A non-invasive glucose sensor based on 3D graphene oxide-MXene composite electrode for the detection of saliva glucose

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Abstract

Regular monitoring of blood glucose levels is crucial in diabetes management. Commonly used procedures may be invasive and can lead to cross-infection and inflammation. Therefore, a safe, non-invasive blood glucose-monitoring technology is needed. Herein, a 3D reduced graphene oxide (rGO) electrode was modified with MXene (Ti$_3$C$_2$) and gold nanoparticles (AuNPs) to construct a non-invasive, saliva glucose detection electrode. The Au/rGO-Ti$_3$C$_2$ electrode exhibited good detection performance for glucose concentrations in the range of 10 µM–21 mM at a working potential of 0.6 V, with a detection limit of 3.1 µM glucose, and a sensitivity of 355 µA mM$^{-1}$ cm$^{-2}$. The Au/rGO-Ti$_3$C$_2$ electrode showed almost no response to the addition of interfering substances, and no effect was observed upon subsequent glucose detection. The sensor could detect glucose in artificial saliva and saliva supernatant. The modified electrode showed a significant response to low glucose concentrations, even at 10 µM. These results indicate the suitability of the Au/rGO-Ti$_3$C$_2$ electrode for saliva glucose detection. The electrode developed in this study has great potential in improving the efficiency of diabetes monitoring through pain-free, non-invasive glucose detection in saliva.

1. Introduction

Diabetes is the second-most dangerous disease worldwide, after cancer. According to the International Diabetes Federation, the number of people with diabetes is expected to reach 700 million by 2045 [1]. Elevated blood glucose levels can affect the function of the heart, eyes, kidneys, and other organs, causing serious complications and endangering health [2, 3]. Therefore, regular monitoring of blood glucose levels is crucial for people at risk for diabetes. The procedures used with most blood glucose meters on the market are invasive and may easily lead to cross-infection and inflammation, which can increase patient pain [4]. One solution to this problem is the development of non-invasive blood glucose-monitoring technology. Non-invasive glucose monitoring can be classified as optical, microwave, or electrochemical [5–7]. The optical method is complicated to perform and has a low correlation between measured and actual values. Further, microwave sensors are highly penetrating and portable but have low sensitivity and selectivity [8]. In contrast, electrochemical methods have low detection limits, high sensitivity, low cost, and simple operating procedures. Currently, the main electrochemical non-invasive glucose-monitoring methods use biofluid samples, and the glucose levels in saliva (normal: 0.23–0.38 mM, diabetes: 0.55–1.77 mM), tears (normal: 0.05–0.5 mM, diabetes: 0.5–5 mM), and sweat (normal: 0.06–0.11 mM, diabetes: 0.01–1 mM) were found to positively correlate with measured blood glucose levels [9].

In recent years, several biofluid-based sensors have been developed. Lee, et al. [10] used glucose oxidase (GOx) and Prussian blue to develop a sweat glucose sensor, and Cui, et al. [5] used MXene and GOx to develop a tear glucose sensor. The instability of GOx can lead to poor stability and repeatability of electrode measurements [11]. Usually, sweat and tears are extracted through exercise and external stimuli, but residual skin substances may interfere with the test results. This makes it challenging to accurately
measure glucose in sweat and tear samples. In contrast, saliva extraction is simpler and less invasive, making it a more suitable biofluid for glucose detection. Kadian, et al. [12] modified indium tin oxide with poly (3-hexylthiophene) (PET)-titanium dioxide (TiO$_2$) film and GOx to develop a saliva glucose sensor. However, the electrode preparation was complex and prone to reproducibility- and stability-related issues. Gu, et al. [13] prepared a glucose sensor by immobilizing GOx in a composite structure of reduced graphene oxide (rGO) and MXene; they used it to successfully detect serum glucose at a high detection limit (100 µM in air, 130 µM in O$_2$). We evaluated the previous methods and concluded that the development of a non-invasive, highly sensitive, interference-resistant glucose sensor with good stability and repeatability has become necessary.

