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Graphene
A Revolutionary Material ?

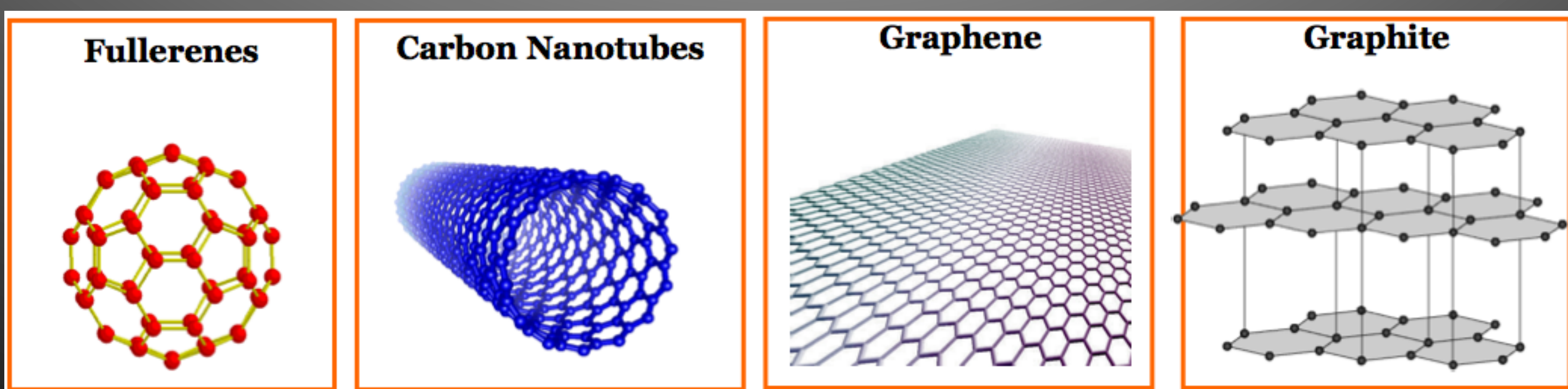
StéRéO Team's Bibliographic Seminar

Julien Botton - November 25th 2014

Carbon

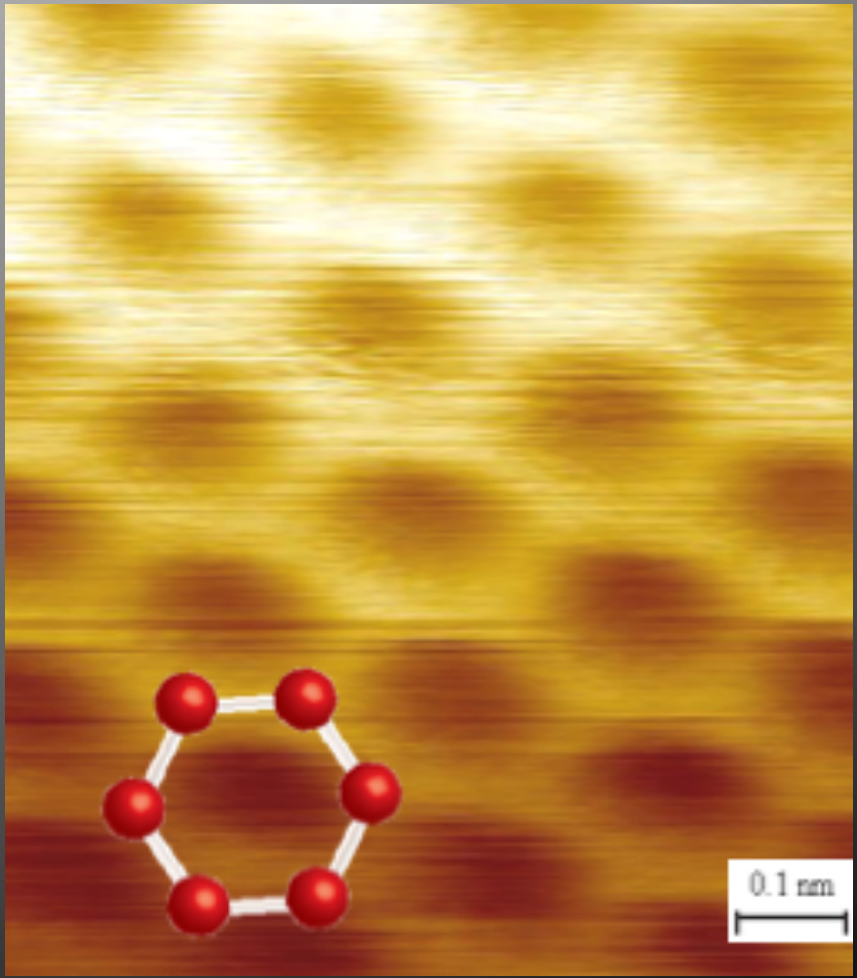
Allotropic Forms of sp² Carbon

0 D   1 D   2 D   3 D



Graphene

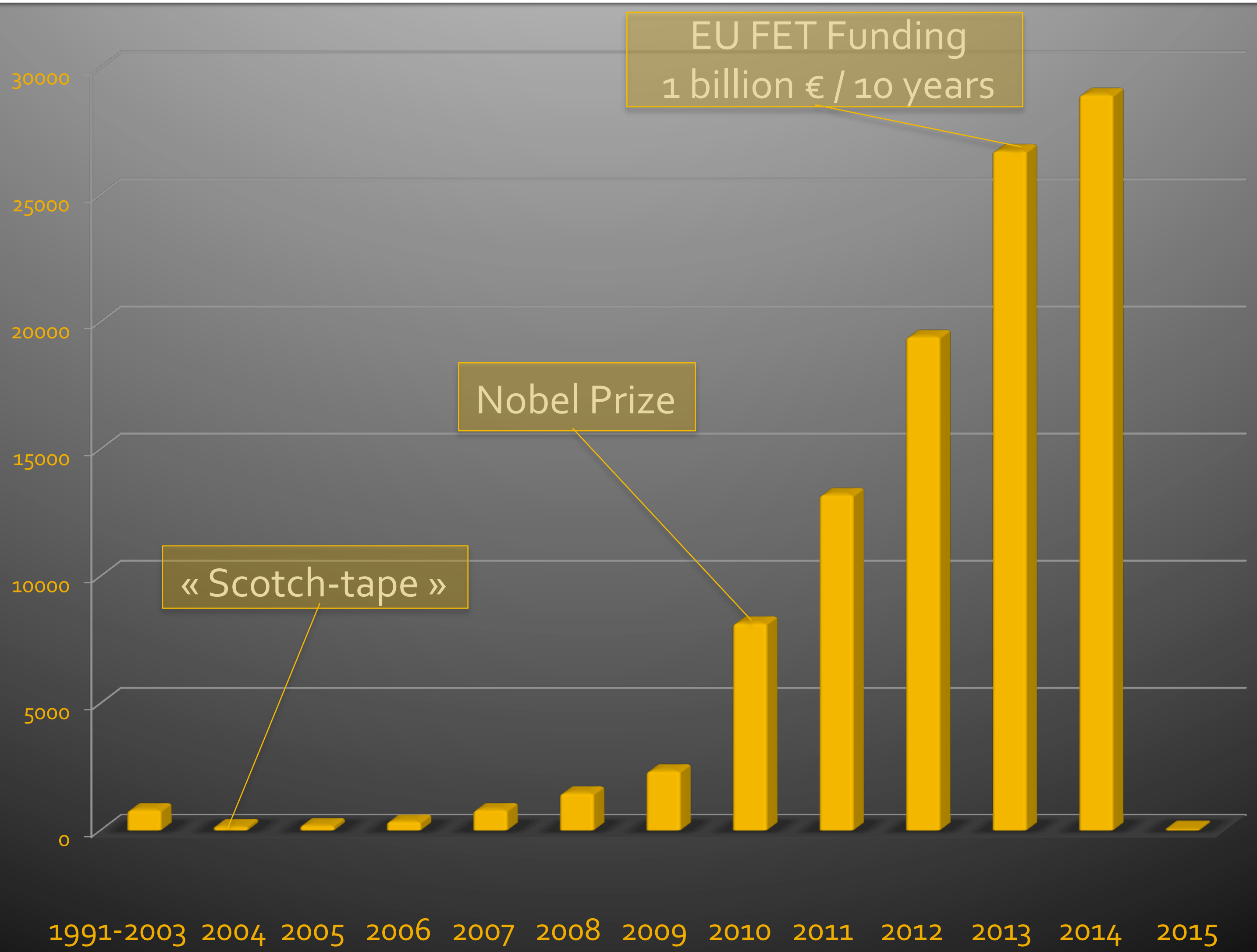
- Single-layer atomic monocrystal
- Semi-metal
  - High mobility of charge carrier
  - Thermal conduction
- Mechanical resistance
  - Stiff honeycomb architecture



A Short Story

Publications on graphene

data obtained from Web Of Science



- How to Synthesize Graphene ?
- How to Functionalize Graphene ?
- Which Perspectives for this Field ?

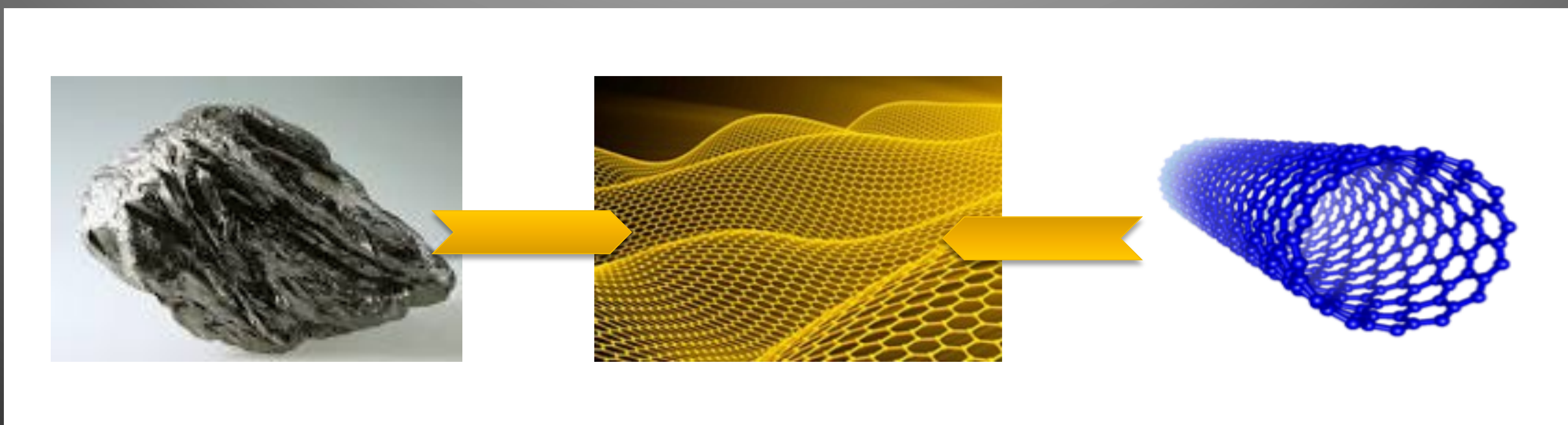
How to Synthesize Graphene ?

- ✓ Top-Down Approach
- ✓ Bottom-Up Processes

General Strategies

- Top down *vs.* Bottom-up
  - **Top-down**: Synthesis from a bulk material
  - **Bottom-up**: Growth of the material from a support

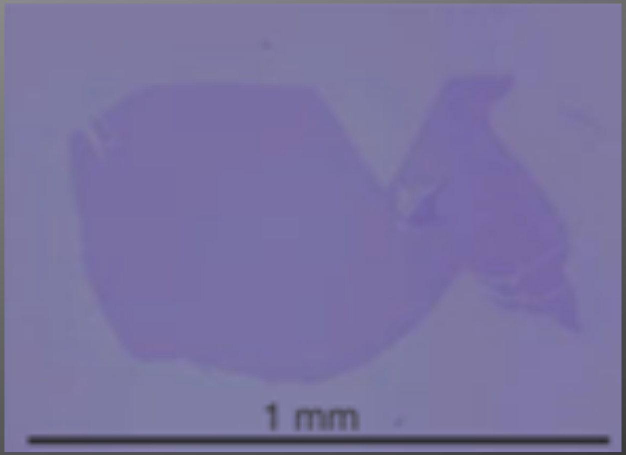
Top-down Approach



Graphite Graphene Carbon Nanotube

Mechanical Exfoliation of Graphite

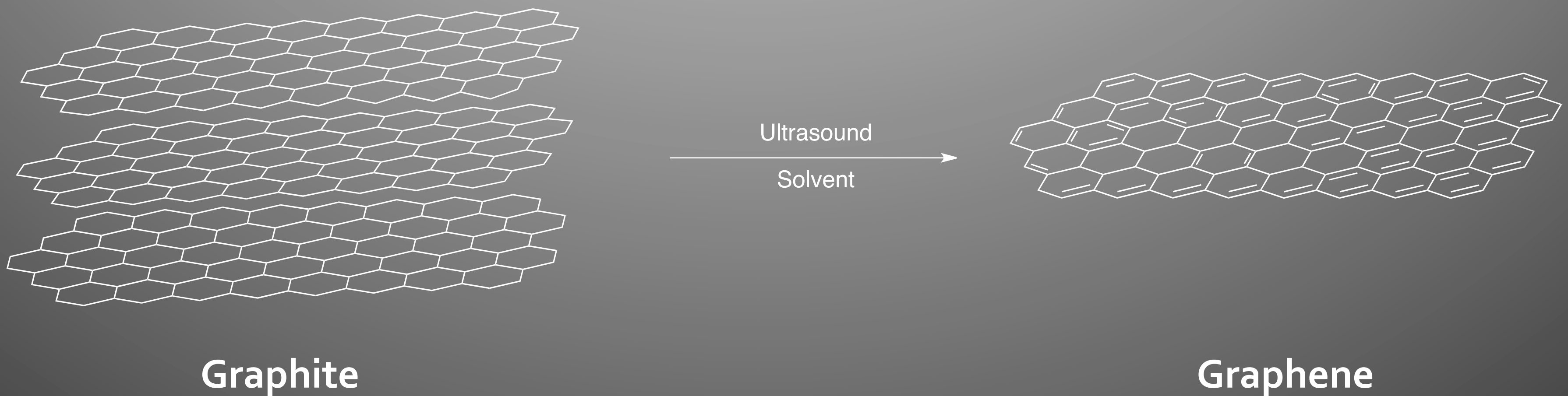
- « **Scotch-tape method** »
  - Peel off several times graphite with an adhesive
    Transfer on substrate (SiO_2)
  - Large flakes of
    monolayered graphene
  - No alteration,
    simple technique
    - **Pristine graphene** (highest quality)
  - Impossible to scale-up



