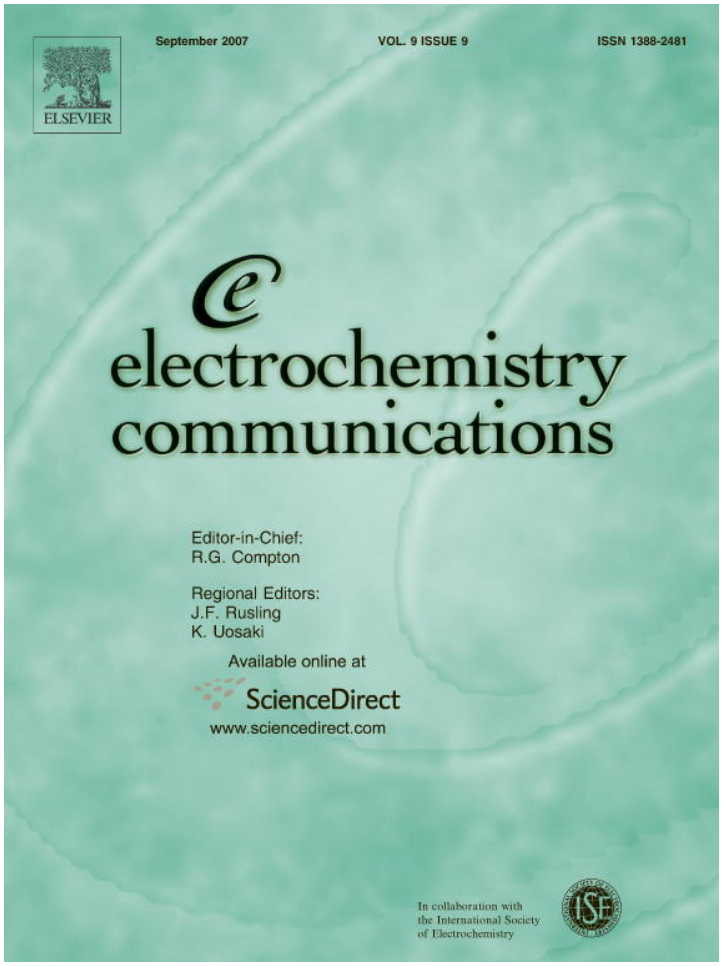

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TiO_2 nanotube arrays fabricated by anodization in different electrolytes for biosensing

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Abstract

Titania nanotube arrays were fabricated by anodic oxidation of titanium foil in different electrolytes. The morphology, crystallinity and composition of the as-prepared nanotube arrays were studied by XRD, SEM and EDX. Electrochemical impedance spectroscopy (EIS) was employed to investigate their electrical conductivity and capacitance. Titania nanotube arrays co-adsorbed with horseradish peroxidase (HRP) and thionine chloride (Th) were studied for their sensitivity to hydrogen peroxide by means of cyclic voltammetric and galvanostatic measurements. The experiments showed that TiO_2 nanotube arrays possessed appreciably different sensitivities to H_2O_2 due to their different conductivity. Further experiments revealed that TiO_2 nanotubes have noticeably different ability of adsorbing HRP and Th, and the best sensitivity was achieved when the density of HRP is the highest. The TiO_2 nanotube arrays fabricated in potassium fluoride solution demonstrated the best sensitivity on hydrogen peroxide in the range of 10^{-5}–3×10^{-3} M at pH 6.7 and at a potential of −600 mV (vs. Ag/AgCl).

Keywords: Titania nanotubes arrays; Biosensors; Hydrogen peroxide; Electrochemical impedance spectroscopy

1. Introduction

Various nanomaterials have been used as supports or matrices to immobilize protein or enzyme for the development of enzyme-based biosensors [1–4]. In order to immobilizing enzyme effectively, the nature of the nanomaterials must have considerable impacts on an enzyme's expressed activity and apparent kinetics. Besides, the surface area, porosity and the physical characters of the nanomaterials will also affect the adsorption of enzyme.