Graphene is a single-atom, 2D carbon material with excellent electrical conductivity, high specific surface area, and good catalytic activity, mechanical properties, and biocompatibility [14]. Through the “bottom-up” method, π-π superposition interactions transform 2D GO into 3D graphene hydrogels [4, 15]. 3D rGO prevents the aggregation of 2D graphene, which gives 3D rGO a larger specific surface area, better catalytic activity, higher conductivity, and wider electrochemical window than in 2D graphene [16–18]. 3D rGO is widely used in electrochemical sensors. Graphene-based electrodes have a wider linear range for glucose detection than carbon materials, such as carbon nanofibers and carbon nanotubes [19, 20]. Ye, et al. [21] used rGO, carbon nanofibers, and CuO to develop a glucose sensor with a wide linear range (1 µM–5.3 mM).

MXenes are novel 2D transition metal carbides/carbonitrides [14]. Their chemical formula is $M_{n+1}X_nT_x$, where M represents an early transition metal, X is C or N, $T_x$ denotes surface functionalization (e.g., -OH or -F), and n = 1, 2, or 3 [22]. MXenes exhibit excellent electrical conductivity, hydrophilicity, layer-spacing, and catalytic properties [23–25]. The large layer spacing of multilayer MXenes allow various particles to be interspersed in opposite directions, creating a strong adsorption force. A single layer (Ti$_3$C$_2$) can increase the specific surface area of MXene, providing more active sites and improving its catalytic performance. Gopal, et al. [26] used MXene and CuO to develop a glucose sensor that responded to glucose in human serum samples.

Under alkaline conditions, gold nanoparticles (AuNPs) exhibit good electrical activity, high response currents to glucose, and high catalytic activity, stability, and resistance to interference [11]. Su, et al. [27] used Au and CuO to develop a glucose sensor that measured the glucose content in pharmaceuticals.

Herein, we developed a salivary glucose biosensor based on 3D rGO-immobilized MXenes and AuNPs. Further, we performed electrochemical characterization of the Au/rGO-Ti$_3$C$_2$ electrode and investigated its stability, interference immunity, and measurement repeatability.

2. Materials and Methods

2.1. Chemicals and materials
D-Glucose monohydrate, chloroauric acid (HAuCl$_4$·4H$_2$O), and dichloromethane (CH$_2$Cl$_2$) were purchased from Aladdin (Shanghai, China). NaCl, NaOH, KCl, CaCl$_2$, potassium hydrogen sulfate (KSCN), potassium ferricyanide (K$_3$[Fe(CN)$_6$]), potassium dihydrogen phosphate (KH$_2$PO$_4$), sodium sulfate (Na$_2$S), urea (UR), ascorbic acid (AA), uric acid (UA), dopamine (DA), and L-cysteine were obtained from Macklin (Shanghai, China). Graphene oxide (GO) was bought from Ashine Advanced Carbon Materials Co., Ltd. (Changzhou, China). MXene (single layer Ti$_3$C$_2$) was purchased from Beike 2D Materials Co., Ltd. (Beijing, China). Apiezon WAX W was obtained from Madison Technology Co., Ltd. (Beijing, China). Glucose Assay Kit with O-toluidine was bought from Beyotime Biotech Inc Co., Ltd. (Shanghai, China). In all experiments, deionized water with a specific resistivity of 18.25 MΩ cm$^{-1}$ was used.

