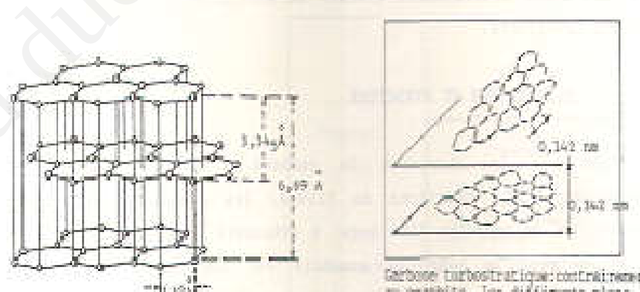
GRAPHENE

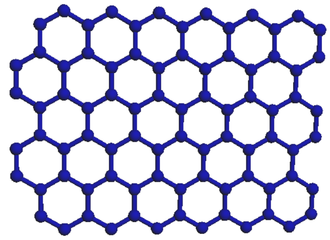
CARBON MONO SHEETS



Carbone turbostratique: contrairement au graphite, les différents plans formés par les hexagones (plans graphitiques) sont désorientés les uns par rapport aux autres

Structure du graphite et des fibres de carbone.

Properties of Graphene?



Graphene sheet

Graphene sheets are predicted to possess outstanding properties:

- ~1100 GPa modulus (stronger than steel)
- Density 2.2 g/cm^3 (lightweight yet strong)
- Thermal conductivity 3000 W/m-K
- Electrical conductivity (ballistic electron transfer)
- Open to the full repertoire of synthetic organic chemistry for 'chemical tuning'

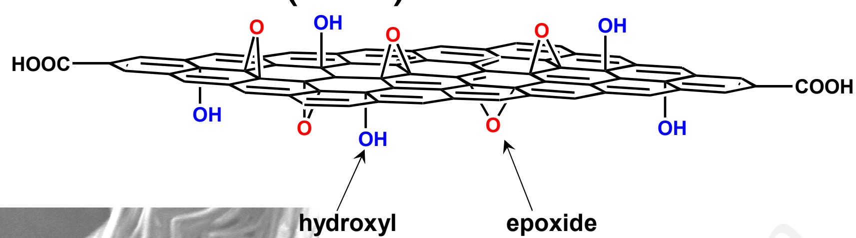
However, getting individual graphene sheet is a very difficult challenge

Alternative Approach: Graphite Oxide

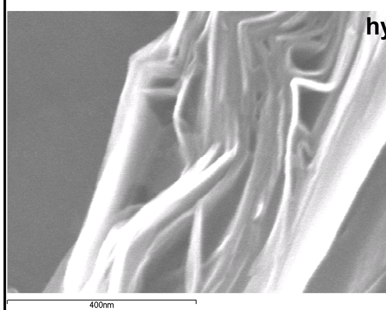
Graphite $\xrightarrow{\textbf{Oxidant}}$ **Graphite oxide (GO)**

Graphite oxide suspended in water

Structure of Graphite Oxide (GO)



Graphene oxide sheet

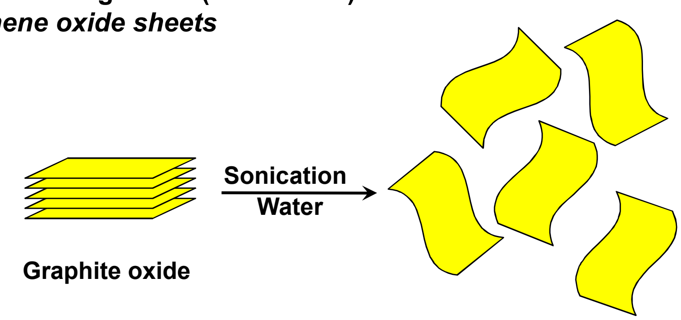


SEM image of GO

- **Layered structure preserved**
- **Sheets held by hydrogen bonds**

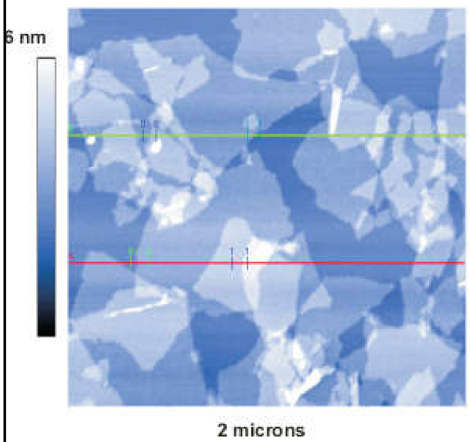
Exfoliation of GO in Water

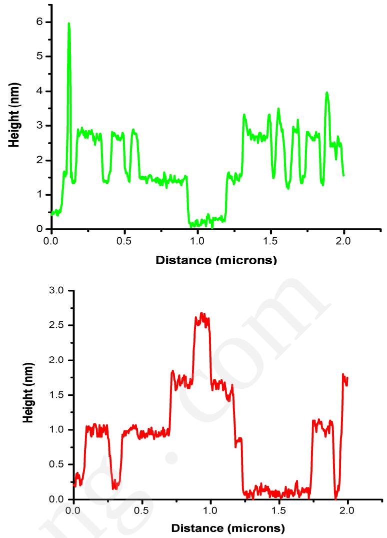
- **Oxygenated graphene layers are hydrophilic**
- **Water can penetrate the interlayer galleries**
- **Mechanical agitation (ultrasound) ➔ exfoliation down to *single graphene oxide sheets***



Graphene oxide sheets

AFM Images of Exfoliated GO





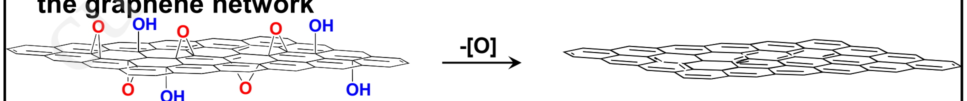
Sheets ~ 1 nm thick deposited on a mica surface.

These are individual graphene oxide sheets!

