Self-Doping Polyaniline Nanofibres

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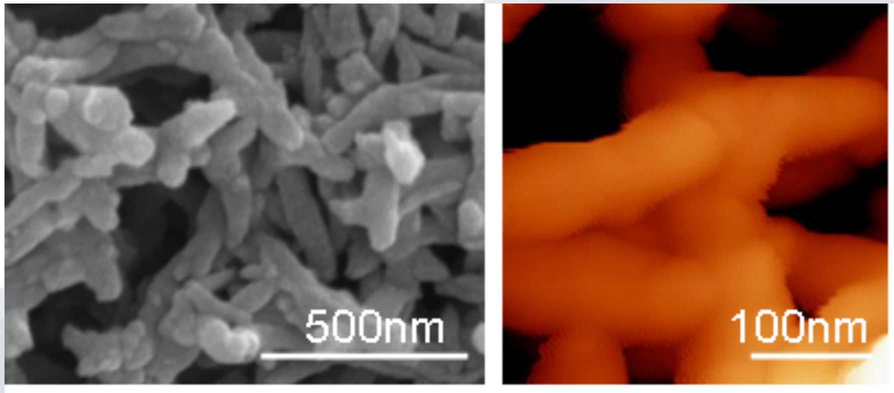
Outline

- Background
- Polyaniline Nanofibres Synthesis
- Functionalisation of Polyaniline Nanofibres
- Complete characterization of the modified nanofibres
- Applications
- Conclusions



Background

Polyaniline Nanofibres

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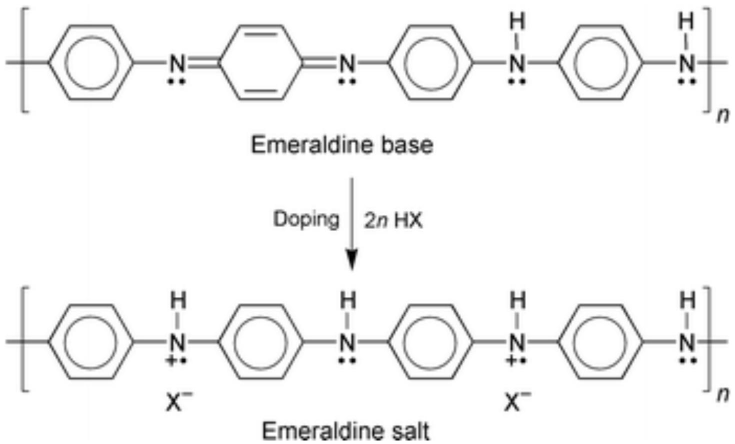
Advantages

- 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 acid[3]

- Polymerization of aniline derivatives[4]

- 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

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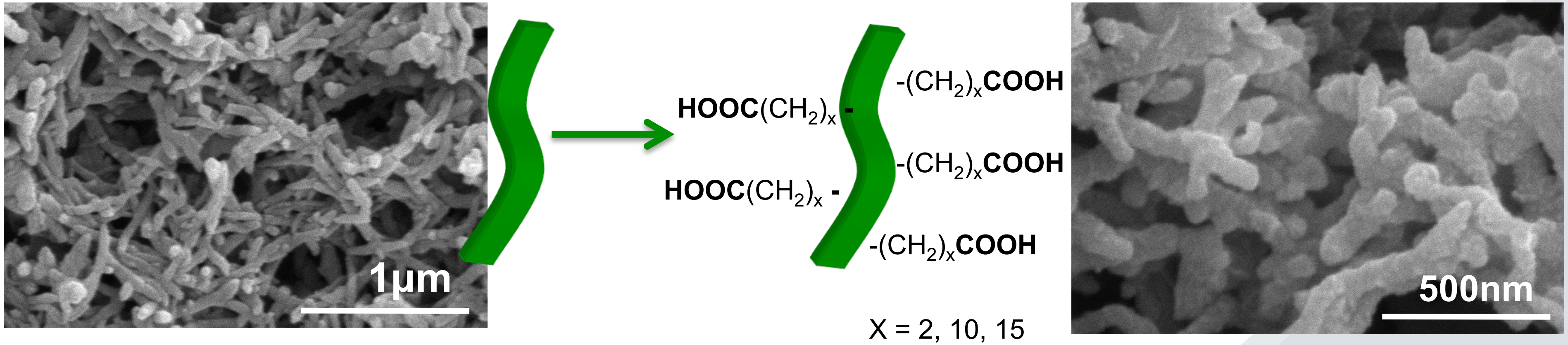
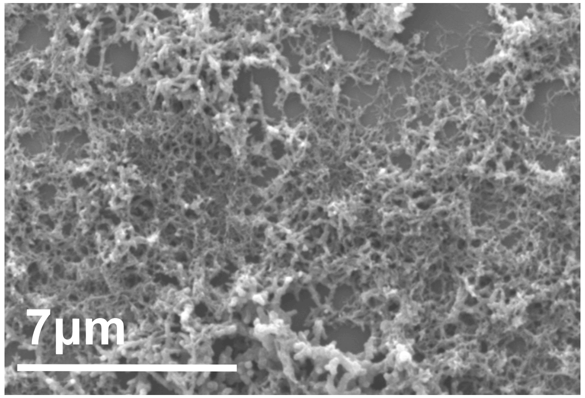
Our Approach

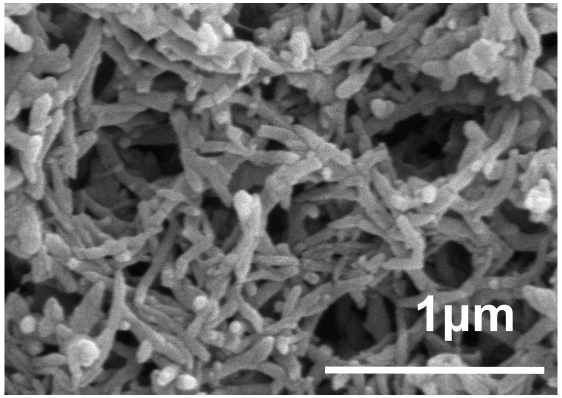


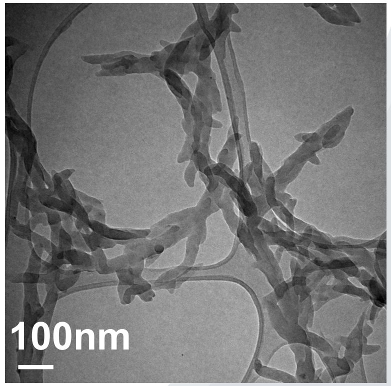
- Cheap and Scalable Process
- Maintain the Nanomorphology of PAni

