Graphene, an incredible material: the role of chemistry in realizing the promise of technological innovation

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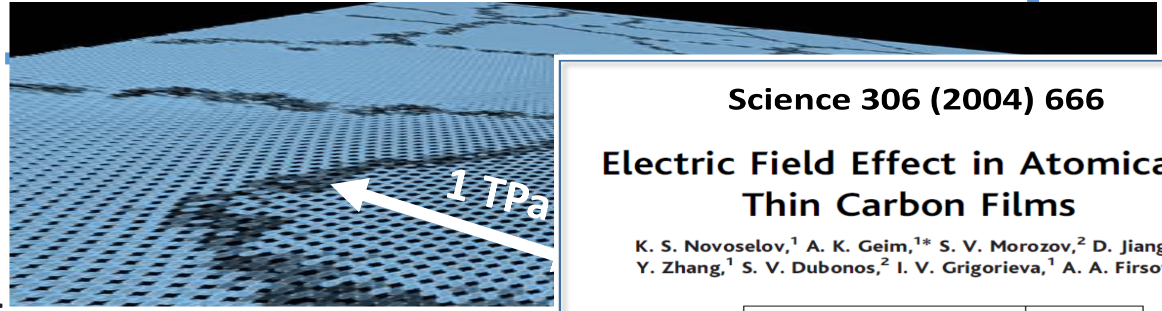
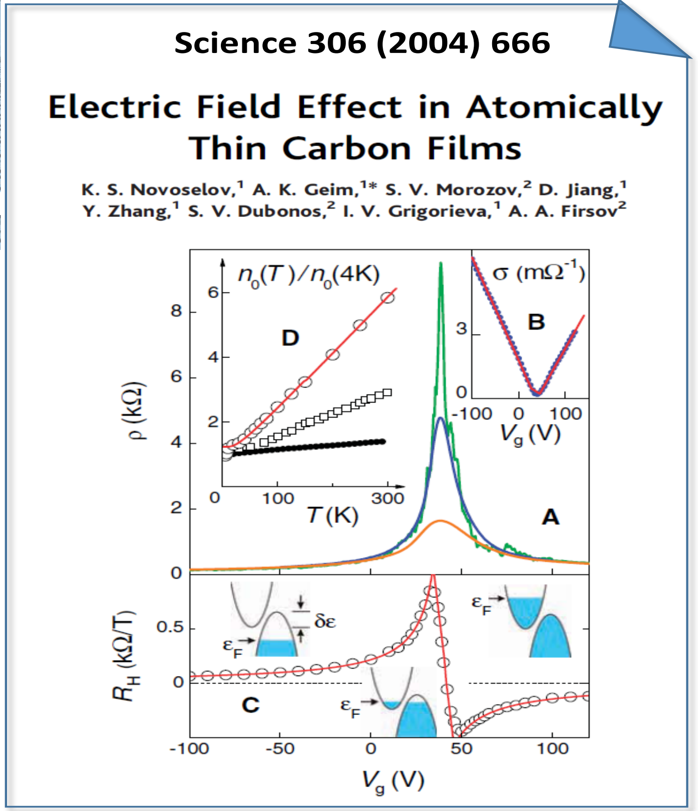
Why is graphene "incredible"?

Commonly mentioned incredible (?) properties of graphene

- **Thin**
- **Transparent**
- **Flexible**
- **Strong**
- _ _ _ _ _ _ _
- _ _ _ _ _ _ _
- _ _ _ _ _ _ _

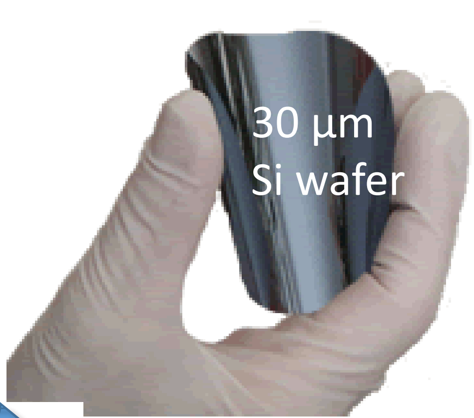
Lambert–Beer law
A = k*t

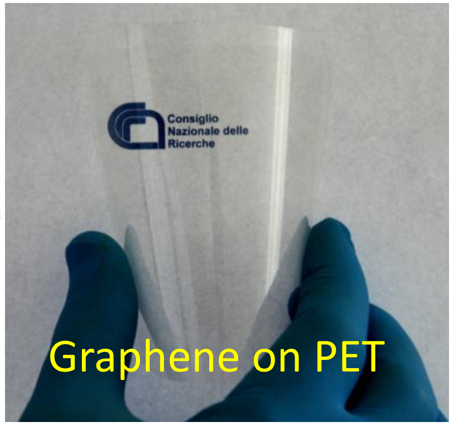



Science 306 (2004) 666

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]





High room-temperature mobility (~10,000 cm^2/Vs)

Strong ambipolar electric field effect

OUR ANSWER

GRAPHENE IS AN INCREDIBLE MATERIAL SINCE IT CAN BE CONSIDERED AS…

QUASI-METAL

It provides very good conductivity and supports surface plasmons

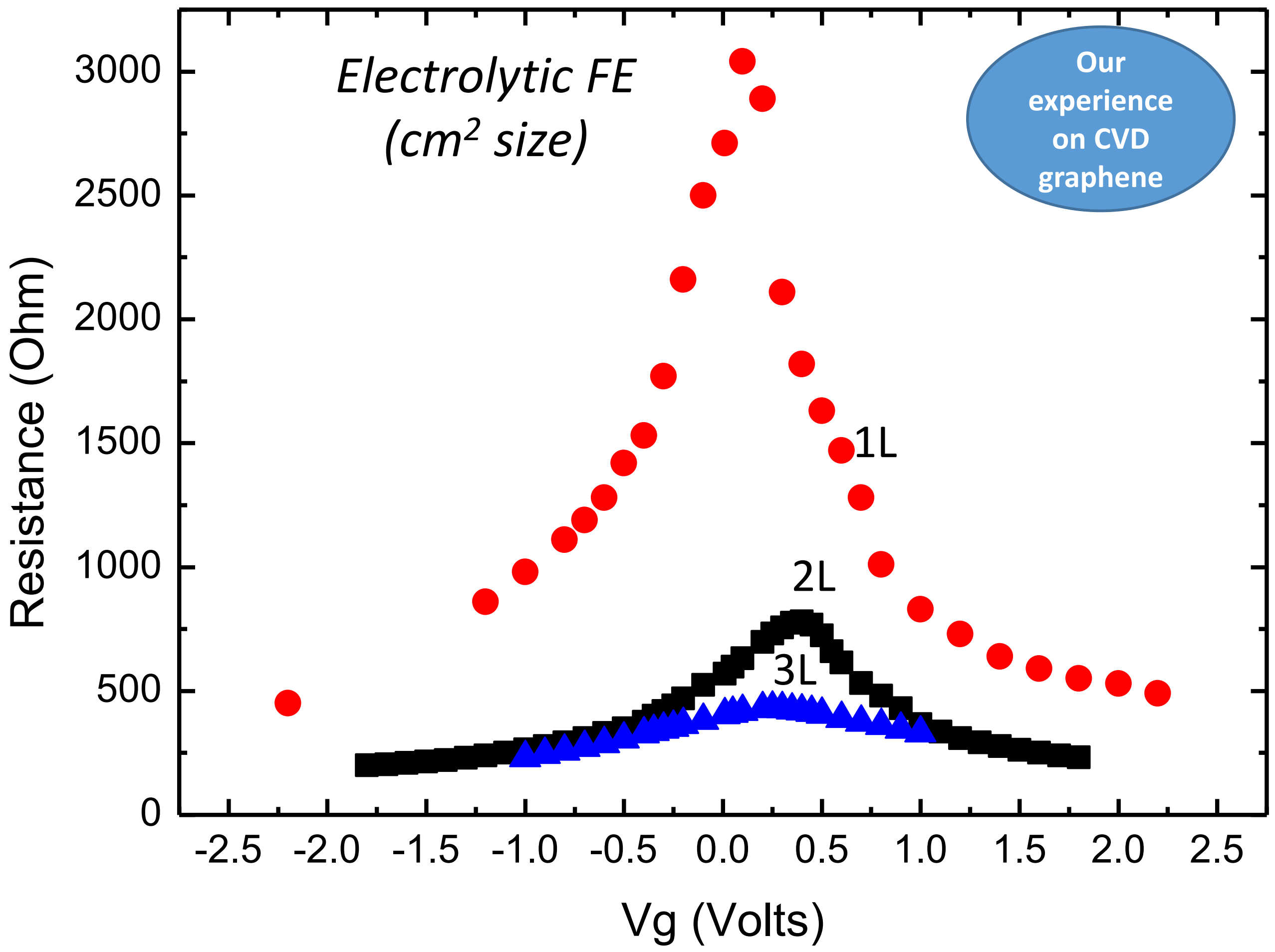
QUASI-SEMICONDUCTOR

Its transport and optical properties can be tuned by or p/n doping

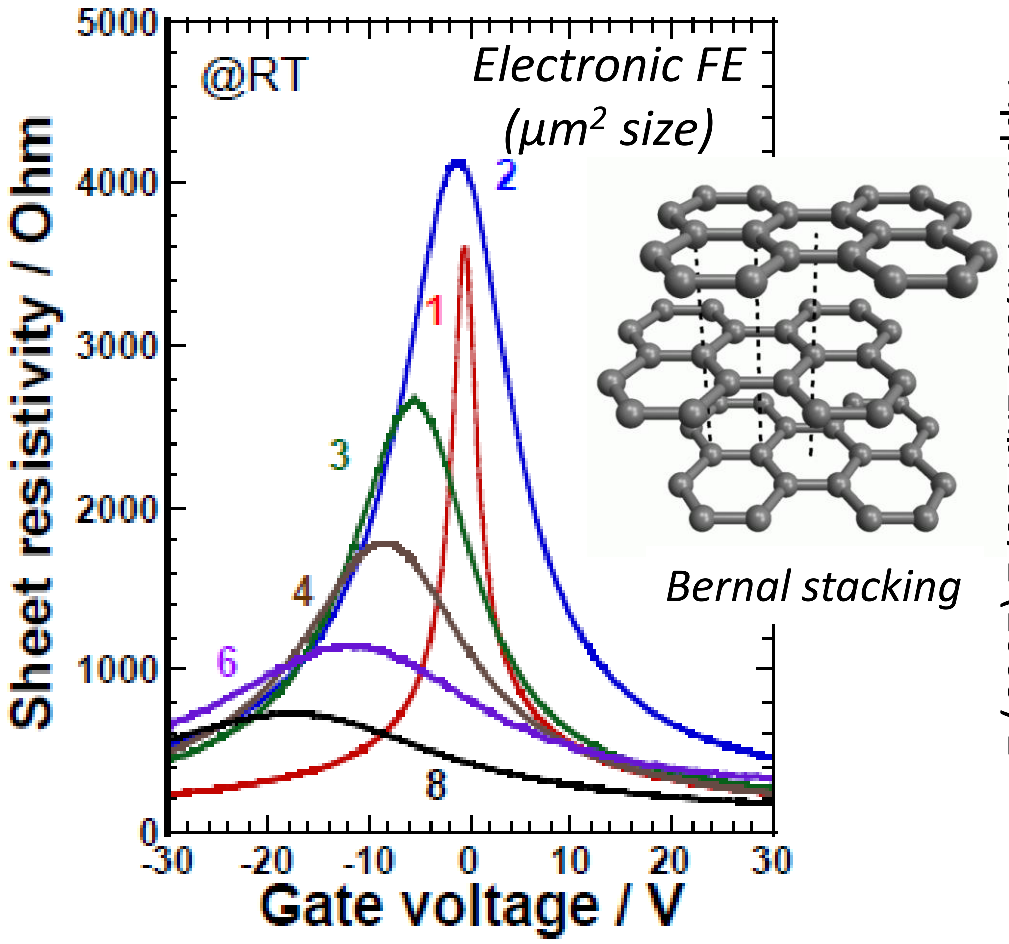
When does graphene material became graphite?

The demonstration of ambipolarity/tunability can be exploited to discriminate univocally a **graphenic** material from a **graphitic** one

CVD graphene



Mechanically Exfoliated graphene



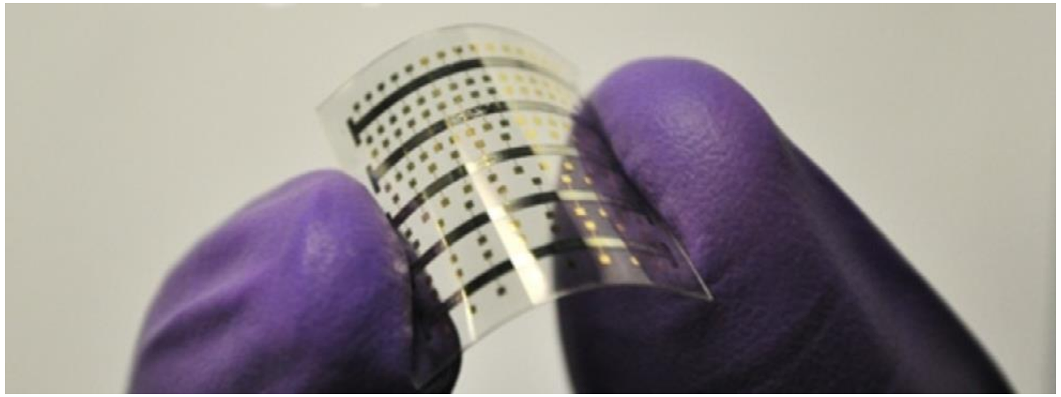
Applied Physics Express. 2 (2009) 2

The graphene promises

Potential graphene applications

- **Electronics**
- **Optoelectonis**
- **Photonics**
- **Sensing**
- **Energy**
- **…**

Flexible transistor

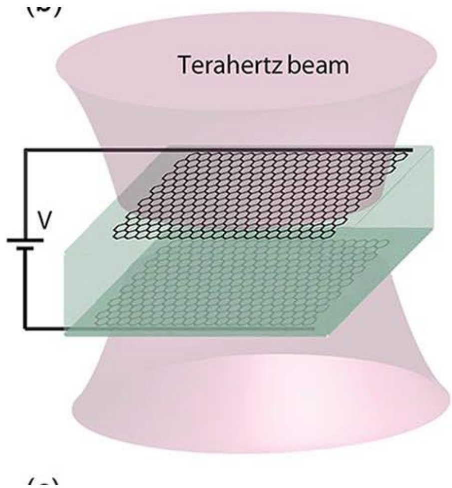


touch-screens

ACS Nano, **2014**, *8* (1), pp 950-956

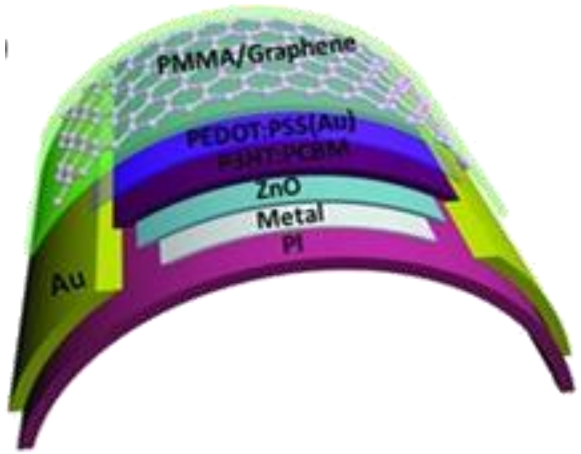
THz modulators and antennas

Proceedings of the IEEE, 101, (2013)1705



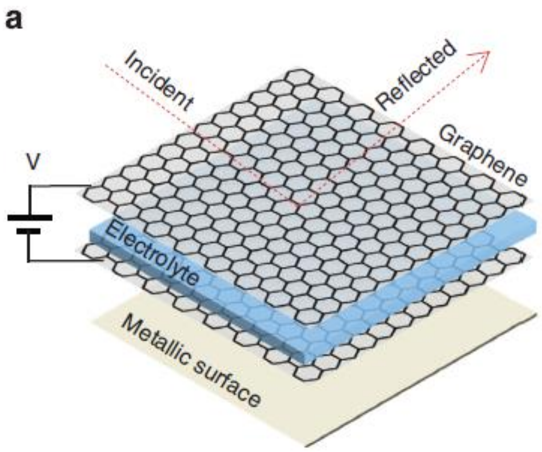
OPV devices

Adv. Mater. **2013**, *25*, 4296–4301



EMI shield

NATURE COMMUNICATIONS, 6 (2015) 6628

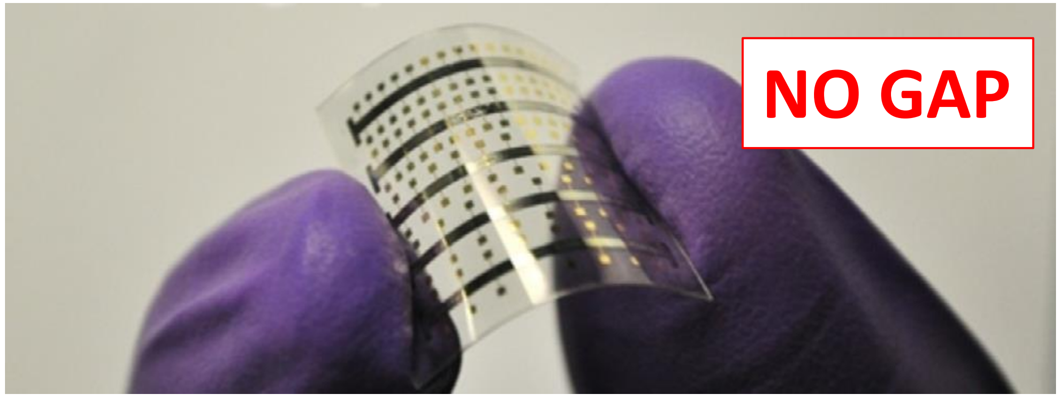


The graphene ~~promises~~ DRAWBAKS

Potential graphene applications

- Electronics
- Optoelectonis
- Photonics
- Sensing
- Energy
- …

Flexible transistor



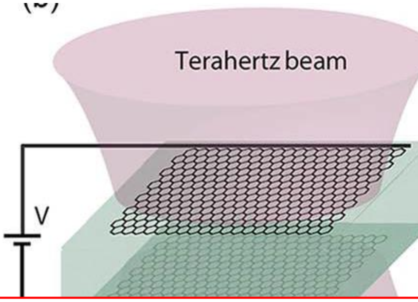
NO GAP

ACS Nano, **2014**, *8* (1), pp 950-956

touch-screens

HIGH Rs

THz modulators and antennas

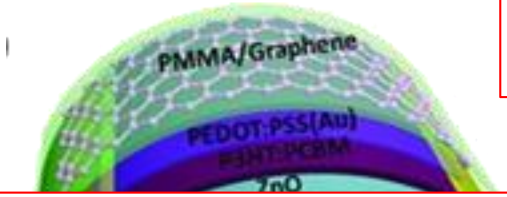


DIFFICULT TUNING OF OPTICAL CONDUCTIVITY (especially on large area)

