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Zinc oxide nanocones as potential scaffold for the fabrication of ultra-high sensitive hydrazine chemical sensor

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Abstract

The fabrication and characterization of ultra-high sensitive hydrazine chemical sensor based on zinc oxide (ZnO) nanocones are reported. The ZnO nanocones were synthesized by a low-temperature solution process and examined by various techniques in terms of their morphological, structural, compositional and optical properties. The studies revealed that the synthesized ZnO materials possessed good-crystallinity and defined nanocone morphologies and exhibited good optical properties. The hydrazine chemical sensor was fabricated on the amperometric principle and shows ultra-high sensitivity and low detection limit. The estimated sensitivity and detection limit of the fabricated hydrazine chemical sensor were 50×10^4 μA μM^{-1} cm^{-2} and 0.01 μM, respectively. The observed response time was < 2 s.

Keywords: B. Electron microscopy; E. Electrodes; E. Sensors; ZnO nanocones; Hydrazine

1. Introduction

Literature witnessed that extensive research has been done to develop robust and reliably smart sensors for the efficient recognition of technologically and environmentally important but hazardous analytes [1–5]. Hydrazine and its derivatives are the compounds which have numerous applications and widely used in pesticides, pharmaceuticals, air bags, rocket fuel, fuel cells, in organic reactions etc. [6–9]. Even though hydrazine is used for various high technological applications but according to the U.S. Environmental Protection Agency, it is considered as highly toxic and unstable chemical as its exposure leads to highly adverse effects to human and animals. The exposure of hydrazine, even at low concentration, may cause headache, nausea, dizziness, coma, irritation to eyes, nose and throat. Further, hydrazine shows carcinogenic and mutagenic effects, and can cause damages to liver, kidneys and central nervous system [10–13]. Therefore, due to these important applications and highly toxic nature, it is highly desirable to detect the leak and exposure of hydrazine very efficiently. Several techniques like fluorescent, chemodosimetric, colorimetric, and electrochemical are available for the qualitative and quantitative analysis/detection of hydrazine [14–17]. Out of these various methods, electrochemical technique is proving itself as one of the most promising, accurate, fast, sensitive and cost effective technique [18]. For fabricating electrochemical sensors, normally the working electrodes are modified with electron mediators. Nowadays, nanomaterials are being used as efficient electron mediators due to their special electronic and optical properties [19–21]. Recently, Chen et al. have used Au@Pd core–shell nanoparticles supported on amino-functionalized TiO_2 nanotubes for electrochemical sensing of hydrazine [19]. In another report, Wang et al. have demonstrated electro-catalytic sensor based on silver nanocubes for sensing hydrazine and hydrogen peroxide [20]. Anu Pratapa et al. have reported the fabrication of electrochemical

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hydrazine sensor based on $Ni(OH)_2$–MnO_2 hybrid material [21]. Among various electron mediators, ZnO nanoparticles have received a considerable attention due to its special properties and wide applications. The properties of ZnO include its biocompatibility, wide band gap, high-electron communication features, enhanced electrochemical response etc. [22–29]. Due to these excellent properties, ZnO nanomaterials have been used as efficient electron mediators for the fabrication of electrochemical hydrazine sensors as reported in the literature [30–36]. The previously demonstrated hydrazine sensor exhibited low sensitivity and high detection limits; hence, still there is a need to develop a highly sensitive, robust and reliable hydrazine chemical sensor based on ZnO nanomaterials.

This paper reports a simple and facile large scale synthesis of well-crystalline ZnO nanocones and its utilization as an efficient electron mediator for the fabrication of highly sensitive and robust hydrazine chemical sensor. The synthesized ZnO nanocones were characterized in terms of their morphological, structural and compositional properties. From the detailed sensing experiments, it was realized that the hydrazine chemical sensor based on ZnO nanocones exhibited very high sensitivity and lower detection limit. To the best of our knowledge, the observed sensitivity for the fabricated hydrazine sensor is highest among the entire reported hydrazine sensor fabricated based on ZnO nanomaterials.