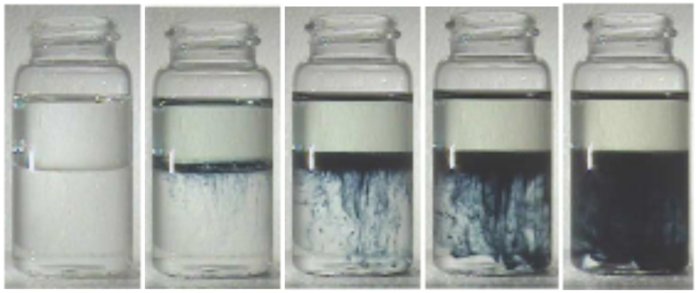
Polyaniline Nanofibres Synthesis

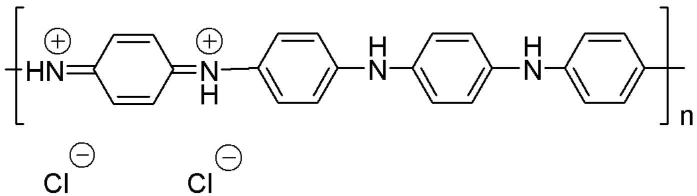
- interfacial polymerization









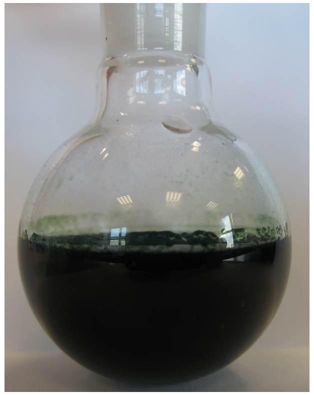


- Diameters : 30 - 50 nm
- Lengths: 500nm - several µm

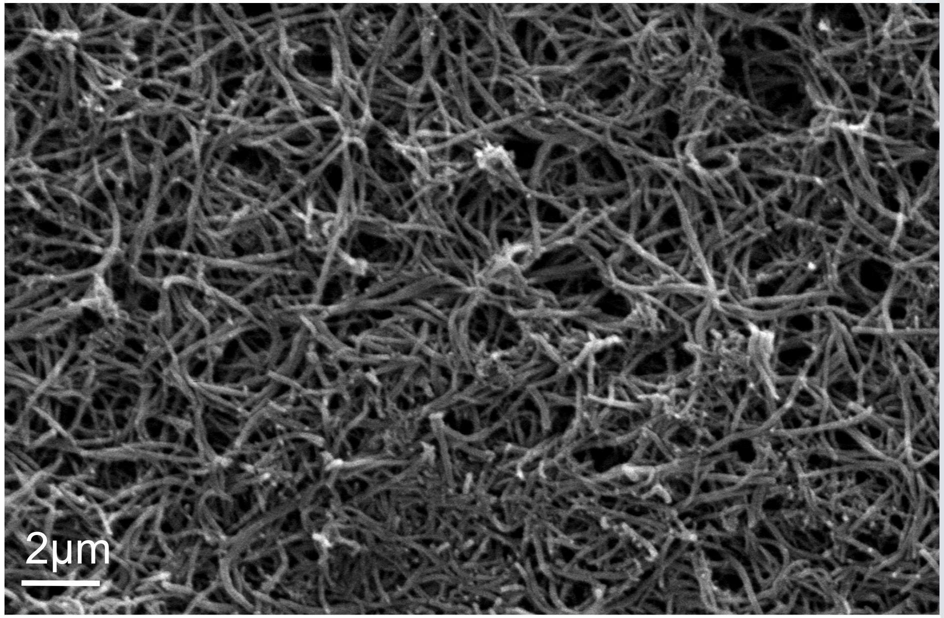
J.X. Huang, S. Viril, B.H. Weller, R.B. Kaner, *J.Am.Chem.Soc.* 125 (**2003**),314-315

Extra-long Polyaniline Nanofibers

- rapidly mixed method



Initiator : N-Phenyl-p-Phenylenediamine
Oxidant : Ammonium Persulfate
Acid : p-Toluenesulfonic acid

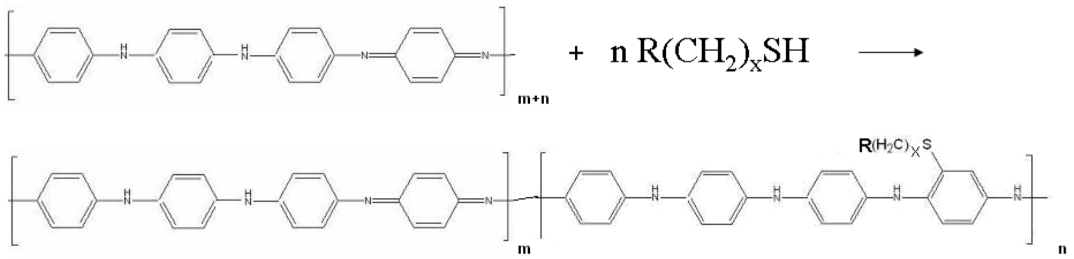


- diameter: approximately 100nm
- average length:30μm

Yue Jessica Wang, Henry D. Tran, and Richard B. Kaner - Synthesis of Extra-long Polyaniline Nanofibers

Polyaniline Functionalisation

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



R = COOH

Thiol Derivative	Carbon Length	End group	Mmol thiol added/ 45 mg Pani
Mercaptopropanoic acid (C3COOH)	3	COOH	0.2 ; 0.5; 1; 5; 20
Mercaptoundecanoic acid (C11COOH)	11	COOH	0.05, 0.1, 0.2; 0.5; 1
Mercaptohexadecanoic acid (C16COOH)	16	COOH	0.2; 0.5; 1

