FUNCTIONALISED POLYANALINE NANOFIBERS

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POLYANALINE 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

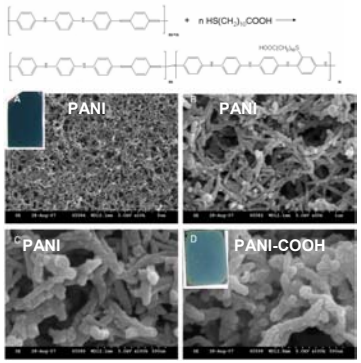
Nanofibres are synthesised by interfacial polymerisation [1]. The process is complete within 24 hours, and the technique can be easily scaled up by increasing the volume of reactants.

Interfacial polymerisation. Time (min)

12 20 30 40 50 60 250 1440 (24hrs)

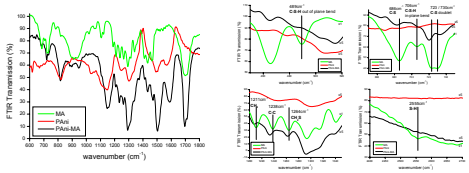
NANOFIBRE FUNCTIONALISATION

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 nucleophic 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).

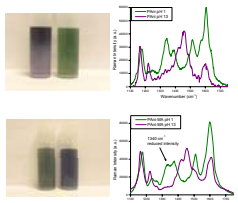
EVIDENCE FOR COVALENT ATTACHMENT



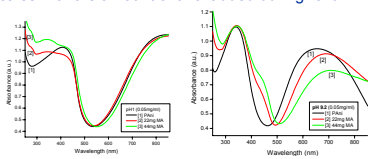
FTIR spectra show characteristic mercaptoundecanoic acid (MA) peaks alongside those of polyaniline. Characteristic thiol peaks are eliminated – supporting the covalent bonding structure suggested. Other peaks are shifted slightly, which is consistent with a change in the local chemical environment and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

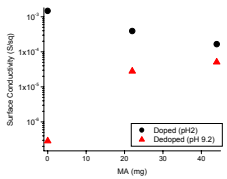


UV-vis spectra (below, pH2) support covalent functionalisation, as indicated by the peaks at 310nm. At higher pHs, PAni nanofibres de-dope. Modified fibres however, show a peak at 450nm suggesting self-doping may be occurring in COOH functionalised fibres. The intensity of this peak scales with the amount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

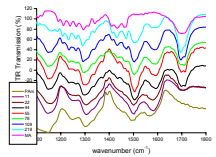


SELF-DOPING BEHAVIOUR

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

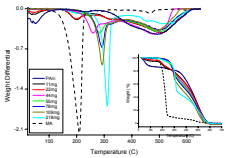


CONTROLLING FUNCTIONALISATIO



The intensity of -COOH bands in FTIR scales with th of thiol added during reflux. A plot of the band intensity at 16 =O) versus that at 1587cm^{-1} (a PAni band) reveals a linear trend

QUANTIFYING FUNCTIONALISATION



PAni-COOH fibres show two significant decomposi ratures. The first, at 220°C, is assigned to a modified PAni-COC component. The second, at 495°C, is due to unmodified PAni. of the PAni peak is inversely proportional to the degree of functi

TGA confirms a linear trend in the level of functi

CONCLUSION

In this work, we focus on polyaniline nanofibre . Using the technique described, carboxylate terminated side-ch e covalently bound to solution based fibres.The degree of coval ment can be controllably altered. These functionalised nanomate self-doping behaviour, thus reducing the need for an extern . They also provide a template which can be further modif velop more sophisticated structures, for applications such as bio

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