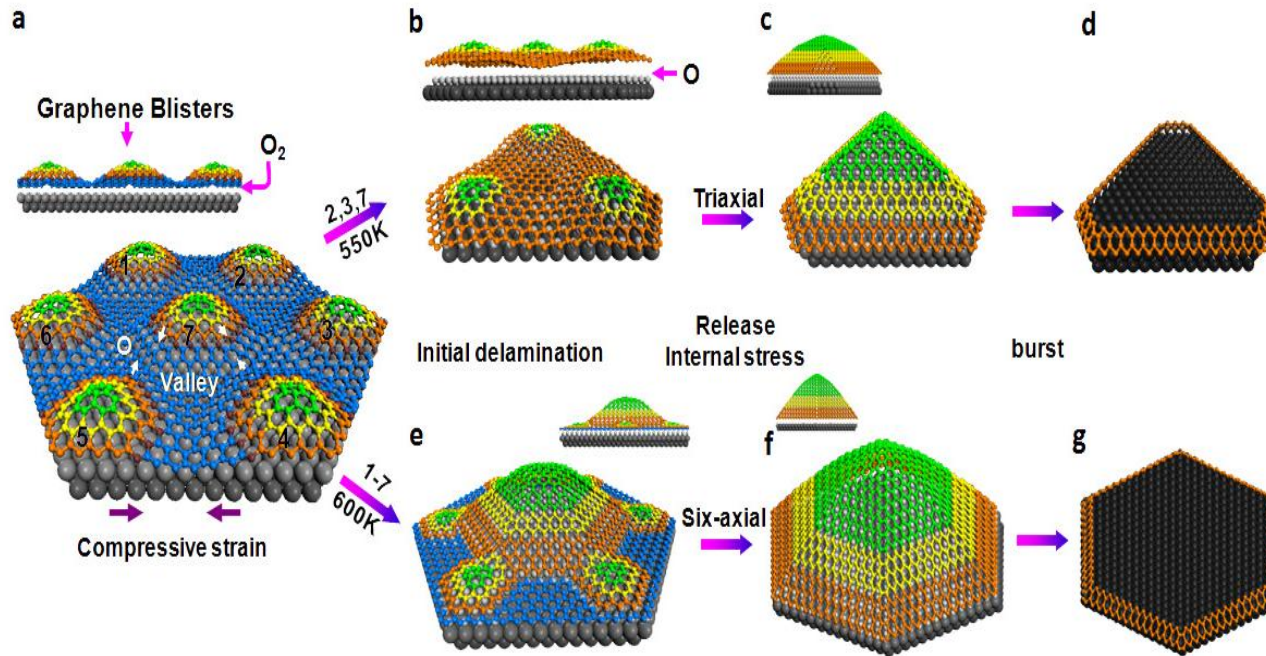
944–950



2. Engineering Strain in Graphene by forming Bubbles

- (a) Couple dirac particles to strain via pseudomagnetic field**
- (b) How to control such strain patterns at the nanoscale ?**

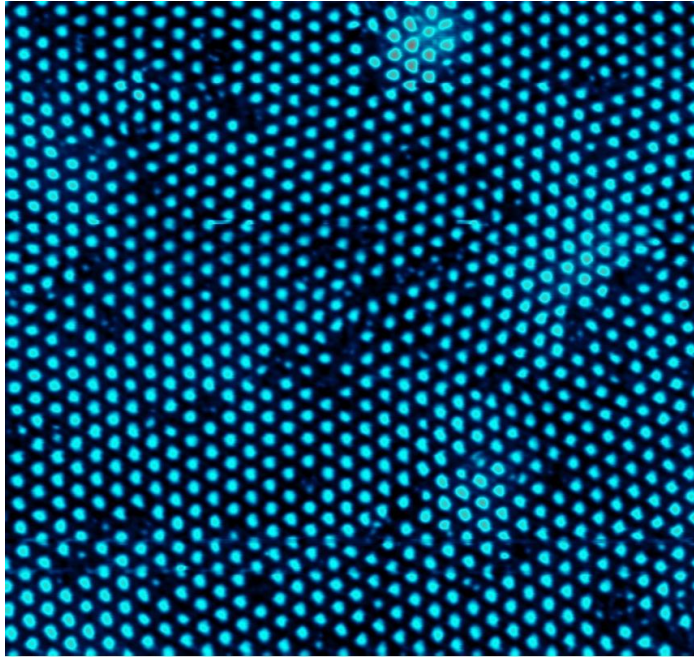
Engineer Graphene Nanobubble from the Moire Blisters



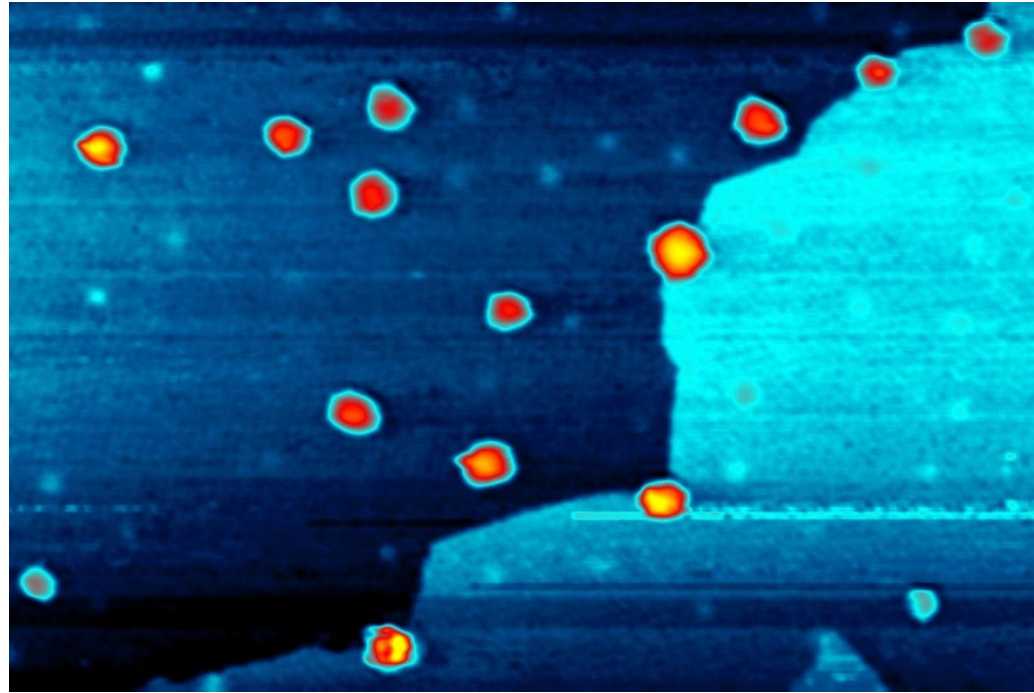
1. Graphene blisters are formed due to the uniform compressive strain associated with the lattice-mismatched ruthenium and graphene.

2. Oxidation releases Elastic Strain and Moire Blisters sinter to form bubbles

- Defective Moire Pattern due to sub-surface defects on metal
- Bubbles are more inclined to appear on defective Moire Site



150x150 nm

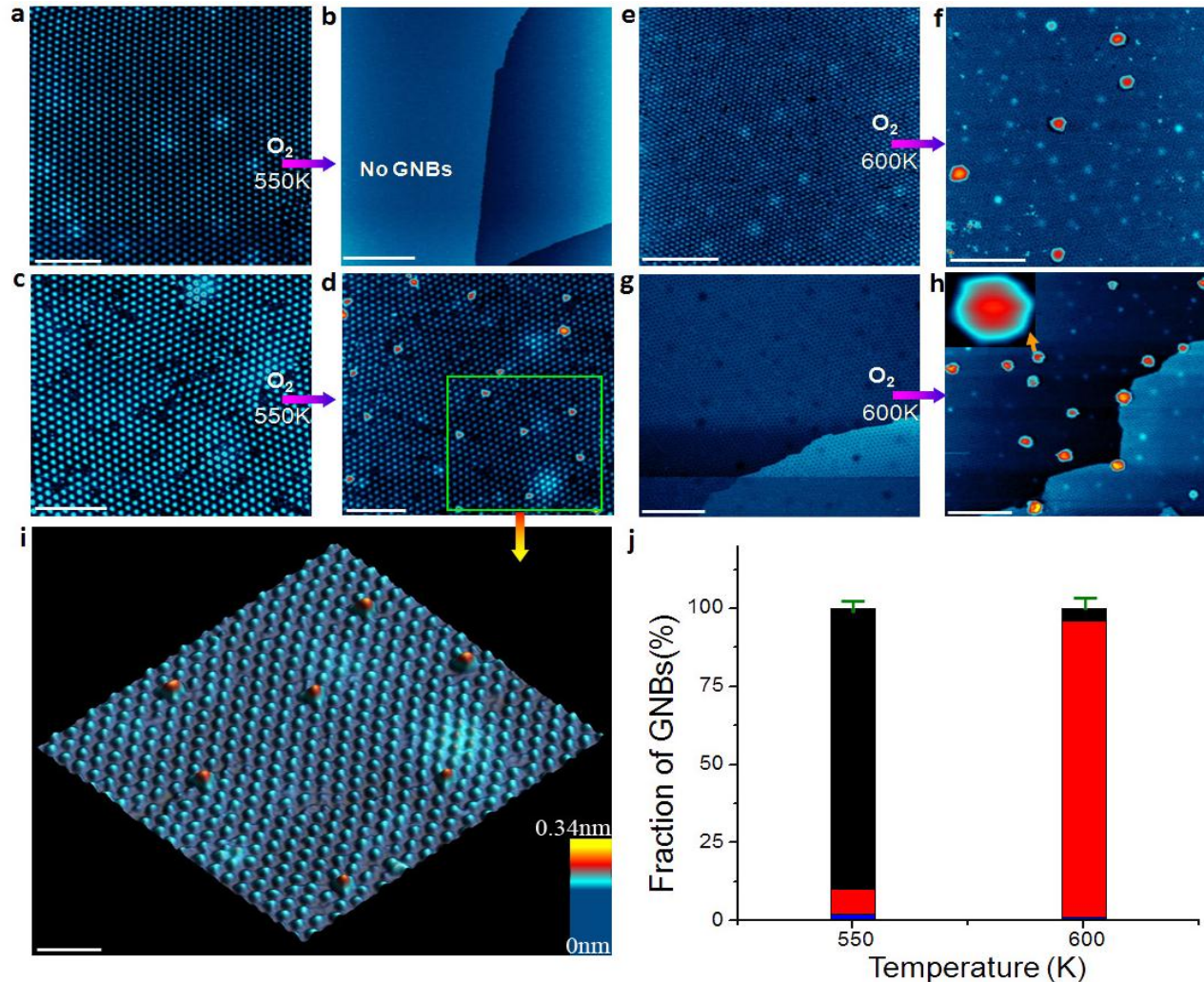


Transforming Graphene Moire Blisters into Geometric Nanobubbles

Jiong Lu, Antonion C. Neto, Kian Ping Loh*,

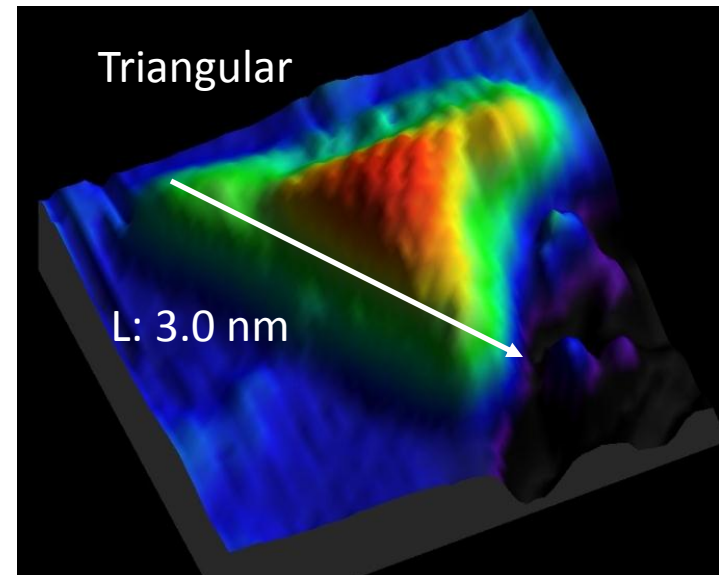
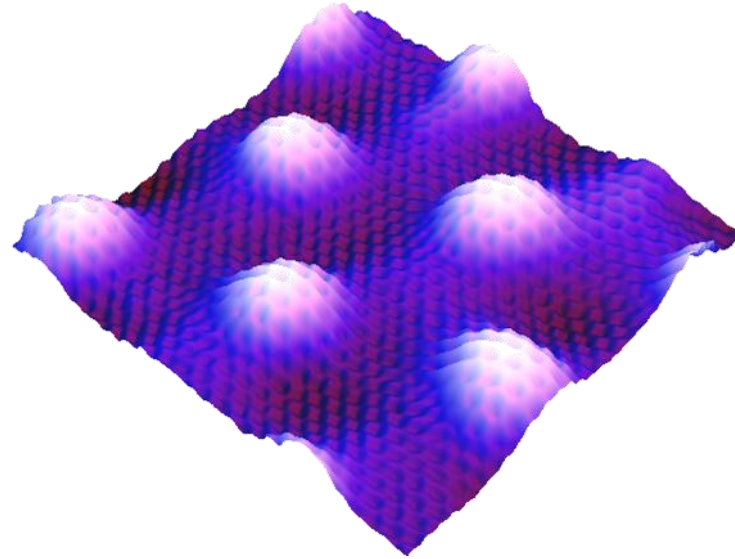
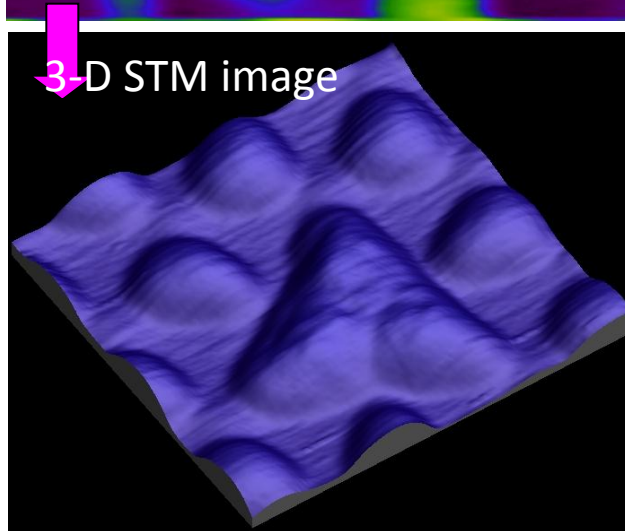
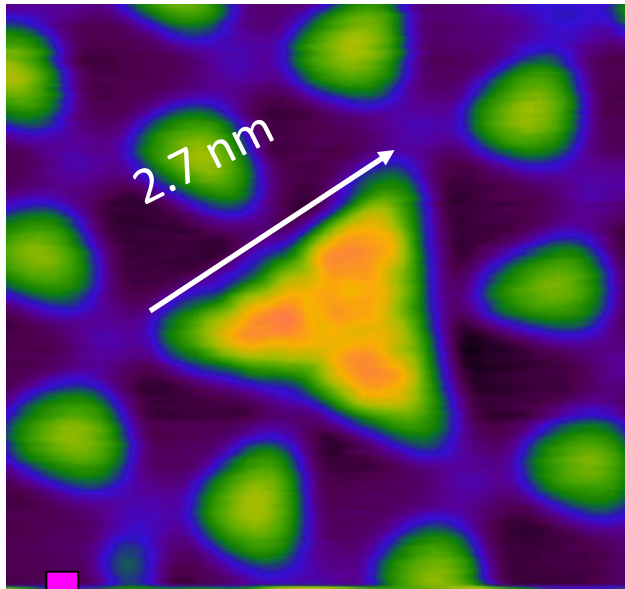
Nature Communcations, 8;3:823.(2012)

