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Improving the detection of hydrogen peroxide of screen-printed carbon paste electrodes by modifying with nonionic surfactants

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ABSTRACT

Nonionic surfactants, such as Triton X-100 and Tween-20, were shown in this study to improve the electrocatalytic activity of screen-printed carbon paste electrodes (SPCE). The electrochemical response of SPCE to hydrogen peroxide increased 8–10-fold with the modification of nonionic surfactants. In addition, the glucose biosensors fabricated from nonionic surfactant-modified SPCE exhibited 6.4–8.6-fold higher response to glucose than that fabricated from unmodified SPCE. A concentration effect is proposed for nonionic surfactant to bring neutral reactants to the surface of electrode. Moreover, nonionic surfactant-modified SPCE exhibits a capability of repetitive usage and good reproducibility (R.S.D. < 5%) in the measurement of H_2O_2. Interestingly, the nonionic surfactant-modified SPCE exhibited an opposite effect to ascorbic acid, a common electroactive agent, which causes interference during clinical diagnosis. The differential responses of nonionic surfactant-modified SPCE to H_2O_2 and ascorbic acid suggest its potential in the development of biosensors for clinical diagnosis.

1. Introduction

Surfactants are usually amphiphilic organic compounds that contain both a hydrophilic (water-loving) head and a hydrophobic (water-hating) tail. The amphiphilic property allows surfactants to self-assemble into single or ordered stacks of bilayer with many functions, including microporosity, selective permeability and binding biomolecules on or within the bilayers. Due to this property, surfactants have been used in the development of electrochemical sensors to entrap proteins in the surfactant bilayer, to arrange proteins into a correct orientation and to facilitate the electron transfer between proteins and electrode [1–6]. The modification of electrode surface by a thin layer of cationic surfactant cetyltrimethylammonium bromide (CTAB) was demonstrated to enhance the sensitivity and the dynamic range of detection for adriamycin [6] estrogen [2] and bisphenol A [3]. Presumably, modification of ionic surfactants changes the electrochemical properties of an electrode by its ability to absorb and concentrate the reactants near the electrode [6,7]. Moreover, the surfactant modification may change the surface property of an electrode and facilitate the access of analytes to the electrode surface [8–11].

Although ionic surfactants were demonstrated to be capable of enhancing the responses of electrodes to various electroactive species, the use of nonionic surfactants, such as Triton X-100 (TX100) and Tween-20 (TW20), in the biosensor design is rare. In some cases, TX100 was used as a matrix to incorporate heme proteins, such as hemoglobin, myoglobin and horseradish peroxidase (HPR) [12,13], for the fabrication of biosensors. The embedded heme proteins may conducted a proper orientation in the TX100 matrix and exhibit an improved electron transfer between heme proteins and the electrodes [13]. In a different report, TX100 was shown to facilitate the incorporation of uniquinone or menaquinone, a redox mediator, in pasting binder of the carbon paste electrode, by which the sensitivity of the fabricated glucose biosensor was enhanced [14]. These reports indicate that nonionic surfactants may enhance the direct electrochemistry of proteins by arranging a proper orientation of active site of the protein to the electrode [12,13]. However, the effect of nonionic surfactants in the electrocatalytic activity of electrodes to hydrogen peroxide (H_2O_2) has not been studied.

H_2O_2, one of the products of oxidases, is broadly utilized as a detection target in different areas, such as clinical diagnosis, food analysis, pharmaceutical and environmental analyses [15–17]. However, the presence of interferants in clinical samples, such as L-ascorbic acid, uric acid, and acetaminophen, often causes problem during measurement. The enhancement of the electrocatalysis of H_2O_2 may help not only to enhance the sensitivity of measurement, but also to reduce the effect of interferants. Attempts have been made to improve the electrocatalysis of H_2O_2 on electrodes, such

Abbreviations: TX100, Triton x-100; TW20, Tween-20; SPCE, screen-printed carbon paste electrode.

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as deposing transition metals [18–20], metal oxides [21,22], carbon nanotube (CNT) [18,23] and oxidoreductive enzymes [24,25] on the surface of electrodes. Although these methods are effective in enhancing the electrocatalytic activity of electrode to H_2O_2, they are often tedious, costly and less stable.

In this study, evidence is presented to demonstrate that the electrocatalytic activity of a screen-printed carbon paste electrode (SPCE) to H_2O_2 can be markedly improved by the modification of nonionic surfactants. Further investigation was carried out to explore the feasibility of using TX100- and TW20-modified SPCEs for the fabrication of oxidase-based biosensors. This work shows that surface modification using nonionic surfactants is simple, effective and economic to substantially improve the electrocatalytic and sensitivity of SPCE.

