AVT-373 Research Specialists' Meeting on
"Emerging Technologies for Proactive Corrosion Maintenance"

Nanomaterials-Based Sensors for Corrosion Detection and Monitoring for Proactive Aircraft Management

Lucy Li[1*], Mounia Chakik[2], Shiva Ashoori[2],
Eyal Rosesheter[3], Ravi Prakash[2], and Jingwen Guan[4]

[1*] Aerospace Research Centre, National Research Council Canada, Ottawa, CANADA
[2] Department of Electronics Engineering, Carleton University, CANADA
[3] Department of Physics, Carleton University, CANADA
[4] Security and Disruptive Technologies, National Research Council Canada, Ottawa, CANADA

Canada NRC·CNRC

Oct 9-11, Bastad, Sweden

Carleton UNIVERSITY

NRC Aerospace

1 Structures and materials

2 Aerospace manufacturing

3 Aerodynamics

4 Propulsion

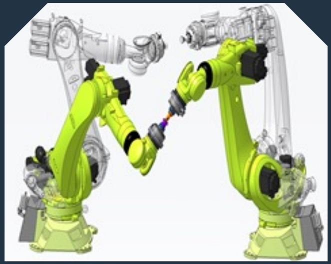
5 Flight research

Programs and Focus Areas

Low Emission Aviation

Integrated Aerial Mobility

Aeronautical Product Development & Certification



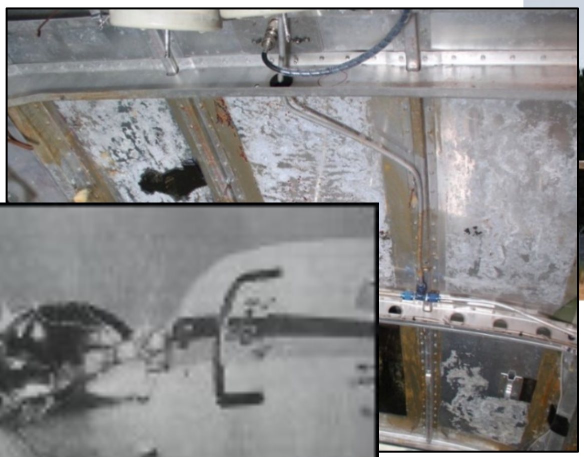
Advanced Digital Aerospace Manufacturing

Defence Technology Sustainment

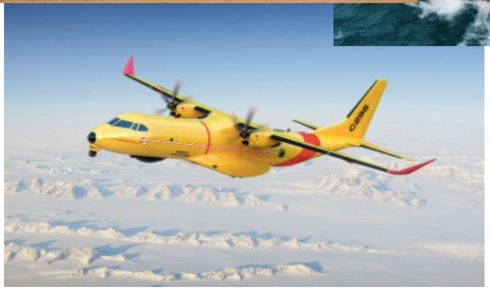
Air Travel Research

Key Objectives

- Chromate-free coating – the Future is Not Without its Challenges:
  - Study Li- and Mg- rich chromate-free systems
  - Environmental corrosion sensors for on-aircraft application
  - *Research and development of onboard sensors for direct corrosion detection (Low TRL)*

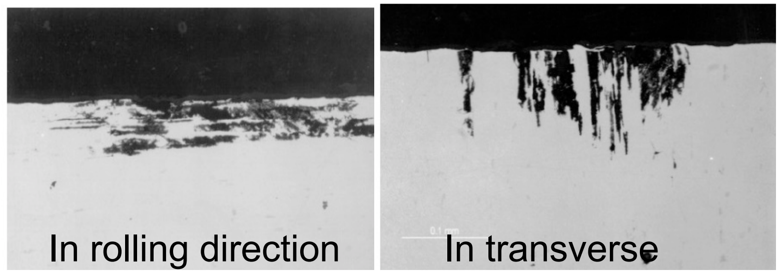


(Aloha, 1988)



Corrosion Types

Unform corrosion

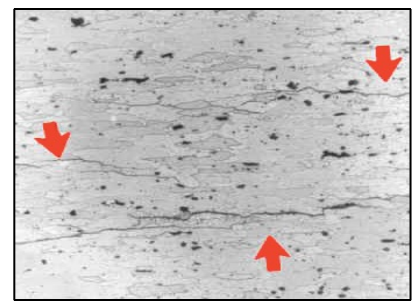


Pitting Corrosion

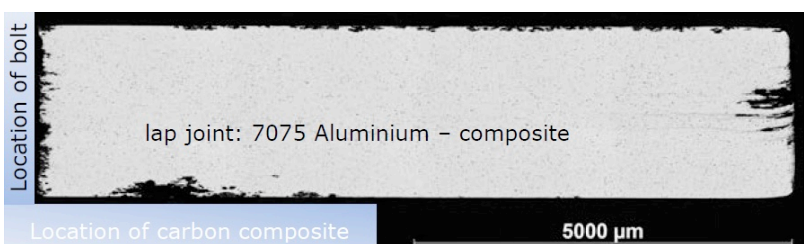
Fretting corrosion

Exfoliation of 7178-T6

Filiform corrosion



Intergranular corrosion of 7075-T6 (including stress corrosion)



