Super-hydrophobic graphene-based materials: impact of surface properties on wettability

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Alcereco / Grafoid

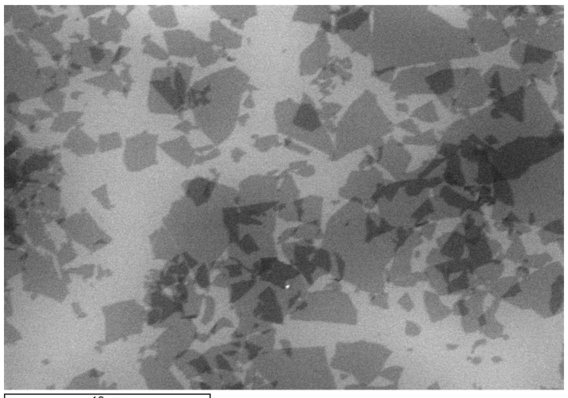
- Alcereco is an advanced materials company wholly-owned subsidiary of Grafoid.

- Alcereco is based at the former Novelis/Alcan Global R&D site & retains stewardship of a variety of important (and some proprietary) equipment and the expertise to operate them at a high technical level.

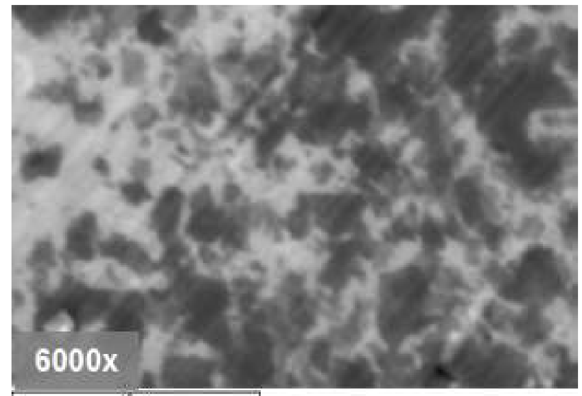
- Competencies cover a wide range of aluminum-related technologies:
    - Casting custom alloys, Rolling, Heat treating
    - Coatings: organic, inorganic, roll-bonded, sprays, films, etc.
    - Material Characterization
        - Mechanical properties, microstructure, composition, XRD, Raman, XPS, XRF, HRTEM, DSC, OES, SEM-EBSP, FIB, etc.

Graphene coatings at Alcereco / Grafoid

GrafeneX: Proprietary technology to deposit graphene on many types of substrates: glass, metals, polymers



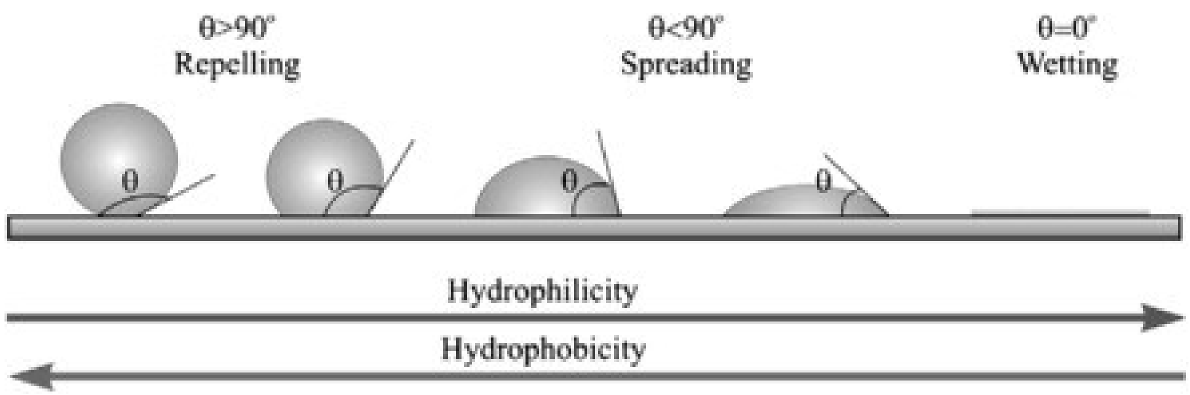
Graphene on Si wafers



Graphene on Al sheet

- Our coatings are “polygranular”, few-layer graphene (in contrast with single layer, “monocrystalline” CVD deposited graphene).
- GrafeneX is a scalable, continuous, environmentally friendly method which produces graphene coatings customized to client’s needs.
- Three main areas of graphene materials:
  - **Hydrophilic graphene:** pre-treatments, adhesion promoting, wettable and printable coatings…
  - **Hydrophobic graphene:** printable electronics, EM shielding, battery materials…
  - **Super-hydrophobic graphene:** self-cleaning, water repellant, anti-fogging coatings…

Hydrophobic surfaces



(Super)hydrophobic: (very) afraid of water!

