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Tungsten oxide (WO_3) nanoparticles as scaffold for the fabrication of hydrazine chemical sensor

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ABSTRACT

This paper reports the fabrication and characterization of hydrazine amperometric sensor based on tungsten oxide (WO_3) nanoparticles. The WO_3 nanoparticles were prepared by facile aqueous solution process. The detailed morphological and structural characterizations revealed that the prepared nanoparticles are spherical shape and possessing well-crystalline monoclinic structure. The prepared nanoparticles were used as effective electron mediators for the fabrication of efficient hydrazine amperometric sensors. The fabricated hydrazine sensor exhibited a good sensitivity of 0.18,471 $\mu A/\mu M/cm^2$ and detection limit of 144.73 μM. Importantly, to the best of our knowledge; this is the first report in which WO_3 nanoparticles are efficiently used as effective electron mediator for the fabrication of sensitive hydrazine amperometric sensor.

1. Introduction

Hydrazine and its derivative class of compounds are extensively employed in several fields namely agriculture, chemical and pharmaceutical industry, as propellant for satellites, aircrafts, rockets, as blowing agents, plant growth regulators, antioxidants, photographic agents, corrosion inhibitors, insecticides and also engaged as fuel for direct fuel-cell system [1–4]. Regardless of such multitudinous worth, even acute exposure of hydrazine and its derivatives, which enter our biosphere from industrial or aerospace emissions, can result in dizziness, temporary blindness, irritation of eyes, nose and throat, nausea [5]. The Environmental Protection Agency (EPA) has authenticated this chemical as human carcinogen and cataclysmic to central nervous system, liver and brain [6]. Keeping in view its myriad of applications, a rational and ingenious method for sensing and detection of hydrazine and its derivatives is desired. Several techniques such as spectrophotometry, titration, chromatography, fluorescence are extensively used for the detection of hydrazine or its derivatives [7–12]. However, all these strategies are time-consuming, unreasonably pricey and sample pre-treatments are often required. Among various detection techniques, the electrochemical method presents itself as easy method which exhibited portability, wide linear range and greater sensitivity [13–16].

Previously, Wang et al. have demonstrated the sensing of hydrazine using 3,4-dihydroxy benzaldehyde functionalized electrode [17]. Further, palladium plated boron-doped diamond micro-disc array has also been exploited by the Compton group for electrocatalytic oxidation and detection of hydrazine [18]. In addition, gold nanoparticles–polypyrrole nanowire modified glassy carbon, gold electrode modified with iron–phthalocyanine complex coupled to mercaptopyridine, palladium nanoparticles on poly(vinylferrocenium) have displayed attractive electro-activity toward oxidation of hydrazine along with Pd/WO_3, Pd/TiO_2 films [19–23].

Recently, the semiconducting oxide nanomaterials have received a great attention due to their excellent chemical and physical properties and wide applications [24–41]. Among various semiconducting oxide, the tungsten oxide (WO_3) is one of the most promising materials due to its functionalities and wide applications. It is a wide band gap (ranging from 2.4 to 2.8 eV) and n-type semiconductor material with excellent photochromic, electrochromic, thermochromic and catalytic properties. [42–45].

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Due to these above mentioned properties, WO_3 are widely used for various applications such as electrode materials for secondary batteries, heterogeneous catalyst, solar energy devices, photocatalysts, field-emission devices, and so on [46–50]. In addition to this, WO_3 nanomaterials are widely used as electrode material for the detection of various gases such as O_3, O_2, NO_2, NO, NH_3, H_2S, H_2, ethanol, *etc.* [51–54]. Even though WO_3 possess various interesting properties and widely used for variety of application, but, to the best of our knowledge, the utilization of WO_3 nanomaterials for the fabrication of electrochemical hydrazine sensor has never been reported in the literature.

This work demonstrates the simple and facile aqueous solution synthesis of WO_3 nanoparticles. The prepared nanomaterials were characterized in detail in terms of their morphological, structural and optical properties. Finally, the prepared nanomaterials were used as potential electrode material for the fabrication of efficient electrochemical hydrazine sensor.

2. Experimental details

2.1. Chemicals

Cetylpyridinum bromide (CPyB) (purity >99%) and Tungsten(VI) chloride (WCl_6, 99.9%) were obtained from Sigma-Aldrich. Ammonia solution (25%, v/v) was purchased from Merck. Acetone (98–100%) and ethanol (99.9%) were obtained from BDH and Changshu Yangyuan (China), respectively. All reagents were used as received without further purification. De-ionized (DI) water was used for solution preparation

2.2. Synthesis of WO_3 nanoparticles

For the synthesis of WO_3 nanoparticles, in a typical reaction process, CPyB was dissolved in DI water to make a 7.0 mM solution and then was stirred for 2 h. Consequently, aqueous ammonia was slowly added to the resultant CPyB solution under continuous stirring. Finally, 0.9279 g of WCl_6 was added into the obtained solution and stirred for 4 h at room temperature. The product was then aged at ambient temperature for 3 days. The resultant product was filtered and washed with DI water and ethanol, sequentially and dried at room-temperature. The obtained material was then calcined at 600 °C for 2 h and finally WO_3 nanoparticles were obtained.