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

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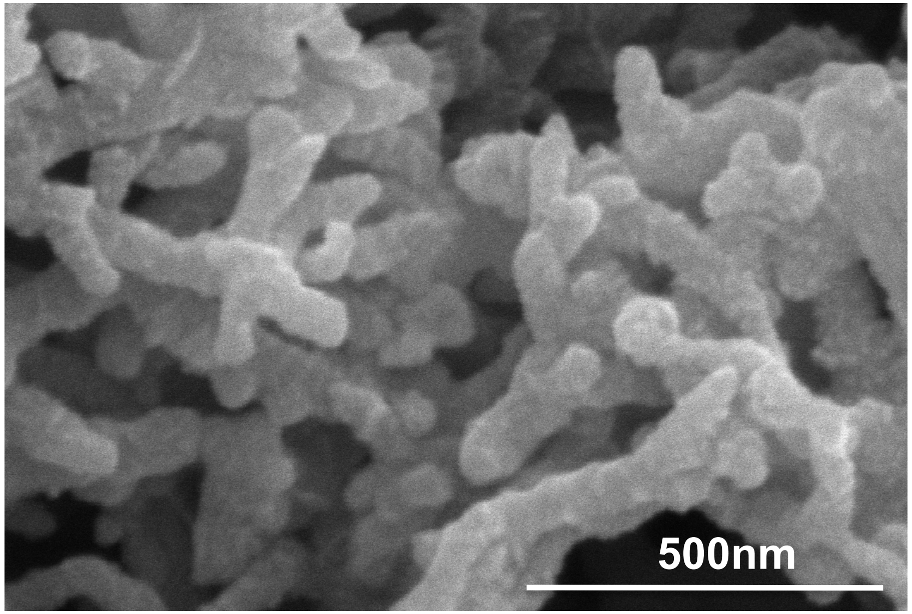
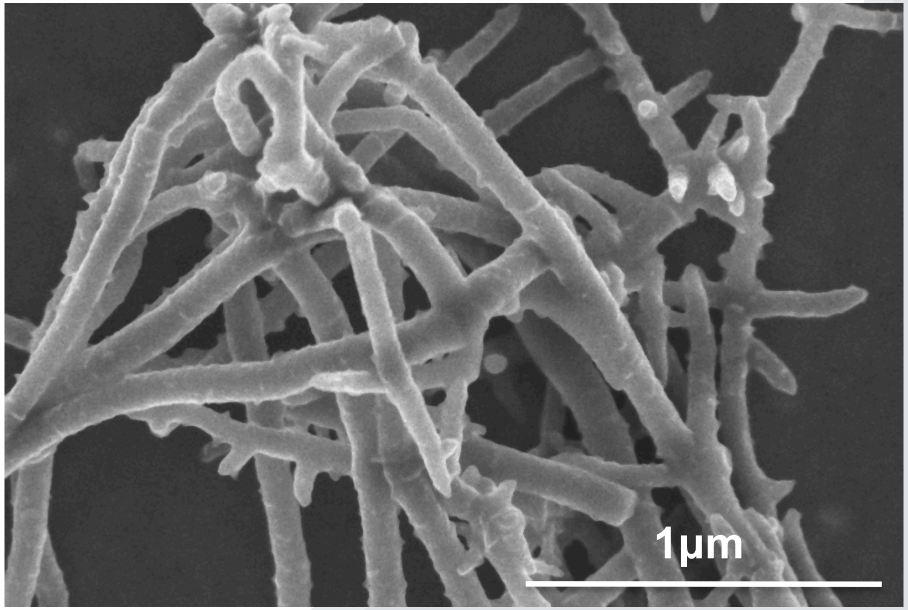
Scanning electron microscopy (SEM)





➢Nanomorphology **is maintained post-functionalisation.**

Fourier Transform Infrared Spectroscopy (FTIR)

