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# A glucose biosensor based on the synergistic action of nanometer-sized TiO<sub>2</sub> and polyaniline

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## ABSTRACT

Polyaniline/active carbon (PANI) and nanometer-sized TiO<sub>2</sub> (n-TiO<sub>2</sub>) were prepared by oxidation and sol-gel methods, respectively, and were then used as a zymophore to modify a glassy carbon electrode (GCE) and a GOx/n-TiO<sub>2</sub>/PANI/GCE sensor with a synergistic effect was established. A series of performance evaluations for the modified material and sensor was studied in detail through cyclic voltammetry (CV) and a chronoamperometry (CA) method. The results showed that the sensor had a good response to glucose and that the electron of the GOx molecule was transferred directly onto the sensor, and a linear relationship between the GOx redox peak current and the sweep speed was found. The apparent transmission speed constant, *k*, for dissimilar electrode charges was 1.35 s<sup>-1</sup>, 95% of the maximum steady current for the GOx/n-TiO<sub>2</sub>/PANI/GCE sensor could be reached in 10 s, the linear range of the detected glucose concentration was from 0.02 mM to 6.0 mM, the sensitivity was 6.31 μA mM<sup>-1</sup> cm<sup>-2</sup>, and the limit of detection was 18 μM. The sensor had good selectivity and stability and could be maintained at 82% of the initial activity for 30 days.

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## 1. Introduction

Diabetes mellitus is a serious disease that is harmful to human health, and currently, the effective way to treat it is to severely restrict the diet and control the blood sugar. The blood sugar content is the objective indicator for diabetes mellitus, and it is therefore of great significance to establish a quick, efficient, and inexpensive detection method for glucose. The development of a glucose sensor meets this developmental requirement. Conductive polymer and nanometer-sized materials have received much attention due to their good electrical conductivity, large specific surface area, and small size. Both of these materials have broad application in biosensors.

Nanometer-sized TiO<sub>2</sub> (n-TiO<sub>2</sub>), a new inorganic material with a special crystal structure, has been used to affix to biomacromolecules such as enzymes to achieve good biocompatibility and electron transfer ability. n-TiO<sub>2</sub> therefore has a good prospective application in the area of bioelectrochemistry. Li et al. accomplished the fixation and the direct electron transfer process of myohemoglobin, hemoglobin, and cytochrome C to a nanometer-level TiO<sub>2</sub> membrane [1,2]. Zhang et al. prepared a glucose sensor

with a detection limit of 0.1 μM by using a multi-walled carbon nanotube/n-TiO<sub>2</sub>/gold nanoparticle to modify a GCE [3]. Li et al. made a direct electron transfer of GOx happen on the electrode surface by using mesoporous n-TiO<sub>2</sub>/multi-walled carbon nanotube material [4].

Polyaniline, when used as a typical conducting polymer to establish an enzyme-type sensor, has been a topic of intense research interest over the past few years. Due to the conjugated structure that exists in the polyaniline molecule, the electron has a high degree of transferability. In polyaniline, “mixing” could change its electronic structure, magnetic properties, optical properties, electrical conductivity, and structural features remarkably [5]. Lee et al. modified the GOx with functionalized polyaniline and a multiwalled carbon nanotube and accomplished the direct electrochemistry of an enzyme sensor [6]. Dhand et al. found that the GOx showed good electrochemical activity after being wrapped by nanoscale electro-deposited polyaniline, which indicated that the polyaniline has good biocompatibility [7]. Zhai et al. prepared a highly sensitive glucose enzyme sensor based on Pt nanoparticles–polyaniline hydrogel heterostructures, which exhibited unprecedented sensitivity, as high as 96.1 μA mM<sup>-1</sup> cm<sup>-2</sup>, with a linear range of 0.01–8 mM, and a low detection limit of 0.7 μM [8].

Polyaniline/active carbon (PANI) and n-TiO<sub>2</sub> were prepared by oxidation and sol-gel methods, respectively, and they were then used to co-modify the electrode surface. By utilizing the good electrical conductivity and the effects of the small sizes of the two

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types of materials, an amperometric glucose sensor with a synergistic effect was established, and the detection limit, response time, linear detection range, stability, and anti-jamming capability were studied systematically.

## 2. Experimental

### 2.1. Main instruments and reagents

The working electrode was a glassy carbon electrode (GCE, GC130,  $\varnothing$ 3 mm) from Tianjin Aidahengsheng Technology Co., Ltd. The aniline, chitosan, and tetra-*n*-butyl titanate were of analytical purity from the Sinopham Chemical Reagent Co., Ltd., and the GOx, uric acid (UA), L-cysteine, and ascorbic acid (AA) were of biochemical purity from Sigma.

### 2.2. Preparation of *n*-TiO<sub>2</sub>

Five milliliters (mL) of isopropanol was added into 10 mL of tetra-*n*-butyl titanate, and component A was obtained by stirring for 30 min. Component B consisted of 2 mL of distilled water, 2.5 mL of isopropanol, and a small amount of glacial acetic acid. Component C was obtained by adding the appropriate amount of Polyethylene glycol into 2.5 mL of isopropanol. During the stirring process, component B was dropped into solution C first, and component A was then added dropwise to the BC solution. The duration of the reaction was 0.5 h. The solution that was obtained was aged for 1 day, and then a yellow and transparent sol was obtained. Afterwards, the sol was put into a dryer at 80 °C for 10 h. A xerogel was obtained and was then calcined in the muffle furnace at 500 °C for 2 h, resulting in the TiO<sub>2</sub> powder.