Novoselov, Geim *et. al.*, *Science* **2004**, 306, 666

Solution-based Exfoliation of Graphite

- Use of NMP, DMF,… as solvent

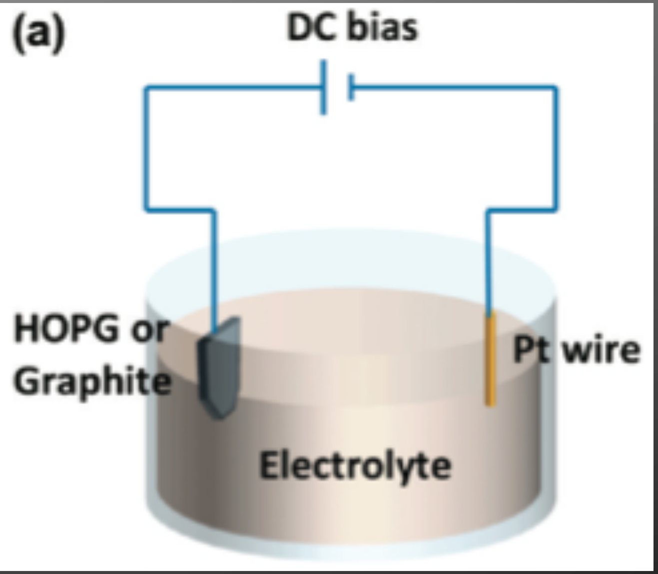


- Small amount of defects but graphene sheets breaks into tiny flakes
- Up to 90 % single-layered graphene

Coleman *et. al.*, *Nature Nano.* **2008**, 3, 563
Novoselov *et. al.*, *Nano Lett.* **2008**, 8, 1704

Electrochemical Exfoliation of Graphite

- Intercalation of electrolytes between the graphite sheets followed by exfoliation upon a current induced by electrodes
  - H_2SO_4
  - Poly(styrenesulfonate)
- Environmental friendly
- Partial Oxidation
- Not reproducible



Li *et. al.*, *ACS Nano.* **2011**, 5, 2332
Wang *et. al.*, *Carbon* **2009**, 47, 3242

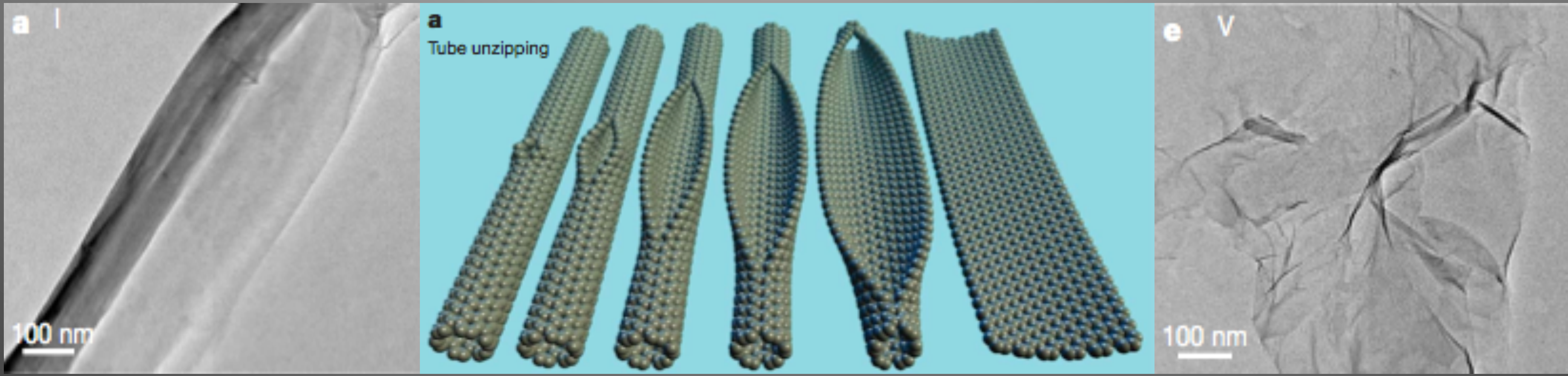
Oxidation, Exfoliation and Reduction

- Oxidation of graphite to graphite oxide
  - $KClO_4$: Brodie (1859), Staudenmaier (1898), Hofmann (1937)
  - $KMnO_4$: Hummers (1958), Tour (2010)
- Exfoliation by intercalating agents
- Reduction of graphene oxide
  - Thermal: 1000 °C ; formation of a lot of defects
  - Chemical: Hydrazine, LAH, $NaBH_4$, Hydroquinone, Vitamin C, Bacteria,…
  - Electrochemical

Ruoff *et. al.*, *Chem. Soc. Rev.* **2010**, 39, 228

Unzipping Carbon Nanotubes

- Graphene Nanoribbons (Width < 50 nm)



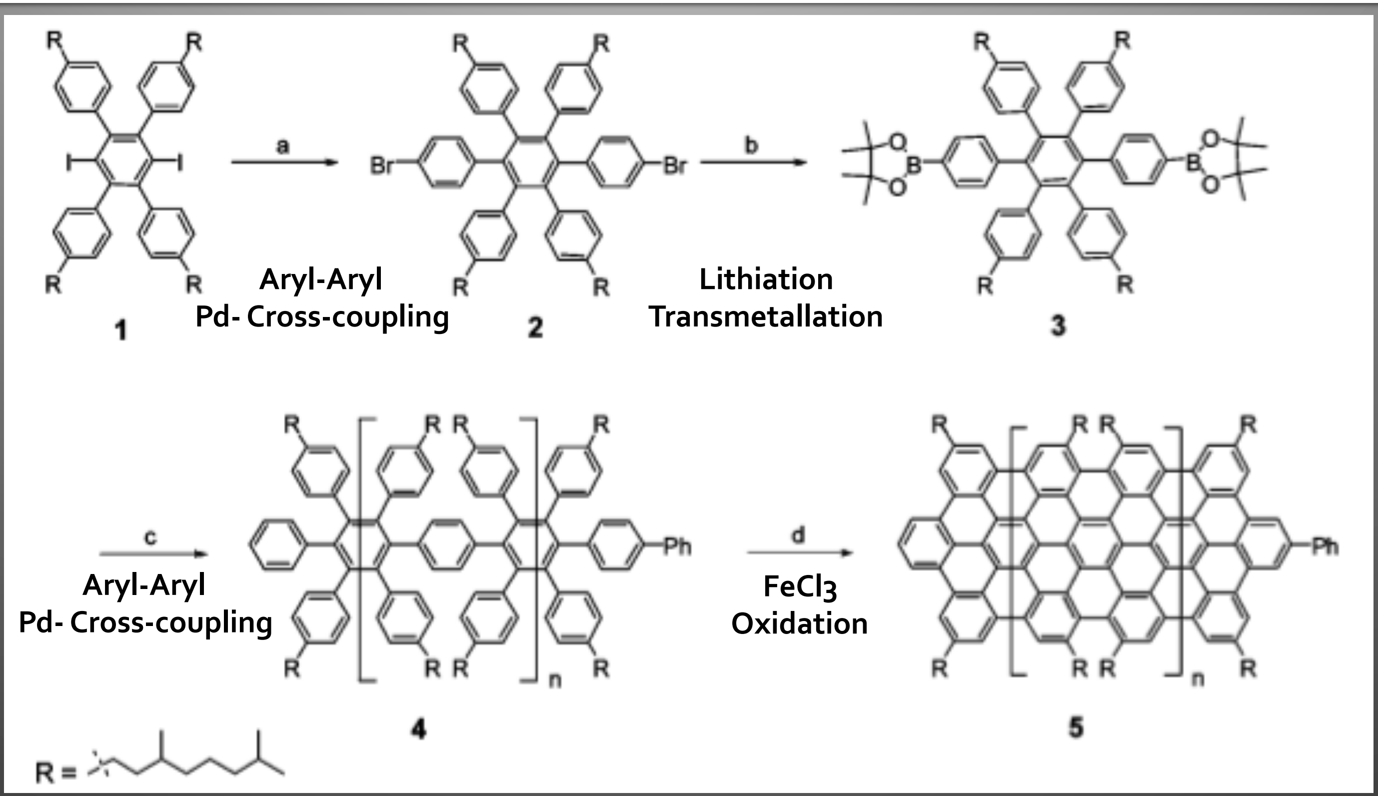
- Use of strong oxidant: $H_2SO_4/KMnO_4$
- Heating with $K_{(m)}$: Pristine Nanoribbons

Tour *et. al.*, *Nature* **2009**, 458, 872
Tour *et. al.*, *ACS Nano* **2011**, 5, 968

Bottom-up Processes

- Chemical Synthesis
- Epitaxial growth
- Chemical Vapor Deposition (CVD)

Chemical Synthesis



- Up to 30 nm wide nanoribbons
- No defects

Müllen *et. al.*, *J. Am. Chem. Soc.* **2008**, 130, 4216

Epitaxial Growth on SiC

- SiC is heated at high temperature under UHV
- Si subblimates and Carbon atoms rearrange to graphene
- Very thin film
- Impurities
- Promising industrially

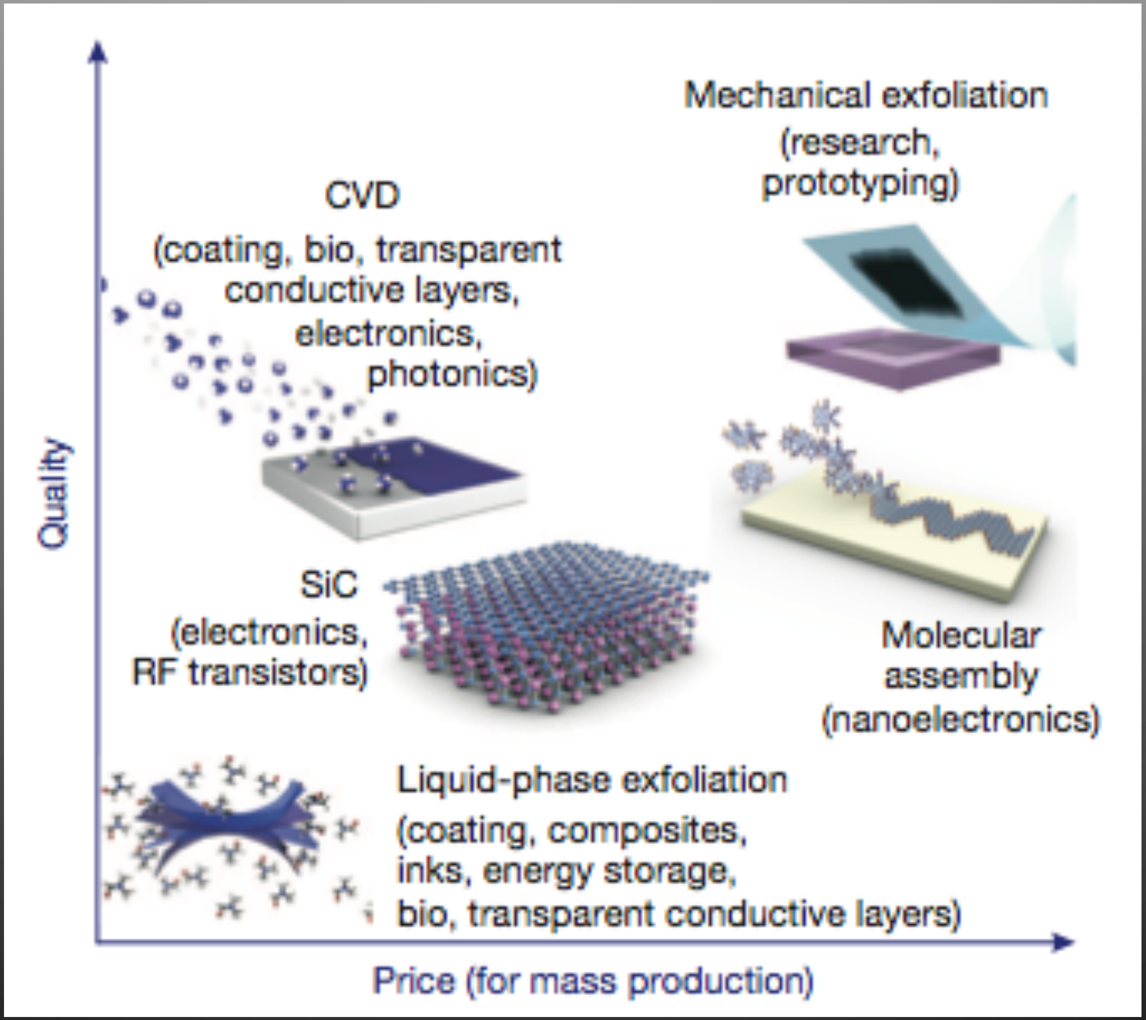
Berger *et. al.*, *Science* **2006**, 312, 1196

Chemical Vapor Deposition (CVD)

- Decomposition of a Carbon source that rearrange on a metal foil to sp^2 honeycomb that is transfered on other substrates
- High performance even with defects
- Further optimization are needed (controlled growth, transfer)
- Promising industrially

Novoselov *et. al.*, *Nature* **2012**, 490, 192

Summary


Mechanical exfoliation
(research,
prototyping)
CVD
(coating, bio, transparent
conductive layers,
electronics,
photonics)
Quality
SiC
(electronics,
RF transistors)
Molecular
assembly
(nanoelectronics)
Liquid-phase exfoliation
(coating, composites,
inks, energy storage,
bio, transparent conductive layers)
Price (for mass production)

How to Functionalize Graphene ?