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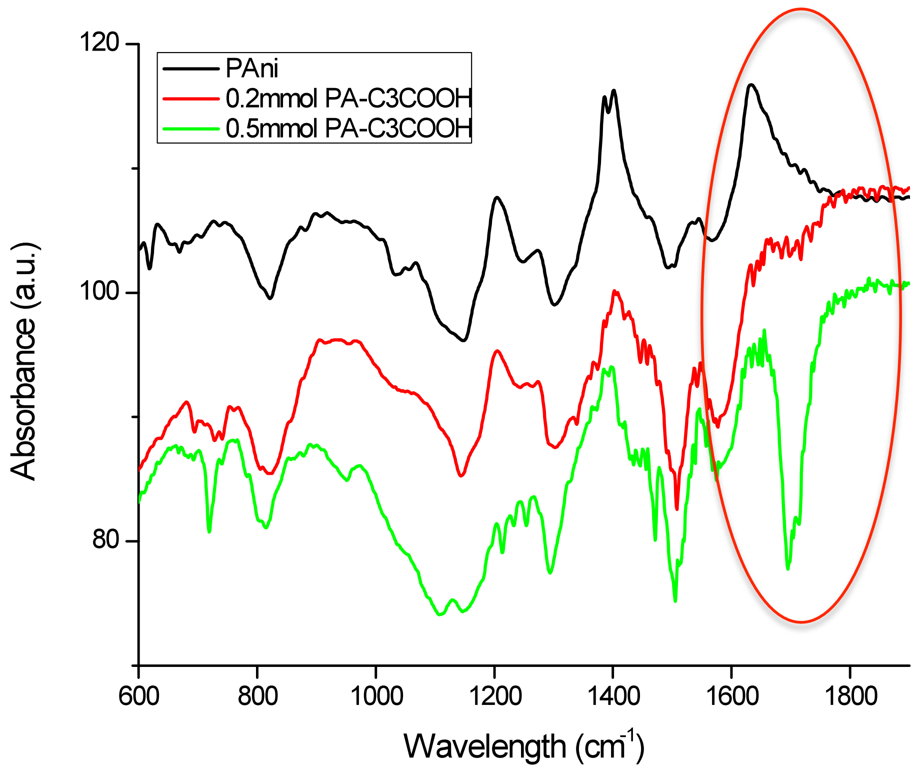
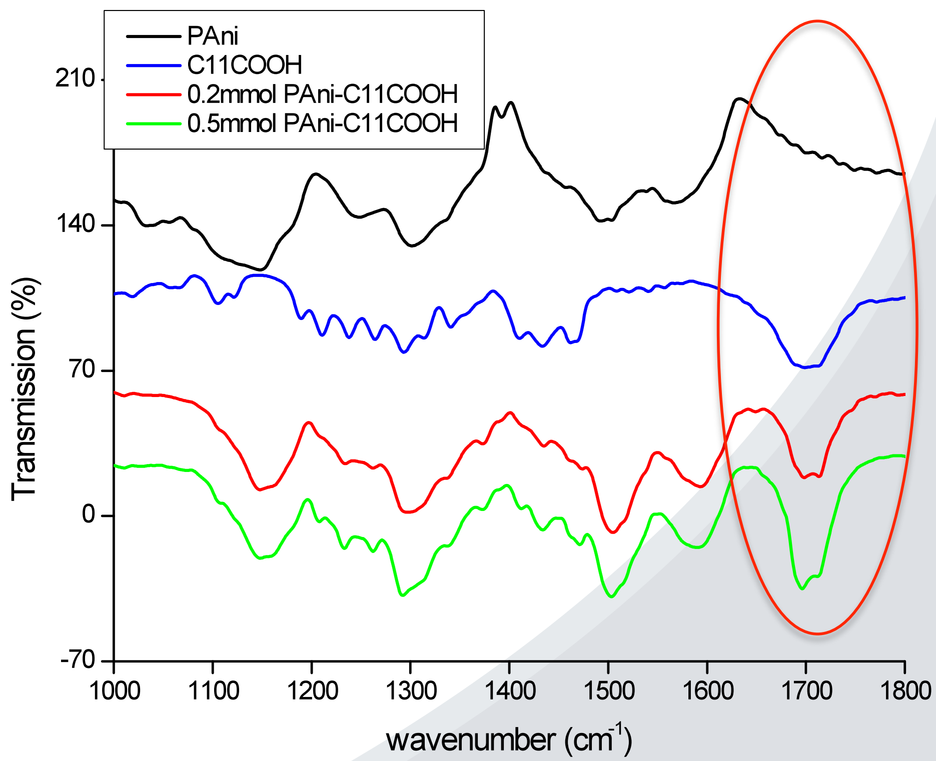
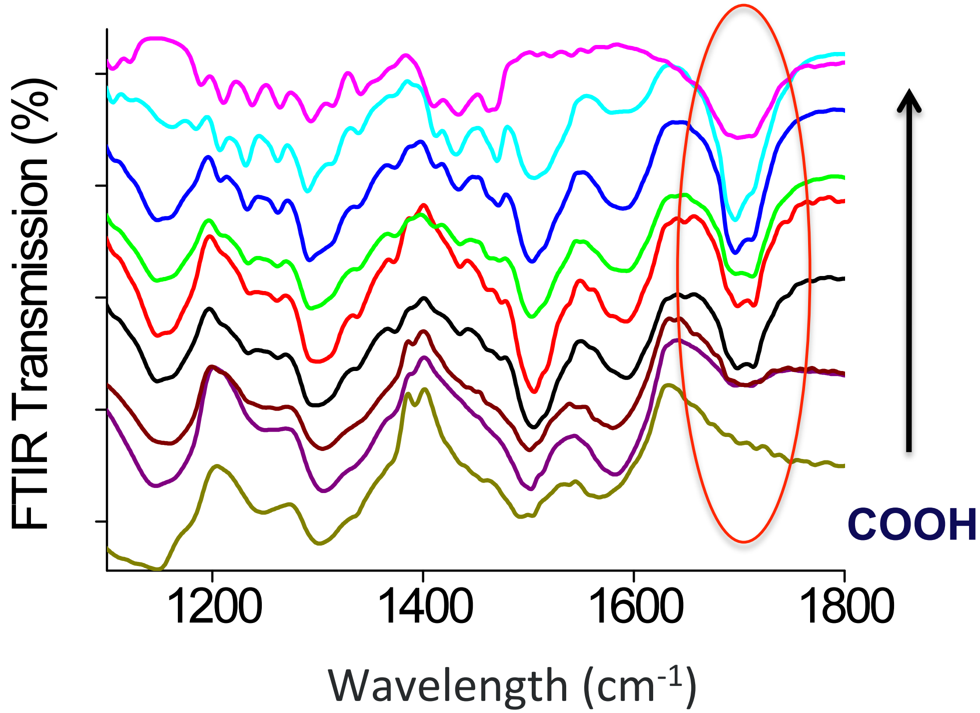
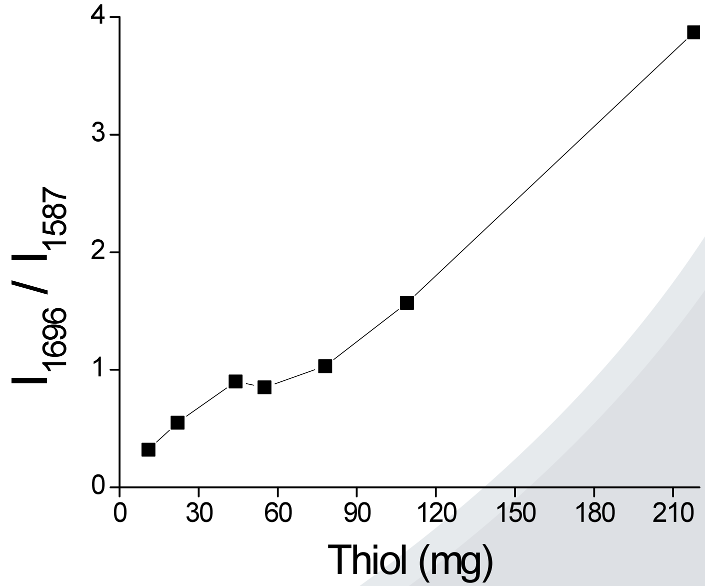




