Enzyme-MXene Nanosheets: Fabrication and Application in Electrochemical Detection of H₂O₂

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Abstract: Two-dimensional MXene nanosheets with vertical junction structure has been employed for easy immobilization of horse radish peroxidase enzymes for fabrication of the electrochemical hydrogen peroxide (H₂O₂) biosensor. The synthesized MXene nanosheets exhibited large specific area, excellent electronic conductivity and good dispersion in aqueous phase. Horse Radish Peroxidase (HRP) enzymes molecules immobilized on MXene/chitosan/GCE electrode demonstrated good electrocatalytic activity toward reduction of H₂O₂. The fabricated HRP@MXene/chitosan/GCE biosensor exhibited a wide linear range from 5 to 1650 μmol/L, a limit of detection of 0.74 μmol/L and good operation stability. The fabricated biosensor has also been successfully employed for detection of trace level of H₂O₂ in both solid and liquid food.

Key words: horse radish peroxidase; MXene nanosheets; biosensor; hydrogen peroxide

Hydrogen peroxide (H₂O₂) is widely used as antimicrobial, oxidizing, reducing and bleaching agents in many fields including pharmaceutical, medical, textile, paper, and food processing[11]. The United States Food and Drug Administration (USFDA) has affirmed the Generally Recognized As Safe (GRAS) status of H₂O₂ for use in food with a maximum permitted concentration in specified foods and residual must be removed by appropriate processing[12]. Excessive amount of H₂O₂ has been reported to have a destructive impact on central nervous system of human body and can result in oxidative stress which is associated with many diseases including neurodegenerative disorders, diabetes, atherosclerosis and cancers[13-4]. Therefore, monitoring H₂O₂ residual in food is of practical significance to both academic and industry. To date, a variety of techniques including fluorometry[5], spectrophotometry[6-7] and electrochemistry[8-9] have been developed for detection and quantification of H₂O₂.

Electrochemical biosensing technique has generated much interest due to its advantages of simple instrumentation, easy miniaturization, high sensitivity and selectivity, as well as rapid response[10]. At present, very few electrochemical biosensors have reached practical application and commercialization mainly due to its inconsistent operational stability[11]. The sensitivity, selectivity and operational stability of electrochemical biosensors are strongly dependent on structure and properties of electrode materials and enzyme immobilization matrixes[11,12-13].

Two-dimensional (2D) transition metal carbides, nitrides and carbonitrides (MXene) are produced by etching layers of sp elements (MXene) from their corresponding three-dimensional (3D) MAX phases which correspond to the general formula Mₙ₊₁AXₙ (n = 1, 2, 3) where M represents early d-block transition metals (Ti, Sc, V, Cr, Ta, Nb, Zr, Mo, Hf), A represents main group sp elements and X is either C or N atom[14-15]. MXenes have generated a lot of interest due to their hydrophilic surfaces, good structural and chemical stabilities, excellent electrical conductivities, and environment-friendly characteristics[16-17]. As MXene surfaces can be used for easy immobilization of enzymes/protein to achieve accelerated reaction kinetics, low detection limits, high sensitivity and selectivity, it is suitable for use as highly sensitive and selective detection platform for biosensing applications[18-21]. Understanding of the sensitivity,
selectivity and long term operational stability of MXene electrochemical biosensors are important for application of MXene biosensors for various purposes.