2.2. Preparation of the Au/rGO-Ti$_3$C$_2$ electrode

Preparation of the Au/rGO-Ti$_3$C$_2$ electrode is shown in Scheme 1. First, a 3:1 (v/v) mixture of GO (2 mg mL$^{-1}$) and Ti$_3$C$_2$ (2 mg mL$^{-1}$) was ultrasonically dispersed for 1 h. Second, the resulting suspension and a copper wire (diameter 0.3 mm) were sealed in a 5 mL Teflon-lined autoclave and maintained at 180°C for 3 h. The obtained rGO-Ti$_3$C$_2$ hydrogel was then dried at 50°C for 1 h. Finally, the rGO-Ti$_3$C$_2$ was immersed in 4 mM HAuCl$_4$·4H$_2$O for 30 s, upon which the film changed from black to reddish-brown. The sides of the cylinder were then encapsulated in wax. The rGO and rGO-Ti$_3$C$_2$ electrodes were prepared using the same method. In this study, copper wire acted as a conductor.

2.3. Electrochemical measurements

All electrochemical measurements were performed using a three-electrode system which included the Au/rGO-Ti$_3$C$_2$ electrode, a Pt wire (diameter 0.1 mm), and Ag/AgCl as the working, counter, and reference electrode, respectively. Origin 2018 software (Origin 9.1; OriginLab, Northampton, MA, USA) was used to analyze all the measurement data. Scanning electron microscopy (SEM) (Nova 450; FEI Inc., Eindhoven, Holland) was used to investigate the morphology of the Au/rGO-Ti$_3$C$_2$ electrode.

2.4. Artificial saliva and saliva supernatant

Artificial saliva samples were prepared by mixing 0.064 mM Na$_2$S, 3.087 mM KSCN, 6.834 mM NaCl, 5.369 mM KCl, 5.07 mM KH$_2$PO$_4$, 7.207 mM CaCl$_2$, 16.667 mM UR, and 1 L deionized water, based on the method described by Chen et al. [28]. The pH was adjusted to 12.8 by using 1 M NaOH. Human saliva samples were collected from healthy volunteers. The process of collecting saliva samples was approved by the ethics committee of Xinxiang Medical University. All volunteers signed informed consent forms. For saliva collection, the volunteers rinsed their mouths and placed clean cotton balls inside their mouths until they were completely moistened. The liquid was then extracted from the cotton balls and centrifuged at 8000 rpm for 10 min. The final pH of the collected supernatant was adjusted to 12.8 by using 1 M NaOH.

3. Results and Discussion
3.1. Characterization

The surface of the rGO, rGO-Ti$_3$C$_2$, and Au/rGO-Ti$_3$C$_2$ electrodes was investigated using SEM. The rGO surface exhibited a typical wrinkled surface morphology on a scale of 2 µm (Fig. 1A), revealing a folded nanosheet structure after the hydrothermal reaction of GO [29]. Dispersed Ti$_3$C$_2$ was polymerized in the rGO hydrogel (Fig. 1B). The addition of a small amount of Ti$_3$C$_2$ to the GO not only prevented rGO stacking but it also had a synergistic effect with rGO that improved its electrochemical properties [13]. This structure provided a larger specific surface area for the adsorption of AuNPs, improving the electron transfer rate and providing more active sites for electrocatalysis of glucose [30]. AuNPs were uniformly adsorbed onto the surface of rGO-Ti$_3$C$_2$ (Fig. 1C), producing an Au/rGO-Ti$_3$C$_2$ film at a scale of 1 µm (Fig. 1D). Further, XRD and XPS characterization is shown in Fig. S1.

3.2. Direct electrochemical behavior of the Au/rGO-Ti$_3$C$_2$ electrode

Electrochemical impedance spectrum (EIS) measurements were carried out in a mixture of 5 mM K$_3$[Fe(CN)$_6$] and 0.1 M KCl to analyze the electron transfer properties of the electrodes. In the EIS, the high-frequency intercept on the x-axis represents the resistance of the solution [31]. Nyquist plots of the rGO, rGO-Ti$_3$C$_2$, and Au/rGO-Ti$_3$C$_2$ electrodes are shown in Fig. 2A. With the addition of Ti$_3$C$_2$ and AuNPs to the rGO electrode, the resistance to electron transfer decreased significantly, whereas the diffusion rate increased. Therefore, this modification enhanced the conductivity of the electrode and accelerated the electron transfer rate of the electrochemical reaction. Cyclic voltammetry (CV) analyses of different electrodes in the same electrolyte are shown in Fig. S4.

