Covalent attachment of functional side-groups to polyaniline nanofibres

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Abstract: Polyaniline (PAni) is an example of a conducting polymer that can be switched between an insulating and a conductive state. This switching is accompanied by a colour change. Recently, interest has developed in the nanofibre form of PAni as these low dimensional structures have a very high surface area, thus enabling a faster response time. We investigate how the surface chemistry of these nanofibres can be modified by covalently attaching functional side-groups. In particular, we demonstrate the attachment of both amide and carboxylic acid groups. This can be achieved using a simple reflux technique. The modified material retains its nanomorphology and the intrinsic electrochemical, spectroscopic and redox properties of PAni are also preserved. Both acid and amine side-groups are interesting in that they provide a template, which could be further altered to enhance the selectivity of PAni. Acid terminated chains can also be used to introduce self-doping behaviour to PAni.

Keywords: nanomaterials; polyaniline; conducting polymer.

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Silvia Scarmagnani studied Pharmaceutical Chemistry in the University of Padua where in 2006 she received her Master degree (Honours) in Pharmaceutical's Chemistry and Tehcnology. She carried out her Master thesis (based on the synthesis of antitumor agents derived from hydroxybenzaldehyde) in collaboration with Cardiff University, UK. In 2006 she started her PhD in Dublin City University, Ireland, where she is currently investigating the development of adaptive surfaces for optical sensing using molecular photoswitches under the supervision of Prof. Dermot Diamond.

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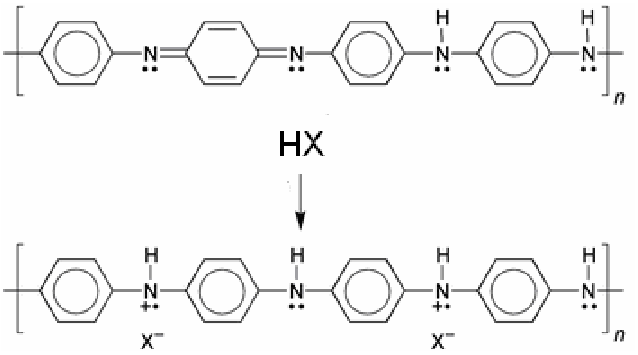
Dermot Diamond received his PhD and DSc from Queen's University Belfast (Chemical Sensors, 1987, Internet Scale Sensing, 2002), and was VP for Research at Dublin City University (2002–2004). He has published over 190 peer-reviewed papers in international journals, is a named inventor in 13 patents, and is co-author and editor of three books. He is currently Director of the National Centre for Sensor Research (www.ncsr.ie) and a PI in CLARITY (www.clarity-centre.com/), a major research initiative focused on wireless sensor networks. In 2002 he was awarded the inaugural silver medal for Sensor Research by the Royal Society of Chemistry, London.

1 Introduction

Much interest has developed in the area of nanostructured conducting polymers (Chiou and Epstein, 2005; Chiou et al., 2007; Huang and Kaner, 2004, 2006; Huang et al., 2003; Tran and Kaner, 2006; Virji et al., 2004, 2005, 2006). These one-dimensional objects combine the advantages of an organic conductor with those of a high surface area material, thus making them ideal for a diverse range of applications such as electronic devices, chemical sensors and actuators (Huang et al., 2003; Virji et al., 2004, 2005a, 2005b, 2006; Small et al., 2007; Baker et al., 2008; Roh et al., 2002). Polyaniline (PAni) is an example of a conducting polymer, which can be switched between distinct states that exhibit dramatically different properties. For example, an external stimulus can be used to switch PAni reversibly between an insulating emeraldine base form and a conducting emeraldine salt form (Scheme 1). Consequently, it has great potential in sensor applications. The nanostructured form of PAni offers a very large surface-to-volume ratio that can lead to the dramatic enhancement of sensitivity and response time. The emeraldine salt form of PAni is also particularly interesting in that its electrical conductivity is much higher than that of traditional polymers. The deployment of PAni in commercial applications, however, is restricted due to issues with its stability. In particular, the leaching of an external acid dopant can be a problem. For commercial sensing applications, the selectivity of PAni is also a limitation.