Richard Piner

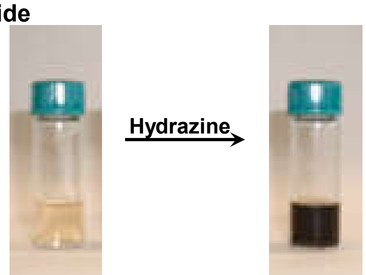
Exfoliation/Reduction Approach

- **Graphene oxide sheets are not conductive**
- **Reduction (de-oxygenation) can be employed to partially restore the graphene network**



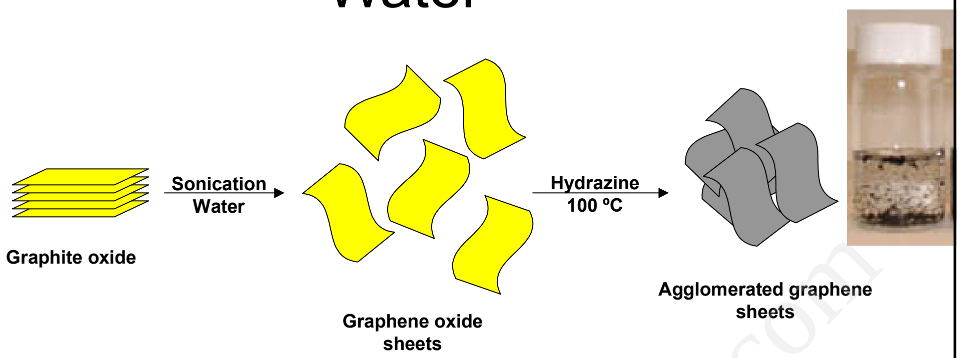
Graphene oxide

Graphene



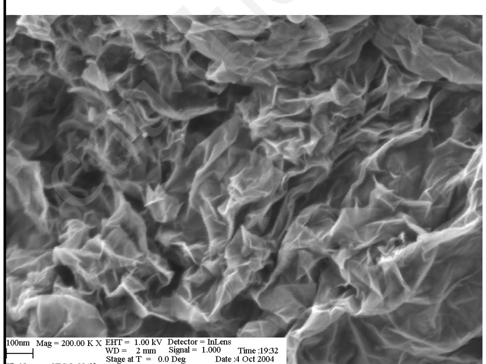
Reduction of graphite oxide with hydrazine

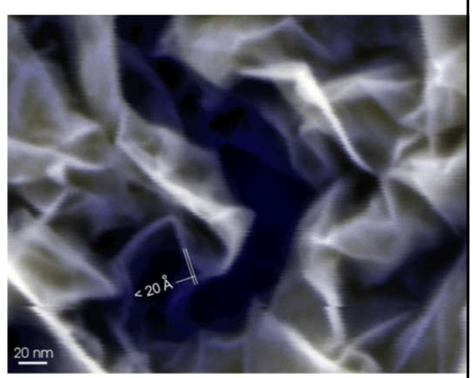
Graphite Oxide Reduction in Water



De-oxygenation of GO sheets ➔ lowering hydrophilic character ➔ agglomeration and precipitation

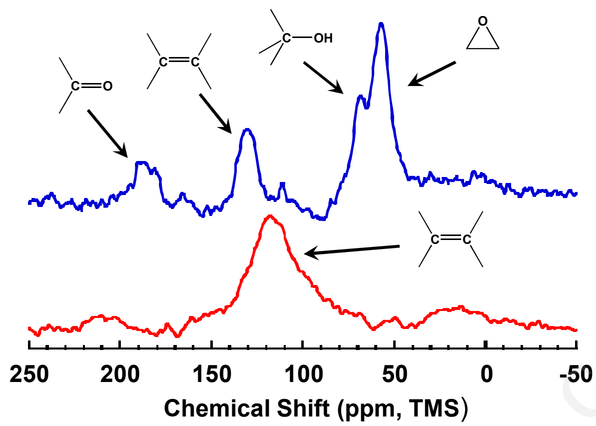
Reduced Graphene Oxide Sheets





- **Highly disordered structure and high specific surface area (~600 m^2/g, theoretical surface area for graphene is ~2,700 m^2/g)**
- **For comparison, activated carbon is ~1000 m^2/g**

Solid State NMR Study

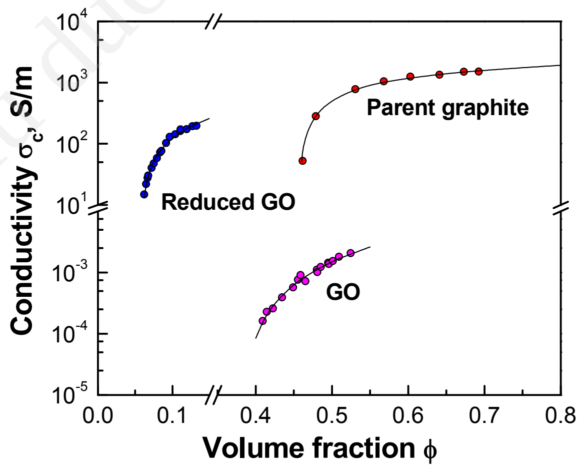


^{13}C MAS NMR spectra of graphite oxide and reduced graphite oxide

Reduction restores sp^2 carbon sites.

Stankovich, S. et al., *Carbon* **2007**, *45 (2007),* 1558–1565

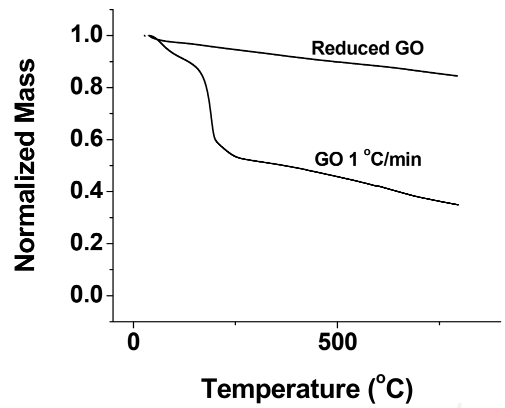
Conductivity or CReGO



Electrical conductivity of the reduced graphene oxide sheets restored ~ parent graphite.

Stankovich, S. et al., *Carbon* **2007**, *45 (2007),* 1558–1565

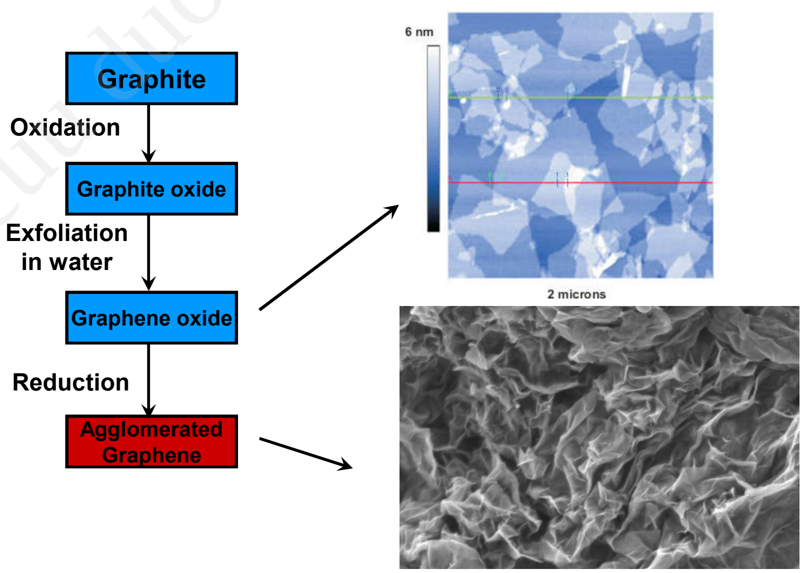
Graphite Oxide Reduction



Reduced graphene oxide sheets are more thermally stable than graphite oxide itself

