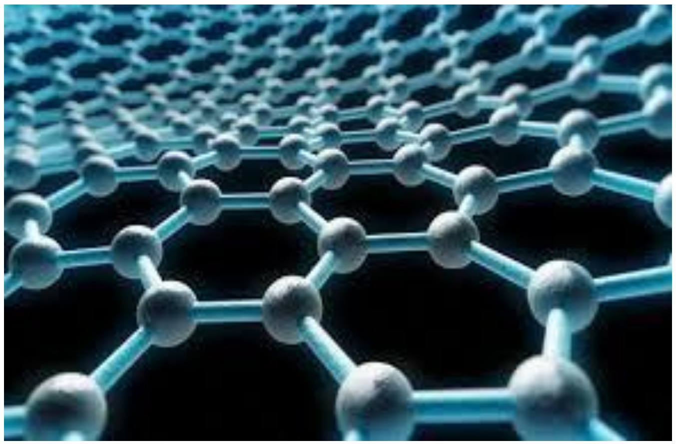

Graphene: potential ITO - replacement as transparent conductive layer

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Outline

- Motivation
- The MEM4WIN Objective
- Graphene
- CVD growth of Graphene
- Doping of Graphene
- Graphene compared to ITO: State of the art
- Graphene beyond ITO
- Applications of Graphene in Windows Technologies
- Conclusions

The Modular MEM4WIN Window Concept

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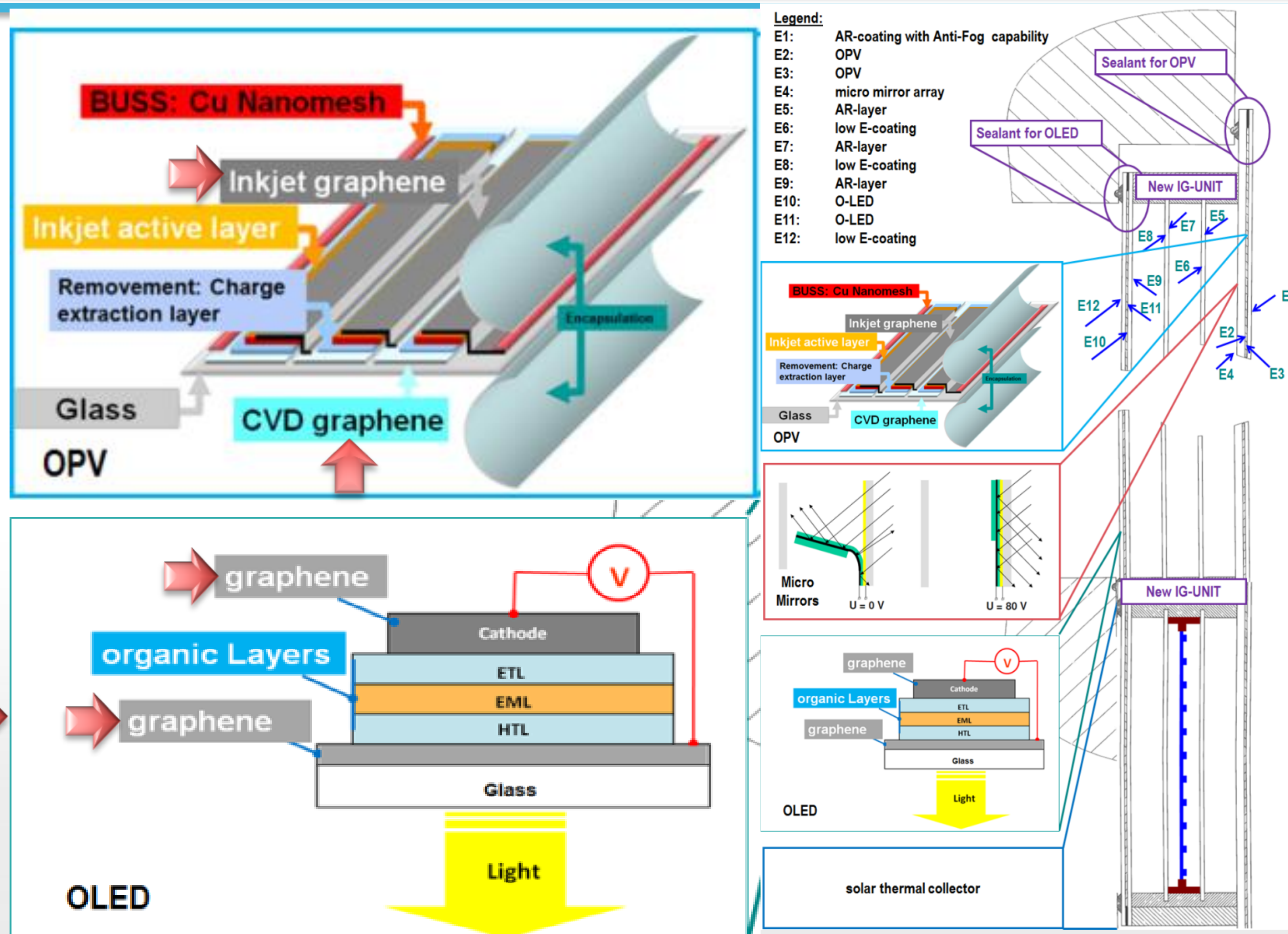
Modular components like

- OPVs
- organic light emitting diodes (OLEDs)
- micro mirrors
- solar thermal collector

will be integrated into a quadruple glazing window

As innovation, in the OPV and OLED, GRAPHENE will replace ITO



Motivation: Getting Graphene into the ITO Replacement market

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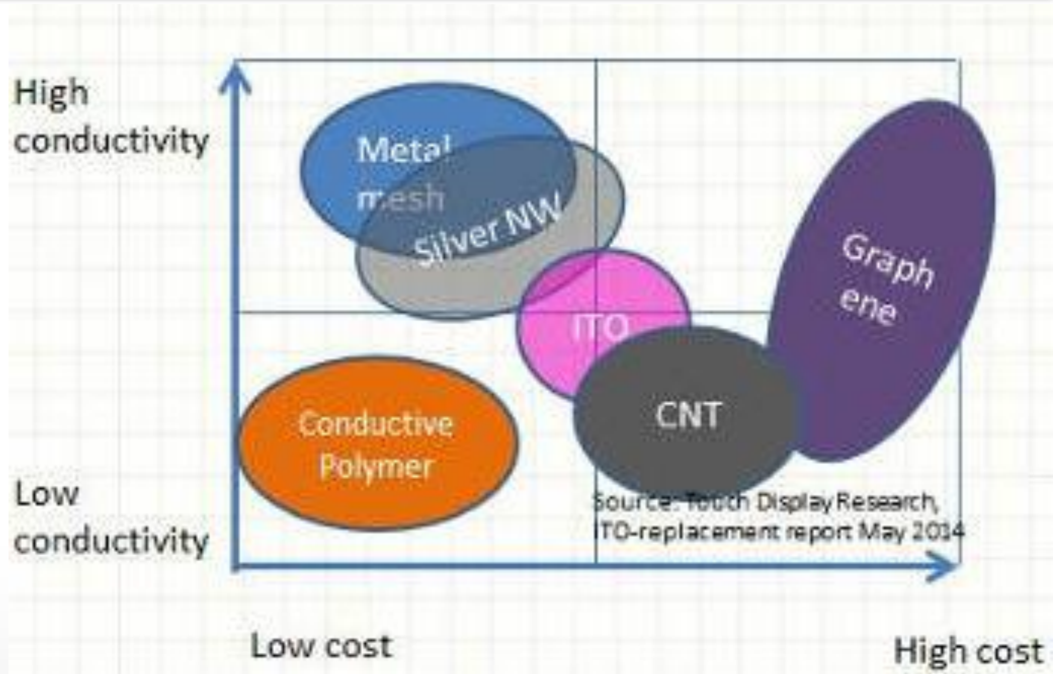
- Materials combining high electrical conductivity and optical transparency are vital for optoelectronic devices, such as solar cells, light emitting diodes and touch screens.
- Doped metal oxides, in particular indium tin oxide (ITO), are the most widely used.
- However, the rising price and limited geographical availability of Indium and the desire for flexible substrates necessitates alternative transparent conductor materials (TCs) for next generation devices.
- There are a number of technologies being developed to address this market, many of which are based on some form of nanomaterials and involve printing or coating processes which can be performed continuously.
- Among the range of intensely studied emerging TCs, graphene shows great promise



