Central European Institute of Technology
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RAJARSHI ROY

POSTDOCTORAL RESEARCHER,
RG PLASMA TECHNOLOGIES
CEITEC, MASARYK UNIVERSITY

GRAPHENE: A PARADIGM SHIFT AND THE ADVENT OF 2D MATERIALS

Funded by European Regional Development Fund-Project "MSCAfellow2@MUNI" (No. CZ.02.2.69/0.0/0.0/18_070/0009846)

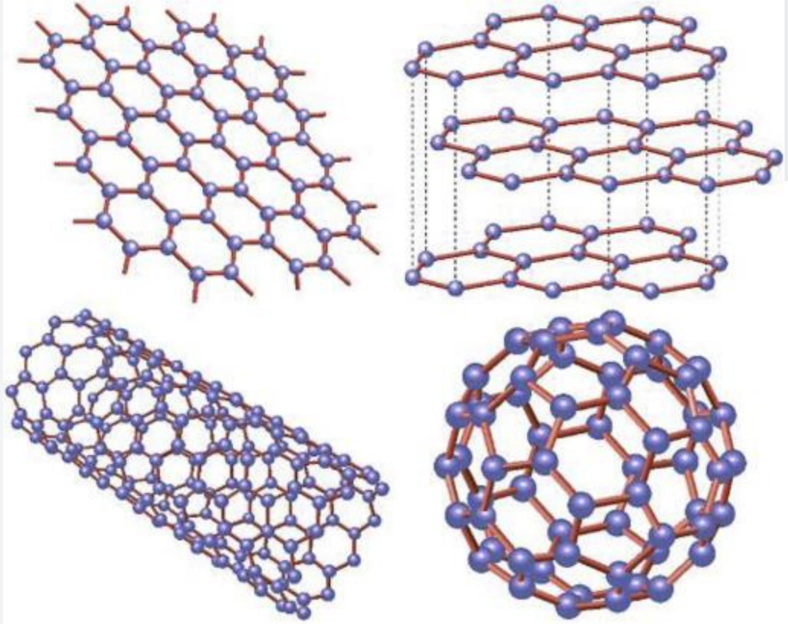
SUMMARY OF DISCUSSIONS

- FUNDAMENTAL PROPERTIES
- SYNTHESIS STRATEGIES
- BASIC CHARACTERIZATIONS
- SOME APPLICATIONS
- CONCLUSIONS

FUNDAMENTAL PROPERTIES

PREMISE

ALLOTROPES OF CARBON IN DIFFERENT DIMENSIONS

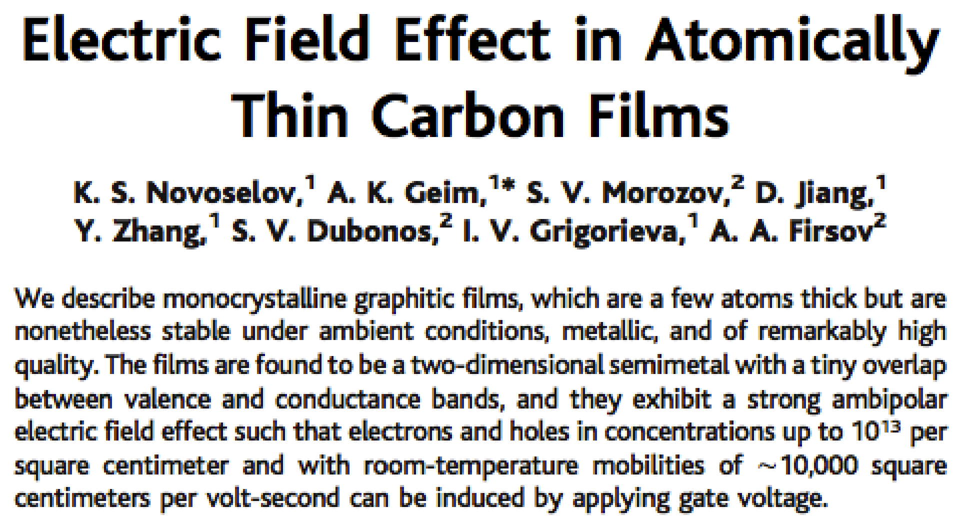


WHY IS GRAPHENE IS IMPORTANT AND WORTHY OF NOBEL PRIZE?

A. GEIM, K. NOVOSELOV
UNIVERSITY OF MANCHESTER, UK

NOBEL PRIZE IN PHYSICS (2010)

FOR GROUNDBREAKING EXPERIMENTS WITH 2D MATERIAL CALLED GRAPHENE



Electric Field Effect in Atomically Thin Carbon Films

K. S. Novoselov,[1] A. K. Geim,[1]* S. V. Morozov,[2] D. Jiang,[1] Y. Zhang,[1] S. V. Dubonos,[2] I. V. Grigorieva,[1] A. A. Firsov[2]

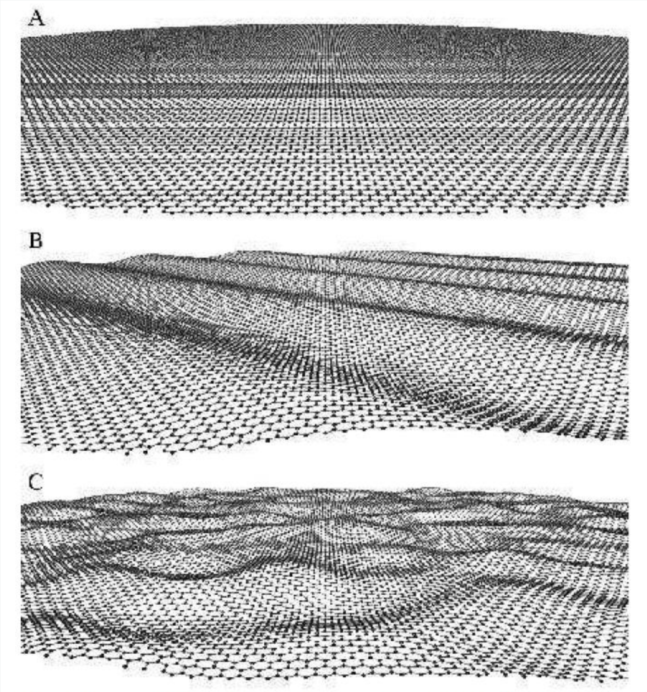
We describe monocrystalline graphitic films, which are a few atoms thick but are nonetheless stable under ambient conditions, metallic, and of remarkably high quality. The films are found to be a two-dimensional semimetal with a tiny overlap between valence and conductance bands, and they exhibit a strong ambipolar electric field effect such that electrons and holes in concentrations up to 10^{13} per square centimeter and with room-temperature mobilities of ~10,000 square centimeters per volt-second can be induced by applying gate voltage.

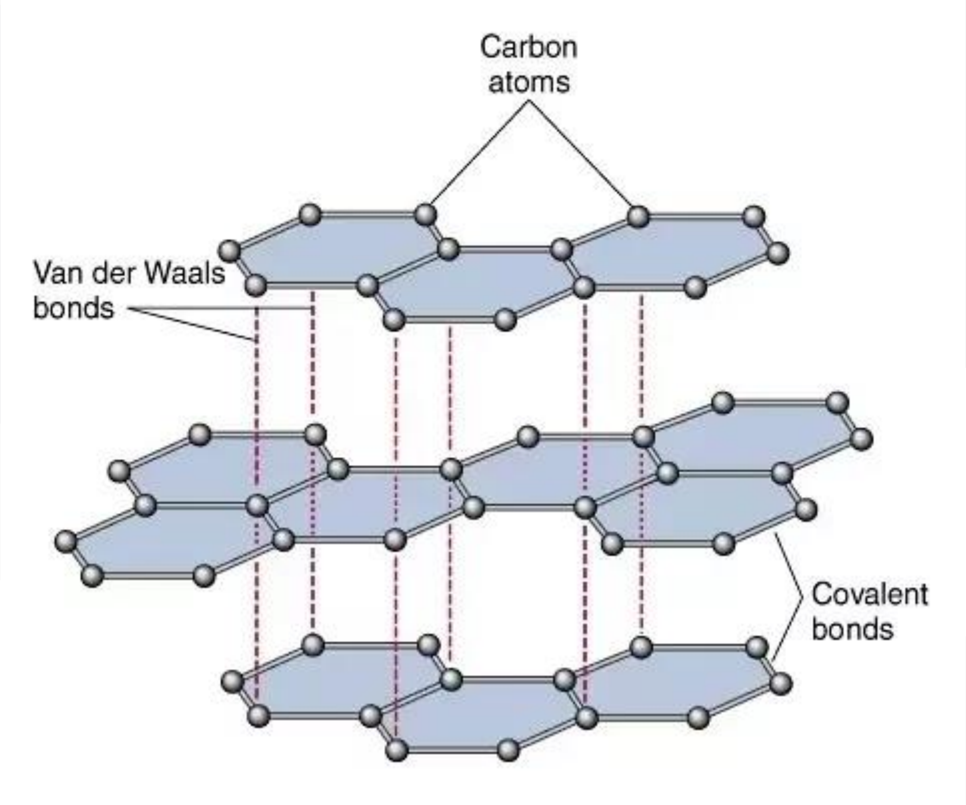
K.S. Novoselov et al., SCIENCE, 2004.

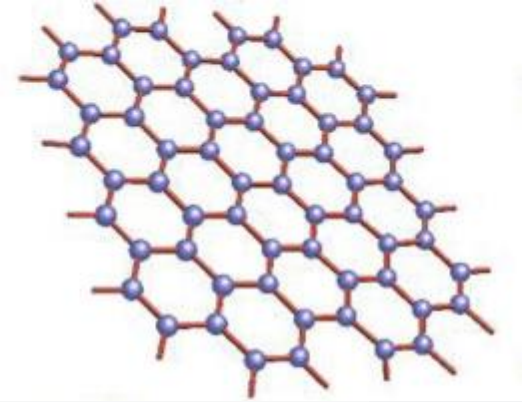
Landau and Peierls argued that strictly two-dimensional (2D) crystals were thermodynamically unstable and could not exist.

Band Theory of Graphite, P. R. Wallace, PRL, 1947.