➢Covalent attachment of the Mercaptoacid to the polymer backbone

Controlling the extent of functionalisation





- Characteristic PAni band at 1587cm^{-1}
- C=O band at 1696cm^{-1}

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

Thermal Gravimetric Analysis

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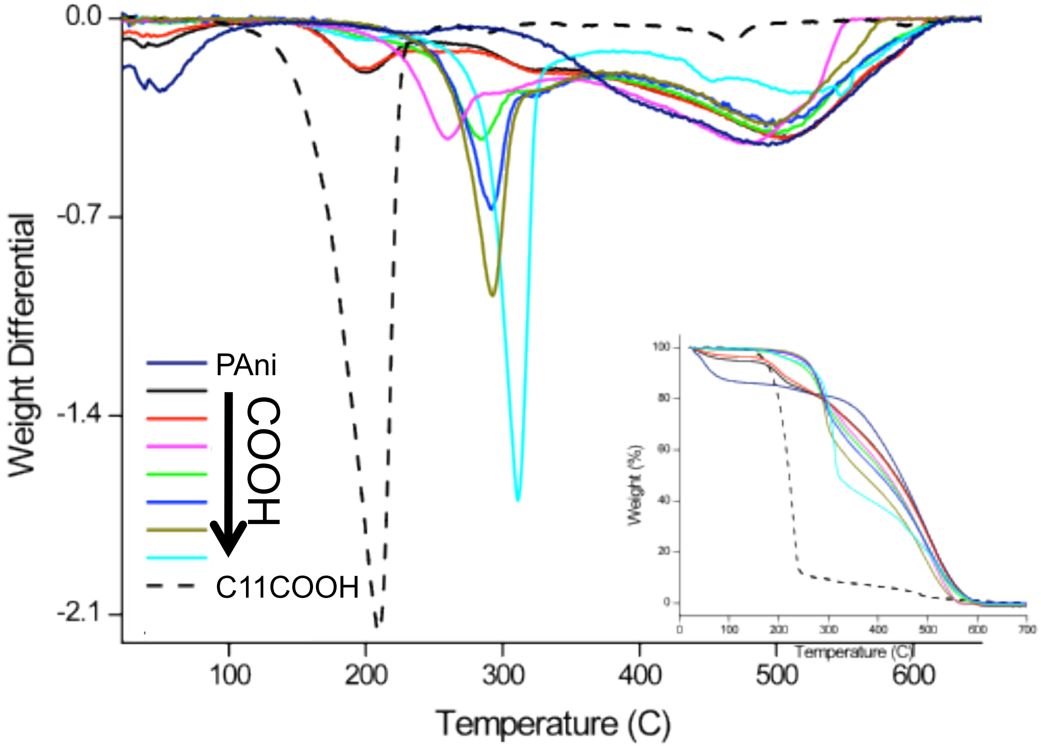
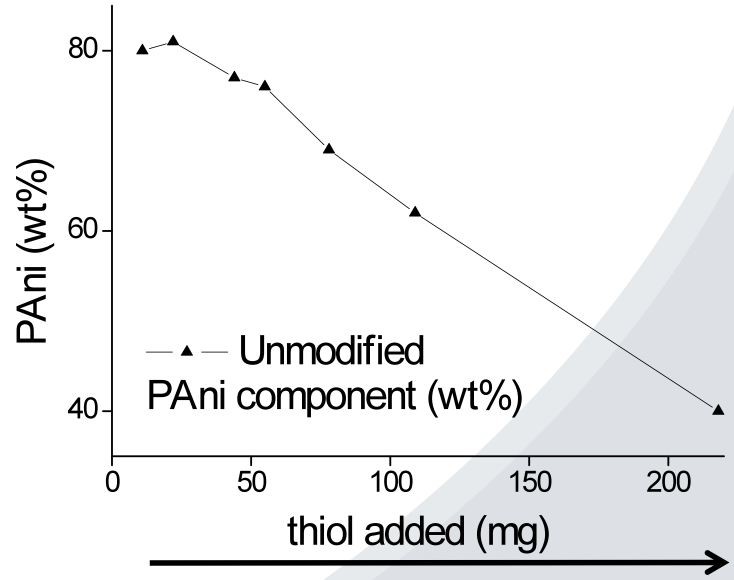
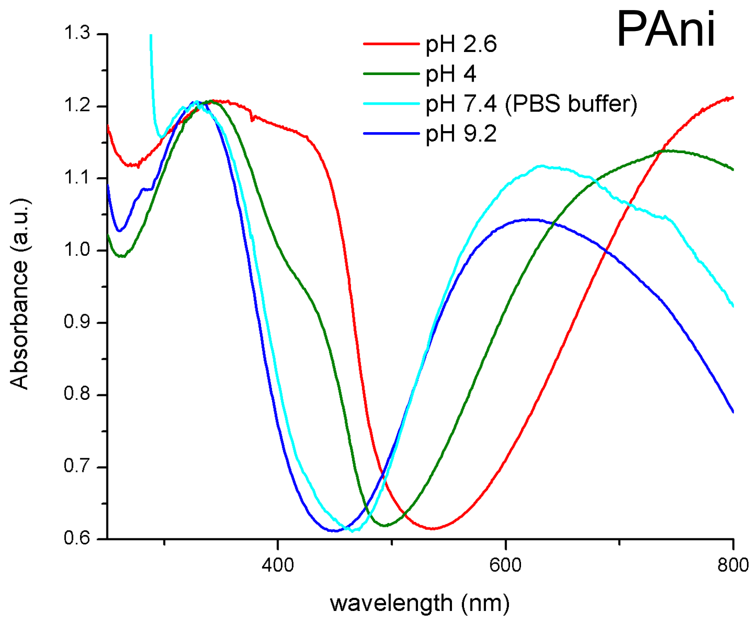