Hydrophobic θ > 90°

Super-hydrophobic θ >120°

Swarthmore College Biology Department,, Hans J. Ensikat et al., Beilstein J. Nanotechnol. 2011, 2, 152–161.

Hydrophobic surfaces

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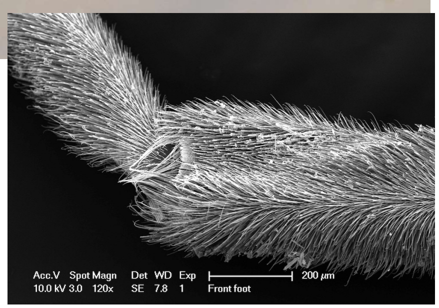
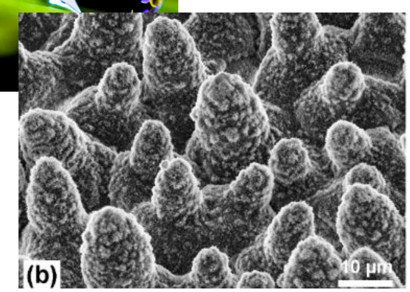
Hydrophobicity in nature





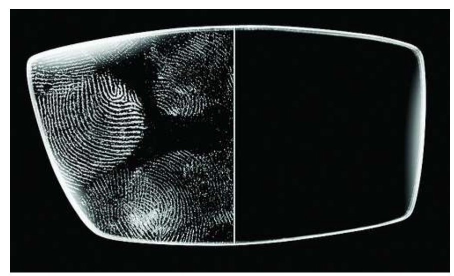
“Lotus” effect: non-wettable (apolar or “waxy”) chemistry + microstructure/nanostructure

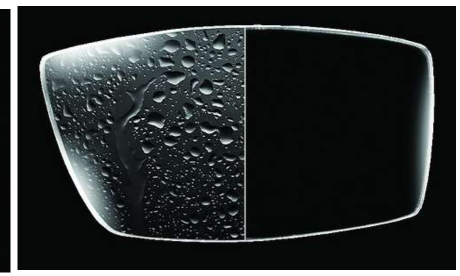
Swarthmore College Biology Department,, Hans J. Ensikat et al., Beilstein J. Nanotechnol. 2011, 2, 152–161.

Applications

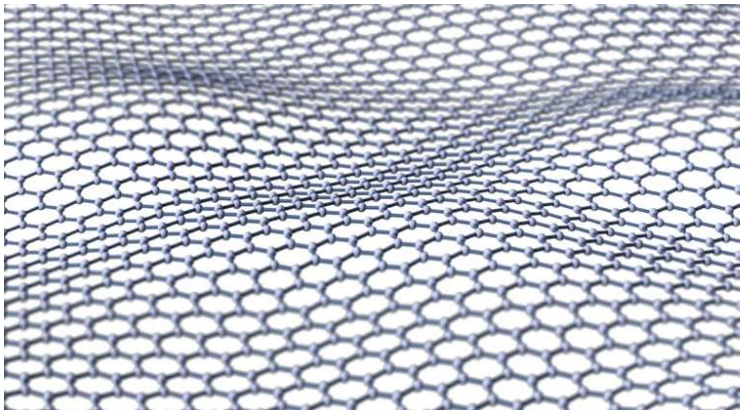
Hydrophobic / super-hydrophobic coatings

- Anti-fogging, anti-smudge, self-cleaning, anti-icing coatings
- Corrosion protective coatings

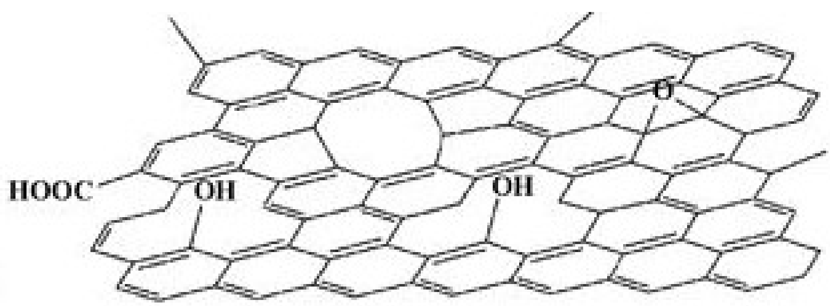




Graphene



- Theoretically, graphene is simply a 2-D mesh of a single layer of carbon atoms (apolar structures)
- Graphene-based coatings are expected to be hydrophobic
- Water contact angle (WCA) measured on Gr surfaces ≈ 70 - 90^{o} (similar to polymeric surfaces, e.g. PP, PS!)



