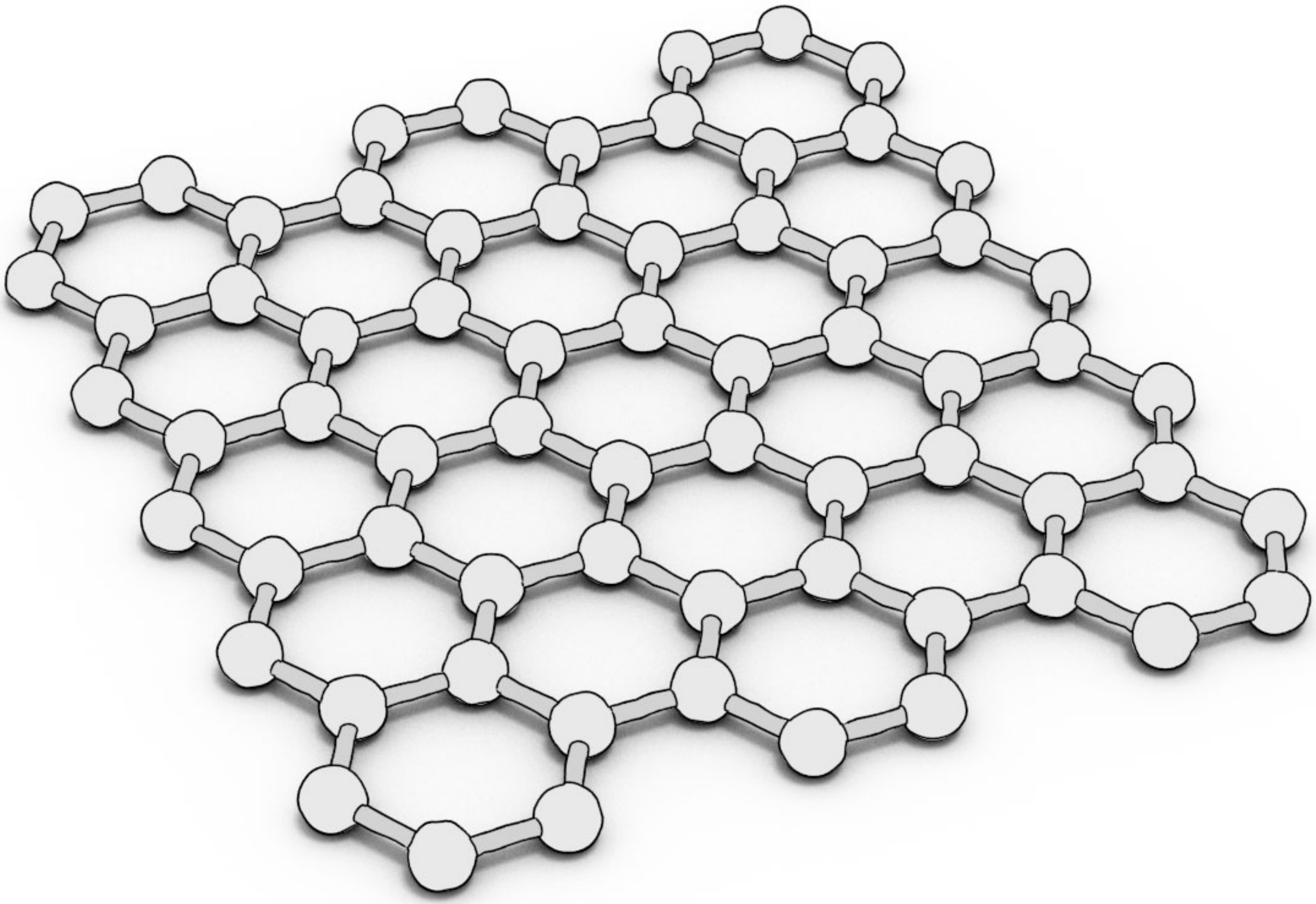
Graphene



Graphene is an allotrope (form) of carbon consisting of a single layer of carbon atoms arranged in an hexagonal lattice.

It can be considered as an indefinitely large aromatic molecule, the ultimate case of the family of flat polycyclic aromatic hydrocarbons.

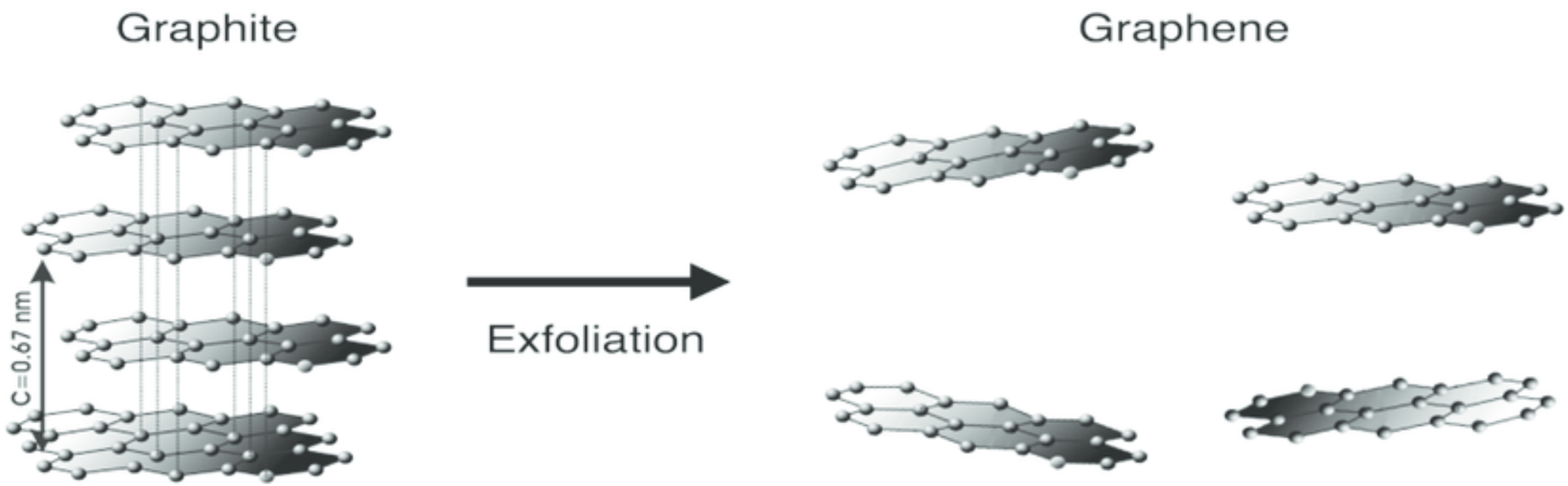
The material was rediscovered, isolated, and characterized in **2004** by **Andre Geim** and **Konstantin Novoselov** at the University of Manchester.

This work resulted in the two winning the **Nobel Prize in Physics in 2010** "for groundbreaking experiments regarding the two-dimensional material graphene".

Andre Geim

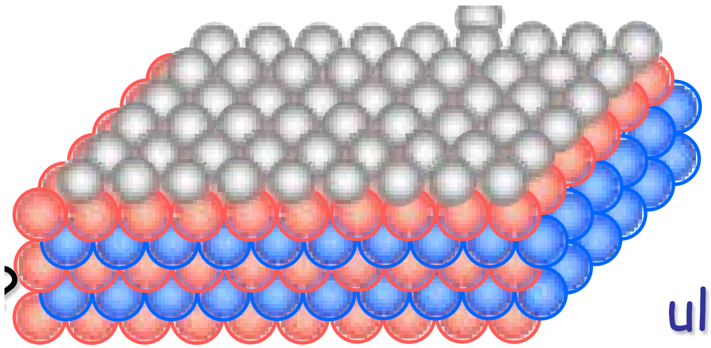
Konstantin Novoselov

exfoliation



highly oriented pyrolytic graphite (HOPG)

Epitaxial growth



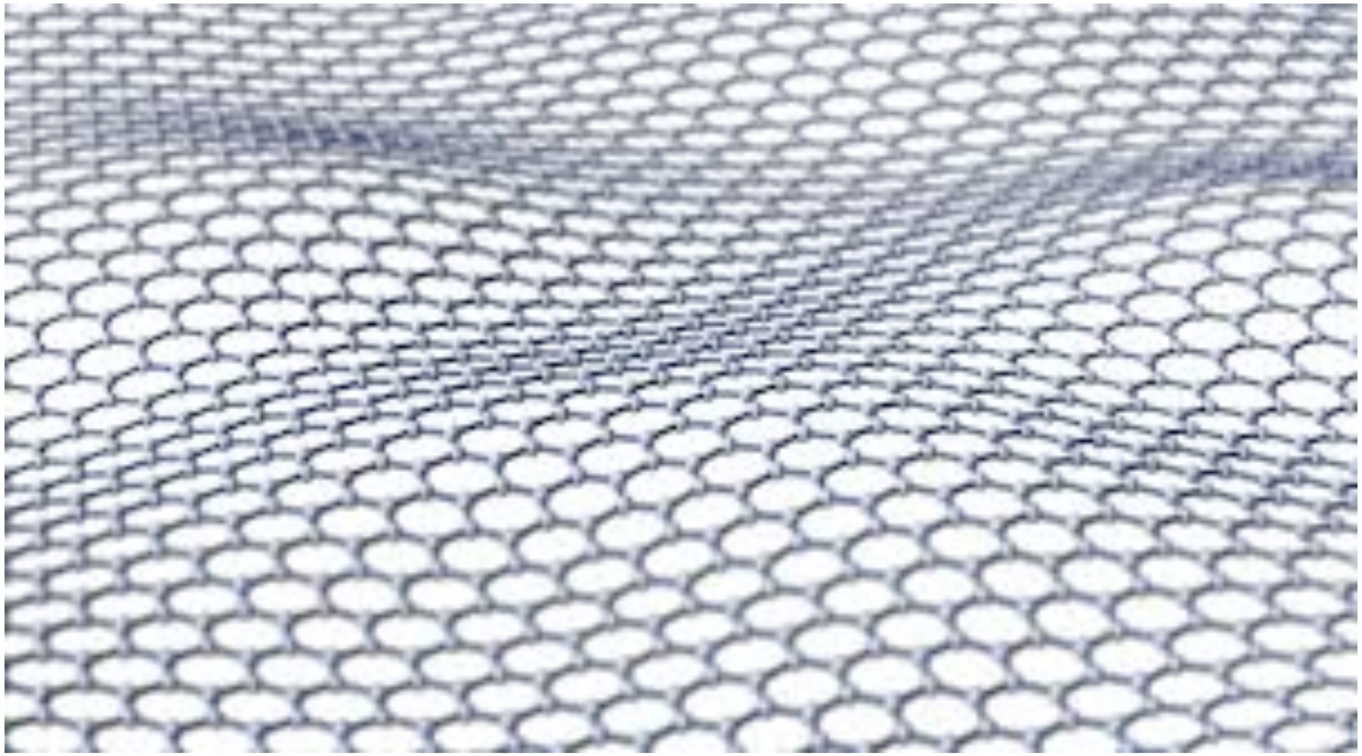
chemically remove the substrate

↓

ultra-thin monocrystal

"Graphene" is a combination of "graphite" and the suffix -ene, named by Hanns-Peter Boehm, who described single-layer carbon foils in 1962.

Graphene can be considered an "infinite alternant" (only six-member carbon ring) polycyclic aromatic hydrocarbon



nanoscale corrugation

Electric Field Effect in Atomically Thin Carbon Films

2 OCTOBER 2004 VOL 306 SCIENCE, p. 666

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.

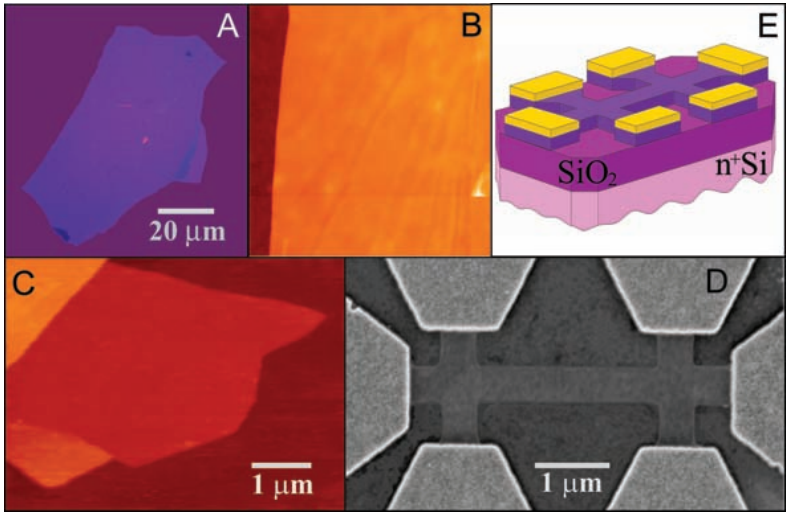


Fig. 1. Graphene films. (**A**) Photograph (in normal white light) of a relatively large multilayer graphene flake with thickness ~3 nm on top of an oxidized Si wafer. (**B**) Atomic force microscope (AFM) image of 2 µm by 2 µm area of this flake near its edge. Colors: dark brown, SiO_2 surface; orange, 3 nm height above the SiO_2 surface. (**C**) AFM image of single-layer graphene. Colors: dark brown, SiO_2 surface; brown-red (central area), 0.8 nm height; yellow-brown (bottom left), 1.2 nm; orange (top left), 2.5 nm. Notice the folded part of the film near the bottom, which exhibits a differential height of ~0.4 nm. For details of AFM imaging of single-layer graphene, see (*15*). (**D**) Scanning electron microscope image of one of our experimental devices prepared from FLG. (**E**) Schematic view of the device in (D).

