Conducting Polymer-Catalytic MIP Hybrid Sensor for Electrochemical Detection of Catechol

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Brief Blurb:
Cranfield University

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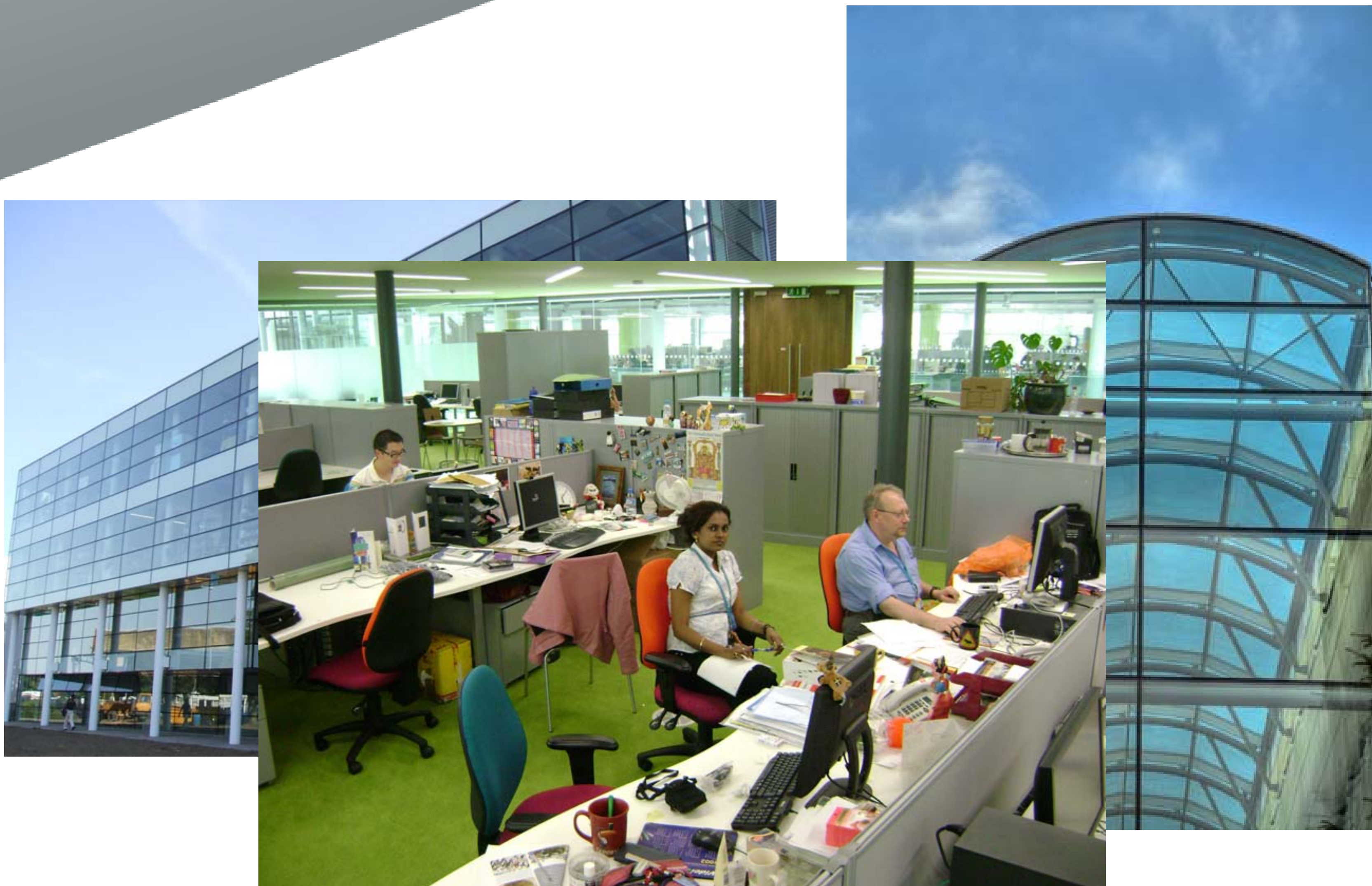
- Postgraduate-only University
- Emphasis on Business, Science and Technology
- On two sites in southern England
    - Cranfield main campus adjacent to Cranfield village
    - The Ministry of Defence college at Shrivenham

Cranfield Health: Our strength



Overview of the TALK

- Brief introduction about Molecularly Imprinted Polymers (MIPs)

- Catalytic MIPS and sensors

- Application of Conducting Polymer-Catalytic MIP HYBRID Sensor for electrochemical detection of catechol and derivatives

- Future work

Why Molecularly Imprinted Polymers?

