

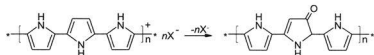
A Novel Molecularly Imprinted Electromodulated Overoxidized Polypyrrole Modified Carbon Fiber for Chiral Separation of Amino Acids

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Aim: To design ultra sensitive and enantioselective on-line sensor for commercial applications.

Introduction: The area of resolution of racemic mixture of amino acids and its derivatives have attracted a great deal of attention during past decade because of their particular interest in food, pharmaceutical and medical industry. A variety of separation techniques have been explored with a great potential for commercial applications. Among them, molecular imprinting technique is one of the most powerful tool for the preparation of artificial polymers to recognize target molecule. Although, conducting polymers can detect molecular details in more precise manner through a cavity created by a dopant, based on molecular imprinting protocols. However, it has not yet been reported that such recognition becomes possible if polypyrrole film is dedoped by overoxidation. In the present work, overoxidized polypyrrole (OPPy) film having versatile molecular recognition system through doping of L-glutamate as a template molecule have been used as a molecularly imprinted polymer matrix (Fig. 1).

Results: Polypyrrole is overoxidized chemically or electrochemically to cause dedoping as follows^{1,2}.



To give clear evidence to overoxidation process, we have carried out FT-IR, ESR and STM characterization to identify carbonyl group, evaluate spin concentration as a measure of degree of conjugation and see some rearrangement of polymer packing. Optimization of overoxidation parameters have been carried out by EQCM technique. Effect of overoxidation applied potential and electrolyte were studied to yield uniform, porous and dopant free OPpy film. At optimized conditions the OPPY(L-glu) film shows the substantial difference with analyte chirality at pH 1.7 and 0.0

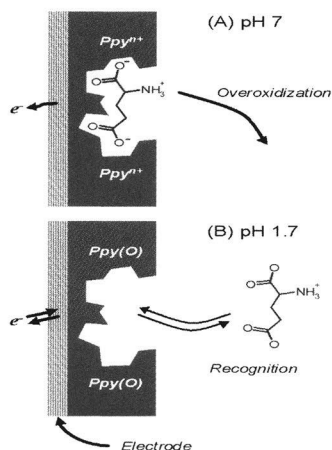


Fig.1 Model for cavity formation and recognition with overoxidized polypyrrole.

V(p1,2). A potential is playing significant role in uptake and release of amino acids. This OPPY(L-glu) system has excellent selectivity for L-glutamate not only over D-glu acid but several other amino acids. We have extended these investigations to sense or separate L-glu from D-glu using OPPY(L-glu) modified carbon fiber packed in electromodulated column, keeping in mind to prepare on-line sensor in conjugation with Cu detector. The repetitive response of column for L- or D- glu is shown in fig. 3.

Discussion: The OPPY film doped with one of the isomer of glu can serve well as a chiral sensor with high chiral selectivity due to closer fit between cavity and target molecule and charge of the OPPY film. The highest transition energy on uptake and release, resulting from such a fit, can be shifted down and up by electrochemical charging of the film. The maximum uptake for L-glu was obtained at 1.7 pH. Glutamic acid preferentially exist as a cation at a pH below 2.2. The uptake dependence agrees well with the distribution of cation (p.2). Thus, this technique enables the use of more precisely traced cavities, which are not accessed by thermal uptake.

Future Work: The present method put forward a new approach for chiral discrimination and will be utilize for determination of free amino acids in food samples.

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References:

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Publications:

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Experimental:

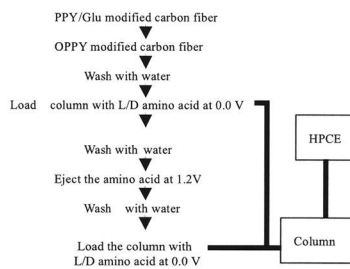


Fig 2. Operation and Functional flow chart of OPPY(L-glu) modified carbon fiber

2. Potential-Induced enantioselective uptake of amino acid into molecularly-imprinted overoxidized polypyrrole, Bhavana Deore, Zhidong Chen and Tsutomu Nagaoka, Analytical Chemistry, 72(17), 3989, 2000
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4. Overoxidized polypyrrole films: A model for the design of enantioselective electrodes (under preparation).
5. Electromodulated OPPY(l-glu/L-lactic acid) modified carbon fiber column for Chiral separation. (Under preparation).
6. Pulsed amperometric detection of underivatized amino acids using copper electrode at acidic pH (Under Preparation).

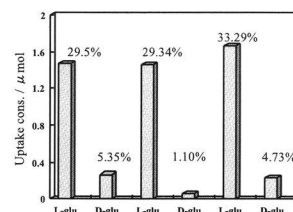


Fig 3. Repetitive response of OPPY(L-glu) modified carbon fiber column for L- or D- glu acid in 1.7 pH at 0.0 V.

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