Core levels and NEXAFS spectroscopy of multilayer vein graphite oxide (GO) membrane

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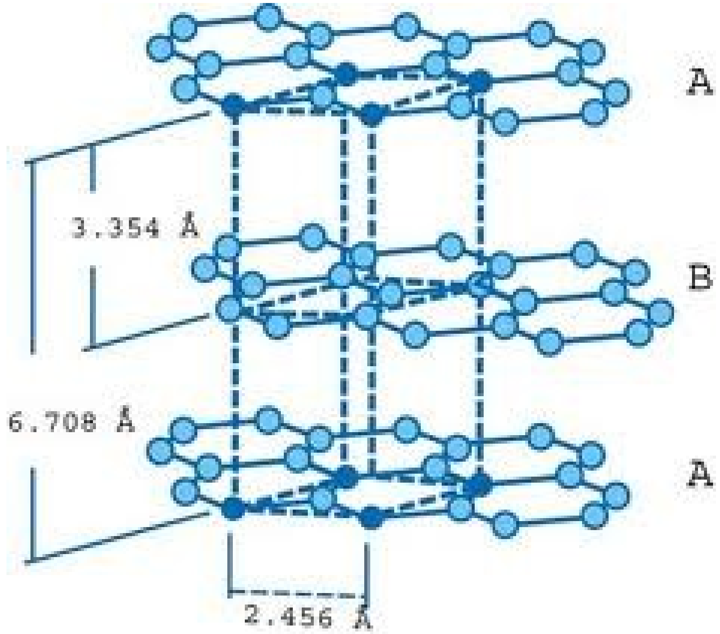
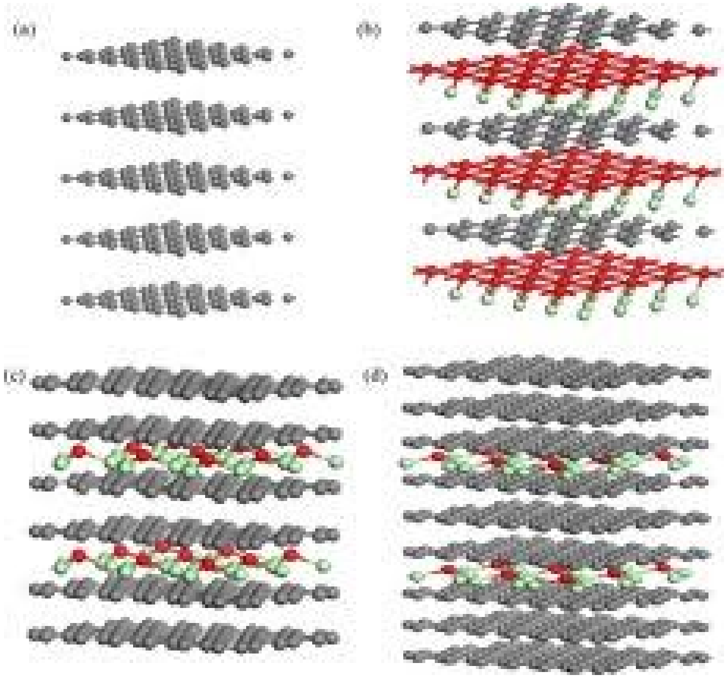
Brief History of graphite oxide (GO)

GO and GIC were first synthesized in 1840s → By Schafhaeul using natural graphite



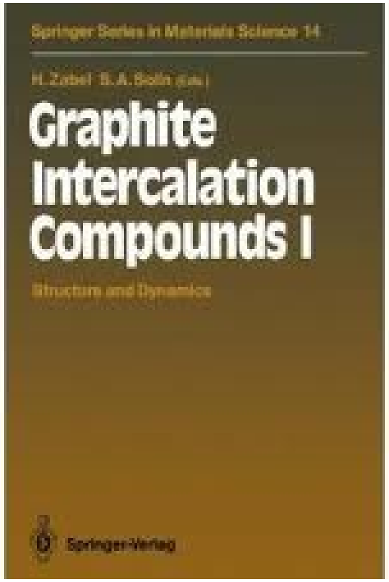
Acids/alkali Metals (K) →



1. Stacked carbon structure
2. Interlayer spacing is 3.354 Å
3. Electronic coupling between 2pz orbitals
4. Excellent thermal and electrical conductor.

1. Stacked carbon structure
2. Interlayer spacing widened
3. Electronic decoupling between 2pz orbitals → some times leads even to Superconductivity effects

Brief History of graphite oxide (GO)



Springer Series in Materials Science 14

H. Zabel S.A. Solin (Eds.)

Graphite Intercalation Compounds I

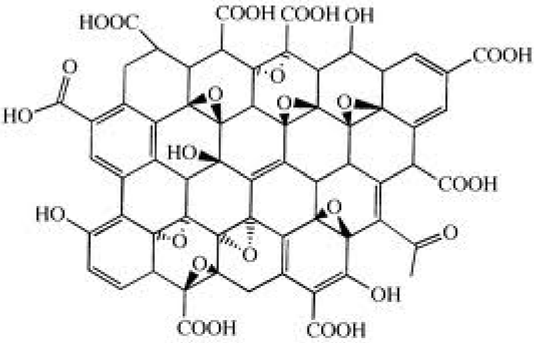
Structure and Dynamics

Springer-Verlag

Chemical reaction

Oxidation
With an oxidant
Such as $KMnO_4$ and
H_2SO_4 as an intercalant.

Oxidation of graphite matrix where
Peripheral carbon atoms at plane edges
And in defects bonded to oxygen contai
groups

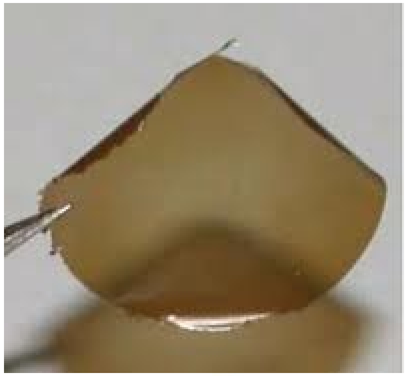


Ultrasound

Graphite Intercalation Compounds I: Structure and Dynamics (Springer Series in Materials Science)

Such a process was in the scientific literature since 1849- Benjamin Brodie ($KClO_3$).

1950 – to date- USE THE METHOD developed by Hummers and Offman.



Exfoliated graphite oxide

Why GO !! Now ???

Graphite

oxidation

(1^{st} product)
Research finished

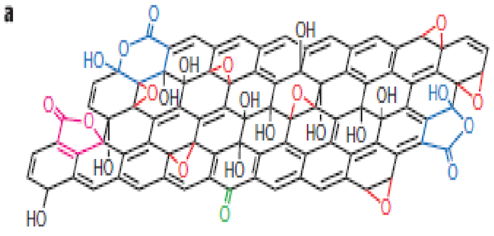
Graphite Oxide (GO)

(2^{nd} product

Graphite nanoplatelets (GNP)

(3^{rd} product
Future !!!)