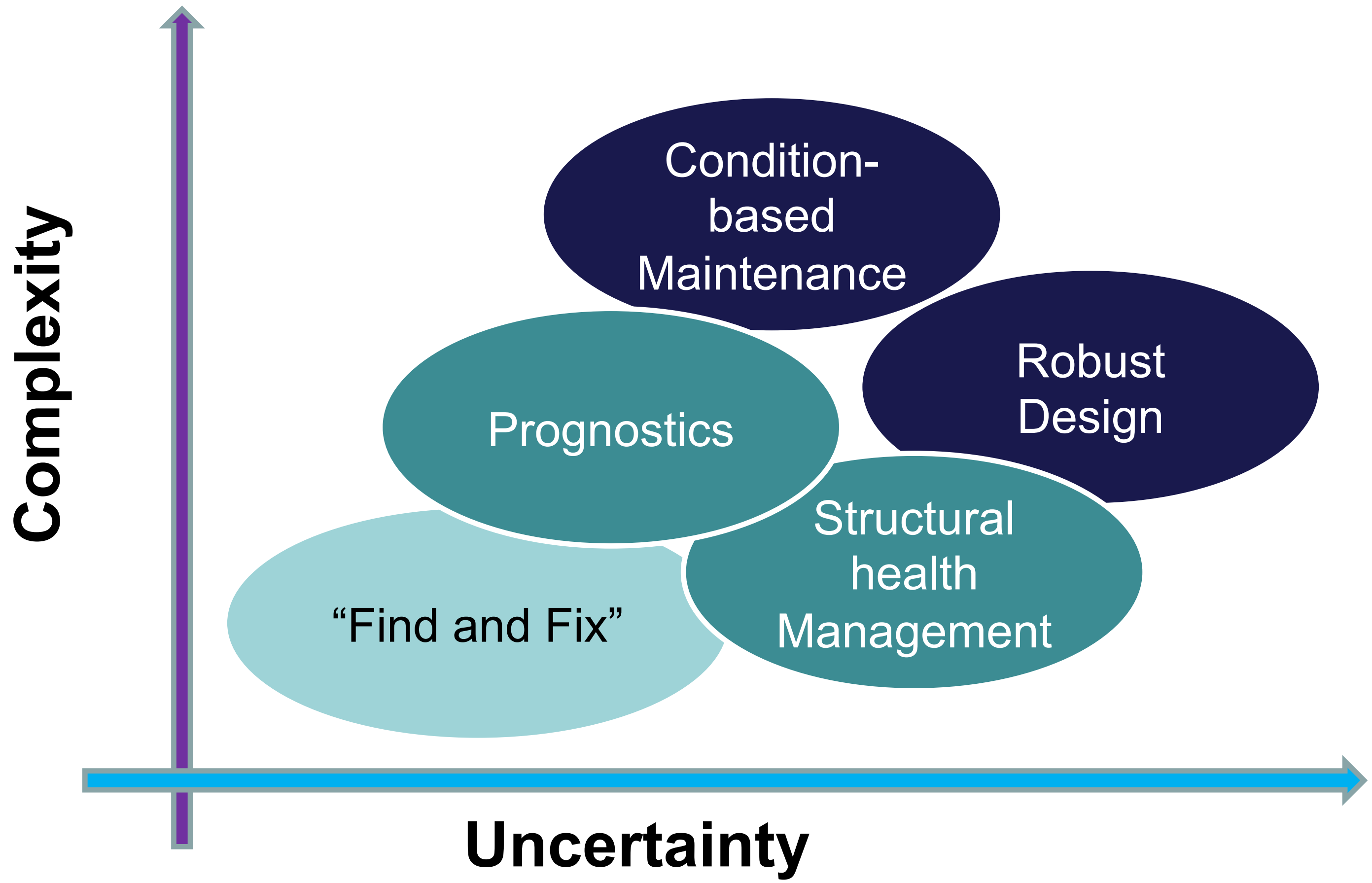
Galvanic corrosion (Ludmila, 2019)

Challenges of Corrosion

- **Costs of Corrosion**
  - For the US Air Force, the cost of corrosion in the FY2018 was $5.67 billion, or 23.6% of total maintenance costs*.
  - 14% of total Non-available Days (NAD) for the Air Force aviation and missiles
- **Challenges**
  - Fixed schedule inspection could lead to “unnecessary” inspection, and/or unexpected and sometimes severe corrosion – downtime and costs;
  - Chromate-free paint systems poses challenges in corrosion management;
  - Galvanic corrosion an prevalent issue at the joints of Al/CFRP (carbon fibre reinforced plastic) with the increase in composites usage
  - No good method to detect or predict breakdown coating / sealants – a key factor in corrosion onset;

*Logistics Management Institute: Tysons, VA, USA, 2018.

Proactive Corrosion Management

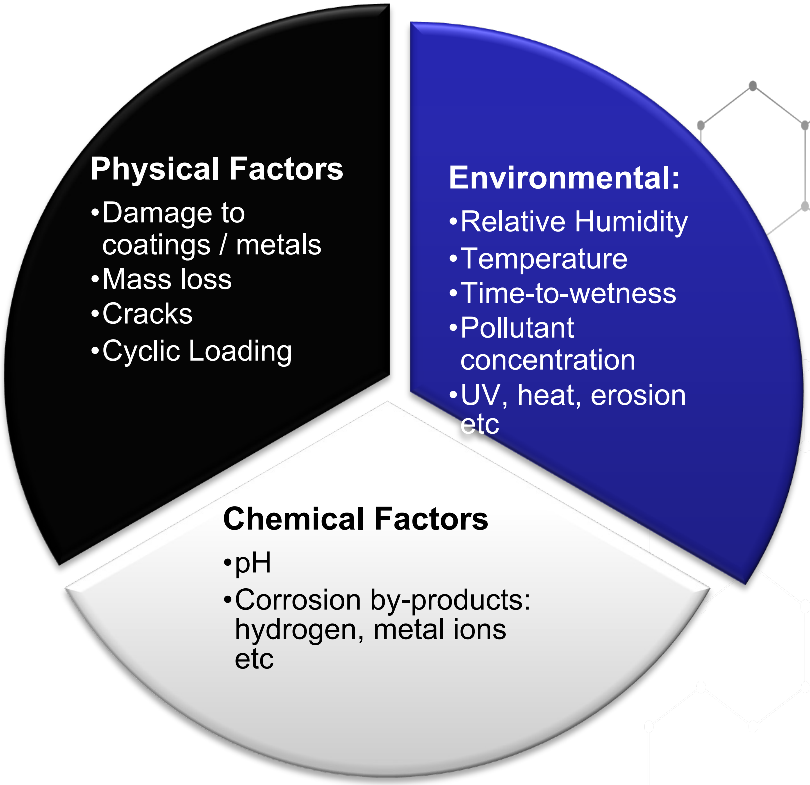


Advanced corrosion sensing as part of structural heath management is key to proactive management

Matrix for Corrosion Detection

Key parameter to inspect for corrosion detection:

- Temperature
- Relatively Humidity
- Time-to-wetness
- Concentration of chloride ions: increases rate of corrosion and prevent generation of protective oxide layers on certain metals;
- Metal ions: high concentration of metal ions from water evaporation promotes corrosion
- Hydrogen and pH:
- UV and other electrolyte



Li *et al. Sensors* **2021**, *21*(9), 2908

Direct detection of corrosion events + continuous measurement of environmental parameters pertaining to corrosion = foundation for reliable corrosion management

Sensor Requirements

- Ultra-high sensitivity to detect corrosion by-products
- Tunable selectivity
- Compact
- Low power consumption
- Low cost fabrication
- Durable
- Wireless transmission on the ground only

Corrosion sensor types [Li, 2021]