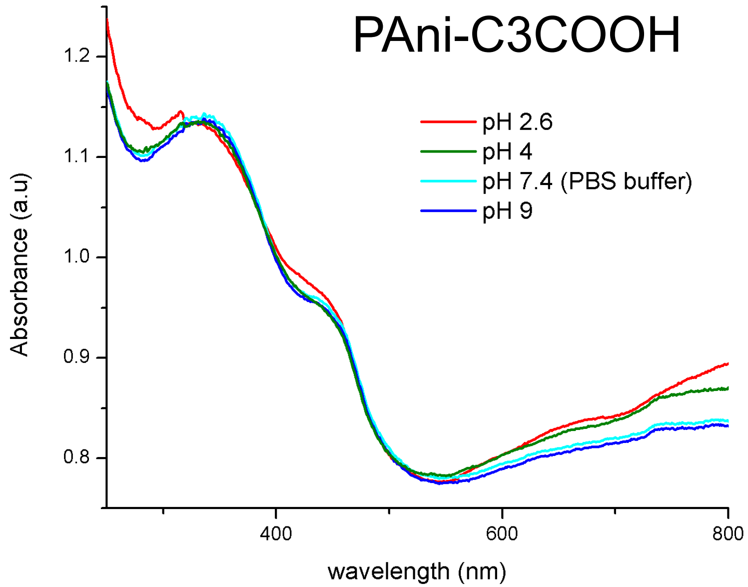


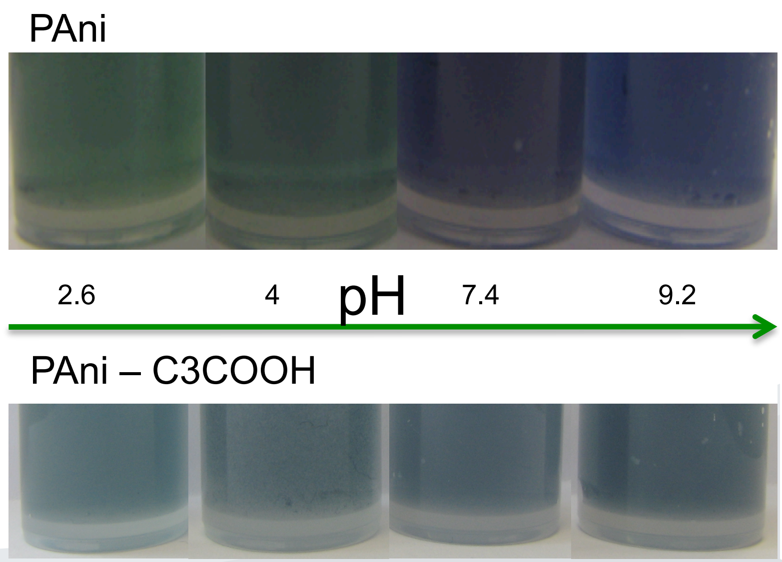
- PAni-COOH fibres show two significant decompositions.
- First peak: a modified PAni-COOH surface component.
- Second peak: unmodified PAni.

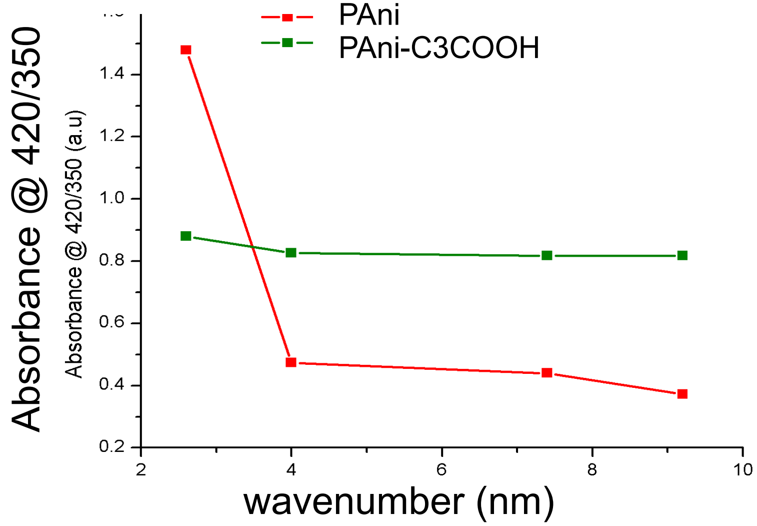
TGA confirms a controllable trend in the level of functionalisation

