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Research article

Nitrite sensing: Utilizing titanium dioxide and copper-doped titanium dioxide in electrochemical detection

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Abstract

Importance of the work: This study is essential for food safety. Detecting nitrite with electrochemical sensing prevents bacterial growth and mitigates health risks.

Objectives: To synthesize titanium dioxide (TiO_2)/copper (Cu)-doped TiO_2 through solution combustion and explore their nitrite detection via electrochemical sensors.

Materials and Methods: TiO_2 and Cu-doped TiO_2 fine particles were synthesized via a solution combustion process, followed by calcination and hydrothermal treatments with multi-walled carbon nanotubes (MWCNTs). The resulting composite was drop-cast onto glassy carbon electrodes and its sensing performance was assessed using cyclic voltammetry.

Results: The solution combustion method reduced the Cu-doped and undoped TiO_2 particles from 500 nm to less than 280 nm. Combined with MWCNTs, these particles were applied as sensing materials in electrodes. Electrochemical tests showed oxidation at 0.55 V and reduction near -0.85 V in a nitrite solution. The Cu-doped TiO_2/MWCNTs had stronger oxidation and reduction peaks compared to the TiO_2/MWCNTs. Sensitivity analyses indicated heightened peak intensity with rising nitrite levels and excellent linearity, suggesting their high potential for nitrite detection.

Main finding: The effectiveness of solution combustion in refining TiO_2 and Cu-doped TiO_2 particles, combined with MWCNTs, enhanced electrode electrocatalysis. This process produced superior materials for effective nitrite detection in environmental and food safety monitoring.

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Introduction

Additives are commonly included in products to satisfy consumer demand and gain a competitive edge in the market, with such items often necessitating the use of chemical additives for various purposes such as enhancing flavor, adding color, preserving freshness or facilitating transportation by Karwowska and Kononiuk (2020). A wide range of additives are utilized in food production, including nitrites, which, when consumed in large quantities, can lead to symptoms including headaches, nausea, bloody stools and even the formation of carcinogenic compounds called nitrosamines within the body (Karwowska and Kononiuk, 2020).

Food additives can be identified using various methods, one of which is high-performance liquid chromatography (HPLC). HPLC separates substances based on their unique properties and is widely used for qualitative and quantitative analyses in fields such as food testing, pharmaceuticals, herbal medicine, and environmental samples. However, HPLC is not suitable for sensor applications due to its limitations in real-time monitoring, portability, cost-effectiveness, simplicity and ease of use according to Meesombad et al. (2021). In contrast, electrochemical sensors are designed for on-site monitoring, with modern sensor technologies being smaller, faster and more precise, often using a potentiostat, an electronic device that controls voltage differences between working and reference electrodes in an electrochemical cell (Meesombad et al., 2021).

The selection of materials for the working electrode in electrochemical sensors is crucial and is contingent on the specific substance being targeted for detection. Commonly used materials for enhancing these electrodes include zinc oxide, nickel oxide, cobalt oxide, iron oxide, silicon, aluminum and brass (Govindhan et al., 2014). Titanium dioxide (TiO_2) is also utilized in electrochemical sensors due to its stability, biocompatibility, high surface area, excellent electron transfer properties and adaptability for specific applications reported by Bagheri et Al. (2014). Furthermore, TiO_2 is cost-effective, making it valuable for a variety of sensor applications (Bagheri et al., 2014).

Doping is a robust method for improving the electrochemical performance of materials in electrochemical sensors. It offers several advantages, including enhanced electrical conductivity, modified band structures for efficient charge transfer, improved charge separation in photoelectrochemical sensors, increased surface area for better sensitivity, enhanced stability and durability, tunable selectivity, expanded material choices and cost-effectiveness (Vazhayil et al., 2022). By selecting appropriate dopants and concentrations, researchers can customize material properties to optimize sensor performance and enhance the efficiency of working electrodes in electrochemical sensors.

