Recyclable Non-Enzymatic Glucose Sensor Based on Ni/NiTiO$_3$/TiO$_2$ Nanotube Arrays

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A non-enzymatic amperometric glucose sensor that can be re-
newed by light irradiation is described. It is composed of Ni/
NiTiO$_3$/TiO$_2$ nanotube arrays (NTAs) prepared by a simple
drothermal treatment of as-anodized TiO$_2$ NTAs in a nickel ace-
tate solution followed by annealing under H$_2$/Ar. The Ni/
NiTiO$_3$/TiO$_2$ NTAs exhibit excellent electrocatalytic activity to-
wards glucose oxidation in a 1.0 M NaOH supporting solution at
a low applied potential of 0.4 V (vs. Ag/AgCl) with a high
sensitivity of 4564 µA cm$^{-2}$·mM$^{-1}$ and a low detection limit of
0.7 µM (S/N = 3). The excellent electrochemical biosensing
properties for glucose detection can be attributed to the or-
derly vertical alignment, large accessible surface, high conduc-
tivity, and electroactive Ni$^2$/Ni$^3$ redox couple. Meanwhile,
owing to their high photocatalytic activity, Ni/NiTiO$_3$/TiO$_2$ NTAs
can readily decompose the organic fouling species generated
on the electrode surface during glucose detection under light
irradiation so that the original sensitivity and selectivity can be
restored. The Ni/NiTiO$_3$/TiO$_2$ NTAs electrode provides a promis-
ing renewable platform enabling long-term glucose monitor-
ing with high sensitivity and selectivity.

Introduction

Diabetes, a global health problem affecting over 200 million
people, can cause disorders of the heart, kidney, retina, and
neural system.[1] Hence, accurate detection of blood glucose
levels is necessary to prevent diabetic complications as diabe-
tes becomes more prevalent in modern society. Conventional
glucose sensors use glucose oxidase immobilized on a solid
electrode to catalyze the oxidation of glucose in the presence
of O$_2$ to produce hydrogen peroxide and thereby monitor the
glucose level.[2] Although such enzymatic glucose sensors are
available commercially, they suffer from some limitations such as
complex enzyme immobilization procedures and instability,
as well as sensitivity to temperature, humidity, chemical envi-
ronment (e.g. pH), and composition of the substrate.[3] As
a result, non-enzymatic glucose sensors are more desirable.[4]
Nickel (Ni) and its oxide or hydroxide exhibit good electroca-
talytic activity towards glucose oxidation[5] and it has been
demonstrated that the faradaic current arising from glucose
oxidation on Ni-based electrodes can be improved by increas-
ing the ratio of the surface area to the geometric area.[6] Thus,
nanostructured Ni-based electrodes, for instance, nanoparticles
(NPs),[7] nanowires,[8] nanosheets,[9] mesoporous structures,[10]
and nanocomposites[11, 12] have been proposed as candidates
for non-enzymatic glucose detection. However, the work po-
tential applied to determine glucose levels at non-enzymatic
glucose sensors is relatively high, (e.g. 0.6 V vs. Ag/AgCl),
which may cause interference for glucose detection.[13] Fur-
thermore, the long-term stability and selectivity are not satisfac-
tory for practical applications of non-enzymatic glucose sen-
sors.[14, 15]

Blood plasma is a complicated liquid medium that mainly
contains proteins, glucose, mineral ions, neurotransmitters,
etc.[16–18] Long-term monitoring of the blood glucose concen-
tration using a non-enzymatic electrode is typically hampered
by rapid surface fouling due to the strong absorption and pas-
sivation of organic biomolecules such as histamine, amino
acids, and serotonin (5-HT), and their oxidized species. This sur-
face fouling process will inevitably attenuate the sensitivity
and selectivity towards glucose oxidation over time.[20–22] Con-
ventional electrode regeneration methods such as mechanical
ablation,[27] and chemical and electrochemical oxidation[28, 29]
are too harsh to implement on nanostructured electrodes as
they may cause significant surface microstructural damage
leading to poor reproducibility and stability.[22, 30] Consequently,
it is imperative to develop a more effective and milder regenerating method to regenerate the electrode surface for long-term glucose monitoring.

