ORIGINAL PAPER

A nanocomposite prepared from platinum particles, polyaniline and a Ti$_3$C$_2$ MXene for amperometric sensing of hydrogen peroxide and lactate

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Abstract

A nanocomposite consisting of platinum particles, polyaniline and Ti$_3$C$_2$ MXene (Pt/PANI/MXene) was used to modify a screen-printed carbon electrode (SPCE) to obtain sensors for hydrogen peroxide and lactate. This nanocomposite was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM) and X-ray powder diffraction (XRD) to determine the physical morphologies and the nanocomposite elements. The modified electrode exhibited the improved current response towards hydrogen peroxide (H$_2$O$_2$) compared with an unmodified electrode and provided a low detection limit of 1.0 μM. When lactate oxidase was immobilized on the modified electrode, the electrode responded to lactate via the H$_2$O$_2$ generated in the enzymatic reaction. The lactate assay was performed by amperometry at a constant potential of +0.3 V (vs. Ag/AgCl). The linear range was found to be from 0.005 to 5.0 mM with a detection limit of 5.0 μM for lactate. Ultimately, this biosensor was used for the determination of lactate in milk samples with high stability and reliability.

Keywords Pt/PANI/MXene nanocomposite · Ti$_3$C$_2$ · Electrochemical sensor · Amperometry · Hydrogen peroxide · Lactate · Milk sample

Introduction

MXenes are materials consisting of transition metal carbide and nitride. They have attracted interest because of their

unique properties, such as high chemical stability, excellent electrical conductivity, large hydrophilic surface area, biocompatibility and easy dispersion in aqueous solutions [1–4]. In general, MXene is synthesized by selectively removing the "A" layer from MAX (M$_{n+1}$AX$_n$) phase by exfoliation using hydrofluoric acid [5] (where M is an early transition metal (e.g. Sc, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo), A is an element from groups 13 and 14 of a periodic table, and X is C and/or N) resulting in the formula of MXene (M$_{n+1}$X$_n$). MXene has been used as a promising material for various applications, such as energy storage [6], supercapacitors [7], gas sensors [8], catalytic material [9], and chemical and biological sensors [10–19]. For sensor applications, MXene patterned field-effect transistor for label-free measurement of dopamine was developed [20]. Furthermore, MXene was applied for specific adsorption of NH$_3$ in a gas sensor indicating the potential application of MXene for gas sensors [21].

The pristine and composited forms of MXene have been used in electrochemical sensors. Pristine MXene was used to modify glassy carbon electrodes and applied for the sensitive

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detection of H_2O_2 and NADH [13]. However, it was found that the oxidation peak of MXene is irreversible and the electrodes possesses a low stability in the oxidation window [13]. Thus, the nanocomposites of MXene with other materials have been investigated to solve these problems. MXene coupled with TiO_2 was reported to entrap and immobilize hemoglobin for mediator-free detection of H_2O_2. This system can improve the stability of sensing compared to pristine MXene [22]. This platform was used for NO_2 detection with high stability [12]. Moreover, the composites of MXene with metallic nanoparticles including gold nanoparticles (AuNPs) have been developed for glucose biosensor with high specificity [11]. MXene composite was used to enhance electron transfer kinetics between electrode and enzyme [11]. A highly stable MXene/Pt electrode was also applied for small molecule detection to improve the stability in an ideal potential window (0 mV vs. Ag/AgCl). Pt has become a common material for electrochemical H_2O_2 detection. Pt can increase the specific electrode surface area and mass transport characteristic towards H_2O_2 over a wide concentration range. To improve electrode conductivity, a conducting polymer, polyaniline (PANI), was selected because of its properties, which include high electrochemical conductivity, biocompatibility and functionality [23]. Thus, the nanocomposites of MXene with metal particle and conducting polymer have potential for electrochemical sensor applications.

There are no previous reports using Pt/PANI/MXene nanocomposite electrodes in electrochemical biosensors. Herein, lactate oxidase (LOx) immobilized on Pt/PANI/MXene nanocomposite modified SPCE was created for H_2O_2 and lactate detection. The analytical performance of this biosensor was investigated and showed high sensitivity towards H_2O_2 and lactate detection with high selectivity and stability. Thus, this platform represents a novel tool for H_2O_2 and lactate biosensor in various applications.