Furthermore, to characterize the electron transfer process and effective surface area of the electrodes, CV analyses were performed at different scan rates (Fig. 2B, Fig. S5). Both the oxidation and reduction peak currents increased linearly with an increase in the square root of the scan rate. The obtained linear relationship is shown in the inset of Fig. 2B. The correlation coefficient ($R^2$) was 0.99, which suggested a typical diffusion-controlled quasi-reversible electron transfer process. The effective surface area of the rGO, rGO-Ti$_3$C$_2$, and Au/rGO-Ti$_3$C$_2$ electrodes was calculated using the Randles–Sevck equation as follows:

$$I_p = (2.69 \times 10^5) A_{\text{eff}} n^{3/2} D_0^{1/2} C_0 v^{1/2}$$

where $I_p$ is the peak current, $A_{\text{eff}}$ is the effective surface area, $n$ is the number of electrons transferred between the electrode and electrolyte ($n = 1$), $D_0$ is the diffusion coefficient of K$_3$[Fe(CN)$_6$] in a 0.1 M KCl solution ($D_0 = 0.673 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$), $C_0$ is the concentration of K$_3$[Fe(CN)$_6$] in solution ($C_0 = 5 \times 10^{-6} \text{ mol cm}^{-3}$), and $v$ is the scan rate. Based on this equation, the calculated effective surface area of the rGO, rGO-Ti$_3$C$_2$, and Au/rGO-Ti$_3$C$_2$ electrodes was 0.031 cm$^2$, 0.034 cm$^2$, and 0.045 cm$^2$ respectively. This
indicated that the prepared Au/rGO-Ti$_3$C$_2$ electrode had a higher effective surface area than that of the MXene-CuO/GCE electrode (0.032 cm$^2$) by Gopal, et al. [26].

### 3.3. Electrocatalytic oxidation of glucose by the Au/rGO-Ti$_3$C$_2$ electrode

To investigate the electrocatalytic oxidation of glucose, CV analysis of the rGO, rGO-Ti$_3$C$_2$, and Au/rGO-Ti$_3$C$_2$ electrodes was carried out at different glucose concentrations in 0.1 M NaOH over a potential range of 0.0–1.0 V. With increasing glucose concentrations, the rGO electrode current response increased as well (Fig. 3). This indicated that rGO was suitable for glucose oxidation. For the rGO-Ti$_3$C$_2$ and Au/rGO-Ti$_3$C$_2$ electrodes, apart from the increase in current, a significant oxidation peak was observed within the 0.4–0.8 V potential range (Fig. 3B and C). Under alkaline solutions, OH$^-$$^-$$^-$ adsorbed onto the Au/rGO-Ti$_3$C$_2$ electrode, forming an AuOH active center. Such a reaction results in dehydrogenation and further oxidation of the glucose molecule and the transfer of electrons to form gluconolactone [32]. Subsequently, the gluconolactone is hydrolyzed to gluconic acid [33]. The electrocatalytic oxidation of glucose is illustrated in Scheme S1.