TiO$_2$ nanotube arrays (NTAs) fabricated by the anodic oxidation of Ti have a large solvated and ion-accessible surface area as well as a direct electron pathway to the underlying Ti substrate. The materials are thus promising as electrodes in biosensors. However, TiO$_2$-NTAs electrodes usually exhibit poor electrochemical activity because of the low conductivity of TiO$_2$. Our recent work demonstrated that carbon-doped TiO$_2$-NTAs (C-doped TiO$_2$-NTAs) could serve as a highly sensitive electrode for the determination of 5-HT due to the enhanced conductivity. The C-doped TiO$_2$-NTAs could be regenerated after 5-HT fouling to recover high sensitivity by UV/Vis light irradiation due to the good photocatalytic activity of the electrode. This work has motivated us to construct a renewable platform for non-enzymatic glucose monitoring with long-term high sensitivity and selectivity.

Herein, we report a promising renewable platform composed of coaxial Ni/NiTiO$_3$/TiO$_2$ NTAs for non-enzymatic glucose detection with high sensitivity and selectivity. The Ni/NiTiO$_3$/TiO$_2$ NTAs are prepared by a simple hydrothermal treatment of as-anodized TiO$_2$ NTAs in a solution of nickel acetate (Ni(OAc)$_2$), followed by annealing under hydrogen (see Scheme 1). The Ni/NiTiO$_3$/TiO$_2$ NTAs combine the aforementioned advantages of Ni NPs with NTAs in biosensing while addressing the conglomeration of Ni NPs and low conductivity of TiO$_2$ NTAs to yield improved sensitivity up to 456.4 $\mu$A/cm$^2$·mm$^{-1}$ and a low detection limit of 0.7 $\mu$m (S/N = 3). Common interfering species such as ascorbic acid (AA) and uric acid (UA) show no significant interference. Organic fouling substances generated on the electrode surface can be decomposed into CO$_2$ and H$_2$O under light irradiation to renew the electrode surface, thus providing reproducible results upon repeated use (see Scheme 1).

**Figure 1.** a–c) SEM images of TiO$_2$ NTAs (a) and hydrothermally treated TiO$_2$ NTAs in a 0.2 M Ni(OAc)$_2$ solution followed by anneal in air (b) and in H$_2$/Ar (c); d) corresponding XRD patterns. e) TEM image of a typical NiTiO$_3$/TiO$_2$ nanotube and EDS spectrum (inset). f) XPS high-resolution Ni 2p spectrum acquired from NiTiO$_3$/TiO$_2$ after annealing in H$_2$/Ar. The inset in (a) is the side-view image of TiO$_2$ NTAs.

**Results and Discussion**

Figure 1a depicts the top-view scanning electron microscopy (SEM) image of the sample prepared by electrochemical anodization of a Ti foil in 0.5 wt% NH$_4$F at 60 V for 1 h. Highly ordered NTAs with inner diameters of about 100–120 nm and a wall thickness of roughly 10 nm were fabricated on the Ti foil. The side-view SEM image (inset in Figure 1a) shows that the NTAs have a smooth outside surface and a tube length of about 12 $\mu$m. After the hydrothermal treatment in a 0.2 M nickel acetate solution, the wall thickness of the NTs increases from about 10 to 30 $\mu$m (Figure 1b) due to cell expansion resulting from the transformation from TiO$_2$ to NiTiO$_3$. After thermal treatment under H$_2$/Ar at 450 °C for 3 h, the morphology of the highly ordered NTAs is retained and the wall thickness and outer diameter of NTs do not change obviously (Figure 1c). The X-ray diffraction (XRD) patterns of the samples after hydrothermal treatment and annealing (in H$_2$/Ar and air) are displayed in Figure 1d. Strong diffraction peaks related to NiTiO$_3$ species appear for the sample obtained after hydrothermal treatment in a 0.2 M nickel acetate solution followed by annealing in air at 450 °C for 3 h. The transmission electron microscopy (TEM) image (Figure 1e) further confirms the tubular nanostructures. The corresponding energy-dispersive X-ray spectrum (EDS) reveals well-resolved and strong signals of Ni,
The presence of the anatase TiO₂, diffraction peak (Figure 1d) suggests that the hydrothermal transformation of TiO₂ into NiTiO₃ may not be sufficient. The remaining TiO₂ is connected to the in situ generated NiTiO₃ layer resulting in the formation of heterojunction Ni/NiTiO₃ NTAs, similar to that observed for SrTiO₃/TiO₂. When the hydrothermal NiTiO₃/TiO₂ NTAs are annealed under H₂/Ar instead of air at 450 °C for 3 h, XRD peaks attributed to metallic Ni species are observed, and simultaneously the intensity of the NiTiO₃ peaks decreases, suggesting that partial reduction occurs and metallic Ni species are formed. X-ray photoelectron spectroscopy (XPS) reveals two chemical states of Ni (Figure 1f), namely metallic Ni (Ni 2p3/2, 852.3 eV; Ni 2p1/2, 855.4 eV; Ni 2p1/2, 873.0 eV), further supporting the presence of metal Ni. These results clearly indicate the formation of heterostructured Ni/NiTiO₃ NTAs under these conditions.

