Mechanistic Studies of Dopamine Electrochemistry at Carbon-Based Electrodes

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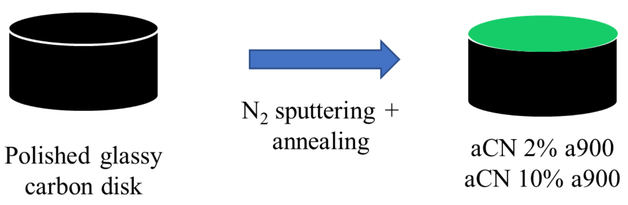
Introduction

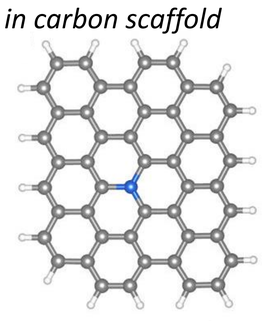
Due to its role in the operation of nervous response and renal, hormonal and cardiovascular systems, quantitation of dopamine (DA) *in vivo* has received great interest. Electrochemical sensing allows detection of nanomolar concentrations, and carbon-based electrodes are particularly suitable for this application due to their bio-compatibility, ease of manufacture, low cost and functionalisation potential. However, their current response depends on DA-surface interactions which might be adversely affected by adsorption and accumulation of oxidised by-products, collectively referred to as 'polydopamine' (PDA). We present a study of the fouling behaviour of carbon electrodes functionalised with N- and O-groups in DA detection at physiological pH, along with spectroelectrochemical studies of the deposited fouling films. Electrodes with smooth, reproducible morphology, tuneable functionality type and concentration and tuneable sp^3/sp^2 ratio were synthesized via sputtering deposition and thermal/electrochemical treatments. The effect of graphitization and functional groups on DA surface coverage was used to rationalise the connection between DA adsorption and electrode fouling. Our results suggest effective methods for optimizing carbon electrode composition as a means of minimizing fouling in DA electroanalysis.

Surface Preparation

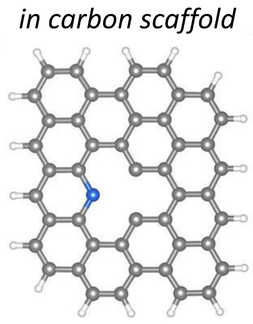
Preparation procedure for N-doped carbon surfaces



Graphitic N-site (blue) in carbon scaffold

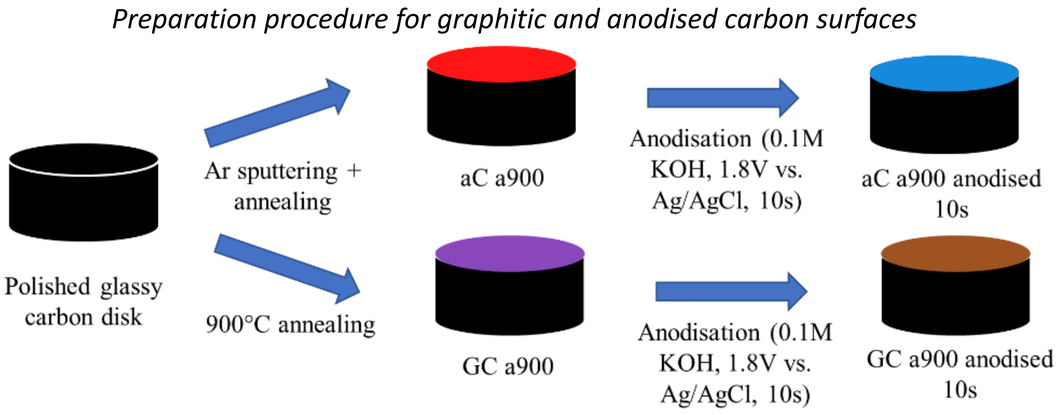


Pyridinic N-site (blue) in carbon scaffold



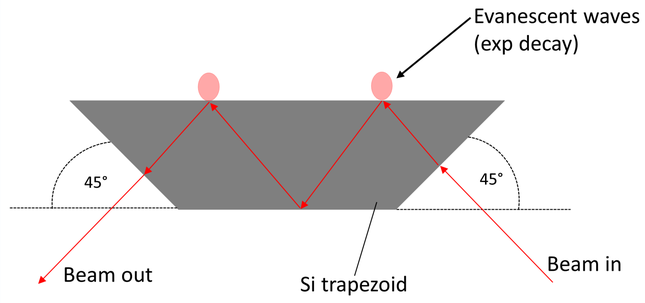
Sputtering in Ar/N_2 followed by annealing results in *ca.* 2% N/C at. concentration and 25:75 pyridinic:graphitic sites, while degree of graphitisation is greater for 2% vs 10%.

