Double Self-Assembly Graphene Thin Films for Copper to Protect from Salt Water Corrosion

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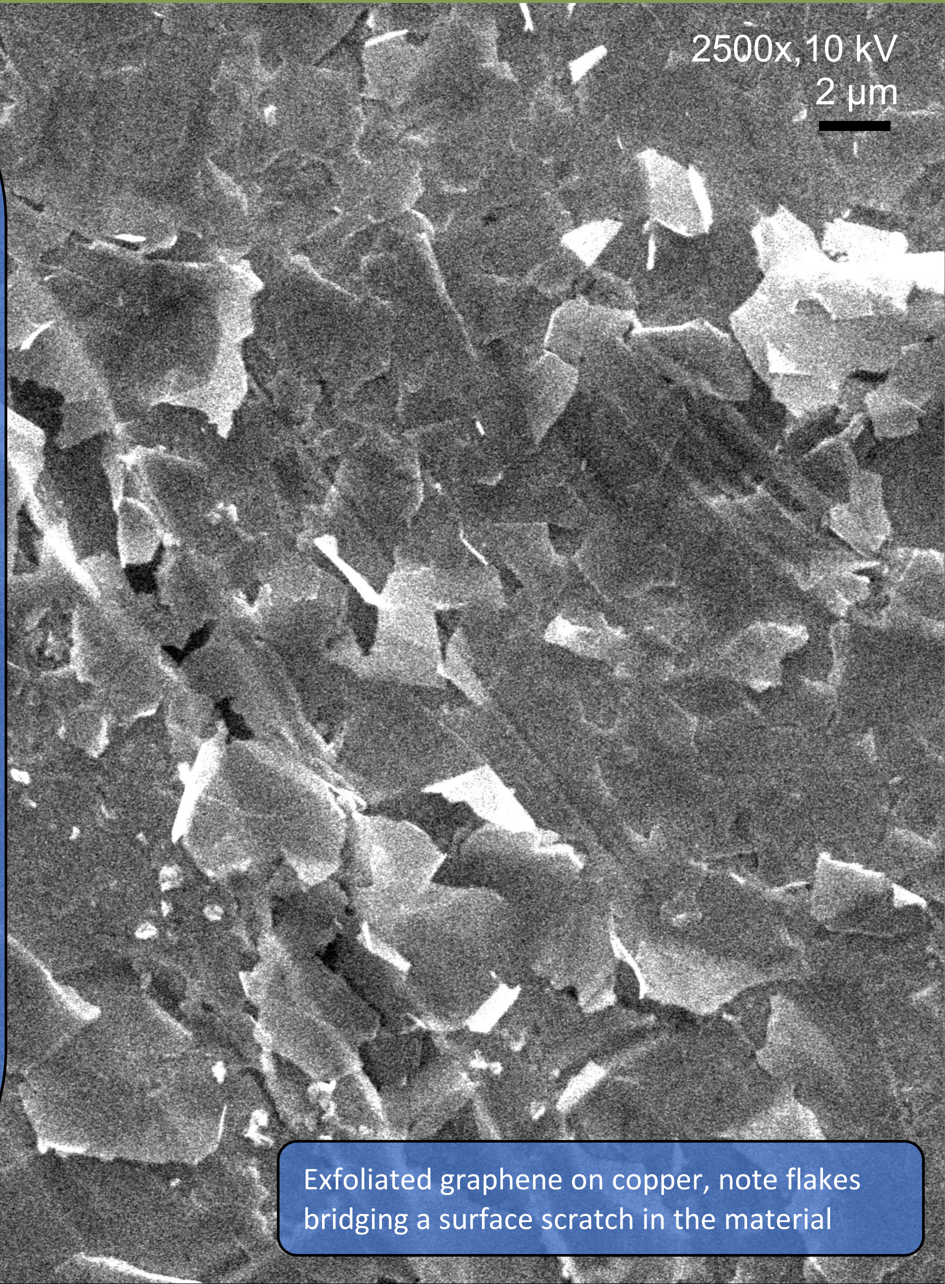
Overview

- Introduction
  - Copper, Corrosion, and Current Mitigation
  - Graphene: A viable candidate for corrosion resistance
  - Double Self-Assembly Coatings
- Method and Testing
- Characterization and Results
  - Raman
  - Optical Microscopy
  - Scanning Electron Microscopy (SEM)
  - Energy-Dispersive X-Ray Spectroscopy (EDX)
- Discussion
- Summary



Exfoliated graphene on copper, note flakes bridging a surface scratch in the material

Copper, Corrosion, and Current Mitigation

- Copper has great conductivity, mild corrosion resistance, and workability.
- Used in the creation of electronics, plumbing, and desalinization

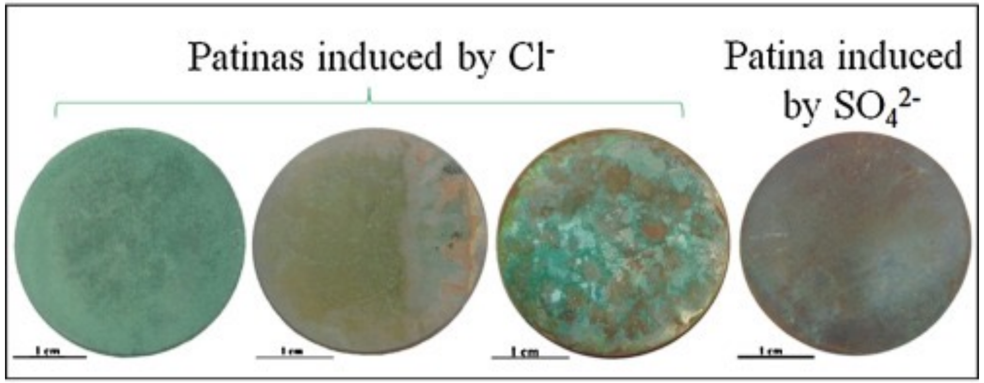


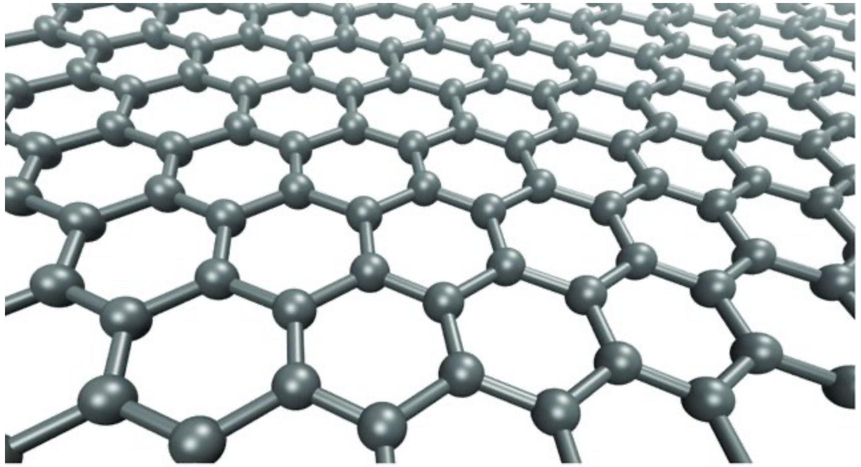
Image Credit: Carlo et. al., from "Artificial patina formation onto copper-based alloys: Chloride and sulphate induced corrosion processes"

Image Credit: Cleanipedia Team, https://www.cleanipedia.com/gb/floor-and-surface-cleaning/polished-plumbing-how-to-clean-copper-pipes.html

- Despite mild corrosion resistance, Copper can still be corroded by ions like Cl^- and SO_4^{2-}
- Current polymer coatings are thick and can alter the copper substrate's physical properties