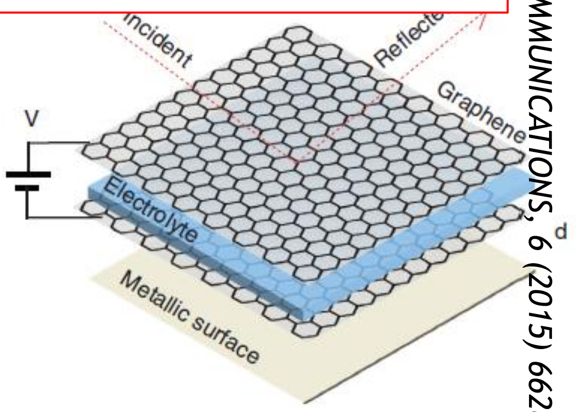
Proceedings of the IEEE, 101, (2013)1705 *NATURE COMMUNICATIONS*, 6 (2015) 6628

Adv. Mater. **2013**, *25*, 4296–4301

OPV devices



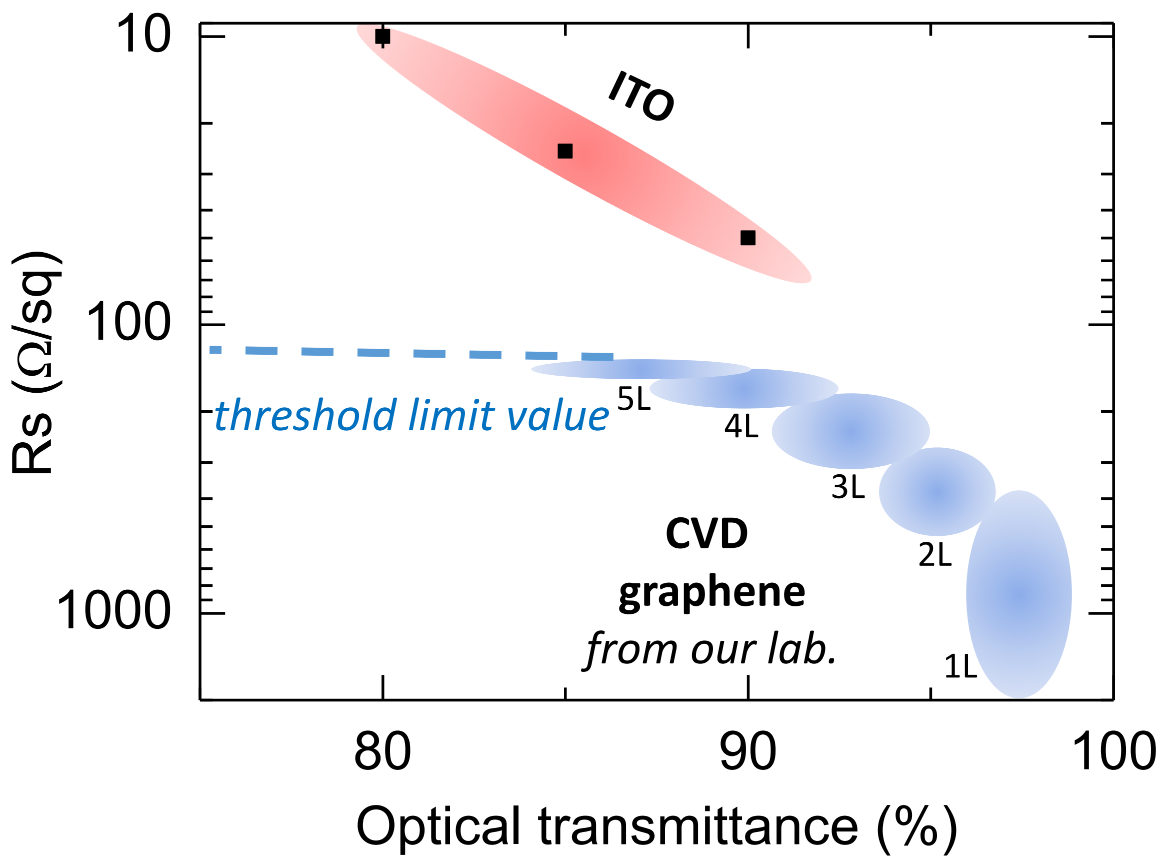
DIFFICULT INTERFACING WITH OTHER MATERIALS (low wettability, high contact resistance,..)



Main “nontransistor” application of Graphene

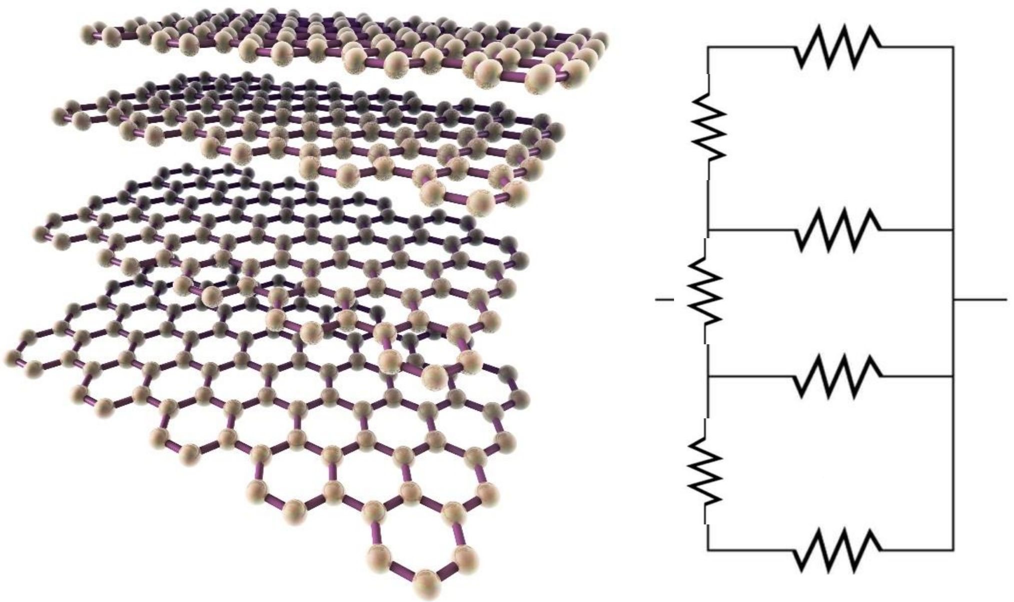
Graphene as Transparent and Flexible conductive film to replace ITO

(very strong competitor!!!)



Lowering the sheet resistance of CVD graphene

by using multiple layers of CVD graphene

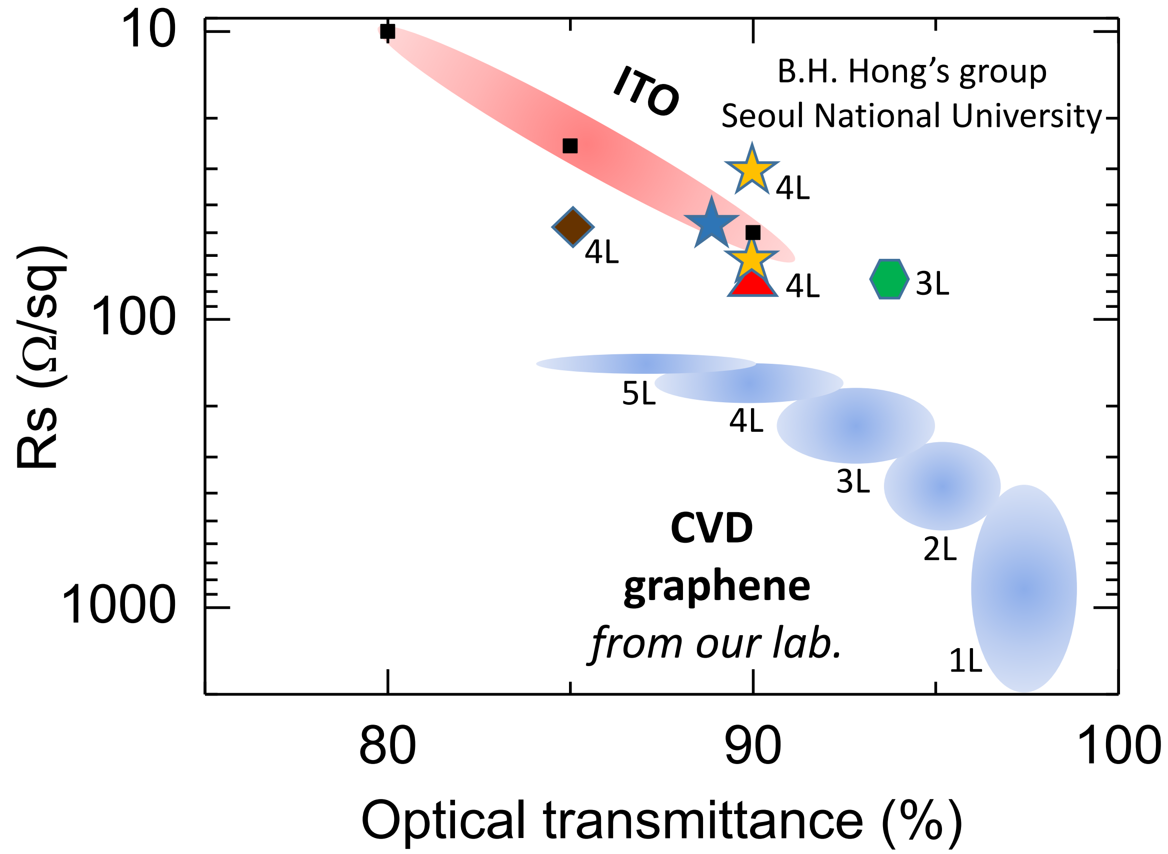


Partial contact or presence of impurities contribute to contact/series resistances between graphene layers

Main “nontransistor” application of Graphene

Graphene as Transparent and Flexible conductive film… to replace ITO

(very strong competitor!!!)



Lowering the sheet resistance of CVD graphene

by doping

- HNO_3 doped graphene (30Ω/sq)
  [Nat. Nanotechnol., **2010**, 5, 574–578]
- $AuCl_3$ doped graphene (54Ω/sq)
  [ACS Nano, **2010**, 4, 4595]
- HNO_3 doped graphene (63Ω/sq)
- $AuCl_3$-CH_3NO_2 doped graphene (43Ω/sq)
  [Nano Lett. **2011**, 11, 5154–5158]
- $FeCl_3$ doped graphene (72Ω/sq)
  [Nanotechnology, **2014**, 25, 395701]
- CL_2 doped graphene (70Ω/sq)
  [Nanoscale, **2014**, 6, 15301–15308]

Chemical Treatment for Lowering R_s of CVD Graphene: HNO_3 Doping

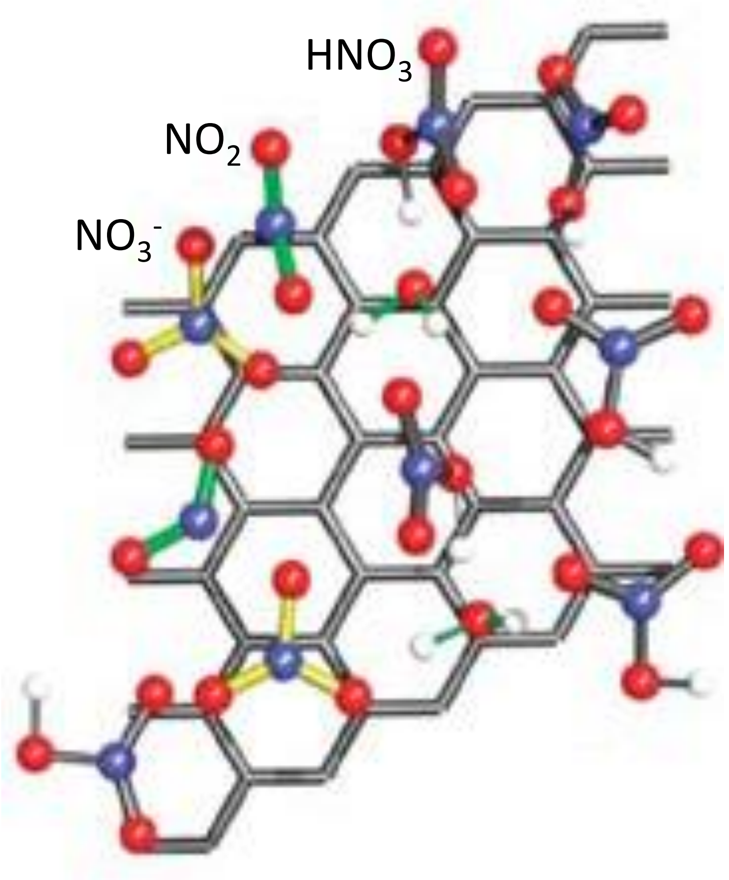
State of the art: 30Ω/sq

4L graphene treated with HNO_3

[Nat. Nanotechnol., **2010**, 5, 574–578]

Graphene **p-**doping by HNO_3

$$10HNO_3 + 50C \rightarrow (6HNO_3)2NO_3^- C_{50}^+ + 2NO_2 + 2H_2$$



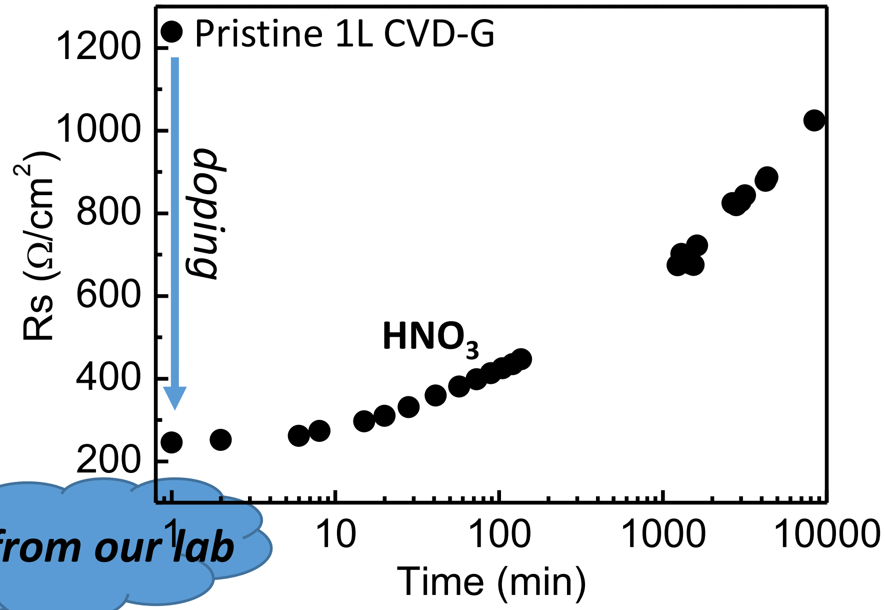
[ACS Nano, **2011**, 4, 3096]

HNO_3, NO_3^- and NO_2 adsorbed on graphene by <u>non covalent interactions</u>

σ=neμ

Increasing the graphene carrier density (holes) without introducing charge trapping center (C-sp3)

