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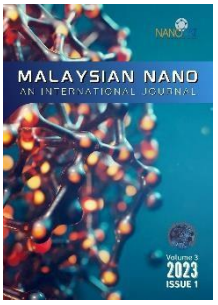

Research article

Multilayered Nano Ti_3C_2Tx Electrode: An Ultrasensitive Electrochemical Sensor for Rutin Antioxidant Detection

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Abstract

Multilayer two-dimensional (2D) structures (MXenes) provide promising advantages in biomedical applications. Using SEM and XRD characterization techniques, the synthesized substance was identified. Our results show that Ti_3C_2Tx-GCE possesses a significant number of active sites, enhancing its electrocatalytic activity and electrochemical sensing abilities for RT oxidation. The multilayered Ti_3C_2Tx-GCE that was produced had good electrochemical properties and acceptable pore structures. Additionally, it exhibited remarkable linearity starting from 1 to 10 µM and demonstrated high sensitivity for the electrochemical measurement of RT, with an impressively low limit of detection (LOD) of 0.345 µM. EIS studies revealed that the synthesized multilayered Ti_3C_2Tx possessed a significantly low charge transfer resistance and a high electron transfer rate constant. Our research lays the groundwork for designing a multilayered Ti_3C_2Tx network, which opens up intriguing possibilities for creating high-performance electrochemical sensors for use in biomedicine and clinical settings.

Keywords: Multilayered Ti_3C_2Tx, Wet Chemical Etching Method, Electrochemical Sensor, Rutin Sensor

1. Introduction

This template serves as a manual for crafting manuscripts to be submitted. For comprehensive instructions and submission protocols, kindly refer to the instructions for Authors or a recent journal issue. The need for a rutin sensor arises from the growing demand for accurate and reliable detection methods for antioxidants in various fields. Rutin, a flavonoid compound found in many fruits and vegetables, possesses significant antioxidant properties and plays a crucial role in human health [1,2].

The Multilayered Ti_3C_2Tx electrode is an innovative electrochemical sensor designed for ultrasensitive detection of the antioxidant rutin. This sensor exhibits remarkable sensitivity and selectivity, making it a valuable tool for various applications in the field of antioxidant detection [3]. The unique composition and structure of the electrode enable the efficient detection of rutin molecules, offering a reliable and accurate analytical technique. The Ti_3C_2Tx electrode is composed of multiple layers of titanium carbide nanosheets, which are known for their excellent electrical conductivity and large surface area. These nanosheets are synthesized using a well-established method, ensuring the electrode's stability and reproducibility. The multilayered architecture of the electrode provides enhanced electrochemical performance by facilitating efficient charge transfer and maximizing the exposure of the active sensing surface [4,5]. One of the key advantages of the Multilayered Ti_3C_2Tx electrode is its ultrasensitivity in rutin detection. The electrode exhibits a remarkably low detection limit, allowing for the detection of rutin molecules at extremely low concentrations. This attribute is crucial in many fields, such as pharmaceuticals, food science, and environmental monitoring, where the accurate measurement of antioxidants is of paramount importance.