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- Problems Associated with Natural Compounds

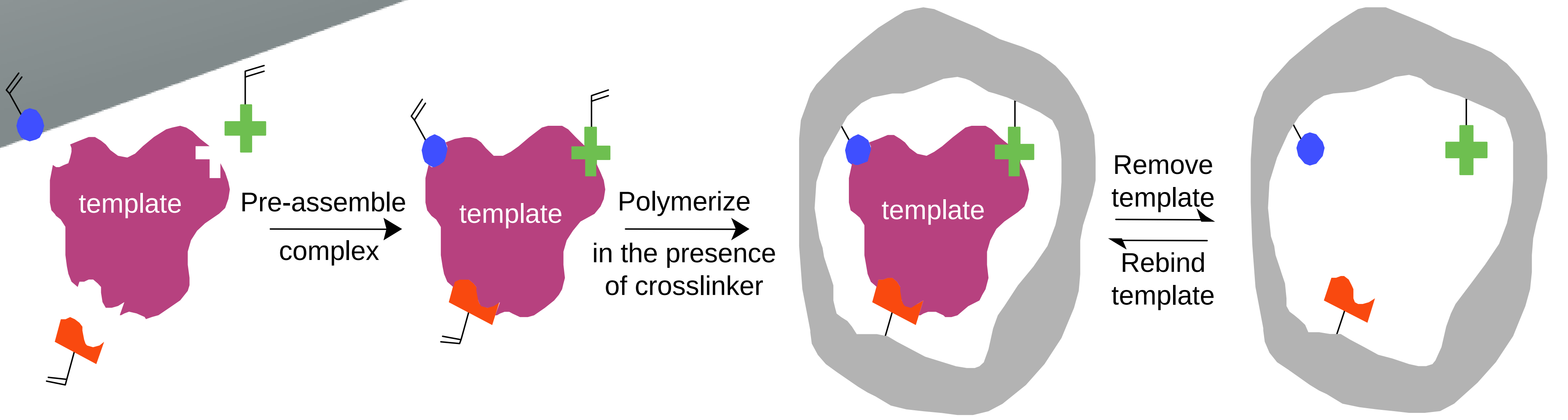
✓ Low stability of the biomolecules

✓ High price of enzymes and receptors

✓ Poor performance in non-aqueous media

✓ Poor compatibility with micro fabrication technology, resulting in difficulties with design of sensors

Molecular Imprinting



- Cross-linked polymer formed around a molecule that acts as a template, template subsequently removed.

- Imprints containing functional groups complementary to those of template are left behind

- Covalent or non-covalent approach

Advantages of MIPs

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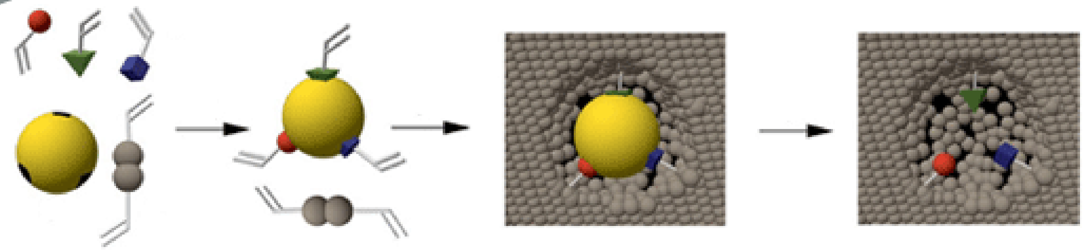
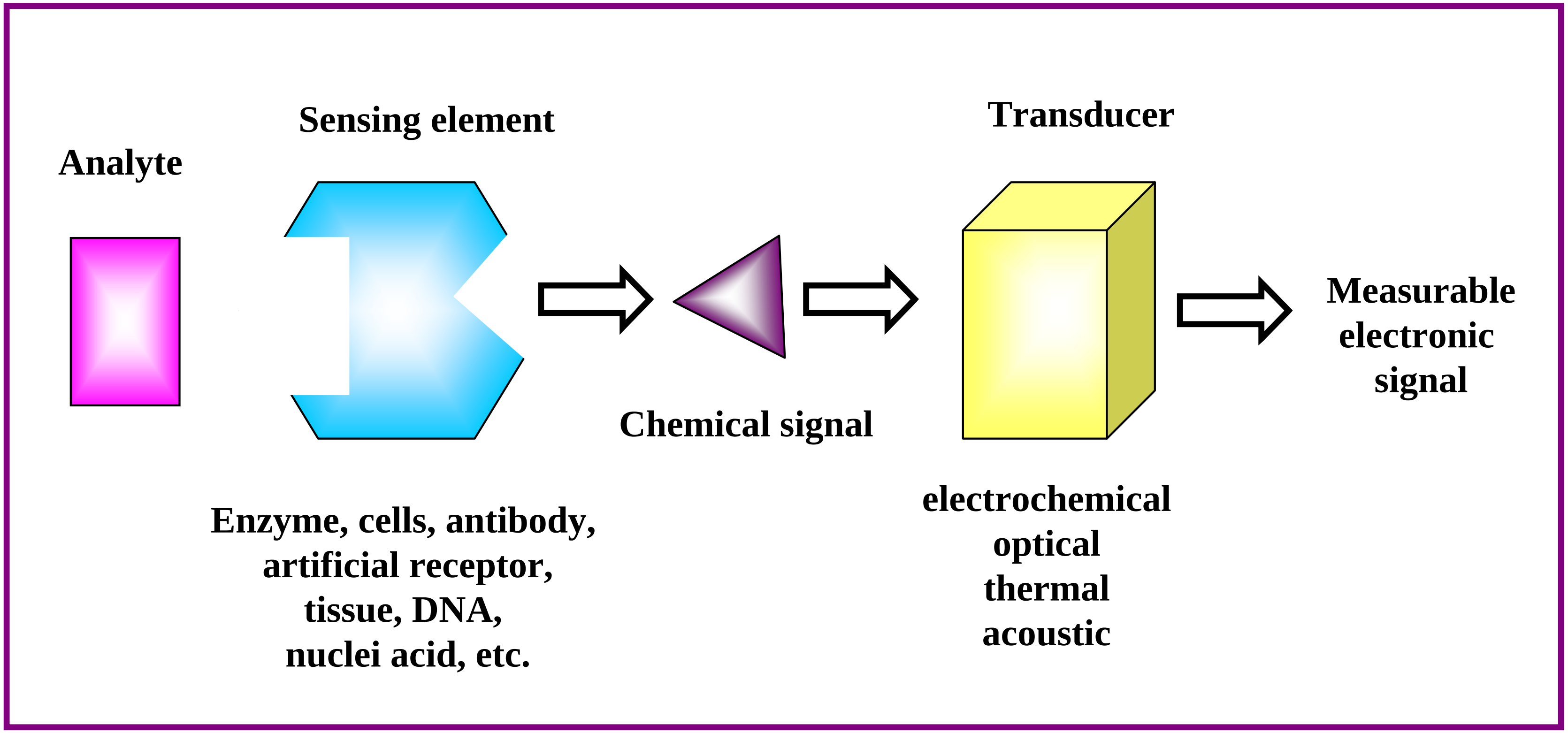


