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Zinc Oxide Quantum Dots as Efficient Electron Mediator for Ultrasensitive and Selective Electrochemical Sensing of Mercury

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ABSTRACT

Heavy metals especially mercury represents one of the most hazardous substances that need to be estimated and monitored. Even though various qualitative and quantitative methods have been used to classify or eliminate mercury, but most of the processes entailed complex routes and refined instrumentations. Here, in this work, we developed a highly efficient, ultrasensitive and selective electrochemical sensor for the trace level measurement of mercury on zinc oxide quantum dots by using Linear Sweep Voltammetry (LSV). The prepared nanosensor possesses a very high detection limit of 5 ppb with sensitivity of 4.6 μA cm^{-2} ppm^{-1} in response time of <2s. The fabricated sensor is reproducible and stable upto three months. Considerably this is the lowest detection limit attained for the determination of mercury amongst other reported electrochemical sensors for mercury. In addition, the selectively of sensor towards mercury is very high even in the presence of other common interfering ions. The practicability of the current sensor has also been measured in real environmental samples with good recoveries and with consistent results as verified with other standard technique.

1. Introduction

Ecological contamination due to fast industrial development is one of the major reasons behind the scarcity of clean and drinkable water across the globe. Rapid growth in consumer market with smart products has resulted in release of harmful toxins including heavy metals and harmful non-biodegradable chemical into the water bodies without proper treatment. Out of all these toxins, heavy metals especially mercury cause an immense danger to the environment. Hg species contaminate water bodies and eventually become part of food chain through soil, air or water. Different sources including coal burning power plants, breaking mercury products, spilling mercury, medical waste incinerator, alkali metal processing, tanning industries, volcanic eruptions, vaporization from water bodies and flood are the main causes for presence of mercury in the environment. The existence of mercury has direct influence on the developmental and behavioural abnormalities and impaired reproduction in human beings. Because of the prolonged half life and lack of decomposition, mercury is considered as most fatal contaminant as it accumulates and retained in human body for long time and interferes with various proteins, enzymes, lipids, DNA and other molecules inside body and results in neurological, cardio vascular, respiratory, GIT (gastrointestinal tract) skin related and neurophysiological disorders [1–4]. It has been reported that over 60,000 babies are born annually with neurological disorders caused by mercury poisoning of their mothers [5]. Therefore, the identification and estimation of harmful substances is of prime importance for devising strategies to combat ecological hazards of mercury.

Currently, several techniques such as absorption spectroscopy, optical emission spectroscopy (OES), ICP-MS (inductively-coupled plasma-mass spectrometry), X-ray fluorescence spectrometry, WD-XRF (Wavelength dispersive X-ray fluorescence spectrometry) have been employed to identify and estimate mercury. Amongst the variety of techniques reported, there is hardly any simple and portable device or system that can provide accurate and sensitive in-situ detection of toxic Hg species. All the available methods have certain limitations in terms of sample preparation, need of expertise, large sample volume, high cost and maintenance. Moreover, all these techniques are laboratory bound [6–8].

Out of all the above mentioned conventional ways, electrochemical sensing of mercury is one of the most potential mean for detecting such harmful pollutant. The redox active nature of mercury makes it a suitable candidate for electrochemical detection. The current approach has the prospective to attain high sensitivity (ppb to ppt) and selectivity toward mercury. The portability,

