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Electrochemical determination of semicarbazide on cobalt oxide nanoparticles: Implication towards environmental monitoring

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Highlights

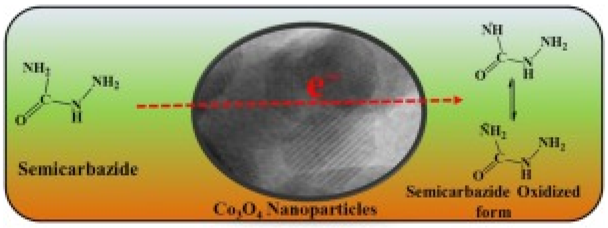
- An economical fabrication of Co_3O_4 nanoelectrode for electrochemical sensing of Semicarbazide (SCB)
- Ultra-low LOD and LOQ were found to be 0.13 and 0.46 respectively for semicarbazide (SCB).
- This article investigates the non precious metal highly stable electrochemical sensor for semicarbazide (SCB) determination.

Abstract

The electrochemical determination of semicarbazide (SCB) executed by using cobalt oxide (Co_3O_4) nanoparticle modified electrode which was fabricated by using simple precipitation method. The as-synthesized nanoparticles have been well characterised by X-ray diffraction (XRD), Furrier transform infra-red (FTIR), UV-visible (UV-Vis) spectroscopic techniques, energy dispersive analysis of X-ray (EDAX), BET surface area, thermogravimetric (TG) analysis and transmission electron microscopic (TEM) techniques. The XRD shows face centred cubic (FCC) structure, the FTIR demonstrated a major bands appeared at 574 cm^{-1} and 669 cm^{-1} are suggesting the (Co-O) vibrational mode of Co_3O_4. The TEM of Co_3O_4 NPs has been confirmed its ultra-small particle size is of ~2 nm ± 0.5 nm. Whereas, EDAX shows the only cobalt and oxygen are available confirms Co_3O_4 having high BET surface area. The fabricated Co_3O_4 acted as a highly sensitive electrochemical sensor for the determination of SCB by using linear Sweep voltammetry (LSV), cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) in 0.5 M KOH solution. Significantly, anodic onset potential observed at 0.2 V vs. SCE, linear range of scan rate and concentration (1 mM–100 mM) with (LOD 0.13 and LOQ 0.46) and high current and potential stability with pH dependent behaviour confirms Co_3O_4 based electrocatalytic system is good for oxidative determination of SCB. The selectivity of the sensor also tested by using mixture of other environmental active species with SCB by using LSV measurements. This proposed system is applicable in food and pharmaceutical industries for the determination of SCB as an amperometric sensor.

Graphical abstract

The cobalt oxide (Co_3O_4) modified electrode was fabricated by using simple precipitation method for oxidative determination of semicarbazide (SCB). This proposed system is applicable in food and pharmaceutical industries for the determination of SCB as an amperometric sensor.



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Introduction

Semicarbazide (SCB) is the organic complex, odourless, derivatives of urea with chemical formula O-C(NH_2)(N_2H_3), and is soluble in water having melting point of 356–363 °F [1]. SCB has been commonly synthesized by condensation of urea and hydrazine [2]. It is used as to prepare pharmaceuticals contains nitrofuran, antibacterials and dizatrifone also stable metabolite of antibiotic nitrofurazone. The blowing agent azodicarbonamide (ADC) on degradations obtained product [3], [4]. In recent time, SCB has been originate in foodstuffs in jars wrapped with cap liners and adulteration of milk [5], [6]. SCB have prepared by azodicarbonamide (ADC) which degrade beneath temperature and moisture content which are having cap liners [7]. Again, Nitrofurans which are widely used for prevention and cure of gastrointestinal and dermatological contagions caused by microorganisms and as growth promoters in calves, fish and shrimps. They are metabolized quickly *in-vivo* and importantly decreases the levels in plasma and formed the stable tissue bound metabolites. These metabolites are realised in acidic conditions which are carcinogenic and mutagenic effects on human being. In addition to this, the SCB is bind with protein in animal and formation of stable complex in body and which is detectable [8]. Therefore, there is an urgent necessity to develop a method for determination and sensing of the SCB to prevent illicit misuse of ADC in foodstuffs by analytical methods, which should have simple operation, quick response during its determination [9] (Scheme 1).

