

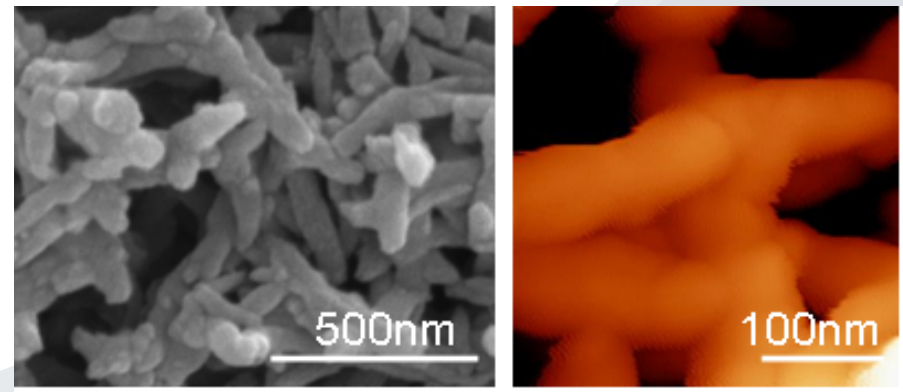
Self-Doped Carboxylated Polyaniline Nanofibres

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Outline

- Polyaniline Nanofibres Synthesis
- Functionalisation of Polyaniline Nanofibres
- Nanofibre characterization
- Applications

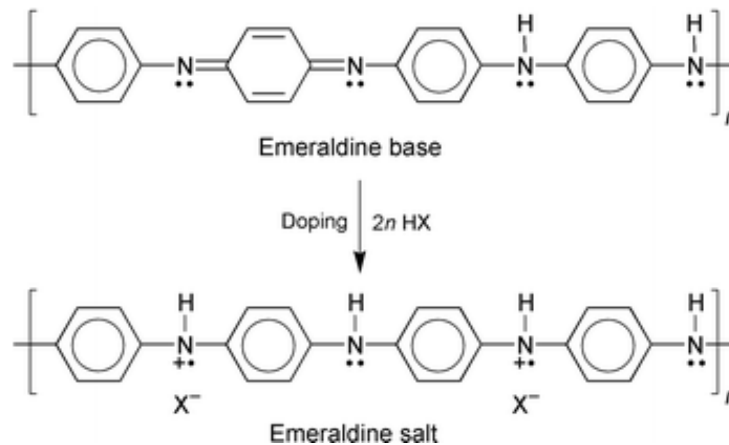


Background

Polyaniline Nanofibres

Advantages

- low cost, easy synthesis
- reversible acid-base doping-dedoping chemistry



Insulating State
Blue/Violet Colour

Conducting State
Green

Limitations

- electroactivity and conductivity of PANi strongly depend on the solution pH
- neutral pH : Pani is electro-inactive and nonconducting



Self-doping Polyaniline



Common Approach

- Doping Pani with anionic species
e.g. : poly(acrylic acid)¹, poly(styrene sulfonate)²
- Copolymerization of aniline with derivatized aniline monomers
e.g. : ortho (or meta)-aminobenzene-sulfonic acid³
- Polymerization of aniline derivatives⁴
- Layer-by-layer assembling

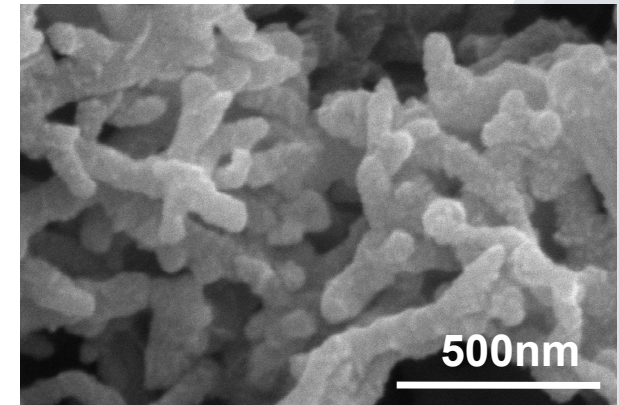
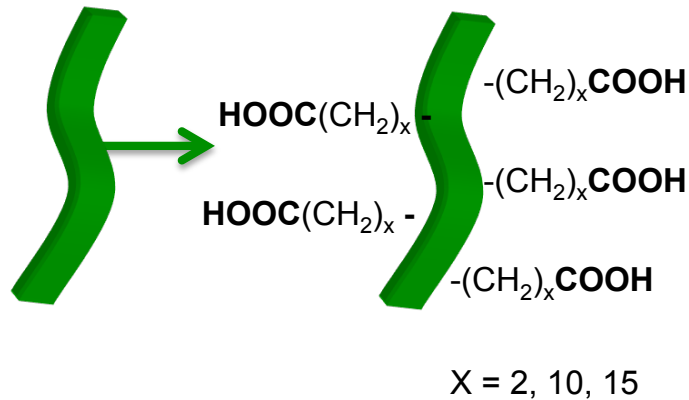
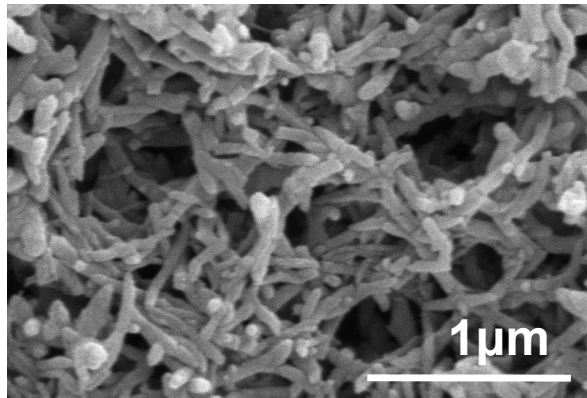
[1] P. N. Bartlett and E. Simon, Phys. Chem. Chem. Phys., 2000, 2,2599.

