Nanomaterial-based electrochemical sensors for arsenic - A review

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ABSTRACT

The existence of arsenic in the environment poses severe global health threats. Considering its toxicity, the sensing of arsenic is extremely important. Due to the complexity of environmental and biological samples, many of the available detection methods for arsenic have serious limitations on selectivity and sensitivity. To improve sensitivity and selectivity and to circumvent interferences, different electrode systems have been developed based on surface modification with nanomaterials including carbonaceous nanomaterials, metallic nanoparticles (MNPs), metal nanotubes (MNTs), and even enzymes. Despite the progress made in electrochemical sensing of arsenic, some issues still need to be addressed to realize cost effective, portable, and flow-injection type sensor systems. The present review provides an in-depth evaluation of the nanoparticle-modified electrode (NME) based methods for the electrochemical sensing of arsenic. NME based sensing systems are projected to become an important option for monitoring hazardous pollutants in both environmental and biological media.

1. Introduction

Among various heavy metals, arsenic (As) is one of the most significant environmental hazards because it threatens the lives of several hundred million people (Clancy et al., 2013; Smedley and Kinniburgh, 2002; Smith et al., 2002). In natural waters, arsenic species are generally found in the form of arsenite (As(III)), arsenate (As(V)), monomethyl arsonic acid (MMA), and dimethyl arsinic acid (DMA). Among these, the inorganic forms of As(III) and As(V) are the predominant species in natural water that have enhanced toxicity and greater mobility. The guideline values for the permissible amount of As in drinking water is set at 10 ppb by the World Health Organization (Aragay et al., 2011). Therefore, sensitive and selective analysis of inorganic arsenic in various environmental matrixes, such as ground and drinking water, is of high importance to identify the contaminated source, to increase the efficiency of water treatment processes, and to establish proper regulation (e.g., by public health agencies) (Nath et al., 2014).

Some of the well-known analytical methods reported for the determination of inorganic As include inductively-coupled plasma mass spectrometry (ICP-MS), hydride-generation atomic absorption and emission spectrometry (HG-AAS/AES), atomic fluorescence spectrometry (AFS), and high-performance liquid chromatography (HPLC) (Luong et al., 2007). However, these methods require expensive and sophisticated instruments, high operating costs, and complicated sample preparation processes (e.g., digestion or clean-up steps). Additionally, as these techniques are time-consuming, they may not be suitable for routine and on-field analysis.

Electroanalytical techniques have been proven to be a promising alternative for both qualitative and quantitative analysis to replace the conventional methods. The electrochemical sensing systems offer the advantages of simple instrumentation, high sensitivity, selectivity, ease of use, miniaturization, minimal sample pretreatment, short analysis time, and portability. Considerable research efforts have been made to develop portable electrochemical sensors to analyze inorganic arsenic in the environment. In the development of electroanalytical sensing systems for the determination of inorganic arsenic, the sensing electrodes are often modified with suitable materials to achieve desired enhancements in sensitivity and selectivity.