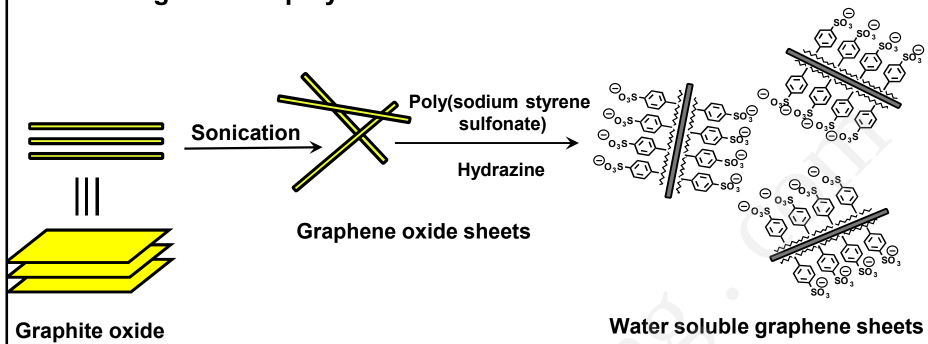
Stankovich, S. et al., *Carbon* **2007**, *45 (2007),* 1558–1565

Progress thus far…



" Water-Soluble" Graphene Sheets

- **PSS needs to be present in high concentration**
- **Coating with the polymer is irreversible**

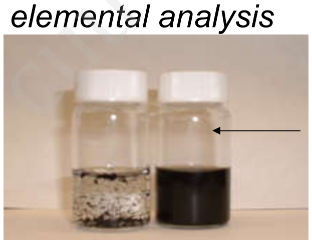


It works!

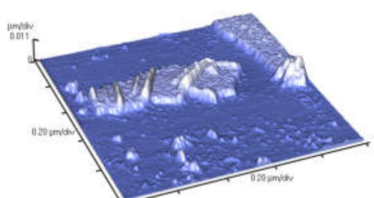
Stankovich, S. et al, *J. Mater. Chem.* **2006**, *16*, 155-158.

"Water-Soluble" Graphene Sheets

- *Stable "water-soluble" graphene/polymer complex isolated*
- *Polymer-coated sheets contain ~40% polymer-determined by elemental analysis*



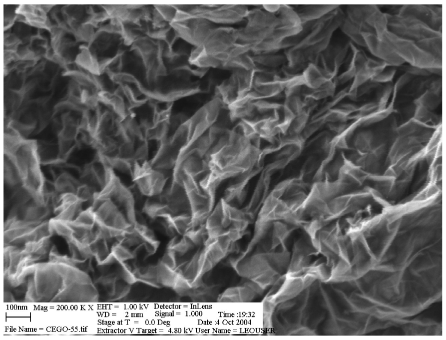
Stable suspension produced by reducing 1 mg/mL solution of GO in water in the presence of poly(sodium styrenesulfonate)

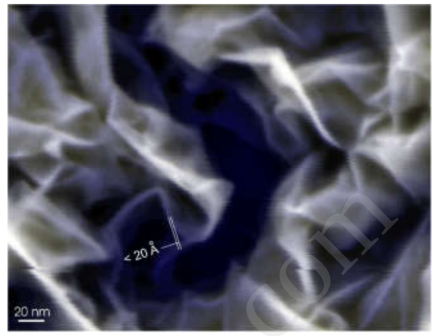


AFM images show that the "solution" contains mainly individual sheets ~ 4 nm thick

Stankovich, S. et al, *J. Mater. Chem.* **2006**, *16*, 155-158.

Reduced GO Nanoplatelets: CReGO





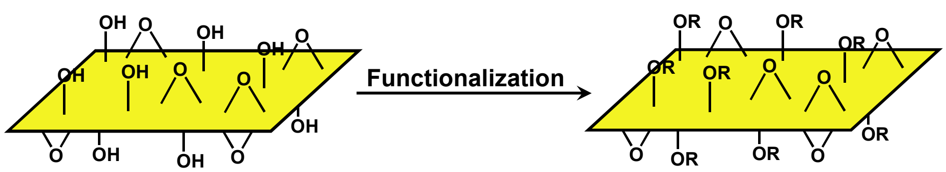
- Reduction of GO nanoplatelets leads to precipitation and irreversible agglomeration
- The precipitated material cannot be re-dispersed

Graphene in Organic Solvents

Can we exfoliate graphite oxide in organic solvents?

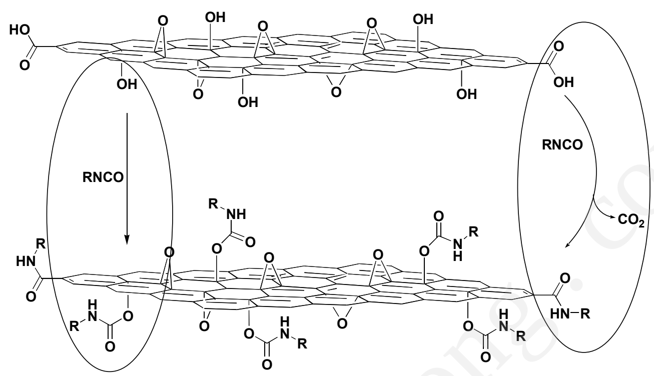
Approach:

- **Derivatize hydrogen bonding groups**
- **Graphene oxide sheets should become less hydrophilic**
- **Strength of interlayer bonding should attenuate**

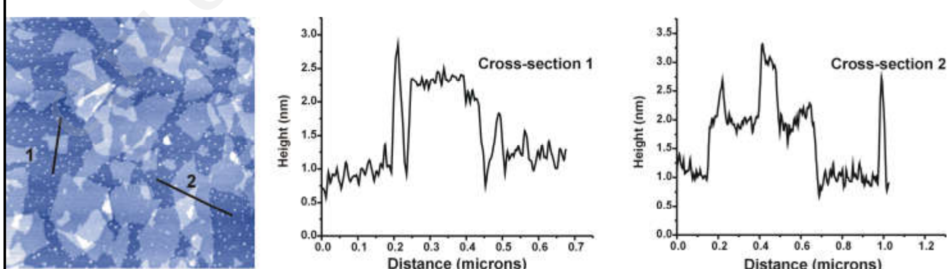


Functionalized Graphene Oxide

- **Surface hydroxyl groups of GO can be chemically modified by derivatization with organic isocyanates**
- **Isocyanate-treated GO loses ability to exfoliate in water but exfoliates in polar aprotic solvents**



Exfoliation of Functionalized GO



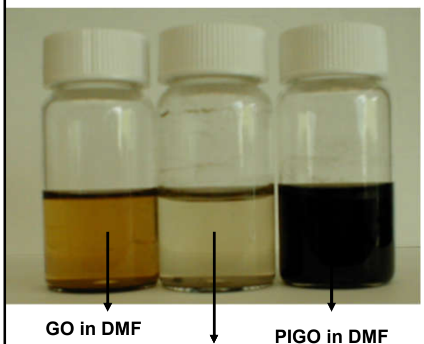
Phenyl isocyanate-treated GO (PIGO) exfoliated in DMF

Functionalized graphene oxide sheets in organic solvents.

