MONASH University

SMaCLab Soft Materials and Colloids

Science

Turning graphite into gold – unpeeling molecular solids at the nano-scale

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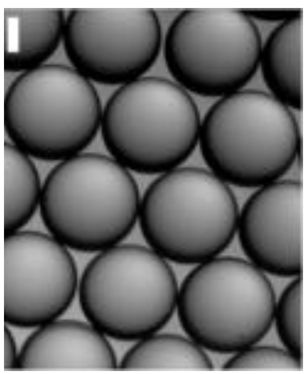
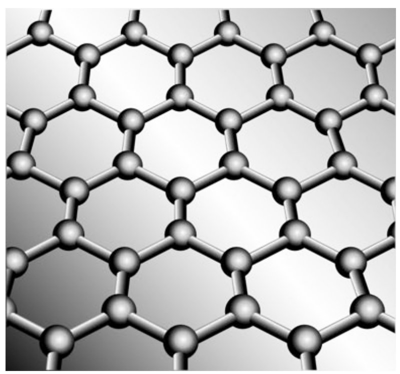
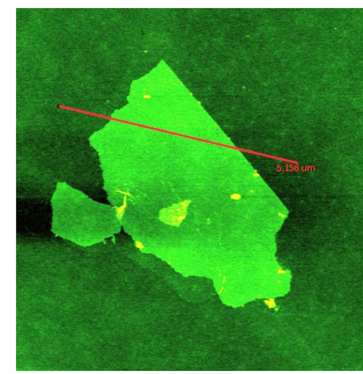
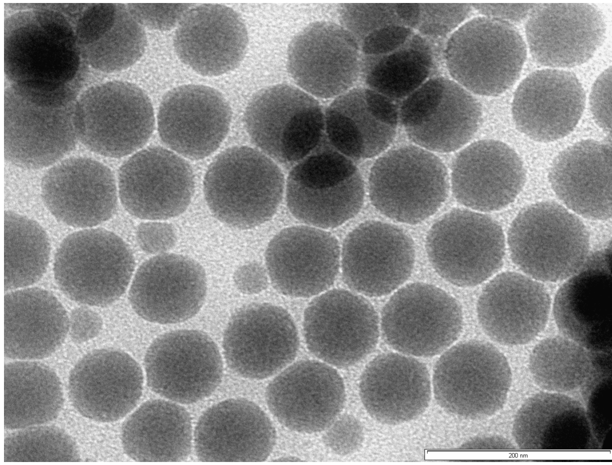
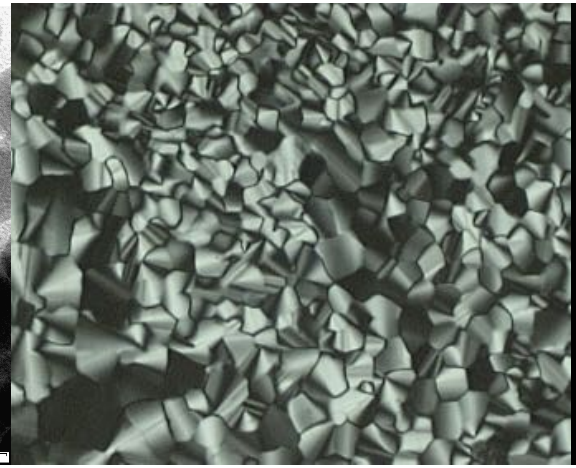






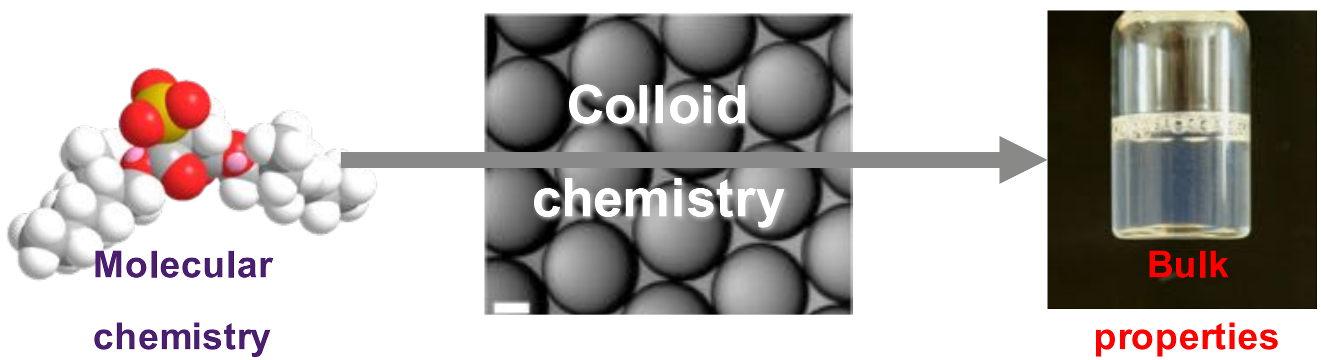
CEA November Lectures, 18th November 2016





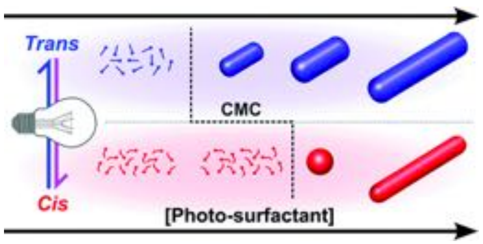
Colloids: **a group of materials characterised by a length scale (nm to μm)**

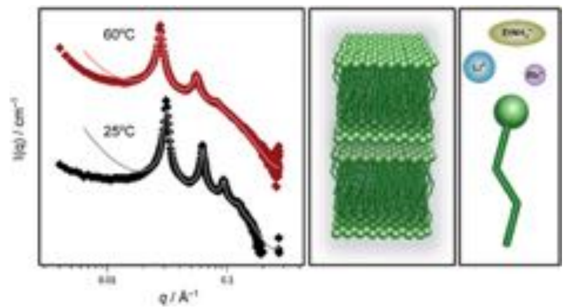
- **Droplets**: emulsions – mayonnaise, milk, butter, ice cream; liquid aerosols
- **Bubbles**: foams – sea foam, polystyrene foam, Champagne, fizzy drinks
- **Particles**: paints, engine oil, powders, solid aerosols
- **Squishy things**: liquid crystals, biological cells

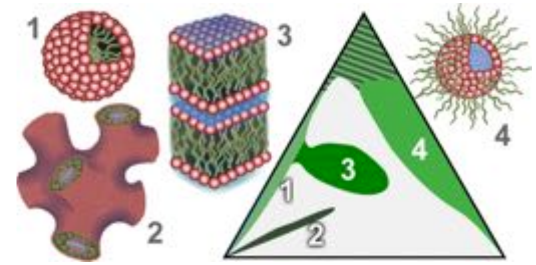


Responsive colloidal systems – for applications

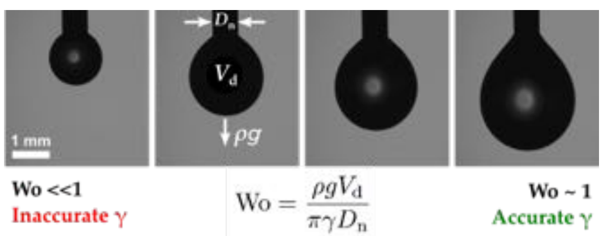
Surfactant mesophases: decontamination, stabilisation, lubrication, templating, liquid crystals, photosurfactants

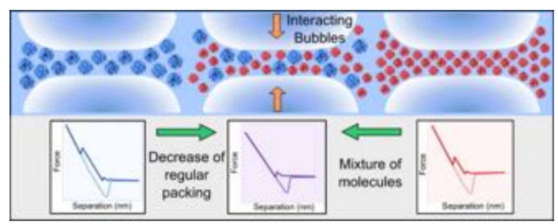


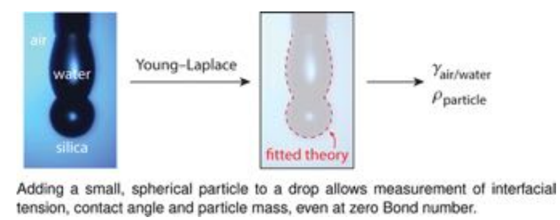




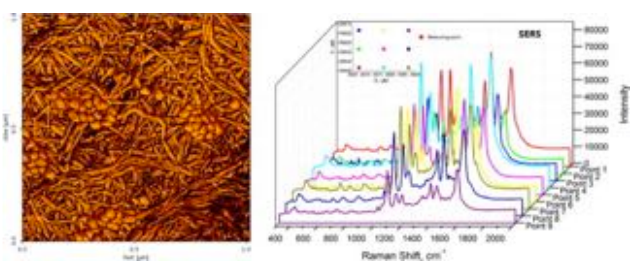
Drops and bubbles: single droplets, emulsions, foams, complex fluids, soft colloidal arrays

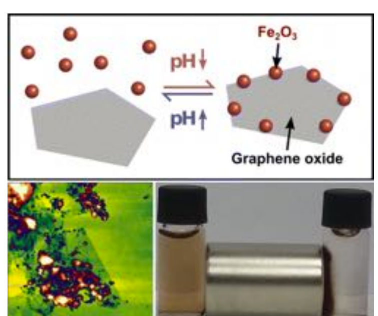


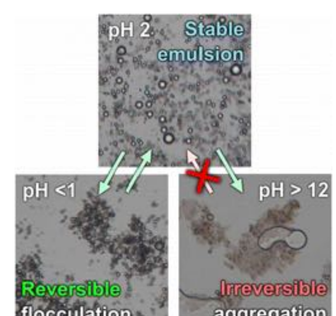


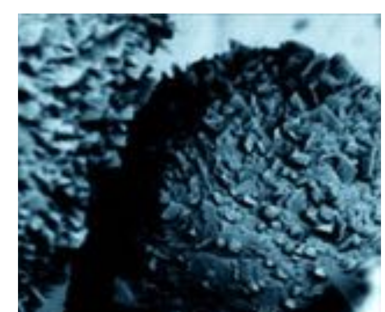


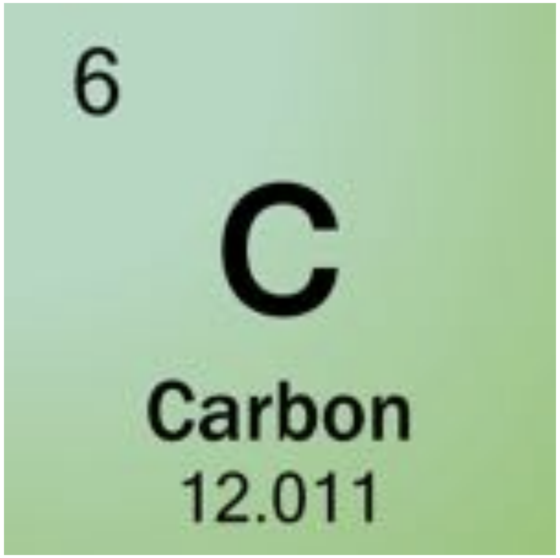
Nanomaterials: graphene, graphene oxide, composites, templating, nano-celluloses









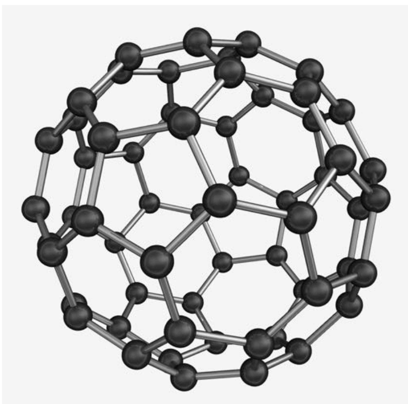


Mantra to 1st year undergrads in synthetic unit:

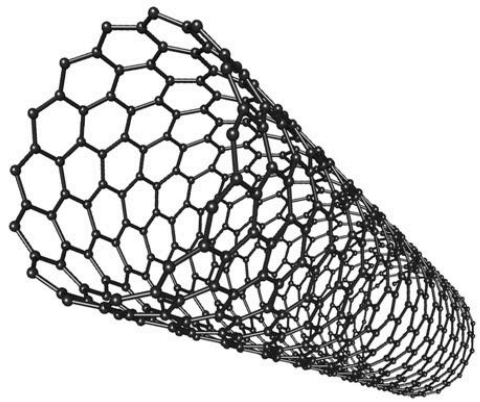
In a stable compound, carbon always has 4 bonds!