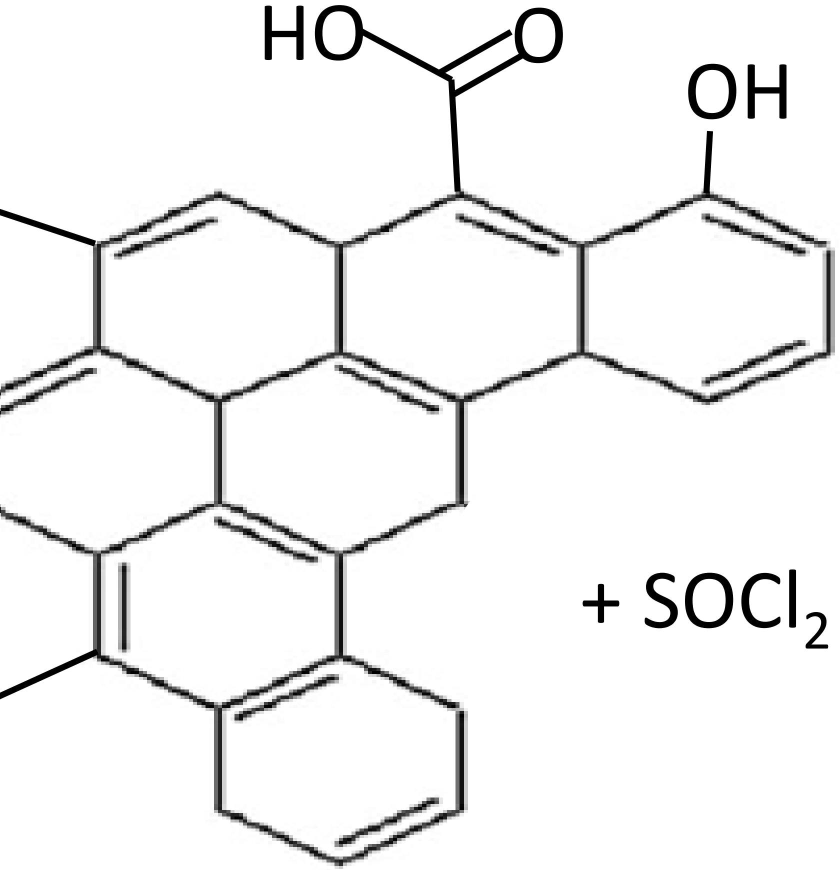
not stable upon air exposure



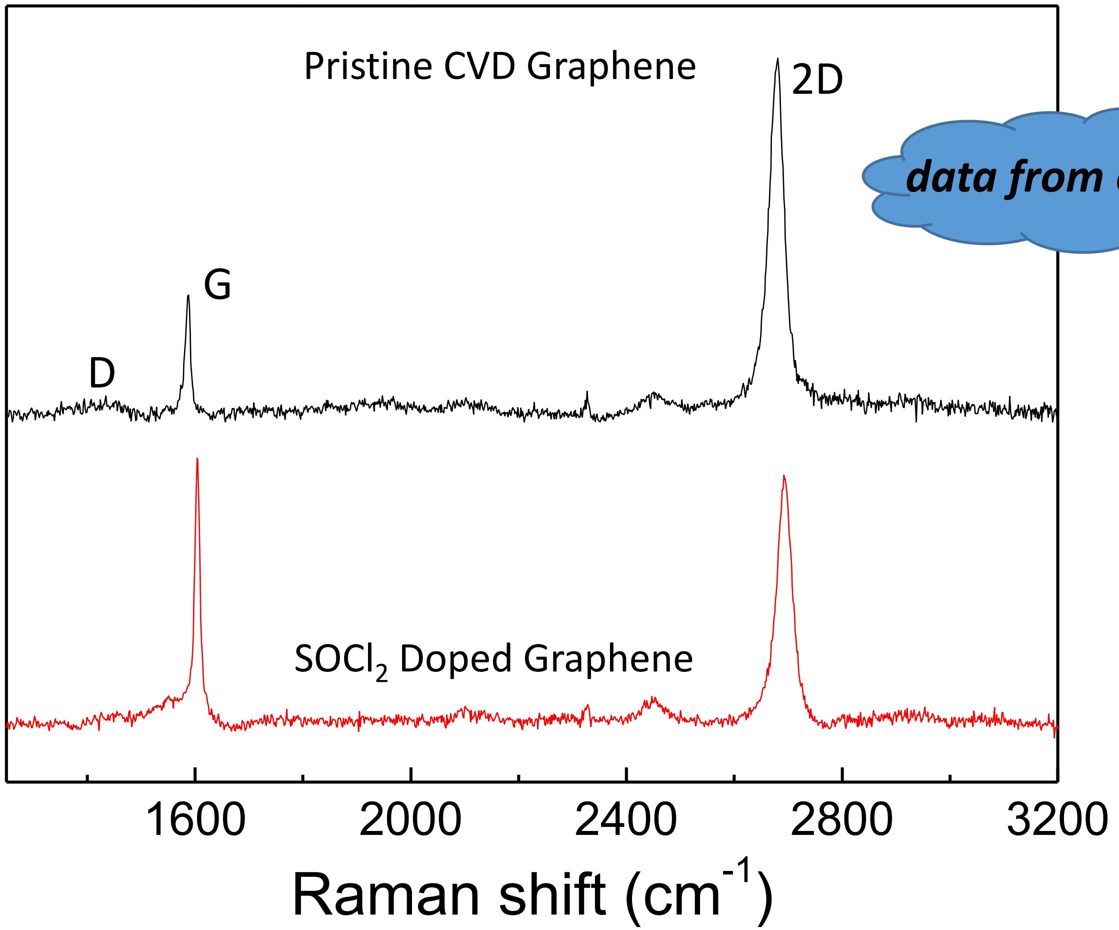
data from our lab

Covalent attachment of electron acceptor species (-Cl) without creating new C-sp^3 charge scattering center

Taking advantage of intrinsic chemical defects in CVD graphene



+ $SOCl_2$



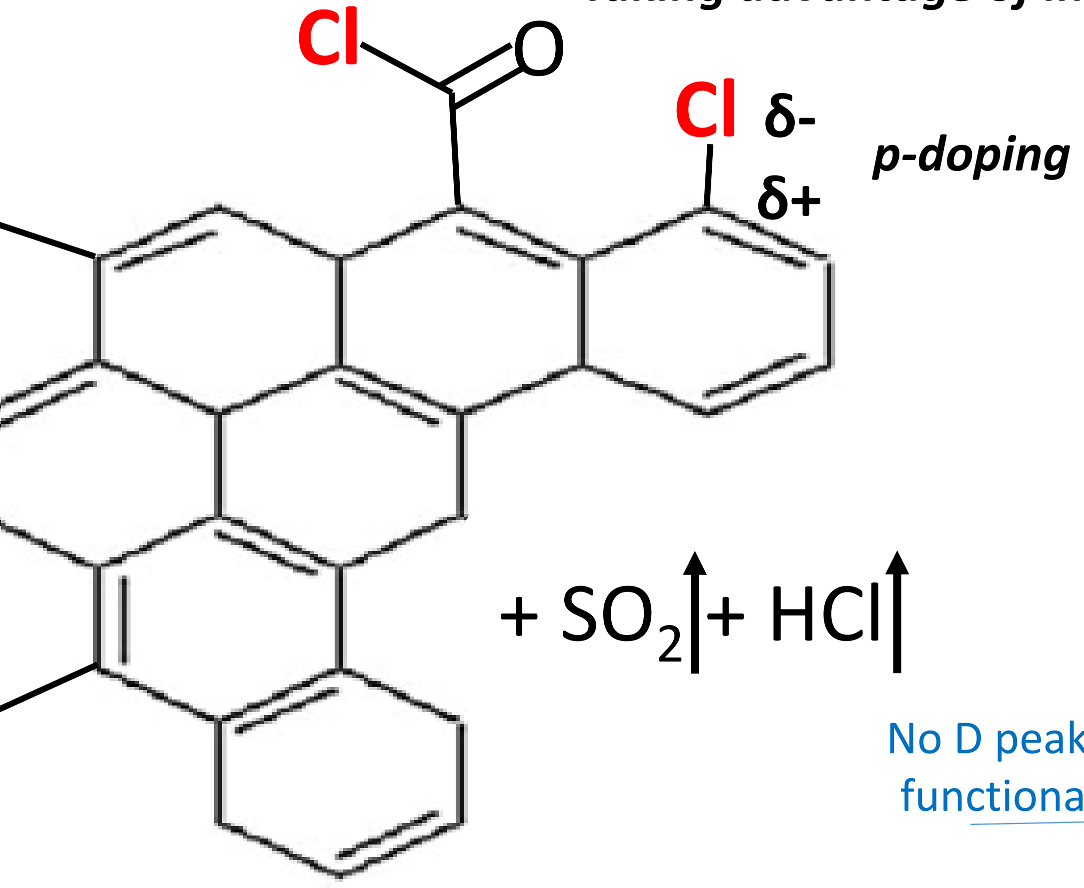
data from our lab

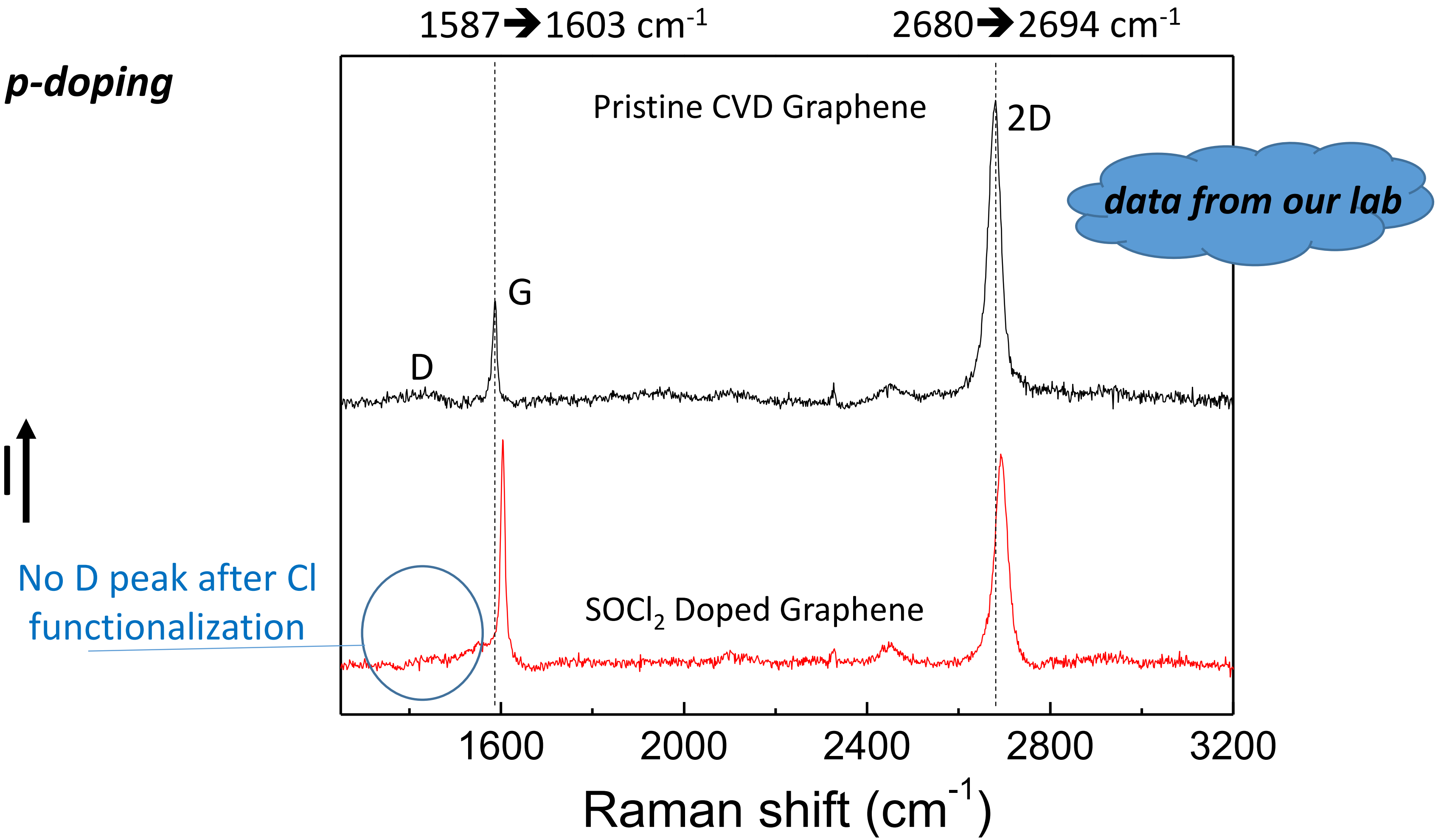
“nucleophilic substitution reaction”

Chemical Treatment for Lowering R_s of CVD Graphene : **$SOCl_2$ Doping**

Covalent attachment of electron acceptor species (-Cl) without creating new C-sp^3 charge scattering center

Taking advantage of intrinsic chemical defects in CVD graphene





"nucleophilic substitution reaction"

Chemical Treatment for Lowering R_s of CVD Graphene : **$SOCl_2$ Doping**

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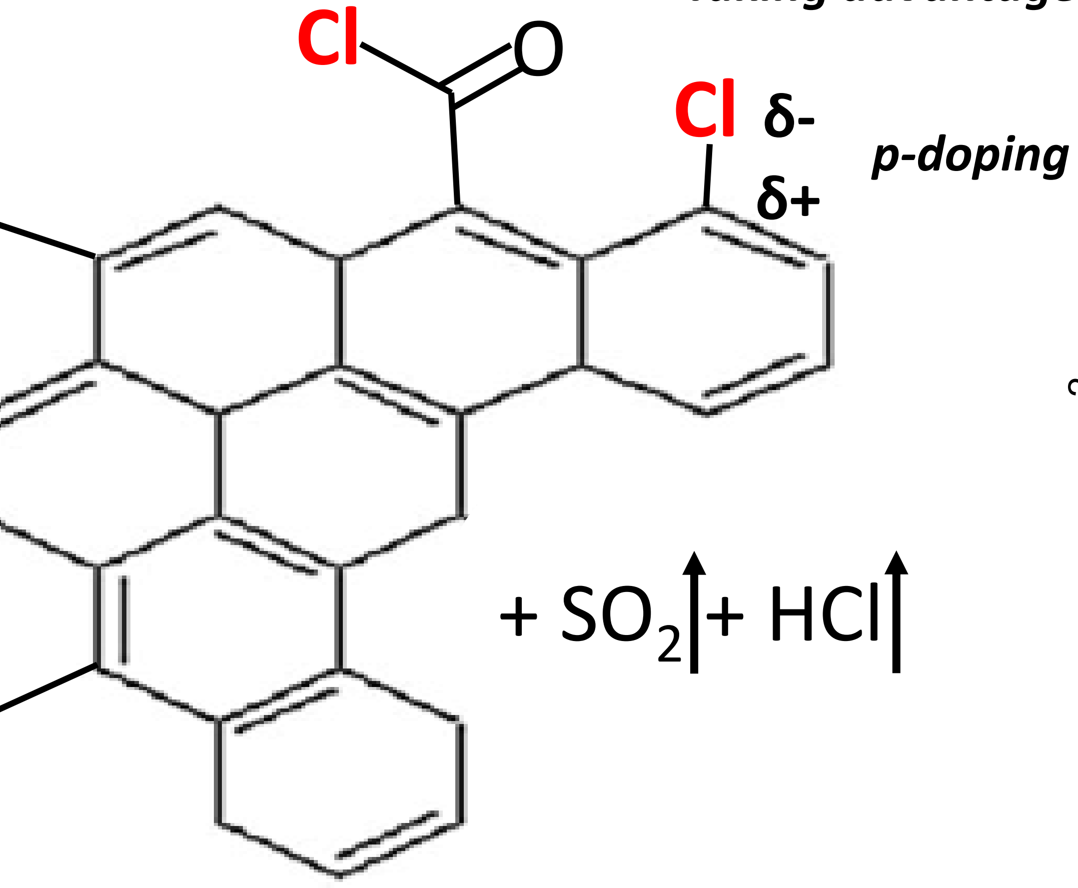
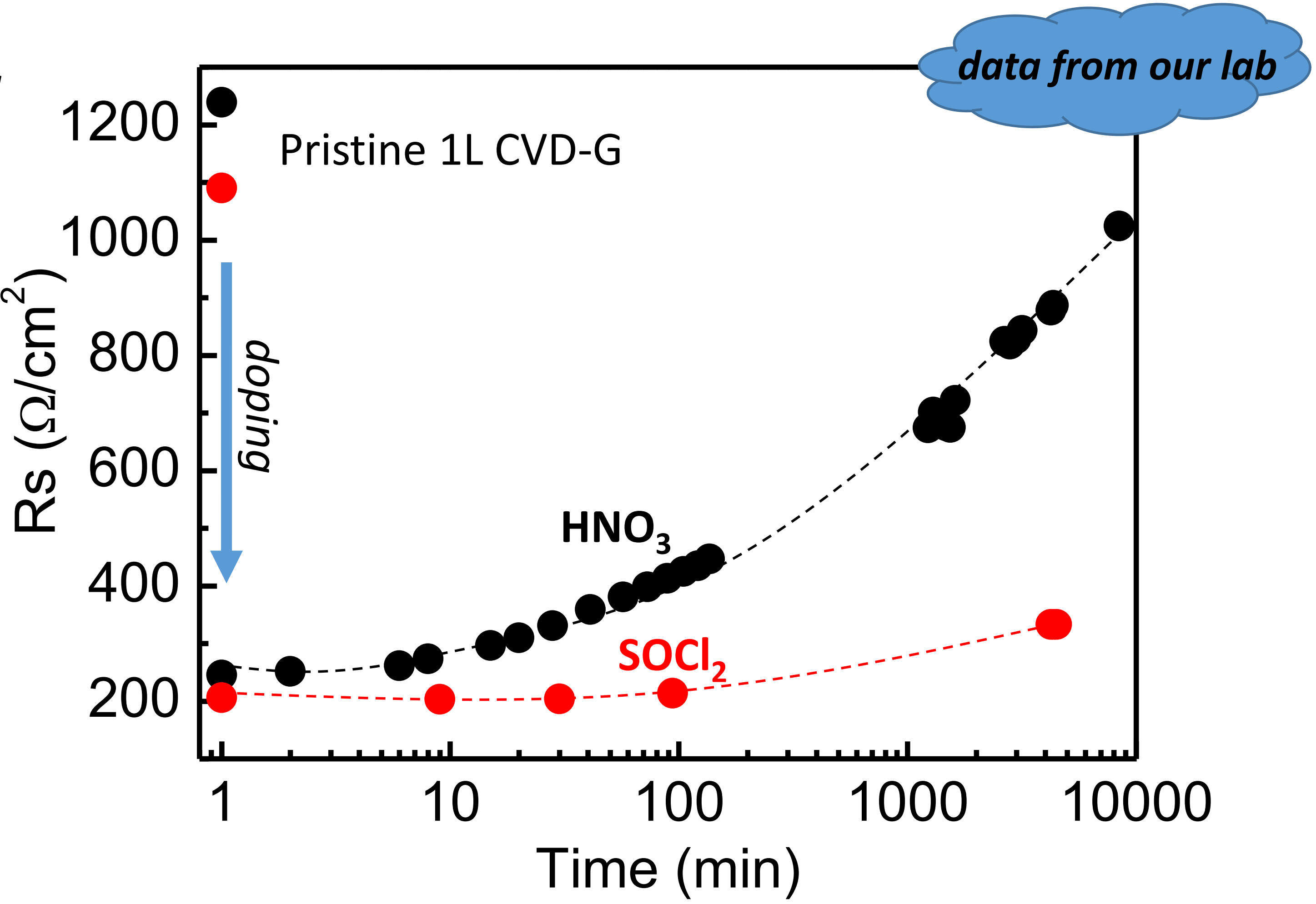
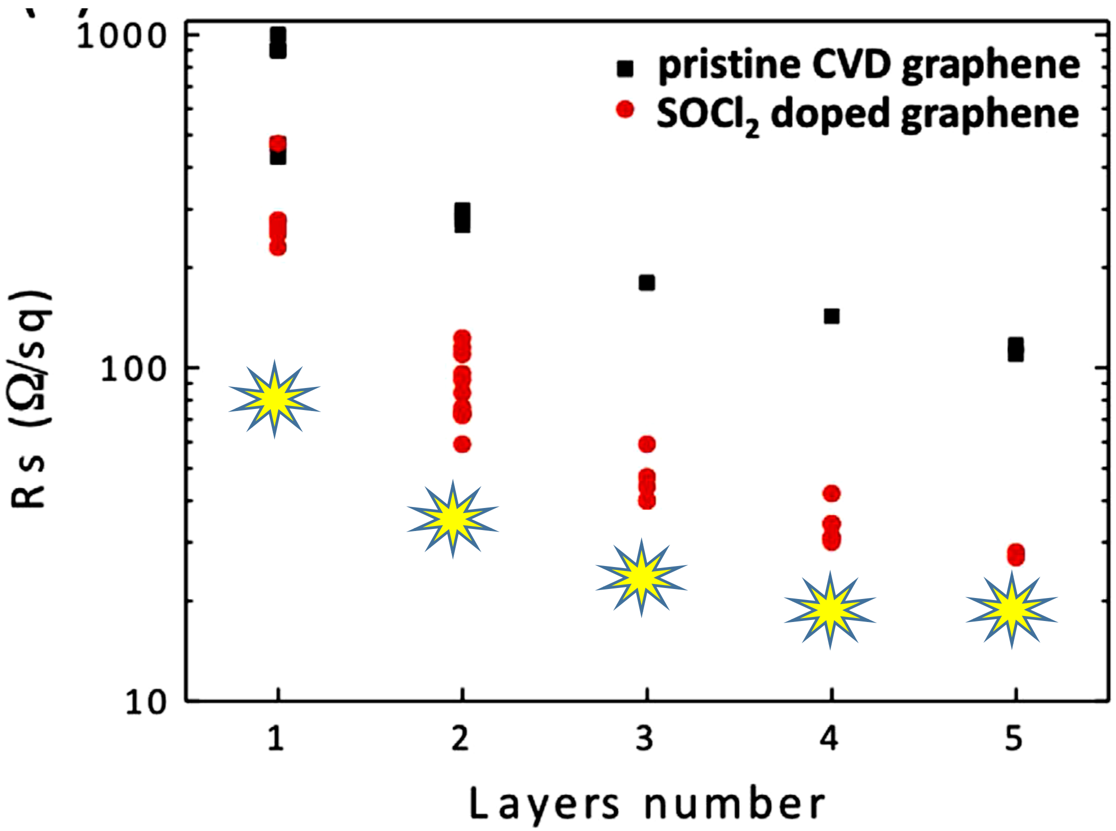




