Environmental fate of 2D materials in aquatic ecosystems: the case of graphene oxide 2D membranes

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Credit: Institute of Water

Outline

1

The issue of sustainability

2

Towards a Sustainable Materials Ecosystem

3

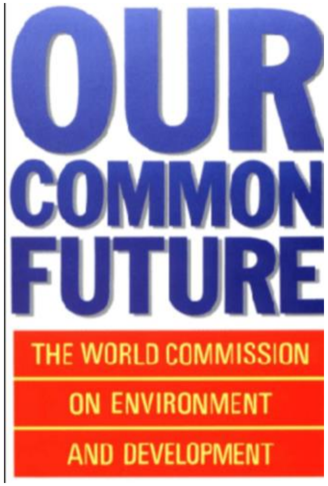
The case of graphene oxide

3

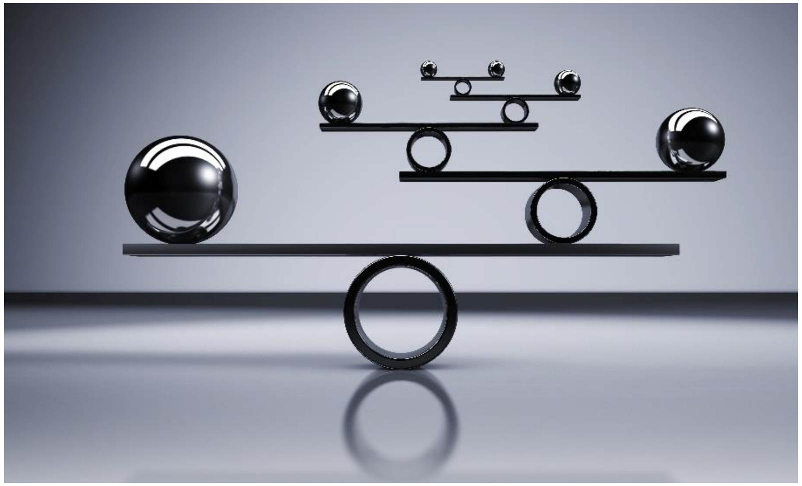
Challenges and Opportunities

The Issue of Sustainability!!!

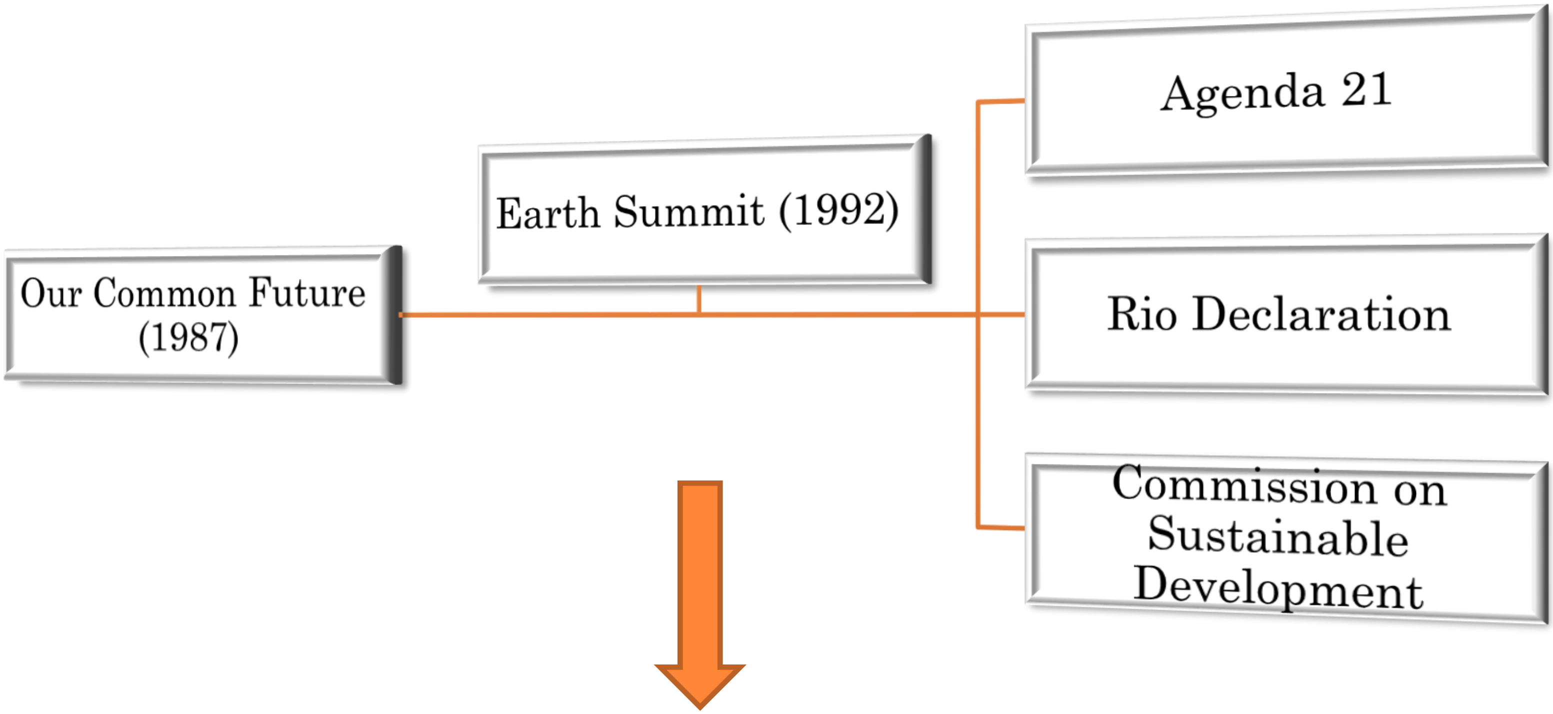
What is Environmental Sustainability?



“Meeting the needs of the present without compromising the ability of future generations to meet their own needs”



What is Environmental Sustainability?

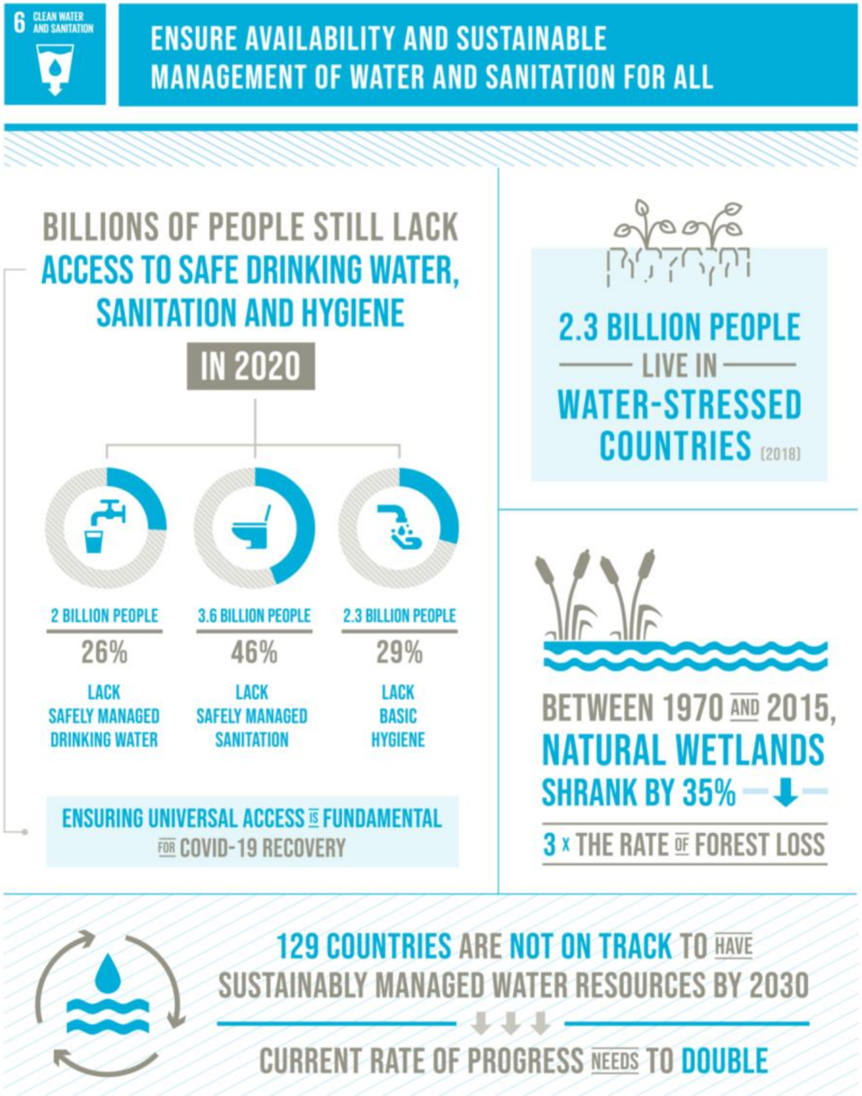


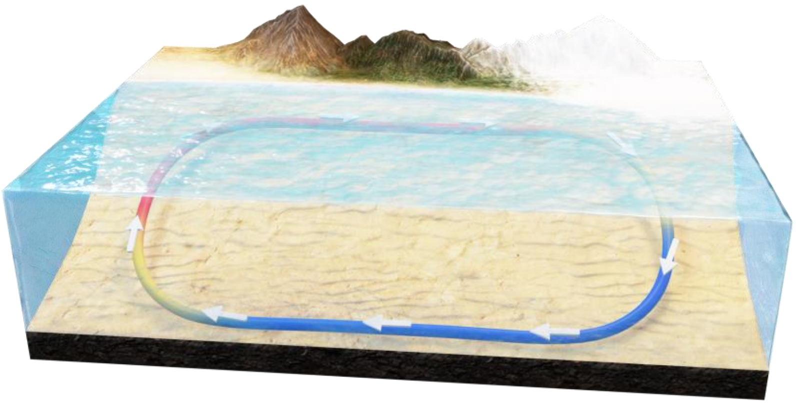
Interlocking Crises Definition

What is Environmental Sustainability?