- ✓ ***MIP sensors/assays provide a viable alternative to the current methods used for analyte detection***
- ✓ MIPs can be prepared for practically any compound
- ✓ MIPs have similar affinity as compared to natural biomolecules and often better specificity
- ✓ MIPs can work in organic solvents
- ✓ MIPs are stable at low/high pHs, pressure and temperature
- ✓ Polymers are inexpensive
- ✓ Polymers are compatible with microfabrication

MIP-based Sensors: one of the applications



Drawback(s) of MIP-based Electrochemical Sensors

- The lack of a direct path for the conduction of electrons from the active sites to the electrode.
- MIPs are insulating materials and normally prepared as intractable powders
- Attaching MIP particles to an electrode gave no signal
- We need a better interface between MIP active sites and the electrode surface

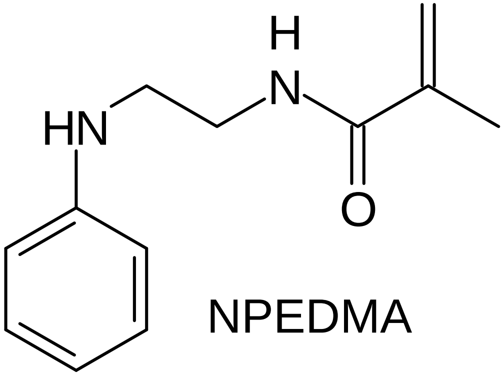
Our Approach

- We have sought to address this problem through the preparation and characterisation of novel hybrid materials containing an electrically conducting polymer and a MIP for electrochemically active templates.

- In this way a network of molecular wires can be prepared which allow for more or less direct electrical connection between the electrode and the active sites within the MIP.