### 2.3. Preparation of the PANI composite material

Aniline monomer (0.9 mL) and the activated carbon powder (0.84 g) were dispersed in 30 mL of a 1 mol L<sup>-1</sup> hydrochloric acid solution, and N<sub>2</sub> was blown into the solution to deoxidize it for 30 min. After stirring the solution at a constant speed for 1 h, the aniline monomer was uniformly adsorbed onto the AC surface. An appropriate amount of ammonium peroxydisulfate (APS) was added to 20 mL of the 1 mol L<sup>-1</sup> hydrochloric acid solution. Then, N<sub>2</sub> was blown into the solution, and the APS was dissolved after stirring. The prepared APS hydrochloric acid solution was dropped into the aniline hydrochloric acid solution gradually over 1 h, the reaction temperature was maintained at 0 °C, and the reaction lasted for 5 h with stirring. After the reaction, the product was washed and filtered repetitively with hydrochloric acid, alcohol, and distilled water to eliminate any oligomer that had not reacted or had not reacted completely. After 24 h of drying in a vacuum oven at 60 °C, the PANI composite material with an atrovirens color was obtained. The optimum molar ratio of AC:ANI:APS for the PANI material was 7:1:1.

### 2.4. Preparation of the GOx/*n*-TiO<sub>2</sub>/PANI/GCE

**Electrode Pre-treatment:** Alumina powder with particle diameters of 0.3  $\mu$ m, 0.1  $\mu$ m, and 0.05  $\mu$ m was put on a polishing cloth and soaked in distilled water. The form of the GCE in the alumina powder turbid liquid was the "8" type. The electrode was then polished, and the polished electrode was placed in nitric acid aqueous solution with a volume ratio of 1:1 for 20 min. The electrode was washed with distilled water and alcohol, and the electrode underwent distilled water ultrasonic cleaning. The treated electrode was scanned by cyclic voltammetry (CV) in a solution of 0.1 M KCl and 5 mM K<sub>3</sub>[Fe(CN)<sub>6</sub>], as  $\Delta E_p < 80$  mV, and

the electrode was taken out, re-washed with the distilled water, and preserved.

**Dispersion of the modified material:** PANI or *n*-TiO<sub>2</sub> powder (1 mg) was put into a 0.5% chitosan solution respectively, and then dispersed uniformly in the chitosan solution after being treated with ultrasound.

**Preparation of the GOx solution:** Two milligrams of GOx and 15 mg of BSA was placed in 200  $\mu$ L of standard phosphate buffer, which was then vibrated until the GOx was well distributed and placed in a refrigerator.

**PANI/GCE or *n*-TiO<sub>2</sub>/GCE:** PANI dispersion (6  $\mu$ L) or *n*-TiO<sub>2</sub> dispersion (6  $\mu$ L) was coated onto the GCE surface respectively, and dried with infrared irradiation.

***n*-TiO<sub>2</sub>/PANI/GCE:** 6  $\mu$ L of the *n*-TiO<sub>2</sub> dispersion liquid was dropped and coated onto the PANI/GCE surface and dried with infrared irradiation.

**GOx/*n*-TiO<sub>2</sub>/PANI/GCE:** An appropriate amount of GOx solution and 2.5% glutaraldehyde were rapidly mixed by the glutaraldehyde crosslinking method. The mixture above (6  $\mu$ L) was quickly placed onto the *n*-TiO<sub>2</sub>/PANI/GCE, dried in the air, and put in the refrigerator at 4 °C for 1 h to complete the GOx and glutaraldehyde crosslinking. The modified electrode was taken out, dried in the air, and preserved in the refrigerator at 4 °C.

### 2.5. Characterization and detection method

The *n*-TiO<sub>2</sub> and PANI materials were characterized using SEM, XRD, and electrochemical methods. The preparation method for SEM was that PANI dispersion (6  $\mu$ L) or *n*-TiO<sub>2</sub> dispersion (6  $\mu$ L) was coated onto the GCE surface respectively, and dried with infrared irradiation. The modified electrode was tested in a glucosidic or non-glucosidic situation with CV, electrochemical impedance spectroscopy (EIS), and chronoamperometry (CA). The reproducibility and stability of the sensor were also determined.

## 3. Results and discussion

### 3.1. Properties of *n*-TiO<sub>2</sub>

#### 3.1.1. SEM characterization

Fig. 1 shows that the prepared TiO<sub>2</sub> reached sizes on the scale of nanometers, which was directly related to the formation of the sol particles and TiO<sub>2</sub> anatase. Thus, the TiO<sub>2</sub> prepared with the sol-gel method could have good electrical conductivity and the metal ion nanometer effect, and could easily be imbedded into the active center of the enzyme molecule.

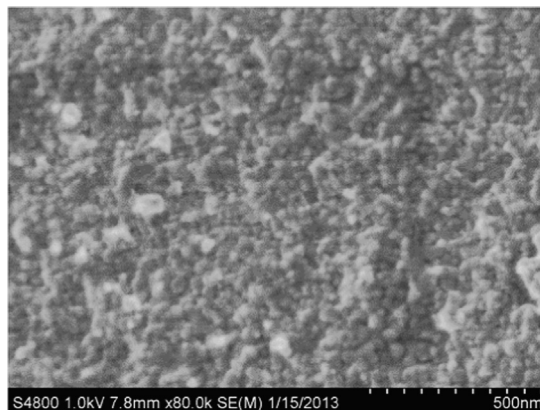


Fig. 1. SEM image of nano-titanium dioxide (80,000  $\times$ ).

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