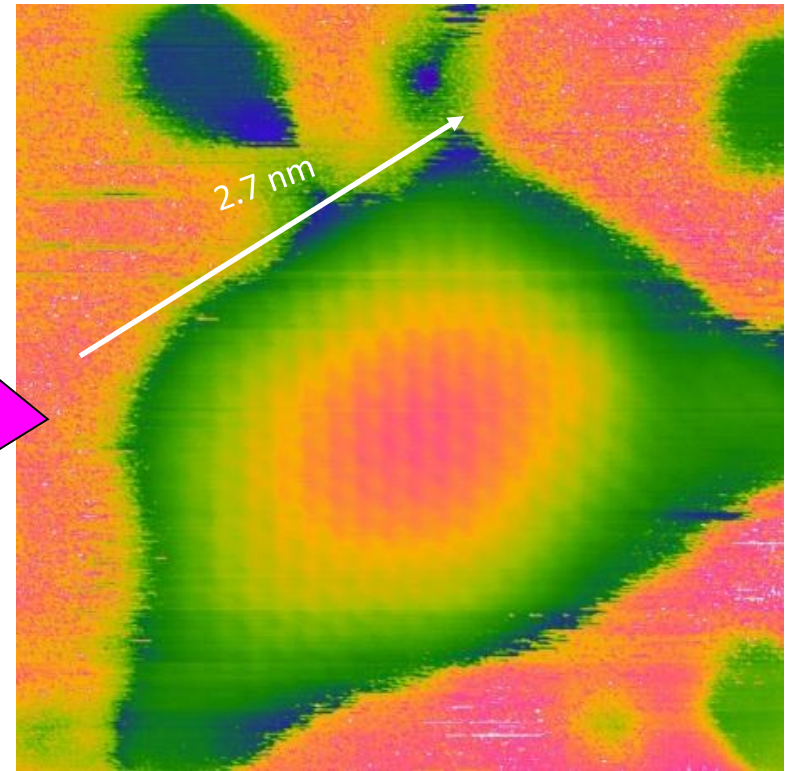
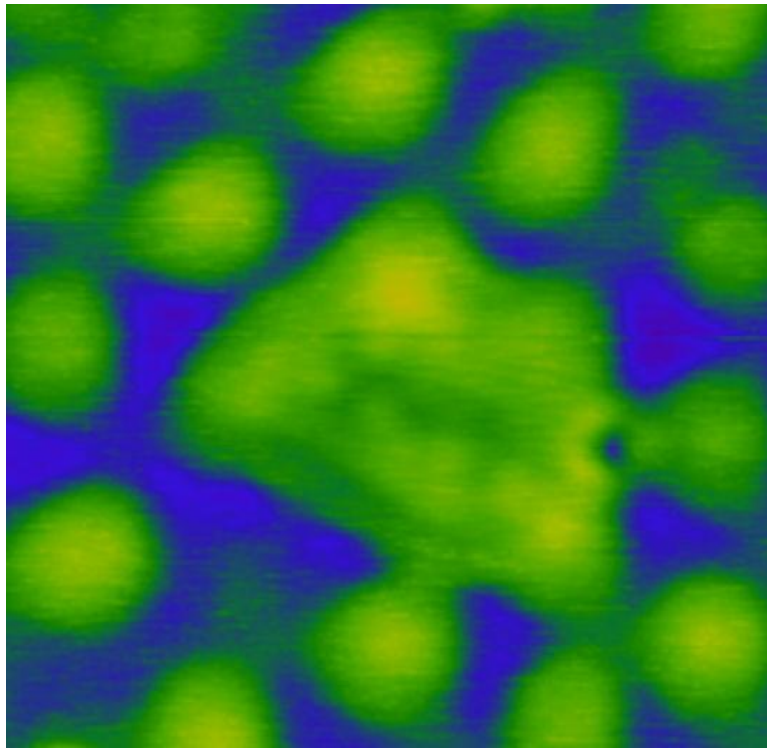
Bubbles appear on site that has defective Moire pattern, and these can be seeded by Ion Beam Irradiation



Transforming Graphene Moire Blisters into Geometric Nanobubbles

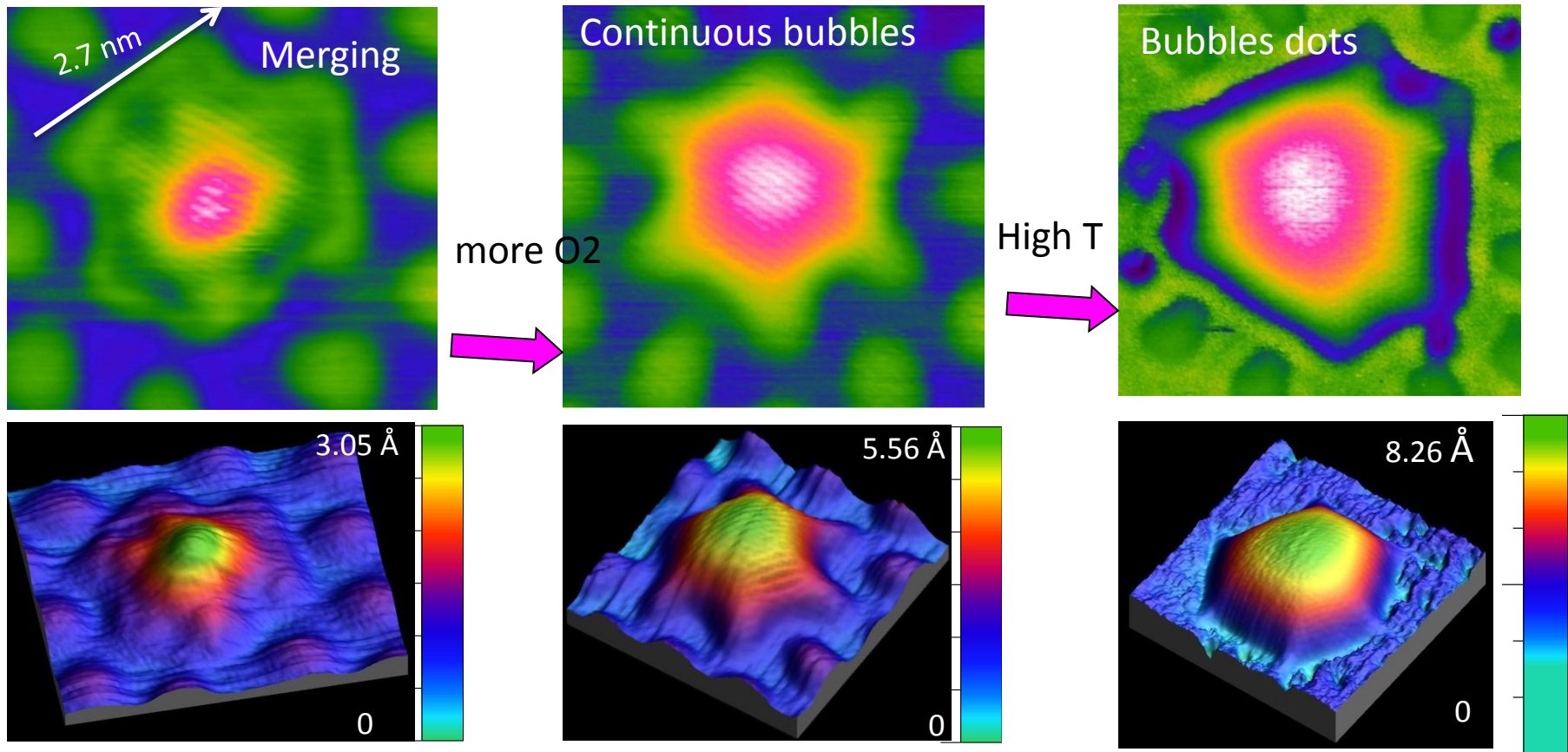
Jiong Lu, Antonion C. Neto, Kian Ping Loh*,
Nature Communcations, 8;3:823.(2012)





Decouple graphene and
merging of 5 blisters

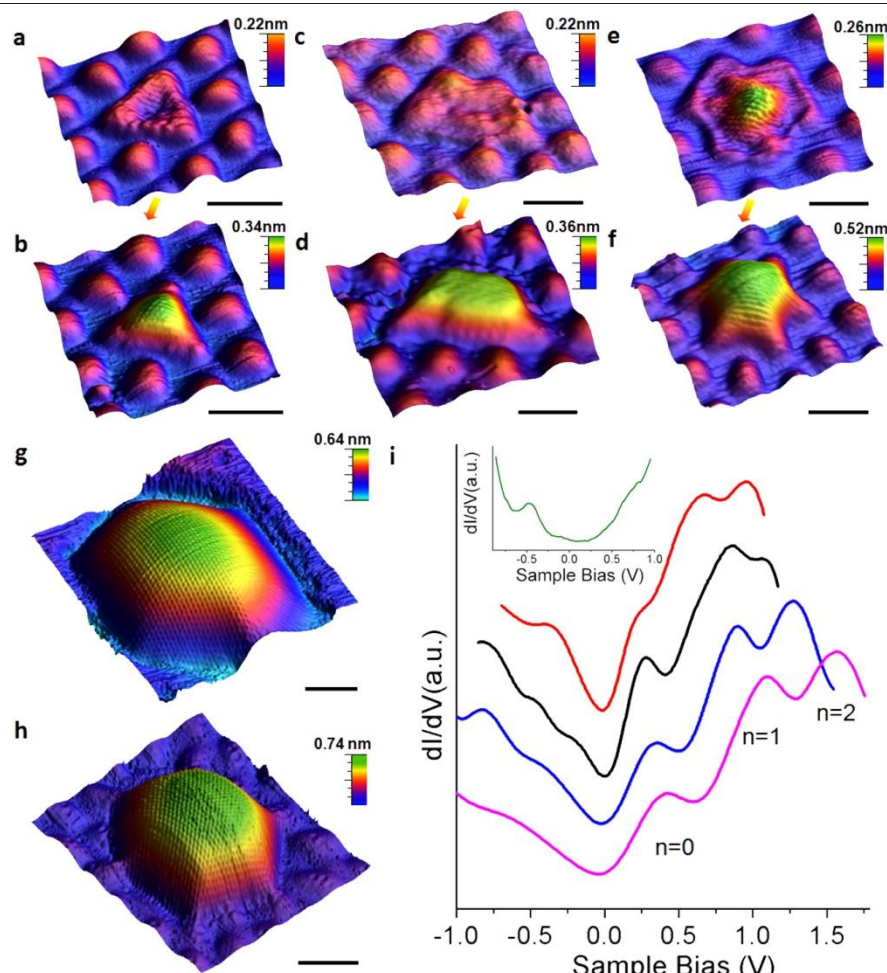
Merging of 7 blisters to form hexagonal bubbles



STS: More-like free-standing graphene

Transforming Graphene Moire Blisters into Geometric Nanobubbles,
Jiong Lu, Antonion C. Neto, Kian Ping Loh*,
Nature Communcations, 8;3:823.(2012)

Sintering the Moire Blisters to Make Geometrically well defined Graphene Bubbles With Giant Pseudomagnetic Field



$$E_n = \text{sgn}(n) \sqrt{2e\hbar v_F^2 |n| B_s + E_{Dirac}} \quad n = 0, \pm 1, \pm 2 \dots \dots (1)$$

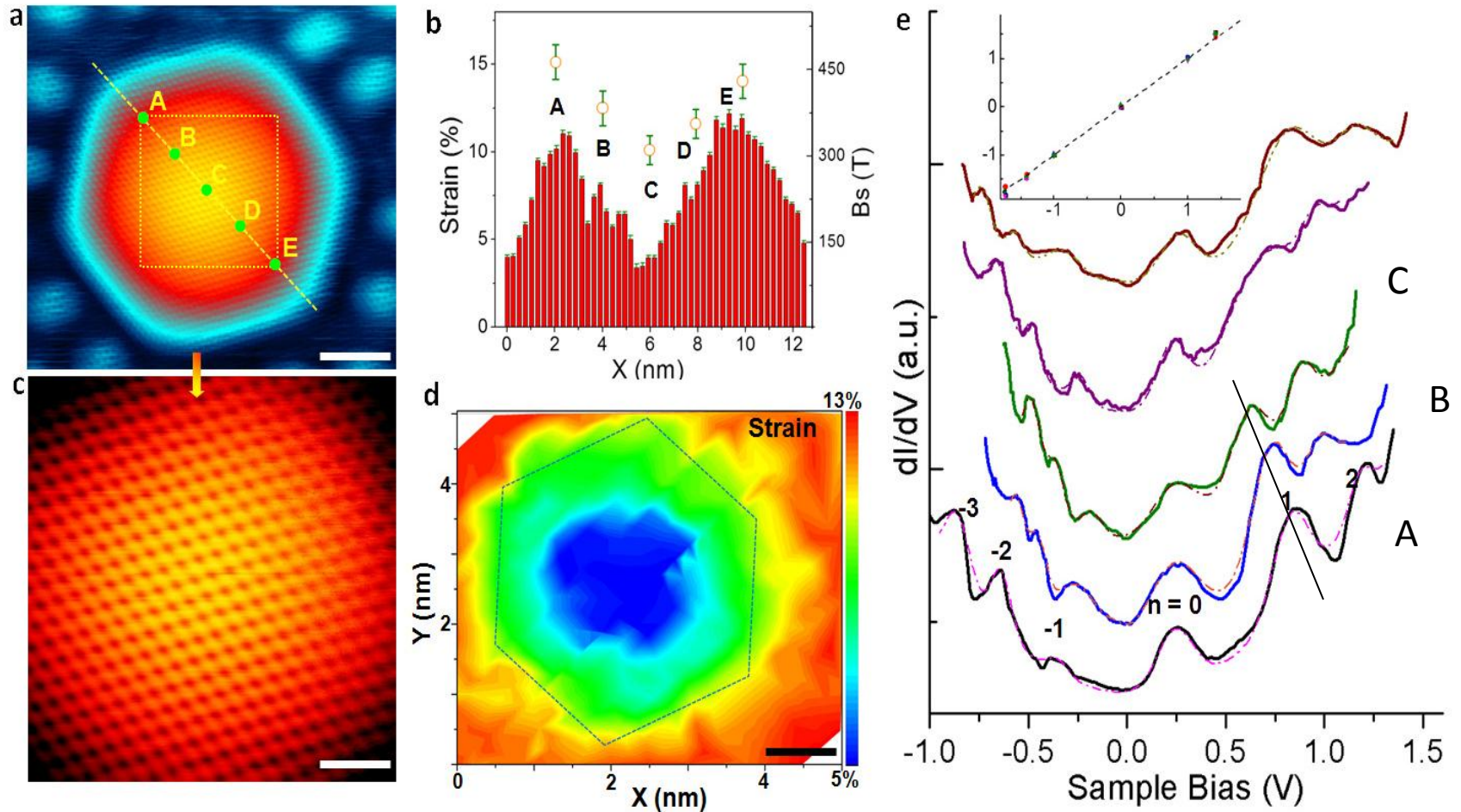
the LL energy expected in graphene scales according to $E/B^{1/2}$

pseudo-magnetic fields as large as 650 T and electronic gaps of order of 0.8 eV.