Present study aims to fabricate a horse radish peroxidase@MXene electrochemical biosensor for detection of H₂O₂ in food. HRP, a heme-containing enzyme, has been widely used to catalyze oxidation of a wide variety of substrates including hydrogen peroxide[22-23]. MXene with vertical junction structure in which MXene sheets are perpendicular to the plane of graphite has been demonstrated to have good electromagnetic absorption properties[24]. We proposed that this vertical junction structure will improve HRP immobilization and demonstrate good electron transfer properties which made it a suitable enzyme immobilization matrix for fabrication of H₂O₂ electrochemical biosensor. We have synthesized and characterized MXene using X-ray powder diffraction (XRD), fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). MXene was then used as HRP immobilization matrices to fabricate HRP@MXene/chitosan/GCE biosensor. Electrochemical behavior of the fabricated HRP@MXene/chitosan/GCE biosensor was investigated and optimized using cyclic voltammetry (CV) and different pulse voltammetry (DPV). Amperometric method was used to detect concentration of H₂O₂ in real food samples. Selectivity and storage stability of the HRP@MXene/chitosan/GCE were also elucidated.

1 Experimental

1.1 Materials and chemicals

Horseradish peroxide (HRP, activity 250 units mg⁻¹) was purchased from Sigma Aldrich. Natural flake graphite (300 mesh), Ti powders (300 mesh, purity of 99.9%), Al powders (300 mesh, purity of 99.9%), Hydrogen peroxide solution (30 wt%), hydrogen peroxide (HQ), chitosan (deacetylation 95%), potassium chloride, acetic acid were obtained from Aladdin, China. Other reagents including NaCl, KCl, sodium hydroxide (NaOH), K₃[Fe(CN)₆], K₄[Fe(CN)₆]· 3H₂O were obtained from Sinoreagent, China. 0.1 mol/L phosphate buffer solutions (PBS, pH 7.0) comprising NaH₂PO₄ and Na₂HPO₄ were used as the electrolyte. All aqueous solutions were freshly prepared with ultra-pure water (18 MΩ•cm).

1.2 Synthesis of MXene (Graphite/TiC/Ti₃C₂)

G(graphite)/TiC/Ti₃C₂ were fabricated according to a previously reported method with slight modifications[24]. Graphite powder (300 mesh), Ti powders (300 mesh, purity of 99.9%), Al powders (300 mesh, purity of 99.9%), NaCl and KCl were mixed at a molar ratio of 4:4:1:10:10, placed in alumina crucible and packaged in a tube furnace. The tube furnace was heated to 800 °C at a heating rate of 4 °C min⁻¹ under argon protection and kept for 300 min. Following that, the mixtures were heated to 1100 °C at a heating rate of 4 °C min⁻¹, kept for 180 min and finally cooled to room temperature at a cooling rate of 4 °C min⁻¹. The resulting product (G/TiC/Ti₃AlC₂) was washed by deionized water to remove salts and dried at 80 °C. G/TiC/Ti₃C₂ were obtained by etching process using HF to remove the Al atoms.

1.3 Characterization of MXene

MXene was characterized using XRD, FTIR and SEM. XRD analysis were conducted at room temperature using Bruker D8 Discover XRD (Cu radiation, λ=0.1540596 nm) over the 2θ range of 5°~70° at room temperature. FTIR spectra was obtained in the range of 500 to 4000 cm⁻¹ by using a Fourier-transform infrared (FTIR) spectroscopy (Nicolet 6700, Thermo, USA).

The microstructures of the powders were examined by a field emission scanning electron microscopy (FEI...
Quanta FEG 250) equipped with an EDS system and a TEM instrument (FEI Tecnai F20).

1.4 Fabrication of the HRP@MXene/chitosan/GCE biosensor

Fabrication of the HRP@MXene electrochemical biosensor is illustrated in Fig. 1. Glassy carbon electrodes (GCE, 3 mm) was firstly polished using Al2O3 (1.0, 0.3, 0.05 μm), cleaned by ethanol and water for three times, and finally dried under gentle N2 stream. Ten microliter of HRP solution [10 mg/mL, PBS (0.1 mol/L, pH 6.0)] and 20 μL of MXene aqueous solution (5 mg/ml) were mixed and shake at 200 rpm for 10 h at low temperature. Following that, 10 μL chitosan solution (6 mg/ml, adjusted to pH6.0 by 10−1 M NaOH) was added to the mixture and vibrated for 3 min. Chitosan solution has been previously reported to be positively charged and have good electrical conductivity at pH 6.0 due to the protonation of amino groups. As MXenes synthesized in present study is negatively charged due to the abundance of hydroxyl or fluoride groups, it could be well adhered in chitosan solution via Coulomb effect and formed a unique film on the surface of GCE. 5 μL of the resultant HRP@MXene/chitosan was drop cast onto the surface of a freshly polished GCE. The prepared electrodes (HRP@MXene/chitosan/GCE) were dried and stored in 0.05 M PBS (pH 7.5) in a refrigerator (4 °C) prior to usage.