[2] P. N. Bartlett and E. N. K. Wallace, J. Electroanal. Chem., 2000,486, 23.

[3] Z. Wang, L. Jiao, T. You, L. Niu, S. Dong and A. Ivaska, Electrochem. Commun., 2005, 7, 875

[4] H. Tran and R. B. Kaner, Chem. Commun., 2006, 3915

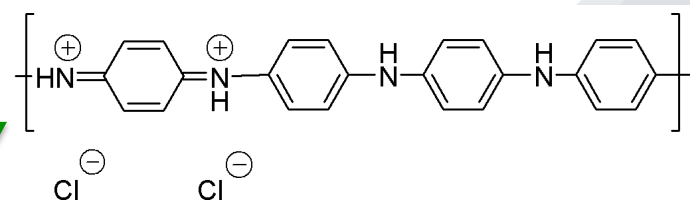
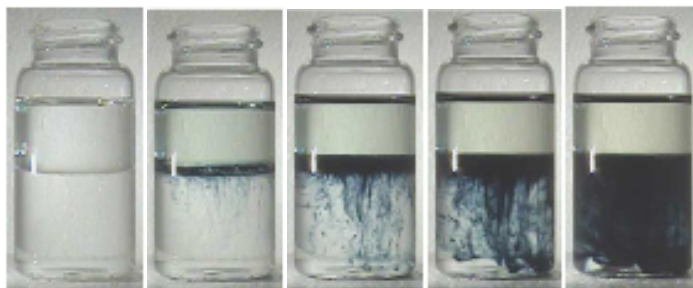
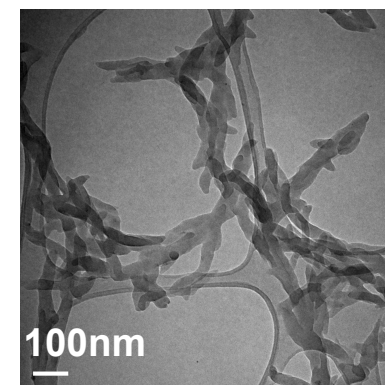
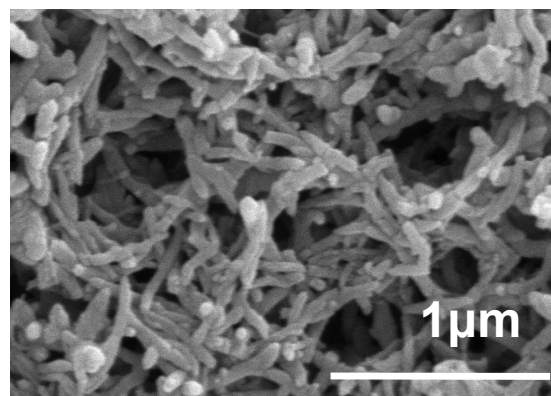
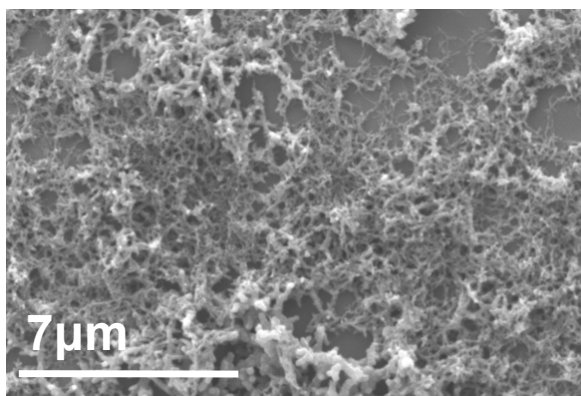
Our Approach



