Conducting polymers in environmental analysis

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As a family of materials, conducting polymers (CPs) elicit the possibility of both exploiting the chemical and physical attributes of the polymer for chemical analysis and incorporating its electronic and electrochemical properties to enhance the analytical figures of merit. This review article provides a snapshot of current investigations in many research laboratories on the use of CPs for sensors, separations and extraction techniques.

This review focuses primarily on polyaniline, polypyrrole, and polythiophene and their substituted composites. It includes applications in gas, ion and organic molecule sensors, and solid-phase extraction and microextraction. We also discuss the broad challenges and the accomplishments in preparing analytical devices from CPs.

Keywords: Analytical device; Biosensor; Chemical analysis; Conducting polymer; Environmental analysis; Extraction; Sensor; Separation; Solid-phase extraction (SPE); Solid-phase microextraction (SPME)

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1. Introduction

The emergence of conducting polymers (CPs) has constituted a significant milestone in modern analytical science [1]. The typical CPs includes polyaniline (PAn), polypyrrole (PPy), polythiophene (PTh), and their derivatives. The most common forms of CPs in their neutral states are insulators called conjugated polymers. However, these neutral conjugated polymers can be converted into semi-conductive or conductive states through chemical or electrochemical redox reactions. To extend the functions or to improve the performances of these polymers, CPs are frequently doped with other functional materials to form composites. The general characteristics of these forms were reviewed recently [2,3]. Due to their unique conductive properties, they are usually employed in significant applications in chemistry, physics, electronics, optics, materials and biomedical science, which has prompted the need for analytical methodologies to characterize and to control the quality of these materials [3,4].

Furthermore, construction of sensors, and separation and extraction devices based on CPs is an exciting area of development for modern analytical science [1,5]. The properties of CPs (e.g., high electronic conductivity and mechanical resistance) have driven impressive research efforts in electroanalytical applications in recent years [6]. CPs and their composites are good electrodes or electrode-modifying materials, and can give electrocatalytic activity towards the electro-oxidation of molecules (e.g., formic acid or hydrazine) [7,8]. The intrinsic property allows small ions and molecules to diffuse easily into CP matrices, and thus greatly increases the active sites for electrochemical reactions, which leads to applications in dehydrogenase or oxidase-enzyme-based electrochemical biosensors [9,10]. Besides an increased active surface area of electrode, which gives rise to enhanced electrochemical responses, and a demonstrated anti-fouling capability of electrode surfaces upon modification with CPs, there are important practical advantages over conventional electrode materials. Other reviews specifically dealt with electrochemical biosensors based on CPs and their composite materials [11,12]. We briefly summarize specific applications of CPs in sensors for monitoring pH, inorganic ions, organic molecules and gases.

Another potential application of CPs is in the field of sample preconcentration,

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0165-9936/$ - see front matter © 2012 Elsevier Ltd. All rights reserved. doi:http://dx.doi.org/10.1016/j.trac.2012.06.003

such as solid-phase extraction (SPE) or microextraction (SPME). As previously published [13], large surface area, the ability to establish π–π interactions, and excellent chemical, mechanical and thermal stability make CPs very attractive as SPE or SPME sorbents for extraction or isolation of trace amounts of compounds.

CPs are easily prepared by chemical or electrochemical methods. The chemically obtained CPs can be packed in conventional SPE columns [14]. Similarly, the electrochemically obtained CPs can be deposited on metallic wire or metallic capillary internal walls used in SPME systems [15,16]. Moreover, CPs' sorptive properties can be modified by changing the type of dopant and additives during synthesis. In this sense, many efforts have been made to develop new selective SPE or SPME sorbent materials with CPs and analytical aids. We outline in this review several applications to the trace enrichment of contaminants in water, soil and gas samples.

Considering the huge number of publications concerning analytical applications of CPs and a couple of available reviews focused in this field, we confine this review to significant contributions to the field in recent literature. Thus, we critically review the role of CPs in recent developments of new designs of sensors, separations and extraction devices.

2. Fabrication of conducting polymers

Various methods are available for the fabrication of CPs. However, the most widely used techniques involve oxidation reactions by chemical or electrochemical methods [17–19]. In general, these methods have inherent advantages and characteristics, as summarized in Table 1 [20].

Chemical methods mainly include condensation polymerization or addition polymerization. Condensation polymerization is a step-growth polymerization and proceeds via the loss of small molecules (e.g., hydrochloric acid or water), while addition polymerization (i.e. chain-growth polymerization) is a technique where unsaturated monomer molecules add to a growing polymer chain one at a time. Chemical synthesis not only provides many different possible routes to synthesize a variety of CPs, but also permits the scale-up synthesis of these materials, which is currently impossible with electrochemical synthesis.

Electrochemical synthesis is rapidly becoming a common alternative for preparing CPs because of its simplicity and reproducibility [21]. Electrochemical methods have many advantages over chemical methods, in the sense that they offer control of the polymerization and doping level, and could be produced over a number of substrates in order to fabricate devices directly. The three-electrode system (working, counter, and reference electrodes) was frequently employed in electrochemical procedures. By using electrochemical methods, these polymers can be synthesized by anodic oxidation of the monomers in suitable electrolytes (aqueous or non-aqueous) at constant potential, at constant current, or by cycling the potential. In addition, the nature and the size of counter ions used also have a great effect on the physical properties of CP coatings (e.g., morphology, porosity, mechanical property and thermal stability). Improved mechanical and thermal properties can be achieved for CP coatings incorporating sulfonated aromatic counter ions [22].

From the point of view of separation applications, we recommend the chemical route because large amounts of polymers are needed. Their sorptive properties can be modified by changing the counterions incorporated during the preparation procedure. The chemically-obtained CP can be easily packed in conventional SPE columns.

If the polymeric product is intended for use as a polymer-film electrode, thin-layer sensor, or in SPME, electrochemical polymerization is preferable because potential control is a prerequisite for the production of good-quality material and the formation of the polymer film at the desired spot in order to serve as an anode during synthesis. In brief, all CPs can be synthesized chemically, but electrochemical synthesis is limited to those systems in which the monomer can be oxidized in the presence of a certain potential to form reactive radical-ion intermediates for polymerization.

Table 1. Comparison of chemical and electrochemical polymerization of conducting polymers (CPs) [20]

Polymerization approach	Advantages	Disadvantages
Chemical polymerization	• Larger-scale production possible • Post-covalent modification of bulk CP possible • More options to modify CP backbone covalently	• Cannot make thin films • Synthesis more complicated
Electrochemical polymerization	• Thin film synthesis possible • Ease of synthesis • Entrapment of molecules in CP • Doping is simultaneous	• Difficult to remove film from electrode surface • Post-covalent modification of bulk CP is difficult