Corrosion Factors	Sensors	Description	Pros and cons
Physical	• Visual/enhanced visual inspection • Eddy current • Radiography • Thermography • Electrical/inductive Resistance based mass loss sensors • Ultrasonic Sensors • Corrosion Potential-electric conductivity. • Linear Polarization Resistance • Galvanic corrosion sensor [17] • Electrochemical Impedance Spectroscopy [18] • Electrochemical noise [19] • Acoustic emission	• Inspection of surface, intergranular, exfoliation and pitting corrosion. • Measurements of mass loss, defects, cracks and coating degradation due to corrosion. • Measurement of change in resistance, galvanic current, potential, impedance and acoustic emissions due to the presence of corrosion and the resulting mass loss.	• Low-cost and broad applications. • Mature technologies. • Online or offline measurements. • • May not be able to distinguish corrosion from cracks. • May be applicable to uniform corrosion only. • Difficult to implement in distributed systems. • Difficult to detect corrosion in hard-to-reach locations.
Environmental	• Ion Selective Sensors (ISFET) [20] • Electrochemical/biological sensors [20] • Capacitive sensors [21][22] • Fiber Optics • Photosensors [23] • Surface Acoustic Waves (SAW) • Radio Frequency Identification (RFID) • Hydrogen probes [24]	• Monitoring of environmental factors responsible for corrosion events such as moisture, temperature and pollutants. • Monitoring of environmental factors through change in electrical, optical and acoustic responses of the sensors.	• Real time on-board monitoring. • Easy to integrate into moving components and hard-to-access locations. • May be integrated into distributed networks. • Possibility of wireless signal transfer. • • Prone to electromagnetic interference. • May be affected by exposure to harsh environments. • Prone to signal noise.
Chemical	• ISFET [20] • Electrochemical sensors • Capacitive sensors [22] • Fiber Optics [25] • Photosensors [23] • pH sensors [[26] • Color-indicating-paints [27]	• Detection of by-products of corrosion such as, pH variation and metal ions. • Change in electrical and optical response of sensors is induced by the presence of corrosion by-products.	• Real-time on-board monitoring. • Easy implementation in distributed systems. • Versatile, compact and sensitive for chemical detection. • High selectivity toward specific chemical species. • Lack of long-term stability and vulnerability to noise. • Selectivity issues in the presence of other chemical species.

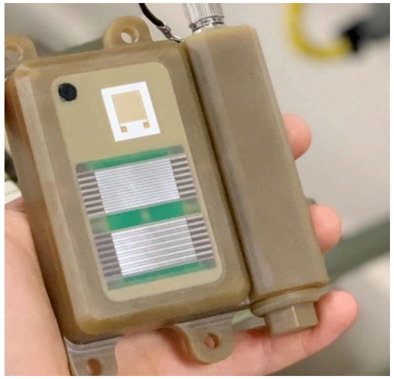
Emerging Sensors

- **Commonly used Methods**
  - Visual inspection
  - Ultrasonic
  - Eddy current
- **Emerging Sensing Approaches**
  - Environmental sensors
  - Fiber optics, phototransistors
  - Chemical sensors
  - Capacitive sensor
  - Acoustic sensors
  - Electrochemical sensors

Examples of Environment and Corrosivity Monitoring Device

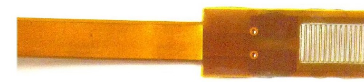
Luna corrosion sensor

- **Temperature and RH**
- **Conductance**
- **Free corrosion rate**
- **Galvanic corrosion rate**

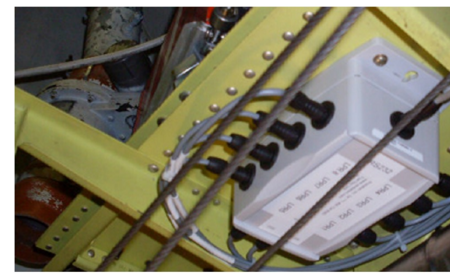


Galvanic Probe (Emerson)

Micro Linear Polarization (LPR) Sensors - Embedded installed in the rear fuel bay bulkhead



Thin film μLPR sensor size of a stamp



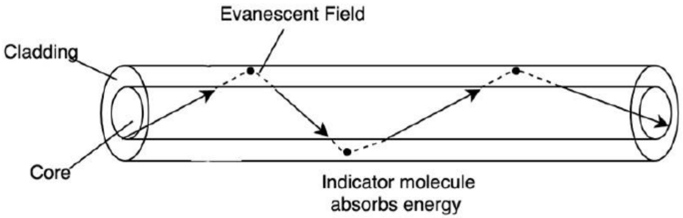
(Brown, 2014)

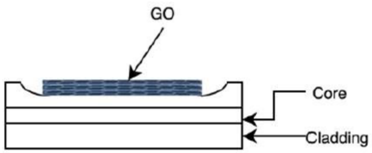
Ultrasonic sensor monitoring petroleum pipeline (Emerson)

Acoustic Emission Sensor (Marposs)

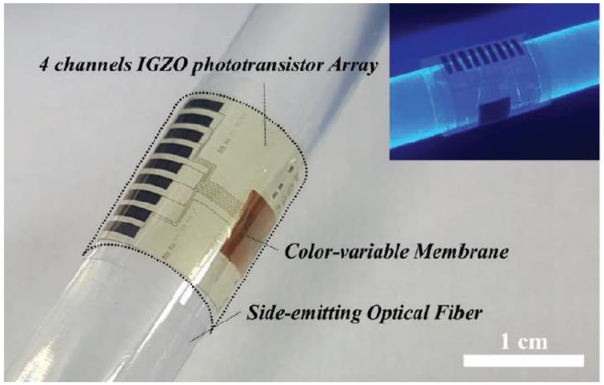
Electrochemical Impedance Spectroscopy (EIS)

Fiber Optic Based Sensors

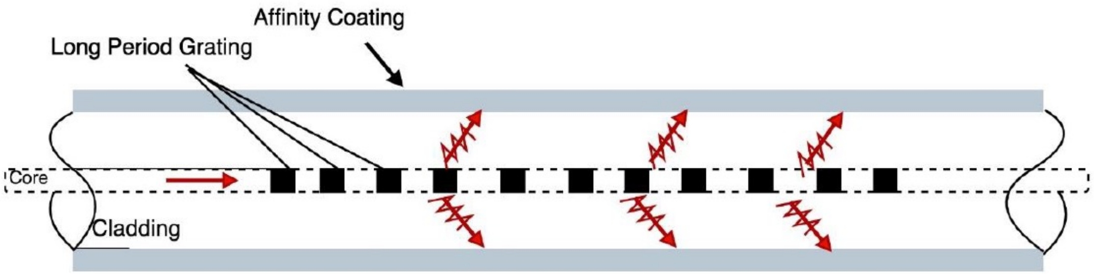




Backscattering optical fiber sensing with graphene coated fiber (Zhang, 2014)



- Multifunctional colorimetric light-transmittance-based durability diagnostic system (Im, 2019)