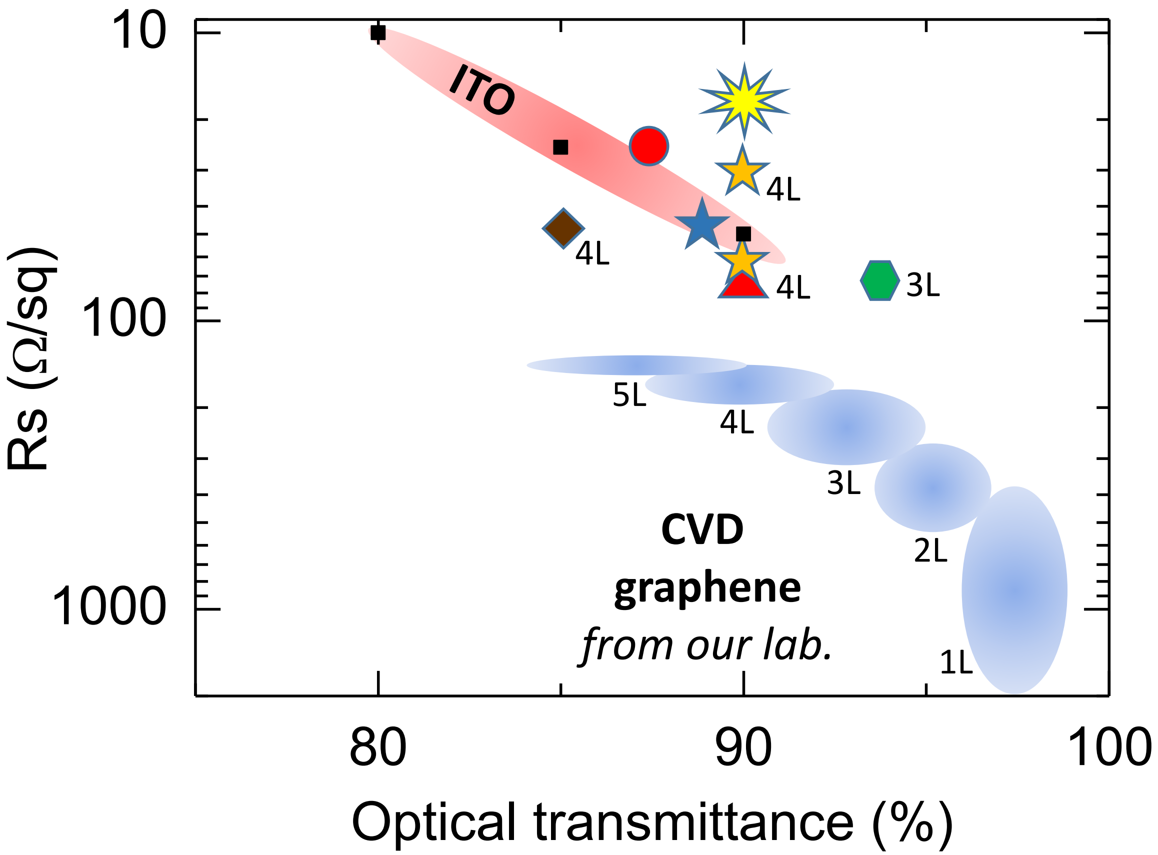
nucleophilic substitution reaction

[data from our lab.]

Towards Very Low Rs CVD Graphene



New result from the lab
Rs = 18 Ω/sq
T = 90%



M. Grande, G. V. Bianco, et al, Scientific Reports 5 (2015) 17083

Electromagnetic response of graphene at microwave frequencies

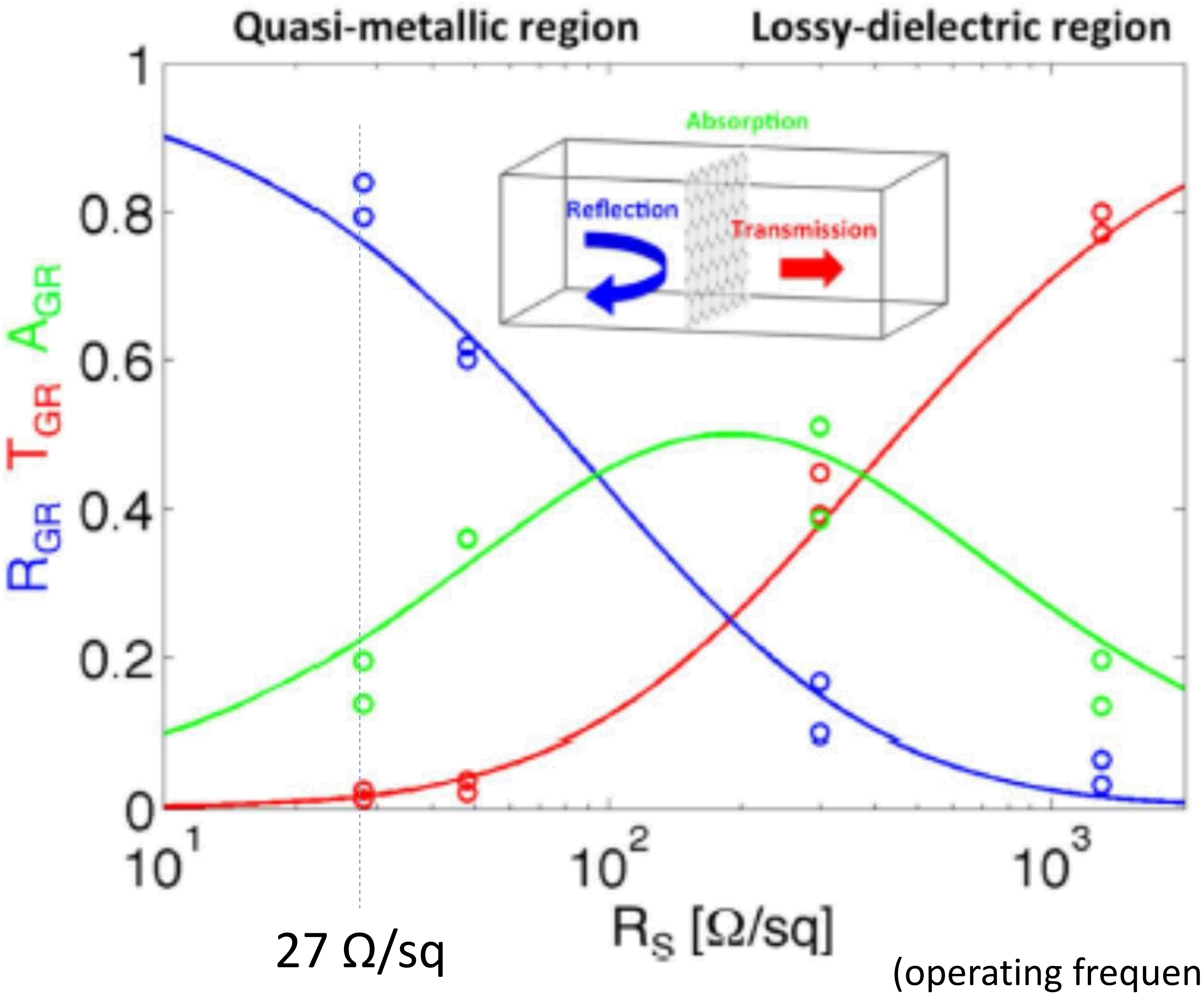
$$\sigma(\omega) = \sigma_{DC}/(1 - i\omega\tau)$$

Drude-like optical conductivity

Quasi-metallic graphene for developing flexible and transparent microwave devices (shields, polarizers, antennas, etc)

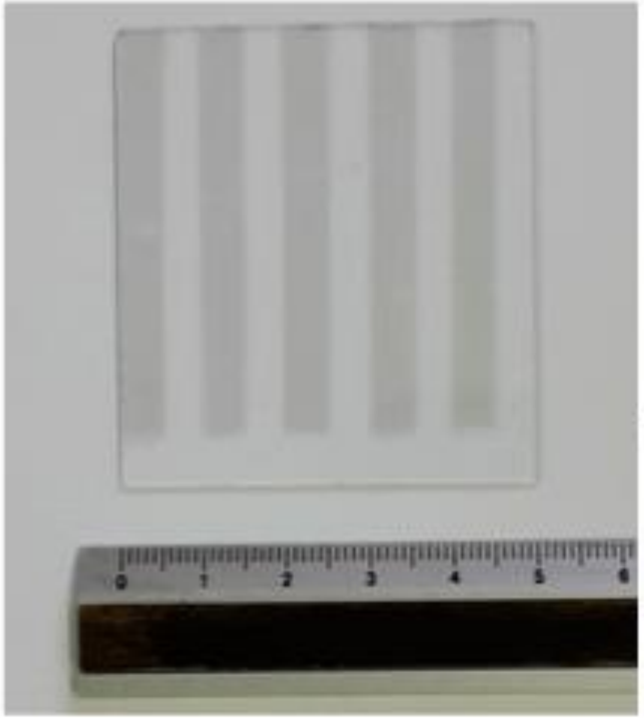
- CNR-NANOTEC, Bari, Italy
- Politecnico di Bari, Italy
- Redstone Arsenal, Alabama-USA

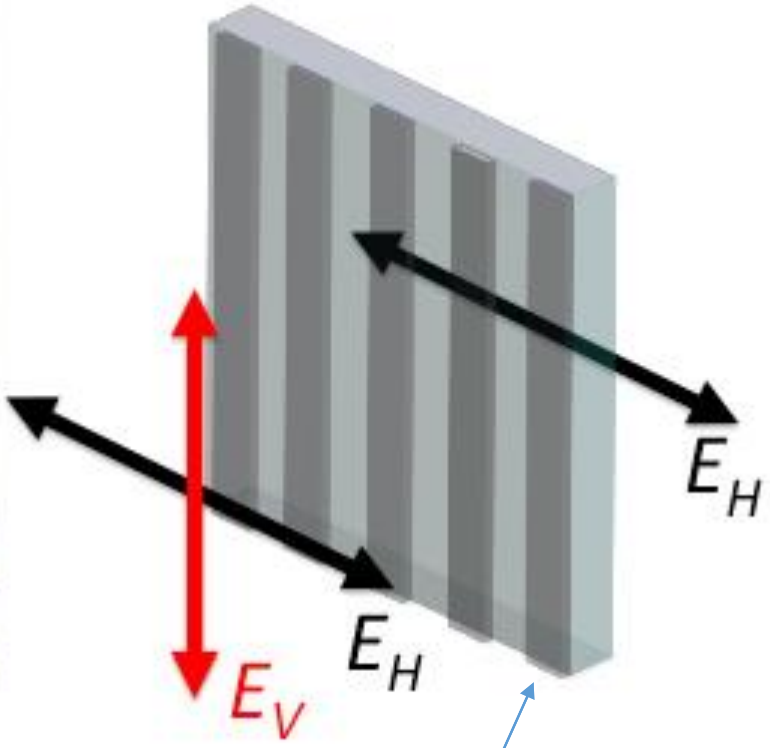
Scientific Reports 5 (2015) 17083

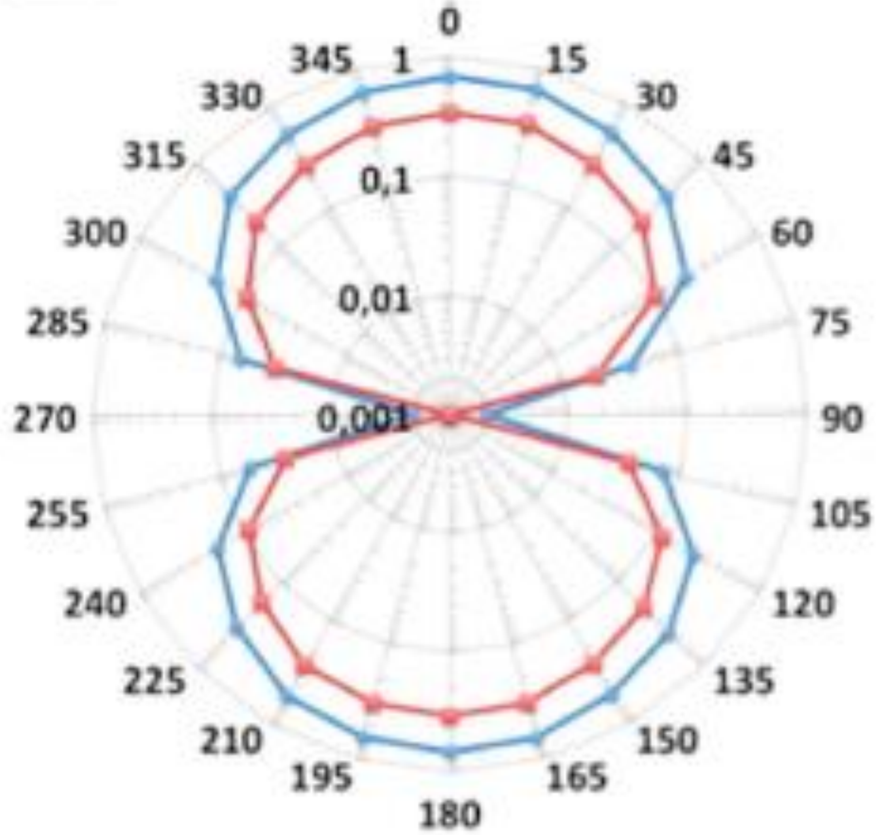


(operating frequency:9 GHz)

Optically Transparent Microwave Polarizer Based on Graphene







M. Grande, G. V. Bianco, et al,
Scientific Reports, 5 (2015) 17083

- CNR-NANOTEC, Bari, Italy
- Politecnico di Bari, Italy
- Redstone Arsenal, Alabama-USA

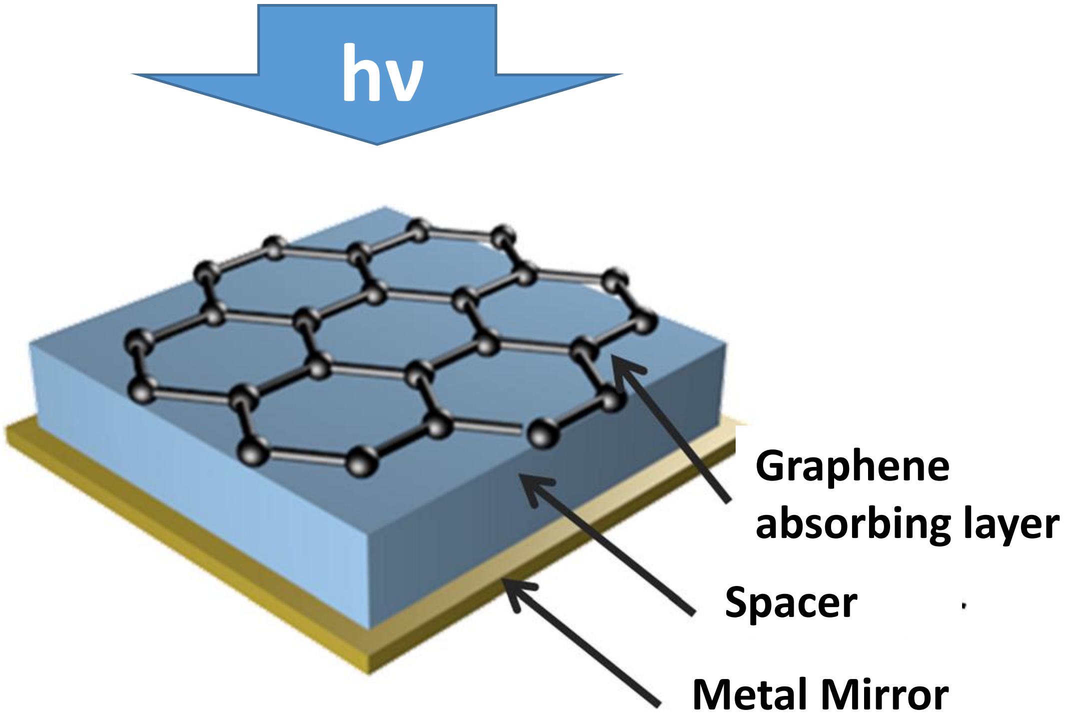
4L graphene stripes (4mm)
Rs : 40 Ω/sq
T : 90%