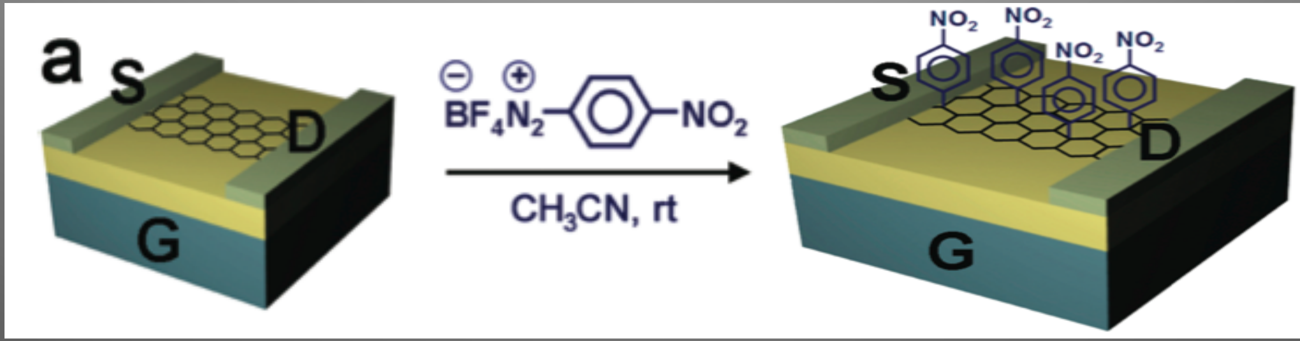
- ✓ Covalent Modifications
- ✓ Non-Covalent Modifications
- ✓ Nanoparticules Adsorption
- ✓ Doping
- ✓ Localized Modifications

Covalent Modifications

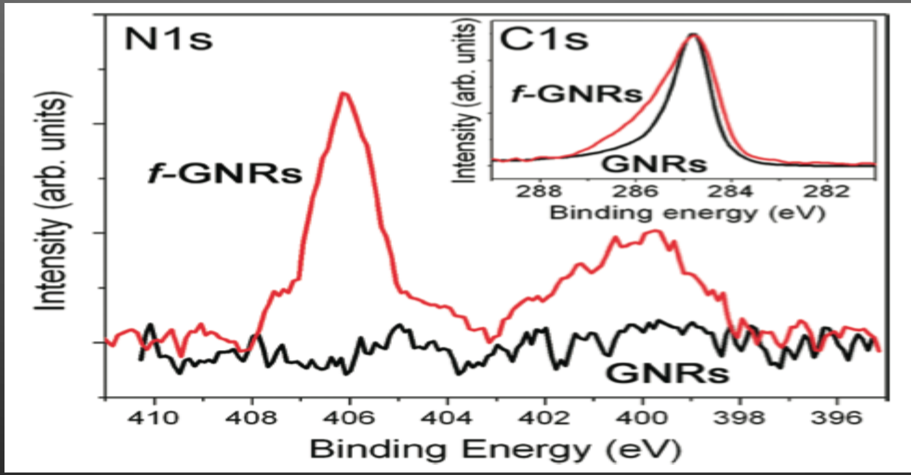
- Two major strategies:
  - Reactivity on sp^2 Carbon of Graphene
    - Free-Radical
    - Dienophiles
  - Reactivity on oxidized Carbon of Graphene Oxide

Diazonium salts

- *In-situ* generation of aryl radical grafted on Graphene Nanoribbons



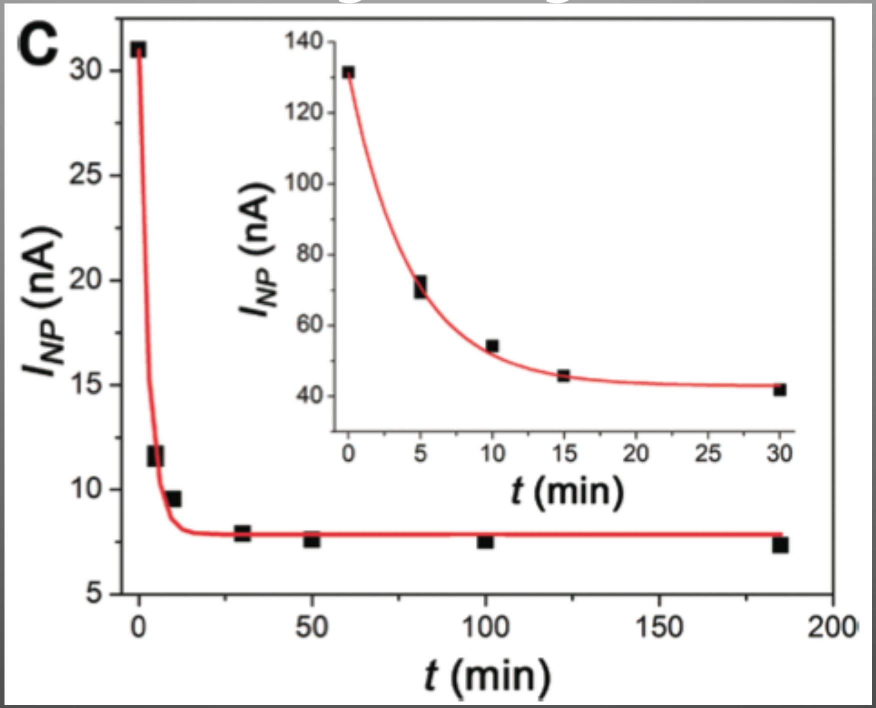
- XPS



Tour *et. al.*, *ACS Nano* **2010**, 4, 1949

Diazonium salts

- Time-control over the grafting:

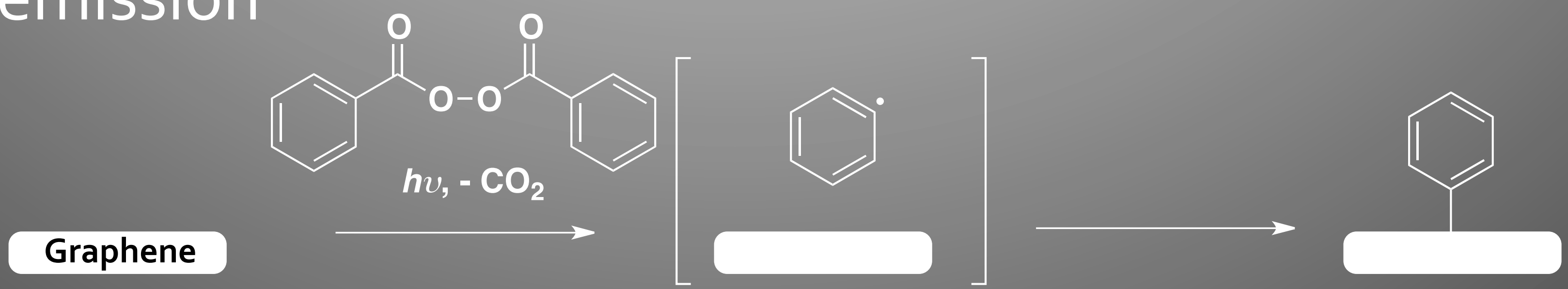


- Increase of grafting means an increase of C – sp³ and therefore a drop in conductivity.

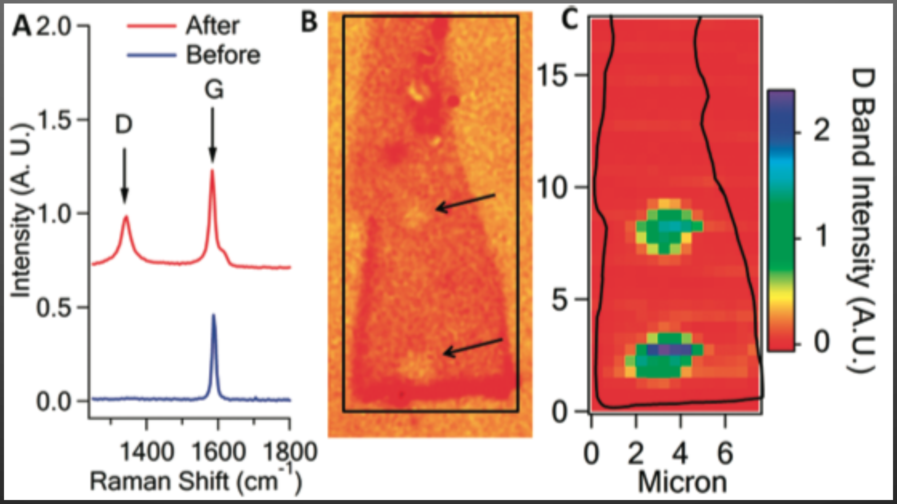
Tour *et. al.*, *ACS Nano* **2010**, 4, 1949