Graphene

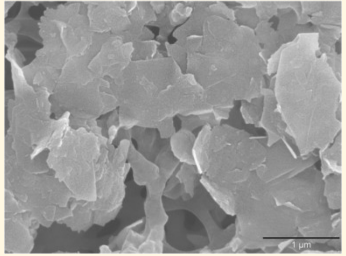


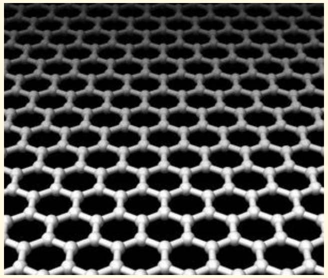
GO: 4.08 x 10^{-1} S m^{-1}

C:O = 1:3

Many layers of graphene oxide

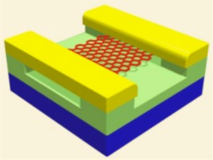
Reduction



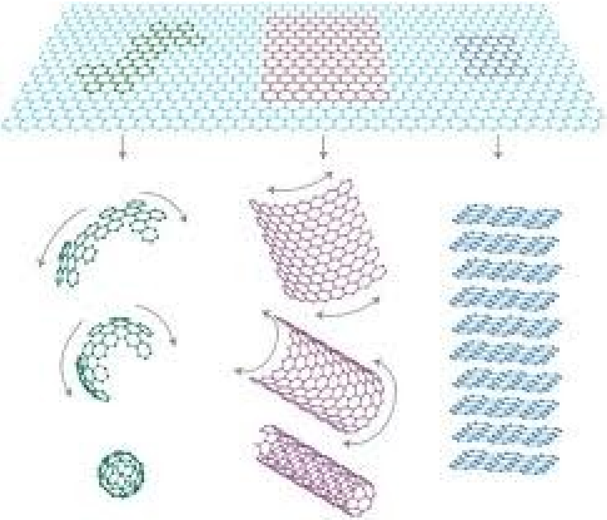


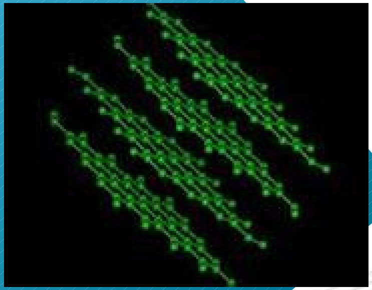
Next generation Electronics.

> 5 micron



What is GNP ?





Few Layers Of graphene (GNP)

- NGPs provide a wide range of performance characteristics including:

Conductivity

- The highest thermal conductivity known today (up to ~ 5,300 W/(mK), five times that of copper, at a density that is four times lower

- Exceptional in-plane electrical conductivity (up to ~ 20,000 S/cm)

- **Strength**
- Fifty times stronger than steel
- Ultra-high Young’s modulus (approximately 1,000 GPa) and highest intrinsic strength (~ 130 GPa estimated)

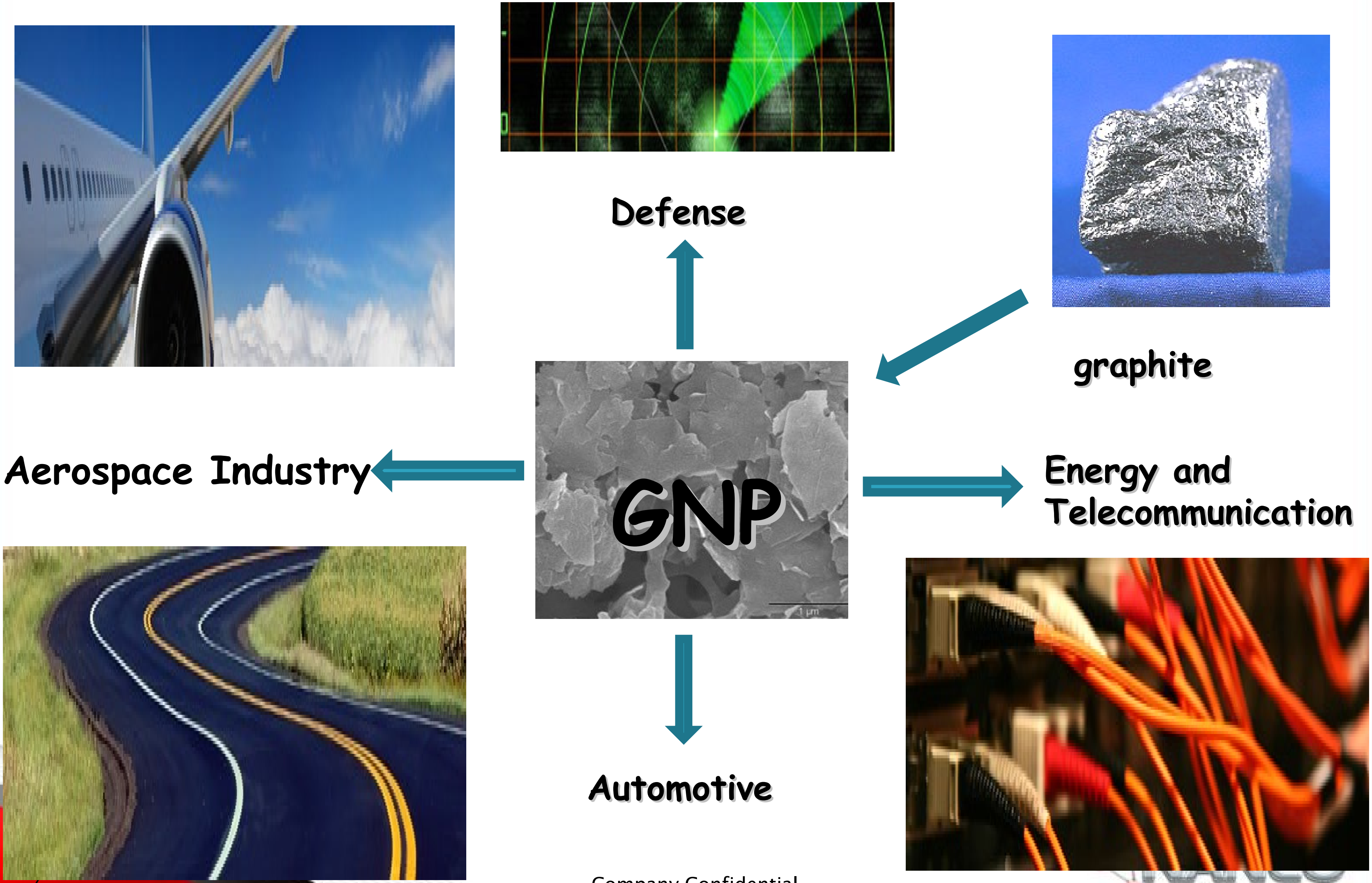
- **Surface Area**
- High specific surface area (up to ~ 2,675 m2/g) twice that of CNTs

- **Density**
- Low density (2.25 g/cm3)

- **Dimensions**
- Available in a wide range of platelet lengths (typically 1-20 µm) and thicknesses (approximately 0.34 nm to 100 nm)

- Single layer graphene as thin as 0.34 nm.

Rationale of GO !!!!!!



