Voltammetric sensor array based on differently doped polypyrrole molecularly imprinted polymers for the simultaneous detection of acetaminophen, uric acid and ascorbic acid

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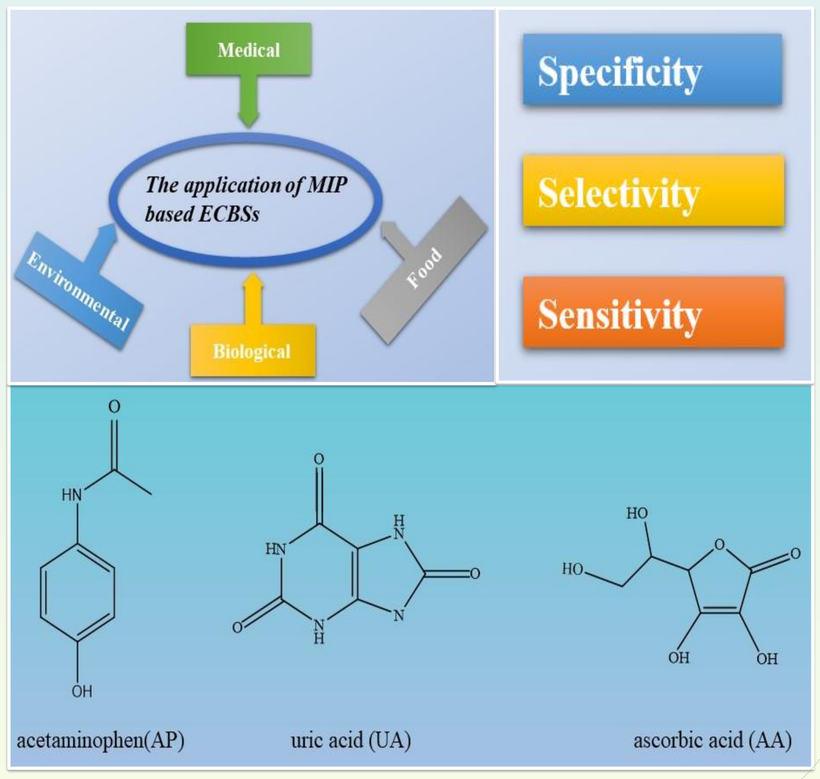
GRUP DE SENSORS I BIOSENSORS

ABSTRACT

Molecularly imprinted polymers (MIPs) are synthetic receptors with complimentary cavities towards a chosen template molecule (the target analyte), able to rebind it with high affinity and specificity. Those interactions are similar to the ones between the antibodies and antigens, but with superior chemical, mechanical, thermal and pH stability, and reusability. Thus, with the goal of obtaining of low-cost artificial receptors with high selectivity towards a desired analyte, highly suitable for applications in diverse many fields, such as the environmental, medical or agro-alimentary. In this regard, MIPs have become a significant research hotspot in the development of electrochemical sensors given their ability to selectively rebind to the target analytes with high specificity even in the presence of complex matrix; thus simplifying the analysis process and improving chemosensors performance.

In this work, MIP films are in-situ electro-synthesized from a monomer (pyrrole) solution, in the presence of the template molecule and different doping anions as a facile approach for the tuneability of the MIP morphology. A systematic evaluation on the effect of a series of anions as counter ion dopant integrated into the polypyrrole (PPy) backbone was carried out, including perchlorate ($ClO4^-$), p-toluene sulfonate (pTS^-), dodecyl sulfonate (DS^-) and dodecyl benzene sulfonate (DBS^-). The target compounds being evaluated were acetaminophen (AP), uric acid (UA) and ascorbic acid (AA), and the performance of the resulting MIPs modified electrodes was evaluated by means of cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Finally, combination of the different MIP modified electrodes as well as the NIP (non-imprinted polymer) into a sensor array will be evaluated to carry out the analysis of mixtures of the above-mentioned compounds, with the aid of chemometric methods such as principal component analysis (PCA) and artificial neural networks (ANNs).



