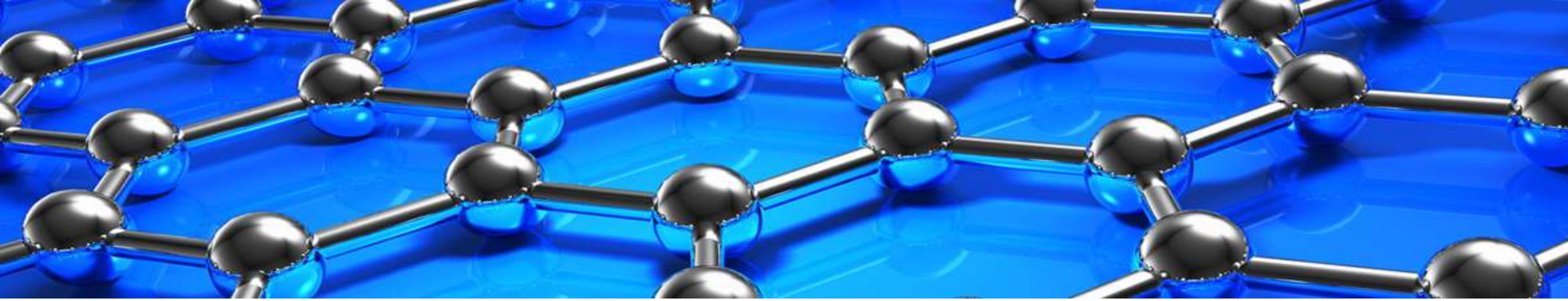

Applied Graphene Materials

Towards A Novel, Non-Metal Graphene Nanoplatelet Hybrid Anti-Corrosive System for Tomorrow's Protective Coatings

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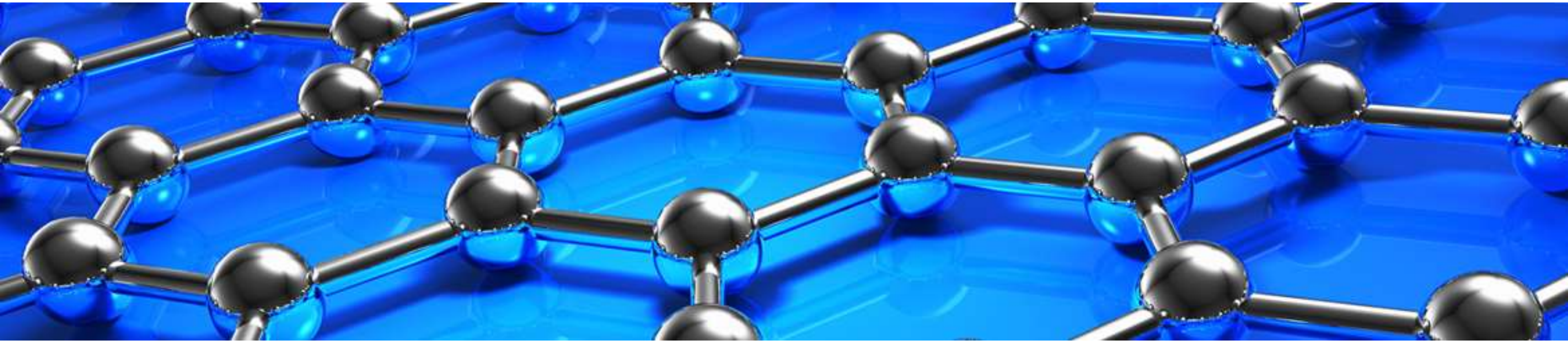
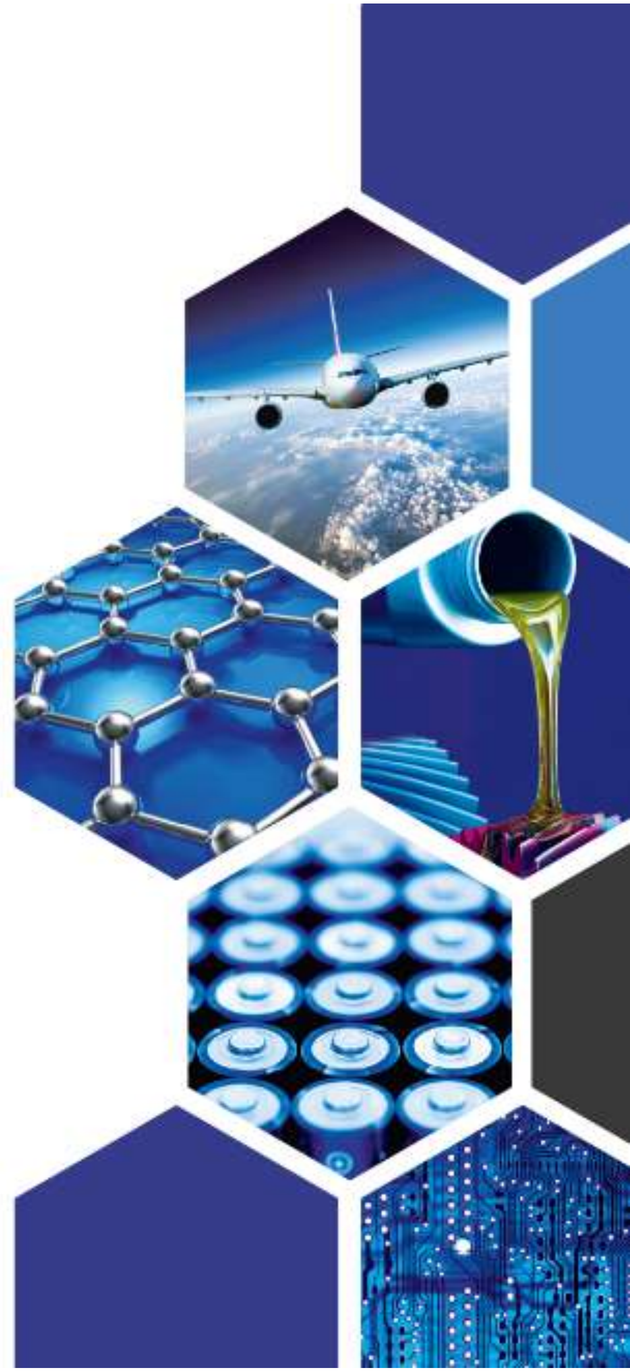
19 March 2019