Field effect

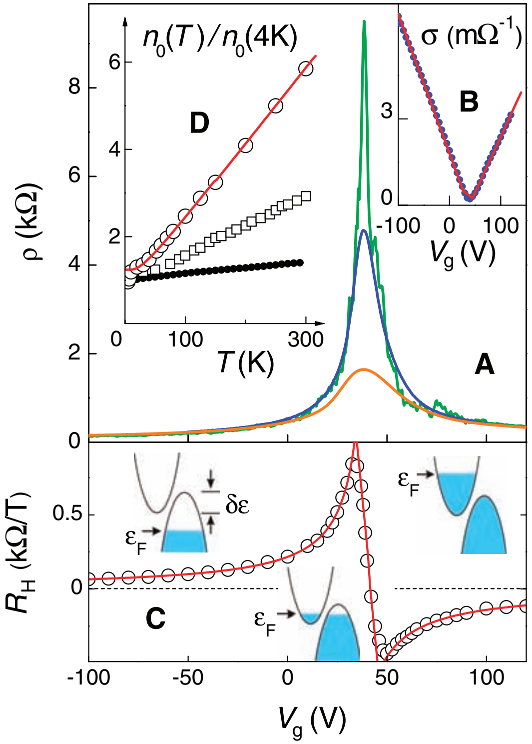
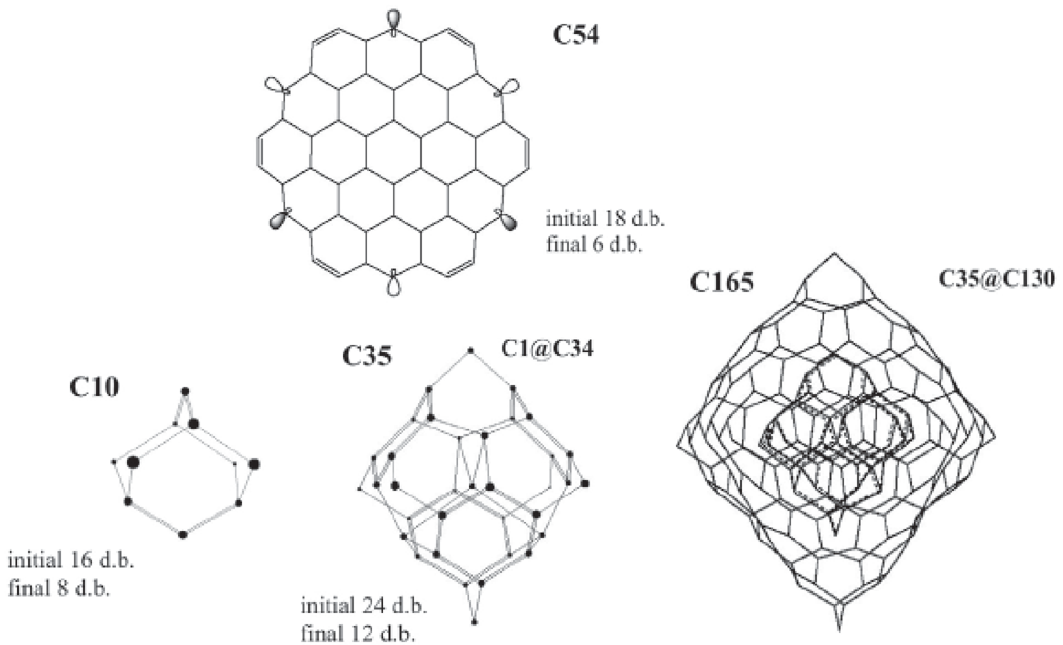


Fig. 2. Field effect in FLG. (**A**) Typical dependences of FLG's resistivity ρ on gate voltage for different temperatures (T = 5, 70, and 300 K for top to bottom curves, respectively). (**B**) Example of changes in the film's conductivity $\sigma = 1/\rho(V_g)$ obtained by inverting the 70 K curve (dots). (**C**) Hall coefficient R_H versus V_g for the same film; T = 5 K. (**D**) Temperature dependence of carrier concentration n_0 in the mixed state for the film in (A) (open circles), a thicker FLG film (squares), and multilayer graphene ($d \approx 5$ nm; solid circles). Red curves in (B) to (D) are the dependences calculated from our model of a 2D semimetal illustrated by insets in (C).

THERMODYNAMIC STABILITY



graphene:
thermodynamically unstable
for <24,000 atoms or size < 20 nm

Shenderova, Zhirnov, Brenner *Crit Rev Mat Sci* 2002

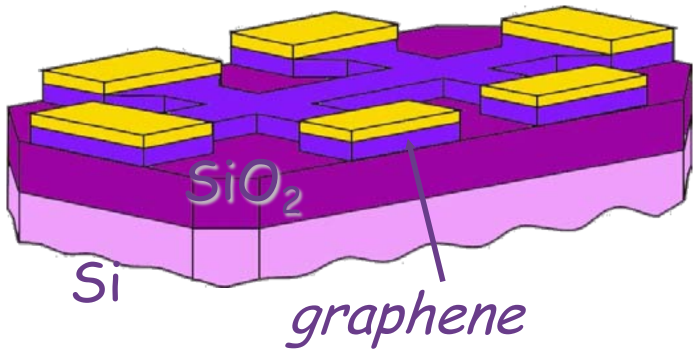
graphene sheets
should scroll

Kaner *Science* 2003
Braga *et al Nanolett* 2004

THERMODYNAMICALLY UNSTABLE
does not mean IMPOSSIBLE
-JUST METASTABLE-

WHY THIS PAPER IMPORTANT

- observation of large isolated graphene crystals
- simple and accessible method for their isolation



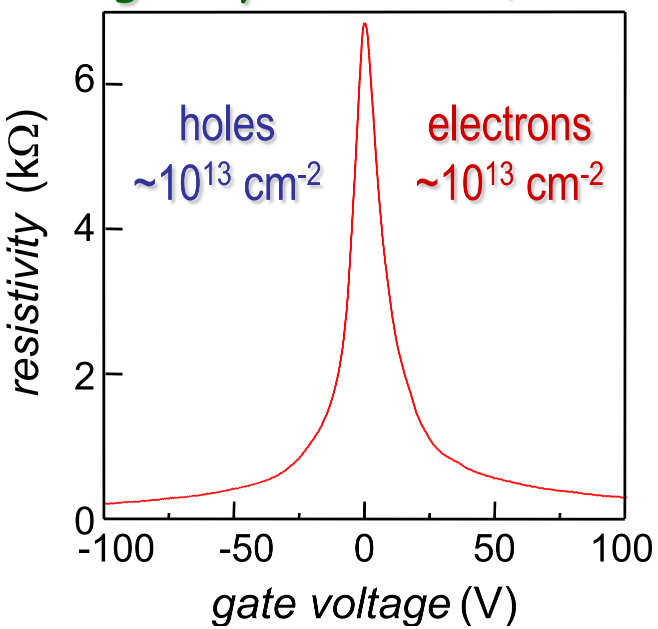
- CONTROL ELECTRONIC PROPERTIES

ambipolar electric field effect

- ASTONISHING ELECTRONIC QUALITY

ballistic transport on submicron scale under ambient conditions

changes by 100 times, not ~1%



NOT JUST AN OBSERVATION OF GRAPHENE:

GRAPHENE REDISCOVERED IN ITS NEW INCARNATION

DISCOVERY OF GRAPHENE

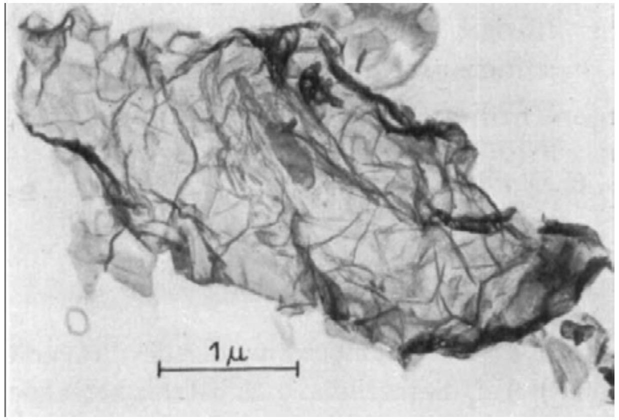
digging through old literature

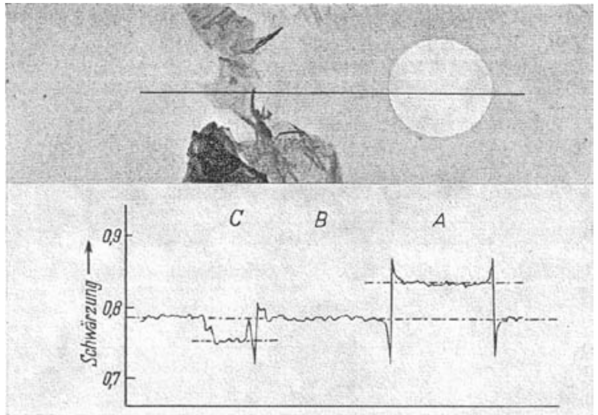
Benjamin Brodie
Phil Trans. 1859

"carbonic acid"

"Graphon 33"

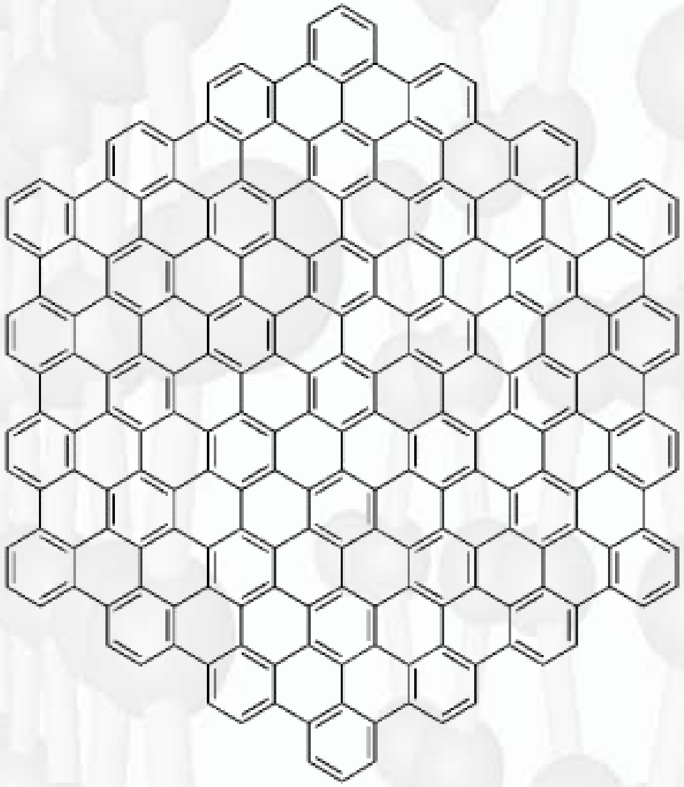
suspension of graphene oxide crystallites





TEM studies of the dry residue
Ruess & Vogt 1948; Boehm & Hofmann 1962

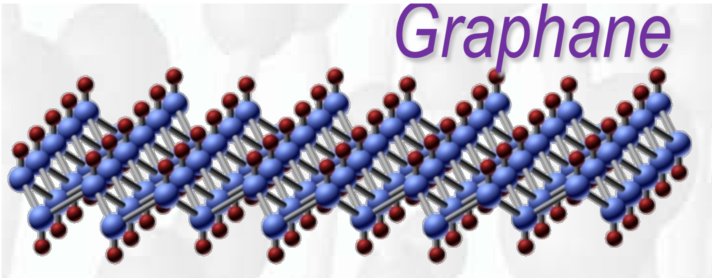
remained the best observation for over 40 years!