Copper (Cu) was selected as a dopant in TiO_2 electrocatalysts in the current study due to its ability to enhance catalytic activity during electrochemical reactions. This improvement is associated with the variable oxidation states of copper, which facilitate charge transfer processes on the surface of TiO_2, with the resulting Cu-doped TiO_2 nanocomposite attracting considerable attention due to its elevated specific surface area, enhanced transfer of charge carriers, numerous active sites and robust chemical and mechanical stability by Zhou et al. (2020), Song et al. (2022) and Nassef et al. (2023). As a result, it has been applied in diverse fields, as indicated by various research studies (Zhou et al., 2020; Song et al., 2022; Nassef et al., 2023).

Electrocatalytic activity was further enhanced by using a combination of Cu-doped TiO_2 and nanocarbon materials, specifically multi-walled carbon nanotubes (MWCNTs). The Cu-doped TiO_2-MWCNTs combination resulted in improved surface area and enhanced electrical conductivity and stability, with the enhancement of sensor electrochemical performance attributable to this combination having been documented by Rao et al. (2017).

The current research focused on preparing TiO_2/MWCNTs and Cu-doped TiO_2/MWCNTs composites for use as sensing materials in electrochemical sensors and explored their potential application for nitrite detection. The importance of this study primarily lies in the utilization of the solution combustion method for refining TiO_2 and Cu-doped TiO_2 particles, which were used as sensing materials that showcased improved electrochemical performance and enhanced nitrite detection capabilities when tested on pond water and sausage samples. The research results should contribute insights into the synthesis, material characterization, and electrochemical testing of sensors, providing valuable knowledge in the areas of electrocatalysis and chemical detection. Additionally, the results should contribute to enhancing food safety and mitigating health risks related to the consumption of nitrites.

Materials and Methods

Synthesis and characterization of Cu-doped titanium dioxide powder

TiO_2 and Cu-doped TiO_2 were prepared using the combustion method. Submicron-sized TiO_2 powder with an average particle size close to 500 nm (99% purity; Sigma Aldrich®)

was dissolved in sulfuric acid (H_2SO_4, 95–97% purity; Emsure®) and then diluted with deionized water (DI) to achieve a 6 M concentration. Copper (II) nitrate Cu $(NO_3)_2$ (Daejung) was added to the mixture in a copper-to-titanium mole ratio of 3:100. Subsequently, glycine (NH_2CH_2COOH, 99% purity; Fluka Analytical®), serving as the fuel for the combustion process, was introduced to the mixture in a 1:1 ratio with TiO_2. The mixture underwent combustion by heating at close to 400°C. The powder obtained from the combustion was collected and underwent calcination in an MFL1200 muffle furnace (Nano Generation Co., Ltd) (maker) at 500°C.

The synthesized TiO_2 and Cu-doped TiO_2 powders were examined for their phase using X-ray diffraction analysis with an X'Pert X-ray diffractometer (Philips) in the range 20–80°, with a step size of 0.02°. Additionally, surface area analysis was performed using the Brumaire-Emmett-Teller (BET) method with a 3Flex surface area analyzer (Micromeritics). The particle size and morphology of the powders were examined using scanning electron microscopy (SEM; Quanta 450; FEI).

Preparation of sensing materials for working electrodes

The synthesized Cu-doped TiO_2 powder was mixed with MWCNTs using DI (1:1 volume ratio). The mixture underwent 30 min of sonication at high-frequency vibration to ensure uniformity. The solution was subjected to the hydrothermal method by placing it in an autoclave at 120°C for 5 hr. Following the hydrothermal treatment, the solution was filtered to remove excess water and then dried at 80°C for 24 hr. The Cu-doped TiO_2/MWCNTs composite was mixed in ethanol, along with a Nafion (Sigma-Aldrich), binding agent, in a 1:0.95:0.05 volume ratio. The mixture was sonicated for 30 min to ensure homogeneity and subsequently drop-cast onto working electrodes made of glassy carbon. Prior to drop-casting, the glassy carbon electrodes were polished with diamond paste (particle size: 15 µm) and rinsed with aluminum powder and DI water. After this preparation, the electrodes were allowed to dry overnight.