Comparison of the various nanomaterials competing in the ITO replacement space. [Source: Touch Display Research]

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Graphene: Revolution in Waiting

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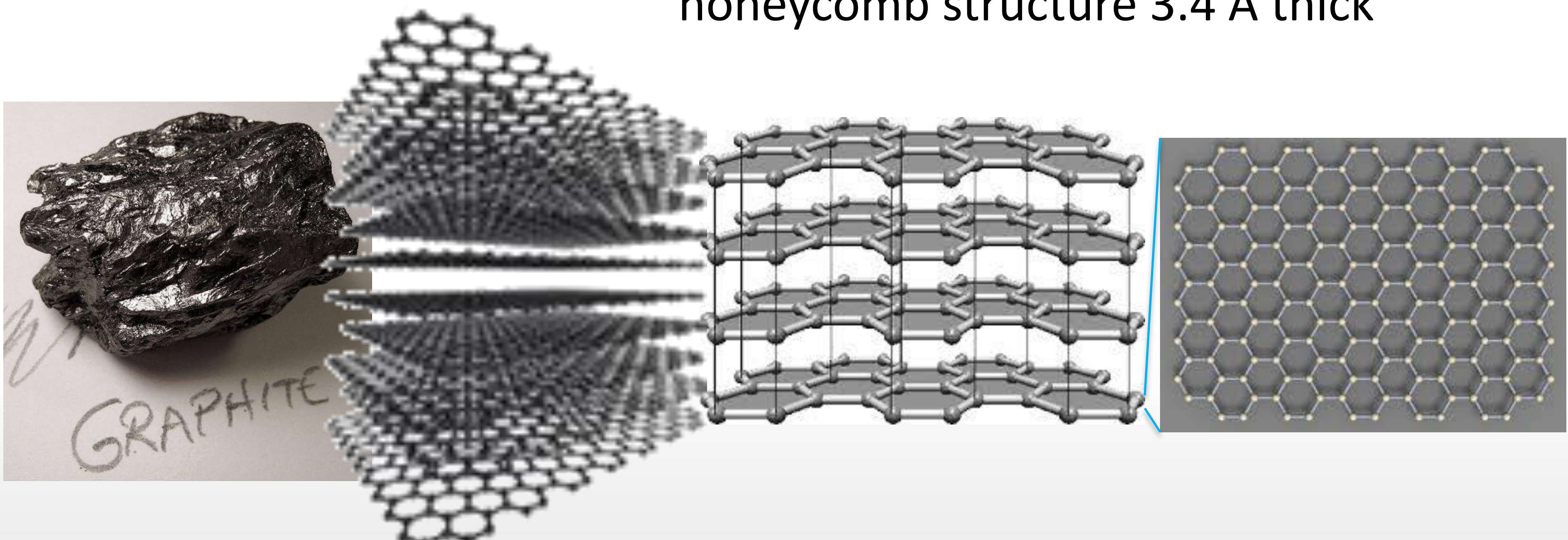
- From Graphite to Graphene: a single layer of Carbon atoms in a honeycomb structure 3.4 Å thick



Graphene is the thinnest material ever made; It is transparent, conducts electricity and heat better than any copper wire and weighs next to nothing. Its thinness makes the material ultra-flexible, even rollable.

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Why Graphene is so Popular?-1

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Its history leading to the Nobel Prize in Physics in 2004

- The term graphene first appeared in 1987 to describe single sheets of graphite
- In the 1930s, Landau and Peierls showed thermodynamics prevented 2D crystals in free state, an article in Physics Today reads:

- "Fundamental forces place insurmountable barriers in the way of creating 2D crystals...Nascent 2D crystallites try to minimize their surface energy and inevitably morph into 3D structures. But there is a way around the problem. Interactions with 3D structures stabilize 2D crystals. So one can make 2D crystals sandwiched between or placed on top of the atomic planes of bulk crystals"

- In 2004, Andre Geim and Kostya Novoselov at Manchester University managed to extract single-atom thick crystallites (graphene) by the Scotch tape technique from bulk graphite and transferred them onto SiO_2 on a Si wafer .

- Since 2004, an explosion in the investigation of graphene in terms of synthesis, properties and applications have been reported.

Why Graphene is so Popular?-2

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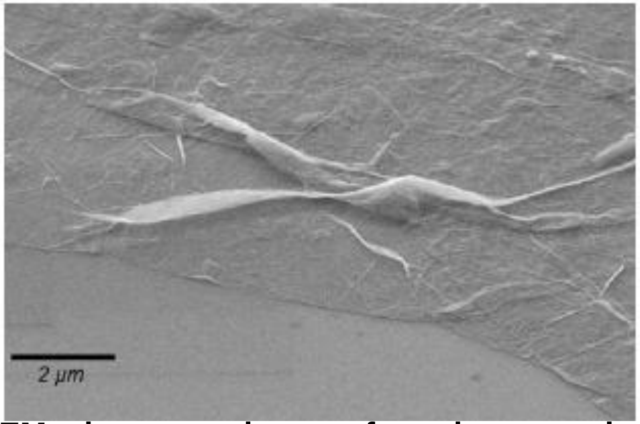
Its Outstanding (theoretical) Properties

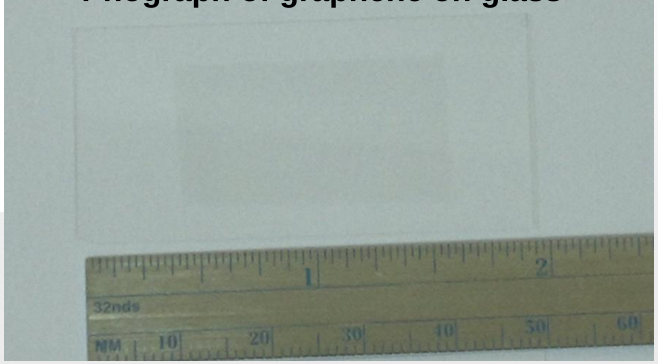
	Graphene	**Competitor**
High Electron Mobility (cm^2/Vs)	200.000	Silicon 1400
High Electrical Conductivity (S/m)	10^8	Silver $63x10^6$
Optical Properties	97.7% Transmittance (monolayer)	
Thermal Conductivity (W/mK)	5300	Silver 429 Copper 400
Mechanical Properites	High Young's modulus 1100 Gpa High Fracture Strength 125 GPa	200 times stronger than steel
Anomalous quantum Hall effect		

How it appears



SEM microscopy image of graphene on glass

Phograph of graphene on glass



Why Graphene as ITO-Replacement?