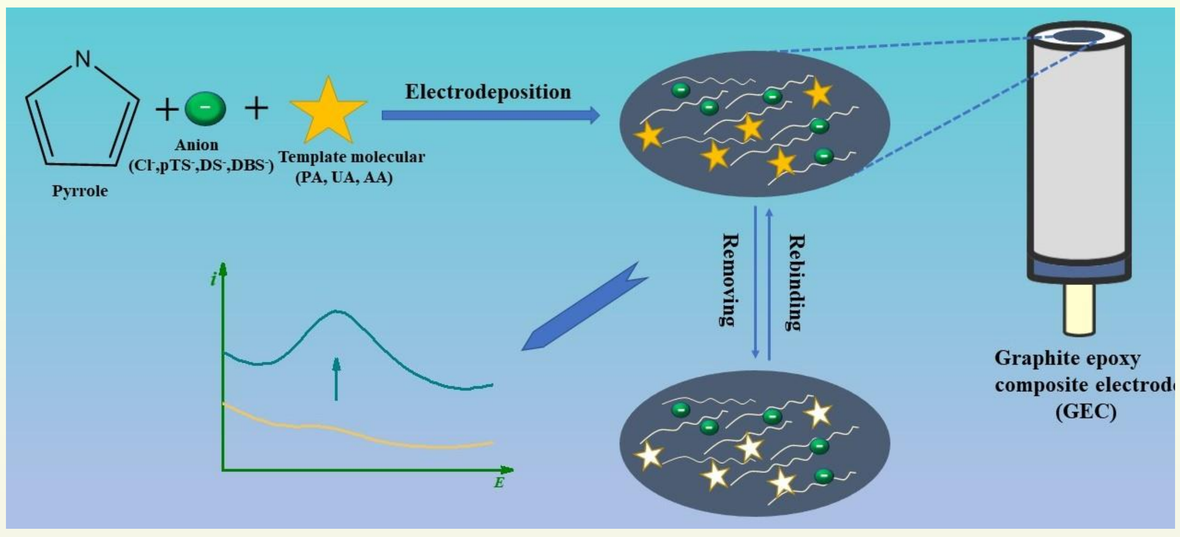


Fig.1 The fabrication process and working principle of the PPy/A^- MIPs sensor.

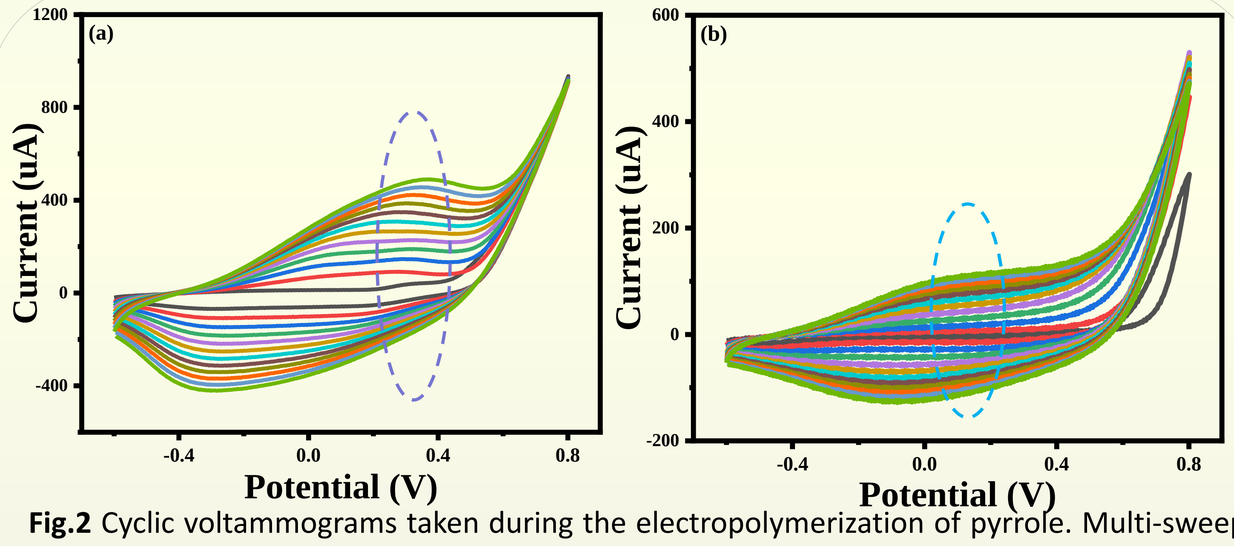


Fig.2 Cyclic voltammograms taken during the electropolymerization of pyrrole. Multi-sweep CV (a) with and (b) without acetaminophen onto a GEC electrode (scan rate: 50mVs^{-1}; supporting electrolyte: 0.1M $NaClO_4$; number of scans: 12).