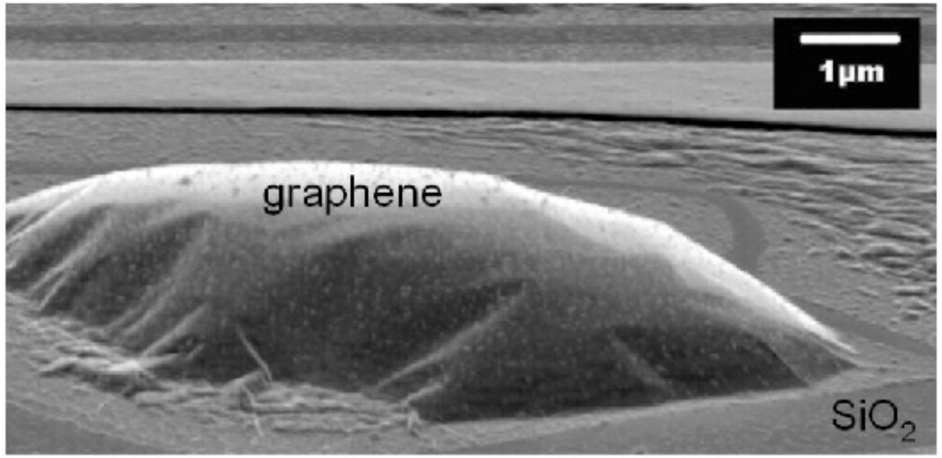
Graphene: A viable candidate for corrosion resistance

- Graphene, an sp^2 hybridized hexagonal network of carbon atoms may provide ultra-thin corrosion resistance
  - Graphene sheets are chemically inert
  - At its thinnest is one atom thick
  - Impermeable to ions and gases



Note: A ball and stick model of the described graphene structure

Image Credit: Armano et. al., from "Two-Dimensional Carbon: A Review of Synthesis Methods, and Electronic, Optical, and Vibrational Properties of Single-Layer Graphene"



Note: Gas trapped is HF, displaying both graphene's inert and impermeable qualities simultaneously.

Image Credit: Stolyarova et. al., from "Observation of graphene bubbles and effective mass transport under graphene films"

Current corrosion resistant graphene coating methods

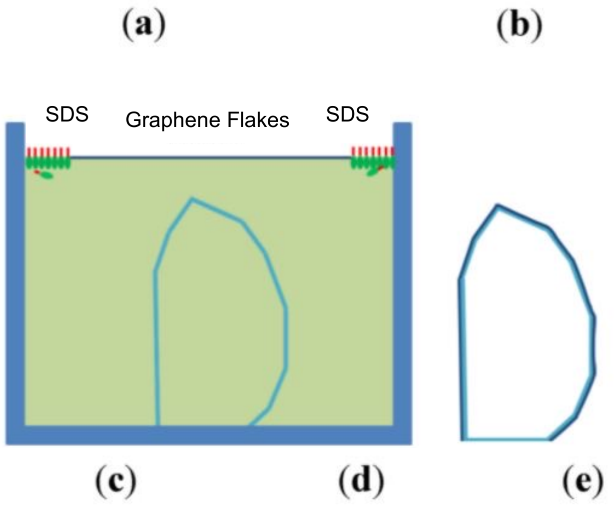
- Currently chemical vapor deposition (CVD) creates anti-corrosive graphene on copper and nickel
  - Good for flat surfaces
  - Layers can be transferred to other materials
    - However, limited to flat and slightly convex surfaces
  - Transfer process is complex and low yield
- **Good in situations where flat coatings are required, however not as good for 3D objects.**

Note: Easy Tube101, CVD Equipment Corporation Gas cabinets AGA-K, model DS 52 4B. Maximum Substrate size 2.5 cm X 5 cm

Image Credit: UseScience, https://scientificservices.eu/item/device-for-synthesis-of-graphene-cvd-equipment-corporation/1569

New Method for corrosion resistance – Double self-assembly

- One new method called double self-assembly (DSA) by Jia et. al. may offer one solution to this
  - Allows for coatings of smaller flakes to conform to 3D substrates
  - Multiple coatings may offer corrosion resistant layer
  - Will be performed with pristine exfoliated graphene without surface modification rather than the reduced graphene oxide the authors used, less defects in flakes
  - Corrosion resistance for this method will be tested on copper 2D copper samples to establish feasibility before trying more complex shapes



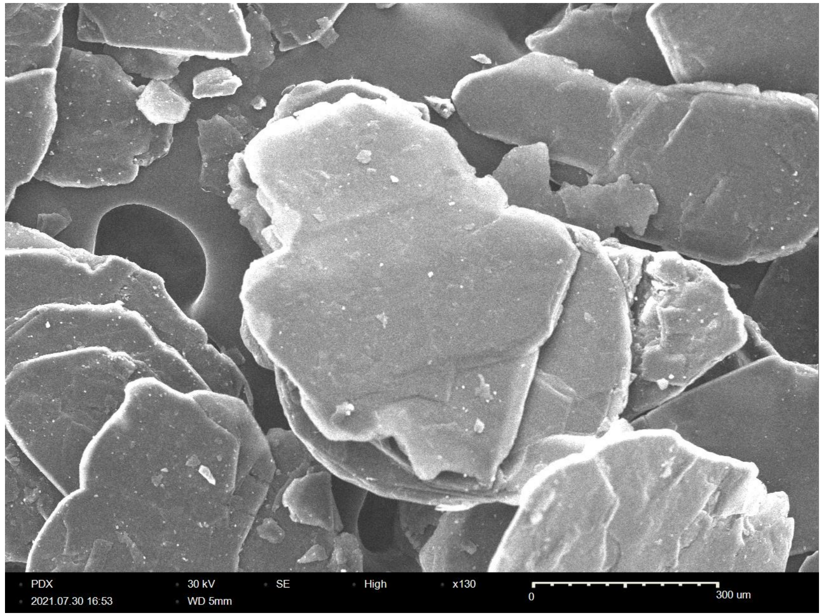
Example of DSA films of graphene flakes on 3D substrate, a and b showing film conformation.

Image Credit: Jia et. al. from “Large Area Graphene Deposition on Hydrophobic Surfaces, Flexible Textiles, Glass Fibers and 3D Structures”

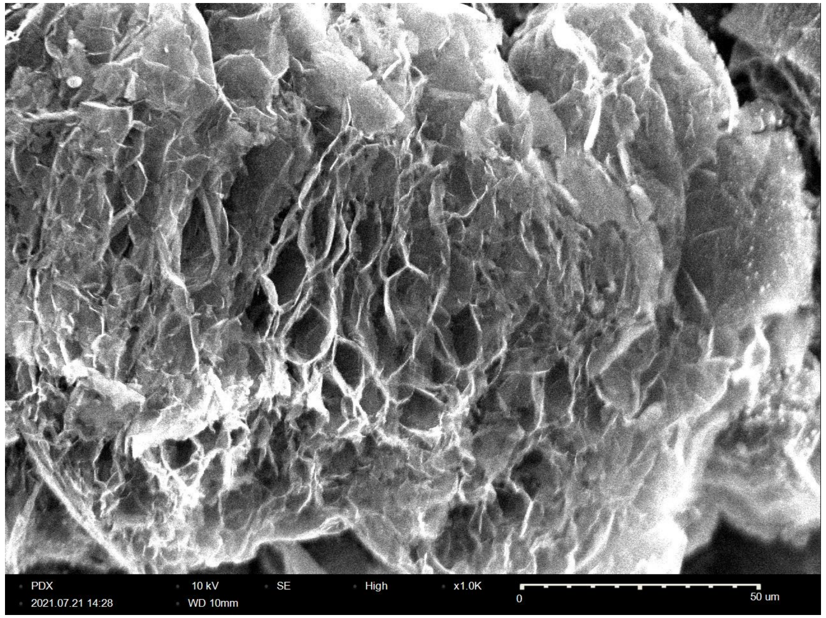
Experimental Setup

Expandable Graphite → Expanded Graphite → Sonicate Expanded Graphite → Centrifuge → Solvent replacement → Use to make loose film on DI water → Densify film with SDS → Lift substrate through, dry with Vacuum

- Exfoliation by Wen et al, Kaleb Hood, and Ben Hughes
- DSA by Jia et. al.