J. C. Mayer et al. NATURE **446**, 60 ,2007



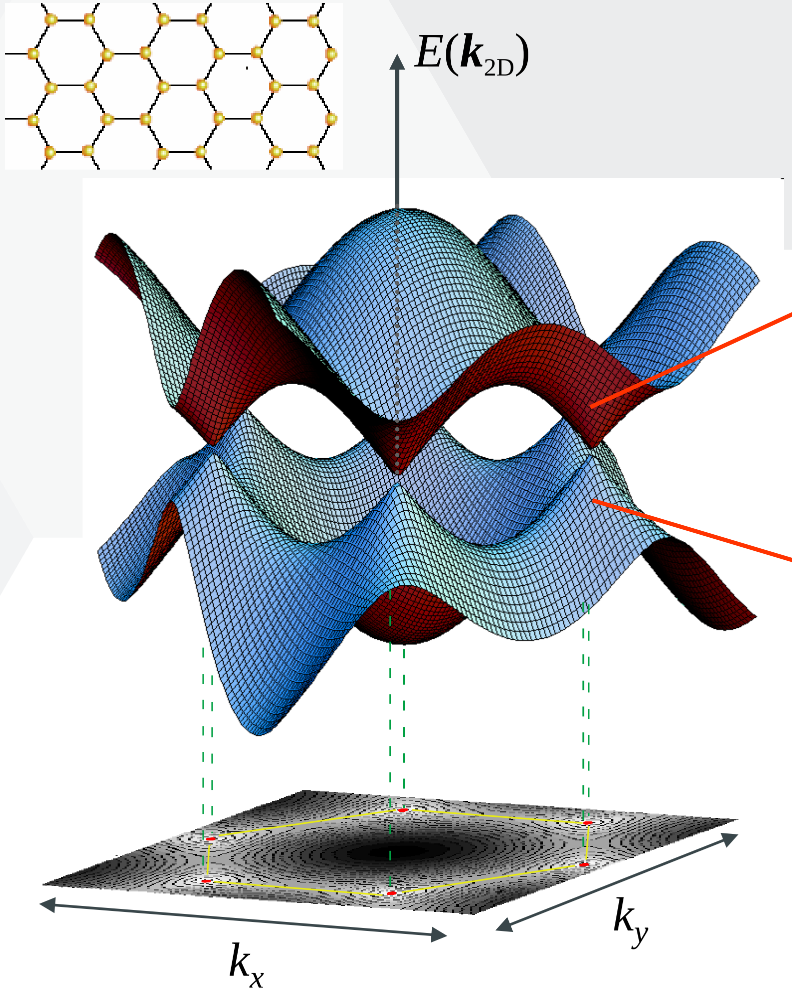




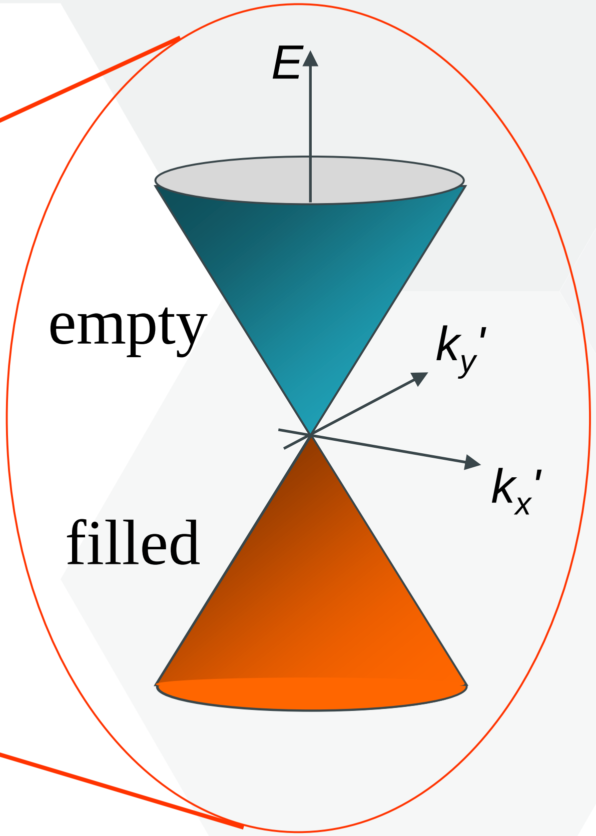
GRAPHENE IS A ONE-ATOM THICK LAYER OF GRAPHITE WHERE THE CARBON ATOMS ARE ARRANGED IN A 'HONEYCOMB' LATTICE

'HONEYCOMB' LATTICE → *HEXAGONAL, Sp2*

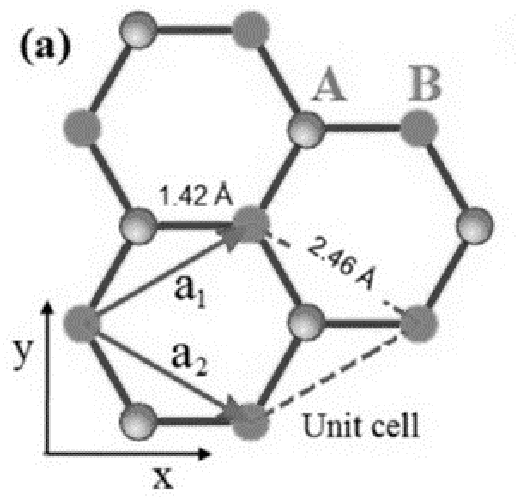
Band structure of graphene (Wallace 1947)

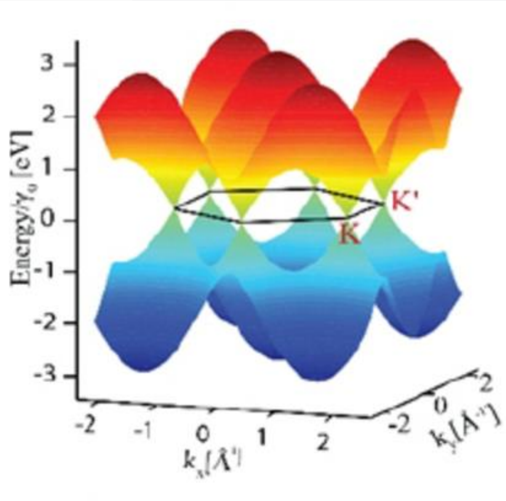


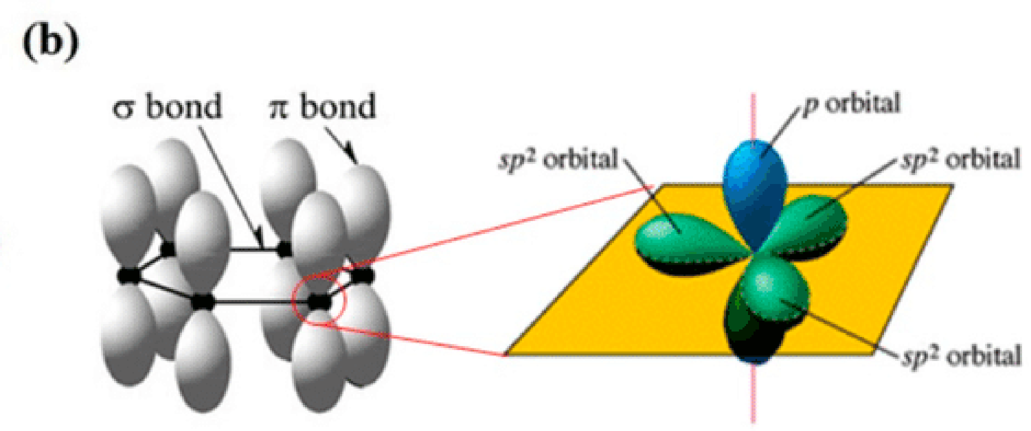
$$E \approx \hbar v_F \left| \vec{k}'_{\perp} \right|$$



Zero effective mass particles moving with a constant speed $v_F = c/300$







Follows Dirac Equation from relativistic QM and correlation to quantum electrodynamics

$$(i\partial\!\!\!/ - m)\,\psi = 0$$

Effective mass (m^*) ~ $[dE^2/dk^2]^{-1}$

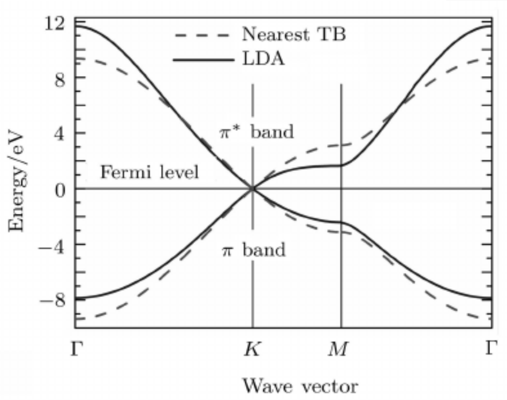
Most semiconductors, $0.1\ m_0 < m^* < 1\ m_e$
Graphene, $m^* < 0.01\ m_0$ *(depending on number of carriers)*
Therefore, expect VERY high mobility in graphene both holes and electrons can be carriers

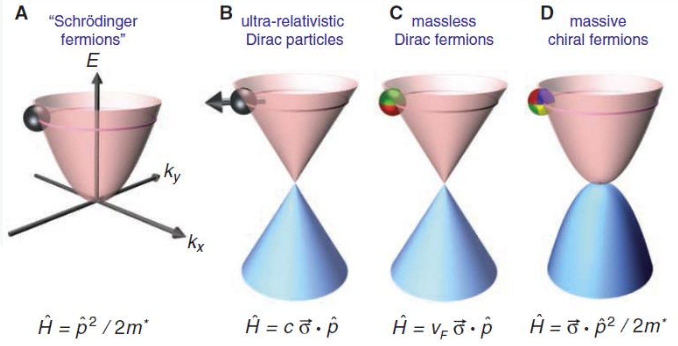
The velocity of an electron at the Fermi level (v_F) is inversely related to m^*

$$m^* \simeq \frac{p}{v_g} \simeq \frac{\hbar k}{v_f}.$$

Relativistic Realm: 10^6 m/s ~ c/300 ~ V_F

Electron mobility ~ 200000 $cm^2 \cdot V^{-1} \cdot s^{-1}$; Resistivity ~10^{-6} Ω·cm (at room temperature)