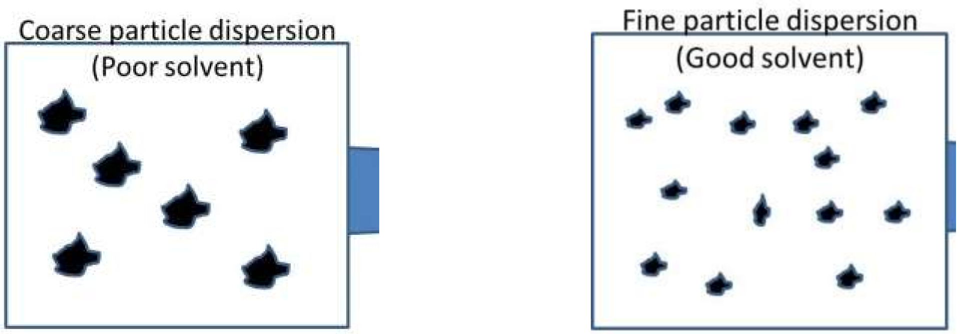
- Real-life graphene flakes (e.g. obtained by chemical exfoliation) have detects (e.g. holes, O-groups, dangling bonds, deformed structures, etc) originating from either the deposition or transfer / reduction process.
- These detects locally disturb the electron distribution, thereby introducing permanent dipoles (like polar moieties).

Graphene

Graphene-based coatings can be super-hydrophobic if:

- They are defect-free or low-defect structure with apolar groups ("waxy" chemistry), and
- Have micro/nano structures at the surfaces:
  - μ-texturing of the substrate vs.
  - μ-texturing of the coating

Idea: solvent –GO flakes interactions would control the conformation of the flakes affecting the morphology (wettability) of final GO and (r-GO) films

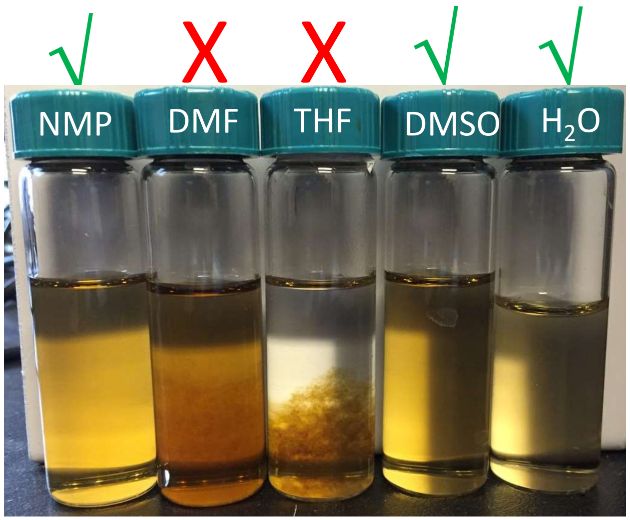


TEM image of a single layer GO film

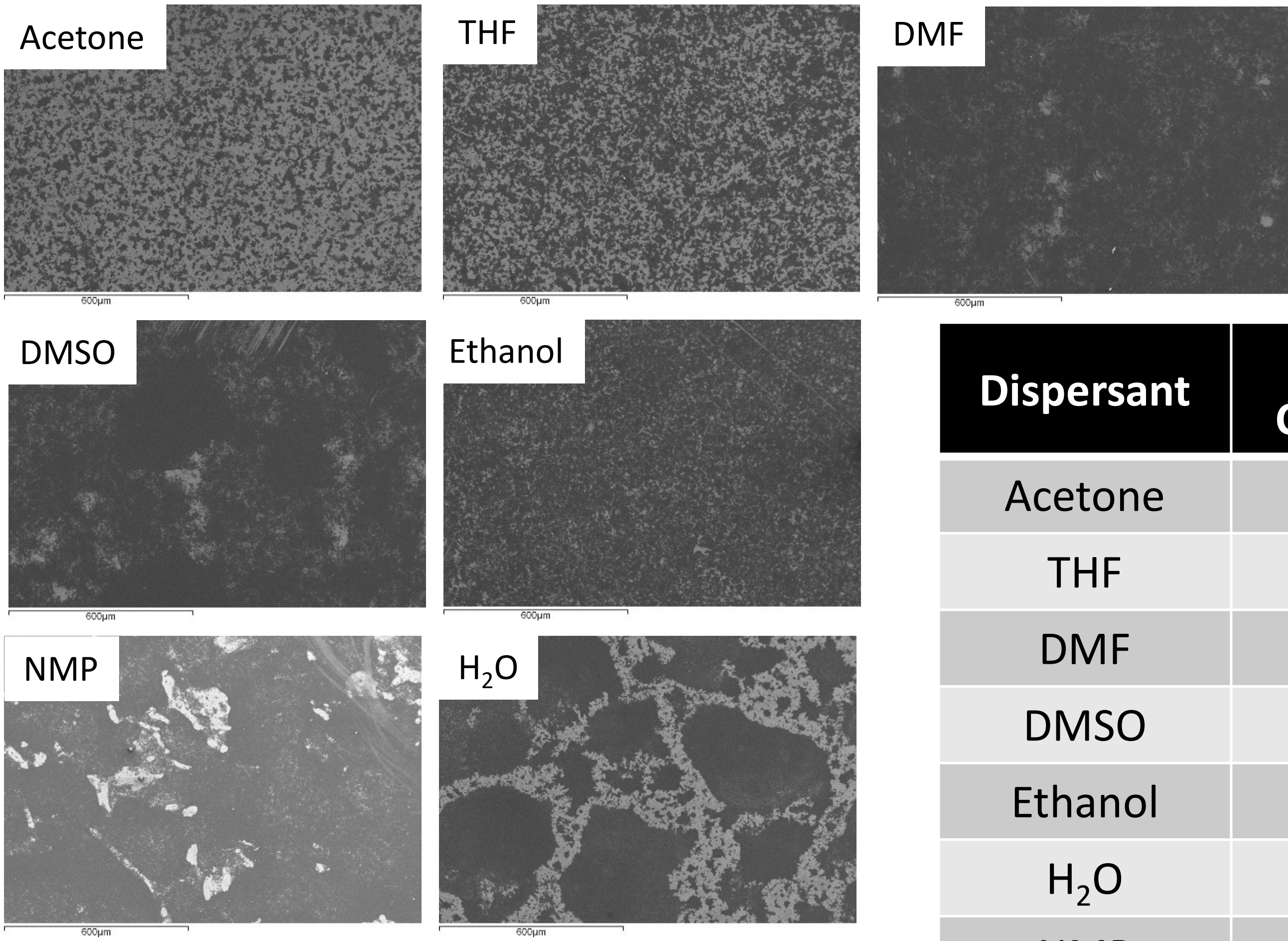
C. Gomez-Navarro, J. C. Meyer, R. S. Sundaram, A. Chuvilin, S. Kurasch, M. Burghard, U. Kaiser, *Nano Lett.* **2010**, *10*, 1144.