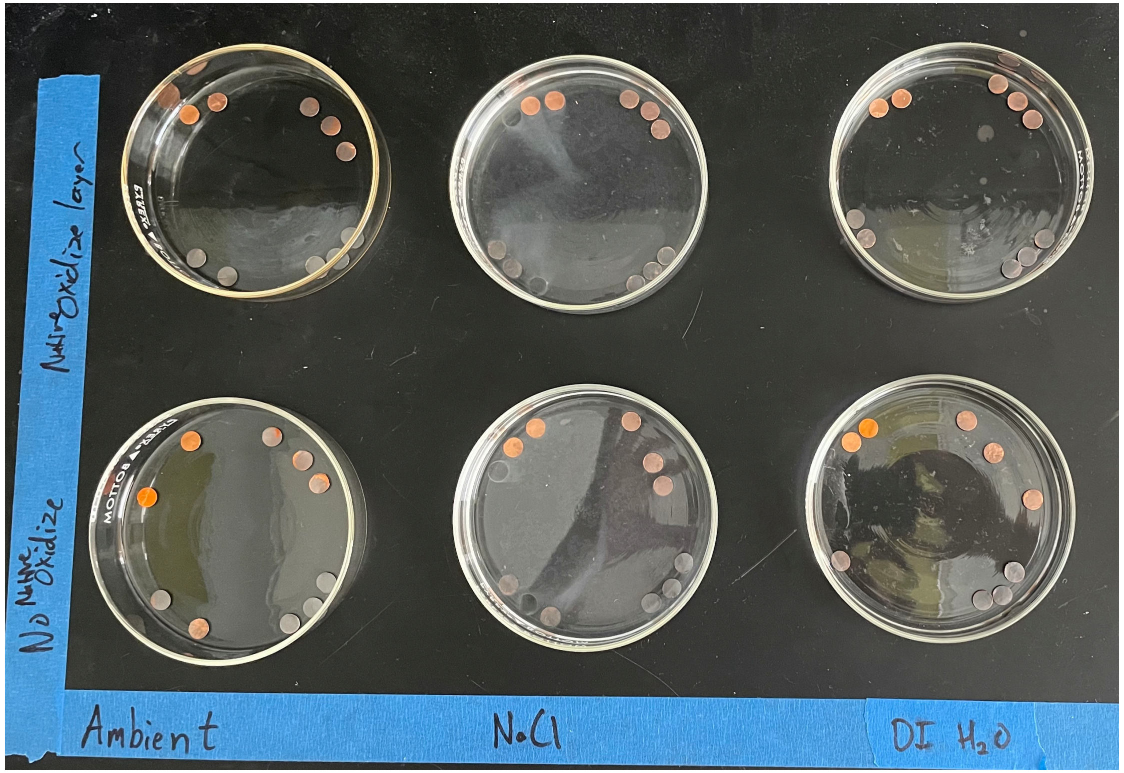
SEM image of expandable graphite, individual flakes that make up the larger piece can be seen on the surface of some pieces.



SEM image of expanded graphite, note the large gaps between layers caused by thermal expansion process. Expands in volume by 250x

Testing Setup

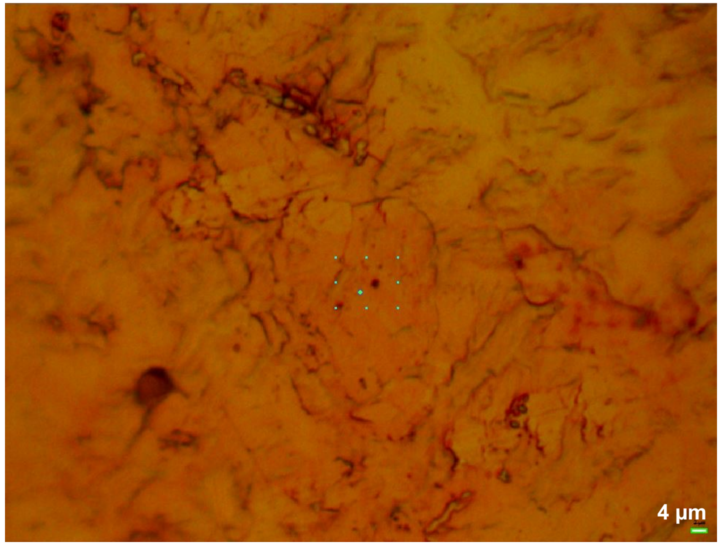
Samples with different numbers of depositions created → Samples placed in 5% Salt Water, with dry and DI water controls → Samples checked at 1, 3, and 5 days → Optical microscopy, Raman, SEM, and EDX used to characterize



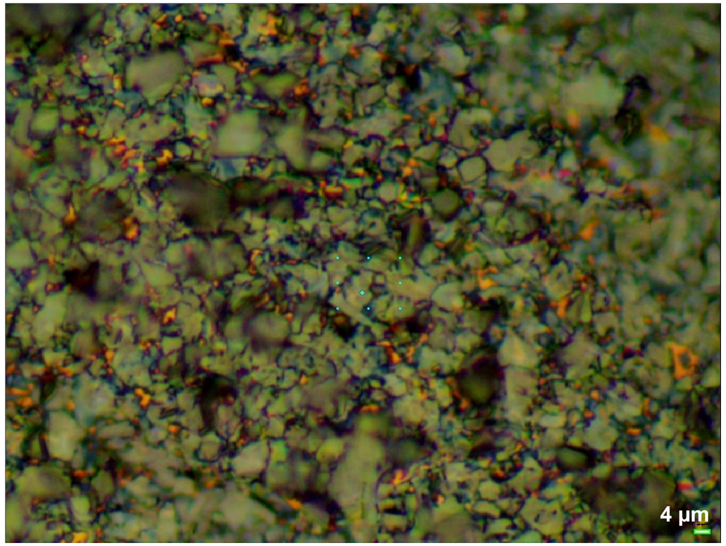
Corrosion Testing Setup

Optical Microscopy – Coating Quality Analysis

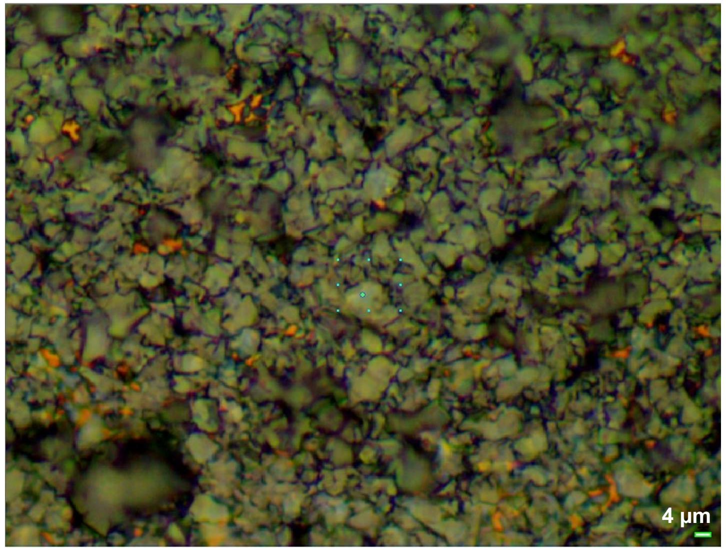
- With increasing numbers of depositions the coverage of the film increases, as does its thickness
- Surface topography elevates parts outside depth of focus
- Even at 5 coats small spots of bare copper can be seen on the optical micrograph (Circled).
- It was observed while making coatings that some of the previous coat can be lost, creating inconsistent coats.