Electrochemical impedance spectroscopy (EIS) is performed on the TiO₂ NTAs, NiTiO₃/TiO₂ NTAs, and Ni/NiTiO₃ NTAs all with the same geometric area (9 x 9 mm²) in a 1.0 M KCl solution containing 5.0 mM K₃[Fe(CN)₆] and 5.0 mM K₄[Fe(CN)₉] and the results are shown in Figure S1 in the Supporting Information and Figure 2. The Nyquist plots can be fitted by an equivalent circuit (inset in Figure 2a) in which Rₑ is the bulk resistance of the electrochemical system, Rₛ is the Faradic charge-transfer resistance, and W is the Warburg impedance. The NiTiO₃/TiO₂ electrode exhibits a smaller Rₛ (ca. 130 Ω) than the TiO₂ NTAs (ca. 80 kΩ; Figure S1). Rₛ is further reduced to ca. 15 Ω for the electrode of Ni/NiTiO₃/TiO₂ NTAs indicating high conductivity, which can be attributed to the metallic Ni species generated in situ along the walls of the NTs, and oxygen vacancies in TiO₂, and/or NiTiO₃ introduced by H₂/Ar annealing at 450 °C. This heterostructured Ni/NiTiO₃/TiO₂ NTAs facilitate electron transfer and result in enhanced electrocatalytic activity in glucose oxidation and photoelectrochemical properties.

Cyclic voltammograms (CVs) are acquired on the Ni/NiTiO₃/TiO₂ NTAs electrode in the absence and presence of 1.0 mM glucose as shown in Figure 2b. Anodic and cathodic peaks positioned at 420 and 325 mV are observed from 1.0 M NaOH at a scanning rate of 50 mV s⁻¹ corresponding to the Ni⁢(OH)₂ electrode couple. When 1.0 mM glucose is added, the anodic peak current increases apparently (about 300 μA) but the cathodic current does not change significantly. No redox response to glucose is observed for the TiO₂ NTAs annealed in air and H₂/Ar (Figure S2a,b) and Ni/NiTiO₃/TiO₂ NTAs (Figure S2c), suggesting that metallic Ni is responsible for electrocatalytic oxidation of glucose. The CVs in Figure S2a,b indicate that the currents are enhanced by 2 orders of magnitude on the TiO₂ NTAs annealed in H₂/Ar compared to those annealed in air due to the increased conductivity stemming from H₂/Ar annealing at 450 °C. The H₂ annealing can significantly increase the charge-carrier (electron) concentration and induce obvious n-type doping of TiO₂ nanotubes. This is a possible explanation for why Ni/NiTiO₃/TiO₂ NTAs exhibit good conductivity and electrocatalytic activity towards glucose oxidation.