However, literature reflects, there are several advanced methods available for the determination of the SCB form food and pharmaceutical samples in aqueous solutions. For example, Anklam *et.al* summarizes analytical methods for SCB from foodstuff and complete information has elaborated to govern qualitative and quantative evaluation of SCB [10]. Nitrofurazone and SCB detected by the HPLC coupled UV, fluorescence detectors by Du group [11], Danaher et.al studied, UHPLC-MS/MS method [12] for the determination of SCB form plasma like bovine, ovine, equine and porcine. The 2-nitrobenzaldehyde was used to derivativesed plasma samples afterwards extracted with solvent and analysed by UHPLC-MS/MS. Comparative studies of azo-dicarbonamide, biuret and semicarbazide hydrochloride were carried out by FTIR and surface-enhanced Raman spectroscopy (SERS) while the difference between them well demonstrated by Yao et.al. [13]. Although, these methods are available but are having serious limitations like tedious analysis procedure, high cost, need of huge amount of gases/chemicals and expertise, also suffered with poor selectivity and sensitivity etc. Electrochemical sensing and determination have become the predominant analytical methods for the qualitative and quantitative detection of numerous molecules [14], [15], [16]. In addition to this, the electro analytical techniques involves highly selective, they have low detection limit order up to 10^{-10} mole per lit with a wide range of concentrations of electro-active molecules in the form of pure or combined form i.e. in the presence of foreign substances. Electrochemical based or electro-sensing methods have applicable in various branches like nanotechnology, molecular biology, biochemistry to develop the electrochemical sensors with advanced analysis ways [17], [18], [19], [20]. Again, various forms poisonous substances, drug active compounds and biological substances monitoring and with environmental pollutants analysis have performed in short time. In literature number of volumetric electro analytical sensor have reported for the qualitative and quantitative determination of pharmaceutical and environmental particulates viz., chlorpromazine, folic acid, dopamine, sudan etc. [21], [22], [23], [24], [25], [26], [27], [28]

Very few reports are available in literature for electrochemical determination of SCB. For example, anodic oxidation of SCB by Contursi et.al, on IrO_2 electrode by using cyclic voltammetry at room temperature [29]. SCB has been quantified on Pt crystal electrode in aqueous solution by Aldaz and co-workers [30]. Zhao et.al studied volumetric determination on graphene modified metal free electrode [31]. However, these methods are having some boundaries like, use of high cost noble metals, are highly poisonous and their earth abundance is low.

Furthermore, the nanotechnology having broad range of applications especially in the field of electronics, pharmaceutical, to tackle energy and environmental sciences, information technology, catalysis, painting etc. In the line of this nanoparticle (NP) is the primery central basic unit with 10–100 nm in size, i.e. having at least one of the dimension in one billionth meter approximately. The nanoparticles reveals distinctive biological, chemical and physical assets as compared to its own bulk counterpart. Occurrences of these different properties significantly altered due to enhanced surface area to volume ratio, good quantum confinement and enriched reactivity, stability, mechanical strength with good recovery. Also, fabrication of metal oxide based nanomaterials and their potential tuneable applications opens the new door in electrocatalysis, as it is having surface alteration with anionic, cationic, hydrophobic and hydrophilic stabilizers resulted in different morphologies with own bulk counterpart. The electrochemical reactions having important role in electrocatalysts as it is greener approach for the conversion, determination/sensor, redox reactions, energy conversation etc. Under experimental considerations the productivity of transformation have dependent on properties of electrolytes, effect of pH, the phases of catalyst, conductivity of the electrolyte, voltage applied within the working potentials etc. [32], [33], [34], [35].