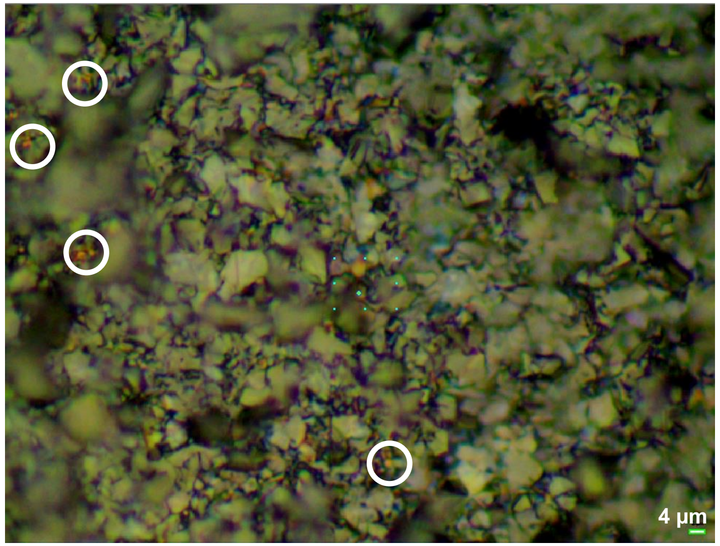
Bare copper with native oxide



Single Deposition on copper with native oxide



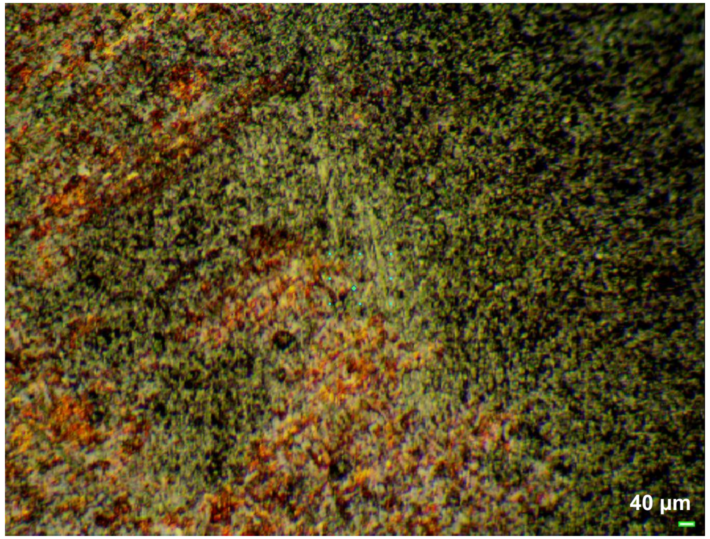
Triple Deposition on copper with native oxide

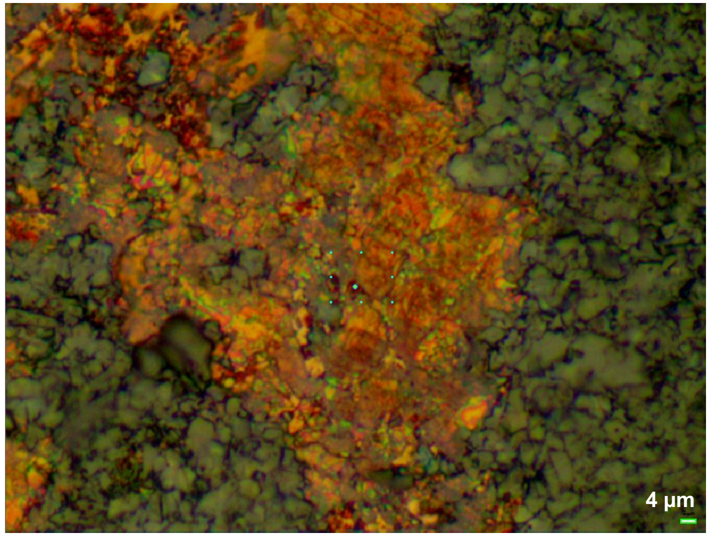


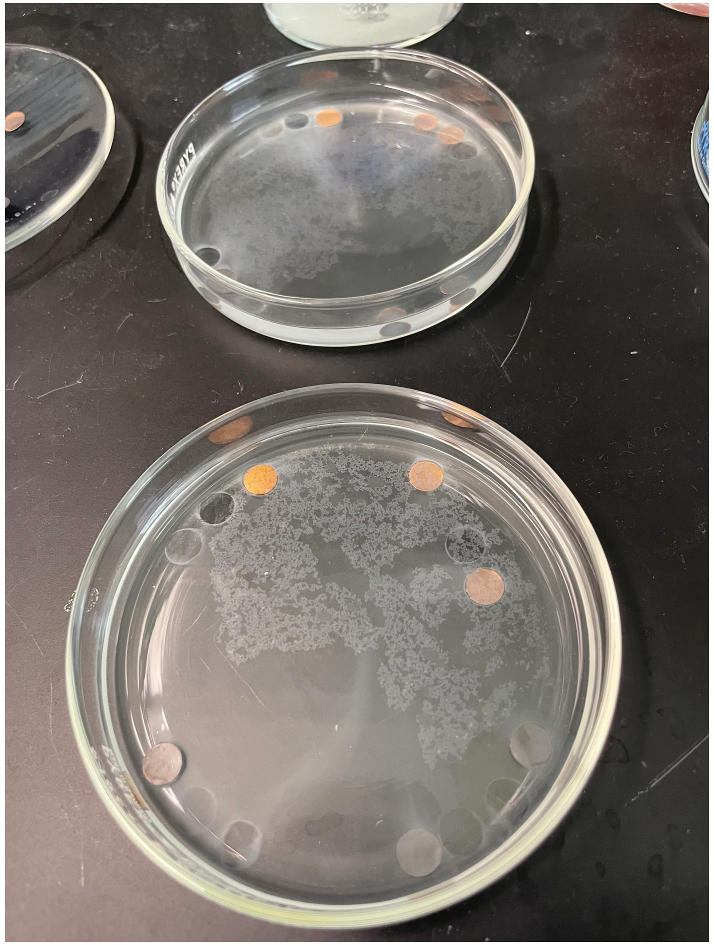
5 Coat Deposition on copper with native oxide

Optical Microscopy – Coating Stripping

- Even with 5 coats, salt water was able to reach the copper surface and start the corrosion process.
- As time went on the coatings in the NaCl solution began to flake off, drifting to the surface.
- This was seen floating at the top of the dish the corrosion trials took place in.
- Control samples did not see this happen.





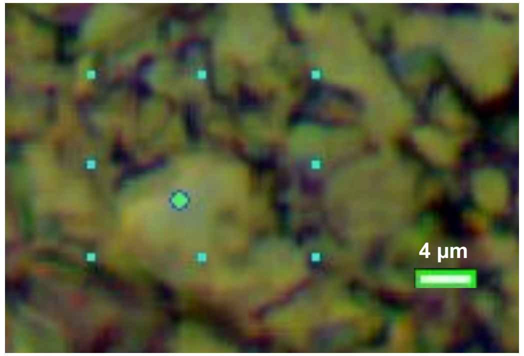


5 coatings after 3 days in the NaCl solution at 100x (top left) and 1000x (bottom left). Note the exposed copper. Right shows the graphene flakes that have detached and floated to the surface.