The Importance of Water

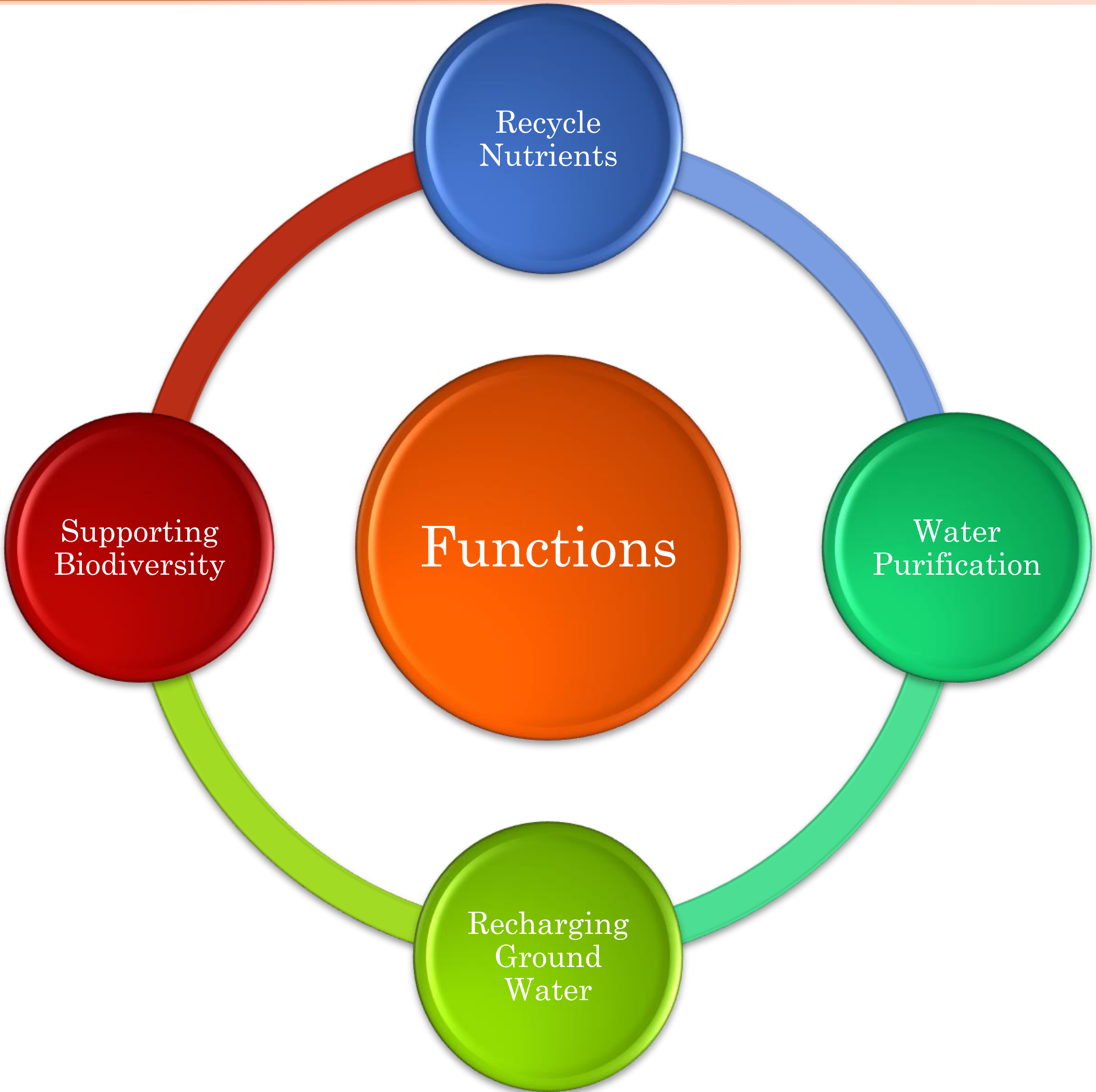
The importance of Water





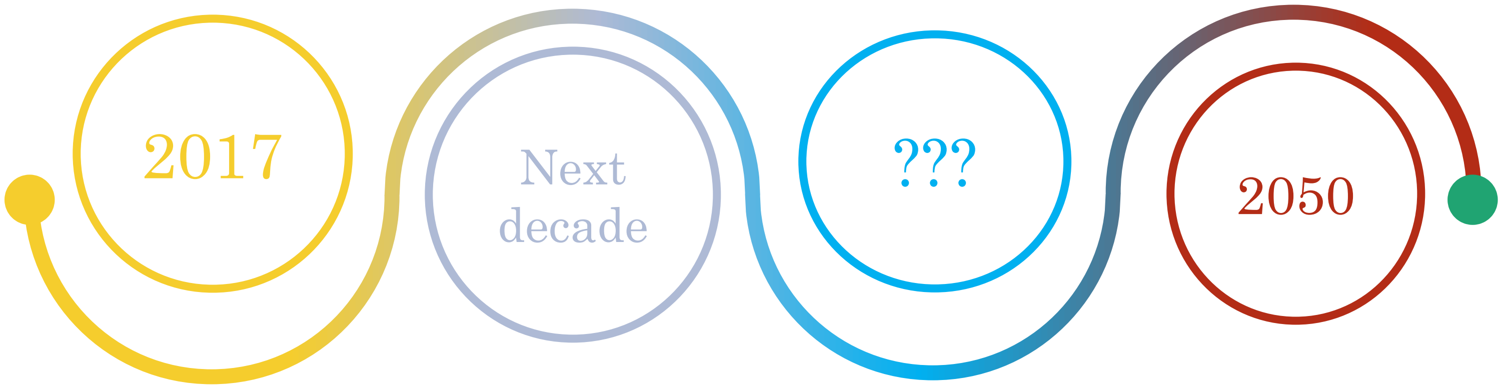
THE SUSTAINABLE DEVELOPMENT GOALS REPORT 2021: UNSTATS.UN.ORG/SDGS/REPORT/2021/

The importance of aquatic ecosystems



Towards a Sustainable Materials Ecosystem

Sustainable Materials System Roadmap



Global Raw Materials Use

More than 90 billion metric tons

More than 60% is extracted in Asia

Global Raw Materials Use

Mostly extracted in Africa

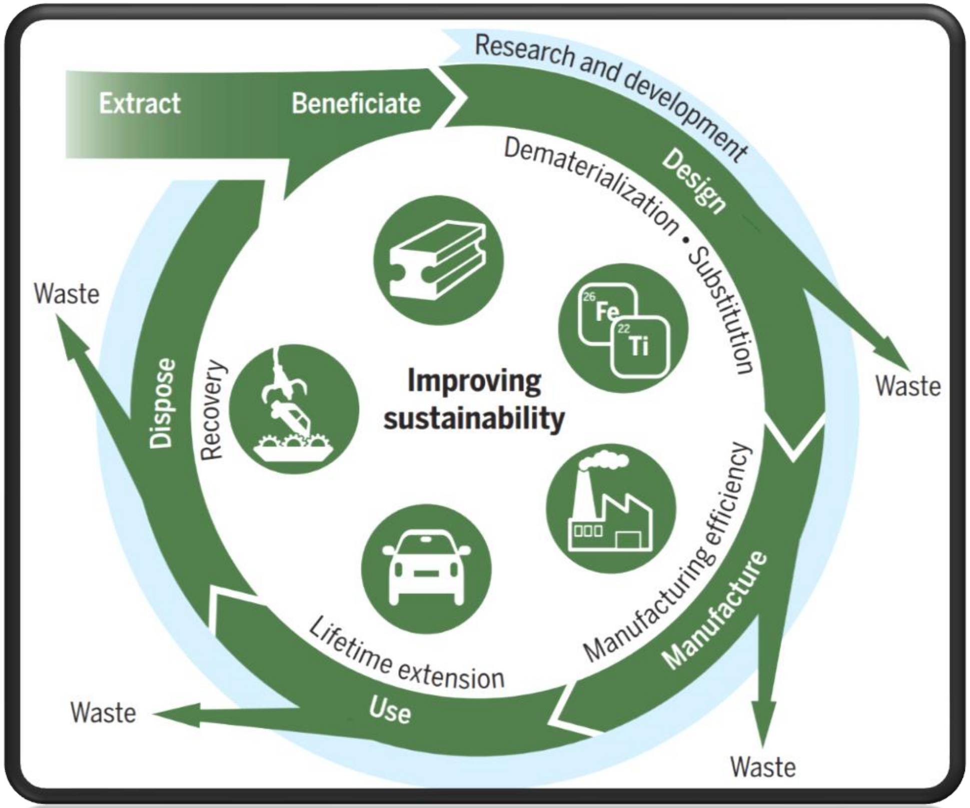
Environmental Threats

Bio-diversity. Land-use change, climate impacts, biogeochemical flows

Global Raw Materials Use

More than 180 billion metric tons

Environmental Life-Cycle of Materials



Beginning in the mid-50s

The shift from biomass or renewable materials to nonrenewable substances

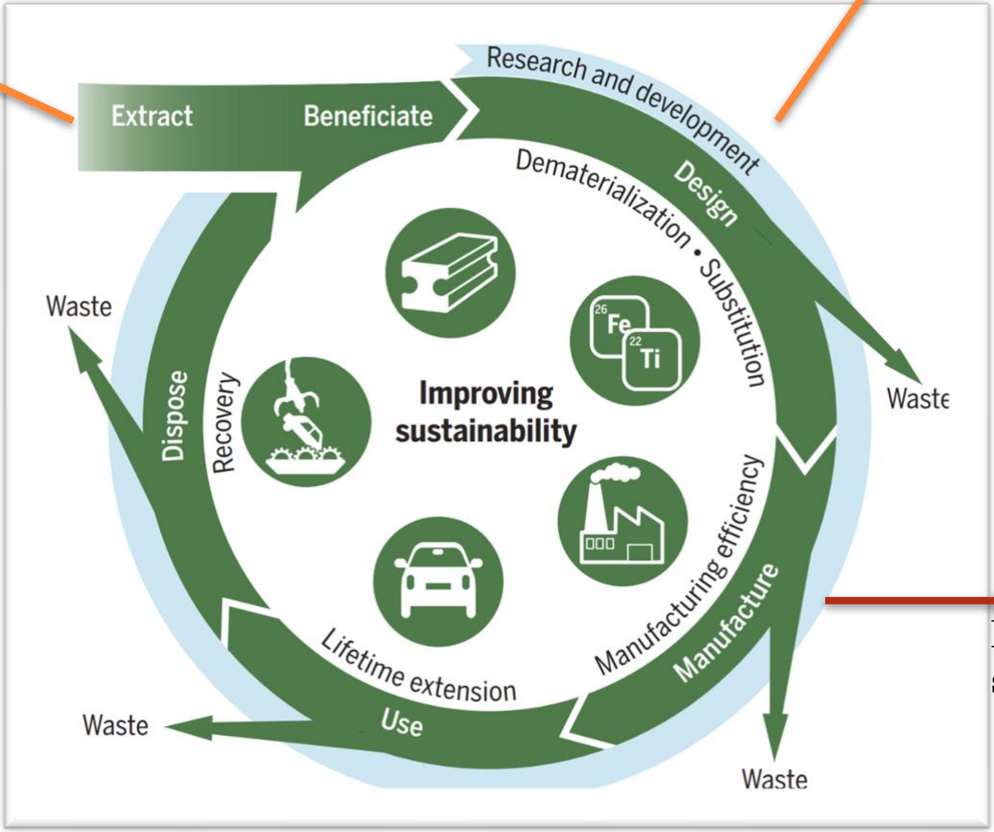
Toward a sustainable materials system, DOI: 10.1126/science.aat6821.

Environmental Life-Cycle of Materials

Primary metal extraction accounts for 8% total global Energy Consumption

Expected to increase even more

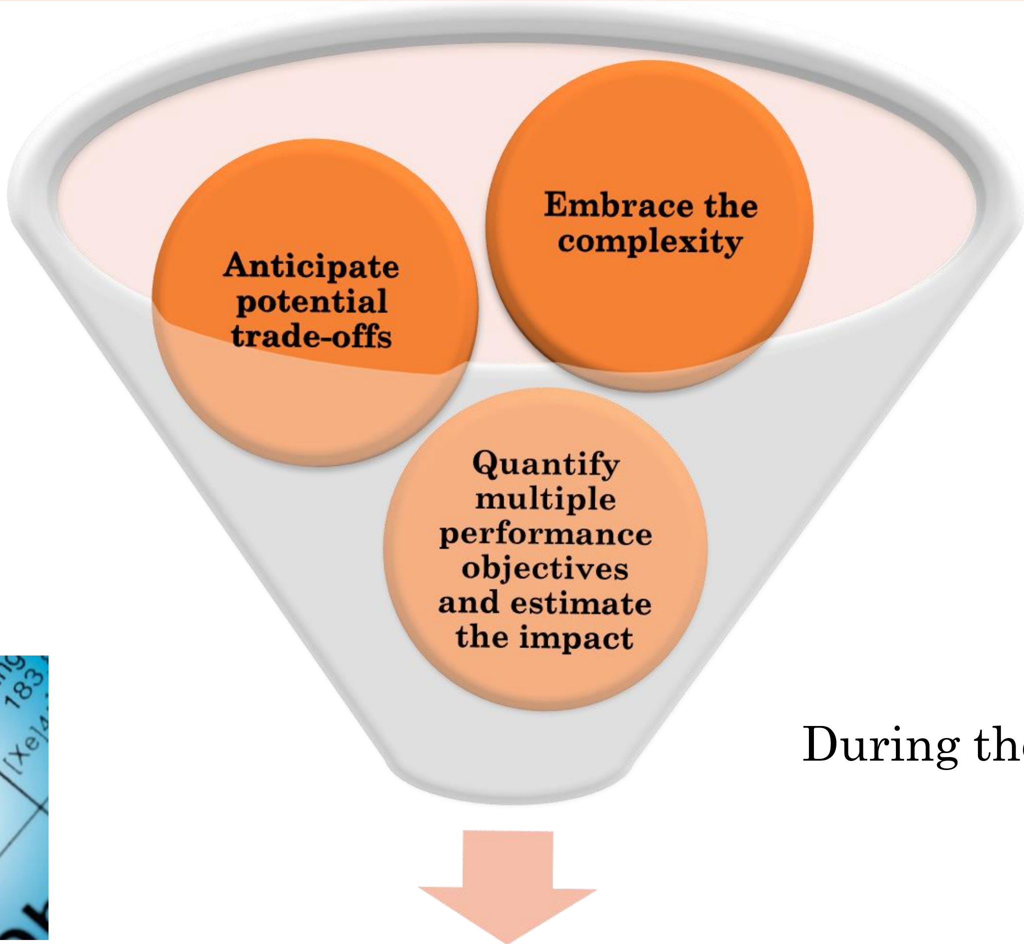
Cement production: 50% of direct CO2 emission comes from just one stage

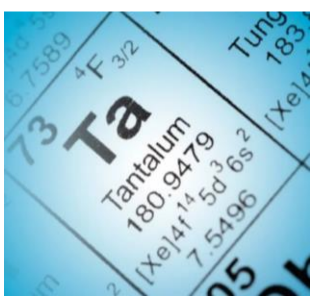


Direct air, water and soil emission

An unprecedented effort is needed to achieve sustainable materials production and use

Charge to technical community





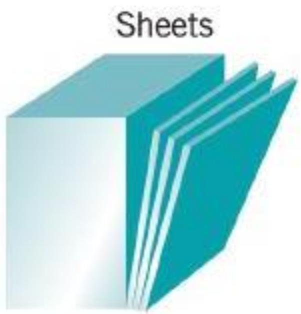
During the initial R&D stage

The Current Sustainability Challenge!!!

Towards a Sustainable Materials Ecosystem

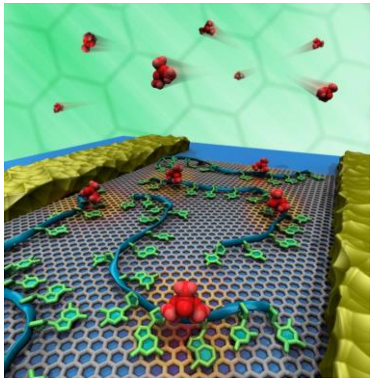
The case of 2D materials

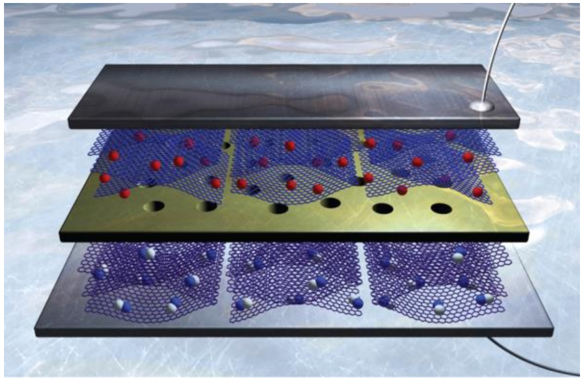
So why 2D materials?

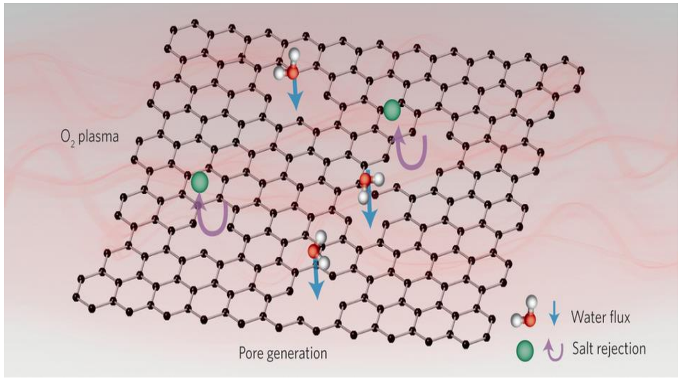


Increase in surface area/volume

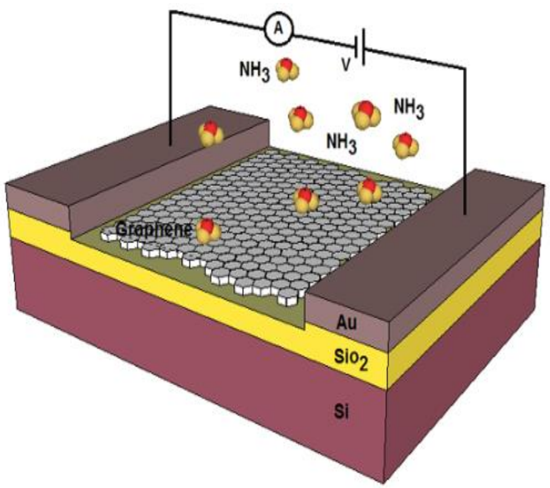
Emergence of different properties

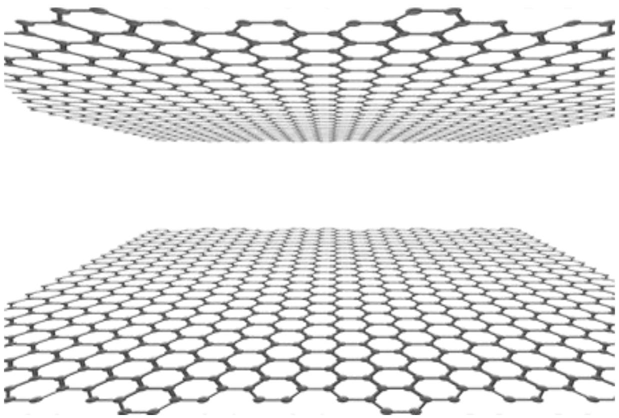


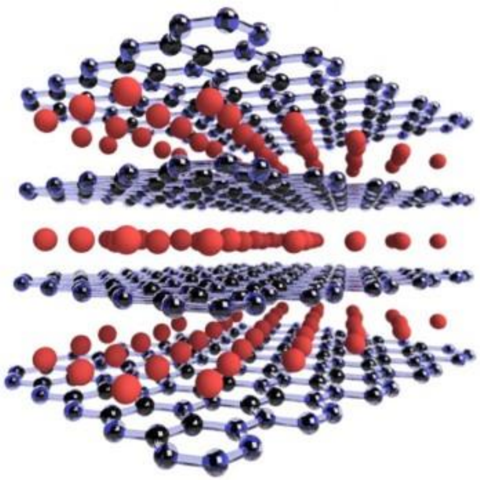




Why 2D?



