Topics included in this group meeting: Graphene background, synthesis, application as catalysts, characterization and perspectives.

Not covered in this group meeting: Applications in photocatalysis, sensors, supercapacitors, drug delivery and Full cells/ORR.

IUPAC definition: Graphene is a single carbon layer of the graphite structure, describing its nature by analogy to a polycyclic aromatic hydrocarbon of quasi infinite size.

Why study graphene and its derivatives?
Graphene is an exciting and unique material which shows peculiar electronic, optical, mechanical and chemical properties, among others, which have found application in numerous scientific and technological areas.

Synthetic Organic Chemistry? Graphene?
Can we make organic synthesis on two-dimensional planes?
“Organic chemistry can be defined as the the study of the structure, properties, reactions, and preparation of carbon-containing compounds …”

Graphene, as others hydrocarbons, can undergo many reactions in order to afford necessary flexibility to adapt it into specific performances.

Timeline of selected events in the history of the preparation, isolation and characterization of graphene.

Graphite oxide prepared by Schafhaeutl, Brodie, Staudenmaier, Hummers and others
Morgan and Somorjai obtain LEED patterns produced by small-molecule adsorption onto Pt(100)
Blakely and co-workers prepare monolayer graphite by segregation carbon on the surface of Ni(100); several subsequent reports follow
Boehm and co-workers recommend that the term “graphene” be used to describe single layers of graphite-like carbon
Ruoff and co-workers micromechanically exfoliate graphite into thin lamellae comprised of multiple layers of graphene
Geim and co-workers prepare graphene via micromechanical exfoliation, numerous reports follow

1840-1958
1962
1968
1969
1970
1975
1986
1997
1999
2004
2010

Boehm and co-workers prepare reduced graphene oxide (rGO) by the chemical and thermal reduction of graphite oxide
May interprets the data collect by Morgan and Somorjai as the presence of monolayer of graphite on the Pt surface
van Bommel and co-workers prepare monolayer graphite by subliming silicon from silicon carbide
IUPAC formalizes the definition of graphene: “The term graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed”

Dreyer et al. ACIE. 2010, 49, 9336.
Graphene Chemistry

Overview of Principals Methods of Synthesis for Graphene-based Materials:

Chemical Oxidation
- **Hummers method (1958)**
- Other methods: Brodie, Staudenmaier, Hofman and Tour.
- **Advantages:** Most Used method, Large scale production, Medium quality GM.
- **Disadvantages:** Impurities and defects, GM of low electrical conductivity, Large production of liquid wastes.

Chemical vapor deposition (CVD)
- **Advantages:** High cost, Large scale production, Green synthesis method, easy doping.
- **Disadvantages:** Low production.

Pyrolysis of precursors
- **Advantages:** Low cost, Large scale production, Green synthesis method, easy doping.
- **Disadvantages:** Medium quality graphene.

Mechanical exfoliation
- **Advantages:** High quality graphene
- **Disadvantages:** Time consuming, Low production.

**Synthesis of Graphene and its derivatives**

Graphene layers without functionalization are insoluble and infusible, which limits their application capabilities.

The essential purpose of graphene derivatisation is to tailor its physical and chemical properties. The synthesis of graphene derivatives can be divided in two major process: a) bottom-up and b) top-down.

**Graphene oxide (GO)**

*Proposed structure of GO based on the Lerf Klinowski model*

GO is currently the principal precursor used for the synthesis of graphene materials. Moreover, GO itself has attracted considerable attention due to the oxygen functional groups on its surfaces. GO has attracted considerable attention as potential material for use in photovoltaic cells, capacitors, sensor and catalysis.


**Synthesis of Graphene-based Materials:**

GO as starting material:

\[
\text{GO} \rightarrow \text{GO} + e^{-} \rightarrow \text{GO} + N_{2}\]

Graphene (G) as starting material:

\[
\text{G} + N_{2}^+ + e^- \rightarrow \text{G} + N_{2}
\]

Fluorographene (FG) as starting material:

\[
\text{FG} + \text{BrMg} \rightarrow \text{R}
\]

GO - simplified structure

Diagram of Active Sites of Graphene-Based Nanomaterials

**Navalon et al. Chem. Rev. 2014, 114, 6179.**

**Ma et al. ACS Catal. 2016, 6, 6948.**
Application as catalysts: GO

GO as catalyst

C-C coupling

C-H coupling

Synthesis of thioethers

Iodination

Sulfoxidation

Alkylation of Arenes

57-99% yield
15 examples

82-95% yield
2 examples

60-92% yield
15 examples

5 x recycled

34-80% yield
21 examples


Zhang et al. ACS Appl. Mat. Interfaces 2015, 7, 1662.

Gao et al. ACIE 2016, 55, 3124.


Hu et al. JACS 2015, 137, 14473.


Proposed mechanism

Alkylation of Arenes

Hu et al. JACS 2015, 137, 14473.

GO, air

CHCl₃, 100°C
Graphene Chemistry

**C-C coupling**

\[
\begin{align*}
R - H & \xrightarrow{\text{GO (40mg)}} R - \equiv - H \\
& \xrightarrow{\text{CH\textsubscript{3}CN, 100°C, argon, 12h}} R - \equiv - R
\end{align*}
\]

*Proposed mechanism*


**Iodination**

\[
\begin{align*}
\text{GO (20mg), I\textsubscript{2} (1.1 equiv)} & \xrightarrow{\text{CH\textsubscript{3}NO\textsubscript{2} (0.7 mL)}} \text{Ar or Ar} \\
& \xrightarrow{120°C, 1h, air} \text{Ar or Ar}
\end{align*}
\]

*Proposed mechanism*


**Application as catalysts: rGO**

\[
\begin{align*}
\text{rGO} & \xrightarrow{H_2O_2} \text{rGO} \\
& \xrightarrow{k_2} H_2O + O_2
\end{align*}
\]

*Proposed mechanism*


18% yield
5 x recycled
Graphene Chemistry

Karla S. Feu

Baran Group Meeting
10-06-18

Characterization Techniques:

Analytical Techniques:
* Atomic emission (AES), *absorption spectroscopy (AAS) or *inductively coupled plasma mass spectrometry (ICP-MS): Presence of metal impurities.
* Combustion elemental analysis: composition
* TPD: thermal stability

Microscopy (M):
morphology and single layer confirmation
* Transmission electron M (TEM)
* Scanning electron M (SEM)
* Atomic force M (AFM)
* Elemental mapping (Energy dispersive X-ray)

Spectroscopy:
functional groups and metal oxidation date
* Raman
* FT-IR
* XPS
* UV-Vis
* Solid-state NMR

Textural characterization
BET: surface area of powders
XRD: crystallinity and stacking

Thermal Analysis:
interaction with oxidizing reducing agents
* Thermogravimetry
* Thermodesorption

Raman

FT-IR

XPS

UV-vis

SS-NMR

Adsorption isotherm: BET

PXRD

Thermal analysis: ATG
Others Applications and Perspectives:

- Lithium ion battery
- Solar cells
- Supercapacitors
- Bio applications
- Sensors
- Water desalination
Applications: Biosensors

Schematic of the Desorption Mechanism of the Probe DNA adsorbed on GO, driven by the addition of (A) cDNA and (B) Non-cDNA

Perspectives

# More complex derivatives of graphene;
# The research should also focus on well defined graphene;
# A more intensive collaboration between synthetic chemists, polymer chemists and biologists;
# In the field of catalysis, the exploration in the unchartered territory of enantioselective transformations;
# The potential of the graphene-based materials are huge and still in the begin.