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

Advantages

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

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

Our Approach

- Cheap and Scalable Process
- Maintain the Nanomorphology of PAni
Polaranine Nanofibres Synthesis

- interfacial polymerization

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

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
Poylanilne Functionalisation

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

\[
\begin{align*}
\text{[Polyaniline]} & \quad + \quad n \, R(CH_2)_xSH \\
\text{[Thiol Derivative]} & \quad \rightarrow \\
\text{[Product]} & \quad R = \text{COOH}
\end{align*}
\]

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

Scanning electron microscopy (SEM)

- Nanomorphology is maintained post-functionalisation.
Fourier Transform Infrared Spectroscopy (FTIR)

- Covalent attachment of the Mercaptoacid to the polymer backbone
Controlling the extent of functionalisation

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

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

- 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

**PAni**

![Graph showing UV-vis spectroscopy for PAni across different pH values.](image1)

**PAni-C3COOH**

![Graph showing UV-vis spectroscopy for PAni-C3COOH across different pH values.](image2)

**Absorbance @ 420/350**

![Graph showing absorbance at 420/350 nm for PAni and PAni-C3COOH across different wavenumbers.](image3)

**PAni**

- pH 2.6
- pH 4
- pH 7.4 (PBS buffer)
- pH 9.2

**PAni – C3COOH**

- pH 2.6
- pH 4
- pH 7.4 (PBS buffer)
- pH 9
Raman spectroscopy

C3COOH = mercaptopropanoic acid  
C16COOH = mercaptohexadecanoic acid

➢ Prove self-doping behaviour
Conductivity measurements

\[ \sigma_s = G \cdot \frac{S}{l} \]

\( \sigma_s \) – surface conductivity

\( G \) – conductance of the circuit

\( \sigma_s \approx 10^{-6} \text{ to } 10^{-7} \text{ S/cm} \) \([1,2]\)

Applications

Nanofibre Biosensors

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

= Primary antibody
= Secondary antibody labelled with HRP

ELISA

- HRPO

Antibody-functionalized Pani Nanofibres
Antibody-functionalized Pani Nanofibres

Applications
Antibody-functionalized Pani Nanofibres
Pani Nanofibres
Pani Nanofibre Blanks

Electrocatalytic oxidation of Ascorbic Acid

\[
\text{C}_6\text{H}_8\text{O}_6 \quad \rightarrow \quad 2\text{e}^- \quad 2\text{H}^+ \quad \rightarrow \quad \text{C}_6\text{H}_6\text{O}_6
\]

(Ascorbic acid) \quad \text{(Dehydroascorbic acid)}
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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