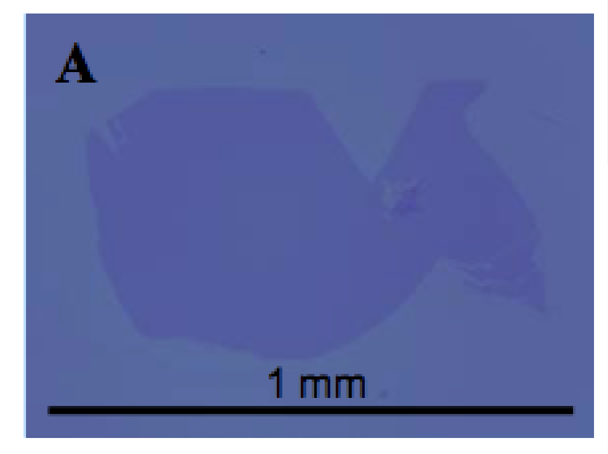




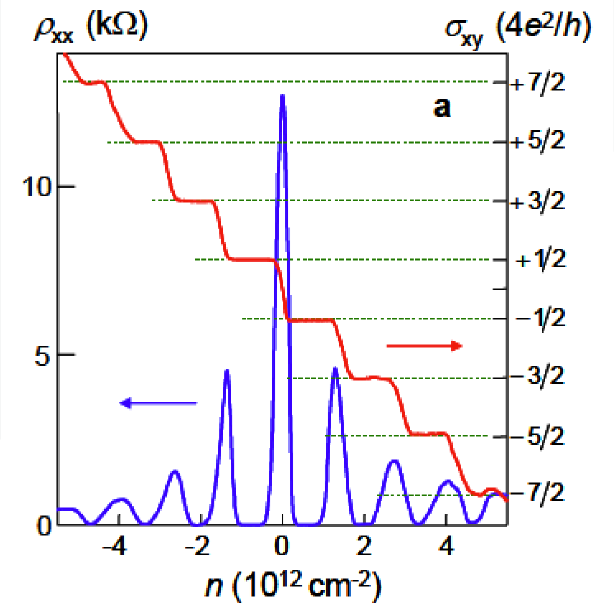
A. Geim, SCIENCE 384, 1530, 2009.

EXOTIC PROPERTIES OF GRAPHENE

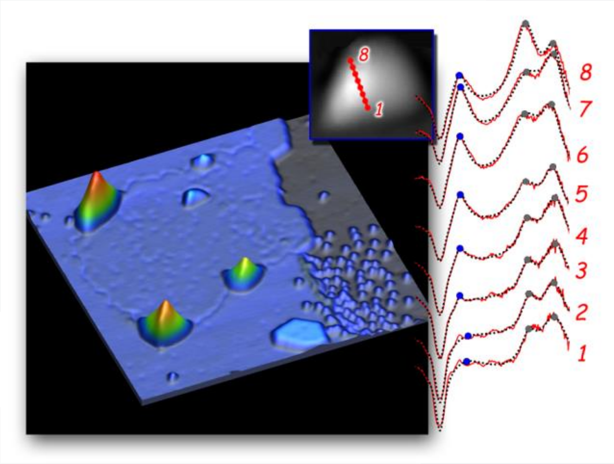
K.S. Novoselov et al., SCIENCE, 2004.
Katnelson et al., NAT. PHYS., 2006
Levy et al., SCIENCE, 2010



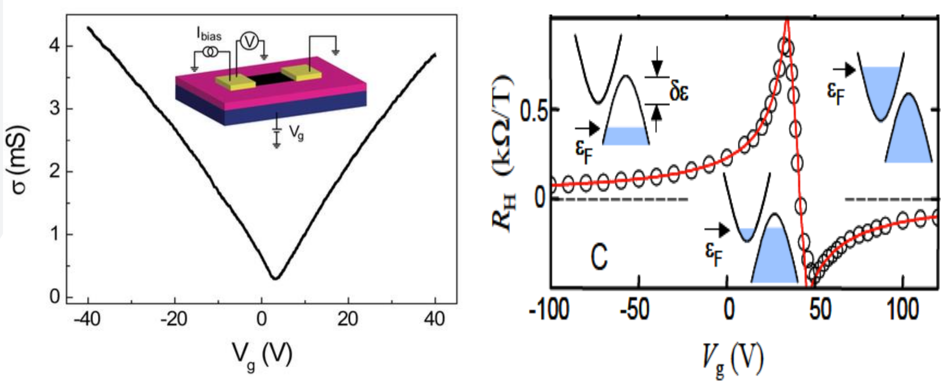
SLG ON 285 nm Si/SiO2



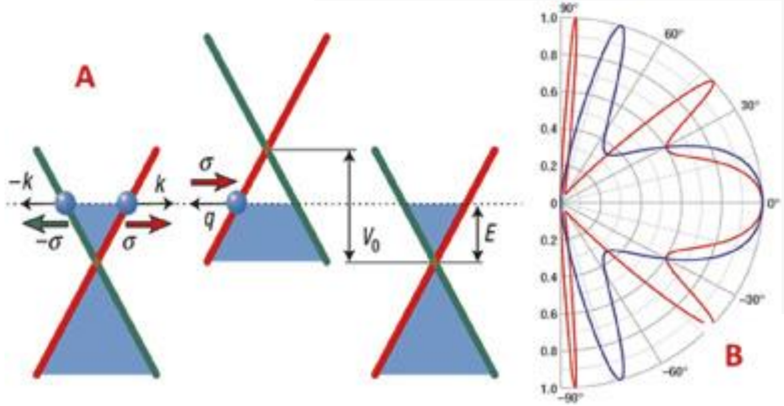
FQHE



PSEUDOMAGNETIC FIELD QUANTIZATION

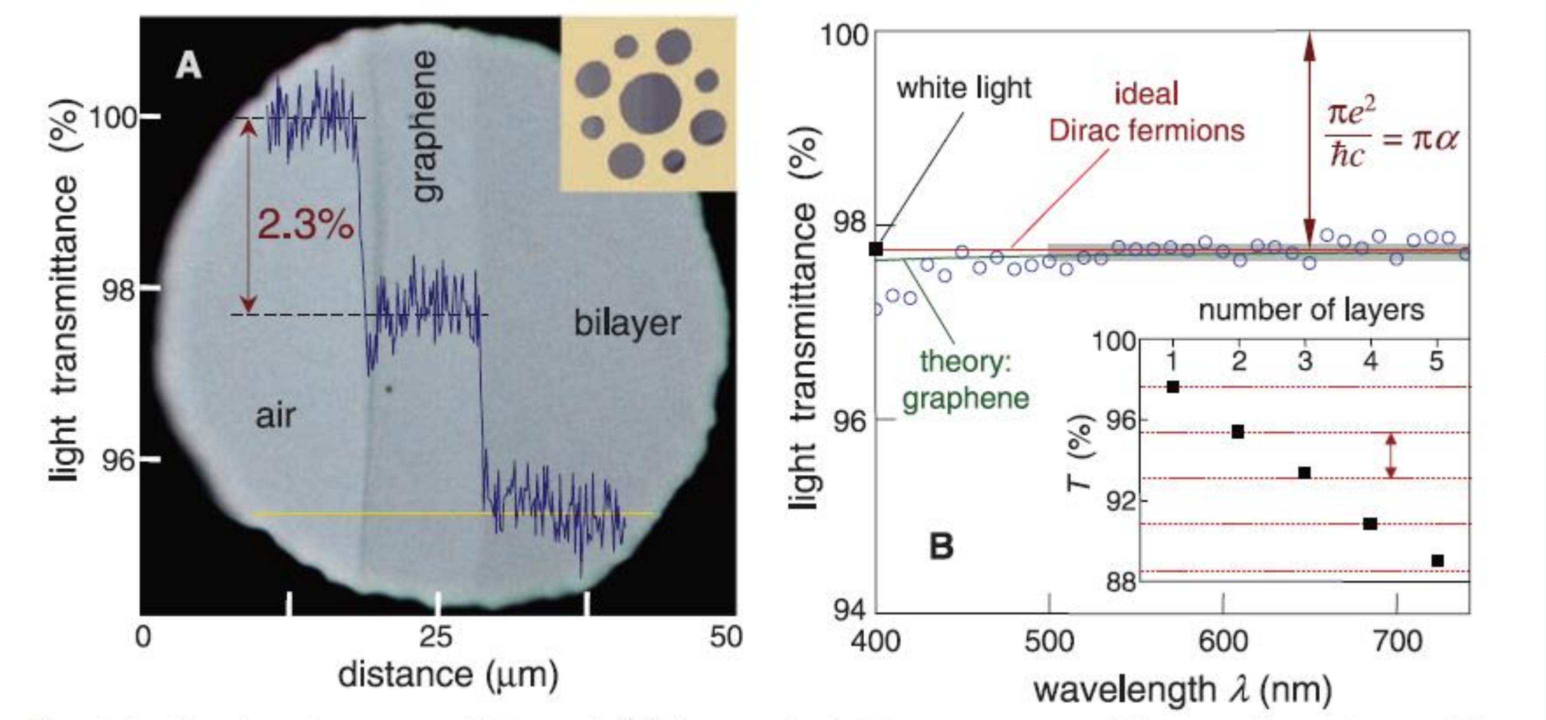


AMBIPOLAR ELECTRIC FIELD EFFECT



KLEIN TUNELLING

METALLICITY AND TRANSPARENCY IN GRAPHENE



- Opacity of suspended graphene (1) is defined solely by the fine structure constant, a = e2/ℏc ≈ 1/137 (where c is the speed of light), the parameter that describes coupling between light and relativistic electrons
- Despite being only one atom thick, graphene is found to absorb a significant (pa = 2.3%) fraction of incident white light, a consequence of graphene’s unique electronic structure.

