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Direct ultrasensitive redox sensing of mercury using a nanogold platform

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ABSTRACT

Rapid industrialization and innovative material processing routes have resulted in the contamination of natural resources. Qualitative and quantitative estimation of mercury in food, beverages, water sources, and other environmental media has become of prime importance for human well-being. The present healthcare sector desires cheap, easy to use, and portable field-based monitoring kits for the detection of hazardous pollutants like mercury. In view of these facts, there is a strong need for robust, cost effective, reproducible, ultrasensitive, selective, and portable technology for the detection of mercury in samples. Here, we report the facile direct redox sensing of mercury ions at the ppb level. In this work, a combined application of linear sweep voltammetry (LSV) and chronoamperometry techniques was made for the direct electrochemical sensing of mercury ions on a nanogold platform. This is the first report in which the direct electrochemical sensing of mercury is demonstrated based on LSV & chronoamperometry techniques without the use of any biomolecule/co-coordinating ligand. LSV works in one direction/sweep, thereby diminishing the possible occurrence of interfering agents in a reverse sweep. This new approach is more reliable, robust, ultrasensitive, and user friendly relative to previous methods. The fabricated Au/Nafion/GC electrode showed ultra-high sensitivity of 11.75 μA cm^{-2} ppb^{-1} [detection limit of 3.78 ppb (19 nM) with a linearity ranging up to 50 ppm] at a response time of <2 s, demonstrating wide applicability and efficacy of this technique for sensing mercury.

1. Introduction

The agricultural community is facing an uphill battle for producing sufficient quantity and quality of food to feed the continuously increasing global population without compromising ecosystems. Domestic and commercial industries are producing large amounts of toxic waste that are exceedingly dangerous to the environment as well as to human health. Most natural resources have become victim to human technological advancements. Despite great progress in fabrication technology, process automation, packaging, and portability of devices, there is still a great challenge regarding simplified processes for the estimation, handling, and management of hazardous substances that are released into the environment as a consequence of technical development. Industries are therefore engaged in competition to produce complex, lightweight, portable, and multifunctional products to detect waste emerging from different chemical and physical processes.

Advancements in technology have resulted in the generation of higher concentrations of heavy metals into the ecosystem. In many aquatic environments, water quality is not properly observed and poses an ecological hazard to animals and humans. As such, the problem of waste disposal has become a serious socioenvironmental issue [1–3]. The qualitative and quantitative estimation of these harmful contaminants is mandatory and is desired at regular intervals to keep track of sources that emit these dangerous substances. The problem is quite severe in that metals are non-biodegradable, are persistent in the environment, can be transported with sediments, and are bio-accumulated in the food chain. Of the various toxic heavy metals, mercury is one of the major contaminants present in the environment. Mercury cells, mercury bulbs, metal plating industries, run-off from industrial waste and croplands, and flood and mining industries are the major sources of mercury [3]. This toxic substance becomes part of the food chain through exposure in the water, soil, and air. In humans, mercury interferes with many proteins, DNA, enzymes, and other biomolecules resulting in numerous poisonous and mutagenic effects. It also disturbs cholesterol levels and several kidney-related diseases are the consequence of mercury poisoning [3–5].

For quality management, the qualitative and quantitative estimation of mercury is of prime importance to effectively lower concentrations of mercury in air, food, and beverages/drinking water below permissible limits. A number of instrumental systems including absorption and emission spectroscopy, ICP-MS (inductively-coupled plasma-mass spectrometry), and WD-XRF (wavelength dispersive X-ray fluorescence spectrometry) have been used for the determination of mercury in different samples. All these techniques have certain limitations such as the need for large sample volume, skilled personnel, sample pretreatment, costly instrumentation, high cost per sample, and time consuming protocol [6–8]. Moreover, most of these conventional techniques cannot be