- Cheap and Scalable Process
- Maintain the Nanomorphology of PAni

Polyaniline Nanofibres Synthesis

➤ interfacial polymerization

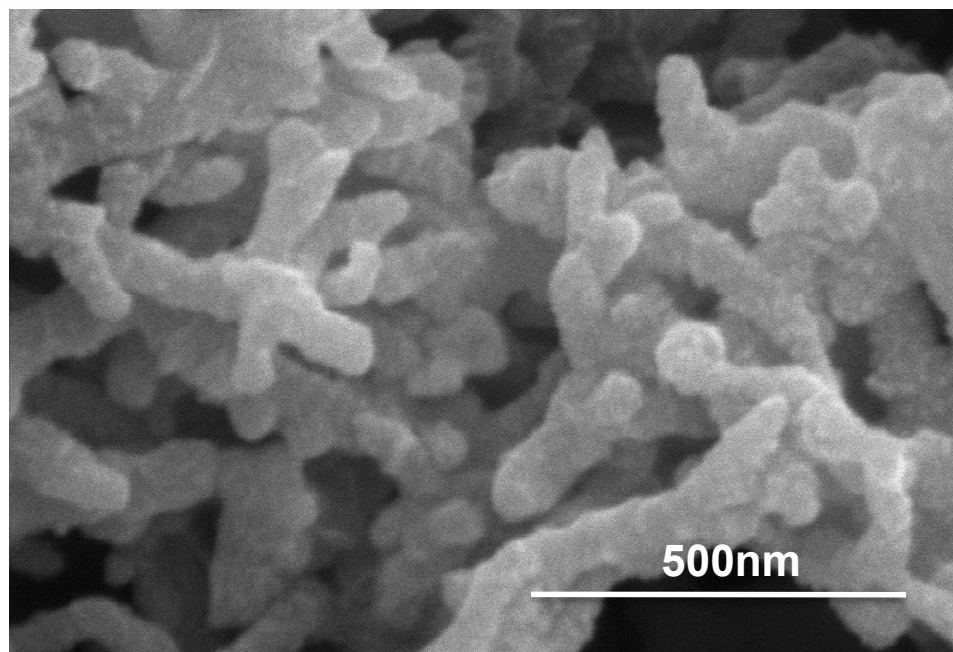
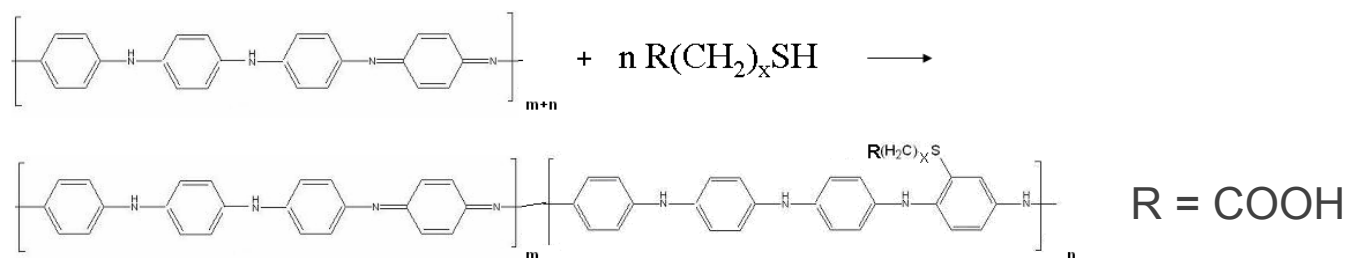


- Diameters : 30 - 50 nm
- Lengths: 500nm - several μm

J.X. Huang, S. Viril, B.H. Weller, R.B. Kaner, *J.Am.Chem.Soc.* 125 (2003),314-315