Experimental

Chemicals and materials

MAX (Ti_3AlC_2) powders were synthesized according to the previous report, with a slight modification [24]. 50% hydrogen fluoride (HF) was obtained from Ajax Finechem Pty Ltd. (www.npchemsupply.com). 30% hydrogen peroxide (H_2O_2) was purchased from Merck Schuchardt OHG 85662 Hohenbrunn Germany (http://www.merckmillipore.com). Aniline monomer, chloroplatinic acid (H_2PtCl_6), potassium ferricyanide ($K_3[Fe(CN_6)]$), potassium ferrocyanide ($K_4[Fe(CN_6)]$), phosphate buffer (PB, 0.1 M, pH 7.4), lactate standard solution, and 50.0 $U·mL^{-1}$ lactate oxidase (LOx) were purchased from Sigma–Aldrich (St. Louis, MO, USA, https://www.sigmaaldrich.com/). All solutions were prepared in deionized (DI) water (Millipore, USA, R ≥ 18.2 MΩ cm^{-1}).

Apparatus

The morphologies and elemental composition of MXene were characterized by using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) (JSM-6400; Japan Electron Optics Laboratory Co., Ltd., Japan, https://www.jeol.co.jp/en/), respectively. Transmission electron microscopy (TEM) was used for investigating MXene dispersion and polyaniline/MXene (PANI/MXene) nanocomposites. X-ray diffractometer (XRD) was used to identify the structural composition of MXene. All electrochemical measurements were performed using CHI 1240B potentiostat (CH Instruments, Inc., USA, https://www.chinstruments.com/) and controlled with CHI 1240b software. All standard solutions were prepared in 0.1 M PB (pH 7.4).

Synthesis of MXene

MAX was pounded into powder, sieved, and dispersed in 20.0 mL of 50% HF. Then, the dispersed MAX solution was sonicated for 3 h using an ultrasonicator and followed by neutralizing with DI water. After that, MAX solution was centrifuged at 3000 rpm for 10 min. The supernatants were kept for freeze-dry. The black powders were collected and used as MXene for all further experiments.

Modification of Pt/PANI/MXene on screen-printed carbon electrode

The dispersion solution of MXene was prepared by adding 0.5 mg MXene in 1.0 mL of DI water. The mixture solution was dispersed by using a probe ultrasonicator for 1 h to obtain a well dispersed MXene solution. 1.0 μL of MXene was dropped on the surface of SPCE and dried at a room temperature. After that, 0.1 M aniline was used to produce the nanostructure of PANI on MXene surface by electropolymerization by using CV with a scanning potential in a range from −0.5 to +1.0 V (vs. Ag/AgCl) for 2 cycles and 100 $mV·s^{-1}$ of scan rate. Finally, 10 mM H_2PtCl_6 was used to perform the platinum particles (Pt) on PANI/MXene electrode using electrodeposition via amperometry with a constant potential of −0.2 V (vs. Ag/AgCl) for 120 s.

Electroanalytical measurement

All the electrochemical measurements were performed on a potentiostat using cyclic voltammetric and amperometric techniques. Cyclic voltammetry (CV) was used to optimize the parameters for electrode modification and electrode characterization for hydrogen peroxide detection by scanning the potential between −0.8 to +0.8 V (vs. Ag/AgCl) with a scan rate of 100 $mV·s^{-1}$. Amperometry was used to determine

H_2O_2 and lactate with a constant potential of +0.3 V (vs. Ag/AgCl) for 240 s.

Real sample analysis

Commercially available pasteurized milk samples were mixed with 0.8 mL of 24% trichloroacetic acid (TCA) and centrifuged for 10 mins at a speed of 10,000 rpm. Then, the supernatant was collected for all further experiments. For the standard addition method, different lactate concentrations (1.0, 1.5, 2.0, 2.5 and 3.0 mM) were spiked into the supernatants [25] and the electrochemical measurements were performed.