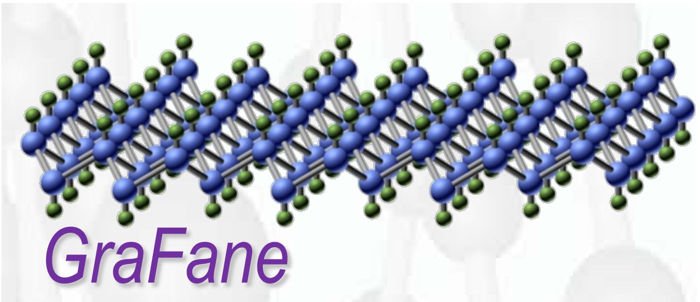
largest known
flat hydrocarbon:
222 atoms or 37 benzene rings

(K. Müllen 2002)

hydrogenation of graphene



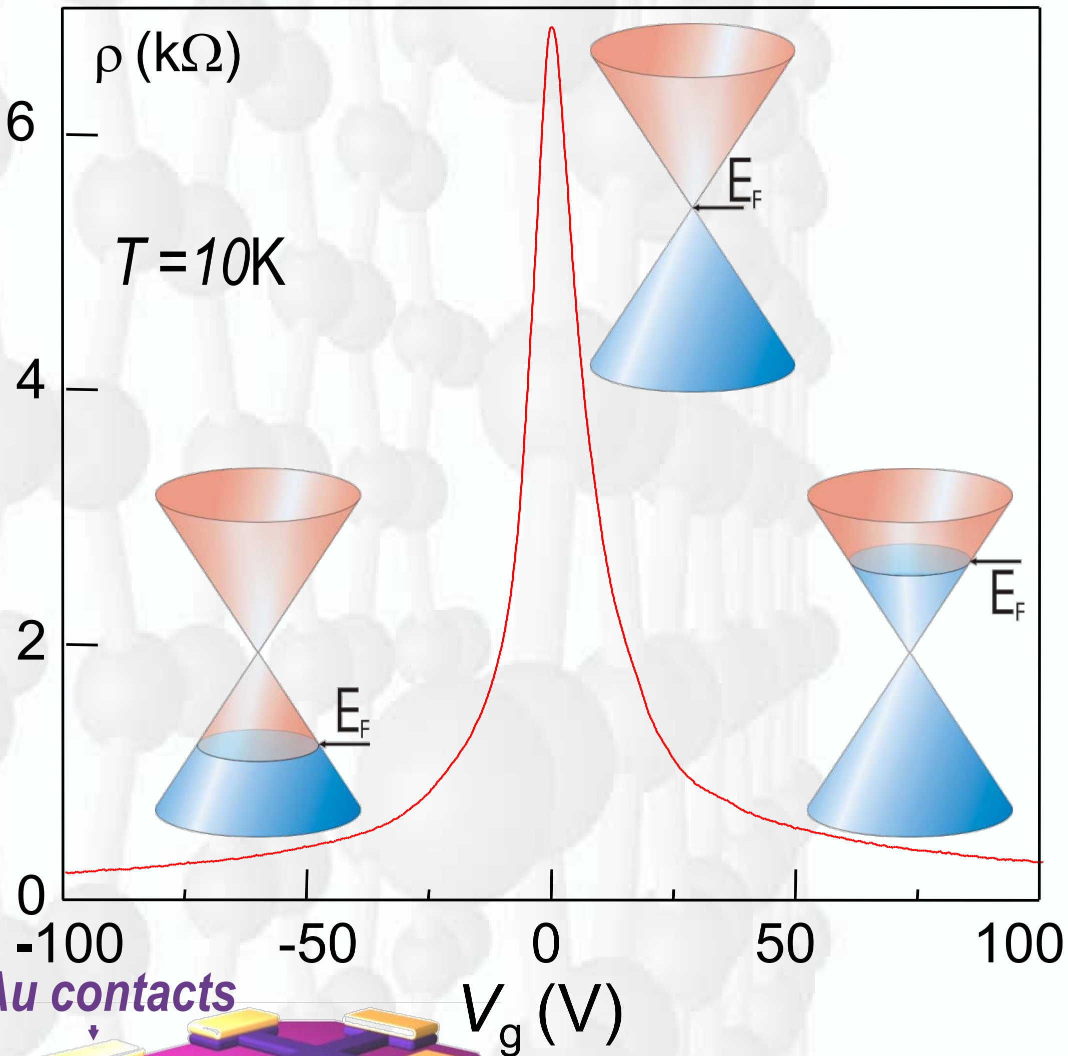
Science 2009

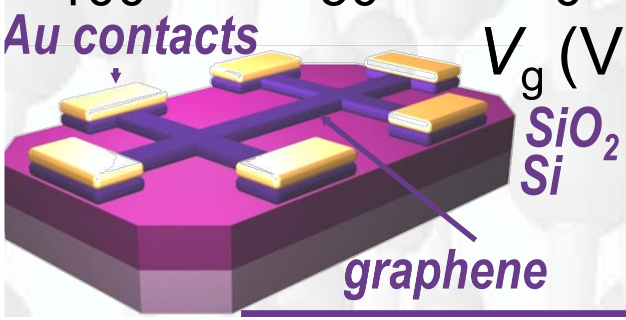


fluorographene

Small 2010

Graphene Field Effect Transistors



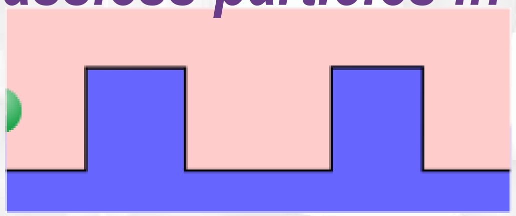


carrier mobility <u>currently</u>:
up to ~50,000 $cm^2/V\cdot s$ at 300K
even when strongly doped

~1,000,000 $cm^2/V\cdot s$ at 4K
(Andrei, Kim & Manchester group)

<u>intrinsic (phonon-limited)</u>:
>200,000 $cm^2/V\cdot s$ at 300K
(higher than in any other material)

Massless particles in 2D:



Klein paradox

NEVER LOCALIZED

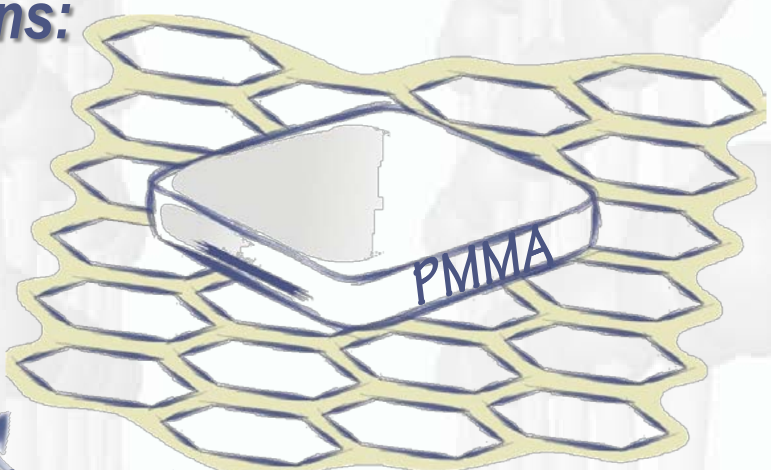
O. Klein, Z. Phys 53,157 (1929); 41, 407 (1927)
M.I.Katsnelson et al Nature Physics (2006)
Young et al Nature Physics (2009)

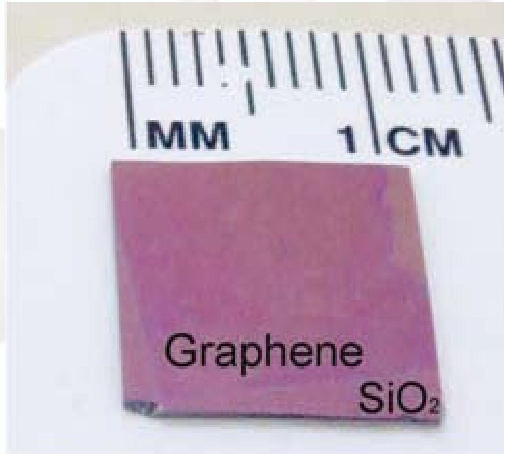
Mass Production of Graphene

CVD growth on Ni, Cu... as part of 3D structure

to quench flexural phonons:

Bommel 1975 (SiC)
McConville 1986 (on Ni)
Land 1992 (on Pt)
Nagashima 1993 (on TiC)
Forbeaux 1998 (SiC)
de Heer 2004 (SiC)
… …





Release graphene by etching Ni

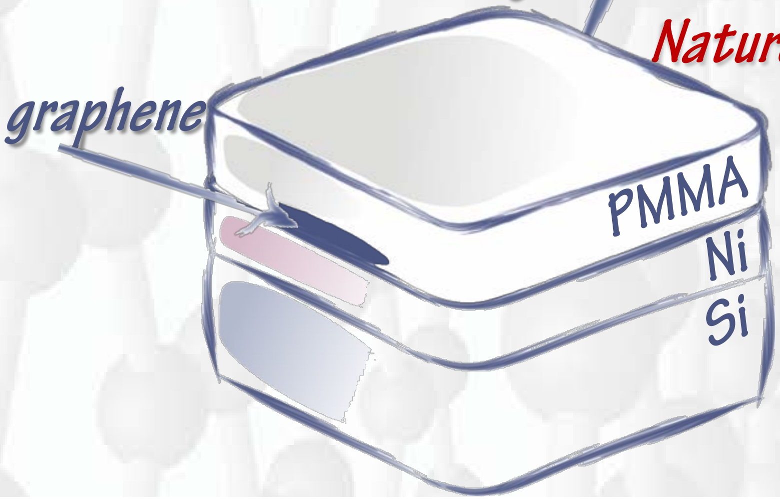
fish by TEM grid

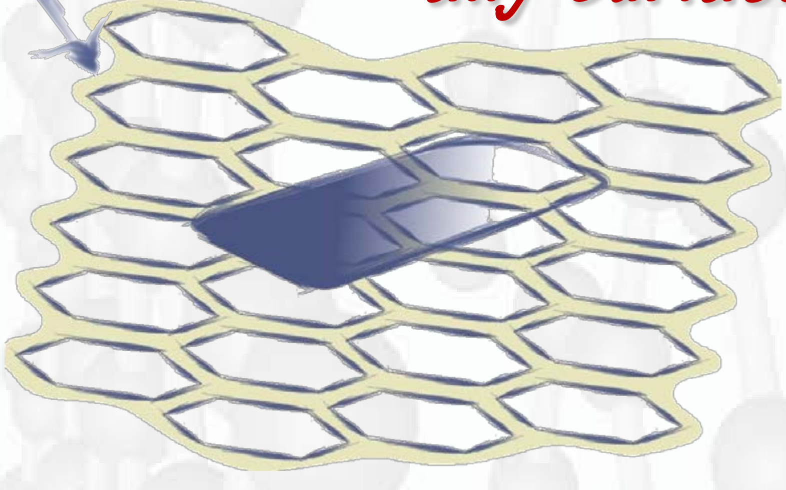
remove PMMA

Direct transfer on any surface

Suggested:
Geim & Novoselov
Nature Mat. (2007)

Realised :
MIT (2008)
Yu(2008)
Hong (2009)
Ruoff (2009)





breaking strength of ~ 40 N/m

Record values for room temperature **thermal conductivity** (~5000 W m–1 K–1)
and **Young's modulus** (~1.0 TPa)

Graphene can be stretched elastically as much as 20%, more than any other crystal

Chemistry of graphene

The associated strain and curvature can markedly influence local reactivity.