TiO_2 nanotube possesses nontoxicity, good biocompatibility and environmental safety, and would offer both large surface area compared to nanoparticles. It has easy coordination with amine and carboxyl groups on the surface and can be fabricated through a variety of methods [5–8]. Thus, it can be used as matrix to immobilize proteins and enzymes for biomaterial and biosensor. Recently, Tsuchiya and Oh formed nanostructure hydroxyapatite (bone-like calcium phosphate) on TiO_2 nanotube layers fabricated by electrochemical anodization of titanium foil [9,10]. Macak and co-workers reported the fabrication of selforganized porous oxide-nanotube layers on the biomedical titanium alloys Ti–6Al–7Nb and Ti–6Al–4V by a simple electrochemical treatment [11]. Bavykin and Liu investigated the adsorption of protein on TiO_2 nanotubes for biosensor design [12,13]. But all of the research was focused on short nanotube arrays which was no more than five hundred nanometers long. In the present study, different length of TiO_2 nanotube arrays fabricated by anodic oxidation in different electrolytes were subsequently co-immobilized horseradish peroxidase (HRP) and thionine chloride (Th) for the study of their sensitivities on hydrogen peroxide

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detection. The ability of co-adsorption of HRP and Th on different length of TiO_2 nanotube arrays and their conductivity were firstly discussed. The results demonstrated that the sensitivity of TiO_2 nanotube arrays was affected not only by the conductivity of the arrays, but also by the adsorption of protein, moreover, HRP was found to be the critical factor in the reaction. The excellent sensitivity on hydrogen peroxide found in the 1.8 μm long TiO_2 nanotube arrays is in the range of 10^{-5}–3×10^{-3} M at a potential of −600 mV (vs. Ag/AgCl), wider than the report of short TiO_2 nanotube arrays [13].

2. Experimental section

2.1. Reagents

Titanium foil (99.94%) of 0.5 mm in thickness, potassium fluoride (KF, 99%), hydrofluoric acid (HF, 40%), ammonium fluoride (NH_4F, 99.3%) and ethylene glycol (100%) were purchased from VWR, and horseradish peroxidase (HRP, 2.5 mg/ml), thionine chloride (Th, 100%) were from Sigma. Chemicals were of reagent grade and were used as received. All the solutions were prepared with DI water (>16 MΩ cm).

2.2. Fabrication of titania nanotube arrays

TiO_2 nanotube arrays were fabricated by anodization of Ti foil in a two-electrode electrochemical cell with a platinum foil as a cathode at a constant potential at room temperature, following the recipe reported in literatures [14–16]. The Ti substrate was chemically etched in 30% HCl aqueous solution at approximately 80 °C for about 20 min. After rinsing thoroughly with DI water, the clean titanium foils were anodized in three different types of electrolytes for 1 h to form TiO_2 nanotube arrays on Ti substrates. The composition of three electrolyte solutions and voltage used for anodization were summarized in Table 1. The resultant TiO_2 nanotube (TNT) arrays are hereinafter designated as: TNT(HF), for the 0.1 M HF electrolyte, TNT(KF), for the mixture electrolyte of 1.0 M $NaHSO_4$ and 0.1 M KF, and TNT(EG), for the ethylene glycol (EG) containing 0.25% NH_4F.

2.3. Preparation of modified electrodes

The as-grown TiO_2 nanotube arrays were first rinsed by DI water thoroughly, sealed with epoxy resin leaving an open area of 0.7×0.7 mm^2, then immersed in 1 ml 5 mM PB solution at pH 7.0 containing 15 μM thionine chloride and 200 μL HRP for 2 days to produce the Th/HRP modified electrodes. For the measurements of HRP and Th loading, UV–Vis absorption spectra of the mixed HRP/Th solution before and after immersion were measured. The absorption peak intensities at 415 nm for HRP and at 603 nm for Th were used to estimate the amount of HRP and Th adsorbed on the TNT surface. The resultant electrodes were stored in 5 mM PB of pH 7.0 at 4 °C.