Electrochemical testing

The electrodes prepared in the previous step were utilized for testing the detection of nitrite compounds using cyclic voltammetry (CV). The concentration of nitrite compounds in the solution was in the range 100–1,000 µM. The process of preparing Cu-doped TiO_2/MWCNTs composite working electrodes and nitrite detection is illustrated in Fig. 1.

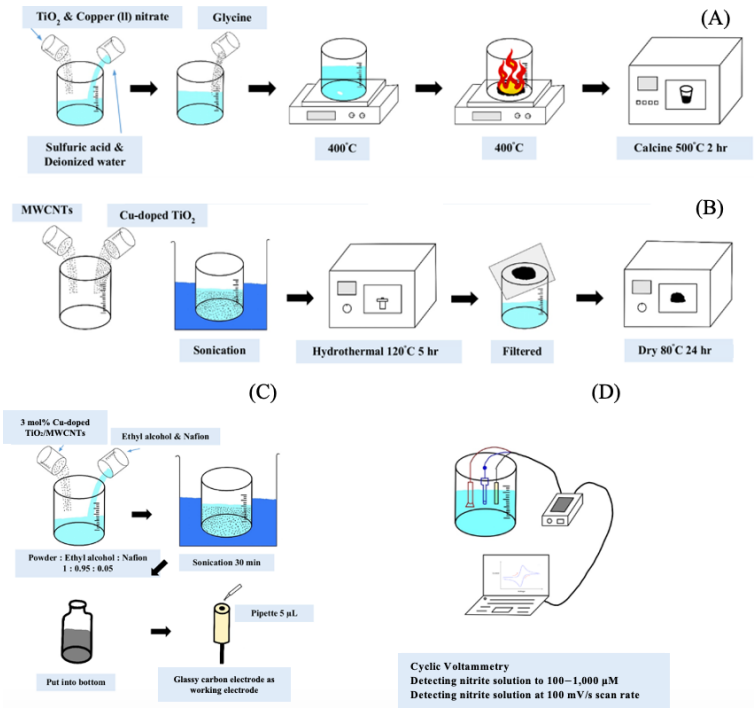

Fig. 1 Schematic representation of the preparation of Cu-doped TiO_2/MWCNTs composite working electrodes and the detection of nitrite using cyclic voltammetry method: (A) synthesis of Cu-doped TiO_2 using the solution combustion technique; (B) preparation of Cu-doped TiO_2/MWCNTs composite using the hydrothermal method; (C) preparation of a glassy carbon electrode containing the Cu-doped TiO_2/MWCNTs composite; (D) electrocatalytic measurement of the electrode

Preparation of real samples for electrochemical measurement

The water from the pond and sausages were used as the actual samples to examine the nitrite content. For the sausage analysis, 30 g of sausages bought at the local market in Bangkok, Thailand, were processed, homogenized, and extracted using a 0.1 M phosphate buffer solution at pH 7. Then, the extracted sample was cooked in a water bath at 75 °C for 30 min and subsequently filtered. The prepared extract served as the analyte for determining the nitrite concentration, following the procedure outlined Guo and Fan (2023).

Results and Discussion

Phase identification

The TiO_2 and Cu-doped TiO_2 produced through the combustion technique were examined and determined to predominantly consist of the anatase phase (JCPDS 96-901-5930), exhibiting 2θ values at approximately 25.26°, 37° and 48° with a very low-intensity rutile peak at a 2θ value of 27.42° (JCPDS 96-900-1682), as depicted in Fig. 2.

Anatase generally has a larger surface area and enhanced catalytic capabilities (Fröschl et al., 2012), while rutile offers increased stability and improved mobility of charge carriers (Miyoshi et al., 2018). The combination of these phases results in a synergistic relationship, leveraging the strengths of each (Zheng et al., 2011). This synergy enhances overall catalytic performance by effectively separating charge carriers. The resulting reduction in charge recombination enhances the efficiency of catalytic reactions. Consequently, the mixed phase of anatase and rutile in TiO_2 achieves a balance between surface area, stability and charge carrier mobility, conveying superior catalytic activity compared to pure anatase in various catalytic applications (Luttrell et al., 2014; Bagheri and Julkapli, 2017).