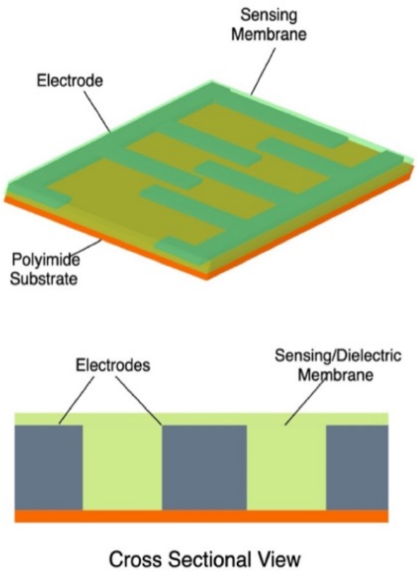
Schematic of long period grating optical fiber sensing mechanism (Cooper, 2001)

Nanomaterials-based Electrochemical Thin Film Sensors

- **Thin Film Transistors**
  - Low-cost fabrication
  - High sensitivity
  - Fast response
  - Small footprint
  - Easy integration

- Organic Semiconductors
  - Abundance and diversity
  - Solution processability
  - Mechanical flexibility
  - Chemical reactivity
  - Chemical functionalization

Nanomaterials-based Capacitive sensors



(a)

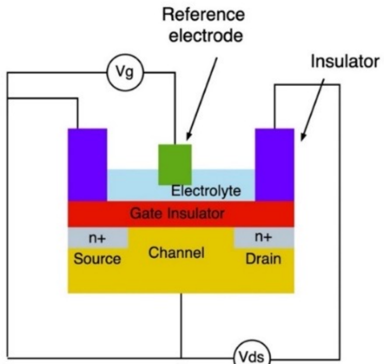
The structure of IDE based chemical sensor. [Khan, 2016]

(b)

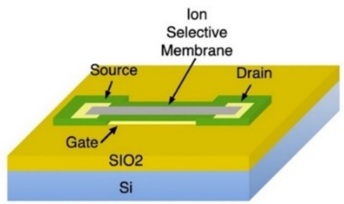
Flexible GO-based capacitive humidity sensor [Alrammouz, 2019]

- Monitor the concentration of chemical species by measuring change in capacitance
- Commonly used for humidity and pH sensing
- An example of capacitive humidity sensor using ion-selective graphene oxide (GO) as the sensing layer
  - Sensitive
  - Porosity of self-assembled GO suited for air flow monitoring
  - Flexible
- Issue with the sensors:
  - Selectivity
  - Long-term stability

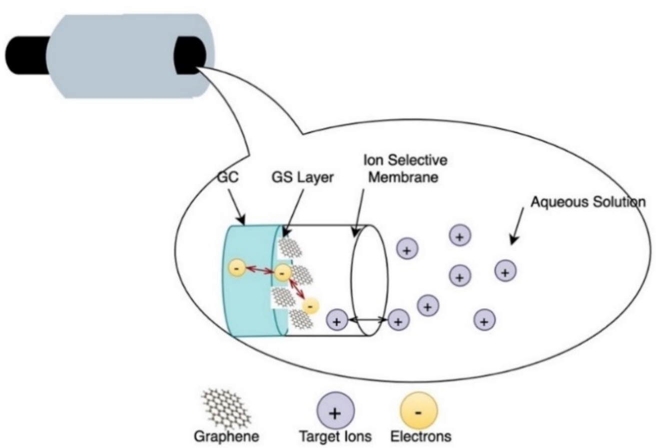
Nanomaterials-based Ion Selective Field Effect Transistor and Ion Selective Probes



Solution ISFET sensing system (Akbari, 2019)



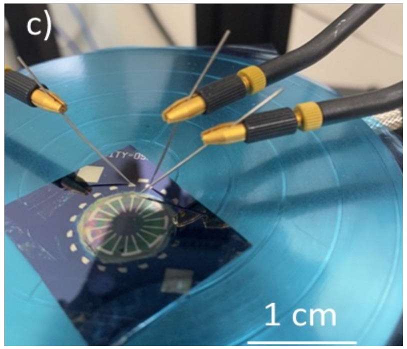
Solid gate ISFET sensor structure (Salvo, 2017)

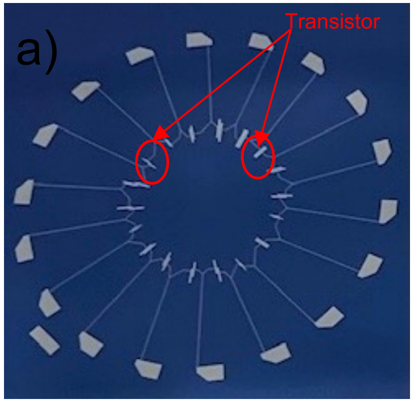


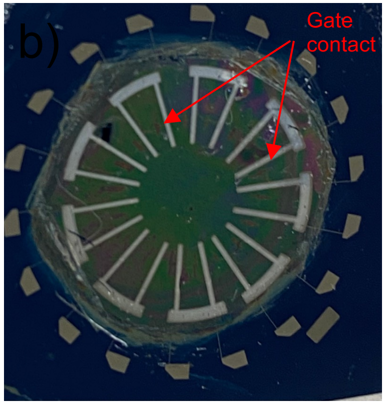
GC/graphene ion selective electrode structure (Li, 2012)

- Potentiometric sensors that produce electrical current or voltage variations in response to changes in ionic distribution;
- The sensing is conducted by coaing the gate electrode with an ion-selective materials, such as metal oxides, to which specific ions reversibly bind to and modulate current and surface potential;
- Nanomaterials as gate channel allows for miniaturization of sensor device due to its high surface to volume ratio and high carrier mobility;
- Possibility of real time measurements of multiple ions concentration – such as chloride, other ions, and pH sensing in harsh environments

Sensor Nodes







a) Metal patterned Si/SiO_2 substrate. b) Solution processed OTFTs with top gate metal contact

- Sensor nodes are a multi-parameter integrated sensor network, for real-time monitoring;
- Compact, lightweight;
- On-board prognostic possible;
- Wireless systems possible

Ongoing Corrosion Sensor Development Effort

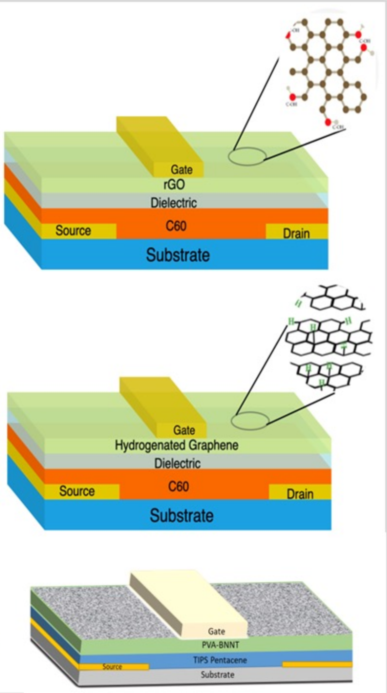
Corrosion Environmental Factors
- Temperature
- Humidity
- Pollutants e.g Salinity, metal ions