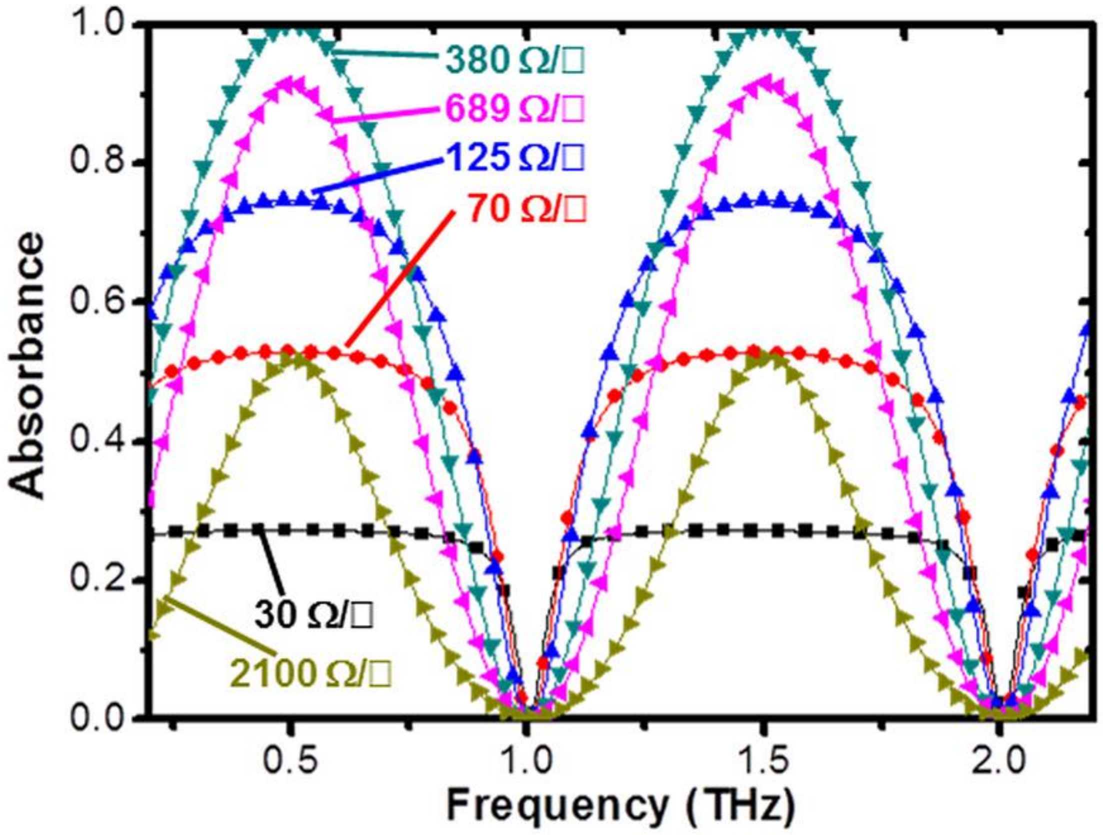
$(T_{90}-T_{pol})/T_{90}$

Graphene polarizer
Copper polarizer

(operating frequency:9 GHz)

SALISBURY SCREEN



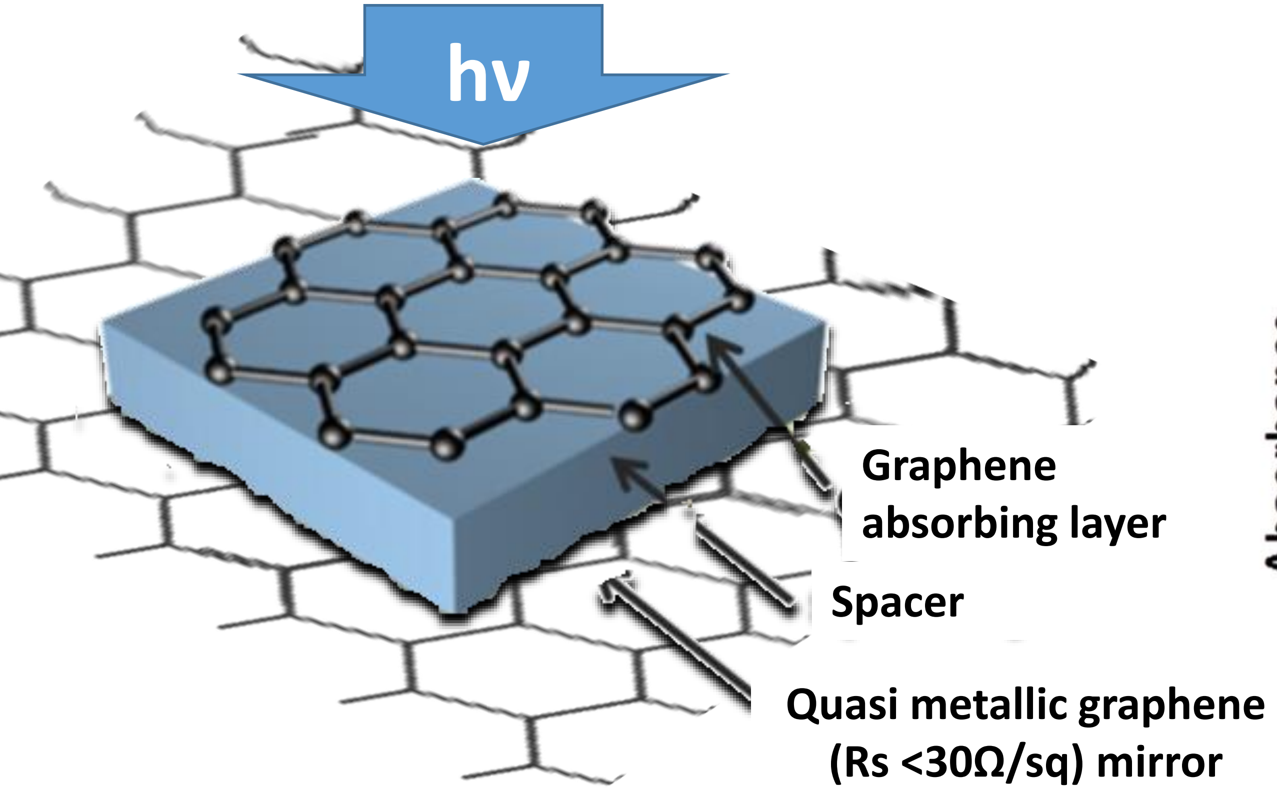


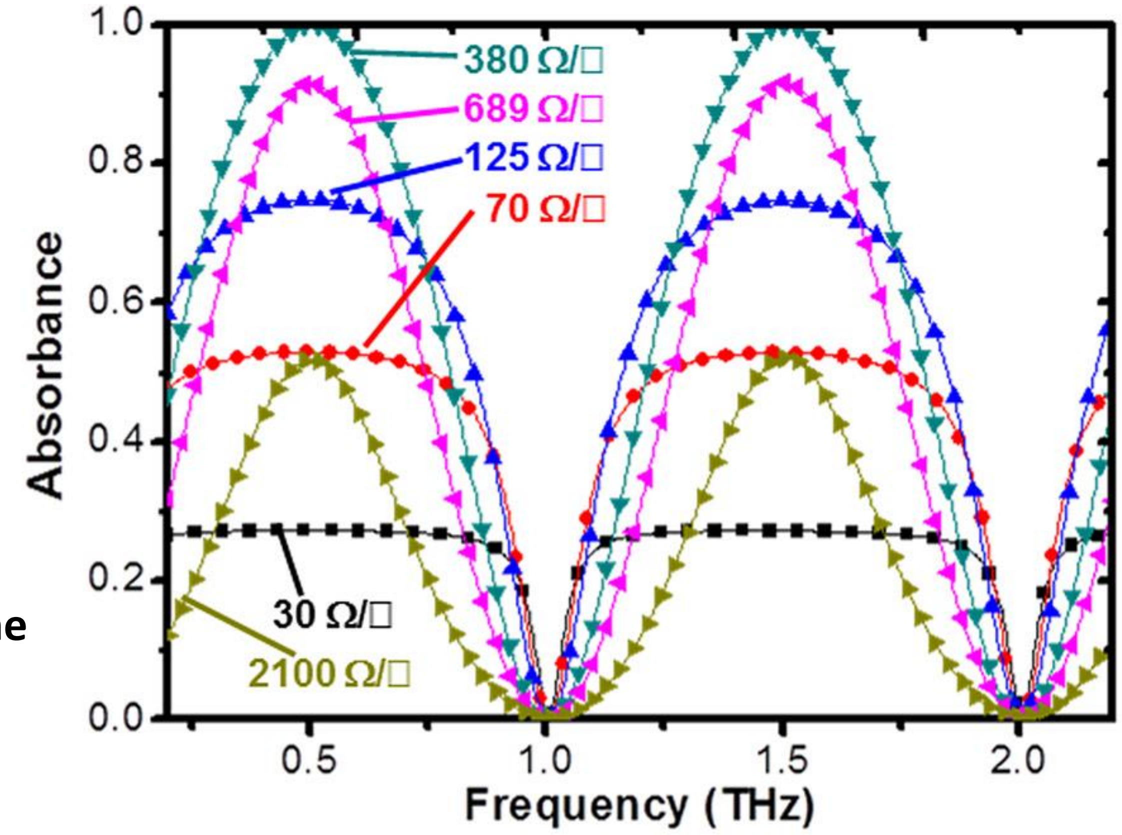
APL 104, 081106 (2014)

The interplay between interference and losses leads to perfect absorption only for specific values of radiation frequencies (defined by the spacer thickness) and of graphene optical conductivity (defined by the Rs)

Graphene EMI shield

SALISBURY SCREEN





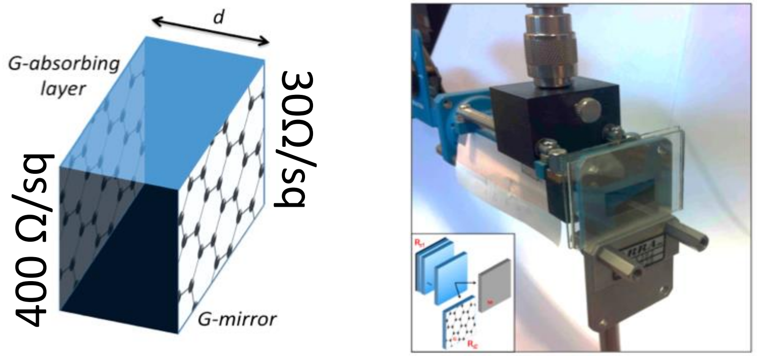
APL 104, 081106 (2014)

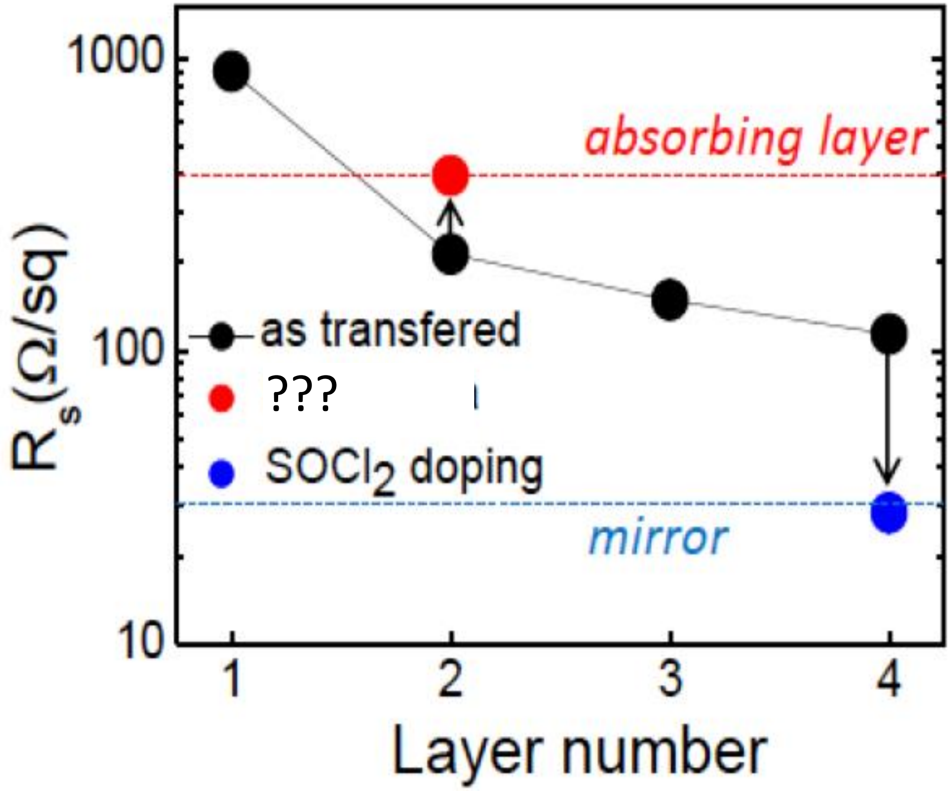
OUR IDEA

Optically transparent EMI shield

Optically transparent Graphene EMI shield

G. V. Bianco, M. Grande, et al Optics Express (2016), in press.





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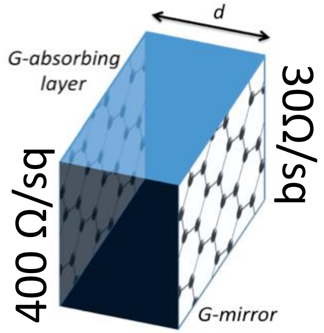
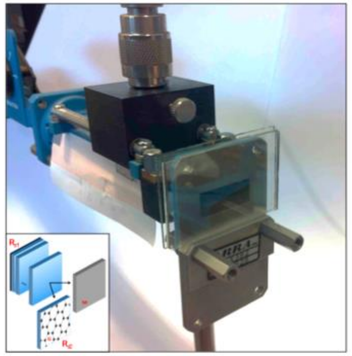
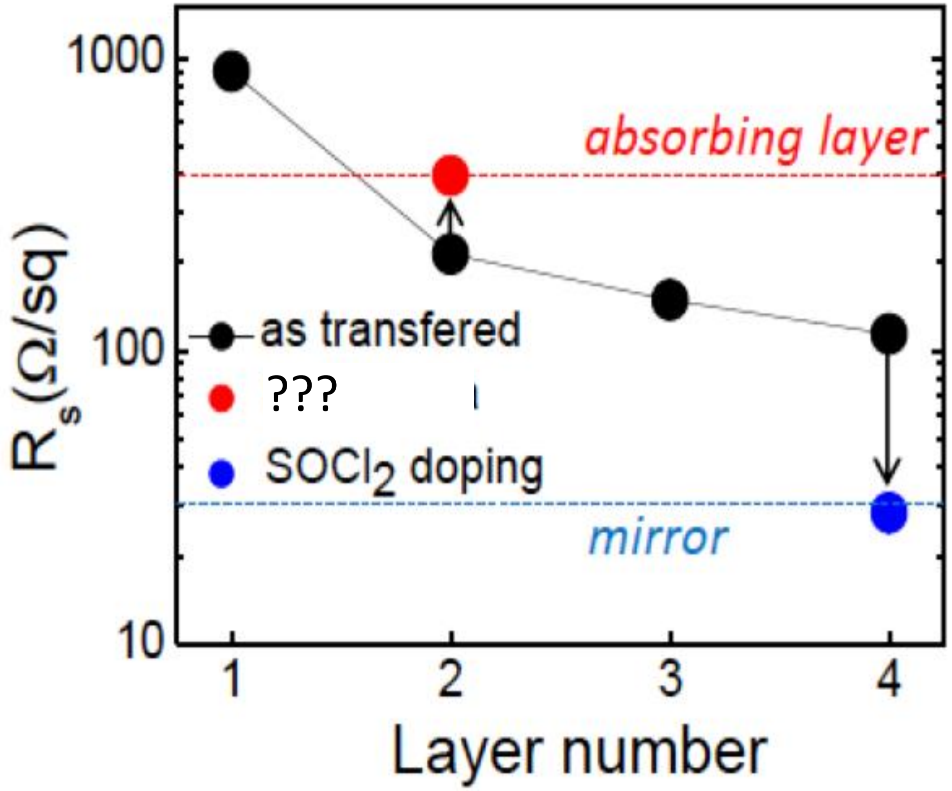
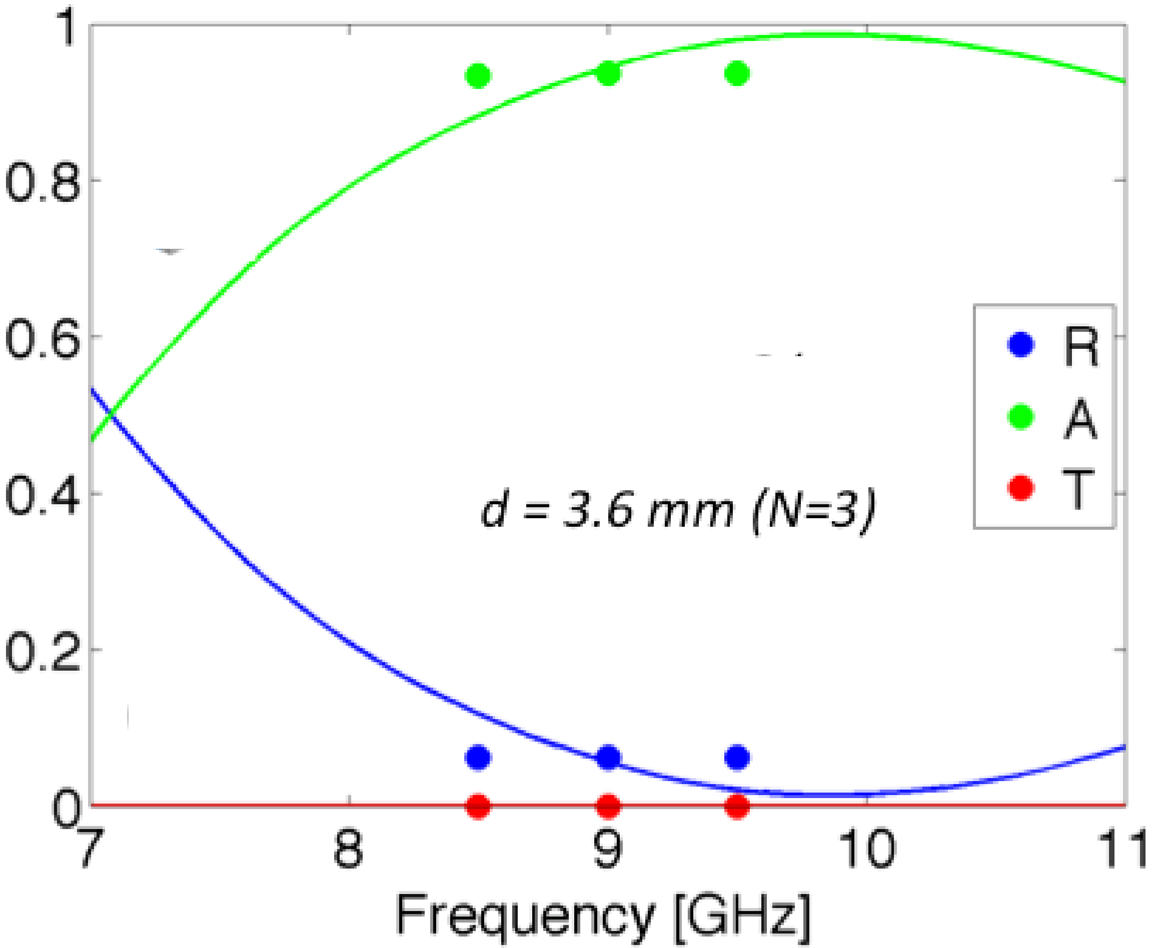