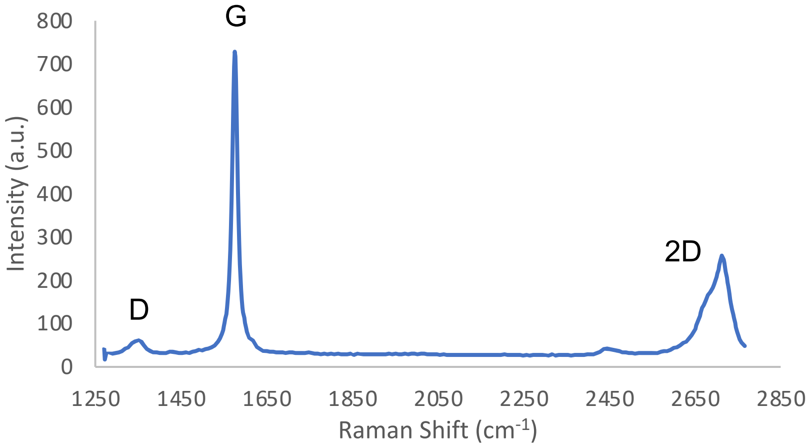
Raman Spectroscopy – Material Verification

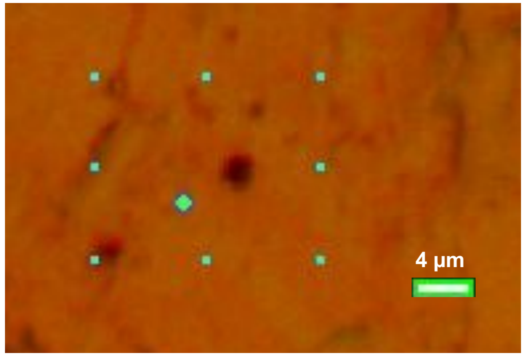
- Average Raman Spectra from exfoliated graphene map (above) and native copper oxide map (background corrected, below).

- The exfoliated graphene spectra is consistent with other spectra produced by this lab.
- Raman spectra of the copper shows peaks at 212 cm^{-1} and 632 cm^{-1}, consistent with reddish Cu_2O, reinforcing that an oxide layer is present.

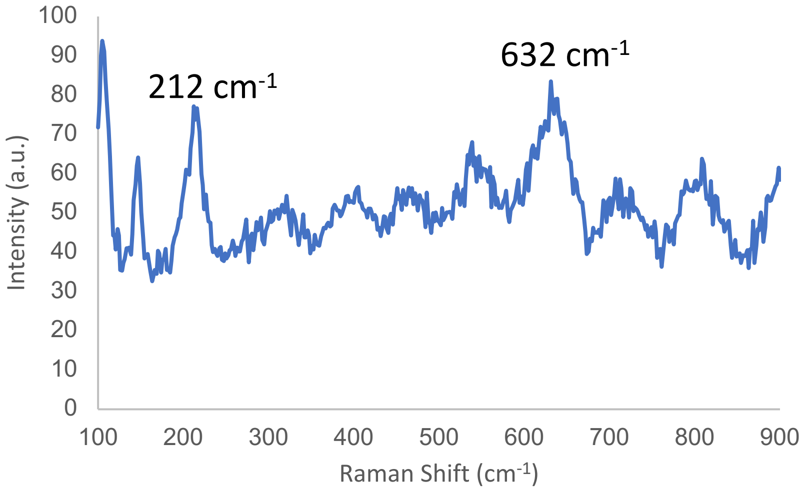


Exfoliated Graphene, 1000x magnification



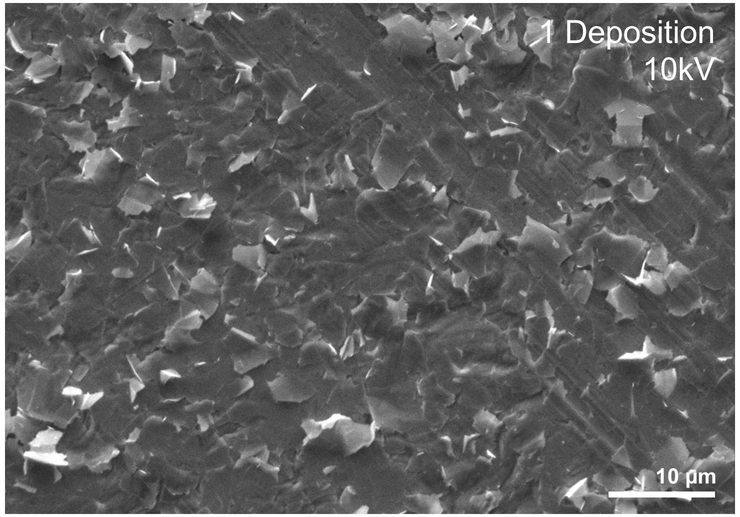


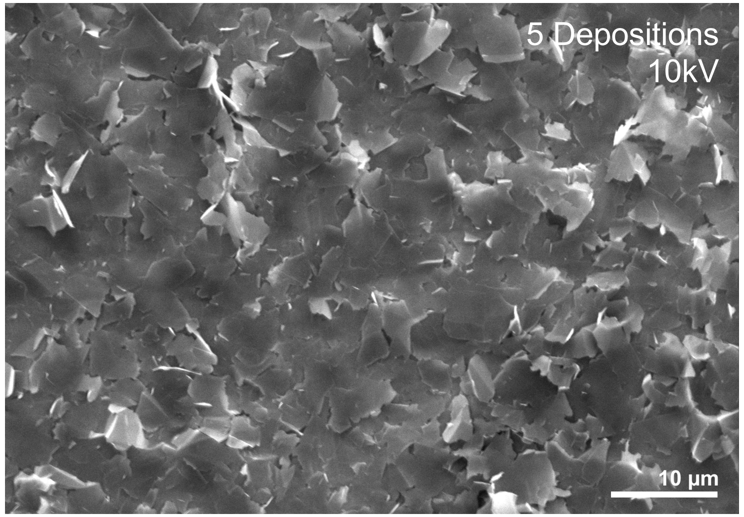
Native copper oxide, 1000x magnification

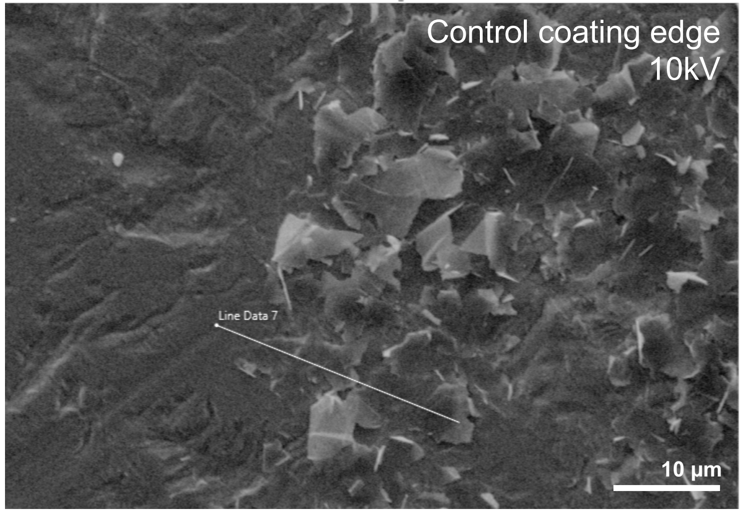


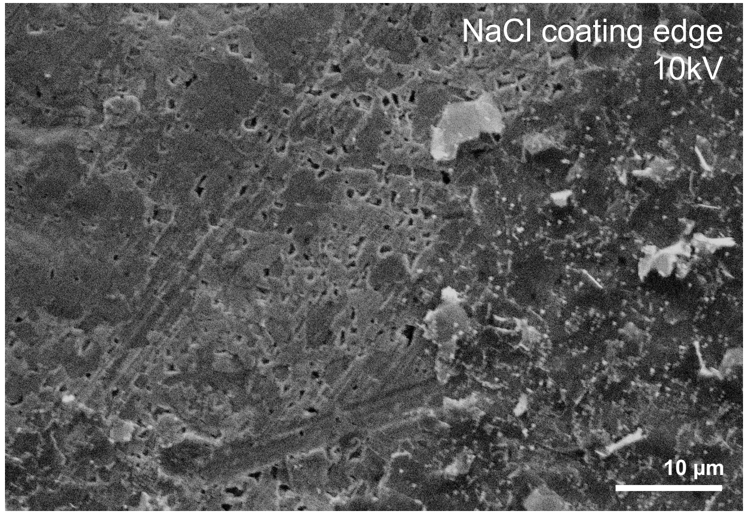
SEM – Coating Topography and Edge Comparison

- SEM reveals the topography of the exfoliated graphene coating, showing that flakes don't lie perfectly flat on the copper surface.
- A comparison of the edges of the coatings (confirmed by EDX) reveals holes in the copper in areas where coating flaked off.









