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Bi_2O_3@Bi nanoparticles for ultrasensitive electrochemical determination of thiourea: monitoring towards environmental pollutants

Ajay V. Munde, Balaji B. Mulik, Raviraj P. Dighole, Somnath C. Dhawale, Lila S. Sable, Ashwini T. Avhale, Bhaskar R. Sathe

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Highlights

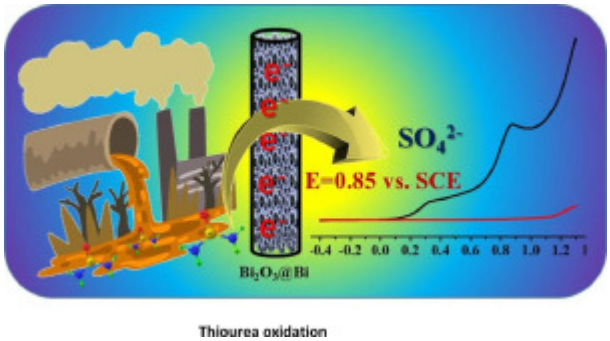
- Bi_2O_3@Bi synthesised by chemical synthesis route having Bi core and Bi_2O_3 shell.
- Electrochemical thiourea (TU) sensing on Bi_2O_3@Bi shows ultra-low LOD of 2.90 µM.
- Outstanding reusability, excellent stability, wide range calibration linearity and high stability pH of Bi_2O_3@Bi towards TU sensing.
- Bi_2O_3@Bi shows excellent selectivity and activity towards TU sensing from their active surface features.

Abstract

Thiourea and other sulphur containing organic molecules are commonly present in industrial waste water and because of their toxic nature are environmental pollutants. Thiourea oxidation constructed on cost effective and proficient catalyst to substitute/alternative with noble metals (Pt, Au, Ir, Rh, Pd and others) based electrodes. Herein, this report for the synthesis of Bi_2O_3@Bi (~ 4-5 nm) nanoparticles by using polyfunctional citric acid is a surface protecting molecule for electrocatalytic thiourea oxidation reactions as a one of the environmental hazardous monitoring system at room temperature. These as-synthesized nanoparticles were well characterized by scanning electron microscopy (SEM), Furrier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD), thermogravimetric analysis (TGA) and further studied for electrochemical determination of thiourea (TU). These structural and morphological studies were further confirms the rhombohedral crystal structure with thermogravimetric analysis (TGA) shows 20 wt% citrate molecules on the surface of Bi_2O_3@Bi nanoparticles. The electrochemical studies on Bi_2O_3@Bi nanoparticle reveals that, it's having ultra-low detection limit, higher sensitivity and better activity at ultralow potential for a current density of 11.2 mA/cm^2 for oxidation of thiourea (TU). Moreover, chronoamphrometric (i-t) measurement shows proposed Bi_2O_3@Bi based system is having stable and long term current performance at a potential of 0.85 V vs. SCE towards the TU oxidation. This work affords with noble metal free electrocatalyst for novel appliance and remarkable consequence as a thiourea determination and conversion as a part of waste management.