Experimental

1. GO dispersions in water (4 mg/mL) were further diluted till a concentration of 0.1 mg/mL using polar solvents:
    - N-methyl-2-pyrrolidone, NMP, aprotic polar, 4.1D
    - Dimethyl sulfoxide, DMSO, aprotic polar, 3.96D
    - Dimethylforamide, DMF, apriotic polar, 3.86D
    - Acetone, apriotic polar, 2.91D
    - Water, priotic polar, 1.86D
    - Ethanol, priotic polar, 1.69D
    - Tetrahydrofuran, apriotic "borderline" polar, 1.63D
2. Dispersions were studied visually and using Dynamic Light Scattering (DLS)
3. GO films were obtained by spraying the dispersions onto clean surfaces of SiO_2/Si wafers followed by drying under vacuum @ 80 ^oC for 1h
4. GO films were reduced under vacuum @ 1100^{o}C for 2 h
    - SEM, AFM-morphology, thickness and surface coverage
    - XPS, Raman Spectroscopy-chemistry
    - CAG + Cassie-Baxter model-wettability



GO Coating Characterization by SEM & AFM



Dispersant	Surface Coverage (SEM)	Coating Height (AFM)
Acetone	28%	52 nm
THF	31%	21 nm
DMF	83%	3 nm
DMSO	92%	2 nm
Ethanol	96%	14 nm
H_2O	76%	14 nm
NMP	86%	9 nm