Benzoyl Peroxides

- *In-situ* generation of aryl radicals upon light emission



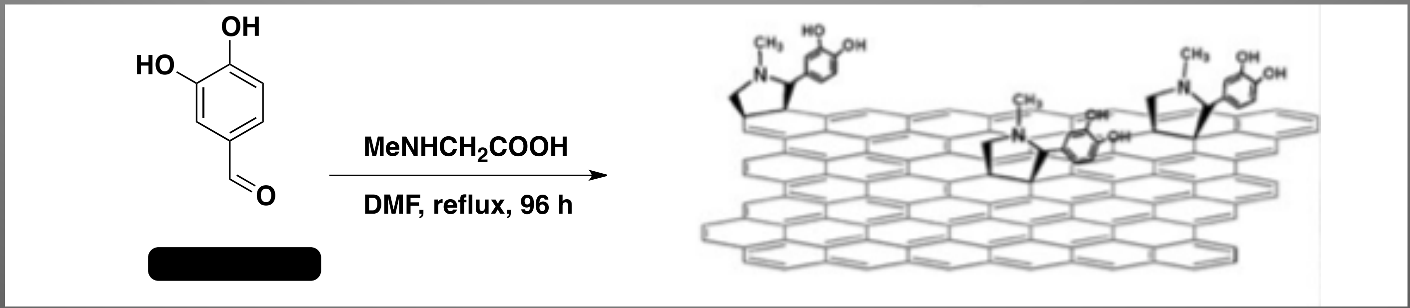
- Raman spectroscopy



Brus *et. al.*, *JACS* **2009**, 131, 17099

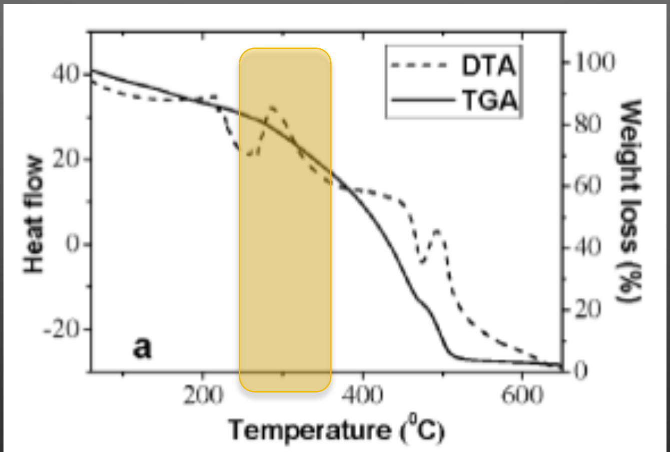
Azomethine Ylides

- Formation of pyrrolidine rings via 1,3 dipolar cycloadditions



- Thermogravimetry

Around 25 % weight loss

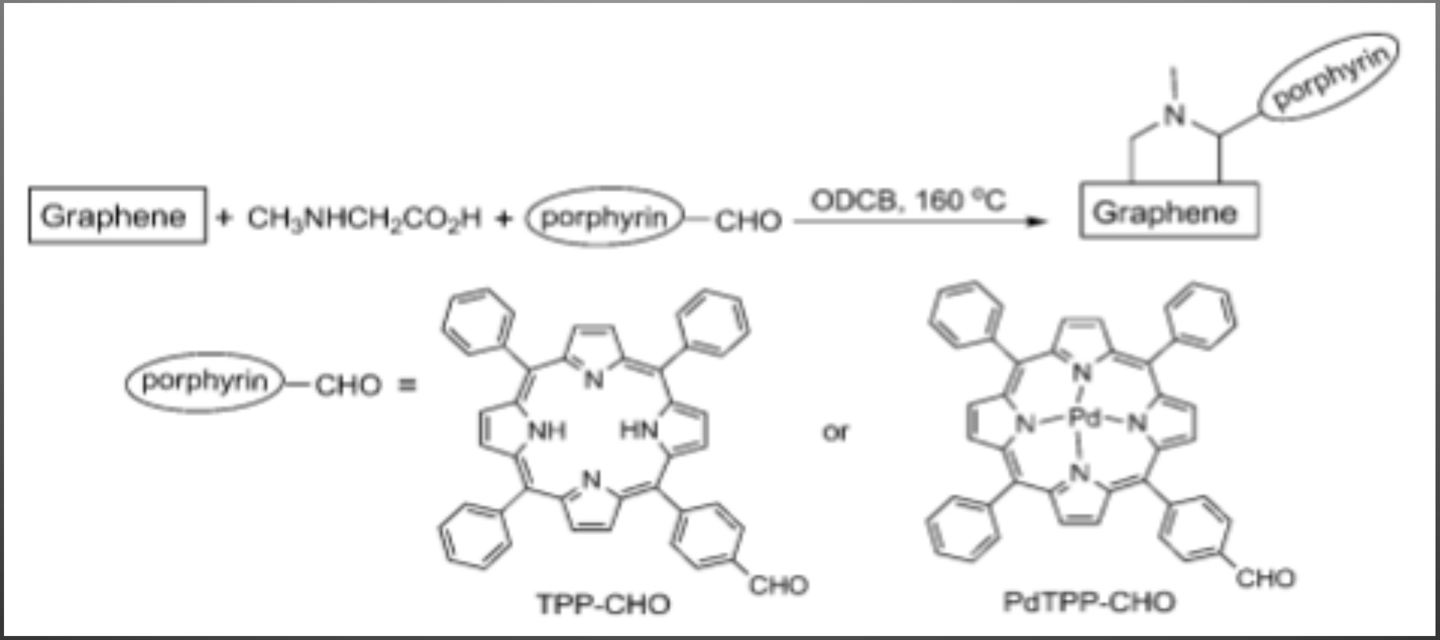


1 functionalization / 40 C

Georgakilas *et. al.*, *Chem. Commun.* **2010**, 46, 1766

Azomethine Ylides

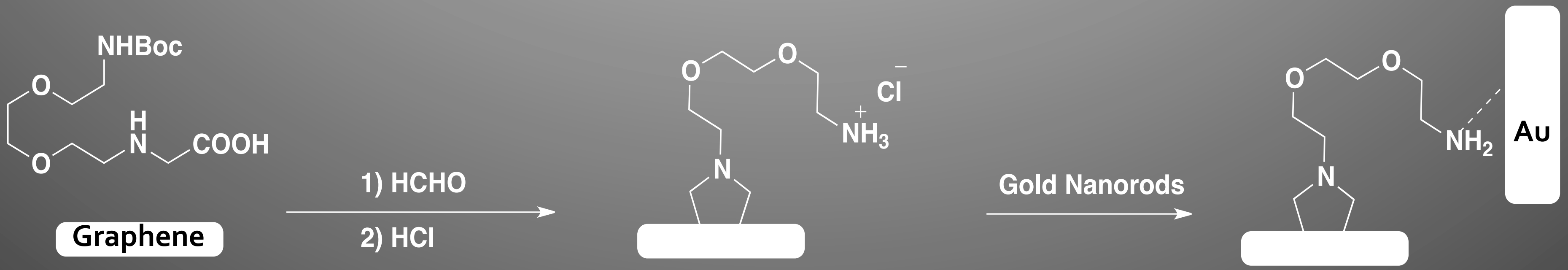
- Wide range of functionnalization
  - (Metallated) Porphyrins

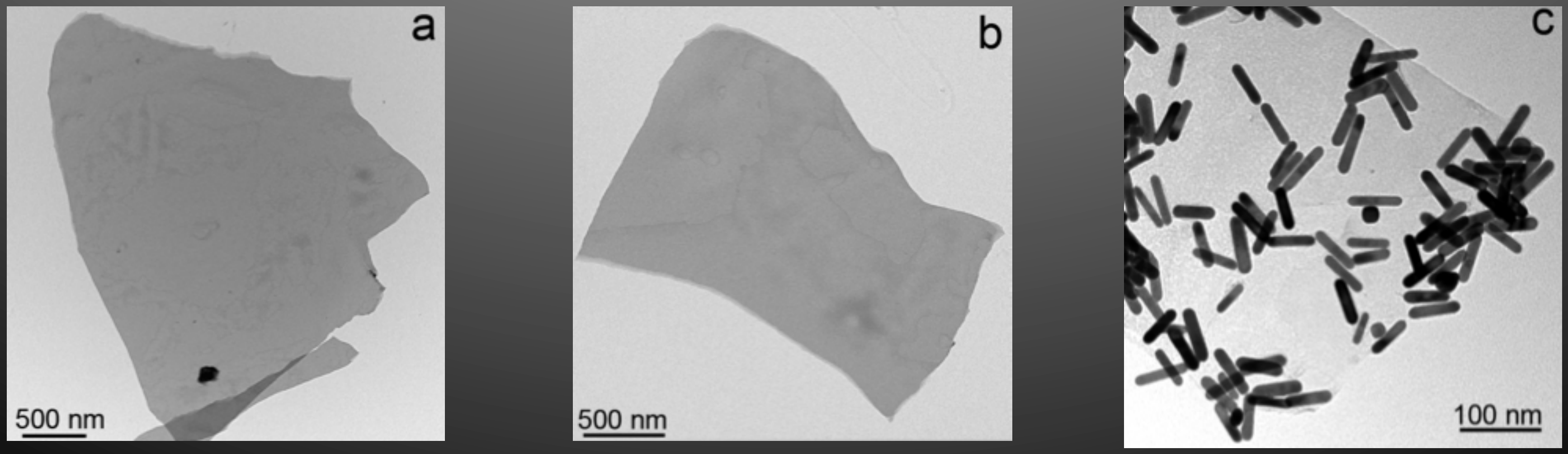


Feringa *et. al.*, *Chem. Eur. J.* **2011**, 17, 8957

Azomethine Ylides

- Wide range of functionalization
  - Gold Nanorods

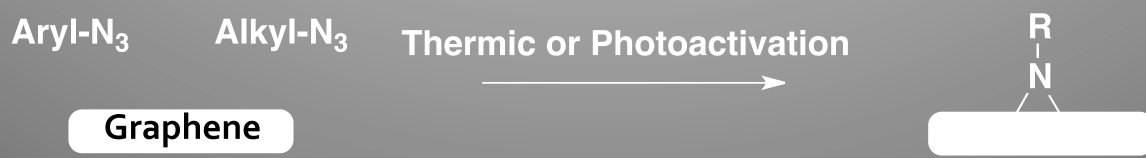




Prato *et. al.*, *ACS Nano* **2010**, 4, 3527

Nitrenes

- Wide Range of Functionalization

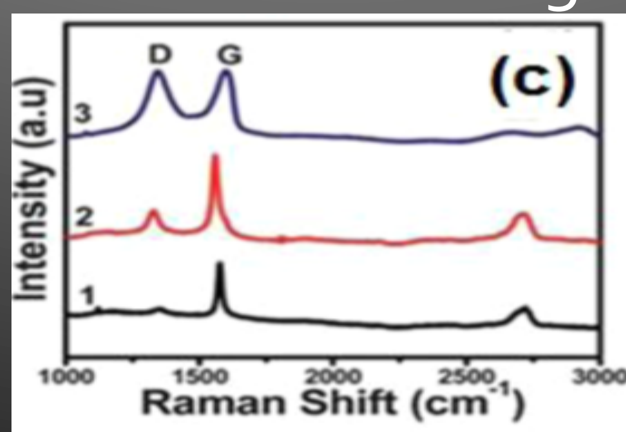


Liu *et. al.*, *Nano Lett.* **2010**, 10, 3754

- Up to 1 Azide / 13 C with BocPheN$_3$

Strom *et. al.*, *Chem. Commun.* **2010**, 46, 4097

- Concentration-control over the grafting



10 equiv. Azide

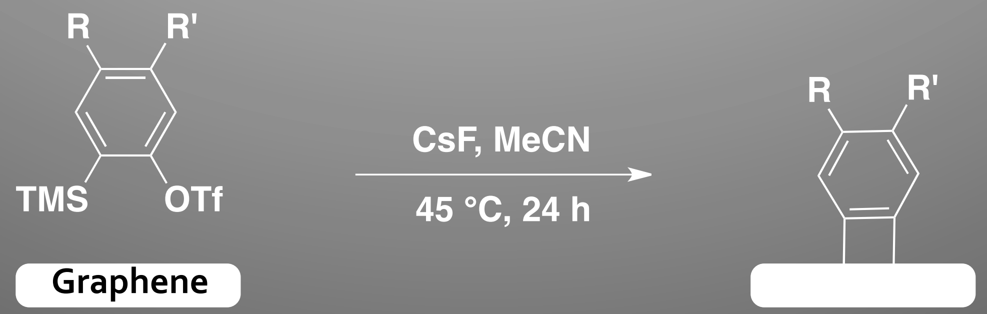
1 equiv. Azide

Graphene

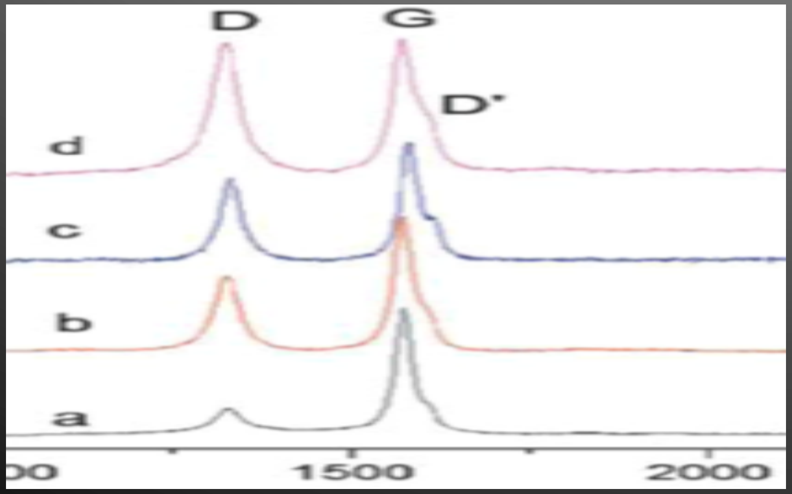
Vadukumpully *et. al.*, *Nanoscale* **2011**, 3, 303

Arynes

- *In-situ* generation of benzyne and formation of a cyclobutane



- Substitution-control over grafting



R = R′ = H	$I_D/I_G = 0.97$
R = Me, R′ = H	$I_D/I_G = 0.69$
R = R′ = F	$I_D/I_G = 0.55$
Pristine Graphene	$I_D/I_G = 0.24$