The electronic gaps associated with these pseudo-magnetic fields are of the order $\Delta E(\text{eV}) \approx 0.03 [B(\text{T})]^{1/2}$ and hence they vary from 0.3 eV to 0.8 eV

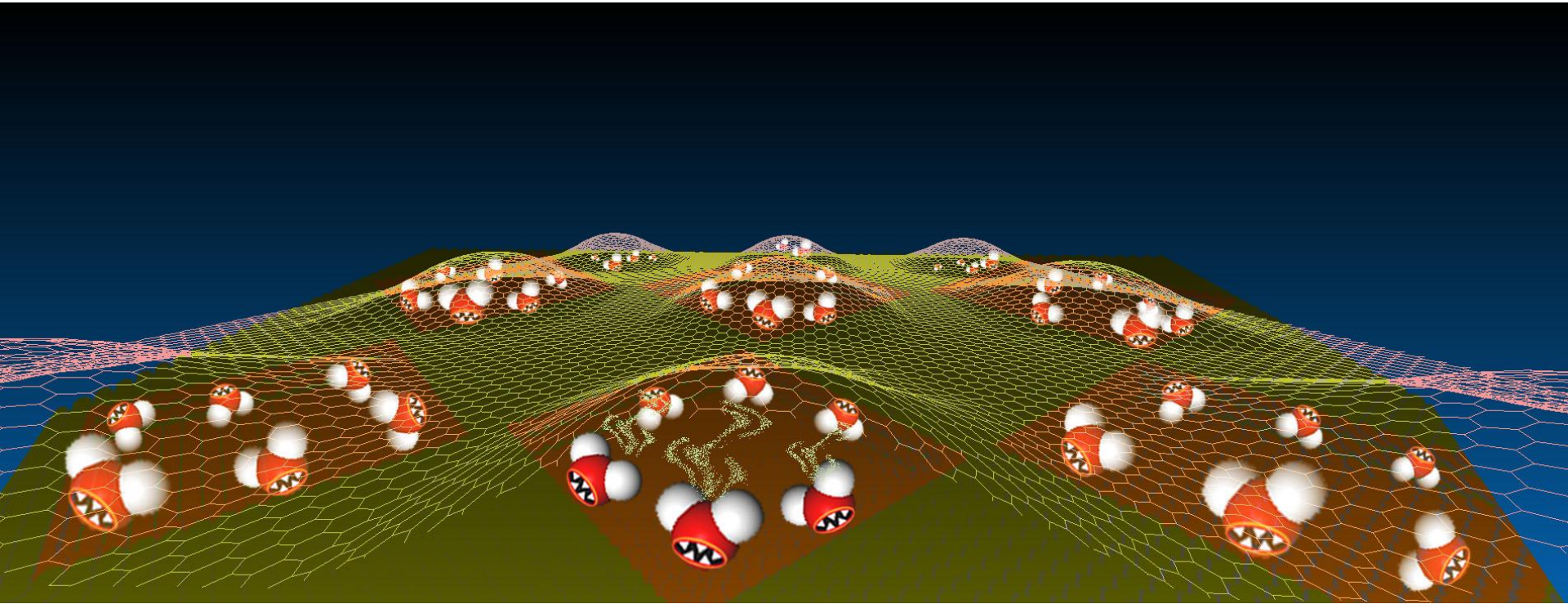
Strain field higher at the edges of graphene bubble versus the center

This results in shifts of the Landau level peaks in the STS curves towards higher energies for regions of bubbles near the edges

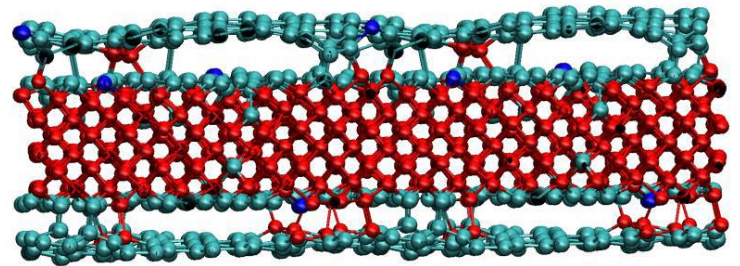
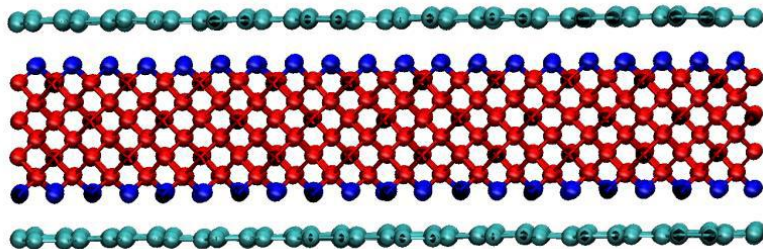


3. Observing Chemistry Inside Graphene Nanobubbles

A hydrothermal anvil made of graphene bubbles ?

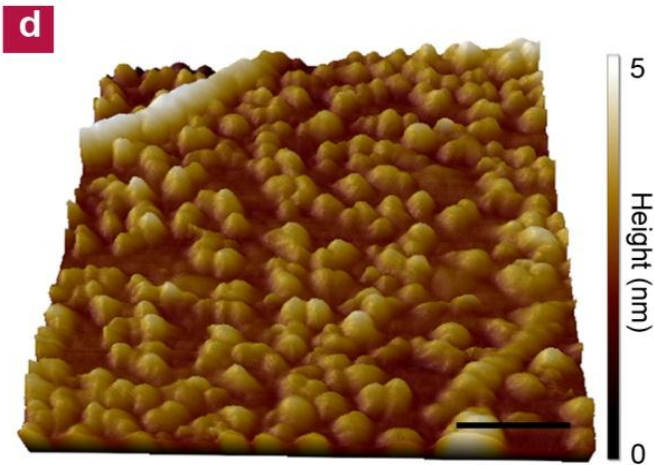
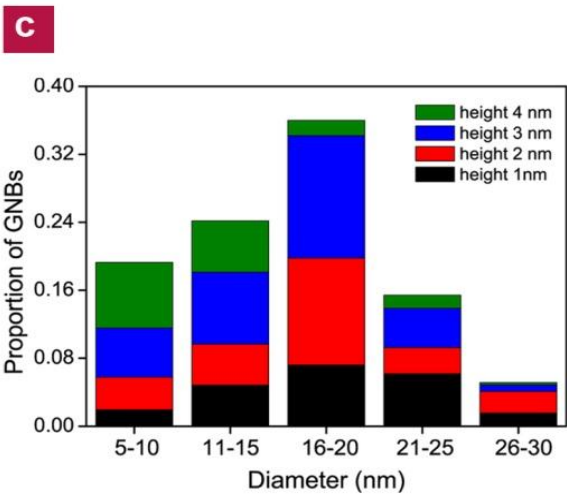
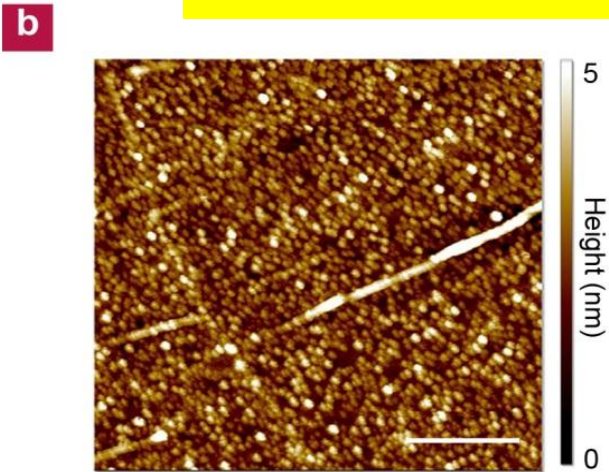
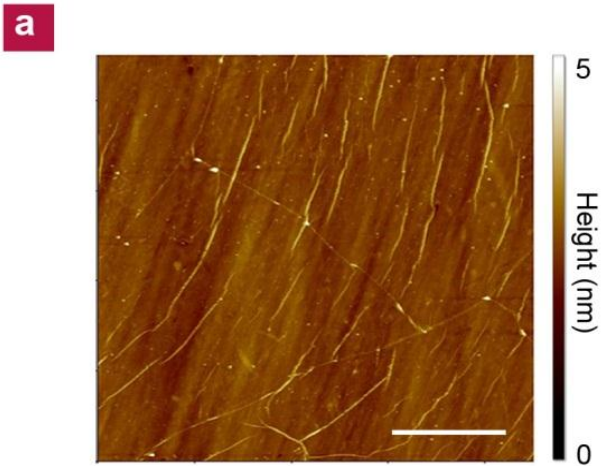


No clear insight into how graphene interfaces with diamond



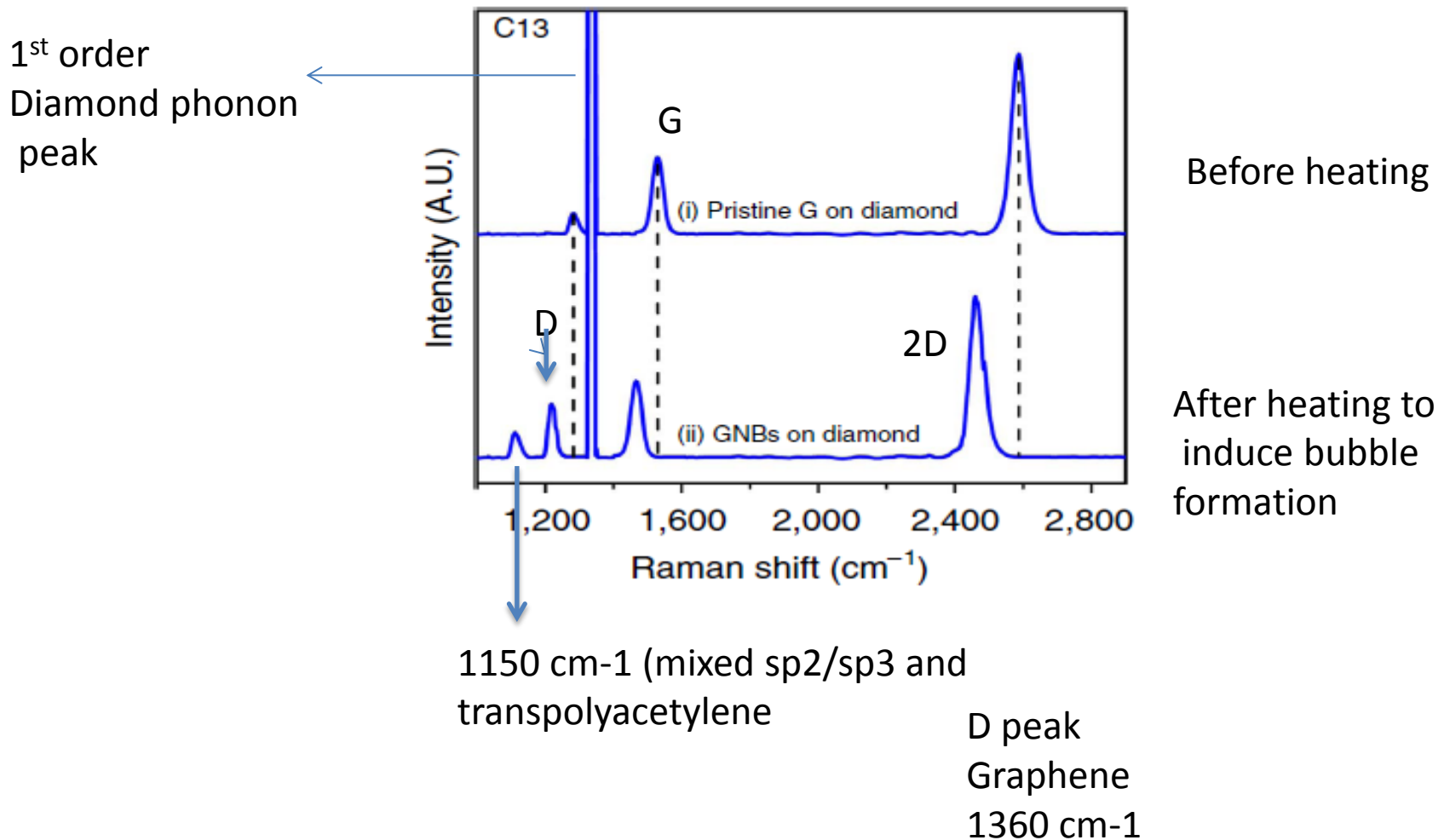
GRAPHENE NANOBUBBLE MAT FORMED ON DIAMOND

A hydrothermal Anvil made of Graphene nanobubbles on diamond
Candy Su, Kian Ping Loh*
Nature Communications 4, 1556, (2013)



The pressure that is built up in a typical Graphene nanobubble of 2 nm in height and 10 nm in radius is calculated to be approximately 1 GPa

Red shift upon the formation of bubbles - These observations suggest that the lattice of graphene is biaxially strained



Graphene Bubbles are electrochemically more active than flat surface !!