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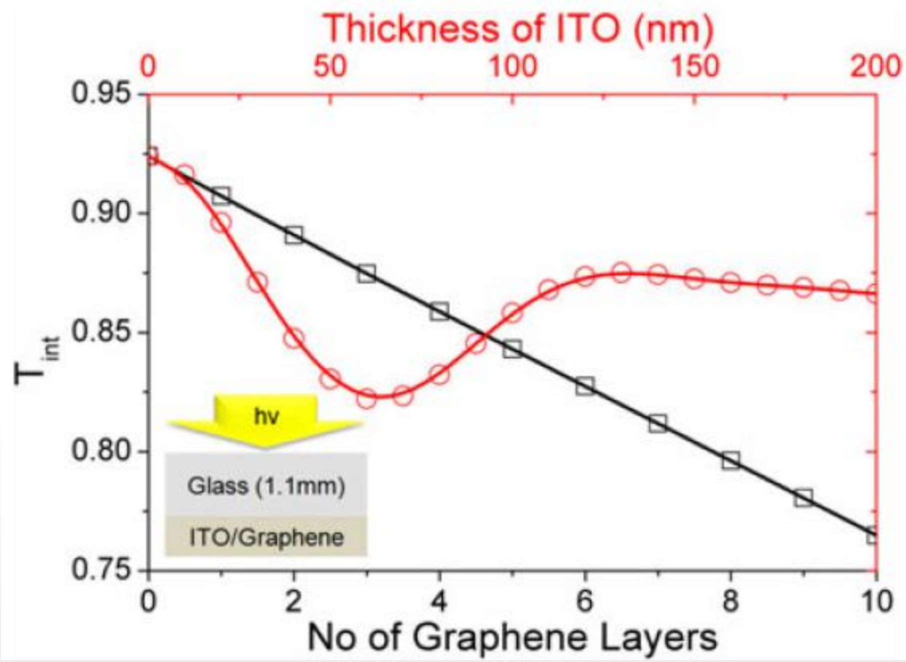
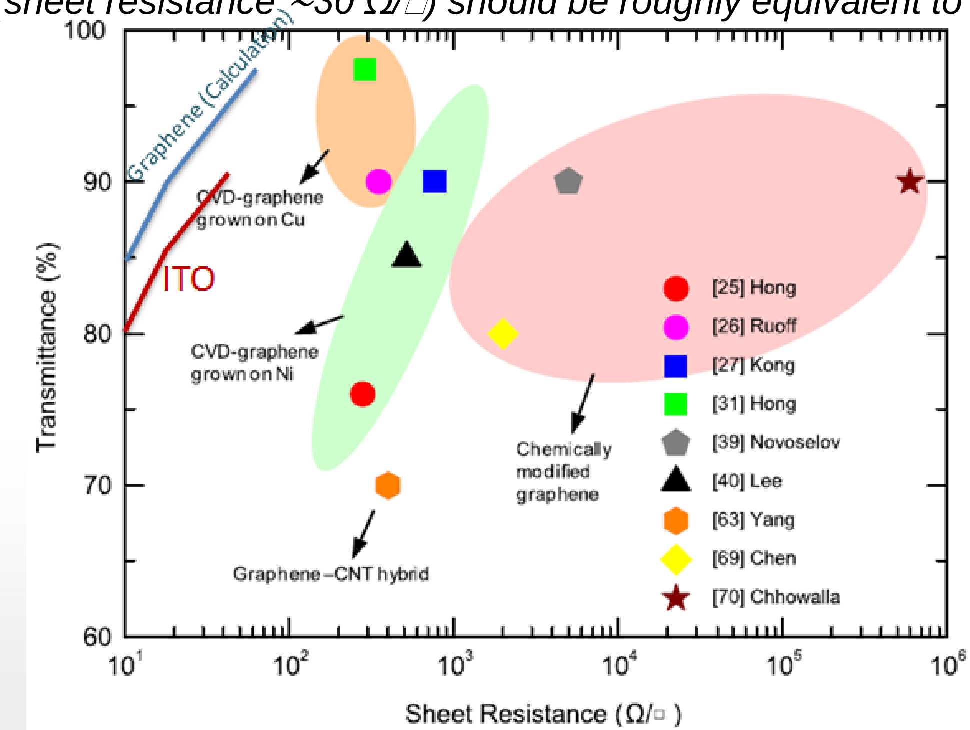
Focusing on Transmittance and Sheet Resistance

- 1-4 layers of graphene have comparable or even higher transmittance than ITO.
- In terms of sheet resistance, *4 layers of graphene (sheet resistance ~30 Ω/□) should be roughly equivalent to ITO on glass (sheet resistance ~20–30 Ω/□).*



Integral transmittance *of light (λ = 350–800 nm) illuminating* 1.1-mm-thick glass and graphene (ITO) as a function of number of graphene layers and ITO thickness



•Experimentally, it is challenging to achieve a sheet resistance < 100 Ω/sq with optical transmittance > 90%

•Sheet resistance also strongly depends on graphene synthesis

Synthetic Routes to Graphene

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Mechanical Exfoliation of Graphite

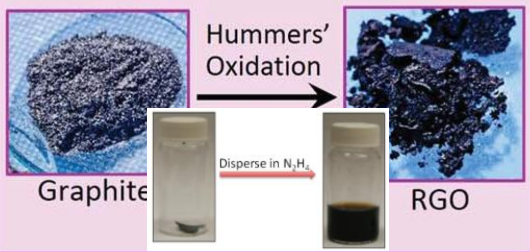
- Also known as the "**Scotch™ tape**" method
- Individual layers are peeled off of Kish graphite and deposited on an arbitrary substrate with little interfacial hybridization

Graphite flakes on "**Scotch™ tape**"

Limit: small hundreds μm-size flakes
Not scalable production

Chemically Derived Graphenes

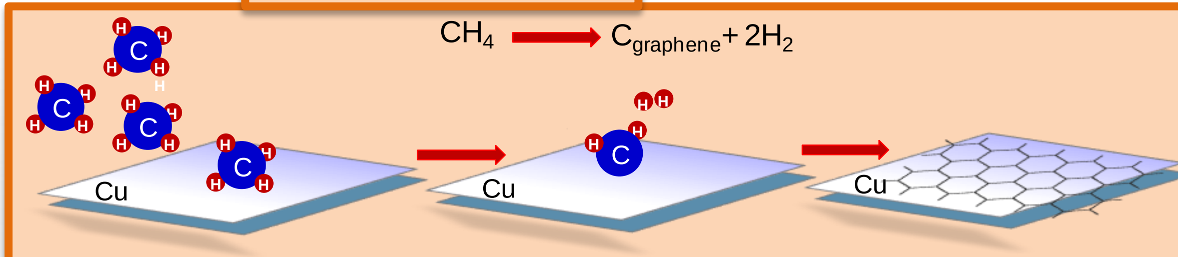
Reduced Graphene Oxides (RGO)



Limit: poor quality

CVD from Transition Metals (Cu, Ni, Pt, Ru,..)

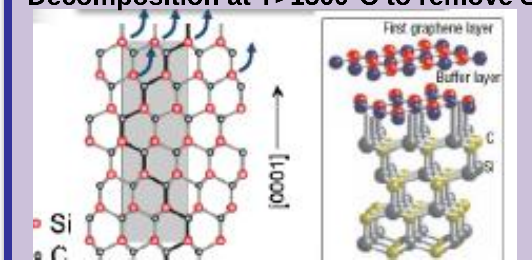
Dehydrogenation of metane CH_4 on Copper catalytic surfaces at T=1000°C



✓ **Advantages: large area, industrially scalable, good quality**

Growth from SiC

Decomposition at T>1500°C to remove Si



Limit: high price of SiC wafer
Size limited from SiC wafer

CVD Growth of Graphene

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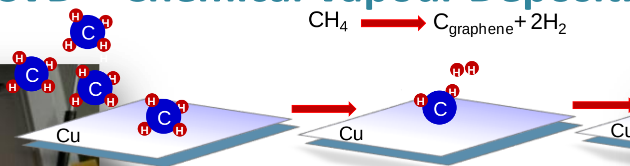
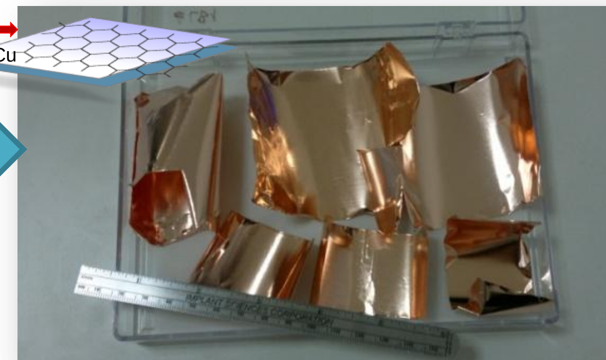
CVD – Chemical Vapour Deposition