Scheme 1



Notes: PAni is a redox active material and switches state in response to changes in its local chemical environment. Protonation (with acid HX) results in the doping of an insulating emeraldine base to form the conducting emeraldine salt. Acid leaching results in the degradation of PAni properties over time.

These problems can be addressed by the covalent attachment of side-groups to PAni. Functionalisation of PAni with acid side-groups results in a self-doping material, thus reducing the need for external dopants, which can leach from the system. Covalent functionalisation of PAni has been reported previously for the bulk material (Jiang Yue, 1990; Salavagione et al., 1999; Acevedo et al., 2005, 2006; Barbero et al., 1999). For example, substituents such as sulphonic acid groups have been added (Jiang Yue, 1990; Salavagione et al., 1999; Barbero et al., 1999). Derivatives of PAni have also been used, whereby monomers are first functionalised and then subsequently polymerised. This approach has been reported for the synthesis of polyanisidine and polyethylaniline nanofibres (Tran and Kaner, 2006). However, polymerisation using this approach can be complicated due to steric effects, and the properties of the resulting materials are compromised when compared to the unmodified PAni (Acevedo et al., 2005).

We demonstrate how covalent functionalisation of PAni nanofibres can be achieved post-polymerisation. This is achieved by refluxing PAni nanofibres in the presence of a nucleophile. Using this approach, we functionalise only the surface of the nanofibres and hence, can maintain the intrinsic characteristics of PAni, which make it such an interesting material to work with. Functionalised nanofibres retain their pH sensitivity, spectroscopic, redox and electrochemical properties. The nanomorphology of the polymer material is preserved during modification. The method we describe for producing functionalised nanomaterials is inexpensive, convenient and scalable.

2 Experimental details

2.1 *Materials*

Aniline (BDH), HCl (Fisher Scientific), ammonium peroxydisulfate (Aldrich), mercaptoundecanoic acid (Aldrich), cysteamine (Aldrich) and pH 4 buffer (Fluka) were used. The aniline monomer was purified by vacuum distillation before use. Other chemicals were used as received.

2.2 *Synthesis of PAni nanofibres*

Nanofibres were synthesised under ambient conditions by interfacial polymerisation between an aqueous and an organic layer (Huang and Kaner, 2004). The aqueous layer contained 200 ml of 1 M HCl as the dopant acid and ammonium peroxydisulfate $[(NH_4)_2S_2O_8]$ (60 mmol) as the oxidising agent. The organic layer contained 200 ml of purified aniline (200 mmol) dissolved in toluene.

2.3 *Modification of PAni nanofibres*

Once purified, PAni nanofibres were subsequently modified with either mercaptoundecanoic acid (MA) or cysteamine (CA). Nanofibre colloids were reacted with the alkane thiol in an aqueous pH 4 buffer. The solution was refluxed at 100°C for two hours without stirring. After reflux, functionalised PAni nanofibres were centrifuged at 3000 rpm for 30 minutes to remove by-products and any remaining unreacted species. The supernatant was removed and the solution made up to the original volume with deionised water. Centrifugation was repeated for three cycles.

2.4 *Characterisation of nanofibres*

2.4.1 *Field emission scanning electron microscopy*

Field emission scanning electron microscopy (FESEM) was carried out at an accelerating voltage of 20 kV on a S-4300 Hitachi system. Samples were cast as films onto silicon wafers and coated with 10 nm Au/Pd prior to imaging.

2.4.2 Nuclear magnetic resonance

Nuclear magnetic resonance (NMR) spectra were obtained using a Bruker 400 MHz instrument. Solid samples (2 mg) were sonicated for two hours in deuterated DMSO solvent (0.5 ml), with undissolved material being filtered out prior to analysis.