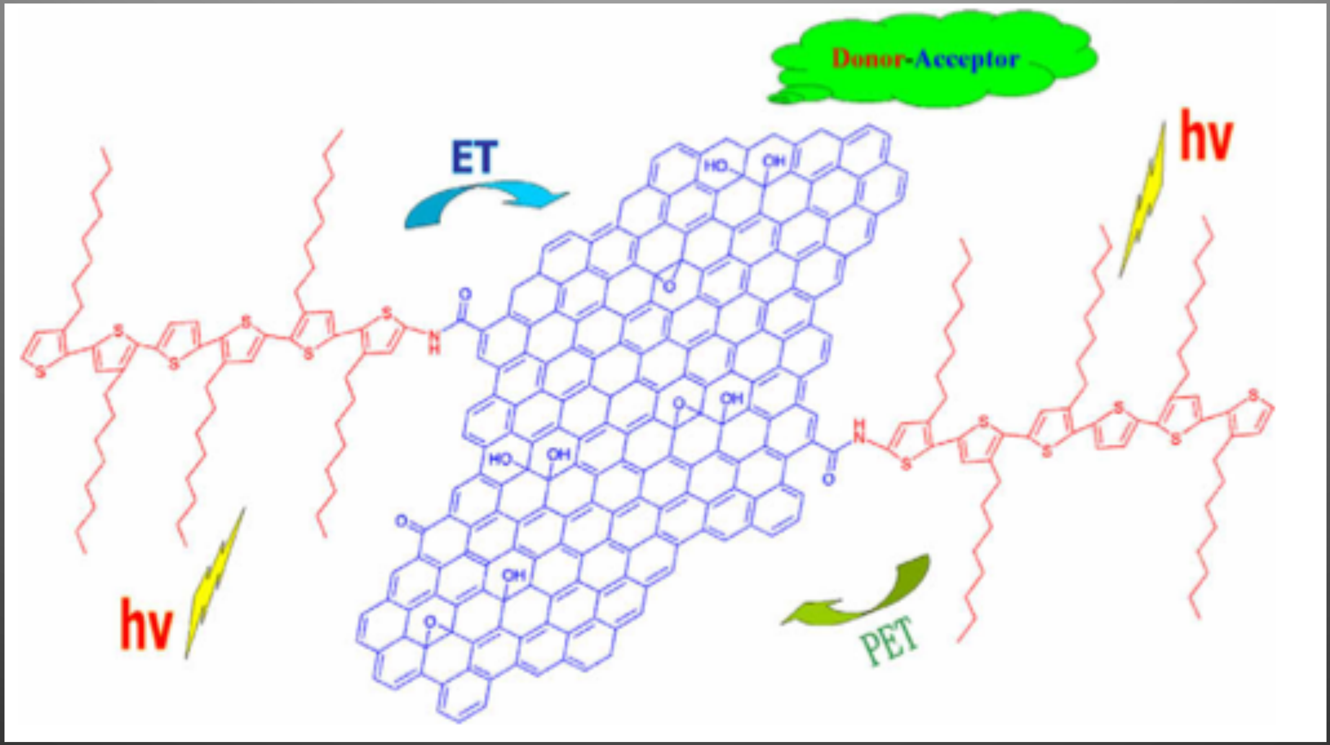
Ma *et. al.*, *Chem. Commun.* **2010**, 46, 7340

Covalent Modifications

- Two major strategies:
  - Reactivity on sp^2 Carbon of Graphene
  - Reactivity on oxidized Carbon of Graphene Oxide
    - Reactivity on Carboxylates
    - Reactivity on Hydroxyles
    - Reactivity on Epoxides

From Carboxylates to Amides

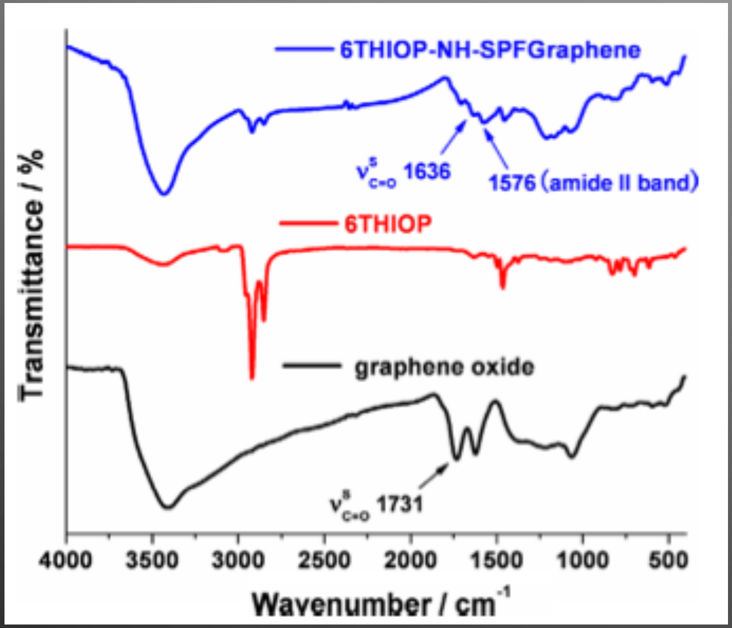
- Polythiophene for Organic Photovoltaic Devices



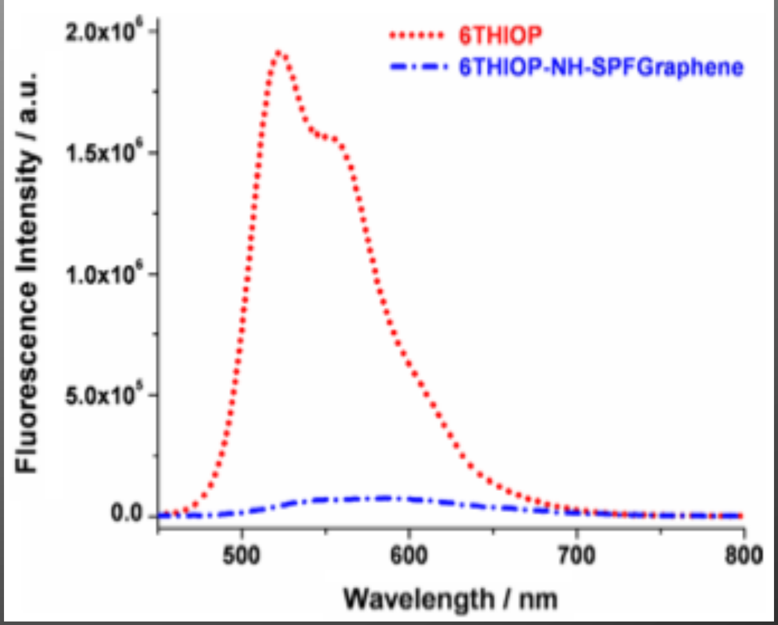
Liu *et. al.*, *Carbon* **2009**, 47, 3113

