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An enzyme free Vitamin C augmented sensing with different ZnO morphologies on SnO_2/F transparent glass electrode: A comparative study

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ABSTRACT

Three types of Zinc oxide (ZnO) nanostructures viz. ZnO nanocrystals (ZnONCs), ZnO nanoparticles (ZnONPs) and ZnO nanobelts (ZnONBs) were synthesized and characterized by UV–Vis, FTIR and SEM. A comparison of signal amplification by these ZnO nanostructures as judged by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and Linear Sweep Voltammetry (LSV) revealed that ZnONCs are better sensing interface for electrochemical detection. When these ZnO nanostructure were compared electrochemically for sensing Vitamin C, ZnONC's sensor outperformed the ZnONP and ZnONB sensor and previously reported sensors. The ZnONCs/MB/FTO electrode showed a wide linear sensing range (0.001 μM to 4000 μM), low detection limit (0.0001 μM), a small response time (5 s) and a storage stability of 6 months. To the best of our knowledge, this elevated sensitivity and remarkable stability for electrochemical Vitamin C detection using ZnONC's have not been reported so far.

1. Introduction

Nano-sized materials are much more captivating than other materials, because of their special electrical, optical and chemical properties arising due to their small size. Zinc oxide (ZnO) nanomaterials have captivated much attention, because of their notable properties such as wide-band gap (3.37 eV), high optical gain, thermal stabilities and luminescent properties. These ZnO nanomaterials have been used in nanodevices such as light-emitting device arrays, logic gate, transistors for short-wavelength, and optoelectronic-device applications like solar cell, piezoelectricdevices, electro acoustic transducers, laser diodes and semiconductor laser [1–3]. Because of all these remarkable properties, wide application area, and expectations for device miniaturization, the synthesis and characterization of the ZnO nanomaterials has attracted more attention. Structures like nanocrystals, nanobelts and nanoparticles, nanorings, nano-tetrapods are of great attention in photonics research, optoelectronics, nanotechnology, and biomedicine. As a result, the controlled production of different and complex nano architectures of ZnO has been investigated more extensively. In the present study we have prepared three different morphologies of ZnO nanomaterials i.e. ZnONCs, ZnONPs and ZnONBs. Spherical like ZnONPs and crystalline like ZnONCs are zero-dimensional nanostructures while belt-like ZnONBs are quasi-one-dimensional nanostructures were synthesized through controlled chemical synthesis on fluorine doped Tin Oxide glass (SnO_2/F) electrode. SnO_2 is the best choice to be used as an electrode as it is economic in comparison to the various expensive metal electrodes. Moreover, the properties such as high chemical stability, surface area and high capacitive behavior makes it all the more suitable to be used as a photo catalyst and as an electrode material [4–8]. The ZnO nanostructures coated SnO_2/F was further electro-deposited with methylene blue which is used as a redox indicator in the present work. Methylene blue (MB) is an organic dye of phenothiazine family. It is a redox indicator with the formal potential in the range of −0.10 to −0.40 V. This potential range is close to the redox potentials of many biomolecules, and thus, it had been used as an electron transfer mediator [9].

Vitamin C (aka ascorbic acid) is a water-soluble vitamin found in many biological systems and foodstuffs (fresh vegetables and fruits, namely, citrus) [10]. It plays an important role in collagen biosynthesis, iron absorption, and immune response activation and is involved in

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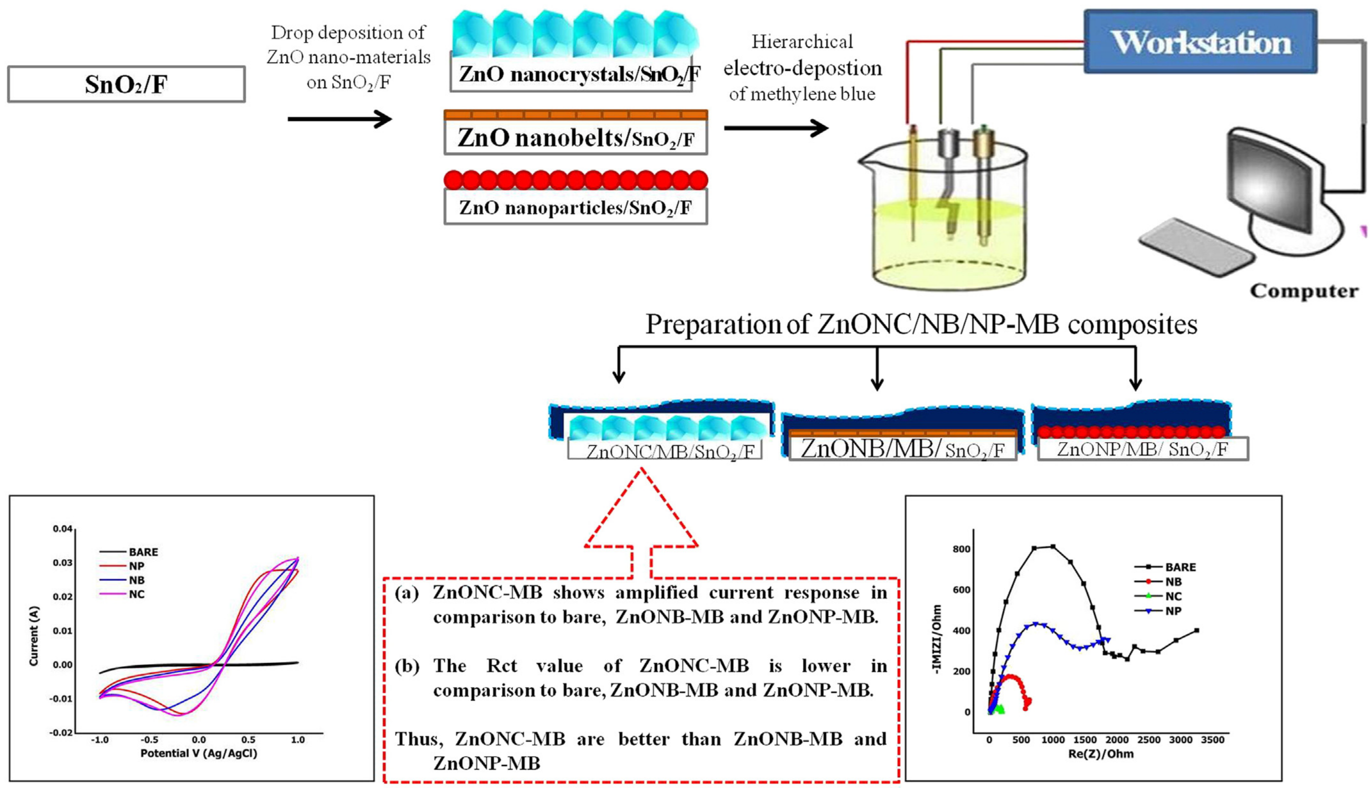