graphite

GNP

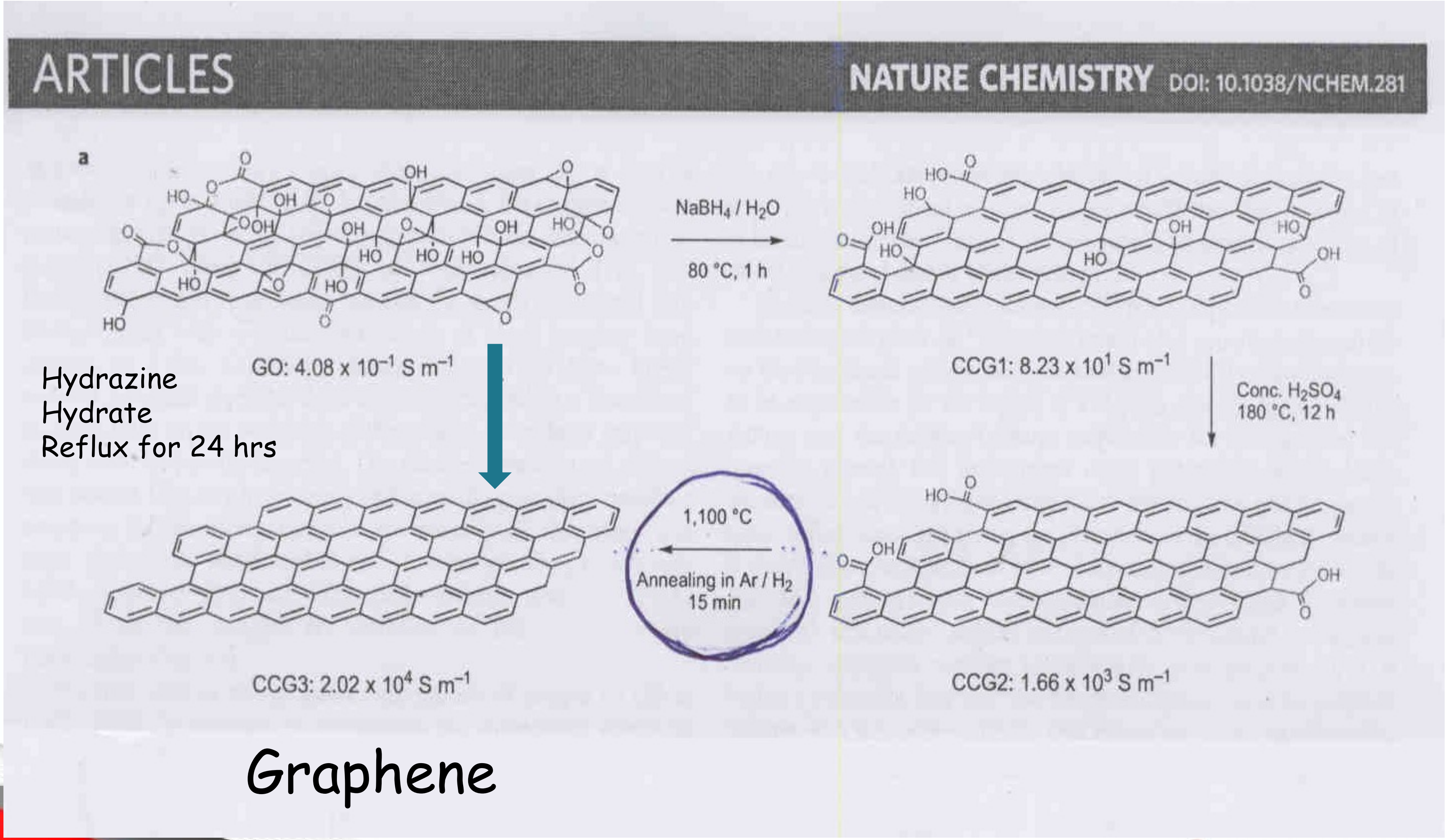
Defense

Aerospace Industry

Energy and Telecommunication

Automotive

What is Graphene !! (wonder material) 2010 Nobel



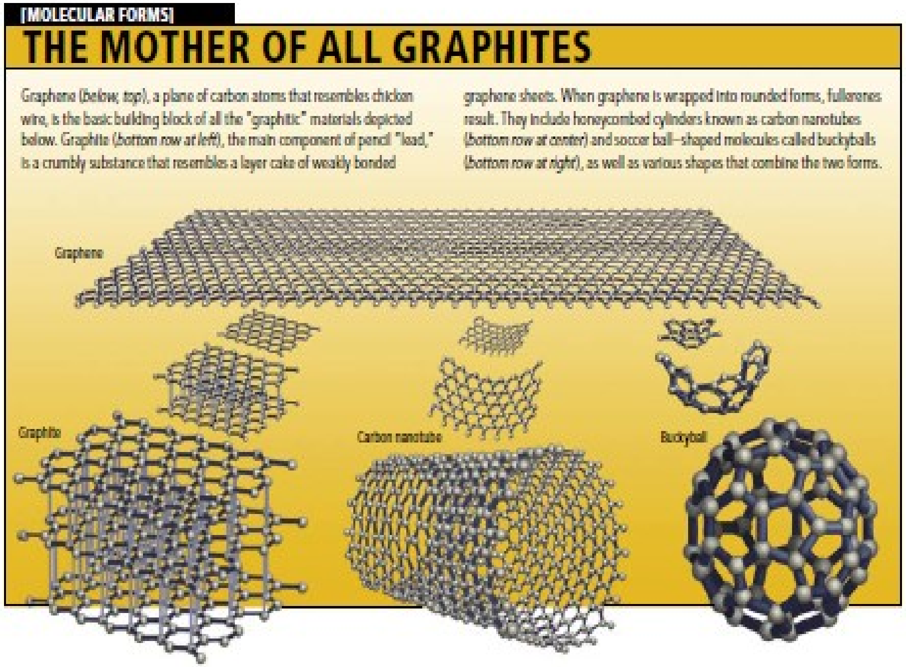
ARTICLES

NATURE CHEMISTRY DOI: 10.1038/NCHEM.281

Hydrazine
Hydrate
Reflux for 24 hrs

Graphene

What So Special about Graphene, CNT and GNP ?



[MOLECULAR FORMS]

THE MOTHER OF ALL GRAPHITES

Graphene (below, top), a plane of carbon atoms that resembles chicken wire, is the basic building block of all the "graphitic" materials depicted below. Graphite (bottom row at left), the main component of pencil "lead," is a crumbly substance that resembles a layer cake of weakly bonded graphene sheets. When graphene is wrapped into rounded forms, fullerenes result. They include honeycombed cylinders known as carbon nanotubes (bottom row at center) and soccer ball–shaped molecules called buckyballs (bottom row at right), as well as various shapes that combine the two forms.

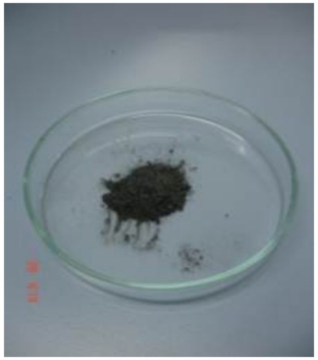
Extremely simple structure
Just simple carbon-carbon atoms network

Graphene superlatives

thinnest imaginable material
Largest surface area (~3000 m^2/g
Strongest material ever measured
Stiffest known material (> diamond)
Most stretchable and pliable
Record thermal conductivity (>diamond)
Highest current density at RT
(million times higher than Cu)
Completely impermeable
Highest intrinsic mobility (100 x Si)
Conducts electricity in the limit of no electron
Lightest charge carriers (zero rest mass)
Longest mean free path at RT(>micron)

Andre Geim, Graphene research update, July 2011, IOP London, UK.