From Carboxylates to Amides

- FTIR



- Fluorescence Quench

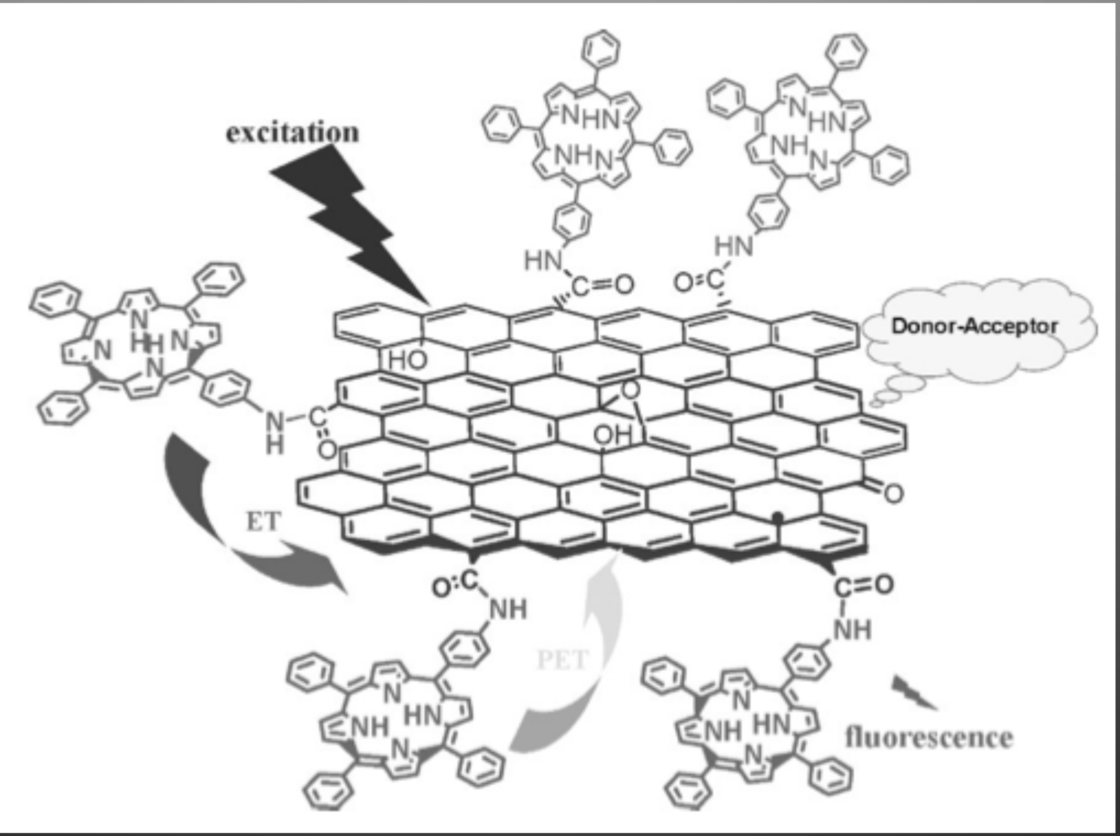


Photoinduced Electron Transfer or Energy transfer

Liu *et. al.*, *Carbon* **2009**, 47, 3113

From Carboxylates to Amides

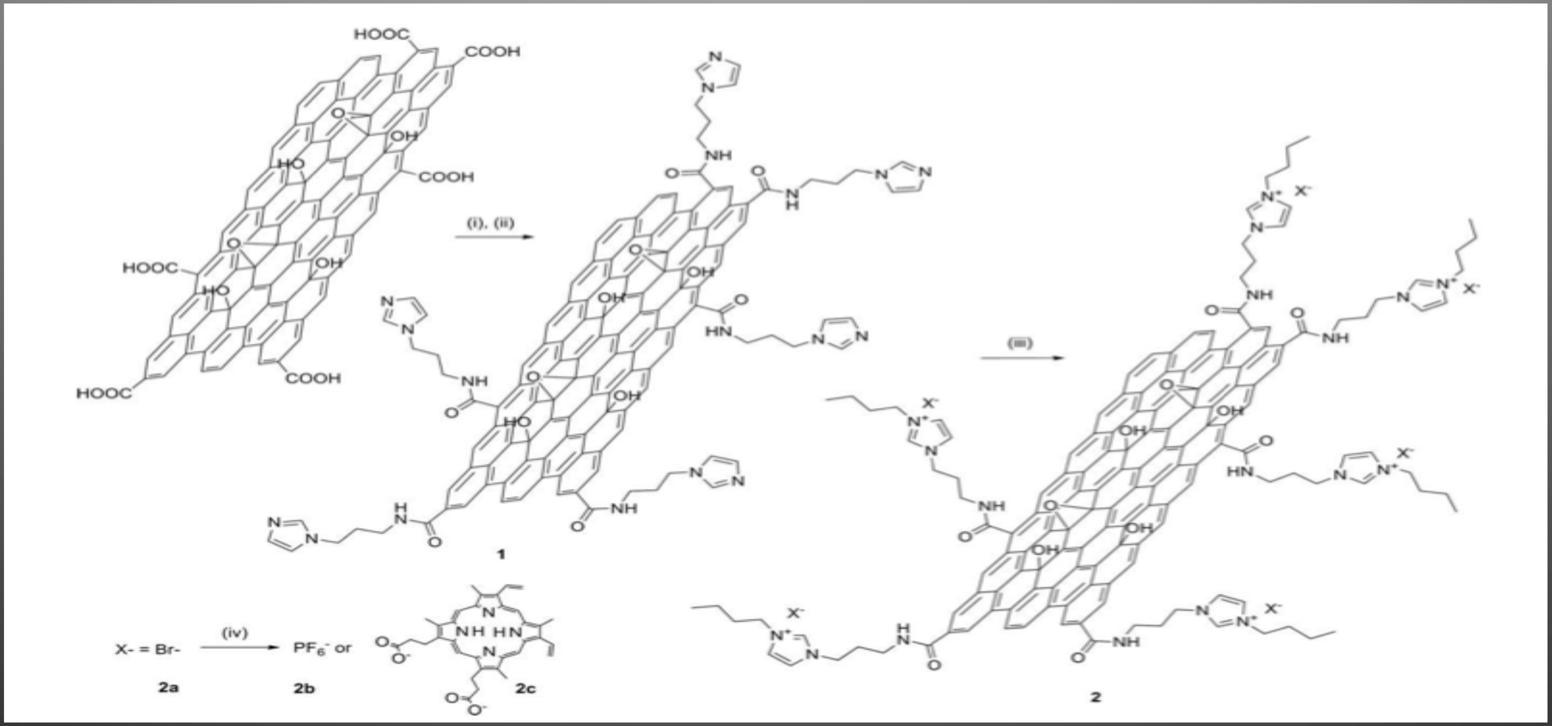
- Porphyrines



Chen *et. al.*, *Adv. Mater.* **2009**, 21, 1275

From Carboxylates to Amides

- Imidazolium

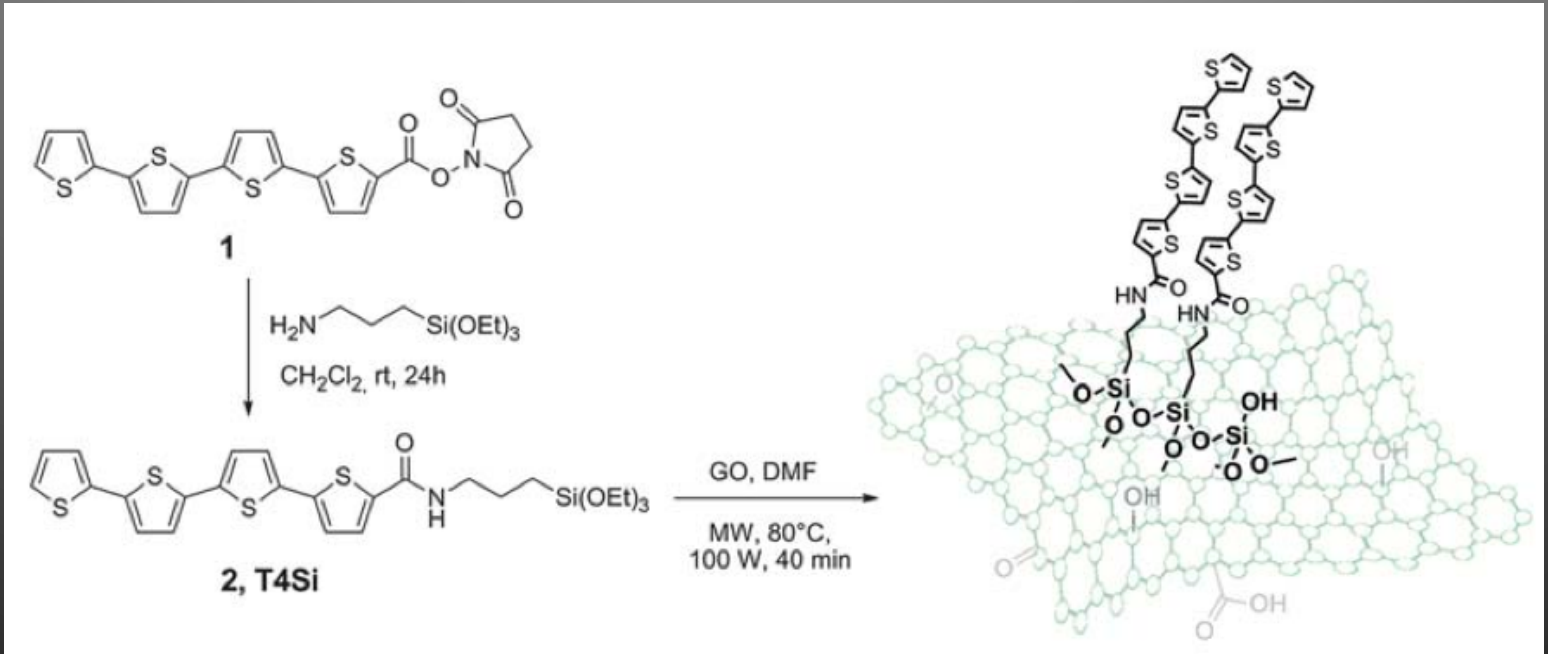


- Anion metathesis allows modulation of the wettability of the materials

Karousis *et. al.*, *Carbon* **2010**, 48, 854

From Hydroxyls to Silyl-ethers

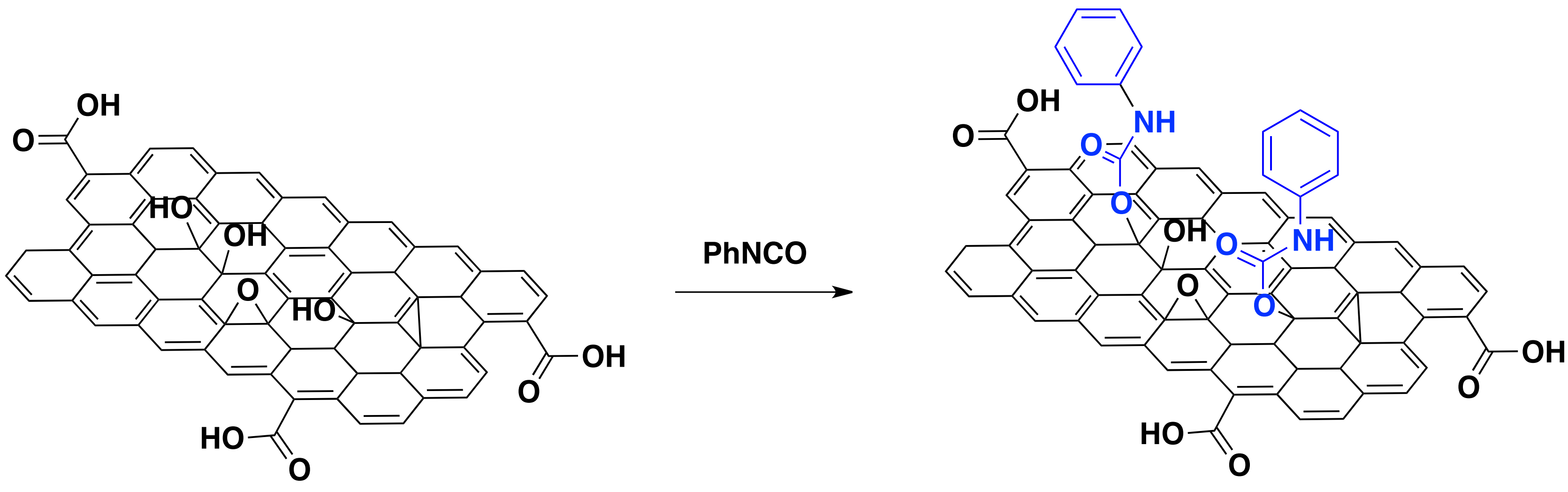
- Use of Triethoxysilanes functionalized polythiophene



Palermo *et. al.*, *J.Mater.Chem.* **2010**, 20, 9052

From Hydroxyls to Carbamates

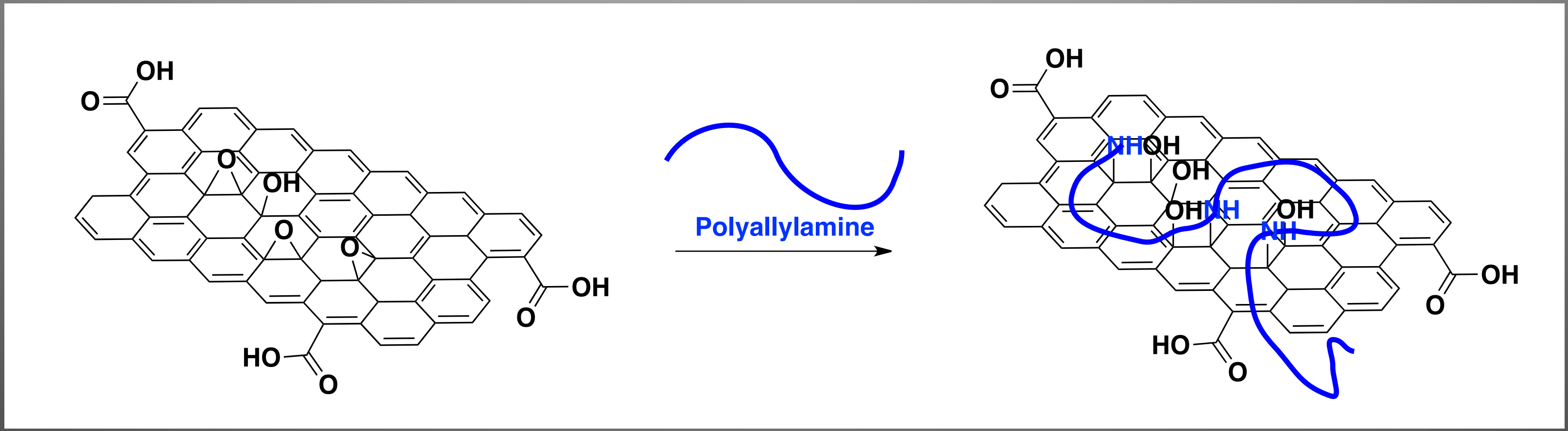
- Use of Phenylisocyanate to improve dispersibility of Graphene Oxide



Ruoff *et. al.*, *Nature* **2006**, 442, 282
Chen *et. al.*, *Adv. Mater.* **2008**, 20, 3924

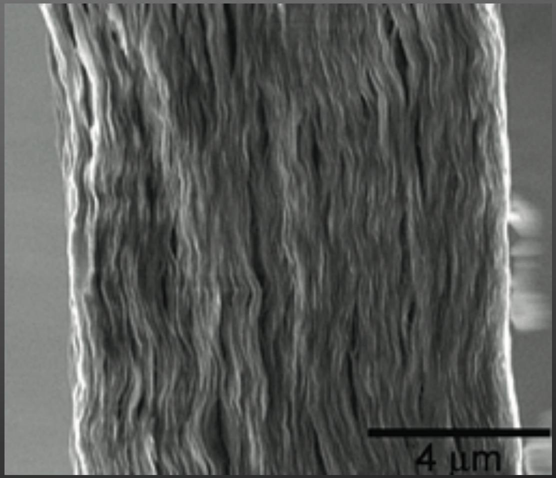
From Epoxides to Aminoalcohols

- Polymer cross-linking with polyallylamine



- Dispersion in organic solvents and water

- Obtention membrane paper-like by filtration



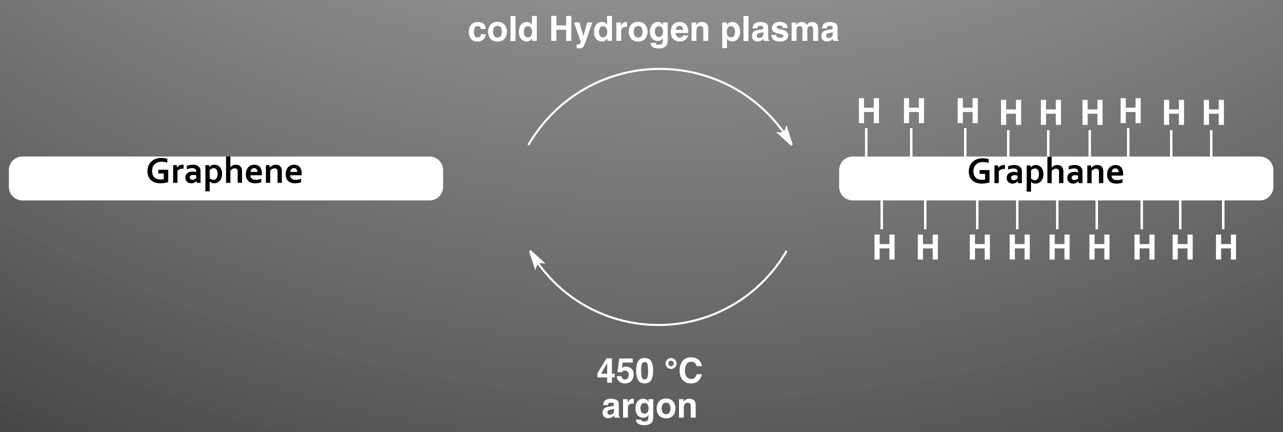
Ruoff *et. al.*, *J.Phys.Chem.C* **2009**, 113, 15801

Covalent Modifications

- Two major strategies:
  - Reactivity on sp^2 Carbon of Graphene
  - Reactivity on oxidized Carbon of Graphene Oxide
- An alternative strategy:
  - Graphane
  - Halographene

Graphane

- Prediction of a sp^3 Carbon monolayer by DFT calculations
- Synthesis

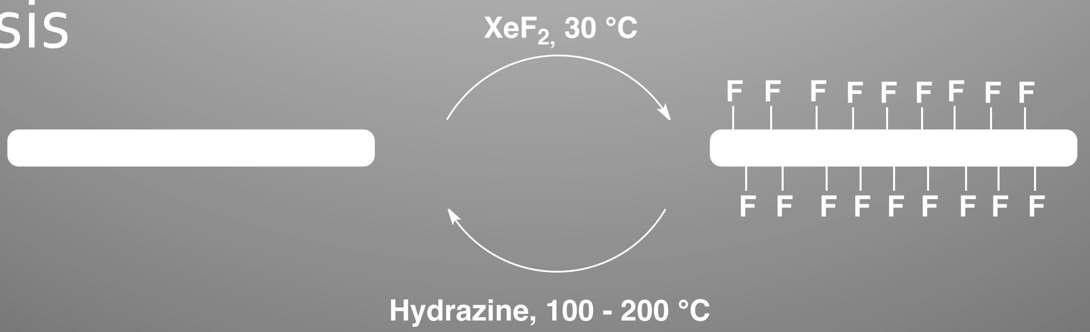


- Insulator-like: Charge mobility is reduced 3x

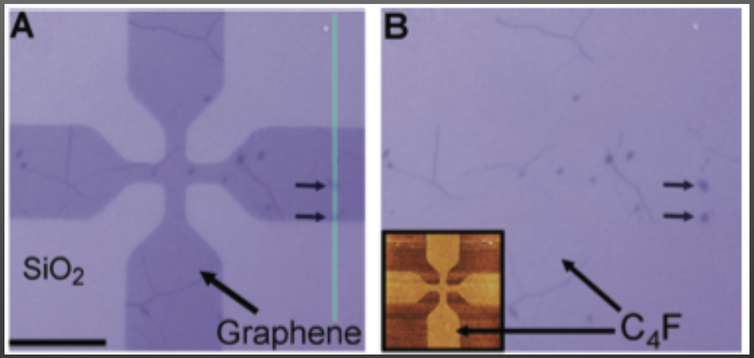
Novoselov *et. al.*, *Science* **2009**, 323, 610
Sofo *et. al.*, *Phys. Rev. B* **2007**, 75, 153401