Nair et al., SCIENCE, 2008

OVERVIEW

Properties	Values	References
Optical transparency	97.7%	Nair et al., 2008
Electron mobility	200,000 $cm^2 v^{-1} s^{-1}$	Bolotin et al., 2008
RT Thermal conductivity	5,000 $W m^{-1} K^{-1}$	Balandin et al., 2008
Specific surface area	2,630 $m^2 g^{-1}$	Edwards and Coleman, 2013
Breaking strength	42 $N.m^{-1}$	Hsu, 2009
Elastic modulus	1 TPa	Lee et al., 2008
Fermi velocity	1×10^6 $m s^{-1}$	Du et al., 2008

Bleu et al., FRONTIERS IN CHEMISTRY, 2018

SYNTHESIS STRATEGIES

MICROMECHANICAL CLEAVAGE OF HOPG (SCOTCH TAPE METHOD)

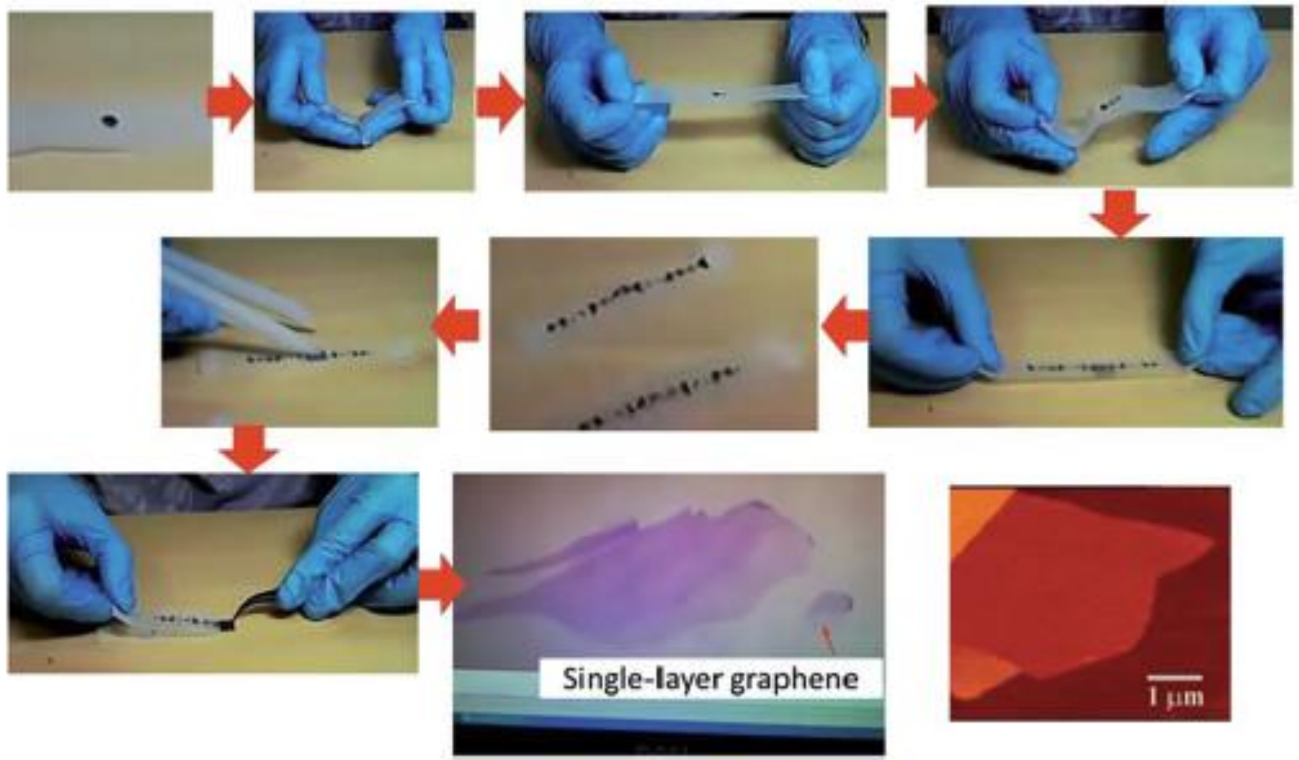
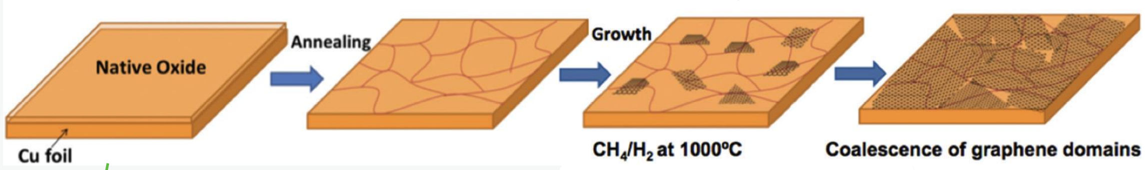


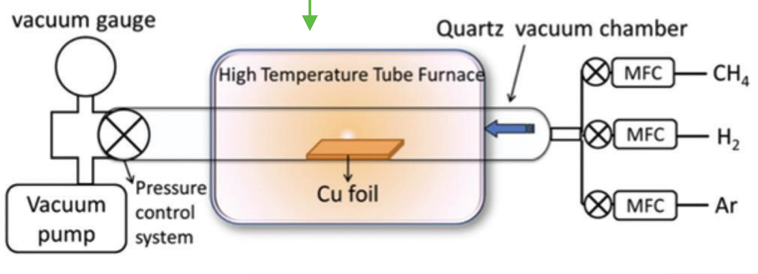
Fig. 2 An illustrative procedure of the Scotch-tape based micro-mechanical cleavage of HOPG.

Yi et al., J. MATER. CHEM. A, 2015.

CHEMICAL VAPOUR DEPOSITION (CVD)

GROWTH





(Cu, Ni, Ga, Pt)

LP PRESSURE CVD

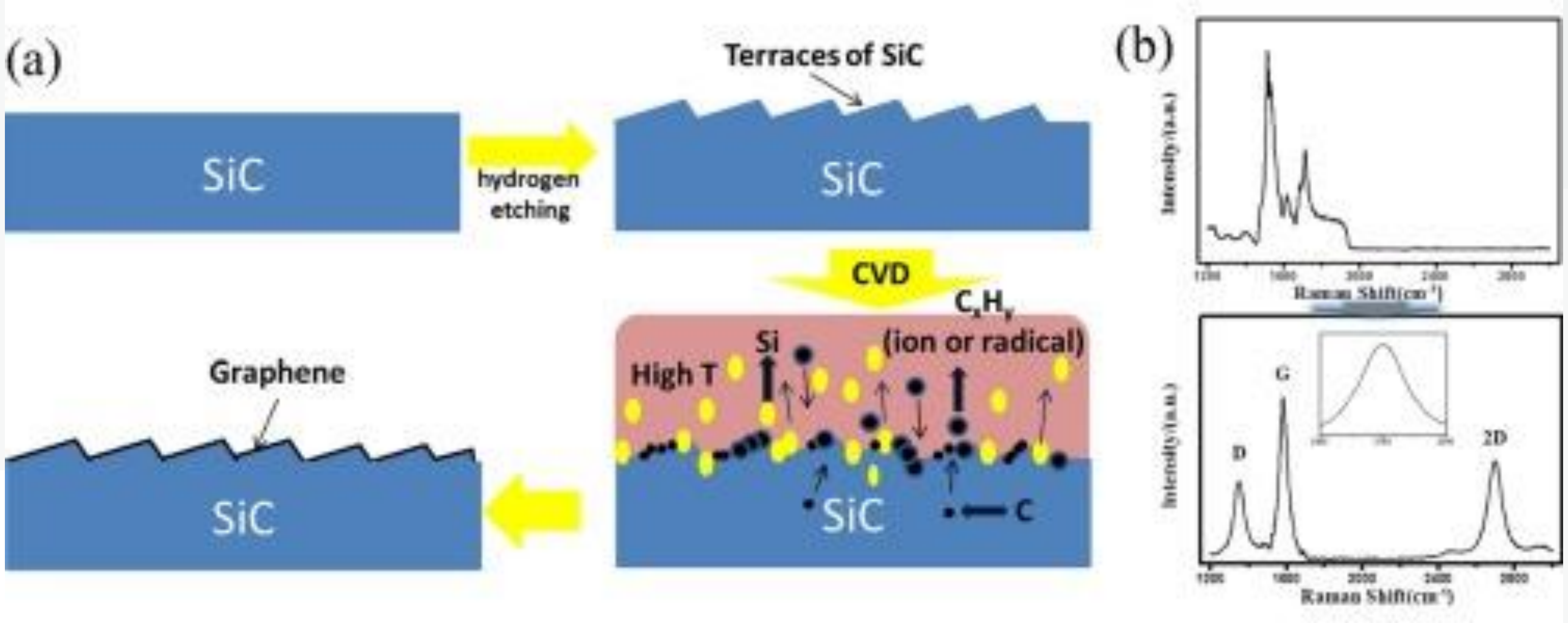
- POLYCRYSTALLINE
- THICKNESS CONTROL NOT POSSIBLE
- LESS TIME TO GROWTH IN LARGE AREA
- SUBSTRATE QUALITY IS IMPORTANT