The dimensionality of carbon

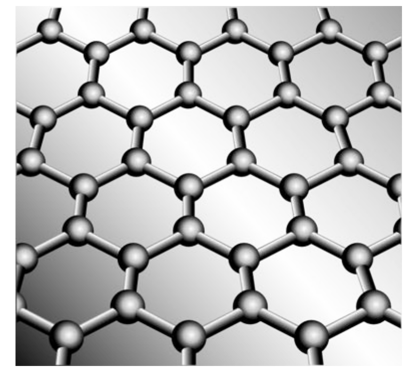
0D Buckyball



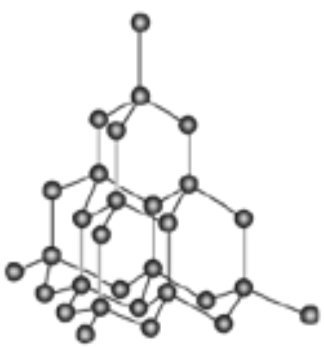
1D nanotube



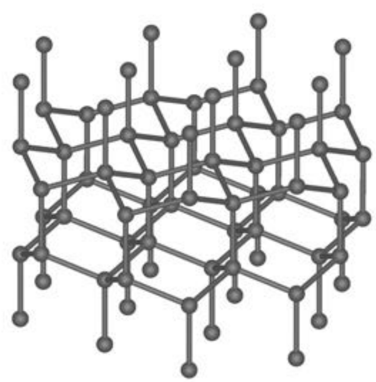
2D graphene



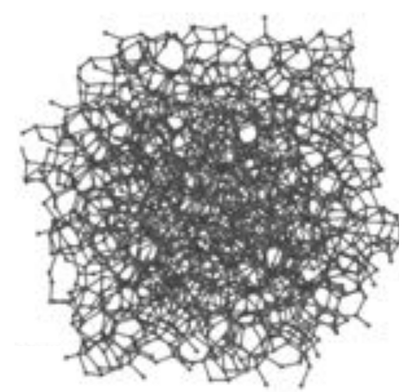
Diamond



Lonsdaleite

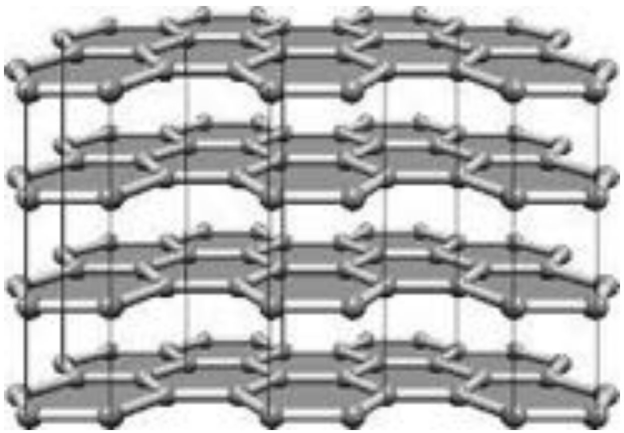


Glassy carbon



Starting with graphite…

- Layered structure: sp2 carbon atoms, 0.142 nm apart in plane (aromatic)
- ‘Spare’ electron for in-plane conduction
- Inter-plane distance 0.355 nm
- Intra-plane bonds strong (covalent); inter-plane bonds ’weak’ (Van der Waals)
- Hence layers can slide past each other under shear = lubricating



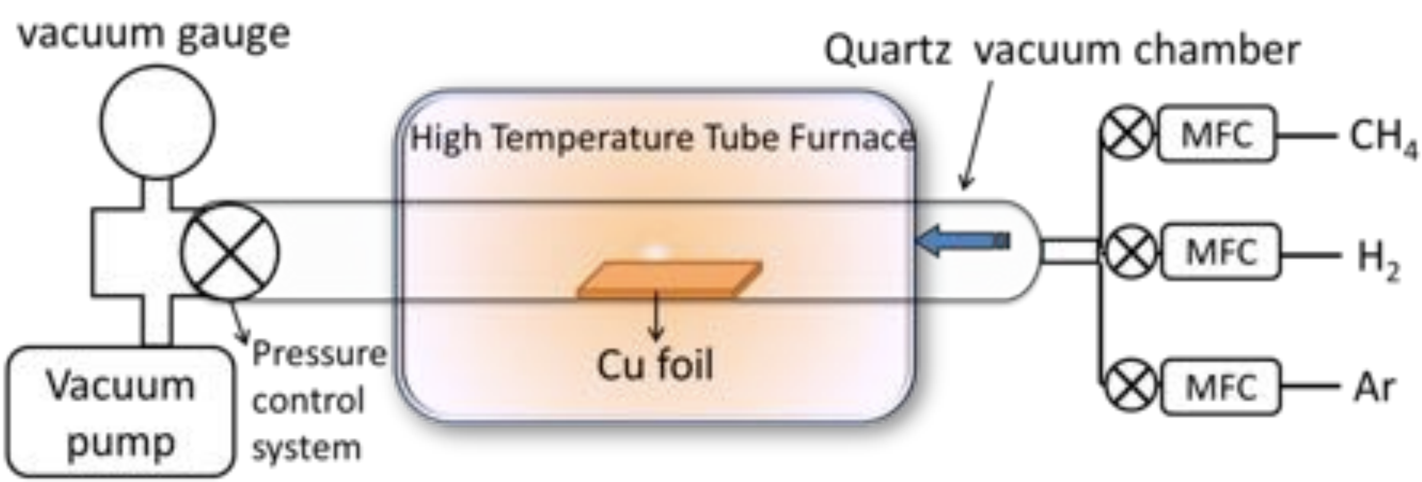
Graphite → graphene

- Three major classes of technique:
  - 1) **Bottom-up**
    - Chemical vapour deposition
    - Synthesis from molecular building blocks (hypothesised)
  - 2) **Top-down**
    - Mechanical exfoliation via shear (Scotch® tape)
    - Liquid shear processes (sonication)
  - 3) **Oxidation/reduction (wet chemical) route**
    - Oxidise graphite to graphene oxide (GO), then reduce to ‘graphene’*

[*actually, reduced graphene oxide, rGO)

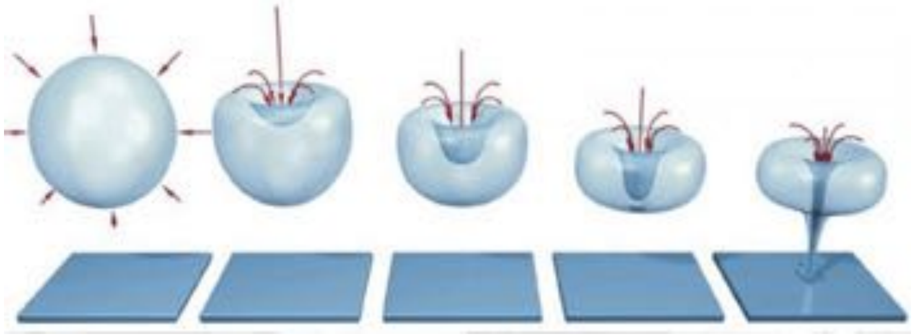
Chemical vapour deposition (CVD)

- Makes *very* perfect graphene (no defects)
- Good if you want one layer (e.g. electronics)
- Expensive, not very scalable



Mechanical exfoliation

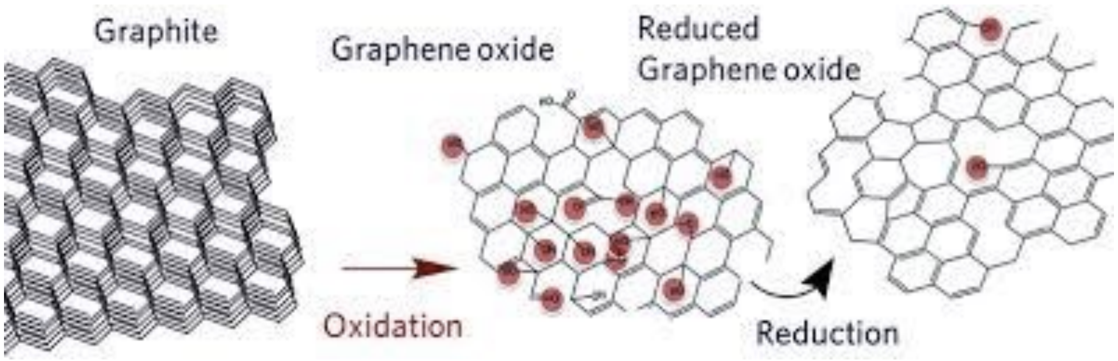
- Makes *fairly* perfect graphene (few defects)
- Good if you want solution processable, often few layer (rarely monolayer)
- High energy, slow, not very scalable



The wet chemical route

We are chemists, after all!!