1.5 Electrochemical behavior of the HRP@MXene/chitosan/GCE biosensor

All electrochemical experiments were carried out using CHI760E electrochemical workstation (Chenhua, Shanghai) with GCE as working electrode, platinum wire as counter electrode and saturated calomel electrode (SCE) as reference electrode. The electrochemical impedance spectroscopy (EIS) and cyclic voltammograms (CVs) of electrodes fabricated using chitosan of different pH was conducted in N2-saturated 0.1 mol/L KCl solution containing 5.0 mmol/L Fe(CN)63−/4− at open circuit potential in the frequency range from 0.1 Hz to 105 Hz with the amplitude 5 mV. The EIS data were analyzed using ZVIEW software.

1.6 Electrochemical biosensing of H2O2 by HRP@MXene/chitosan/GCE biosensor

CVs were carried out in N2-saturated 0.1 mol/L PBS (pH 7.5) in the presence of 2.0 mmol/L H2O2 and 1 mmol/L HQ (dissolved in methanol) at a scanning rate of 50 mV s−1. Differential pulse voltammetry (DPV) was performed in N2-saturated 0.1 mol/L PBS (pH 7.5) containing 2 mmol/L H2O2 and 1 mmol/L HQ (dissolved in methanol) with amplitude of 5 mV and pulse width of 0.2 s after five times of CV at a scanning rate of 50 mV s−1 ranging from 0.8 V to -0.8 V. The effects of electrolyte PBS buffer pH (5.5 to 8) and the concentration of MXene were evaluated and optimized in terms of CV and DPV signal.

1.7 Electrochemical detection of H2O2 in spiked dried scallop and milk

Amperometric current-time curves for H2O2 were carried out to construct a calibration curve of current response at different H2O2 concentration. Measurements were performed in 10 mL of stirred 0.1 mol/L PBS (pH 7.5) in the presence of 1mmol/L HQ with successive addition of H2O2 at room temperature under an applied peak potential value of -0.1V. LOD was determined according to the following equation:

\[
\text{LOD} = 3\text{SD}/K
\]

whereby SD refers to the standard deviation of the control measurement and K refers to slope of the calibration curve.

Milk and dried scallop were chosen as model of liquid and solid food. Milk sample was used directly for H2O2 detection. Dried scallop was pre-treated according to the following procedure to extract H2O2 residual. Briefly, 2 g of dried scallop was immersed in 5 ml of H2O2 aqueous solution (3%) for 1 h. Following that, the scallop was immersed in 5 ml of water for 0.5 h to extract H2O2 residue. H2O2 concentration in spiked dried scallop test solution and milk solution (12.5, 50 and 125 μmol/L H2O2) were detected using the amperometric current-time curves for H2O2. Recovery of the HRP@MXene/Chitosan/GCE was calculated.

1.8 Selectivity of the biosensor

Selectivity of the fabricated HRP@MXene/chitosan/GCE biosensor was evaluated using potentially interfering substances including uric acid, glucose and ascorbic acid [100 μmol/L in 0.1 mol/L PBS (pH 7.5)].

1.9 Storage stability of the biosensor

Storage stability of the HRP@MXene/GCE was evaluated by monitoring reduction peak in CVs in 0.1 mol/L PBS with 1 mmol/L HQ and 2 mmol/L H2O2 during electrodes storage in 0.05 mol/L PBS at 4 °C.