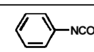
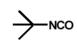
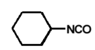
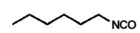
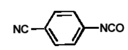
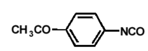
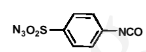
Stankovich, S. *et al.*, *Carbon* **2006**, 44(15), 3342-3347.

Chemically-functionalized Graphene Sheets

PIGO = Phenyl isocyanate-treated GO



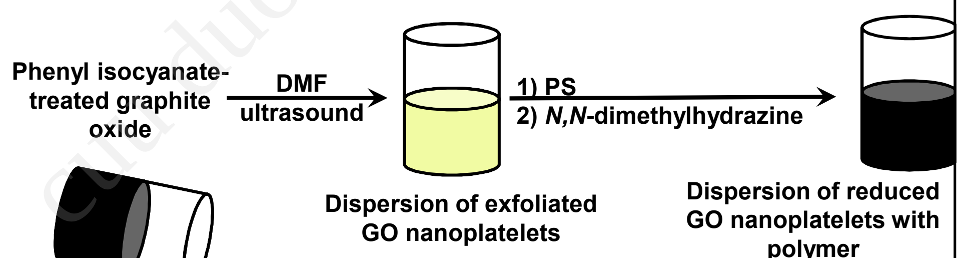
It is possible to control the degree of functionalization.

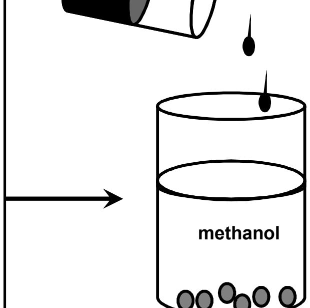
Entry	Isocyanate[a]	Graphene-C/N ratio
1		15.7 (8.7[b])
2		20
3		16
4		18.3
5		12.4
6		7.6
7		16.1

[a] Reaction Conditions: GO (50 mg), isocyanate (2 mmol) in anhydrous DMF (5 mL), 24 h. [b] Reaction time was 7 days.

Stankovich, S. *et al.*, *Carbon* **2006**, 44(15), 3342-3347.

CReGO Nanocomposites





- Reduction without polymer results in agglomeration of the reduced platelets
- Polymer coats reduced nanoplatelets and prevented their agglomeration, giving true nanocomposite

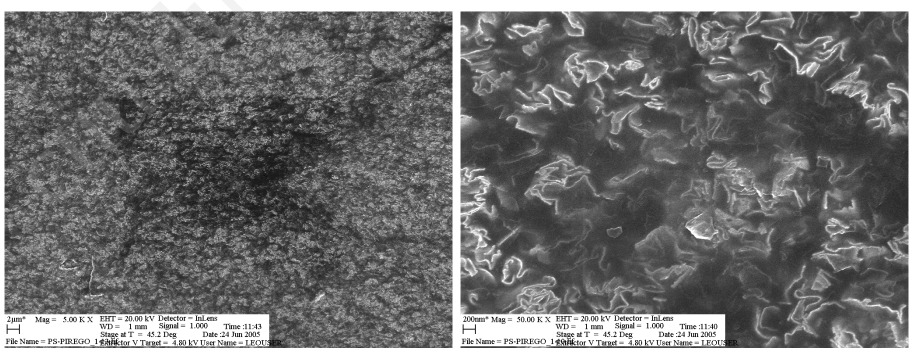
Nanocomposite Synthesis

Reduction of exfoliated PiGO in DMF with polystyrene | Coagulation of the composite with MeOH | Hot-pressing

- **Phenyl isocyanate-treated graphite oxide (PiGO) exfoliated in DMF and reduced with *N,N*-dimethylhydrazine in presence of polystyrene**
- **Graphene/polymer composite isolated by coagulation with antisolvent (methanol)**
- **Reduction without polymer results in agglomeration of the reduced sheets**
- **Polymer coats reduced sheets and prevents their agglomeration**

Stankovich, S. et al., Graphene-based Composite Materials. *Nature* **2006**, *442*, 282-286.

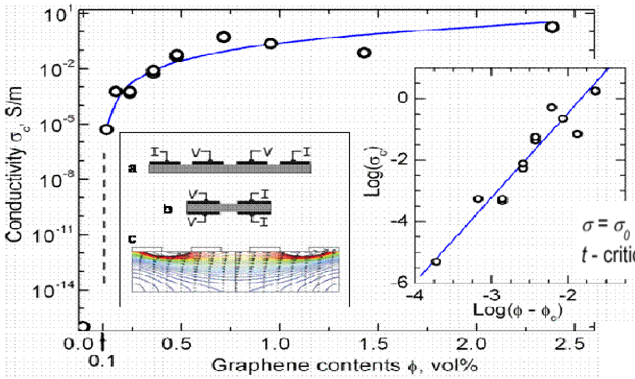
PS/Graphene Composite 1%



- **The reduced sheets have a crumpled morphology**
- **Even at 1% loading the polymer matrix apears completely filled with sheets**

Stankovich, S. et al., Graphene-based Composite Materials. *Nature* **2006**, *442*, 282-286.

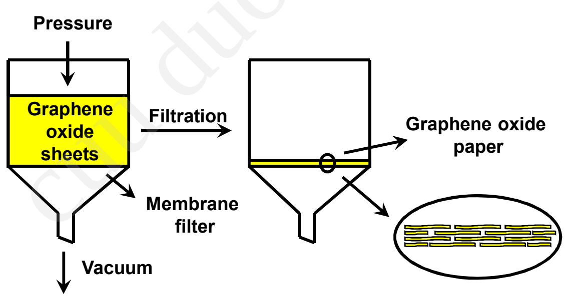
Electrically Conductive Nanocomposites

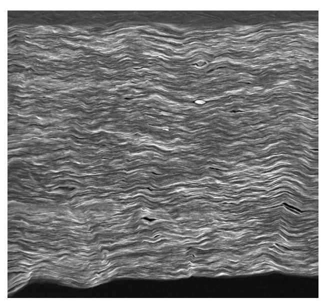


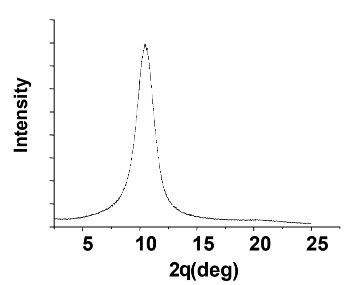
- •Sheets well exfoliated and dispersed in polymer matrix impart electrical conductivity at a very low loading level
- •Low electrical percolation threshold of graphene composite rivals results obtained with carbon nanotubes

Stankovich, S. *et al*., Graphene-based Composite Materials. *Nature* **2006**, *442*, 282-286.