Results & discussion

Electrode characterization

The morphologies of MXene, PANI/MXene and Pt/PANI/MXene-modified working electrode surface were characterized by SEM with EDX as shown in Fig. 1. A typical accordion-like structure of layered MXene powder was observed (Fig. S1a) due to the selective removal of Al layer using the HF exfoliation method. Moreover, the absence of Al atoms in MXene was confirmed by SEM-EDX as shown in Fig. S1c. In addition, the XRD spectrum of MXene was also obtained (Fig. S1b), and the results correspond well with the previous report [4] confirming that MXene was successfully synthesized. The high surface area of MXene ($10 \ m^2 \cdot g^{-1}$) makes it attractive for biosensor applications. Comparing with graphene and its derivatives, the unique multilayer structure of MXene has the ability to enhance the specific surface area and preserve the enzymatic activity on the electrode surface leading to increased enzymatic stability of biosensor [4]. For an electrochemical biosensor, MXene was used to modify a screen-printed carbon working electrode. The accordion-like structure of MXene was deposited on the carbon electrode surface via physical adsorption as shown in Fig. 1a. After electropolymerization of aniline, the nanostructured of sponge-like PANI was formed on the surface of MXene modified electrode as shown in Fig. 1b. Furthermore, the presence of
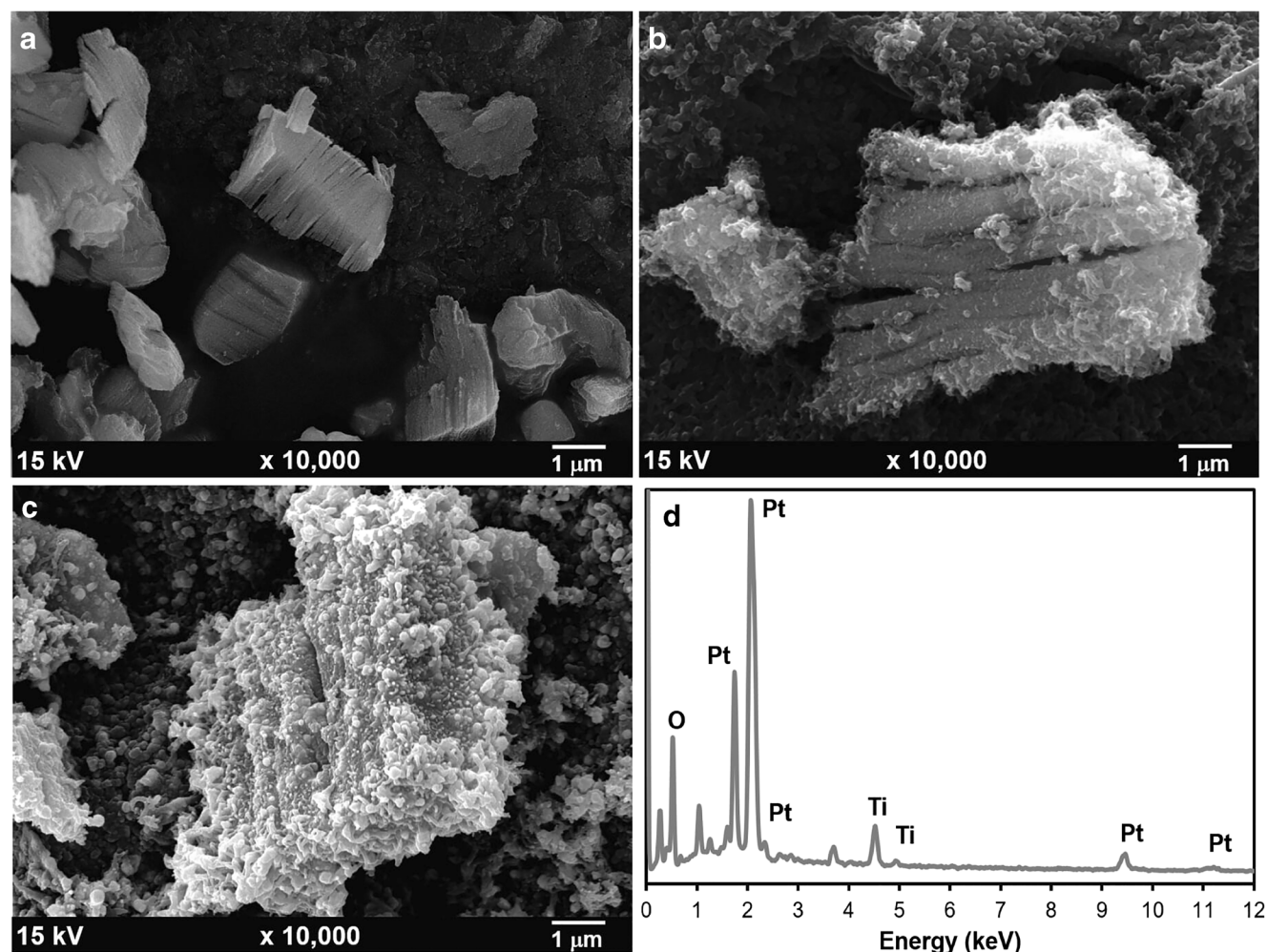