2. Materials and methods

2.1. Materials

The SPCE were obtained from ApexBichem (Hsinchu, Taiwan). Glucose oxidase (EC 1.1.3.4, GOx) was bought from Fluca. H_2O_2 (30%) and glucose were purchased from Sigma. TX100 and TW20 were obtained from Biobasic Inc. Single walled carbon nanotube (SWCNT) with an average external diameter of 20–40 nm and length of 5–15 μm were obtained from Conyuan Biochemical Technology Co. (Taipei, Taiwan). Polyvinyl alcohol functionalized with methyl pyridinium methyl sulfate (PVA-SbQ) was the product of Toyo Gosei Kogyo Co., Japan. Other chemicals used were analytical grade. All of the solutions were prepared with double deionized water.

2.2. Enzyme electrode preparation

Stock solutions of TX100 (0.5–10%), TW20 (0.5–10%) and Nafion (0.5% and 5%) were prepared by dissolving in 99.5% ethanol. SWCNT stock solutions were prepared by dissolving SWCNT in 99.5% ethanol, TX100, TW20 or Nafion stock solution to give a concentration of 2 mg mL^{-1} via a mild sonication. The surface modification of SPCE was performed by spreading 2 μL of SWCNT or nonionic surfactant stock solutions on the working area of SPCE. The coated surface of SPCEs was allowed to dry at the room temperature for 24 h. GOx (13 U μL^{-1}) was mixed with 50% PVA-SbQ in a 1:1 (v/v) ratio. The enzyme electrode was then prepared by spreading 1.5 μL GOX/PVA-SbQ mixture on the active area of nonionic surfactants-modified SPCE, followed by exposing under the light for 2 h on ice. The fabricated GOx electrodes were kept at 4 °C for 24 h before use.

2.3. Apparatus

The static contact angle was determined based to the sessile drop method. The CCD camera was used to capture the side image of water drops on the surface of SPCE. Images from the CCD camera were transferred to a PC (Pentium 1.8 GHz) for analysis. Scanning electron micrographs were obtained using a Hitachi S-4200 microscope.

2.4. Electrochemical measurement

Amperometric measurements were performed on an electrochemical analyzer (model CHI 440, West Lafayette IN, USA). All experiments were carried out with a conventional three-electrode system with the enzyme electrode as the working electrode and a standard platinum electrode as the counter electrode. An Ag/AgCl electrode was used as a reference. Input and output signals from the potentiostat were coupled to a PC (Pentium 1.8 GHz). The amperometric measurements were carried out by adding 0.1 mL H_2O_2 into a cylindrical cell containing 9.9 mL PBS buffer (pH 7.0) under the indicated working potential vs. Ag/AgCl. Unless otherwise stated, all experiments were carried out at room temperature. The baseline current must be achieved prior to the injection of test solution. Magnetic stirring during the operation was used to ensure the homogeneity of the solution. The difference between the baseline and the steady-state current was designated as the response current.

3. Results and discussion

3.1. Effect of nonionic surfactant on the electrocatalytic activity of SPCE

The effect of nonionic surfactants on the electrochemical catalytic activity of SPCE was investigated by coating the working area (4.8 mm^2) of commercial SPCE with various concentrations of TX100 or TW20 (0.5, 1, 2, 5, 7.5 and 10%). As shown in Fig. 1A, the