$CH_4 \rightarrow C_{graphene} + 2H_2$

Batch reactor-furnace heating





Growth Conditions

- CH_4:H_2 precursors
- 1000°C
- 1 Torr

(max size = 50cm* 30cm)

The CVD process include the following steps:

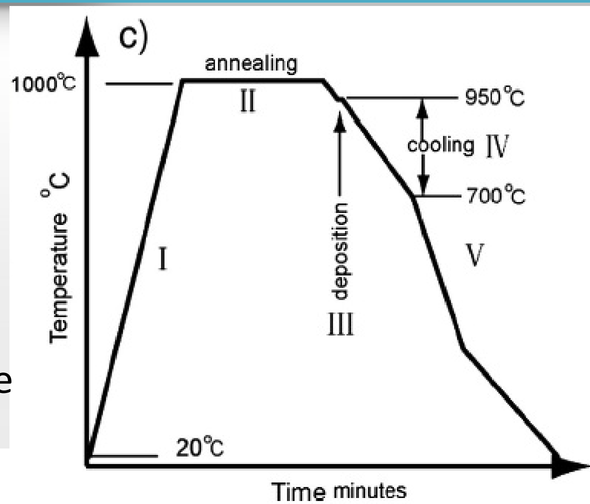
I) Thermal ramping up in H_2

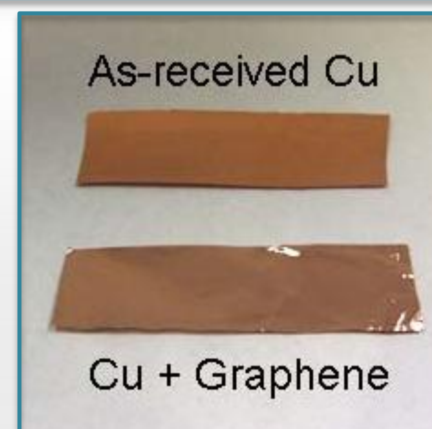
II) Annealing in H_2 of Cu foil

III) Deposition using CH_4

IV) Cooling down

All those steps determine graphene quality





[M. Losurdo et al. Phys. Chem. Chem. Phys. 13, 20836 (2011)]

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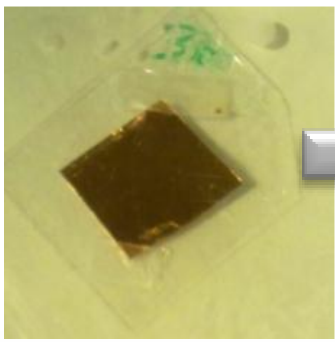
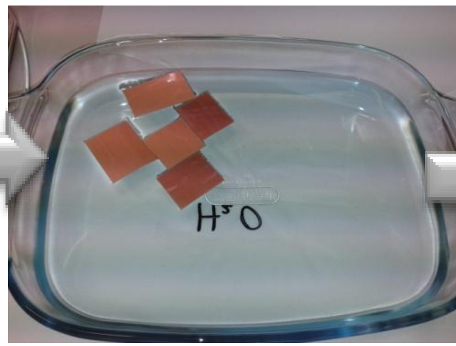
Transferring Graphene onto Substrates

Various additional steps are involved in the transferring of graphene to glass or any other substrate. The thermal tape release method involves the etching of the Cu foil

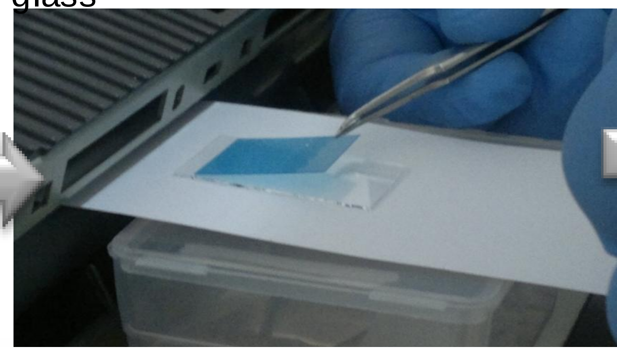
Tape on G/Cu



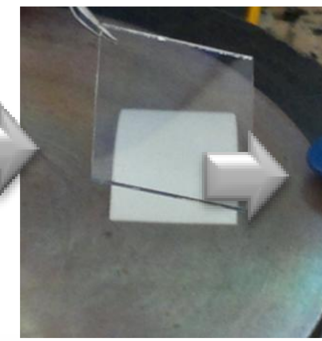
Cu dissolution



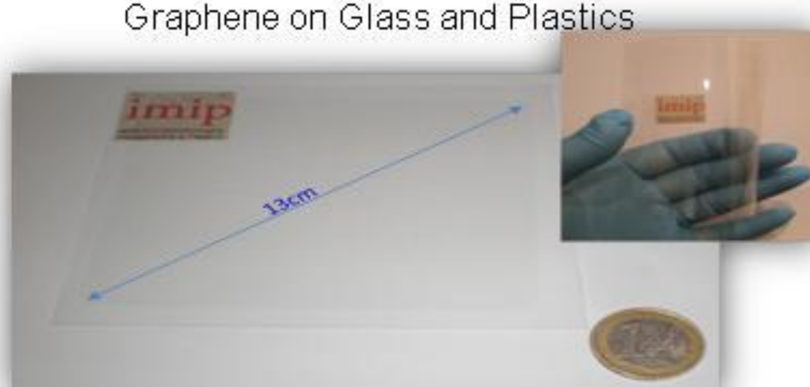
Lamination of Thermal Tape /G on glass



Thermal detaching of tape



Graphene on Glass and Plastics



Properties of Graphene on Glass

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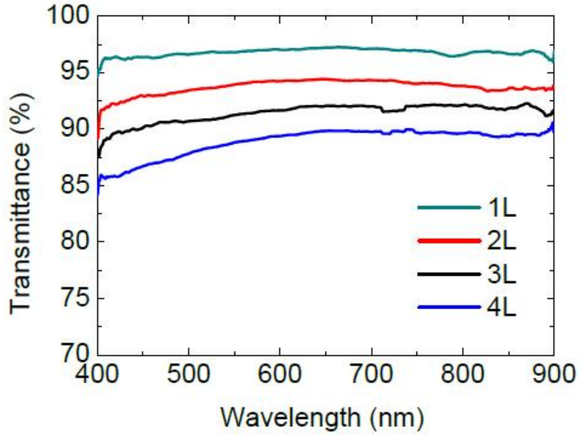
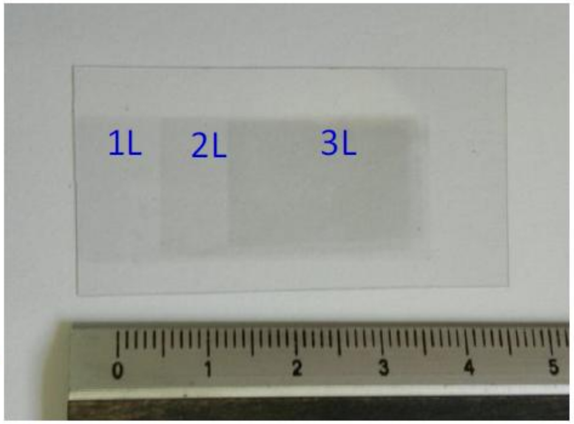
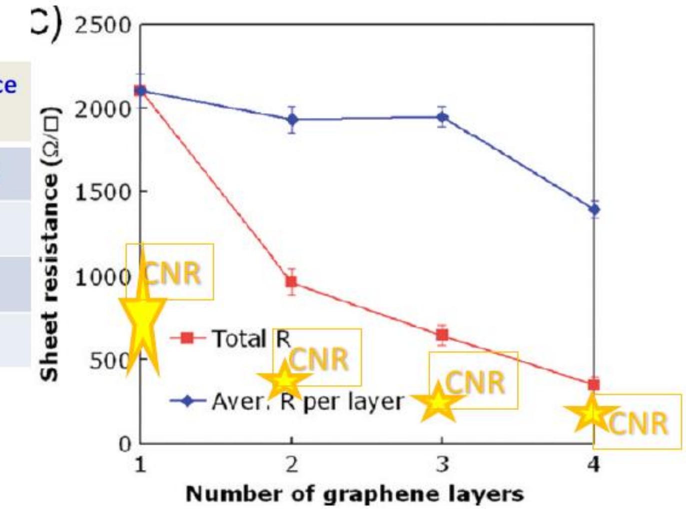
Thickness Dependence