SEM – Corrosion Comparison

- Additionally comparisons of the NaCl sample's copper areas to other works that study the same type of corrosion reveal similarities in their appearance
- Comparison sample soaked for 3 hours at 3% salinity, our sample 5 days at 5% salinity.
- Our coating helped some by comparison, but its poor adhesion caused failure.

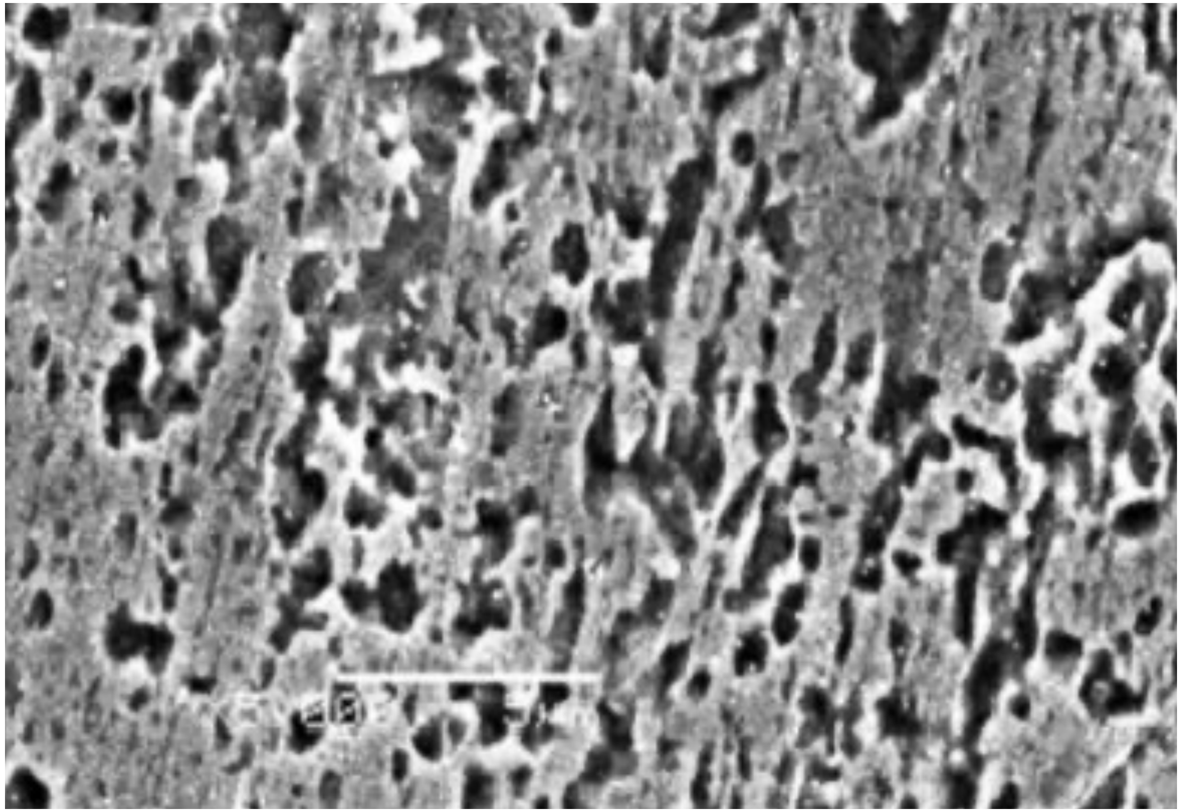
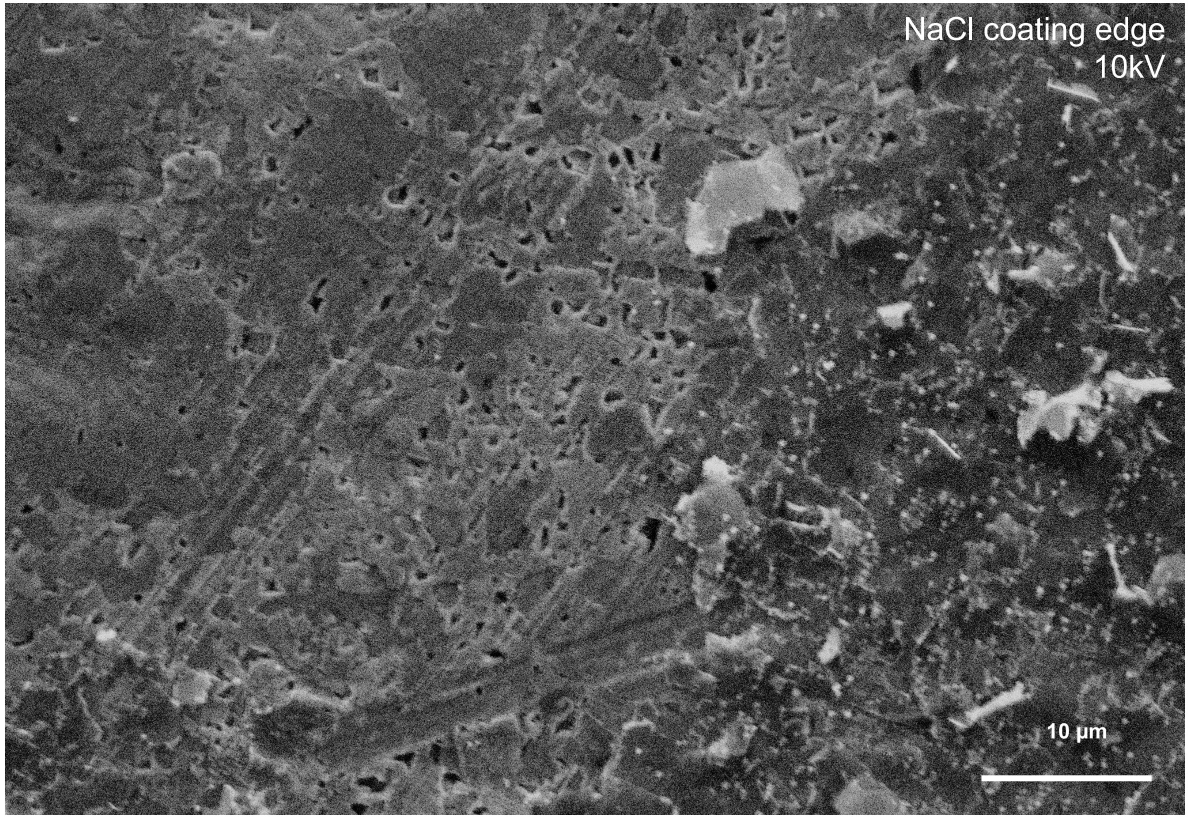
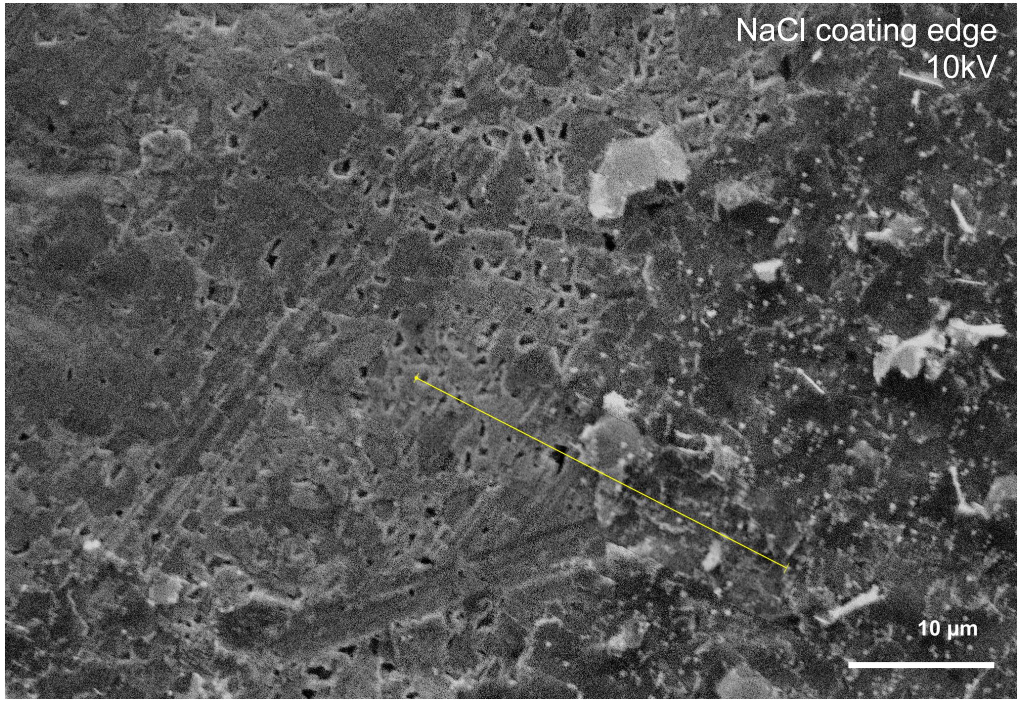