At a potential of 0.6 V, a linear fitting relationship was observed between the glucose concentration and current response for all the three electrodes, with the Au/rGO-Ti$_3$C$_2$ electrode exhibiting the largest response to glucose (Fig. 3D). At the same potential, the amperometric response of the Au/rGO-Ti$_3$C$_2$ electrode was recorded by adding different glucose concentrations at 100 s intervals. When glucose was added to the 0.1 M NaOH, the current responded rapidly within 5 s (Fig. 4A). The current response of the Au/rGO-Ti$_3$C$_2$ electrode exhibited a good linear relationship over a glucose concentration range of 10 µM–21 mM (R$^2$ = 0.998), with a sensitivity of 355 µA mM$^{-1}$ cm$^{-2}$ and a detection limit of 3.1 µM (S/N = 3) (Fig. 4B). Further, a comparison of Au/rGO-Ti$_3$C$_2$ electrode with other enzyme-free glucose sensors is summarized in Table 1. Compared with other literature, Au/rGO-Ti$_3$C$_2$ electrode was having the advantage of a wide linear range and a low detection limit.
Table 1
Table of comparison of Au/rGO-Ti$_3$C$_2$ electrode with other enzyme-free glucose sensors

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Linear range (mM)</th>
<th>LOD (µM)</th>
<th>Sensitivity</th>
<th>Samples</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/rGO/CNF/GCE</td>
<td>0.01–5.3</td>
<td>0.1</td>
<td>912.7 µA mM$^{-1}$ cm$^{-2}$</td>
<td>Saliva</td>
<td>[21]</td>
</tr>
<tr>
<td>Ti$_3$C$_2$Tx-Cu$_2$O/GCE</td>
<td>0.01–30</td>
<td>2.83</td>
<td>11.064 µA mM$^{-1}$ cm$^{-2}$</td>
<td>Serum</td>
<td>[26]</td>
</tr>
<tr>
<td>Au@Cu$_2$O/Nafion/GCE</td>
<td>0.05–2</td>
<td>18</td>
<td>715 µA mM$^{-1}$ cm$^{-2}$</td>
<td>Pharmaceutical</td>
<td>[27]</td>
</tr>
<tr>
<td>Bronze</td>
<td>0-0.32</td>
<td>6.6</td>
<td>480 µA mM$^{-1}$ cm$^{-2}$</td>
<td>Saliva</td>
<td>[28]</td>
</tr>
<tr>
<td>n-FeOOH</td>
<td>0.015–3</td>
<td>7.8</td>
<td>12.13 µA mM$^{-1}$</td>
<td>-</td>
<td>[34]</td>
</tr>
<tr>
<td>CoNi$_2$Se$_4$-rGO@NF</td>
<td>0.001–4</td>
<td>0.65</td>
<td>18.89 mA mM$^{-1}$ cm$^{-2}$</td>
<td>Serum</td>
<td>[35]</td>
</tr>
<tr>
<td>CNTs-Au/GCE</td>
<td>0.2–10.6</td>
<td>-</td>
<td>20.3 µA mM$^{-1}$ cm$^{-2}$</td>
<td>-</td>
<td>[36]</td>
</tr>
<tr>
<td>Au/rGO-Ti$_3$C$_2$</td>
<td>0.01–21</td>
<td>3.1</td>
<td>355 µA mM$^{-1}$ cm$^{-2}$</td>
<td>Saliva</td>
<td>This work</td>
</tr>
</tbody>
</table>

*GCE-glassy carbon electrode, NF-Ni foam substrate, PN-porous nanostructure

Moreover, long-term stability of the Au/rGO-Ti$_3$C$_2$ electrode was demonstrated by periodically recording the amperometric response to 1.5 mM glucose (Fig. 5A). Glucose oxidation was maintained at 98.4% of the initial value after 10 d. The response current to 1 mM glucose showed almost no change over 30 min (Fig. 5B). Subsequently, after another 1 mM of glucose was added to the electrolyte, the current response remained very close to the original value demonstrating the stability during testing (Fig. 5B inset).