To further understand the electrocatalytic oxidation of glucose on the Ni/NiTiO₃/TiO₂ NTAs, we compare the XRD results before and after electrochemical detection of glucose. New diffraction peaks associated with Ni(OH)₂ species are observed after glucose detection in addition to metallic Ni on the Ni/NiTiO₃/TiO₂ NTAs (Figure S2d). Electrocatalytic oxidation of glucose on the Ni/NiTiO₃/TiO₂ NTAs can be expressed as follows:

\[ \text{Ni} + 2 \text{OH}^- - 2 \text{e}^- \rightarrow \text{Ni(OH)}_2 \]  \hspace{1cm} (1)

\[ \text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiO(OH)} + \text{H}_2\text{O} + \text{e}^- \]  \hspace{1cm} (2)

\[ \text{NiO(OH)} + \text{glucose} \rightarrow \text{Ni(OH)}_2 + \text{glucolactone} \]  \hspace{1cm} (3)

The formation of Ni(OH)₂ species can be ascribed to the oxidation of metallic Ni on the Ni/NiTiO₃/TiO₂ NTAs in the alkaline medium. Electrocatalytic oxidation of glucose to glucolactone is therefore catalyzed by the NiO(OH)/Ni(OH)₂ redox couple.

The high electrochemical activity of the in situ generated Ni species and large specific surface area and high conductivity of the Ni/NiTiO₃/TiO₂ NTAs lead to fast response and high sensitivity in the amperometric detection of glucose. The amperometric response is evaluated at 0.1, 0.2, 0.3, 0.4, and 0.5 V by successive injections of 0.02 mM glucose into 1.0 M NaOH under continuous stirring to optimize the working potential and achieve high sensitivity, fast response, and low detection limit towards glucose oxidation. The maximum sensitivity is obtained at 0.4 V (vs. Ag/AgCl) as suggested by Figure S3a. The influence of pH on the oxidation current and potential of glucose is also studied in a series of NaOH solutions with different concentrations by cyclic voltammetry (Figure S4a). The peak potentials decrease and corresponding peak currents increase when the NaOH concentration increases from 0.05 to 1.0 M. Since a highly alkaline environment may result in additional reactions that would disturb the detection of serum glucose due to the fact that the blood samples have so many other small analytes, proteins, etc. which would interfere with the measurement, 1.0 M NaOH is selected as the supporting solution because of the satisfactory response current and peak poten-
tial. The amperometric response to successive injections of glucose (5, 10, 20, 40, 80, and 100 μM) on the Ni/NiTiO$_2$ NTAs in 1.0 M NaOH at 0.4 V (vs. Ag/AgCl) is shown in Figure 3a. A well-defined steplike increase in the amperometric response is observed in the i–t curve. The oxidation reaction on the Ni/NiTiO$_2$ NTAs is very quick and the current reaches a stable value within 5 s after addition of glucose. The response to glucose at low concentrations is shown in the inset in Figure 3a. The Ni/NiTiO$_2$ NTAs display two linear ranges to glucose oxidation (Figure 3b), one from 5.0 to 500 μM with a correlation coefficient of 0.9995 and sensitivity up to 456.4 μA cm$^{-2}$ mM$^{-1}$ and another from 0.5 to 1.7 mM with a correlation coefficient of 0.9989 and sensitivity of 335.9 μA cm$^{-2}$ mM$^{-1}$. The detection limit is estimated to be 0.7 μM (S/N = 3), which is lower than reported results acquired from the Ni-nanoparticle-loaded carbon nanofibers paste electrode.[41] Ni/Al hydroxide nanosheets,[30] and nanoscale nickel hydroxide modified electrode.[42] Table 1 compares the biosensing performance of common non-enzymatic electrochemical glucose sensors illustrating the excellent biosensing characteristics of our electrode. The stability of the electrode is evaluated by successive injection of 20 μM glucose to 1.0 M NaOH during amperometric detection. A relative standard deviation (RSD) of 5.8% is obtained from 30 injections (Figure 3c), indicating the good reliability of the Ni/NiTiO$_2$ NTAs in glucose oxidation.

Some species such as AA and UA that normally co-exist with glucose in human blood[32,12] are interferences towards glucose detection by non-enzymatic biosensors although the physiological level of glucose in human blood (3–8 mM) is much higher than those of AA and UA.[10] The selective determination of glucose by the Ni/NiTiO$_2$ NTAs is demonstrated in Figure 3d by measuring the amperometric response at 0.4 V via successive addition of 1.0 mM glucose, 0.1 mM AA, and 0.02 mM UA to 1.0 M NaOH. AA does not exhibit any observable response and the interference caused from AA is also negligible (less than 5%), indicating the Ni/NiTiO$_2$ NTAs have high selectivity in glucose detection.