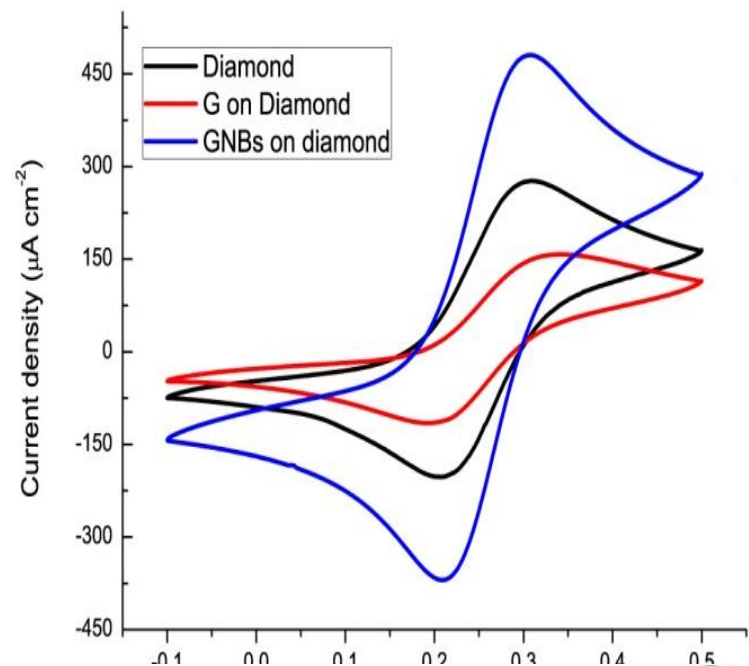


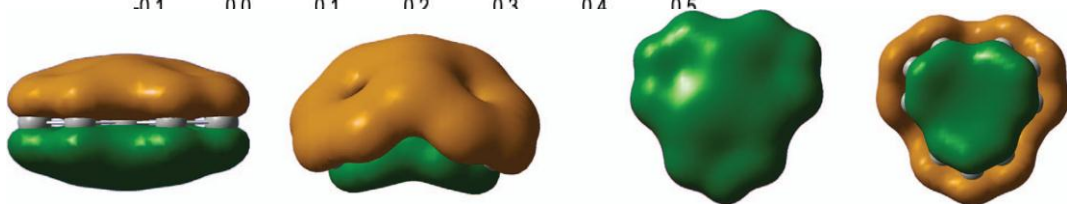
Table 1 | Calculated apparent heterogeneous electron-transfer rate constants and capacitances.

Electrode	ΔE_p (mV)	Rate constant k (cm s^{-1})	Capacitance at 0.3 V ($\mu\text{F cm}^{-2}$)
Diamond	105	0.0740	207.7
G on diamond	146	0.00277	34.27
GNBs on diamond	89	0.0909	397.4

GNBs on diamond > Diamond > flat G on diamond

Cyclic voltammetry of $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple

- Inner sphere redox couple , sensitive to density of electronic states and surface microstructure
- Charge transfer rate calculated follows the order of



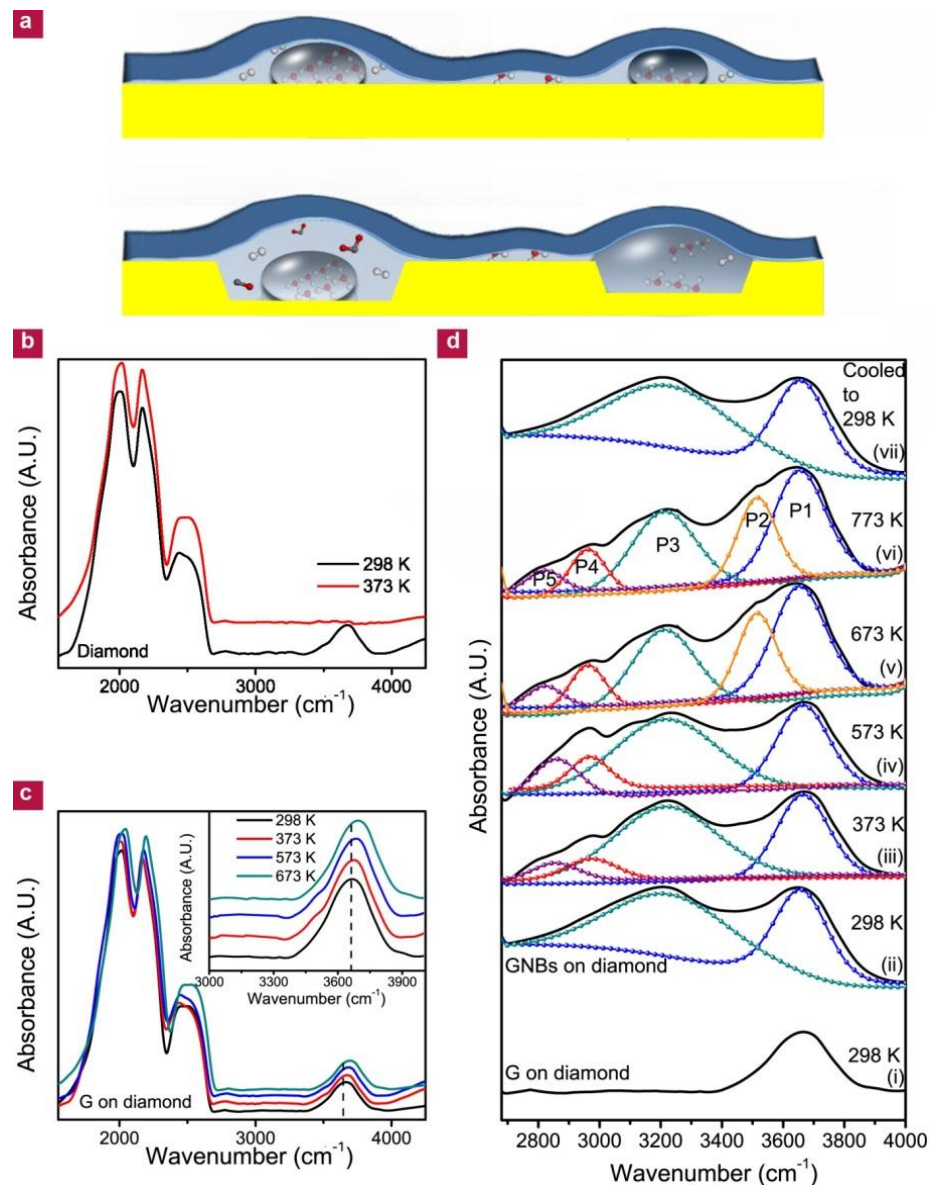
Outward rotation of orbitals enhances local density of states and bestows higher reactivity on the outer surface of the GNB, however Inner surface is less reactive

p_z orbital isosurface wavefunction of flat and curved graphene calculated using density functional theory (DFT, at B3LYP/6-31G*).

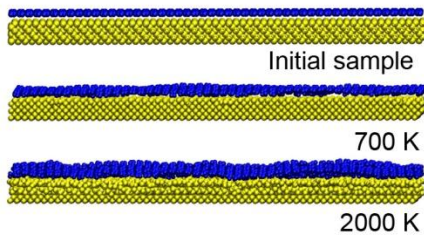
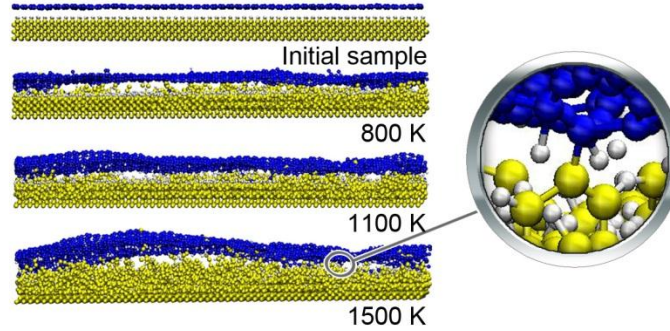
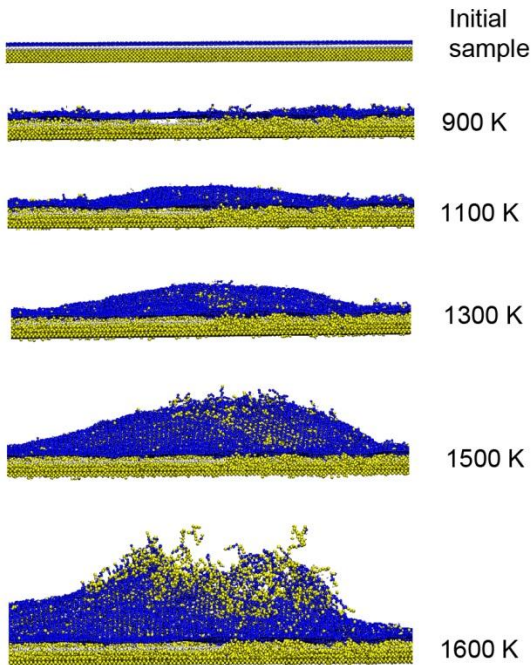
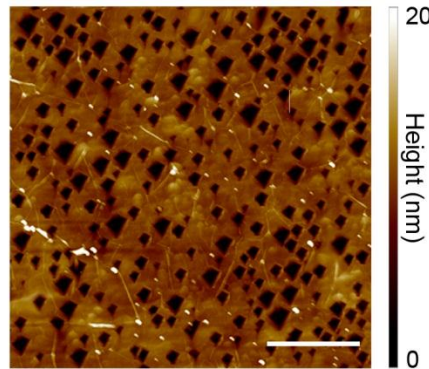
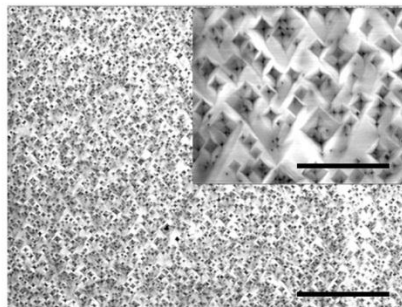
Probing the bonding dynamics of water trapped within Graphene nanobubbles using FTIR: Bench top hydrothermal anvil cell

The critical temperature of water is 647 K, 2 MPa

A hydrothermal Anvil made of Graphene nanobubbles on diamond
 Candy Su, Kian Ping Loh*
Nature Communications 4, 1556, (2013)



Strong hydrogen bonding results in a weakening of the OH oscillator, a red shift in energy and a broadening of the spectral peak.

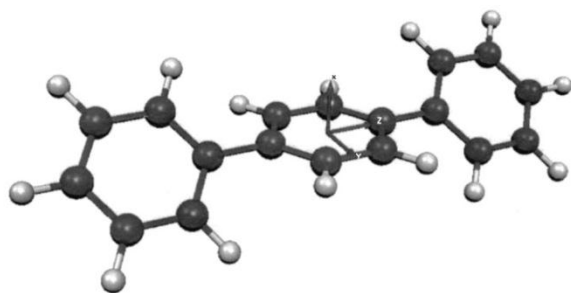
a**b****c****d****e**

**DIAMOND CAN BE
CORRODED
BY SUPERHEATED
WATER !**

A significantly reduced dielectric constant of supercritical water allows it to act as an aggressive solvent for organic material

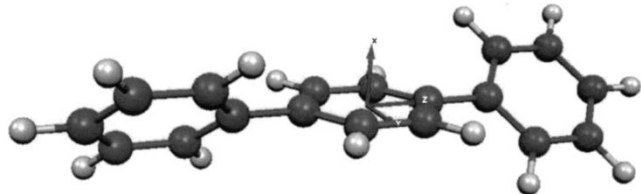
The pressure that is built up in a graphene nanobubble 2 nm in height and 10 nm in radius is calculated to be approximately 1 GPa

Calibrating the pressure inside the bubbles using pressure sensing molecules



C_{2h}

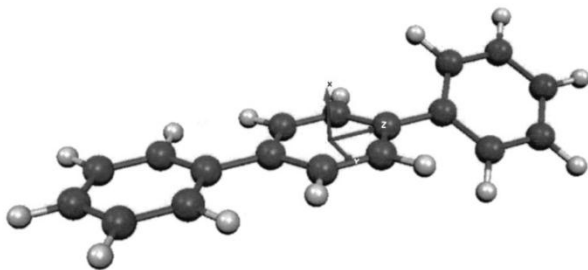
IR-active modes in polyphenyl molecules that become inactive upon the phase transition from the twisted to the planar conformation.



D_2

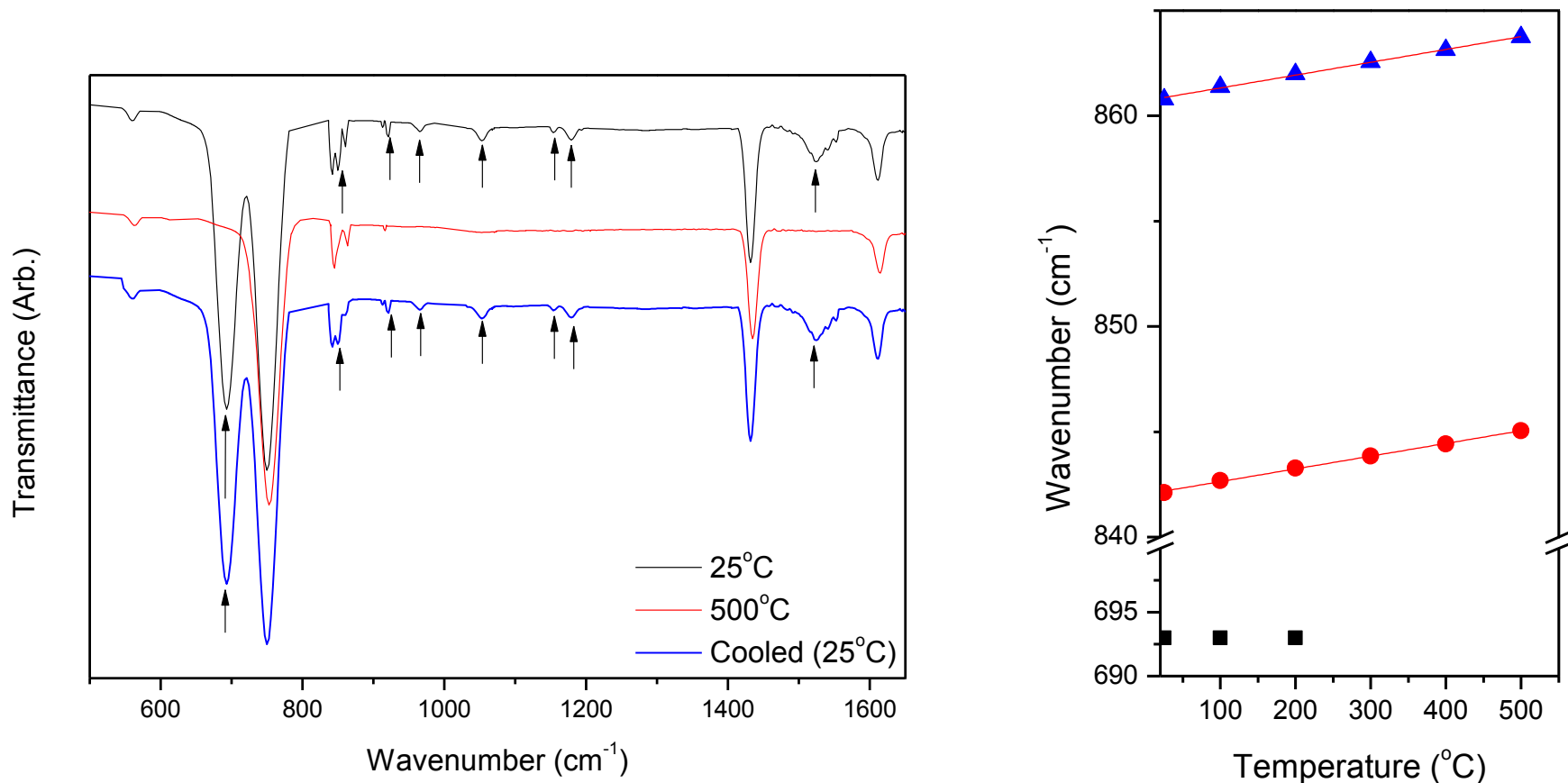
Upon planarization, certain IR-active peaks become IR-forbidden.