Preparation procedure for graphitic and anodised carbon surfaces



Anodisation of GC or sputtered films introduces O-moieties (-OH, C=O, C_2O) and disrupts the carbon scaffold, increasing the sp^3/sp^2 ratio and the defect density.

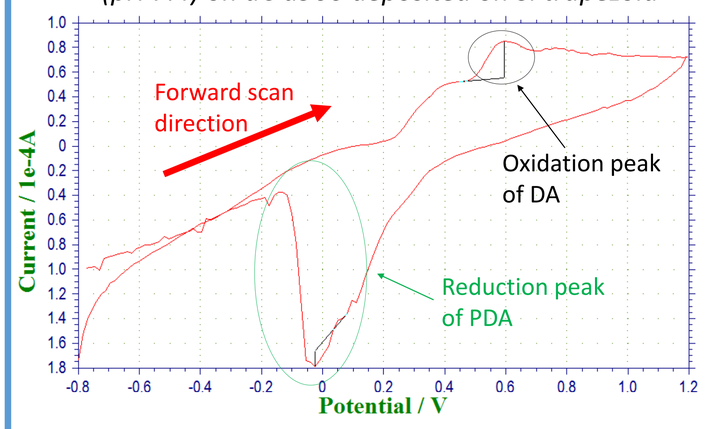
Spectroelectrochemistry Basics



Evanescent waves can probe for molecules near the Si interface.
Deposition of carbon films on Si trapezoids facilitates combining electrochemistry to investigate PDA formation and IR spectroscopy to observe the film evolution as a function of the applied potential.