Graphene Oxide Paper

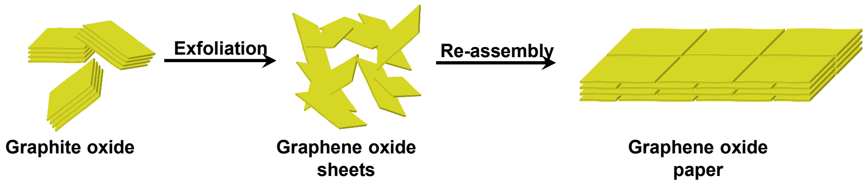


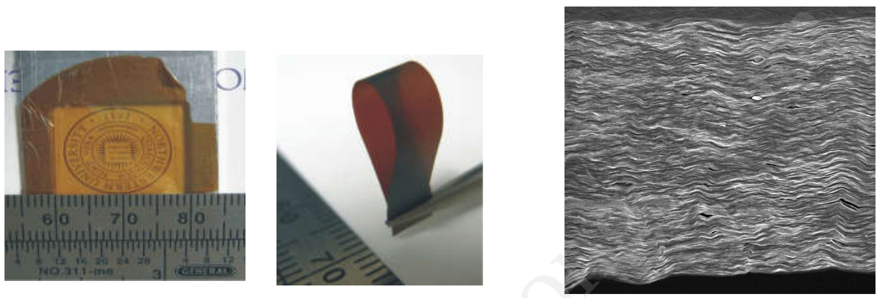




Stankovich, S. *et al*. *Nature* **2006**, *448*, 457-460.

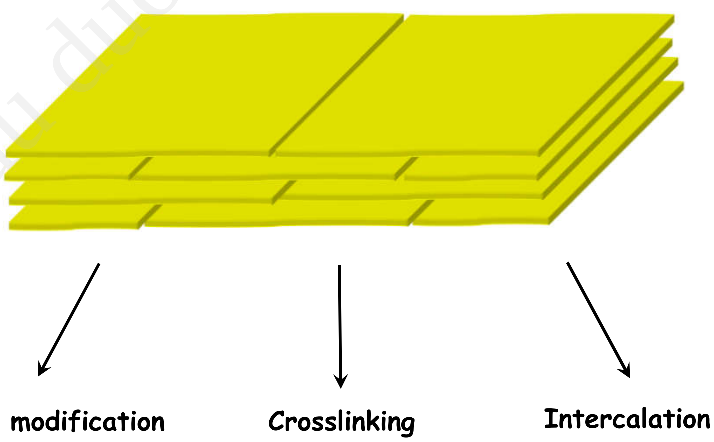
Processing Scheme





Stankovich, S. *et al*. *Nature* **2006**, *448*, 457-460.

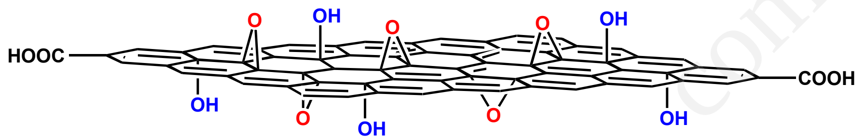
Possibilities



A number of new materials can be prepared!

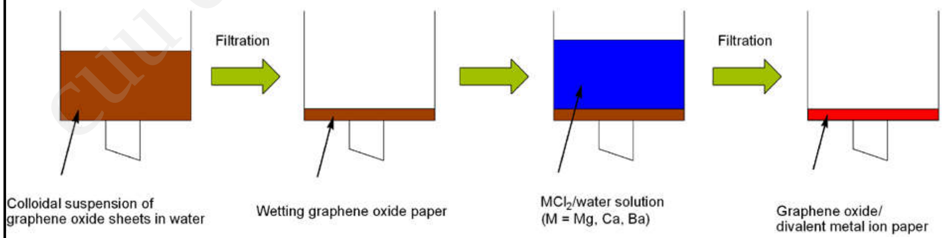
Strategy for Enhancement of Mechanical Properties

- Introducing divalent cations (Mg^{2+}, Ca^{2+}, Ba^{2+})
- Carboxylic acid groups on edges or hydroxyl and epoxy groups on basal planes <—> cross-linking individual graphene oxide sheets?



Graphene oxide sheet

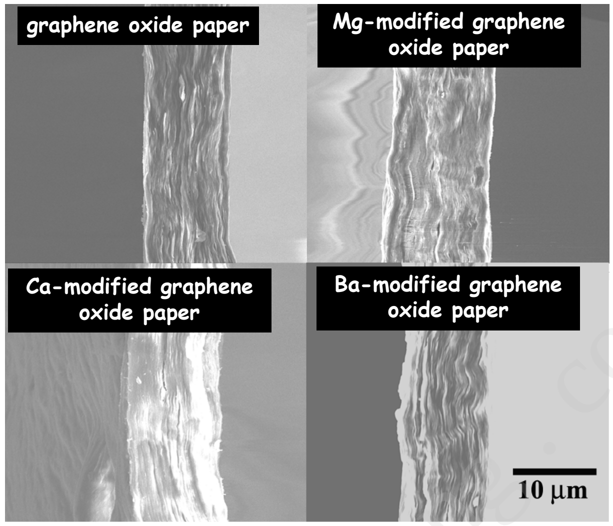
Preparation of M-Modified Graphene Oxide Papers by Continuous Filtration Method