We would expect to see 6 modes disappear from the spectrum if *p-terphenyl* belongs to the C_{2h} group, 29 modes if it belongs to the D_2 group, and 51 modes if the molecule has C_2 symmetry. These “disappearing peaks” comprise a special subset of vibrational modes



C_2

Monitoring the vanishing of out-of-plane vibrational modes in P-Terphenyl: “ pressure induced flattening of the molecules”

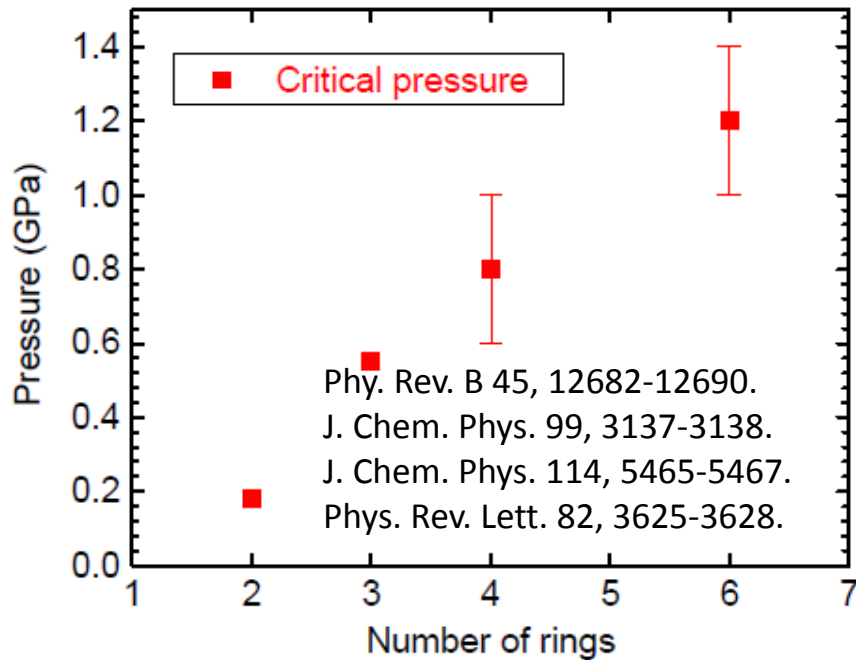


Similarly, by increasing the temperature, certain out-of-plane modes of p-terphenyl were found to disappear. These peaks are indicated by arrows.

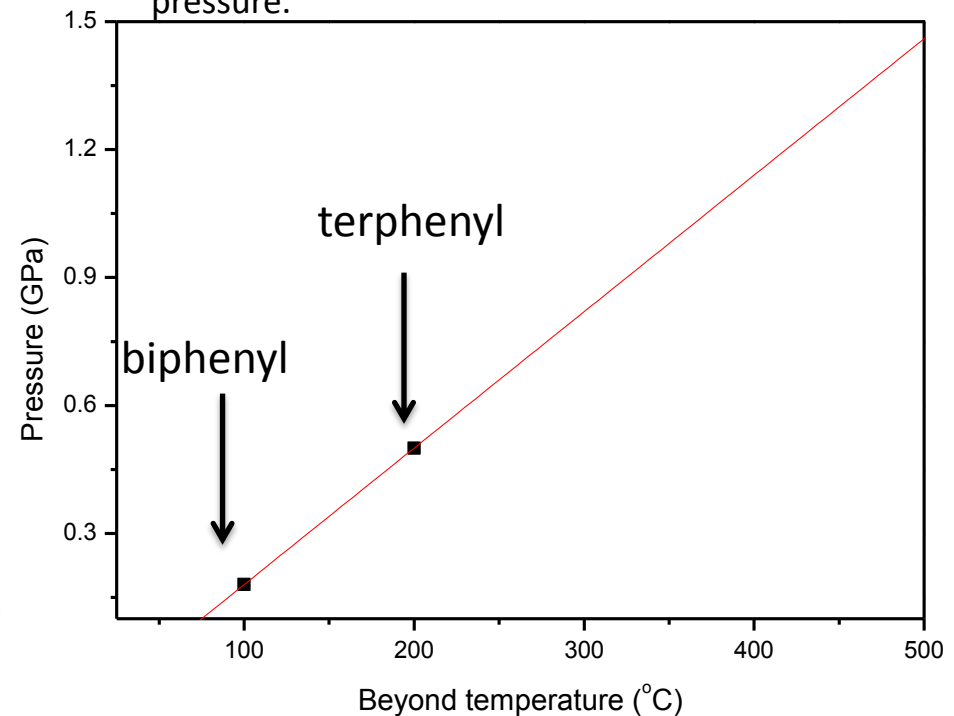
The recovery of these peaks are also observed upon cooling of the sample.

What is the pressure in Graphene Nanobubbles?

Graph plotted based on values that has been reported

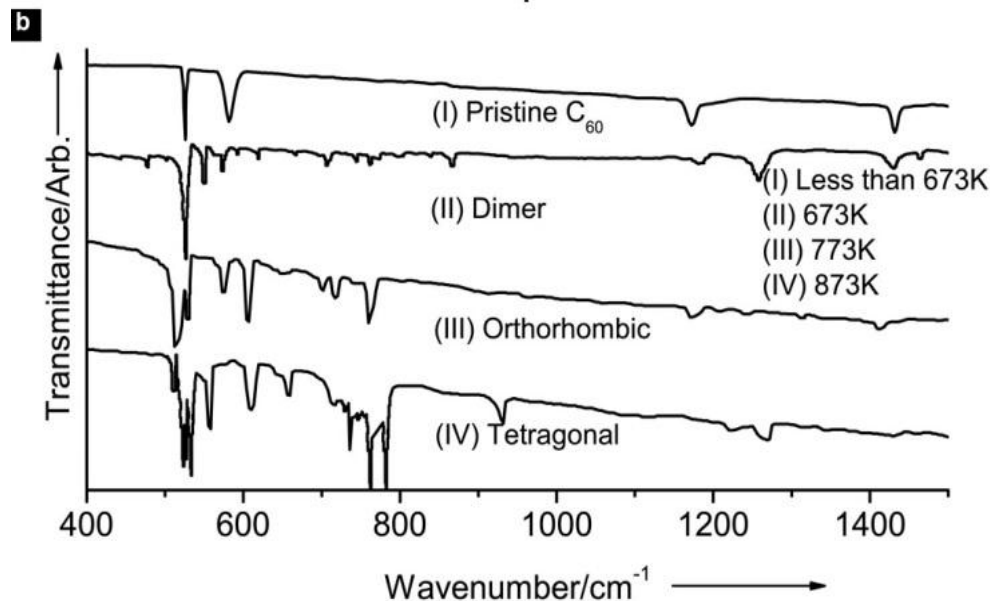
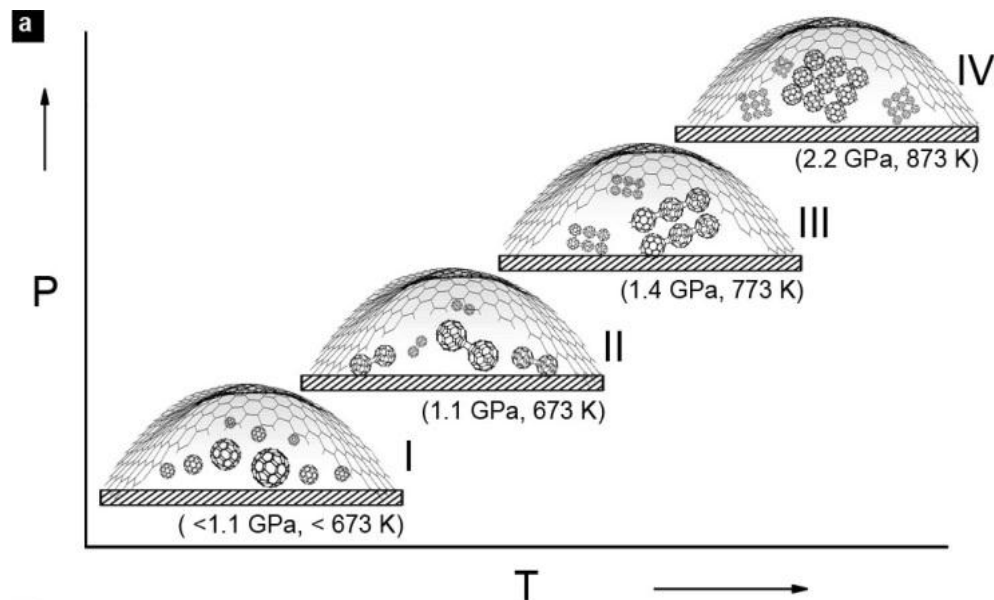


Based on our experiments and with reference from previously reported values, we could draw a correlation between temperature and pressure.



Using this relationship that we derive, we can heat the sample with C60 and determine the pressure at which it undergoes polymerization.

Oligomerization/Polymerization of Fullerene: Pressure-driven [2+2] Cycloaddition



[2+2] cycloaddition of C₆₀ is symmetry forbidden due to mismatch of MOs.

- Molecular C₆₀: 4 sharp IR modes
- Intermolecular bonding (lowers symmetry) changes vibrational spectra drastically
- Phase transformation of C₆₀ in GNB under different stages of polymerization

Angewandte Chemie
Candy Lim, Kian Ping Loh*
(Accepted) 2013

4. Technological Implications of Graphene Nanobubbles

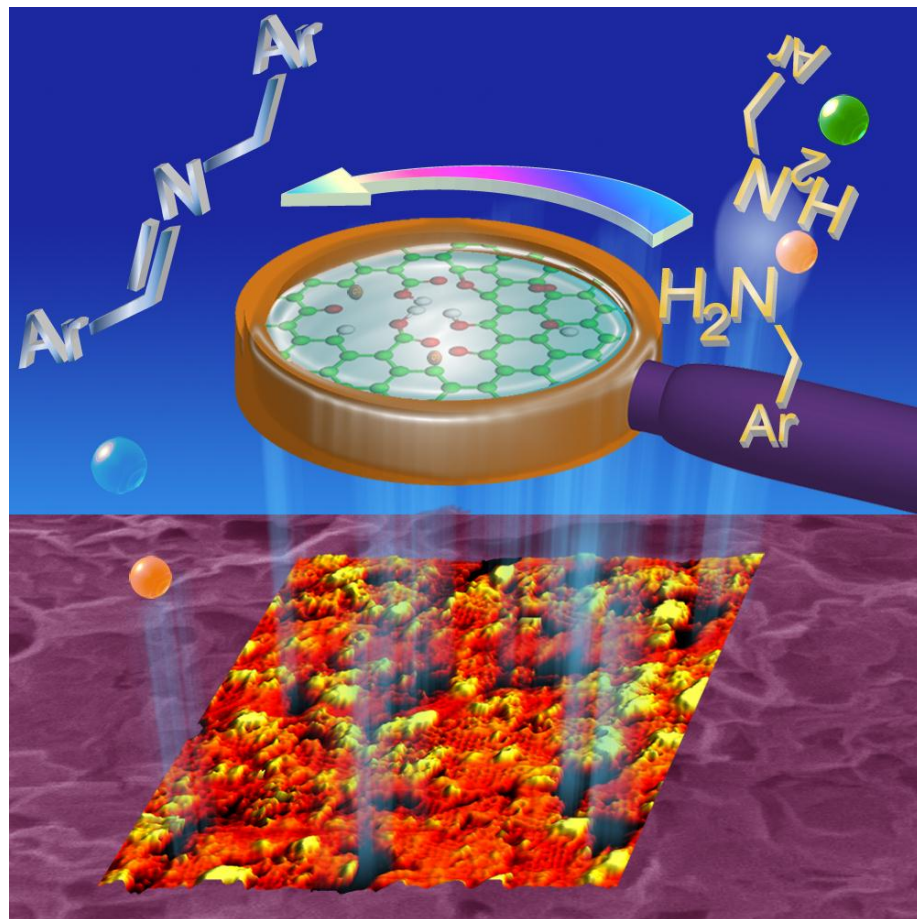
(a) Optical effects

(b) Surface Tension effects

Part II

- **Porous Graphene Oxide**
- Highly defective relative to CVD graphene/mechanically exfoliated graphene

Our Study-Part I: GO as a carbocatalyst

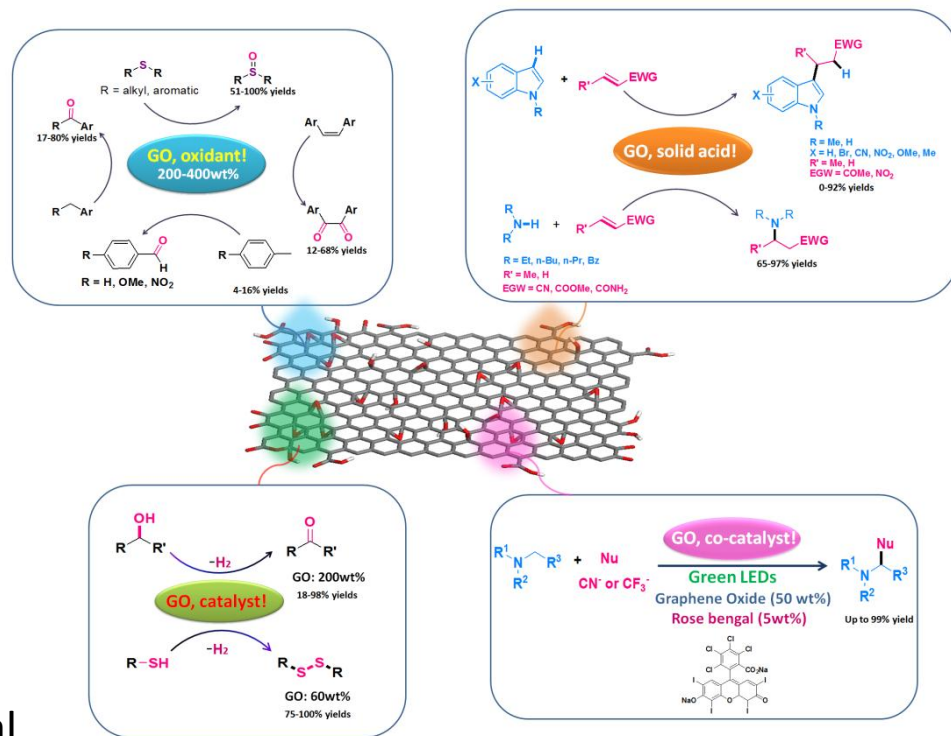
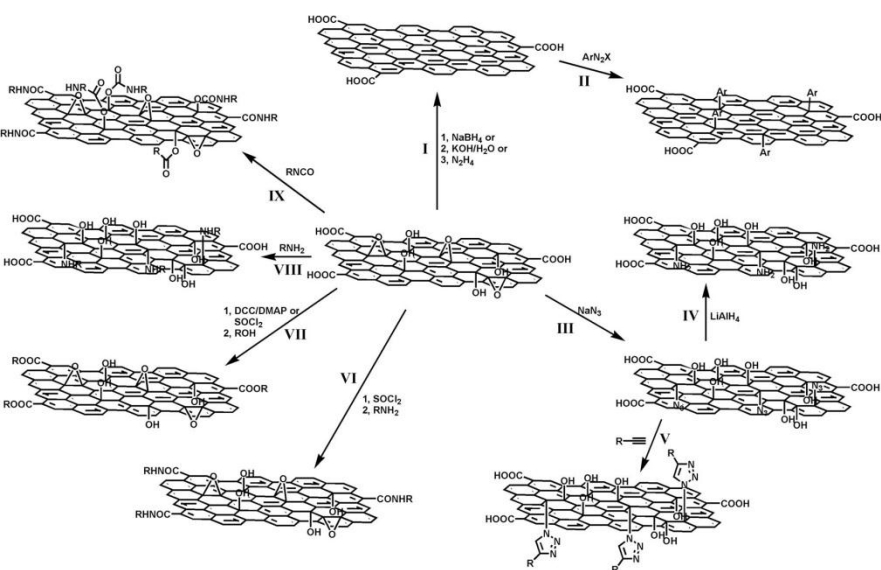


