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Review

Applications of nanomaterials in potentiometric sensors

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ABSTRACT

Nanomaterials play an important role in the fabrication of chemosensors and biosensors, due to their unique physical and chemical properties, such as large surface area/volume ratio, good conductivity, excellent electrocatalytic activity and high mechanical strength. We review recent advances in the applications of these nanomaterials in potentiometric sensors. We highlight the development of stable solid-state polymeric membrane ion-selective electrodes (ISEs). We describe ISEs based on ionophore-modified nanomaterials. Also, we present highly-sensitive potentiometric biosensors based on nanomaterials.

Contents

1. Introduction

Potentiometric sensors are an important class of electrochemical sensors, which detect the relationship between the activity of analyte species and the observed potential response with the two-electrode system comprising an indicator electrode and a reference electrode. Ion-selective electrodes (ISEs) with polymeric membranes containing selective carriers (ionophores) are the most commonly-used potentiometric sensors. They have been widely used for directly determining various inorganic and organic ions in medical, environmental and industrial analyses [1,2]. Compared

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with other analytical techniques, ISEs have some unique characteristics, such as small size, ease of operation, portability and low cost. In the past few years, ISEs have made great progress in improving the lower limit of detection (LOD), exploiting new membrane materials, proposing new sensing concepts and developing deeper theoretical research about potentiometric responses [2].

Nanomaterials, including nanotubes, nanowires, nanofibers, nanorods, nanoparticles, nanocomposites and other nano-structured materials, have been widely applied to fabricate a variety of chemosensors and biosensors based on their unique physical and chemical properties, such as large surface area/volume ratio, good conductivity, excellent electrocatalytic activity and high mechanical strength [3]. In recent years, nanomaterials were gradually introduced into potentiometric sensors (Fig. 1). For example, the exceptional electrical properties and good hydrophobicities of nanomaterials make them suitable as solid contacts for solid-state ISEs. The immobilization of the ionophore on nanomaterials not only eliminates its leaching from the ion-selective membrane, but also develops an alternative sensing membrane. Also, potentiometric biosensors with new sensing concepts have been developed based on the functionalization of nanomaterials with receptors. The most important contributions of nanomaterials to the field of potentiometry are shown in Table 1.

Based on the significant development of advanced materials, this review summarizes the applications of nanomaterials in potentiometric sensors, including the stable solid-state ISEs based on nanomaterials as solid contacts, ISEs based on ionophore-modified nanomaterials and nanomaterial-based potentiometric biosensors.

2. Nanomaterial-based solid-state ion-selective electrodes

2.1. Nanomaterials as solid contacts

Solid-contact ISEs are regarded as the most promising generation of potentiometric ion sensors, due to their durability, ease of miniaturization and low maintenance. A solid contact between an electronic conductor and an ion-selective membrane is the essential element for fabricating a stable solid-state polymeric membrane ISE, since its intrinsic property significantly influences the potential stability and reproducibility for long-term use [4]. In the past few decades, various electroactive materials with ionic and electronic conductivities have been extensively investigated as solid contacts in order to obtain stable analytical performance. Conducting polymers, such as polypyrrole (PPy), poly(3-octylthiophene) (POT) and poly(3, 4-ethlyenedioxythiophene) (PEDOT), are commonly used ion-to-electron transducer materials, as reviewed by Bobacka et al. [2,5]. However, these materials suffer from some limitations, such as light sensitivity [6], uptake of POT by the membrane [7], remnants of salt from the polymerization process that

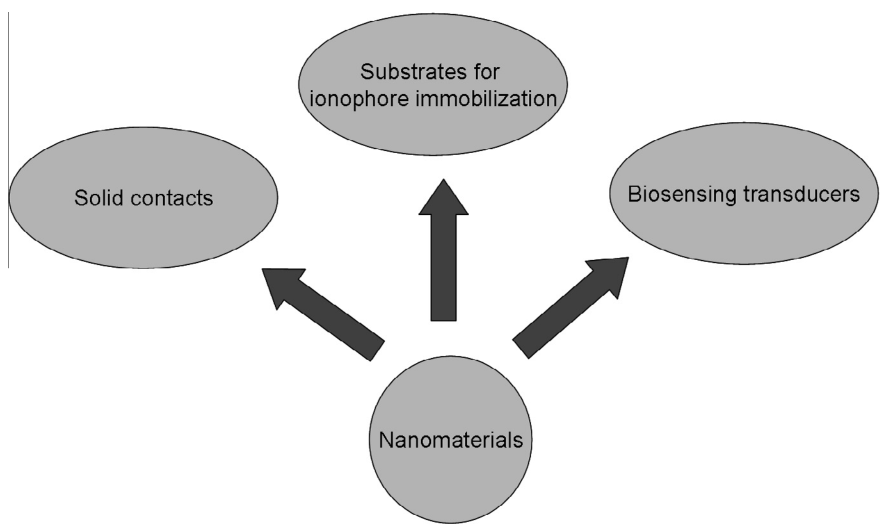

Fig. 1. The most important applications of nanomaterials in potentiometric sensors.

Table 1
Timeline of the most important contributions of nanomaterials to the field of potentiometry

Year	Nanomaterials	Applications
2003	Biotin-modified gold nanopores	Label-free potentiometric protein sensor
2007	3DOM carbon[a]	Solid contact
2008	Carbon nanotubes	Solid contact
2009	Polycarbonate nanopore membrane	Ion-channel mimetic sensor for protein detection
	Aptamer-modified carbon nanotubes	Potentiometric aptasensor
2010	Ionophore-modified gold nanoparticles	Ionophore immobilization
2011	Gold nanoparticles	Solid contact
	Graphene	Solid contact
	Ionophore-modified carbon nanotubes	Ionophore immobilization
	Ionophore-modified gold nanopores	Solid-state ion-channels
2012	Gold nanocluster	Solid contact
	Ionophore-modified gold nanoparticles	Potentiometric sensing membrane

[a] 3DOM carbon, Three-dimensionally ordered macroporous carbon.