

# FUNCTIONALISED POLYANILINE NANOFIBERS

Emer Lahiff<sup>1</sup>, Silvia Scarmagnani<sup>1</sup>, Gordon Wallace<sup>2</sup> and Dermot Diamond<sup>1\*</sup>

<sup>1</sup>National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland.

<sup>2</sup>Intelligent Polymer Research Institute, University of Wollongong, Australia.

## POLYANILINE NANOFIBERS

Polyaniline (PAni) is a conducting polymer which switches between distinct states exhibiting dramatically different properties. The colour, conductivity and redox state of PAni all depend on the local chemical environment of the material. Consequently PAni has great potential for sensing applications. The nanostructured form of PAni is particularly interesting as it provides a very large surface-to-volume ratio that can lead to dramatic enhancement of sensor sensitivity and response time. In this work, we focus on derivatising polyaniline nanofibres. Using the technique described, carboxylate terminated side-chains can be covalently bound to solution based fibres.

## NANOFIBER SYNTHESIS

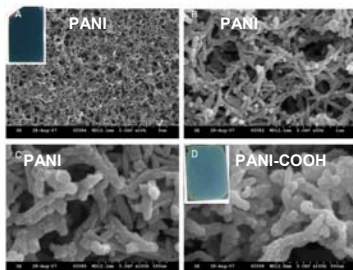
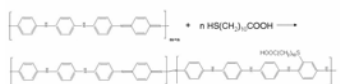
Nanofibres are synthesised by interfacial polymerisation [1]. The process is complete within 24 hours, and the technique can be easily scaled up by increasing the volume of reactants.



Interfacial polymerisation. Time (min)  
12 20 30 40 50 60 250 1440 (24hrs)

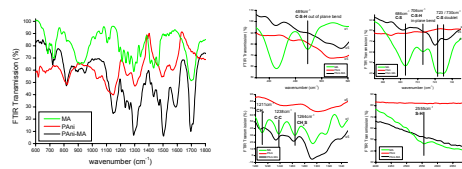
## NANOFIBRE FUNCTIONALISATION

Nanofibres are refluxed for two hours in the presence of a thiol (mercaptoundecanoic acid) [2]. During this time, reactive thiol groups attach onto quinoid rings by nucleophilic addition.



Functionalised nanofibres retain their nanomorphology post-modification (as shown by SEM). Nanofibres can be cast from solution to form films, on substrates such as silicon (insets above).

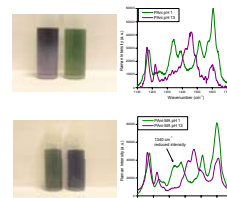
## EVIDENCE FOR COVALENT ATTACHMENT



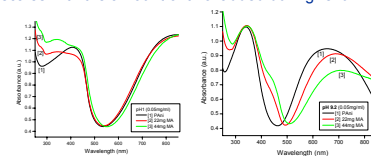
FTIR spectra show characteristic mercaptoundecanoic acid (MA) peaks alongside those of polyaniline. Characteristic thiol peaks are eliminated – supporting the covalent bonding structure suggested. Other peaks are shifted slightly, which is consistent with a change in the local chemical environment and again confirms covalent attachment.

## SWITCHING

Functionalised nanofibres retain the ability to switch optical properties in response to changes in the local environment. This is reflected in Raman spectra, and also colour changes in the material (right).

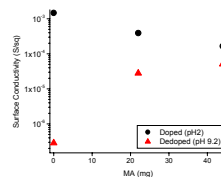


UV-vis spectra (below, pH2) support covalent functionalisation, as indicated by the peaks at 310nm. At higher pHs, PAni nanofibres de-dope. Modified fibres however, show a peak at 450nm suggesting self-doping may be occurring in COOH functionalised fibres. The intensity of this peak scales with the amount of thiol added during reflux.

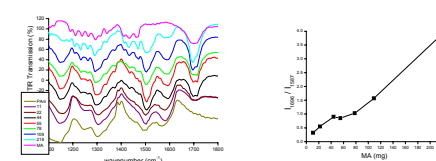


## SELF-DOPING BEHAVIOUR

Functionalised nanofibres show enhanced conductivity in an alkaline environment. This suggests some self-doping due to protonation by covalently bound acid side-groups.

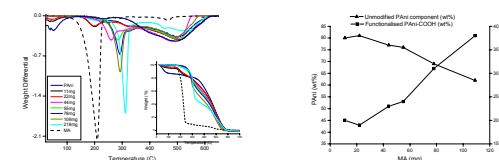


## CONTROLLING FUNCTIONALISATION



The intensity of -COOH bands in FTIR scales with the amount of thiol added during reflux. A plot of the band intensity at 1696cm<sup>-1</sup> (C=O) versus that at 1587cm<sup>-1</sup> (a PANi band) reveals a linear trend.

## QUANTIFYING FUNCTIONALISATION



PAni-COOH fibres show two significant decomposition temperatures. The first, at 220°C, is assigned to a modified PANi-COOH surface component. The second, at 495°C, is due to unmodified PANi. The area of the PANi peak is inversely proportional to the degree of functionalisation.

TGA confirms a linear trend in the level of functionalisation

## CONCLUSION

In this work, we focus on polyaniline nanofibre derivatives. Using the technique described, carboxylate terminated side-chains can be covalently bound to solution based fibres. The degree of covalent attachment can be controllably altered. These functionalised nanomaterials show self-doping behaviour, thus reducing the need for an external dopant. They also provide a template which can be further modified to develop more sophisticated structures, for applications such as biosensing.

## REFERENCES

- [1] Li, D.; Kaner, R. B., Chemical Communications, (2005), 3286.
- [2] E. Lahiff, T. Woods, W. Blau, G.G. Wallace, D. Diamond. Synthetic Met. (2009), doi:10.1016/j.synthmet.2008.12.029accepted.

\*Contact e-mail: dermot.diamond@dcu.ie

UNIVERSITY COLLEGE DUBLIN

DUBLIN CITY UNIVERSITY

TYNDALL NATIONAL INSTITUTE