2 Results and discussion

2.1 Characterization of the synthesized MXene
and HRP@MXene

XRD pattern of the synthesized MXene (G/TiC/Ti3C2) and G/TiC/Ti3AlC2 are showed in Fig 2(A). G/TiC/Ti3C2 demonstrated a dominant phase of graphite (peak at ≈26°) and TiC (peak at 35.9°, 41.8°). This is in agreement to previously reported finding[24]. In addition, after HF etching, the peak at 39° corresponds to the (104) plane of Ti3AlC2 disappears compared to the XRD pattern of Ti3AlC2 which indicates the elimination of Al during the G/TiC/Ti3C2 syntheses process.

As shown in Fig 2(B), FTIR spectra of MXene did not demonstrate any absorption peaks from 3800 to 400 cm⁻¹. Meanwhile, HRP demonstrated characteristic peaks at 2961, 1647, 1541, and 1080 cm⁻¹. The amide I band (1700–1600 cm⁻¹) can be assigned to the α-helical conformation of the HRP; meanwhile, the amide II band can be assigned to the β-sheet structure of the HRP[3]. Following immobilization of HRP onto the two dimensional MXene nanosheets, the major bands of HRP can be observed on the FTIR spectra of HRP@MXene indicating successful immobilization process without any conformational change in the secondary structure of HRP.

SEM analysis shows a two dimensional multilayered structured of Ti3C2 (< 1 μm) standing perpendicular to the plane of G/TiC forming interfacial junctions (Fig 1C). The multilayer Ti3C2 also demonstrated typical MXene morphology of two- dimension structure (Fig 1D). This two-dimensional multilayered interfacial junctions structure provides a large specific surface area for efficient enzyme immobilization/entrapment.

2.2 Electrochemical behavior of the fabricated GCE biosensor

Chitosan, a natural film-forming agent, is commonly used in fabrication of enzyme electrodes. It is positively charged at pH<6.3 due to protonation of amino groups[8, 27]. At pH>6.3, chitosan demonstrated decreased solubility in aqueous solution with the decline of adhesion. Fig S1(A) shows the effects of pH of chitosan solution on charge transfer resistance (Rct) of chitosan/GCE electrodes. Rct was found to slightly increase with pH increased from pH 5.0 to pH 6.0. However, a dramatic increase in Rct from 0.347 kΩ to 1.304 kΩ can be observed as pH of the chitosan solution was increased from 6.0 to 6.5 and reached 4.663 kΩ at pH 7.0.

In addition, according to Fig S1(B), redox peaks current decreased with increased pH, and ΔEp became bigger when pH from 6.0 to 7.0. The increasing Rct reflected the degressive electrical conductivity of chitosan because of protonation of amino groups, and the increasing ΔEp indicated the declined ability of electronic transfer. Consider the film-forming and electrical conductivity of chitosan, in addition, HRP has been reported to be most active at nearly neutral[28, 29], chitosan solution at pH 6.0 was used in the fabrication of HRP@MXene/chitosan/GCE biosensor Fig. 3(A) shows the Nyquist plots of chitosan/GCE, MXene/chitosan/GCE and HRP@MXene/chitosan/GCE. All three electrodes (chitosan/GCE, MXene/chitosan/GCE and HRP@MXene/chitosan/GCE) demonstrated a electron transfer-limited process in the high frequency area. Chitosan/GCE electrode had an Rct value of 174.40 Ω. Incorporation of MXene onto the chitosan/GCE matrix resulted in a decreased of Rct value of MXene/chitosan/GCE to 52.88 Ω indicating good electron transfer property of MXene from the redox probe of [Fe(CN)₆]³⁻/⁴⁻. Nevertheless, immobilization of HRP onto the MXene/chitosan/GCE matrix had increased the Rct value of HRP@MXene/chitosan/GCE to 542.60 Ω. Increased in the Rct value is mainly caused by steric hindrance, electrostatic interactions and partial blockage of interfacial electrons by enzyme molecules which has poor conductivity[10]. Cyclic voltammetry (CV) for the different electrodes were carried out in 5.0 mmol/L Fe[CN]₆³⁻/⁴⁻ and 0.1M KCl (Fig. 3(B)).