UV-vis spectroscopy

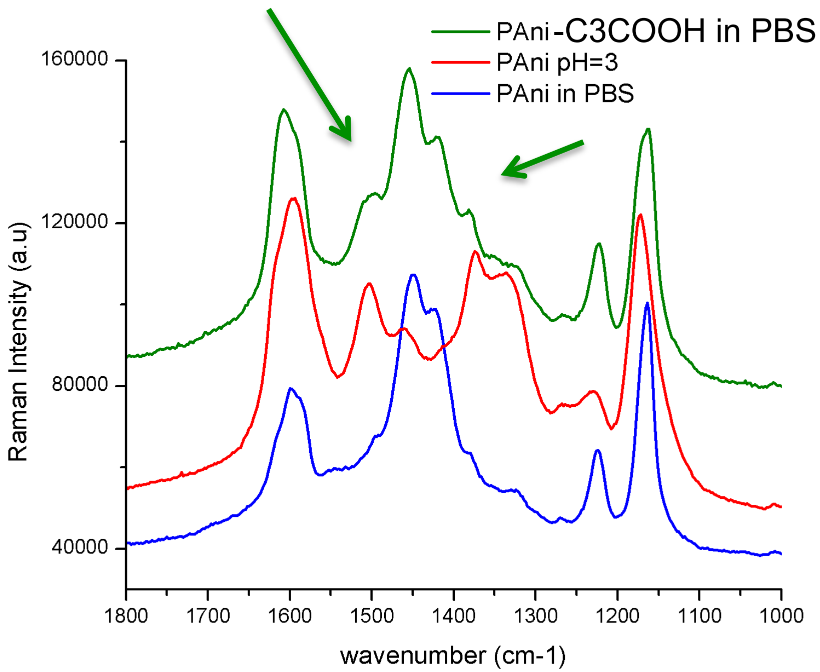


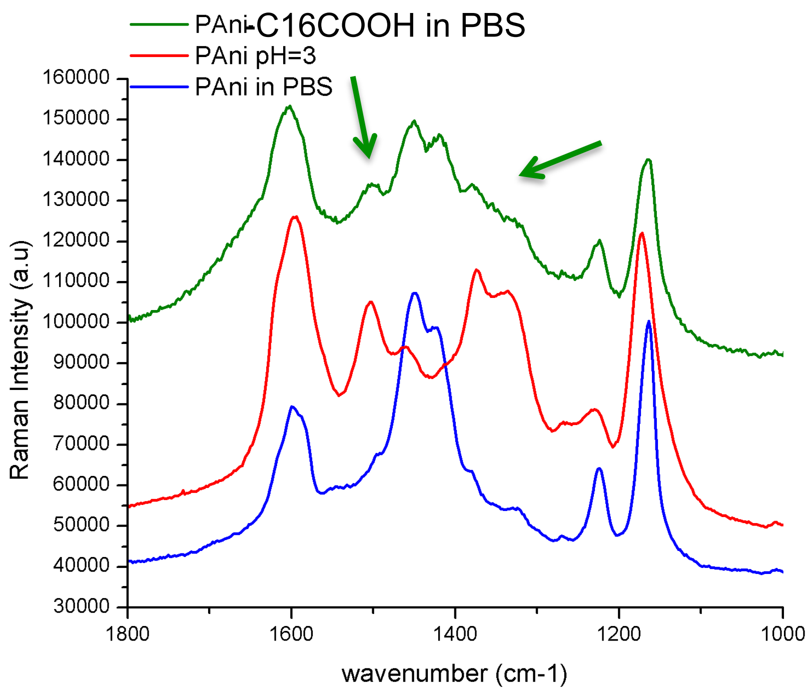






Raman spectroscopy





C3COOH = mercaptopropanoic acid C16COOH = mercaptohexadecanoic acid

➢ Prove self-doping behaviour

Conductivity measurements

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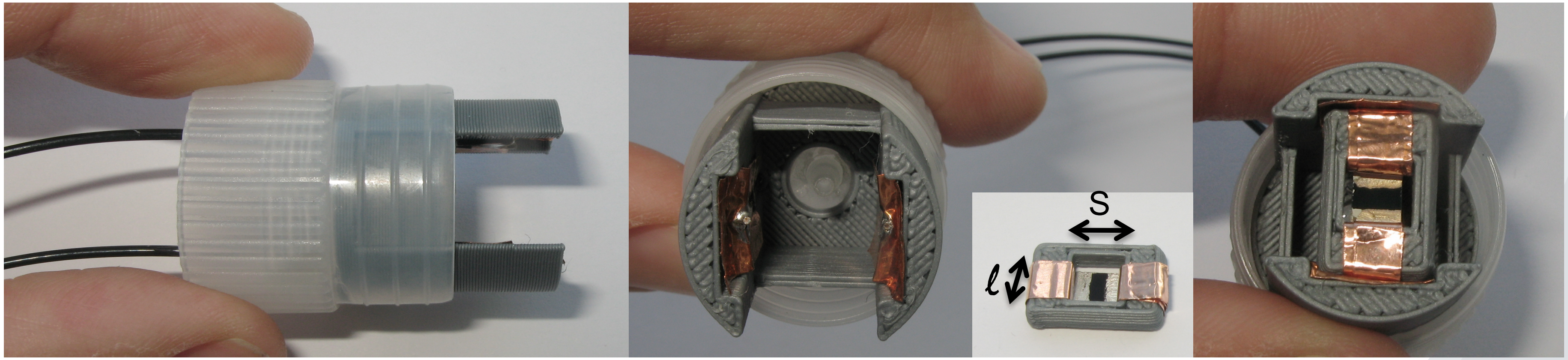
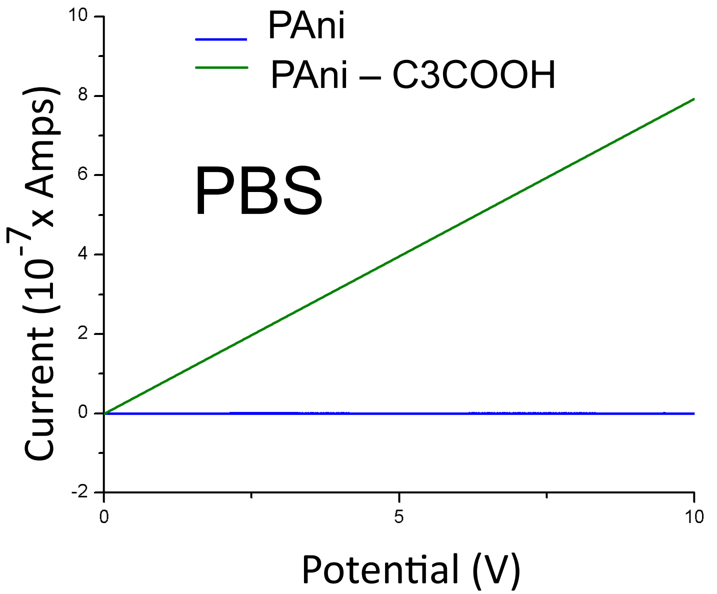




$\sigma_S = G * S/\ell$

σ_S – surface conductivity

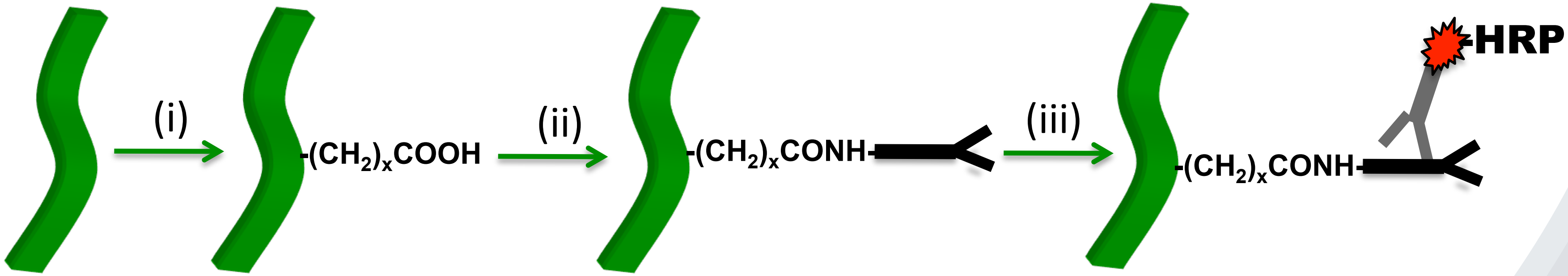
G – conductance of the circuit

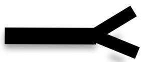
$\sigma_S \approx 10^{-6} - 10^{-7}$ S/cm [1,2]