Wettability-WCA

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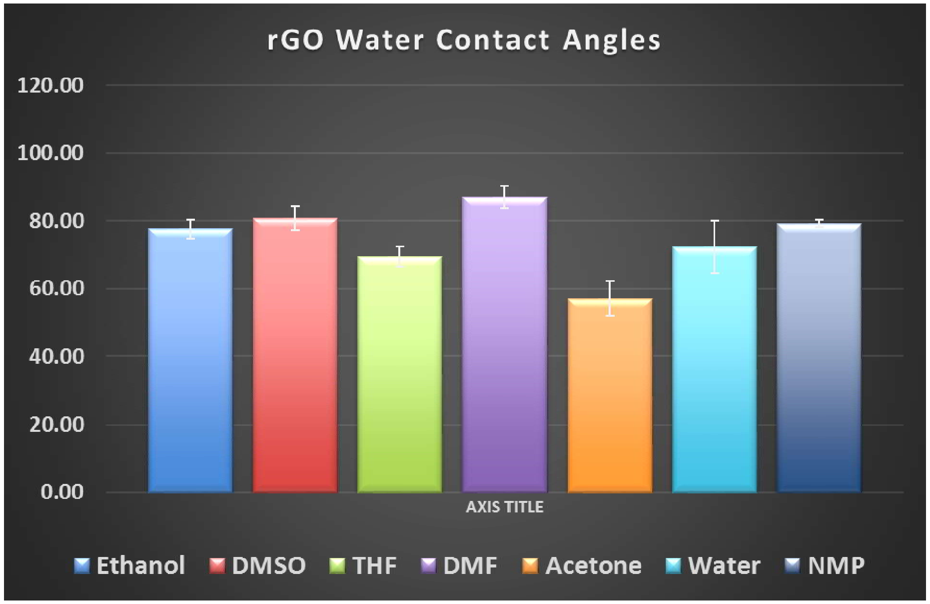
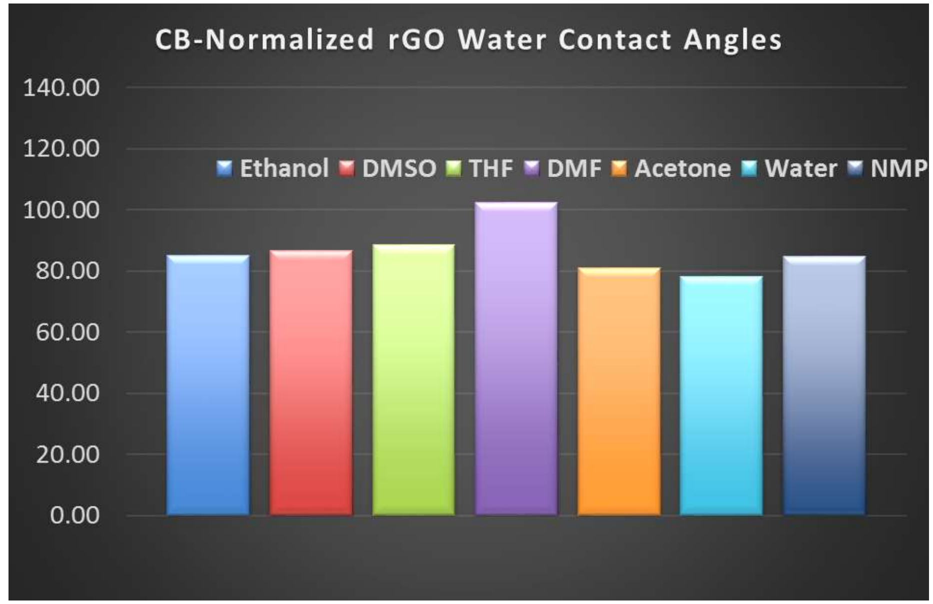




- WCA values are not a function of either the polarity of the solvent nor the film morphology
- Different surface coverage values may impact the measured values of the WCAs

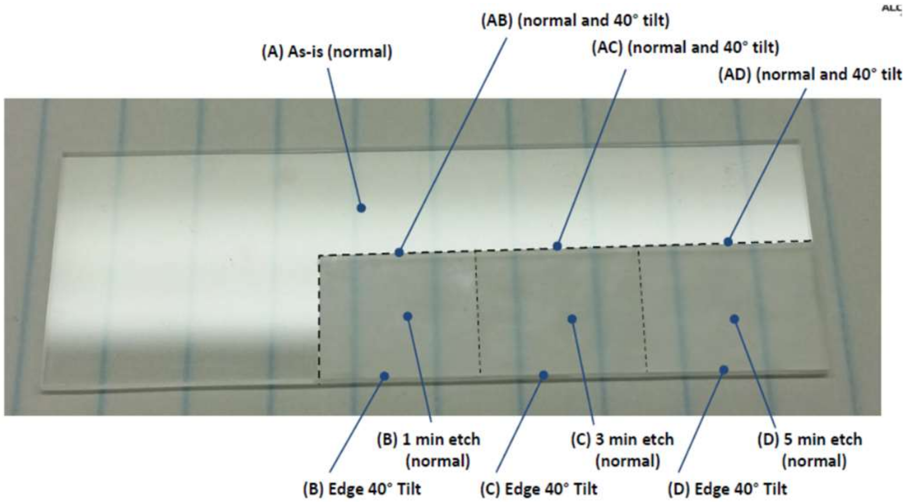
Cassie-Baxter Equation:

$$\cos(\theta_{100\%} = f * cos\ \theta + (1\text{-}f)*\cos(\theta_{substrate})$$

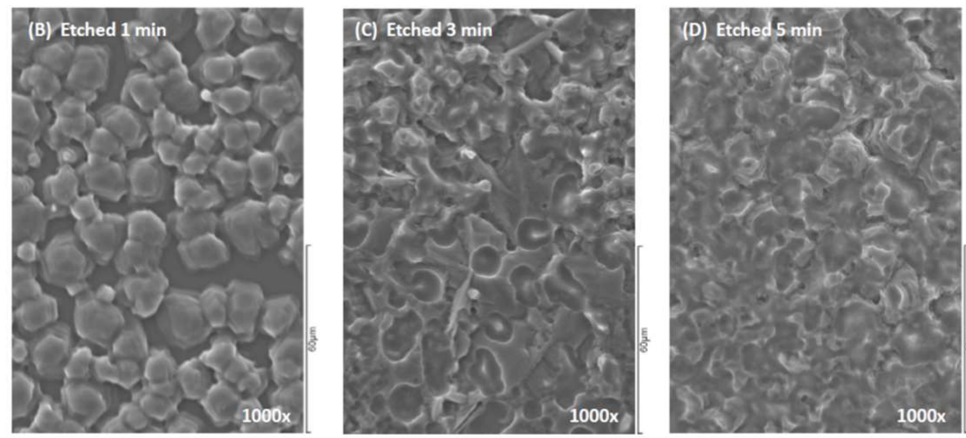
- f: fractional surface coverage of the film (determined by SEM)
- θ : measured water contact angle
- $\theta_{substrate}$: WCA on bare substrate (SiO_2)