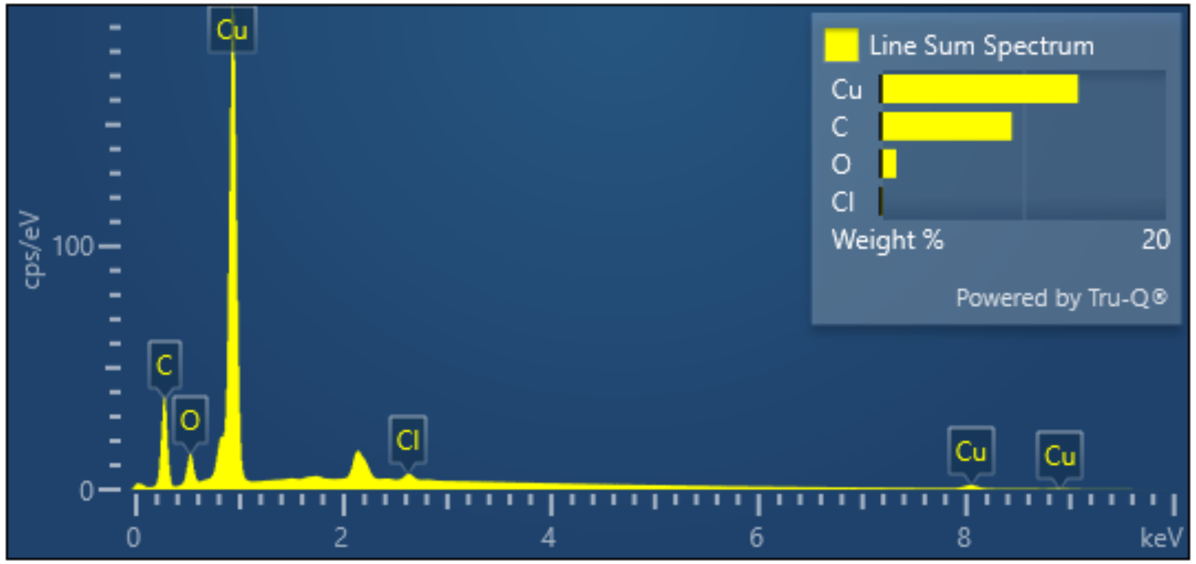
Image Credit: Wei et. al. from "Facile construction of a polydopamine-based hydrophobic surface for protection of metals against corrosion"

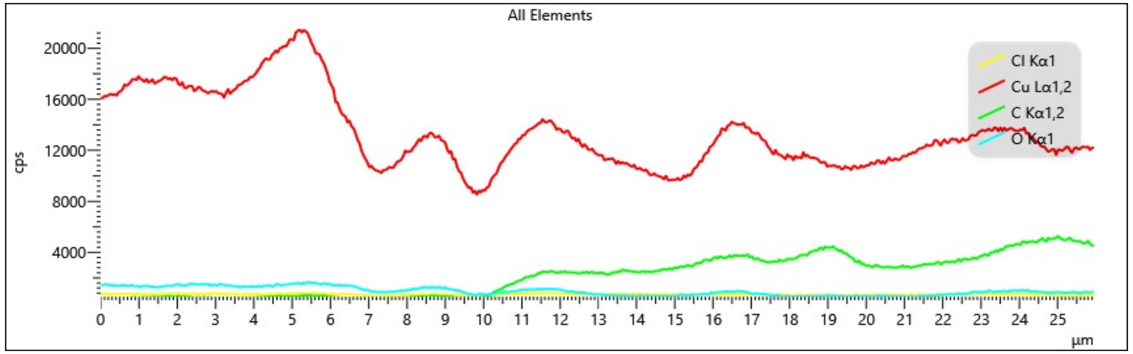


EDX – Graphene Edge and Corrosion Product Verification

- Line scan verifies areas of bare copper where the graphene was removed from solution and verifies the presence of Cl in the sample in absence of Na.
- This supports the idea that rather than the Na being a part of NaCl, the Cl is a part of a different compound, which may be the corrosion product containing chlorine.
- Additional testing methods needed to verify this.