Sensors and Detectors
- Fiber Optic Sensors
  Resistive Sensors
  Capacitive Sensors
- Thin Film Transistors
  Ion Selective Sensors

Nanomaterials of Interest
- Reduced Graphene Oxide (rGO)
- Hydrogenated Graphene
- Carbon Nanotubes (CNT)
- Boron Nitride Nanotubes (BNNT)

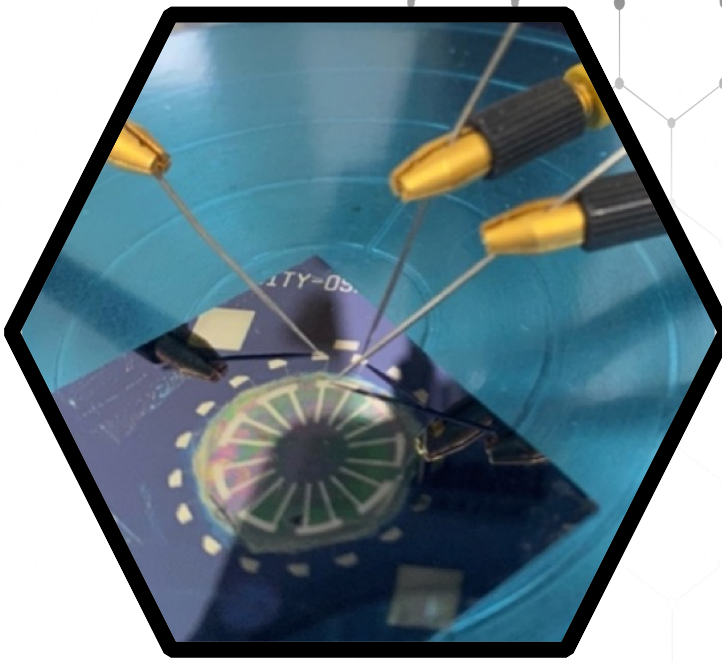
Targets
- Surface Wetness (Qualitative Measurement of wet condition)
- Chloride Ions (measured concentration range:1-100ppm)
- Implemented for temperature sensing and regulation
- Investigated to improve device performance and longevity

Sensor Configuration



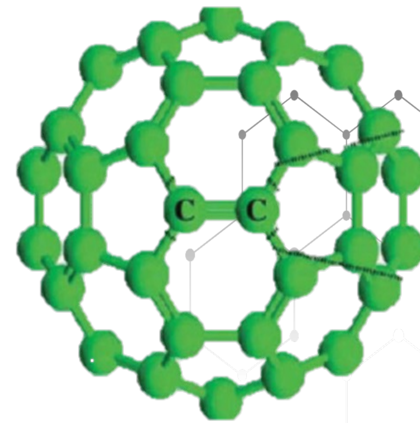
Moisture and Chloride Ion Sensing

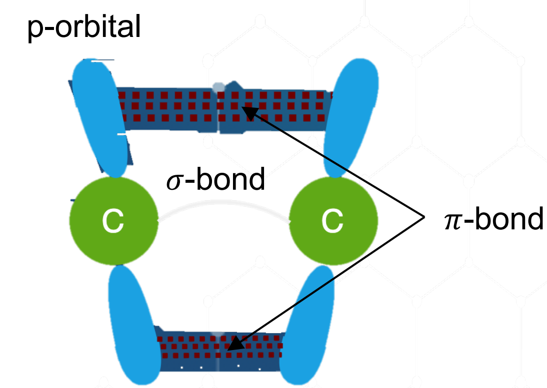
- **Corrosion Monitoring**
  - Surface moisture
  - Chloride ion (Cl^-)
- **Organic Thin Film (OTFT) Sensors**
  - Fullerene C_{60} modified electrodes
  - Functionalized graphene oxide (GO)
  - Functionalized graphene nanoparticle



Fullerene C_{60}

- **Molecular Structure: Conjugated molecules**
  - Buckyball comprising 60 carbon atoms arranged in 20 hexagons and 12 pentagons.
  - Conjugated molecules forming molecular crystals in FCC lattice through van der Waal bonds.
- **Electronic structure and attributes**
  - Totally filled HOMO band → Semiconductor
  - Partially filled LUMO band → Electron affinity
  - Charge transport : Hopping mechanism
  - Carrier mobility: 0.5 – 1.5 $cm^2/V.s$
  - Bandgap: 1.5 - 2.3 eV

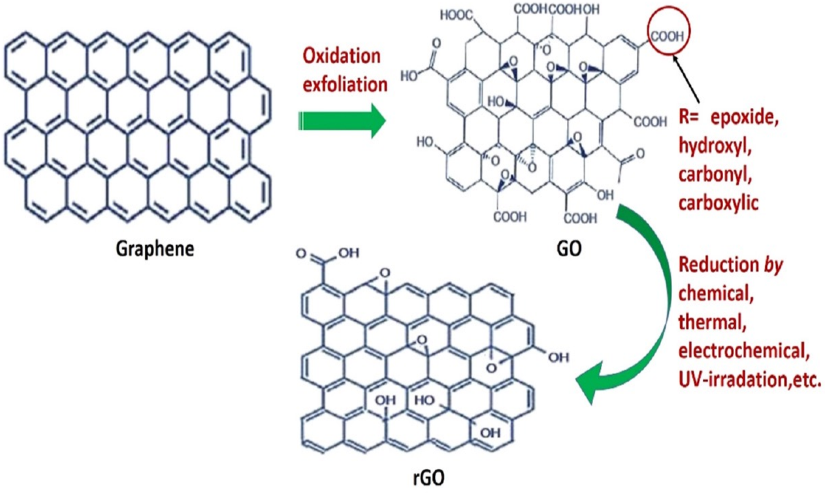




Muhammad *et al.*, J, Mater. Chem.C. (2013)

Reduced Graphene Oxide

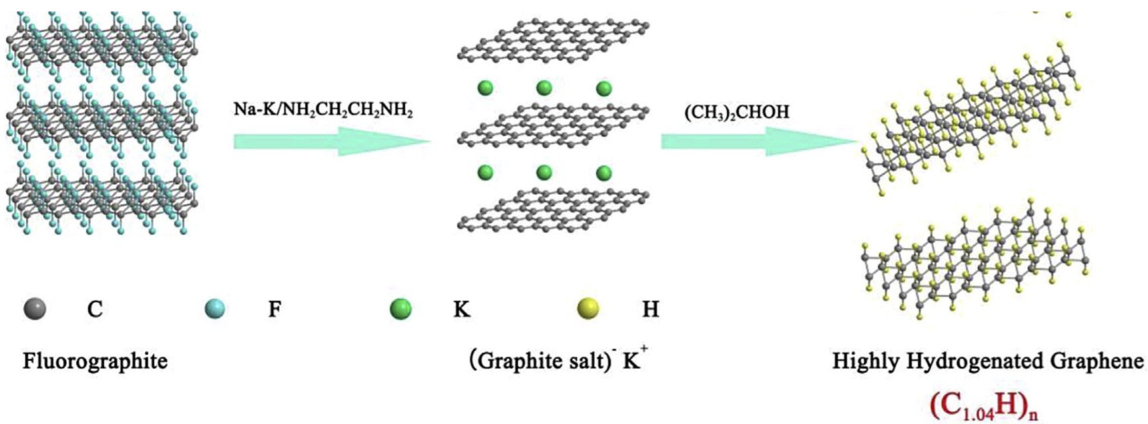
- **Oxidation + Reduction**
  - Improve solubility
  - Chemical affinity toward water molecules
- **Sensing mechanism**
  - Electrical conductivity increases due to the increase in hole density resulting from bonding between water molecules and H_3O^+.



