



Mixed metal oxide nanocomposites for enhanced electrochemical detection of nitrite in food products

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ABSTRACT

Mixed metal oxide nanocomposites comprising Manganese, Copper, and Vanadium oxides (Mn/Cu/V₂O₅) were synthesized via a modified hydrothermal technique. Synthesized nanocomposites (Mn/Cu/V₂O₅ NCs) were characterized using FT-IR, FE-SEM with EDAX, TGA, X-ray diffraction, and UV-vis spectroscopic techniques. For the electrochemical detection of nitrite in food samples, a working electrode was specifically designed and constructed utilizing ternary NCs of Mn/Cu/V₂O₅. The electrochemical behavior of the fabricated working electrode towards sensing nitrite ion was investigated using voltammetric methods such as Cyclic Voltammetry (CV), Differential Pulse Voltammetry (DPV), and Linear Sweep Voltammetry (LSV). The electrochemical impedance spectroscopic approach was employed for the structural study of interface created at the interface of working electrode and the analyte. The impact of scan rate and electrolytic pH on the electro-oxidation behavior was examined. The novel working electrode achieved a very low detection capability of 0.01 μM in a detection range of 0–300 μM. The fabricated electrochemical food sensor shows high sensitivity for sensing nitrite in both reference and real food samples. This study offers valuable insights into the fabrication of cost-effective and reliable sensors for detecting additives, colorants, and preservatives in food samples.

1. Introduction

Since ancient times, the problem of maintaining food quality during prolonged storage and transportation has been a significant concern which compels the utilization of food preservatives to prevent natural degradation (Smith-Palmer et al., 2001). Food preservatives are a class of chemical compounds used in food storage and packaging to retard or inhibit the growth of microbes responsible for food deterioration (Russell and Gould, 2003). Throughout history, natural and artificial chemicals have been used to extend the shelf life of food. Commonly used food preservatives are sorbates, benzoates, nitrite, nitrates, and sulfates. For decades, nitrite (NO₂), a common inorganic compound, recognized as a food preservative and fertilizer.

There is a great interest in the detection of nitrite due to its significant role across various domains. Nitrite salts, including sodium nitrite (E250) and potassium nitrite (E249), are frequently used as food additives to prevent processed vegetables, animal-based products, and various other food items (Khanfar et al., 2019); (Phuong Thoa et al., 2009). Nitrite ions play a vital role in food preservation by inhibiting the growth of harmful pathogenic microorganisms, thereby preventing

decomposition and enhancing the flavor and color of specific food items. Nitrite prolongs the shelf life of processed food by acting as an antimicrobial agent and assuring its safety for consumption. The structural of Sodium Nitrite is shown in Fig. S1.

However, despite their importance in food preservation, excessive consumption or exposure to nitrites can present health hazards to humans. Surpassing the recommended safety threshold for nitrite in food items can have fatal consequences for human health (Chan, 2011; Balasubramanian et al., 2017). Nitrite readily binds with hemoglobin, forming methemoglobin, consequently diminishing the blood's ability to transport oxygen (Chen et al., 2019; Miao et al., 2011a, 2011b; Van Staden et al., 2018). Nitrites have the potential to interact with naturally present compounds in specific foods, like amino acids, resulting in the formation of nitrosamines. These nitrosamines are recognized carcinogens and have been correlated to an increased risk of cancer, particularly stomach cancer (Chan, 2011).

Prolonged exposure to high levels of nitrites can cause respiratory problems. Inhaling nitrite-containing dust or fumes, particularly in industries, may irritate the respiratory tract and lead to coughing, wheezing, and other respiratory symptoms. Therefore, to reduce these

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risks, regulatory agencies closely monitor and impose limits on the permissible levels of nitrite in processed food. However, the Maximum Residue Levels (MRLs) in processed foods generally range from 50 to 150 mg kg⁻¹ (Correia et al., 2010). Furthermore, the Environmental Protection Agency has set the highest contamination threshold of 1.0 ppm for Nitrite ions in the public domain water supplies since groundwater contains inorganic nitrite that may get into drinking water (primarily from fertilizers) (Liu et al., 2019).

NO₂ is also recognized as a significant pollutant in many countries. Due to its resemblance to salt, some individuals will use NO₂ to make fake salt (Han et al., 2020; Juskowiak et al., 1996). The advancement of accurate and targeted techniques for the electrochemical detection of nitrite is essential for maintaining food safety and protecting human health (Chen et al., 2008; Safavi et al., 2008). Later significant attention was paid to advanced voltammetric techniques for nitrite determination.

Different analytical methods have been developed to effectively monitor and ensure food quality and safety. These include various spectroscopic methods (Guevara et al., 1998; Ohta et al., 1986; Senra-Ferreiro et al., 2010) like chemiluminescence (Pelletier et al., 2006), fluorescence (Guo et al., 2023; Zhang et al., 2023), nanoplasmonic colorimetry (Keivani et al., 2017), Raman spectrophotometry (Sepahvand et al., 2021), chromatographic methods like GC, HPLC (Tran et al., 2017), GC-MS, LC-MS (Bord et al., 2005; Hassan, 2001; Kodamatani et al., 2009; Lippsmeyer et al., 1990; Miura and Hamada, 1999; Srijaranai et al., 2002; Stutelberg et al., 2014), electrophoretic (Masár et al., 2015), and electrochemical methods (Aksu and Alanya-hoğlu, 2017; Diariso et al., 2018; Manea et al., 2010; Menart et al., 2015; Pietrzak and Meyerhoff, 2009; Rabi et al., 2016; Sall et al., 2020). The majority of them, however, are not appropriate for online or field monitoring since they need specialized tools, complex procedures, and costly (Wang et al., 2014).

Spectrophotometric methods have emerged as the leading option for nitrite detection, thanks to their remarkable sensitivity and simple procedures. Griess Assay is the most prominent among these techniques, which make use of acidified materials containing nitrite to diazotize an appropriate aromatic amine (such as sulfanilamide). The reliability of this approach may significantly vary due to the existence of antioxidants or highly pigmented and heterogeneous matrices frequently encountered in biological and food samples (Gill et al., 2019). To tackle these obstacles, electrochemical techniques provide a remedy, employing either amperometric/voltammetric or potentiometric detection modes.

Among these techniques, electrochemical methods have attracted significant interest in nitrite detection owing to their rapid response, suitability for ambient conditions, affordability, ease of use, as well as their higher sensitivity, and excellent selectivity making them a compelling choice for widespread use. However, conventional electrodes face a challenge in directly oxidizing nitrite due to their higher overpotential (Šetkus et al., 2010).

The practice of modifying the working electrode by specific requirements is recognized as a beneficial approach in the field of electrochemistry. Enhanced conductivity and low electron transfer resistance are desirable properties for chemically modified electrode materials on their specific surfaces. Additionally, possessing a board surface area for the interaction with the target analyte is also favorable (Kumari et al., 2023a, 2023b, 2023c; Samandari et al., 2019). Sensitivity, as well as the selectivity of electrochemical sensors, can be enhanced through the incorporation of various materials into the electrode design, including noble metals, carbon-containing compounds, conducting polymers, and 2D nanomaterials (Li et al., 2015; Li et al., 2019; Pineda et al., 2018; Rhouti et al., 2022; Yang et al., 2021).

Recently, nanomaterials have gained considerable interest in electroanalytical chemistry owing to their high surface-to-volume ratios and customizable properties. The distinctive interatomic bond distances, chemical reactivity, melting points, and optical/electronic properties of nanomaterials play vital roles in their functionality. These materials offer tailored functionalities for specific applications. Their properties

arise from interactions between nanoscale components and their surrounding environment. Electrochemical measurements offer a comprehensive analysis of the electrocatalytic activity of nanomaterials (Kleijn et al., 2014; Zhu et al., 2015). Nanomaterials hold the potential for developing novel devices with unique functionalities designed to detect chemical contaminants.

