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Recent advances for cyclodextrin-based materials in electrochemical sensing

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ABSTRACT

Owing to the hydrophobic inner cavity and hydrophilic exterior of cyclodextrins (CDs), CDs molecules could exhibit excellent properties in water solubility, molecular recognition and enrichment capability, and CDs-based materials attracted considerable attentions in electrochemical sensing. This review shows the unique advantages and detecting mechanism of electrochemical sensors based on CDs functionalized materials, and recent advances for CDs-based materials (including CDs/carbon nanotubes, CDs/graphene, CDs/conducting polymers and other CDs-based nanomaterials) in electrochemical sensing. Finally, we also discussed some critical challenges and prospects in this field.

Contents

1. Introduction

Electrochemical sensing has received many attentions and been used widely in the detection of biomolecules and environmental pollutants due to its cheap and portable instruments, low cost and rapid analysis, high sensitivity and selectivity. And the selection and development of effect materials for modifying electrodes are key factors to improve the sensitivity and selectivity of electrochemical sensing [1–4].

Cyclodextrins (CDs), including α-, β- and γ-cyclodextrins (α-, β- and γ-CD, Fig. 1), are a kind of oligosaccharides composed of six, seven, and eight glucose units, respectively. CDs molecules have a toroidal shape with a hydrophobic inner cavity (due to the presence of a glycosidic oxygen bridges and hydrogen atoms from OH groups) and a hydrophilic exterior (due to the presence of primary and secondary hydroxyl groups) [5,6]. The hydrophobic inner cavity could enable CDs molecules to bind selectively various organic, inorganic, and biological guest molecules in their cavities to form host-guest inclusion complexes or nanostructured supermolecular, showing high molecular selectivity and enrichment capability. And the hydrophilic exterior could make CDs as functional molecules to improve the dispersibility of functional materials in solvents. Furthermore, CDs are environmentally friendly, low-cost and easy-to-get [7–9]. These interesting characteristics resulted that CDs have important promising applications in electrochemical sensing.

In recent years, CDs-based materials attracted many attentions in the field of electrochemical sensing. These materials mainly focused on CDs-functionalized carbon nanomaterials (carbon nanotubes (CNTs) and graphene) and CDs-modified conducting polymers. Herein, we discuss the unique advantages and detecting mechanism of electrochemical sensors based on CDs-based materials, and recent advances for CDs/CNTs, CDs/graphene,

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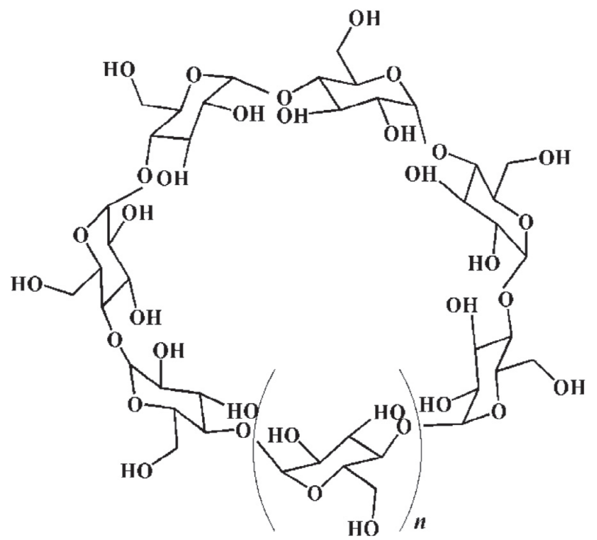

Fig. 1. The structure of CDs ($n = 0$, α-CD; $n = 1$, β-CD; $n = 2$, γ-CD).

CDs/conducting polymers and the other CDs-based materials in electrochemical sensing. In this review, the design proposals, synthesis methods and applications of CDs-based materials were discussed in detail.