2.4.3 Fourier transform infra-red spectroscopy

Fourier transform infra-red spectroscopy (FTIR) were recorded in transmission mode from 400 to 4,000 cm^{-1}, for 100 repeat scans, with a resolution of 8 cm^{-1} and at 1 cm^{-1} intervals on a Perkin Elmer Spectrum GX FTIR. Samples were dried under vacuum at 50°C for four hours prior to FTIR and then mixed with dried KBr.

2.4.4 UV-vis spectroscopy

UV-vis was carried out on a Perkin Elmer UV-vis NIR Lambda 900 Spectrometer at 1 nm resolution.

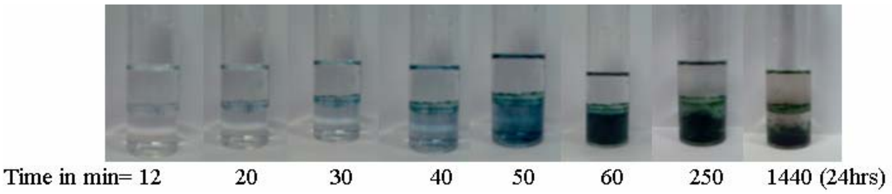
2.4.5 Atomic force microscopy

Atomic force microscopy (AFM) images were recorded in tapping mode on a Veeco Dimension 3100 instrument. AFM images were analysed and processed using WSxM software (http://www.nanotec.es).

3 Results and discussion

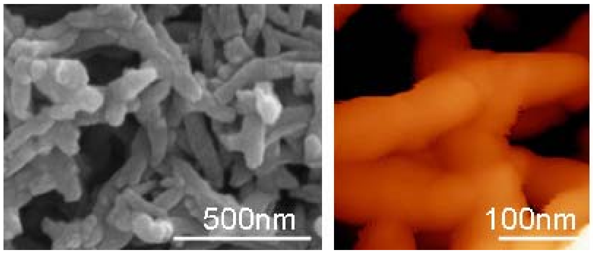
PAni fibres were synthesised by interfacial polymerisation, during which the colourless aniline monomer is oxidised at the organic/aqueous interface. The polymerised material is green and migrates into the aqueous layer, precipitating out of solution over time. The first signs of polymerisation appear after 12 minutes and after 24 hours the process is complete (Figure 1). The product can be collected from the aqueous phase and purified by centrifugation. Synthesised fibres were imaged using both FESEM and AFM to confirm the nanomorphology of the polymerised product (Figure 2). Imaging revealed porous structures with a large exposed surface area. AFM measurements showed some of the larger fibre diameters to be in the region of 100 nm.

Figure 1 Interfacial polymerisation of aniline (see online version for colours)



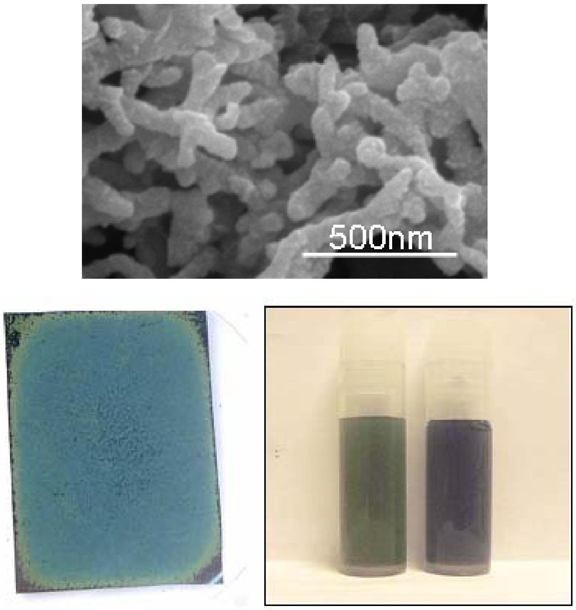
Notes: The green PAni product begins to form after 12 minutes and after 24 hours reaction time the product precipitates to the bottom of the aqueous phase.