Fluorographene

- Synthesis



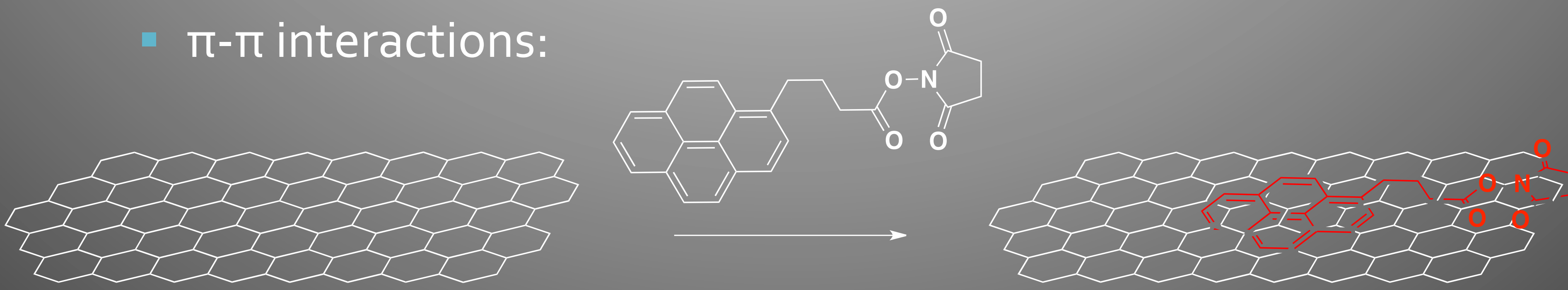
- Support-control over stoecchiometry
  - Graphene/Cu: Single-side functionalization (C_4F)
  - Graphene/Si: Dual-side functionalization (C_1F_1)
- Chemically inert, Teflon-like



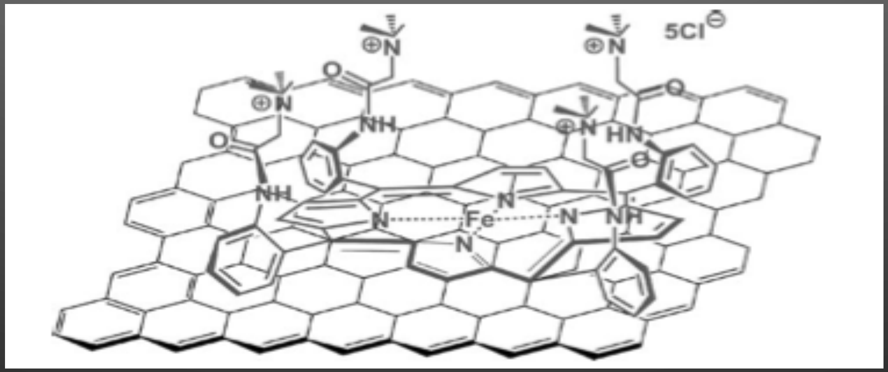
Novoselov *et. al.*, *Science* **2009**, 323, 610
Sofo *et. al.*, *Phys. Rev. B* **2007**, 75, 153401

Non-Covalent Modifications

- Graphene is a rich π-system
  - π-π interactions:



    - Increase of Power Conversion Efficiency from 0,21 to 1,71 %
  - Cation-π interactions:



Wang *et. al.*, *Appl. Phys. Lett* **2009**, 95, 063302
Ju *et. al.*, *Chem. Eur. J.* **2010**, 16, 10771

Nanoparticules Adsorption

- General Strategy:
  - Metal salts are injected in a solution of graphene oxide
  - A reductive process allows the formation of NPs that are adsorbed on the graphene sheet.

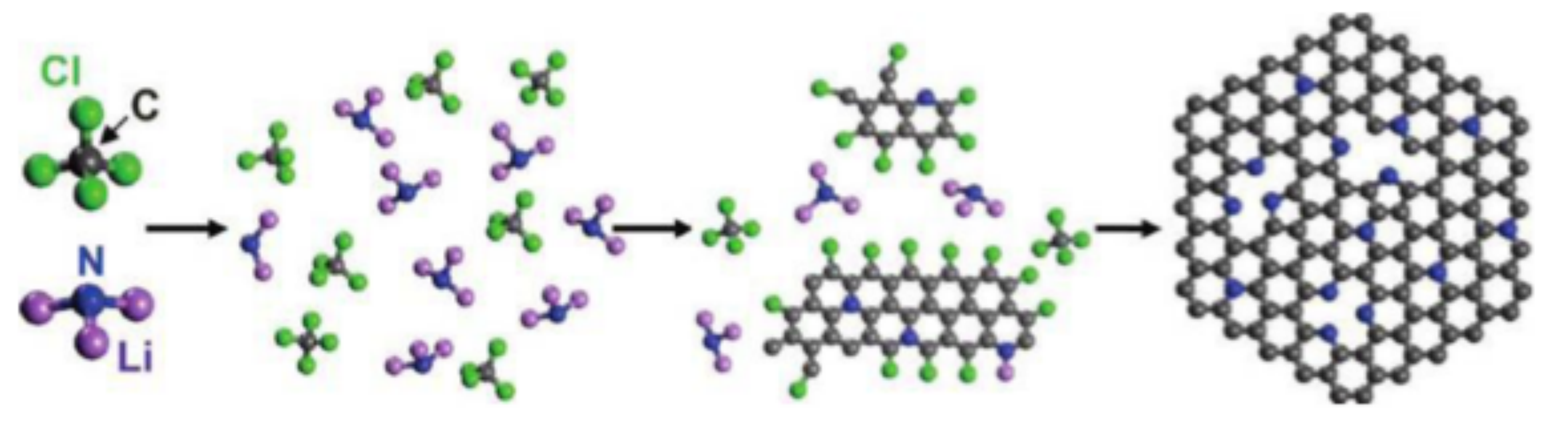
Kim *et. al.*, *Chem. Rev.* **2012,** 112, 6156

- Noble Metal affinity
  - Pd >> Au > Ag
  - Pd-graphene interaction through dative bond

Hozba *et. al.*, *J. Phys. Chem. C* **2012,** 116, 14151

Doping for semi-conductor

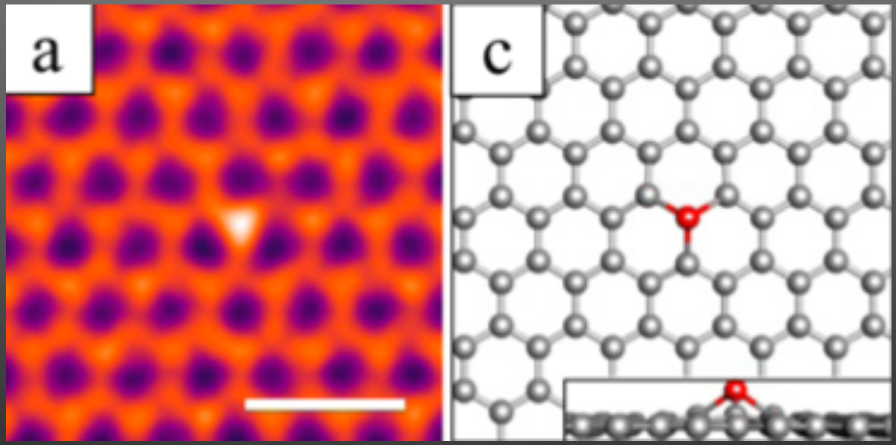
- Nitrogen doping:
  - 3 sp^3 orbitals
  - 1 lone pair conjugated with π-system
  - n-type doping



Chen *et. al.*, *Chem. Soc. Rev.* **2014**, 43, 7067

Doping for semi-conductor

- Boron doping:
  - 3 sp^3 orbitals
  - 1 vacancy
  - p-type doping
- Metal doping:



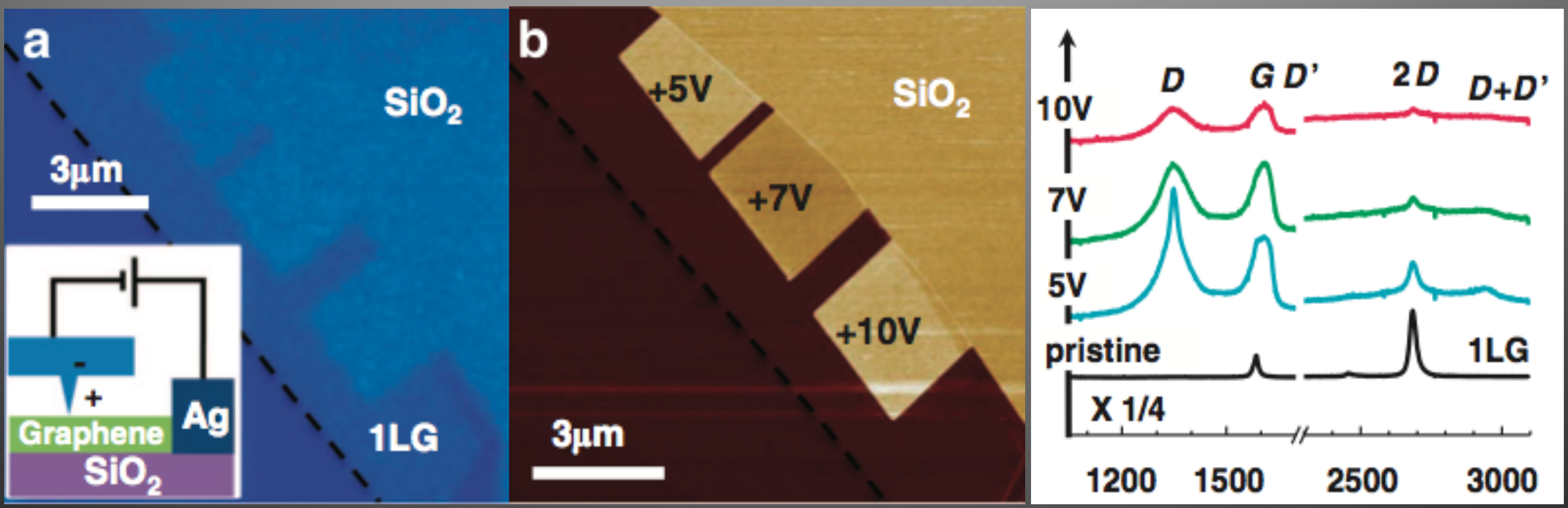
Chen *et. al.*, *Chem. Soc. Rev.* **2014**, 43, 7067
Warner *et. al.*, *Nano. Lett.* **2014**, 14, 3766

Local Functionalizations

- Use of Scanning-Probe Microscopy techniques:
  - Local Oxidation
  - Local Arylation
  - Local Adsorption