2.4. Electrochemical measurements

Cyclic voltammetric and galvanostatic measurements were performed with a CHI605IC electrochemical station, and electrochemical impedance spectroscopy (EIS) was carried out in a Salon 1260 impedance/gain-phase analyzer. Electrochemical software *Z*-plot was employed for impedance data acquisition. A Pt foil and Ag/AgCl electrode were used as counter electrode and reference electrode respectively. The amplitude of the modulation potential for EIS measurement was 10 mV, the range of the frequency was from 400 kHz to 0.05 Hz. All solutions were deaerated with ultrapure nitrogen before measurements, and nitrogen was passed over the top of the solution during the experiments. All measurements were conducted at room temperature (about 20 °C).

2.5. Characterization

For characterizing TiO_2 nanotubes morphology, diameter, and length, a scanning electron microscope (SEM, Philips, JEOL JSM7000) was employed with an accelerating voltage 10 kV. X-ray diffraction (XRD) was performed on a Philips 1820 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å).

3. Results and discussion

3.1. Characteristic of titania nanotube arrays

Fig. 1 is the SEM images of TiO_2 nanotube arrays prepared by anodization in different electrolytes for 1 h. The as-grown TiO_2 nanotube arrays vary significantly in length depending on the applied DC voltage and the type of electrolyte solutions. The average pore diameters of TiO_2 nanotubes as estimated from the SEM images are 100 nm (TNT(HF)), 110 nm (TNT(KF)), and 80 nm (TNT(EG))

Table 1
Summary of electrolyte compositions and anodization voltages as well as the diameters, length, and specific surface area of the resultant titania nanotube arrays

Samples	Electrolyte composition	Voltage (V)	Diameter (nm)	Length (μm)	Surface area (mm^2/mm^2)
TNT(HF)	0.1 M HF	20	100	0.5	8
TNT(KF)	0.1 M KF + 1.0 M $NaHSO_4$	20	110	1.8	26
TNT(EG)	0.25%NH_4F + ethylene glycol	60	80	12	692

