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Synthesis and Characterization of Poly(pyrrole) Nanopores and Nanowires and Application as Ammonia Sensors

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Abstract – In this work, two types of nanostructured poly(pyrrole) were synthesized in an attempt to obtain ammonia sensors with good performance in terms of sensitivities and response times. Nanoporous poly(pyrrole) (Fig. 1, left) was obtained through template deposition over poly(styrene) colloidal particles, while poly(pyrrole) nanowires (Fig. 1, right) were formed potentiostatically from a 0.15 M Py + 0.2 M Na₂HPO₄ + 10^{-3} M NaClO₄ solution. The sensitivities of nanostructured sensors towards ammonia were higher than those obtained with analogous bulk sensors, due to increased surface area and easier analyte diffusion through the nanostructures.

The development of efficient sensors basically depends on the performance of the transducer and its interaction with the analyte, in a way to provide reasonable sensitivities and short response times. In that sense, a good strategy is to nanostructure the transducer, causing an increase in its electroactive area and enabling an easier diffusion of the analyte through the nanostructures. Many procedures are available to nanostructure a polymeric film, and in this work two of them will be presented: (a) the use of poly(styrene) colloidal crystal template [1] to obtain nanoporous poly(pyrrole), and (b) template-free synthesis of poly(pyrrole) nanowires [2]. These films were employed then as ammonia amperometric sensors, since this analyte is a clinically important compound related to hepatic disorders as cirrhosis and severe hepatitis.

Experimental: (a) The spherical colloidal poly(styrene) particles were deposited on a Pt electrode and then were kept at 100 °C for 4 h. Then pyrrole (Py) is polymerized (potentiostatically, at 0.7 V vs. Ag/AgCl/KCl_{sat}, from a solution containing 50 mM Py + 25mM DBSA) and subsequently nanospheres are removed by immersion in toluene for 24h. (b) Poly(pyrrole) nanowires were grown potentiostatically (0.795 V vs. Ag/AgCl/KCl_{sat}, from a 0.15 M Py + 0.2 M Na₂HPO₄ + 10⁻³ M NaClO₄ solution) on a gold surface deposited over glass. The electrodes were characterized with scanning electron microscopy before ammonia detection tests. Ammonia amperometric detection was performed at 0.35 V in borate buffer (0.1 M and pH 10.0), under constant stirring. Amounts of ammonia were periodically added to the solution, increasing its total concentration in 20 µM per addition.

The procedures used to nanostructurate poly(pyrrole) film were both successful, as depicted in Figure 1. In the case of nanoporous PPy, sensitivities towards ammonia were higher than those obtained with analogous bulk sensors. Figure 2 shows an ammonia detection amperogram (a), and the respective analytical curve (b), obtained when nanoporous PPy was employed as working electrode. The sensitivity in this case was 93.3 μ A cm⁻² mM⁻¹. Other studies concerning a systematic comparison between both nanostructured film performances towards ammonia detection are under development, and will be presented during the meeting.



Figure 1: SEM images of nanostructured PPy: nanopores (left) and nanowires (right)



Figure 2: Ammonia detection at nanoporous PPy.

[1] V. R. Gonçales, M. P. Massafera, T. M. Benedetti, D. G. Moore, S. I. Córdoba de Torresi and R. M. Torresi, J. Braz. Chem. Soc. 20, 4 (2009) 663.

^[2] C. Debiemme-Chouvy, Electrochem. Commun. 11 (2009) 298.