- Using multiple transferring, we can produced bilayer, trilayer and four-layer graphene on glass.
- The sheet resistance decreases going from monolayer (1L), to bilayer (2L), trilayer (3L) and to four-layers (4L) stacked graphene layers, with corresponding transmittance decreasing, still being >90%.
- The table summarizes the transmittance at 550nm and the measured sheet resistance values.
- CNR-IMIP achieved sheet resistance values, indicated by stars better than data from literature
- **The sheet resistance of unintentional doped graphene is still higher than that of ITO!**



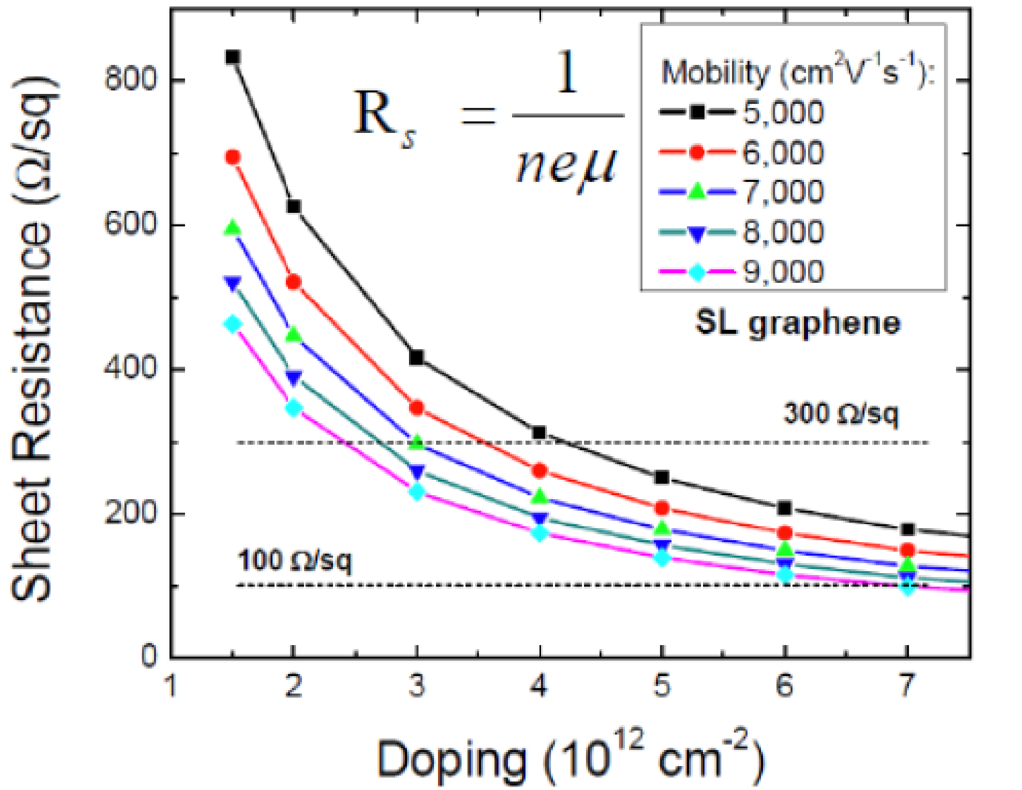


Graphene layers	Transmittance (%) @550cm-1	Sheet Resistance Ω/□
1L	96.8	470 ÷ 1100
2L	93.9	260 ÷ 320
3L	91.2	200 ÷ 290
4L	88.8	~150



Doping of Graphene: The Challenge!

- Typically, the sheet resistance, Rs, of pristine or undoped single layer CVD graphene is of the order of 1000-5000 Ω/□ — too large to for use as a transparent conductor!
- The sheet resistance can be lowered by doping graphene
- The challenge: it is difficult to achieve doping of graphene stable in time!

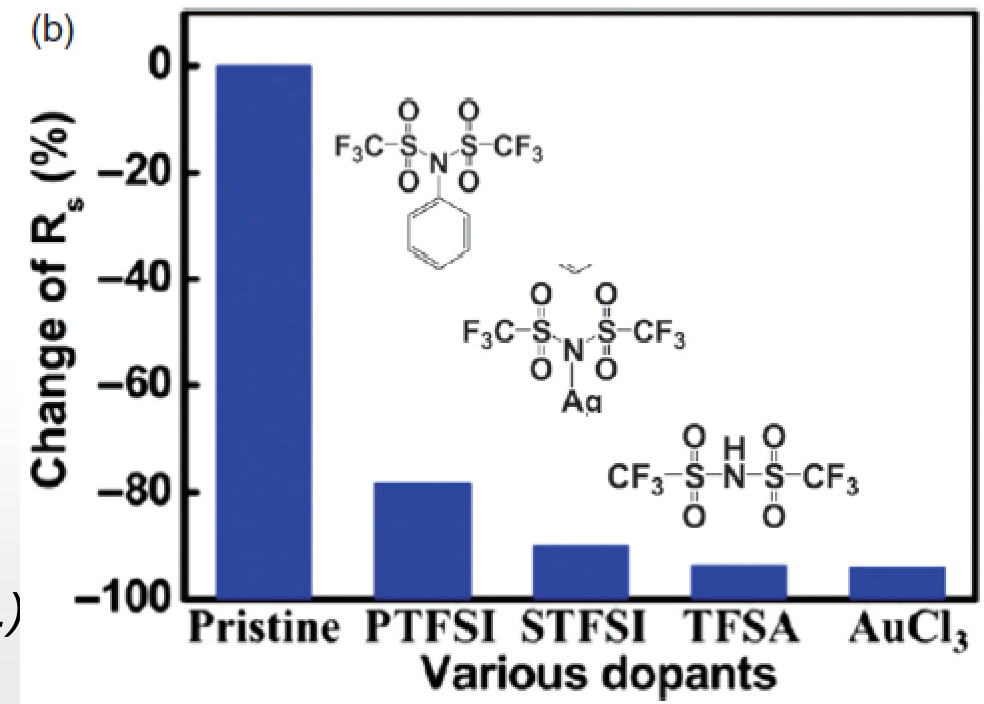


[S.Bae et al. Phys. Scr. T146 (2012) 014024

Doping of Graphene

For the application of graphene in various fields, doping is one of the efficient ways because it can tailor the electrical properties of graphene. Many researchers have investigated graphene doping methods through various processes, and they could be categorized into

- Electrical doping
  (e.g. gate-controlled doping)
- Wet doping
  - *Acid Treatment* (HNO_3)
  -*Metal Chloride Treatment ($AuCl_3$)*
- Molecular doping
- Chemical Doping
  (e.g. Thermal treatment in NH_3)
- Metallic cluster-induced doping *(Au, Ag,..)*
- Plasma Doping
  (e.g. hydrogenation, fluorination,..)



Sheet resistance of pristine and doped graphene using organic dopants. The data are compared with doping with AuCl3.