Flexible membrane-graphene oxide membrane



40 µm
Graphite particles

oxidation

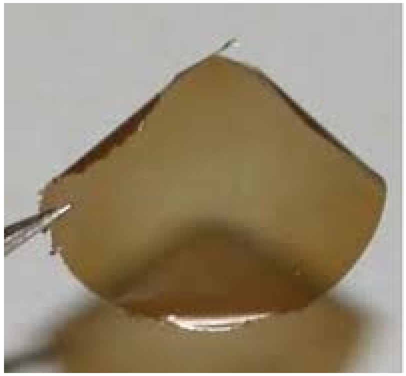
Self-assembling

Thick GO paper
t >>> 200µm

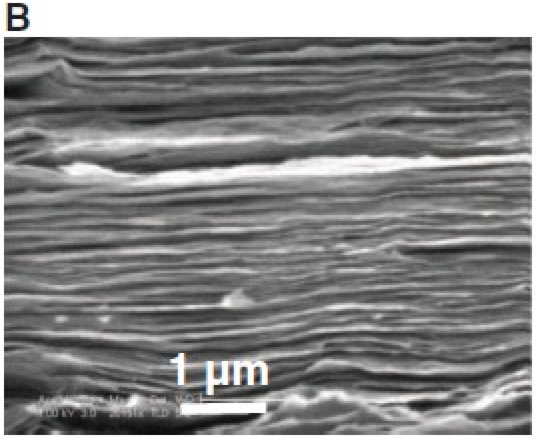
Dilution

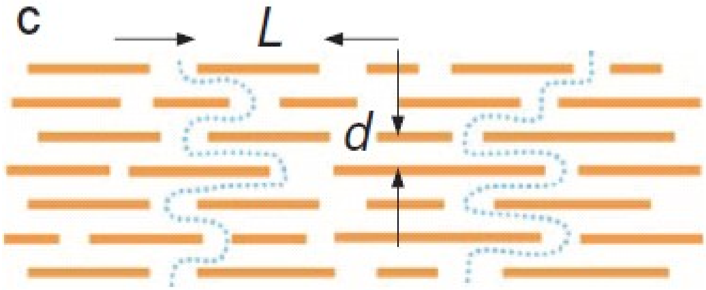
Thin GO paper
t >> 100 µm

Exfoliation



t = 0.5 µm





Full of nano-capillaries Science, 335, 442, 2012

Unimpeded permeation for water

Size of a water molecule = 0.278 nm

Graphene oxide membrane- Applications

Transparent flexible conductive films

composite and free-standing paper like material

Energy related material

Applications in biology and Medicine-DNA sequencing

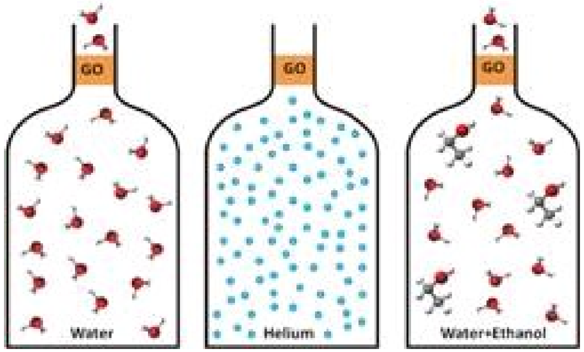
Antibacterial material

Surfactant

Research Material

Replace expensive ITO

Distil Vodka



Nanostructured Hybrid Transparent Conductive Films with Antibacterial Properties

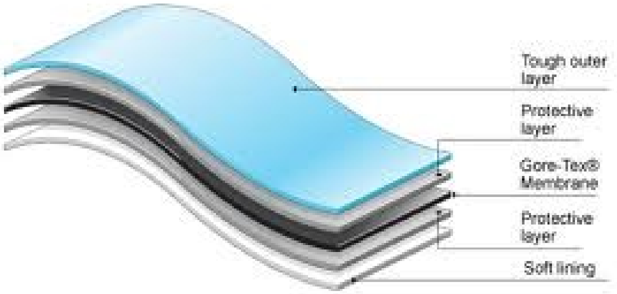
Iskandar N. Kholmanov, Meryl D. Stoll

Craig Barnhart, Jeffrey R. Potts, Richard

Artistic view: Water easily evaporates through graphene oxide membranes but they represent an impermeable barrier for other molecules.

Some applications of free-standing paper-like materials

1. As protective layers



2. Chemical filters
3. Components of electrical batteries or super-capacitors

4. Adhesive layers
5. Electronic or opto-electronic components and molecular storages

Given all these information

It is fair to raise fundamental question such as to How These Properties of multi-layer Graphene Oxide membrane change on

1. The **content of carbon** present in the parent graphite.

2. The **crystalinity** of the parent graphite.

3. The **purity** of the parent graphite.

4. The **electronic structure** of the parent graphite.

More importantly

Whether we could use our own raw material, vein graphite, to do this ???? To see whether it produces the similar materials but with different characteristics.

As the nature of origin of **vein graphite** is different to that in **flake graphite**.

Objective is to see whether the properties **intrinsic** to vein exists- as a result of its **distinct nature of origin**.

Synthesis of GO membrane

With less problems, we can prepare GO multilayer membrane from vein graphite powder using, for example, Hummers method .

Also we can gather a breadth of information on multilayer GO using, for example, XRD, FT-IR, SEM, AFM,TGA and solutions of them using UV-Visible and optical microscopy for its structural, optical, topographical and thermal properties.

The Job in Hand ? has more gravity !!

- Is to "claim" (register) that your materials are "better and marketable" than existing materials, internationally.

High-end applications those require answers to problems with fundamental nature originating from the electronic properties of GO - requiring **in depth (finer) information** of your samples.

Electronic properties (finer details) of GO

- X-ray (tunable) absorption spectroscopy (XAS) to investigate the electronic properties of GO-Synchrotron Radiation.

- Core level photoemission spectroscopy
- (*sp*^{2} and *sp*^{3} carbon, oxygen functional groups, atomic vacancies, C:O ratio, degree of oxidation etc. by using BE of C 1s)

- BE is a unique character for an orbital- resolve features lying < 100 meV resolution.

- NEXAFS-distribution of the density of states in unoccupied orbitals, above Fermi energy, of GO and vein graphite, the orientation of graphite planes, the purity of the samples, and the relative size of the planer ring system etc.

What is Synchrotron Radiation ?

A synchrotron is a huge scientific machine designed to produce very intense beams of x-rays and ultraviolet light.

*This "synchrotron light" can penetrate deep inside matter and allows scientists to investigate the world around us at the scale of atoms and molecules-

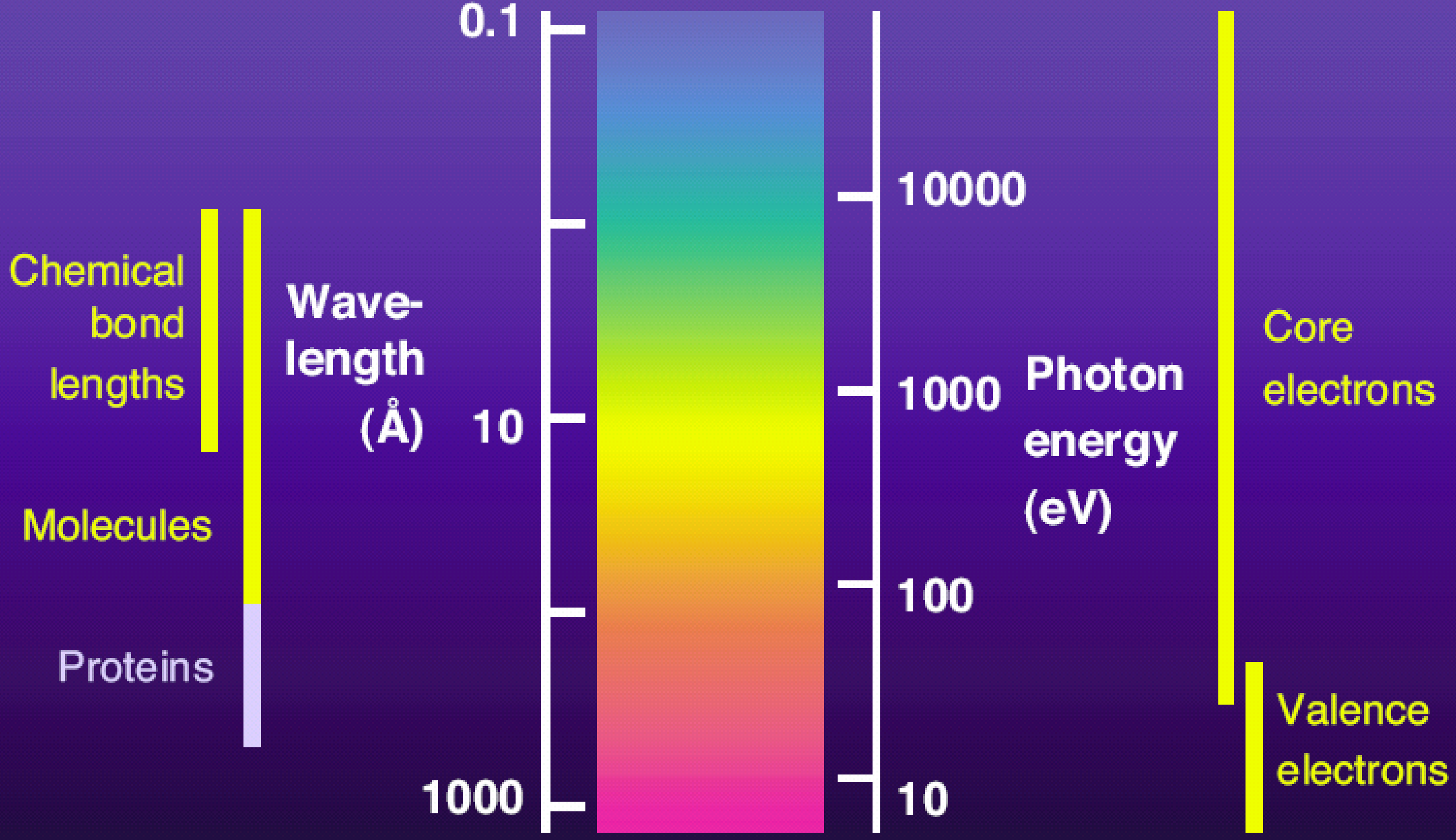
-Excellent tool for nanoscience and nanotechnology.