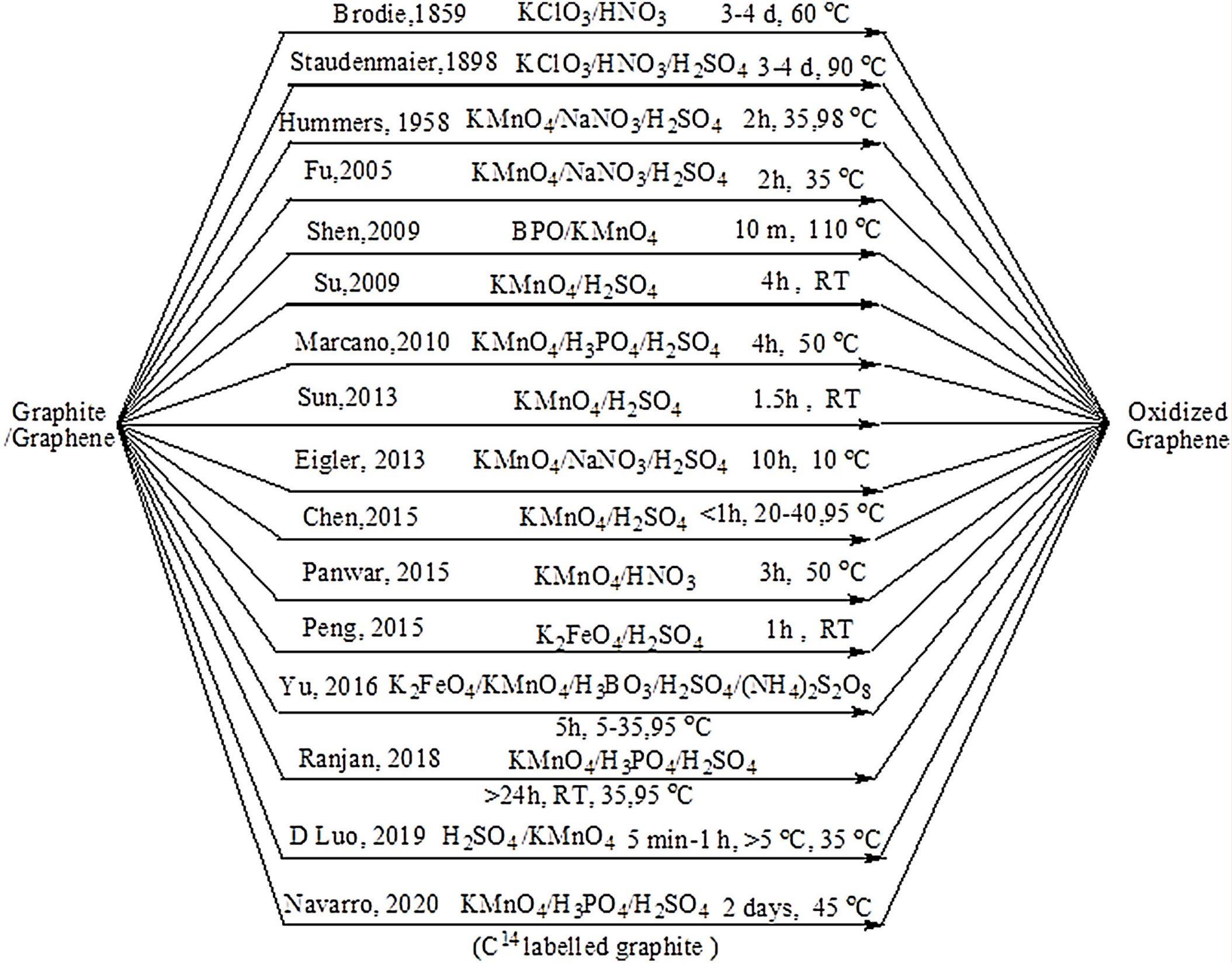




Flat, conductive, transparent, high surface area: Dream material for Sensing and energy application

Graphene: Its all surface

Why do both chemists and material scientists like it??? **HUGE surface area**



Graphite
/Graphene
Brodie,1859 KClO3/HNO3 3-4 d, 60 °C
Staudenmaier,1898 KClO3/HNO3/H2SO4 3-4 d, 90 °C
Hummers, 1958 KMnO4/NaNO3/H2SO4 2h, 35,98 °C
Fu,2005 KMnO4/NaNO3/H2SO4 2h, 35 °C
Shen,2009 BPO/KMnO4 10 m, 110 °C
Su,2009 KMnO4/H2SO4 4h, RT
Marcano,2010 KMnO4/H3PO4/H2SO4 4h, 50 °C
Sun,2013 KMnO4/H2SO4 1.5h, RT
Eigler, 2013 KMnO4/NaNO3/H2SO4 10h, 10 °C
Chen,2015 KMnO4/H2SO4 <1h, 20-40,95 °C
Panwar, 2015 KMnO4/HNO3 3h, 50 °C
Peng, 2015 K2FeO4/H2SO4 1h, RT
Yu, 2016 K2FeO4/KMnO4/H3BO3/H2SO4/(NH4)2S2O8
5h, 5-35,95 °C
Ranjan, 2018 KMnO4/H3PO4/H2SO4
>24h, RT, 35,95 °C
D Luo, 2019 H2SO4/KMnO4 5 min-1 h, >5 °C, 35 °C
Navarro, 2020 KMnO4/H3PO4/H2SO4 2 days, 45 °C
(C14 labelled graphite)
Oxidized
Graphene

Graphene dashboard

China

Largest Layered Crystals Producer in the world

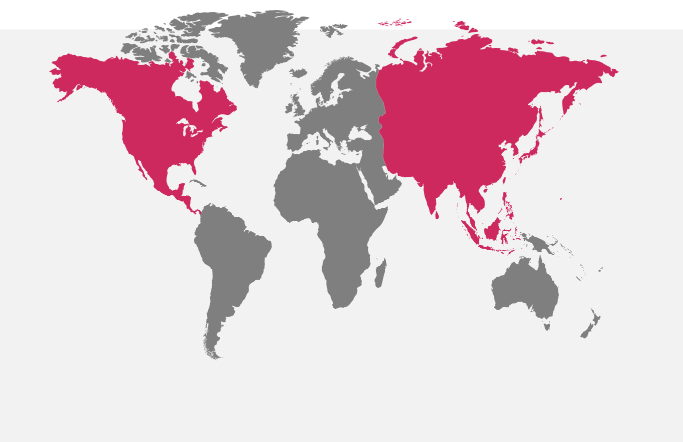
Accounts for 62% graphite mining activities

Key future Industry

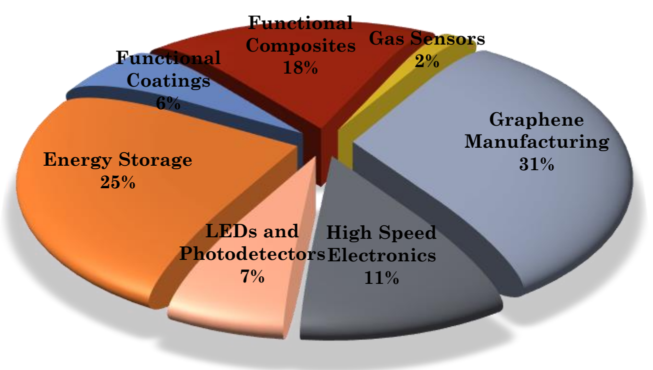
- 10 separate Strategic Research Zones
- More than 67% of patents filed in the world on 2D materials

Total number of companies: 200

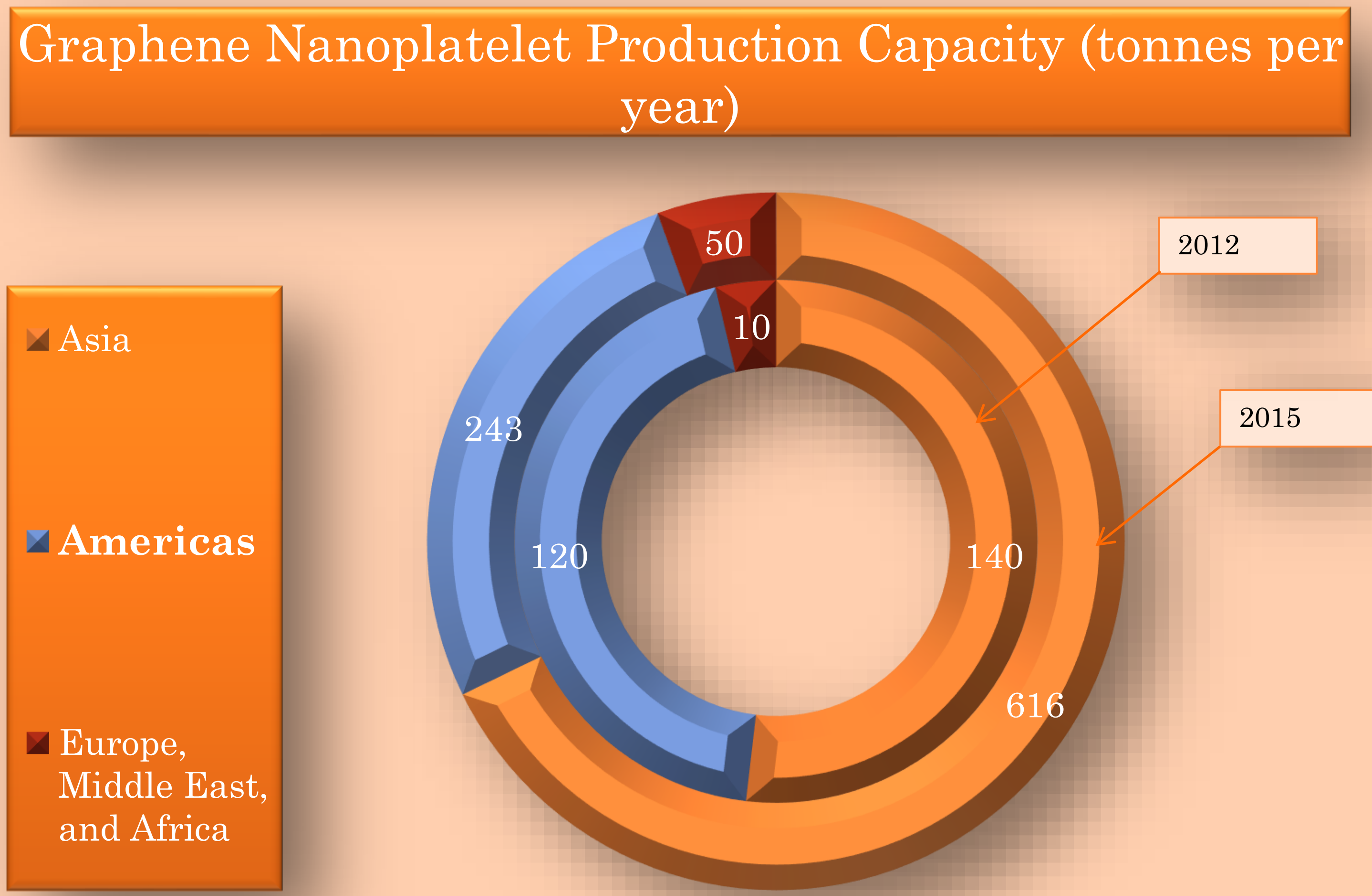
Market Location



Graphene Patents as of 2015



Graphene: The Interest



Graphene: The production

Founded in 2014
Capacity: 450 tons of GNPs
Capacity: 1500 tons of Graphite Oxide

The Sixth Element Inc.

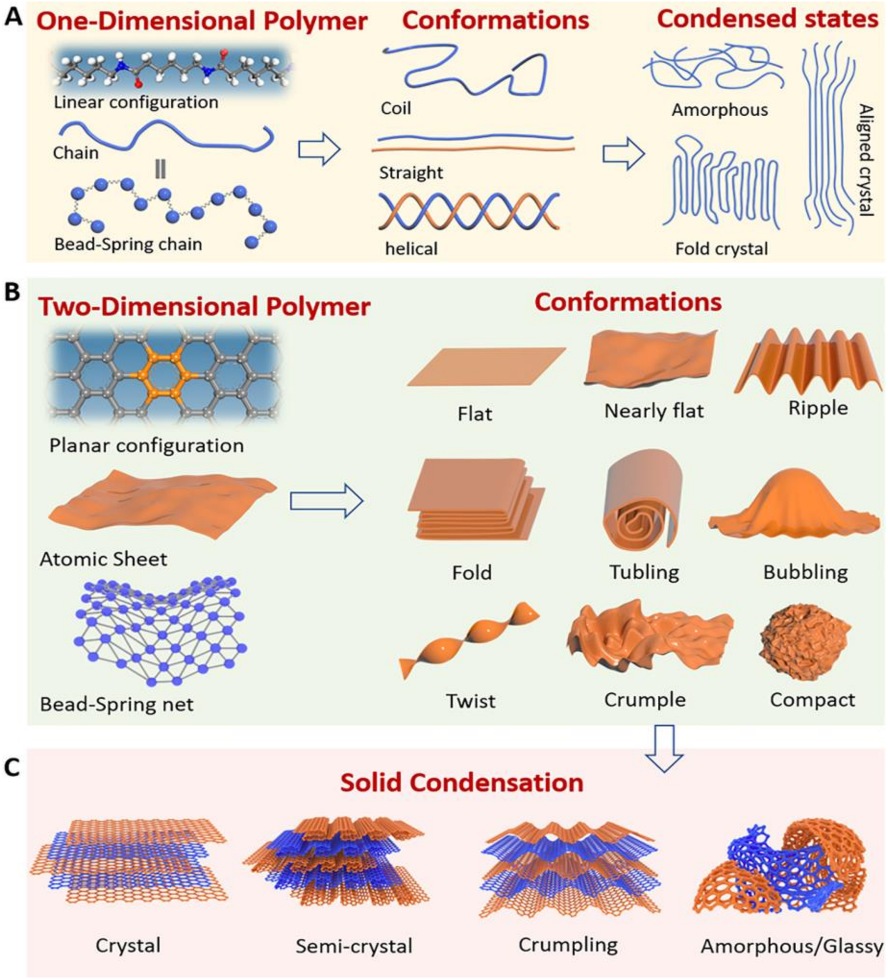
Graphene Used As An Additive in Polym...
2021-09-02

Image Credit: The Sixth Element (Changzhou) Materials Technology Co.,Ltd.