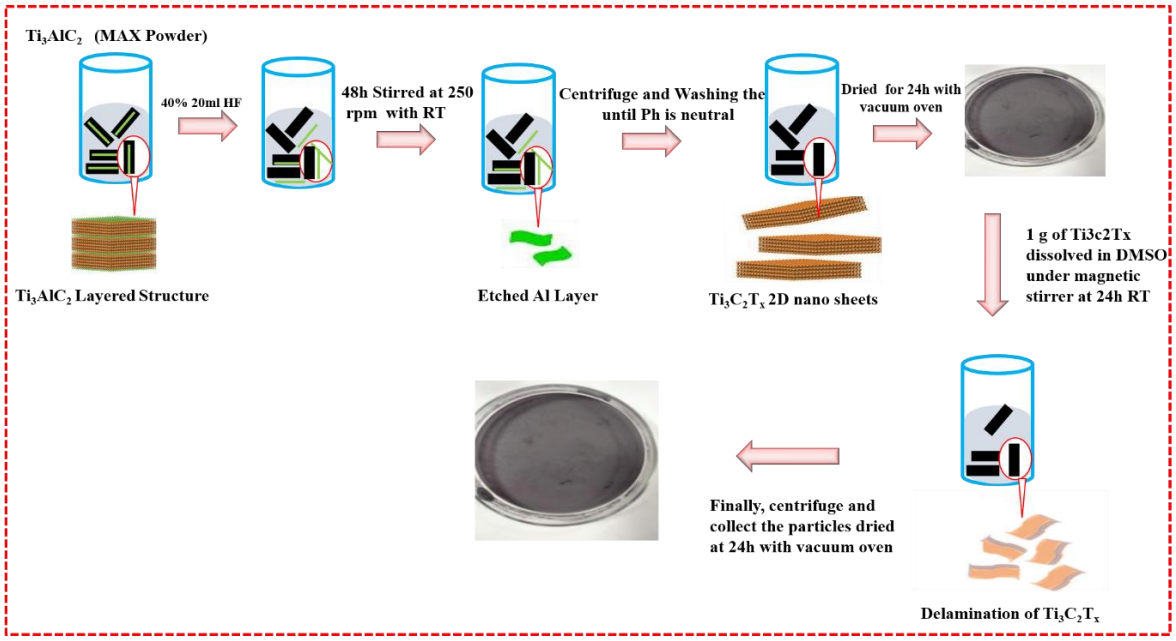
Moreover, the Multilayered Ti_3C_2Tx electrode demonstrates high selectivity towards rutin detection, even in the presence of other interfering species. This selectivity is attributed to the unique surface properties of the Ti_3C_2Tx nanosheets, which interact specifically with rutin molecules, resulting in a highly specific sensing mechanism [6]. Consequently, the electrode can distinguish rutin from other compounds, enabling reliable and precise analysis. In addition to its exceptional performance, the Multilayered Ti_3C_2Tx electrode offers practical advantages in terms of ease of fabrication and integration into existing electrochemical sensing platforms [7]. Its synthesis process is well-established and can be easily scaled up, making it feasible for large-scale production. Furthermore, the electrode's compatibility with standard electrochemical measurement techniques simplifies its implementation in various analytical setups. In conclusion, the Multilayered Ti_3C_2Tx electrode represents a significant advancement in ultrasensitive

electrochemical sensing for rutin antioxidant detection. Its unique composition, enhanced sensitivity, and selectivity make it a promising tool for a wide range of applications [8,9]. By enabling accurate and reliable detection of rutin, this electrode contributes to the development of more efficient and precise antioxidant analysis methods, ultimately benefiting industries and research fields focused on health, food, and environmental sciences. In this research work, the multilayered Ti_3C_2Tx was synthesized, and structural and morphological analysis was conducted. The performance of the rutin sensor based on the prepared multilayered Ti_3C_2Tx was investigated under optimal conditions. The developed electrochemical sensor exhibited ultra-high sensitivity, good stability, and selectivity when tested. This innovative approach, based on nanocomposites, holds great potential for advancing antioxidant detection. It can contribute to improved health monitoring and enable advancements in diverse scientific and industrial applications.

2. Materials and Methods

The MAX phase powder (Ti_3AlC_2) Titanium Aluminium Carbide nano powder Purity: 98%, APS: <40 μm) Saveer Matrixnano Private Limited. 48% Con Hydrofluoric acid. Powder X-ray diffraction (PXRD) profiles were captured throughout a diffraction angle range of 10 to 80 degrees using Cu-K radiation (Smart Lab-Rigaku X-ray diffractometer). TESCAN VEGA3 SBH was used to perform morphology under a high vacuum Electrochemical experiments were carried out in a three-electrode cell with a GCE as working electrode, a platinum as a counter electrode, and Ag/AgCl as a reference electrode using an Auto lab PGSTAT302.

2.1 Wet Chemical Etching Method



Scheme 1. Ti_3C_2Tx Electrode Preparation Method.

Ti_3C_2Tx (MXene) was synthesized through the wet chemical etching method. 0.5 g Ti_3AlC_2 (MAX) powder was slowly added to 40% of concentrated 20ml of hydrogen fluoride and stirred at 300rpm at room temperature for 48 hours. The solution was centrifuged several times with deionized water and ethanol until it reached a pH of 7. Following that, the Ti_3C_2Tx powder was collected by drying it for 24 hours in a vacuum oven at 75 °C. Delamination of the multilayer Ti_3C_2Tx was accomplished by dissolving 0.5 g of Ti_3C_2Tx in 30 ml of DMSO and stirring it for 24 hours at room temperature [10]. Finally, the solution was centrifuged at 3000 rpm for 15 minutes before being filtered and dried at 75 °C to obtain a few layers of Ti_3C_2Tx in Scheme 1.