Nurazzi *et al*., Nanotechnol. Rev. (2021)

Hydrogenated Graphene

Wet Chemical Synthesis: Modified Birch reduction

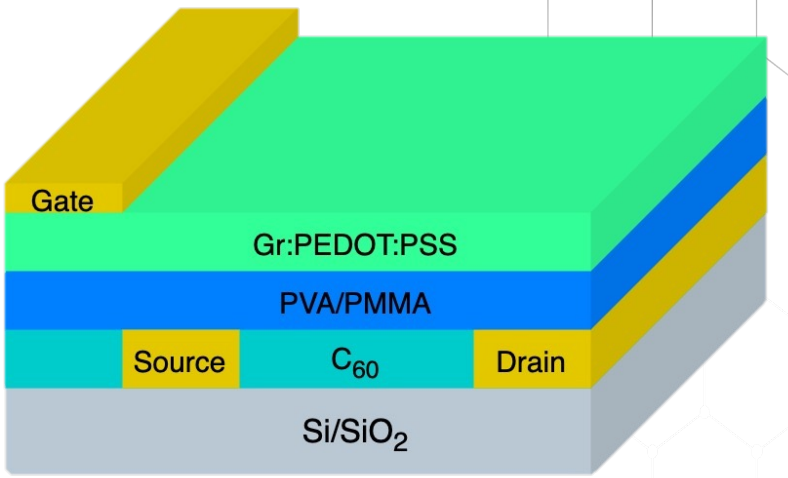


Y. Yang et al. / Carbon 107 (2016)

- Chemical affinity and selectivity toward Cl^-.
- Sensing Mechanism: Ionic bonds between H^+ and Cl^- reduces the charge density in hydrogenated graphene and decreases its electrical conductivity.

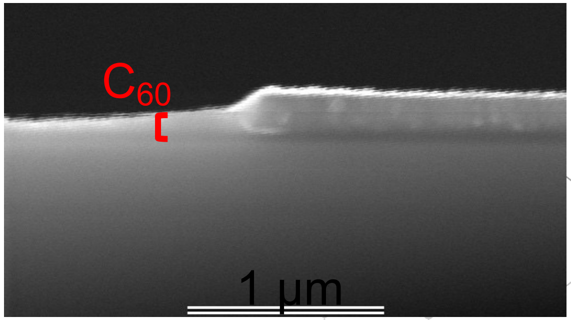
OTFT Architecture and Structure

- **Device configuration**
  - Top Gate Bottom Contact
- **Structure**
  - Substrate : Si\SiO_2
  - Metal contacts: Chromium
  - Semiconductor: Fullerene C_{60}
  - Multilayer gate dielectric: PVA\PMMA
  - Gate conductive polymer: Gr:PEDOT:PSS



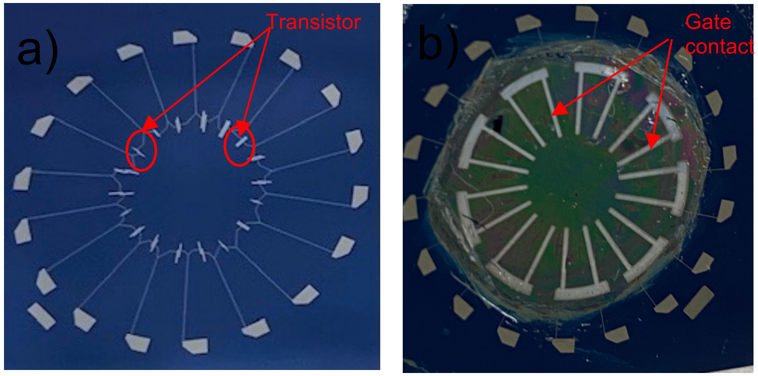
C_{60} OTFT device configuration and structural layers.

OTFT Fabrication



SEM cross sectional image of C_{60} thin film

- **Metal Patterning**
  - UV-photolithography
  - Negative lift off
- **Material deposition**
  - C_{60} in 1,2 dichlorobenzene: 120 nm
  - PVA: 125 nm
  - PMMA: 200 nm
  - PEDOT:PSS: 1000nm
  - Gr:PEDOT:PSS : 500nm
  - Cr top gate contacts: 200nm

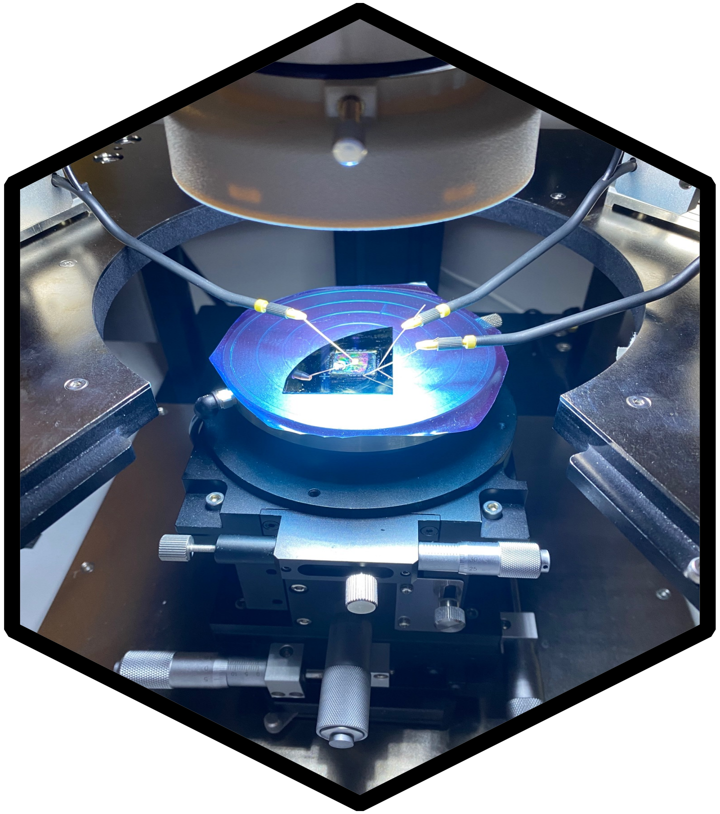


a) Metal patterned Si/SiO_2 substrate. b) Solution processed OTFTs with top gate metal contact