Figure 2 FESEM and AFM images show PAni nanofibres with diameters in the region of 90 nm (see online version for colours)



Nanofibres were subsequently modified by refluxing with either mercaptoundecanoic acid or cysteamine. During this time, the reactive SH nucleophile of the alkane thiol attaches onto the electrophilic quinoid rings in the PAni backbone, as quinoimine units suffer nucleophilic attack with addition on the ring (Salavagione et al., 1999). Functionalised nanofibres were then purified by centrifugation. FESEM imaging shows that post-functionalisation, the nanomorphology of the material is maintained. Nanofibres can either be cast onto substrates such as silicon or used in solution (Figure 3). Like PAni, the functionalised material is redox active and changes colour in response to the pH of its environment. At low pHs, the PAni is green, indicating a doped conductive form. At higher pH values (> 4), the material is purple indicating a dedoped insulating state.

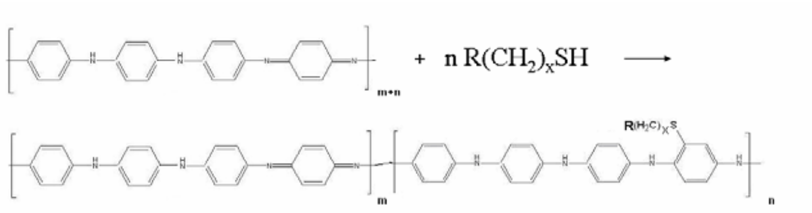
Figure 3 Functionalised nanofibres maintain their morphology (see online version for colours)



Notes: They can be cast as film onto substrates (such as silicon) or dispersed in solvents (such as water). The material retains its ability to switch colour in response to changes in the local pH.

Scheme 2 shows the proposed chemical structure of functionalised PAni. Alkane thiols attach onto some quinoid rings of the PAni backbone. The extent of this side-chain attachment can be controlled by varying the amount of thiol added during reflux, as demonstrated previously by the authors. Covalent attachment of side-chains was verified using NMR.

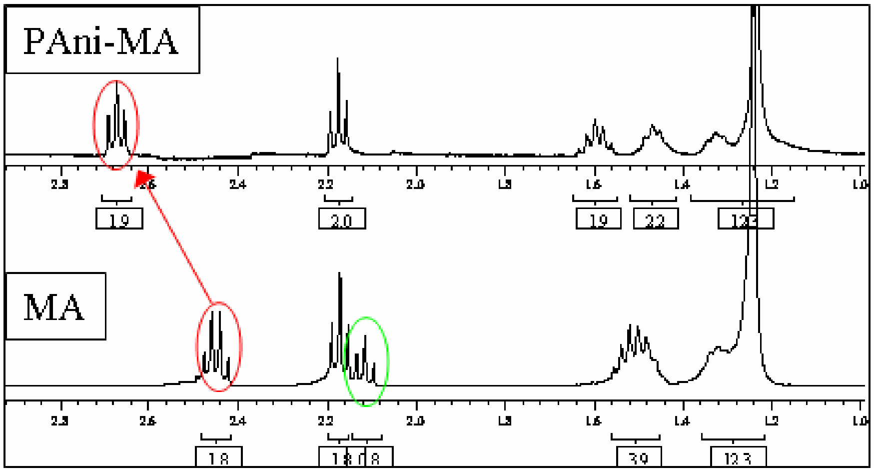
Scheme 2



Notes: Thiol attachment occurs at the quinoid ring of the PAni backbone. The ratio of n:m is dependent on the pH of the environment and also on the extent of functionalisation. ($X = 2$ where $R = NH_2$, and $X = 10$ where $R = COOH$)

PAni is a difficult material to dissolve and therefore only side-chain protons appeared in the NMR spectra (Figure 4). Results for ^1H NMR of mercaptoundecanoic acid (400 MHz, DMSO-d_6) were: δ 12.01 (1H, s), 2.46 (2H, m), 2.17 (2H, t, J = 7.33), 2.11 (1H, t, J = 7.71), 1.50 (4H, m), 1.32 (2H, m), 1.20–1.28 (10H, br). For the functionalised PAni-MA ^1H NMR (400 MHz, DMSO-d_6) results were: δ 2.67 (2H, t, J = 7.33), 2.18 (2H, t, J = 7.33), 1.60 (2H, m), 1.47 (2H, m), 1.33 (2H, m), 1.18 – 1.28 (10H, br).