GRAPHENE OXIDE (GO) SHEETS ADOPT A CRUMPLED CONFIGURATION IN WATER

They impose minimal environmental risks

Conformational Phase map of Graphene Oxide



DOI: (10.1021/accountsmr.0c00027)

To Crumple, or Not To Crumple, That is the question.

nature

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nature > letters > article

Published: 30 January 1992

Crumpled and collapsed conformation in graphite oxide membranes

Xin Wen, Carl W. Garland, Terence Hwa, Mehran Kardar, Etsuo Kokufuta, Yong Li, Michal Orkisz & Toyoichi Tanaka

Nature **355**, 426–428 (1992) | Cite this article

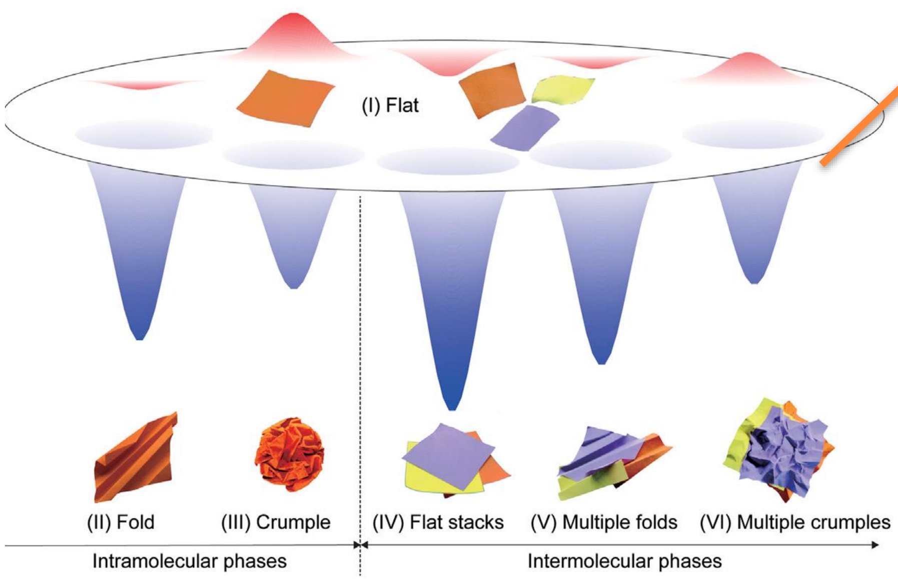
GO sheets in water are fractals with dimension of 2.5

↓

GO sheets adopt a crumpled conformation, akin to that of a crumpled paper ball

Conformational Phase map of Graphene Oxide

DOI: (10.1021/accountsmr.0c00027)

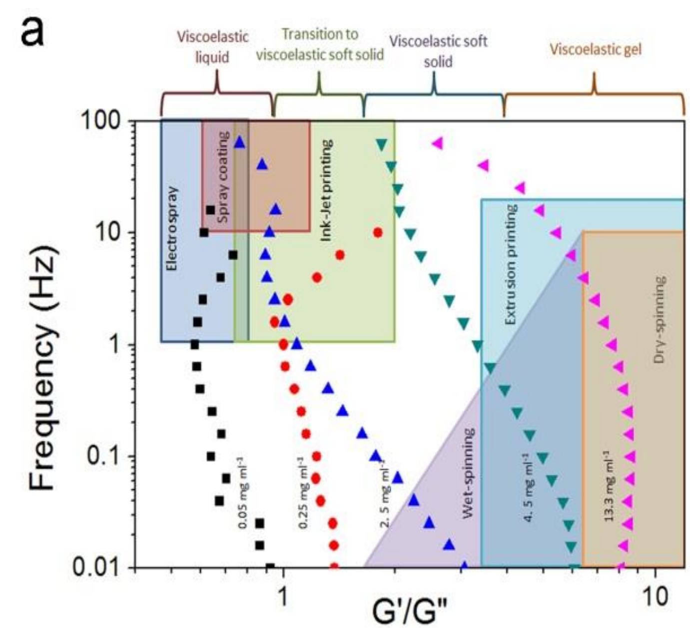


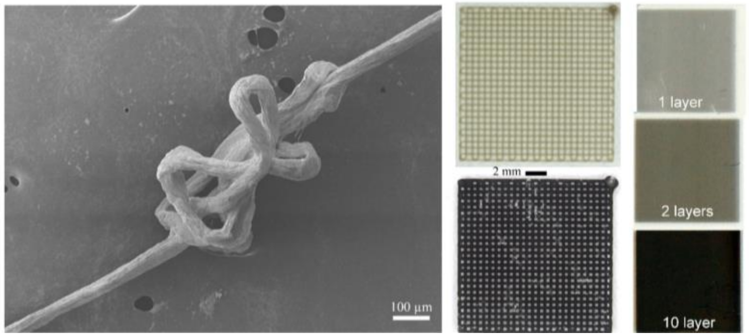
Dilute Regimen ~0.01 wt%

Concentrated Regimen ~0.01 wt%

Environmental impact

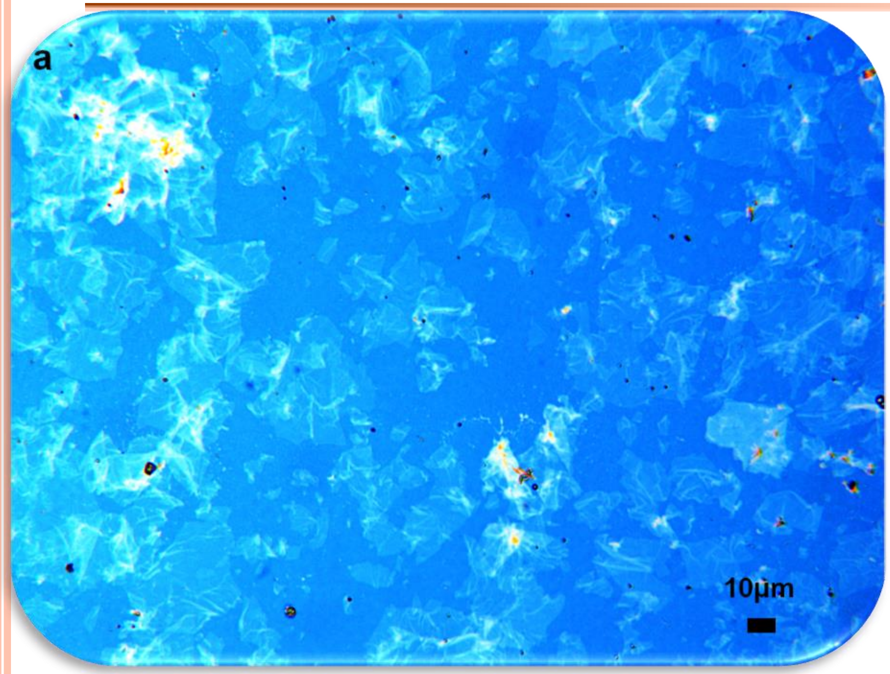
Technical importance in solution processing