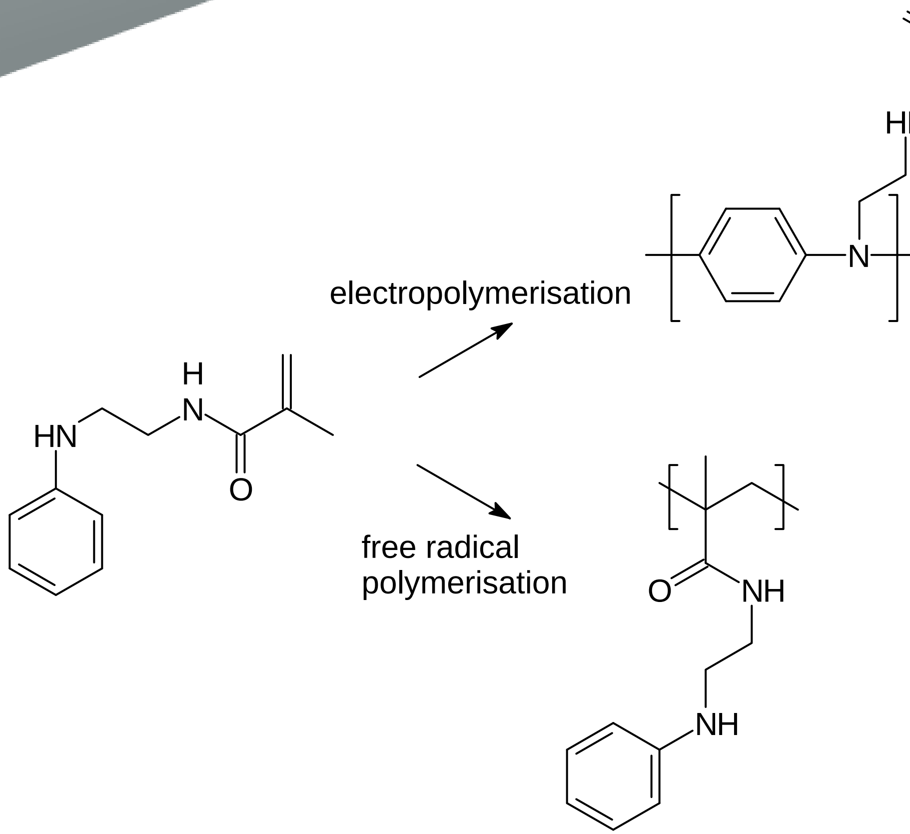
Solution: synthesis of new monomer

- A new monomer was designed and synthesised based on aniline
- The monomer, NPEDMA, has both aniline and double bond functionalities



NPEDMA

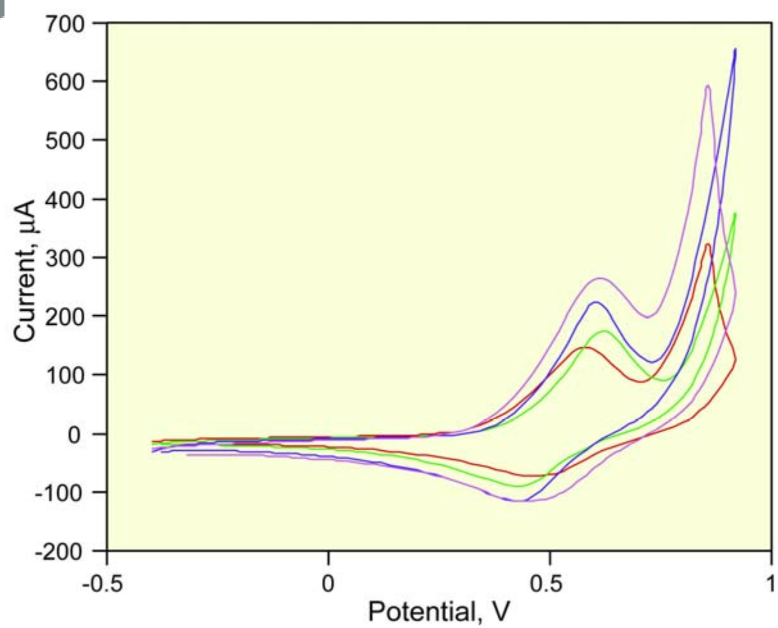
“orthogonal” monomer



polyaniline

Poly(methacrylamide)

Electropolymerisation



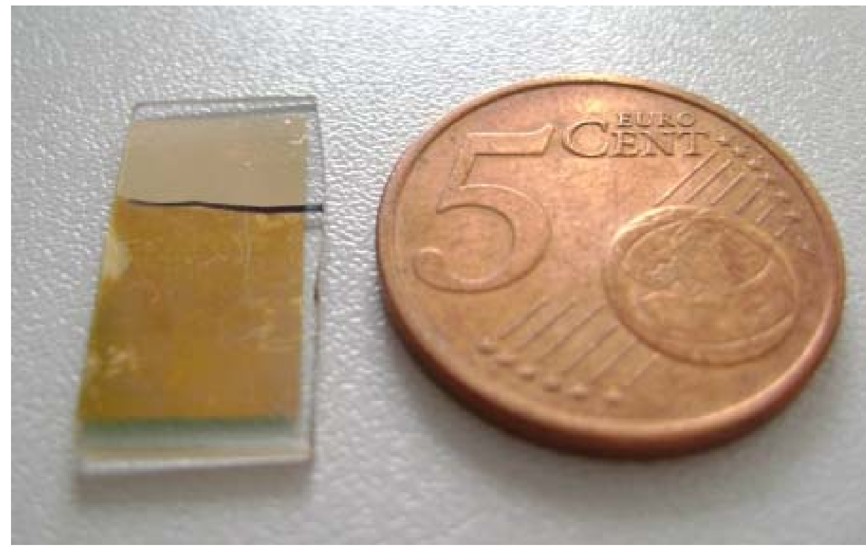


Figure. Cyclic voltammograms for electropolymerisation NPEDMA. The gold electrode was cycled between -0.4 V and +1.0 V (*vs*. Ag/AgCl) at a scan rate of 50 mV/s in a solution of NPEDMA (24 mM) in 50 mM HClO4 (15 cycles)