ATMOSPHERIC PRESSURE CVD

- SINGLE CRYSTAL DOMAIN
- THICKNESS CONTROL
- MORE TIME TO GROWTH IN LARGE AREA

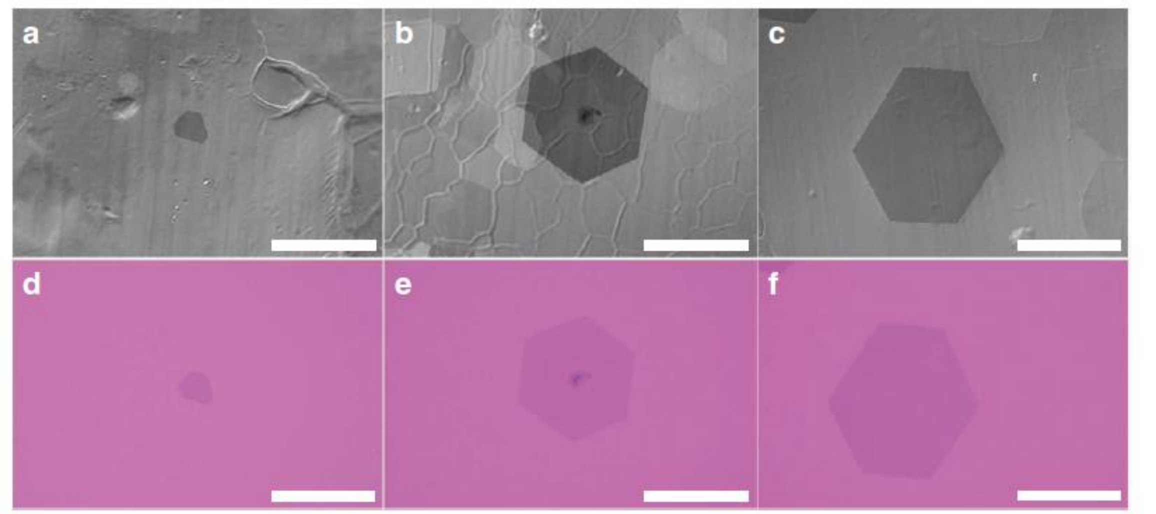
ECS J. Solid State Sci. Technol. 2017

CVD on SiC

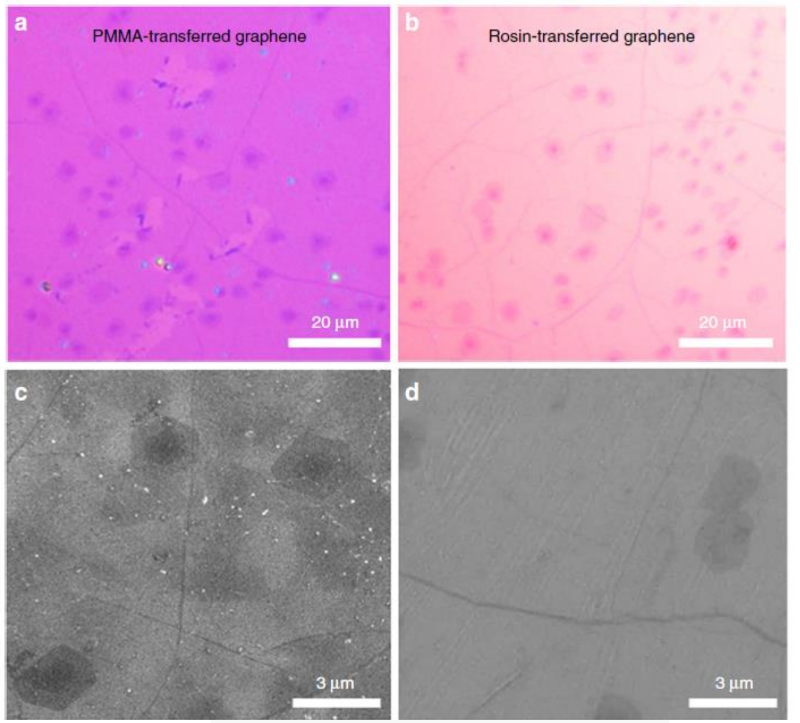


YANG ET AL., APPL. SURF. SCI., 2018.

ATMOSPHERIC PRESSURE CVD



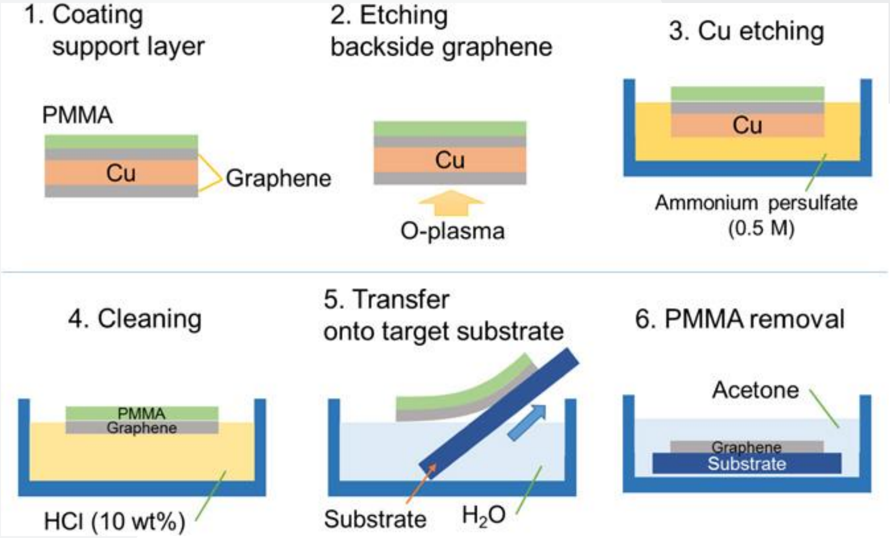
LOW PRESSURE CVD (1mbar)



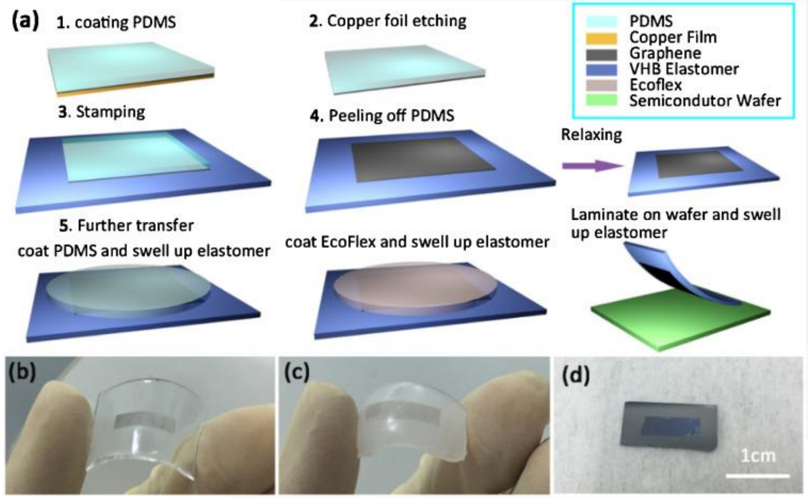
ZHANG ET AL., NAT. COMMUN. 2016
GAO ET AL. NATURE COMMUN., 2011