3. Results and discussion

3.1 Structural Analysis

The lattice parameters have been ascertained based on the corresponding structures, and their values are presented in Table 1. The visuals can be seen in Figure 1 [X].

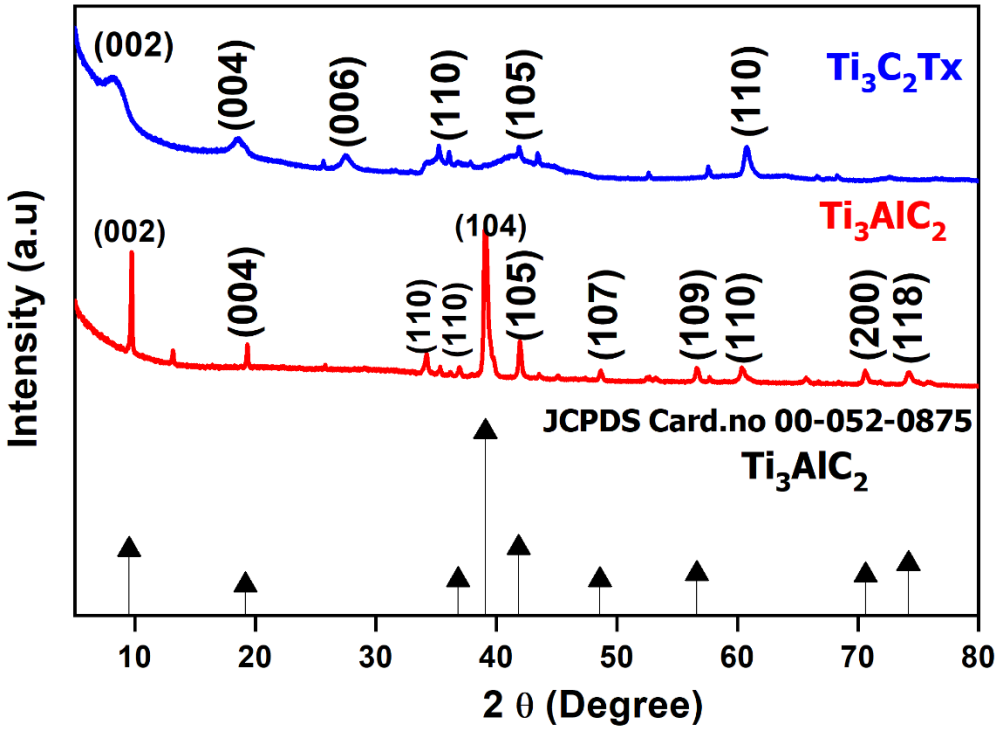


Figure 1. PXRD Pattern of Ti_3C_2Tx Electrode.

X-ray diffraction (XRD) spectrum of bulk Ti_3AlC_2-MAX and etched Ti_3C_2Tx-MXene is shown in Figure 1. The XRD spectrum of the bulk MAX that was collected matched the JCPDS no. 052-0875, which corresponds to Ti_3AlC_2, quite well. After 48 hours of etching the aluminum (Al) with hydrofluoric acid (HF), the XRD peak intensity and crystallinity were decreased lower angle side [11]. The broad peak shifted from 9.9 to 8.3, resulting in an increase in the *d*-spacing for MXene. The structural study shows that the MAX phase resulted in effective Al etching.