However physicists study things even beyond nanotechnology using SR.

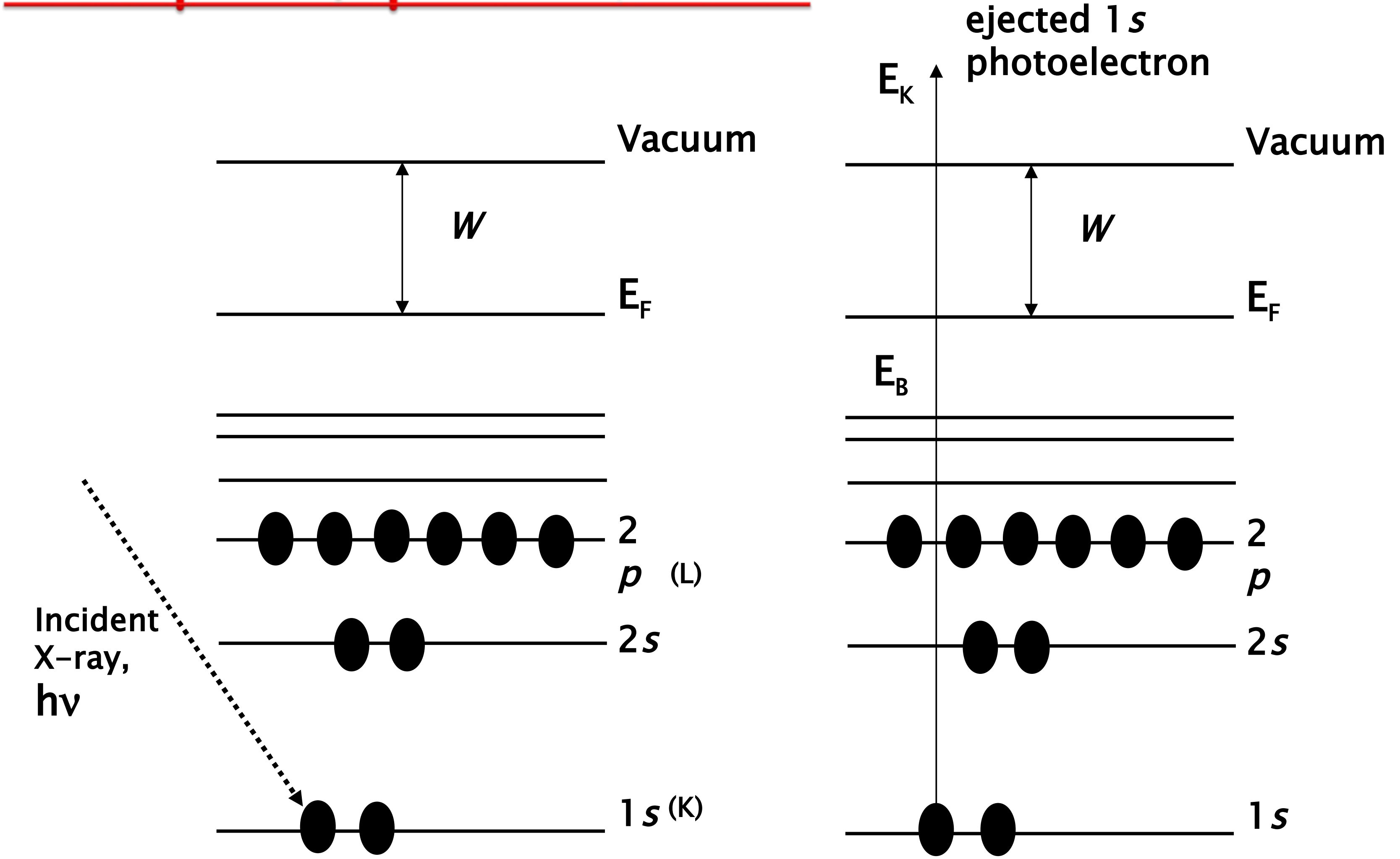
ELETTRA Synchrotron, Trieste

ICTP-ELETTRA Users Program, www.elettr

Why x-rays and ultraviolet?