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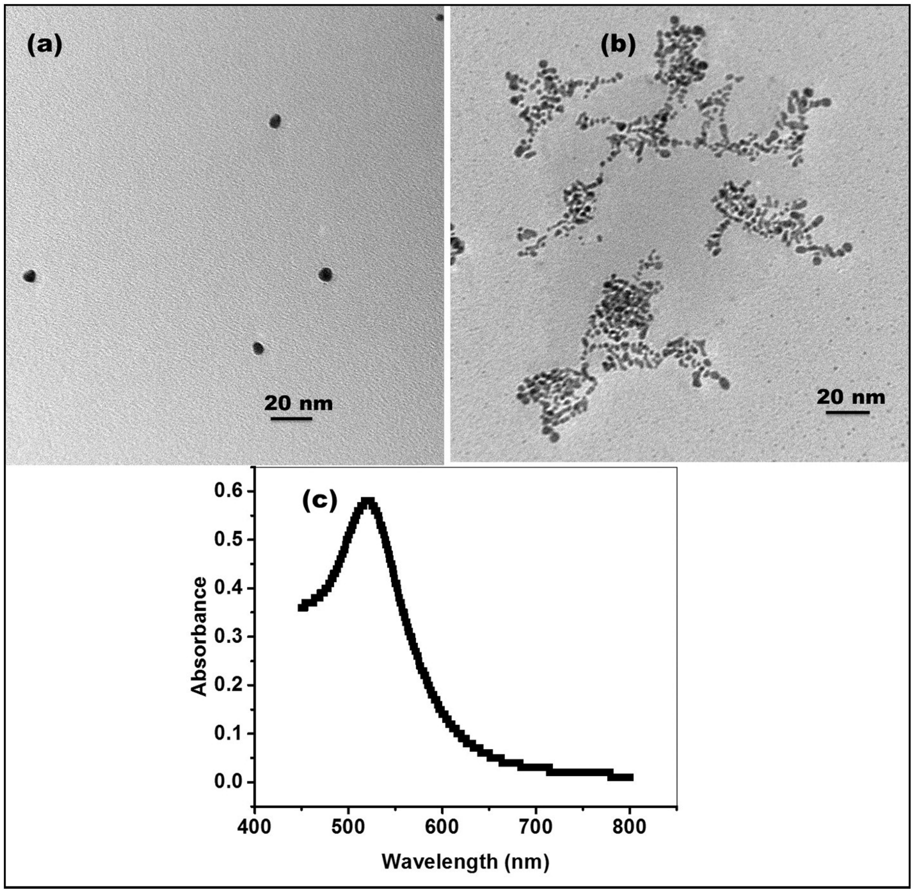

Fig. 1. TEM images of gold nanoparticles (Au NPs) in the (a) segregated and (b) aggregated form. (c) A UV–Visible plot of as synthesized Au NPs.

used for the on-site detection of mercury in real field conditions. Further, the limit of detection with these techniques sometimes cannot go beyond a specific value without pretreatment. Electrochemical and optical detection of heavy metals has gained attention among scientific community in recent times. Chemically and biochemically electrodes modified with nanomaterials are being utilized for electrochemical determination of various heavy metals. Different materials like amalgams, alloys, macromolecules, caged molecules, proteins and nucleic acid have been used as recognition elements for selective and sensitive determination of different heavy metals including mercury. Light absorption, light emission and fluorescence techniques with synthetic receptors have been explored for optical detection of these heavy metals [9–12].

The underlying principle behind the present work on mercury detection is that mercury is a redox active species with specific electrode potential. Thus, it can be detected with the help of electrochemical sensing. Due to its unique and specific electrode potential value, the chances of interference with ionic species other than mercury diminishes during electrochemical sensing. In recent years, the electrochemical detection of certain analytes (drugs, pesticides, biologically active compounds, antigens, and pathogens) has revolutionized the field of sensor technology [13–15]. Likewise, several techniques for the electrochemical sensing of mercury have been reported in recent years. Of these, a few studies dealt with stripping voltammetry for the detection of mercury species, while others relied on the fabrication of a sensing element like DNA or another metal-coordinating group on the electrode surface. Stripping voltammetry detection of mercury requires pre-concentration steps, expert handling, large sample volume, and significant time. Toxicity of the mercury electrode used in stripping voltammetry in and of itself poses a problem when disposing mercury; hence, it represents a major disadvantage along with other limitations. Recent advances in electrode fabrication by modification with a variety of materials for electrochemical sensing has shown great potential towards the identification and estimation of different analytes in varying atmospheric conditions like temperature, pH, and other interfering compounds [16–21]. Major limitations associated with the electrochemical biosensing of mercury include limited shelf life of the electrode, complex procedure, reproducibility, and lack of stability.

The utilization of nanomaterials and their hybrids can assist in the rapid, on-site, selective, and ultrasensitive electrochemical sensing of mercury. Mercury contained in a minimum sample volume as small as a few microliters can be quantified through electrochemical detection without any pretreatment. Modification of the electrode surface using a suitable nanomaterial to render a high surface area, enhanced electron communication feature, and efficient electron shuttle between mercury ions/analyte and the electrode is required [22,23]. Out of the different metal nanoparticles, gold has been used extensively in sensing applications. Various optical, electrochemical, fluorescent, electrical, SPR (surface plasmon resonance), and surface enhanced Raman scattering (SERS)-based sensors have been reported using gold nanoparticles (Au NPs). A number of advantages, including ease of synthesis, high conductivity, enhanced catalytic properties, and large surface area, are attractive to make Au NPs an excellent choice in electrochemical sensing. These extra ordinary features help make the sensor ultrasensitive, robust, selective, and with higher affinity towards the analyte of interest [24].

This research reported here describes the facile chemical synthesis of Au NPs and the fabrication of an Au/Nafion/GC electrode for the robust and uncomplicated redox sensing of mercury ions using a LSV (linear sweep voltammetry) technique. The LSV technique is easy to operate and requires less than a minute for recording output. Further, the sensing profile is observed without any pre-concentration steps or the need for skilled personnel. Easy handling and portability provides the Au/Nafion/GC electrode as a nice platform for utilization in point of care analysis.