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

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March 2017
Barcelona
Alcereco / Grafoíd

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

- 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 / Grafoïd

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

- 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 $\theta > 90^\circ$

Super-hydrophobic $\theta > 120^\circ$

Hydrophobic surfaces

Hydrophobicity in nature

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

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° (similar to polymeric surfaces, e.g. PP, PS)

- Real-life graphene flakes (e.g. obtained by chemical exfoliation) have defects (e.g. holes, O-groups, dangling bonds, deformed structures, etc) originating from either the deposition or transfer / reduction process.

- These defects 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

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
   - Dimethylformamide, 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 °C for 1h
4. GO films were reduced under vacuum @ 1100°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

<table>
<thead>
<tr>
<th>Dispersant</th>
<th>Surface Coverage</th>
<th>Coating Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>28%</td>
<td>52 nm</td>
</tr>
<tr>
<td>THF</td>
<td>31%</td>
<td>21 nm</td>
</tr>
<tr>
<td>DMF</td>
<td>83%</td>
<td>3 nm</td>
</tr>
<tr>
<td>DMSO</td>
<td>92%</td>
<td>2 nm</td>
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<tr>
<td>Ethanol</td>
<td>96%</td>
<td>14 nm</td>
</tr>
<tr>
<td>H₂O</td>
<td>76%</td>
<td>14 nm</td>
</tr>
<tr>
<td>NMP</td>
<td>86%</td>
<td>9 nm</td>
</tr>
</tbody>
</table>
Wettability-WCA

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

- $f$: fractional surface coverage of the film (determined by SEM)
- $\theta$: measured water contact angle
- $\theta_{substrate}$: WCA on bare substrate ($\text{SiO}_2$)
Substrate Topography-WCA

Fischer microscope glass slides etched with Armour Etch paste

SEM images normal to the surface
Substrate Topography-WCA

r-GO

GrafeneX Coatings

r-GO on etched glass

![Graph showing WCA for GO films, r-GO films, and Teflon Disk on Smooth Glass and Etched Glass](image)

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

Films were deposited on smooth Al foil.
• 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 ≥ 120°) 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

• Rejean Lemay, John Ward, Victoria Vander Byl (Alcereco Inc.)

• NSERC-Engage program funding

• Mary Gallerneault is thankful for an NSERC Industrial Postgraduate Scholarship for her MSc @ Queen’s University & Alcereco Inc.

• Thank you!