Principle of photoemission



The equation which describes photoemission process

$E_B = h\nu - E_K - W$ *(Einstein equation)*

The Origin of NEXAFS spectra-information on electronic structure

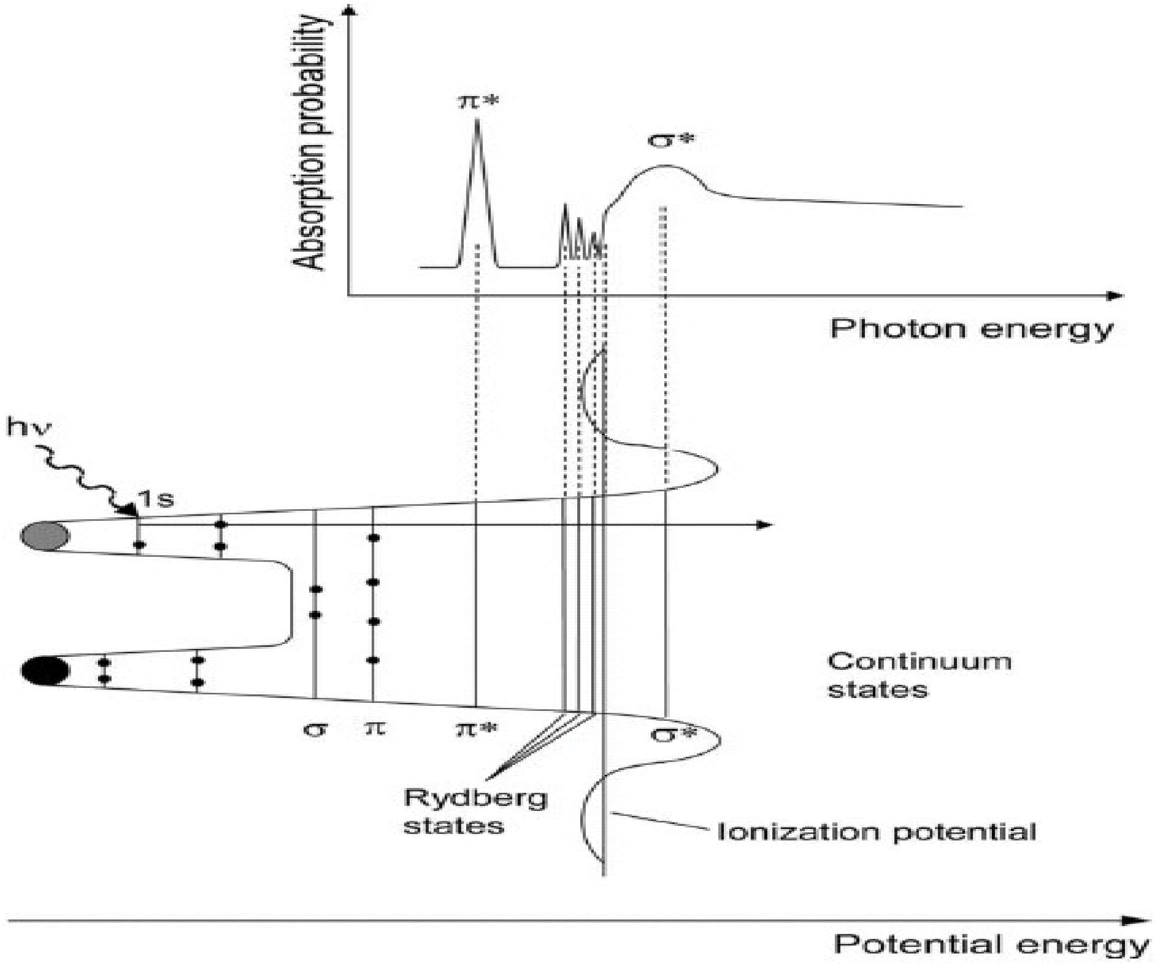
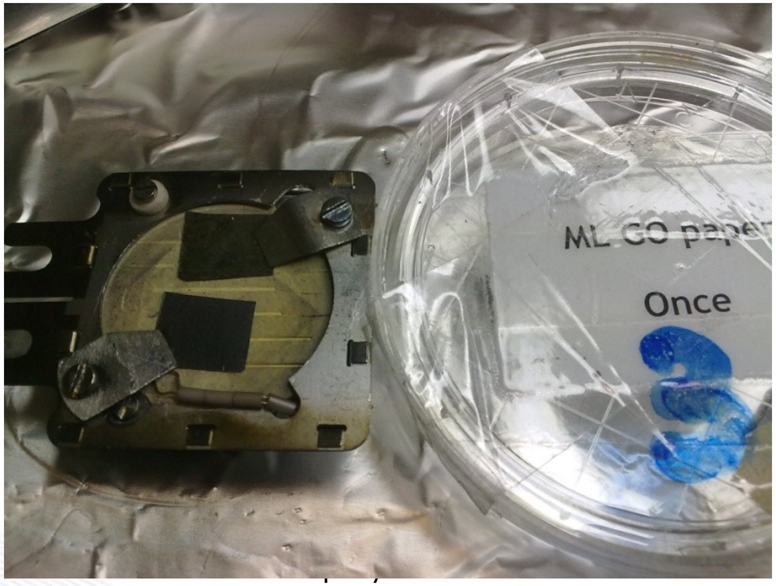
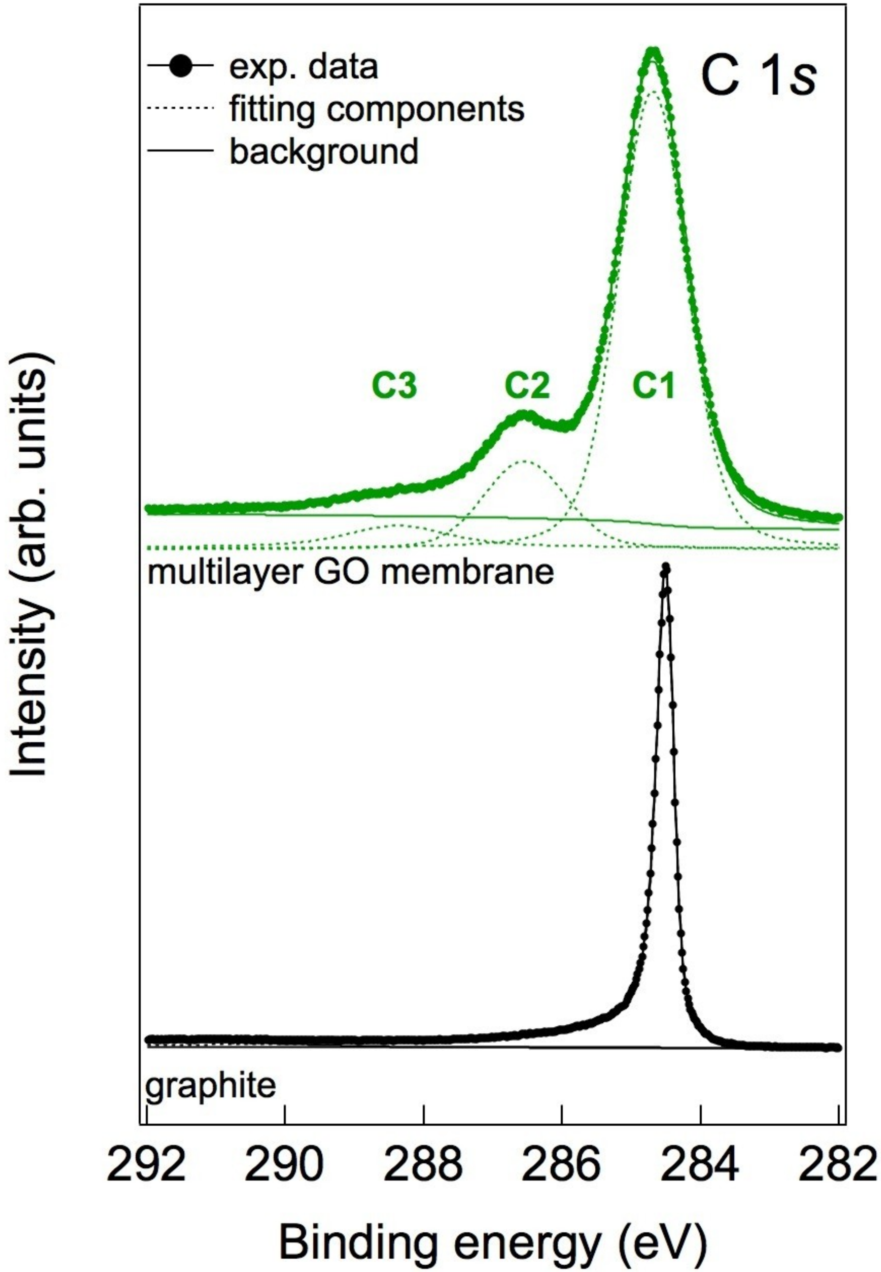


Fig. 3 Schematic potential (bottom) and corresponding NEXAFS K-shell spectrum (top) of a diatomic molecular (sub)group. In addition to Rydberg states and a continuum of empty states similar to those expected for atoms, unfilled molecular orbitals are present, which is reflected in the absorption spectrum.

Sample mounting



Core level spectroscopy (May 2012)