In comparison to Chitosan/GCE (curve a), MXene/chitosan/GCE (curve b) demonstrated an increase in current response and similar ΔEp value (differences between anodic and cathodic peaks potential) indicating MXene is an excellent electric conducting material. Meanwhile, HRP@MXene/chitosan/GCE (curve c) demonstrated a decreased in current response and an increased in ΔEp value indicating HRP hindered the electron conductivity.

2.3 Electrochemical biosensing of H₂O₂ by the biosensor
Fig. 2 XRD patterns of G/TiC/Ti$_3$AlC$_2$ and G/TiC/Ti$_3$C$_2$ (A); FTIR spectra of the MXene, HRP and HRP@MXene (B); SEM images of the MXene (C and D).

Fig. 3 EIS of Chit/chitosan/GCE electrode (a), MXene/Chit/GCE electrode (b), HRP@MXene/Chit/GCE electrode (c) electrodes cycled in 0.1 M KCl aqueous solution containing 5 mM [Fe(CN)$_6$]$_{3^-}$/4^- (A); CV curves of Chit/GCE (a), MXene/Chit/GCE (b), HRP@MXene/Chit/GCE (c) electrodes cycled in 0.1 M KCl aqueous solution containing 5 mM [Fe(CN)$_6$]$_{3^-}$/4^-; (potential window: -0.1 V-0.5 V vs. SCE) (B).

Fig. 4 CV curves of Chit/GCE (curve a, black line), MXene/Chit/GCE (curve b, red line), HRP/Chit/GCE electrode (curve c, pink line), HRP@MXene/Chit/GCE (curve d, blue line) electrodes cycled in N$_2$-saturated 0.1 M PBS (pH 7.5) containing 1.0 mM HQ and 2.0 mM H$_2$O$_2$ at a scanning rate of 50 mV s$^{-1}$ (potential window: -0.8 V-0.8 V vs. SCE).

Fig. 4 shows the CV of chitosan/GCE, MXene/chitosan/GCE, HRP@chitosan/GCE, and HRP@MXene/chitosan/GCE electrodes obtained in 0.1 mol/L N$_2$-saturated PBS (pH 7.5) containing 1 mmol/L HQ and 2 mmol/L H$_2$O$_2$. Chitosan/GCE electrode demonstrated a pair of well-defined redox peaks.
with potentials at about 0.14 and −0.07 V which is characteristic of redox process of HQ and H$_2$O$_2$[30]. In comparison to the signal obtained from chitosan/GCE, modification of the GCE with MXene/chitosan resulted in signal enhanced of the redox peaks. Following HRP immobilization, both HRP@chitosan/GCE and HRP@MXene/chitosan/GCE demonstrated further enhanced of the reduction peak with HRP@MXene/chitosan/GCE showing highest increase in reduction peak’s current (52 $\mu$A). Increased in the reduction peak current can be attributed to reduction process of H$_2$O$_2$ catalyzed by HRP at its reducing state (HRP$_{\text{RED}}$) (Fig. 1). During this reduction process, the redox centre of HRP$_{\text{RED}}$ turned into its oxidizing state (HRP$_{\text{OX}}$). HRP$_{\text{OX}}$ were then regenerated into HRP$_{\text{RED}}$ with the aid of HQ which was oxidized to form benzoquinone. Finally, benzoquinone exchanged electrons with the electrode to electro-chemically produced HQ. The redox processes of H$_2$O$_2$ and hydroquinone were in agreement with those previously reported findings[30]. The aforementioned findings showed HRP@MXene/chitosan/GCE biosensor can be used for electrochemical biosensing of H$_2$O$_2$ and MXene provided a favorable microenvironment to retain the bioactivity of HRP.