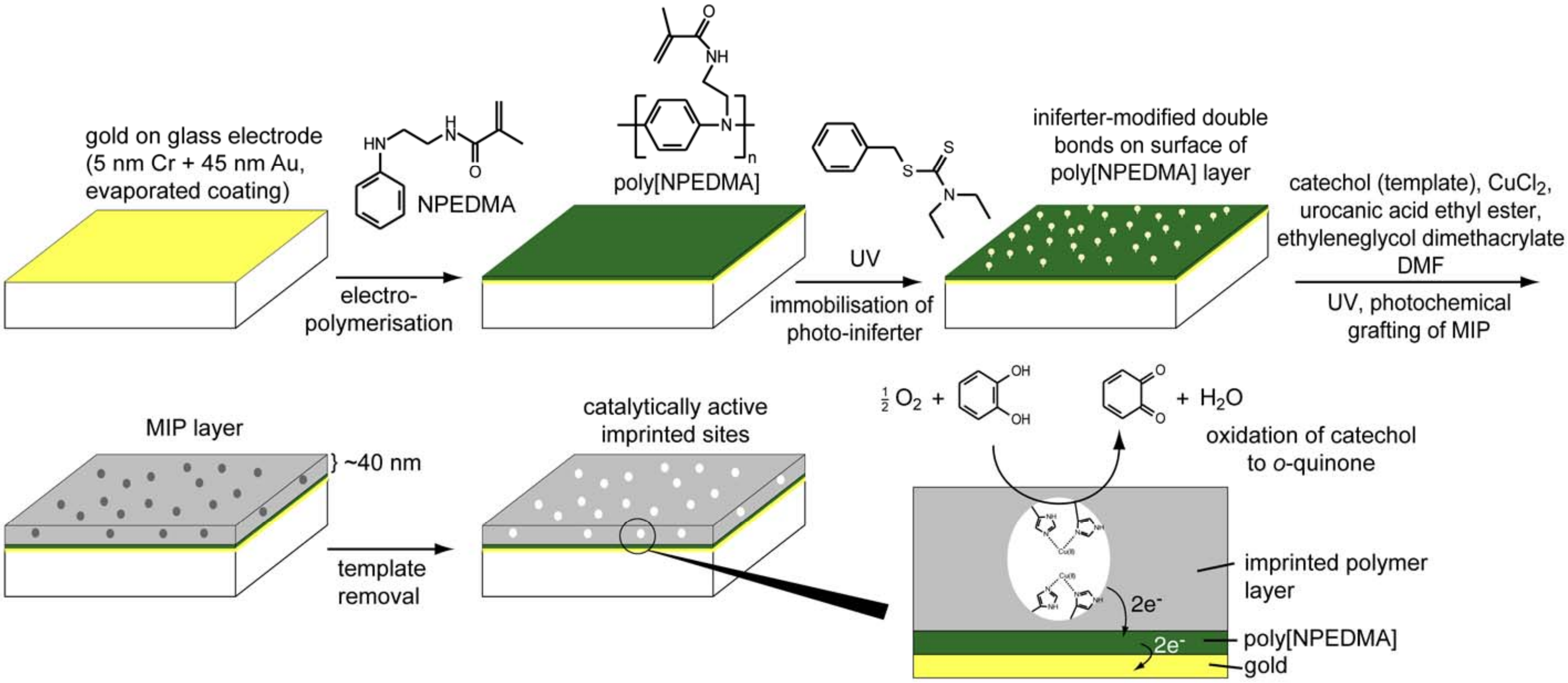
MIP-Hybrid Sensor

- We set out to prepare an electrochemical sensor using a catalytic molecularly imprinted polymer (MIP) as the recognition element
- MIP is constructed from catechol (template), Cu (II) (metal catalyst), urocanic acid ethyl ester (functional monomer) and ethylene glycol dimethacrylate (crosslinker) in DMF (porogenic solvent)
- MIP is a Tyrosinase mimic
- Oxidation of substrate (catechol) should release electrons which should give rise to a signal

Piletsky, S.A. *et al*. *Ukr. Biochem. J*., 2005, **77**, 67-78.