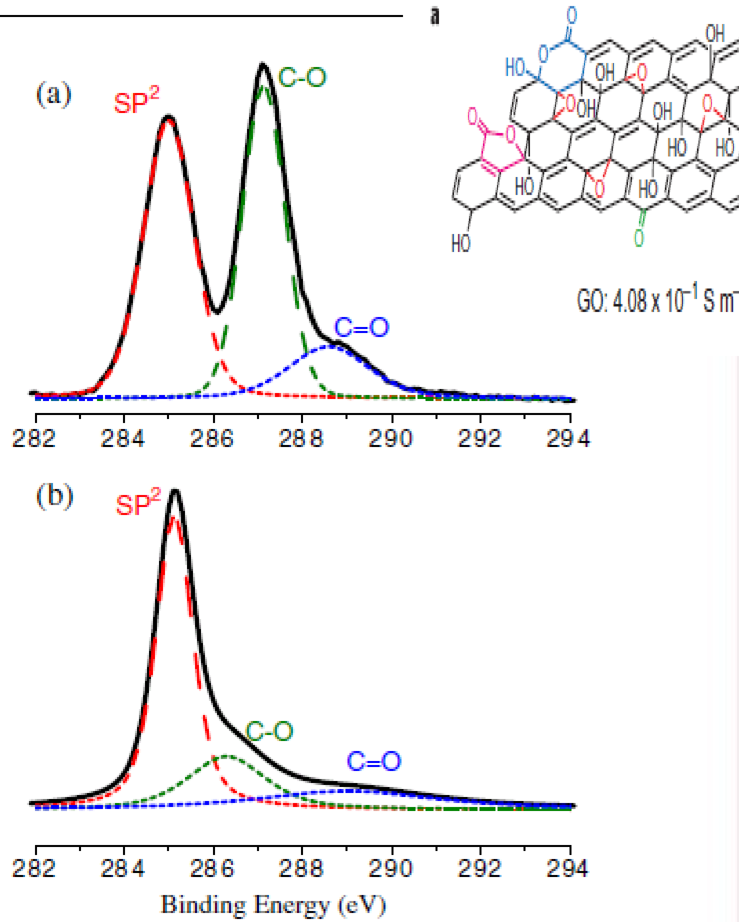
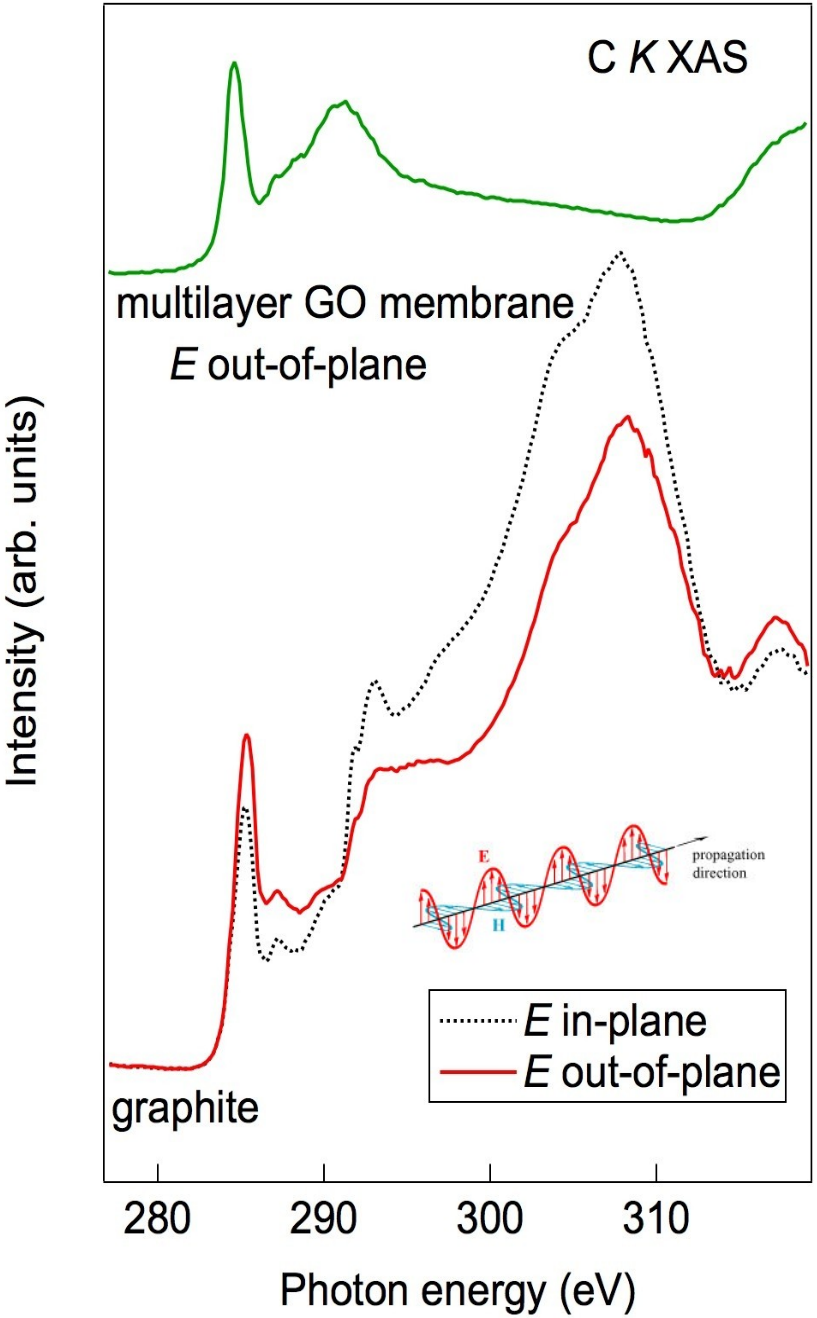


Fig. 1 – High resolution XPS spectra of GO (a) and tRGO (b). The black solid lines are original spectra; the deconvoluted dashed lines in red, green and blue are assigned to sp^2-C, C–O (hydroxyl and epoxy groups), C=O (carboxyl groups), respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Zhan, D, Carbon 49, 2011, 1362 and Kim, S, Nature Materials, May 2012 DOI:10.1038

NEXAFS



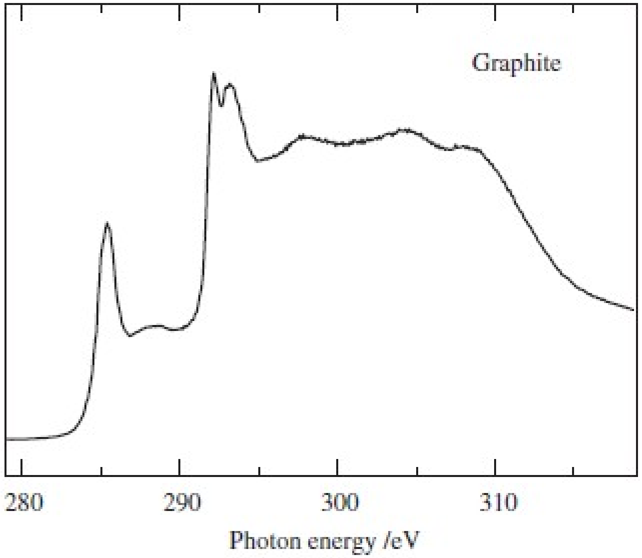


Fig. 2. NEXAFS C K-edge spectra of FIB-CVD DLC, IP DLC and graphite.

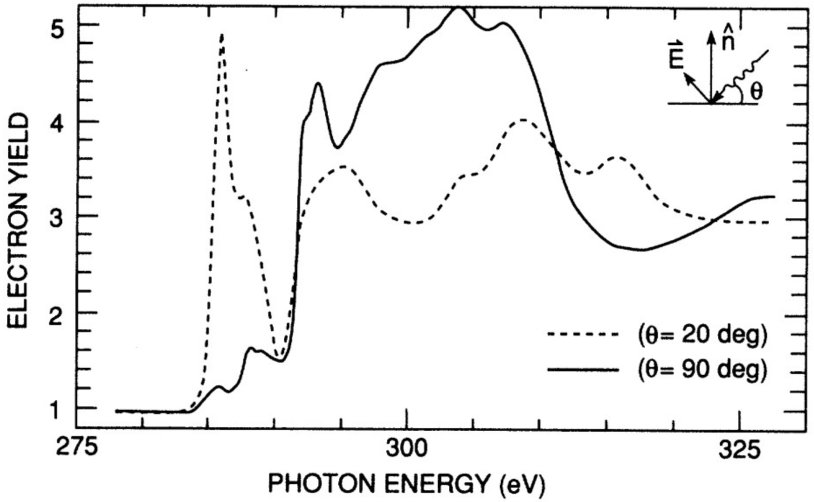
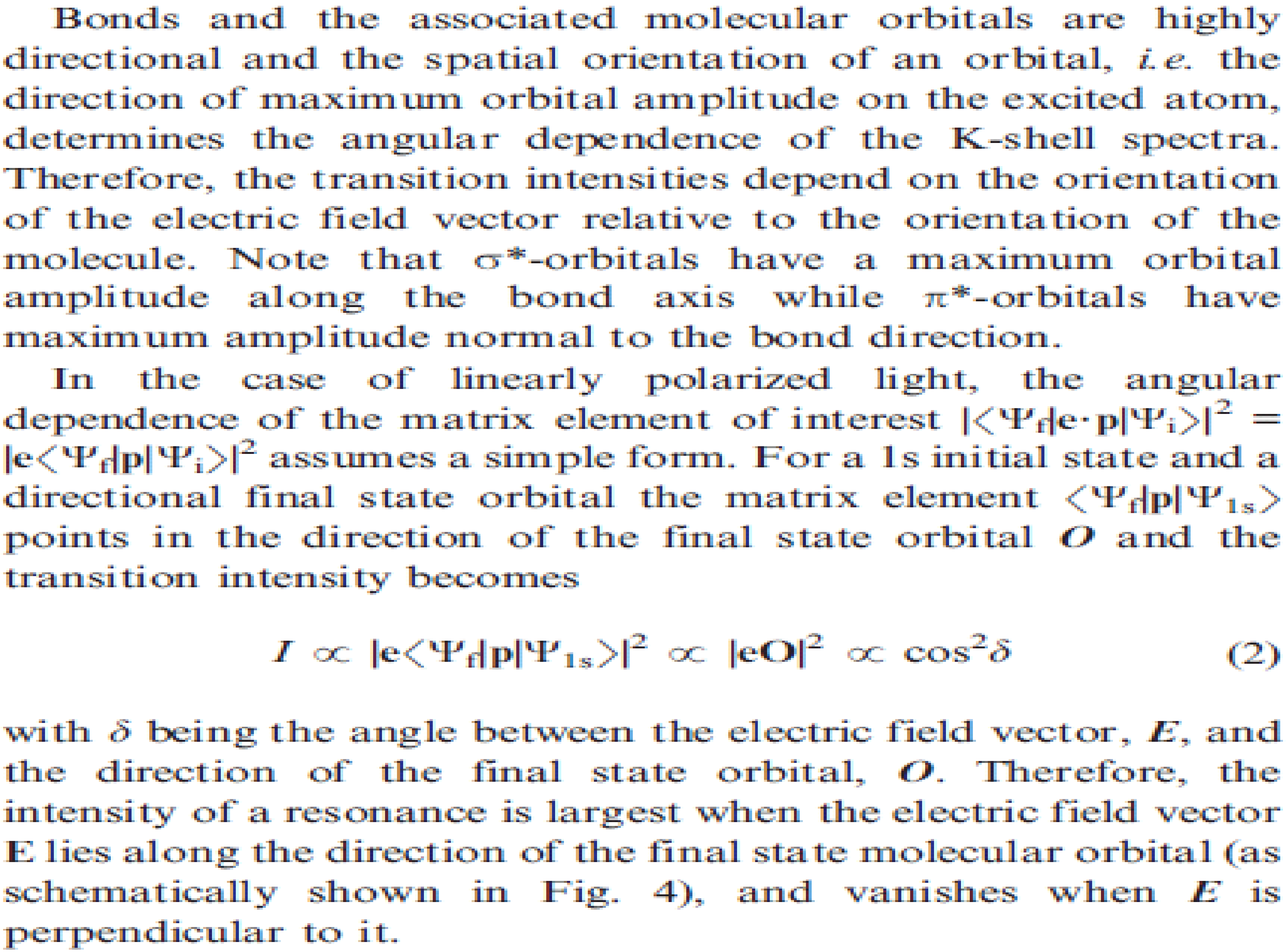