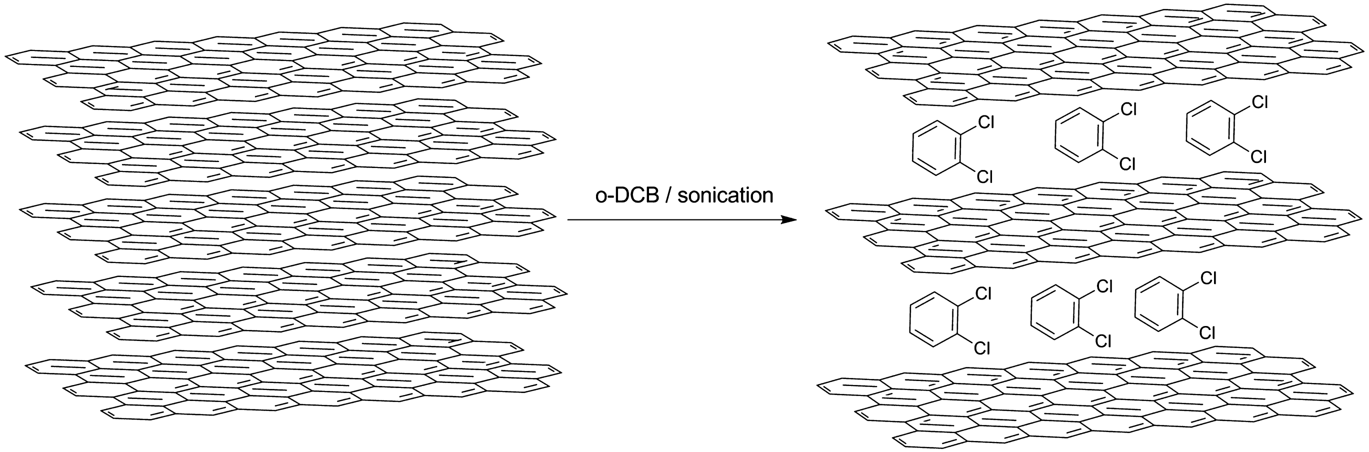
reagents can attach to both graphene faces

Covalent Functionalization Strategies for Graphene

many of the strategies already used for fullerenes or CNT may be applied to covalently decorate graphene

Exfoliation strategies

use of solvent to disrupt Wan der Waals interactions

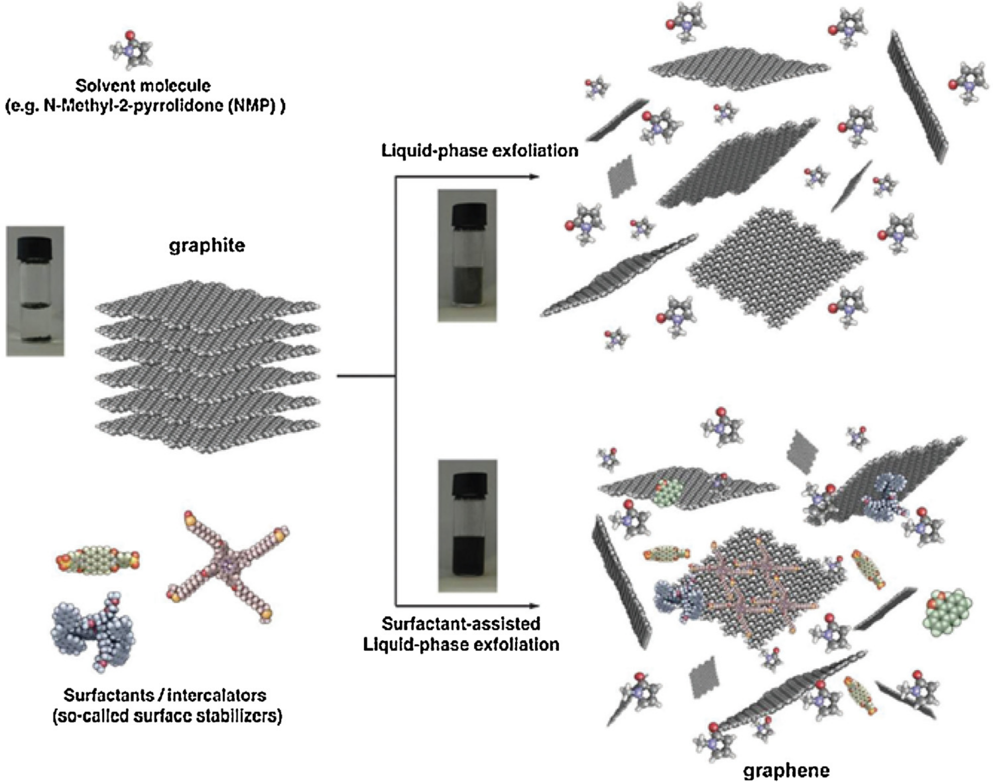


use of surfactants

electrochemical esfoliation

Supercritical fluid exfoliation

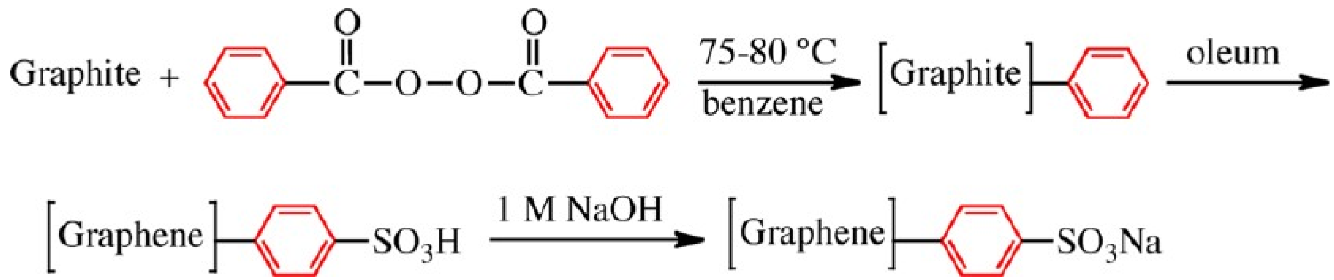
Esfoliation of graphene



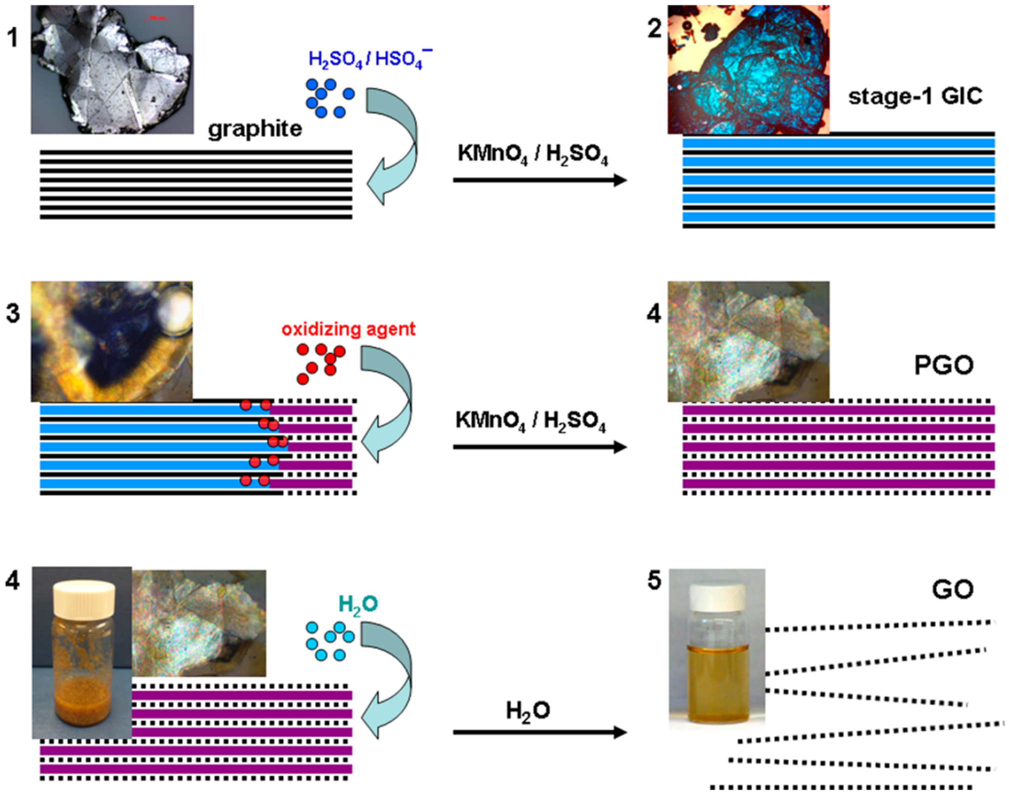
Schematic representation of the liquid-phase exfoliation (LPE) process of graphite in the absence (top-right) and presence (bottom-right) of surfactant molecules.

N-methylpyrrolidone (NMP, 40 mN/m), N,N'-dimethylformamide (DMF, 37.1 mN/m), γ-butyrolactone (GBL, 35.4 mN/m), and ortho- dichlorobenzene (o-DCB, 37 mN/m), are the best media for the exfoliation of graphite