2. The unique advantages and detecting mechanism

CDs can be viewed as "molecular shape sorters" and have a hydrophobic inner cavity and a hydrophilic exterior. The inner cavity provides the ability to selectively bind and retain analytes of proper geometrical fitting in their cavities. Different targets have different binding constant and bonding strength with CDs' cavities. Whereas the exterior could make CDs as functional molecules to improve the dispersibility of functional materials, this is very important for the high stability and sensitivity of snesors. For CDs-based carbon nanomaterials, the CDs molecules could be anchored to the carbon substrates surface by many methods, such as noncovalent and covalent reactions, and the nanomaterials could exhibit the synthetic properties of both CDs and carbon nanomaterials [10–12]: CDs could improve the dispersibility, molecular recognition and enrichment capability of nanohybrids (pure CNTs and graphene are insoluble in solvents and tend to form irreversible agglomerates due to the high hydrophobic surface), carbon nanomaterials could provide large surface area, high conductivity, and even high electrocatalysis, thus resulted the excellent electrochemical sensing performance of CDs-based carbon nanomaterials. The selectivity, sensitivity, and detection limit based on CDs-based carbon nanomaterials are mainly determined by the amount of CDs molecules on carbon substrates surface and enrichment capability towards analytes. For CDs/conducting polymers, CDs could be incorporated into polymeric films and attached to the backbone by nucleophilic attack reaction and etc. Besides of the host-guest interaction and molecular enrichment capability of CDs, the conducting polymers could offer featured charged groups (positive or negative charge), and most of conducting polymers have high electrocatalysis toward guests [13–15], thus further improving the sensitivity and selectivity of CDs/conducting polymers in electrochemical sensing owing to the unique effects of CDs and conducting polymers.

3. CDs based carbon nanomaterials

3.1. CDs/CNTs

CNTs, including single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs), are comprised of single or multiply-nested graphene sheets that are seamlessly wrapped into cylindrical tubes with diameters of between 0.4 and 100 nm. The lengths of these nanotubes can range from a few nanometers to several micrometers. The CNTs possess high electrical conductivity (1000–2000 S/cm), large theoretical surface areas (~1315 m^2/g; the actual values are scattered from 1315 m^2/g for SWCNTs to ~50 m^2/g for MWCNTs), excellent physical and chemical properties (low density, high mechanical strength, good chemical and thermal stability) that enable a wide range of electrochemical sensing applications [16–19]. However, the intrinsic van der Waals interactions between the pristine tubes make CNTs bundle together on a large scale and are insoluble in routine solvents, resulting in the severe restriction of the applications [20]. By combining CDs and CNTs, a novel nanomaterial possessing the synergetic properties of both CDs and CNTs could be obtained. In this section, we outline the recent advances in CDs/CNTs based electrochemical sensors.

Initially, many scientists prepared CDs/CNTs nanocomposites be simply mixing CNTs and CDs in different solvents and used the nanocomposites for electrochemical sensing of rutin [21], tyrosine [22], dihydroxybenzene isomers [23], chlortetracycline [24] and etc. In these systems, the interactions between CDs and CNTs are mainly hydrophobic interactions and Van der Waals attraction forces [25]. For instance, by dispersing MWCNTs in DMF solution containing β-CD, Shen and Wang [26] prepared a nanocomposites of β-CD and MWCNTs. Then, the nanocomposites were deposited on glassy carbon electrodes (GCE) and used for the simultaneous determination of guanine, adenine and thymine. The voltammograms of bases adenine and thymine exhibit just two small hump peaks and the voltammograms of base guanine could not be observed at the bare GCE. In the case of nanocomposites of β-CD and MWCNTs modified GCE, the peak current of adenine and thymine enhance significantly, and meanwhile the base guanine could be also detected. Diao's group [25] prepared β-CD polymer functionalized MWCNTs via mixing β-CD polymer and MWCNTs in water under sonication for 2 h, and the β-CD polymer-MWCNTs nanocomposites were used for supramolecular recognition of ferrocenemethanol and p-aminothiophenol. Although the CDs/CNTs hybrids prepared by these methods could exhibit the synthetic properties of CDs and CNTs, the structure and morphology of the obtained hybrids are not uniform, and the CDs molecules are peeled easily away from CNTs surfaces due to the weak binding force between CNTs and CDs.

Recently, Wang and Huang et al. [27] prepared a SWCNTs/pyrenecyclodextrin (SWCNTs/PyCD) modified GCE for the determination of 3,3′,4,4′-tetrachlorobiphenyl using an electrochemical impedance spectrum (Fig. 2). With the aid of a pyrenyl group, PyCD could tightly attach to the sidewall of SWCNTs by means of π–π stacking interactions. If 3,3′,4,4′-tetrachlorobiphenyl molecules are captured by the cavities of the PyCD hosts, the formation of guest–host complexes could create a barrier for the electrochemical process, thereby hindering the access of the redox probe to the electrode surface, resulting in an increase in the electron-transfer resistance. Next, Wang and Huang et al. [28] used the obtained SWCNTs/PyCD nanohybrids for the first time on the redox-reaction-based electrochemical detection of p-nitrophenol. The advantages of this nanohybrid are that p-nitrophenol molecules could be captured by PyCD, the different complex formation constants of PyCD with other guest molecules results in the ultrahigh selectivity, and the rapid electron transfer of the π-electron systems (pyrene rings) linked CD and SWCNTs result in high sensitivity via a direct redox reaction. The SWCNTs/PyCD shows a sensitivity of