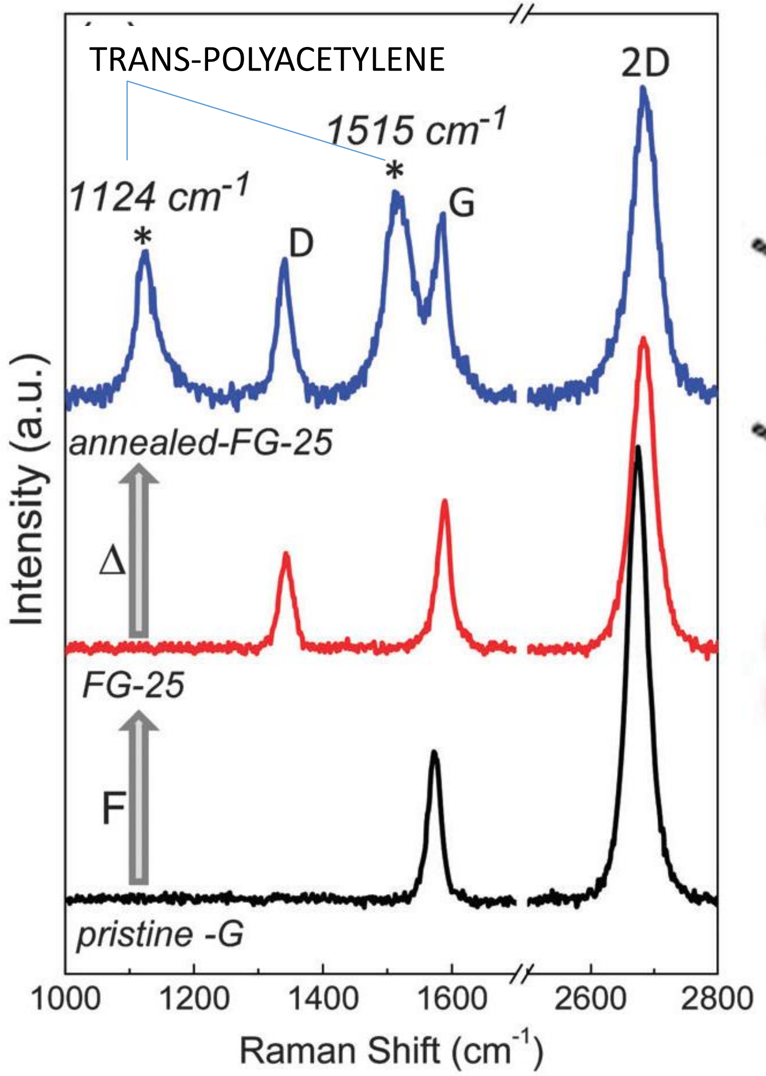




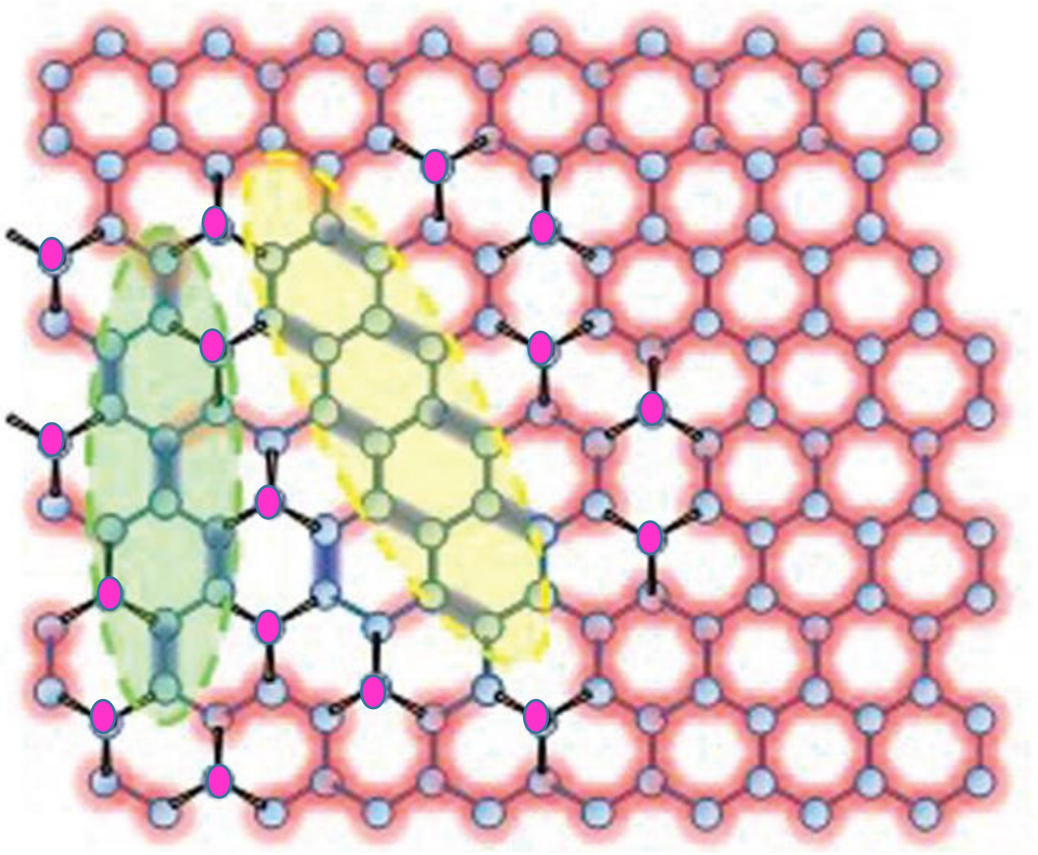
Device performances: comparison between theory and experimental findings.

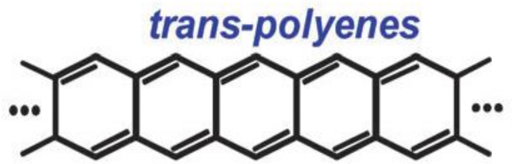


PhotoThermal-Active Plasma-Fluorinated Graphene



G. Bruno, G.V. Bianco, et al,
Phys.Chem.Chem.Phys., 16 (2014) 13948

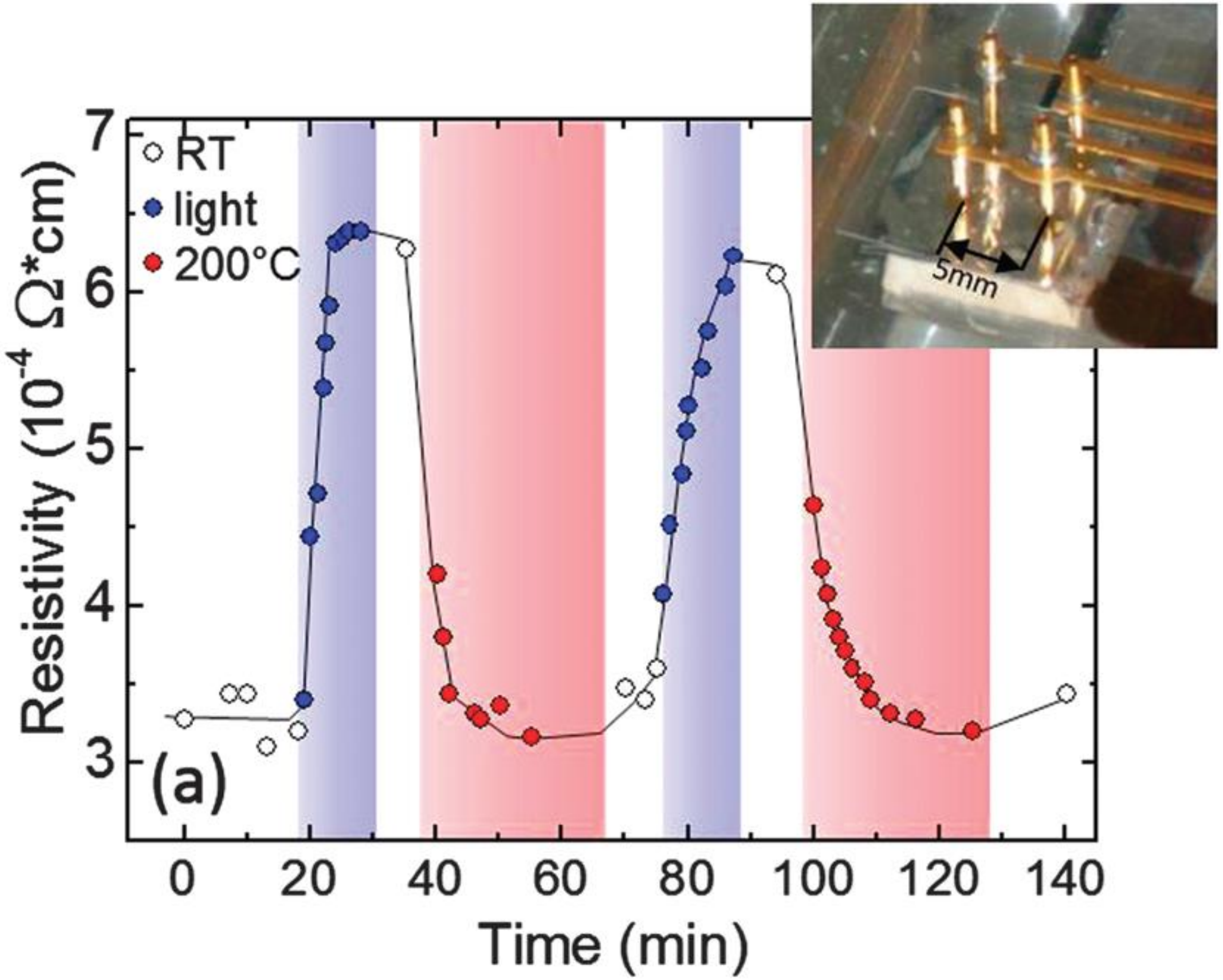


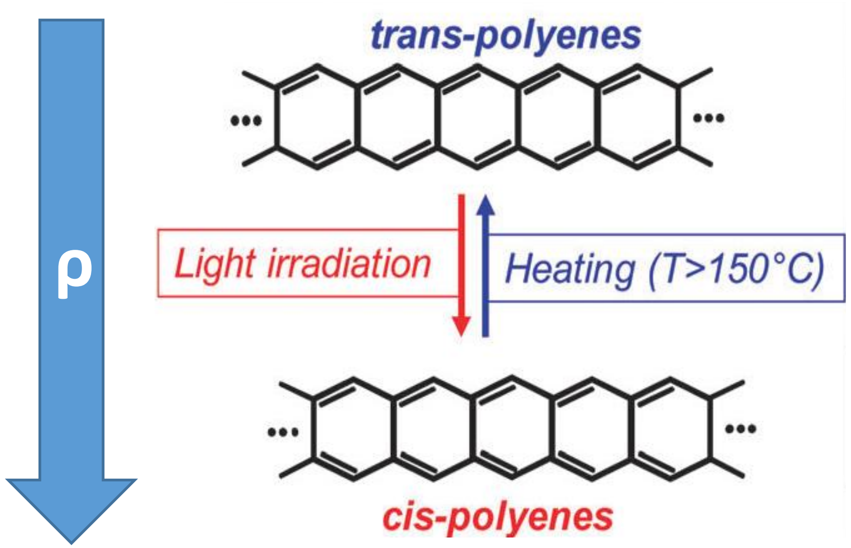


Raman spectroscopy reveals the formation of polyenes in plasma-fluorinated graphene (low fluorine coverage)

PhotoThermal-Active Plasma-Fluorinated Graphene

Monitoring of fluorographene resistivity under light irradiation and annealing





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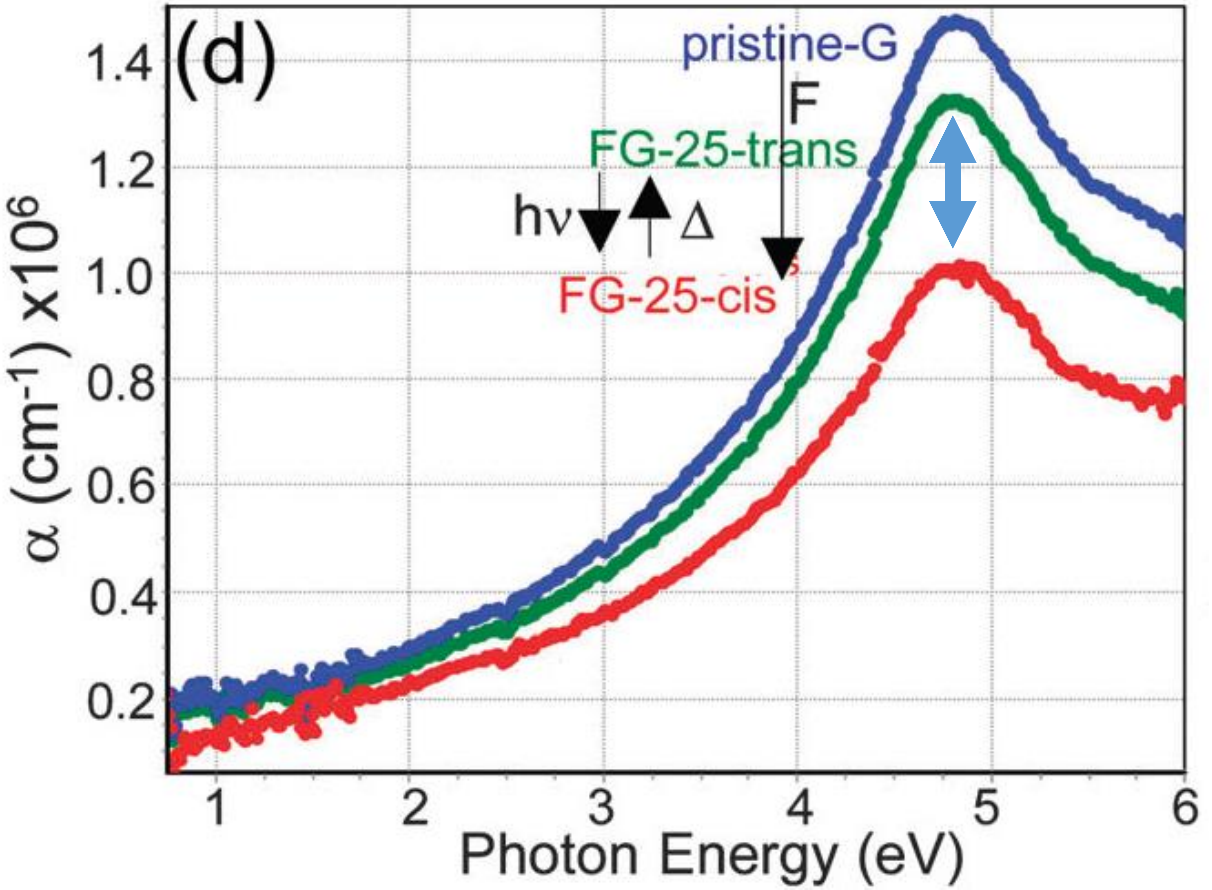
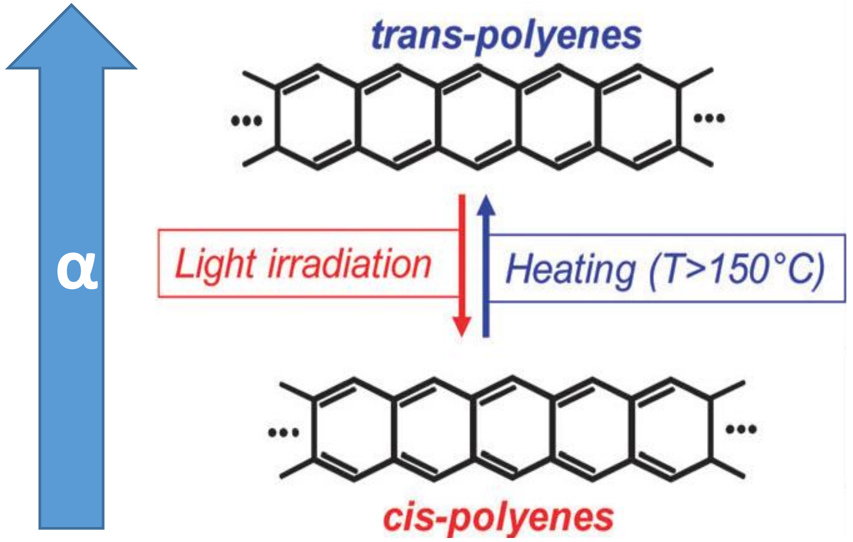
PhotoThermal-Active Plasma-Fluorinated Graphene

Ellipsometric analysis of fluro graphene absortption coefficient under light irradiation and annealing