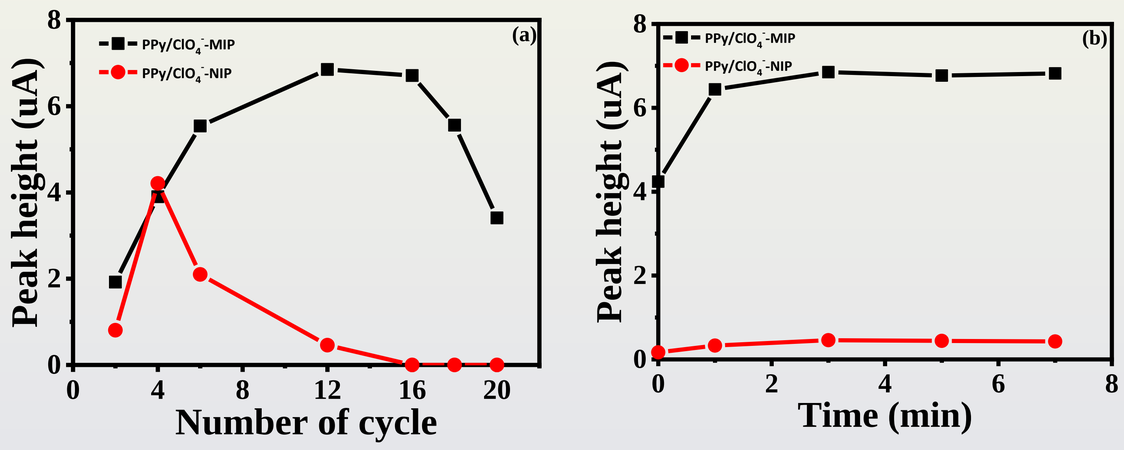


Fig.3 Effect of (a) the number of cycle (b) incubation time on the response of MIP and NIP modified GEC electrodes. Responses were measured through the in 5ppm AP with PBS.

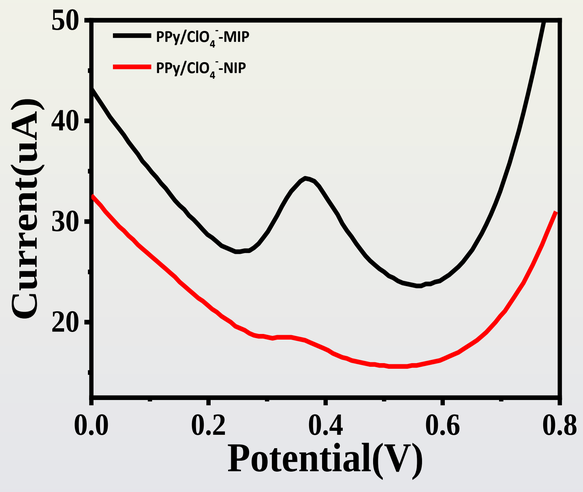


Fig.4 DPV response curves of the PPy/ClO4⁻ MIP and NIP towards a 5ppm AP solution in PBS after incubating for 3min.

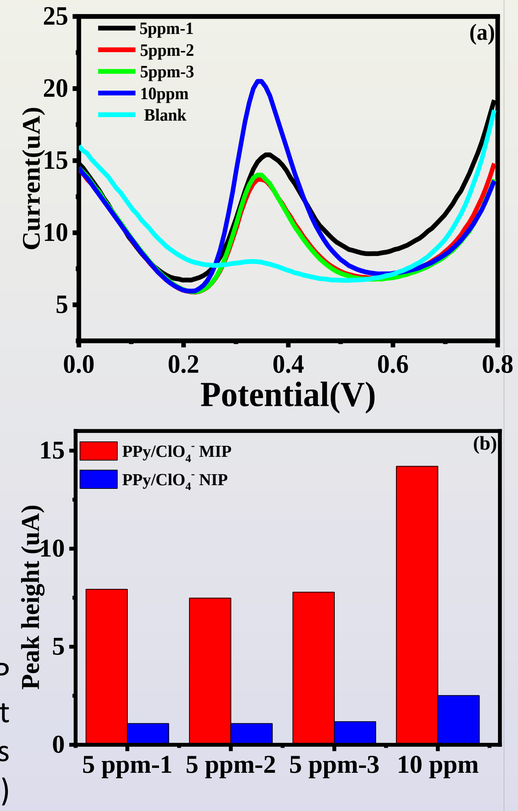


Fig.5 Repeatability of the PPy/ClO4- MIP and NIP response towards a 5ppm AP solution in PBS, and next towards a 10ppm solution. The incubation time was 3min. (a) Raw voltammetric responses for the MIP, (b) peak height for both the MIP and NIP against the run order.

Conclusions

In summary, a facile and rapid electrochemical method for the in situ deposition of PPy/ClO_4^- MIP and NIP films onto the surface of GEC electrodes was proved to be feasible. Particularly, in the response towards acetaminophen, PPy/ClO4⁻ MIP was more effective than PPy/ClO4⁻ NIP.

Future work should focus on the fabrication of other anion doping PPy MIP, especially some organic anions that may contribute to the interaction with polypyrrole plus porous structures, for the more efficient detection of other analytes and further general comparisons of their morphology, structure, and performance. This work will demonstrate the further application prospect of MIP-based electrochemistry biosensors.

Acknowledgements

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References

[1] Rijun Gui, Hui Jin, Huijun Guo and Zonghua Wang, Recent advances and future prospects in molecularly imprinted polymers-based electrochemical biosensors, Biosensors and Bioelectronics 100 (2018) 56-70.

[2] Xavier Cetó, Christopher P. Saint, Christopher W.K. Chow, Nicolas H. Voelcker, Beatriz Prieto-Simón, Electrochemical detection of N-nitrosodimethylamine using a molecular imprinted polymer, Sensors and Actuators B 237 (2016) 613–620.

[3] L. Ozcan, Y. Sahin, Determination of paracetamol based on electropolymerized-molecularly imprinted polypyrrole modified pencil graphite electrode, Sensors and Actuators B 127 (2007) 362–369.