SCHEME 5. Synthesis of Water-Soluble Graphene

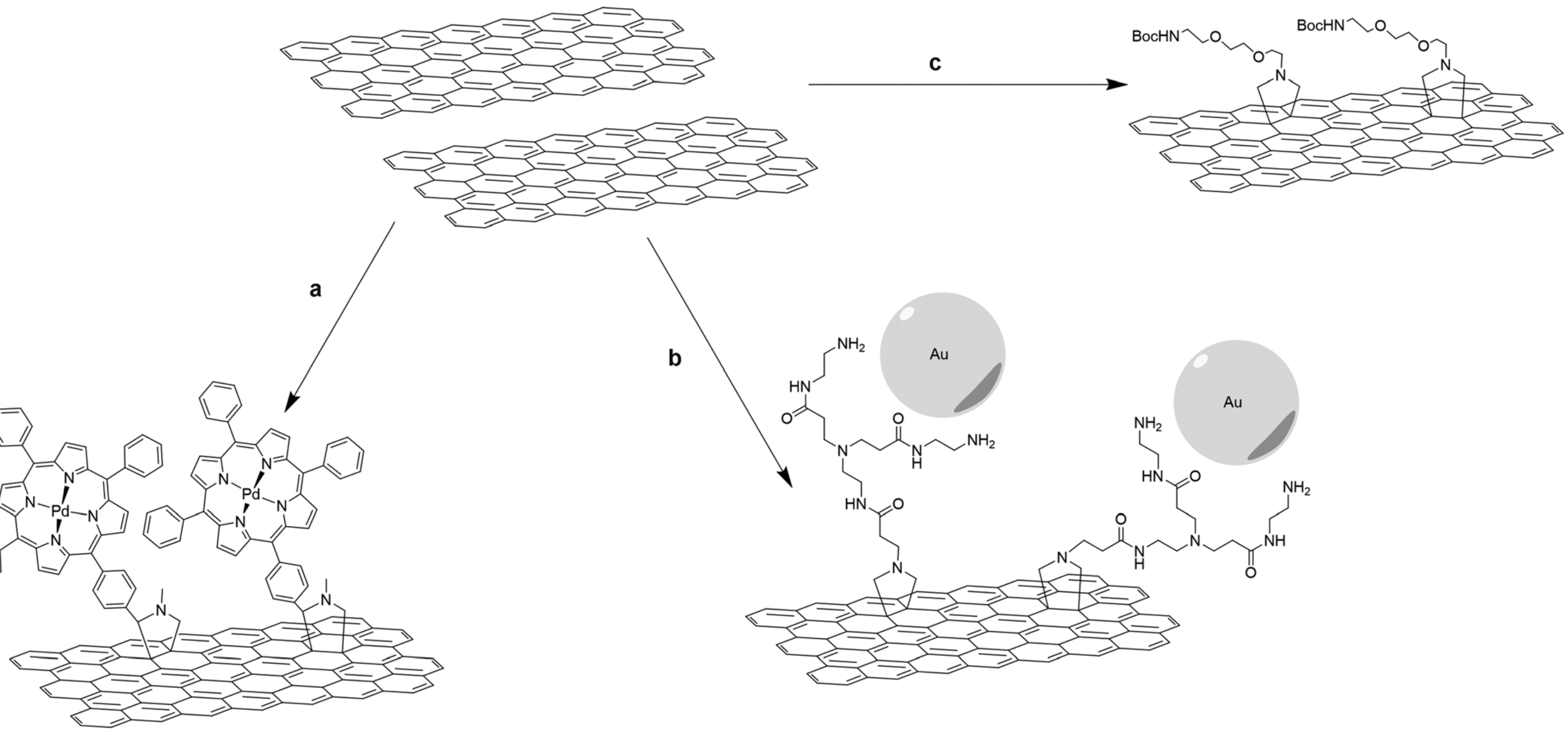


Mechanism of Graphene Oxide Formation

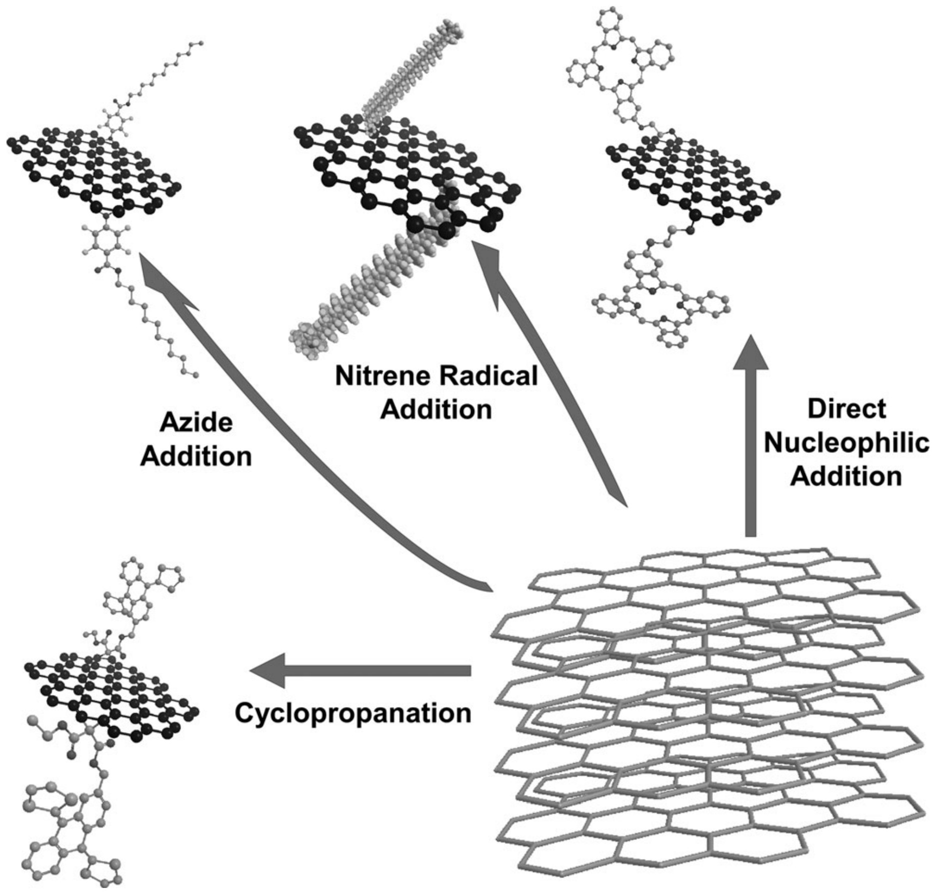


Schematics of conversion of bulkgraphite into GO with corresponding micrographic images or sample appearances at each phase. The three steps signify formation of the two intermediate products (stage-1 GIC and PGO) and the final GO product. The solid black lines represent graphene layers; dotted black lines represent single layers of GO; wide blue lines represent H_2SO_4/HSO_4 intercalant; wide purple lines represent a layer of the mixture of H_2SO_4/HSO_4 intercalant with the reduced form of oxidizing agent.

Prato's reaction

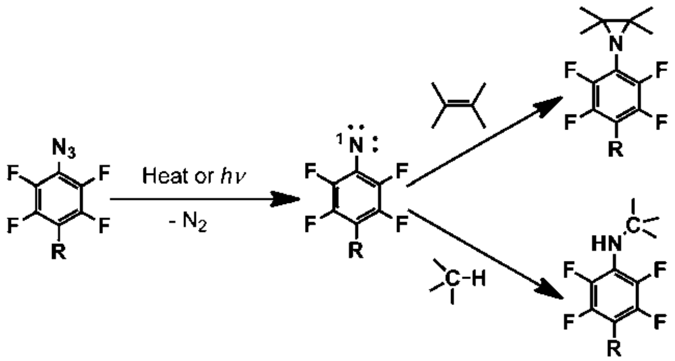


Schematic representation of various 1,3-dipolar cycloaddition reactions of azomethine ylides for the functionalization of graphene sheets. a) i) Exfoliation using o-DCB, ii) sarcosine, porphyrin-CHO, 160 °C, 7 days ;
b) i) Exfoliation using DMF, ii) $BocNHCH_2CH_2NHCH_2COOH$, HCHO, 130 °C, 3 days, iii) TFA, 12 h, iv) PAMAM dendrons, EDC, DMAP, HOBt, 12 h;
c) i) Exfoliation using NMP, ii) $BocNH(CH_2CH_2O)_2CH_2CH_2NHCH_2COOH$, HCHO, 125 °C, 5 days.

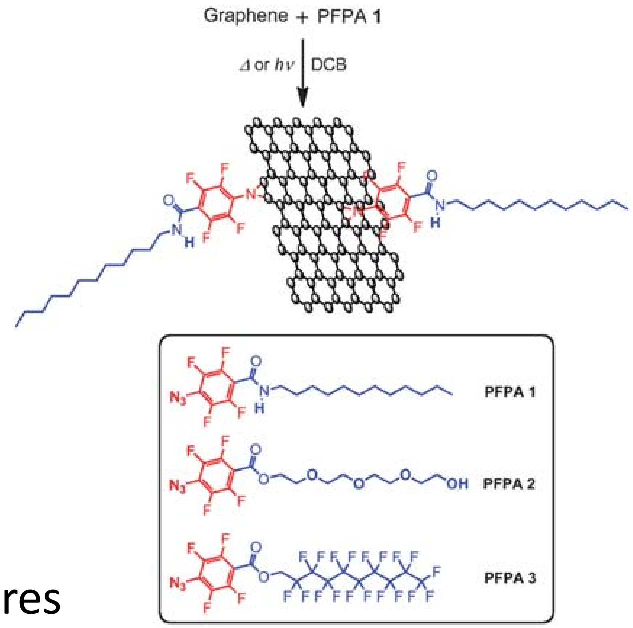


Azide
Addition
Nitrene Radical
Addition
Direct
Nucleophilic
Addition
Cyclopropanation

Nitrene radical addition

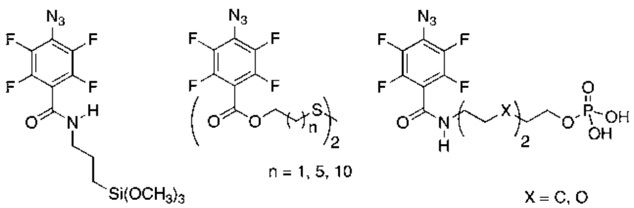


Insertion and addition reactions of singlet perfluorophenylnitrene generated from photolysis or thermolysis of PFPA



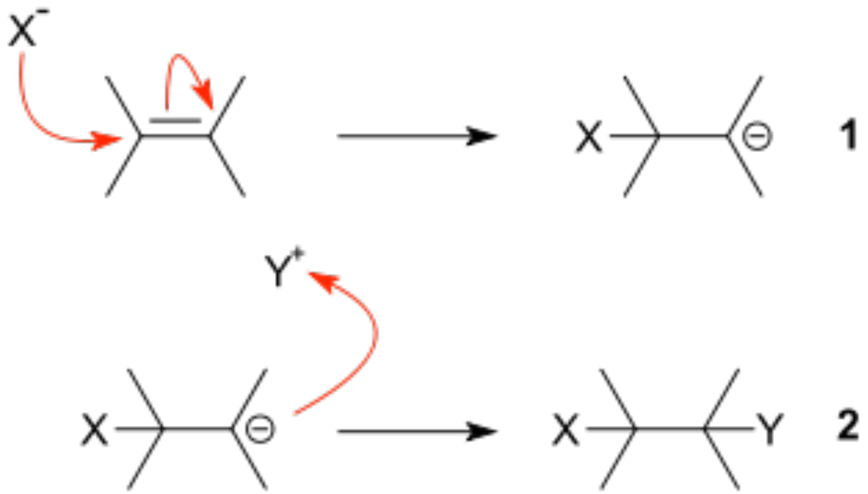
Solution-phase functionalization of pristine graphene with PFPAs.

Immobilization of graphene films and patterned structures



PFPAs derivatized with silane, disul- fide and phosphate

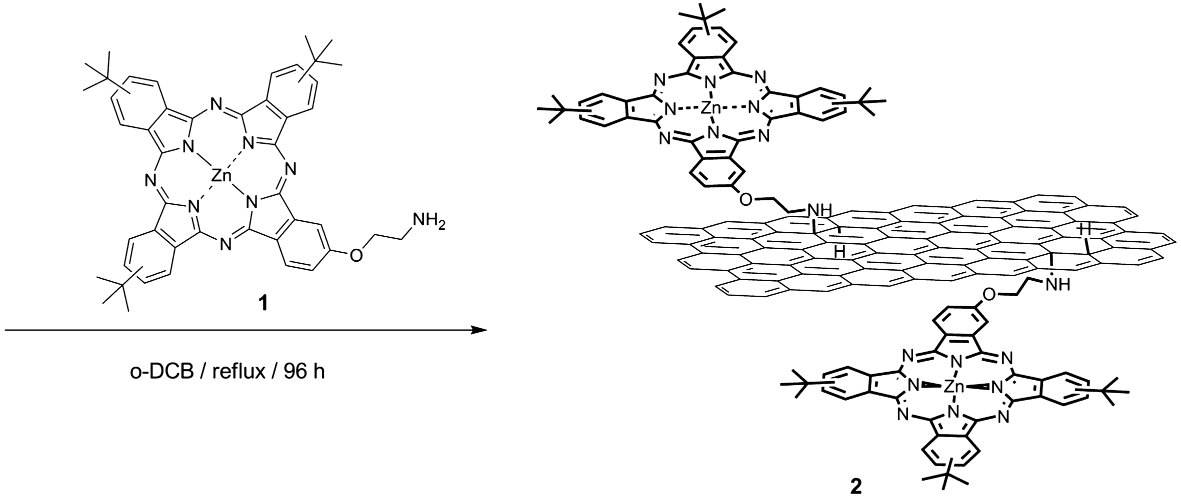
Nucleophilic addition to an alkene.

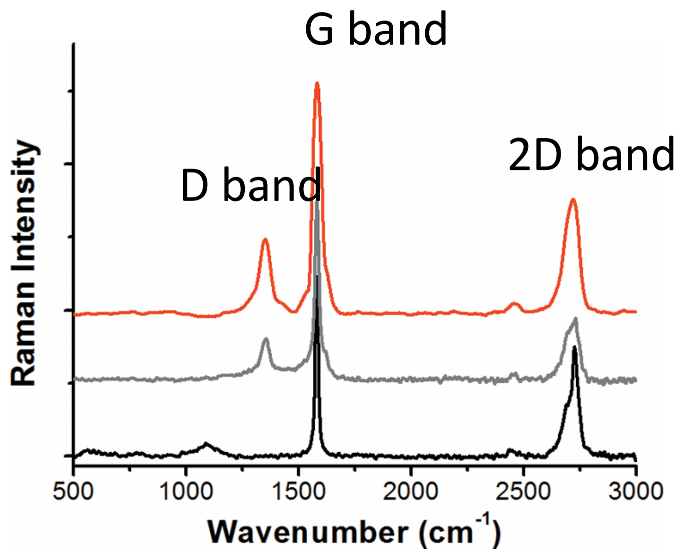


The driving force for the addition to alkenes is the formation of a nucleophile X− that forms a covalent bond with an electron-poor unsaturated system -C=C- (step 1). The negative charge on X is transferred to the carbon – carbon bond.

