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Electrocatalytic activity of Pt doped TiO_2 nanotubes catalysts for glucose determination

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ABSTRACT

A hybrid system of titanium dioxide nanotubes (TNTs) incorporated with poly(amidoamine) dendrimers-encapsulated platinum nanoparticles (Pt-DENs) was constructed in a neutral aqueous solution through electrostatic interaction. The TNTs/Pt-DENs nanohybrids immobilized glucose oxidase (GOx) was used to modify a glassy carbon electrode (GCE) for detecting the electrocatalytic response to the reduction of glucose. The structures of nanohybrids were characterized by TEM, XRD and FT-IR, the performance of modified electrodes was characterized by cyclic voltammetry (CV) and amerometric measurements, respectively. The modified electrodes, which had a fast response of glucose oxidase less than 3 s, could be used for the determination of glucose oxidase ranging from 2 μM to 12 mM. The detection limits were 1 μM at signal-to-noise ratio of 3.

1. Introduction

The direct electrochemistry of enzymes has received increasing attention in the last few years, which provide a platform for fabricating new kinds of mediator free biosensors, battery application and biomedical devices [1,2]. However, enzymes exhibit a rather slow rate of heterogeneous electron-transfer at conventional electrodes, because of the deep burying of the electroactive prosthetic groups, the unfavorable orientations of enzymes at electrodes [3]. Therefore, the studies are focusing on selecting ideal electrode materials, such as carbon nanotubes [4], iron oxide nanoparticles [5–7] and biomaterials [8–10] to enhance the direct electron-transfer between the enzymes and underlying electrodes.

Since various TiO_2 nanostructures which have favorable physical optical and electrical properties have been reported in the last few years. Much attention has been given to the study of structural characteristics, properties, and applications [11,12]. TiO_2 nanotubes, owing to their large length–diameter ratio, continue to be involved in bioelectrochemistry field due to their chemical inertness, rigidity, nontoxicity, high hydrophilicity and good biocompatibility [13–18]. However, a common problem occurred when using metal oxide semiconductors to modify electrodes is poor charge transport [19–21].

Metal nanoparticles such as Au [22], Ti (III) [18], Ag [23], and Pt [24] were introduced to dope with TiO_2 nanotubes to overcome the deficiency mentioned above. These kinds of metal nanoparticles have excellent conductivity, catalytic property and biocompatibility. They can perform as “electronic wires” to enhance the electron-transfer between redox centers in enzymes and electrode surfaces, and as catalysts to increase electrochemical reactions [25–28]. However, these nanoparticles are intended to agglomerate, it is necessary to use protective agents, such as small organic molecules or polymers to prevent aggregation. Highly branched dendritic macromolecules poly (amidoamine) (PAMAM) could be used to modify electrode surface due to their good biocompatibility and adequate functional groups for chemical fixation [29]. It was reported that the dendrimers were capable of increasing the concentration of hydrophobic molecules at the electrode–solution interface, improving the sensitivity as well as the selectivity of certain specific electrochemical reactions [30].

Therefore, our main concern in the present work is to enhance the conductivity and sensitivity of TNTs, and further the direct electron-transfer of glucose oxidase. In order to improve the conductivity and sensitivity of TNTs, Pt-DENs nanoparticles were used to dope with TNTs, then the TNTs/Pt-DENs were loaded with the model protein, glucose oxidase (GOx). The TNTs/Pt-DENs/GOx biosensor could be obtained by immersing TNTs/Pt-DENs composites in the GOx-contained buffer solution. Much better conductivity to the resultant TNTs/Pt-DENs/GOx biosensor can be achieved attributing to the doping treatment. Direct electrochemistry of GOx has been observed. The biosensor further exhibits fine

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bioelectrocatalytic characteristic of fast response, high sensitivity for the amperometric detection of glucose.

2. Experimental

2.1. Materials

Glucose oxidase (GOx, EC.1.1.3.4, TYPEVII, 150 U/mg) was purchased from Fluka, which was modified by the periodate-oxidized GOx (IO_4-GOx) according to the literature [31]. And glucose was from Sigma–Aldrich. Pt-DENs were synthesized according to the previous literature [32]. Phosphate buffer solutions (PBS, 0.1 M) with various pH values were prepared by mixing stock standard solutions of Na_2HPO_4 and NaH_2PO_4, and adjusting the pH with H_3PO_4 or NaOH. Doubly distilled and deionized water was used through this work.

2.2. Preparation of TNTs

Titanate nanotubes were synthesized by hydrothermal method using commercial TiO_2 nanoparticles powder (P25, Degussa, Germany) as a starting material. A conversion from nanoparticles to nanotubes was achieved by treating the nanoparticle powder with 10 M NaOH at different temperatures, for 24 h, in the autoclave. The precipitates were neutralized thoroughly with distilled water for 5 times, soaked with 1 M NaOH for 10 h, then filtered and dried at atmospheric condition. The detailed procedure is reported elsewhere [33,34].

2.3. Preparation of Pt-DENs/TNTs/GOx nanocomposites

0.3 g TiO_2 nanotubes (TNTs) was dispersed in 10 mL of a Pt-DENs colloid solution (pH 7) and shaked for 1 h. The result solution was centrifuged at a speed of 6000 rpm to get the product of Pt-DENs/TNTs hybrid materials. The hybrid material (10 mg) prepared above was dispersed in a solution of GOx (20 mg/mL, pH 6) and shaken for 1 h for enzyme absorption. The bioconjugates were then centrifuged and washed with distilled water three times.