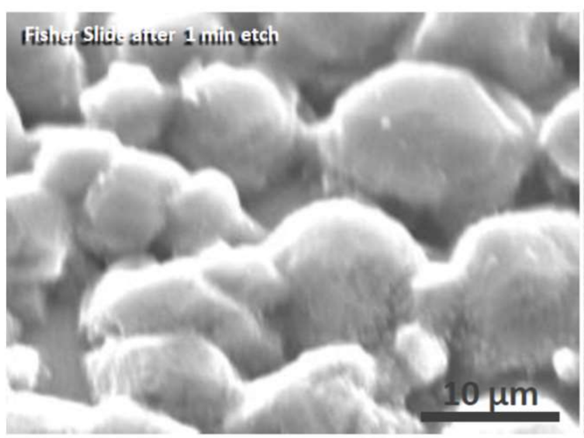
Substrate Topography-WCA

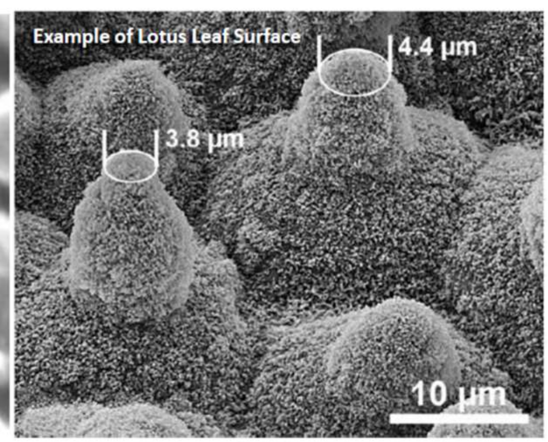
Fischer microscope glass slides etched with Armour Etch paste



SEM images normal to the surface







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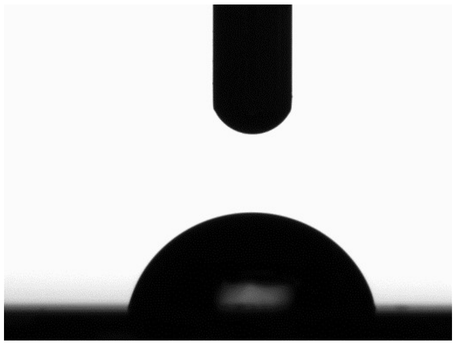
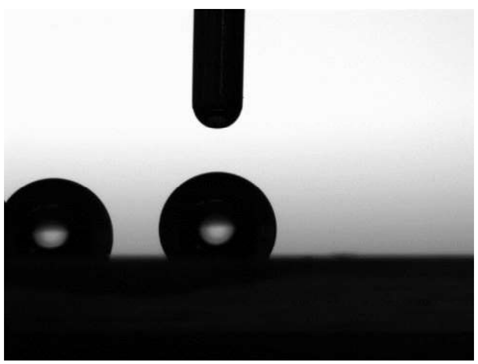
Substrate Topography-WCA