From the experimental results, it was concluded that the combustion technique was a suitable method for synthesis that met the chemical composition requirements.

Particle size, morphology and specific surface area of Cu-doped TiO_2

The TiO_2 and Cu-doped TiO_2 powders had a spherical morphology, as depicted in Fig. 3. Through image analysis using Image J, the average particle sizes were determined to fall within the range 250–280 nm, indicating that the solution combustion technique effectively refined the particle size, reducing it from the initial size of approximately 500 nm to one-half its original size.

In addition, the scanning electron micrographs revealed the particle sizes of both powders were in comparable ranges. Despite their fine size, these particles tended to aggregate into clusters, which led to a reduction in the specific surface area, which, in turn, would influence the electrochemical properties. This observation was supported by the analysis of the relatively low specific surface area using the BET technique, yielding results of less than 10 m^2/g.

Typically, when the BET surface area is lower in a catalytic reaction, it implies that the available surface for the reaction is limited. This reduced surface area might hinder the catalyst's ability to interact effectively with the reactants. As a result, the catalyst might exhibit lower activity and efficiency in promoting the desired chemical transformation (Sun et al., 2018).

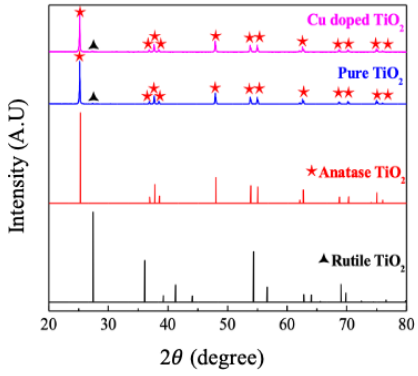

Fig. 2 X-ray diffraction patterns of undoped TiO_2 and Cu-doped TiO_2

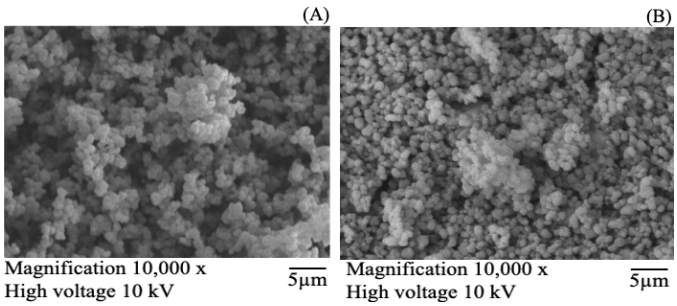

Fig. 3 Scanning electron micrographs: (A) undoped TiO_2; (B) Cu-doped TiO_2

Electrochemical activities

Electrochemical impedance spectroscopy (EIS) investigations offer valuable insights into the kinetics of electron transfer processes occurring at the interface between the electrode and electrolyte on a working electrode (Wang et al., 2014; Terbouche et al., 2016). In this particular investigation, EIS measurements were carried out on glassy carbon electrodes (GCE) containing Cu-doped TiO_2/MWCNTs and undoped TiO_2/MWCNTs composites. These measurements were conducted in a solution containing 5 mM standard potassium ferrocyanide ($K_4[Fe(CN)_6]$, 99% purity; Daejung) in 0.1 M of potassium chloride (KCl, 99–100% purity; Kemaus). The assessments encompassed a frequency range of 100–10 mHz at an applied voltage of 0.2 V. The obtained results manifested as a Nyquist plot, illustrating the values of charge transfer resistance (R_{ct}) for Cu-doped TiO_2/MWCNTs and undoped TiO_2/MWCNTs, of 11 kΩ and 30 kΩ, respectively. This outcome is depicted in Fig. 4, highlighting an amplified electrical conductivity in the Cu-doped TiO_2/MWCNTs composite electrode. The mechanism by which Cu-doped TiO_2/MWCNTs facilitated electron transfer could be explained as follows.