Figure 4 NMR spectra strongly support covalent attachment to an electron withdrawing group (see online version for colours)



Notes: Most significantly, the triplet at 2.11 p.p.m., assigned to the thiol proton, disappears for PAni-MA. Also, a change from multiplet to triplet, is consistent with the loss of the S-H bond in the PAni-MA.

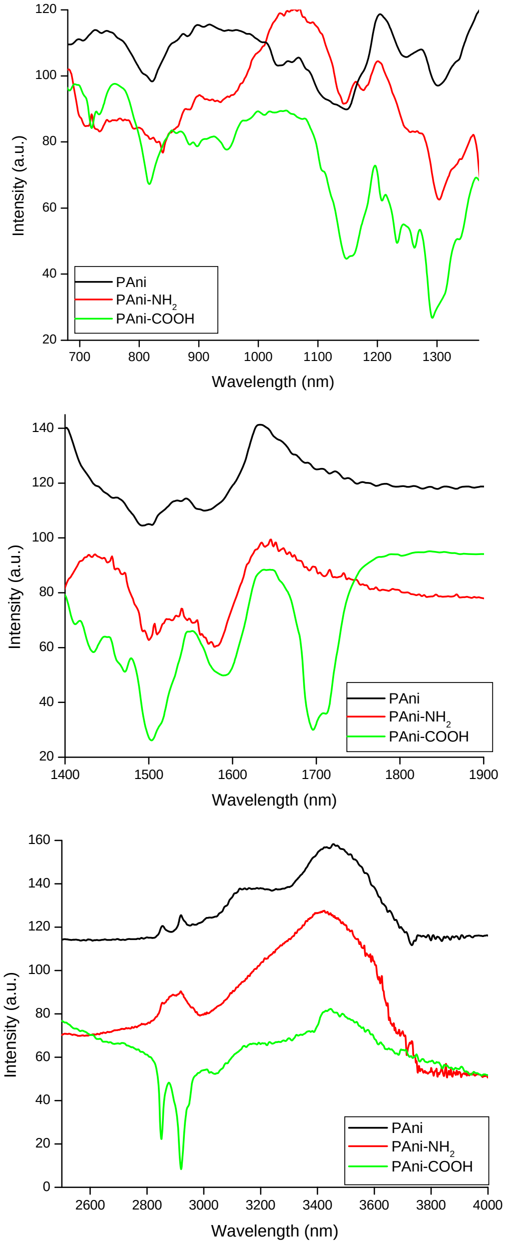
Therefore, 22 hydrogen atoms are seen for MA ($HS(CH_2)_{10}COOH$), as expected. A triplet at 2.11 p.p.m. was assigned to the thiol proton and this disappears in the PAni-MA spectrum, suggesting covalent attachment. In PAni-MA, there is a general downfield shift for protons in the MA alkyl chain, which suggests a decrease in the electron density surrounding these protons. This is consistent with the covalent attachment to electron withdrawing (quinoid) units on the PAni backbone. For example, the two protons at 2.46 are shifted downfield to 2.67 consistent with deshielding. We suggest that these protons may be assigned as being attached to the carbon adjacent to the sulphur bond. The shift is accompanied by a change from multiplet to triplet, consistent with the loss of the S-H bond in the PAni-MA. NMR evidence therefore strongly supports covalent attachment of the MA group to an electron-withdrawing group. The four protons at 1.5 p.p.m. split due to a change in the local environment. We suggest that these can be assigned as the protons adjacent to the carboxylic acid group and splitting are consistent with deprotonation of this group. The carboxylic acid proton was observed at 12.01 p.p.m. for MA and was absent for PAni-MA, suggesting deprotonation of the bonded MA sidechain. This observation is consistent with self-doping of the PAni by covalently attached acid side-chains.