Electrochemical sensors built with nanomaterials are a hotbed of research, brimming with the potential to revolutionize analysis in environment and food science. These next-generation tools could significantly improve or even replace traditional sensing approaches (Nagaraj et al., 2014). Miao et al. designed and later fabricated an electrochemical sensor using platinum (Pt) nanoparticles for the selective estimation of NO₂ ions in ambient lake water with a detection limit of 5 µM (Miao et al., 2011a, 2011b). In another work, a sensor for the electrocatalytic estimation of nitrite was developed by coupling gold nanoparticles (Au NPs) with a multi-walled carbon nanotube (MWCNT) (Afkhami et al., 2014). The resulting sensor exhibited good sensitivity towards nitrite detection. Similarly, Amatatonchai et al. reported a method for amperometric detection of another preservative sulfite using a Carbon Nanotube (CNT) incorporated with Au NPs and polymer (PDDA) (Amatatongchai et al., 2015). The sensor demonstrated a range (2–200 mgL⁻¹) having a limit of detection of 0.03 mgL⁻¹ for determining sulfite levels in fruit juice and wines. Maduraiveeran et al. developed a simultaneous electrochemical sensor for detecting and quantifying toxic hydrazine, sulfite, and nitrite utilizing Au NPs embedded amine-functionalized silicate-modified electrode (Maduraiveeran and Ramaraj, 2007). In another study, researchers reported the use of Au-loaded SnO₂ hollow microtubes for non-enzymatic detection of H₂O₂ using amperometric methods (Liu et al., 2014). An electrochemical sensor was fabricated to detect p-nitrophenol by modifying a glassy carbon electrode with poly(methylene blue). The sensor achieved a low detection limit of 90 nM. It was successfully utilized for detecting p-nitrophenol in real samples using differential pulse voltammetry (Giribabu et al., 2013). Graphene coupled with TiO₂ NCs was employed for the electrochemical determination of p-chlorophenol (Bai et al., 2014). In a separate study, Fang and colleagues investigated the electrochemical interactions between Au NPs deposited onto dendrimers of poly (amido amine) that were adsorbed onto the surfaces of gold or platinum electrodes for the development of chemically modified electrodes (Fang et al., 2011). In a separate study, an electrochemical sensor was reported for nitrite detection utilizing Ag NPs stabilized by Polyamidoamine (PAMAM) dendrimers (Ning et al., 2014). An electrochemical sensor was fabricated utilizing Carbon Nanotubes (CNTs), dendrimers, enzymes, and Pt NPs. This approach facilitated swift and efficient detection of low volumes on printable chips, potentially offering a cost-effective and disposable solution (Siriviriyannun et al., 2013).

A highly sensitive electrolytic sensor for heavy metal ions detection in water solutions was fabricated by combining fiber-in-tube Solid Phase Microextraction (SPME) with anodic stripping voltammetry (Song et al., 2013). In another work, researchers utilized an amperometric sensor based on quantum-dot decorated nanocrystals for detecting formaldehyde in the environment (Kumar et al., 2022). Recently, mixed metal oxide nanocomposite-modified working electrodes were utilized for the sensitive determination of Vanillin (Kumari et al., 2023a, 2023b, 2023c) and Sudan-I, and Tartrazine dyes (Kumari et al., 2024; Kumari et al., 2023a, 2023b, 2023c) in different food samples.

In this work, a modified working electrode consisting of Mn/Cu/V₂O₅ NCs electrochemical sensors was developed to determine nitrite preservatives in food samples. The superior performance of the sensor can be attributed to the unique properties of the Mn/Cu/V₂O₅ NCs, synthesized through a hydrothermal route, which provided a wide surface area and facilitated efficient electron transfer kinetics at the electrode interface. However, low-cost substances that are found in all chemical laboratories were used to modify the electrode. The proposed electrochemical sensor shows high sensitivity with very good stability toward the detection of nitrite ion preservatives in real food products

and may be extended to the sensitive determination of different preservatives in food samples.

2. Experimental

2.1. Materials

All chemicals and reagents used were of analytical grade and were directly employed without additional purification. Manganese dioxide (MnO_2), Vanadium pentoxide (V_2O_5), Copper oxide (CuO), and Sodium hydroxide were purchased from CDH Chemicals Ltd. (New Delhi, India). Sodium Nitrite (NaNO_2), HCl, and Acetone were obtained from Sigma-Aldrich (Bengaluru, India). Sodium phosphate monobasic and dibasic salts were acquired from Sisco Research Laboratory Chemicals Pvt. Ltd. (Mumbai, India). Ultrapure double-distilled H_2O was utilized for synthesizing NCs. Ethanol (purity 99.9 %) was procured from Chanshu Hongsheng Fine Chemicals (China).

2.2. Instrumentation

FT-IR (Diamond ATR, Bruker ALPHA, Germany), TGA (Thermogravimetric and Differential Thermal analyzer, DTH-60H, Shimadzu Japan), FESEM 7610 F Plus/ZEOL (USA), UV-VIS (UV-2600 Shimadzu, Japan), P-XRD Smart Lab 3.0 kW/Rigaku, (Japan), were used to characterize the synthesized metal NCs. An electrochemical workstation (Metrohm, AUTOLAB, Netherlands) was employed to investigate the behavior of NCs toward nitrite detection. The setup comprised a three-electrode system, with a saturated Ag-AgCl electrode serving as the reference electrode, a Pt-metal wire as the auxiliary electrode, and a Mn/Cu/ V_2O_5 NCs modified electrode as the working electrode. Thermo Fisher Scientific pH meter was used for all pH measurements.

2.3. Hydrothermal synthesis of Mn/Cu/ V_2O_5 NCs

Mn/Cu/ V_2O_5 NCs were synthesized using the versatile hydrothermal method, which is widely employed for the preparation of metal NCs (Sharma et al., 2024; Rabenau, 1985). We have used specifically, the hydrothermal method over Sol-gel and Co-precipitation methods, because the hydrothermal method has better control over particle size and shape. The hydrothermal method often results in high purity and greater crystallinity of metal NPs due to high pressure and temperature inside the Teflon chamber. Other advantages of hydrothermal methods are energy efficiency, eco-friendly, and minimum agglomeration of particles.

Firstly, a metal salt solution of Manganese di-oxide (MnO_2), Copper oxide (CuO), and Vanadium pentaoxide (V_2O_5) was prepared in distilled water with constant stirring to ensure homogeneity. Poly-vinylpyrrolidone (PVP) was added to the metal salt. The stabilizing agent helps in controlling the size and shape of the NPs and prevents their aggregation. Sodium hydroxide (0.5 M) was added to the metal salt solution, acting as a reducing agent that facilitates the reduction of metal ions to metal NPs. After sealing the mixture tightly, it was placed in an SS autoclave and raised the temperature to 130°C for 24 h. Then reaction mixture was allowed to return to ambient temperature.

Following the completion of the hydrothermal reaction, the reaction mixture naturally cooled to room temperature. The resulting metal NCs was obtained by centrifugation process to separate it from the solution. Collected NCs were washed many times with an ethanol-water mixture to remove any residual impurities or unreacted reagents. After washing, the product underwent a drying phase for a duration of 8 h at 100°C . The end product was finely grounded and subsequently stored in glass Vials.