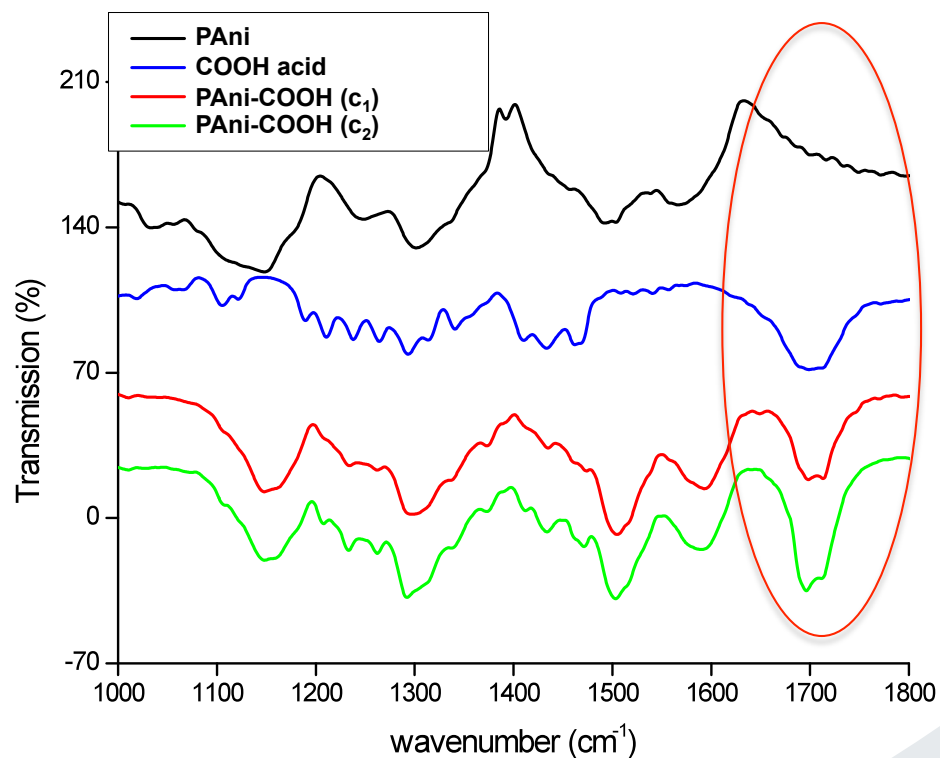
Polyaniline Functionalisation

- Thiol reflux - 100°C for 2 hours in aqueous pH 4 buffer.
- Reactive thiol groups attach onto quinoid rings by nucleophilic addition.



E.Lahiff, T. Woods, W. Blau, G.G. Wallace, D. Diamond, *Synth. Met.* 159 (2009), 741-748.

Evidence of Covalent Bonding



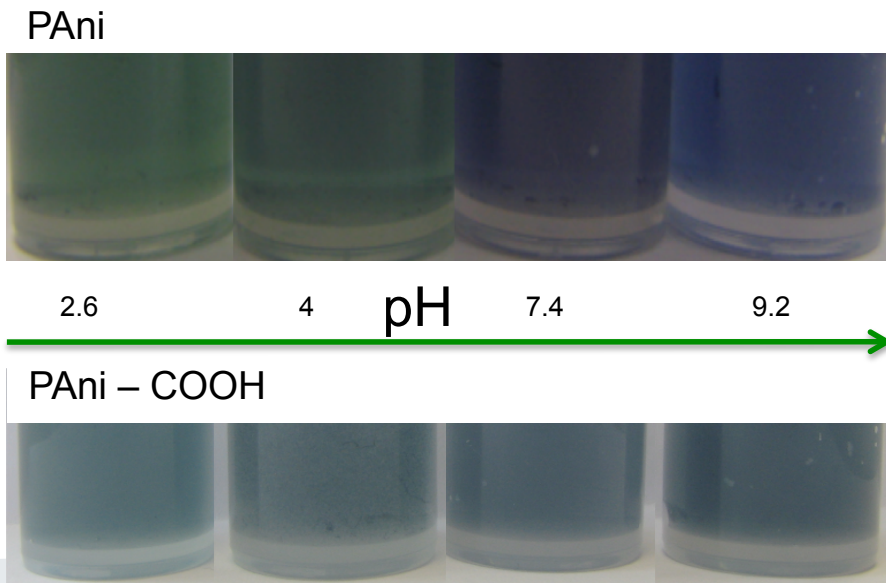
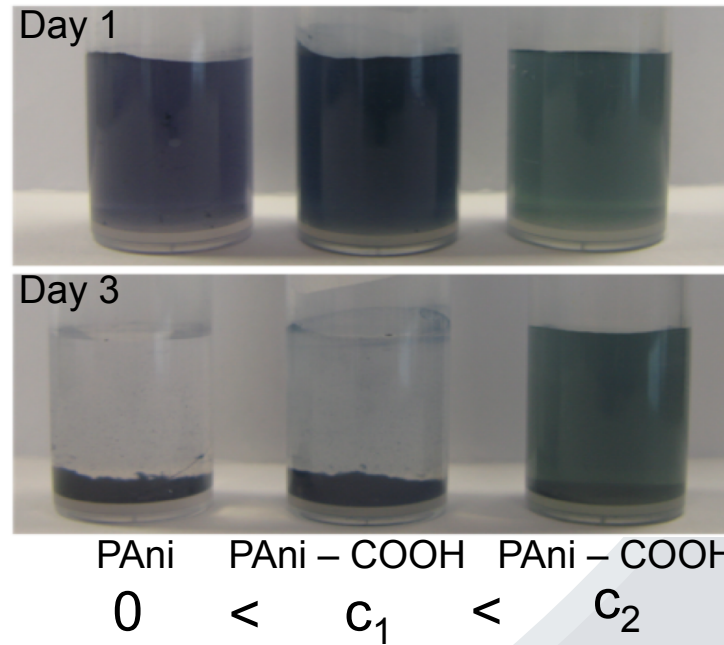
➤ Covalent attachment of the acid to the polymer backbone

The degree of side-chain attachment can be controllably altered.

E.Lahiff, T. Woods, W. Blau, G.G. Wallace, D. Diamond, *Synth. Met.* 159 (2009), 741-748.