Fig. 1 SEM images of **a** MXene, **b** PANI/MXene, **c** Pt/PANI/MXene nanocomposites, and **d** SEM-EDX spectra of Pt/PANI/MXene modified electrode
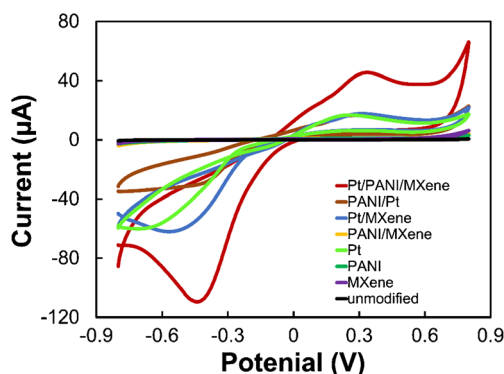
Fig. 2 Cyclic voltammograms of 1.0 mM H_2O_2 measured on 8 different electrodes including unmodified, MXene, PANI, Pt, PANI/MXene, Pt/MXene, Pt/PANI and Pt/PANI/MXene modified electrodes, with a scan rate of 100 mV·s^{-1}

Fig. 4 Nyquist plots of 0.1 M KCl containing 5.0 mM $[Fe(CN)_6]^{3-/4-}$ on unmodified, Pt/PANI/MXene and LOx/Pt/PANI/MXene modified electrodes

PANI on MXene was also characterized by TEM as shown in Fig. S2. PANI was successfully grown on MXene surface (Fig. S2b) leading to easy electrolyte access, fast ion diffusion, and enhanced electrochemical performance [26]. To further improve the electrocatalytic activity of the electrode towards H_2O_2 detection, Pt was selected to modify the PANI/MXene electrode via electrodeposition. The presence of Pt was confirmed by SEM-EDX (Fig. 1c–d). Platinum particles were uniformly deposited on the PANI/MXene electrode surface after electrodeposition via amperometry. The average size of Pt was found to be 137 ± 70 nm ($n = 40$). In addition, SEM-EDX results (Fig. 1d) showed a high intensity of Pt confirming the presence of Pt within Pt/PANI/MXene nanocomposite electrode.

Electrode optimization and electrochemical characterization

In this work, MXene, PANI and Pt play the important role for electrode surface modification not only for enhancing the electrochemical sensitivity but also improving the stability of enzymatic immobilization. The influence of MXene concentration, number of electropolymerization PANI cycles and the electrodeposition time for Pt particle growth were systematically investigated. As shown in Fig. S3, the best conditions for
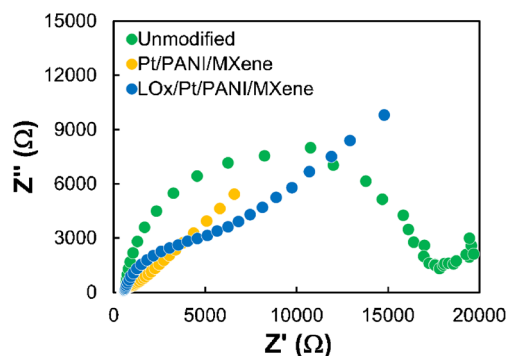
the preparation of Pt/PANI/MXene modified electrode are 0.5 mg·mL^{-1} MXene, two cycles of PANI electropolymerization, and 2 min of electrodeposition, and these optimal conditions were used for all experiments.