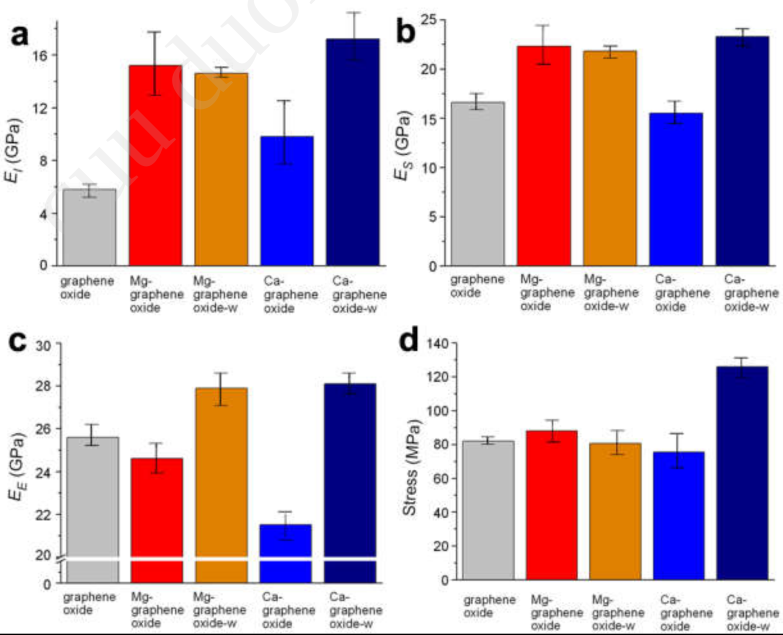
As-Prepared or

Rinsed: 3 times by adding water

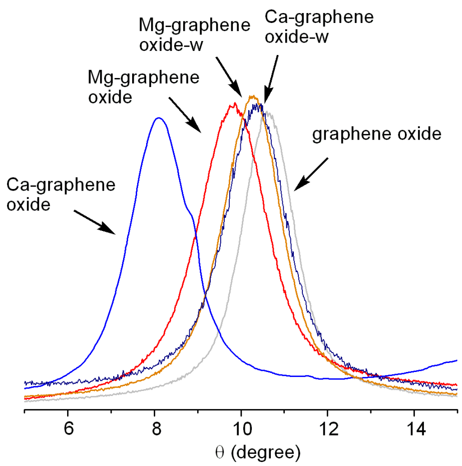
SEM Images of M-modified Graphene Oxide Papers



Mechanical Properties of Unmodified and M-modified Graphene Oxide Papers



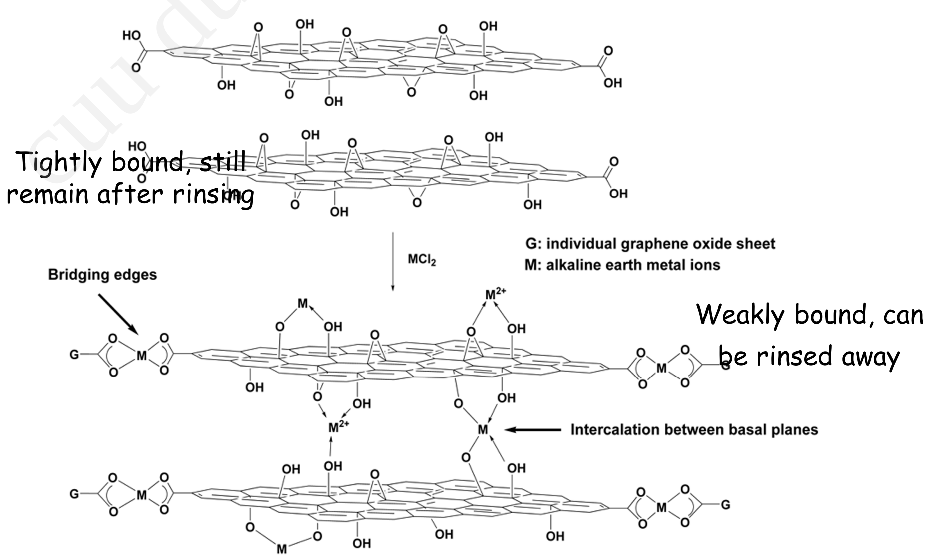
XRD data of Graphene Oxide Papers



Sample #	*d*-spacing (nm)
As-prepared Mg-modified graphene oxide paper	0.90
As-prepared Ca-modified graphene oxide paper	1.09
Rinsed Mg-modified graphene oxide paper	0.86
Rinsed Mg-modified graphene oxide paper	0.85
graphene oxide	0.83

Mg and Ca-modified samples contain intercalated metal species which can be removed by water washing.

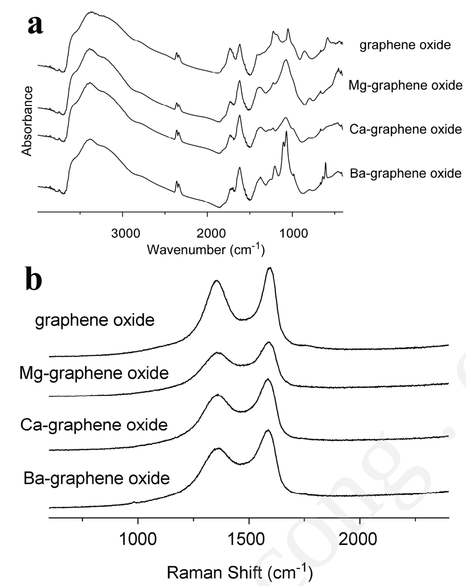
Model for connections between Graphene Oxide and MCl_2



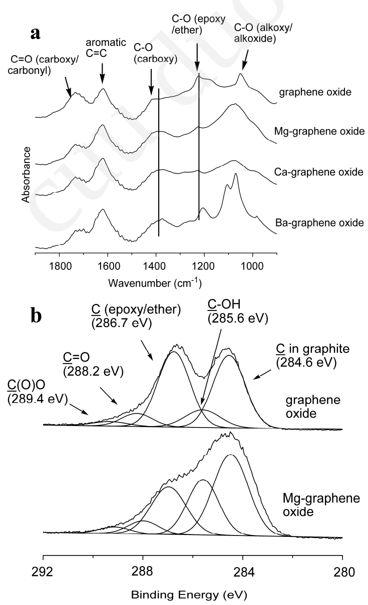
IR and Raman Spectra of Unmodified and M-Modified Graphene Oxide