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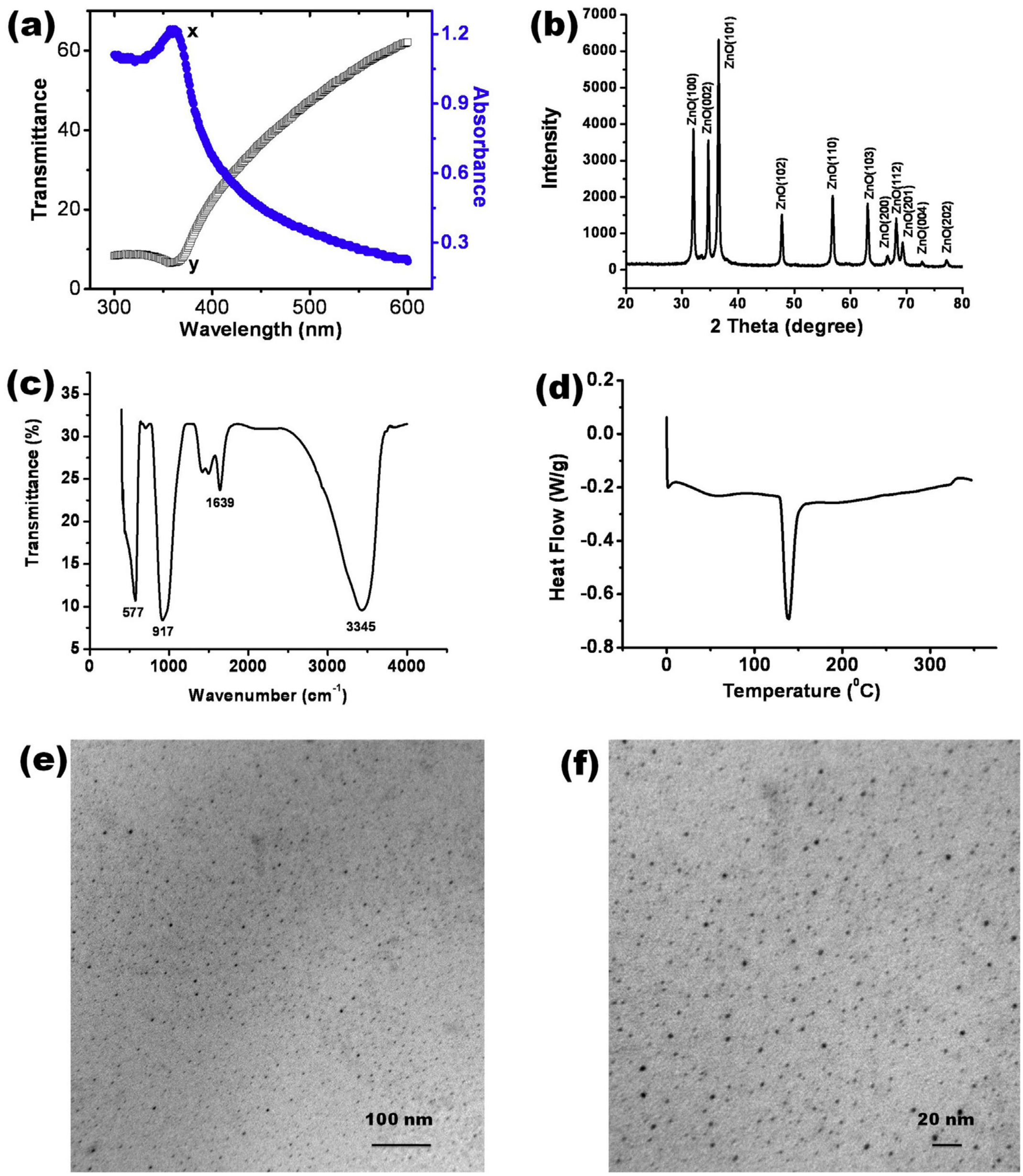

Figure 1. (a) UV-Visible spectra, (b) XRD analysis, (c) FTIR spectra, (d) DSC graph and (e, f) TEM images of as synthesized ZnO quantum dots.

simplicity and readiness for field applications also enhance the utility of electrochemical sensing. Among different electrochemical means, Stripping voltammetry technique has been much exploited for sensitive and selective determination of mercury by scientists. Whereas, certain limitations in terms of pre concentration steps, time consuming behaviour and need of expert handling [9–13,15] restricts the use of such technique, toxicity of mercury electrode required in stripping voltammetry also confines this technique only to wastewater management. In addition, interference of mercury with proteins in case of biological fluids is major drawbacks with stripping voltammetry for detecting mercury. Further, other electrochemical sensing processes require the fabrication of electrodes with different kinds of biomolecules and other coordinating ligand. In these techniques electrode is modified with some biomolecule or ligands which are specific to certain heavy metal ions. This makes the electrode selective and affinitic towards that specific heavy metal ion. Detection of various heavy metal ions including lead, cadmium, chromium, cobalt, nickel and mercury have been carried out by these techniques in recent past [4,10,14–17]. Although these techniques are reliable for estimation of heavy metal ions yet suffer from major limitations in terms of handling, storage and reproducibility. The modulations of electrode require expert handling during fabrication and proper storage conditions like optimum temperature and pH. Furthermore, shelf life of such fabricated electrode is less [18–23].

Consequently, by an easy yet effective nanoengineering process, i.e employing a hybrid nanostructured material for formulating working electrodes enhances the sensitivity and selectivity issues in electrochemical sensing [24]. Out of various nanomaterials used, zinc oxide nanoparticles have attained a unique position due to their enormous physicochemical properties. Zinc oxide (ZnO) is generally one of the essential and multipurpose nanomaterials in the family circle of metal oxides. ZnO is used for diverse range of high-technological appliances due to its intrinsic characteristics, such as optical band gap energy (3.37 eV), high-exciton binding energy (60 meV), biocompatibility, high-electron communication features, etc. Moreover, quantum dots of ZnO nanocrystals have also demonstrated outstanding sensing abilities due to their