Ordinary alkenes are not susceptible to a nucleophilic attack.
Perfluorinated alkenes (alkenes that have all hydrogens replaced by fluorine) are highly prone to nucleophilic addition,

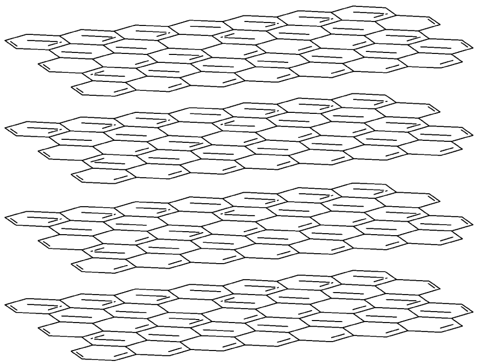
nucleophilic addition of primary amines to carbon nanostructured materials

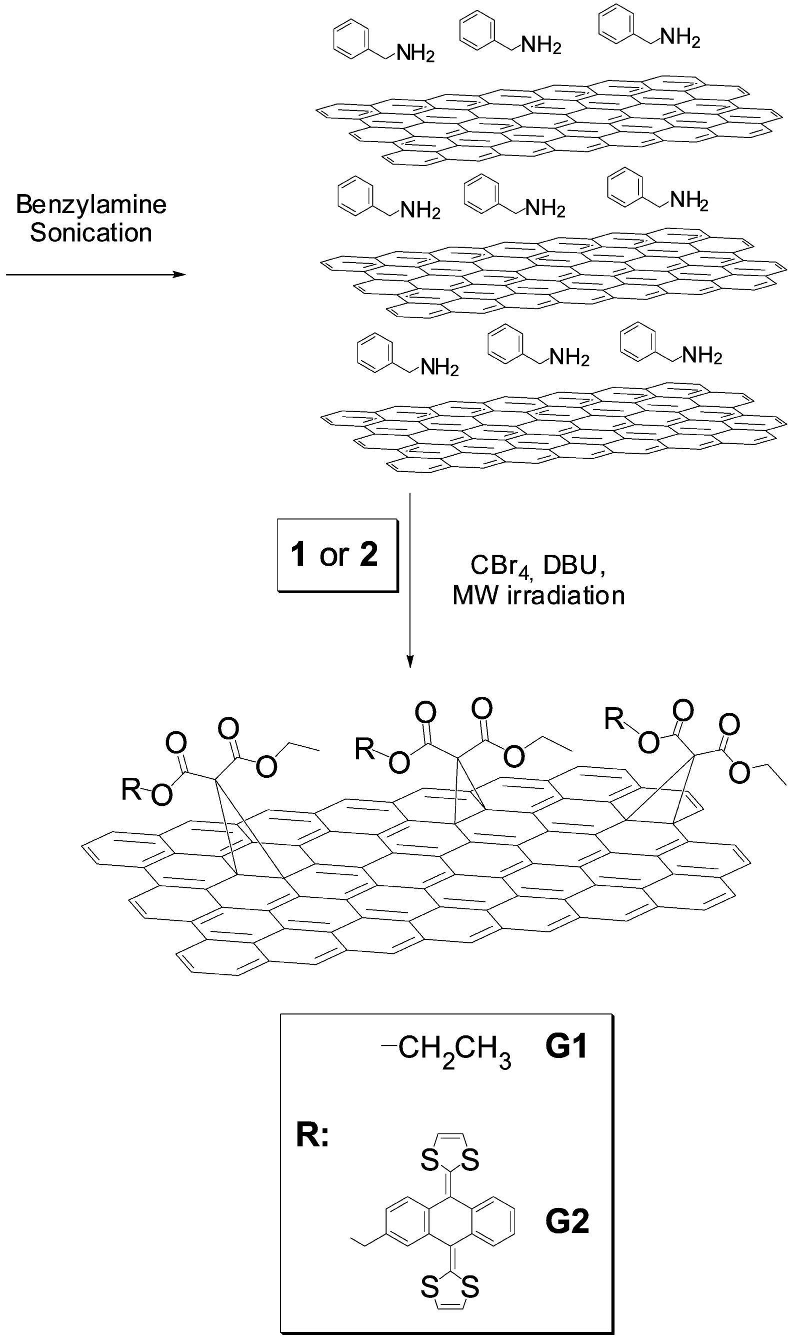




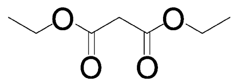
Raman spectra of pristine graphite (black), exfoliated graphene (gray), and ZnPc−graphene hybrid material 2 (red), obtained at λexc = 514 nm.

Bingle Cyclopropanation

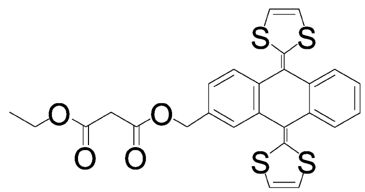




formation *in situ* of alfa-bromo derivative of malonic ester

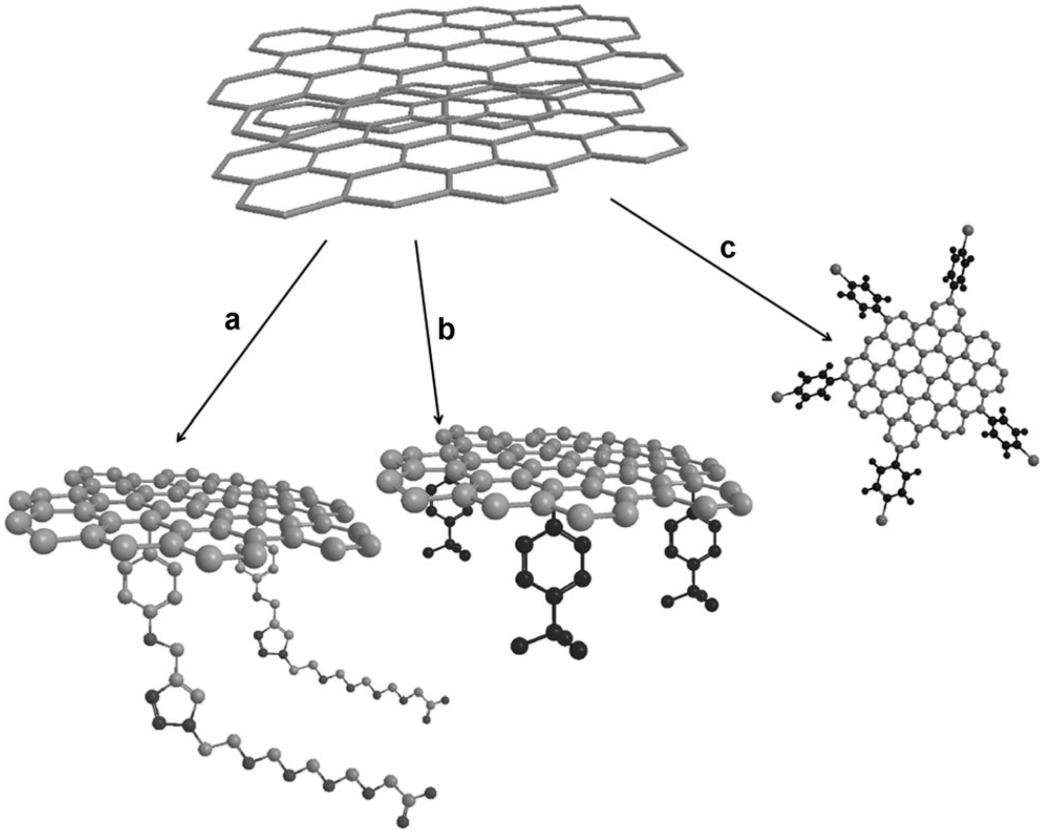


1



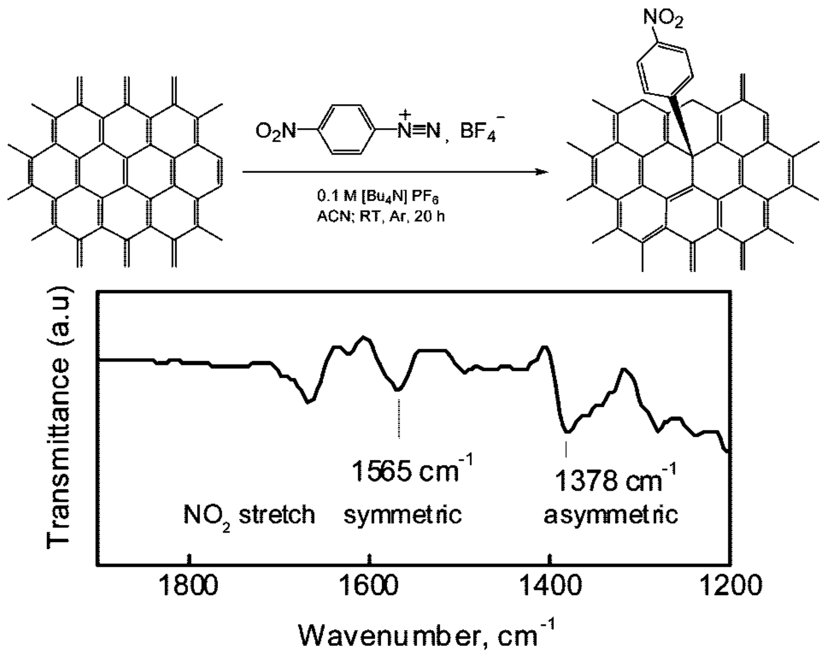
2

Aryl diazonium salt reaction

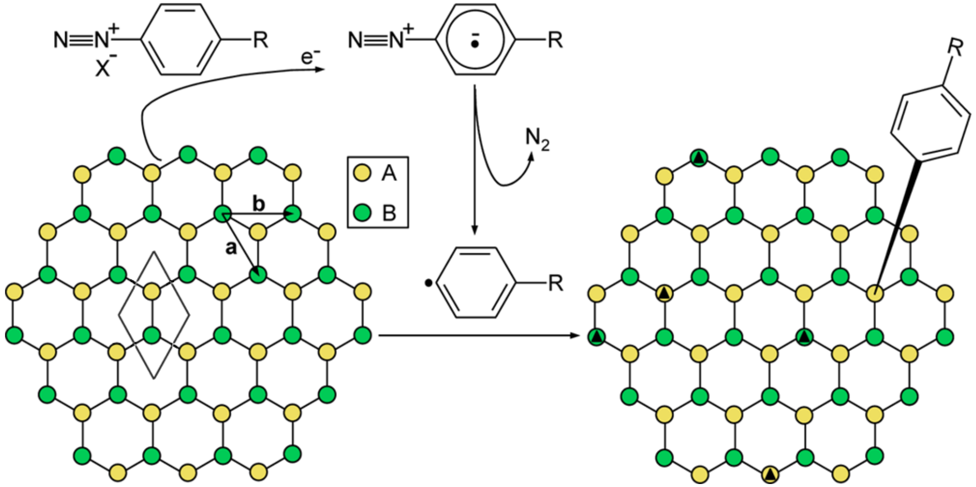


Diazonium salt functionalization processes on graphene. a) i) Exfoliation using SDS, azide, 8 h, ii) Azide-(dPEG)$_4$-acid, sodium ascorbate, $CuSO_4$, THPTA, 18 h;
b) i) Exfoliation using NaK, 3 days, ii) 4-tert-butylphenyldiazonium tetrafluoroborate;
c) i) Dispersion of expanded graphene using $HClSO_3$, ii) $NaNO_2$, cat. AIBN, bromoaniline, iii) sonication in DMF.

Chemical Modification of Epitaxial Graphene: Spontaneous Grafting of Aryl Groups

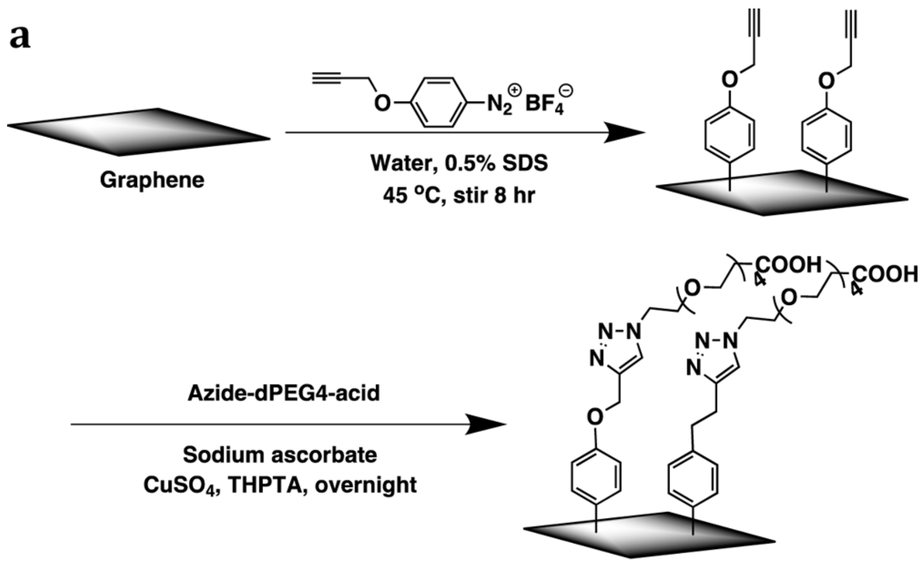


The reaction (below) is due to spontaneous electron transfer from the graphene layer and its substrate to the diazonium salt.