- Oxidise graphite using very strong oxidants
- Water spontaneously exfoliates the oxidised graphite structure
- Chemical reduction to remove oxygen functionalities (hydrazine is good)
- Fast, cheap, scalable, gives monolayer product
- Lots of defects, reduced conductivity, waste issues…

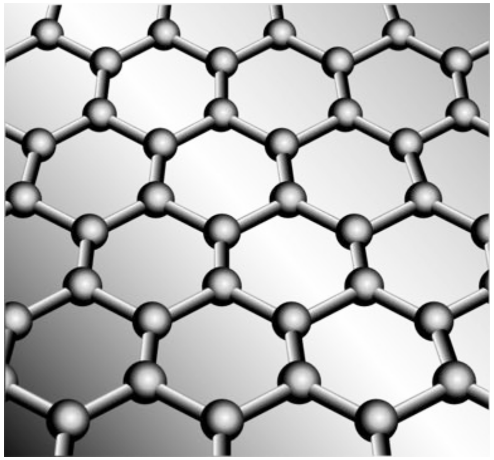


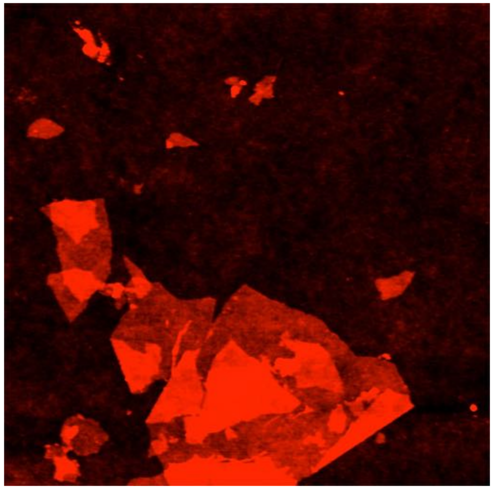
Graphene oxide

- For a colloid scientist, graphene oxide is **much more interesting** than graphene!
- Water dispersible, surface active, forms liquid crystals, etc.
- Very pH sensitive – responsive materials and interfaces
- Acts as a stabiliser for emulsions – **is it a surfactant?**

= interesting colloidal properties, and

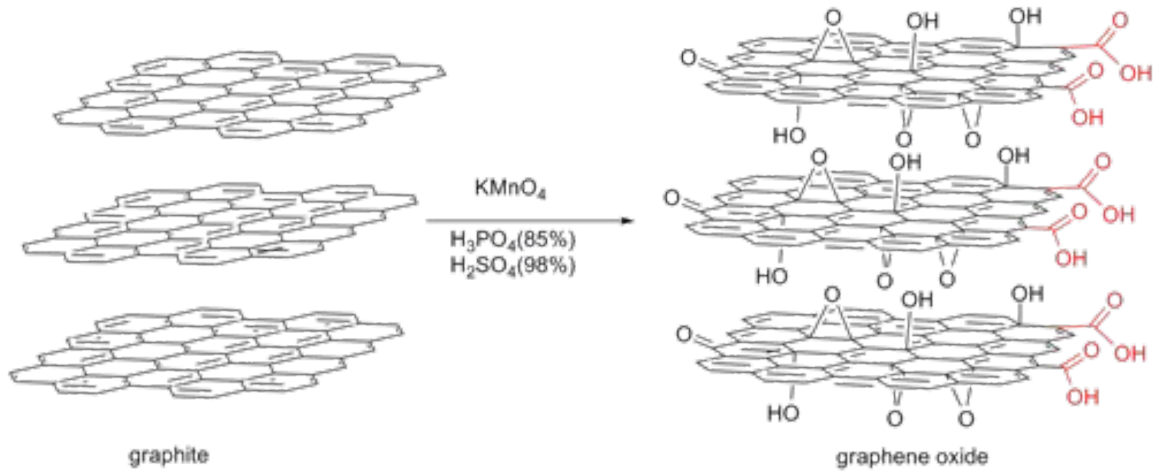
- We can make graphene oxide by the bucket-load





Graphene oxide synthesis

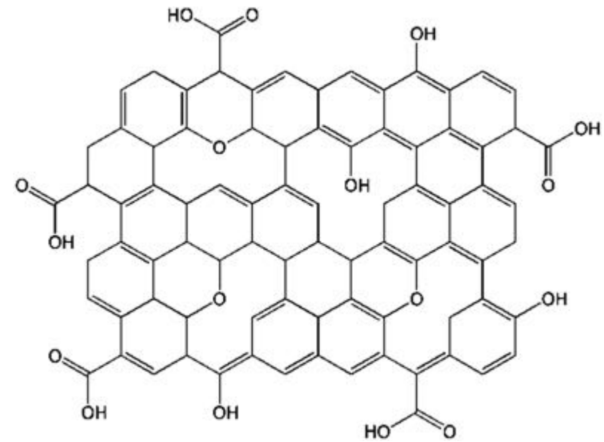
1) Oxidise
2) Exfoliate
3) Purify
    a) Centrifuge
    b) Centrifuge
    c) Centrifuge
    d) Dialyse



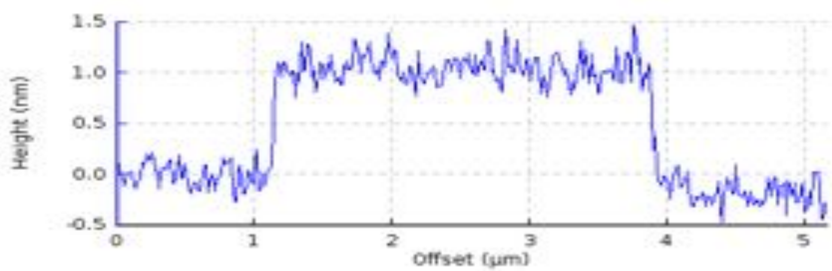
= graphene oxide, *diam*. = 1–4 µm, *thx* = 1 nm (monolayer)

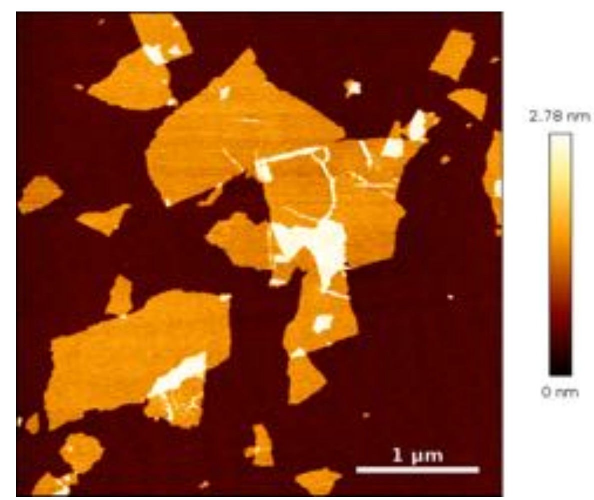
(outcome predicated on starting graphite and route)

Graphene oxide

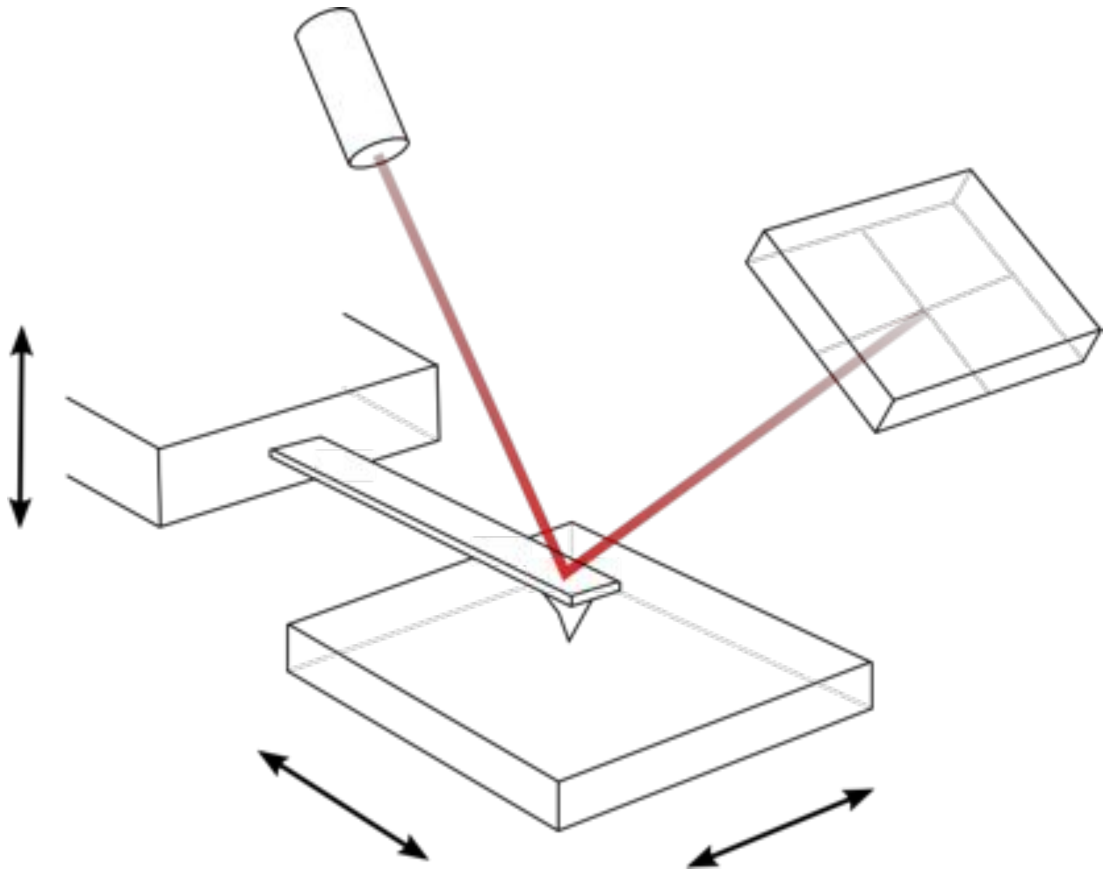


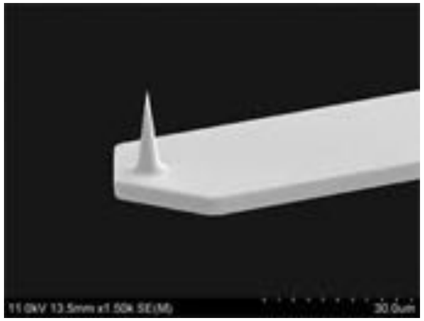
- Single sheets of sp2/sp3 carbon, decorated with many oxygen-containing functional groups:
    - Hydroxy, epoxy, carboxy
- All ~1 nm thick (monolayer)
- **Great adsorbent** for metal ions and organics
- **Can it be a stabiliser/emulsifier?**