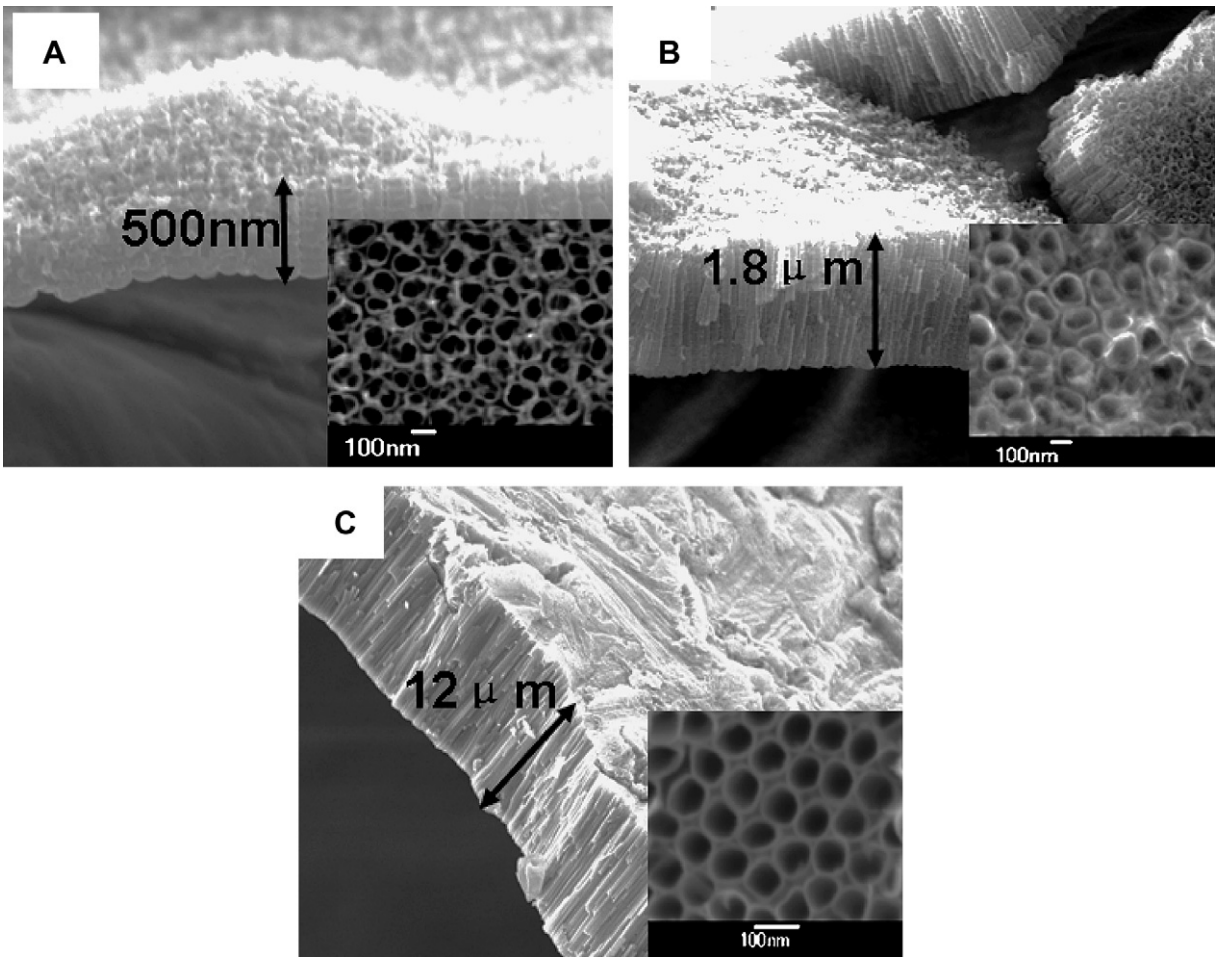

Fig. 1. SEM images of TiO_2 nanotubes prepared in (A) 0.1 M HF acid solution at 20 V (B) 1.0 M $NaHSO_4$ containing 0.1 M KF at 20 V and (C) ethylene glycol containing 0.25% NH_4F at 60 V for 1 h.

and the lengths of the nanotubes are 500 nm (TNT(HF)), 1.8 μm (TNT(KF)) and 12 μm (TNT(EG)), respectively. The specific surface area are estimated to be 8 (cm^2/cm^2) (TNT(HF)), 26 (cm^2/cm^2) (TNT(KF)) and 692 (cm^2/cm^2) (TNT(EG)), respectively. The length of nanotube arrays is affected by both the pH value and the concentration of electrolyte solutions as reported in literatures [17,18]. In hydrofluoric acid containing electrolyte (pH 1.2), it is not possible for nanotube length to grow longer than 500 nm as reported in literature [14]. In a KF electrolyte at a pH 4.0, adjusted by addition of sodium hydrogen sulfate and sodium hydroxide, the length of TiO_2 nanotubes could get up to 1.8μm, similar to the literature data [15]. While in the organic electrolyte, much longer TiO_2 nanotubes were grown, which has been attributed to the reduction of water content that reduces the solubility of the TiO_2 and thus promotes the growth of longer nanotubes [16]. The spectra curves of the EDX analyses for the TiO_2 nanotube arrays indicated that there exist trace F in TNT(HF) and TNT(KF), while in the TNT(EG), C was observed. The latter suggests that the organic carbon species in the electrolyte has been incorporated into TiO_2 nanotubes. All the as-grown TiO_2 nanotube arrays are amorphous as determined by XRD, agreed well with the report of Beranek [19].

3.2. EIS measurements

All as-grown TiO_2 nanotube arrays were characterized by means of EIS, which is a powerful technique widely used to study porous electrodes [20–22]. Fig. 2 presents EIS curves of three TNT electrodes fabricated in different electrolytes, all measured at the electrode potential 0.1 V in 0.1 M Na_2SO_4 at frequencies ranging from 0.05 Hz to 40 kHz. Plot A is the Bode graph showing the impedance as a function of frequency; while plot B is the Nyquist plot. The equivalent circuit shown in Fig. 2C was used to fit the EIS data. The fitting curves are shown in Fig. 2B as solid lines together with the experimental data denoted as symbols. In this circuit, R_1 represents the solution resistance, the parallel combination R_2C_2 is associated with the conductivity and capacitance of the TiO_2 nanotube electrodes. The parallel combination of the interface charge transfer resistance (R_3) and the constant phase element (CPE) leads to a depressed semicircle in the corresponding Nyquist impedance plot. The constant phase element (CPE) is