2.4. Preparation of NCs-based electrode sensor

To establish effective electrical connectivity between the analytical solution and potentiostat/galvanostat circuit Cu-wire was used. Initially,

a copper wire was polished with emery paper followed by gentle flattening of the tip of the wire to improve the working area and electrical conductance. The flattened Cu wire was threaded from end to end into an empty plastic syringe. To prepare the slurry for the proposed electrochemical sensor, a mixture of paraffin light, Mn/Cu/ V_2O_5 NCs, KCl, and graphite powder were blended. Using a syringe, the slurry was carefully injected into the plastic syringe electrode through which the Copper wire passed (Kumar et al., 2022; Kumari et al., 2023a, 2023b, 2023c). The lower tip of the prepared electrode was tightly sealed using resin to prevent electrolyte leakage. The top section (uncovered) of the fabricated electrode was coated with wax, to prevent any electrolyte spillage. The incorporation of synthesized NCs was intended to improve the conductance and working area as well as the sensitivity of the electrochemical sensor.

2.5. Electrochemical techniques

For all measurements, the three electrodes-based Potentiostat/Galvanostat with Ag/AgCl as the reference electrode, Mn/Cu/ V_2O_5 NCs as a working electrode, and Pt-wire as a counter electrode were used. The electrolytic solution was placed in a beaker containing the three electrodes. Throughout the experiment, a 0.1 M NaPO_4 buffer (PB) served as the analytical electrolyte. Electrochemical characterizations of nitrite were carried out using different voltammetric techniques like CV, DPV, and LSV. In amperometric measurements, the potential was swept from -1.0 to 1.0 V against saturated Ag/AgCl as a reference electrode with a 10 mVs^{-1} scan rate for the electrochemical detection of nitrite ion preservative. Electrochemical Impedance Spectroscopy was employed for surface analysis of Mn/Cu/ V_2O_5 NCs working electrode.

2.6. Nitrite sample preparation

For the reference sample, sodium nitrite was continuously stirred as it was dissolved in distilled water to yield a clear solution. This solution was then immediately utilized for the electrooxidation study. For the real sample, nitrite extraction was accomplished by leaving 4 g of crushed cheese in 250 mL of distilled water at 70°C . The sample was ultrasonicated for 40 minutes. Following sonication, the suspension was filtered through Whatman filter paper to get a cleared filtrate. This filtrate was then used as the real sample for the electrochemical nitrite detection (Balasubramanian et al., 2018).

3. Results and discussion

3.1. FT-IR spectra of Mn/Cu/ V_2O_5 NCs

Fourier Transformation Infrared (FT-IR) spectroscopic measurements were performed to analyze the synthesized Mn/Cu/ V_2O_5 NCs. The FTIR graph of Mn/Cu/ V_2O_5 NCs showed signals in the fingerprint region as displayed in Fig. S2. In the FT-IR spectrum signals were observed at 537 , 714 , 896 , 958 , and 1623 cm^{-1} . A distinct peak that appears at 537 cm^{-1} suggests the bending vibration of Cu-O (Balasubramanian et al., 2018). The signal at 1623 cm^{-1} indicates the bending mode of the O-H-O. The vibration of the V-O-V bond is represented at 714 cm^{-1} . Furthermore, the two peaks at 896 cm^{-1} and 958 cm^{-1} correspond to the symmetric and asymmetric stretching bands of manganese oxide (Raul et al., 2014).

3.2. UV-visible study of Mn/Cu/ V_2O_5 NCs

UV-visible study of synthesized metal NCs is depicted in Fig. S3. Maximum absorbance of 0.541 was shown by Mn/Cu/ V_2O_5 NCs at 190 nm wavelength. The optical band gap (E_g) an energy gap separating the HOMO and LUMO, controls the optical absorption and conductivity characteristics of ternary metal oxide NCs. The optical band gap can be determined using the Tauc relation (Eq. 1) as given below.

$$\alpha h\nu = B(h\nu - E_g)^n \quad (1)$$

The value of the absorption coefficient, α , at the corresponding wavelength was calculated using the Lambert-Beer Law. The optical band gap of ternary metal oxide NCs was found to be 3.15 eV. $h\nu$ is calculated using the relation $h\nu = 1242 \alpha/\lambda$ (Kumari et al., 2024; Sharma et al., 2024).

3.3. FE-SEM study of Mn/Cu/V₂O₅ ternary metal NCs

FE-SEM technique was used for evaluation of surface morphology like roughness, and homogeneity of the ternary metal oxide NCs. It provides high-resolution 3D images of the sample to calculate average particle size and surface area. The SEM images of Mn/Cu/V₂O₅ NCs at different magnifications are displayed in Fig. S4. A prominent globular crystalline structure was visible in the SEM images of Mn/Cu/V₂O₅ NCs. The synthesis of metal NCs was confirmed by average particle size, which was in the nano range (<100 nm). Fig. S4E illustrates SEM enabled with EDAX analysis of Mn/Cu/V₂O₅ NCs. Elemental data reveals the weight percentage of Vanadium, Manganese, and Copper elements 54.7 %, 6.7 %, and 38.6 %, respectively. These findings serve as further evidence of the sample's purity, with no observable elemental peaks other than those mentioned elements in the EDAX spectra of NCs.

3.4. XRD analysis of Mn/Cu/V₂O₅ NCs

X-ray diffraction study was used to calculate precise structure, crystal lattice, miller indices, space group, and cell parameters of the metal NCs. Rietveld refinement method was used to find out the structural parameters of metal NCs. The diffraction pattern can be analyzed using the most popular Bragg's Law. Fig. S5 displayed the XRD pattern of Mn/Cu/V₂O₅ metal NCs. Mn/Cu/V₂O₅ NCs are crystalline as shown in Fig. S5. XRD peaks at 20, 23, and 28° correspond to V₂O₅ NPs (Kleijn et al., 2014; Kumari et al., 2023a, 2023b, 2023c; Zhu et al., 2015). XRD peaks at 42, and 46° correspond to manganese oxides (Chaudhary et al., 2024). XRD peaks at 2 theta of 45, 50, and 74° correspond to CuO NPs (Kumari et al., 2023a, 2023b, 2023c; Raul et al., 2014).

3.5. Thermogravimetric analysis of Mn/Cu/V₂O₅ NCs

Thermogravimetric analysis (TGA) is a reliable method for evaluating the thermal stability of most of the compounds by monitoring the variation in weight of the specimen with increasing temperature. Approx. 100 mg of sample was put in platinum pans and heated up to 800 °C at a rate of 10 °C/min while being purged with nitrogen at a rate of 30 mL/min. There was a sudden decrease in weight of NCs at 100 °C due to the removal of moisture content in the Mn/Cu/V₂O₅ NCs sample as shown in Fig. S6. Another weight loss takes place at 250 °C and 350 °C due to the loss of other adsorbed gases or one or two metal oxide NPs. Up