TRANSFER MECHANISM

STANDARD WET TRANSFER

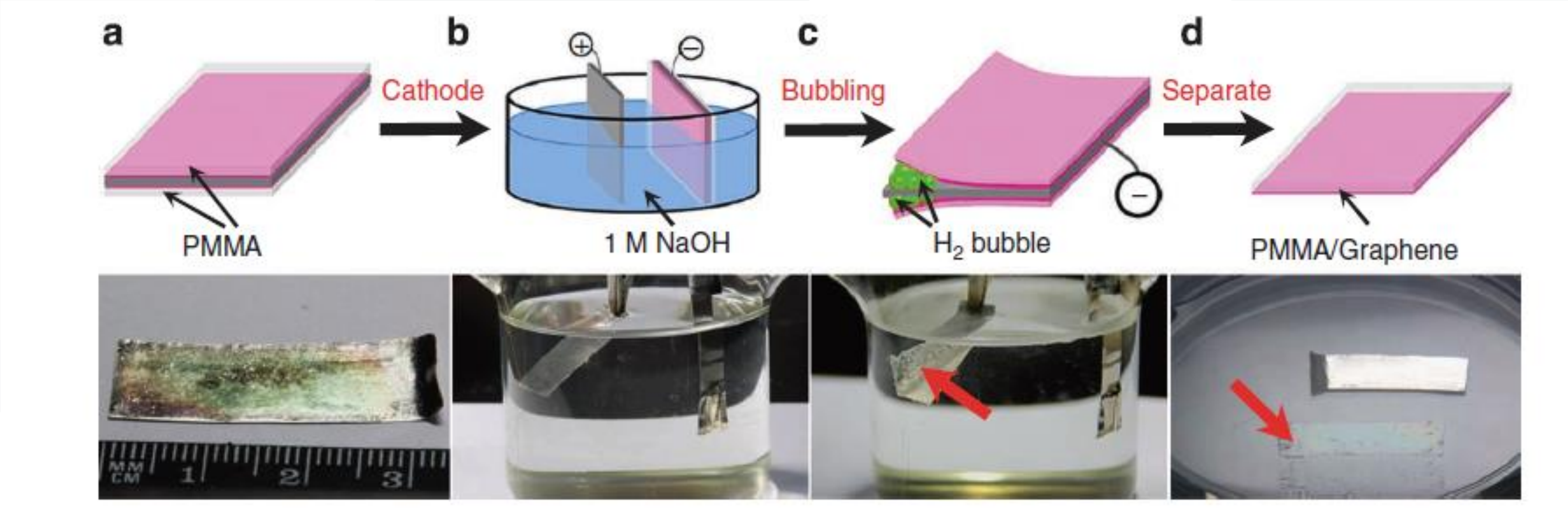


STAMPING METHOD



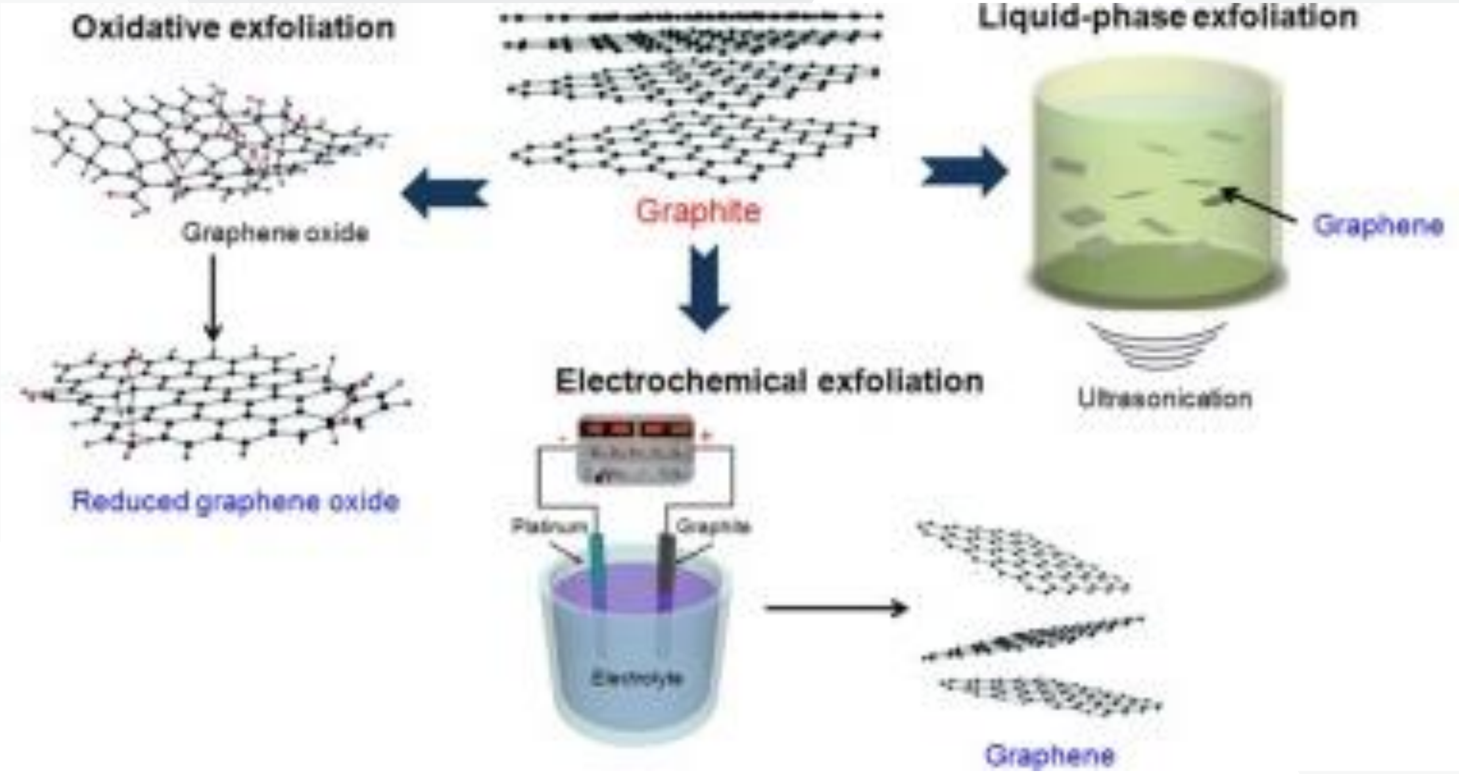
Bleu et al., FRONTIERS IN CHEMISTRY, 2018

BUBBLE TRANSFER



GAO ET AL. NATURE COMMUN., 2011

CHEMICAL METHODS



Parvez et al. SYNTHETIC METALS, 2015

MERITS AND DEMERITS

Micromechanical Exfoliation

- Low Yield
- Adhesive residue
- However can expect very clean samples if processed correctly

CVD

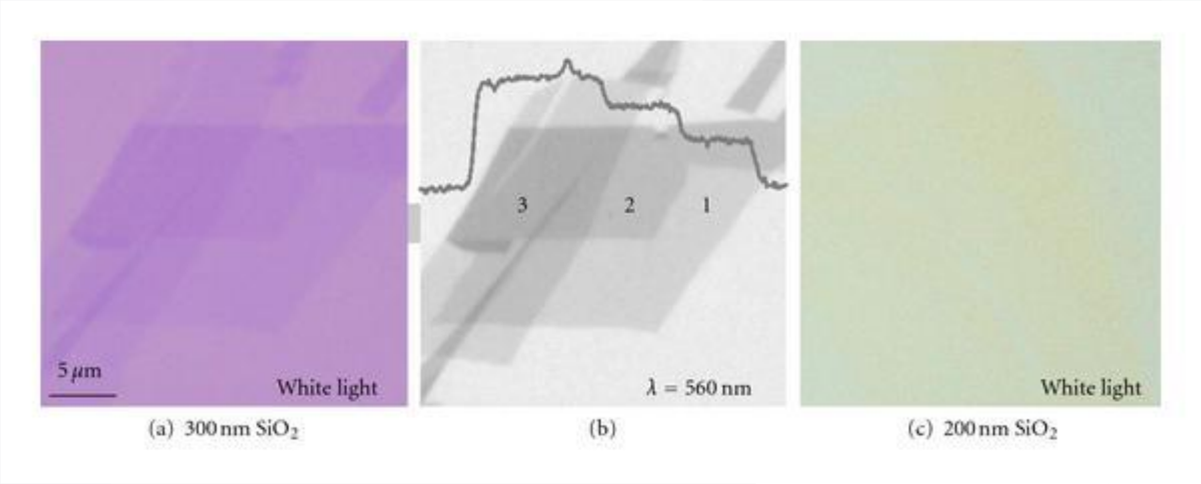
- Can be obtained as thin films for large area device applications. For example: solar cells, sensors, photodiode
- Precise layer thickness could be manipulated
- Careful Transfer to substrate is essential otherwise there could be presence many defects
- Added doping and residues of PL tend to stick to the surface and effects graphene’s performance

Chemical Methods

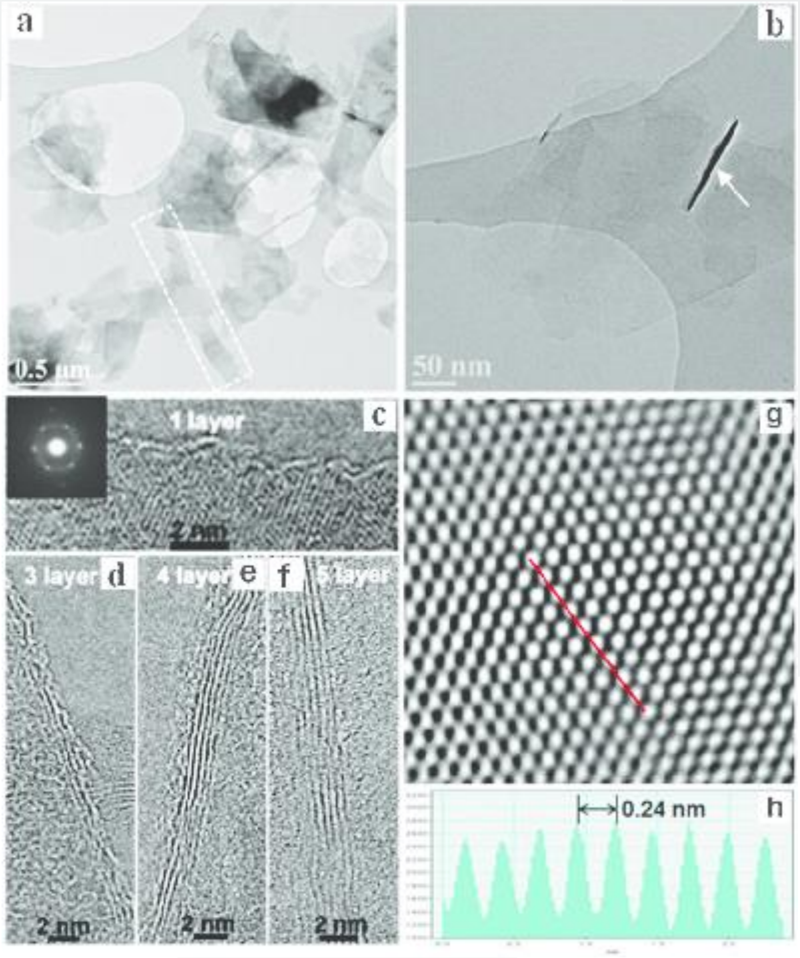
- Very high yield which are essential for composite preparation in mechanical and energy related applications
- Can be obtained in solution or powder form
- Ease of handling
- Some of the species may not be graphene at all but rather derivative of graphene like RGO which is a semiconductor
- Presence of multilayers and more defects are present in many cases