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

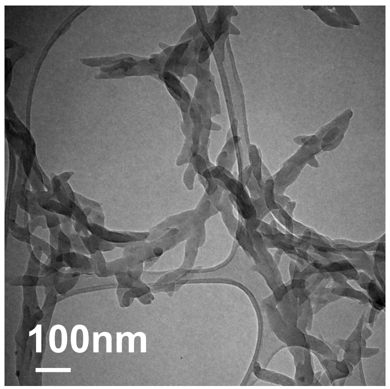
Nanofibre Biosensors



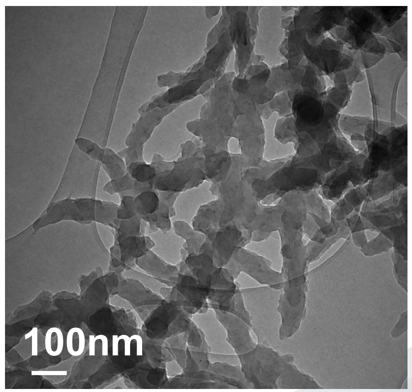
 = Primary antibody

= Secondary antibody labelled with HRP

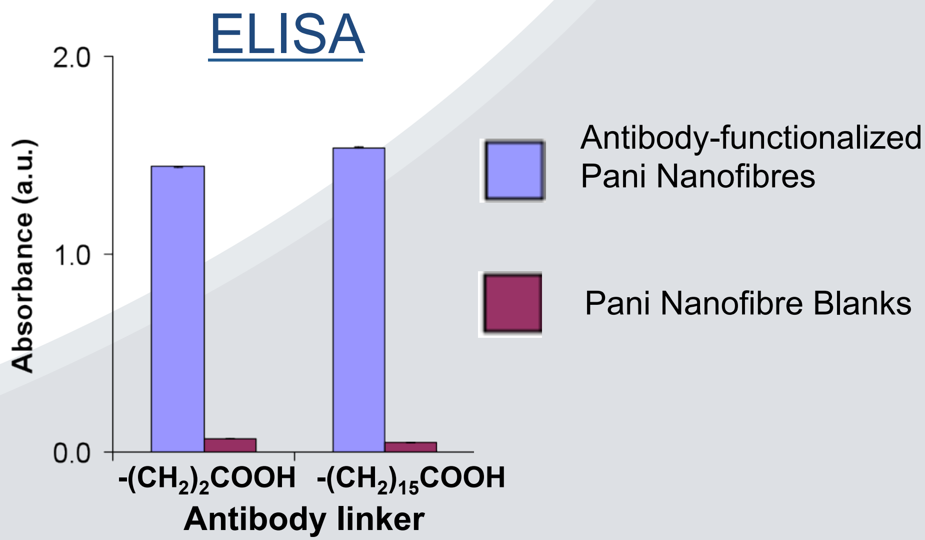
(i) Thiol reflux
(ii) EDC coupling of primary antibody
(iii) Incubation with HRP-labelled secondary antibody



Pani Nanofibres



Antibody-functionalized Pani Nanofibres



[1] Emer Lahiff, Carol Lynam, Niamh Gilmartin, Gordon Wallace, Richard O'Kennedy,Dermot Diamond. Controllable Chemical Modification of Polyaniline Nanofibres.Mater. Res. Soc. Symp. Proc. 2009, Symposium WW.

Electrocatalytic oxidation of Ascorbic Acid

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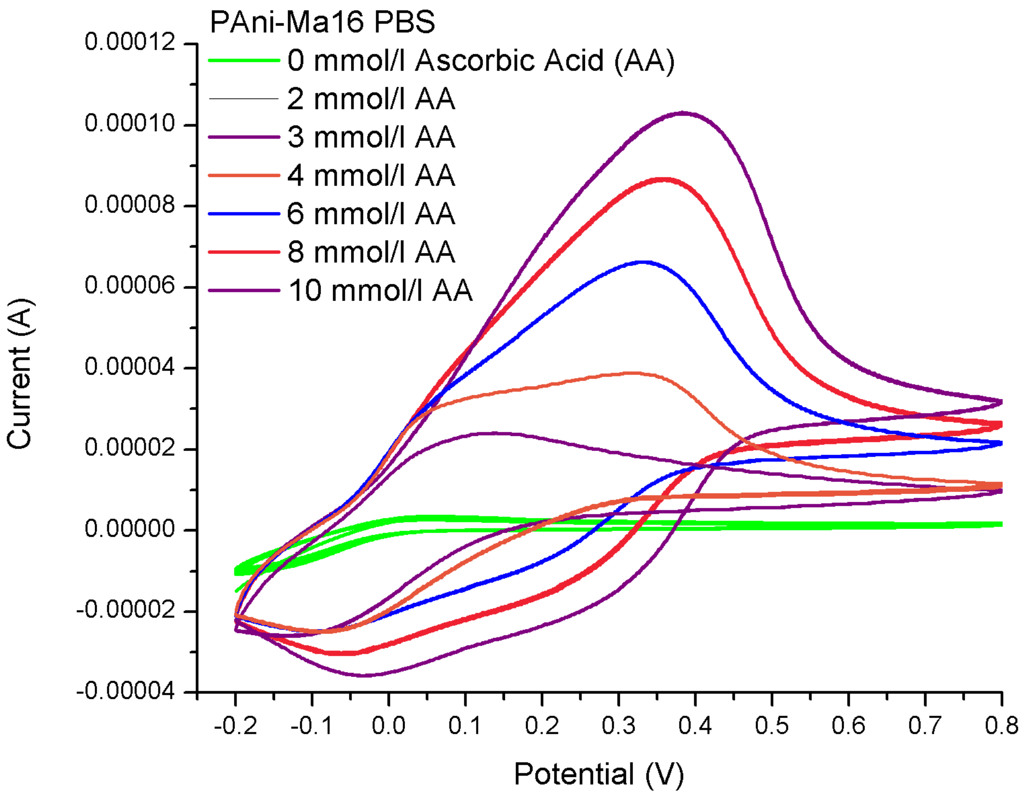

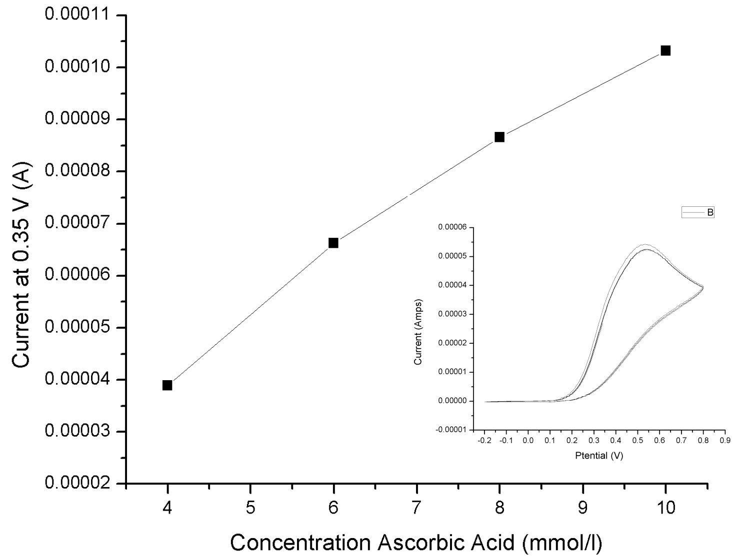

$$\underset{\text{(Ascorbic acid)}}{C_6H_8O_6} - 2e^- - 2H^+ \rightarrow \underset{\text{(Dehydroascorbic acid)}}{C_6H_6O_6}$$

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Conclusions

- Successful functionalisation of solution based Pani nanofibres
- Control over the side-chain attachment
- Maintained nanomorphology
- Self-doping behavior
- A new route for manipulating the surface chemistry of nanofibres

Acknowledgments

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