Introduction



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Introduction

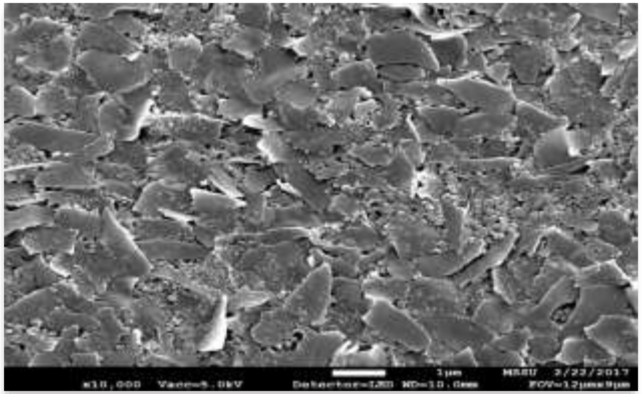
Graphene's two-dimensional structure in the nanoplatelet form results in materials with:

- very high aspect ratio
- high surface area

These materials are particularly suited for use as multi-functional additives in paints and coatings.

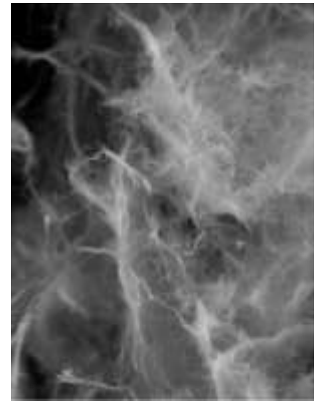
The proposed mechanism by which graphene delivers anti-corrosion performance is a combination of physico-chemical process restricting uptake of water (combined with oxygen and salt) and electro-chemical activity.

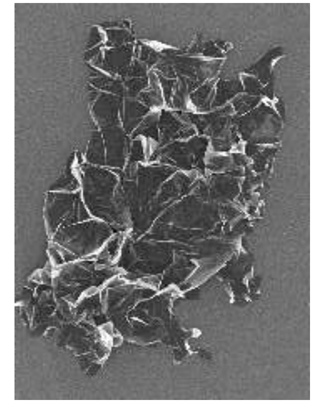
AGM Graphene Nano Platelets



Reduced Graphene Oxide

- Composed of mixture of nanoplatelet type sheets
- Excellent barrier properties
- Moderate density and surface area gives high loading levels in most matrices
- Typically 10% in dispersion for further dilution in final formulation





Graphene

- Very thin, crumpled sheets. (of 5-15 atomic layers)
- Very low density and high surface area, enabling enhanced corrosion
- Typical loading levels 0.5-1% by weight in dispersion for further dilution in final formulation

AGM supplies its graphenes in dispersion format

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Objectives

1. Can graphene give significant uplifts corrosion resistance when applied direct to substrates in C4 / C5 environments?

2. Can performance of zinc rich systems be further extended by using graphene enhanced tiecoat layer?
   - Combining the sacrificial protection of a zinc rich primer with the excellent barrier properties of a graphene coating