The selectivity of the Au/rGO-Ti$_3$C$_2$ electrode is illustrated in Fig. 4C. In the human saliva, the levels of potentially interfering substances, such as AA, UA, and DA, are below 10 µM [28]. The current response of the Au/rGO-Ti$_3$C$_2$ electrode was recorded upon successive addition of 100 µM glucose, 10 µM interfering species, such as AA, UA, DA, NaCl, and L-cysteine, and then 100 µM glucose again in 0.1 M NaOH solution. The Au/rGO-Ti$_3$C$_2$ electrode showed almost no response to the 10 µM of interfering substance, whereas a significant response was measured upon the addition of successive aliquots of 100 µM glucose. AA is usually negatively charged [38]. Owing to the corrosion of the metal surface, Ti$_3$C$_2$ is usually negatively charged [39]. Homogeneous charges repel each other, making the Au/rGO-Ti$_3$C$_2$
electrode almost no response to AA. This indicated that the addition of interfering substances had no immediate or lasting effect on glucose detection.

The measurement repeatability of the Au/rGO-Ti$_3$C$_2$ electrode was investigated using an amperometric study with five Au/rGO-Ti$_3$C$_2$ electrodes prepared using the same method and tested with 1.5 mM glucose. The responses were very similar for all five electrodes (Fig. 5D). The relative standard deviation (RSD) of the electrodes was 0.0038. The above analysis showed that the modified electrodes exhibit high stability, interference resistance, and measurement repeatability.

3.4. Glucose detection in artificial saliva and saliva supernatant

To demonstrate the practical applications of the Au/rGO-Ti$_3$C$_2$ electrode, the concentration of glucose was detected in artificial saliva and saliva supernatant samples using the standard titration method [40]. At intervals of 100 s, a glucose standard concentration (10, 20, and 50 µM) was added to the electrolyte (artificial saliva and saliva supernatant) (Fig. 6). The glucose concentration was determined using the linear regression equation: $I$ (µA) = 15.99 $C$ (mM) + 0.22 (linear relationship, as shown in Fig. 3B). The glucose detection results are provided in Table 2. The electrode showed a similar response to glucose in 0.1 M NaOH and artificial saliva; however, the response to glucose in the salivary supernatant was slightly decreased. This may have been due to the matrix effect of the biological or chemical components present in the saliva [13]. These components may have interfered with the experimental results to some extent and reduced the electrode response to glucose compared with the other two electrolytes.

To demonstrate the effect of highly pH on real saliva samples on glucose detection, the concentration of glucose was detected in pH = 12.8 and pH = 7 saliva supernatant samples using the Glucose Assay Kit with O-toluidine (Fig. S6A and B). It can be concluded that high pH on real saliva samples have less effect on glucose detection (Fig. S6C). These results indicate that the Au/rGO-Ti$_3$C$_2$ electrode can also detect glucose in saliva.
### Table 2
Determination of glucose in artificial saliva and saliva supernatant samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added glucose (µM)</th>
<th>Determined by our sensor (µM)</th>
<th>RSD (%)</th>
<th>Mean recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Artificial saliva</td>
<td>10</td>
<td>10.1</td>
<td>0.7</td>
<td>101</td>
</tr>
<tr>
<td>Artificial saliva</td>
<td>20</td>
<td>20.4</td>
<td>1.4</td>
<td>102</td>
</tr>
<tr>
<td>Artificial saliva</td>
<td>50</td>
<td>50.9</td>
<td>1.2</td>
<td>101</td>
</tr>
<tr>
<td>Saliva supernatant</td>
<td>10</td>
<td>9.8</td>
<td>1.4</td>
<td>98</td>
</tr>
<tr>
<td>Saliva supernatant</td>
<td>20</td>
<td>19.2</td>
<td>2.8</td>
<td>96</td>
</tr>
<tr>
<td>Saliva supernatant</td>
<td>50</td>
<td>49.4</td>
<td>1.1</td>
<td>98.8</td>
</tr>
</tbody>
</table>