Example of NH_3 Graphene Doping

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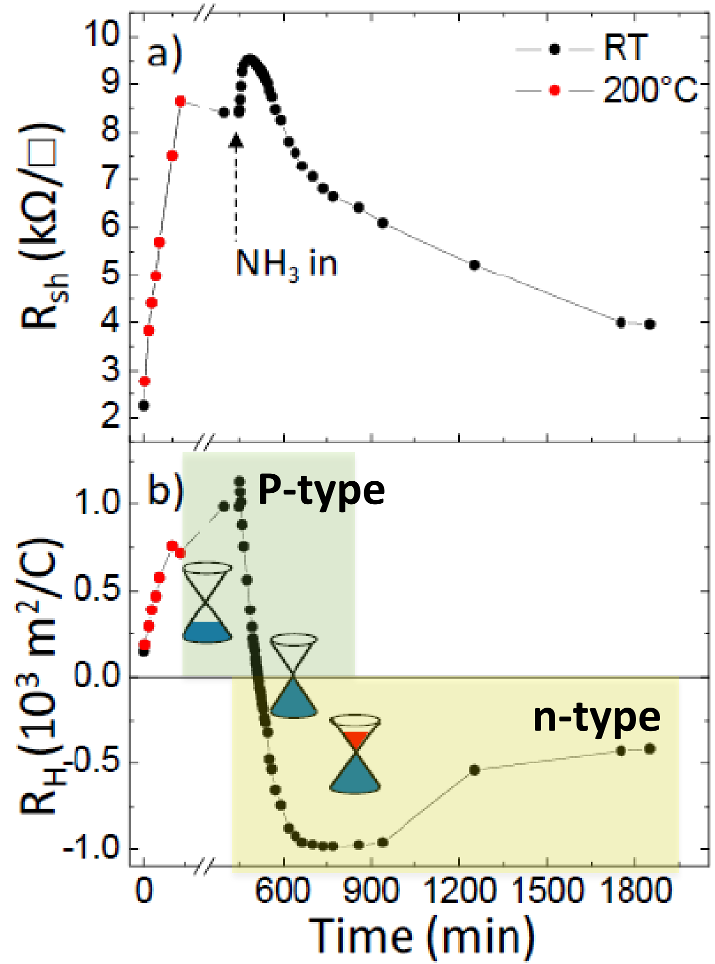
- Real time monitoring of the (a) sheet resistance (Rsh) and (b) Hall coefficient (RH) for a CVD graphene transferred on glass upon ammonia (NH_3) exposure (500 Torr)
- The NH_3 exposure time determines the doping concentration and sheet resistance
- With increasing NH_3 exposure time the graphene changes from p-type to n-type



[G.V. Bianco et al. Phys. Phys. Chem. Chem. Phys. 16, 3632 (2014)]

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Graphene Compared to ITO in Devices

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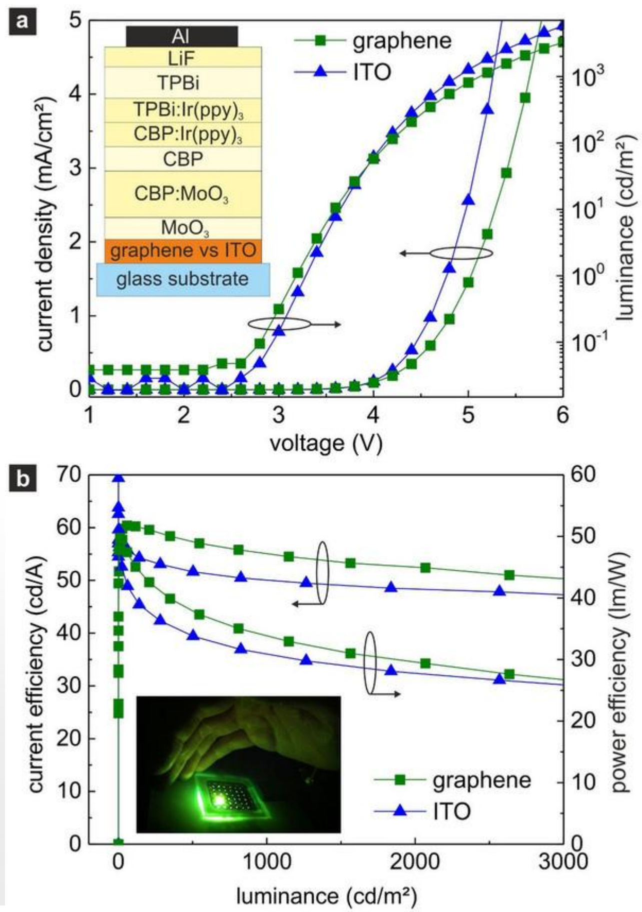
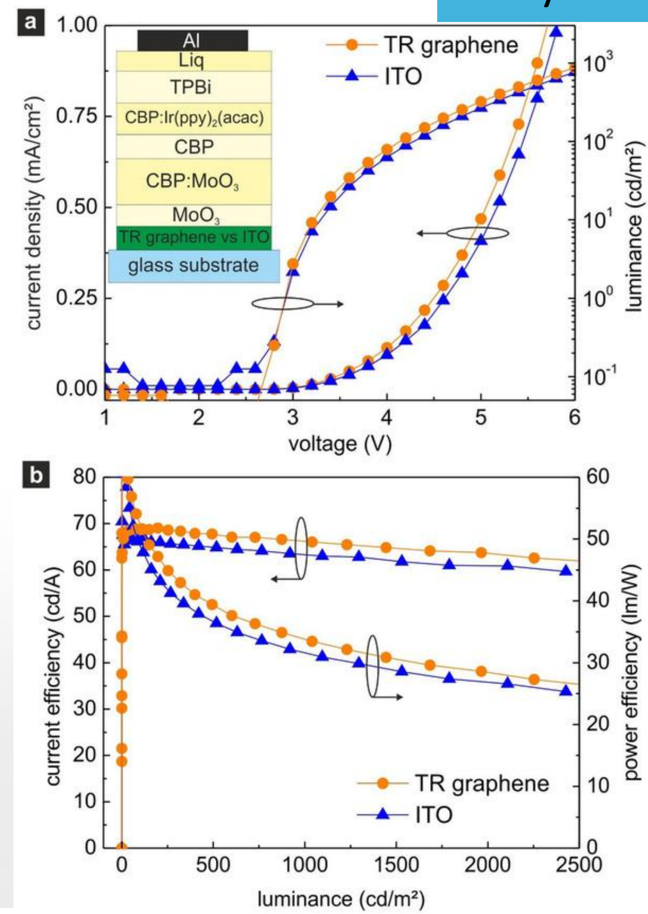
Graphene electrodes achieved same good performance as ITO in OLED

Trilayer G

- Current density, power efficiency and luminance versus voltage for OLED layer stack comprising ITO or graphene bottom electrode.
- Inset shows photograph of powered graphene-based OLED at high brightness level.
- Graphene can perform better than ITO!





[J. Mayer et al. Scientific Reports 4, Article number: 5380 doi:10.1038/srep05380 (2014)]

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Graphene for Heatable Smart Windows

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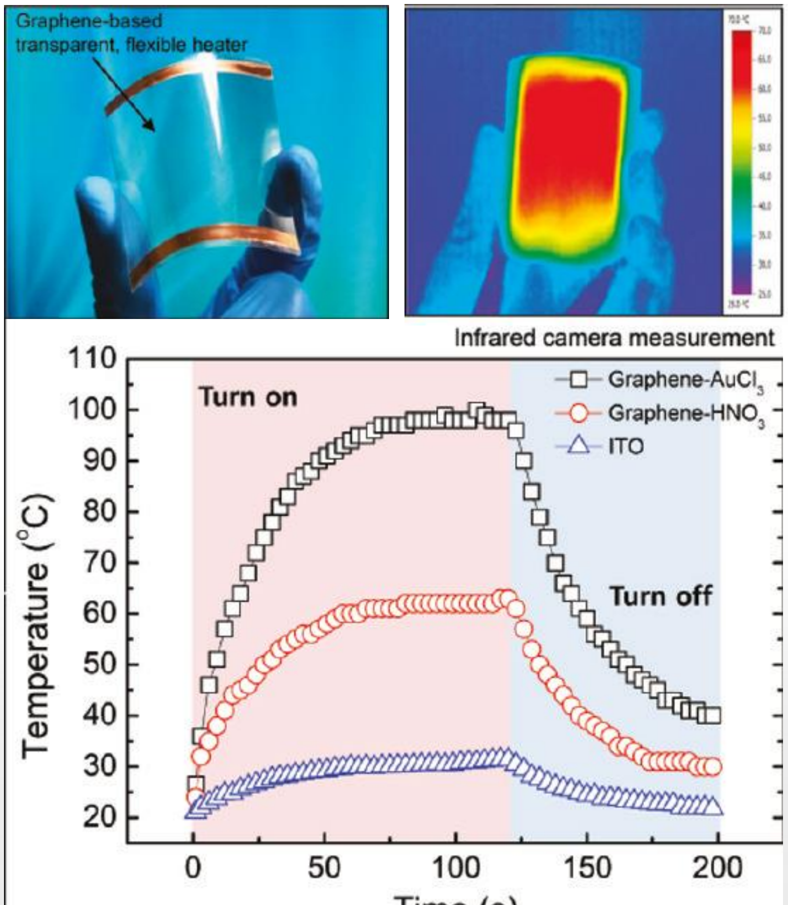
Going beyond ITO