The Ni/NiTiO$_2$ NTAs electrode was evaluated in practical analysis, which was applied to measure the glucose concentration in human serum. A 20 μL serum sample was added to 10 mL of 1.0 M NaOH solution, and the current response was recorded at 0.4 V. The recovery of glucose was determined by standard addition of pure glucose to the solutions containing the serum samples and the corresponding results are summarized in Table 2. The results obtained by electrochemical detection at the Ni/NiTiO$_2$ NTAs electrode match well with those obtained by application of a routine enzymatic method in a local hospital, indicating the potential application of the Ni/NiTiO$_2$ NTAs electrode for the non-enzymatic detection of glucose in biological fluids.

### Table 1. Comparison of biosensing properties on the Ni/NiTiO$_2$ NTAs electrode with other reported nonenzymatic sensors for glucose detection.

<table>
<thead>
<tr>
<th>Glucose sensor</th>
<th>Sensitivity [μA cm$^{-2}$ mM$^{-1}$]</th>
<th>Detection limit [μM]</th>
<th>Linear range [mM]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiCFP electrode</td>
<td>420.4</td>
<td>1</td>
<td>0.002–2.5</td>
<td>[43]</td>
</tr>
<tr>
<td>Ni/Al hydroxide nanosheets</td>
<td>24.45</td>
<td>5</td>
<td>0.005–10.0</td>
<td>[9]</td>
</tr>
<tr>
<td>Ni(OH)$_2$-modified electrode</td>
<td>202</td>
<td>6</td>
<td>0.05–23</td>
<td>[42]</td>
</tr>
<tr>
<td>gold nanoparticles</td>
<td>179</td>
<td>0.05</td>
<td>0–8</td>
<td>[4]</td>
</tr>
<tr>
<td>ruthenium oxide/prussian blue mesoporous platinum</td>
<td>6.2</td>
<td>40</td>
<td>0.3–20</td>
<td>[3]</td>
</tr>
<tr>
<td>copper nanoparticles</td>
<td>9.6</td>
<td>10</td>
<td>0–10</td>
<td>[6]</td>
</tr>
<tr>
<td>Cu-modified ITO[42]</td>
<td>415.02</td>
<td>0.2</td>
<td>0.001–1.7</td>
<td>[12]</td>
</tr>
<tr>
<td>Au nanocages</td>
<td>2.79</td>
<td>5</td>
<td>0.2–13.4</td>
<td>[46]</td>
</tr>
<tr>
<td>Pd nanoparticle/ CNTs[42]</td>
<td>160</td>
<td>0.2</td>
<td>0.5–17</td>
<td>[47]</td>
</tr>
<tr>
<td>Re-structured CNTs[48]</td>
<td>60</td>
<td>1</td>
<td>1–11</td>
<td>[48]</td>
</tr>
<tr>
<td>oxidized</td>
<td>157</td>
<td>5</td>
<td>1–9</td>
<td>[48]</td>
</tr>
<tr>
<td>Ni/NiTiO$_2$ NTAs</td>
<td>438.4</td>
<td>0.7</td>
<td>0.005–0.5</td>
<td>this work</td>
</tr>
</tbody>
</table>


![Figure 3](image-url)
A good electrochemical biosensing platform should have good reproducibility and stability in addition to high selectivity and sensitivity. Electrode fouling and passivation are the main reasons for attenuated signals as well as reduced sensitivity and selectivity over time in electrochemical sensing. Hence, the self-cleaning ability is an important aspect that needs investigation in order to maintain the long-term monitoring of blood glucose levels. Serotonin, histamine, amino acids, and NADH in the blood plasma can foul electrodes due to the accumulation of oxidation products that passivate the electrode surface. Among these biomolecules, serotonin is the most deactivating substance. Therefore, serotonin was selected in our work as a pollutant model. As indicated by Figure S5, the Ni/NiTiO$_2$/TiO$_2$ NTAs show obvious signal drops after cyclic voltammetry was conducted for 100 cycles in the 2.0 mM serotonin solution (Figure S5). Since TiO$_2$ and NiTiO$_2$ have good photocatalytic activity, the accumulated organic species, especially those from the intermediates of serotonin on the Ni/NiTiO$_2$/TiO$_2$ NTAs surface, can be readily decomposed by irradiation with UV light so that the electrocatalytic activity of the electrode can be restored. The typical amperometric responses towards glucose on the original, fouled, and photo-renewed Ni/NiTiO$_2$/TiO$_2$ NTAs are shown in Figure 4a. The fouled electrode shows abated sensitivity when 15 μM glucose is introduced successively into the stirred 1.0 M NaOH solution at an applied potential of 0.4 V. However, after photo-renewal, the Ni/NiTiO$_2$/TiO$_2$ NTAs exhibit almost the same electrochemical behavior as the original electrode, indicating the good recovery efficiency.