Fig. S2(A) shows the CV of HRP@MXene/chitosan/GCE obtained in 0.1 mol/L N$_2$-saturated PBS (pH 7.5) containing 1mM HQ and 2mmol/L H$_2$O$_2$ at various scan rates. The redox peaks of HRP@MXene/chitosan/GCE increased linearly versus the square root of scan rates from 20 to 500 mV s$^{-1}$ (Fig. S2(B)). The electrochemical behaviors were in accordance with a diffusion-controlled process occurring at the surface of the biosensor[31]. Similar results with different electrodes with mediator were also reported[28, 32].

Based on aforementioned findings, PBS buffer’s pH of 7.5 and MXene concentration of 5 mg/ml were used for fabrication of HRP@MXene/chitosan/GCE in the subsequent analysis.

Electrochemical biosensing of H$_2$O$_2$ by HRP@MXene/chitosan/GCE was optimized in terms of electrolyte PBS buffer’s pH (pH 5.5-8.0) and concentration of MXene (0.5-10 mg/mL). The pH value of the electrolyte is important for the performance of enzyme electrode as HRP activity is greatly affected by pH. Fig. S3(A) shows the peak current of HRP@MXene/chitosan/GCE increased linearly with pH 5.5 and reached maximum at pH 7.5. The value of pH was chosen for further studies and was also in agreement with...
with previous observations reported\textsuperscript{33}. Fig. S3(B) shows the peak current of cyclic voltammograms of HRP@MXene/chitosan/GCE fabricated with different concentration of MXene. Peak current of HRP@MXene/chitosan/GCE was the highest at 5 mg/mL MXene with a ratio of MXene to HRP of 1:1. At this concentration of MXene, HRP was fully immobilized on the surface of MXene and the biosensor demonstrated most effective performance. In terms of

2.4 Electrochemical detection of H$_2$O$_2$ in spiked dried scallop and milk

The current-time curve which is a potential-controlled electrochemical analysis method was used to build a calibration curve of amperometric response at a series of H$_2$O$_2$ concentration. Fig 5(A) shows the amperometric response of HRP@MXene/chitosan/GCE following successive additions of H$_2$O$_2$ to PBS buffer (Potential = -0.1 V). The corresponding calibration curves of HRP@MXene/chitosan/GCE biosensor were presented in Fig. 5(B), which was linear at two concentration ranges (5~190 μmol/L and 190~1650 μmol/L H$_2$O$_2$) with a linear regression equation of $Y = 0.02644X + 0.55914$ ($R^2 = 0.999$) and $Y = 0.01959X + 1.84114$ ($R^2 = 0.996$). Moreover, the fabricated biosensor also showed very low detection limit of 0.74 μmol/L. A comparison of linear range and detection limit for H$_2$O$_2$ with other H$_2$O$_2$ sensors reported in literature are summarized in Table S1. The data demonstrated that both the linear range and detection limit for H$_2$O$_2$ are comparable or even better than those detected using sensors recently reported. The excellent biosensing performance of HRP@MXene/chitosan/GCE can be ascribed to the unique vertical junction structure of the two dimensional MXene nanosheets which provided a suitable matrix for HRP immobilization and also platform for H$_2$O$_2$ and HQ redox reactions.