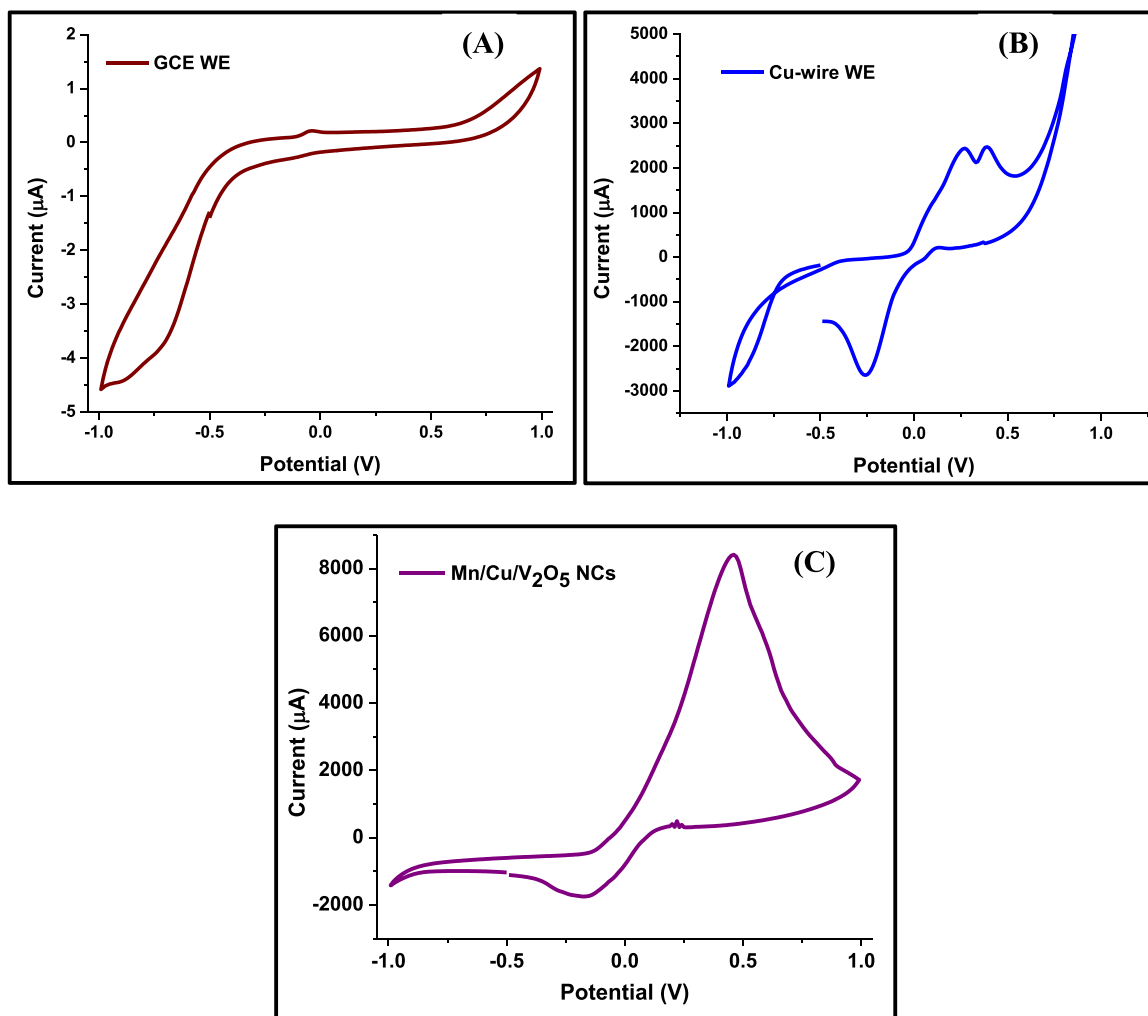


Fig. 1. Cyclic voltammogram at unmodified GCE (A), unmodified Cu-wire electrode (B), Mn/Cu/V₂O₅ NCs modified working electrode (C) in the presence of 100 μ M Nitrite ion in 0.1 M PBS (6 pH) at 10 mVs⁻¹ scan rate.

to 800°C, Mn/Cu/V₂O₅ NCs were found to be stable.

3.6. Electrocatalytic oxidation of nitrite ion using working electrode

The sensitivity of three distinct electrodes: the unmodified glassy carbon electrode (GCE), a basic copper wire (Cu-wire), and a working electrode modified with Mn/Cu/V₂O₅ NCs was evaluated using the Cyclic Voltammetry technique to facilitate electrochemical analysis. Fig. 1 illustrates the cyclic voltammograms of nitrite ions obtained using GCE (Fig. 1C), the bare copper wire (Fig. 1B), and the Mn/Cu/V₂O₅ NCs modified electrode (Fig. 1A). These measurements were conducted in a 0.1 M sodium PBS containing 100 μ M of the reference sample of Nitrite ion, utilizing 10 mVs⁻¹ scan rate. As depicted in Fig. 1C, the unmodified GCE displays a small oxidation peak (0.211 μ A) occurring at - 0.0496 V in the presence of nitrite ions. In Fig. 1B, the unmodified copper wire displays an anodic peak (2437 μ A) around 0.390 V upon exposure to Nitrite, while the Mn/Cu/V₂O₅ NCs working electrode (Fig. 1A) demonstrates a pronounced oxidation peak (8408 μ A) at about 0.460 V for nitrite, exceeding both the GCE and bare copper wire electrodes attributed to the two-electron oxidation of nitrite (NO₂⁻) to nitrate (NO₃⁻). This emphasizes the exceptional charge transfer capability of the Mn/Cu/V₂O₅ NCs modified working electrode in Nitrite oxidation (Wang et al., 2009).

Observations indicate a noticeable improvement in the voltammetric peak current when utilizing the Mn/Cu/V₂O₅ NCs modified working electrode, in contrast to the bare GCE and copper wire. This suggests that the Mn/Cu/V₂O₅ NCs working electrode significantly facilitates the

electrooxidation of nitrite. Consequently, the Mn/Cu/V₂O₅ NCs modified working electrode promotes an expansion in the active area and improves the e-transfer rate between the nitrite ion and the surface of the working electrode. These findings collectively signify the potential of the Mn/Cu/V₂O₅ NCs modified working electrode as a promising modifier for the determination of the electro-oxidation behavior of Nitrite.

3.7. Effect of pH

The electrooxidation of nitrite ions in a three-electrode electrochemical system can be significantly influenced by the pH of the solution due to its effects on nitrite speciation, electrode surface charge, reaction kinetics, and the existence of competing reactions. Using 0.1 M PBS at various pH values, from 4 to 11, the impact of the electrolytic solution's pH on the anodic current peak was investigated to identify the nitrite preservative using cyclic voltammetry, as illustrated in Fig. 2A. The anodic peak current was increased with electrolytic pH up to pH 6 and decreased at higher pH values. A sharp oxidation peak was investigated at pH 6 which was clearly shown in Fig. 2B. Therefore, PB of pH 6 was considered as an optimum pH for nitrite determination and used for further studies. Furthermore, there was no significant impact of the pH of the electrolyte on the anodic peak potential of nitrite oxidation indicating a kinetically controlled electro-oxidation process.

Additionally, the conversion of NO₂ to NO at a lower pH (lower than pH 6) might result in a fall in peak current, as shown in (Eq. 2) given below:

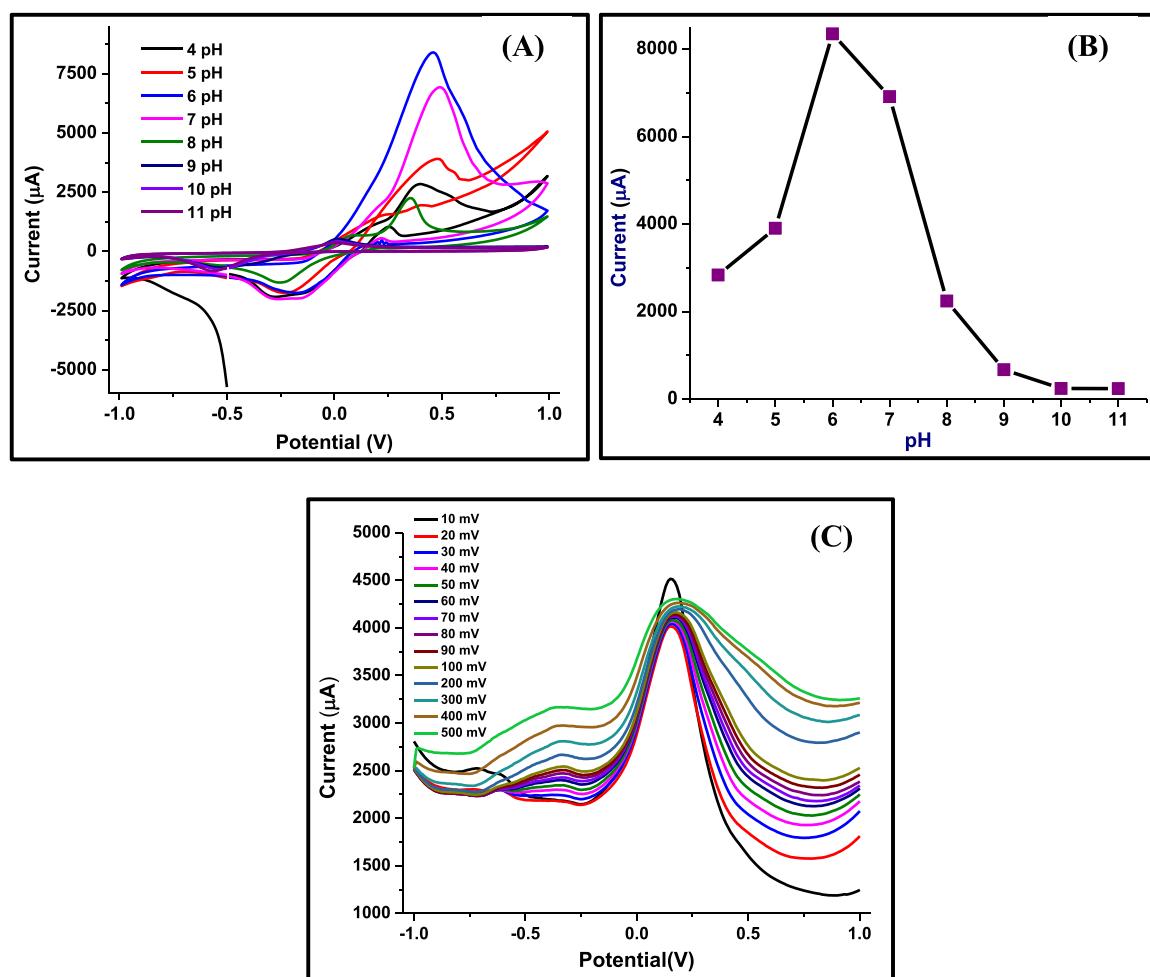


Fig. 2. CV curves of 100 μ M Nitrite ion at different pH 4–11 (A), Peak current (μ A) vs. pH using Mn/Cu/V₂O₅ NCs modified working electrode (B). Effect of scan rate of Mn/Cu/V₂O₅ NCs working electrode on electro-oxidation of 100 μ M concentration of nitrite ion in 0.1 M PBS of pH 6 (C).



Additionally, the alkaline solutions could facilitate the accumulation of oxide layers on the surface of the proposed working electrode which could hinder the electro-oxidation of nitrite. Moreover, the decrease in oxidation peak currents observed at elevated pH levels (above pH 6) can be attributed to a proton deficiency, which impacts the electro-catalytic oxidation of nitrite (Balasubramanian et al., 2018; Kamyabi and Aghajanloo, 2008).

3.8. Effect of scan rate

The correlation between the potential sweep of nitrite oxidation at various scan rates and the resulting redox current can be utilized to identify the electroanalytical parameters that relate to the current responses of nitrite. The impact of scan rate on the electro-oxidation behavior of Mn/Cu/V₂O₅ NCs modified working electrode towards nitrite ion was investigated using Differential Pulse Voltammetry (DPV). Fig. 2 (C) shows the differential voltammetric curve of nitrite (100 μM concentration) in 0.1 M PB (pH 6.0) at Mn/Cu/V₂O₅ NCs modified electrode with the scan rate in the range of 10–500 mVs^{-1} . The oxidation current exhibits an increase with the scan rate i.e., 10–500 mVs^{-1} . However, a sharp anodic peak with maximum current appeared at 10 mVs^{-1} scan rate. The electrochemical reaction becomes less reversible due to a slow electron transfer rate at higher scan rates. Hence, 10 mVs^{-1} was used as the optimum scan rate.

3.9. Effect of concentration

3.9.1. Linear Sweep Voltammetry (LSV)

Linear Sweep Voltammetry (LSV) stands as a crucial pivotal technique in electrochemistry, due to its quantitative capabilities, remarkable sensitivity, wide-ranging applicability, and ability to provide kinetic information about electrochemical reactions. LSV facilitates the precise quantitative analysis of electroactive species dissolved in a solution. This technique was employed to electrochemically determine the presence of nitrite ion preservatives in food samples. Fig. 3 depicts the LSV curve of the electro-oxidation of nitrite ion present in a sodium PBS of pH 6 at 0.01 Vs^{-1} scan rate. By monitoring the current response as a function of applied potential, LSV can determine the concentration of analytes in a sample. An oxidation peak current of $-0.0692 \mu\text{A}$ was observed at a peak potential of -0.0669 V . A linear current response was observed with a rise in oxidation current w.r.t. to the nitrite ion concentration in the electrolytic solution. A well-defined anodic peak current of $1738.94 \mu\text{A}$ with a peak potential of 0.30 V was observed at a

10 μM concentration of nitrite ion. At higher concentrations (at 300 μM) an intense current peak arose at $12538 \mu\text{A}$ and was investigated at a potential of 0.435 V which is 8 folds higher than the 10 μM concentration of nitrite ion. Additionally, a regression equation was also computed to support the reliability of the fabricated sensor with a calibration coefficient (R^2) of 0.9975 shown below (Eq. 3) (Committee, 1988; Van Loco et al., 2002; Araujo, 2009).

$$I (\mu\text{A}) = 2.418 \times (\mu\text{M}) + 3.138 \quad (3)$$

The above equation suggested that the oxidation of nitrite on Mn/Cu/V₂O₅ NCs modified electrode is controlled by the diffusion process.

3.9.2. Differential Pulse Voltammetry (DPV)

Differential pulse voltammetry (DPV) is an important analytical approach frequently used for simultaneous or individual compound analysis. DPV approach provides many analytical advantages such as improved resolution and a decreased detection limit. Therefore, using a Mn/Cu/V₂O₅ NCs modified working electrode, the DPV approach was applied under optimal conditions to quantitatively detect nitrite ions in the food sample. Initially, the electrochemical behavior of Mn/Cu/V₂O₅ NCs modified working electrode at different nitrite concentrations of 0–300 μM was investigated for the reference (control) (0.1 M NaNO₂ solution).

A calibration plot was obtained by DPV under the experimental conditions shown in Fig. 4B. The oxidation current shows a direct correlation with the nitrite ions from 0–300 μM , as shown in Fig. 4 (A and B). DPV curves of Mn/Cu/V₂O₅ NCs modified electrode show a Regression Eq. (4) having $R^2 = 0.9981$ given below (Fig. 4 B):

$$I (\mu\text{A}) = 2.031 \times (\mu\text{M}) + 4.329 \quad (4)$$

Differential Pulse Voltammograms for nitrite at the modified electrode were also investigated for the real sample (cheese sample). The DPV curve (Fig. 4 A.) for nitrite was recorded after the deposition step of 20 s w.r.t. reference electrode (Ag/AgCl) at a PB of 6 pH with 10 mVs^{-1} scan rate. The peak current was increased correspondingly with the concentrations of the real sample (Fig. 4 C).

The electroanalytical performances of the working electrode modified by Mn/Cu/V₂O₅ NCs were compared with those of several nitrite electrochemical sensors that have been described in the literature, as shown in Table 1. The Mn/Cu/V₂O₅ NCs modified working electrode has shown a large linear range and a very good limit of detection compared to the majority of other electrochemical sensors. The low-cost materials/compounds present in almost all chemical laboratories were used to modify the working electrode.