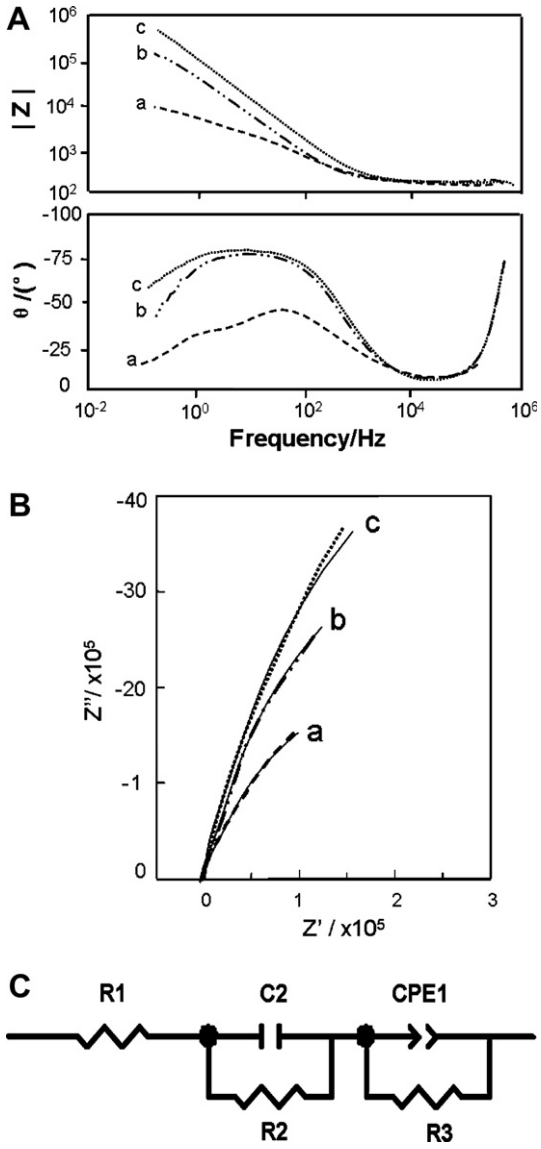

Fig. 2. Niquist (A) and Bode (B) plots of (a) TNT(HF): dash line (b) TNT(KF): dash and dot line (c) TNT(EG): dot line in 0.1 M Na_2SO_4 solution. The solid line is the fitting curve in polt B. Plot C is the equivalent circuit used in the simulation.

defined by CPE-T and CPE-P. If CPE-P equals one approximately, then the CPE is identical to a capacitor, C_{dl} [20]. In the present study, the fitting of the present data results in 0.79, 0.94 and 0.81, respectively. Thus the CPE-T values obtained in this work are close to C_{dl}. The parameters determined by the fitting of the experimental EIS data in the solution are summarized in Table 2.

The electrical resistance R_2 of TiO_2 nanotube arrays increases in the following order: TNT(HF) (0.16 MΩ) < TNT (KF) (0.59 MΩ) < TNT(EG) (1.43 MΩ), and the capacitance C_1 changes as: TNT(HF) (1.9 μF) < TNT(KF) (3.4 μF) < T NT(EG) (5.5 μF). The low electrical conductance also explains well the experimental results that a well-defined reduction peak appears at −0.6 V for the TNT(HF) and TNT(KF) electrodes when tested with electroactive probes $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ by means of cyclic voltammetry, while no reduction peak is observed for the TNT(EG) electrode in the same potential range. This result is consistent with the electrochemical and spectroelectrochemical studies of nanoporous TiO_2 films by Topoglidis et al. [23,24]. The capacitance is related to the surface area, however, later study will present that the amount of adsorbed protein is not proportional to the surface area for long length TNT electrode.

