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Heterogeneous Carbon Electrodes and Nano-Sized Materials: Some Current Trends

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Abstract

Nanomaterials have stimulated another renaissance in the development of chemical sensors and biosensors during the past decade. Heterogeneous carbon electrodes (carbon paste and screen-printed carbon electrodes) are particularly prone to serving as substrates due to the ease of simple surface or bulk modification.

Key words: carbon paste, screen printed electrodes, nanoparticles, nano-sized material, graphene.

Introduction

After the invention of voltammetry by Heyrovsky in the 1920s a few technical innovations and developments in measurement techniques had significant impacts on electroanalysis leading to its renaissances, such as instrumental and methodical refinements, modification of electrodes and, recently, exploitation of nano-sized materials in the recognition layer of electrochemical sensors. A brief overview will be given in the following paragraphs.

Electrode Materials

Due to a more or less pandemic mercury phobia glassy carbon and noble metals have become predominant, either as direct electron-mediating substrate or as supports of various film electrodes, such as bismuth, antimony, gold and others. Heterogeneous electrodes, in particular carbon paste (CPE) and screen-printed carbon electrodes (SPCEs) have attracted enormous attention due to their feature of being easily modified under mild bio-compatible conditions. Thus, multiple modification with biological components or labile systems is easily possible leading to broad applicability of such sensing systems to a wide variety of analytes..

Nano-Sized Materials

Nanomaterials are currently extensively used to modify sensor surfaces. Gold nanoparticles as "pioneers" in nano-particle-assisted sensorics are still appreciated because of their pronounced ability to chemisorb sulfur-containing compounds, yielding a simple platform for enzyme immobilization. Apart from noble metal nanoparticles from oxides and sulfides, composites and organic compounds and polymers are widely used. Core-shell nanoparticles offer a variety of features, such as specific binding of substrates or easy handling due to magnetic properties [1].

Carbon-based nanomaterials, i.e., graphene nanodots, carbon nano-tubes and nanoribbons, graphene (which is mostly reduced graphene oxide) and graphene nanoplatelets play an almost dominant role nowadays. Functionalization of graphene and its composites with hetero-atoms, functional groups or nanoparticles uncover almost endless possibilities to equip sensors with specific properties and characteristics. Even quantum dots, artificial quasi-atoms with discrete electronic states and fluorescence properties due to electronic space restriction, are exploited for electrochemical purposes.

Nanomaterials have created a new dimension for the design of electrochemical sensors, a tendency that will persist due to the enormous variability with respect to size, shape and composition. Nevertheless it can be noticed already that possibly not all applications where nanomaterials are involved display an inherent necessity to use them, but that authors just follow a fashionable trend to increase the attractiveness of their work [2]. Additionally, disadvantages of the work with nanoparticles are frequently time-consuming and sophisticated operations in combination with poor robustness and short lifetimes (storage and operation). Furthermore, nanomaterials are becoming emerging environmental pollutants [3] with insecure future how legislation will act on their industrial exploitation.

Analytes

The spectrum of analytes covers inorganic and organic ones, supposed they provide an electrochemical or electrocatalytical signal. There is a growing interest in inorganic analytes, for example, in heavy metals. The assays include electrocatalysis [4], accumulation via ionic liquids [5], or enzymatic inhibition [6]. But the main concern of electrochemical sensors are organic compounds of environmental and biological interests. Cancer markers are one topic among many others, such as herbicides, pesticides, toxins, alkaloids and drugs.

Biosensors

Biosensors make up the majority of literature on electrochemical sensors. Enzyme-based sensors, especially oxidoreductases according to the chemical nature of amperometric detection, contribute the biggest share. Wiring of the enzyme for direct electron transfer is one of the main topics as demonstrated with nanoribbons (third generation of oxidase sensors [7]).

Nucleic acids are electroactive and can be directly determined via sorptive accumulation on CPEs. Electro-sorbed double-stranded deoxyribonucleic acid (dsDNA) serves either as accumulator for intercalating species or for interaction studies. Single-stranded DNA is the basis for genosensors via hybridization with target strands.

Immunosensors with immobilized antibodies are concurred by aptamer sensors and molecularly imprinted polymers mimicking synthetic antibodies.

Cytosensors recognize specific cells, most often applied to detect cancer cells; they are usually designed as immunosensors.

Unfortunately, biosensors suffer from many drawbacks with respect to routine analysis and commercialization. Many of them behave like individuals with only fair reproducibility and storability.

Future Prospects

Electrochemical sensors have again undergone some renaissance due to the use of nanoparticles in the receptor of sensors. Modifying enzymes and biological components will increase their stability and robustness. Miniaturization of sensors on chips, sensor arrays for simultaneous determinations and for designing electrochemical noses, tongues or complete micro total analysis systems (µTAS) becomes more efficient by nano-sized materials being applicable in point-of-care testing (POCT). Combination of implanted sensors with micro-electromechanical systems (MEMS) powered by biofuel cells will be extremely useful therapeutic aids in the future.

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