BASIC CHARACTERISATIONS

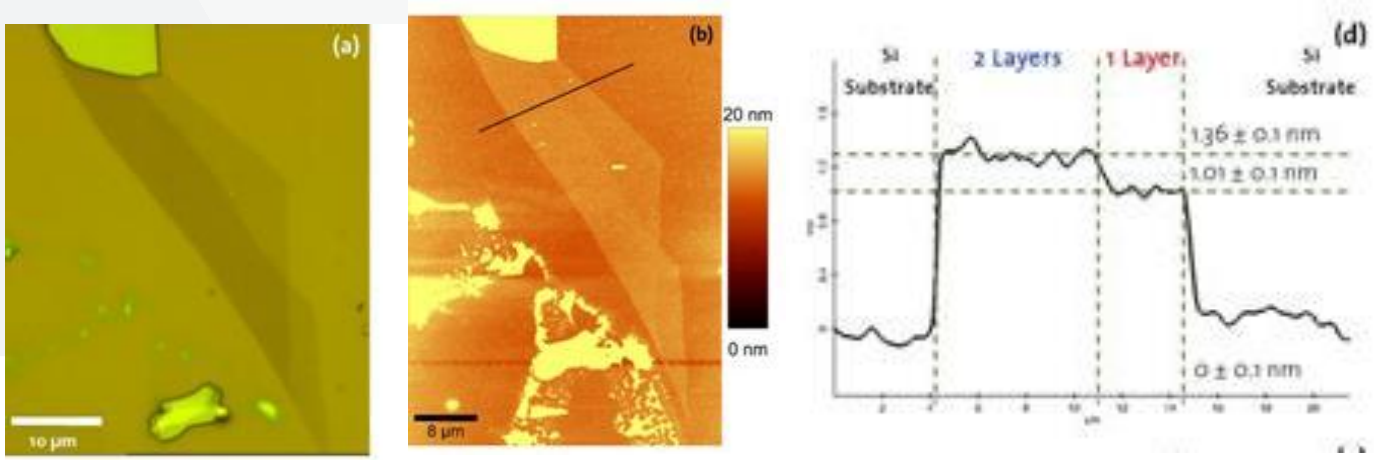
OPTICAL MICROSCOPY



HRTEM



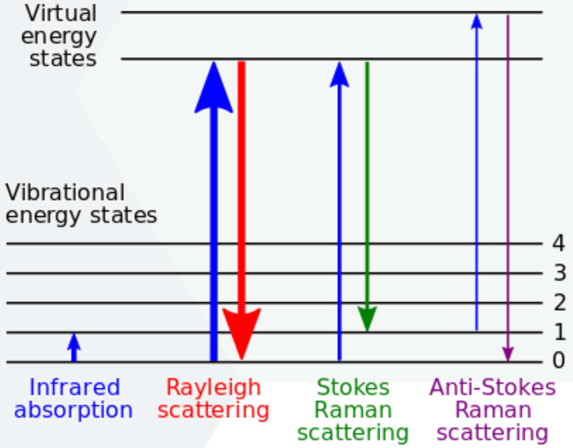
ATOMIC FORCE MICROSCOPY

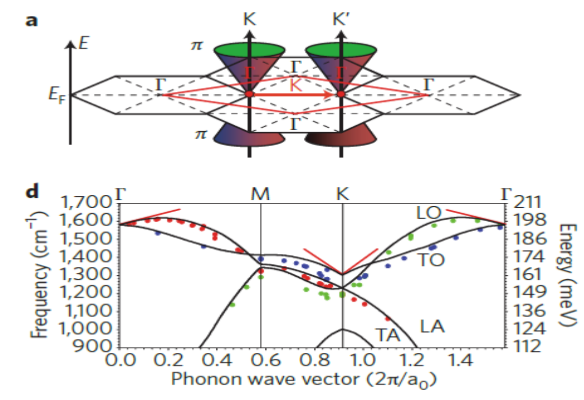


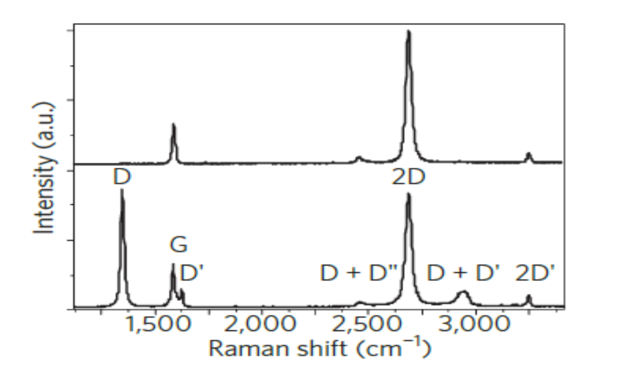
1 Cooper et al., ISRN Condensed Matter Physics, 2012
2 WITEC, gmbh, Germany

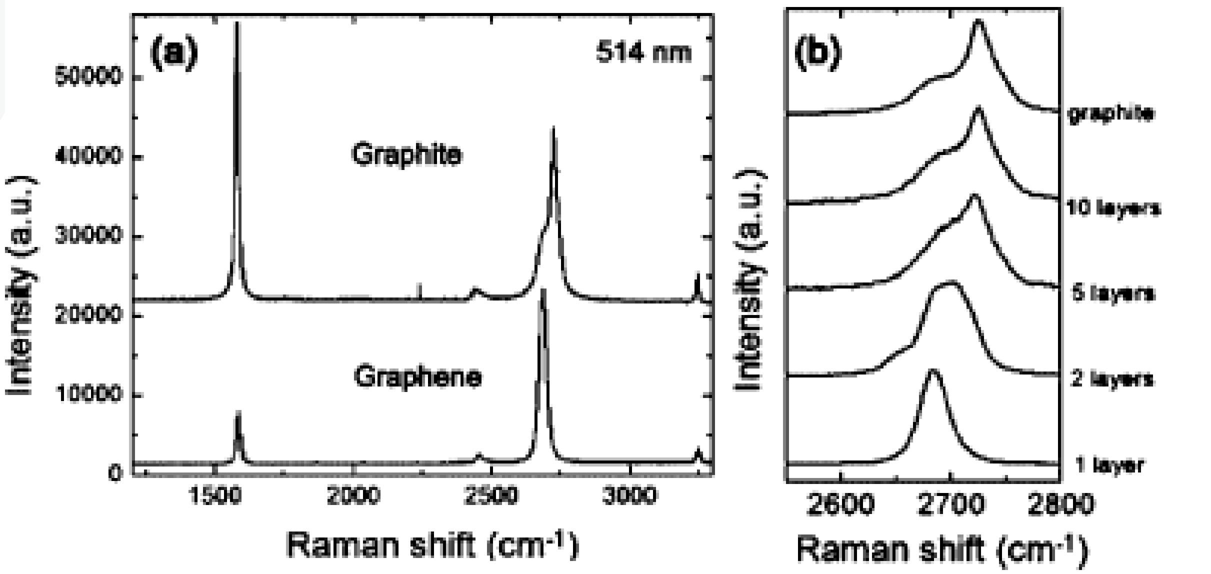
RAMAN

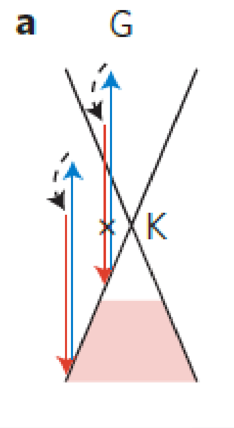
1 Ferrari et al. Nat. Nanotech. 8, 235, 2013
2 Ferrari et al. PRL **97,** 187401 (2006).
3 Dresselhaus et al. Nano Lett. (2010).

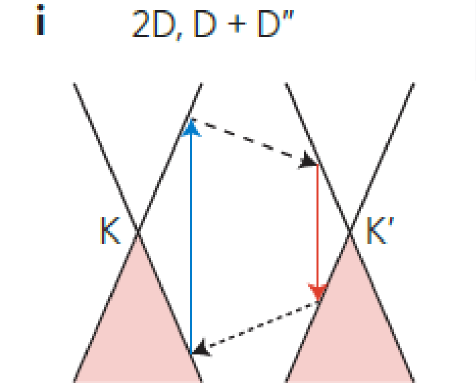




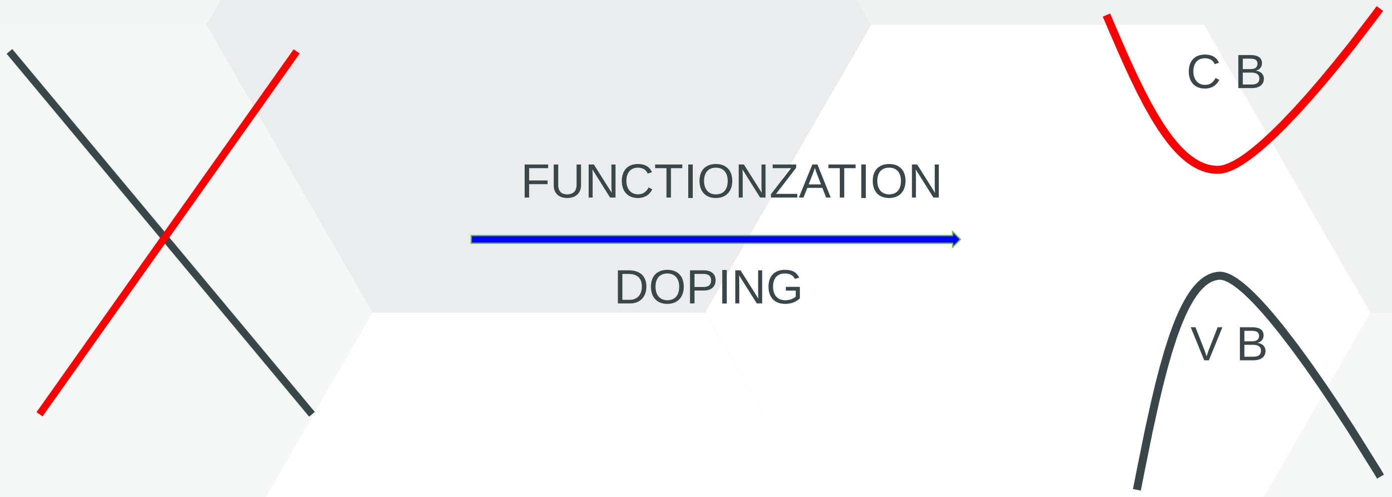








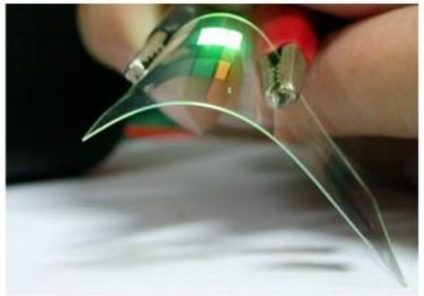
ROADBLOCK



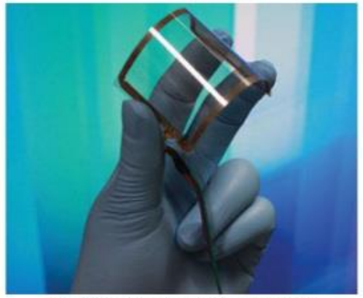
- GRAPHENE WITH ZERO BANDGAP IS ENTICING FOR EXOTIC PHYSICS BUT NOT FOR ELECTRONICS
- ULTRA HIGH MOBILITY IN GRAPHENE TRANSISTORS CANT BE USED AS THEY DON'T SWITCH OFF [DEADLOCK]
- ON-OFF RATIO ~10^{6}-10^{10} IS NEEDED IN MOSFET
- BANDGAP CAN BE OPENED IN GRAPHENE BY FUNCTIONALIZATION OR DOPING