IR

Raman



FT-IR and XPS Data



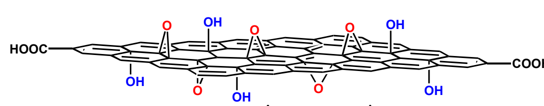
After M-modification

C=O (carboxy/carbonyl): decrease

C-O (carboxy): broad and shift

C-O (epoxy/ether): decrease

C-O (alkoxy/alkoxide): broad and increase



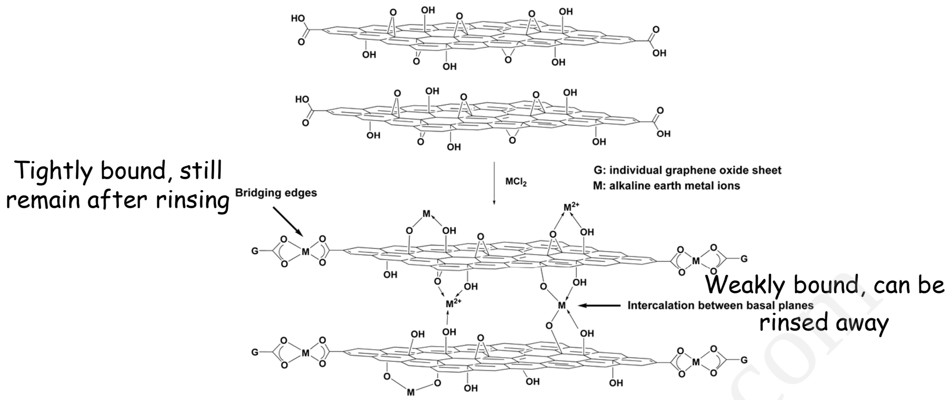
Graphene oxide

<u>C</u> (epoxy/ether): decrease

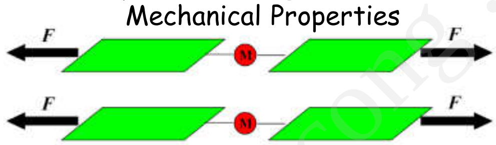
<u>C</u>-OH: increase

<u>C</u>(O)O and <u>C</u>=O: slightly shift to lower energy

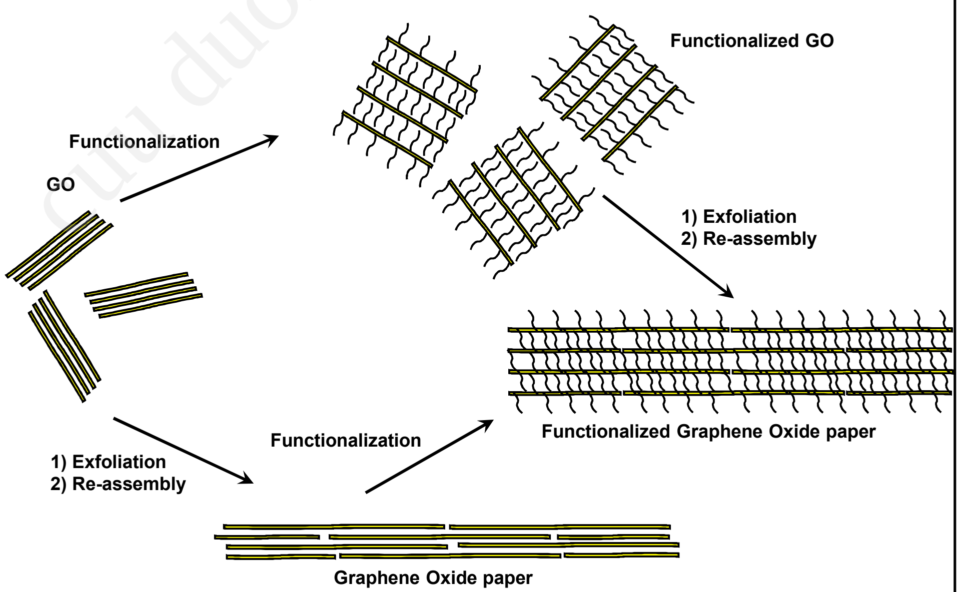
Model for Interactions between Graphene Oxide and MCl_2



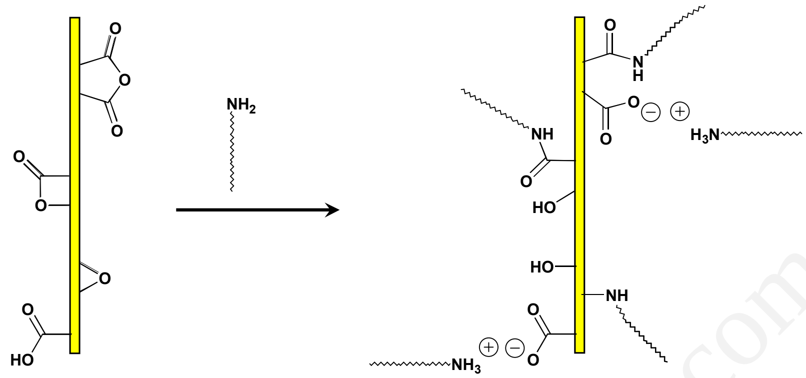
Edge-linked M-carboxylate works against Tensile Force to Enhance Mechanical Properties



Chemical Modification in Gallery



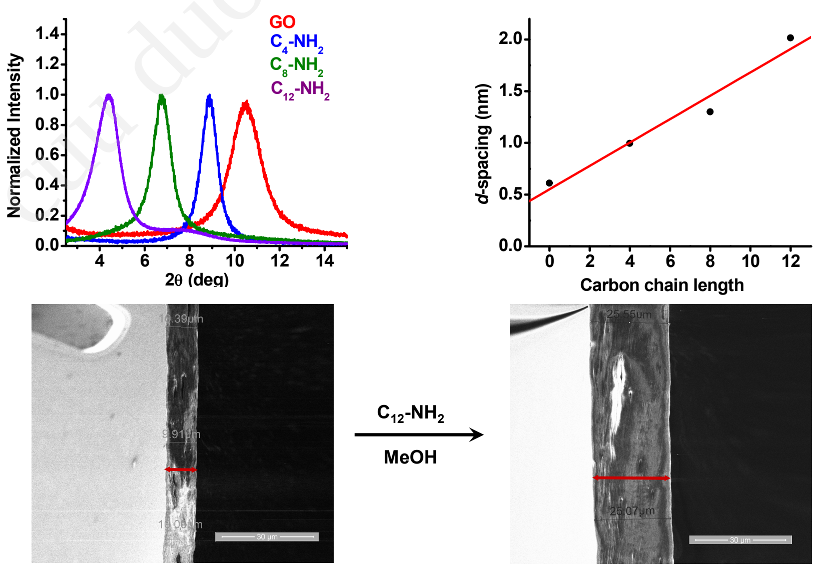
Amine Chemistry of GO



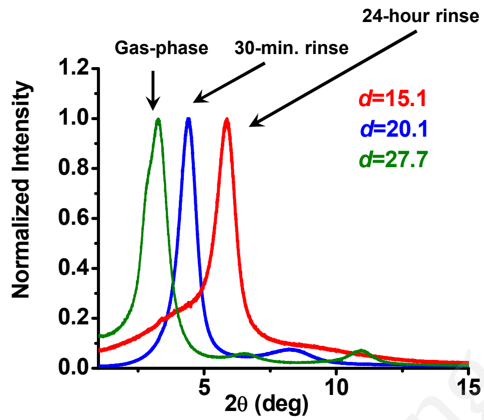
Graphene oxide paper —Alkylamine (0.1 M / MeOH→ Amine-functionalized graphene oxide paper