Device Testing and Validation Results

Device Characterization and Performance

- **Dielectric Characterization using impedance analyser**
  - C = 7.82 nF/cm^2
- **Output Characteristic: I_{DS} Vs V_{DS}**
  - V_{DS} = -2V to 30V
  - V_{GS} = 80mV, 500mV, 1V
- **Transfer Characteristic: I_{DS} Vs V_{GS}**
  - V_{DS} = -1V to 5V
  - V_{DS} = 50mV, 100mV, 200mV



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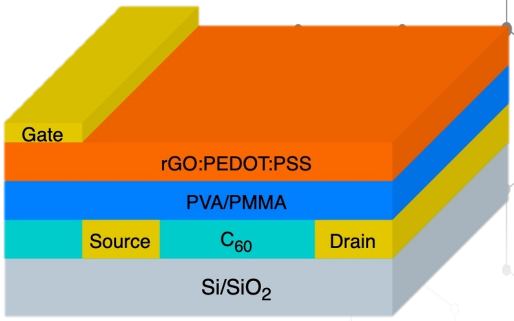
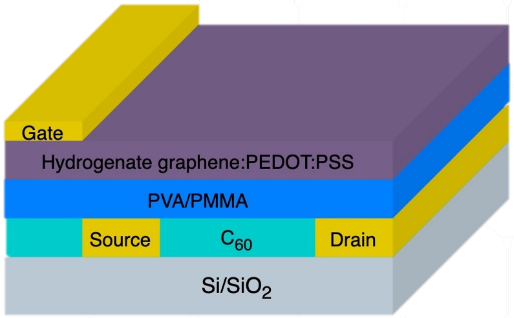
NATO Unclassified + EOP Slide 25

OTFT Sensor Configuration

- **Humidity Sensor**
  - Sensing material: rGO
  - Response: increased electrical conductivity in the presence of water molecules.
- **Chloride ion sensor**
  - Sensing material :Hydrogenated graphene
  - Response: decreased electrical conductivity in the presence of Cl^-.

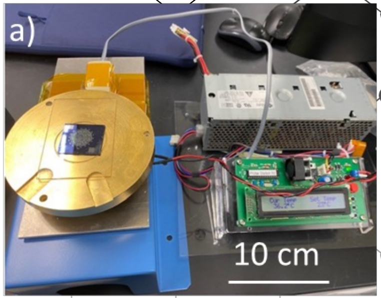


Humidity sensor device configuration and structural layers.



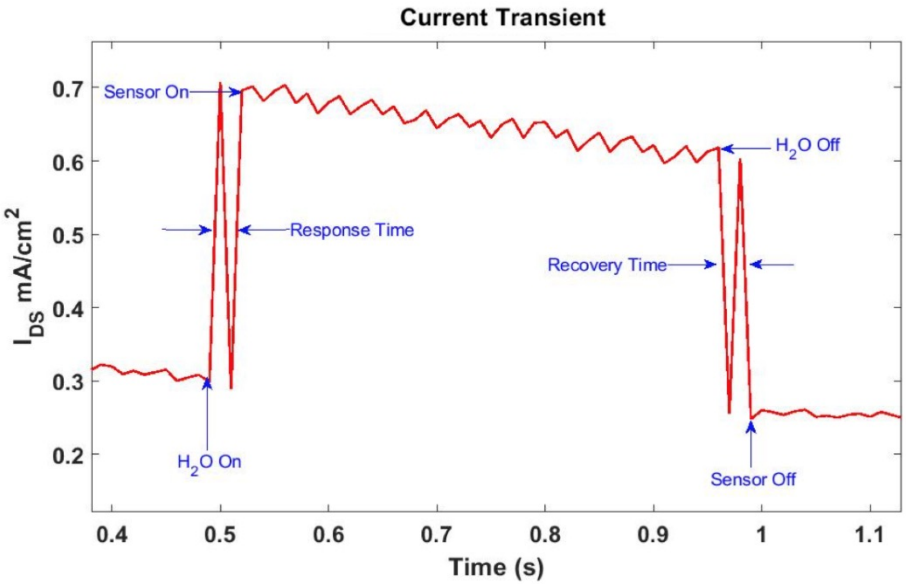
Cl^- sensor device configuration and structural layers.

Humidity Sensor Performance



- rGO OTFT wetness sensor designed for qualitative measurements of surface moisture;
- Qualitative measurement of surface moisture → 95%RH
  - Responsivity:

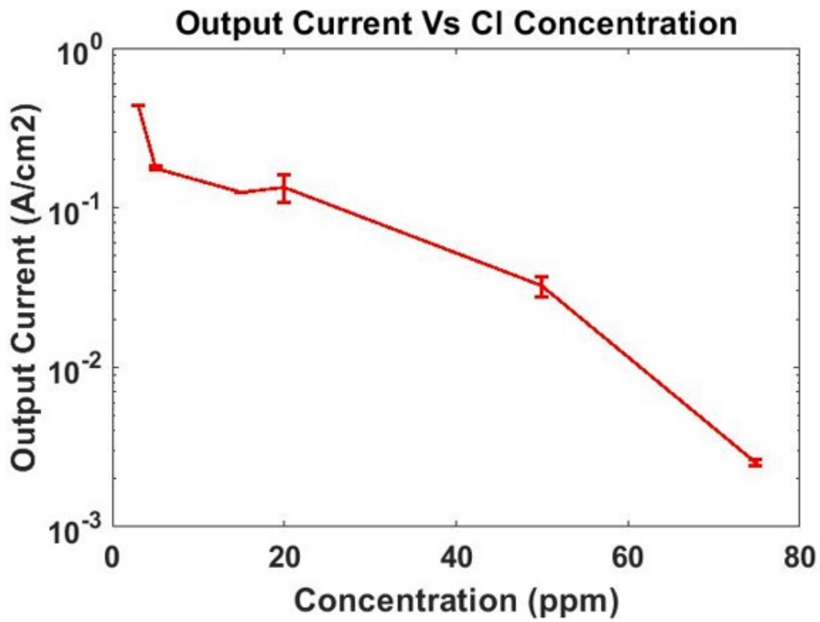
    $\Delta I/I_{dry}$ = 122.6%
  - Response time: 20 ms
  - Recovery time: 20 ms



Current response of rGO coated OTFT sensor to the presence of surface moisture (95%RH)