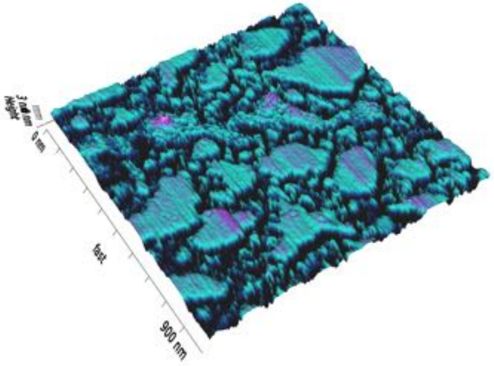


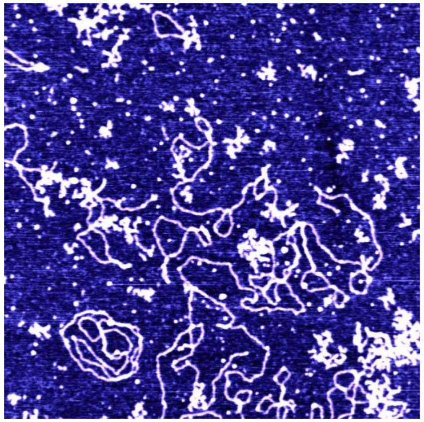


The Atomic Force Microscope

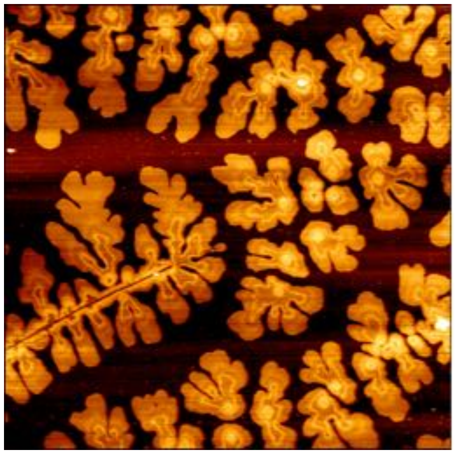
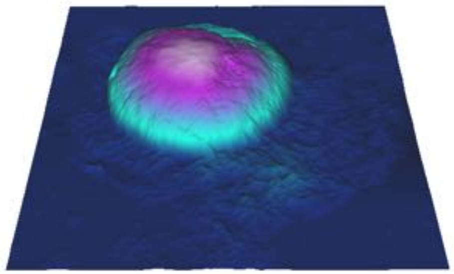
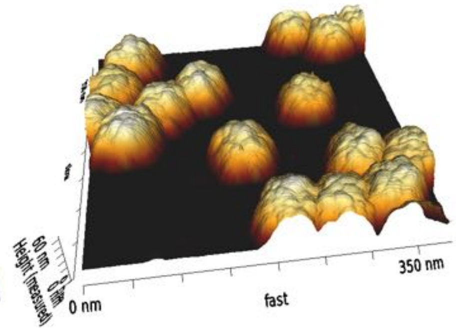


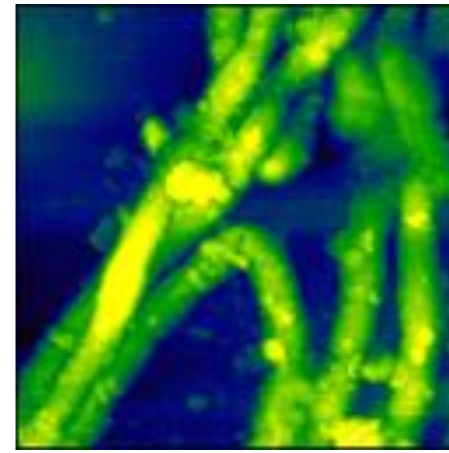
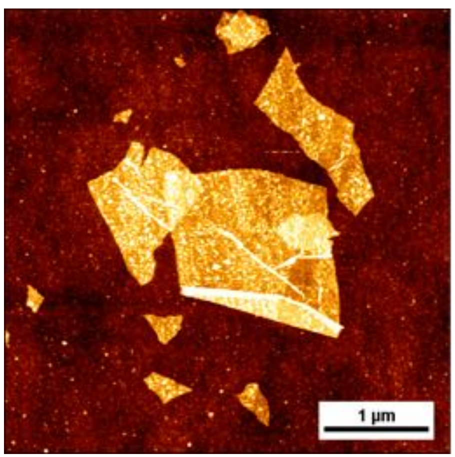


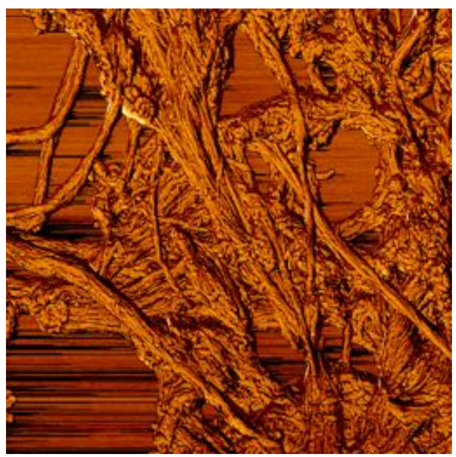
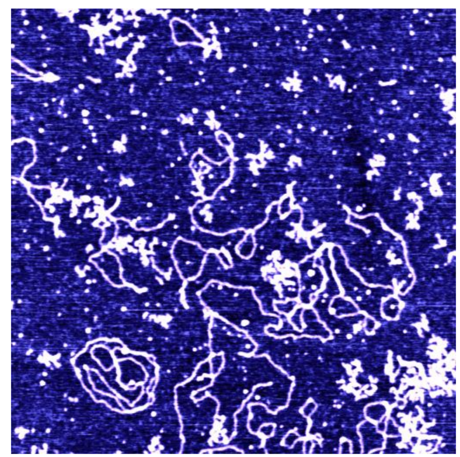
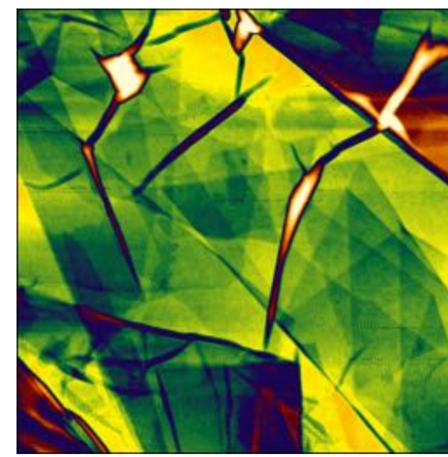




Atomic force microscopy (supported by MCATM)

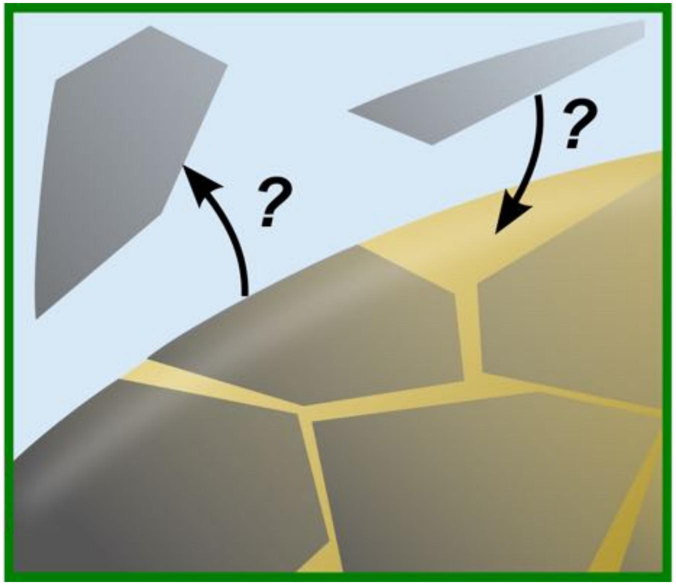



Graphene oxide at interfaces

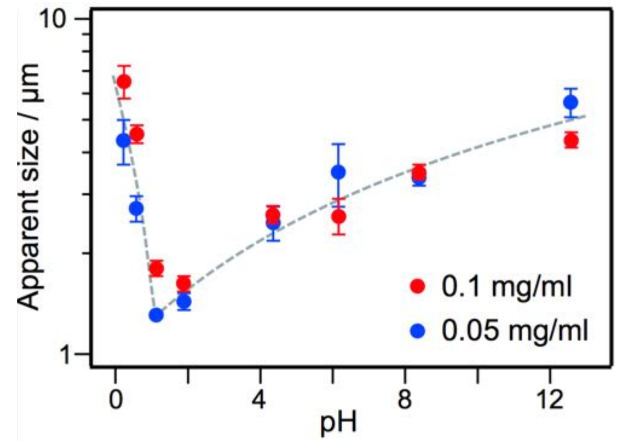
- What drives adsorption?
- Can desorption occur? If so, under what conditions?
- Need to know:

1) Charges on surfaces
2) Hydrophobicity/hydrophilicity (short range)
3) Van der Waals? (weak)

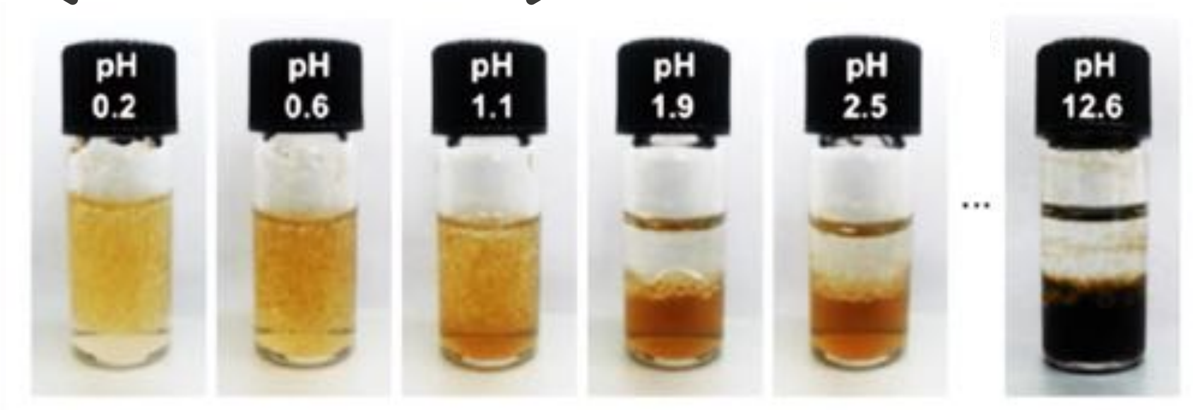


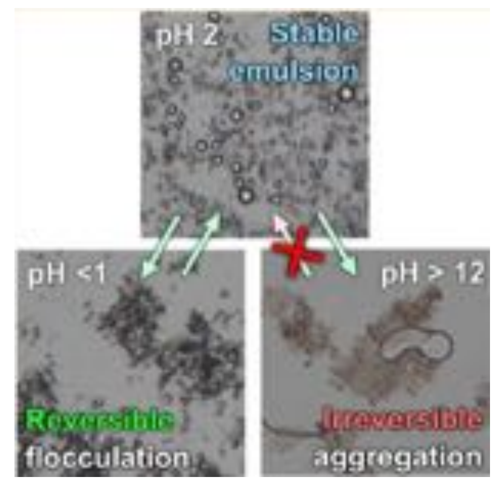
Graphene oxide – directing assembly

- Use our understanding of colloidal forces to increase adsorption at oil-water interface
- Use hydrophobia to flocculate/gel droplets
- Readjusting pH up can redisperse droplets
- At high pH, chemistry irreversibly changes, and readjusting pH does *not* restore stability