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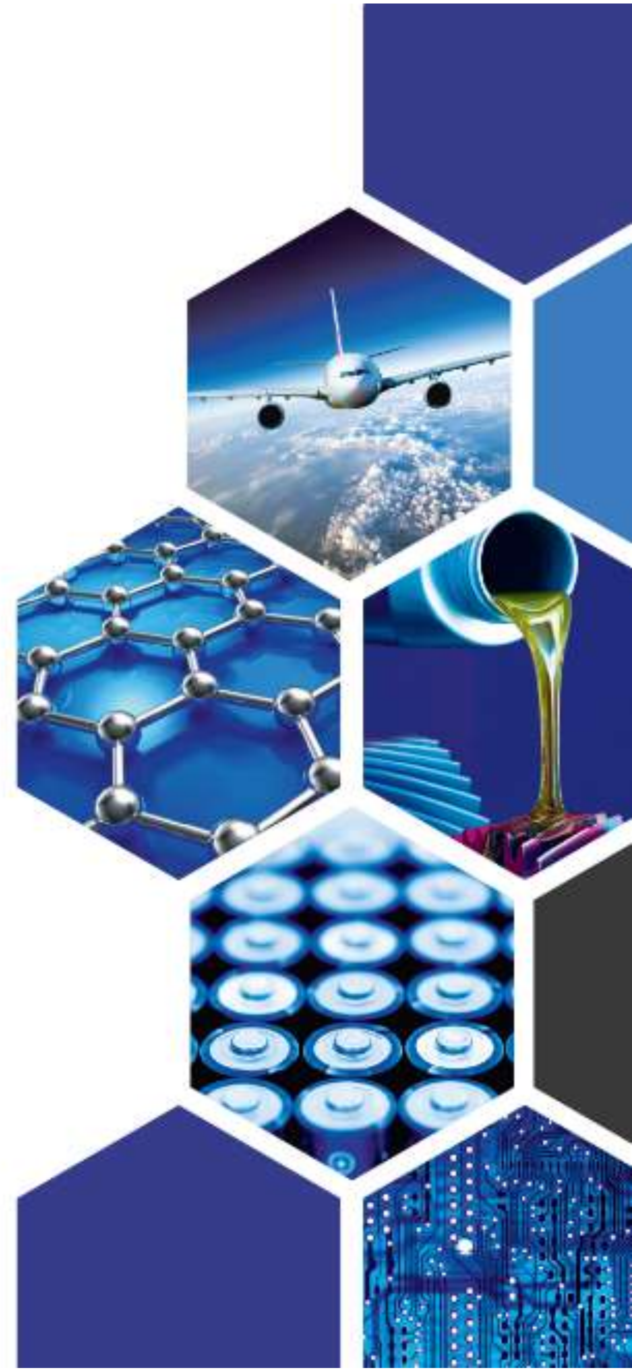
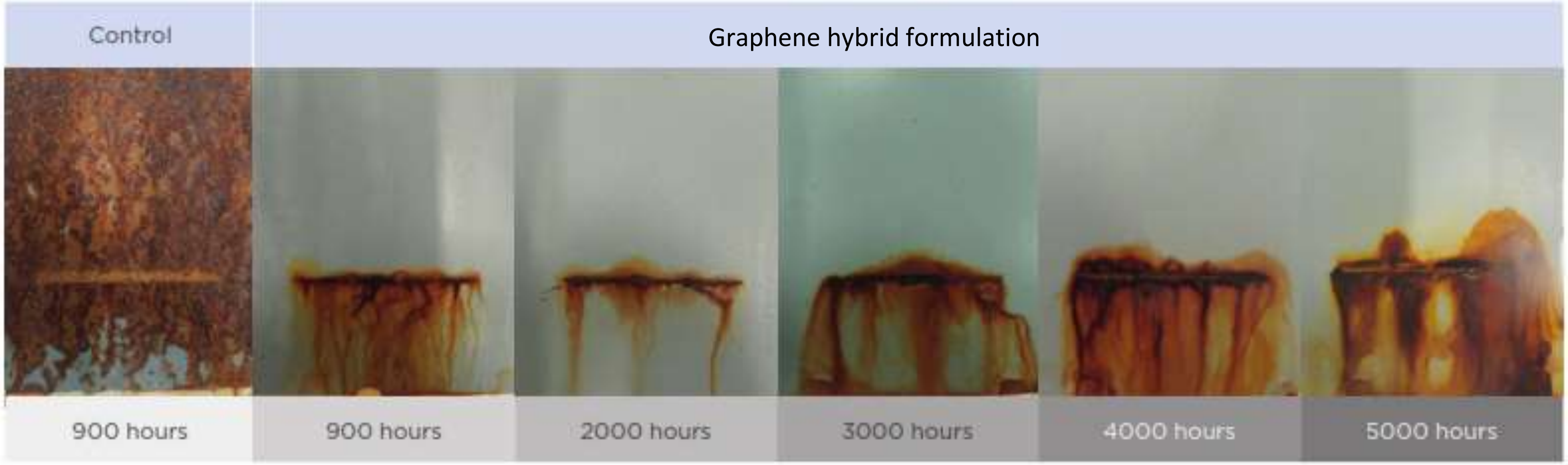
Experimental



Previous Developments

- Previously, AGM has developed and reported meaningful anti-corrosive performance gains in epoxy coatings for C3 (ISO12944) environments, against zinc phosphate systems, using a hybrid primer solution incorporating graphene nanoplatelets .
- Performance on ASTM G85 prohesion test was extended from 1000 to 5000 hours by using graphene in combination with metal free active inhibitors



Test Program

Demonstrate performance in a C4 / C5 environment

- Preliminary investigations carried out using Neutral Salt Spray (ISO 9227)
- Electrochemical studies carried out to aid further understanding of mechanism of protection

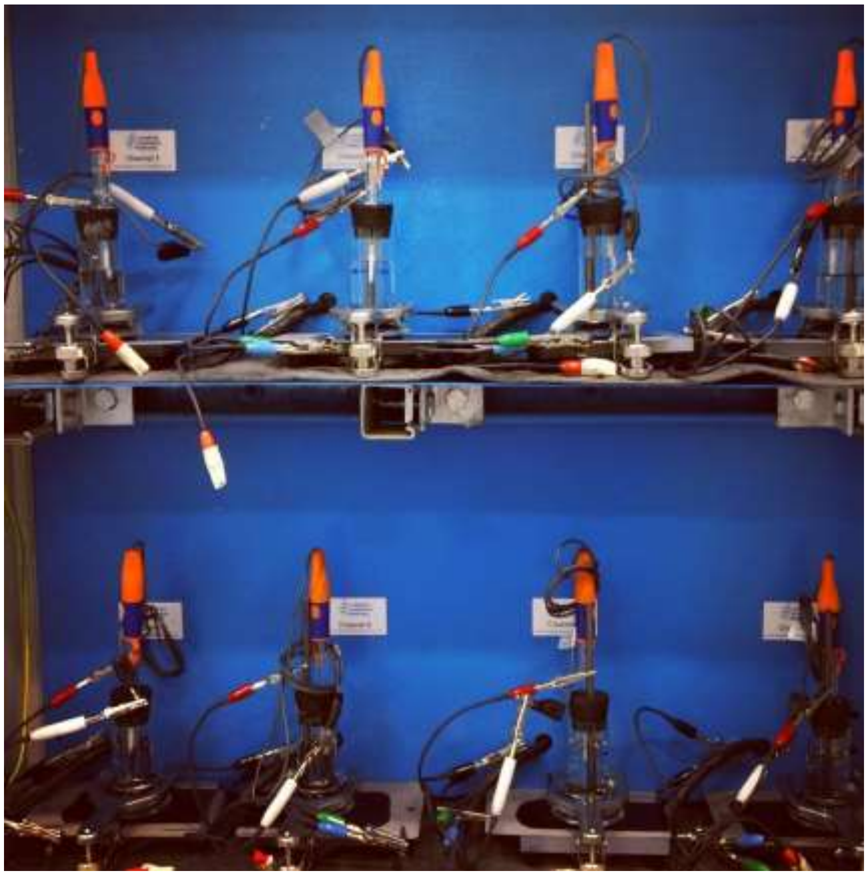
Systems tested

- Single layer of primer applied direct to substrate at 50-60 microns
- Three layer systems
  - Zinc rich primer direct to substrate
  - Graphene systems (and control) in intermediate layer as a tiecoat
  - Polyurethane topcoat