2.4. Preparation of Pt-DENs/TNTs/GOx biosensor

Glass carbon (GC, 3 mm diameter, Model CHI 104, CH Instruments) electrodes were polished with 1.0, 0.3 and 0.05 mm alumina powder, respectively, then cleaned in a piranha solution (a 1:3 mixture of 30% H_2O_2 and concentrated H_2SO_4) and finally sonicated thoroughly in double distilled water. Next, the polished electrode was sonicated in acetone and doubly distilled water and then allowed to dry at room temperature. Then, 5 μL of the Pt-DENs/TNTs/GOx bioconjugates prepared above this suspension colloid was deposited on the surface of the pretreated GCE. The electrode was then left to dry and was stored for at least 24 h at 4 °C. The biosensor was stored under the same conditions when not in use. The TNTs or Pt-DENs modified GCE were fabricated using the same GCE by the same method.

2.5. Characterization

Morphology and microstructure of the synthesized materials were examined by Transmission electron microscopy (TEM, JEOL HF-2010 TEM), FT-IR (Nicolet AVATAR360) and X-ray Diffract meter (RIGAKU, D/MAX 2550 VB/PC). All electrochemical experiments were performed on a CHI 660A electrochemical workstation (CH Instru. Co., Shanghai, China) at 20 °C (±2) °C. The working electrode was a modified GCE. A saturated calomel electrode (SCE) served as reference electrode, and a Pt wire served as counter electrode. The working solutions were deoxygenated with nitrogen gas for 15 min before measurement and a nitrogen atmosphere was maintained over the solutions during experiment.

3. Results and discussion

3.1. Structural characteristic of TNTs and Pt-DENs/TNTs composite

Fig. 1 is a typical X-ray diffraction (XRD) data taken from the TiO_2 nanotube samples. The strong diffraction peak at 2θ angles of 25.0°, 37.4° and 48.5° may correspond to the spacing of (1 0 1), (0 0 4) and (2 0 0) of the anatase (tetragonal) phase, two diffraction peaks at 2θ angles of 27.4°, 36.3° may correspond to the spacing of (1 1 1), (1 0 1) of the rutile phase. Because the nanotubes may form by rolling up the two-dimensional sheets of TiO_2 structure, some diffraction peaks of rutile phase TiO_2 may not appear in the XRD pattern [35,36].

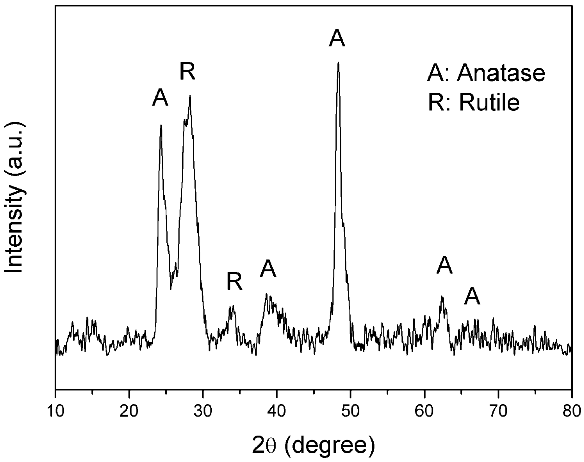

Fig. 1. XRD pattern of TiO_2 nanotube.

FT-IR spectrum of TNTs is shown in Fig. 2. Some bands can be observed: at 3390 cm^{-1}, assigned to the stretching of a hydroxyl group that was chemisorbed on a surface defect site, and 1623 cm^{-1}, pertaining to H–O–H bending for molecular water. The absorption band at 1380 cm^{-1} represents the symmetric bending of CH_3 groups. These groups can help the conjunction and dispersion of Pt-DENs nanoparticles. The band at 500 cm^{-1} was associated with the Ti–O–Ti stretching mode of TiO_2 [37].

Partially quarternized poly (amidoamine) (PAMAM) dendrimers having both quaternary ammonium groups and primary amines can be used as a polymeric template reservoir to prepare stable platinum–dendrimer nanocomposites. It was found that the resulting nanocomposites remain stable for several months. As shown in Fig. 3b, TEM image showed that well-defined nanosized platinum nanoparticles were almost monodispersed, with average particle diameter of ca. 3 nm and narrow size distribution. The inset of Fig. 3b also showed a high-magnification TEM image of a single Pt nanoparticle and the single crystal structure was observed. Similar results have been reported in the literate [32,38]. Fig. 3a illustrated that the as-prepared TNTs have nearly uniform diameters of around 10 nm and nanotube walls of around 5 nm. It can be seen from Fig. 3b that Pt-DENs nanoparticles on TNTs surface were slightly flattened with sizes in the range of 2–3 nm. The modification of Pt-DENs with positively charged could be easily attracted onto TNTs through electrostatic interaction in aqueous and form the TNTs/Pt-DENs composite.

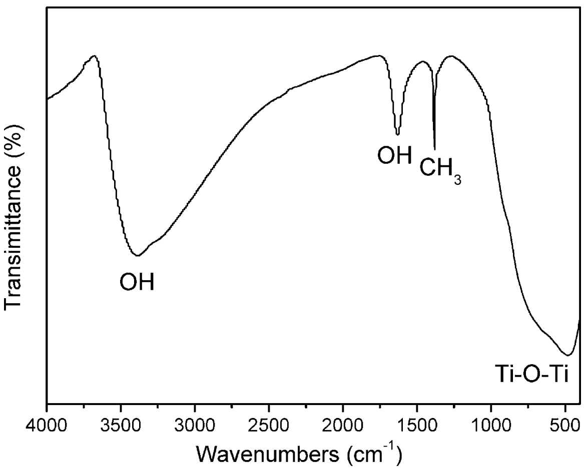

Fig. 2. FT-IR spectrum of TiO_2 nanotube.