IEP window region





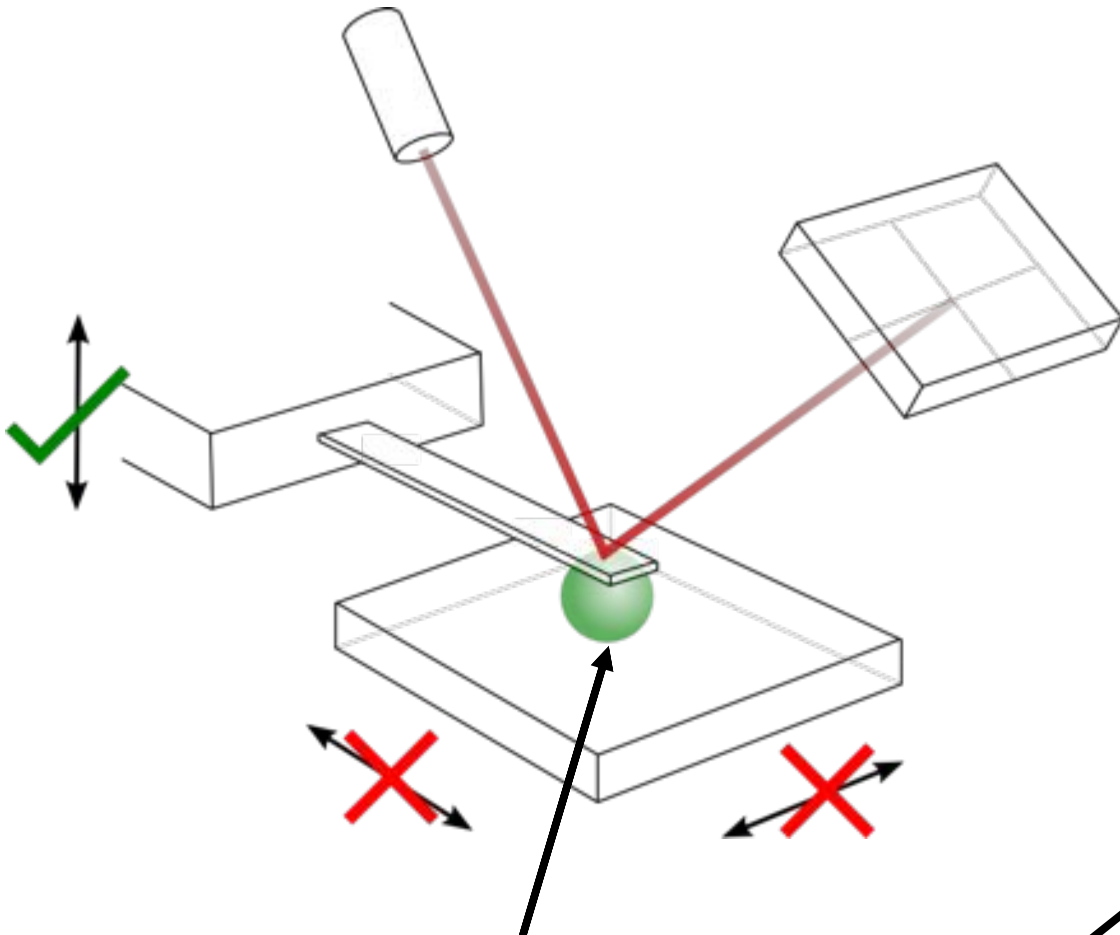
McCoy, Pottage and Tabor; *J. Phys. Chem. C* 118 (2014) 4529-4535

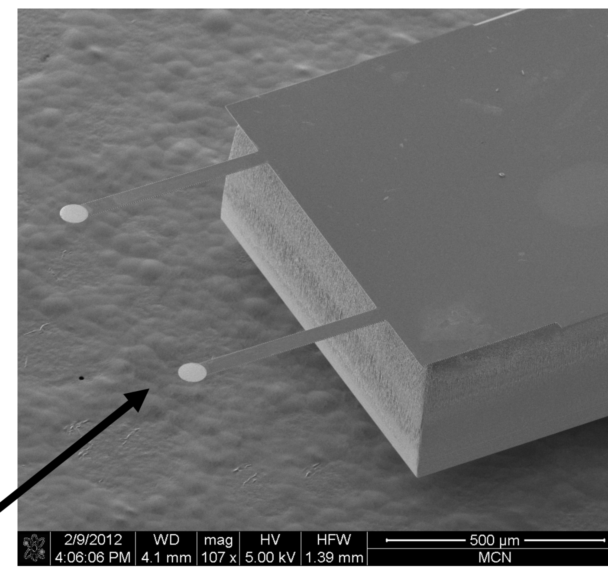
Soft colloidal AFM

AFM for colloidal forces:

- Tipless, custom cantilever to pick up drops/bubbles

- Only movement in Z-direction (up/down)



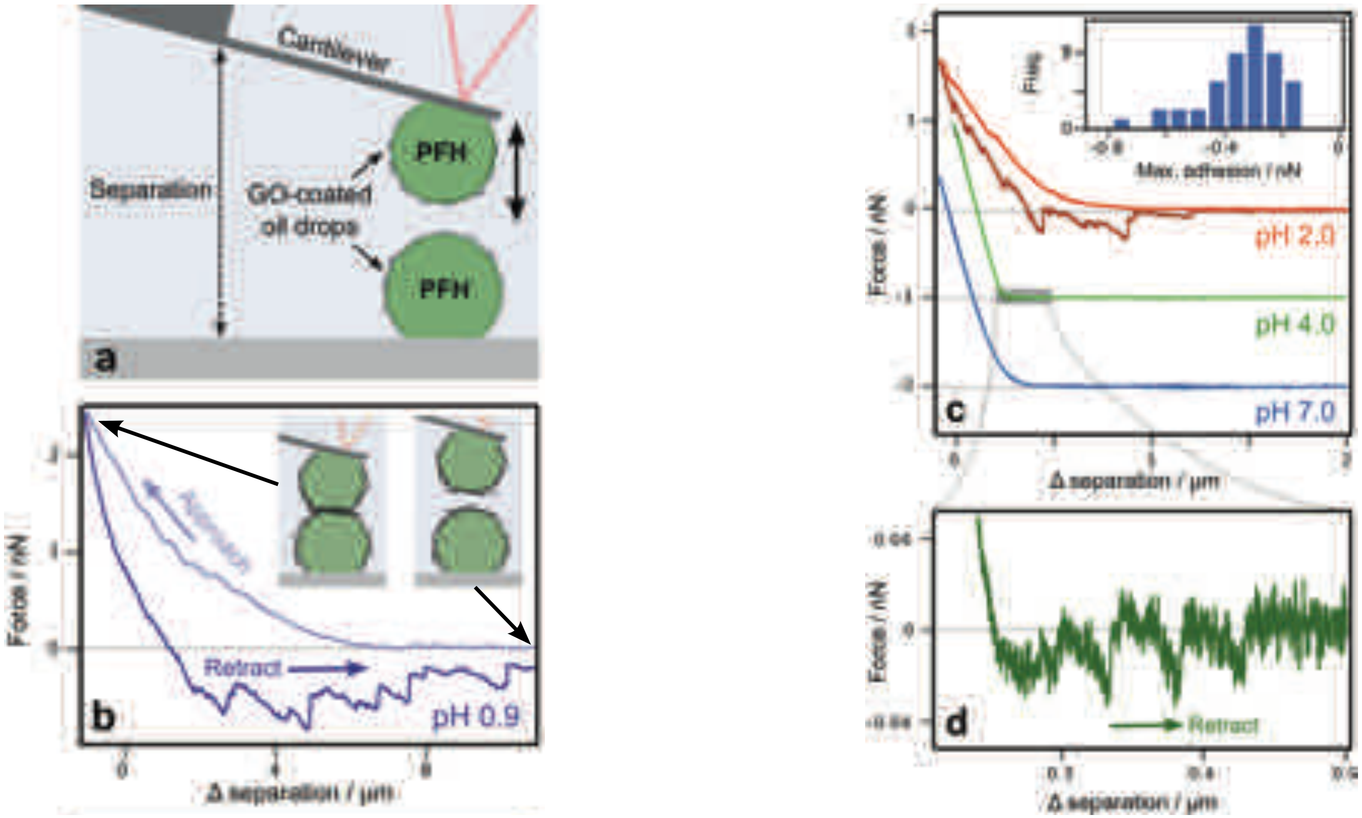


~100 µm diameter

Bottom side with gold disc:

Graphene oxide – droplet interactions

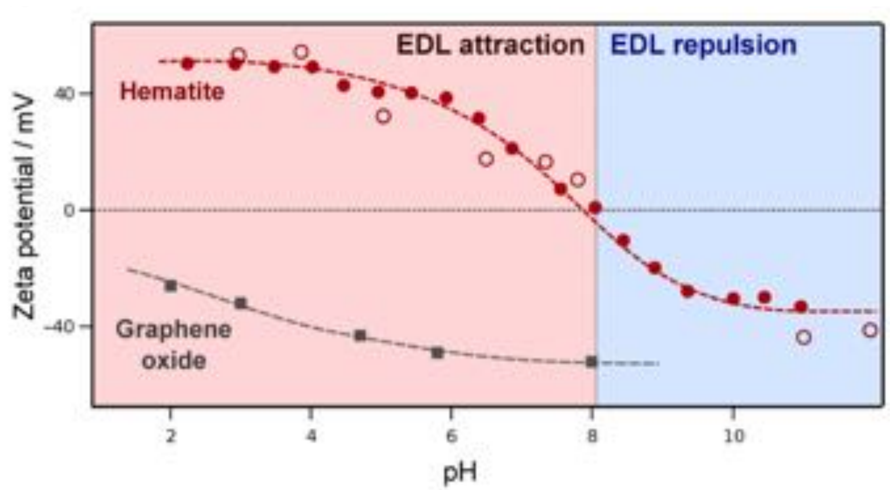
- Use AFM to directly measure interactions between pairs of droplets
- Can see detachment events at low pH, explaining flocculation