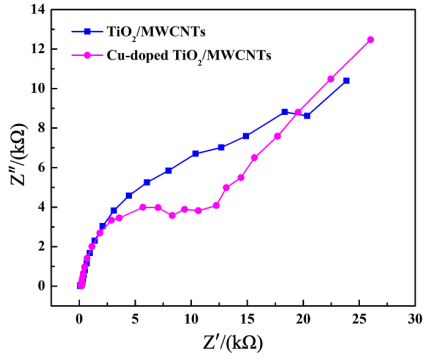

Fig. 4 Nyquist plots of composite electrode Cu-doped TiO_2/MWCNTs and TiO_2/MWCNTs electrodes in 5 mM solution of $K_4[Fe(CN)_6]$ in 0.1 M KCl with frequency range of 10–100 kHz and 0.2 V applied voltage

Doping, the introduction of impurities into a semiconductor to modify its band structure, is a well-established and cost-effective method for enhancing catalyst performance (Berger, 2020). Dopants can reduce the bandgap energy, making it easier for electrons to be excited from the valence band to the conduction band; in addition, the dopants can inhibit the transition from anatase to rutile by infiltrating the anatase lattice and altering oxygen vacancy levels, which affects the material's electronic properties (Hanaor and Sorrell, 2011).

In the context of Cu-doped TiO_2, the Cu acted as a dopant that enhanced electron transfer rates and electrocatalytic performance due to several factors. First, Cu doping reduced the bandgap energy of TiO_2, facilitating easier electron excitation and enhancing the material's conductivity. Second, metals, particularly transition and noble metals like Cu, serve as traps for charge carriers, thereby reducing the recombination of electron-hole pairs. This prolongs the lifetime of the charge carriers and increases the probability of electron transfer to the electrode surface (Ola and Maroto-Valer, 2015; Tahir et al., 2017). Finally, Cu doping increases the number of active sites on the TiO_2 surface, which facilitates more efficient electron transfer and improves the overall electrocatalytic activity as stated by Ola and Maroto-Valer (2015) and Tahir et al. (2017).

Furthermore, integrating MWCNTs into the composite electrode enhanced the electron transfer rates and electrocatalytic performance. The MWCNTs had several advantageous properties as they have a high specific surface area, providing more active sites for electrochemical reactions and increasing the efficiency of the electrode. They also have outstanding electron conductivity, facilitating rapid electron transfer between the electrode and the electrolyte. Additionally, their chemical stability ensures that the electrode maintains its performance over prolonged use and under various conditions (Yang et al., 2017; Hussain et al., 2020).

The low charge transfer resistance observed in the EIS results indicated that integrating Cu-doped TiO_2/MWCNTs into sensing materials substantially improved the electron transfer efficiency between the electrode and electrolyte, thereby enhancing electrocatalytic activity. This enhancement was consistent with findings in the existing literature on metal-doped oxides (Manibalan et al., 2022).

Since there was superior charge transfer and amplified electrical conductivity in the Cu-doped TiO_2/MWCNTs, this was chosen for further testing of electrocatalytic activity. CV was used to measure the electrochemical reactions of the composite containing multi-walled carbon nanotube and Cu-doped TiO_2/MWCNTs in a nitrate solution with concentrations in the range 100–1,000 µM. The scanning rate was set at 100 mV/s. It was observed that the oxidation and reduction reactions occurred at potential differences close to 0.55 and -0.85 V, respectively.

The mechanism of nitrite sensing could be explained through the electrochemical reactions involved during the oxidation and reduction processes. The oxidation peak at 0.55 V corresponded to the oxidation of nitrite (NO_2-) to nitrate (NO_3-) on the surface of the Cu-doped TiO_2/MWCNTs electrode. This process could be represented by the following reaction (Rashed et al., 2020):

$$NO_2^- + 2H^+ + O_2^- \rightarrow NO_3^- + H_2O + 2e^-$$

The reduction peak at -0.85 V might be attributed to the reduction of nitrite (NO_2-) to ammonia (NH_3), which could be described by the following reaction (Dreyse et al., 2011):