Chloride Ion Sensor Performance

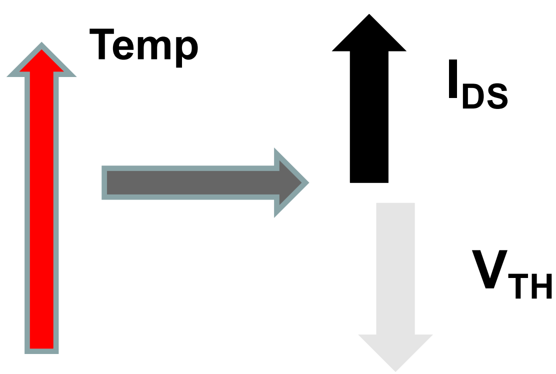
- Logarithmic response to increasing Cl^- concentration.
- Decreasing output current with increasing Cl^- concentration.
- Sensitivity to extra low concentrations far below corrosion onset thresholds (100ppm-3500ppm)
- Sensitivity:
  - $\Delta I/(I_{ref}\,C)$ = 4% per ppm
- Sensor response stability after repeated measurements

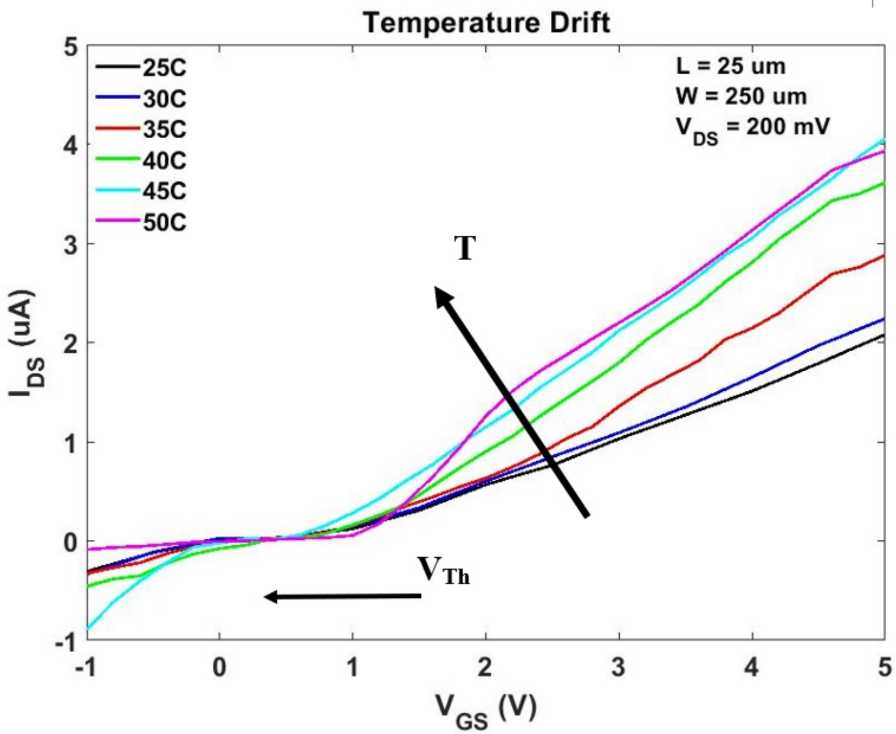


Sensor Drift

- **Thermal effects : 25℃ to 50℃**

  Increase in device performance due to thermal excitation of free and localized charge carriers.





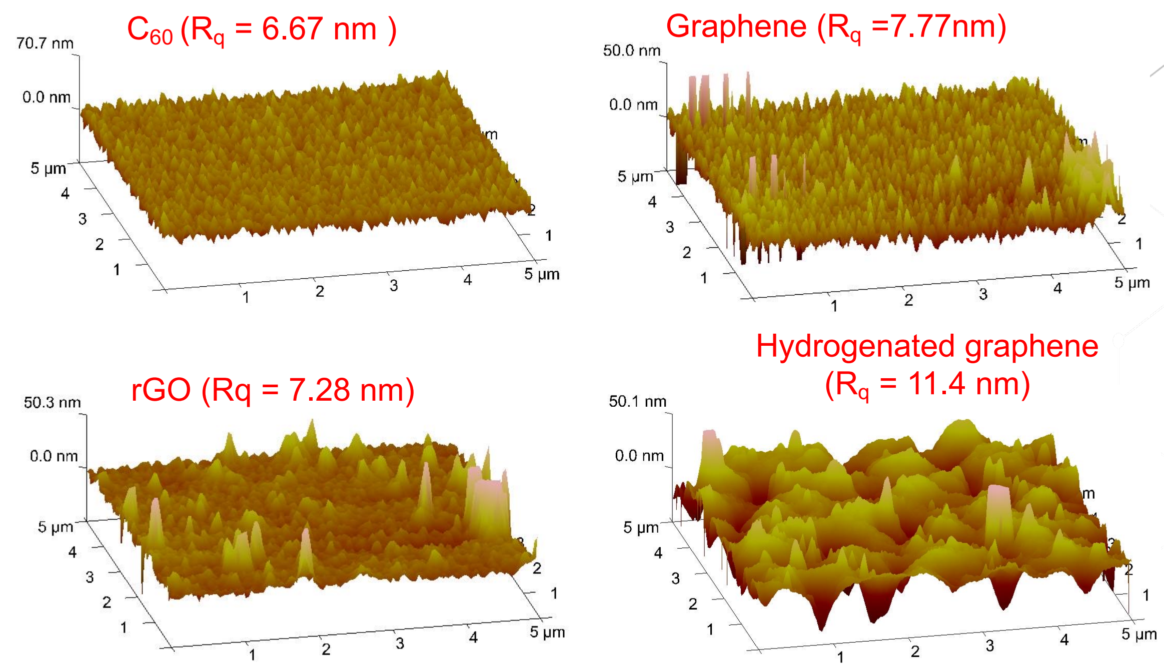
Transfer characteristic of OTFT sensor at increasing ambient temperature

Conclusion

- Low-cost and small footprint sensors targeting chemical and environmental for corrosion sensing;
- Solution processed organic thin film transistors.
- High responsivity (122%) and fast response (20ms) to surface moisture.
- Sensitivity (4%/ppm) to ultra fine concentrations of Cl^- (3ppm-75ppm)
- Consistent response after recurring measurements.
- Sensor experiences drift at increasing temperature, and temperature compensation needed.
- Ongoing work on carbon nanotube and boron nanotubes for new sensing functions (i.g. pH, metal ions…) and sensor durability
- Multi-analyte corrosion monitoring systems using arrays of OTFTs.

Thank You

Surface topology and roughness (R_q)



3D AFM images of C_{60} thin film electrode and the functional gate layers: graphene, rGO and hydrogenated graphene