3.3. Co-adsorption of HRP and Th on titania nanotube arrays

Immobilization of both HRP and Th on the titania nanotube arrays reached saturation after immersing TNT arrays in the mixture solutions of HRP and Th for 2 days. Fig. 3 shows the absorbance spectra of the as-prepared mixture solution (dash line) and remaining solution (solid line) with HRP and Th adsorbed by TNT(EG) electrode for 2 days. Absorption peaks of HRP at 415 nm and Th at 603 nm are appreciably reduced, indicating both HRP and Th were removed from the solution and co-immobilized on the TNT(EG) electrode. The amounts of HRP and Th adsorbed were estimated from the change of peak intensities. For TNT(HF) and TNT(KF) electrodes, it revealed the similar results of co-adsorption of HRP and Th, though with varied amounts being adsorbed. Table 3 summarized the amount of HRP and Th adsorbed on three different TNT samples. These results revealed that both HRP and Th can be effectively immobilized on TNT arrays by a co-adsorption procedure. However, the amounts of Th adsorbed on TNT electrodes increased significantly from 1.1 μg/mm^2 on TNT(HF), to 2.7 μg/mm^2 on TNT(KF), to 3.8 μg/mm^2 on TNT(EG), while a less significant variation in the amount of HRP on different TNT arrays was found: 0.3 μg/mm^2 on TNT(HF), 0.5 μg/mm^2 on TNT(KF), and 0.2 μg/mm^2 TNT(EG). It should be noted that TNT(EG) adsorbed the highest concentration of Th, whereas TNT(KF) adsorbed the highest amount of HRP per surface area. It will become clear in the next section that the amount of HRP adsorbed per surface area plays a critical role in sensitivity of H_2O_2.

Table 2
Impedance components for titanium nanotubes electrodes determined by fitting EIS experimental data measured in 0.1 M Na_2SO_4 at 0.1 V using the equivalent circuit shown in Fig. 2C

Electrodes	R_1 (Ω)	R_2 (MΩ)	C_2 (μF)	R_3 (MΩ)	CPE-P	CPE-T (μF)
TNT(HF)	327	0.16	1.9	0.1	0.79	5.0
TNT(KF)	322	0.59	3.4	0.1	0.94	4.0
TNT(EG)	314	1.43	5.5	0.2	0.81	3.3

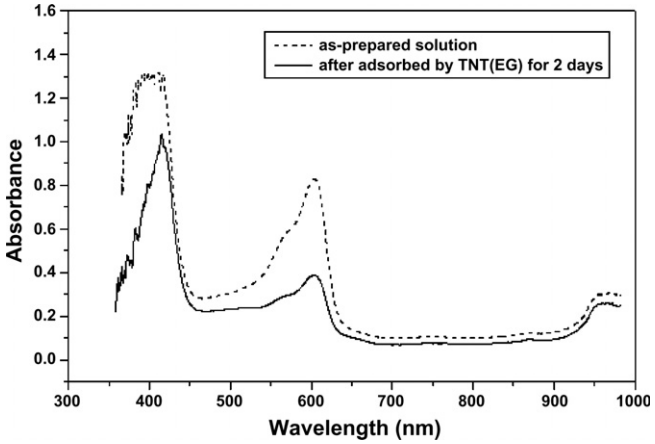

Fig. 3. Absorbance of HRP and Th in as-prepared mixture solution of 15 μM Th and 200 μL HRP in 1 ml of 5 mM PB (dash line) and remains solution (solid line) after adsorbed by TNT(EG) electrode for two days.

Table 3
The amount of Th and HRP adsorbed on different TNT electrodes

	Th (μg/mm^2)	HRP (μg/mm^2)	Th/HRP ratio
TNT(HF)	1.1	0.3	3.67
TNT(KF)	2.7	0.5	5.19
TNT(EG)	3.8	0.2	15.8

