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Thiourea sensor development based on hydrothermally prepared CMO nanoparticles for environmental safety

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ABSTRACT

Low-dimensional cobalt oxide codoped manganese oxide nanoparticles (CMO NPs; dia. ~ 25.6 nm) were synthesized using the hydrothermal method in alkaline phase. The optical, morphological, and structural properties of CMO NPs were characterized in details using FT-IR, UV/vis., FESEM, XEDS, XPS, TEM, and XRD techniques. Glassy carbon electrode (GCE) was fabricated with a thin-layer of CMO NPs by conducting coating binders for the development of selective and sensitive thiourea (TU) sensors. Electrochemical responses along with higher sensitivity, large-dynamic-range, and long-term stability towards TU were performed by electrochemical I-V approach. The calibration curve was found linear over a wide linear dynamic range (LDR) of TU concentration. From the gradient of the calibration plot, limit of detection (LOD), and sensitivity were calculated as 12.0 ± 0.05 pM and 3.3772 $nAnM^{-1}$ cm^{-2} respectively. It is an organized route for the development of chemical sensor based on very low-dimensional CMO NPs/GCE using electrochemical reduction phenomena. As far as we know, this report is the maiden publication on highly sensitive TU sensor based on the CMO NPs/GCE. This method could be a pioneer developer in TU sensitive chemical sensor development using doped NPs in the simple I-V method for the important sensor applications with useful doped materials coupled nanotechnological systems for environmental safety.

1. Introduction

Thiourea (TU) often considered as a severe ecological chemical containing organic sulphur in it, having detrimental effects on mammals and nitrifying bacteria (Safavi et al., 2015; Manea et al., 2006). It is a carcinogenic (Rosin and Rachmilewitz, 1954) and allergenic (Kanerva et al., 1994) substance. Furthermore, TU causes the disturbance of carbohydrate metabolism (Giri and Combs, 1970) and inhibits nitrification in soil and water (Smyth and Osteryoung, 1977). However, it is extensively used in numerous fields of science and technology such as electroplating industry (Spataru et al., 2005), rubber industry (Puig et al., 1996), photography (Abbasi et al., 2009), analytical chemistry (He et al., 1999), and agriculture (Pérez-Ruiz et al., 1995). Thus, a suitable, selective, low-cost method is needed to investigate this harmful chemical in waste water and environment. Several analytical methods have been reported for determination of TU such as titrimetry (Amin, 1985), piezoelectric method (Yao et al., 1992), high-performance liquid chromatography (HPLC) (Rethmeier et al., 2001), Fourier transform infrared (FTIR) spectrometry (Kargosha et al., 2001), chemiluminescence (He et al., 1999), flow-injection methods (Pérez-Ruiz et al., 1995), UV/vis. Spectrophotometry (Wang et al., 2011) and electrochemical methods (Manea et al., 2006; Spataru et al., 2005; Stara and Kopanica, 1984). Electrochemical methods are often simple, rapid, and highly selective and more sensitive compared to other methods (Safavi et al., 2015; Rahman et al., 2011a). However, the electrochemical response of the TU at a bare electrode is kinetically slow and often associated with high over-potential (Conway et al., 1973; Morales-Guio et al., 2014; Rahman et al., 2017, 2011b; Anantharaj et al., 2016). Consequently, searching for new materials for the modification of electrodes to enhance the rate of electron transfer and reduce the over-potential is necessary. Very few redox mediators such as alumina modified Pt electrode (Nematollahi and Rafiee, 2003) and a monolayer of an oxadiazole derivative and with silver nanoparticles (Moghadam et al., 2016) have been so far developed for the modification of electrode in TU detection. But these are either time consuming or needs sophisticated instrument so not cost effective at all. These drawbacks of different methods can be reduced if GCE electrode is coated with CMO NPs that gives a selective and specific redox reaction. The exceptional electronic, catalytic and optical properties of metal oxide

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nanoparticles make them suitable for potential applications in the electrochemical and optical sensors (Rahman et al., 2016, 2011c). Recently, several metal oxide nanoparticles modified electrochemical sensors have been reported for the determination of different important analytes (Rahman et al., 2012a, 2013; Temerk and Ibrahim, 2016). In electrochemical sensors, metal oxide nanoparticles catalyze electrochemical reactions and also enhance the transfer of electron (Rahman et al., 2012b).

During the detection of ultra-trace amounts of hazardous proficiently, nanomaterial has better properties than their bulk substance, for example, mechanical strength, heat tolerance, electro-catalytic property, electrical conductance, electro-magnetic property, and photo-catalytic property (Lee et al., 2009; Rahman et al., 2016; Umar et al., 2008). Lately, nano-structured doped metal oxides have become more important in research field due to their excellent electrochemical properties. MnO_2 shows important roles as an electro-catalyst among all other metal oxides. Till today, only a few nanostructured metal oxide (doped or undoped) has been prepared and reported for developing TU sensor. To enhance the electrochemical property of the MnO_2 herein, we propose the facile hydrothermal method to prepare CMO NPs in the form of aggregated spherical nanoparticles. The direct electrochemical oxidation of TU at different carbon-based electrodes such as conductive diamond (Spataru et al., 2005; Akeneev et al., 2005), graphite and pencil graphite electrodes (Levent et al., 2011; Rahman et al., 2011d) has also been investigated and large over potentials have been reported. To the best of our knowledge, this is the first report on TU determination using CMO NPs/GCE. In this approach, the electro-catalytic performance of the CMO NPs/GCE towards TU was studied by I-V measurements which show that the CMO NPs/GCE has excellent catalytic activity. Since the improvement of the electro-chemical properties of metal oxides, by doping them, is cost effective and quick relative to other methods specified in the literature, herein, we propose an electrochemical sensor for the determination of TU in aqueous solutions (even at pico molar level) using CMO NPs fabricated GCE. To the best of our knowledge, TU sensor based on CMO NPs fabricated GCE has not yet been reported and displays the lowest detection limit (LOD = 12.0 ± 0.05 pM) than any other published reports.