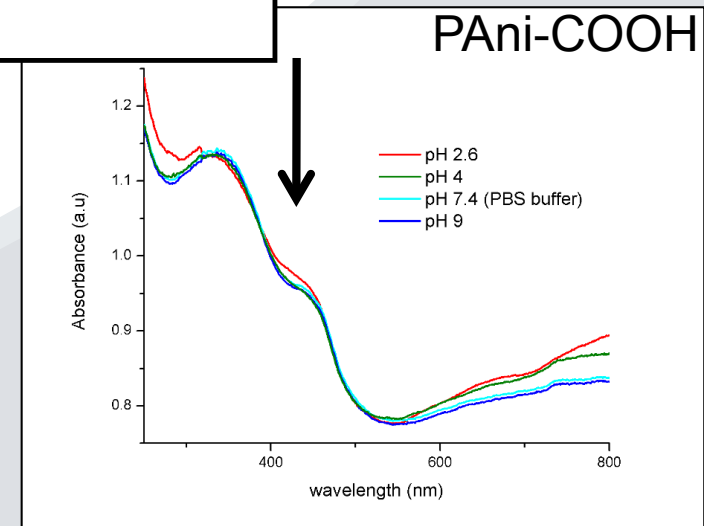
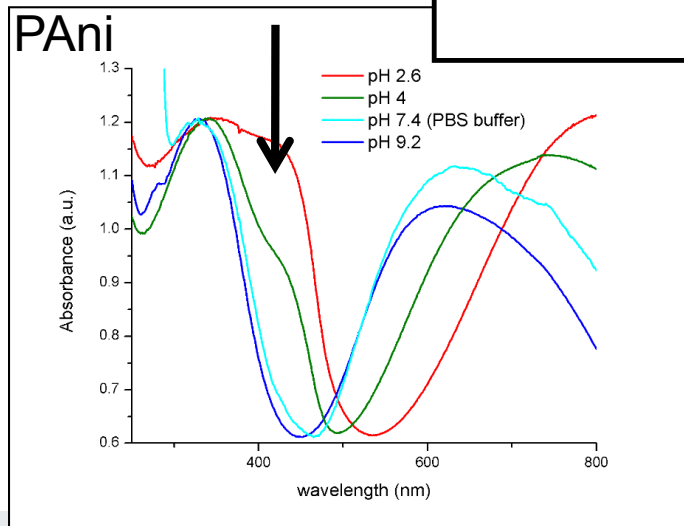
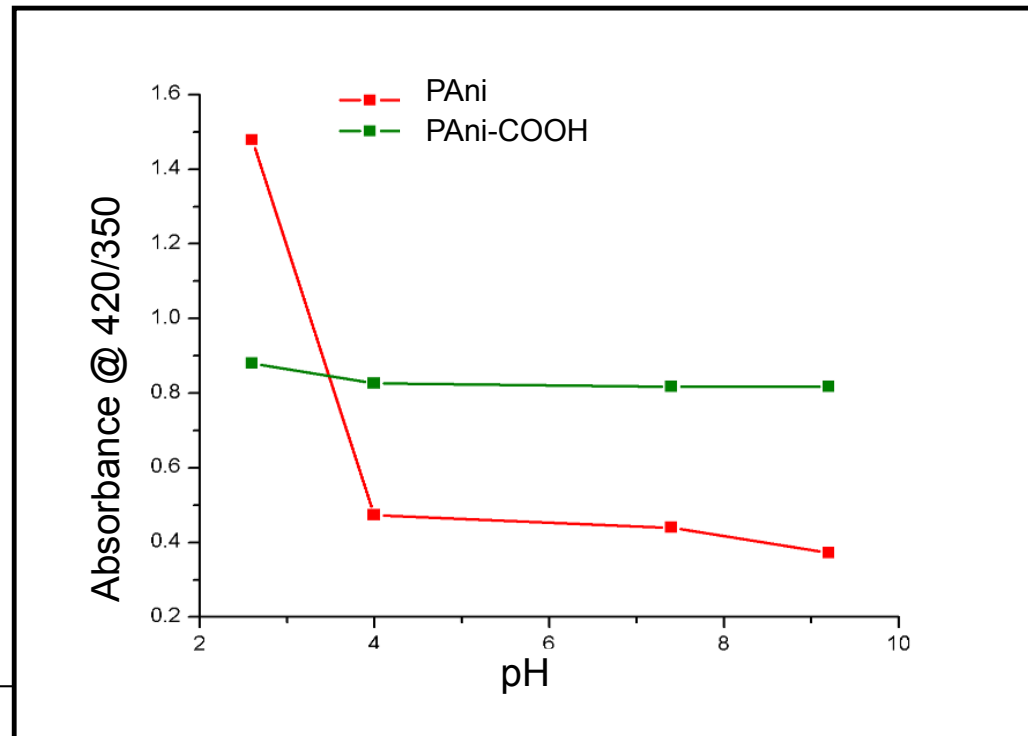
Polyaniline Dispersions