Graphical abstract

Thiourea oxidation



Thiourea oxidation

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Introduction

Thiourea (TU) is one of the majorly used sulphur containing molecule having diverse and enormous industrial, agricultural and biological applications, including in dyes, pulp, and agriculture as herbicides and fertilizer, in photoshop as a photo-developers, electronic and many more industries [1]. TU is also commonly used in metal leaching processes, electroplating industries as a source of sulphur and other compounds of sulphur i.e. CdS commonly used for solar cells and also for the large scale extraction processes of Cu via. Cu_2S formation [2,3]. Moreover, the controlled reactions of TU with H_2O_2 produces highly reactive bleaching agents and is commonly used in textile industries [1]. In view of fertilizer point, TU and its derivatives are well introduced to control the edifice in saline soil and it increases the quality of wheat and maize crop. Moreover, TU is having exceptionally high content of N (36%) and S (42%) and these compositions are having great deal with hydrollic conductivity, and reduced cost compared to N, P, K based fertilizers [4]. Moreover, bio-comfortable sulphur containing chemicals are commonly used for fruit treatment in food industries to increase their shining also in sugar treatment. Unfortunately, overdose of sulphur through these compounds having serious effects on human body to disturbance the carbohydrate metabolism system [5,6]. On the other hand, once TU is heated to its decomposition temperature it emanates very toxic fumes of nitroxides ($H_2N\text{-}O^-$) and sulfoxides ($RR'SO$). Therefore, even though all these good merits of TU contributes more on the industrial development but and indirect use of TU based organo-containing sulphur substances, sulphur containing functional aromatic compounds in dye industries are carcinogenic and allergic in nature [9,10]. It also inhibits the N_2-cycle dependent ecosystems in the fertile soil and also having serious effect on human health [7], [8], [9], [10], [11]. According to human health assessment group (HHAG) in EPA's (EPA- stands for environmental protection agency), TU is commonly used in a thyroid depressant in patients with hyperthyroidism treatment. For example, daily dose of <15 mg (<0.2 mg/kg body weight per day for a 70 kg adult) in adults did not lead to measurable depression of the thyroid gland function, while an overdose of 70 mg/day (1.0 mg/kg body weight/day) produced a hyperthyroidism [9,[11], [12], [13]]. These serious environmental and health issues of TU and of its derivatives motivates to develop an efficient methods for the determination, monitoring and sulphur extraction processes from various sulphur containing resources. Commonly used determination techniques include UV-Vis spectroscopy [14], chromatography [15], Raman spectral analysis [16], chemiluminance [17], electroanalytical and electrochemical sensors [18,19] and many more. Unfortunately, among these techniques most of those are

having serious issues like longer analysis time, high costs, tedious sample preparation, low sensitivity, selectivity etc. and hence it limits their further commercialization.

Among these, electrochemical approach having several merits over others, includes the solvent has been fully recycled and selectivity can be maintained by controlling the electrode potential, high sensitivity and cost effective system. For example, electrochemical systems are having even single molecule detection capability. Researchers are having more interest in electrocatalyst with special characteristics of nanoparticles like electronic, catalytic and better stability towards the metal and metal oxide nanomaterials as an electrochemical sensor [18], [19], [20]. Literature reports the numerous materials like metals, metal oxides and their carbon based materials including graphene, graphene oxide, functional carbon nanotubes and fullerene are commonly used materials for electrochemical sensing and bio-sensing applications [4,[21], [22], [23]]. Moreover, modern trend in electrochemical sensor involves the development in TU oxidation from waste water using different hybrid electrodes even containing lower concentration at various pH. Interestingly, among metals, chemically inert/noble metals (Pt, Ag and Au) are having outstanding activity towards TU oxidation but their high cost limits its commercialization and industrial applications [24], [25], [26]. Therefore, to further resolve these issues researcher are devoting towards developing a new catalytic systems for cost effective and increasing electrochemical activities based on chemical nature of elements like Co, Cu, Sn, Mn and their carbon composition which will be prodigious deal with TU oxidation reactions. For example, Amini et al. demonstrated the synthesis of MnO_2 nanosphere immobilized on DNA template and was found active catalyst towards TU oxidation in PBS-7 (phosphate buffered saline pH-7) [27]. Hasnat and co-workers examined TU oxidation on Pd surface and proposed mechanistic path based on kinetic studies at different pH. Interestingly, it was concluded that the overall electrochemical oxidation of TU follows a stepwise oxidation initially, at lower potential (<0.40 V vs. Ag/AgCl) and concerted one at relatively higher potential (>0.40 V) [28]. Moreover, Rahman and co-workers reported SnO_2/V_2O_5 NPs for TU sensing and the high performance might be from their higher surface area and active surface sites, also availability of additional electrons in its conduction band [29].

Recently, Bi and its oxides/hydroxide/bimetallic based materials are found tobe important because of having special characteristics like its earth abundance and higher surface area contributes faster electron transfer, lower band gap, and good chemical and electrochemical stability for long term operation. Literature survey reflects that Bi and Bi_2O_3 materials were commonly used for electrochemical sensing of biomolecules like glucose, phenol, catechol, ascorbic acid, nitrate, heavy metal detection (Pb, Cd, Cr), energy storage materials, degradation of organic pollutants and CO_2 reduction selectively to formate [30], [31], [32], [33]. Moreover, Bi in combination with noble metals like Pd and Pt (Pd-Bi and Pt-Bi) further increases the electrocatalytic activity for fuel cells [34],