Local Oxidation

- Local positive bias induced by conductive AFM tip

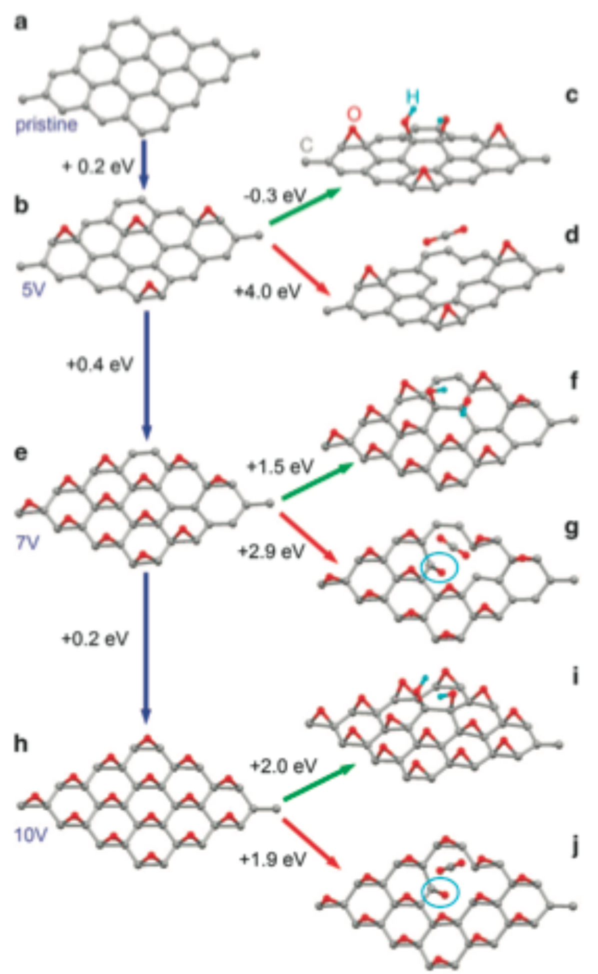


Friction Topography Raman

Byun *et. al.*, *NPG Asia Mat.* **2014**, 6, e102

Local Oxidation

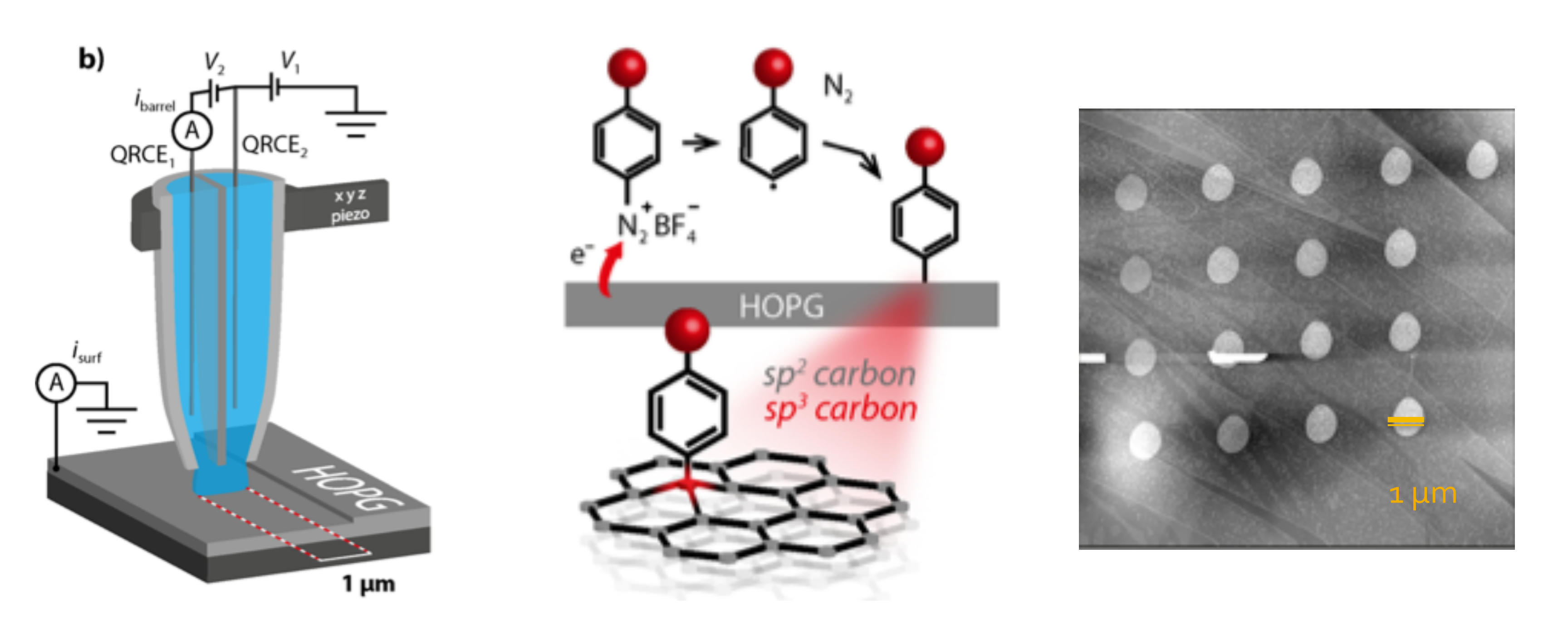
- DFT Calculations
  - Increase of oxygen coverage with higher voltage
- Easily tuned system up to 94,9% coverage in O



Byun *et. al.*, *NPG Asia Mat.* **2014**, 6, e102

Local Arylation

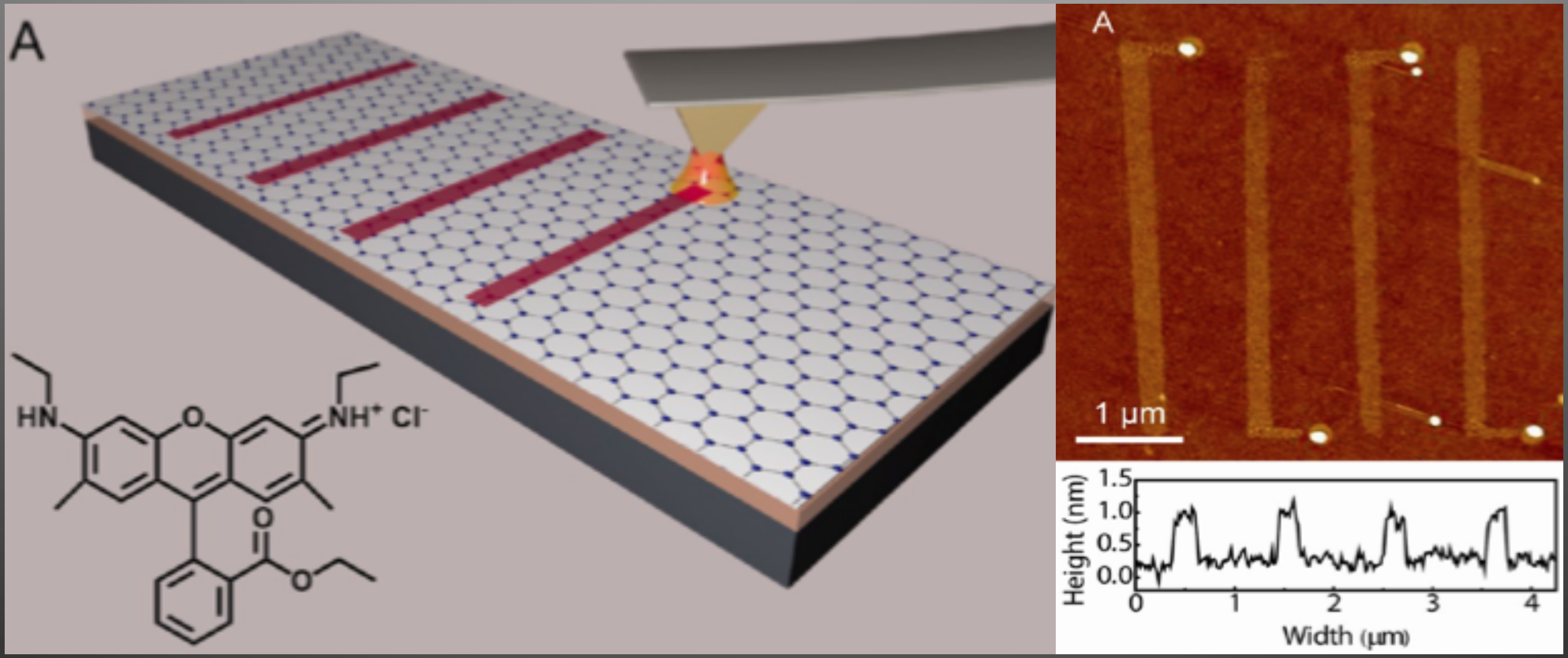
- Tip induced local formation of aryl radicals



Unwin *et. al.*, *J.Am.Chem.Soc.* **2014**, 136, 36

Local Adsorption

- Dip-pen Nanolithography on Graphene



- Up to 90 nm wide
- n-doping of graphene

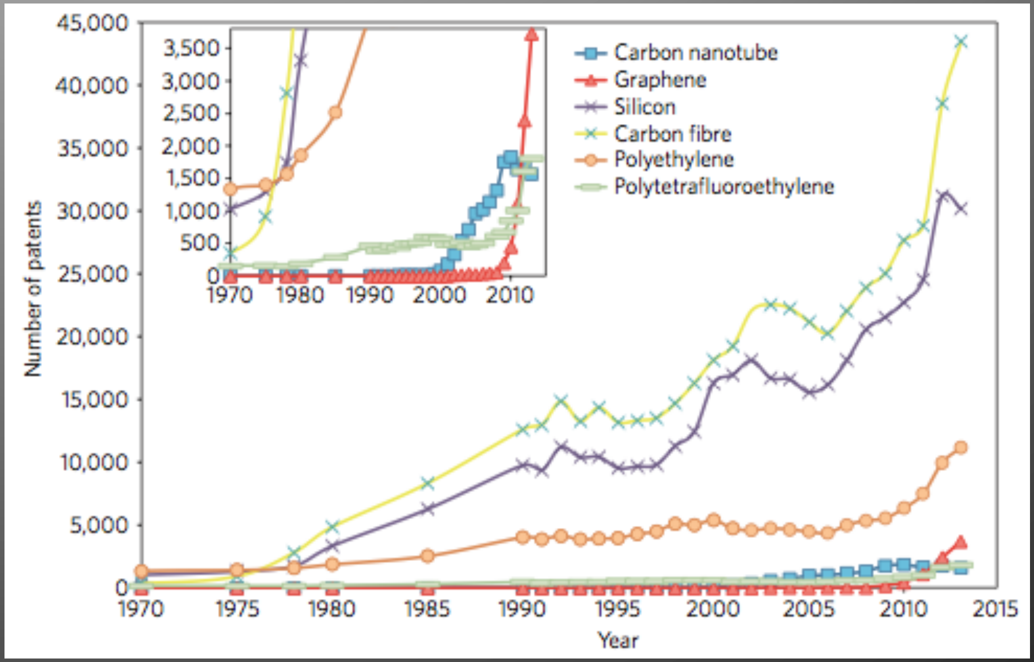
Mirkin *et. al.*, *Nano Lett.* **2013**, 13, 1616

Which Perspectives for this Field ?

- ✓ Economic forecast
- ✓ Industrial perspectives

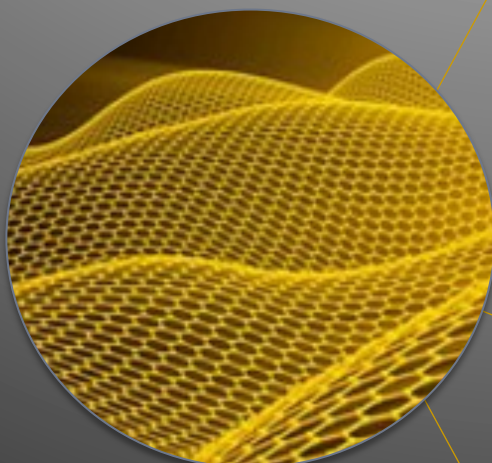
Economic Forecast

- High industrial activity
- Few products on the market (Head's tennis racket, Samsung's touch screen,...)
- Increase of large scale production of large sheet of graphene



Nature Nano. **2014**, 9, Graphene special issue

Some Industrial Perspectives

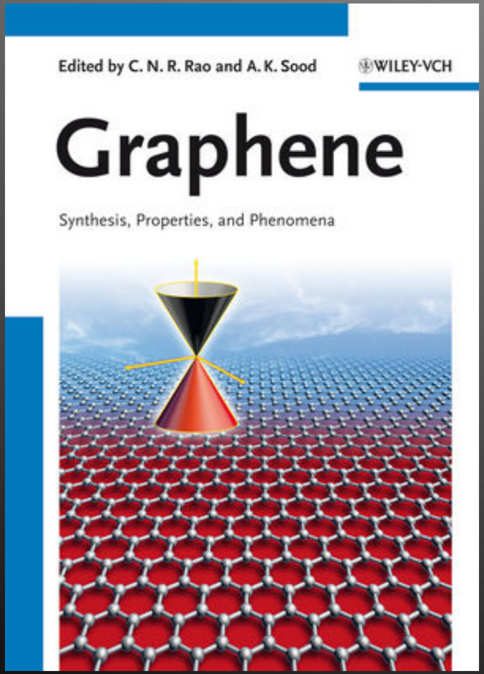


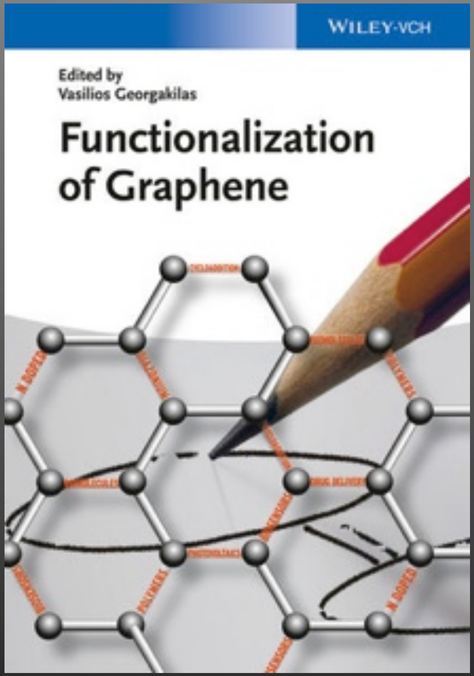
- Imper-meable to gaz
  - Anti corrosion
- Heat conductive
  - Anti tumoral
- Transpa-rency
  - Touch screen
- High surface area
  - Energy Storage

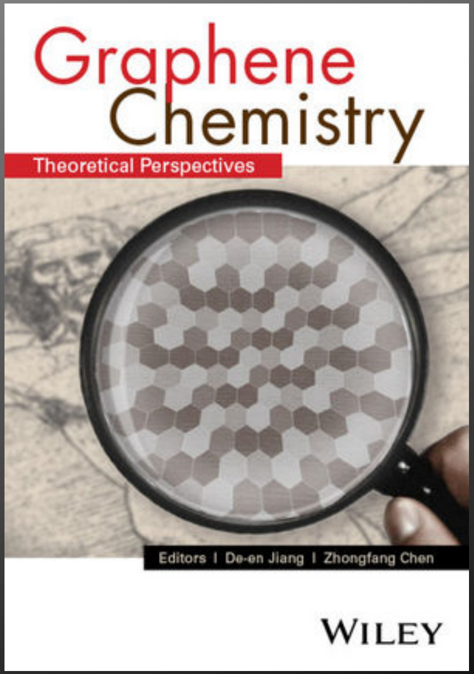
Nature Nano. **2014**, 9, Graphene special issue

To Go Further

- *Chem. Rev.* **2012**, *112*, 6156
- *Chem. Soc. Rev.* **2010**, *39*, 228
- *Chem. Rev.* **2014**, *114*, 7150
- Special issue in *Nature Nano* **2014**







Thank you for your attention