→ Improved stability
over time in neutral pH

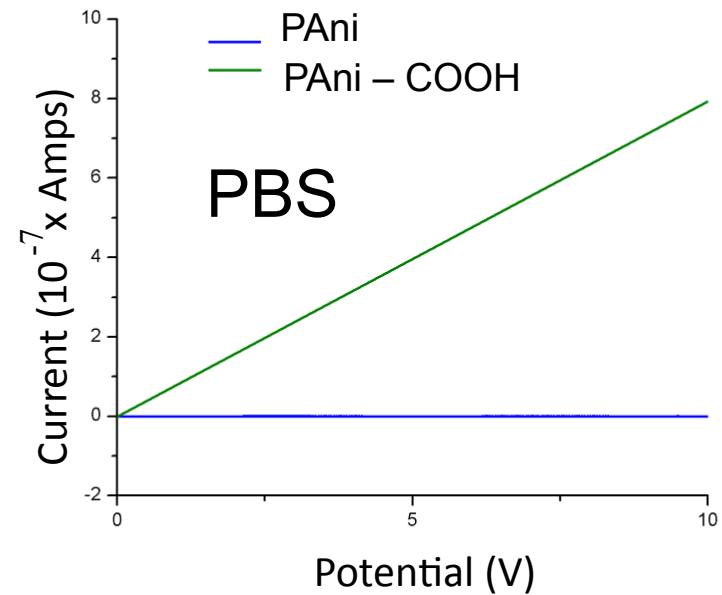
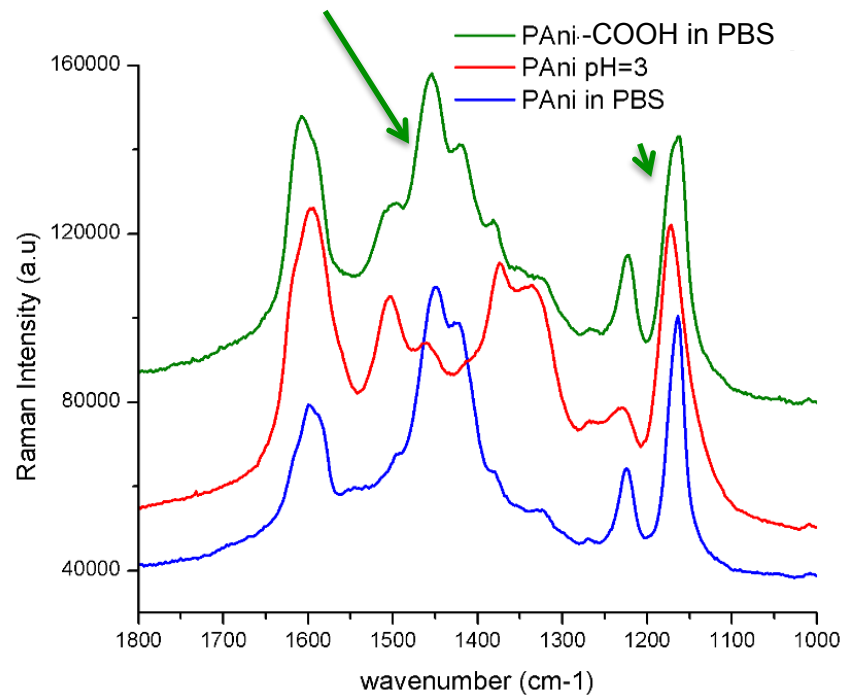