The chemical compositions of the electrode surfaces of the original, fouled, and photocatalytically renewed Ni/NiTiO$_2$/TiO$_2$ NTAs are determined by XPS (Figure 4c). The N1s peak at 400.3 eV observed from the fouled electrode arises from amide or amine (N–C) generated from adsorbed organic species during serotonin oxidation. These organic substances on the electrode surface impede subsequent electrochemical oxidation of glucose, resulting in reduced sensitivity for glucose. After light irradiation for 1 h, the N1s peak in the XPS spectrum (Figure 4d) disappears and the sensitivity of the electrode is recovered, indicating that the adsorbed organic species have been decomposed into H$_2$O, CO$_2$, and NO by light irradiation. The renewed electrode has almost the same electrocatalytic activity towards glucose as illustrated in Figure 4a. It should also be noted that this simple light renewing method does not damage the surface microstructure while the original sensitivity can be restored.

**Conclusion**

A light renewable non-enzymatic glucose sensor based on Ni/NiTiO$_2$/TiO$_2$ NTAs is fabricated by a simple hydrothermal treatment of as-anodized TiO$_2$ NTAs in a nickel acetate solution followed by annealing under H$_2$/Ar. The Ni NPs are formed in situ and decorated uniformly on the walls of the NTs by partial reduction of NiTiO$_2$ by H$_2$/Ar annealing at 450°C; as a result the conductivity and electrocatalytic activity towards glucose oxidation are enhanced with a high sensitivity of 456.4 μA cm$^{-2}$ mm$^{-1}$ and low detection limit of 0.7 μM (S/N = 3). Interferences such as ascorbic acid and uric acid have no influence on the glucose detection, suggesting good selectivity. This glucose biosensor can be readily renewed to maintain the high sensitivity and reproducibility by light irradiation due to its high photocatalytic activity. The high stability, sensitivity, and selectivity towards glucose detection as well as simplicity of the preparation process suggest that the Ni/NiTiO$_2$/TiO$_2$ NTAs have promising applications in glucose measurements and glucose biofuel cells.

**Table 2. Amperometric detection of glucose in human serum samples.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration [mM]</th>
<th>RSD [%]</th>
<th>Added glucose [mM]</th>
<th>Recovery [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.9</td>
<td>7.19</td>
<td>0.1</td>
<td>90</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>103</td>
</tr>
</tbody>
</table>

**Figure 4.**

(a) Cyclic voltammograms of 1.0 mM glucose acquired from the original, fouled, and renewed Ni/NiTiO$_2$/TiO$_2$ NTAs in 1.0 mM NaOH solution. (b) Amperometric response after successive injections of 15 μM glucose into 1.0 M NaOH solution for the original, fouled, and light renewed Ni/NiTiO$_2$/TiO$_2$ NTAs at a scanning rate of 50 mV s$^{-1}$. (c) XPS survey spectra and (d) High-resolution N 1s spectrum acquired from the original, fouled, and light renewed Ni/NiTiO$_2$/TiO$_2$ NTAs.
Experimental Section

Reagents and materials

Analytical-grade ammonium fluoride (NH₄F), ethylene glycol (EG), methanol (CH₃OH), nickel acetate (Ni(CH₃COO)₂·4H₂O), potassium ferrocyanide (K₃[Fe(CN)₆]), and potassium ferrocyanide (K₃[Fe(CN)₆]) were purchased from Tianjin Chemical Company (China), whereas glucose, serotonin, ascorbic acid (AA), and uric acid (UA) were obtained from Sigma. Titanium foils (1 mm in thickness, 99.6% purity) were bought from Advent Materials. Other chemicals were analytical grade and used without further purification. Doubly distilled water (DDW) was used to prepare the solutions and clean the electrodes. The phosphate buffer solution (PBS, 0.1 M) was prepared by dissolving NaH₂PO₄ and Na₂HPO₄ in DDW and the pH value was adjusted to 7.4 by adding H₂PO₄ and NaOH.