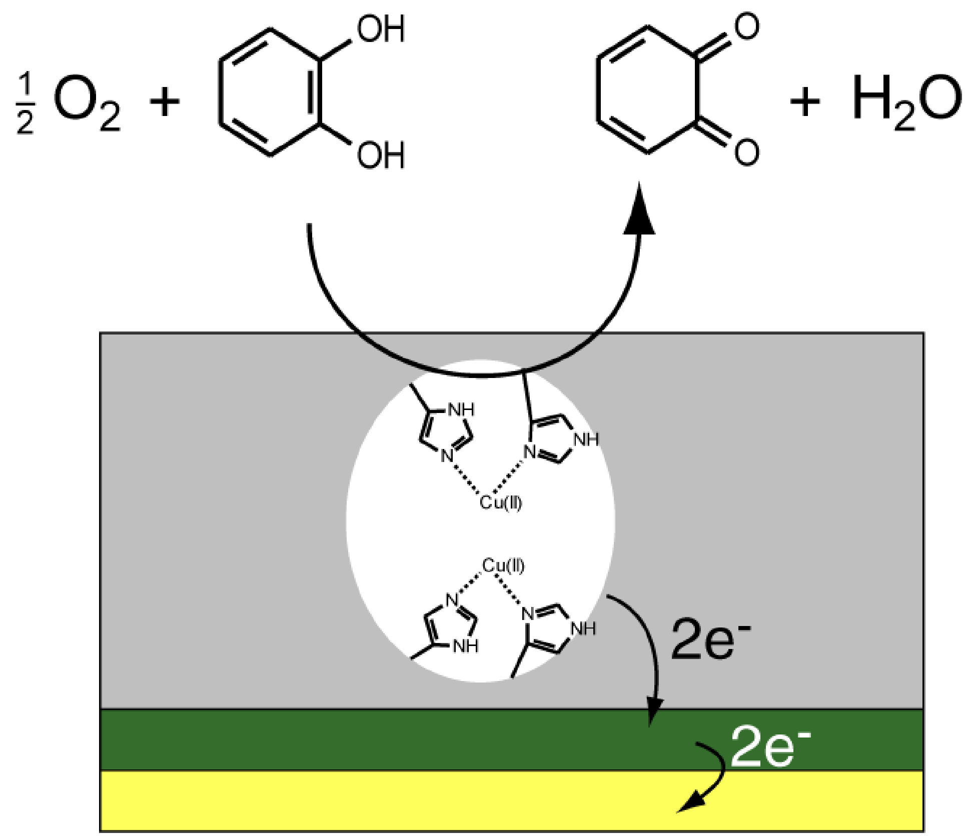
Electrode construction

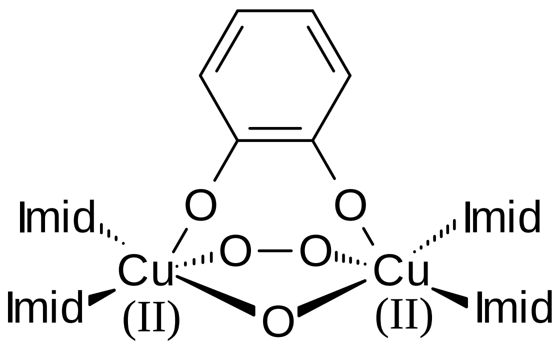
Scheme Construction of the hybrid catalytic MIP electrode for the electrochemical detection of catechol



Catechol oxidase activity of tyrosinase

oxidation of catechol to *o*-quinone





Imid = imidazole

Proposed transition state for the oxidation of catechol

Piletsky, S.A. *et al*. *Ukr. Biochem. J.*, 2005, **77**, 67-78.

MIP and NIP

- Control electrode was constructed with non-imprinted polymer (NIP) (prepared in the absence of template)
- Calibration using cyclic voltammetry (CV) using Ag/AgCl reference electrode
- Calibration performed with 3 separately constructed electrodes