### 4. Conclusions

To develop a highly sensitive, non-invasive glucose detection electrode, rGO-Ti$_3$C$_2$ films were prepared using a hydrothermal reduction method and then modified with AuNPs. The developed Au/rGO-Ti$_3$C$_2$ electrode responded well to glucose in 0.1 M NaOH. The rGO exhibited a catalytic effect on glucose oxidation, and the addition of Ti$_3$C$_2$ increased this catalytic activity, accelerating the electron transfer rate, and providing pores for the attachment of AuNPs. The Au/rGO-Ti$_3$C$_2$ electrode exhibited a wide linear range for glucose detection, high sensitivity, a low detection limit, and good selectivity, stability, and reproducibility. Moreover, the electrode was found to be suitable for real-time detection of glucose in saliva. Through this study, detected glucose in a saliva environment using an Au/rGO-Ti$_3$C$_2$ electrode, which can potentially provide a new approach for non-invasive glucose detection and promote the rapid diagnosis of diabetes.

### Declarations


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Conflicts of Interest: The authors declare no conflict of interest.

References


**Scheme 1**

Scheme 1 is available in the Supplementary Files section.

**Figures**
Figure 1

SEM images of (A) rGO, (B) rGO-Ti$_3$C$_2$, and (C) Au/rGO-Ti$_3$C$_2$ at the scale of 2 µm; and (D) Au/rGO-Ti$_3$C$_2$ at the scale of 1 µm.
Figure 2

(A) EIS of the rGO, rGO-Ti$_3$C$_2$, and Au/rGO-Ti$_3$C$_2$ electrodes in 5 mM K$_3$[Fe(CN)$_6$] and 0.1 M KCl at the frequency range of 0.1–10$^5$ Hz. (B) CV of the Au/rGO-Ti$_3$C$_2$ electrode in 5 mM K$_3$[Fe(CN)$_6$] and 0.1 M KCl at scan rates of 10, 40, 70, 100, 200, 400, 600, 800, and 1000 mV s$^{-1}$ (inset: plot of the oxidation and reduction peak currents vs. square root of the scan rate).
Figure 3

CV of the (A) rGO, (B) rGO-Ti$_3$C$_2$, and (C) Au/rGO-Ti$_3$C$_2$ electrodes at different glucose concentrations (0–5 mM) in 0.1 M NaOH. Scan rate: 100 mV s$^{-1}$, Potential range: 0.0–1.0 V. (D) Calibration curves of the rGO, rGO-Ti$_3$C$_2$, and Au/rGO-Ti$_3$C$_2$ electrodes currents vs. glucose concentration.
Figure 4

(A) Amperometric response of the Au/rGO-Ti$_3$C$_2$ electrode upon adding glucose in 0.1 M NaOH at a constant potential of 0.6 V under continuous stirring (inset: expand view at 10 and 20 µM glucose). (B) Calibration curve of the Au/rGO-Ti$_3$C$_2$ electrode current vs. glucose concentration.
Figure 5

(A) Long-term (10 d) stability of the Au/rGO-Ti$_3$C$_2$ electrode with 1.5 mM glucose in 0.1 M NaOH at a constant potential of 0.6 V. (B) Sensing stability of the Au/rGO-Ti$_3$C$_2$ electrode with 1 mM glucose over 30 min in 0.1 M NaOH at a constant potential of 0.6 V (inset: current response of Au/rGO-Ti$_3$C$_2$ electrode with two additions of 1 mM glucose). (C) Selectivity of the Au/rGO-Ti$_3$C$_2$ electrode to 100 µM glucose, 10 µM interfering species, and 100 µM glucose in 0.1 M NaOH at a constant potential of 0.6 V. (D) Reproducibility study of the five Au/rGO-Ti$_3$C$_2$ electrodes to 1.5 mM glucose.
Figure 6

Amperometric response of the Au/rGO-Ti$_3$C$_2$ electrode upon adding 10, 20, and 50 µM glucose in artificial saliva and saliva supernatant at a constant potential of 0.6 V.

Supplementary Files

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- Scheme.1.tif
- SupplementaryMaterial.docx