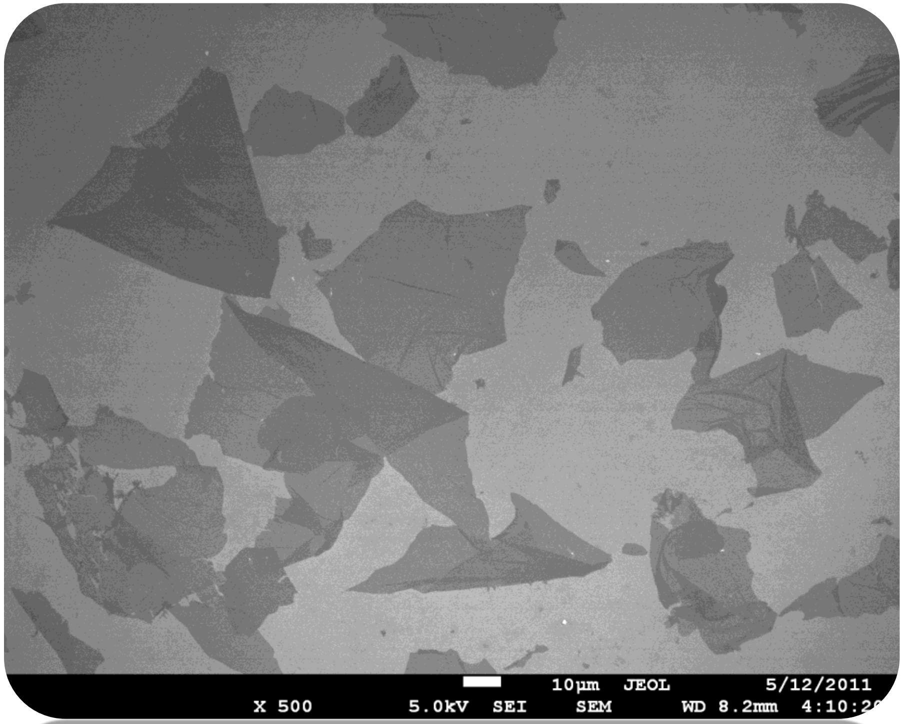




Iranian Journal of Physics Research 20 (3), 515-524

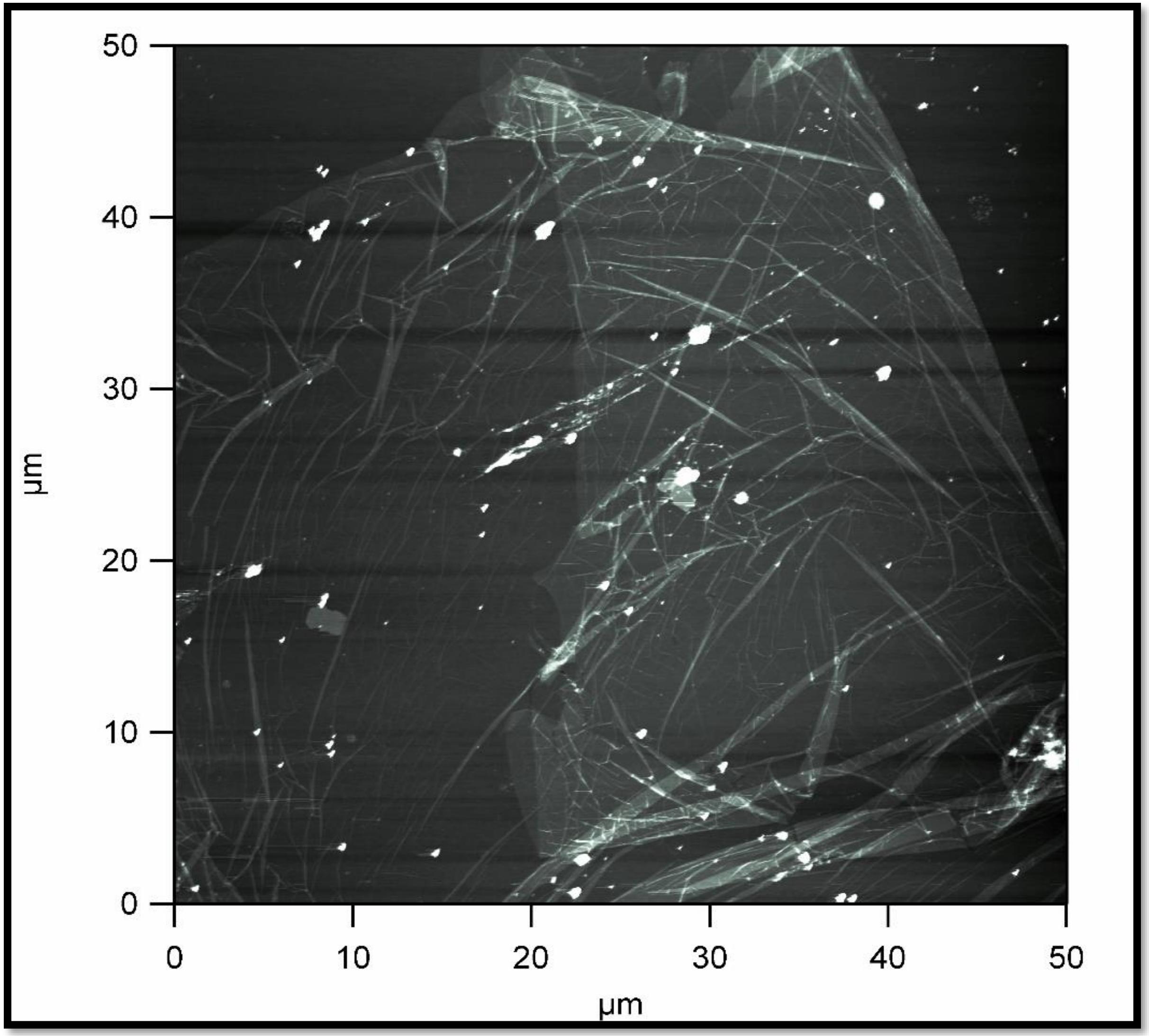
Folds, flat Stacks, and multiple folds



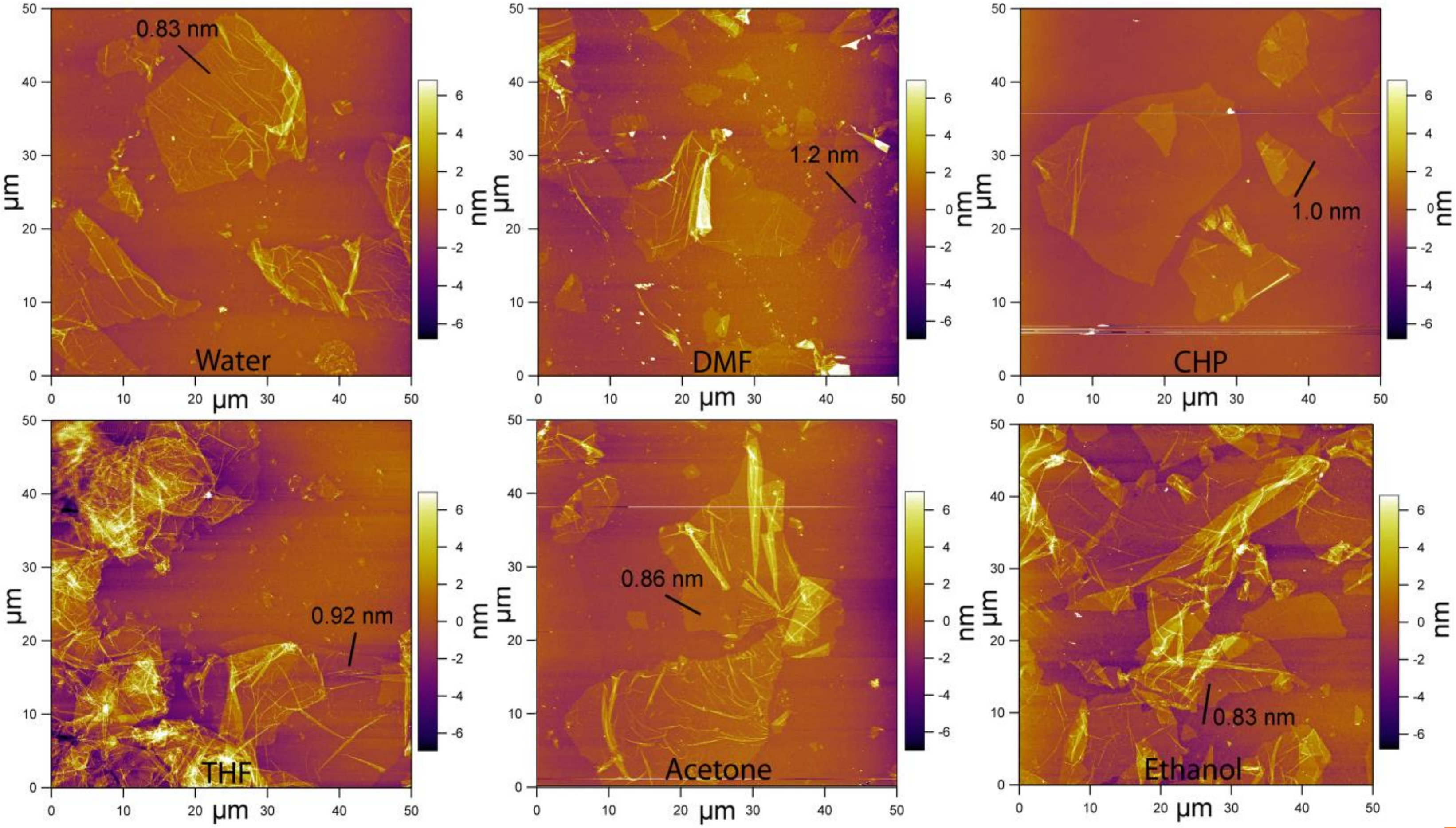


Advanced Functional Materials, 2011. **21**(15): p. 2978-2988.

Folds, flat Stacks, and multiple folds

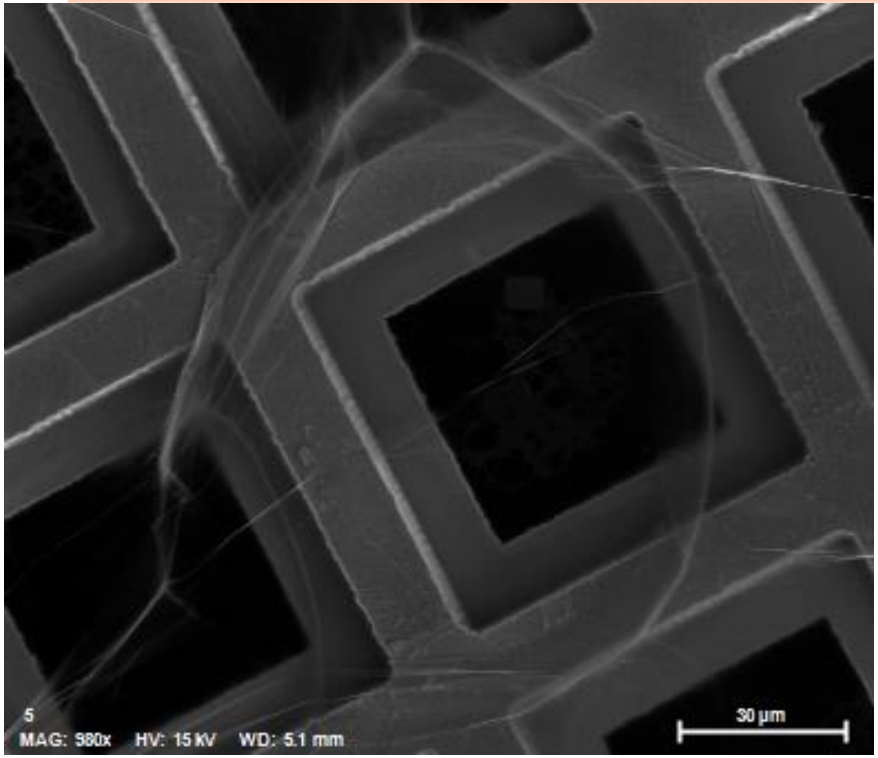


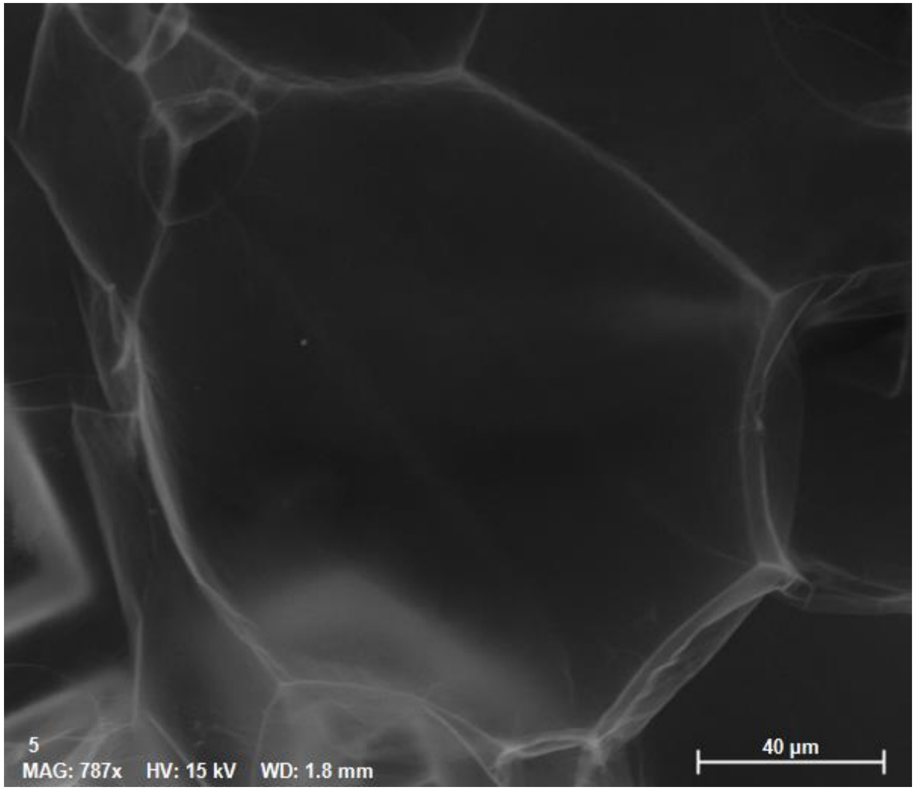
Folds, flat Stacks, and multiple folds in bad solvents



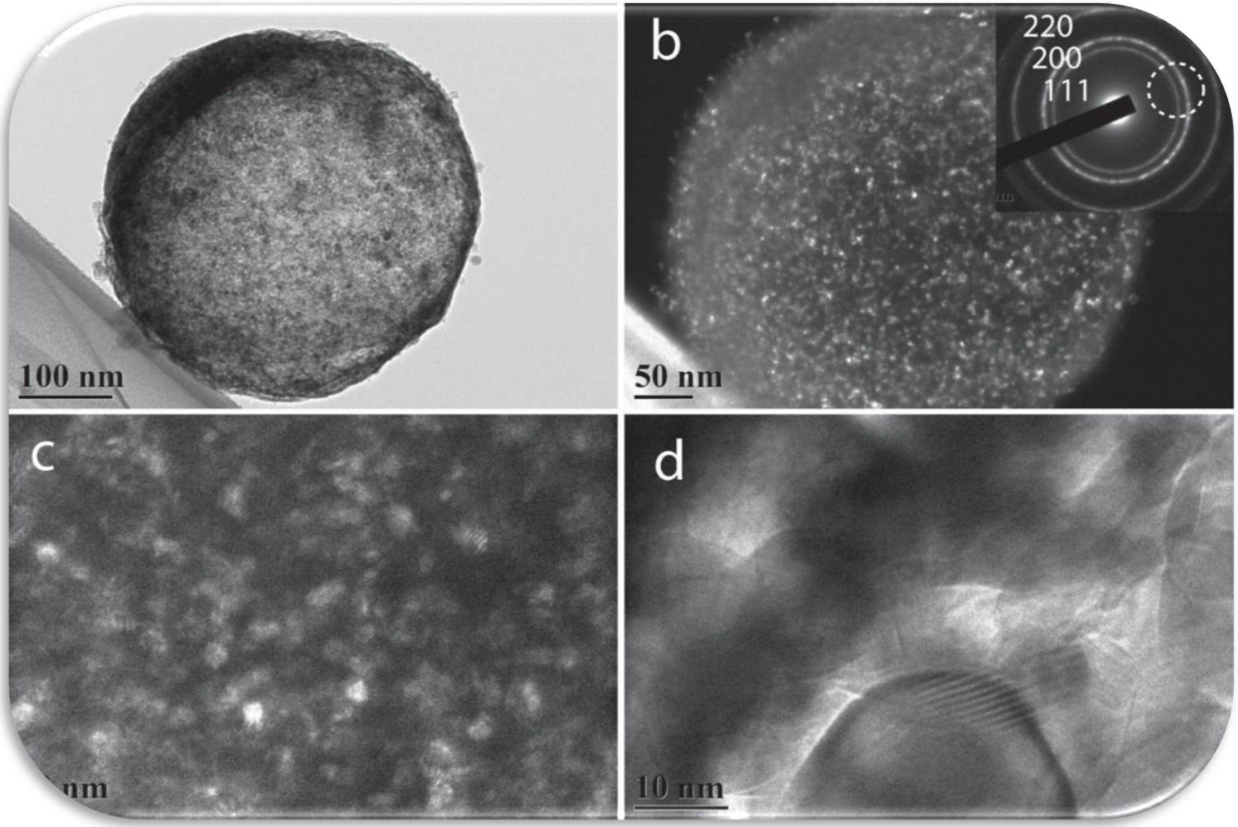
ACS nano, 2013. 7(5): p. 3981-3990.

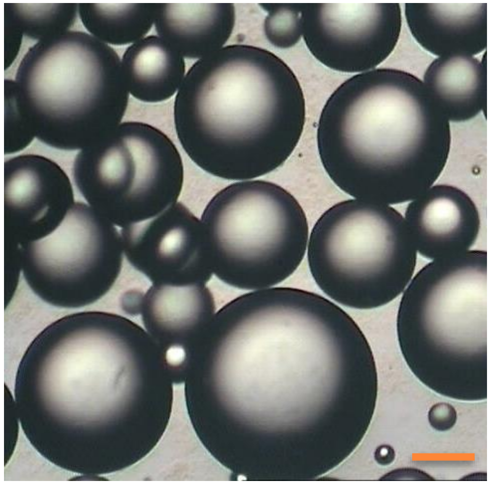
Bubbling





Compact Globular Form Factor





Energy & Environmental Science, **5**(1): p. 5236-5240.

MISCONCEPTION

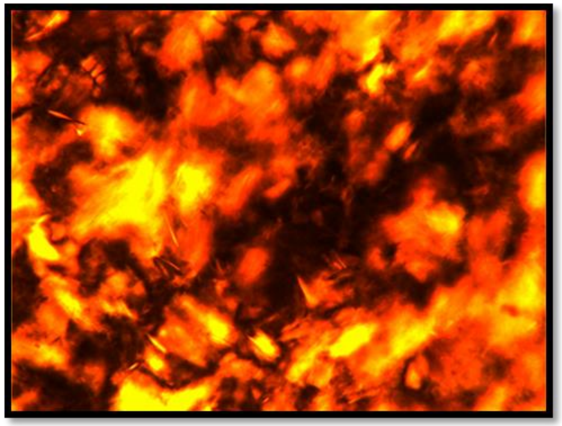
,

Deformed features in GO or graphene sheets are intrinsic to solution processing and unavoidable

RESPONSE

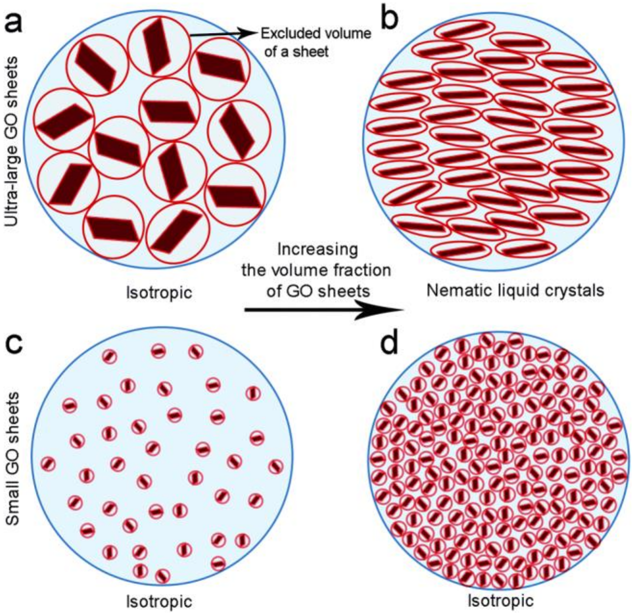
Need for a simple yet effective marker!!!