Calibration

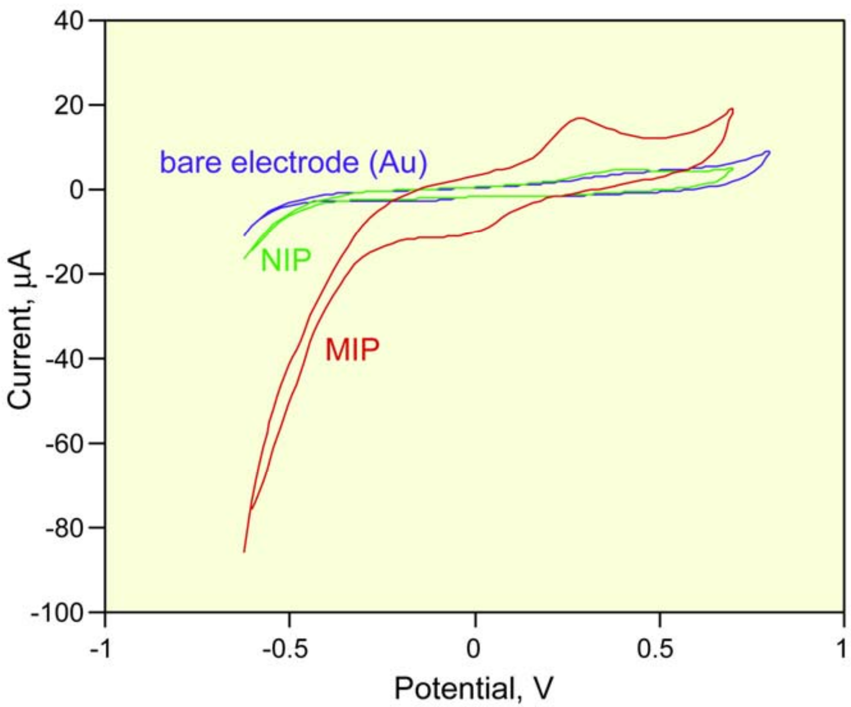


Figure. CV of catechol (0.11 mM) on MIP, NIP and bare electrode

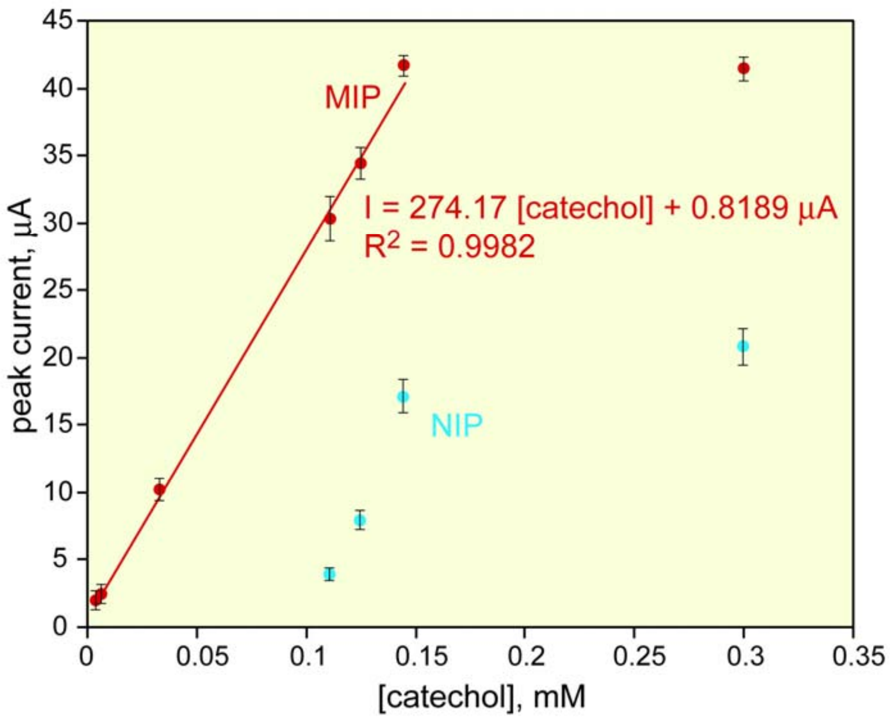


Figure. Calibration plot for catechol detection by anodic oxidation peak

Catalytic performance

- Assessed by chronoamperometry
- Apply potential and follow decay of current over time
- Initial slope, over 0.9 seconds, taken as kinetic data
- No signal in the absence of copper or oxygen
- Phenol, resorcinol and ascorbic acid are not oxidised by the MIP
- Dopamine is oxidised
- Sodium benzoate acts as an inhibitor

