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Electrochemical sensing of heavy metal ions with inorganic, organic and bio-materials

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ABSTRACT

As heavy metal ions severely harm human health, it is important to develop simple, sensitive and accurate methods for their detection in environment and food. Electrochemical detection featured with short analytical time, low power cost, high sensitivity and easy adaptability for in-situ measurement is one of the most developed methods. This review introduces briefly the recent achievements in electrochemical sensing of heavy metal ions with inorganic, organic and bio-materials modified electrodes. In particular, the unique properties of inorganic nanomaterials, organic small molecules or their polymers, enzymes and nucleic acids for detection of heavy metal ions are highlighted. By employing some representative examples, the design and sensing mechanisms of these electrodes are discussed.

Contents

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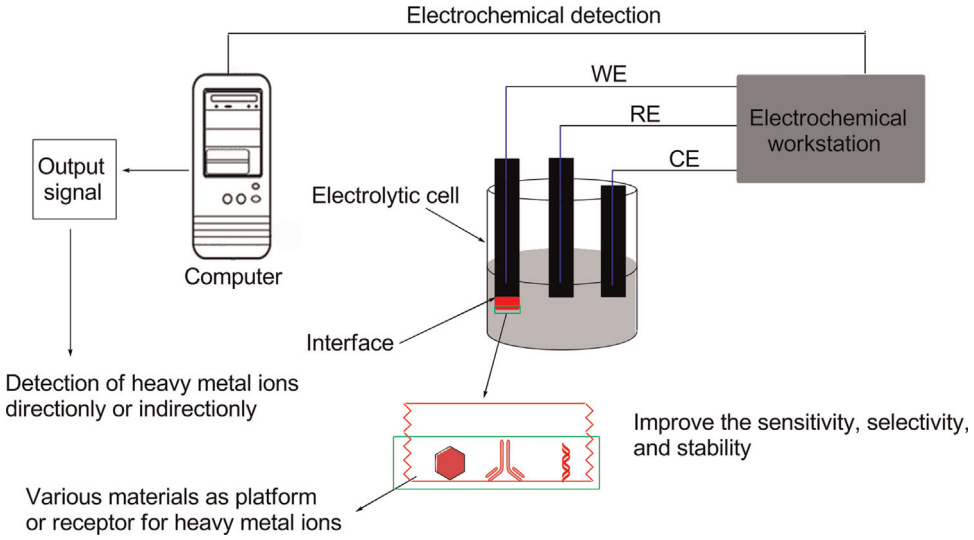

Fig. 1. Schematic illustration of general principle of electrochemical sensing of heavy metal ions.

1. Introduction

Since heavy metal ions are non-biodegradable and can be accumulated in soft tissues, they are considered as the serious source to pollute the biosphere throughout the world and cause many healthy and physiological diseases (Kemper and Sommer, 2002; Tu et al., 2004; Tuzen et al., 2006). Therefore, sensitive and selective determination of toxic heavy metals with a cost-effective and convenient procedure is paramount important. Various techniques have been developed for the detection of heavy metal ions, including electrochemical (Aragay and Merkoçi, 2012), mass spectrometric (Ugo et al., 2001) and optical methods (Kim et al., 2012). For example, atomic absorption spectrophotometry (AAS) has been widely used for the detection of metal ions in industry. This technique can simultaneously detect different ions with high sensitivity, selectivity and accuracy. However, it requires relatively expensive instrument and specialized personnel to carry out the operational procedures. Due to the capability of short analytical time, low power cost, high sensitivity and easy adaptability for in-situ measurement (Wong et al., 2007), electrochemical detection methods have attracted great interest in the detection of heavy metal ions.

The electrochemical detection is normally performed with a three-electrode system containing a working electrode (WE), a reference electrode (RE) and a count electrode (CE) (Fig.1). The WE can be modified with different materials for specific recognition or/and concentration of metal ions (Bontidean et al., 1998; Pan et al., 2009). The presence of heavy metal ions causes the change of current, potential, electrochemical impedance, capacitance or electrochemiluminescence, which can then be used for their detection (Combellas et al., 2008; Fan et al., 2009). Based on these detection signals, the electrochemical sensings can be classified to amperometric, potentiometry, electrochemical impedance, capacitance and electrochemiluminescent methods.

Recent advances in new materials, especially the development of nano- and bio-materials, have opened a new era of analytical techniques. In particular, due to their unique electronic, physical, chemical and mechanical properties, nano- and bio-materials have been explored their extensive applications in electrochemistry (Zhang and Fang, 2010). By tailored functionalization and assembly, these materials can be easily assembled on electrode surface for the fabrication of sensing electrodes and the sensitive and selective detection of heavy metal ions. The assembly of different materials can further improve the electrochemical performance. For example, polymers or biomaterials are frequently assembled on inorganic nanomaterials to construct the highly sensitive electrochemical sensors for heavy metal ions (Chey et al., 2012; Gong et al., 2010; He et al. 2011; Kong et al., 2009; Liu et al., 2010; Pan et al., 2009; Sánchez et al., 2010; Shao et al., 2012; Sudibya et al., 2011; Tang et al., 2013; Wang et al., 2012). This review discusses the design and sensing mechanisms of these electrochemical sensors and introduces the recent advances in electrochemical sensing of heavy metal ions. For clear illustration, the sensing strategies are classified into inorganic, organic and biomaterials modified electrodes, in which the hybrid materials are introduced respectively.

2. Inorganic nanomaterials for electrochemical sensing of heavy metal ions

Benefiting from the intrinsic advantages of regular structure, chemical and thermal stability, high surface reaction activity and catalytic efficiency, large surface-to-volume ratio and strong adsorption ability (Kaushik et al., 2008), inorganic nanomaterials are often used for electrode modification. In particular, metal, metal oxide, carbon and silica based nanomaterials are the most commonly used inorganic nanomaterials in electrochemical detection of heavy metal ions.

2.1. Metal nanoparticles

Metallic nanostructured materials exhibit unique electrical, optical and catalytic properties. Meanwhile, by functionalizing metallic nanoparticles with small chemical and bio-molecules, various detection methods with high specificity have been designed for heavy metal sensing.

Early electroanalytical methods frequently employed the hanging mercury drop and mercury-film based electrodes to detect the heavy metals, because of their wide cathodic potential range, high sensitivity and repeatability (Ensafi et al., 2004; Shams et al., 2004). With the increasing concern about the toxicity of mercury to the environment and the difficulty in handling, storage, and disposal, the use of mercury as an electrode material was banned, and mercury-free solid-state electrodes, such as bismuth and stannum based electrodes, emerged for heavy metals detection. By co-deposition of bismuth and target metals on the glassy carbon or carbon-fiber substrate, bismuth-film electrodes could