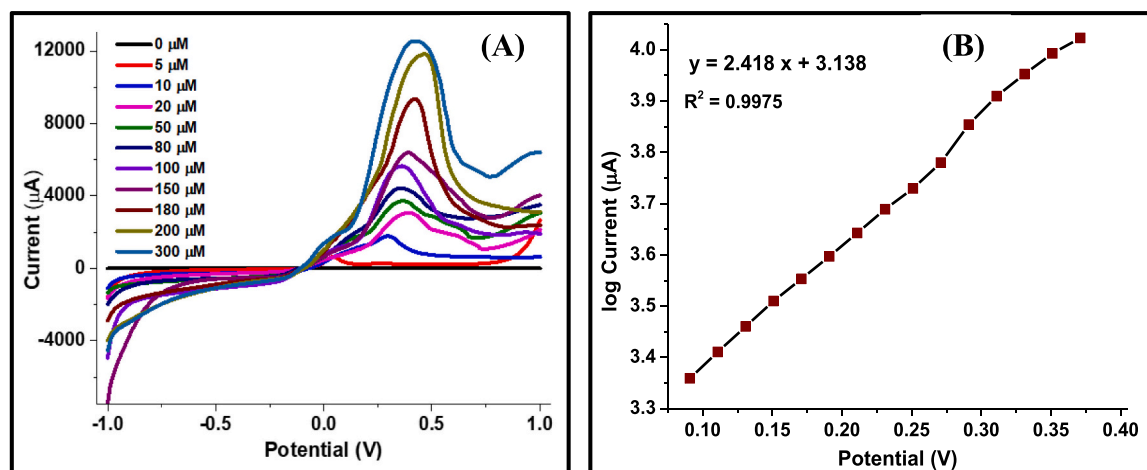


Fig. 3. Linear sweep voltammograms of Mn/Cu/V₂O₅ NCs working electrode (A) towards the electrooxidation of nitrite at different concentrations (0–300 μM), Calibration curve of nitrite ion (B) [for reference sample].

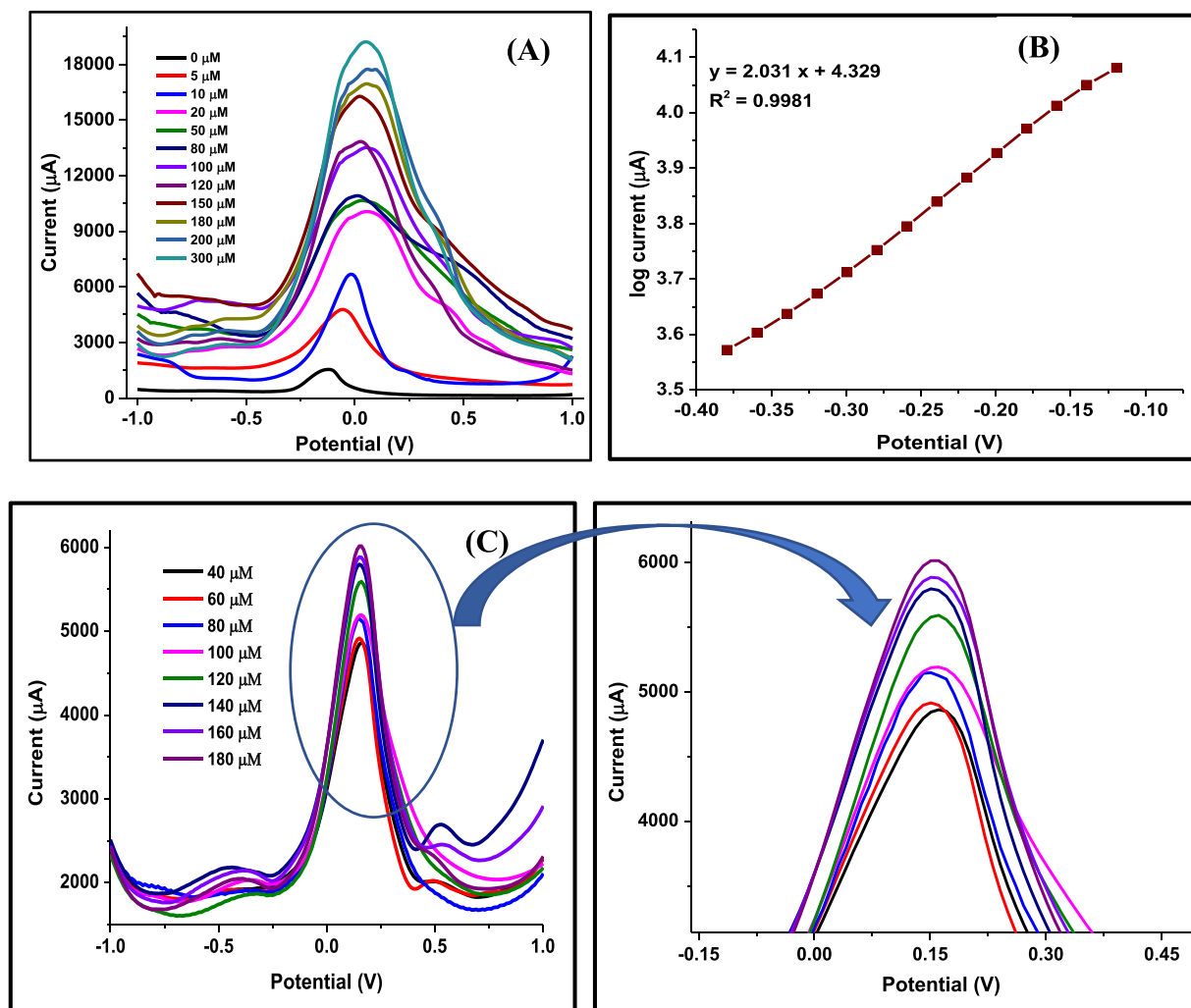


Fig. 4. DPV plots of Mn/Cu/V₂O₅ NCs modified electrochemical sensor towards electrooxidation of nitrite ion with concentrations (0–300 μM), in reference sample in 0.1 M PB with 6.0 pH (A) and, Linear regression curve (B). Differential Pulse Voltammetric curve of electrooxidation of nitrite ion (Cheese sample) towards Mn/Cu/V₂O₅ NCs modified working electrode (C).

Table 1

Comparison of the efficiency of previously reported electrochemical sensors with Mn/Cu/V₂O₅ NCs modified working electrode in electrochemical detection of nitrite ions.