Not included

- Condensation testing
- Cycling ageing test

Electrochemical Testing



EIS

- Combined NSS/EIS Test Method
- Measurements recorded using a Gamry 1000E potentiostat in conjunction with a Gamry ECM8 multiplexer
- The test area of the working electrode was 14.6 cm^2 and run using a 3.5 wt% NaCl electrolyte
- An AC voltage of 10 mV was applied across the samples, with a zero volt DC bias, over a frequency range of 1 MHz to 0.05 Hz
- Samples initially tested before being placed under NSS (T=0) and then retrieved from NSS every 10 days for subsequent testing

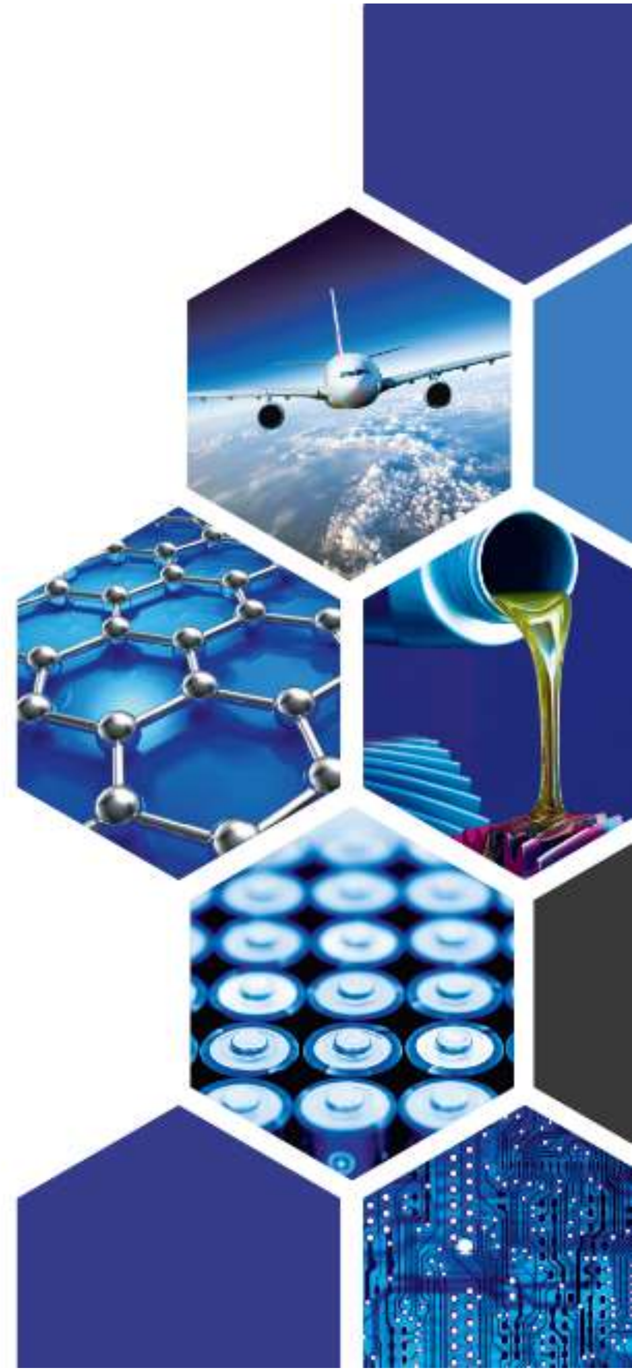
Formulations

Component	Control	D1: Reduced Graphene Oxide Dispersion	D2: Graphene Dispersion	D3: Hybrid Dispersion
Epoxy (EEW 190 g/eq)	15.119	15.119	15.119	15.119
Amino Resin	0.244	0.244	0.244	0.244
Dispersant	0.402	0.402	0.402	0.402
Xylene	15.376	15.376	15.376	15.376
Bentonite thixotrope	0.366	0.366	0.366	0.366
Butanol	1.986	1.986	1.986	1.986
Titanium dioxide	10.966	10.966	10.966	10.966
Blanc Fixe	43.619	43.619	43.619	43.619
Epoxy (EEW 190 g/eq)	**10**	**0**	**0**	**0**
GNP dispersion	**0**	**10**	**10**	**10**
Polyamine hardener	1.922	1.922	1.922	1.922
Total	100	100	100	100
GNP loading %	0	1	0.1	0.5

Panel Preparation

- Steel panels of dimensions 150 x 100 x 2mm, grit blasted to SA2.5
- Coatings were applied using a conventional spray gun.
  - Single coat systems at 50µm DFT
  - Multi-coat systems at 150 -160µm DFT
- For multi-coat samples the over-coating interval used was 3 hours
- All panels were allowed to cure for a period of 7 days at 23°C (+/- 2°C).

Results



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Single Layer – Direct to Substrate

- After 720 hours on Neutral Salt Spray
  - Minimal creep at the scribe
  - Coatings D2 and D3 showed significantly less corrosion across the panel face
  - Formulation D1 was not much better than the control.


Epoxy Prototype Control


D1 Dispersion


D2 Dispersion


D3 Dispersion

Primer	Corrosion	Creep (mm)	Blistering	Adhesion to substrate
Epoxy Prototype (No GNP)	Excessive corrosion	3	-	Good
D1: Graphene Oxide Dispersion	Heavily corroded	1	-	Good
D2: Graphene Dispersion	Mild corrosion	1	1s1	Good
D3: Hybrid Dispersion	Mild corrosion	1	1s1	Good

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Single Layer – Direct to Substrate

- After 1440 hours on Neutral Salt Spray
  - Minimal creep at the scribe
  - Coatings D2 and D3 showed significantly less corrosion across the panel face
  - Formulation D1 was not much better than the control.