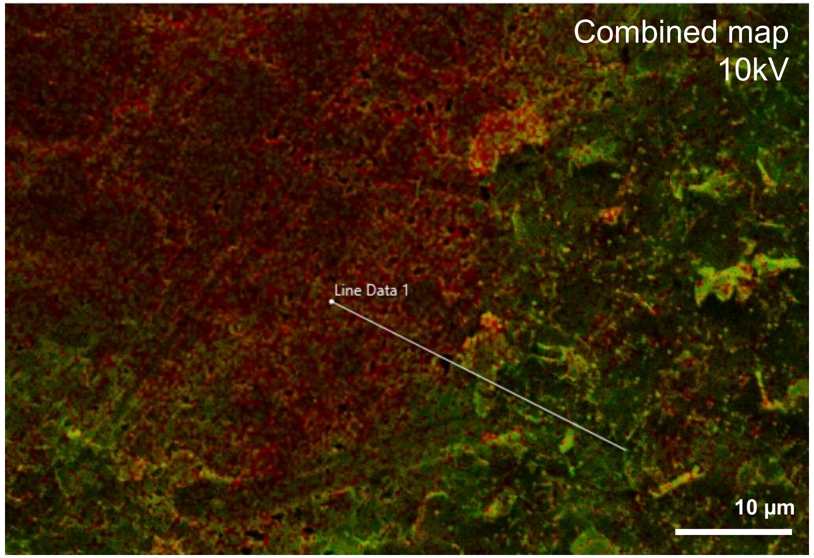


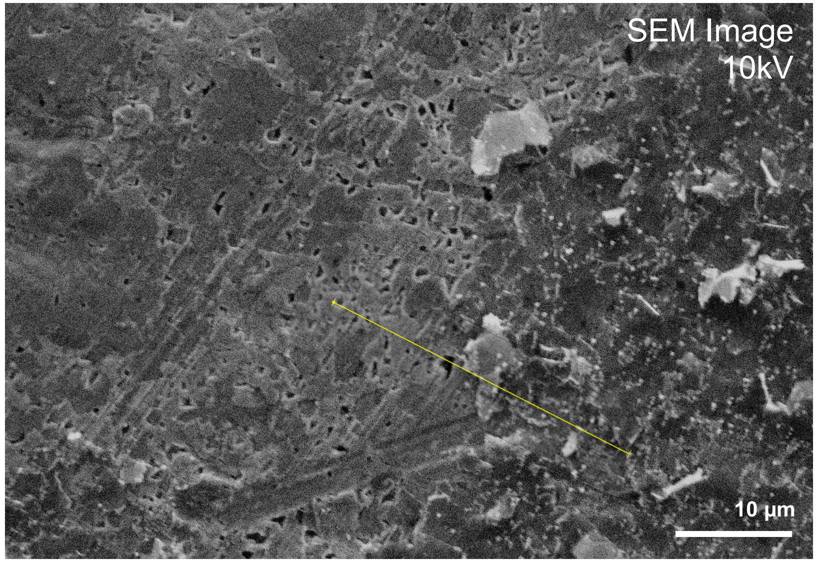


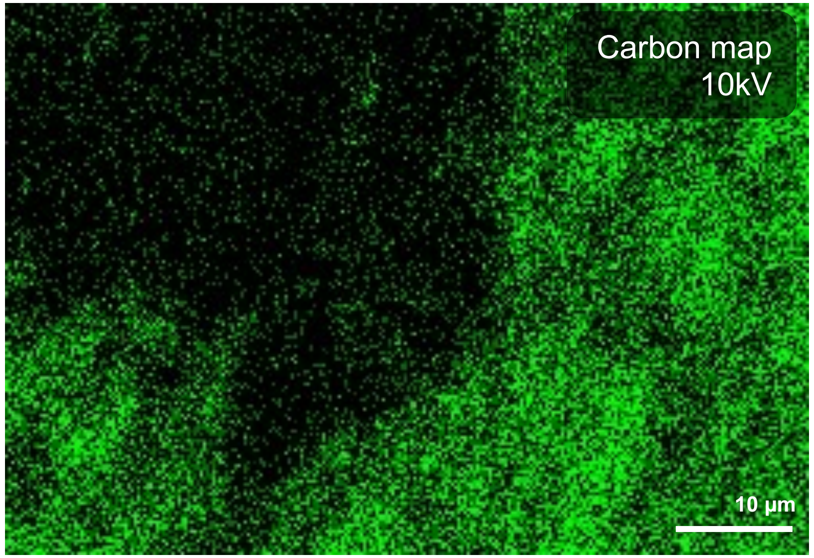


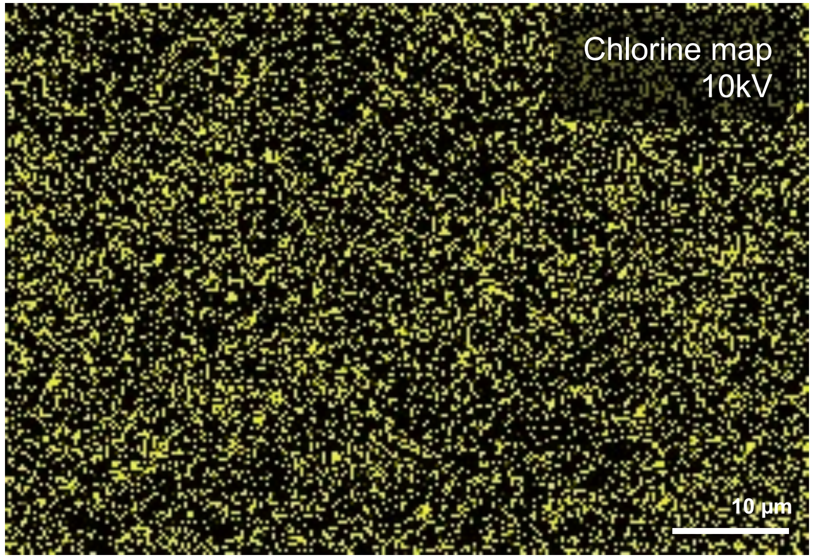
EDX – Graphene Edge and Corrosion Product Mapping

- EDX map of an NaCl exposed sample at an area where coating was removed by the solution. Other elements in layered image:
  - Copper (Red)
  - Oxygen (Blue)
- Again, chlorine present in absence of sodium may be from copper/chlorine corrosion products.









Summary

- Double self-assembly films of exfoliated graphene with different numbers of depositions were created on copper.
- Samples were put in a 5% NaCl solution as well as DI water and air controls and looked at over a period of 5 days.
- Additional coatings after the first resulted in the partial loss of previous coats.
- The NaCl solution samples gradually lost their EG coating, presenting evidence of corrosion, while controls did not.
- This initial testing casts doubt on whether a coating of this material applied via DSA would be able to protect from corrosion.

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References

(1) Fateh, A.; Aliofkhazraei, M.; Rezvanian, A. R. Review of Corrosive Environments for Copper and Its Corrosion Inhibitors. *Arab. J. Chem.* **2020**, *13* (1), 481–544. https://doi.org/10.1016/j.arabjc.2017.05.021.

(2) Di Carlo, G.; Giuliani, C.; Riccucci, C.; Pascucci, M.; Messina, E.; Fierro, G.; Lavorgna, M.; Ingo, G. M. Artificial Patina Formation onto Copper-Based Alloys: Chloride and Sulphate Induced Corrosion Processes. *Appl. Surf. Sci.* **2017**, *421*, 120–127. https://doi.org/10.1016/j.apsusc.2017.01.080.

(3) How to Clean Copper Pipe - How To Polish Copper | Cleanipedia https://www.cleanipedia.com/floor-and-surface-cleaning/polished-plumbing-how-to-clean-copper-pipes.html (accessed 2021 -08 -11).

(4) Armano, A.; Agnello, S. Two-Dimensional Carbon: A Review of Synthesis Methods, and Electronic, Optical, and Vibrational Properties of Single-Layer Graphene. *C* **2019**, *5* (4), 67. https://doi.org/10.3390/c5040067.

(5) Jia, G.; Plentz, J.; Dellith, J.; Dellith, A.; Wahyuono, R.; Andrä, G. Large Area Graphene Deposition on Hydrophobic Surfaces, Flexible Textiles, Glass Fibers and 3D Structures. *Coatings* **2019**, *9*, 183. https://doi.org/10.3390/coatings9030183.

(6) Stolyarova, E.; Stolyarov, D.; Bolotin, K.; Ryu, S.; Liu, L.; Rim, K. T.; Klima, M.; Hybertsen, M.; Pogorelsky, I.; Pavlishin, I.; Kusche, K.; Hone, J.; Kim, P.; Stormer, H. L.; Yakimenko, V.; Flynn, G. Observation of Graphene Bubbles and Effective Mass Transport under Graphene Films. *Nano Lett.* **2009**, *9* (1), 332–337. https://doi.org/10.1021/nl803087x.

(7) Duan, Z. Application of Graphene in Metal Corrosion Protection. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *493*, 012020. https://doi.org/10.1088/1757-899X/493/1/012020.

(8) Jia, G.; Plentz, J.; Presselt, M.; Dellith, J.; Dellith, A.; Patze, S.; Tölle, F. J.; Mülhaupt, R.; Andrä, G.; Falk, F.; Dietzek, B. A Double Self-Assembly Process for Versatile Reduced-Graphene-Oxide Layer Deposition and Conformal Coating on 3D Structures. *Adv. Mater. Interfaces* **2017**, *4* (23), 1700758. https://doi.org/10.1002/admi.201700758.

(9) Device for synthesis of graphene, CVD Equipment Corporation | UseScience https://scientificservices.eu/item/device-for-synthesis-of-graphene-cvd-equipment-corporation/1569 (accessed 2021 -08 -11).

(10) Qian, W.; Chen, Z.; Cottingham, S.; Merrill, W. A.; Swartz, N. A.; Goforth, A. M.; Clare, T. L.; Jiao, J. Surfactant-Free Hybridization of Transition Metal Oxide Nanoparticles with Conductive Graphene for High-Performance Supercapacitor. *Green Chem.* **2012**, *14* (2), 371–377. https://doi.org/10.1039/C1GC16134B.

(11) Wei, N.; Jiang, Y.; Ying, Y.; Guo, X.; Wu, Y.; Wen, Y.; Yang, H. Facile Construction of a Polydopamine-Based Hydrophobic Surface for Protection of Metals against Corrosion. *RSC Adv.* **2017**, *7* (19), 11528–11536. https://doi.org/10.1039/C7RA00267J.