[35], [36], [37], [38]. Herein, these studies Bi_2O_3@Bi NPs synthesized via. chemical reduction approach, to found an effective chemical interactions due to upturn electrochemical properties. Moreover, Bi containing material shows exceptionally high oxophilic nature, because these surface formation of Bi $(OH)_3$ and Bi-O have been opens additional active sites, which are significantly involved in electrochemical oxidation reactions. Accordingly, the electrochemical oxidation of TU on Bi_2O_3@Bi nanoparticles by using LSV, CV, EIS studies demonstrates, is having lower detection limit, higher sensitivity, and better activity at ultra-low potential with its long term stability. These characteristic properties of as-synthesised Bi_2O_3@Bi NPs along with having its low cost, nontoxic nature, its artistic physical and chemical properties has been further encourages towards the promising system for TU detection as one of the model reaction of environmental monitoring processes. Interestingly, from literature, it has been cleared that, the represented Bi_2O_3@Bi NPs based electrocatalytic systems proposed first time for TU oxidation reactions.

Section snippets

Material

Bismuth nitrate [Bi $(NO_3)_3.5H_2O$] and citric acid were purchased from Sigma-Aldrich. Nitric acid (HNO_3), absolute ethanol (99.99%), hydrazine hydrate, Al_2O_3 powders (1, 0.3 and 0.05 μm) were obtained from Fischer Scientific India. All the chemical reagents were of analytical grade and used as received without any further purification. Deionized water was used as a solvent throughout the synthesis of materials as well as for their electrochemical and electrocatalytic studies.
As demonstrated…

…

Result and discussion

Fig. 1(a) displays transmission electron microscopy (TEM) image of as-synthesized Bi_2O_3@Bi NPs, whereas, Bi found to be at the core having average size of 3-4 nm and its shell is of Bi_2O_3 having size of 5-6 nm. The HR-TEM image shown in **Fig. 1(b)** of Bi_2O_3@Bi NPs having dark-black coloured area corresponds to Bi and distinct light grey colored region at the periphery corresponding to Bi_2O_3 shell. **Fig. 1(c)** SAED pattern of Bi_2O_3@Bi shows the glorious spots corresponding to the rhombohedral Bi and …

Electrochemical and electrocatalytic studies of Bi_2O_3@Bi towards TU oxidation

Electrochemical behaviour of as-synthesized nanocomposite has been investigated by using linear sweep voltammetry (LSV) in 0.5 M KOH. Accordingly, **Fig.5(a)** shows the superimposed electrocatalytic performance of bare GC having featureless response for 10 mM TU and with modified Bi_2O_3@Bi response in absence and presence of 10 mM TU in 0.5 M KOH at a scan rate of 50 mV/s. Moreover, from the LSV data, it has been observed that there is no any peak appeared in absence of TU on Bi_2O_3@Bi and also TU…

Mechanism of thiourea oxidation

Dehghani et al. demonstrated the carbon based systems like acid and amine functionalised MWCNTs for TU oxidation and also tested the effect of pH on reactivity, i.e. with acidic pH current density decreases and for basic pH remarkably increase in the current density corresponding to TU oxidation [5]. Moreover, Zang et al. studied the TU oxidation on Au electrode in H_2SO_4 shows the oxidation of TU molecule is two electron and two proton transfer process [24]. Also, Safavi *et al.* proposed TU…

Conclusions

In conclusion, the Bi_2O_3@Bi nanocomposite based electrocatalyst is synthesized by simple chemical reduction appraoch and well characterized by FTIR, XPS, and other studies confirms the formation Bi-O bonding. The elemental analysis by using the EDAX shows the presence of Bi and O (only) corresponding to Bi_2O_3@Bi nanocomposite. XRD shows the Bi_2O_3@Bi NPs having rhombohedral structure, TEM analysis confirms the average size of 4-5 nm with Bi in core and having skin of Bi_2O_3. The improvement in…

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

There are no conflicts to declare…

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Author contributions

AVM designed and conducted all experiments, BBM- data analysis, R.P.D. supervised and contributed for some of the synthesis and functionalization of graphene oxide experiments. SCD- review and editing, LSS- Writing - review and editing, ATA- writing - review and editing, conducted, and BRS proposed and supervised the whole project, funding acquisition and assisted in the writing process and data analysis.…

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