Schematic illustration of grafting a diazonium salt with functional group R and counterion X to a graphene sheet. Two carbon atoms (in the A and B sublattices) make up the unit cell (gray diamond) of the graphene sheet (with lattice vectors a and b). Thermodynamically favored lattice positions for further functionalization are marked with black triangles.

a



Graphene
$N_2^{\oplus}$ $BF_4^{\ominus}$
Water, 0.5% SDS
45 °C, stir 8 hr
Azide-dPEG4-acid
Sodium ascorbate
$CuSO_4$, THPTA, overnight
COOH

Characterization of functional graphene

AFM
TEM
TGA
Raman spectroscopy

Non covalent functionalization of graphene

all the strategies seen for CNT

Graphene: applications

Reinforced plastics

Opto and electronic applications

Sensing application at atomic level, Field effect transistors

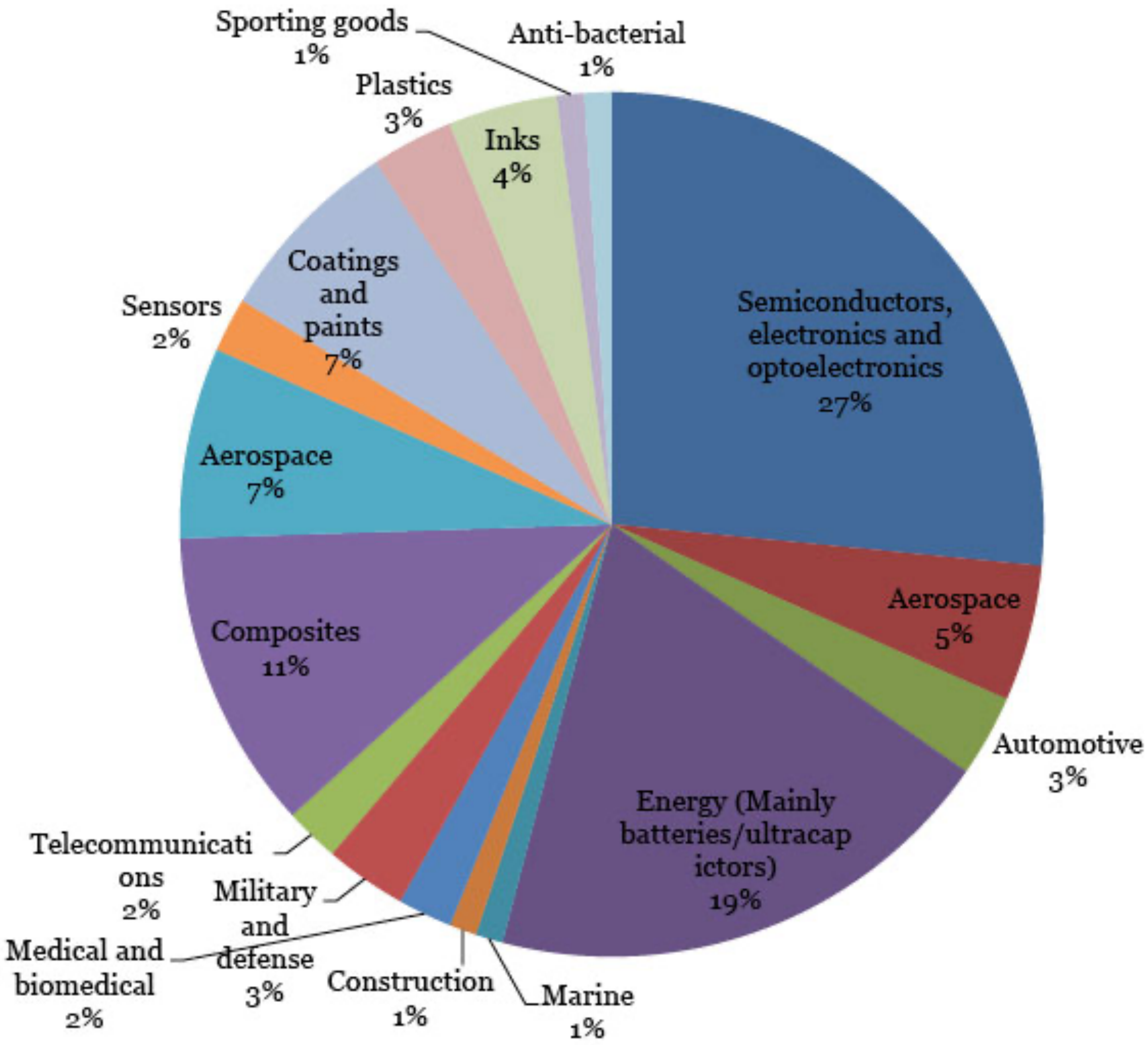
Biomedical applications

Graphene: applications

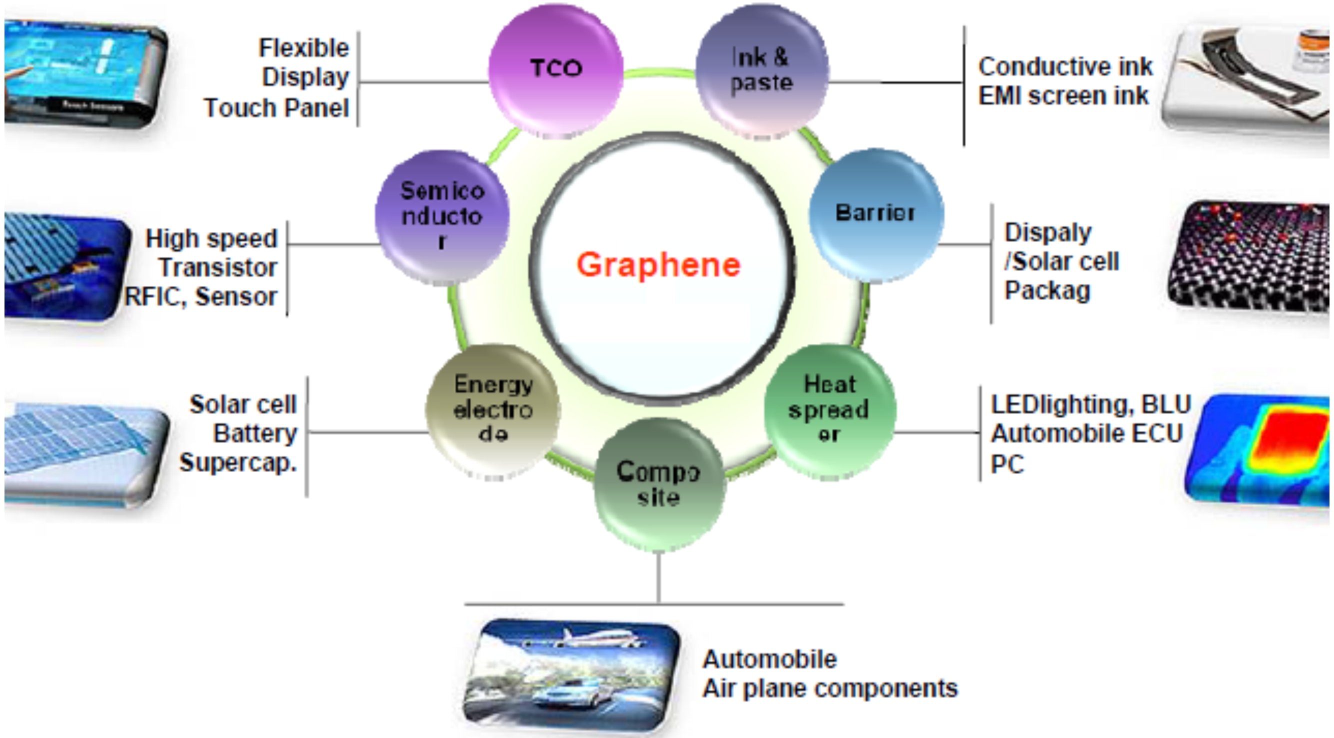
The exceptional electron and thermal transport, mechanical properties, barrier properties and high specific surface area of graphene and combinations thereof make it a potentially disruptive technology across a raft of industries. In 2010, there were over 400 patents issued on graphene and 3,000 research papers published.

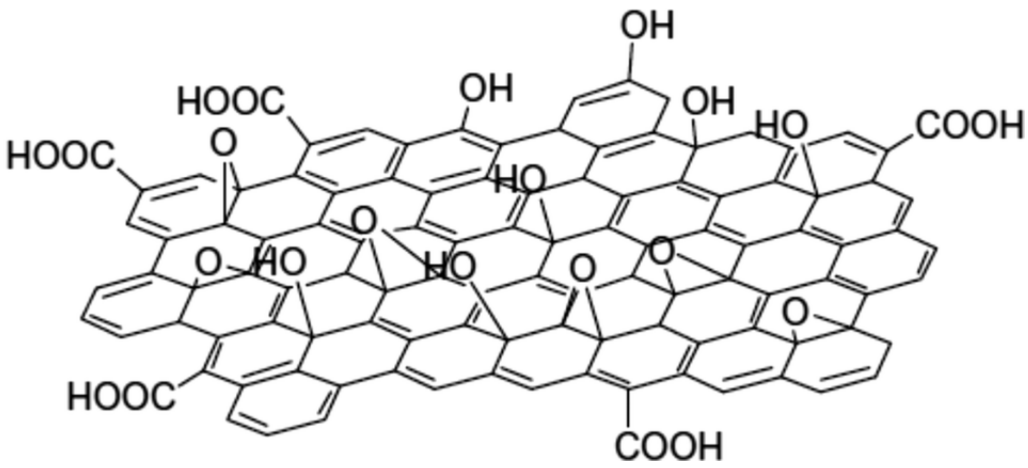
The European Union is funding a 10 year 1,000 million euro coordination action on graphene.
Graphene Flagship
South Korea is set to spend $350 million on commercialization initiatives and the United Kingdom has announced investment of £50million in a new commercialization hub.
The following information refers to end user markets graphene companies are targeting their products to, by percentage. This information was accrued from a comprehensive survey of graphene companies.

2010



Sporting goods 1%
Anti-bacterial 1%
Plastics 3%
Inks 4%
Coatings and paints 7%
Sensors 2%
Semiconductors, electronics and optoelectronics 27%
Aerospace 7%
Aerospace 5%
Composites 11%
Automotive 3%
Energy (Mainly batteries/ultracap ictors) 19%
Telecommunicati ons 2%
Military and defense 3%
Medical and biomedical 2%
Construction 1%
Marine 1%


Graphene
TCO
Ink & paste
Barrier
Heat spread er
Compo site
Energy electro de
Semico nducto r
Flexible Display Touch Panel
Conductive ink EMI screen ink
High speed Transistor RFIC, Sensor
Dispaly /Solar cell Packag
Solar cell Battery Supercap.
LEDlighting, BLU Automobile ECU PC
Automobile Air plane components



OH
HOOC
OH
OH
HO
COOH
HOOC
O
HO
O
O
HO
HO
O
O
O
HOOC
COOH

In the area of biomedical applications, graphene is especially involved in drug delivery, biosensing and tissue engineering, with strong contributions to the whole nanomedicine area.

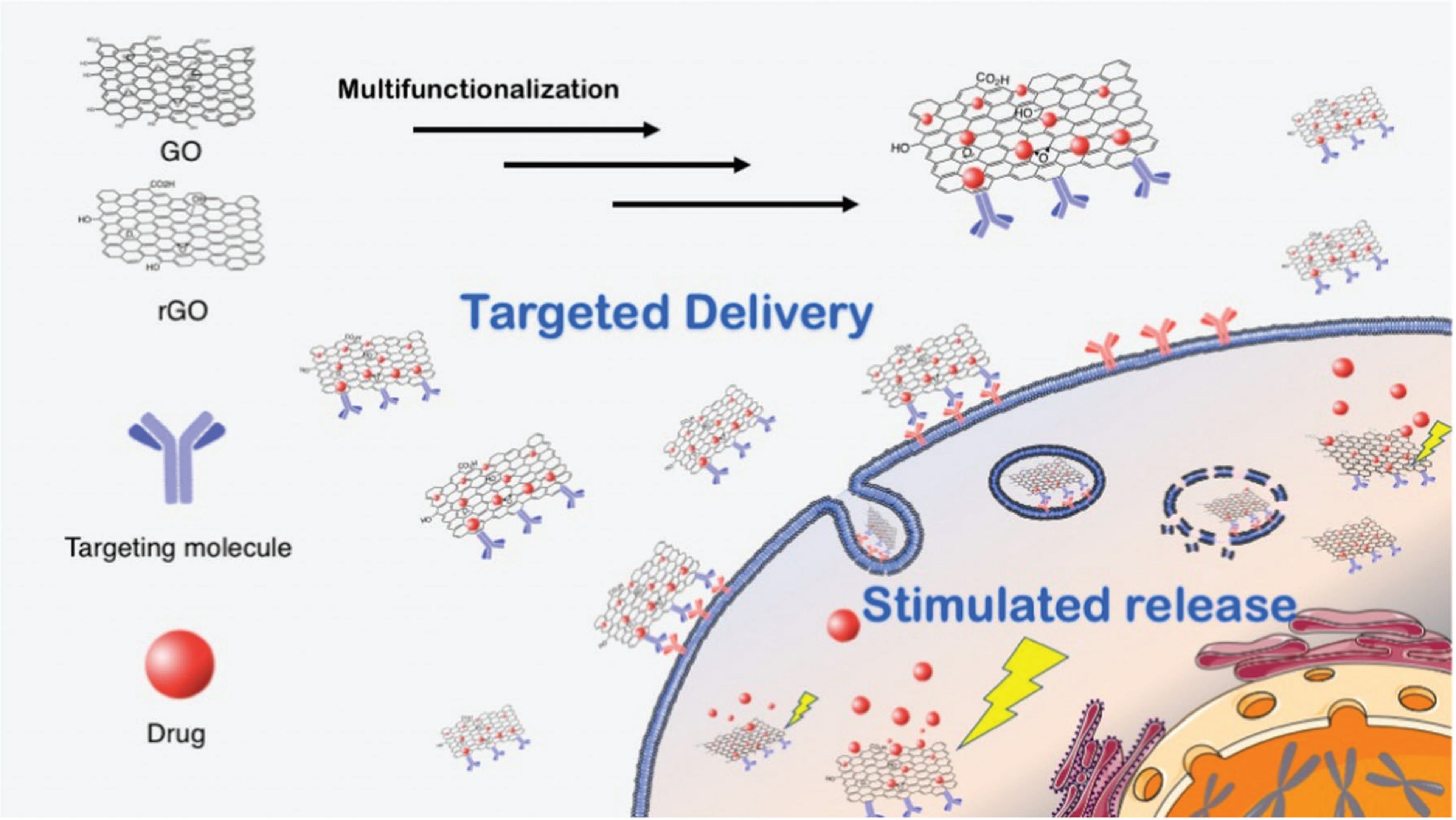
mechanical properties
Biocompatibility
Transparency
Electrical conductivity

graphene is the ideal component for **flexible** biomedical electronic devices or implants, acting as a structural reinforcement or as an integral element.