→ Stability
over a wide pH range

Self-Doping Nanofibres



Self-Doping Nanofibres



➤ Raman indicates self-doping behavior

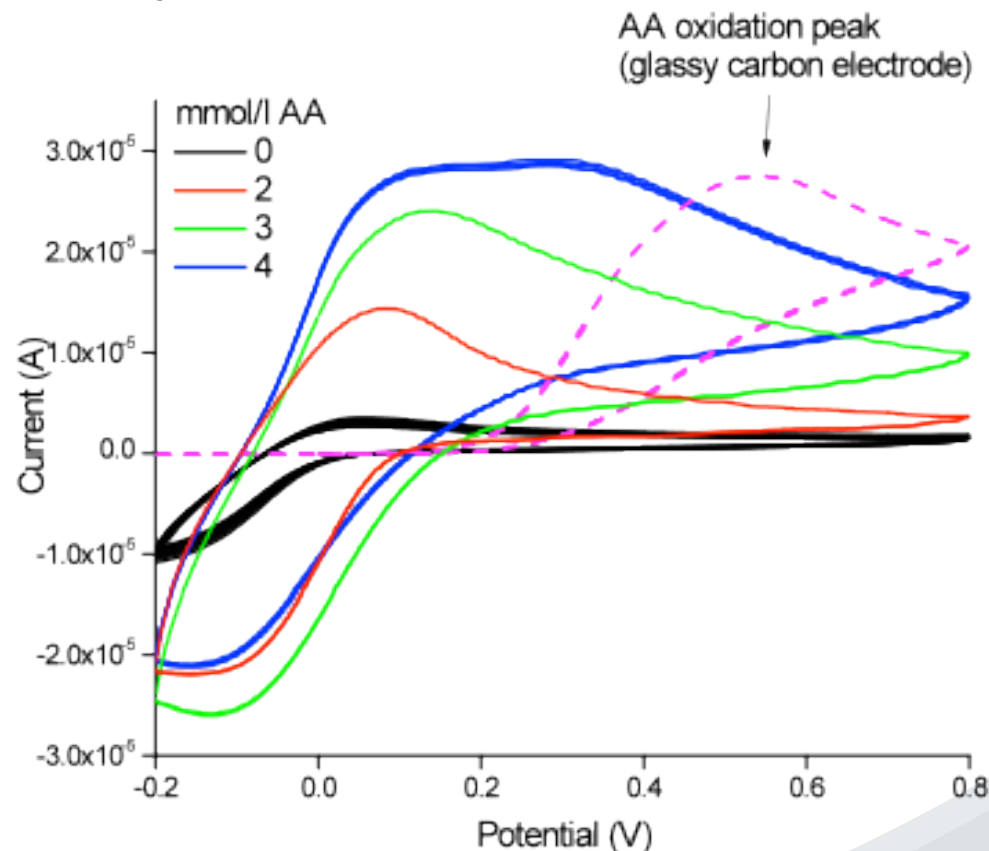
$$\sigma_s \approx 10^{-6} - 10^{-7} \text{ S/cm}$$

1. Lee, R.-H.; Lai, H.-H.; Wang, J.-J.; Jeng, R.-J.; Lin, J.-J., *Thin Solid Films* **2008**, 517, (2), 500-505.

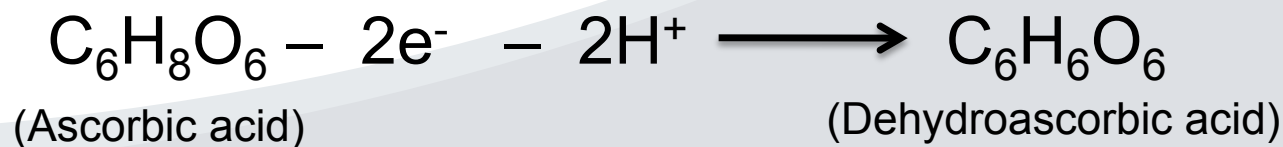
2. Yue, J.; Wang, Z. H.; Cromack, K. R.; Epstein, A. J.; MacDiarmid, A. G., *JACS*, **1991**, 113, (7), 2665-2671.

Applications

Electrocatalytic oxidation of Ascorbic Acid

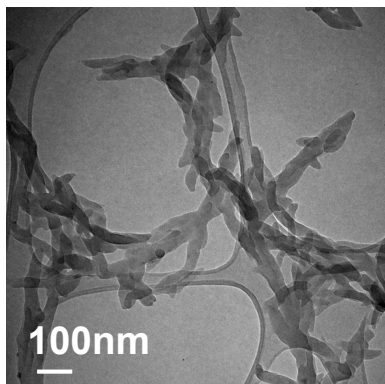
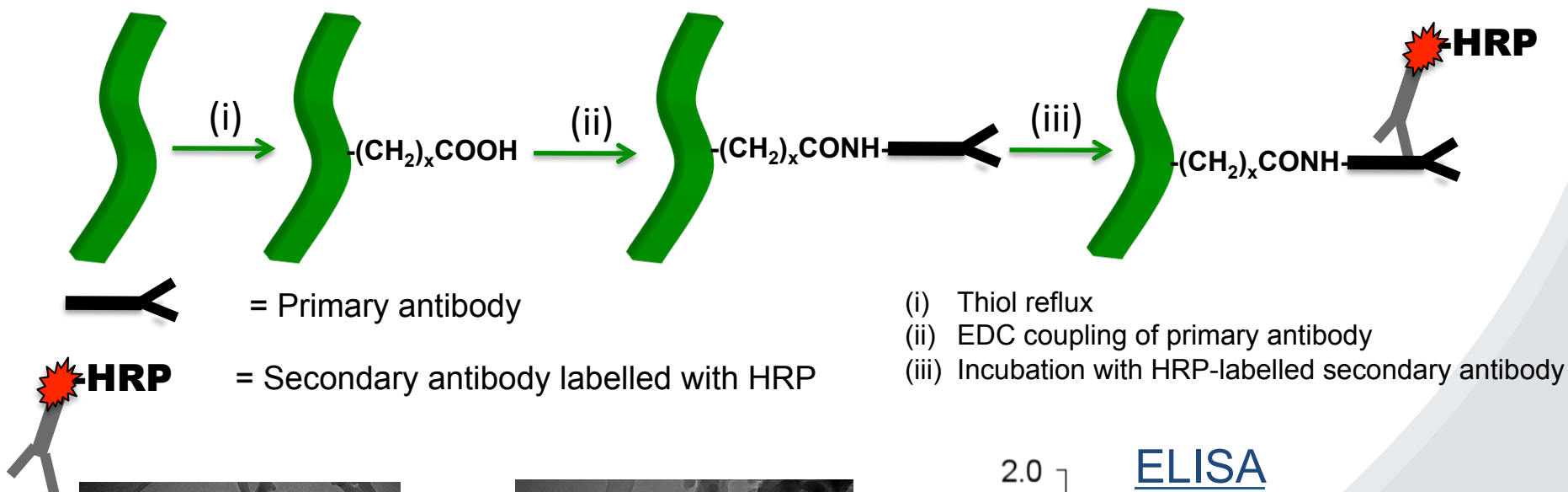