Sr. No.	Material	Technique	Linear range	Detection limit	Sample	Reference
1.	CTABGO/MWNT/ GCE	CV, DPV	5.0–800 μM	1.5 μM	Biological sample	(Yang and Li, 2014)
3.	Fe ₂ O ₃ /RGO	LSV	0.05–780 μM	0.015 μM	Tap Water	(Radhakrishnan et al., 2014)
4.	RGO/MWNT/Pt/Mb/GC	Amperometric	1–2000 μM	0.93 μM	Tap and River water	(Mani et al., 2014)
5.	Au/ZnO/MWNT/GC	CV	0.78–400 μM	0.4 μM	Sausage	(Lin et al., 2011)
6.	Cu/MWCNT/rGO	SWV	0.1–75.0 μM	30 nm	Salami, Sausage, Tap water	(Bagheri et al., 2017)
7.	AuNPs/rGO	Chrono	5.0–2600 μM	500 nm	Tap water	(Zhang et al., 2017)
8.	AuNP/GCFE	Amperometric	1–3350 μM	0.95 μM	Mustard oil	(Wei & Wu, 2019)
9.	Ag/HNT/MoS ₂	CV	2–425 μM	0.7 μM	Water sample	(Ghanei-Motlagh and Taher, 2018)
10.	Carbon powder + CuO	Amperometric	0.1–1.25 mM	0.6 μM	Water sample	(Sljukic et al., 2007)
11.	N-doped graphene quantum dots decorated N-doped carbon nanofibers	CV	5–300 μM	3 μM	Sausage, pickle, lake water and tap water	(Li et al. 2017)
12.	Mn/Cu/V ₂ O ₅ NCs working electrode	CV, LSV, DPV, EIS	0–300 μM	0.01 μM	Water, Cheese sample	Our work

3.9.3. Cyclic Voltammetry (CV)

Cyclic voltammetry (CV) is a highly adaptable methodology for scientific research and innovation since most processes include the transport of electrons. It has been extensively used to monitor the

electrochemical behavior of different compounds due to its ability to find out the relation between structure, potential, and characteristic activities. The fundamental aim of the present work was to utilize the Mn/Cu/V₂O₅ NCs modified working electrode for the sensitive detection

of nitrite ions. The electro-oxidation behavior of the fabricated working electrode towards nitrite ions (reference and real samples) was examined using CV. Fig. 5 shows the CV obtained for a wide linear range of nitrite ions (0–300 μM) present in 0.1 M PB of pH 6.0. In the presence of nitrite ions, an anodic current was detected. There is an overlapping of peak from -0.5 to -0.1 V at 10 μM concentration of nitrite ion may be due to the absence of any electrochemical reaction in this potential window at this specific concentration. With the increase in concentration of nitrite ion, an increase in oxidation peak potential was also observed in CV measurements. The sharp anodic current peak for nitrite was observed as illustrated in Fig. 5 arises from the two-electron oxidation of NO_2^- to NO_3^- as represented in the given Eq. (5) (van Staden et al., 2018).



At the highest investigated nitrite concentration (300 μM) a sharp oxidation peak arose at 14458.48 μA indicates the great sensitivity of Mn/Cu/V₂O₅ NCs modified working electrode towards the electro-oxidation of nitrite ion. The exceptional electron transfer capability and strong synergistic effect of Mn/Cu/V₂O₅ NCs might be responsible for the enhanced electro-catalytic activity of synthesized NCs toward nitrite detection. There is no anodic peak was observed in the absence of

nitrite ion (Kamyabi and Aghajanoloo, 2008).

Similarly, the electro-oxidation behavior of nitrite present in the real sample (cheese sample) was also investigated using CV. The oxidation peak current of different concentrations of nitrite (40–140 μM) at the Mn/Cu/V₂O₅ NCs modified electrode was recorded by CV in PBS solution (0.1 M) of pH of 6 with a scan rate of 10 mVs^{-1} . The sharp anodic peak was recorded at a current of 8348 μA in 100 μM of the real sample of nitrite which is very similar to the oxidation peak current recorded in the reference sample as depicted in Fig. 5. An excellent electron transfer efficiency was observed between the modified Mn/Cu/V₂O₅ NCs working electrode and nitrite ions.

The Mn/Cu/V₂O₅ NCs modified working electrode exhibited strong catalytic action and negligible resistance to charge transfer, resulting in a good electron transfer efficiency between the modified electrode and nitrite ions. As a result, the electrochemical sensor demonstrated exceptional sensitivity and was practical for the electrochemical determination of nitrite in both reference and real samples.

The change in surface area of Mn/Cu/V₂O₅ NCs modified the working electrode before and after CV measurements was calculated using Randles–Ševčík Eq. (6). Peak current (i_p) was observed in a PBS solution (0.1 M) of pH of 6 with a 10 mVs^{-1} scan rate. Peak current was related to the electrochemical surface area (A) of the working electrode using Eq. (6). The quasi-reversible Eq. (7) was also used to find forward

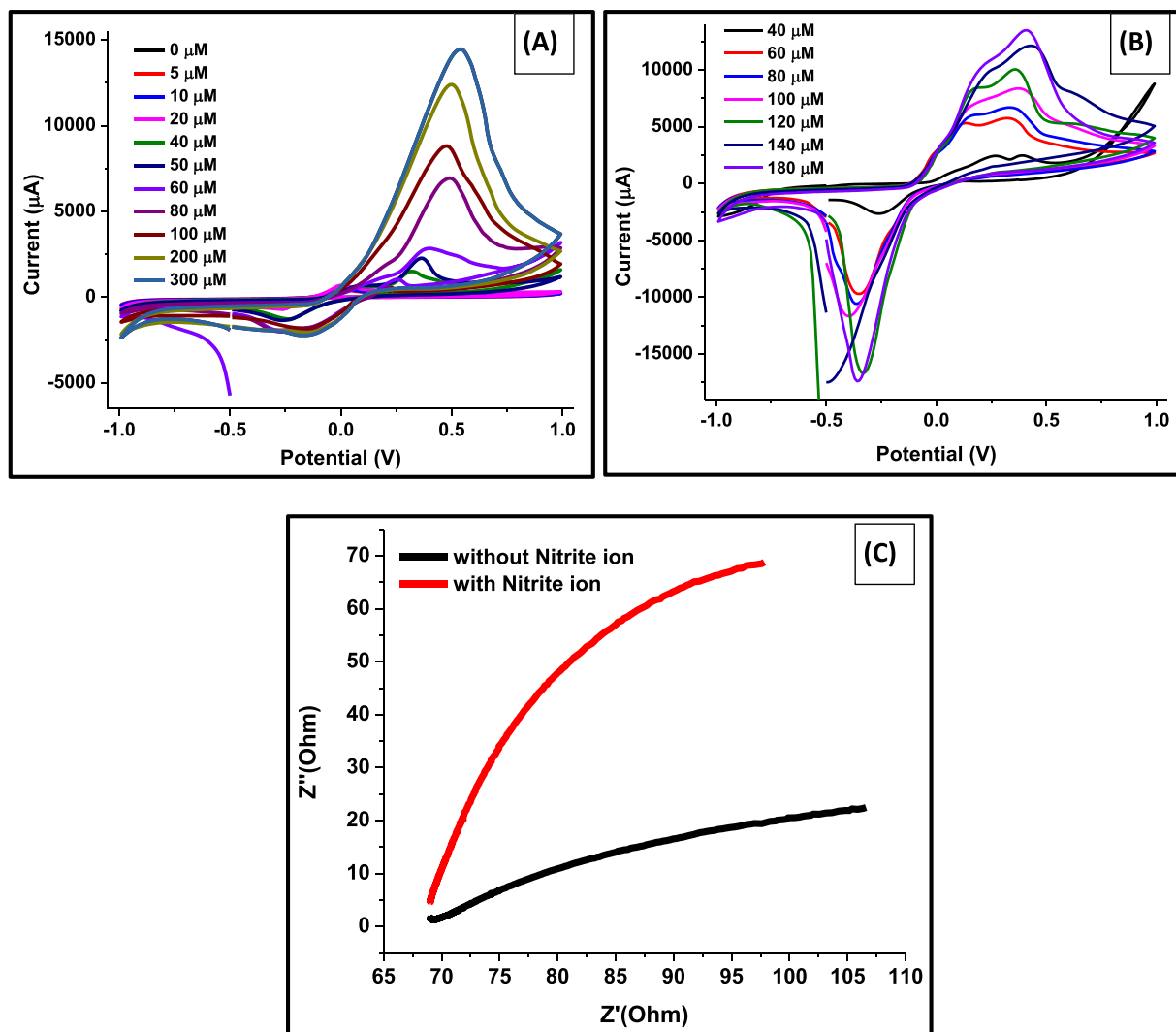


Fig. 5. CV curves of electrooxidation of nitrite ion at various concentrations (0–300 μM) towards Mn/Cu/V₂O₅ NCs-based working electrode in 0.1 M PBS at 6 pH (A). Cyclic Voltammograms of nitrite ion using Mn/Cu/V₂O₅ NCs modified electrode for Real sample (Cheese) analysis (B). Impedance study (Nyquist plot) of Mn/Cu/V₂O₅ NCs modified working electrode without and with nitrite ions (C).

peak current near equilibrium (Crapnell and Banks, 2021).