Probing the Catalytic Activity
of Graphene Oxide and its origin,
Chen Liang Su and Kian Ping Loh* et. al.,
Nature Communications, 3, 1298 (2012)

 to improve its catalytic efficiency

 Study its catalytic origin

GRAPHENE OXIDE MEDIATES MULTIPLE SYNTHETIC TRANSFORMATION



K. P. Loh. Angewandte Chemie International Edition, 49 (37), 2010, pp 6549

K. P. Loh JACS, 2010, 132, 41, pg 14481

K. P. Loh JACS., 2011, 133 (23), pp 8888

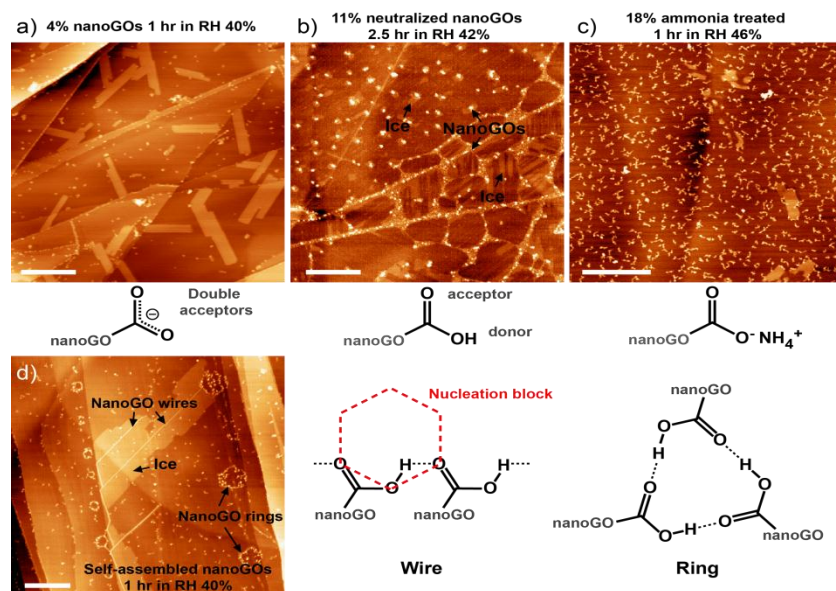
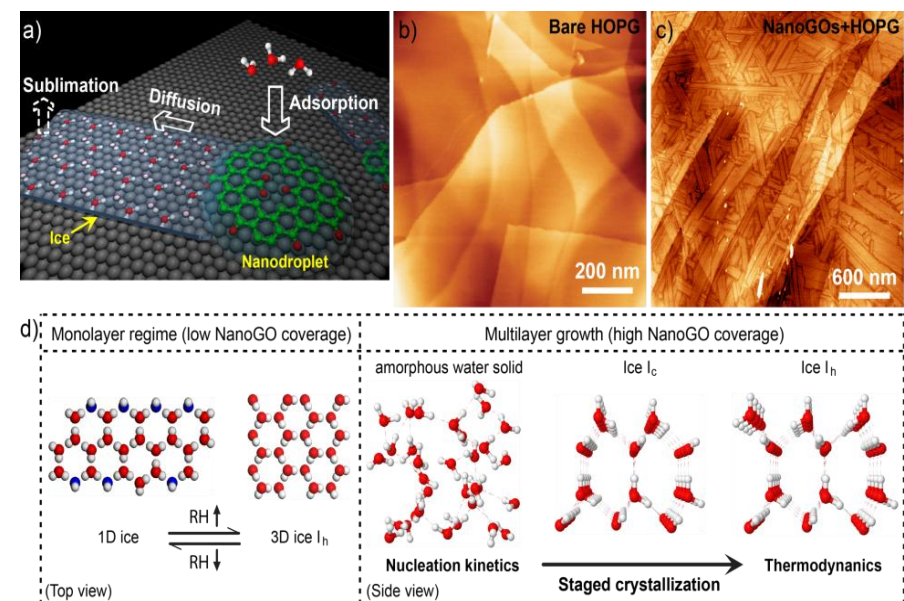
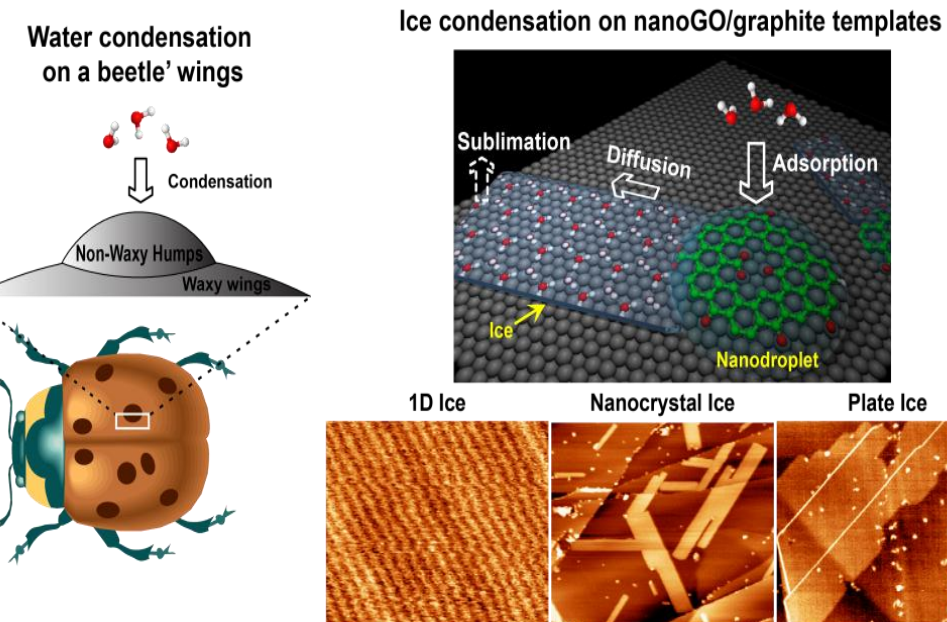
K. P. Loh JACS., 2009, 131 (46), pp 16832

K. P. Loh JACS., 2010, 132 (32), pp 10976

K. P. Loh JACS., 2008, 130 (44), pp 14392

K. P. Loh JACS., 2012, DOI: 10.1021/ja211433h

K. P. Loh, Nature Chemistry 2, 12, 1015 (2011)

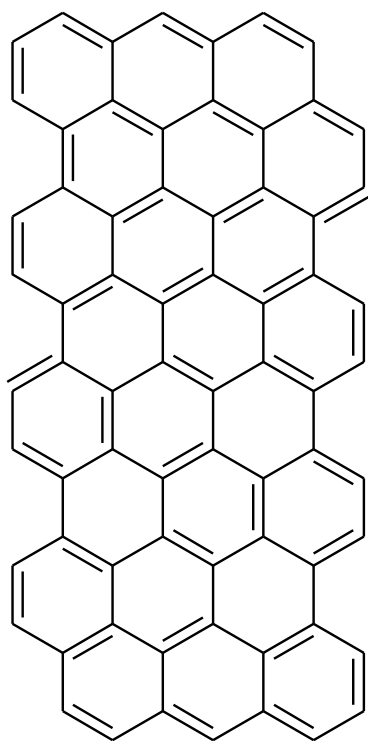


Seeding Ice Growth At Room temperature Using Nano Graphene Oxide

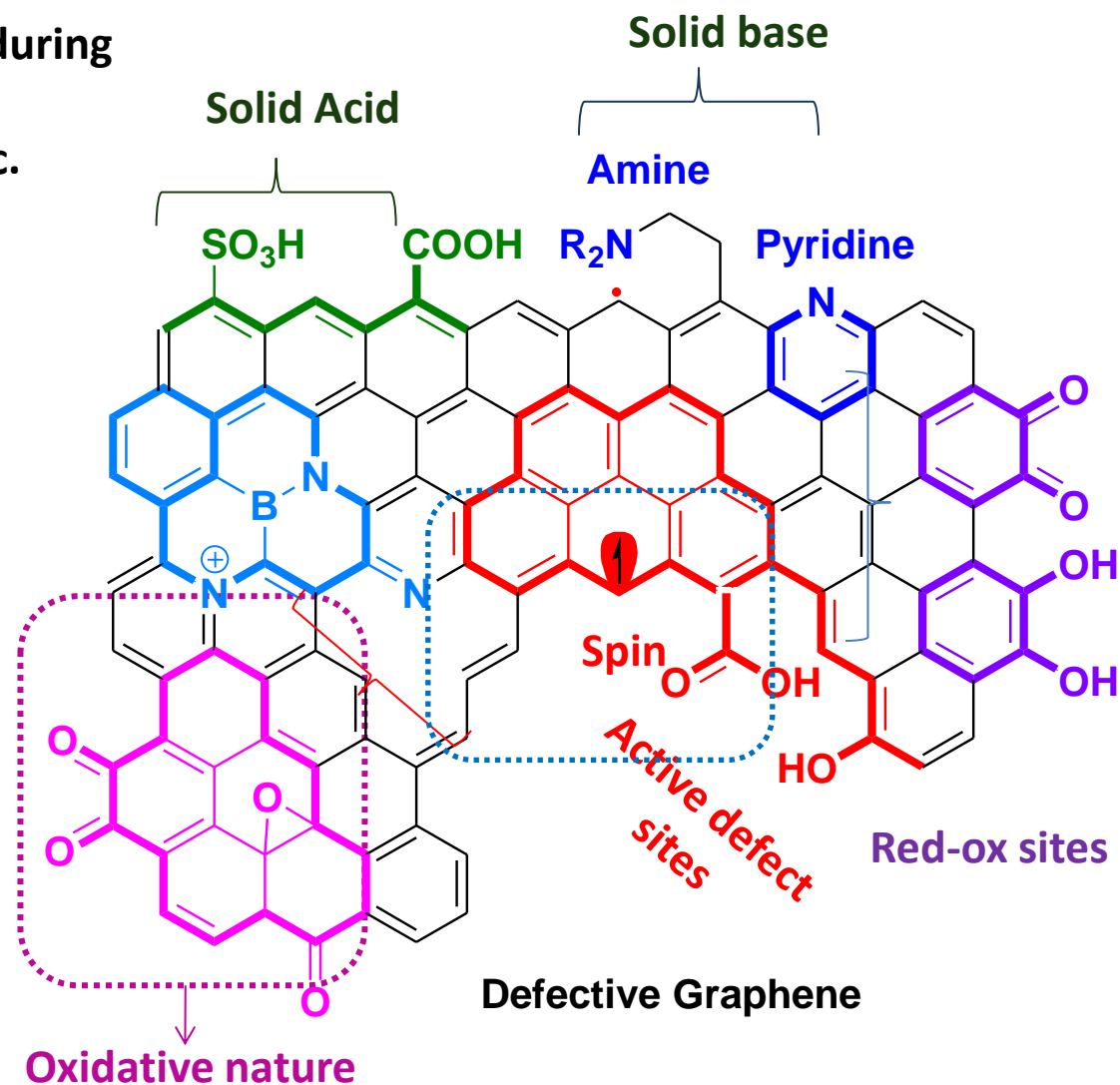
Zheng Yi and K. P. Loh
Angewandte Chemie 2013
[52, Issue 33](#), 8708–8712

Hot spots for catalytic action!

These complex cocktails of functionalities may act in concert during catalysis *via* hydrogen bonding, ionic complexation, radical stabilization etc.