3.2 Surface Morphology Analysis

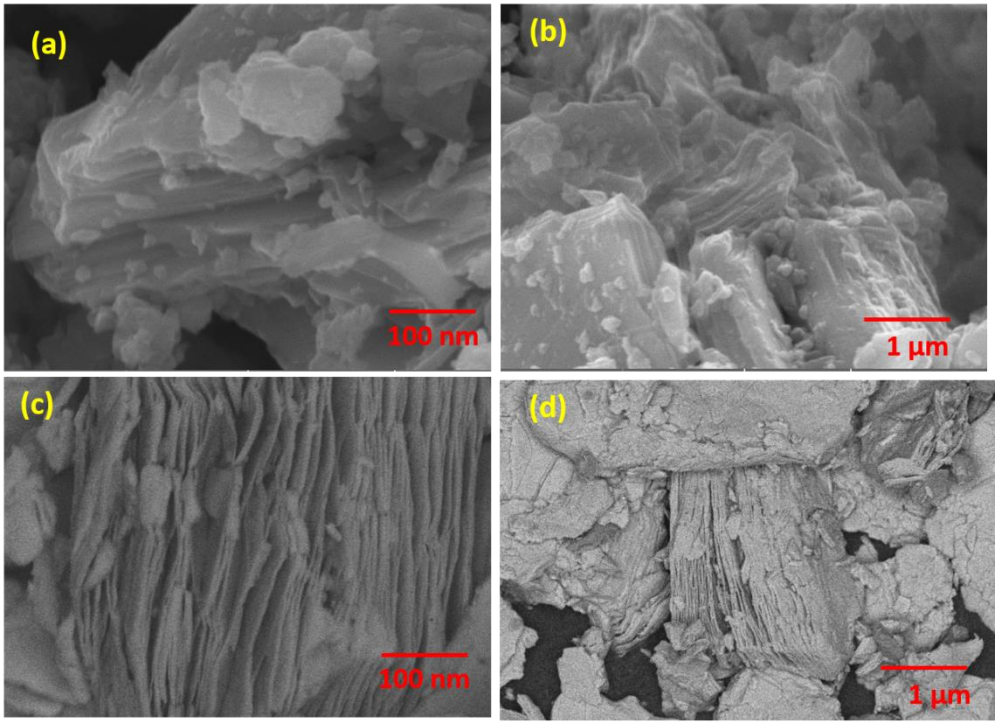


Figure 2. (a, b) SEM Images of Ti_3AlC_2 Electrode. (c, d). SEM Images of Ti_3C_2Tx Electrode.

SEM was used to examine the morphology of the synthesized Ti_3C_2Tx. The Ti_3AlC_2 phase is depicted in Figures 2. (a), (b), and (c), along with a synthesized multilayer of Ti_3C_2Tx with a layered structure that resembles graphene. Extended reaction times of up to 48 hours resulted in complete exfoliation and the production of quasi-2D MXene sheets, as shown in Figure 2(c, d). High magnification made it easy to see how the entire grain had exfoliated into uniformly thin layers. The resulting surface-active spots on the layered structure were subsequently labeled using a multilayered Ti_3C_2Tx electrode to facilitate efficient charge transfer [12].

3.3 Electrochemical Activity of Electrode

Different pH values (3 - 12) were explored using CV to determine the impact of rutin on the Ti_3C_2Tx/GCE. The findings are shown in Figure 3(a). It is known that the peak potentials shifted to the negative and the current values decreased in the pH sequence (3 > 5 > 7 > 9 > 12). This demonstrates the precise proton reaction, and it has been determined that a pH of 7 is suitable for detecting rutin. Peak potential and pH are inversely proportional. The largest redox peak current is observed at pH 7.0, as shown in Fig. 3 (a), among all the pH ranges investigated in this study. The effect of the scan rate on the electrochemical response of rutin was investigated at a Ti_3C_2Tx/GCE electrode in a 0.1 M PBS (pH = 7.0) solution containing a 50 µM rutin solution [13]. The anodic

peak currents steadily increased from 10 mV/s to 40 mV/s with the scan rate (Fig. 3b). The scan rate and oxidation peak currents (Ip) have a strong linear correlation. With an increase in scan rate, the redox peak potentials also moved slightly, indicating an almost reversible electrochemical process.