Primer	Corrosion	Creep (mm)	Blistering	Adhesion to substrate
Epoxy Prototype (No GNP)	Excessive corrosion	10	-	Good
D1: Graphene Oxide Dispersion	Excessive corrosion	7	-	Good
D2: Graphene Dispersion	Mild corrosion	3	1s1	Good
D3: Hybrid Dispersion	Mild corrosion	3	1s1	Good

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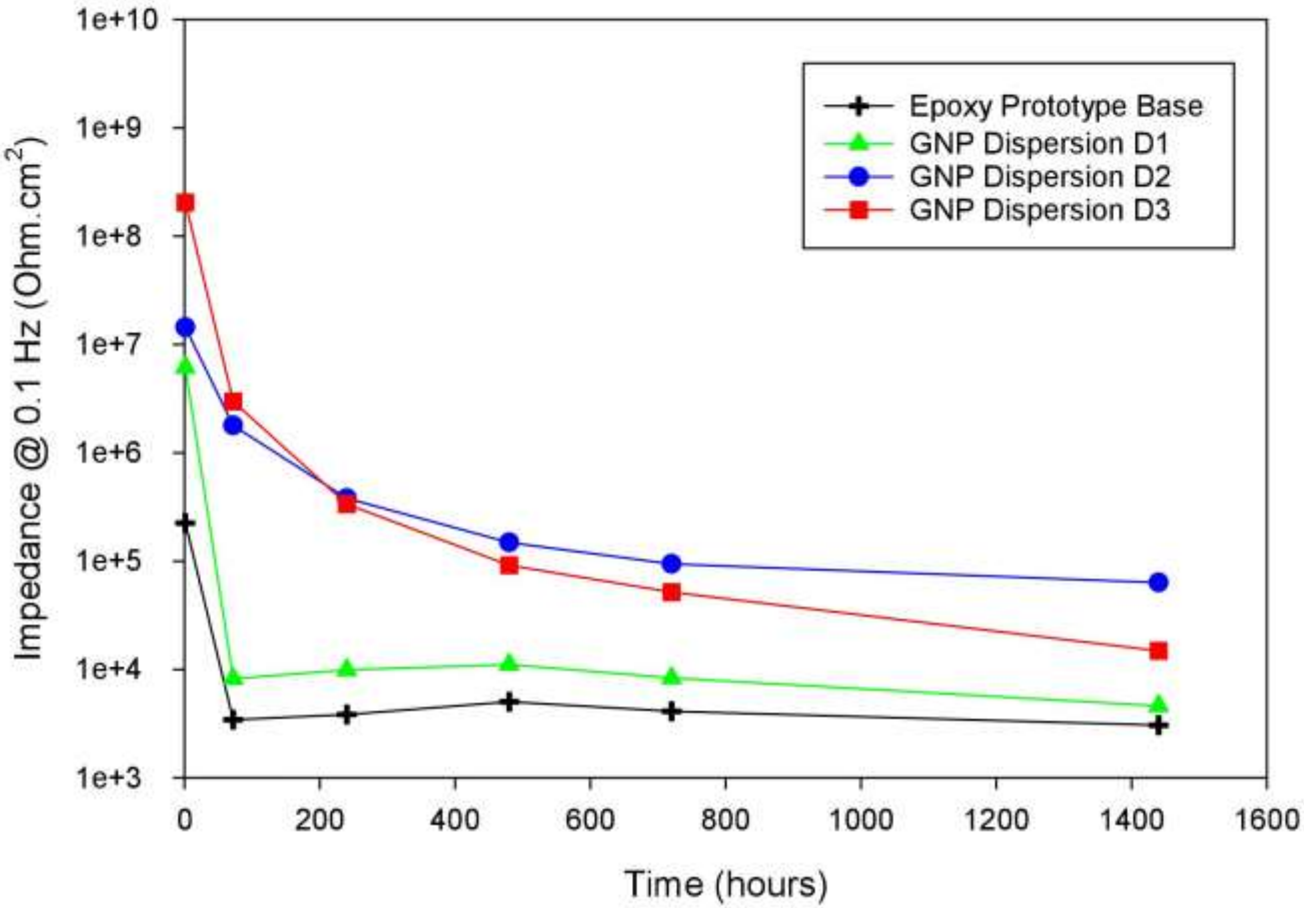
Single Layer - Direct to Substrate



- Impedance measurements carried out at 10 day intervals.
- Graphene enhanced primers showed impedance levels higher than the graphene-free control.
- After 1440 hours, highest impedance levels were achieved with Coating D2.

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Single Layer – Direct to Substrate

Discussion

- After 1440 hours of neutral salt spray testing, D2 and D3 showed significantly better corrosion resistance compared to the graphene-free control system on neutral salt spray.
- Both D2 and D3 showed significantly higher levels of impedance on EIS testing over the 1440 hour period.
- It has previously been demonstrated that graphene significantly reduces water vapour transmission rates. This potentially explains the delay in onset of corrosion and the higher impedance values observed.