FTIR spectra for PAni-MA show characteristic MA bands in the functionalised nanomaterial (Figure 5). Characteristic MA peaks are slightly shifted supporting a change in the local chemical environment consistent with the covalent attachment. Characteristic SH bands are also absent, consistent with thiol attachment. The presence of a carboxylic acid side-chain is confirmed by the FTIR doublet band 1,697 cm^{-1}/1,714 cm^{-1} for PAni-MA. The splitting implies that two slightly different C = O environments exist and suggests some deprotonation of the hydrogen atom attached to the COOH acid group (Goutev and Futamata, 2003). This observation is consistent with NMR results and indicates self-doping behaviour.

Likewise, PAni-CA shows characteristic cysteamine [$HS(CH_2)_2NH_2$] bands alongside those of PAni (Figure 5). These include characteristic CH_2 bands (1189, 1211, 1411, 2850 and 2918) (Goutev and Futamata, 2003; Castro et al., 2004)], C-S bands (686, 723) (Castro et al., 2004), C-C stretch (1105), C-C twist (1238) (Hussain and Kumar, 2003) and 1264 (CH_2-S) (Moller et al., 2007). A band centred around 3,400 cm^{-1} is the characteristic of the amide group. Therefore, FTIR evidence is consistent with covalent attachment of CA.

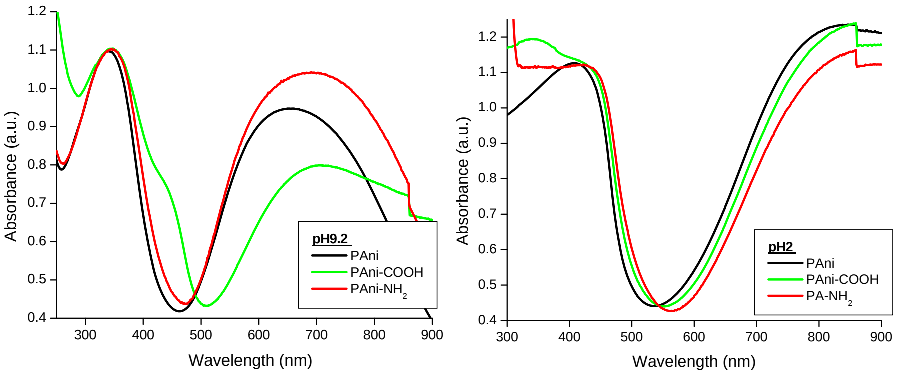
UV-vis spectra reflect changes in the structure of the PAni as it switches between the conformations shown in Scheme 1. At low pH values, a polaron band appears at 450 nm with a tail above 600 nm (Barbero et al., 1994). When PAni fibres are exposed to a higher pH environment these bands disappear, and a π-π^* transition band at 341 nm dominates due to dedoping. Also, a peak at 655 nm can be assigned to the quinoid fraction of the PAni backbone. UV-vis were taken for PAni, PAni-MA and PAni-CA at both pH 9 and pH 2 (Figure 6).

Figure 5 FTIR spectra support covalent attachment of side-chains to the PAni backbone (see online version for colours)



Note: A carboxylic acid band at 1,700 cm^{-1} appears for PAni-MA and an amine band at 3,500cm^{-1} appears for PAni-CA.

Figure 6 UV-vis spectra support acid and amide functionalisation of PAni (see online version for colours)



Notes: The polaron band at 450 nm is the characteristic of the conductive (acid doped) form. A bathochromic peak shift suggests increasing polarity in the immediate vicinity of the PAni, consistent with the attachment of side-chains.