The CVs of a PANi-COOH modified electrode in the presence of 0, 2, 3, and 4 mmol/l ascorbic acid.

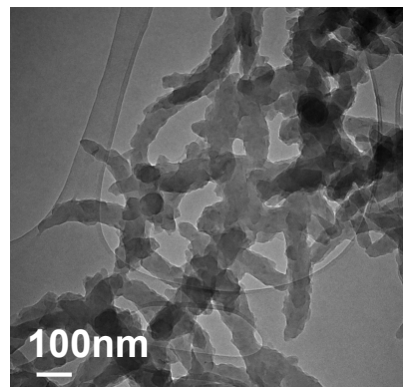


Applications

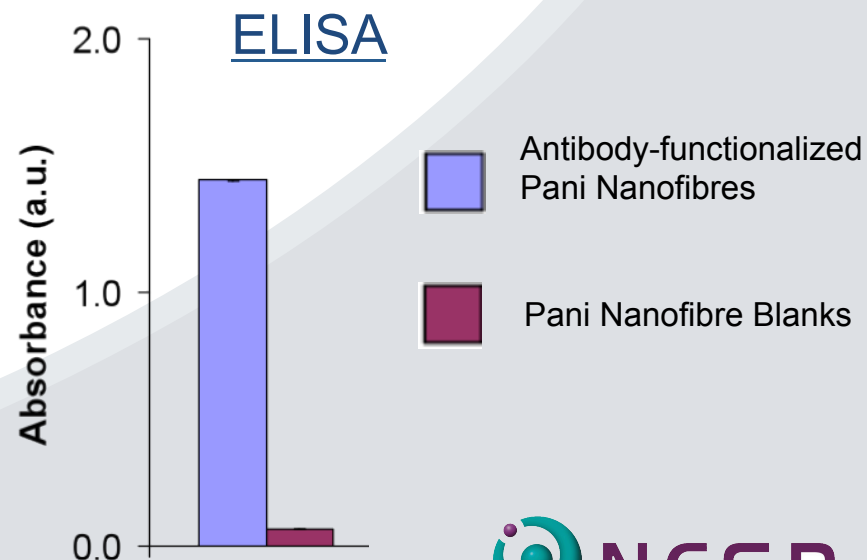
Nanofibre Biosensors



PANI Nanofibres



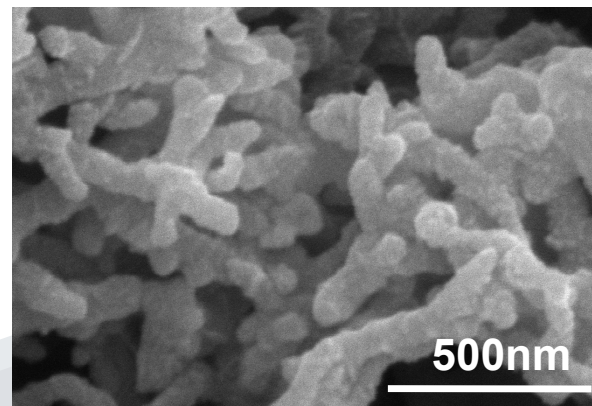
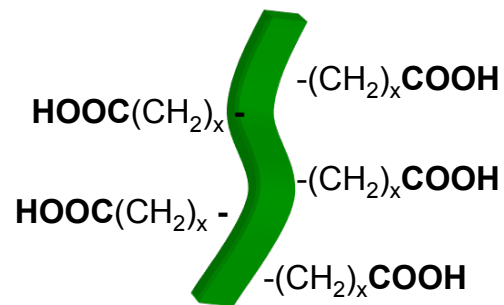
Antibody-functionalized
PANI Nanofibres



Carol Lynam, Emer Lahiff, Niamh Gilmartin, Dermot Diamond, Richard O'Kennedy, *Synth. Met.* (2010), Accepted

Conclusions

- Successful functionalisation of solution based Pani nanofibres
- Control over the side-chain attachment
- Maintained nanomorphology
- Self-doping behavior
- Suitable for bio-applications



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