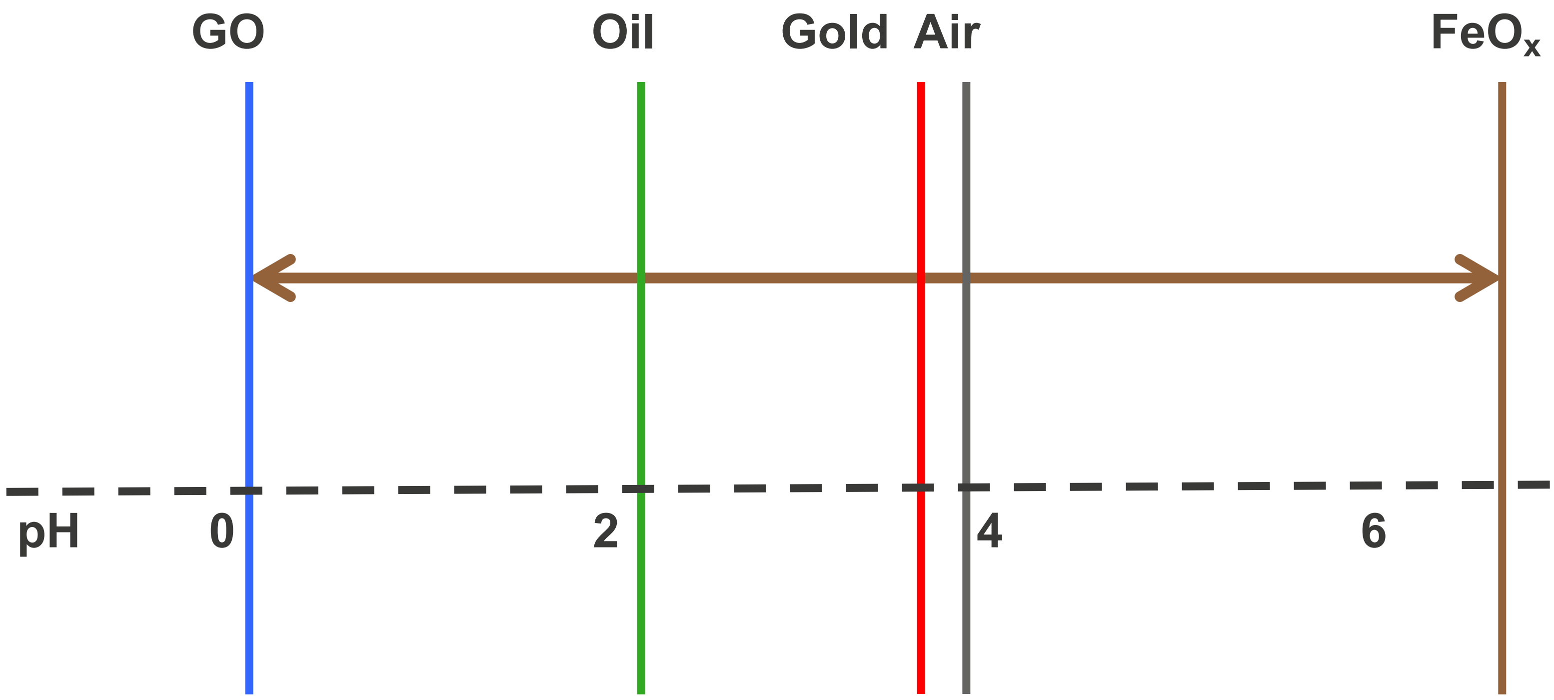
McCoy, Pottage and Tabor; *J. Phys. Chem. C* 118 (2014) 4529-4535

GO and charge-based assembly

- We want to be able to stick magnetic particles onto GO to make it easier to capture from water when used as an adsorbent
- Charge is an appealing way to stick things, as it's non-covalent (doesn't permanently change the properties of the materials)
- Can measure the charge on particles (including GO) using electrophoresis, usually via light scattering
- When charges are opposite sign, attraction expected
- Pick regions for attraction/repulsion based on isoelectric points (IEPs)

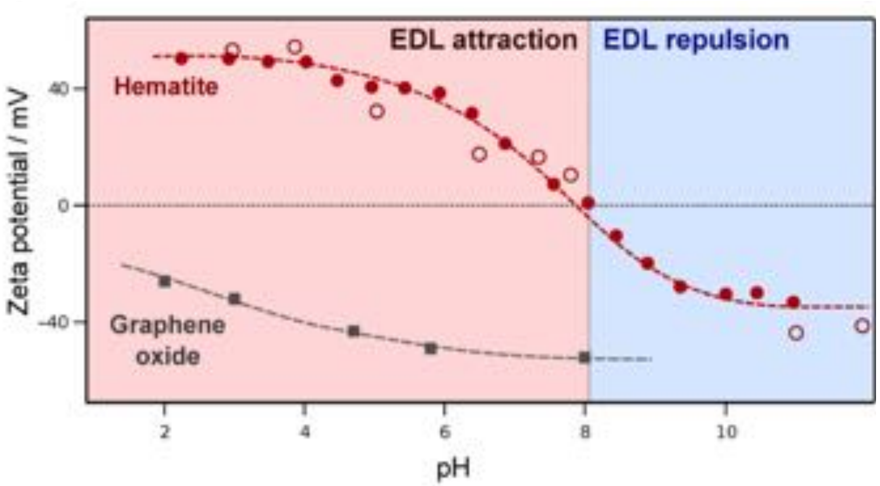


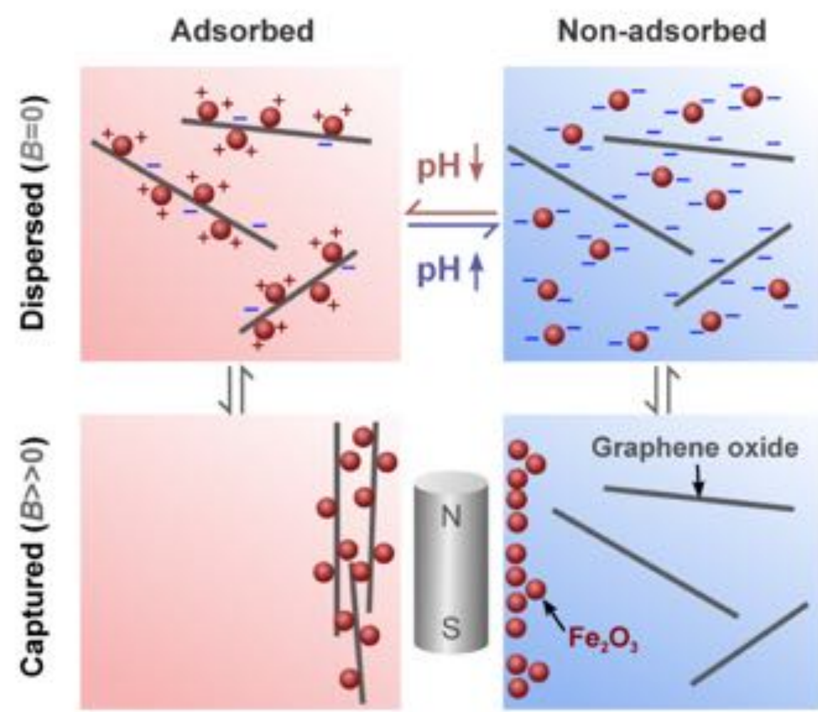
Graphene oxide – directing assembly *via* IEPs



Graphene oxide – particle assembly

- Can we use simple charge chemistry to reversibly tether particles to GO?
- Using magnetic particles, can capture on demand
- Separate using pH → recycling system

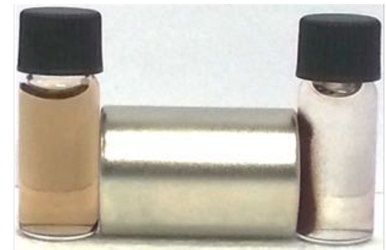


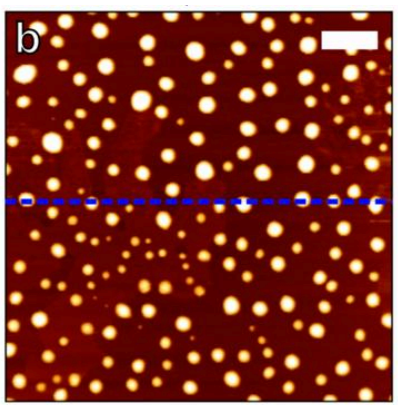


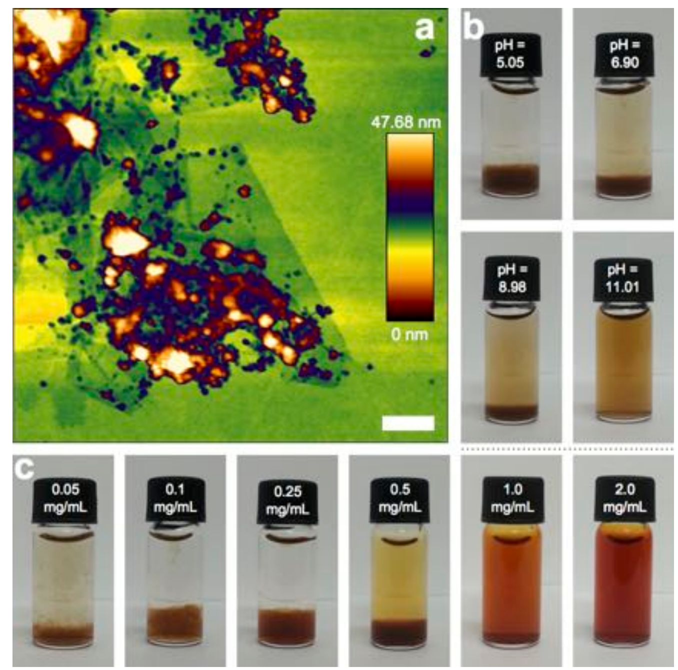
McCoy, Brown, Eastoe and Tabor; *ACS Appl. Mater. Interfaces* 7 (2015) 2124-2133

Graphene oxide – magnetic capture

- FeO_x nanoparticles adsorb to the GO, and cause heteroflocculation
- Modulated – as expected – by pH
- GO-FeO_x complex can be recovered magnetically
- Interesting 'supercharging' effects at high [particles]





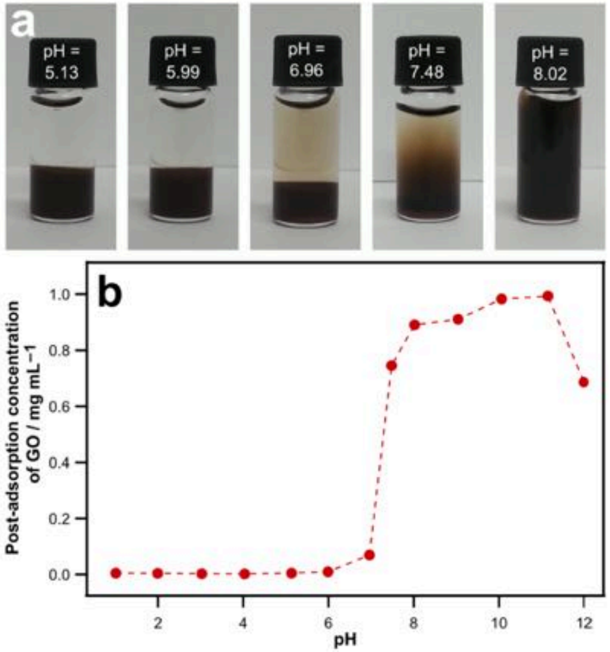


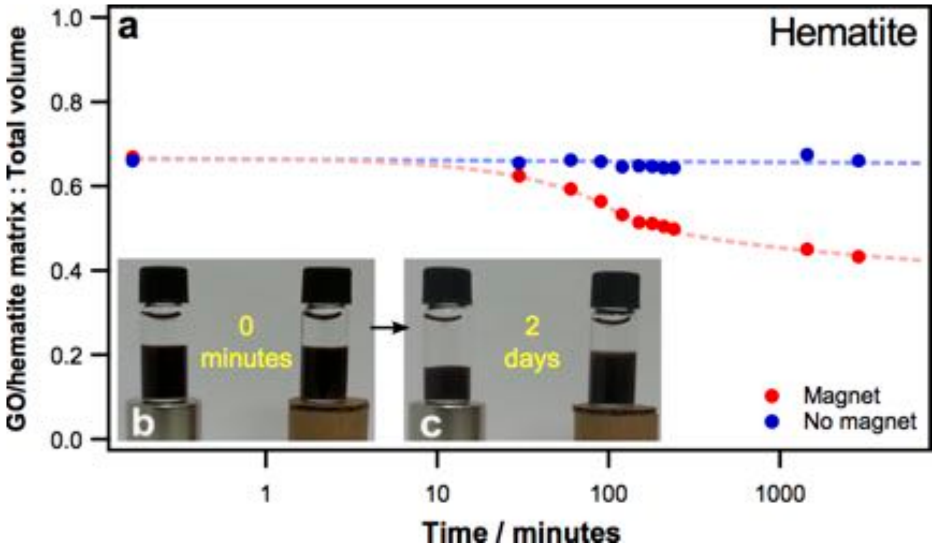
McCoy, Brown, Eastoe and Tabor; *ACS Appl. Mater. Interfaces* 7 (2015) 2124-2133

Graphene oxide – magnetic capture

- Bigger particles (~1 μm) = bigger effects!
- Magnetic dewatering + a new way to study compressional rheology?