In addition, graphene possesses **broadband absorption** and **high transparency** in the visible range (2.3% absorption for single-layer graphene), which grants a unique role in medicine enabling optoelectronic stimulation.

The **electronic properties** of graphene are very important for medical purposes (e.g. 2×10^4 cm^2 V^{-1} s^{-1} carrier mobility and 10^{13} cm^2 carrier density for mechanically Exfoliated graphene), in particular to act as conducting component, electrode or support in bioelectronic devices, exceedingly outperforming current silicon and noble metal analogues.

Graphene materials as platforms for drug delivery



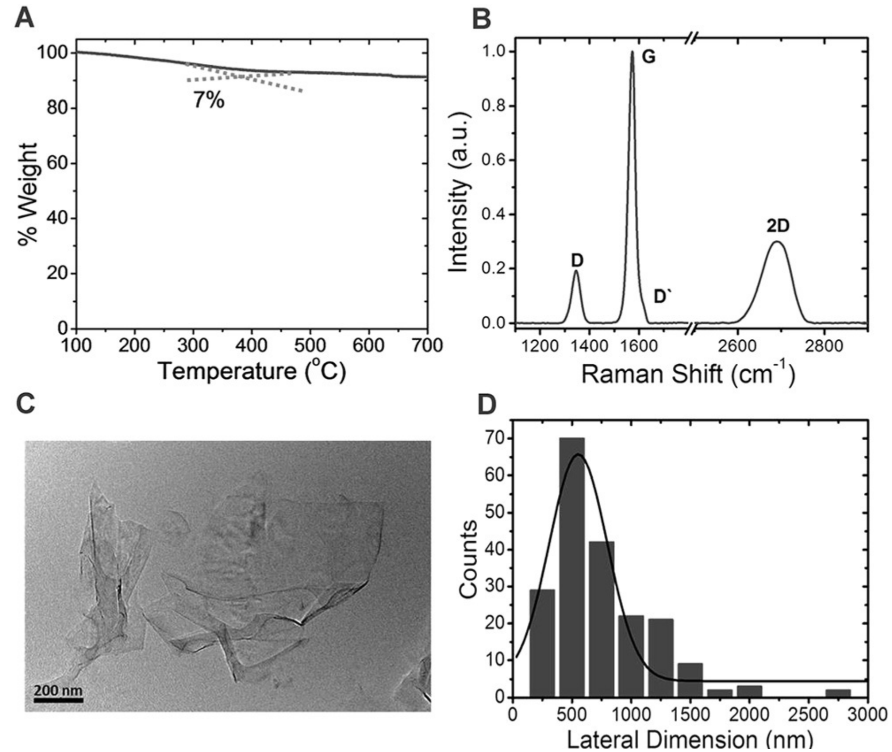
Chem. Soc. Rev., 2017, 46, 4400--4416

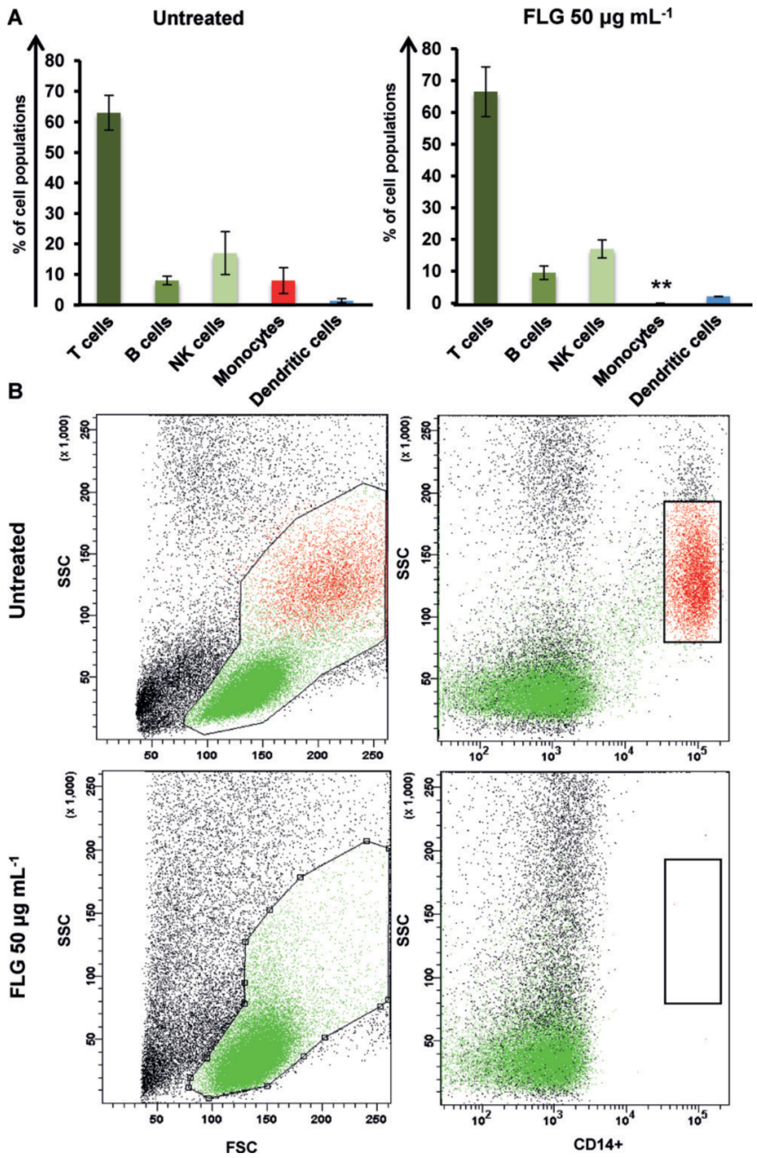
rGO = reduced graphene oxide

Few-Layer Graphene Kills Selectively Tumor Cells from Myelomonocytic Leukemia Patients

Angew. Chem. Int. Ed. 2017, 56, 3014 –3019

FLG dispersions have a specific
killing action on monocytes, displaying neither toxic nor activation
effects on the other immunocompetent cells.
This therapeutic
activity of graphene was applied against an aggressive form of cancer, namely the
myelomonocytic leukemia, where the monocytes are in a malignant form.
In this work it was demonstrated that FLG has the unique ability to cause specifically the
necrosis of monocytic cancer cells.

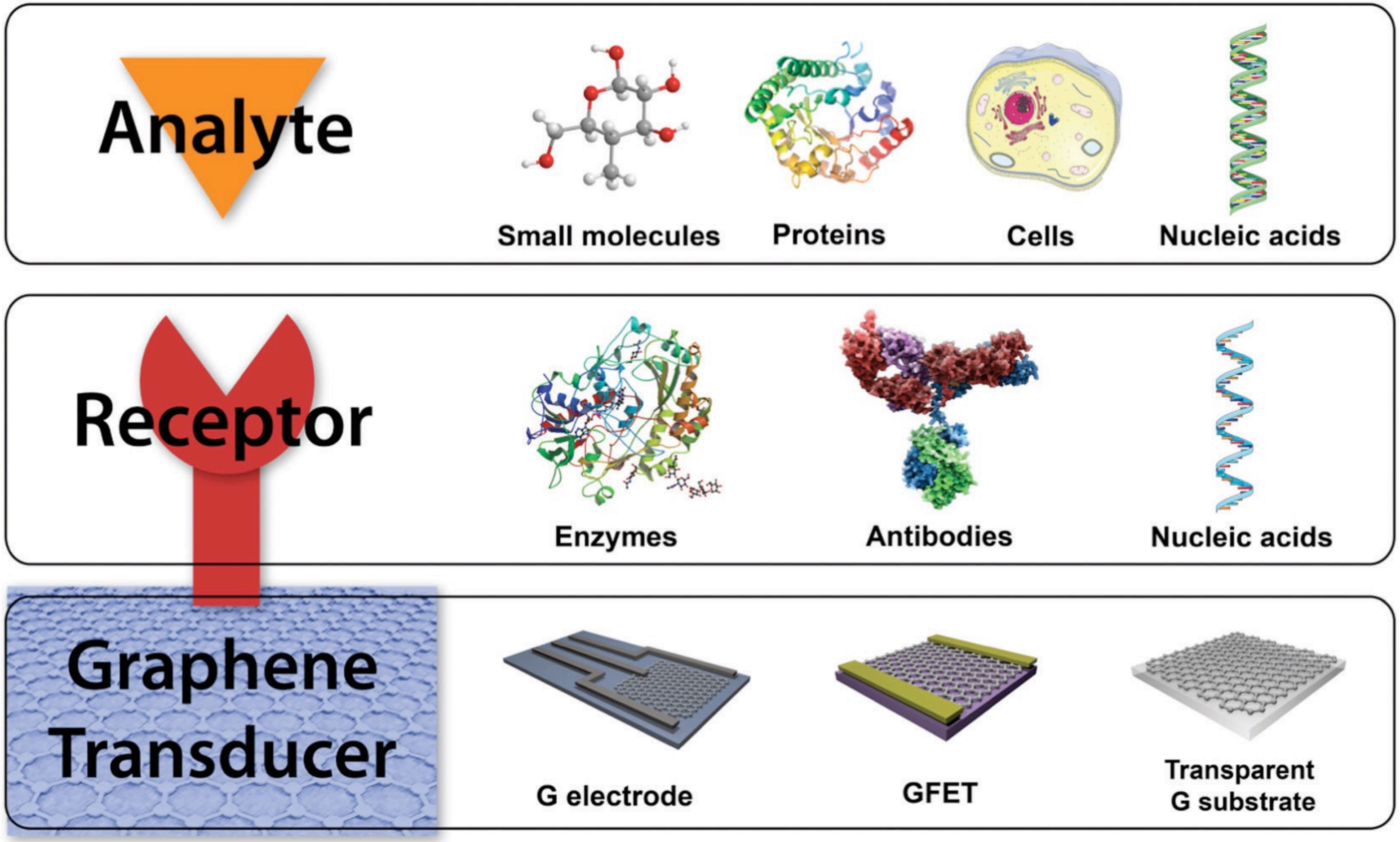




Impact of FLG on different immune cell populations. A) Relative percentage of the different immune cells either incubated for 24 h with 50 mgmL@1 FLG or left untreated. Statistical significance compared to untreated cells (Student’s T-test) is indicated by **=p<0.01. B) Relative morphological dot plots out of at least three experiments of total peripheral blood mononuclear cell (PBMCs) treated with FLG or left untreated. The gate on monocytes was done looking at the CD14 positive events (red dots). The other immune populations are left in green.

the comparison between FLG and a common chemotherapeutic drug confirmed the specificity and higher toxicity of FLG on cancer cells, evidencing the absence of toxicity on other immune cell populations.

Graphene-based bioanalytical devices



The sensing mechanism is produced by the change of the electronic properties of GFET induced by the interactions with the target element

Ex situ bioanalytical sensing
In situ sensing implants