The electrochemical behavior of unmodified, MXene, PANI, Pt, PANI/MXene, Pt/MXene, Pt/PANI and Pt/PANI/MXene modified electrodes was investigated by CV as shown in Fig. 2. The combination of Pt/PANI/MXene (red line) showed the highest anodic and cathodic peak currents towards H_2O_2 detection compared to the unmodified and other modified electrodes (i.e. MXene, PANI, Pt, PANI/MXene, Pt/PANI and Pt/MXene modified electrodes). The presence of MXene enhanced the specific surface area of working electrode due to the multilayer of MXene. The incorporation of PANI on the surface of MXene improves not only electrochemical conductivity but also the surface area of electrode leading to enhanced specific surface area for Pt deposition [27]. Pt on the modified electrodes gives a unique morphology, enhanced electroactive surface area and increased current response towards H_2O_2 detection. Moreover, Pt can effectively accelerate the electron transfer of H_2O_2 detection. Thus, Pt/PANI/MXene modified electrode was selected as a novel electrode for the detection of H_2O_2 produced by enzymatic reaction between LOx and lactate in the further.

Fig. 3 a Hydrodynamic voltammograms of 1.0 mM H_2O_2 (blue line) and background (0.1 M PB pH 7.4: orange line) measured on Pt/PANI/MXene modified electrode, and **b** the signal-to-background ratios (S/B) obtained from hydrodynamic voltammograms
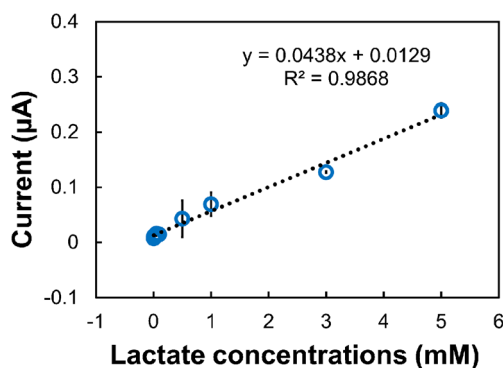
y = 0.0438x + 0.0129
R² = 0.9868
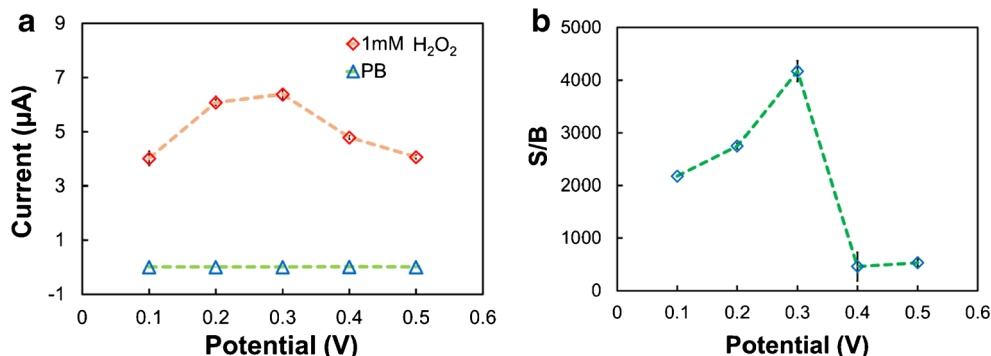
Fig. 5 A calibration plot between amperometric current signals and concentrations of lactate in the concentration range of 0.005–5.0 mM in 0.1 M PB pH 7.4 at +0.3 V (vs. Ag/AgCl) detection potential. The data points were averaged from 3 electrodes ($n = 3$)

Hydrogen peroxide detection

The Pt/PANI/MXene electrode was selected for the detection of H_2O_2 by amperometry. To obtain the optimal conditions for amperometry, the detection potential was optimized in a range of +0.1 to +0.5 V (vs. Ag/AgCl) as shown in Fig. 3. The increase in detection potential from +0.1 to +0.3 V (vs. Ag/AgCl) increased the anodic current signal for H_2O_2 but the background current also increased. The signal-to-background ratios (S/B) was examined instead of the anodic current signal as shown in Fig. 3b. The S/B ratio measured at +0.3 V (vs. Ag/AgCl) not only provides the highest sensitivity for the detection of H_2O_2 but also avoids the interfering effect from real samples due to the low oxidation potential [28]. Hence,

+0.3 V (vs. Ag/AgCl) was chosen as a detection potential for further amperometric experiments.

Pt/PANI/MXene modified electrode was used to detect H_2O_2 at different concentrations, and the amperometric responses were investigated at a steady state current of 240 s to generate a calibration plot of H_2O_2. A calibration plot was linearly proportional to H_2O_2 concentration over a range from 1.0 μM to 7.0 mM with a correlation coefficient of 0.9990 (Fig. S4), showing the ability to use the Pt/PANI/MXene-modified electrode over a wide linear range.