Low pH ⟶ High pH

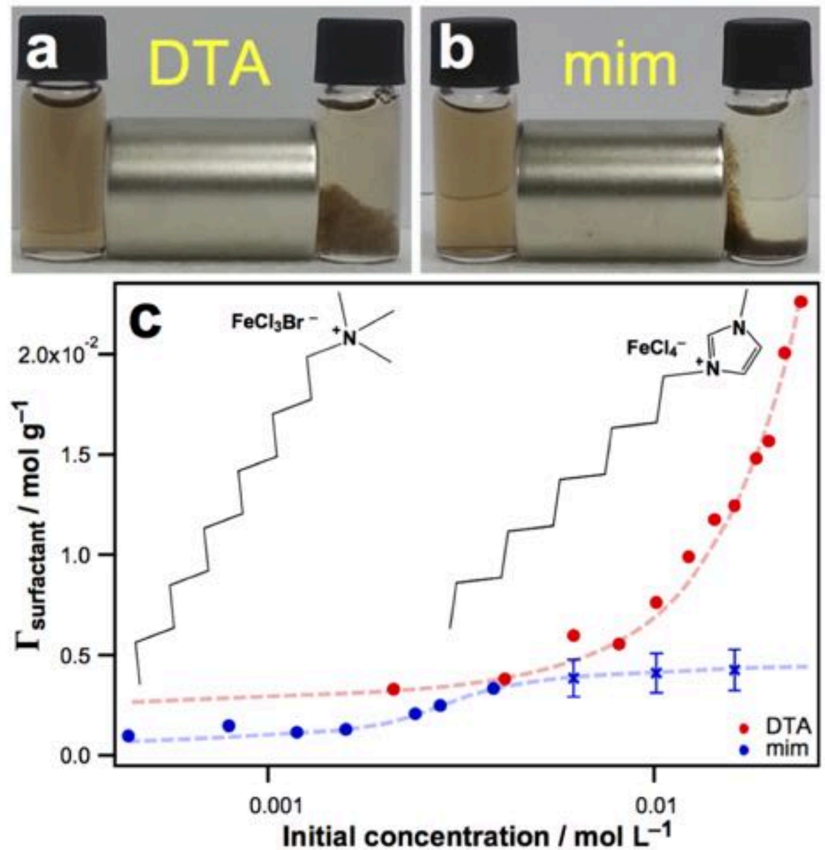




McCoy, Brown, Eastoe and Tabor; *ACS Appl. Mater. Interfaces* 7 (2015) 2124-2133

Graphene oxide – magnetic capture

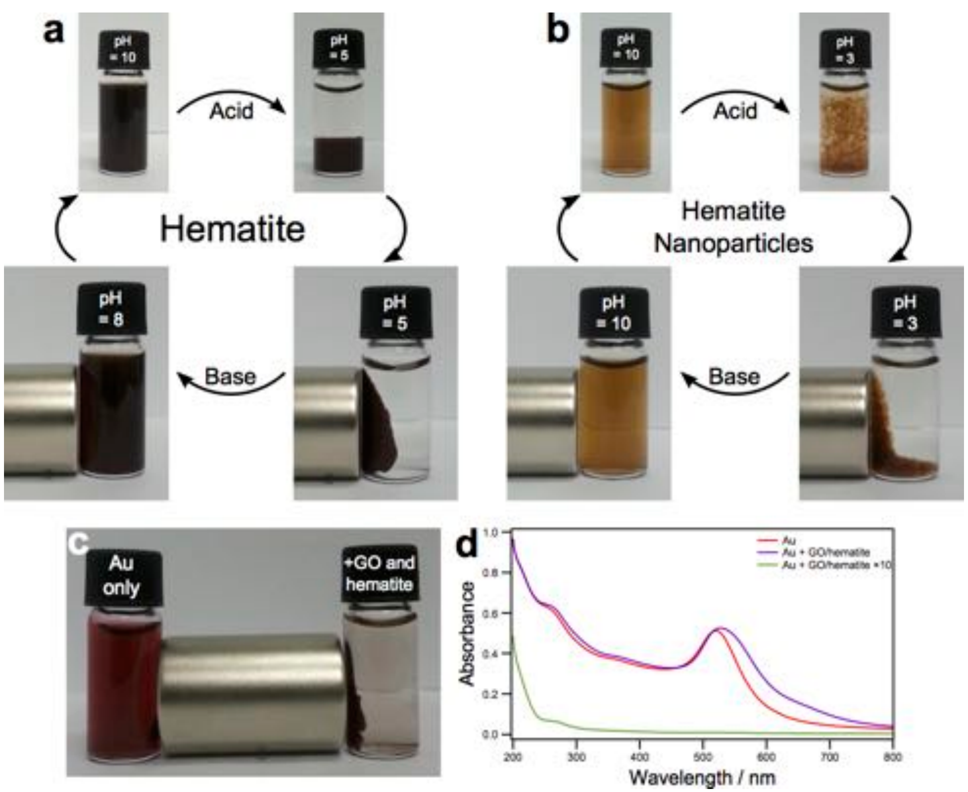
- Magnetic molecules (MILS) can also be used to recover GO
- Effects less pronounced, but easily detectable
- Raises interesting questions about the nature of adsorption
- Hoping to answer these with DFTB modelling (Dr Alister Page, Newcastle)

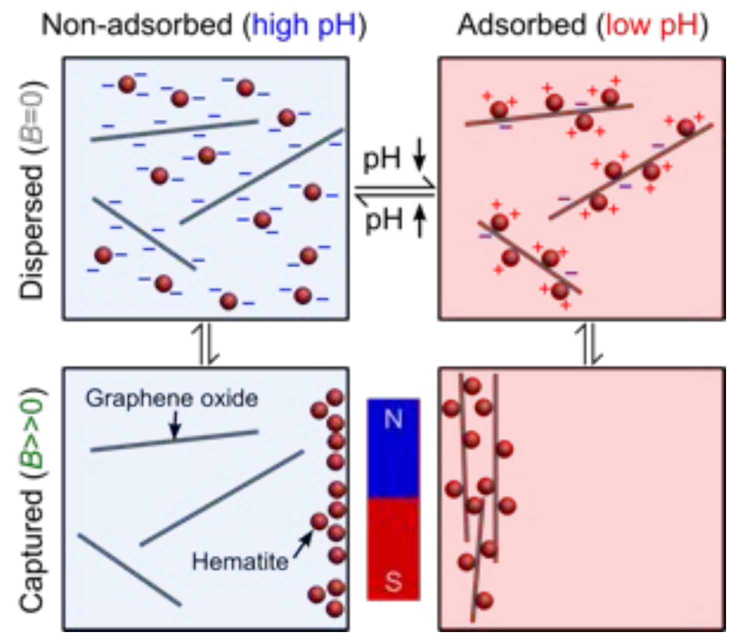


McCoy, Brown, Eastoe and Tabor; *ACS Appl. Mater. Interfaces* 7 (2015) 2124-2133

Graphene oxide – recycling nanomaterials

- Charge interactions are reversible *without loss of function* by changing pH



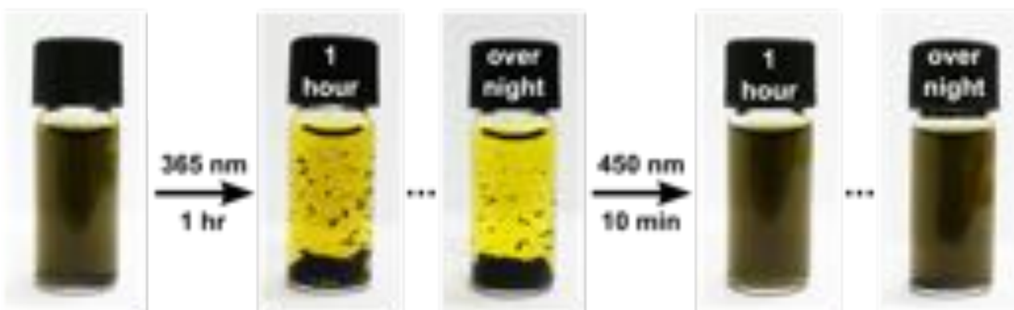


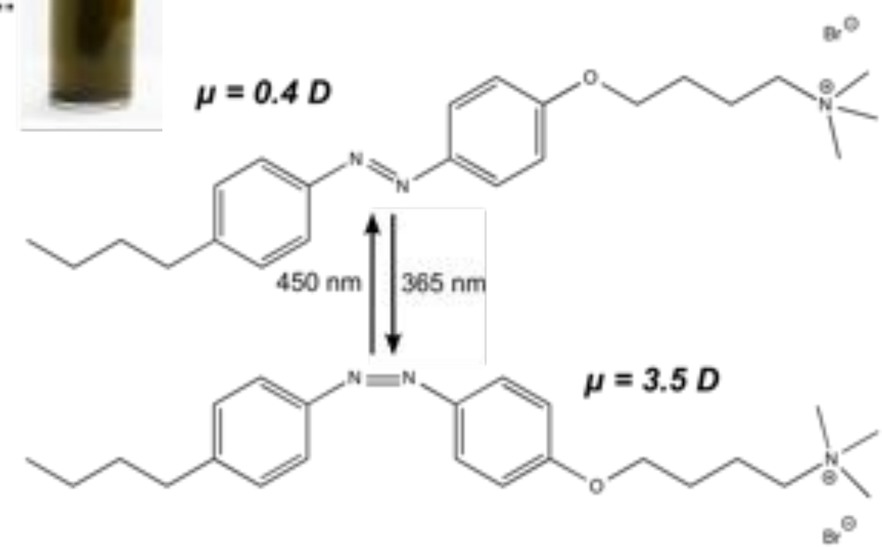
← Can use the GO as a sponge to grab particles, ions, toxins + magnetically capture those too

McCoy, Brown, Eastoe and Tabor; *ACS Appl. Mater. Interfaces* 7 (2015) 2124-2133

GO control – the next generation

- We can even capture and disperse graphene (and graphene oxide, and carbon nanotubes) using light.
- Lower energy than magnets, but not as ‘clean’





Conclusions

- To the colloid chemist, GO is **far more exciting** than pure graphene – water dispersable, tunable surface activity, pH response, *etc*.
- Behaves as a pseudo-molecule – between conventional surfactant, polymer and particle
- Great stabiliser for emulsions
- Fantastic adsorbent (5–20x more effective than activated carbon)
- Unique opportunities for incorporating other response and control mechanisms, *e.g.* magnetism

Uni students tap miracle carbon to cleanse water

JOHN ROSS

Monash University's Thomas McCoy, left, and Rico Tabor

MAGNETS and a Nobel prize-winning wonder material could be used to overcome toxic overload in the world's waterways.