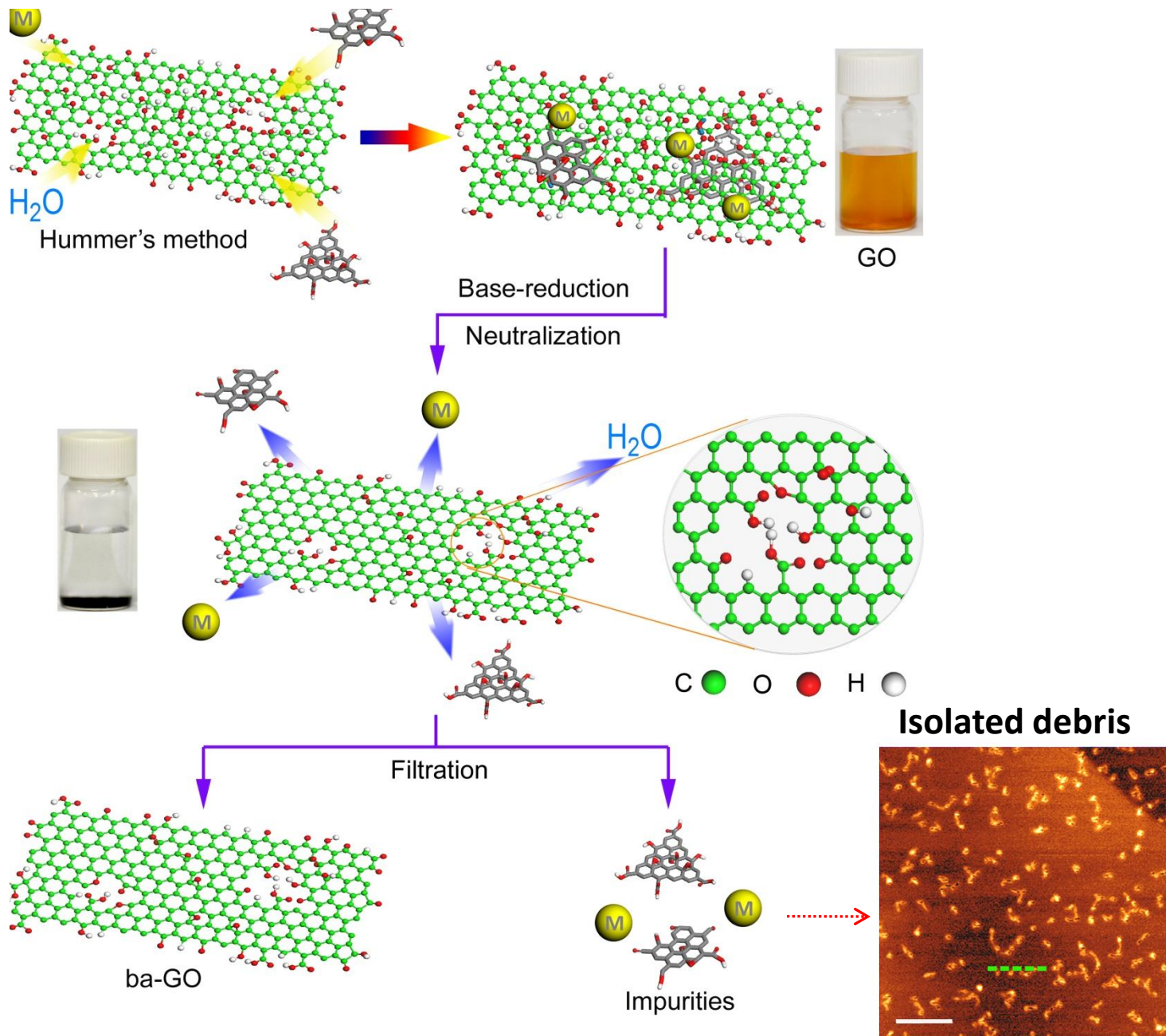
Perfect Graphene



Defective Graphene

All these “imperfections” help to mediate its catalytic properties!

Schematic representation of GO separation



Metal impurities were removed.

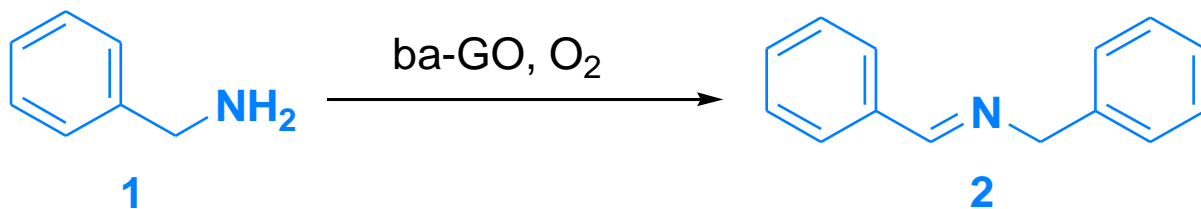
		Before	After
Element	Graphite	GO	ba-GO
Mn	45.085 ppm ^b	304.6516 ppm	< 1.0 ppm
Fe	1050.1785 ppm	204.2784 ppm	96.3118 ppm
Zn	94.8833 ppm	35.71 ppm	2.5735 ppm
Au	3.7233 ppm	1.8551 ppm	N. D.
Ru	N. D.	N. D.	N. D.

ICP-MS (Inductively Coupled Plasma-Mass Spectroscopy) Analysis of GO, Graphite and ba-GO.^a

^a20 mg sample was dissolved by 2 ml of mixture acid (HCl : HNO₃ = 3 : 1) and diluted to 10 ml by 5% DI water. ^bMetal/Sample = 1 µg/g.

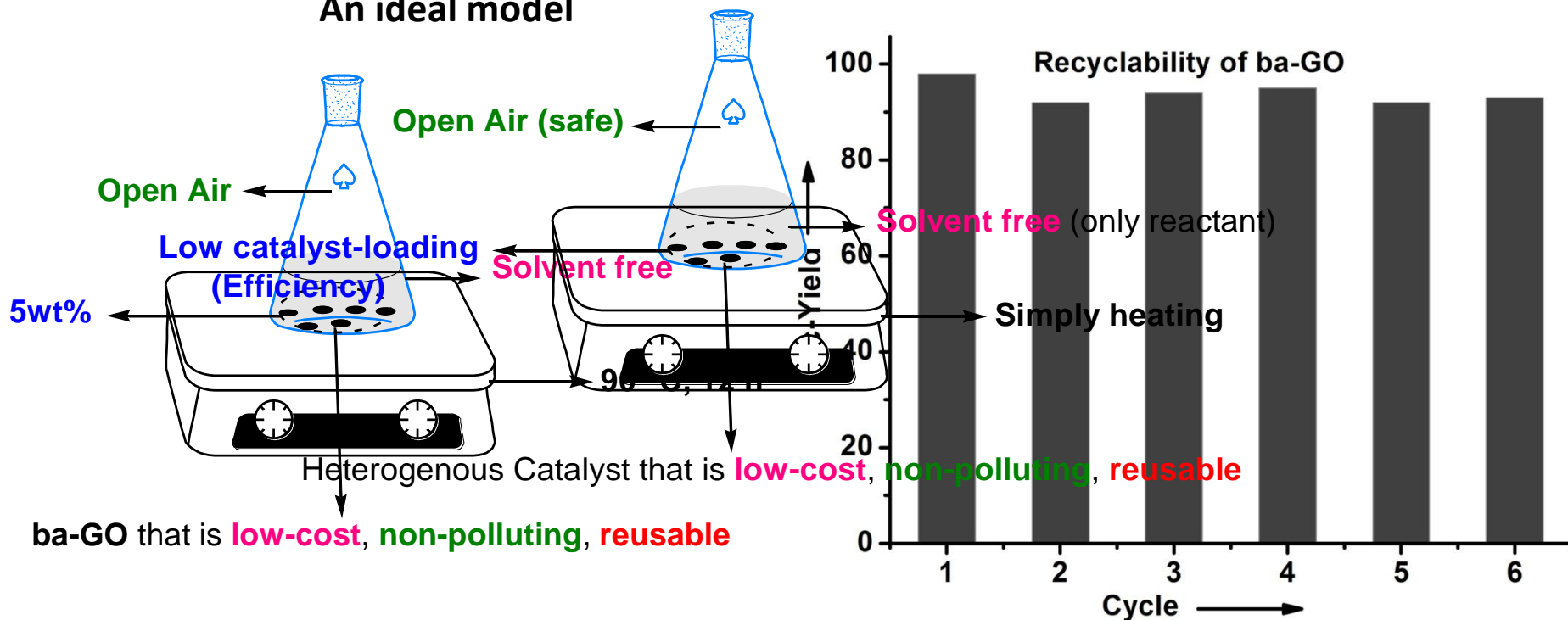
Realization of the ideal model!

Oxidative coupling of benzyl amine as the model reaction



N-Benzylbenzaldimines

An ideal model



Carbocatalyst

Vs

Gold catalyst

ba-GO

Active catalyst: ba-GO

Heterogeneous: self-support

Total catalyst loading: 5 wt%

Active catalyst loading: 5 wt%

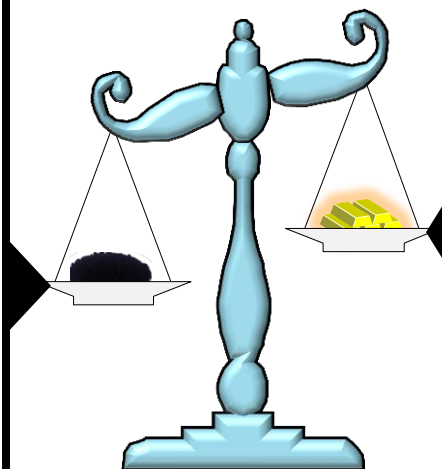
Price of GO/ba-GO: <1 \$/g

Reaction Temperature: 363 K

Oxidant: Open Air

Solvent free

6th reuse: 93% yield



Nano Au/C

Active catalyst: Au

Heterogeneous: carbon support

Total catalyst loading: ~250 wt%

Active catalyst loading: ~2 wt% Au

Price of bulk Au: >40\$/g

Reaction Temperature: 373 K

Oxidant: 5 bar O₂

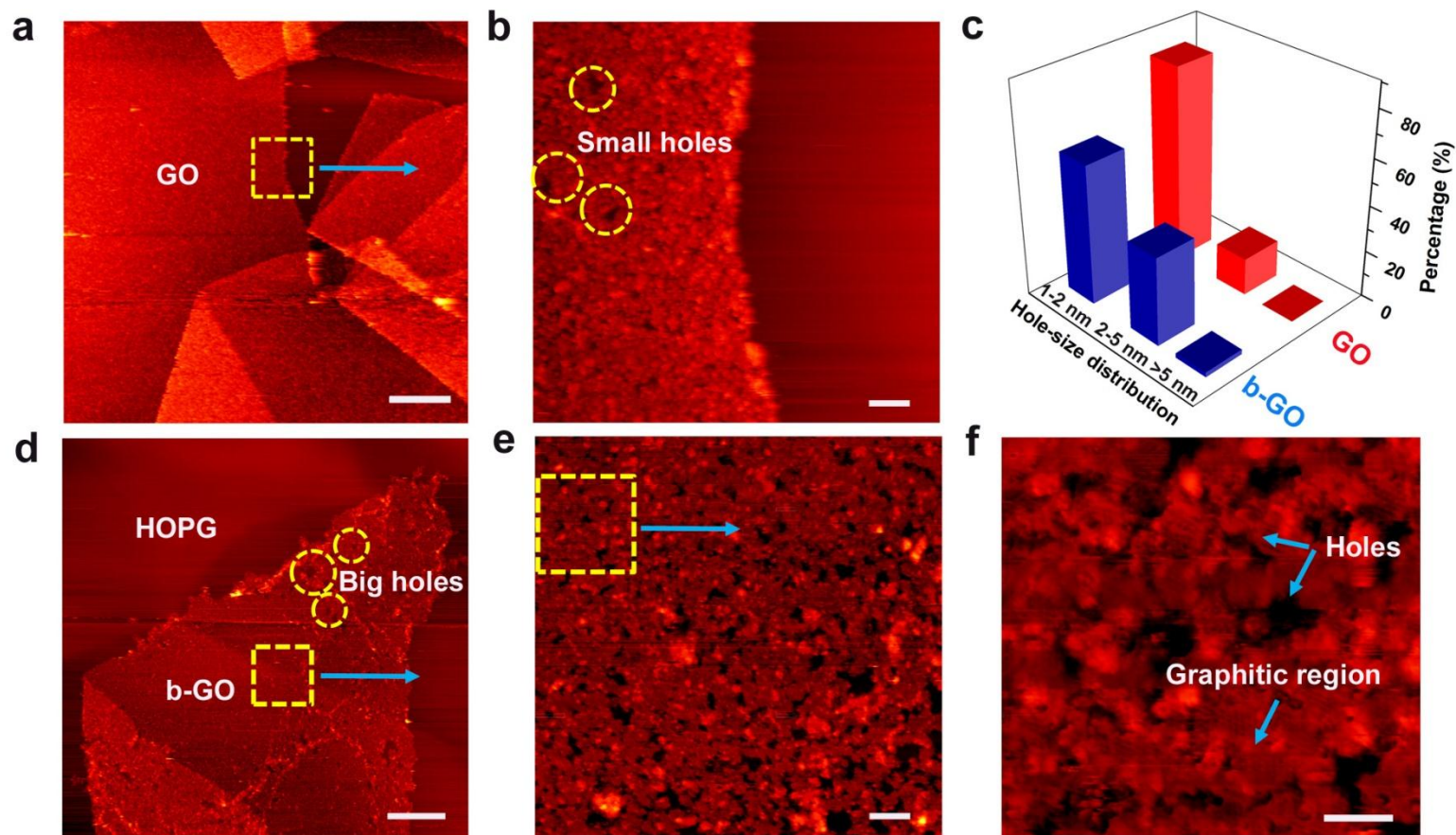
Solvent: PhMe

3rd reuse: 68% yield

Journal of catalysis, 2009, 138-144

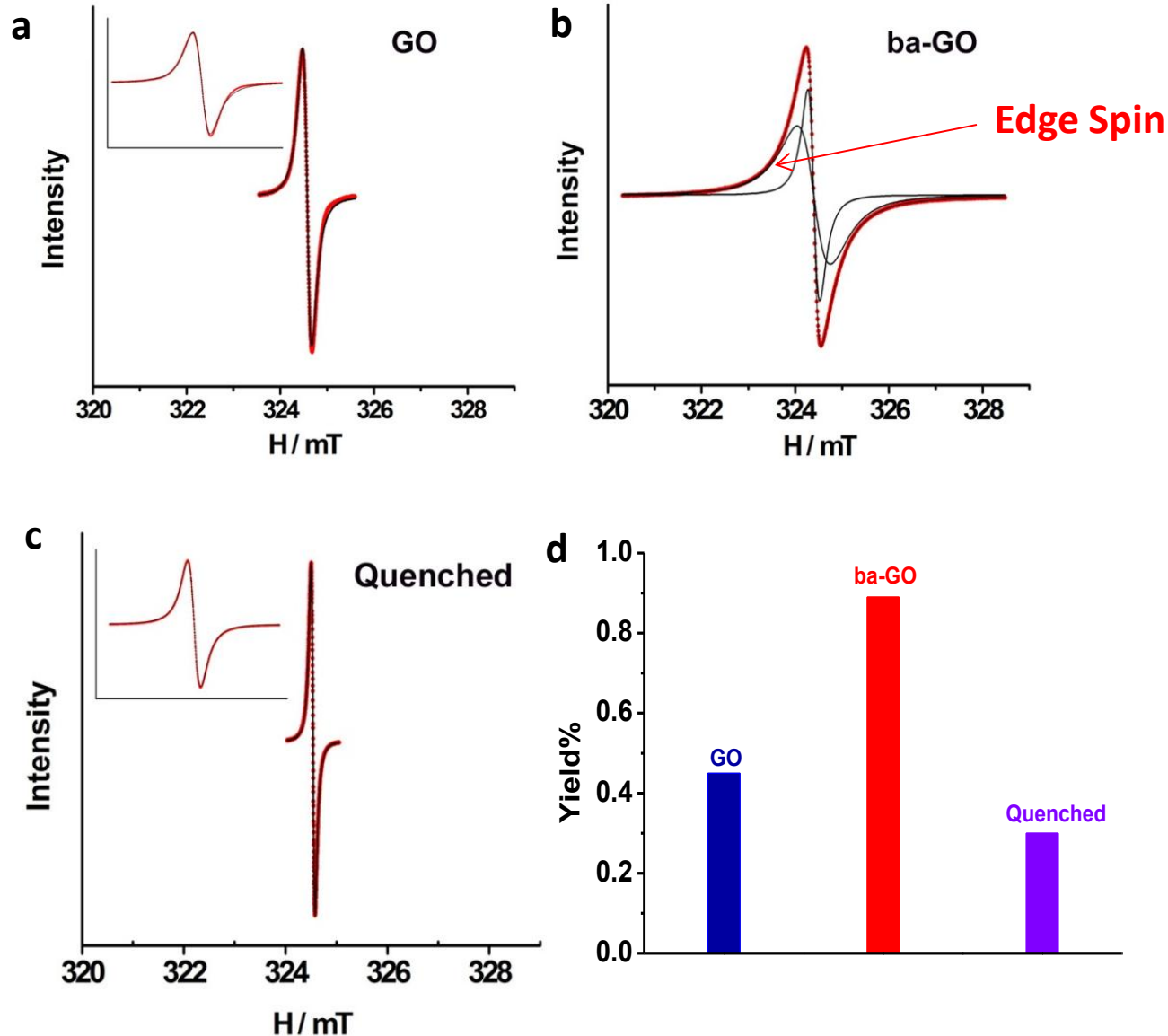
Therefore, this carbocatalyst can be an ideal replacement for metal catalyst.