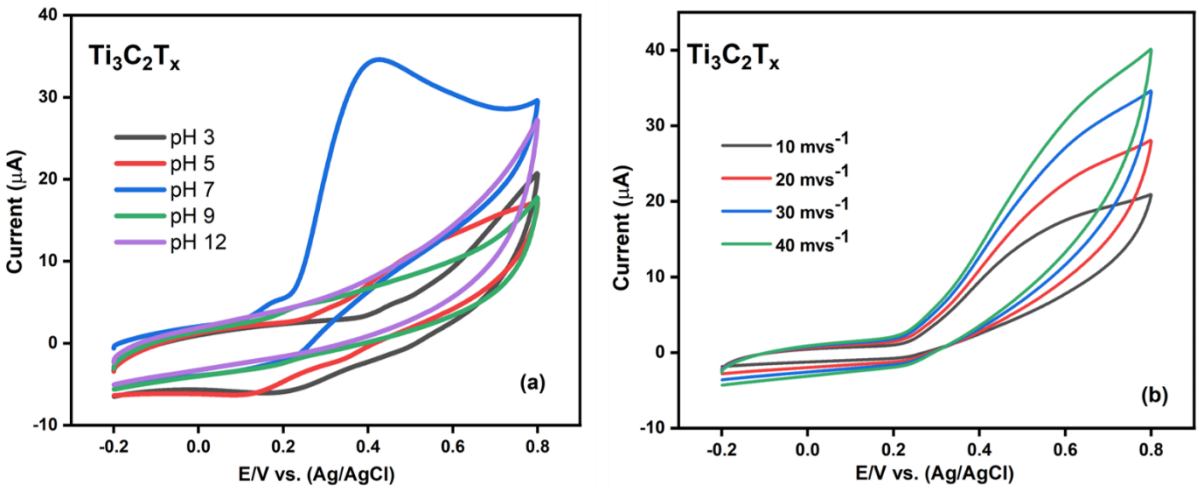


Figure 3. Cyclic voltammetry curves of RT (50 µM) at different pH values. (b) Cyclic voltammetry curves of RT at different scan rates.

In a PBS (pH 7) solution, Ti_3C_2Tx/GCE was added to oxidize rutin, with a scan rate of 50 mV s^{-1}. This is shown in Fig. 4a. No peak is visible in Ti_3C_2Tx/GCE in the absence of rutin. But when rutin is added, a strong and well-defined peak current emerges. With each successive increase in rutin concentration (0-100 M), the anodic peak current rises linearly. The reversible oxidation process in Fig. 4b, used in a rutin molecule, transforms the B-ring of the catechol group into an ortho-quinone derivative. This process demonstrates that the Ti_3C_2Tx/GCE exhibits strong linearity in the range of rutin concentration (0-100 µM) compared to the corresponding current signal. Since the Ti_3C_2Tx/GCE catalyst has a derived regression coefficient of R^2=0.994, it is evident that it exhibits exceptional electrocatalytic activity towards rutin. The electrochemical sensor's analytical capabilities were evaluated using the DPV approach under ideal conditions [14,15]. A series of rutin concentrations ranging from 0 to 10 µM were used to assess the sensor's performance. As shown in Fig. 4c, the oxidation peak current increases with the addition of rutin, and there is a strong linear relationship between the current response and rutin concentration in the range of 1 to 10 µM. The sensor has a low detection limit of 0.345 µM and the Ti_3C_2Tx/GCE modified electrode offers several advantages, including a wide linearity range and a low detection limit. The regression equation was computed with an R^2 value of 0.985 in Fig. 4d.