- Graphene films synthesized by chemical vapor deposition on Cu foils, after multiple transfers and doping, show sheet resistance as low as ~43 Ohm/sq with ~89% transmittance, which are ideal as low-voltage transparent heaters.
- Time-dependent temperature profiles and heat distribution analyses show that the performance of graphene-based heaters is superior to that of conventional transparent heaters based on ITO

[B. H. Kong, N*ano Lett. 11*, 5154 (2011)]

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Graphene for Electro-Thermal Antifog Glasses

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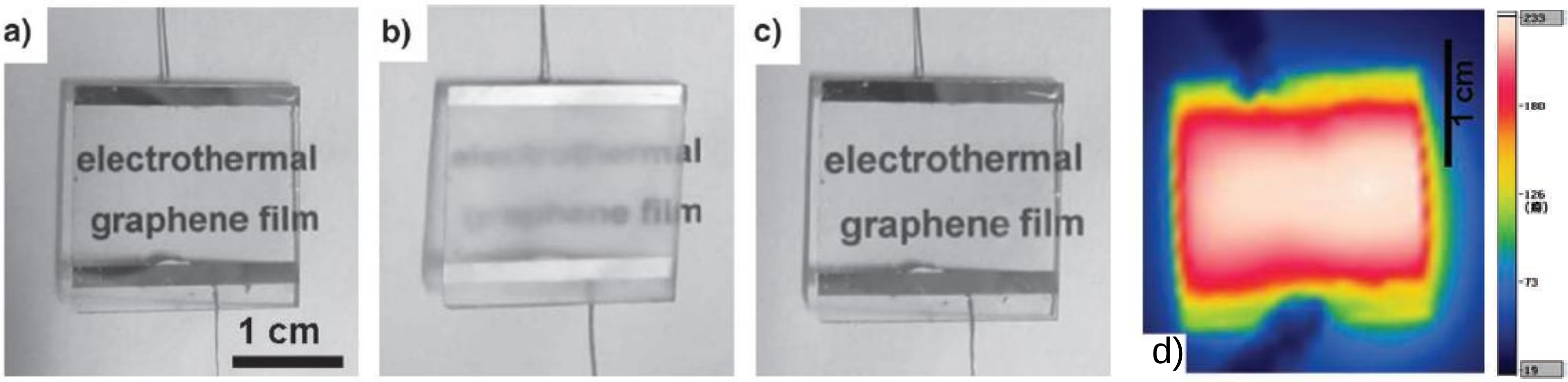
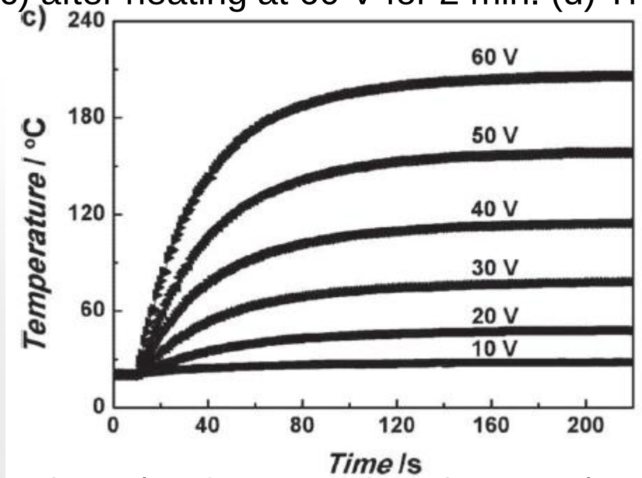


Frost removal performance before (a) and after (b) frost formed on the back of the film at -10°C in a refrigerator, and c) after heating at 60 V for 2 min. (d) The infrared thermal image at 60V



Electrothermal performance of graphene on glass

- Kimberly-Clark, the global health product manufacturer, has received a patent for an anti-fogging coating for glasses, using graphene as one of its components.
- US Patent Number 8398234 describes a transparent coating for optical lenses which also conducts electricity to prevent condensation.

[D. Sui et al. Small 2011, 7, No. 22, 3186].

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Graphene for Electrochromic Smart Glass

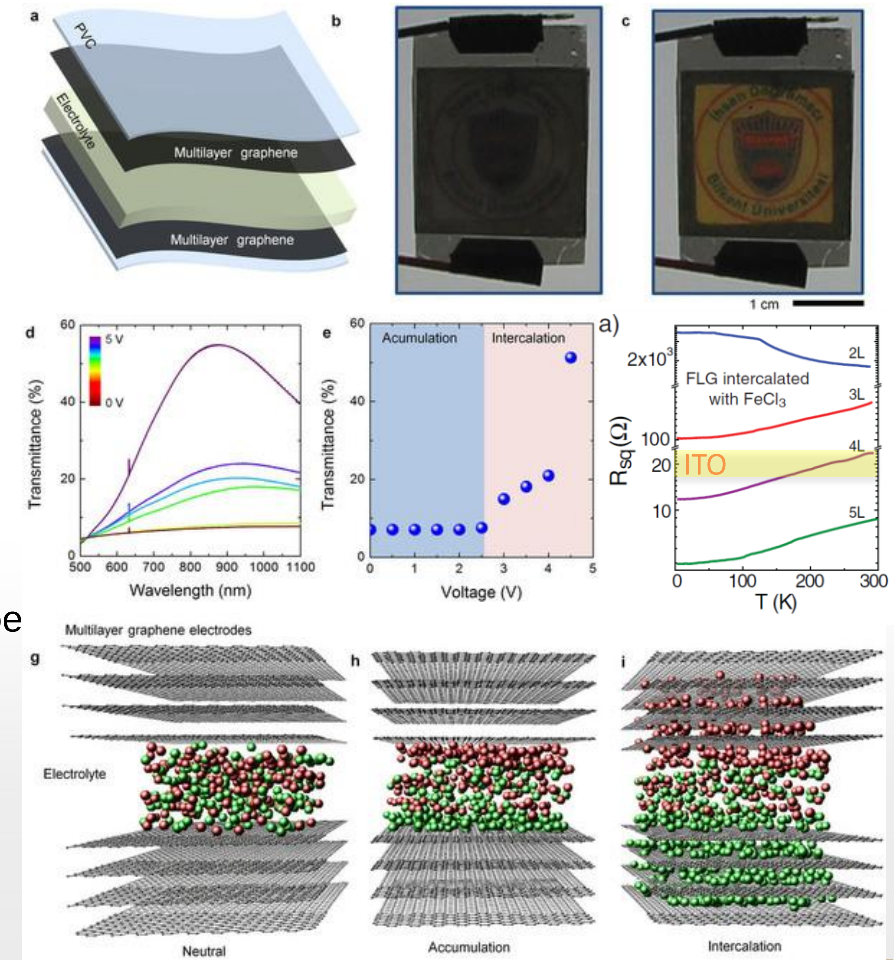
- Glass-backed graphene with specific electrolyte for voltage-tuneable transparency/opacity in an electrochromic window/device.
- The graphene surface can be switched from full transparency to a translucent or opaque darkened state within five seconds. The system is fully reversible to transparency in two seconds.