A proof-of-concept study led by a Monash University undergraduate student has demonstrated an astonishingly simple way to cleanse water of contaminants, from lead and mercury to dye and antibiotics.

The system is based around extraordinarily thin layers of carbon, known as graphene, and magnets commonly used in electronics. "We've been using rare-earth magnets — you can buy them at Jaycar," said co-researcher Rico Tabor. "But any strong magnet does the trick."

Under the approach, the magnets draw charged particles out of water as it flows through a pipe. The particles are attached to tiny sheets of graphene oxide, which attract a huge range of toxins.

Graphene is a revolutionary material that won two Scottish physicists the 2010 Nobel prize. The thinnest known substance, at just one atom thick, it is also the lightest, strongest and most conductive. Its extraordinary flexibility, density and optical properties are being explored for use in products ranging from computer chips to gas sensors and condoms.

The Monash system uses graphene oxide, which is much easier to produce than pure graphene. "If you only want to treat wastewater, you don't care about the conductivity and all that stuff," Dr Tabor said. "(Graphene) has the most surface area possible to make, so it's an amazing absorbent."

He said graphene oxide's ability to "sponge" metal ions made the new system a promising way of treating mine tailing dams. "The goal is not always to get the purest water possible, it's to use cost-effective technology (to achieve) acceptable standards.

"As pressure on water increases, having technologies for the future is key. We might come up against a wall at some stage, where the current processes just don't cut it."

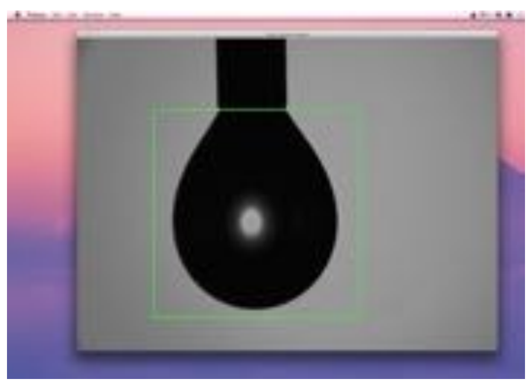
While other groups have researched ways of using graphene to decontaminate water, Dr Tabor's system is the first to use fully recyclable components. "We can separate the graphene oxide from the magnetic materials, so we can reuse (them) pretty much infinitely."

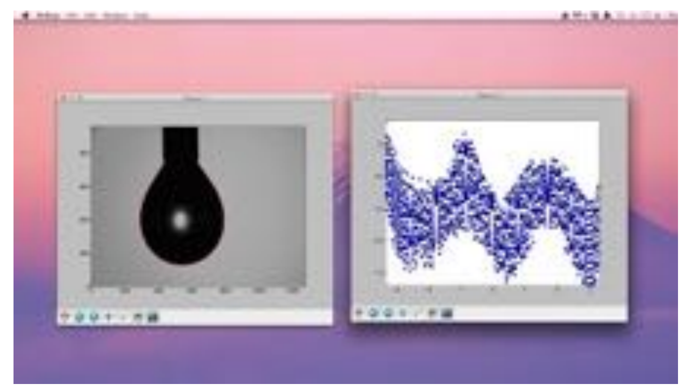
The study, published in the journal *ACS Applied Materials and Interfaces*, also involved the Massachusetts Institute of Technology and Bristol University.

The Australian, Feb 17th 2015

An aside for surface scientists

- We have released our pendant drop fitting software for free!
- Written in Python, GNU GPL license
- Available for free at **www.opencolloids.com**
- *JCIS* **454** (2015) 226–237

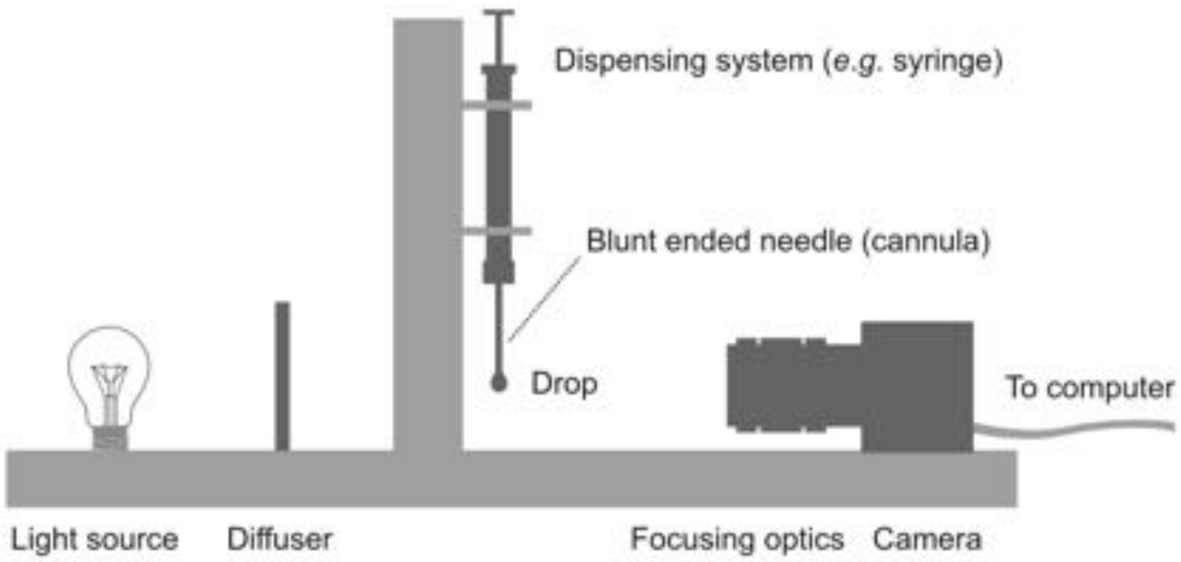




Pendant drop for undergrads & high-schoolers

- Setup cost is minimal
- Powerful piece of surface science (move over, capillary rise!)
- We now use this in undergraduate chemistry labs

powered by open drop 1.0 'Angelshark'



Outlook

- Of the possible 2D materials, three are commonly used:
  - Graphene (and GO, and reduced GO) ($$$$, conductive)
  - Molybdenum disulfide ($, insulator)
  - Boron nitride ($, insulator)

- Many others exist theoretically or in reality:
  - Borophene, germanene, silicene (allotropes)
  - Tungsten diselenide, hafnium disulfide (transition metal di-chalcogenides)

- Around **500 more** 2D materials remain to be explored!

Outlook

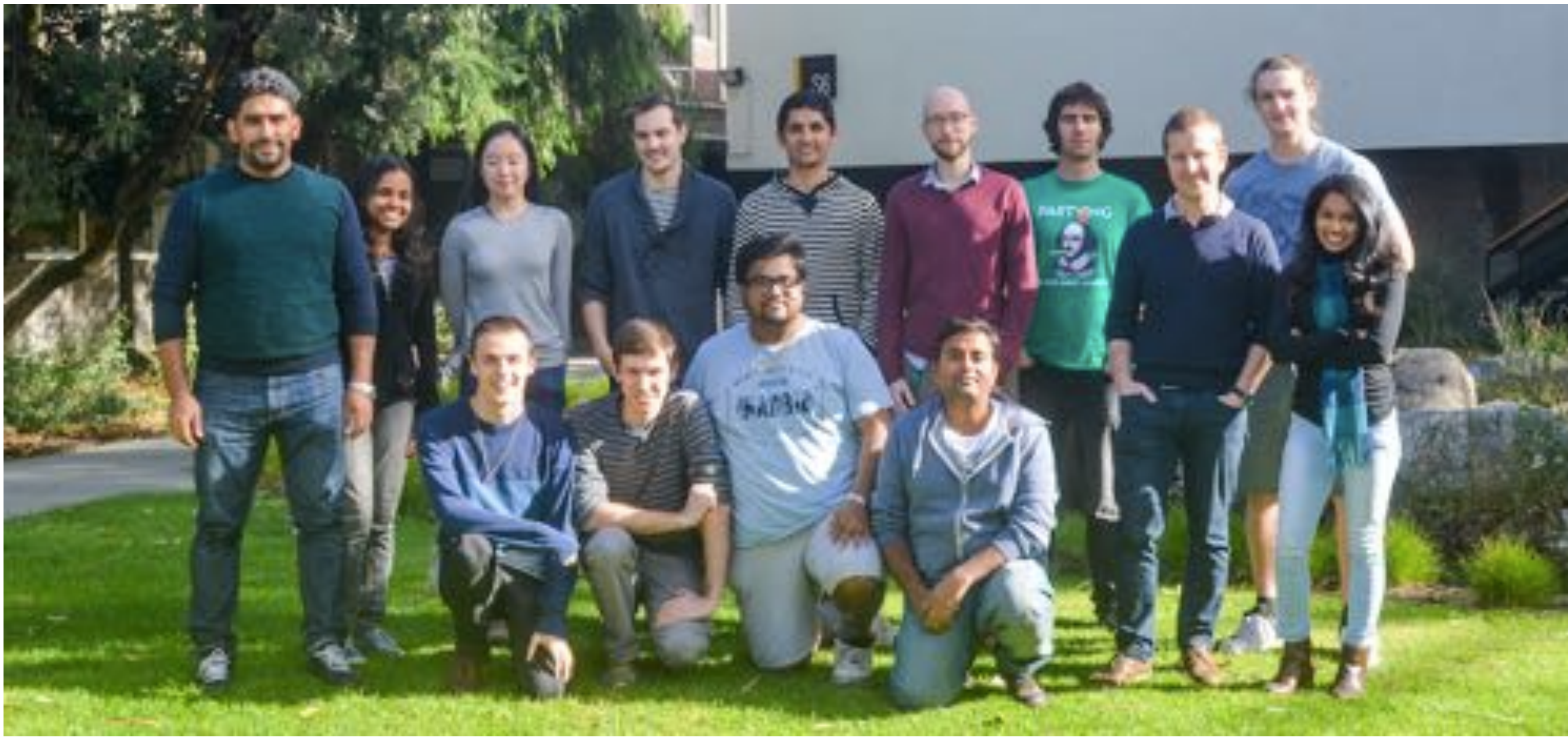
- And for the spectacle-adjusters you meet in the street who tell you that graphene is too expensive to every be used:
- In 2000, 1 g of carbon nanotubes cost $1875
- In 2016, 1 g of carbon nanotubes costs <$2

- In 2006, there wasn’t 1 g of graphene on earth
- Today, 1 g of graphene costs $1
  (medium quality, www.graphene-supermarket.com)

- 1 g of graphene oxide costs significantly <$1!

Acknowledgements

SMaCLab Soft Materials and Colloids



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The Monash Centre for Atomically Thin Materials

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SMaCLab Soft Materials and Colloids

Questions?

Want materials?

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www.opencolloids.com