Preparation and characterization of Ni/NiTiO₃/TiO₂ NTAs

Titanium foils were sliced into 10 × 10 mm² pieces and mechanically polished. After degreasing sequentially in acetone, alcohol, and DDW, the Ti foil surface was dried by nitrogen gas. Electrochemical anodization was conducted on a two-electrode apparatus equipped with a direct current power supply (IT6834, ITECH, China) at room temperature at an applied voltage of 60 V for 1 h. The Ti foil served as the anode and a graphite foil was the counter electrode. The electrolyte was EG containing 0.5 wt% NH₄F, 5 vol% CH₃OH, and 5 vol% DDW. The as-anodized samples were then ultrasonically cleaned in water for 10 min. The samples were immersed in 40 mL of nickel acetate solution (0.2 M) in a 60 mL Teflon-lined autoclave for hydrothermal treatment at 175 °C for 6 h. Afterwards, the samples were removed from the vessel and ultrasonically washed in diluted HCl for 5 min to remove the residues and dried in nitrogen. The samples were placed on a ceramic substrate and inserted into a tube furnace. The furnace tube was purged with pure argon (Ar) several times to remove residual oxygen and moisture and then heated to 450 °C under Ar. Hydrogen (H₂) gas was introduced into the chamber together with Ar at a flow rate (H₂/Ar) of 90 sccm (standard cubic centimeter per minute) at standard temperature and pressure. After 3 h, the tube was cooled to room temperature under Ar. The final products of Ni/NiTiO₃/TiO₂ NTAs were produced directly on the Ti foil. For comparison, NiO/TiO₂ NTAs were prepared by annealing the hydrothermally-treated sample under air at 450 °C for 3 h. The morphology and composition of the products were characterized by field-emission scanning electron microscopy (FE-SEM, FEI Nova 400 Nano), transmission electron microscopy (TEM, JEOL 2010 equipped with an energy-dispersive X-ray spectrometer (EDS), X-ray diffraction (XRD, Philips X’Pert Pro), and X-ray photoelectron spectroscopy (XPS, ESCALB MK-II).

Glucose monitoring and surface regeneration

The electrochemical experiments were conducted on a CHI 660c potentiostat (CH Instruments Inc., Shanghai, China) with a conventional three-electrode system at room temperature. The as-prepared TiO₂, NiO/TiO₂, and Ni/NiTiO₃/TiO₂ NTAs were insulated with epoxy resin leaving an open area of 9 × 9 mm² as the working electrode, whereas a Pt foil was the counter electrode. A 1.0 M NaOH solution was used as the electrolyte. The Ag/AgCl electrode was used as the reference electrode during detection of glucose and the saturated calomel electrode (SCE) was used in the surface regeneration study. Amperometric experiments were carried out under continuous magnetic stirring. Electrode fouling experiments were conducted by performing cyclic voltammetry on the Ni/NiTiO₃/TiO₂ NTAs electrode in 0.1 M (pH 7.4) PBS containing 2.0 mM serotonin for 100 cycles at a scanning rate of 50 mV s⁻¹. The fouled electrode surface was regenerated by exposure to UV light (500 W) for 1 h at room temperature.

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Keywords: glucose sensors · nanotube arrays · photocatalysis · self-regeneration

Easy-to-clean sensor: A non-enzymatic glucose biosensor based on Ni/NiTiO$_3$/TiO$_2$ nanotube arrays shows high sensitivity and selectivity for glucose detection. Owing to its high photocatalytic activity, the sensor can be readily renewed to maintain the high sensitivity and reproducibility by light irradiation.