The change of morphology before and after base treatment



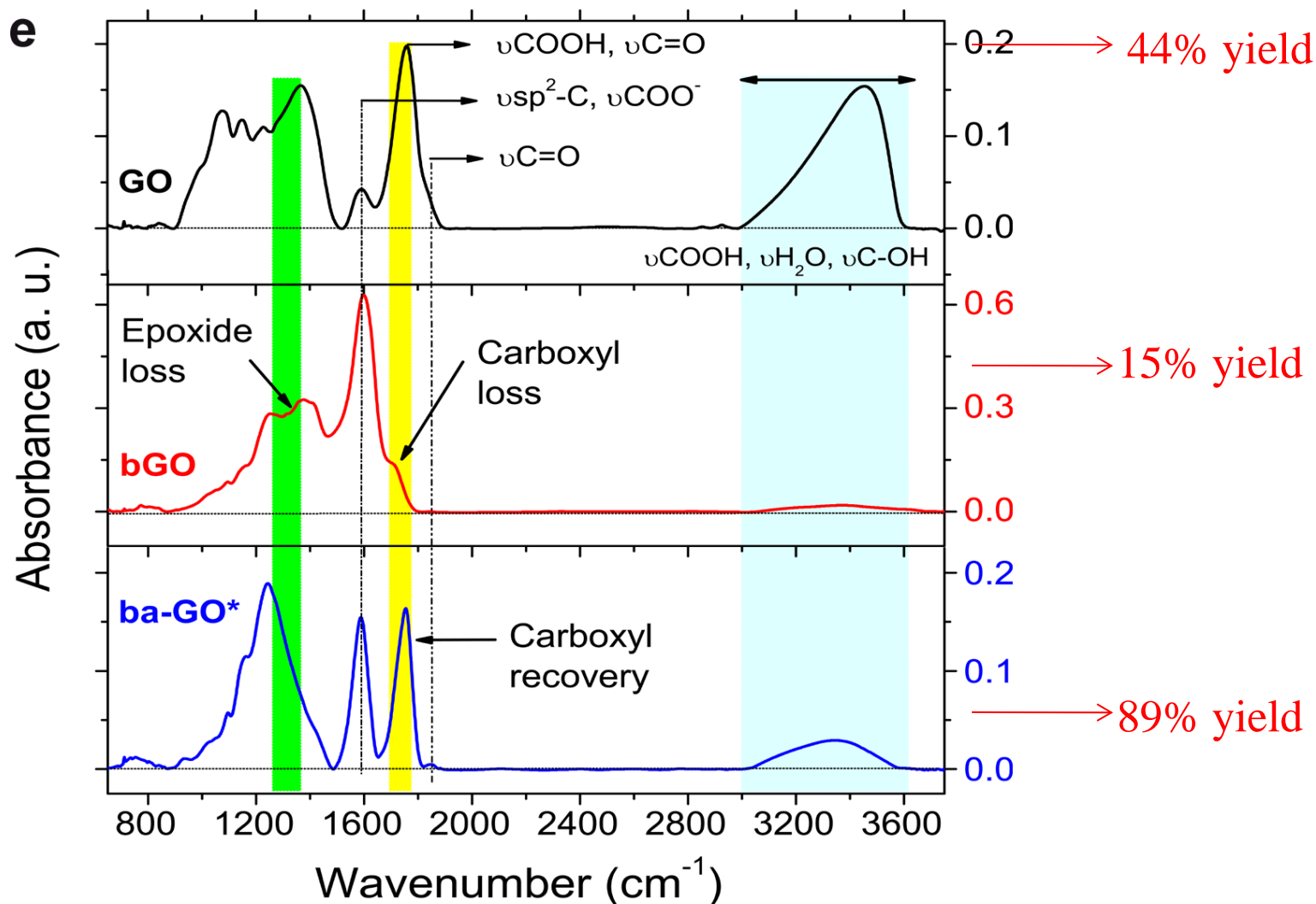
1. Holes could be created and enlarged by the strong base-etching process
2. Some unique functionalities might be introduced in the defects: e. g. spin electron from the non-bonding π electron states are likely to be created at the edges.

Electron Spin Resonance (ESR) measurements confirm the present of unpaired electrons



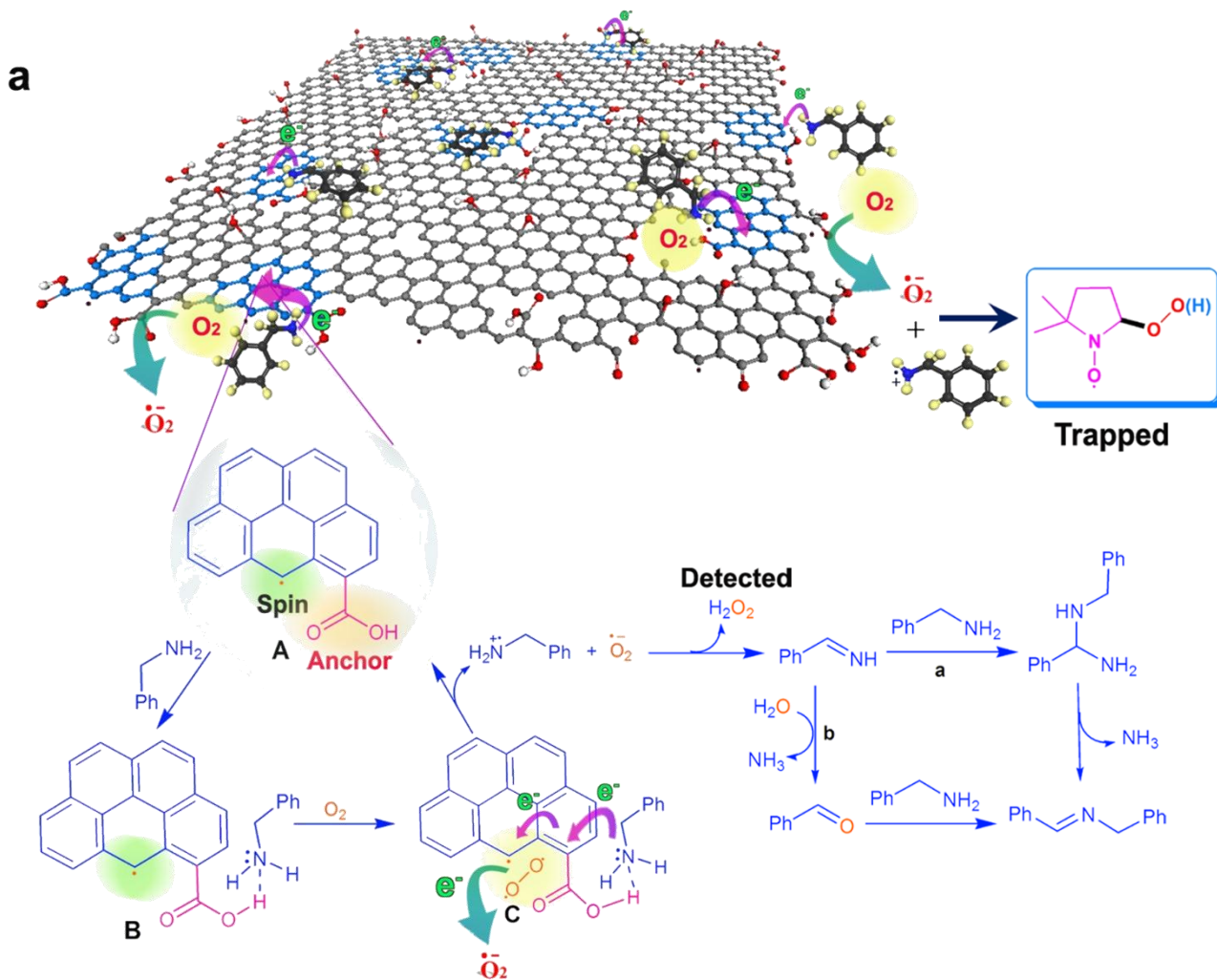
This suggests that **radical states at the edge sites** are important in the catalysis besides **carboxylic acid groups**

Controlling the **acidic functionalities** is important for the reactivity

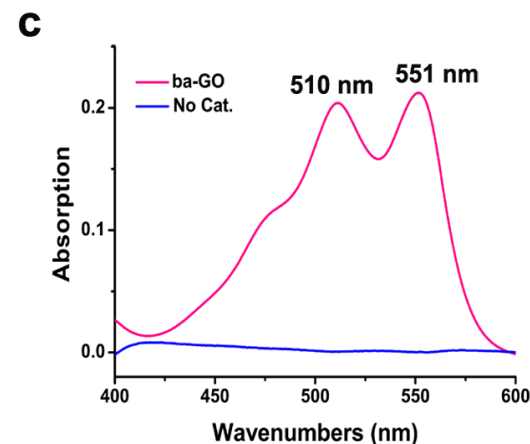
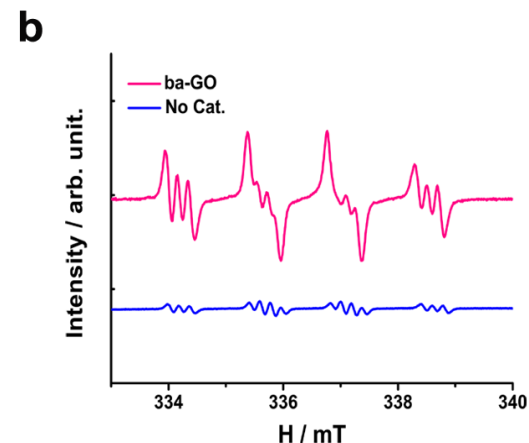


The significant contribution of the **carboxylic acids** in this catalysis could be confirmed

Synergistic effect of acidic groups and spins



The oxygen radical was trapped by the DMPO spin-trapped EPR spectra



H₂O₂ was detected by the UV-visible absorption spectra (Adding DPD and POD.)

Probing the Catalytic Activity of Graphene Oxide
Chen Liang Su and Kian Ping Loh* et. al.,
Nature Communications, 3, 1298 (2012)

Conclusions

- Strained structures like graphene bubbles afford new energy landscape
- The graphene bubbles can be used as a hydrothermal cell for studying reaction dynamics at high pressure and temperature
- Defective, porous graphene oxide can be effective carbocatalyst

References

1. Face-to-Face Transfer of Graphene Films on Silicon Wafer

Libo Gao, A.H. Castro Neto, Kian Ping Loh*

Nature (2013) *Accepted*

2. Order-Disorder Transition in a 2-D B-C-N alloy

Jiong Lu, Kai Zhang, Tze Chien Su,, A. H. Castro Neto, Kian Ping Loh*

Nature Communications (In print, ASAP)

3. Graphene Oxide as a Chemically Tuneable Platform for Optical Applications

Kian Ping Loh*, Bao QL, Eda G, Manish Chowalla.

Nature Chemistry, 2, 12, 1015-1024 (2010)

4. Transforming Fullerene Molecules into Graphene Quantum dots,

Jiong Lu, Pei Shan Emmeline and Kian Ping Loh*

Nature Nanotechnology, 6, 247–252, (2011)

5. Graphene as broadband polarizer

Q. Bao, Y. Wang, D. Y. Tang, Kian Ping Loh*

Nature Photonics, 5, 411–415 (2011)

6. Transforming Graphene Moire Blisters into Geometric Nanobubbles,

Jiong Lu, Antonion C. Neto, Kian Ping Loh*

Nature Communications, 8, 3:823. (2012)

7. Probing the Catalytic Activity of Graphene Oxide and its origin,

Chen Liang Su and Kian Ping Loh* et. al, *Nature Communications*, 3, 1298 (2012)

8. A hydrothermal Anvil made of Graphene nanobubbles on diamond

Candy Su, Kian Ping Loh*

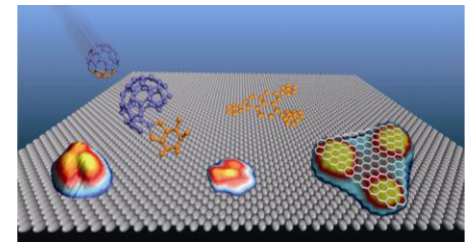
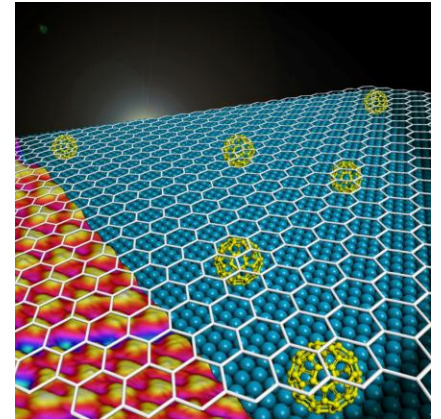
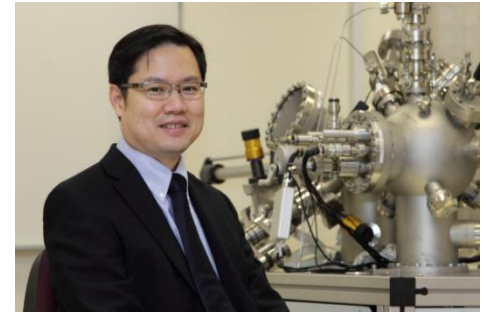
Nature Communications 4, 1556, (2013)

9. High Yield exfoliation of 2-D chalcogenides using Na Naphthanelide

Jian Zheng, Kai Zhang, Kian Ping Loh* et. a. *Nature Communications*

10. The chemistry of ultra-thin transition metal dichalcogenide nanosheets

Manish Chhowalla, Goki Eda, Kian Ping Loh et. al. *Nature Chemistry* 5, 263 (2013)





Thank You!