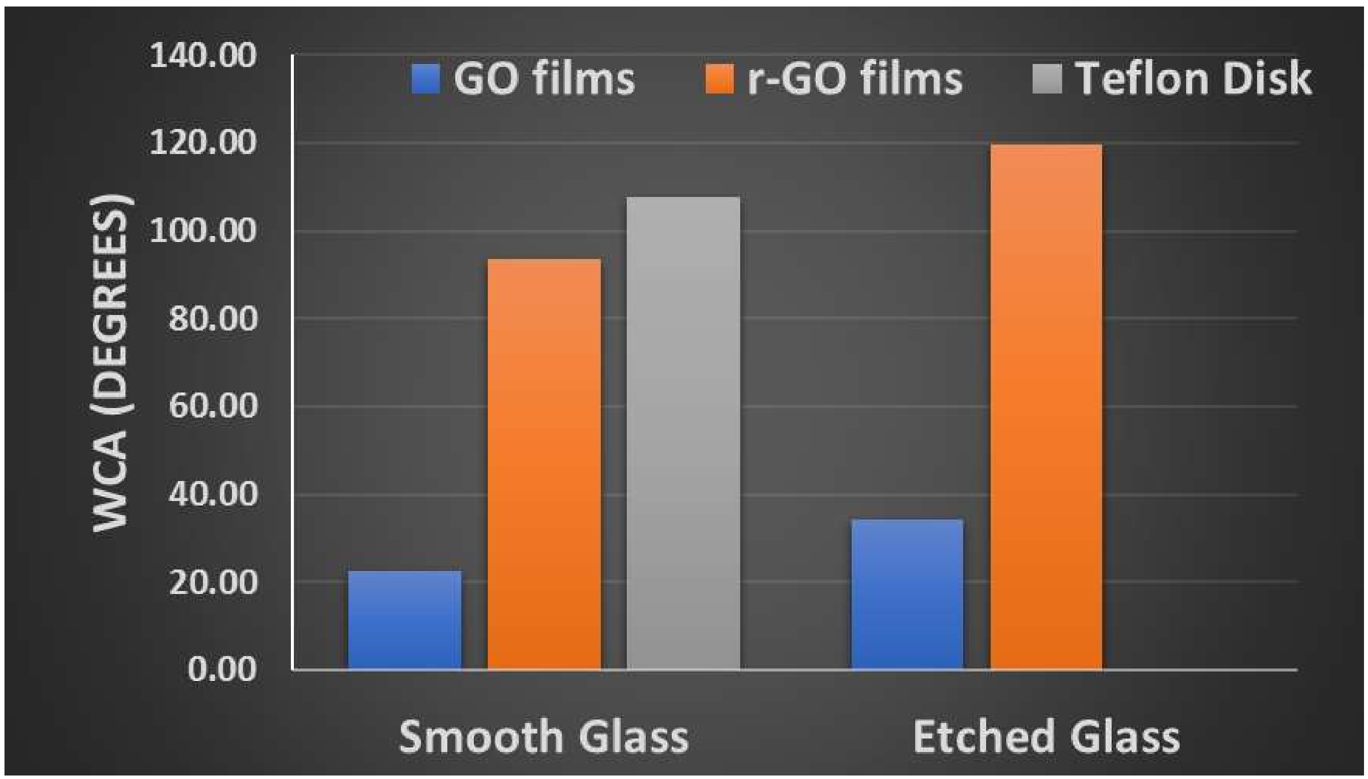
r-GO



r-GO on etched glass

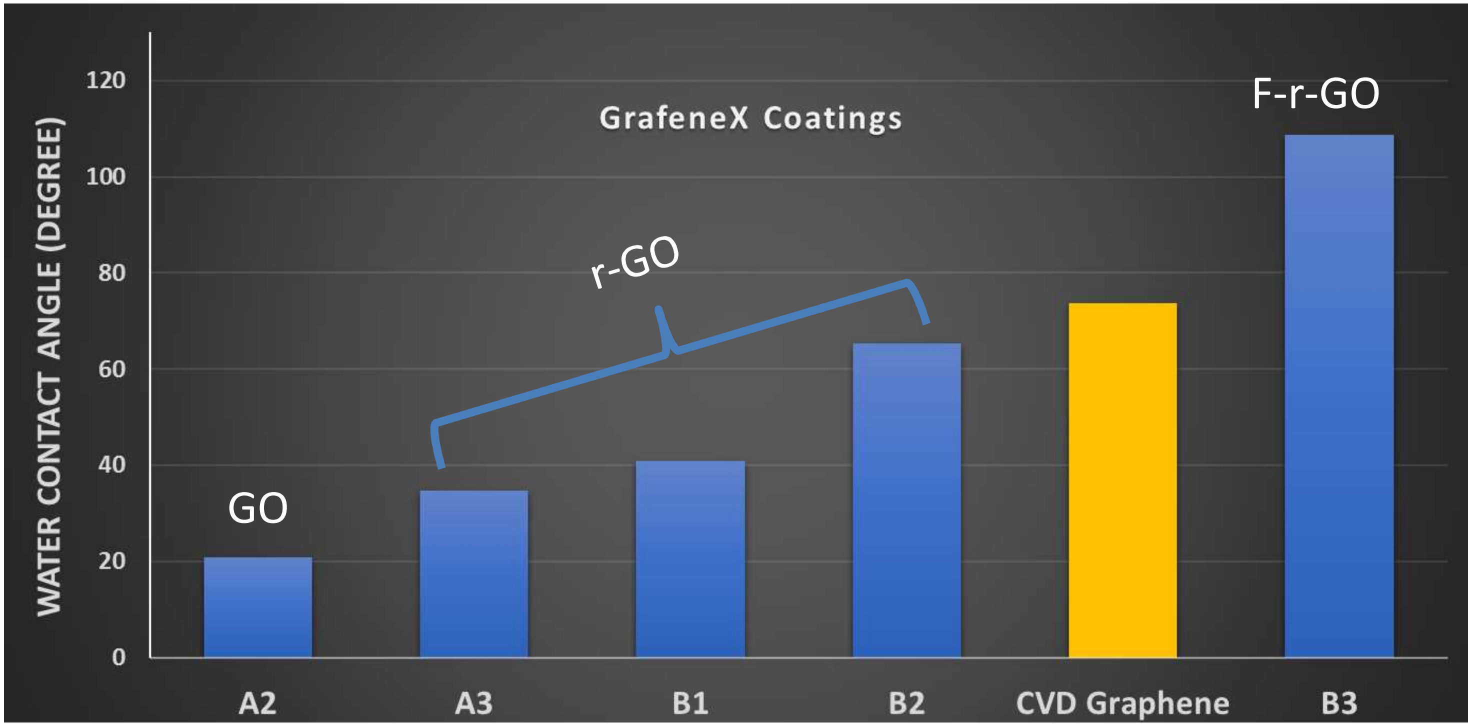


GrafeneX Coatings



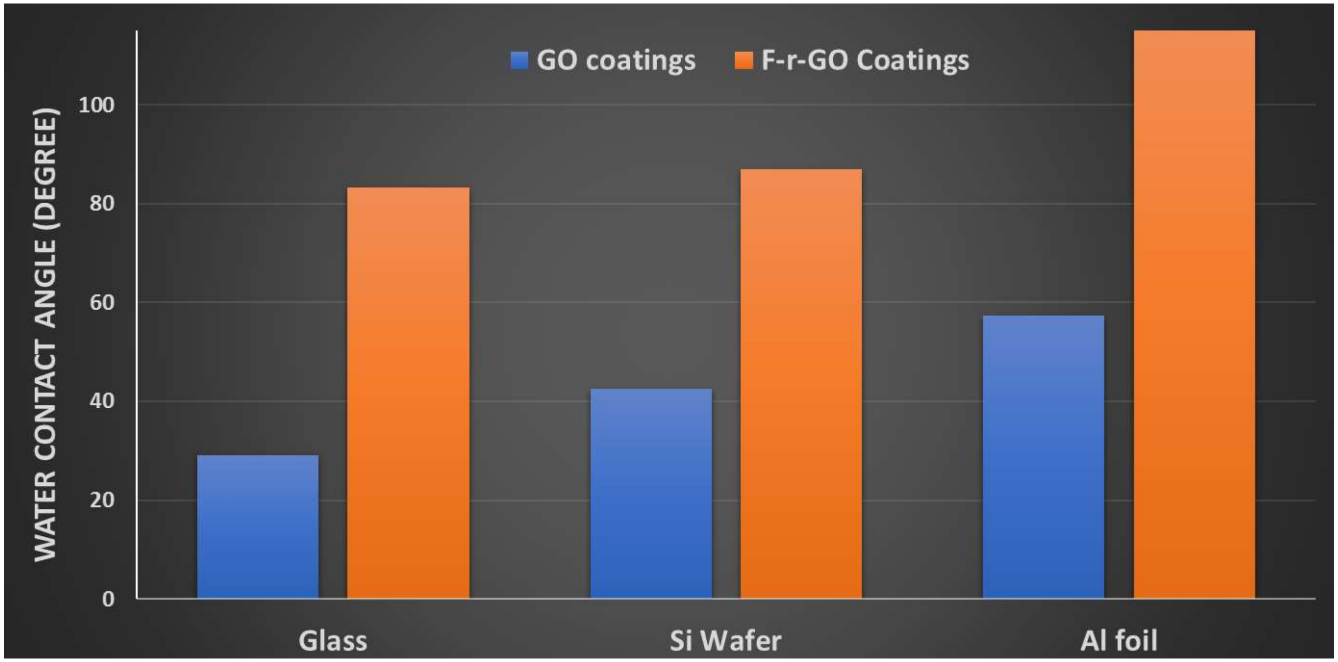
Film Chemistry-WCA

Functional groups can be grafted onto r-GO films: during or after the reduction process



Films were deposited on smooth Al foil

Substrate-WCA



- Differences have been observed between WCAs measured on coatings deposited on various substrates
- Surface coverage and roughness were similar in all cases, so the differences can be explained only by molecular re-arrangements within the coating to minimize interfacial energy with the substrate material.

XPS measurements on GO films showed that O is mostly present in:

- C-O-C groups for GO films on Si and Al substrates,
- C-O and O-C=O for GO on glass

Key Takeaways

- Wettability of graphene coatings is a function of:
  - Chemical composition (e.g. residual O-containing groups, new chemical groups incorporated)
  - Substrate surface coverage, this means composite WCAs are measured when surface coverage is incomplete
  - Substrate topography
  - Type of substrate; due to its very low thickness, molecular re-arrangements at the interface between graphene layer and substrate can be reflected in the values of the WCAs
  - Other?

- Graphene-based super-hydrophobic coatings (WCA ≥ 120º) require:
  - μ-texturing of the substrate
  - Altering the chemistry of the graphene, since C=C, C-C bonds are apolar, but not the most water repellant.

Acknowledgements

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- Thank you!