

# WHOLLY PRINTED POLYPYRROLE-BASED BIOSENSORS ON FLEXIBLE SUBSTRATES



Bo Weng<sup>2</sup>, Roderick Shepherd<sup>2</sup>, Karl Crowley<sup>1</sup>, Anthony J. Killard<sup>3</sup>,  Aoife Morrin<sup>1\*</sup>, Gordon G. Wallace<sup>3</sup>

<sup>1</sup>School of Chemical Sciences, National Centre for Sensor Research, Dublin City University, Dublin 9, Ireland

<sup>2</sup>Intelligent Polymer Research Institute, ARC Centre of Excellence for Electromaterials Science, University of Wollongong, NSW, Australia

<sup>3</sup>Department of Applied Sciences, University of the West of England, Coldharbour Lane, Bristol BS16 1QY, UK

Trends such as aging populations in western countries, increasing environmental legislation, the rise of genetic technology, and the emergence of such ubiquitous computing are all growth drivers for the development of sensor platforms. The markets that can be addressed by sensor manufacturers at present are vast and evolving rapidly. Printed chemical- and bio-sensors represent a unique opportunity within this market, where there is high demand for low-cost, mass-producible sensor products in specific key markets such as point-of-care medical diagnostics and smart packaging. The technique of inkjet-printing has the potential to revolutionize the production of the sensor interface, just as screen-printing in the early 1980s when it was first used for the production of the enormously successful point-of-care glucose biosensor. Screen-printing, a technique surpassed in terms of speed, cost and automation by inkjet printing has, by example, demonstrated the potential of printing as a technique for new sensor production of the future.

Our research looks to develop wholly printable electrochemical sensor chips, using printable metallic and carbon inks, and layers of materials such as conducting polymers and biomolecules to impart functionality and selectivity. This, we believe, is a truly viable, low-cost route to mass producing devices for commercially relevant sensing applications. Conducting aqueous polypyrrole (PPy) nanodispersions<sup>1</sup> have been developed recently at IPRI and are being examined for sensor application at DCU. The PPy formulation is highly processible, and has previously been successfully deposited using piezoelectric inkjet printing. Combining this formulation with the enzyme introduces a biosensing functionality into the ink. Horseradish peroxidase (HRP) was simply mixed into the PPy formulation and the resulting ink was inkjet printed to screen-printed flexible carbon-paste electrodes (CPEs). The linear range of detection of hydrogen peroxide was found to be 10  $\mu\text{M}$  – 10 mM.

This research demonstrates the feasibility of exploiting printing technologies to fabricate biosensors. Further work is ongoing to assess to possibility of fabricating low cost conducting polymer-based immunosensors via rapid printing.

## Profilometry & SEM

The characteristic rough morphology of the CPE diminishes as number of inkjet printed layers of PPy/HRP increases.

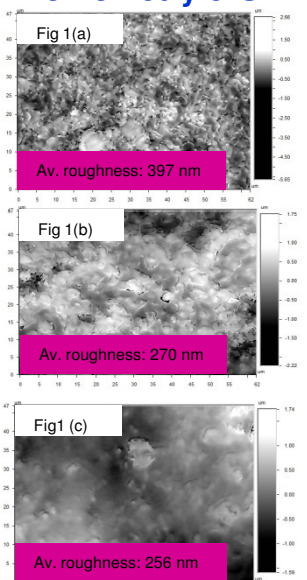


Fig 1a: Profilometry of bare screen-printed carbon paste electrode (CPE)  
Fig 1b: one layer of inkjet printed PPy/HRP (2.5mg/mL) ink on a CPE.  
Fig 1c: Five layers of PPy/HRP (2.5mg/mL) inkjet printed onto a CPE.