Scheme 1. Hierarchical deposition of methylene blue on ZnO nanomaterials layered on SnO_2/F.

wound healing. It also acts as a powerful antioxidant which fights against free-radical induced diseases [11–13]. It is widely used in the treatment of certain diseases such as scurvy, common cold, anemia, hemorrhagic disorders, wound healing as well as infertility [14]. Even so, Vitamin C excess can escort to gastric nuisance, and the metabolic product of Vitamin C (oxalic acid) can cause renal tribulation [15]. In some cases, disproportionate quantities of Vitamin C may result in the inhibition of natural processes occurring in food and can make a payment to taste deterioration [16]. Accordingly, precise strength of Vitamin C concentration is vital for monitoring of food and vegetables class on a daily basis exercise.

Vitamin C concentration can be determined with the ease by various analytical methods such as titrimetric method [17], fluorimetry [18], spectrometry [19–21], chemiluminiscence [22], enzymatic methods [23], capillary electrophoresis [24], and HPLC [25–27]. However, these conventional methods suffers from enormous pretreatment method, time consuming process and requirement of requires lavish equipments and most of these methods overestimate the levels of Vitamin C in different matrices due to the presence of oxidizable species other than Vitamin C [28]. Nevertheless, electrochemical detection methods are very popular for the detection of various compounds because of advantages like low cost, simplicity, low detection limit, fast response time and improved sensitivity. Matos et al. with a palladium modified gold electrode [29], Aoki et al. with a micro multi-band electrode [30], M. G. Hosseini et al. used titanium oxide nanotube films containing gold nanoparticles [31] and electrochemically determined the Vitamin C electrochemically in diverse samples. Amongst the numerous urbanized electrochemical sensors, various nanoporous metal oxide nanomaterials have been used extensively used due to their fascinating properties such as enhanced thermal stability, low cost, biocompatibility, non-toxicity and low temperature of processing.

In the present study, three different types of ZnO morphologies, viz., ZnONCs, ZnONPs and ZnONBs have been synthesized, characterized and used for in vitro electrochemical sensing of Vitamin C. The results have been compared and inferenced to get better nano structure for electrochemical sensing. This is attributed to the fact that nanoparticles tends to aggregate or agglomerate while nanobelts tends to roll over into a ring like structure which reduces its electrical conductivity and electrocatalytic activity; however, ZnONCs remain stable and also shows high electrocatalytic activity. As the current sensor is enzyme-less, electrocatalytical behavior of ZnONCs is greatly exploited for amplified sensing signal.

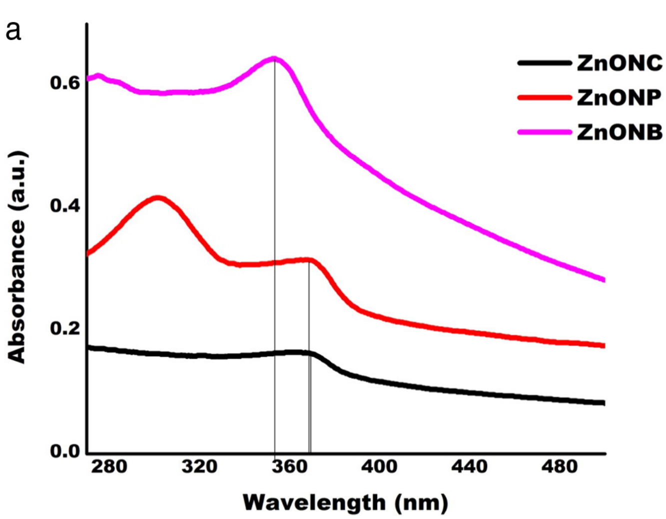

Fig. 1a. UV–Vis spectra of ZnONCs, ZnONPs and ZnONBs.

2. Experimental section

2.1. Chemicals

NaOH, $Zn(NO_3)_2 \cdot 6H_2O$, $ZnCl_2$, SDSN, Na_2CO_3, zinc acetate, ethanol, Lithium Hydroxide were purchased from Sigma-Aldrich, India. All