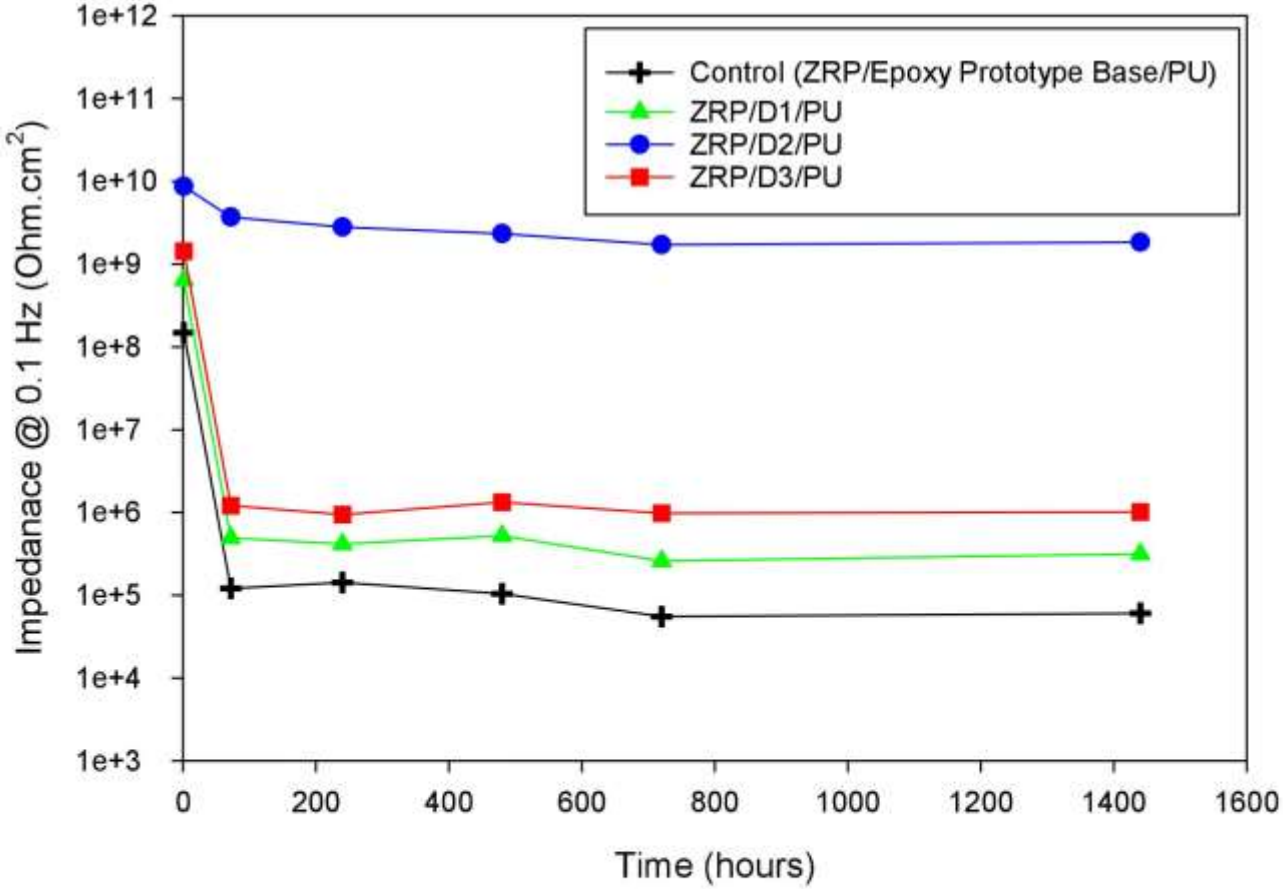
Graphene Enhanced Tiecoat

NSS Testing Results:

- Panels were assessed for blistering, creep and breakthrough corrosion at 240, 480, 720 and 1440 hours
- Electro-chemical assessments were also carried out at the above intervals

1st Coat	2nd Coat	3rd Coat	Corrosion	Creep (mm)	Blistering
Zinc Rich Primer (Commercial)	Epoxy Prototype (No GNP)	Polyurethane Topcoat	No visible corrosion	<1	None
Zinc Rich Primer (Commercial)	D1: Graphene Oxide Dispersion	Polyurethane Topcoat	No visible corrosion	<1	None
Zinc Rich Primer (Commercial)	D2: Graphene Dispersion	Polyurethane Topcoat	No visible corrosion	<1	None
Zinc Rich Primer (Commercial)	D3: Hybrid Dispersion	Polyurethane Topcoat	No visible corrosion	<1	None

Graphene Enhanced Tiecoat



- Impedance measurements were carried out at 0, 72, 240, 480, 720 and 1440 hours.
- All three graphene enhanced primers showed higher impedance values than the graphene-free control.
- Coating D2 in the intermediate layer showed significantly higher impedance.

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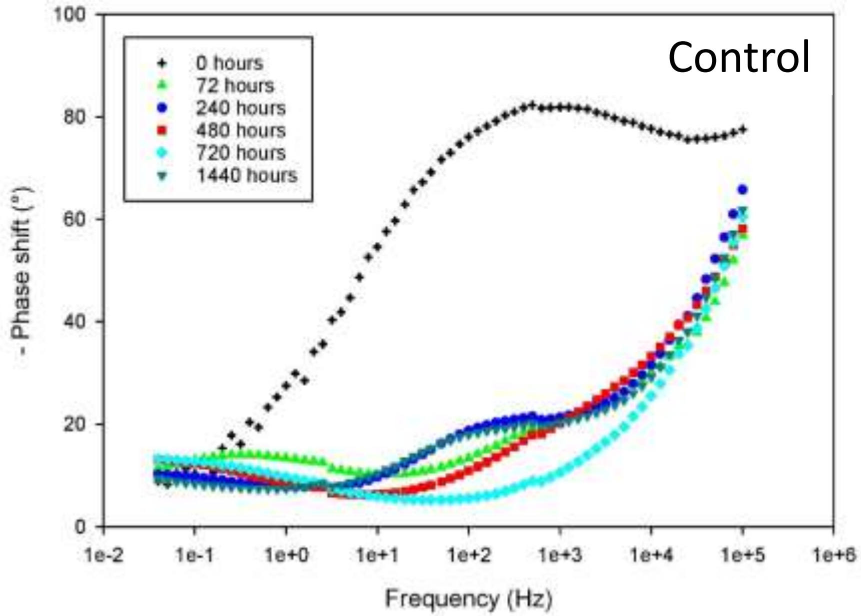
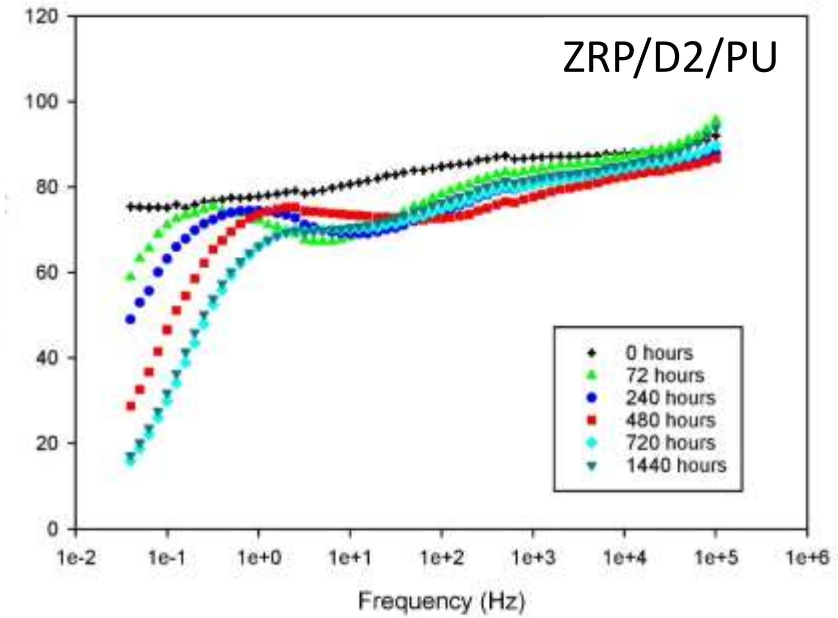
Phase Shifts Bode Plots – Three Layer Systems