Lactate detection

Lactate can be detected via H_2O_2 generation from the enzymatic reaction between LOx and lactate [28] using a LOx/Pt/PANI/MXene-modified electrode. For a lactate detection, LOx (1.0 μL; 50 U·mL^{-1}) was immobilized on Pt/PANI/MXene-modified electrode by a drop casting and drying at a room temperature for 10 min. The presence of LOx on the electrode surface was confirmed by EIS and compared with Pt/PANI/MXene-modified electrode in the absence of LOx and an unmodified electrode by measuring the impedance change. The Nyquist plots showing electron transfer resistance (R_{ct}) between the electrode surface and the redox couple of $[Fe(CN)_6]^{3-/4-}$were investigated [29]. Since LOx is a non-conductive protein, the charge transfer resistance increases after immobilization. As shown in Fig. 4, R_{ct} of the modified electrode immobilized with LOx is higher than the one without LOx. This is resulted from the enzyme immobilization on

Table 1 Comparison of electrodes for lactate detection

Electrode	Linear range (mM)	Detection limit (μM)	Sensitivity (μA·mM^{-1})	Reference
LOx/Pt/GCNF/SPCE	0.01–2.0	6.9	0.0413	[16]
LOx/FSM8.0/Naf/CoPC/SPCE	0.02–1.5	18	0.0036	[30]
Au/MPTS/AuNPs/LOx	0.05–0.25	4.0	3.4	[31]
LOx/MWCNTs/Pt-nano/GCE	0.25–2.0	10.0	3.99	[19]
LOx/ PtNp-CNF-PDDA/SPCE	0.025–1.5	11	0.0368	[17]
LOx/PtNP/GCNF–SPCE	0.01–2.0	6.9	0.0413	[16]
LOx/GPNs/GCE	0–1.0	8.0	3.52	[14]
LOx/PtNPs/PdNPs/carbon	0.05–0.8	0.1	0.003	[32]
LOx/CS/MWCNTs/FcMe/HRP/ BSA/SPBGE	0.03–0.24	22.6	NR	[33]
LOx/Pt/PANI/MXene	0.005–5	5.0	0.62	This work

NR Not report, *LOx* Lactate oxidase, *Pt* Platinum particles, *GCNF* Graphitized carbon nanofibers, *SPCE* Screen-printed carbon electrode, *FSM8.0* Mesoporous silica powder, *Naf* Nafion layer, *CoPC* Cobalt phthalocyanine, *Au* Gold electrode, *MPTS* (3-mercaptopropyl)-trimethoxysilane, *AuNPs* Gold nanoparticles, *MWCNTs* Multiwalled carbon nanotubes, *Pt-nano* Platinum nanoparticle, *PtNp-CNF* Platinum nanoparticle decorated carbon nanofibers, *PDDA* poly(diallyldimethylammonium) chloride, *GPNs* Graphene supported platinum nanoparticles, *PtNPs* Platinum nanoparticles, *PdNPs* Paldium nanoparticles, *CS* chitosan, *FcMe* Ferrocene methanol, *HRP* Horse Radish Peroxidase, *BSA* Bovine serum albumin, *SPBGE* Basal-plane like screen-printed graphite electrodes

Fig. 6 **a** The reproducibility of electrodes and **b** the stability testing (0–30 days) on LOx/Pt/PANI/MXene modified electrode for the detection of 1.0 mM lactate in 0.1 M PB pH 7.4 by amperometry using detection potential of +0.3 V. The standard deviations are obtained from 5 measurements ($n = 5$)
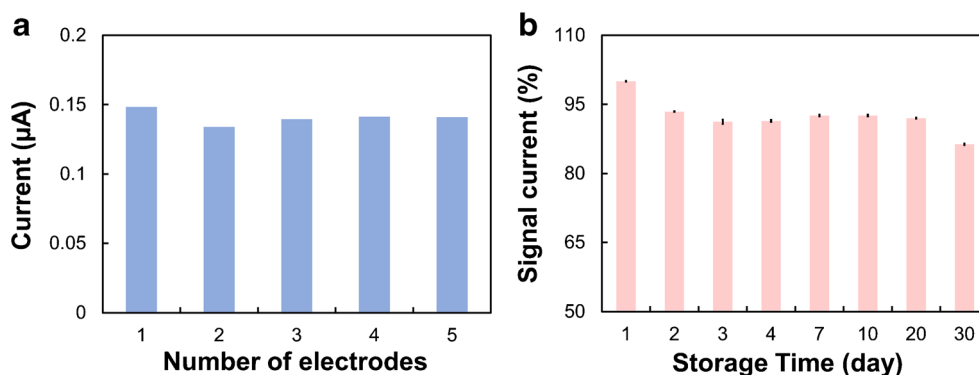
the electrode surface, which reduces the electron transfer rate of the electrode leading to increased charge transfer resistance. Moreover, the lowest charge transfer resistance was exhibited on Pt/PANI/MXene-modified electrode confirming that Pt/PANI/MXene modified electrode (yellow) can accelerate the electron transfer through electrode surface. Hence, the LOx/Pt/PANI/MXene modified electrode is suitable for electrochemical determination of lactate.