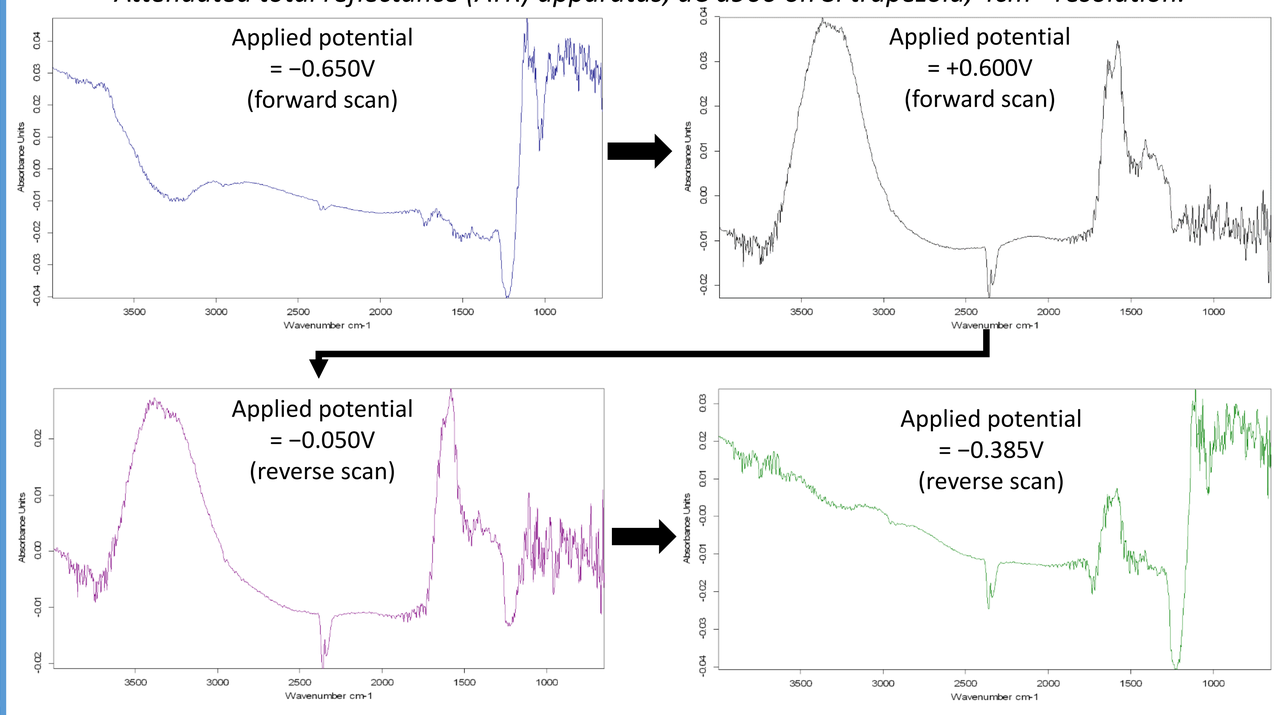
Spectroelectrochemistry of PDA

Representative voltammogram of 1mM DA in PBS (pH 7.4) on aC a900 deposited on Si trapezoid



Experiment involved using staircase voltammetry – 15mV steps every 15s for a "pseudo-1mV/s" measurement.
This enables the collection of IR spectra at a fixed potential – quasi-static conditions.
Extended deposition times lead to thick PDA growth and a large reduction in the peak associated with PDA-type moieties.

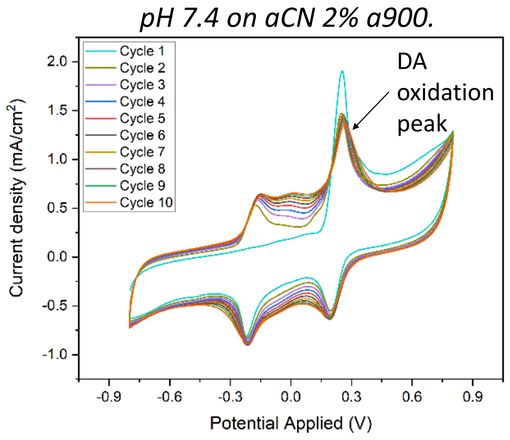
IR spectra collected while scanning the potential using staircase voltammetry.
Attenuated total reflectance (ATR) apparatus, aC a900 on Si trapezoid, 4cm^{-1} resolution.



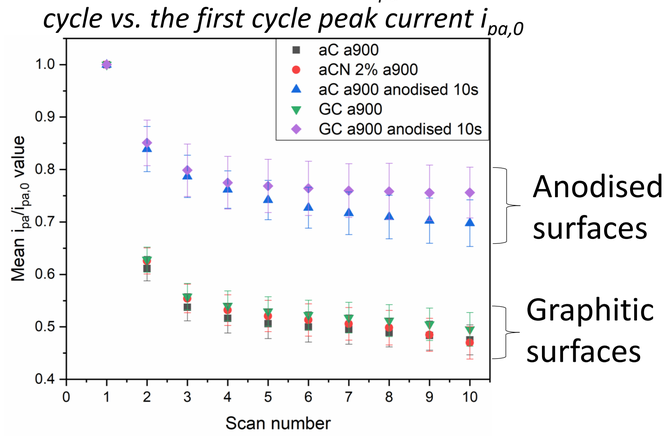
Forward scan – deposition of PDA through oxidation of DA. Characteristic peaks of PDA occur[2] at 1736 cm^{-1} and 1652 cm^{-1}: their increase indicates PDA deposition.
A sizeable change in the intensity of the H_2O stretching mode (~3300cm^{-1}) and the H_2O bending mode (~1640cm^{-1}) is seen going from positive potentials (+0.600V) to negative potentials (−0.385V). We attribute this to the ingress and egress of ions as the PDA network becomes charged.
After the first cycle, the PDA is thick enough to be insensitive to changes at the PDA/H_2O interface and subsequent spectra show no new potential-dependent changes.

Fouling Behaviour of Electrodes

Representative set of CV cycles of DA pH 7.4 on aCN 2% a900.