Over the decades, a wide range of modification protocols was explored, ranging from synthetic metal ionophores to biological receptors such as DNA or proteins (Aragay et al., 2011). Recent reports concluded that the design and construction of nanoparticle-modified electrodes could be very effective in electrochemical sensor technology (Tang and Cheng, 2013). In this context, the development of electrochemical sensors based on nanoparticle-modified electrodes, e.g.
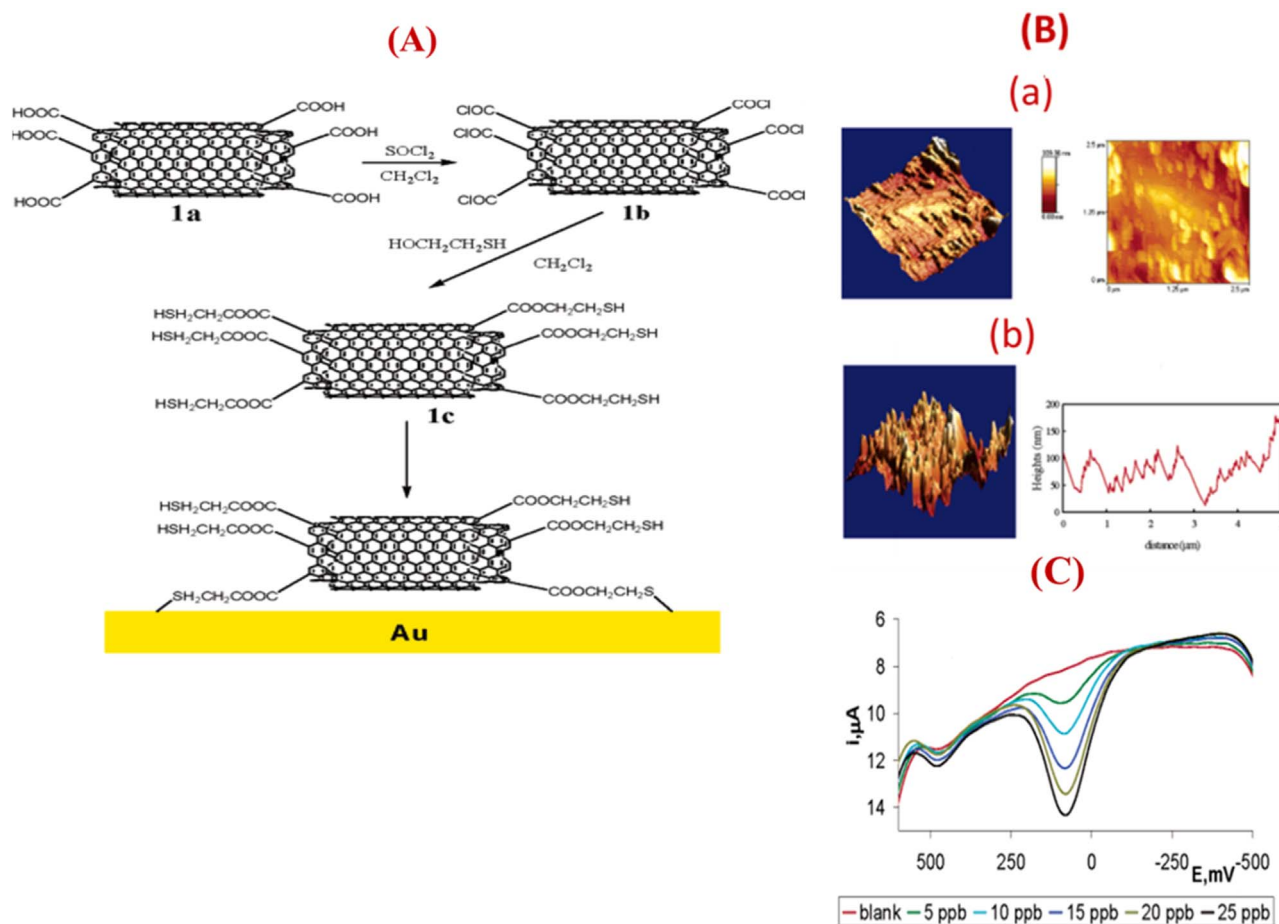
Fig. 1. (A) Schematic for the preparation of chemically modified Au electrode with functionalized MWCNTs: 1a) acylation, 1b) thiolation, and 1c) derivatization of MWCNTS-COOOCH$_2$ SH$_2$ on Au electrode. (B) AFM images: (a) AFM images of a representative portion of MWCNT CME surface. (b) AFM image of a representative portion of SWCNTs CME. (C) Voltammetric curves for As(III) in the presence of As(III) on MWCNTs (Profumo et al., 2006).

carbon nanoparticles, MNPs, and MNTs, has become one of the most active research areas (Chen and Liu, 2014; Fan et al., 2016; Barsan et al., 2015; Oja et al., 2013; Pu et al., 2016). The nanoparticles exhibit unique chemical, physical, and electronic properties that cannot be achieved by other sensory materials or even by the same bulk materials from which the nanoparticles were prepared (Hu and Dong, 2008). The nanomaterial-modified electrodes, when used for electrochemical analysis of heavy metals, exhibit dramatically increased sensitivity due to the enhancement of specific surface area and related surface free energy. The NP-modified electrodes can also be designed as random arrays of microelectrodes and can offer distinct advantages over conventional macro electrodes in terms of increased mass transport, reduced solution resistance, low detection limit, and better signal-to-noise ratio.

This review summarizes recent advances in the development of diverse nanomaterial-modified electrode interfaces for electrochemical sensing of inorganic arsenic (As (III) and As (V)). Such sensor designs have helped to enhance the analytical performance of the existing electroanalytical sensing systems in terms of sensitivity, selectivity, field portability and multiplexed detection capability. The potentials and drawbacks of different systems are addressed and discussed in detail. According to the latest reports, the use of nanoparticle-modified electrodes are set to meet the commercial challenges in developing cost effective, field portable, and highly selective sensors and test kits to monitor arsenic in drinking water and other environmental samples. (Note that some details of Sections 3 through 6 are placed in Supplementary Materials along with relevant data (Tables 1S through 7S) and graphics (Fig. 1S through 14S) because of space limitations.)

2. Types of nanoparticles used for electrode modification and methods to stabilize them

There are many types of nanomaterials employed for the modification of electrodes for electrochemical sensing including: carbon nanoparticles, noble MNPs, metal oxide nanoparticles, and bimetallic nanoparticles (Aragay et al., 2011). Various methods have been developed and employed for the synthesis of the target NPs including chemical reduction, UV-photo activation synthesis, laser pulse methods, and sonochemical methods (Aragay et al., 2011). Among these options, the chemical reduction of metal salts is one of the most popular methods due to several advantages over physical methods (Aragay et al., 2011). The NPs may undergo aggregation to result in an increase in particle size, which affects their catalytic properties. That is, larger particles generally have less activity compared to well-dispersed or smaller nanoparticles. Therefore, it is desirable to minimize aggregation via functionalization of the NPs which, in turn, also provides stability to the NPs dispersions. Surface derivatizations of MNPs can generally be achieved via several approaches including: the deposition of a layer of another inorganic substance (inorganic core-inorganic shell composites), the attachment of organic capping agents, and the covalent binding of biomolecules (i.e., DNA and antibodies) at the interface. The stabilization of MNPs has also been achieved through electrostatic or steric mechanisms.