At pH 9, PAni is in the dedoped form and this is reflected in the spectrum obtained. At pH 9, the PAni-MA functionalised material shows features, which indicate some doping of the PAni and this is consistent with the presence of acidic side-groups. For CA functionalised material, at pH 9, we do not see this doping effect (as NH_2 is basic). However, at both pH 9 and pH 2, we see a bathochromic shift, which is consistent with a change in local pH (consistent with the attachment of side-groups). The amide group is more polar than the acid group and therefore, the peak shift is more significant for PAni-CA than for PAni-MA. Similar bathocromic peak shifts have been reported for PAni when dispersed in solvents of increasing polarity (Yasuda et al., 2003). Therefore, the UV-vis offers further evidence that we have in fact functionalised PAni nanofibres with both COOH and NH_2 side-chains.

4 Conclusions

We have demonstrated the successful attachment of alkane thiol molecules to PAni nanofibres. Alkane chains can be either acid or amine terminated, thus providing a route for controlling the surface chemistry of nanofibres. Acid terminated chains can be used to introduce self-doping behaviour to PAni, hence reducing the need for an external dopant. Amine terminated chains are interesting in that they provide a template which could be further altered to enhance the selectivity of PAni. Carboxylic acid and amine groups are excellent sites for biomolecule attachment (such as proteins and saccharides) (Lisichkin and Kudrinskii, 2007; Yiu and Wright, 2005). Therefore, by functionalising PAni nanofibres, we provide a mechanism to broaden potential applications for the material.

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References

Acevedo, D.F., Balach, J., Rivarola, C.R., Miras, M.C. and Barbero, C.A. (2006) 'Functionalised conjugated materials as building blocks of electronic nanostructures', *Faraday Discuss*, Vol. 131, pp.235–252.

Acevedo, D.F., Salavagione, H.J., Miras, M.C. and Barbero, C.A. (2005) 'Synthesis, properties and applications of functionalized polyanilines', *J. Braz. Chem. Soc.*, Vol. 16, No. 2, pp.259–269.

Baker, C.O., Shedd, B., Innis, P.C., Whitten, P.G., Spinks, G.M., Wallace, G.G. and Kaner, R.B. (2008) 'Monolithic actuators from flash-welded polyaniline nanofibers', *Advance Materials*, Vol. 20, No. 1, pp.155–158.

Barbero, C., Miras, M.C., Schnyder, B., Haas, O. and Kotz, R. (1994) 'Sulfonated polyaniline films as cation insertion electrodes for battery applications 1: structural and electrochemical characterization', *J. Mater. Chem.*, Vol. 4, No. 12, pp.1775–1783.

Barbero, C., Morales, G.M., Grumelli, D., Planes, G., Salavagione, H., Marengo, C.R. and Miras, M.C. (1999) 'New methods of polyaniline functionalization', *Synthetic Metals*, Vol. 101, Nos. 1–3, pp.694–695.

Castro, J.L., Lopez-Ramirez, M.R., Arenas, J.F. and Otero, J.C. (2004) 'Surface-enhanced Raman scattering of 3-mercaptopropionic acid adsorbed on a colloidal silver surface', *J. Raman Spectrosc.*, Vol. 35, No. 11, pp.997–1000.

Chiou, N.R. and Epstein, A.J. (2005) 'A simple approach to control the growth of polyaniline nanofibers', *Synthetic Metals*, Vol. 153, Nos. 1–3, pp.69–72.

Chiou, N.R., Lui, C.M., Guan, J.J., Lee, L.J. and Epstein, A.J. (2007) 'Growth and alignment of polyaniline nanofibres with superhydrophobic, superhydrophilic and other properties', *Nat. Nanotechnol.*, Vol. 2, No. 6, pp.354–357.

Goutev, N. and Futamata, M. (2003) 'Attenuated total reflection surface-enhanced infrared absorption spectroscopy of carboxyl terminated self-assembled monolayers on gold', *Appl. Spectrosc.*, Vol. 57, No. 5, pp.506–513.

Huang, J. and Kaner, R.B. (2004) *Journal of the American Chemical Society*, Vol. 126, p.851.

Huang, J.X. and Kaner, R.B. (2004) 'A general chemical route to polyaniline nanofibers', *Journal of the American Chemical Society*, Vol. 126, No. 3, pp.851–855.