Ratio of the peak current i_{pa} for each cycle vs. the first cycle peak current $i_{pa,0}$



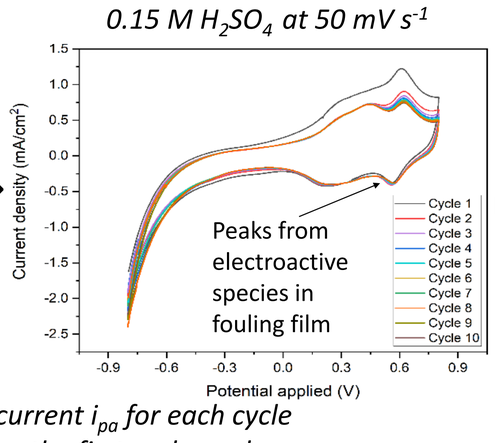
Peak current ratio serves as a measure of fouling susceptibility.[2] Anodised surfaces show greatest resilience to fouling, likely due to greater sp^3/sp^2 ratio and defect density.
No indication that adsorption influences fouling rate – aCN 2% a900 and aC a900 foul at very similar rates.

Effectiveness of Acid Cleaning of Surfaces

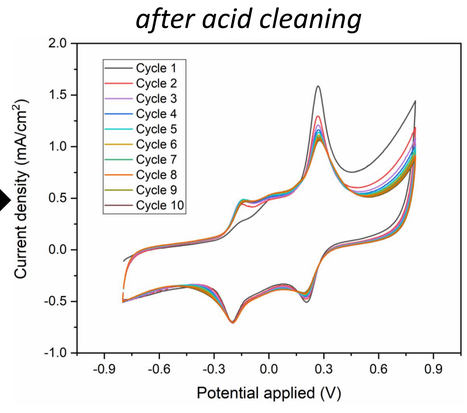
To what extent do the fouled surfaces recover their original sensing ability after cleaning?

Initial 10 cycles in DA, producing fouled electrodes

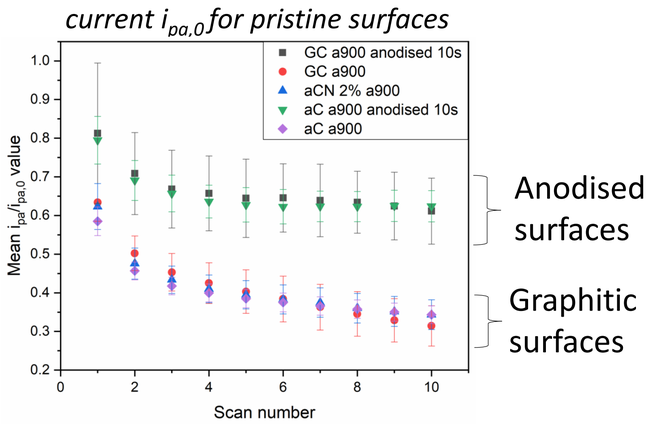
CVs used to clean the surfaces, 0.15 M H_2SO_4 at 50 mV s^{-1}



CVs of DA on aCN 2% a900 after acid cleaning



Ratio of the peak current i_{pa} for each cycle after cleaning vs. the first cycle peak current $i_{pa,0}$ for pristine surfaces



Acid cleaning results in DA oxidation recovery.
The extent of recovery can be monitored by the ratio of the peak currents for the acid cleaned surfaces vs. the initial pristine surface peak.
The recovery on anodised surfaces is greater than on graphitic surfaces, showing that graphitic domains are more susceptible to irreversible fouling.

Conclusions and Future Work

- DA fouling correlates to the extent of DA adsorption; the specific chemical sites appear to be less important than the degree of graphitisation. Graphitisation is crucial as a promoter/inhibitor of PDA adsorption and hence fouling.
- Anodised surfaces show greater resistance to fouling and recovery after cleaning while maintaining fast kinetics, likely due to greater sp^3/sp^2 ratios and defect densities.
- Spectroelectrochemistry reveals the growth of thick PDA on the carbon surfaces.
- The evolution of the IR bands related to H_2O indicates the movement of ions into and out of the PDA matrix as the latter changes its charge state. Future work should investigate this phenomenon using different counterions and charged/uncharged redox probes, to determine the potential of PDA as a redox-switchable ion sensor.

References:

[1]Patel, Tan, Miller, Macpherson, Unwin, *Analytical Chemistry* **2013,** *85* (24), 11755-11764.
[2]Daboss, Lin, Godejohann, Kranz, *Analytical Chemistry* **2020**, 92, 12, 8404–8413

Acknowledgments:

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