The marker is relatively simple:
Formation of nematic liquid crystal phase



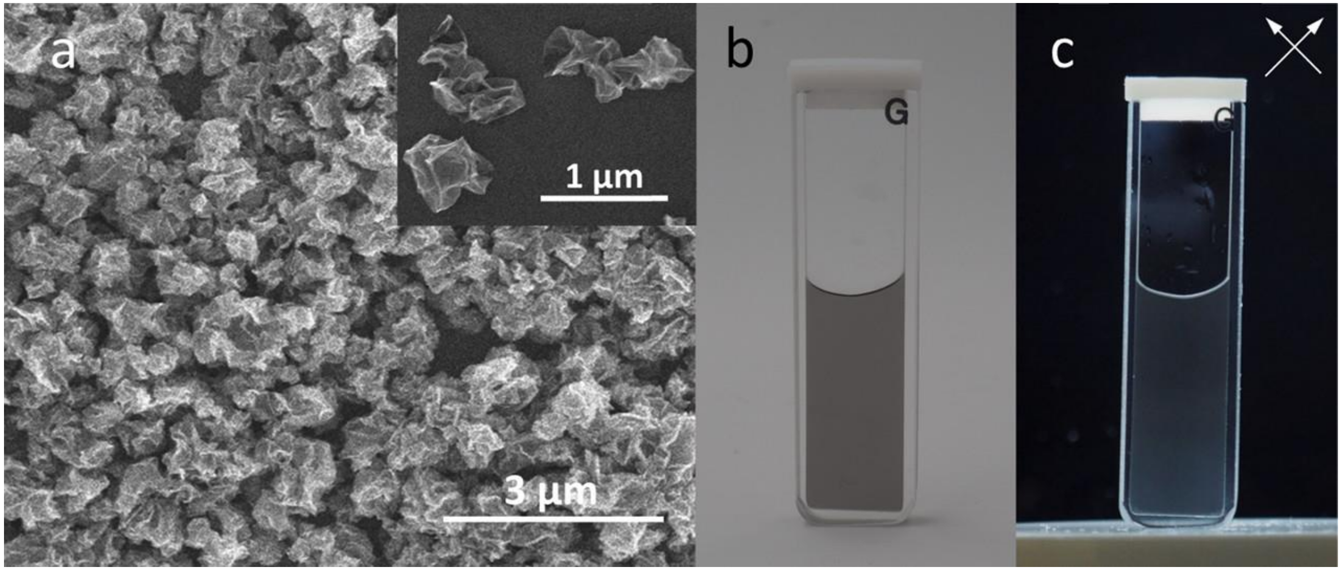
Advanced Functional Materials, 2011. 21(15): p. 2978-2988.

If GO sheets were to transform into a shape like crumpled paper balls or the even denser collapsed form, the resulting particles would not have formed a nematic phase at all because their contour is largely isotropic amid the complexity of the structures



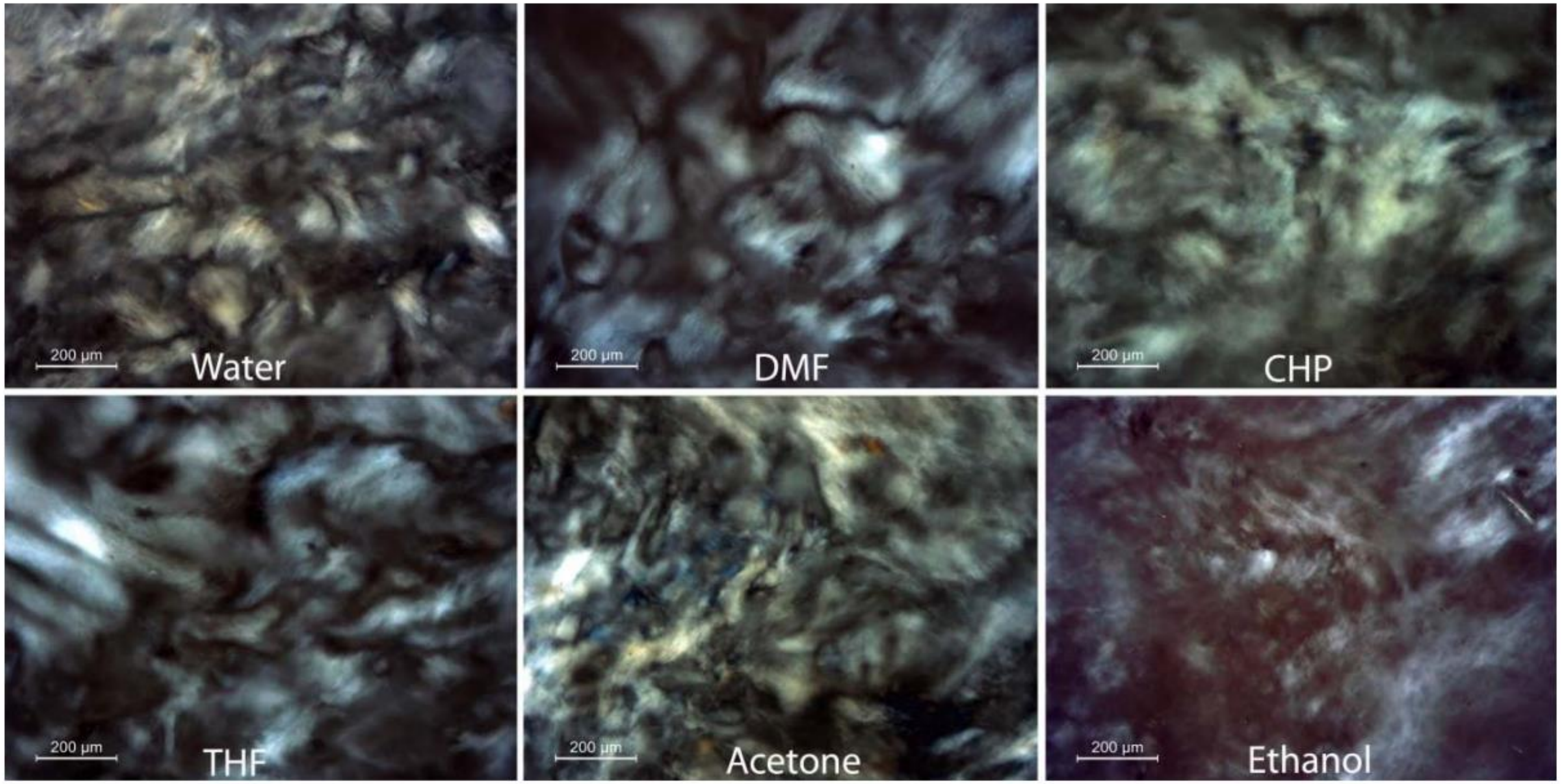
Materials Horizons 1 (1), 87-91

Crumpled paper balls: Can they form liquid crystals?

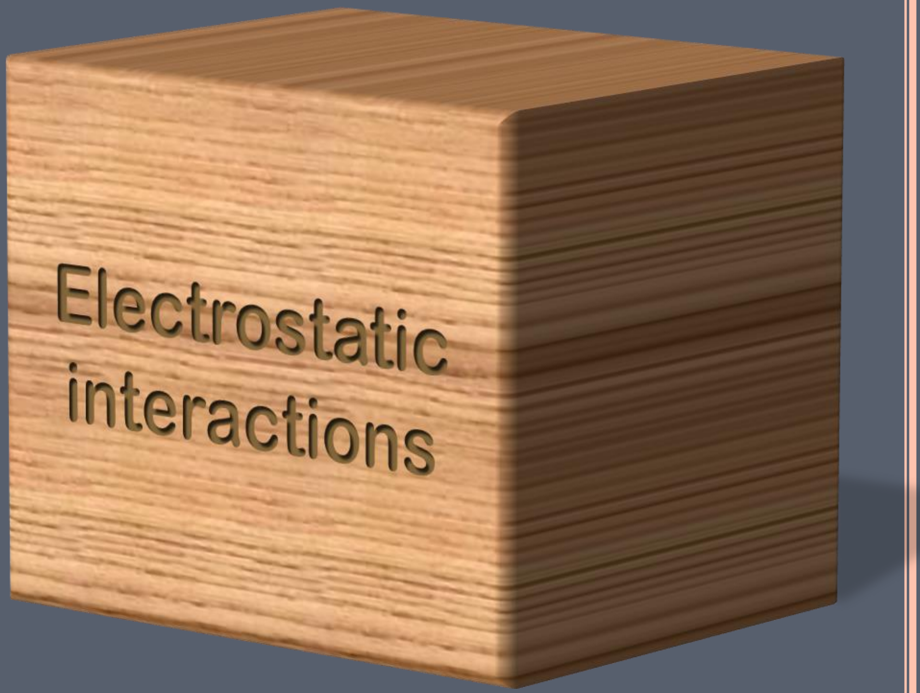


DOI: (10.1021/acsomega.7b01647)

Under poor solvent conditions



It clearly establish that GO sheets do not crumple nor collapse into 3D morphologies with nearly isotropic contour in poor solvent conditions.



Can electrostatic interactions alter the rigidity of GO?

Assumptions

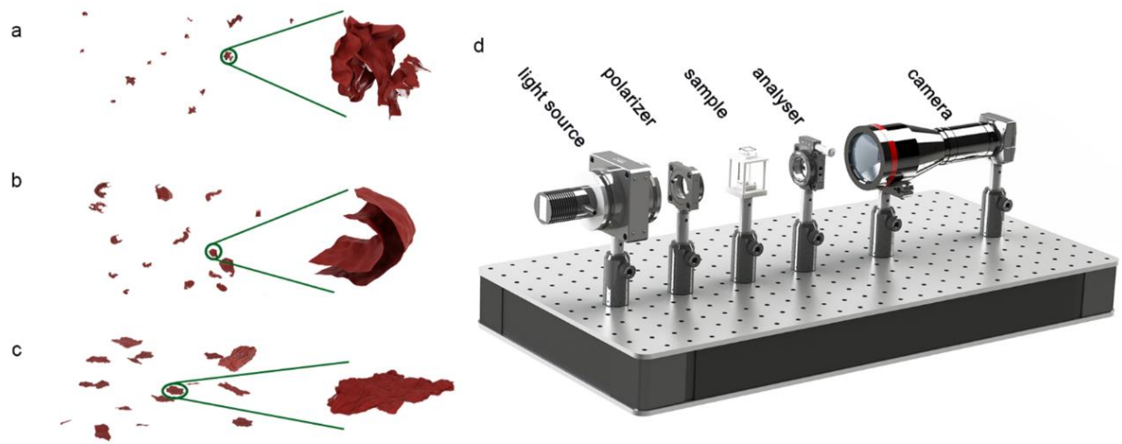
- The behaviour of GO in water is largely controlled by the presence of negatively charged entities on its surface
- Similar to polyelectrolytes, electrostatic interactions tend to rigidify membranes especially those with low intrinsic rigidity

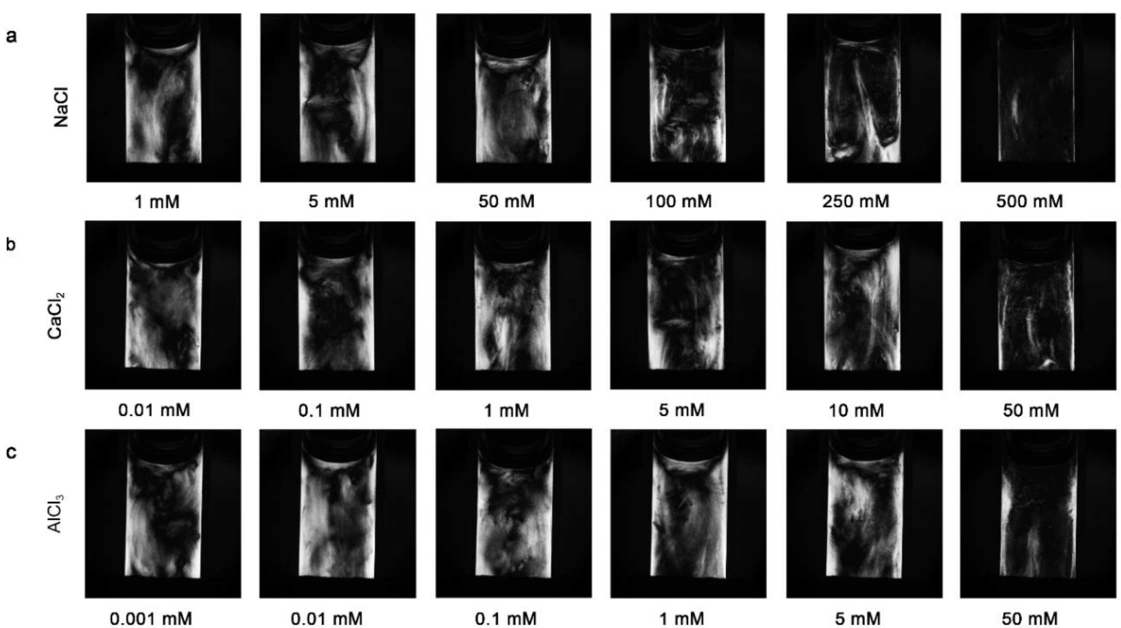
Main questions

How stable are these giant macromolecules in aqueous environment?