FIG. 3. Polarization-dependent C *K* NEXAFS spectra of a bulk sample of HOPG.

Angular dependence of the spectra



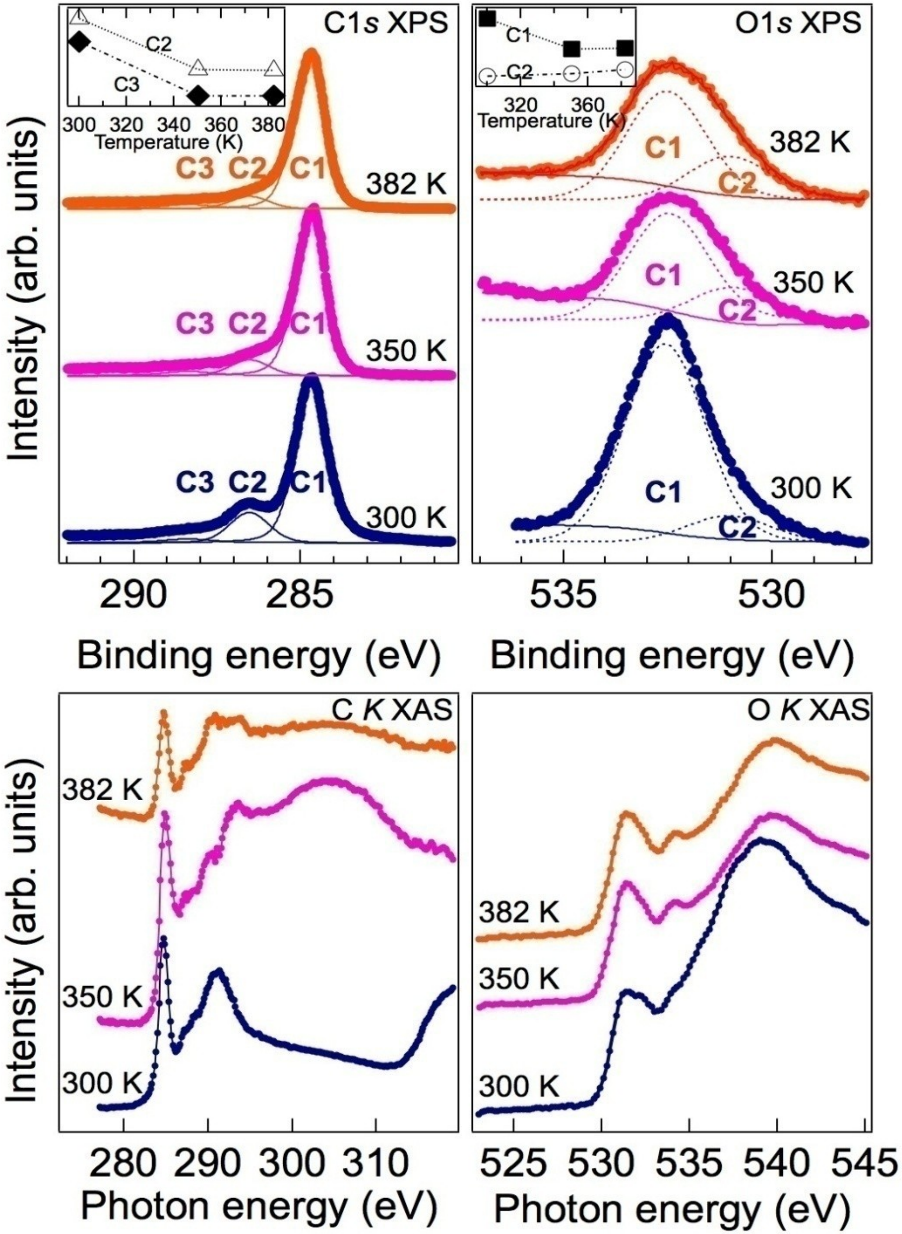
Bonds and the associated molecular orbitals are highly directional and the spatial orientation of an orbital, *i.e.* the direction of maximum orbital amplitude on the excited atom, determines the angular dependence of the K-shell spectra. Therefore, the transition intensities depend on the orientation of the electric field vector relative to the orientation of the molecule. Note that σ^*-orbitals have a maximum orbital amplitude along the bond axis while π^*-orbitals have maximum amplitude normal to the bond direction.

In the case of linearly polarized light, the angular dependence of the matrix element of interest $|\langle\Psi_f|\mathbf{e}\cdot\mathbf{p}|\Psi_i\rangle|^2 = |\mathbf{e}\langle\Psi_f|\mathbf{p}|\Psi_i\rangle|^2$ assumes a simple form. For a 1s initial state and a directional final state orbital the matrix element $\langle\Psi_f|\mathbf{p}|\Psi_{1s}\rangle$ points in the direction of the final state orbital $\boldsymbol{O}$ and the transition intensity becomes

$$I \propto |\mathbf{e}\langle\Psi_f|\mathbf{p}|\Psi_{1s}\rangle|^2 \propto |\mathbf{e}\mathbf{O}|^2 \propto \cos^2\delta \qquad (2)$$

with δ being the angle between the electric field vector, $\boldsymbol{E}$, and the direction of the final state orbital, $\boldsymbol{O}$. Therefore, the intensity of a resonance is largest when the electric field vector E lies along the direction of the final state molecular orbital (as schematically shown in Fig. 4), and vanishes when $\boldsymbol{E}$ is perpendicular to it.

C 1s and NEXAFS on Vein GO membrane following thermal annealing at each step



Final Observations

Vein graphite seems to be more chemically stable than other forms of graphite (core level spectra)

Vein graphite has higher number of sheets per crystallite (XRD) and chemical oxidation breaks this higher order into smaller crystallites and introduce oxygen functionalities which make the basal plane of graphite hydrophilic (core level and FT-IR spectra).

Vein graphite has the highest *cohesive* energy than any other natural graphite (in plane and out-of plane) 8 meV-200 meV.

The electronic structure of vein graphite is similar to that of man-made HOPG and it differs from flake graphite, especially in the higher photon energy range where the distribution of density of states of in the unoccupied orbitals lie-