2. Experimental details

2.1. Synthesis of ZnO nanocones

All the chemicals used for the synthesis of ZnO nanocones were purchased from Sigma-Aldrich and used as received without further purification. For the synthesis of ZnO nanocones, in a typical reaction process, 0.1 M aqueous solution (50 ml) of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) was mixed with 0.1 M aqueous solution of hexamethylenetetramine (HMTA) (50.0 ml) under stirring at room temperature. The resultant mixture was stirred continuously for 20 min at room temperature to mix well. Few drops of 1.0 M NaOH (sodium hydroxide) solution were added to adjust the pH of the solution to10.0. The obtained solution was then heated and refluxed with continuous stirring at 90.0 °C for 7 h in necked round bottom flask. White precipitates were obtained after completing the reaction which were filtered off, washed thoroughly with distilled water and ethanol, and dried in hot wave oven.

2.2. Characterizations of ZnO nanocones

The as-synthesized ZnO nanocones were characterized for their morphological, structural and optical properties. The morphological characterization was done using transmission electron microscopy (TEM). The structural and crystal phases were investigated by an X-ray diffractometer (XRD, Brucker). The elemental and chemical compositions were determined by energy dispersive spectroscopy (EDS) and Fourier transform infrared (FTIR, Shimadzu) spectroscopy, respectively. To determine the optical properties of as-synthesized ZnO nanocones, UV–vis spectroscopy (Shimadzu) was done at room-temperature. The scattering properties of the as-synthesized ZnO nanocones were examined by Raman-scattering spectroscopy.

2.3. Fabrication of hydrazine sensor based on ZnO nanocones

From application point of view, the synthesized ZnO nanocones were used as electron mediators for the fabrication of sensitive hydrazine (N_2H_4) electrochemical sensor. For fabrication, the as-prepared ZnO nanocones were coated on polished gold (Au) electrode (surface area=2 mm^2). For coating, the slurry of ZnO nanocones was made by adding as-prepared nanocones and 5 wt% nafion solution in a particular ratio and the prepared slurry was then coated on Au electrode and dried at 4 °C for 24 h to get a uniform layer and tight binding of nanoparticles over entire electrode surface. All the electrochemical experiments were performed at room-temperature with a μ Autolab GPES-4 electrochemical work-station using three-electrode configuration in which the modified ZnO/Nafion/Au electrode was used as working electrode, a Pt electrode as a counter electrode and an Ag/AgCl (sat. KCl) as reference electrode. For all the measurements, 0.1 M phosphate buffer solution (PBS; pH 7.0) was used.

3. Results and discussion

3.1. Structural, morphological and compositional properties of as-synthesized ZnO nanocones

To examine the crystallinity and crystal phases, the as-synthesized ZnO nanomaterials were examined by X-ray diffraction (XRD) pattern. Fig. 1(a) exhibits the typical XRD pattern of as-synthesized ZnO nanocones and shows several well-defined diffraction reflections which are almost similar to the reported XRD pattern of pure ZnO [36]. The diffraction reflections appearing at various peak positions, i.e. 31.6°, 34.2°, 36.4°, 47.4°, 56.7º, 66.7°, 68.2°, 69.2°, 72.4° and 77.2° are corresponding to various reflections of ZnO (100), (002), (101), (102), (103), (200), (112), (201), (004) and (202), respectively. All the observed diffraction reflections are in close agreement with the reported JCPDS card no. 36-1451 for pure ZnO. The observed XRD result demonstrates that the as-synthesized ZnO nanocones are pure ZnO with wurtzite hexagonal phase. The well-defined reflections are evident for the well-crystallinity of the synthesized nanocones. Except ZnO reflections, no other peak related with any other impurity was detected in the pattern which further revealed that the prepared nanocones were pure ZnO.

The general morphologies of the as-synthesized nanocones were examined by transmission electron microscopy (TEM). Fig. 1(b) demonstrates the typical TEM image of as-synthesized ZnO material. The TEM image revealed that the as-synthesized ZnO nanomaterials possessed cone-shaped morphologies which were grown in very high density. Moreover, due to high-density growth, some agglomeration can be