Key benefits

- The transparent state is completely clear due to the graphene layer.
- A voltage is only applied to switch the system, more efficiently than constant voltage systems.
- The system is tuneable; the degree of opaqueness can be adjusted by voltage.

Applications

- Reduction of solar glare in windows and mirrors.
- Improved temperature and light control in buildings.
- For use in privacy windows in internal glass partitions in offices.



Graphene for Electrochromic Smart Glass

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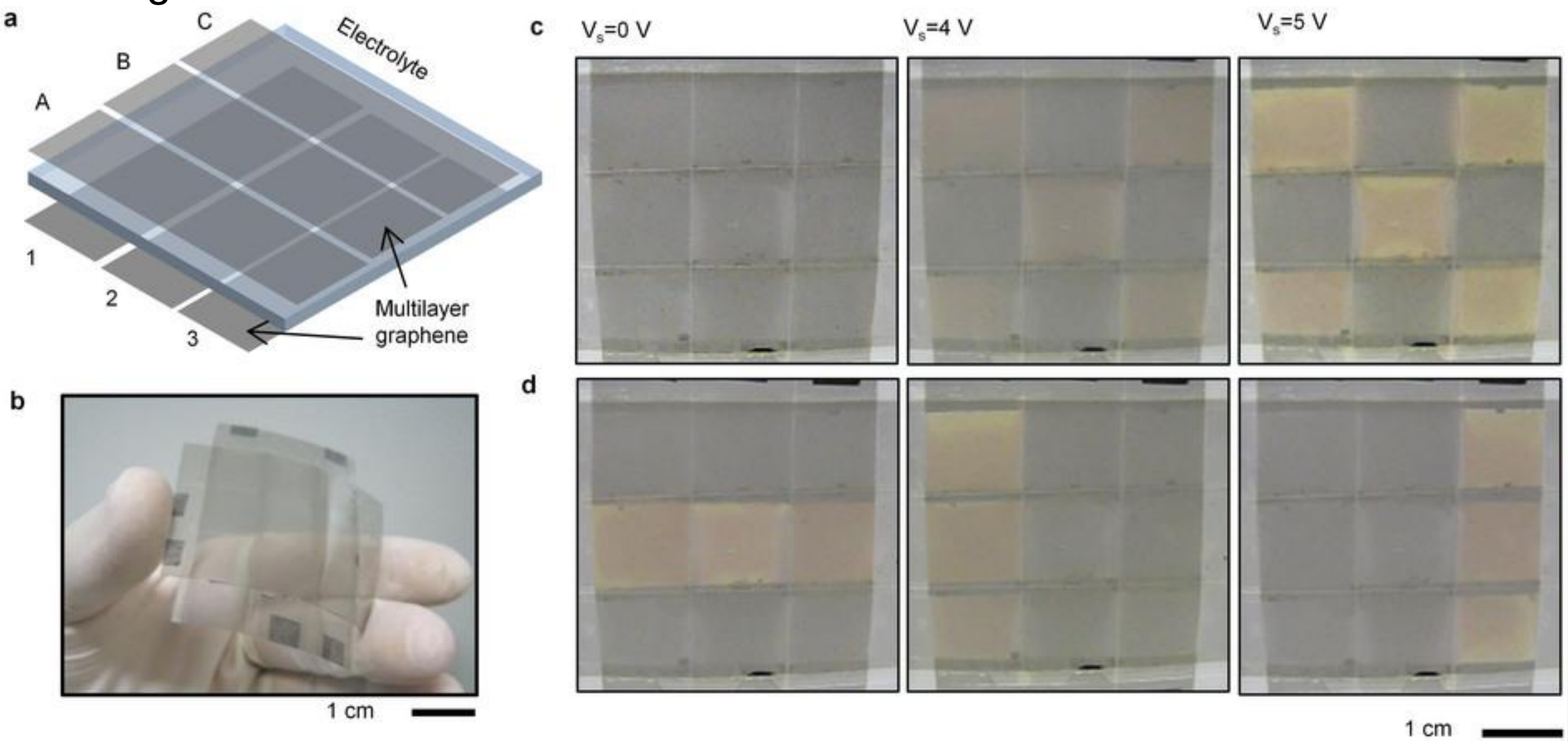
- The graphene electrodes are encapsulating the electrolyte
- The graphene system is tuneable; the degree of opaqueness can be adjusted by voltage.



[E.O. Polat et al. Scientific Reports 4, 648 (2014)]

Graphene for Electrolyte-Free Electrochromic Devices

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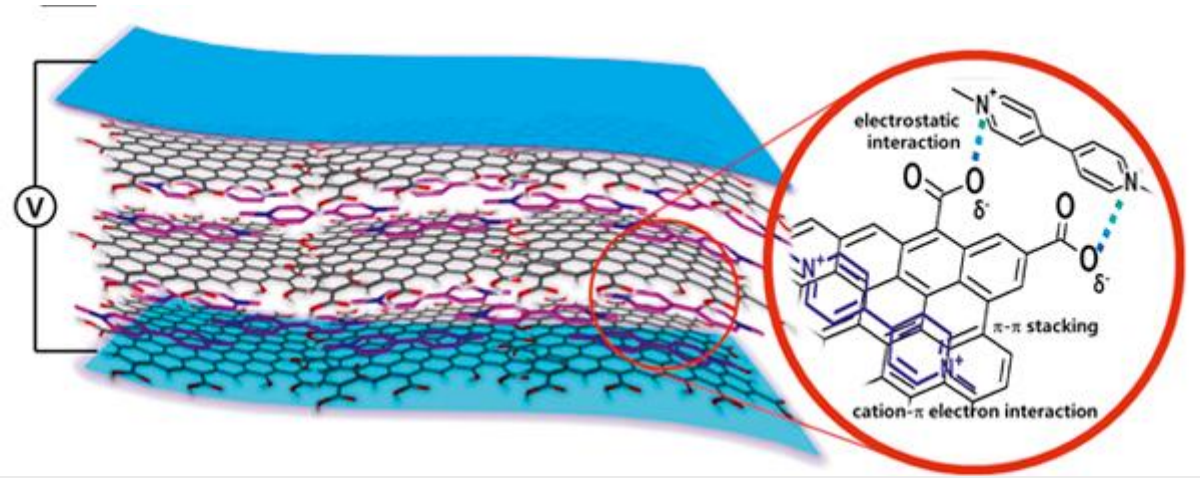
ADVANCED TECHNOLOGIES FOR SMART WINDOWS

Further recent implementation: using graphene as electrodes and graphene quantum dot-viologen nanocomposites as electrolytes eliminating any additional electrolytes

- The use of electrolytes in an ECD system could lead to the unwanted decomposition of metal-ion containing electrochromes at high voltages. In order to combat the negative effect of electrolytes on device stability and performance, the researchers developed a flexible ECD where the electrochrome, methyl-viologen (MV^{2+}) is combined with electrostatically strong, conductive graphene quantum dots (GQDs). There is strong adherence between the MV^{2+} (cation) and GQDs (anion) as a result of strong electrostatic and π-π interactions. The resultant ECDs demonstrate stable electrochromic performance without the use of an electrolyte.



[*Advanced Materials* (DOI: 10.1002/adma.201401201; p. 5129)]

Conclusions

- **CVD large area growth on practical substrates for device development is achieved.**
- **Doping is making graphene approaching ITO standards**
- **Graphene has many opportunities in smart windows technologies**
- **Smart windows including graphene are becoming a reality!**

http://www.futuretimeline.net/forum/topic/1551-samsung-transparent-smart-window/

Acknowledgements

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ADVANCED TECHNOLOGIES FOR SMART WINDOWS

- MEM4WIN Consortium

http://www.mem4win.eu/

- Coworkers at CNR-IMIP:

  Maria Giangregorio, Giuseppe Bianco, Alberto Sacchetti

- European Commission under Grant Agreement GA 314578

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