2.3. Characterizations of WO_3 nanoparticles

The prepared WO_3 nanoparticles were characterized in terms of their morphological, structural and compositional properties. The general morphologies of prepared nanoparticles were observed by field emission scanning electron microscopy (FESEM; JEOL-JSM-7600F) and transmission electron microscopy (TEM; Hitachi-H-7500). The crystallinity and crystal phases of the prepared nanoparticles were examined by the X-ray diffraction (XRD; PANanalytical Xpert Pro.) pattern measured with Cu-*K*α radiation (λ = 1.54178 Å) in the range of 15–55°. The elemental and chemical compositions of synthesized nanoparticles were examined by energy dispersive spectroscopy (EDS) attached with FESEM and Fourier transform infrared (FT-IR) spectroscopy, respectively. FTIR spectrum of prepared WO_3 nanoparticles was carried out using KBr disk technique with Hitachi 270-50 IR spectrophotometer in the range 4000–400 cm^{-1}. Room-temperature UV–Vis. and photoluminescence (PL) spectroscopy were done to examine the optical properties of synthesized nanoparticles.

2.4. Fabrication of hydrazine amperometric sensor based on WO_3 nanoparticles

For the fabrication of hydrazine chemical sensor, the WO_3 nanoparticles were coated on the surface of gold electrode (Au;

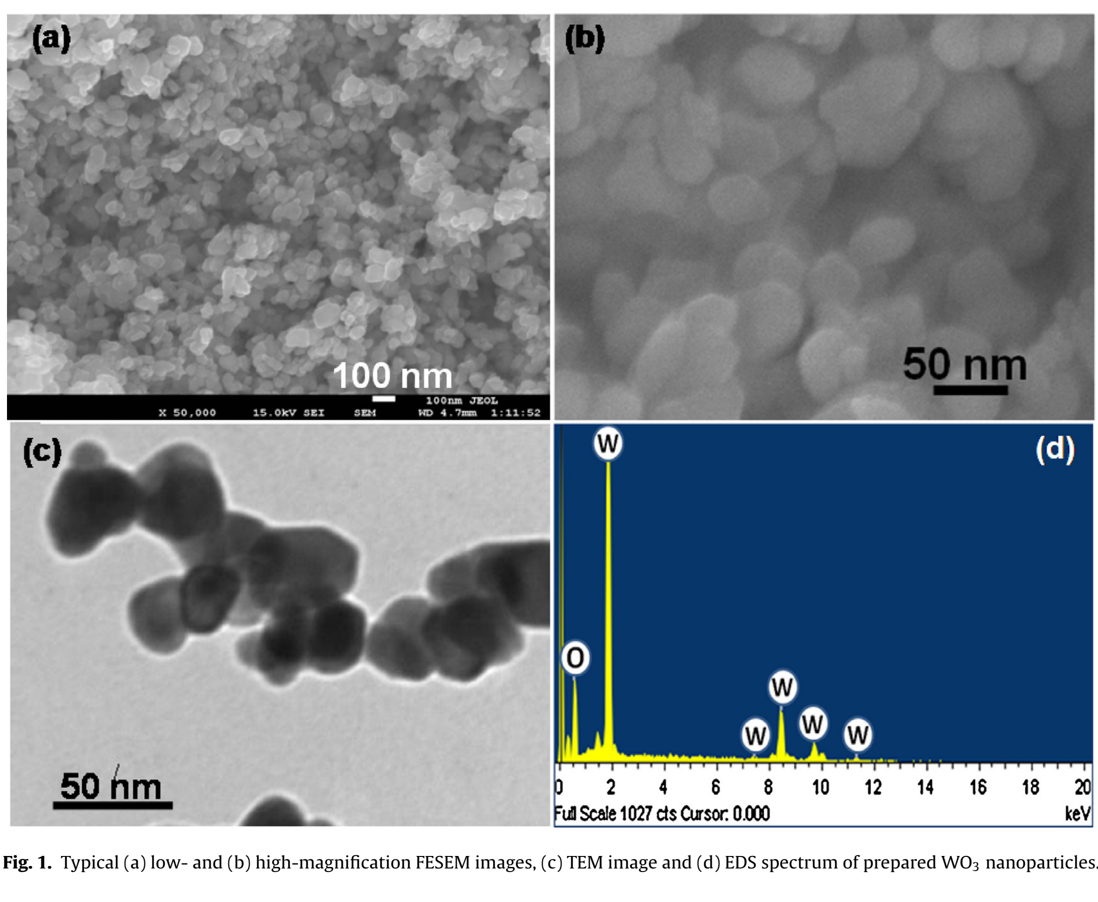

Fig. 1. Typical (a) low- and (b) high-magnification FESEM images, (c) TEM image and (d) EDS spectrum of prepared WO_3 nanoparticles.