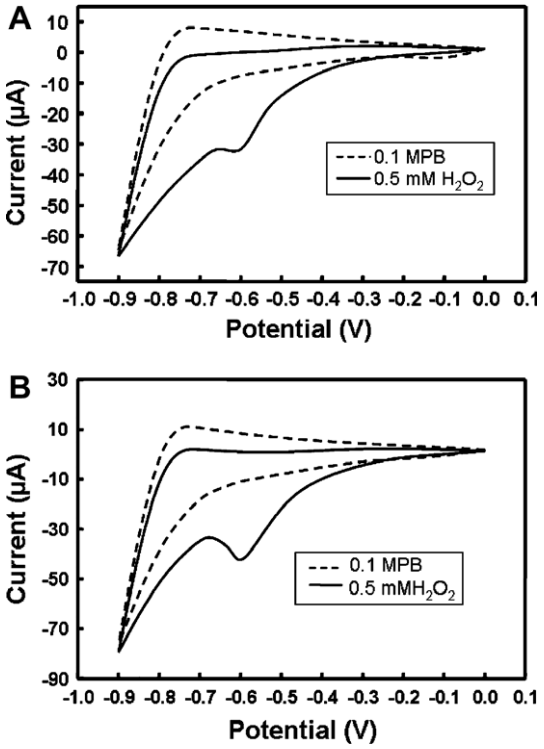

Fig. 4. Cyclic voltammograms of (A) TNT(HF) (B) TNT(KF) in the absence (dash line) and presence (solid line) of 0.5 mM H_2O_2 at a scan rate of 50 mV s^{-1}.

3.4. Hydrogen peroxide biosensors

Fig. 4 presents the CVs of TNT(HF) (curve a) and TNT(KF) (curve b) electrodes co-immobilized with both HRP and Th in 0.1 M PB at pH 6.7 in the absence of H_2O_2 (dash line) and in the presence of 0.5 mM H_2O_2 (solid line) at a scan rate of 50 mV/s. Neither reduction nor oxidation peak were observed in all three electrodes at the absence of H_2O_2. However, a drastic increase of the reduction current of TNT(HF) (plot A) and TNT(KF) (plot B) is observed in the presence of 0.5 mM H_2O_2 (solid line). In contrast, there is no reduction peak when using TNT(EG) electrode in the presence of 0.5 mmol H_2O_2. The difference in three TNT electrodes is likely due to the self-assembly of Th/HRP on the TNT arrays surface. Moreover, the reduction current of TNT(KF) is more negative (−47.3 μA) than TNT(HF) (−34 μA), because the TNT(KF) can adsorb more enzyme due to its larger surface area, thus the more negative increase of reduction peak intensity for the TNT(KF) electrode shows a higher electrocatalytic activity of the immobilized HRP for Th oxidation in the presents of H_2O_2. The response mechanism of the electrodes to H_2O_2 is summarized as follows:

$$\text{HRP (red)} + H_2O_2 \rightarrow \text{HRP (ox)} + H_2O \quad (1)$$

$$\text{HRP (ox)} + \text{Th (red)} \rightarrow \text{HRP (red)} + \text{Th (ox)} \quad (2)$$

$$\text{Th (ox)} + 2H^+ + 2e^- \rightarrow \text{Th (red)} \quad (3)$$

Firstly the immobilized HRP (red) chemically reduces the H_2O_2 to form water and HRP (ox). Secondly the HRP (ox) chemically oxidizes the reduced Th (red) to form HRP (red) and Th (ox). Finally the Th (ox) is electrochemically reduced to form Th (red), resulting in the reduction peak at −0.6 V in the CV curves.

Fig. 5(A) displayed the typical amperometric response curves of TNT(HF) and TNT(KF) electrodes under the optimal experimental conditions. The stable amperometric response could be observed at −0.6V with successive injections of 0.125 mM H_2O_2 into 0.1 M PB solution. Fig. 5(B) presents the sublinear calibration curve of the reduction current vs. the H_2O_2 concentration. The sublinear response range of the sensor to the H_2O_2 concentration is from 5×10^{-5} to 2×10^{-3} M for TNT(HF) (curve d) and from 1×10^{-5} to 3×10^{-3} M for TNT(KF) (curve c). The polynomial fitting results of the two sublinear curves are as follow,

$$C_{\text{TNT(KF)}} = 16.9 + 32.6I - 4.3I^2 \quad (4)$$

$$C_{\text{TNT(HF)}} = 16.8 + 21.2I - 3.4I^2 \quad (5)$$

where C is the concentration of H_2O_2; I refers to the reduction current. The correlation coefficients are 0.998 and 0.997, respectively. When the electrodes were not in use, they were stored in 0.1 mol PB solution in a refrigerator at 4 °C. They retained 80% of its initial current response after one month of storage, showing a good shelf life.