$$NO_2^- + H^+ + e^- \rightarrow NH_3 + H_2O$$

Sensitivity

The sensitivity of the working electrodes was calculated based on the slope of the linear relationship between the concentration of the analyte and the current density. Fig. 5 shows that a higher concentration of nitrite solution resulted in more pronounced oxidation and reduction peaks. For the oxidation reaction, measured at the applied voltage of 0.55 V, the sensitivity value was 1.5×10^{-3} µA/µMmm^2, as depicted in Fig. 5. A similar trend was observed for the reduction reaction, which, at the applied voltage of -0.85 V, had a sensitivity value of 1.4×10^{-3} µA/µMmm^2.

Calibration curves were constructed for the electrode using nitrite solutions across a concentration spectrum range of 100−1,000 µM. As illustrated in Fig. 6, these calibration curves exhibited a linear correlation between the nitrite concentration and the current density, with an coefficient of determination value exceeding 0.97. The sensitivity values of the working electrode, determined from the slopes of these calibration curves, fell within the range $1–1.5\times10^{-3}$ µA/µMmm^2, showing that the sensitivity was in a comparable range to those of the other research studies listed in Table 1.

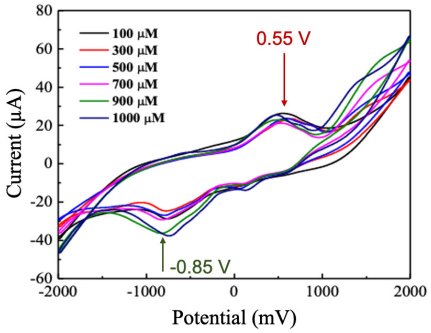

Fig. 5 Cyclic voltammetry curve of Cu-doped TiO_2/MWCNTs at different concentrations of nitrite in range 100–1,000 µM with scan rate of 100 mV/s

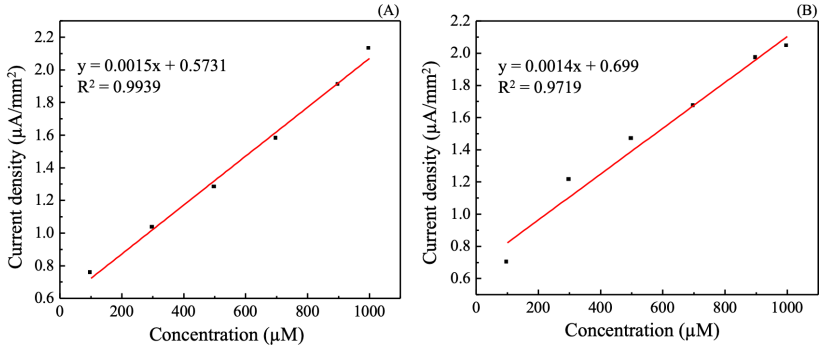

Fig. 6 Calibration curve of Cu-doped TiO_2/MWCNTs electrode in nitrite solution with concentration range of 100–1,000 µM, at applied voltages of (A) 0.55 V for oxidation and (B) -0.85 V for reduction and scan rate of 100 mV/s, where R^2 = coefficient of determination

Table 1 Concentration range and sensitivity of electrodes for detection of nitrite

Type of electrode	Concentration range (µM)	Sensitivity (µA/µM mm^2)	Reference
Pt/Ni(OH)$_2$/MWCNTs modified GCE electrode	100–5,000	1.45×10^{-3}	(Sheng et al., 2017)
Carboxyl functionalized MWCNTs/Co-MOFs/Gr electrode	80–1,160	1×10^{-4}	(Salagare et al., 2022)
Ag-doped zeolite graphite-epoxy electrode	100–1,000	7×10^{-3}	(Manea et al., 2010)
Cu-doped TiO_2/MWCNTs composite GCE electrode	100–1,000	1.4×10^{-3}	This work
		1.5×10^{-3}	