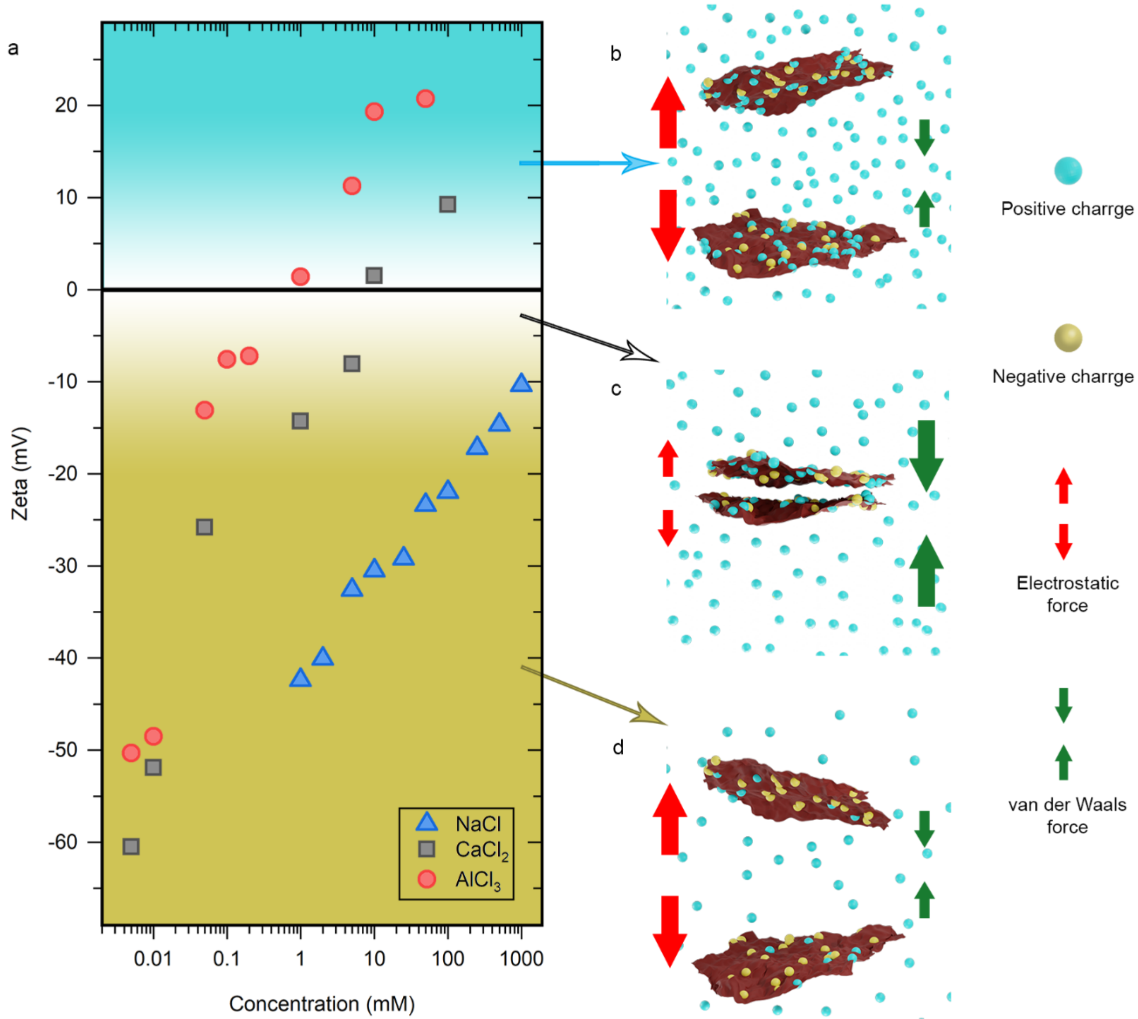
To what extent electrostatic contributions play a role on the structural stability of GO?

Nematic Lyotropic Liquid Crystals (NLLC)

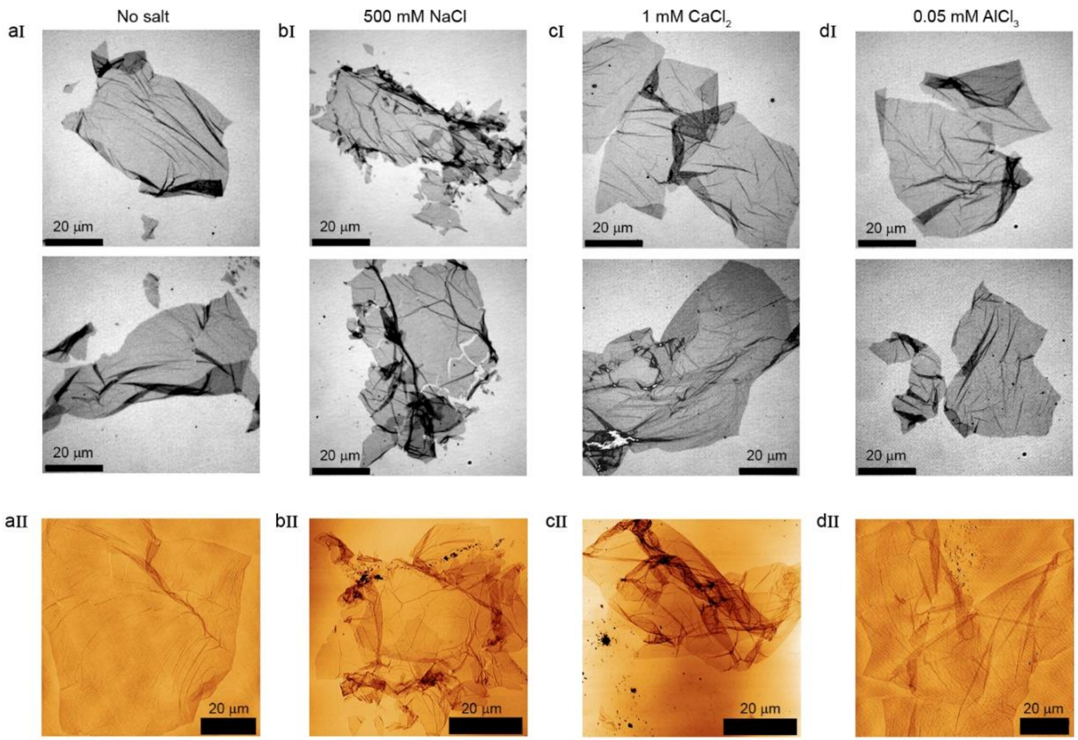




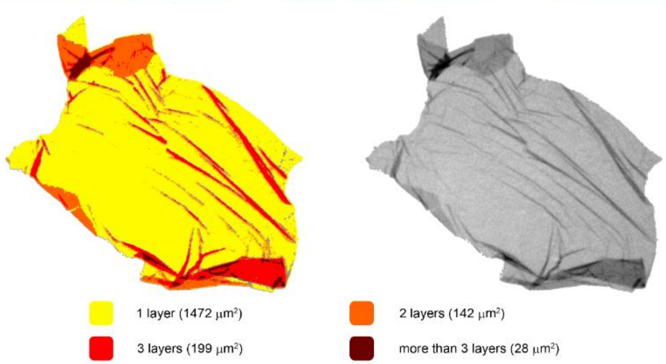
Nematic Lyotropic Liquid Crystals (NLLC)



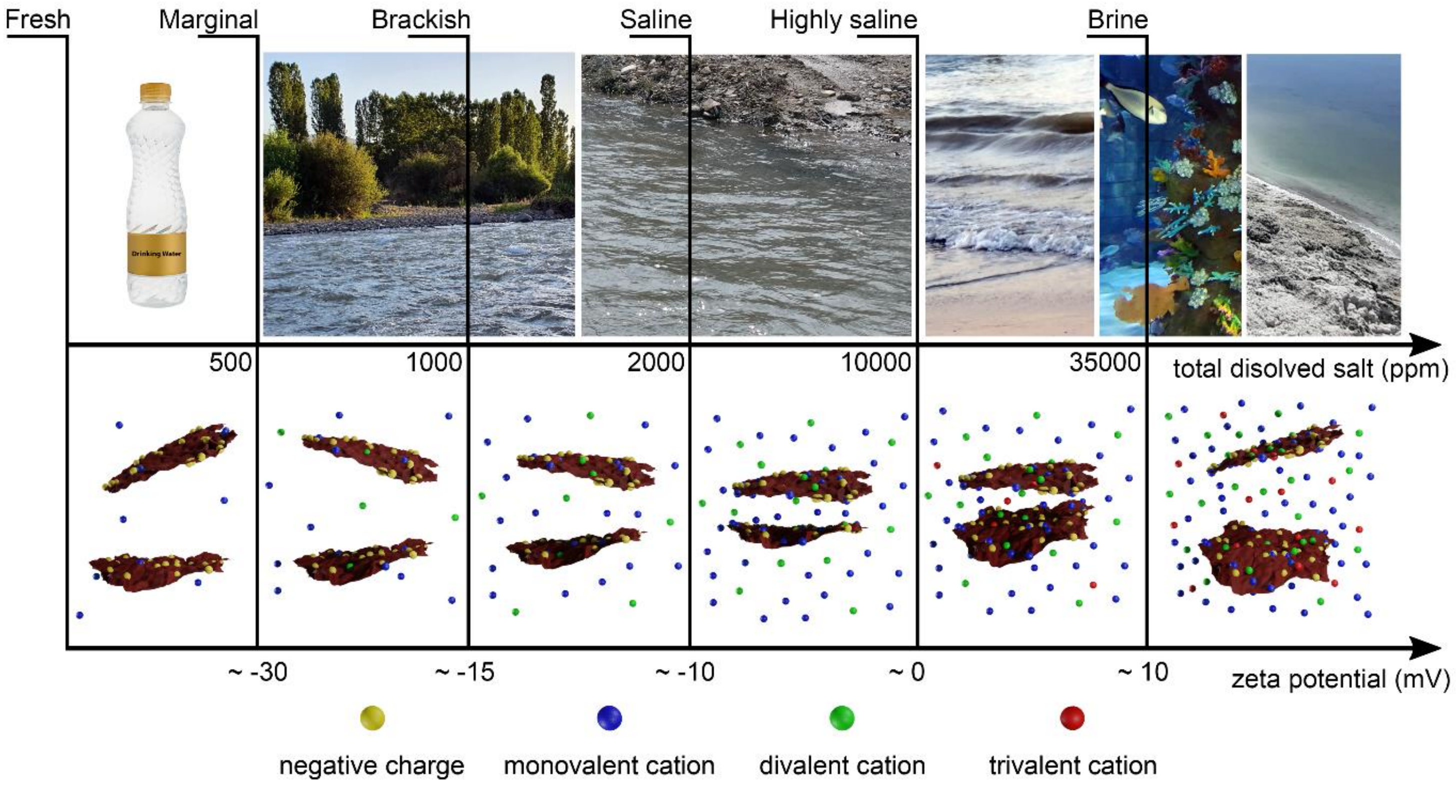
NEMATIC LYOTROPIC LIQUID CRYSTALS (NLLC)



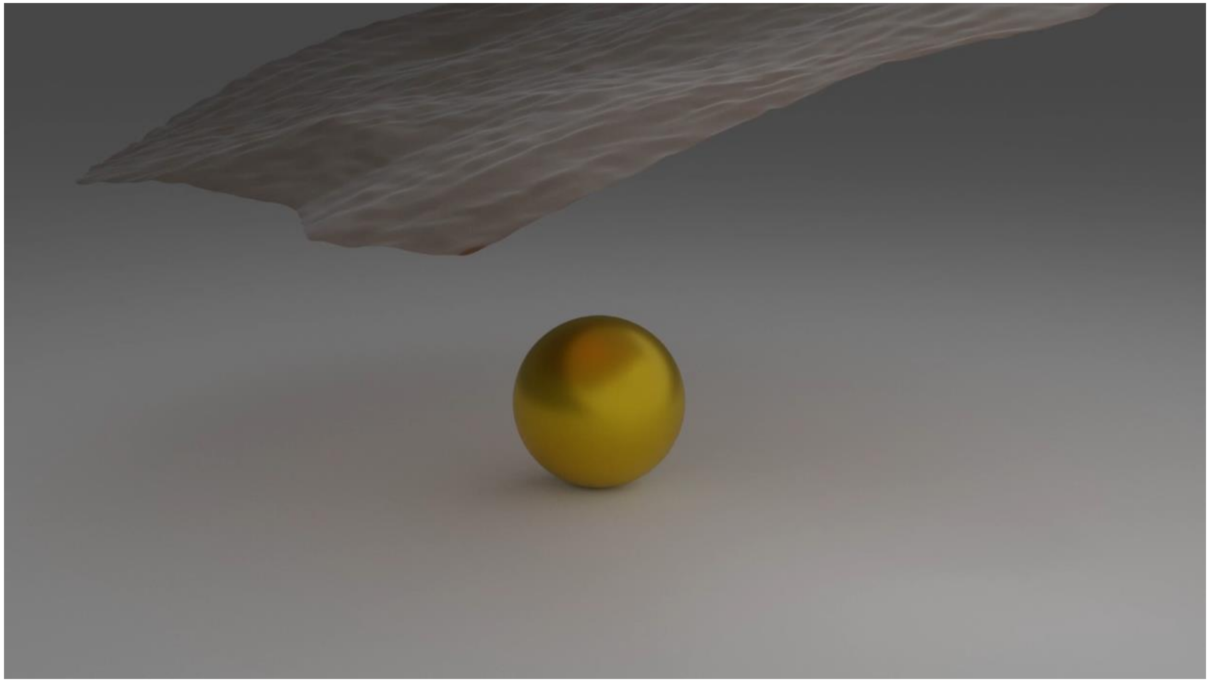
Corresponding grey-scale optical micrographs (I) and atomic force microscopy images (II) of as-deposited GO sheets. GO deposited from dispersions containing no salts (a) and added salts (b-d), exhibits a wrinkled, albeit almost flat morphology. This is due to the very thin (thickness of less than 1 nm) and flexible nature of GO sheets. In addition, as the deposition of GO on the surface is driven by attractive electrostatic forces (and possibly vdW forces), once a part of a GO sheet is anchored to the surface, the rest of the same flake cannot conform to a flat configuration due to the intrinsic thermal fluctuation and undulation.



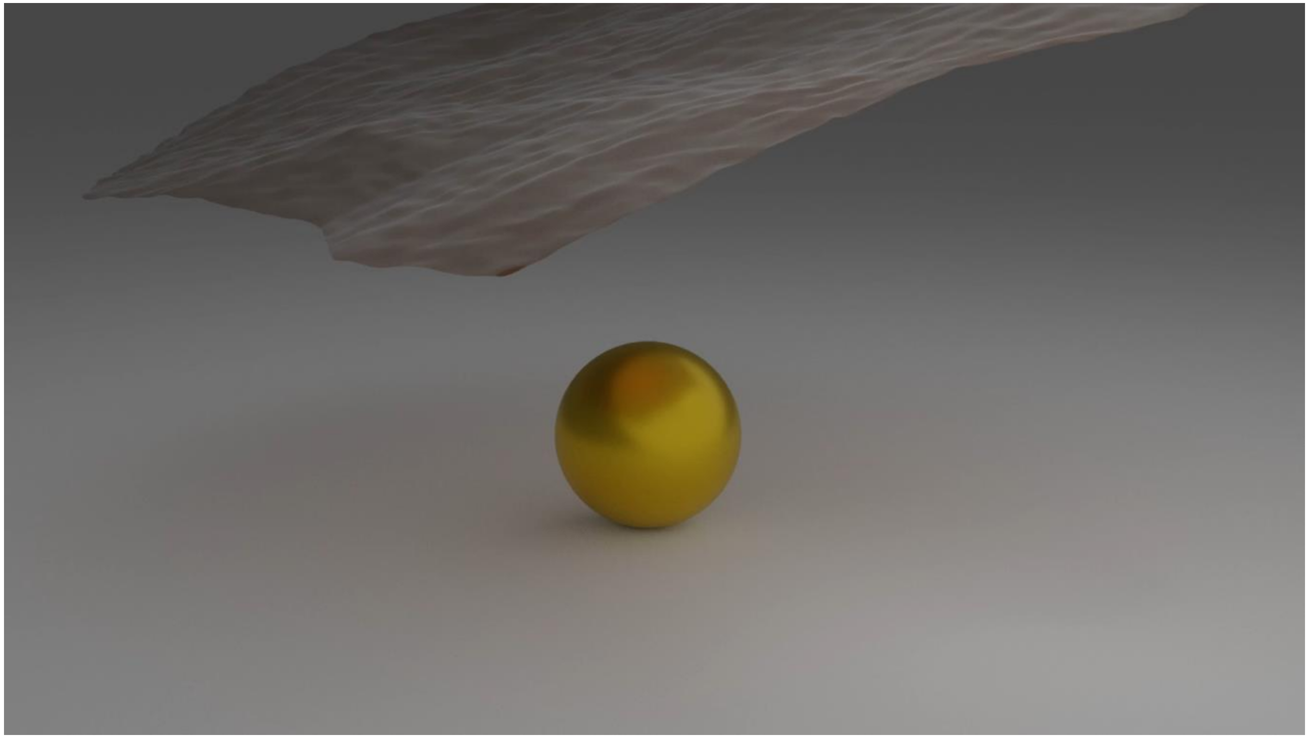
Nematic Lyotropic Liquid Crystals (NLLC)



Effect on microorganisms



Effect on microorganisms



Open questions

By ruling out the effect of the electrostatic force on GO rigidity, what factors are responsible for the rigidity of GO in water?