Present work has used dried scallop and milk as representative of solid and liquid food system to explore the application of HRP@MXene/chitosan/GCE biosensor in detection of H$_2$O$_2$ in food samples. Fig. 5(C,D) shows the amperometric response of HRP@MXene/chitosan/GCE following additions of solutions extracted from milk and dried scallop with different concentration of H$_2$O$_2$. The curves show HRP@MXene/chitosan/GCE were a rapid and sensitive method to detect H$_2$O$_2$ at different concentrations. The recovery of H$_2$O$_2$ in food samples at different concentrations ranged from (90.24±6.97)% to (109.20±3.33)% (Table 1). The results indicated that the fabricated biosensor is reliable tool for detection of residual H$_2$O$_2$ in food samples.

| Sample         | Added H$_2$O$_2$/μM | Found H$_2$O$_2$/μM | Recovery % | RSD % |
|----------------|---------------------|---------------------|------------|-------|
| Milk           | 12.5                | 13.037              | 104.30     | 5.88  |
| Milk           | 50                  | 52.57               | 105.14     | 1.12  |
| Milk           | 125                 | 136.5               | 109.20     | 3.33  |
| Dried scallop  | 0                   | 66.56               | -          | -     |
| Dried scallop  | 12.5                | 77.84               | 90.24      | 6.97  |
| Dried scallop  | 50                  | 120.08              | 107.04     | 1.46  |
| Dried scallop  | 125                 | 189.11              | 98.04      | 8.39  |

2.5 Selectivity and stability of the HRP@MXene/chitosan/GCE

The anti-interference performance of HRP@MXene/chitosan/GCE biosensor was evaluated by detecting 100 μmol/L H$_2$O$_2$ in the presence of the same concentration of ascorbic acid, glucose and uric acid as interfering substances. As shown in Fig. S4(A), there were no noticeable amperometric responses from glucose and uric acid. However, amperometric re-
sponses can be detected by ascorbic acid (34% of H₂O₂) indicating ascorbic acid has the capability to participate in the redox process of HQ and H₂O₂; hence, interfering with the measurement of H₂O₂.

HRP@MXene/chitosan/GCE demonstrated good storage and operational stability. When stored in 0.05 mol/L PBS (pH 7.5) at 4 °C, HRP@MXene/chitosan/GCE was able to retain 84.8% of its initial response to H₂O₂ after a period of 10 d (Fig. S4(B)). This indicated that the vertical junction structure of the MXene (Graphite/TiC/Ti3C2) were able to act as an effective and stable platform for entrapping enzyme HRP.

3 Conclusion

In summary, we have explored a new type of supporting material for immobilizing HRP and fabricated an electrochemical H₂O₂ biosensor for in situ detection of H₂O₂ in food products. The synthesized MXene exhibited large specific area, biocompatibility, excellent electronic conductivity, and good dispersion in aqueous phase. HRP enzymes molecules immobilized on MXene/chitosan/GCE electrode showed good electrochemical behaviors and electrocatalytic activity toward reduction of H₂O₂. The fabricated HRP@MXene/chitosan/GCE biosensor exhibited a wide linear range from 5 μmol/L to 1.650 mmol/L and a low detection limit of 0.74 μmol/L with long-term stability, good reproducibility and high selectivity. The fabricated biosensor has also been successfully employed for detection of trace level of H₂O₂ in real food products (both solid and liquid food). The study provides a good concept for construction of electrochemical H₂O₂ biosensor based on MXene.

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酶-二维 MXene 复合材料的制备及其电化学检测 H$_2$O$_2$ 的应用

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摘 要: 本研究合成了具有垂直栅栏结构的二维 MXene 材料, 与辣根过氧化物酶进行固定, 构筑了过氧化氢电化学酶传感器。合成的 MXene 纳米栅栏具有大的比表面积, 优良的电子传导特性和在水溶液中的良好分散特性; 固定化在酶电极上的辣根过氧化物酶分子表现出了优良的过氧化氢催化效果。结果表明 HRP@MXene/chitosan/GCE 酶电化学传感器在过氧化氢浓度为 5~1650 μmol/L 范围内表现出很好的线性关系, 最低检测限为 0.74 μmol/L, 且具有很好的操作稳定性, 该生物传感器被成功应用于固态与液态食品中过氧化氢残留检测。

关 键 词: 辣根过氧化物酶; MXene 纳米片; 生物传感器; 过氧化氢

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