Pt/Ni(OH)$_2$/MWCNTs modified GCE electrode = platinum nanoparticles loaded on the surface of nickel hydroxide multi-walled carbon nanotubes nanocomposites modified glassy carbon electrode; Carboxyl functionalized MWCNTs/Co-MOFs/Gr electrode = carboxyl functionalized multi-walled carbon nanotubes and cobalt-based metal-organic framework-modified graphite electrode; Cu-doped TiO_2/MWCNTs composite GCE electrode = copper-doped titanium dioxide/multi-walled carbon nanotubes composite glassy carbon electrode

Analysis of nitrite concentration in real samples

The chronoamperometry method was utilized to evaluate nitrite levels in various real samples across a range of nitrite concentrations (100–10,000 µM), as shown in Fig. 7 according to Guo and Fan (2023). With a measured current of 50 µA, the nitrite concentration in the sausages was approximately 8,000 µM, equivalent to 27.6 mg of nitrite per 30 g. This concentration exceeded the allowable nitrite content set by National and EU regulations, which should not surpass 150 mg/kg (Djordjevic et al., 2019). Additionally, the nitrite levels in the pond water from Kasetsart University, Bangkok, Thailand were analyzed, revealing a concentration of 4,000 µM, or 184 mg of nitrite/L, which is above the U.S. Environmental Protection Agency's guideline of 5 mg/L for warm water (United State Environmental Protection Agency, 1986). Notably, nitrite concentrations in water can vary significantly, reaching up to 180 mg/L due to seasonal changes and contamination (Eddy and Williams, 1987).

Conclusion

The solution combustion technique was applied to generate nanoparticles of Cu-doped and undoped TiO_2 powders, leading to a refinement in particle size. The average particle sizes fell below 280 nm, highlighting the effectiveness of this method in reducing the particle size by approximately 50%, compared to the initial size of approximately 500 nm. The synthesized powder, combined with MWCNTs, functioned as the sensing material for the working electrodes. Electrochemical investigations of these electrodes in a nitrate solution revealed oxidation and reduction reactions at applied voltages near 0.55 and -0.85 V, respectively. Notably, the Cu-doped TiO_2/MWCNTs exhibited more pronounced oxidation and reduction peaks compared to TiO_2/MWCNTs.

Further sensitivity analysis of the Cu-doped TiO_2/MWCNTs working electrodes, demonstrated increased peaks with higher nitrite concentrations. For the oxidation reaction, the sensitivity value was 1.5×10^{-3} µA/µMmm^2. Similarly, the reduction reaction had a sensitivity value of 1.4×10^{-3} µA/µMmm^2. As shown in Table 1, the sensitivity values obtained in this study were in a comparable range with findings from other studies. These results underscored the efficacy of the synthesized Cu-doped TiO_2/MWCNTs as a promising material for electrochemical applications, particularly in nitrite detection.

Conflict of Interest

The authors declare that there are no conflicts of interest.

Acknowledgment

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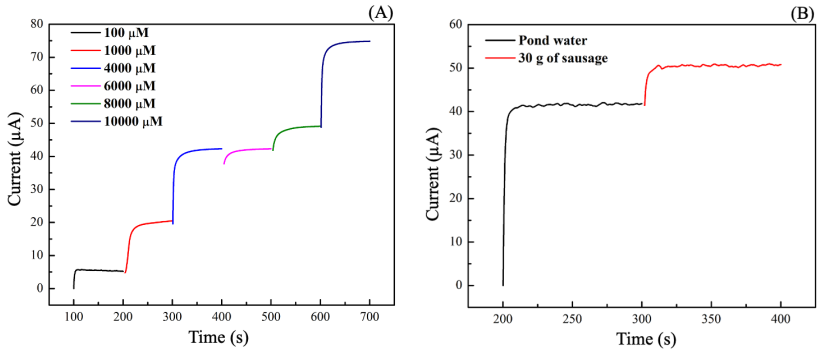

Fig. 7 Chronoamperometry measurements conducted on (A) nitrite concentrations in range 100–10,000 µM and (B) real samples (pond water, sausage) at applied voltage of -0.85 V

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