Co found in the earth's crust abundant in combined form of different alloys, oxides and complexes. Once it separated, it is stable and formation of stable oxides. The Co_3O_4 nanoparticles has spinel type of structure and P-type semiconductor with size and stoichiometry dependent tuneable band gap in the range of 1.48–2.19 eV [36]. Co_3O_4

nanoparticles displays remarkable properties and applications as related with their own bulk counterpart oxide forms. Due to its enormous properties it has been used for large number of potential catalytic and electrocatalytic applications viz., oxidation of biomolecules [37], energy application [38], fuel cell reactions [39], oxygen reduction [40], determination of organic pollutants [41] etc. Herein, Co_3O_4 nanoparticle based electrochemical sensor developed for the determination of SCB and the oxidative determination of SCB on Co_3O_4 NPs has been represented in schematically in Scheme 1. These studies will be helpful for analysis of food and pharma products from pharmaceutical and food industries.

Section snippets

Material

All chemical were purchased from Sigma-Aldrich, cobalt chloride hydrated [$(CoCl_2.)$ $2H_2O$], citric acid, hydrazine hydrate (98%), ethanol, semicarbazide (SCB), urifast drug, urea, tartaric acid, ascorbic acid, potassium hydroxide and all other chemical reagents were of analytical grade from Sd Fine Chemical Pvt Ltd India and used as received without further purification. Deionized water is used as a solvent all over the synthesis of the materials as well as for experimental studies as…

Characterization of Co_3O_4 nanoparticles

As synthesized Co_3O_4 NPs has been well characterised by XRD, FT-IR, UV–vis, TGA, SEM, TEM, EDAX pattern and BET surface area measurement. Accordingly, Fig. 1**(a)** shows the powder XRD pattern of Co_3O_4 NPs, the peaks observed at 19, 31.3, 36.37, 59.2 65.2 and 28, 29 indicates the Co_3O_4 NPs having the face centred cubic structure and is in good agreement with the earlier reports from literature [42]. Moreover, Fig. 1**(b)** shows FTIR spectra of Co_3O_4 which shows the broad peak at 3350 cm^{-1} is assigned …

Conclusion

Herein, cost effective chemical precipitation synthesis approach revealed for Co_3O_4 NPs for electrochemical determination semicarbazide (SCB). The cubic structure of Co_3O_4 NPs have particle size of ~2 nm ± 0.5 nm. The as-synthesized NPs provides as an efficient amperometric electrochemical sensor for the anodic determination of SCB in basic medium. The electrochemical parameters for instance effect of scan rate, concentration and EIS studies, effect of pH and stability of electrocatalyst shows…

Conflict of interest

No any conflict interest.…

Acknowledgements

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2022, Current Opinion in Electrochemistry

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> …On the other hand, the performance of functional molecular devices is strongly dependent on external environmental factors, such as redox reagents [42,43], pH [26], electric field [5,8,29,44,45], photothermal stimulation [26], chelation [46,47], and counterions [42], which can also change the

energy level of molecular junctions (Figure 1). The research on the environmental response is of profound significance to the development of high-performance switches [5–8] and sensors [48–50], especially for environmental monitoring [51,52]. Among these, the modulations on the electronic properties of single-molecule and large-area molecular junctions are different in some aspects.…

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Potential of Piper betle@Co<inf>3</inf>O<inf>4</inf> nanoparticles as high-performance photocatalysts for the removal of industrial dyes

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…On the other side, the materials with a large specific surface area and many available surface active sites can favorably exhibit high photocatalytic activity (Lee et al., 2017). The surface area of P. betle mediated Co3O4 NPs (48.74 m2/g) is higher than those reported for the other comparable materials (e.g., green synthesized Co3O4 NPs (Calotropis gigantea@Co3O4: 46.7 m2/g and green uncapped@Co3O4: 4.4 m2/g), chemically synthesized Co3O4 NPs (NaOH@Co3O4: 44.1 m2/g, H2O2@Co3O4: 36.45, triethanol amine@Co3O4: 31.6 m2/g, and Citric acid@Co3O4: 8.57 m2/g), and other reported materials (MgO: 42.08 m2/g and ZnO: 21.72 m2/g) (Esswein et al., 2009; Liu, J. et al., 2020; Mulik et al., 2021; Ravi Dhas et al., 2015; Sharma et al., 2015; Warsi et al., 2021). Fig. 6 (b) shows the pore size and pore volume distribution in relation to the pore diameters calculated using the Barrett–Joyner–Halenda (BJH) method.…

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