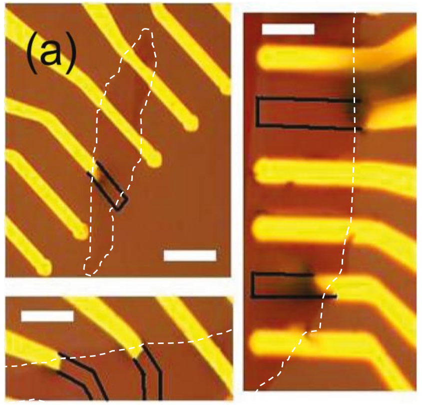
PHOTOTERMAL SWITCHING



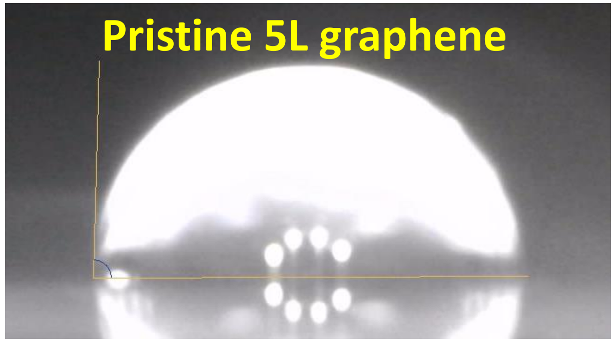
G. Bruno, G.V. Bianco, et al,
Phys.Chem.Chem.Phys., 16 (2014) 13948

Improving graphene wettability by Oxygen plasma

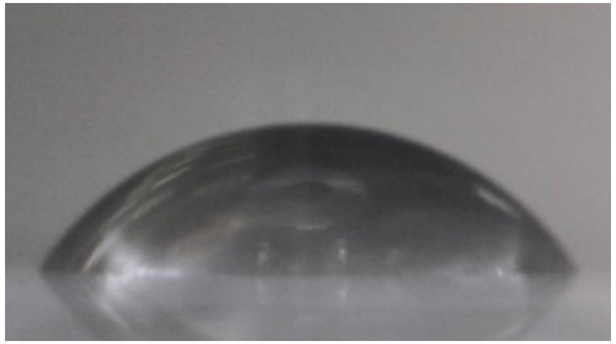
Au contact on graphene

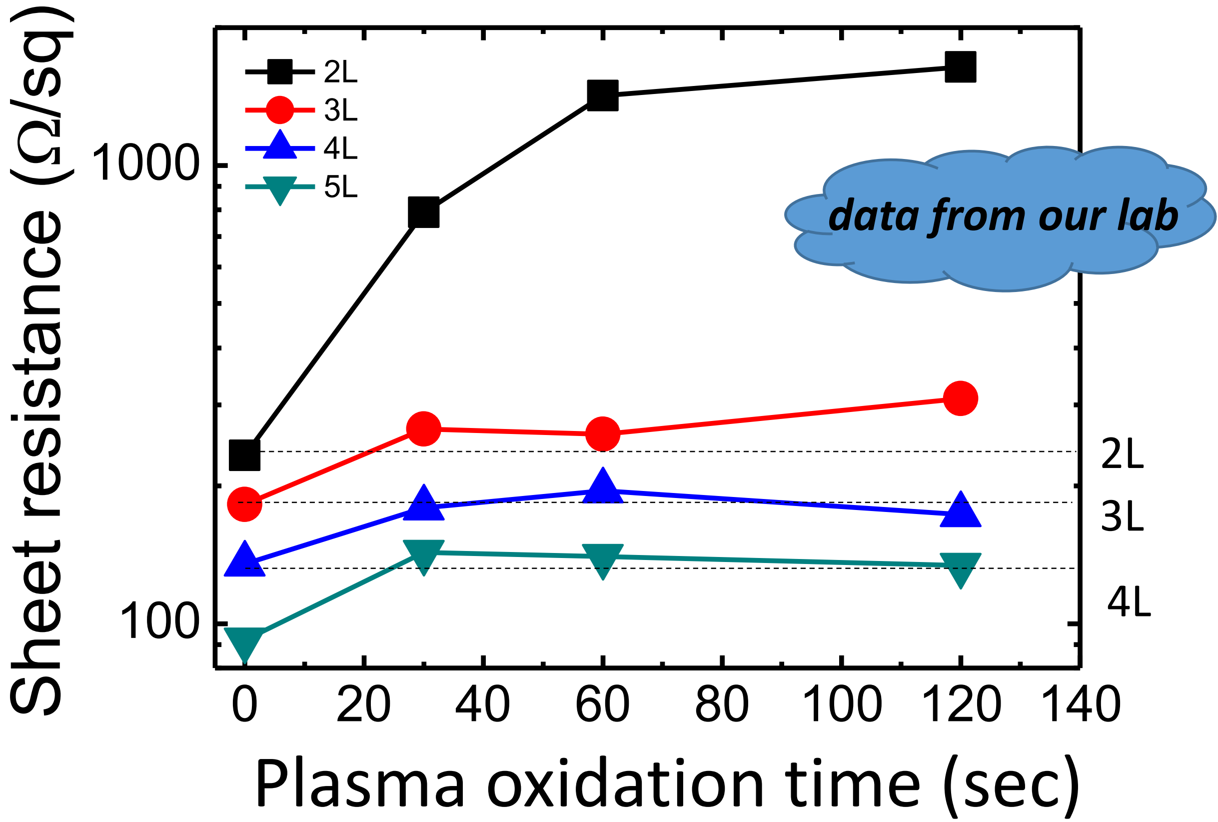


The low surface energy of graphene (70 mJ/m^2) strongly limits its integration with other materials in technological devices



O_2 plasma



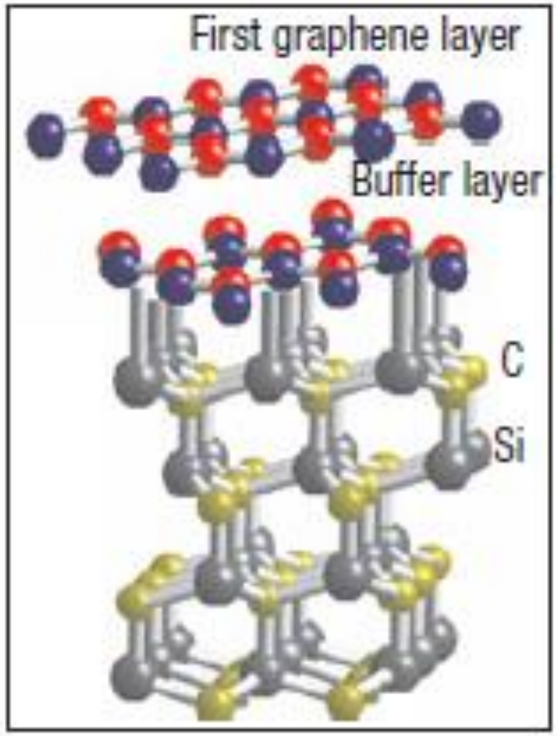


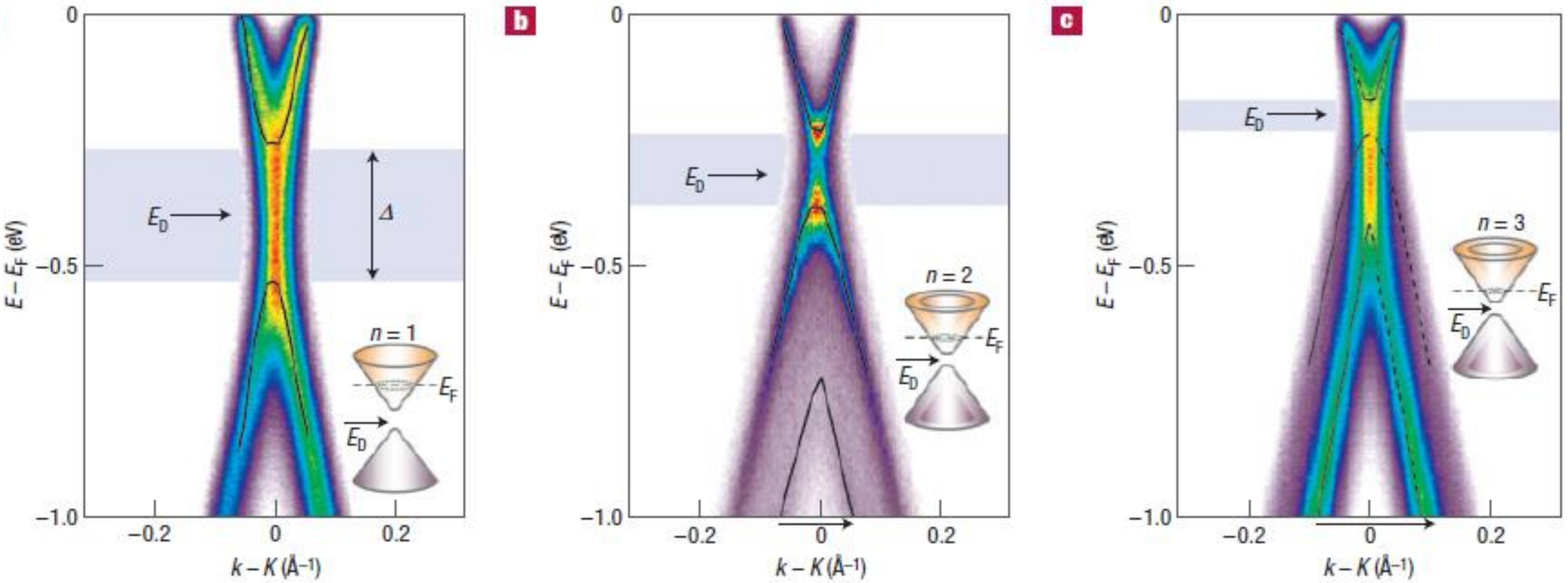
For multilayer graphene, modulated plasma treatment allows surface functionalization without important effects on the transport properties

Looking for a gap in graphene

Several research paths are being targeted at opening a bandgap in graphene: nanoribbon, biased bilayer graphene, chemically modified graphene, bent graphene….

“Substrate-induced bandgap opening in epitaxial graphene”. Nature Materials, VOL 6 (2007) 771



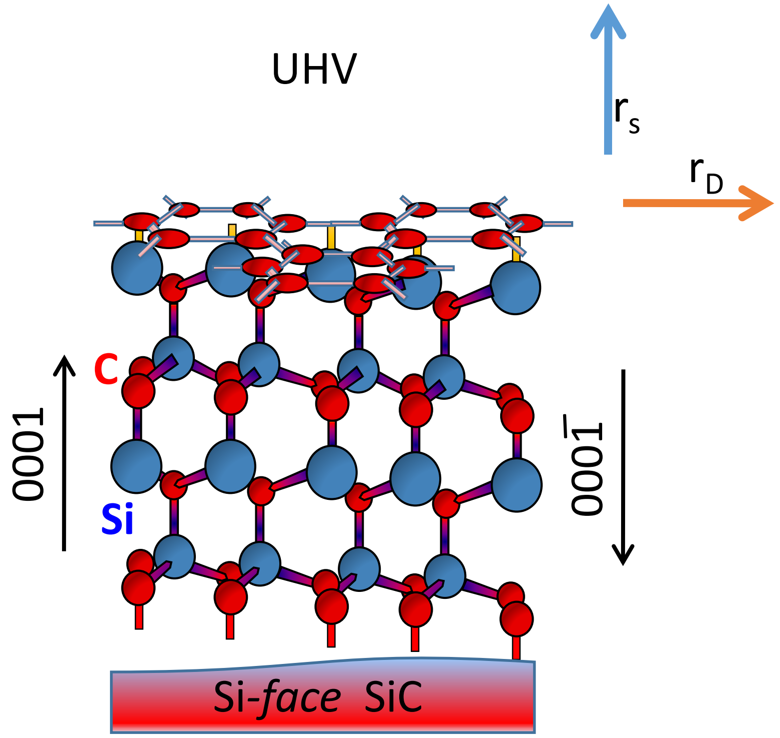


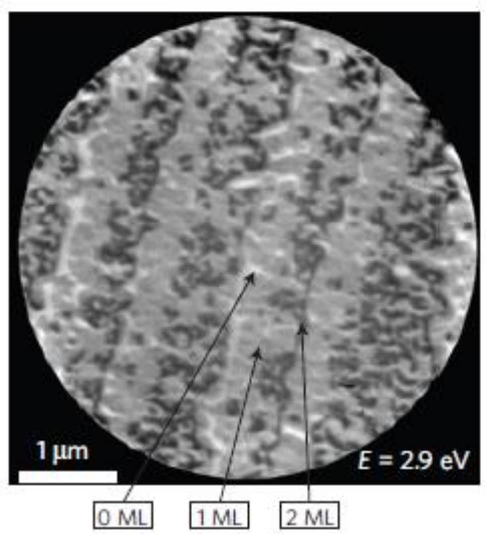
1L **0.26 eV** | **2L** **0.14 eV** | **3L** **0.07 eV**

giuseppevalerio.bianco@cnr.it

Epitaxial Growth of Graphene on SiC

To increase homogeneity and control the thickness one has to lower the sublimation rate (r_s)
while, at the same time, increasing the diffusion length (r_D)



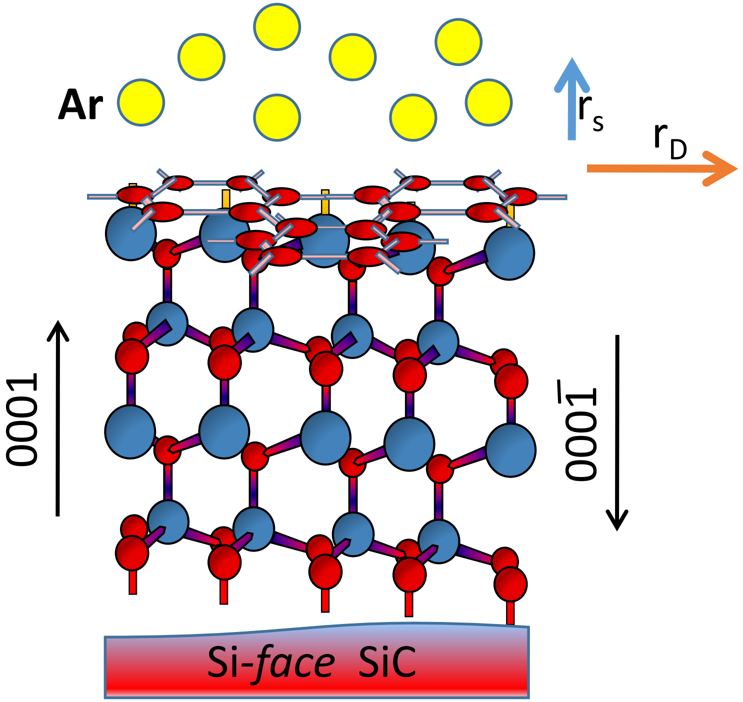


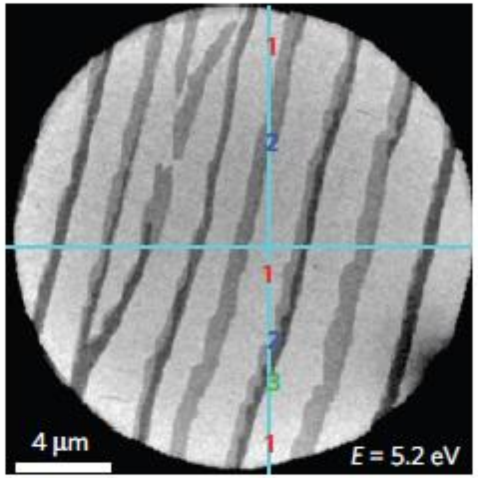
Berger et al., J. Phys. Chem. B ***108, 19912 (de Heer's group)***

Epitaxial Growth of Graphene on SiC

To increase homogeneity and control the thickness one has to lower the sublimation rate (r_s) while, at the same time, increasing the diffusion length (r_D)

Ar atmosphere at ~900 mbar





K. V. Emtsev, ….. T.Seyller, *Nat. Mater.* 8, 203 (2009).

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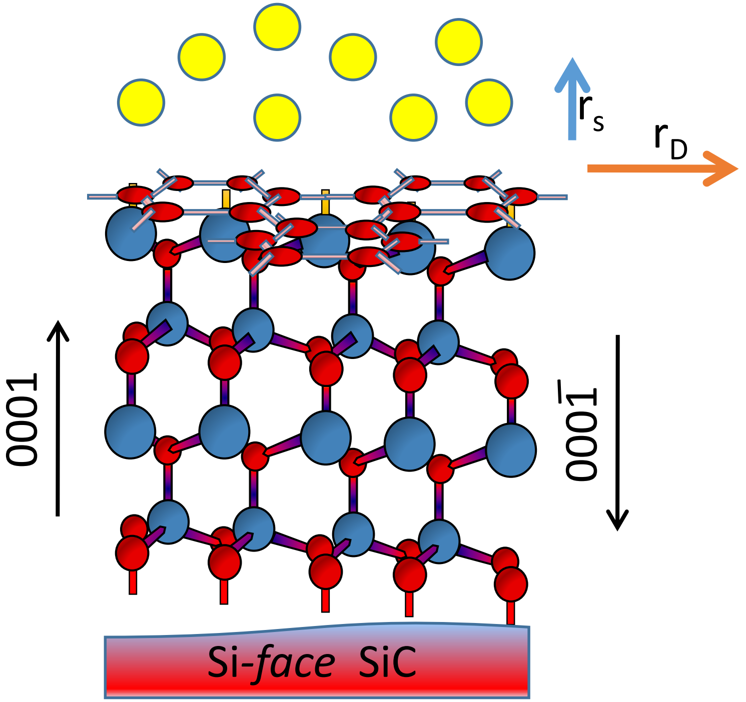
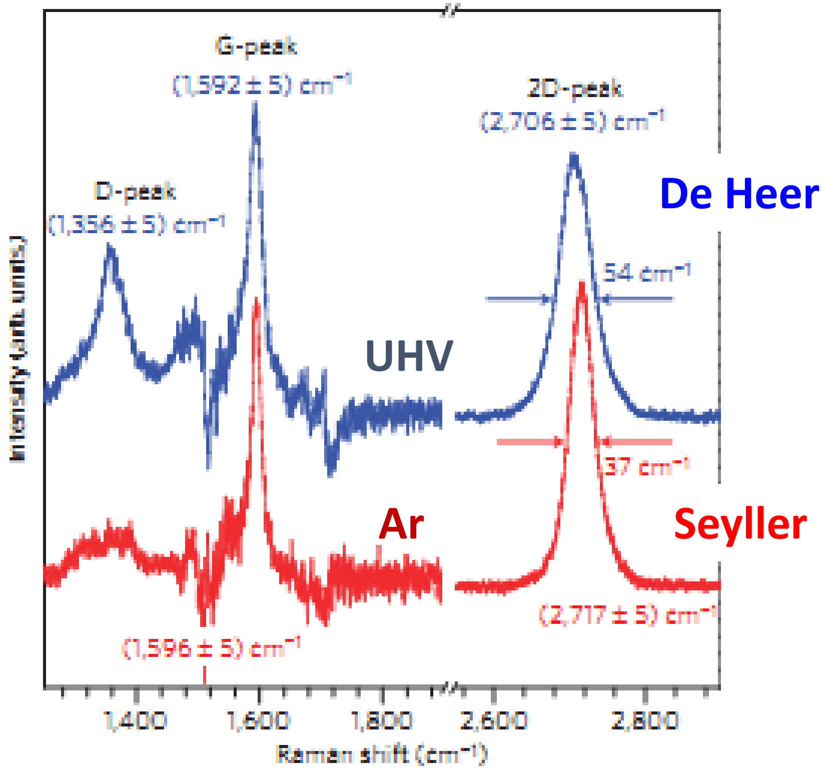