Alkylamines: butyl, octyl, dodecyl

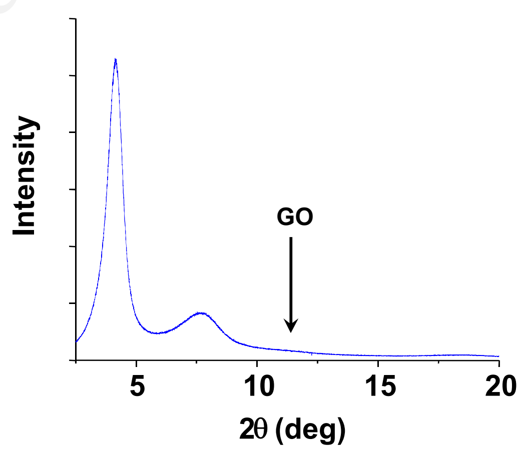
Alkyl Amine-Modified Paper



Amount of Intercalant

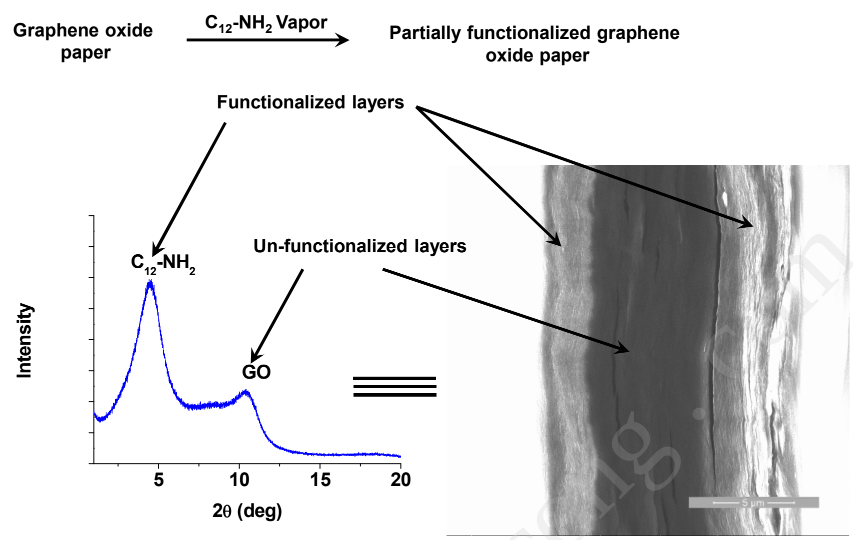


C_{16}-amine

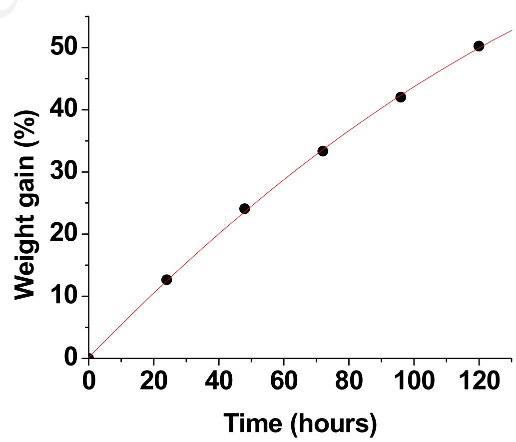


d-spacing lower than expected but sample completely intercalated

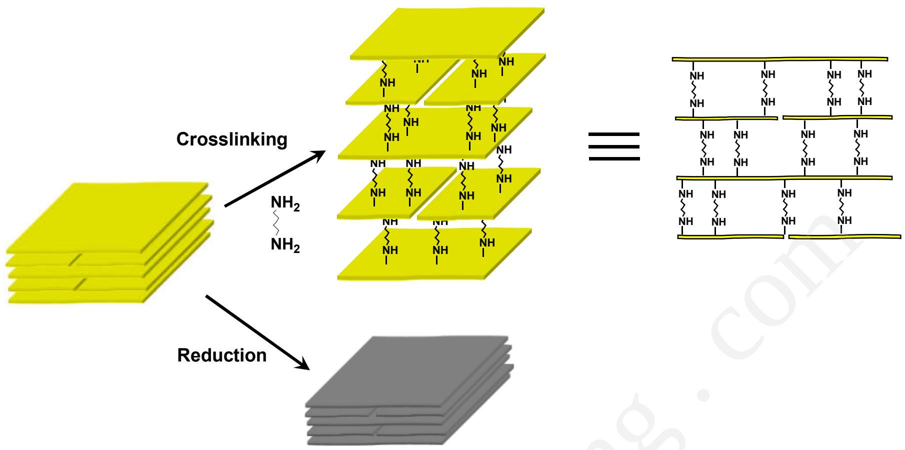
Vapor-phase Reaction



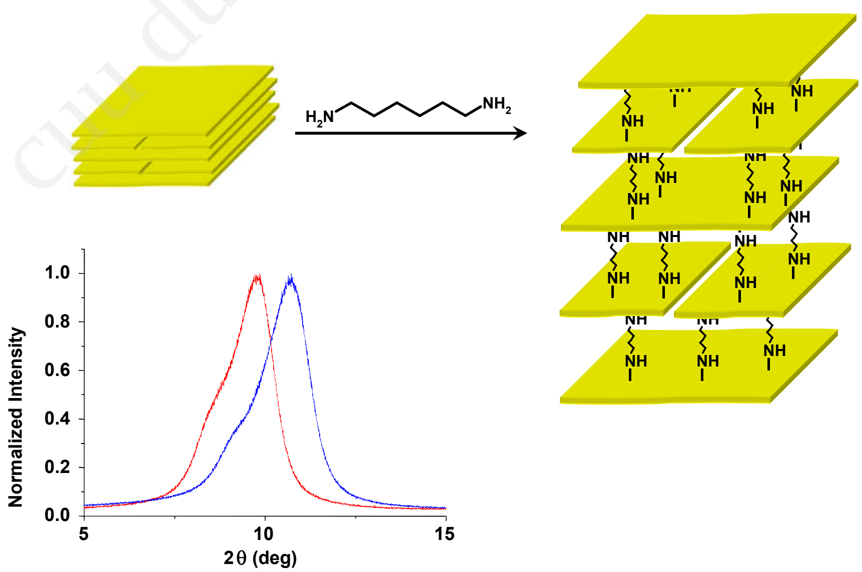
Mass Increase



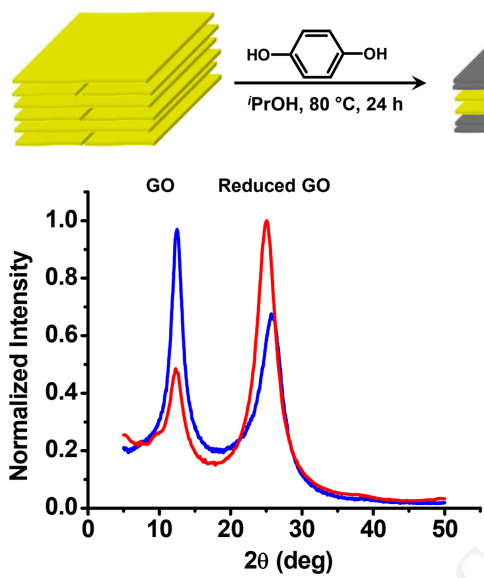
Future Steps



Crosslinked GO Paper



Reduced GO Paper



Conclusions

- **Graphene sheets prepared from graphite oxide via reduction/exfoliation approach**
- **"Water-soluble" graphene sheets prepared by non-covalent surface modification**
- **Exfoliation of graphite oxide in organic solvents was achieved opening the way to prepare graphene/polymer nanocomposites**
- **First graphene paper prepared and studied**
- **Graphite oxide is a promising source of graphene sheets for nanocomposite applications!!!**