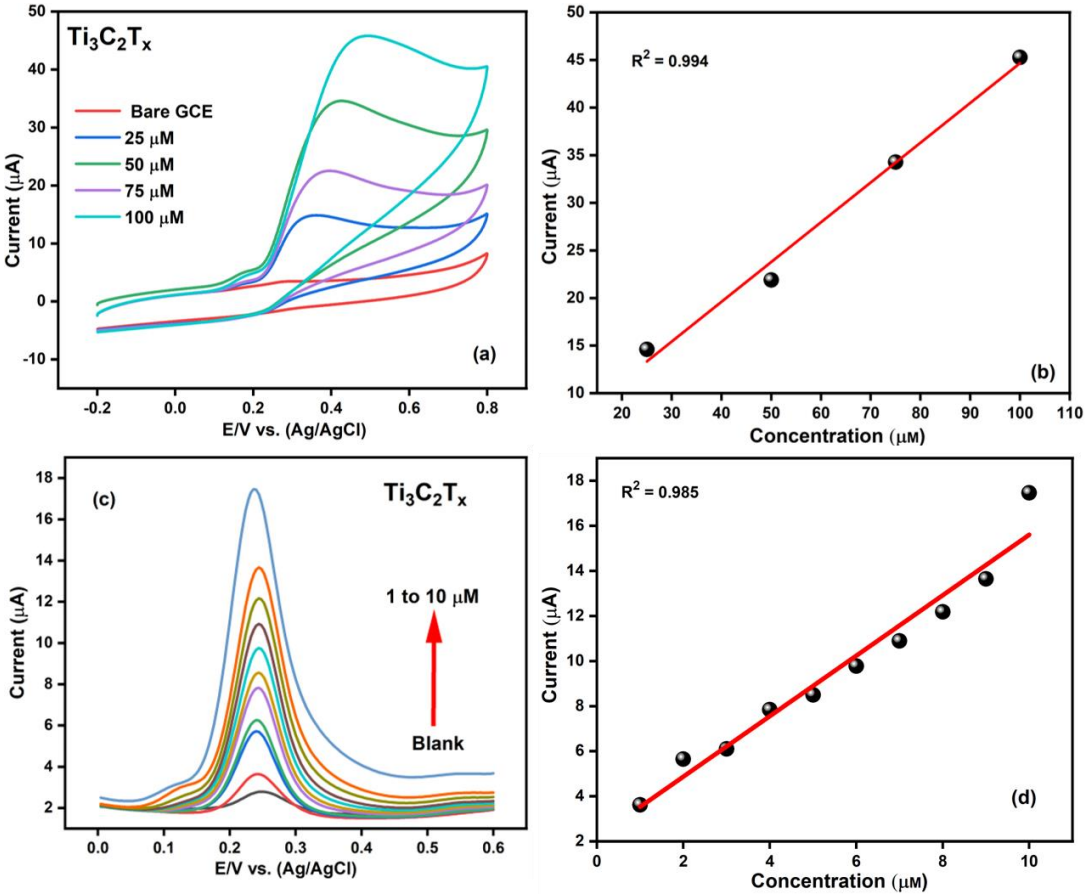


Figure 4. (a) Addition of analyte versus the current. (b) Shows a linear increase in the rate of current. (c) DPV curves of different concentrations of rutin in buffer. (d) Linear relationships between DPV current and lg of rutin concentration.

Figure 5 displays the results of the EIS measurements. The Nyquist story can generally be divided into two distinct portions. One half corresponds to a nearly vertical straight line found in the low-frequency area, indicating the diffusive resistance of the electrolyte to Ti_3C_2Tx/GCE. The other component, a semicircle formed in a high-frequency area, is related to the conductivity of Ti_3C_2Tx/GCE and the charge transfer resistance (Rct).

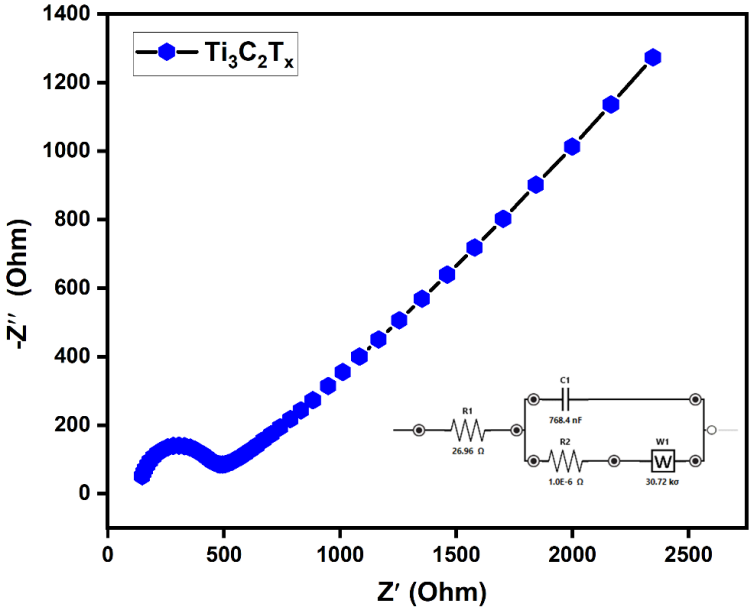


Figure 5: Electrochemical Impeadance Spectrocopy of Ti_3C_2Tx Electrode.

4. Conclusions

In this study, wet chemical etching was successfully used to prepare multilayered Ti_3C_2Tx. Using morphological and structural characterization tools, the synthesized substance was identified. According to our findings, Ti_3C_2Tx-GCE possesses a significant number of active sites, which enhances both its electrocatalytic activity and electrochemical sensing capabilities for RT oxidation. The multilayered Ti_3C_2Tx that was created exhibited suitable pore topologies and excellent interface characteristics. Furthermore, it demonstrated ultra-sensitivity for the electrochemical detection of RT and remarkable linearity from 10 nM, with a very low limit of detection (LOD) of 0.345 μM. The multilayered Ti_3C_2Tx developed exhibited a very low charge transfer resistance and a high electron transfer rate constant, as indicated by EIS measurements. Additionally, the multilayered Ti_3C_2Tx material demonstrated strong selectivity and endurance, indicating its potential use in clinical diagnostics. We believe that the multilayered Ti_3C_2Tx electrode material that has been developed can be effectively and efficiently used as an alternative electrode material for electrochemical sensing of biological samples. Due to the hybrid nature of the manufactured electrode material, it can be utilized as a robust and versatile electrode material within the nanoconfinement range.

Conflicts of 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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