Do the metal cations neutralize the GO surface charge or they just simply react with the multi-functional groups on the surface?

Conclusion

Conclusions

We therefore conclude that the rigidity of GO should have minor electrostatic contributions, although the origin of the super-flexibility of GO sheets yet remains to be understood.

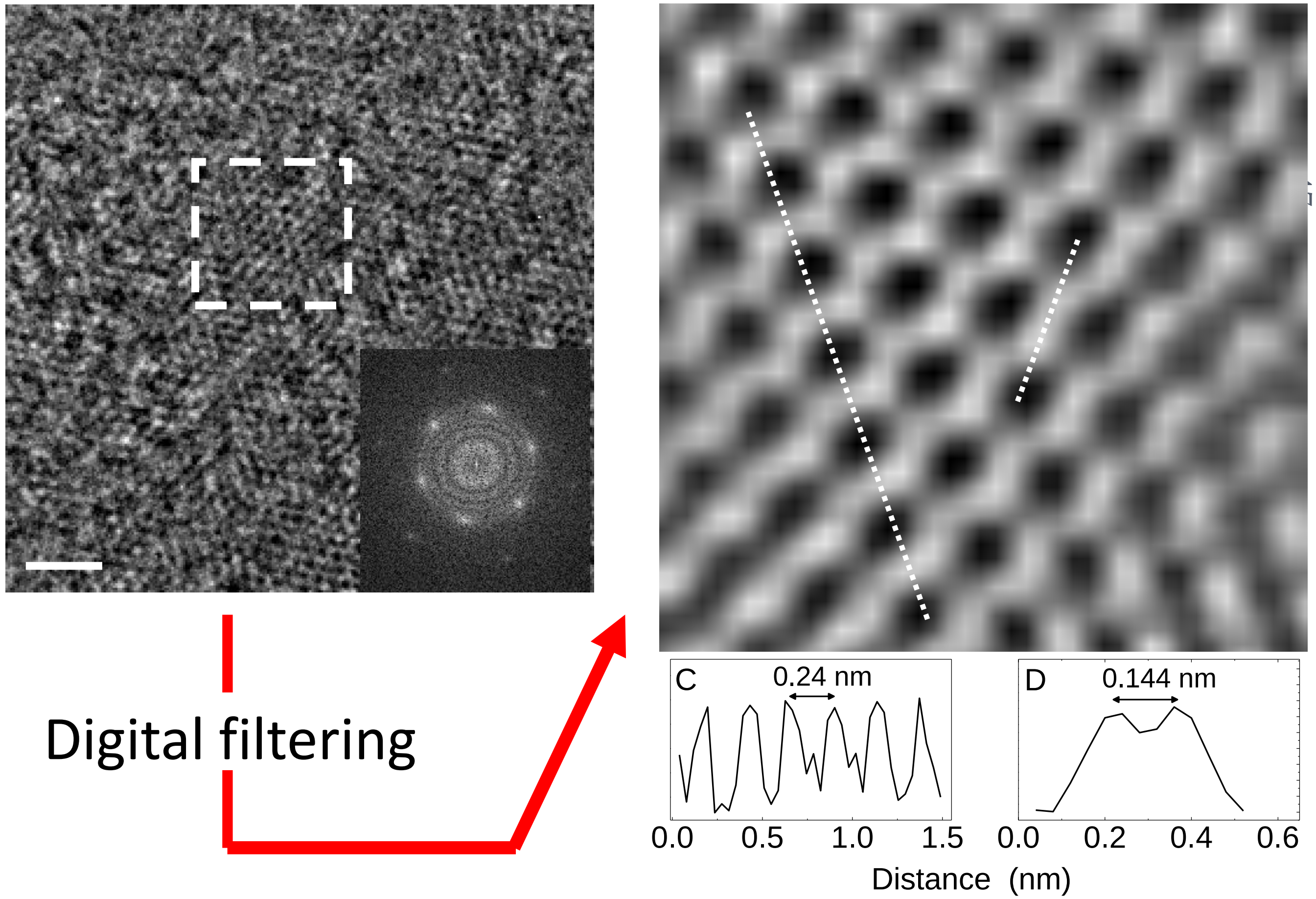
The significance of this finding is that the flat geometry of GO sheets retains its original configuration in a wide range of aquatic environments.

This calls for performing proper safety checks before the final roll-out of true 2D materials for real-world applications.

Thanks!!!

Thanks to:
Dr. Moazzami Gudarzi (National Graphene Institute)
Dr. Taheri (CMNL)
Dr. Sanjari (JETCO)
Dr. Nikfazan (GrapheneX)
Dr. Satalov (f. Leibniz University Hannover)

Aberration corrected scanning TEM



Bad solvents

Table 1. LC formation concentration and GO sheet properties in different solvents.

Solvent	LC formation concentration	Sheet thickness*	d-spacing**
	(mg ml-1)	(nm)	(nm)
Water	0.25	0.83	0.825
DMF	0.25	1.1	1.05
CHP	0.25	1.0	0.101
THF	0.50	0.92	0.937
Acetone	0.50	0.86	0.846
Ethanol	0.25	0.83	0.820

*: Sheet thickness obtained from AFM images

**:*d-spacing* obtained from XRD patterns

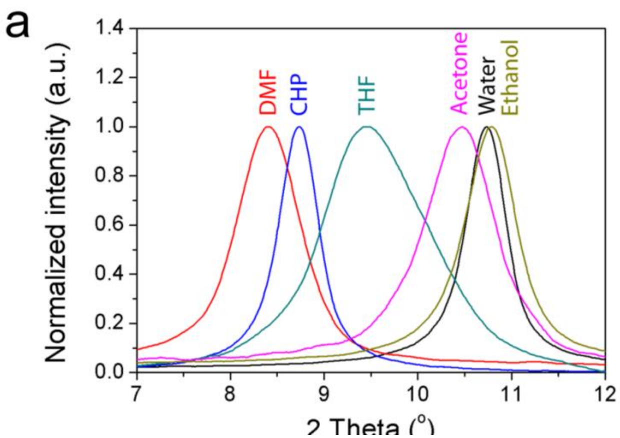
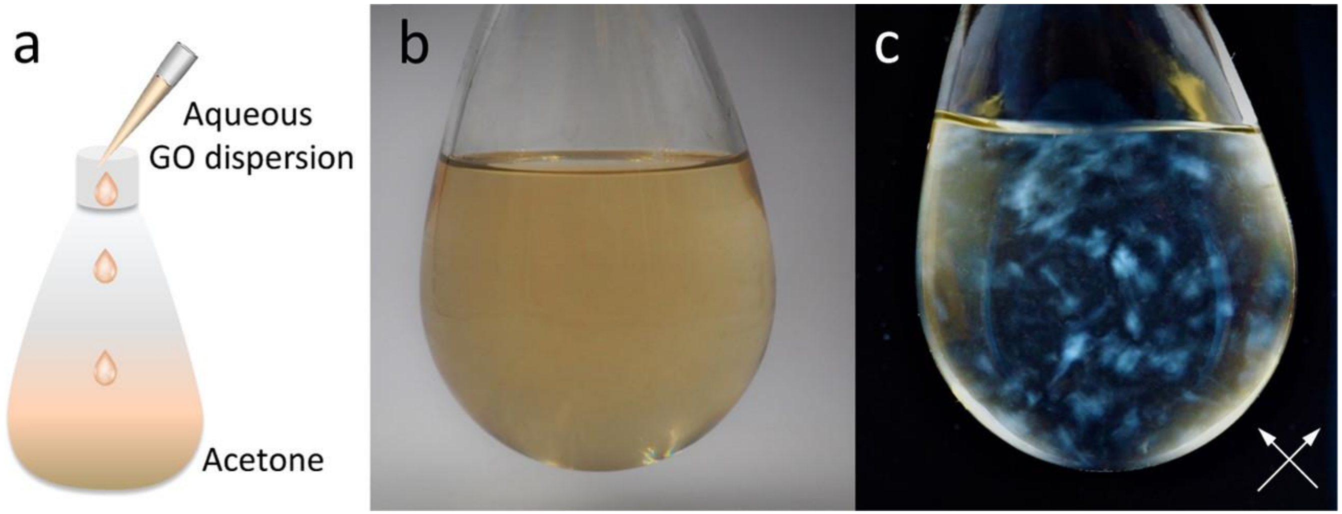


Table 2. Hansen parameters and Gordon parameter for the solvents could support LC GO.

Solvent	LC formation concentration	Hansen Parameter for solvents				Surface tension	Gordon parameter
	(mg ml^{-1})	dispersive	polar	hydrogen	total	(mN m^{-1})	(J m^{-3})
Water	0.25	15.5	16.0	42.3	47.8	72.8	2.77
ethylene glycol	0.25	17.0	11.0	26.0	33.0	47.7	1.25
N-methyl pyrrolidone	0.25	18.0	12.3	7.20	23.0	40.8	0.890
DMF	0.25	17.4	13.7	11.3	24.9	37.0	0.869
dimethyl acetamide	0.25	16.8	11.5	10.2	22.8	36.7	0.810
CHP	0.25	18.2	6.80	6.50	20.5	42.3	0.770
methanol	0.25	15.1	12.3	22.3	29.6	22.7	0.661
THF	0.50	16.8	5.70	8.00	19.5	26.4	0.610
Acetone	0.50	15.5	10.4	7.00	19.9	25.2	0.601
Ethanol	0.25	15.8	8.80	19.4	26.5	22.1	0.569
isopropanol	0.25	15.8	6.10	16.4	23.6	23.0	0.542

Bad solvents



Rheological behaviour

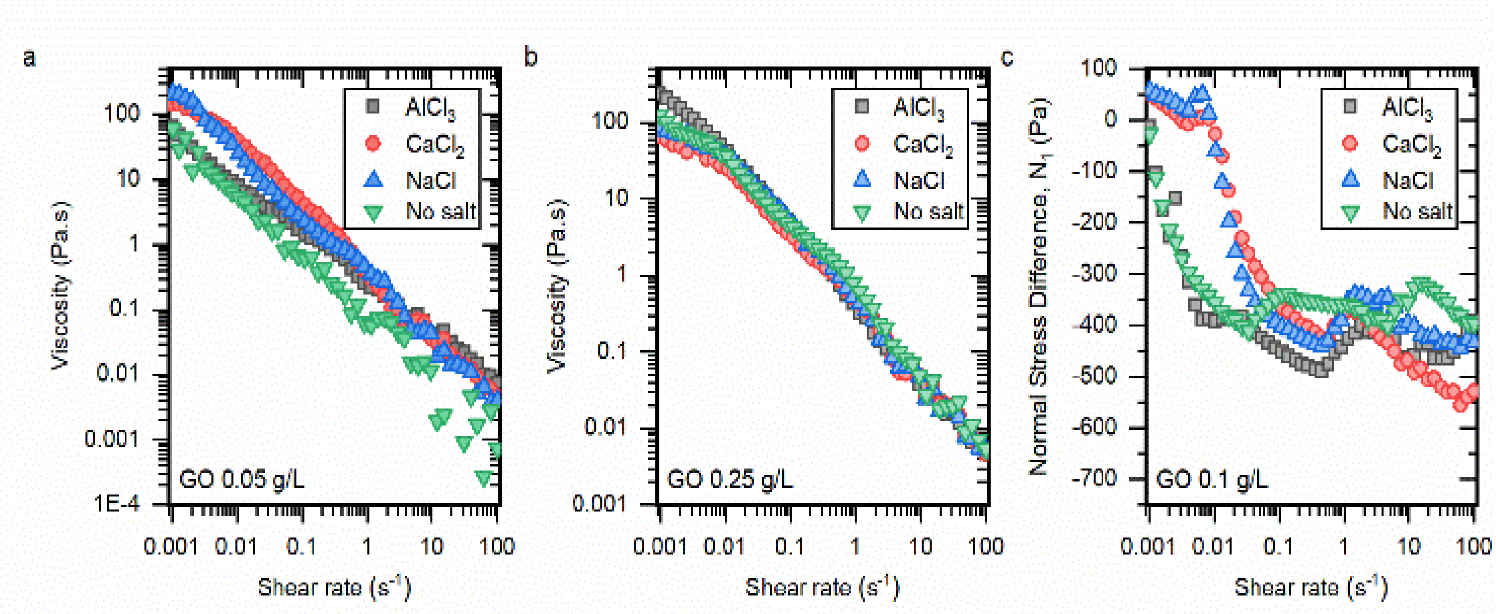


Fig. 4 Rheological behaviour of graphene oxide dispersion containing different salts. Shear viscosity of dilute graphene oxide dispersions as a function of shear rate at different salts concentrations is depicted for graphene oxide concentrations of (a) 0.05 g/L and (b) 0.25 g/L. For other GO concentrations please see Fig. S8. The as-observed almost identical flow behaviour for all dispersions further verifies no change in the aspect ratio of planar GO sheets validating the stable flat conformation of GO sheets in the presence of salts. This is in contrast to the flow behaviour of polyelectrolyte solutions and charged colloidal dispersions Viscosity of the polyelectrolytes solutions normally drops upon the addition of salts due to the large contribution of electrostatic chain rigidity of most polyelectrolytes. (c) The shear alignment of GO sheets results in negative normal stress experienced by the dispersions. This is in contrast to normal polymer liquid crystals. Due to volume filling and packing considerations, increasing the shear rate results in a drop in viscosity and higher absolute normal stress difference. We speculate that the tendency of GO sheets to straighten toward a hypothetically perfect order leads to a compressive force working along the streamlines, consequently resulting in a negative normal stress.