Huang, J.X. and Kaner, R.B. (2006) 'The intrinsic nanofibrillar morphology of polyaniline', *Chemical Communications*, Vol. 4, 367–376.

Huang, J.X., Virji, S., Weiller, B.H. and Kaner, R.B. (2003) 'Polyaniline nanofibers: facile synthesis and chemical sensors', *J. Am. Chem. Soc.*, Vol. 125, No. 2, pp.314–315.

Hussain, A.M.P. and Kumar, A. (2003) 'Electrochemical synthesis and characterization of chloride doped polyaniline', *Bull. Mater. Sci.*, Vol. 26, No. 3, pp.329–334.

Jiang Yue, A.J.E. (1990) 'Synthesis of self-doped conducting polyaniline', *J. Am. Chem. Soc.*, Vol. 112, pp.2800–2801.

Lisichkin, G.V. and Kudrinskii, A.A. (2007) 'Grafted surface compounds in chemical sensors and biosensors', *Russian Journal of General Chemistry* Vol. 77, No. 3, pp.325–335.

Moller, K., Kobler, J. and Bein, T. (2007) 'Colloidal suspensions of mercapto-functionalized nanosized mesoporous silica', *J. Mater. Chem.*, Vol. 17, No. 7, pp.624–631.

Roh, J.G., Hwang, H.R., Yu, J.B., Lim, J.O. and Huh, J.S. (2002) 'Oxidant effects on polypyrrole and polyaniline sensor for several volatile organic gases', *Journal of Macromolecular Science-Pure and Applied Chemistry*, Vol. A39, No. 10, pp.1095–1105.

Salavagione, H., Morales, G.M., Miras, M.C. and Barbero, C. (1999) 'Synthesis of a self-doped polyaniline by nucleophilic addition', *Acta Polym.*, Vol. 50, No. 1, pp.40–44.

Small, W.R., Masdarolomoor, F., Wallace, G.G. and Panhuis, M. (2007) 'Inkjet deposition and characterization of transparent conducting electroactive polyaniline composite films with a high carbon nanotube loading fraction', *Journal of Materials Chemistry*, Vol. 17, No. 41, pp.4359–4361.

Tran, H.D. and Kaner, R.B. (2006) 'A general synthetic route to nanofibers of polyaniline derivatives', *Chemical Communications*, Vol. 37, pp.3915–3917.

Virji, S., Fowler, J.D., Baker, C.O., Huang, J.X., Kaner, R.B. and Weiller, B.H. (2005a) 'Polyaniline manofiber composites with metal salts: chemical sensors for hydrogen sulfide', *Small*, Vol. 1, No. 6, pp.624–627.

Virji, S., Huang, J.X., Kaner, R.B. and Weiller, B.H. (2004) 'Polyaniline nanofiber gas sensors: examination of response mechanisms', *Nano Lett.*, Vol. 4, No. 3, pp.491–496.

Virji, S., Kaner, R.B. and Weiller, B.H. (2005b) 'Hydrazine detection by polyaniline using fluorinated alcohol additives', *Chemistry of Materials*, Vol. 17, No. 5, pp.1256–1260.

Virji, S., Kaner, R.B. and Weiller, B.H. (2006) 'Hydrogen sensors based on conductivity changes in polyaniline nanofibers', *Journal of Physical Chemistry B*, Vol. 110, No. 44, pp.22266–22270.

WSxM-software, Available at http://www.nanotec.es.

Yasuda, T., Yamaguchi, I. and Yamamoto, T. (2003) 'Preparation of N-grafted polyanilines with oligoether side chains by using ring-opening graft copolymerization of epoxide, and their optical, electrochemical and thermal properties and ionic conductivity', *J. Mater. Chem.*, Vol. 13, No. 9, pp.2138–2144.

Yiu, H.H.P. and Wright, P.A. (2005) 'Enzymes supported on ordered mesoporous solids: a special case of an inorganic-organic hybrid', *J. Mater. Chem.,* Vol. 15, Nos. 35–36, pp.3690–3700.