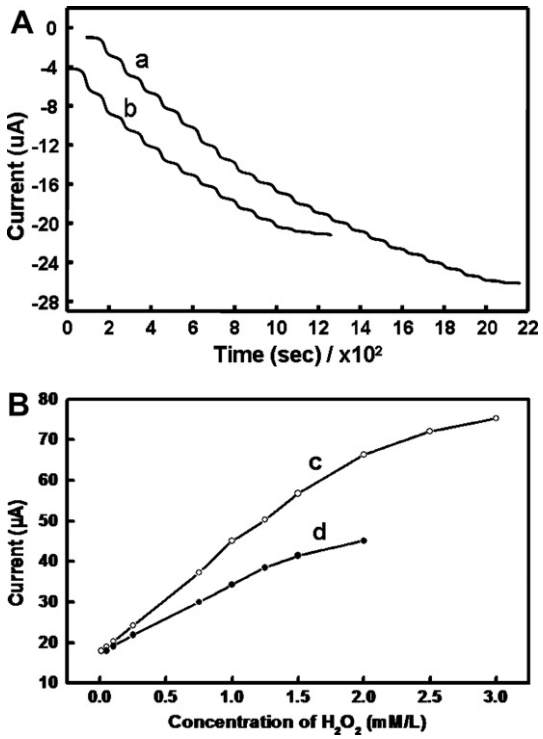

Fig. 5. (A) Amperometric response of TNT(KF) (solid line a) and TNT(HF) (solid line b)at −0.6 V upon successive additions of 0.125 mM H_2O_2 into 0.1 M PB at pH6.7 (B) Calibration curve of reduction current of TNT(KF) (curve c) and TNT(HF) (curve d) vs. the H_2O_2 concentration.

3.5. Sensitivity dependence on the HRP density

The above experimental results have clearly indicated that TiO_2 nanotube arrays grown by anodization in different electrolytes possess significantly different dimensions and thus significantly different surface area. Although all TiO_2 nanotube arrays without post-growth annealing are amorphous according to XRD, some carbon impurity was detected using EDX in TiO_2 nanotubes grown in ethylene glycol electrolyte. The presence of carbon impurity (or other impurity) is expected to affect the surface chemistry and conductivity of the nanotube. The electrical properties of TiO_2 nanotube arrays also vary markedly. Since the sensing of hydrogen peroxide is through interface redox reactions mediated by both HRP and Th, surface area, surface chemistry, and electrical properties of TiO_2 nanotube arrays are all important factors to determine the detection limit and sensitivity. Careful comparison of all the experimental data obtained in the present study implies that the density of HRP adsorbed on the TiO_2 nanotube surface plays a determining role in the sensitivity and detection of H_2O_2. This observation is reasonable considering the following facts:

1. The amount of Th adsorbed on TiO_2 nanotubes is 5–10 times higher than that of HRP.
2. The amount of HRP directly reacts with H_2O_2 and determines the rate of Reaction (1).
3. Reaction (2) involves the charge transfer between HRP and Th molecules with molecular ratio of 1:1. An increased density of HRP will proportionally increase the reaction rate as the concentration of This far higher than that of HRP.
4. Reaction (3) presumably proceeds rapidly as the diffusivity of proton is high as compared to H_2O_2 molecules.

4. Conclusions

In this study, we demonstrated that titania nanotube arrays fabricated by anodic oxidation of titanium foil possess large surface area and good uniformity, are ready for enzyme immobilization, and can be used as biosensor. The sensitivity is related not only to the surface area,but also to the electrical conductivity and surface chemistry of the nanotubes arrays. Although the TiO_2 nanotubes fabricated in organic solution have the longest length and the largest surface area,its conductivity is the lowest. The nanotube arrays fabricated in KF solution has the best sensitivity and the co-immobilized HRP/Th can be electrochemically reduced and redoxidized at the electrode potential −0.6 V in the presence of H_2O_2. This allows us to develop a novel H_2O_2 sensor with a detection range from 10^{-5} to 3×10^{-3} M. It was also suggested by the experiment results that the amount of HRP adsorbed on the electrode plays a critical role in the electrochemical sensing of H_2O_2, as the oxidation of HRP is likely the rate limiting process.

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