2. Experimental sections

2.1. Materials and methods

Cobalt(III)chloride, manganese(IV)chloride, ethanol, monosodium phosphate, disodium phosphate, aspartic acid, bilirubin, TU, cysteine, creatine, fructose, glutamic acid, glutathione, glycine, tyrosine, uric acid, kanamycin, leucine, penicillium G, thionine acetate, nafion (5% ethanolic solution), ammonium hydroxide were used in this work without any further purification, which are procured from Sigma-Aldrich. The calcined CMO NPs was explored with UV/vis. spectroscopy (Evolution 300 UV/visible spectrophotometer, Thermo Scientific). The FT-IR spectrum was measured for the nanocomposites with the NICOLET iS50 FTIR spectrometer, Thermo Scientific, Madison, WI, USA, in the range of 400–4000 cm^{-1}. The XPS spectrum was examined to estimate the binding energy values in eV of Co, Mn, and O on a $K\alpha_1$ spectrometer (Thermo Scientific, Kα 1066). The powdered XRD patterns were evaluated with the ARL X'TRA diffractometer, Thermo Scientific. The morphology of the CMO NPs was studied by FESEM (JEOL, JSM-7600F, Japan). Elemental analysis was carried out by the EDS (JEOL, Japan). The calcined CMO NPs was distributed in ethanol by the ultrasonic vibration to prepare the TEM sample; later by dipping the TEM film into the solution and dry it to investigate further morphological information. The I-V method was applied by an electrometer (Keithley-6517A Electrometer, USA) at room temperature.

2.2. Synthesis of CMO NPs

CMO nanoparticles have been synthesized using an equimolar concentration of $CoCl_3$ and $MnCl_4$ precursor into a Teflon-lined autoclave for 15 h. $CoCl_3$ and $MnCl_4$ solutions (50.0 mL, 0.1 M) were prepared in deionized water separately at room temperature and mixed them with continuous stirring for 30 min. The alkalinity of the reaction mixture was maintained at 10.3 pH value using a basic buffer (NH_4OH/NH_4Cl). Later, the mixture was poured into a Teflon-lined autoclave to put it into an oven for a 6.0 h of heating at 90.0 –100.0 °C. Drop-wise addition of the NH_4OH solution to the precursor's mixture with vigorous stirring to produce a white precipitate at the bottom. After washing the precipitate with deionized water and ethanol successively for removing the organic and inorganic contaminants; dry it at RTP (Room-temperature and pressure; room conditions). Five hours of continuous heating at 400.0 °C in a muffle furnace makes the as-grown precipitate to calcined CMO NPs. The morphology of the calcined CMO NPs is almost consistent with the proposed mechanism of the MnO_2 nanostructure formation. The calcined CMO NPs was characterized scientifically and applied to TU sensing in phosphate buffer phases.

2.3. Fabrication of CMO NPs/GCE

Fabrication of GCE was carried out by the calcined CMO NPs using 5% ethanolic nafion solution as a conducting binder. It was then dried in air for 2 h to get the thin-film on the GCE. In the electrochemical cell, CMO NPs coated GCE, Pt wire, and aqueous TU solution is working electrode (WE), a counter electrode (CE), and electrolyte respectively. To use as a target analyte, aqueous TU solution (0.1 M) was diluted to different concentrations (0.1 M to 0.1 nM) using DI water. By using an electrometer, the simple I-V method was applied to detect the TU in the buffer phase using the CMO NPs/GCE as a WE. All the I-V measurements were carried out in 5.0 mL of phosphate buffer solution (PBS; pH 7.0). From the slope of the calibration plot, sensitivity and lower detection limit of the proposed TU sensor was estimated.

3. Results and discussion

In this approach, the CMO NPs were synthesized by a hydrothermal method in an alkaline medium at 90–100 °C. This technique has several advantages such as facile preparation, accurate control of the reactant temperature, easy to handle, one-step reaction, and high-stability as well as catalytic natures. Optical, morphological, electrical, and chemical properties of CMO materials are of huge significance from the scientific aspect, compared to other metal oxides materials (Rui et al., 2014; Mlowe et al., 2016). Non-stoichiometry, mostly oxygen vacancies, makes it conducting nature in the nanoparticles. The formation energy of oxygen vacancies and metal interstitials in CMO NPs are very low and thus the defects are formed easily compared to other materials, making the material suitable for chemical sensor (Akhtar et al., 2011, 2013; Miners et al., 2016; Mendili et al., 2013; Balaz et al., 2013). The CMO nanoparticles is completely characterized for the Evaluation of binding energy (Ω), Optical and structural evaluation (η), and EIS analysis (ψ) beside morphological as well as elemental analyses, and presented in the Electronic Supplemental Materials (ESM).

3.1. Morphological and elemental evaluation

The morphology and structure of the CMO NPs were investigated by FESEM. Typical morphological information of the calcined CMO NPs is presented in Fig. 1(a-b). Calcined CMO NPs has an average aggregated nanoparticles diameter 25.6 nm in the range of 17.3–35.0 nm. This exceptional structure of CMO NPs provides a large surface area and