SOME APPLICATIONS

TRANSPARENT FLEXIBLE CONDUCTORS



Flexible organic light emitting diode



Flexible transparent conducter with graphene

SENSORS

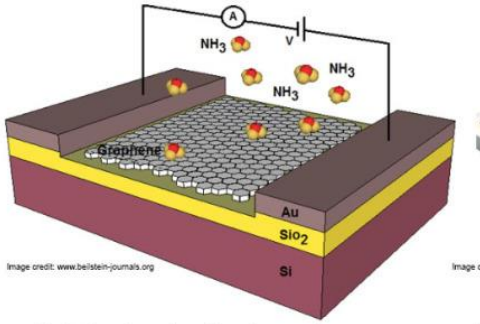


Illustration of graphene based ammonia sensor

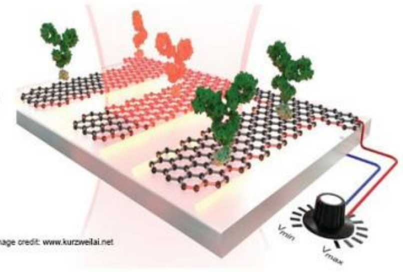


Illustration of graphene based bio-sensor

INK FOR PAINT, COATINGS

Graphene based conductive ink that already in the market

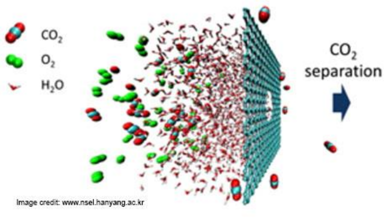
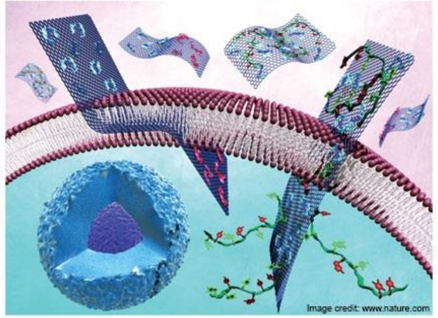
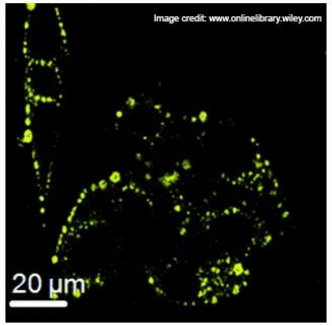


Illustration of graphene based gas barrior for selective gas penetration

DRUG DELIVERY

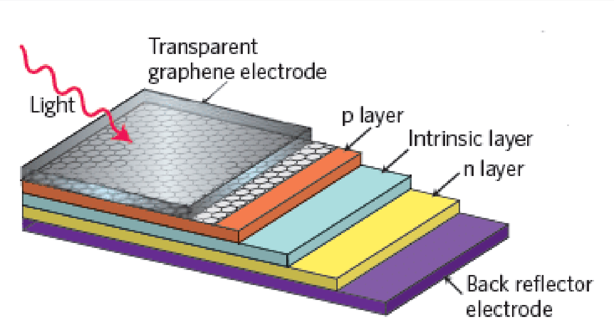


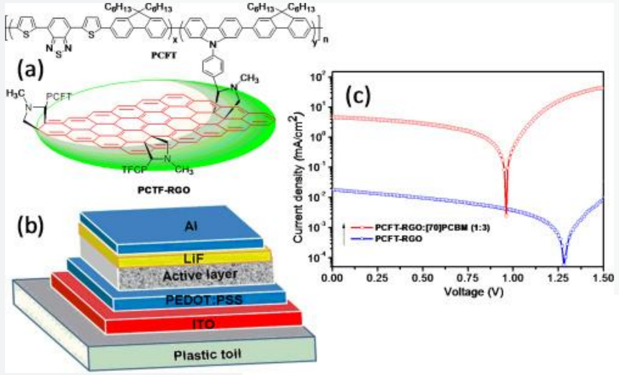
Drug loaded graphenes going through a cell membrane



A cell modified with fluorescent graphene oxide

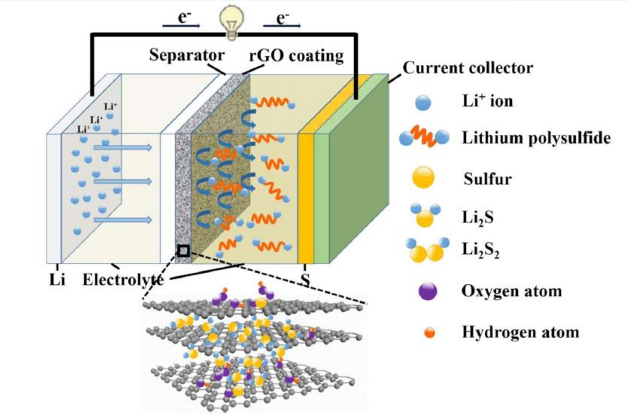
SOLAR CELL

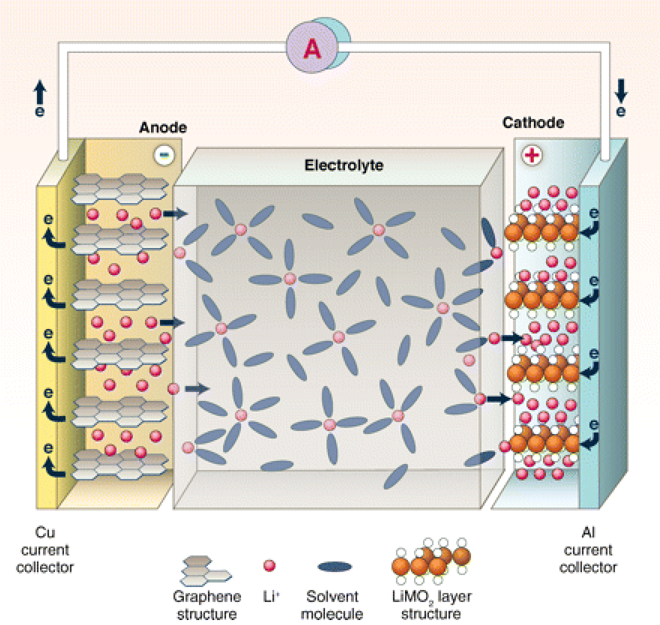




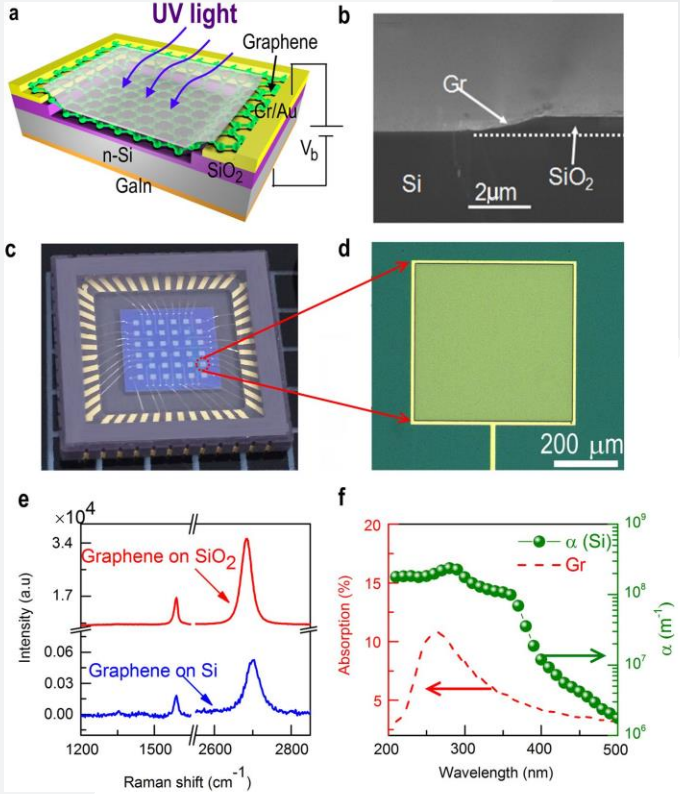
CATALYSIS

Li-ION BATTERY

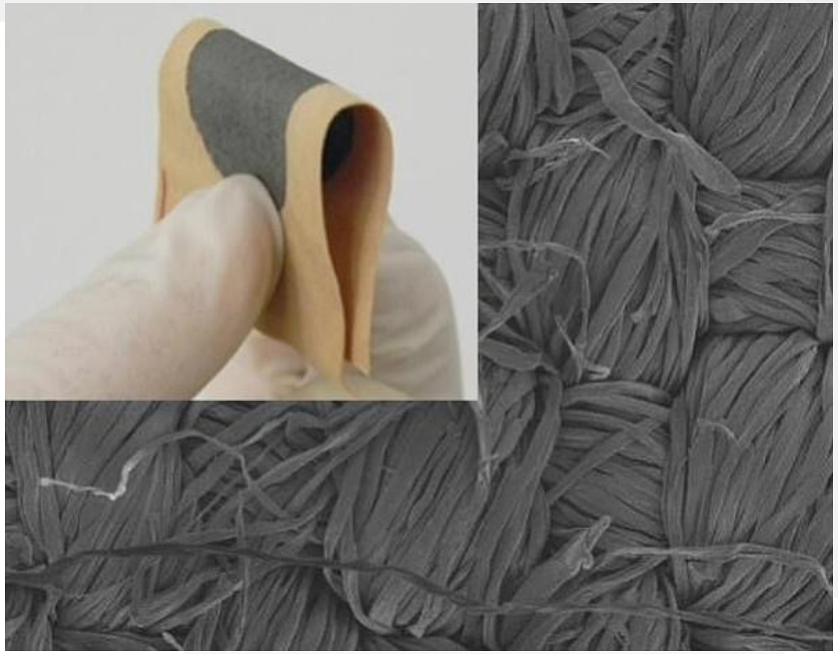




OPTICAL DETECTORS



TEXTILE



CONCLUSIONS

- FIRST SUCH DISCOVERY OF NEW 2D MATERIALS
- EXPLORATION INTO EXOTIC PHENOMENOLOGICAL ASPECTS AND MERGER OF NEW CONCEPTS BETWEEN CONDENSED MATTER AND HIGH ENERGY PHYSICS WITH VALIDATION
- DISCOVERY OF NEW TYPES OF 2D MATERIALS (hBN, TMDC-WS2,MoS2, BOROPHENE, GERMANENE, PHOPHORENE, STANENE ETC.)
- DISCOVERY OF NEW TYPES OF QUASIPARTICLES AND NEW BRANCES OF QUANTUM PHYSICS (VALLEYTRONICS)
- NEW WAY OF DESIGNING MATERIALS: vdW HETEROSTRUCTURES (hBN-GRAPHENE,MoS2-WS2) AND CONCEPT OF WONDER MATERIALS BEING ESTABLISHED WITH WIDE ARRAY OF APPLICATIONS

THANK YOU

CEITEC