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C v^{1/2} \quad (6)$$

$$i_{pf}^{Quasi} = \pm 0.436 n F a_{real} C \sqrt{\frac{n F D v}{RT}} \quad (7)$$

In this case, n is the number of electrons involved in redox reactions, v is the scan rate, D and C are the diffusion coefficient, and the concentration of redox species, respectively. The value of the diffusion coefficient taken was $20 \times 10^{-5} \text{ cm}^2/\text{s}$.

Randles-Ševčík Eq. (6) can be rearranged Eq. (8) to obtain electrochemical surface area (A):

$$A = \frac{i_p}{(2.69 \times 10^5) n^{3/2} D^{1/2} C v^{1/2}} \quad (8)$$

The electrochemical surface area (A) of Mn/Cu/V₂O₅ NCs modified the working electrode before and after CV measurements was 0.315 cm² and 0.324 cm², respectively.

It was observed that both oxidative and reductive peaks were observed at higher concentrations of nitrite ions but only the oxidative peak was observed at low concentrations. This may be due to differences in nitrite ions availability at the working electrode surface at two different concentrations, different electrode kinetics, reaction reversibility conditions, the detection limit of nitrite ions, and surface effects of ions. These factors collectively influence the electrochemical behavior of nitrite ions at two different concentrations which was observed in CV.

The peak potential in the CV of the real sample (Cheese) was shifted more as compared to the reference sample (Fig. 5B) due to different factors that affect the electrochemical environment of the nitrite ions. In real cheese and reference samples both containing nitrite ions, different reasons like the presence of other electroactive species, binding, and interaction with matrix components in the real sample, the difference in ionic strength and diffusion coefficients, presence of complexing agents, viscosity and homogeneity, are few probable reasons that contribute to the shift in peak potential noticed in the real cheese sample as compared to the reference sample of nitrite ions.

3.10. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance spectroscopy (EIS) holds considerable importance as a technique for evaluating film resistance, determining the configuration of the electrified interface, and figuring out the concentration of analyte at the interface. Electrochemical impedance spectroscopy tests were conducted using a conventional three-electrode system in a 0.1 M Na PB with a pH of 6.0 to study the interfacial properties of the fabricated working electrode. The experiments were performed both with and without the nitrite ions. Fig. 5 C depicts Nyquist plots in the absence as well as the presence of nitrite ions in the frequency range of 1–10⁵ Hz in PSB electrolytes. The shape of the Nyquist plot can provide information about the diffusion properties and electron transfer kinetics. A linear portion of impedance spectra represented the diffusion-limiting electrochemical process. The concentration of nitrite ions at the interface is linearly correlated with the resistance of the film and is made possible by the diffusion process, depending on the frequency at which nitrite diffuses.

The rise in charge transfer resistance indicates that the introduction of nitrite ions into the electrolytic solution causes the area of Nyquist plots to expand (Fig. 5C). This phenomenon was proved by the amplification in the thickness of the film at the interface when the nitrite ions were present in the electrolyte. The incorporation of nitrite ions into the electrolytic solution resulted in an enlarged area under the Nyquist plot. The EIS results demonstrate that the Mn/Cu/V₂O₅ NCs electrode surface might reduce the resistance to electron flow during electron transfer.

The surface area (A) of Mn/Cu/V₂O₅ NCs modified the working electrode before and after impedance measurements were obtained from

double-layer capacitance (C_{dl}) using Eq. (9):

$$C_{dl} = \frac{A}{\epsilon \epsilon_0 d} \quad (9)$$

Here, ϵ and ϵ_0 are the dielectric constant of the electrolyte and permittivity of free space. d is the thickness of the double layer. The surface area (A) of the working electrode was calculated by rearranging Eq. (9) as Eq. (10):

$$A = \frac{C_{dl} d}{\epsilon \epsilon_0} \quad (10)$$

The surface area (A) of Mn/Cu/V₂O₅ NCs modified the working electrode before and after impedance spectroscopy measurements was 0.314 cm² and 0.322 cm², respectively.

3.11. Performance and Storage stability study of the working electrode

In electroanalytical chemistry, ensuring the stability of the working electrode is the primary concern. This refers to the capability of reproducing experimental outcomes using the same three-electrode-based setup with equal accuracy and consistency. To investigate the stability of the Mn/Cu/V₂O₅ NCs modified electrode, the CV of nitrite solution was recorded for every 10-day interval. The oxidation current was stable for the 10 repetitive measurements. Periodic monitoring of the current response at 100 μM using the CV technique revealed sustained effectiveness of the Mn/Cu/V₂O₅ NCs modified working electrode over time, with assessments conducted at 10-day intervals for 90 days (Fig. S7).

Significantly, the performance of Mn/Cu/V₂O₅ NCs modified working electrode remains consistent and stable even after prolonged exposure to ambient conditions. This demonstrated durability and reliability, making the proposed working electrode an attractive sensor for various food-sensing applications.

4. Conclusions

The electro-oxidation behavior of nitrite ions (NO₂⁻) in various food samples is determined through an electrochemical sensing platform utilizing a ternary metal NCs-based working electrode. The Mn/Cu/V₂O₅ NCs were synthesized using a hydrothermal method and characterized by different techniques, including FT-IR, UV-Vis spectroscopy, TGA, XRD, and FE-SEM with EDAX. A working electrode modified with Mn/Cu/V₂O₅ NCs was developed and utilized as an electrochemical sensor to investigate the electrocatalytic oxidation behavior of Nitrite ion preservatives in food samples. CV, LSV, DPV, and EIS techniques were used for the accurate and sensitive detection of NO₂⁻ ions. The electrochemical performance of ternary metal oxide-based sensors was compared with glassy carbon-based and platinum-based working electrodes and found to be far better than both. The fabricated sensor presented a wide detection range i.e., 0 and 300 μM concentrations of nitrite, and an excellent detection capacity as low as 0.01 μM. A sharp anodic peak was recorded at a current of 8348 μA in 100 μM of the real sample of nitrite ions. The synergistic activities of NCs were attributed to enhanced electrocatalytic performance necessary for the sensitive determination of nitrite ions. The enhanced electrocatalytic performance was supported by an increase in the active surface area of the electrode after the CV and impedance measurements. Furthermore, the electrochemical sensor provides many advantages, including quick response, relative affordability, and high sensitivity, enabling real-time nitrite monitoring in aqueous solutions. The proposed sensor can accurately detect nitrite in different applications in food security, diagnostic laboratory tests, and environmental monitoring. Future research should focus on optimization, miniaturization of working electrode, selectivity study against another analyte, and exploring eco-friendly synthetic routes.

CRediT authorship contribution statement

Rajni Mohil: Visualization, Validation. **Harish Kumar:** Writing – review & editing, Validation, Supervision, Conceptualization. **Varsha Barman:** Visualization, Validation. **Rajni Kumari:** Writing – original draft, Methodology, Investigation, Conceptualization.

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

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Statement regarding the use of AI tools

We declare that we have not taken the help of any AI tools in writing this manuscript.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jfca.2024.107137](https://doi.org/10.1016/j.jfca.2024.107137).

Data availability

Data will be made available on request.

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