Michaelis-Menten plots

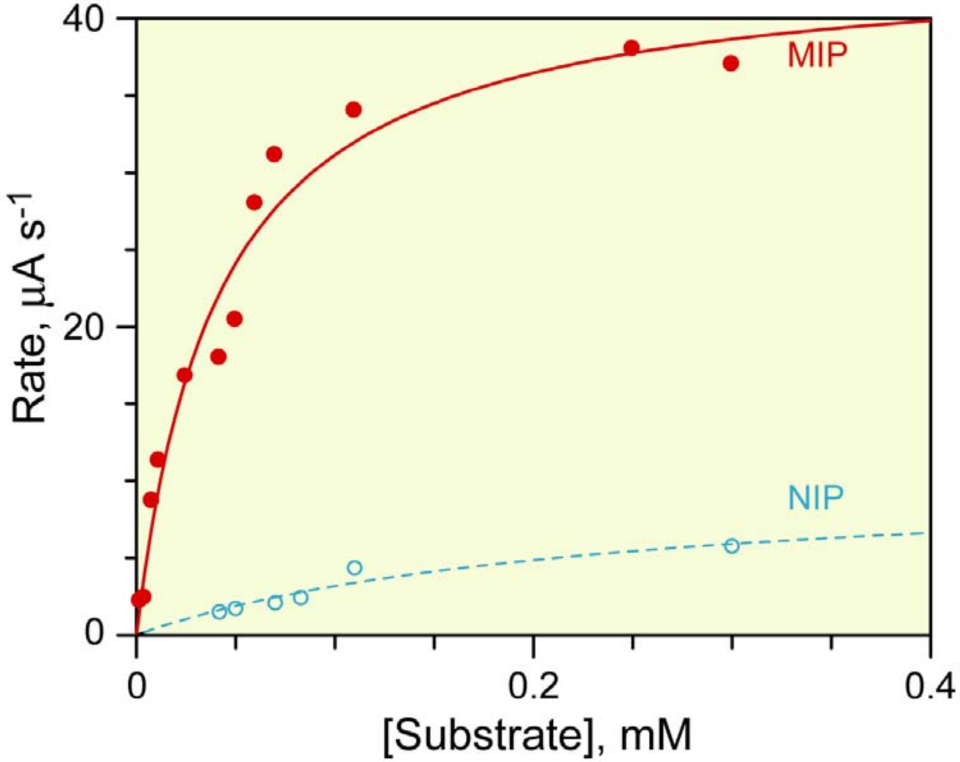


Figure. Michaelis-Menten hyperbolae determined from chronoamperometry data.

Kinetic parameters

Polymer	*Km* (mM)	*Vmax* (μA s^{-1})
MIP	0.041	43.9
NIP	0.200	9.263

Inhibition

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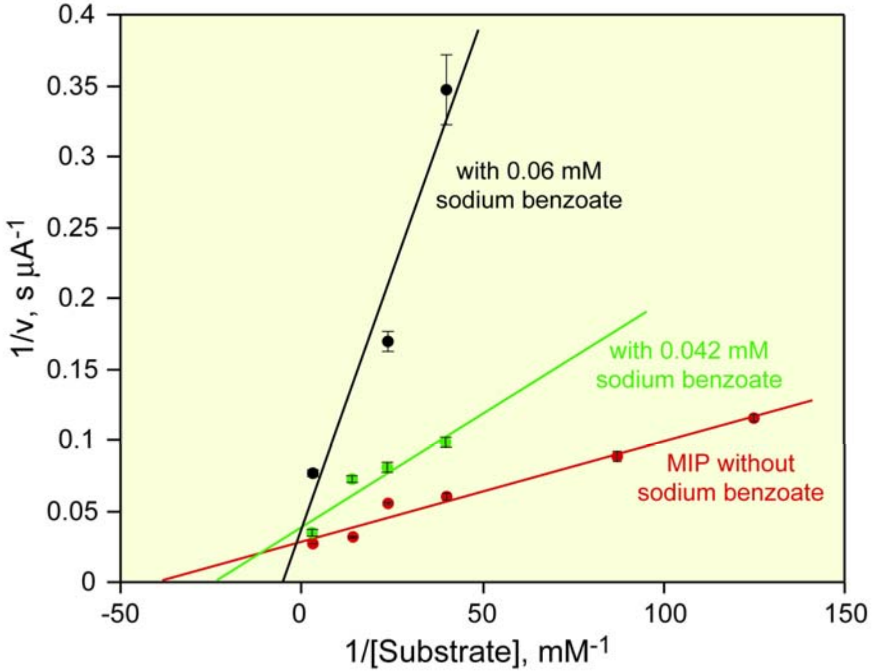

Figure. Lineweaver-Burk plots showing inhibition with sodium benzoate

Summary

- The performance of a MIP-based sensor was markedly improved by the incorporation of a conducting hybrid polymer layer
- This strategy is relatively straightforward and cheaper than carbon nanotubes
- The polyaniline hybrid layer acts as a “molecular wire” to connect the MIP catalytic sites to the electrode
- The sensor construction relies on two advanced polymer formulations

Conclusion

- The experimental results confirm the ability of the NPEDMA polymer layer to mediate conduction of electrons between to the catalytic sites in the MIP and the electrode.
- The MIP exhibits Michaelis-Menton kinetics and competitive inhibition properties similar to those of the enzyme tyrosinase.
- This demonstrates the potential of this approach as a new generation of conducting polymer hybrid material for the development of a variety of functional materials and devices

Future work

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- Lithographic Patterning of Conducting Polymers
- Conducting Membranes (addition polymerisation followed by oxidation)
- Anti-static coatings and radiation shielding (soluble precursors to conducting layers)
- Biofuel cell (as bio anodes)
- Novel Conducting polymeric structures: nano structures, emulsion polymerisation, copolymerisation,
- Possible optoelectronic applications

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Thank you very much