- EIS response at the very beginning of exposure is dominated by a capacitive behaviour (phase shift close to -90 degrees)
- Deviation from a purely capacitive behaviour may arise as water or corrosive species penetrates within the coating pores, developing ionic pathways, creating a resistive contribution (pore resistance) to the overall impedance of the system
- Clear large deviations observed for the control sample compared to the ZRP/D2/PU sample indicates an enhanced barrier performance

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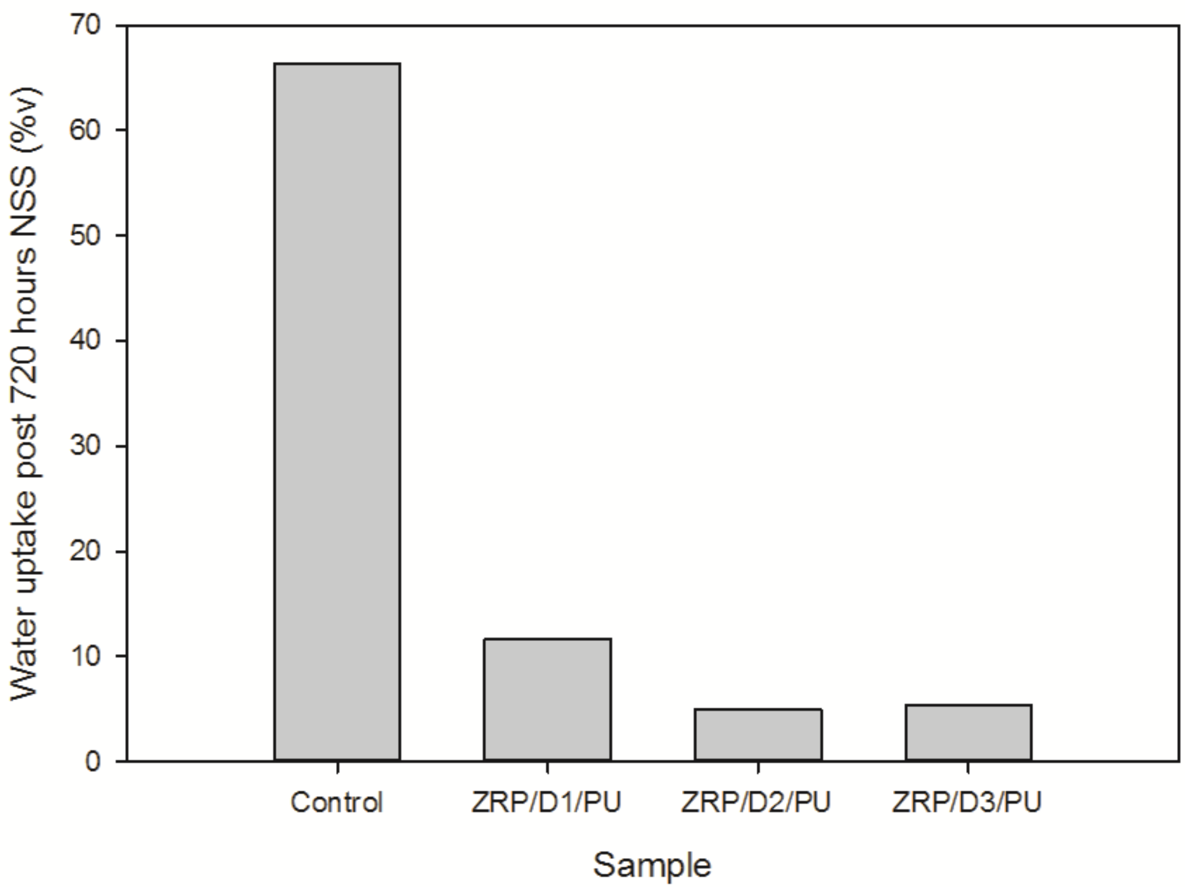
Water Uptake – Three Layer Systems



- Water uptake measurements were extracted from the double capacitance data
- Coatings with a graphene enhanced tiecoat showed a significant reduction in water uptake.
- Coating D2 had the lowest water uptake, which would infer the best barrier properties.