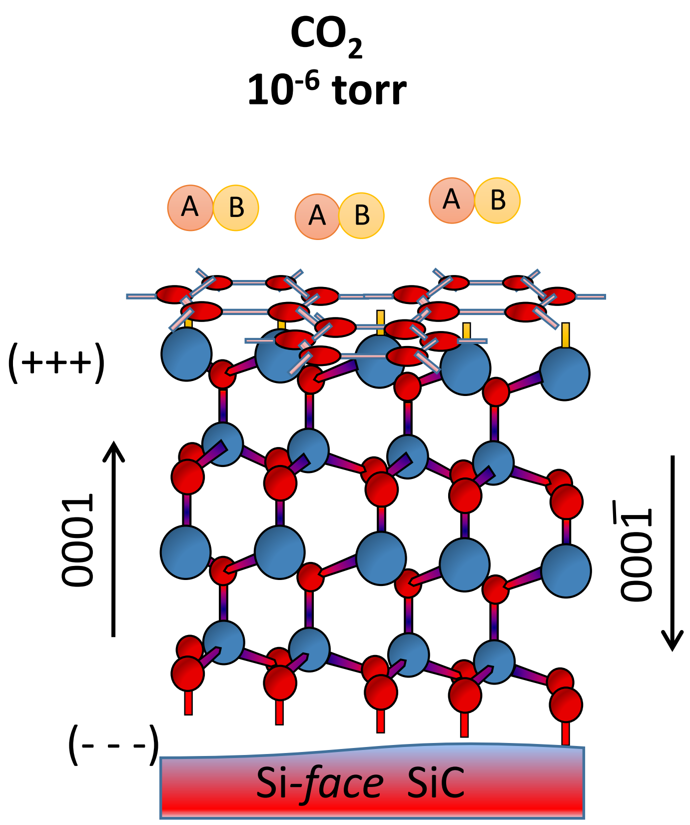


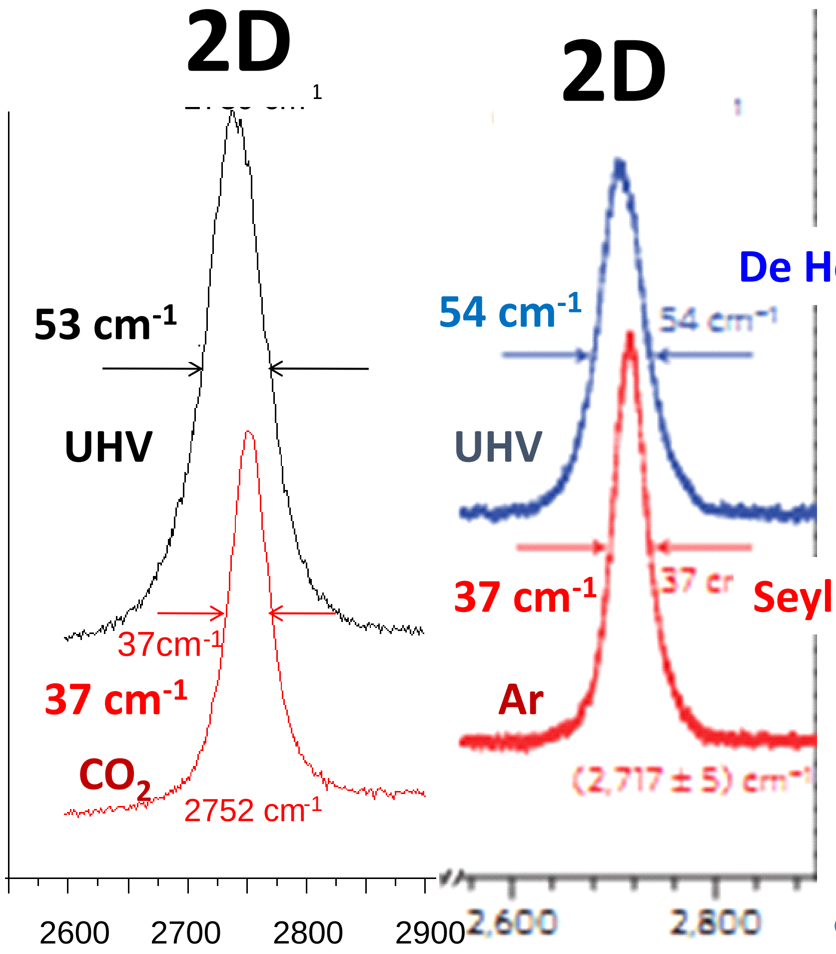
K. V. Emtsev, ….. T.Seyller, *Nat. Mater.* 8, 203 (2009).

The Chemical Route to Epitaxial Graphene

$$2SiC(s) + CO_2(ads) \rightarrow 2SiO(g) + C_3(s)$$

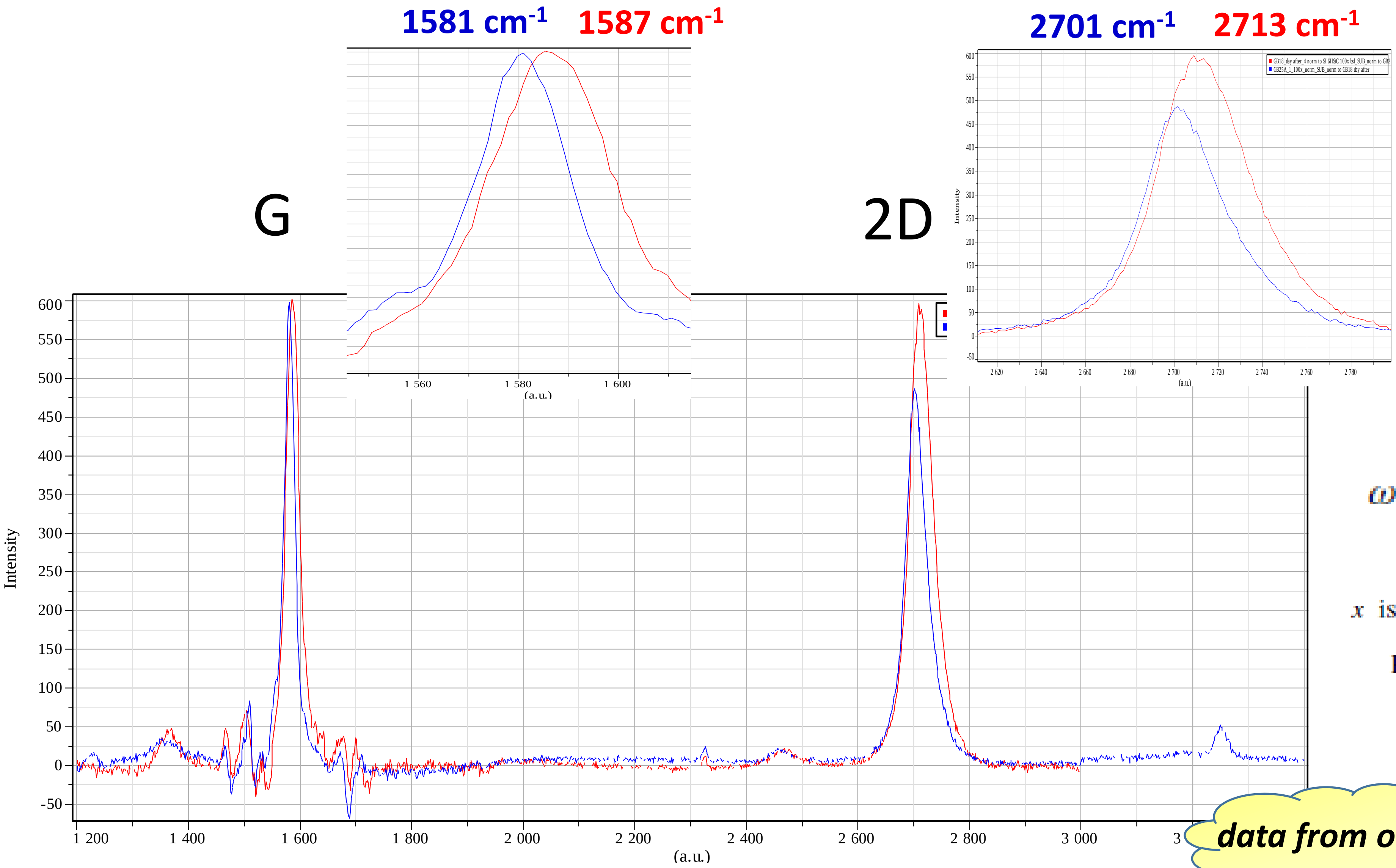
CO_2 Chemistry





data from our lab

Probing ^{13}C isotope effect on graphene



$^{12}CO_2$ Chemistry

$^{13}CO_2$ Chemistry

$$\omega(x) = \omega_{^{12}\mathrm{C}} \sqrt{\frac{m_0}{m_0 + x\Delta m}}.$$

x is the number density of ^{13}C $(0 \leqslant x \leqslant 1)$

PHYSICAL REVIEW B **92**, 125406 (2015)

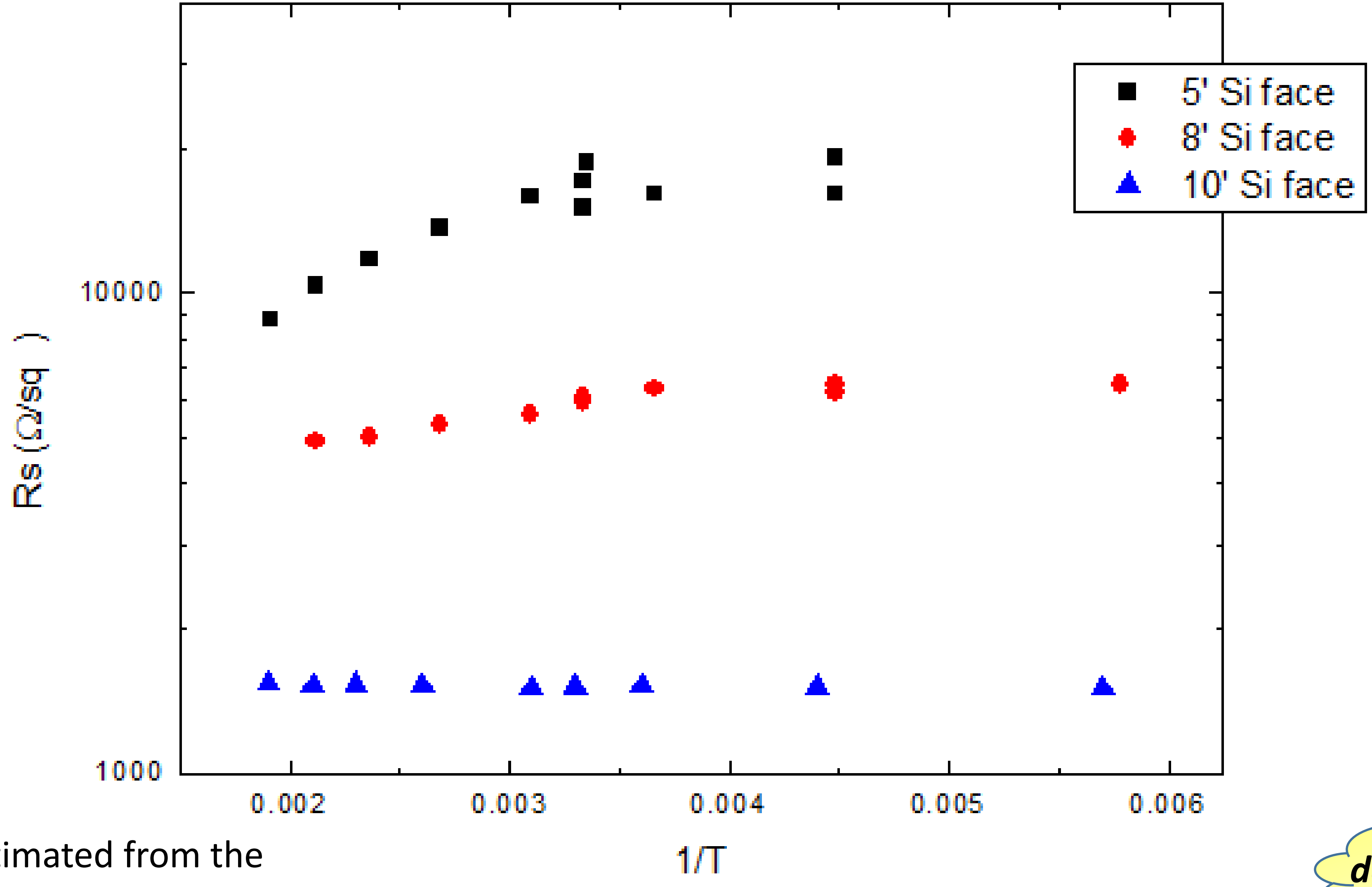
data from our lab

Energy gap in epitaxial graphene

2L

5L

7L



Eg = 60 meV

Eg = 22 meV

Eg = ...

[Thickness estimated from the attenuation of the SiC Raman peaks]

data from our lab

Conclusion

The role of chemistry in realizing the promise of technological innovation:

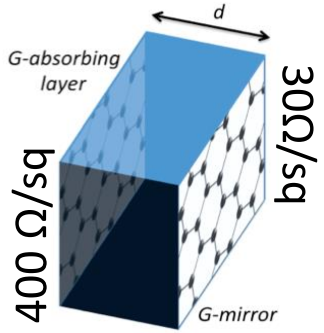
- **Graphene chemical doping by $SOCl_2$** allows the production of very low sheet resistance graphene for TCL and microwave applications.

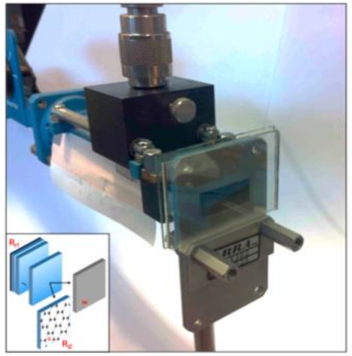
- Graphene functionalization by **modulated plasma treatment** can be exploited for the fine tuning of its optical conductivity in the THz-MW range **(H)**, increasing surface wettability **(O)**, and introducing new properties (**F)**

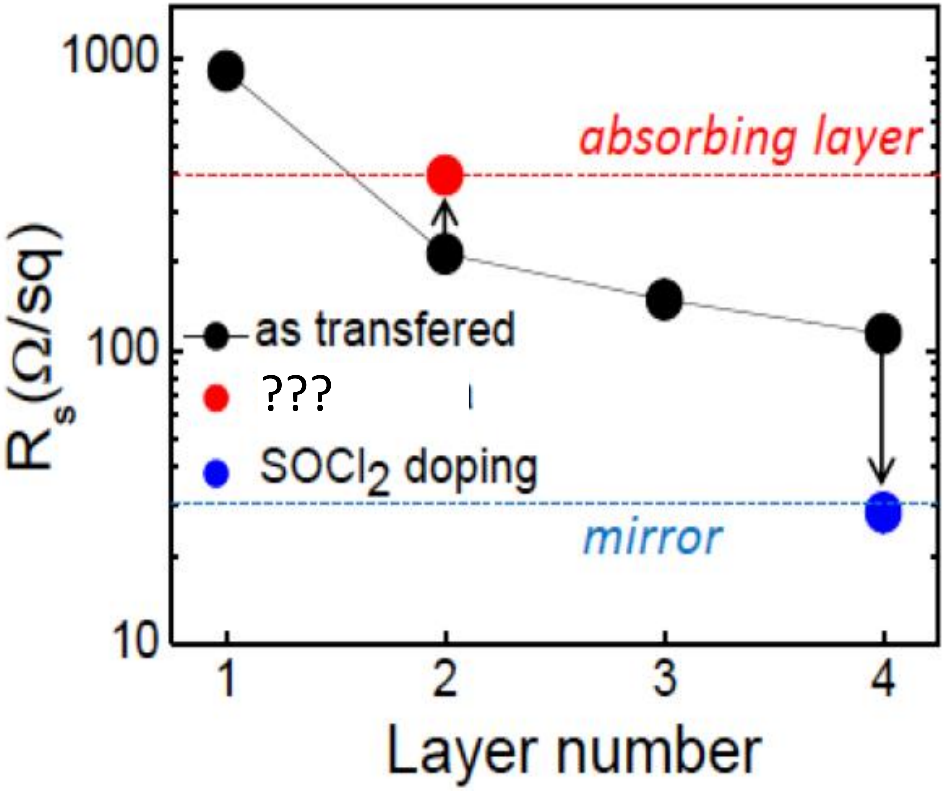
- **CO_2 chemistry** has been demonstrated a promising method for growing "gapped" epitaxial graphene.

Optically transparent Graphene EMI shield

G. V. Bianco, M. Grande, et al Optics Express (2016), in press.







Device performances: comparison between theory and experimental findings.