For the determination of lactate, LOx/Pt/PANI/MXene modified electrodes were incubated for 5 min with different concentrations of lactate under the optimal conditions. The amperometric measurements were made at the steady state current of 240 s to construct a calibration plot for lactate. As shown in Fig. 5, the calibration curve was linearly proportional to the concentration of lactate over the range from 5.0 μM to 5.0 mM with a correlation coefficient of 0.9868. The detection sensitivity of LOx/Pt/PANI/MXene modified electrodes was found to be 0.62 μA·mM^{-1}, and a limit of detection (LOD) for lactate was found to be 5.0 μM ($n = 3$). The electrochemical performances of this biosensor were compared to previously reported systems for lactate detection (Table 1). The biosensor exhibits a relatively high electrochemical sensitivity with a wide linear range for lactate detection. Hence, this information confirms that LOx/Pt/PANI/MXene modified electrode is an alternative system utilized for the detection of H$_2$O$_2$ generated by the enzymatic assay, and it might be a new tool for the detection of other biomarkers for medical diagnosis.

Reproducibility and stability

To investigate the electrode-to-electrode reproducibility, five different electrodes were used to determine 1.0 mM lactate. The current responses for this biosensor offered the reproducible responses with a 3.7% RSD, demonstrating acceptable reproducibility (Fig. 6a). To evaluate biosensor stability, LOx/Pt/PANI/MXene-modified electrodes were prepared and kept in the sealed system at 4 °C for 30 days. The electrodes retained 93% and 86% of their initial signal after storage period of 7 days and 30 days, respectively (Fig. 6b). It is confirmed that this biosensor has a good stability, which might

be the result of the porous structure of PANI and high surface area of multilayers structure of MXene preserving the LOx activity [34].

Determination of lactate in real milk samples

To evaluate the utilization of this biosensor, the analysis of lactate in dairy products was investigated using the standard addition method. Different lactate concentrations (1.0, 1.5, 2.0, 2.5 and 3.0 mM) were spiked into cow's milk followed by a protein precipitation using TCA [35]. The supernatant was kept for further analysis after centrifugation at 10,000 rpm. The biosensor results showed a good agreement with HPLC data using the standard analytical method for lactate (Table S1). This proves that a novel LOx/Pt/PANI/MXene biosensor possesses a high accuracy and applicable for determination of lactate in the real samples.

Conclusions

A Pt/PANI/MXene nanocomposite was successfully fabricated and used to modify screen-printed carbon electrode for hydrogen peroxide (H$_2$O$_2$) and lactate detection. Pt/PANI/MXene-modified electrode can substantially increase the current response signal toward H$_2$O$_2$ detection, which is approximately 180 times higher than an unmodified electrode. For lactate detection, this biosensor provided a linear range of 0.005–5.0 mM with a sensitivity of 0.62 μA·mM^{-1}, and a detection limit of 5.0 μM. In addition, this biosensor provides a relatively low LOD compared to previous reports. Furthermore, the enzymatic activity of LO$_x$ was preserved on this biosensor offering the high stability for at least 30 days with 86% current response retained compared with the initial signal. Hence, this biosensor might be used as an alternative tool for sensitive detection of lactate and it can be further applied for the detection other biomarkers for medical diagnosis.

Compliance with ethical standards

Competing interests The author(s) declare that they have no competing interests.

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