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Graphene Enhanced Tiecoat

Discussion

- After 720 hours, the 3 coat systems show no signs of blistering or corrosion development.
- As expected, there is little evidence of creep development at the scribe. This can be attributed to the sacrificial mechanism of zinc rich primer direct to substrate.
- Furthermore, it’s expected that the barrier protection offered by the graphene enhanced tiecoat is expected to further extend coating lifetime.
- Particularly high impedance values were observed with the use of D2 as a tiecoat. This is likely an effect of the enhanced barrier properties in the tiecoat as demonstrated by the water uptake results.

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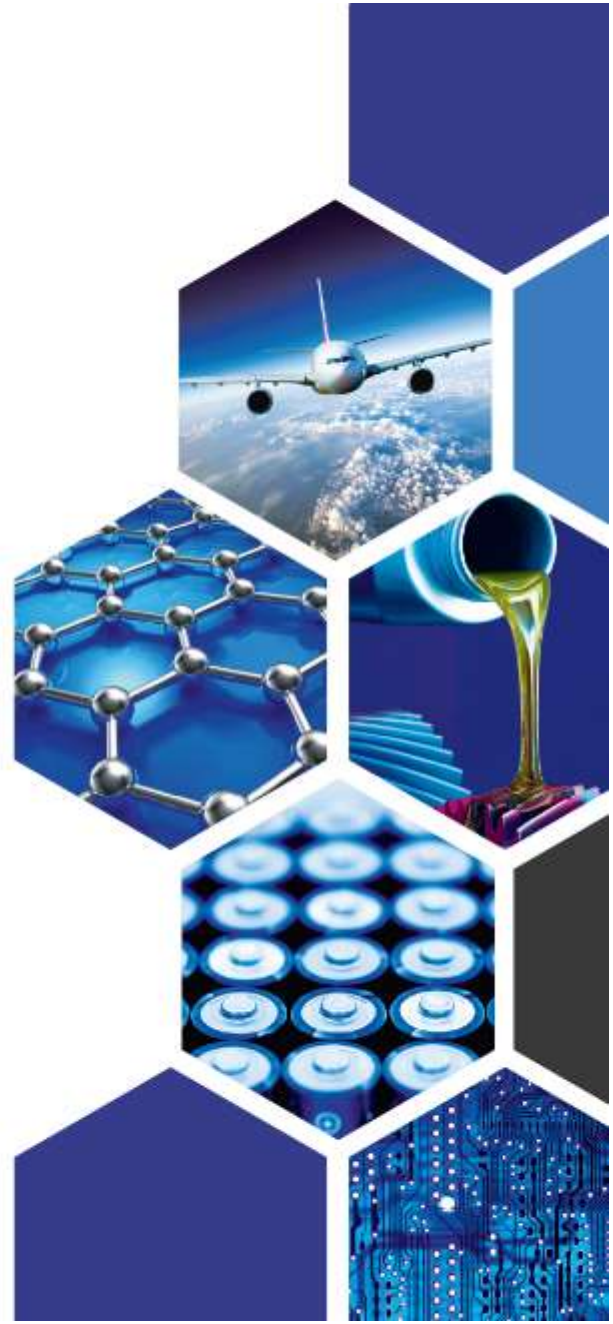
Further Work

1. Further demonstration of performance in C4 / C5 environments:
   - Cyclic ageing test: which could also determine if graphene offers an improvement in thermal stability.
   - Condensation testing: will particularly demonstrate resistance to blistering.
   - Leaching: does the graphene restrict loss of zinc into the local environment?
2. Investigate the direct replacement of zinc rich coatings with graphene enhanced primers. Can a higher level of performance be achieved using a different mechanism of protection?
3. Investigate reduced zinc loadings
   - Reduced zinc in the first layer of a 3 coat system
   - Graphene enhanced zinc-rich formulations

Summary

- Graphene enhanced epoxy primers applied direct metal substrates showed a significant improvement in anti-corrosive performance.
- Improvements seen in the single layers were consistent with the electro-chemical impedance values.
- Early evaluation of the three layer systems showed excellent anti-corrosion performance as expected.
- D2 graphene based coating showed exceptional performance on EIS and is expected to show extended system performance.
    - It is likely that the combination of the sacrificial zinc rich layer and the barrier protection from the graphene enhanced coatings gives extended coating durability and lifetime.



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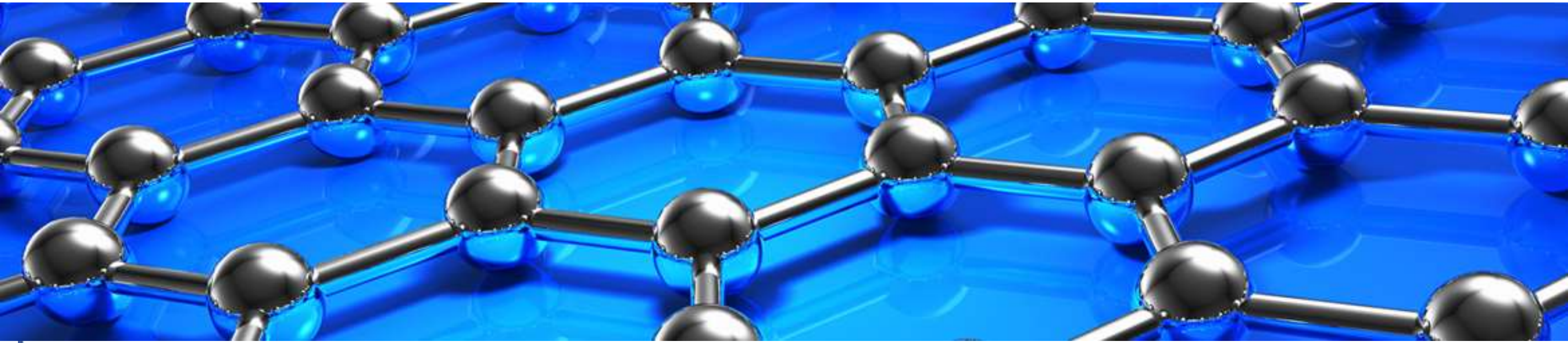

…Graphene in products used by everybody, everyday