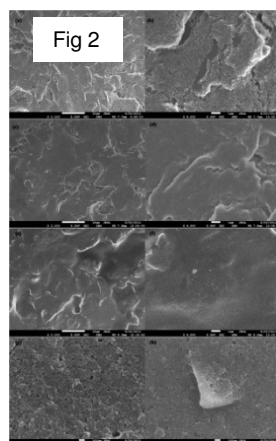
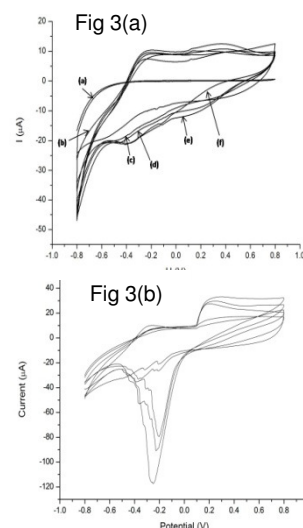


Fig 2a,b SEM of bare CPE; c,d 1 layer; e,f 5 layers PPy/HRP; g PPy; h PPy/HRP

## Cyclic Voltammetry



Voltammetric responses were recorded for PPy and PPy/HRP in the presence of increasing amounts of  $\text{H}_2\text{O}_2$ . Both the anodic and cathodic peak currents increased in the presence of  $\text{H}_2\text{O}_2$  when the PPy/HRP ink was printed to the CPE showing the ability of the film to both oxidise and reduce  $\text{H}_2\text{O}_2$  at appropriate potentials.

Fig.3.(a) Voltammetric response to  $\text{H}_2\text{O}_2$  (1 mM – 1  $\mu\text{M}$ ) of one layer of inkjet printed PPy  
(b) Voltammetric response to  $\text{H}_2\text{O}_2$  (1  $\mu\text{M}$  – 1 mM) of one layer of inkjet printed PPy/HRP (2.5 mg/ml) Buffer used: PBS, pH 6.8 Scan Rate: 100 mV/s

## Amperometry

A potential of -0.2 V vs. Ag/AgCl was selected to monitor the catalytic reduction of hydrogen peroxide. 5 inkjet printed layers of PPy/HRP gave significantly higher responses than 1 layer given the greater loading of HRP as a result of increasing layers. The background response was also greater for higher numbers of layers.

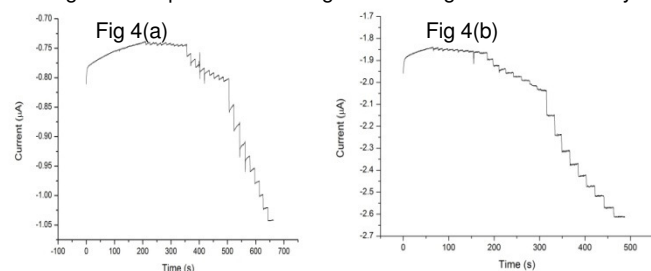


Fig.4. Amperometric responses of CPE-PPy/HRP biosensors to hydrogen peroxide. (a) 1 layer and (b) 5 layers of PPy/HRP (2.5 mg/ml).

## Calibration Curves

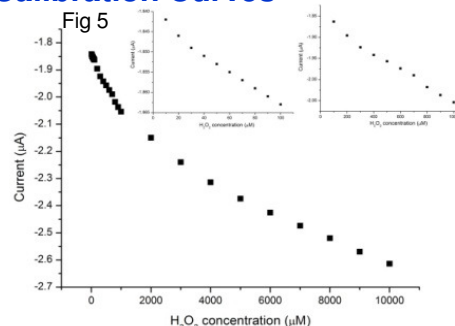


Fig.5. Calibration curves for the printed CPE/PPy/HRP biosensor where 5 layers of PPy/HRP (2.5 mg/ml) were printed. Response shows two linear regions: 1-100  $\mu\text{M}$  and 100 – 1000  $\mu\text{M}$ .

## Conclusion

The feasibility of fabricating a biosensor via a combination of screen- and inkjet- printing has been demonstrated. The HRP enzyme was shown to be inkjet printable in the presence of PPy nanoparticles and to retain activity subsequent to printing.

## Funding

Marie Curie I-RES Program



## References

<sup>1</sup>Bo Weng, Roderick Shepherd, Jun Chen and Gordon G. Wallace, Gemini surfactant doped polypyrrole nanodispersions: an inkjet printable formulation. J. Mater. Chem. 2011, 21:1918-1924.