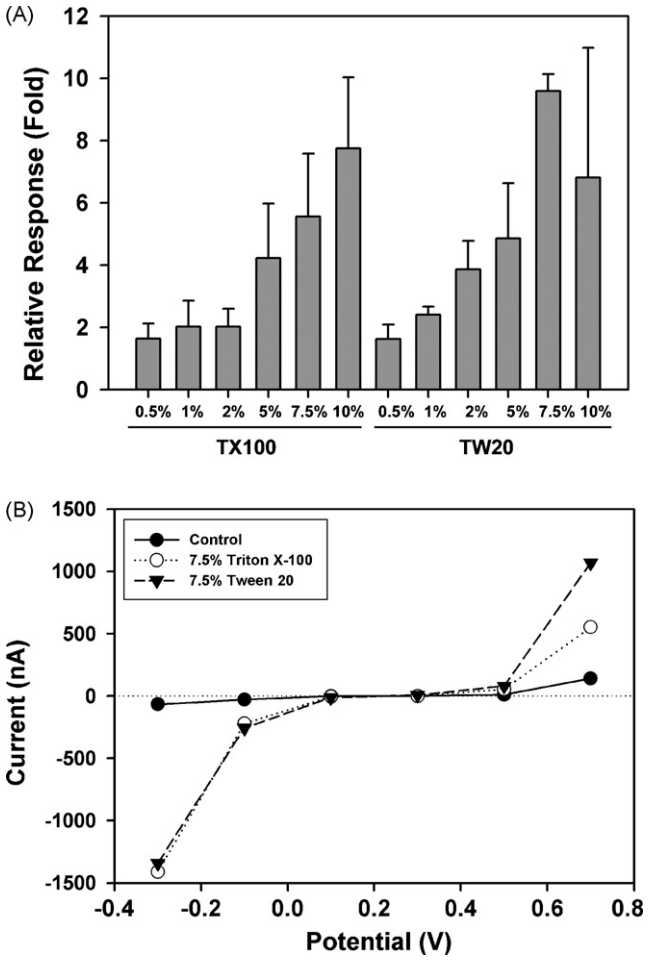


Fig. 1. Nonionic surfactants enhance the electrochemical catalytic activity of SPCE to hydrogen peroxide. SPCEs were modified by various concentrations (0.5–10%) of TX100 and TW20 as described in Section 2. (A) The electrochemical response of nonionic surfactant-modified SPCE to 1 mM H_2O_2 was performed in 100 mM phosphate buffer (pH 7.0) at a working potential of 0.5 V vs. Ag/AgCl. The relative response increase is determined by dividing the responses of nonionic surfactant-modified SPCE to 1 mM H_2O_2 with that of unmodified SPCE to 1 mM H_2O_2. Each data set is presented as the mean ± S.D. from three independent measurements. (B) Hydrodynamic voltammograms of unmodified SPCE (●), TX100-modified (○) and TW20-modified SPCEs (▼). Measurements were carried out at room temperature in 100 mM sodium phosphate buffer (pH 7.0) containing 1 mM H_2O_2 under different working potentials (−0.3 to 0.7 V) vs. Ag/AgCl. The data is presented as the mean of two independent experiments.

electrochemical response of SPCE to H_2O_2 was enhanced by both TX100 and TW20 in a concentration-dependent manner. When modified with 0.5–2% TX100, the electrochemical responses of SPCE to H_2O_2 increased about 2-fold compared to that of unmodified SPCE; whereas, the response increased 4–8-fold when SPCEs were modified with 5–10% TX100. When modified with TW20, the electrochemical response of SPCE to H_2O_2 increased with the concentration of TW20 and reached a maximum (10-fold increase) at 7.5% TW20. The response of TW20-modified SPCE to H_2O_2 then declined with 10% TW20. These results indicate that the electrocatalytic activity of SPCE can be largely enhanced by the modification of nonionic surfactants. The concentration of nonionic surfactant needed for maximum enhancing effect on the electrocatalytic activity of SPCE is found to be 10% TX100 and 7.5% TW20.

The effect of nonionic surfactant on the electrocatalytic activity of SPCE was further investigated by the steady-state hydrodynamic voltammograms. The net steady-state anodic currents of H_2O_2 on unmodified SPCE, SPCEs modified with 7.5% TX100 ($SPCE_{TX100}$) and 7.5% TW20 ($SPCE_{TW20}$) were obtained with potentials ranging from −0.3 to 0.7 V (Fig. 1B). Compared with unmodified SPCE, the electrochemical responses of $SPCE_{TX100}$ and $SPCE_{TW20}$ electrodes to 1 mM H_2O_2 exhibited a marked increase in redox currents to applied potentials higher than 0.3 V and lower than −0.1 V. The steady-state anodic current of the $SPCE_{TX100}$ (i_a = 551.8 nA) and $SPCE_{TW20}$ (i_a = 1070 nA) at a working potential of 0.7 V was enhanced 4–8-fold compared with that of the unmodified SPCE (i_a = 140.2 nA). Whereas, the steady-state cathodic current of the $SPCE_{TX100}$ (i_c = 1411 nA) and $SPCE_{TW20}$ (i_c = 1342 nA) was enhanced about 20 times at −0.3 V compared with that of the unmodified SPCE (i_c = 65.6 nA). In contrast, the steady-state anodic current response of the unmodified SPCE to H_2O_2 exhibited little change or even remained unchanged within the potential range tested. Apparently, the improved sensitivity of the SPCE to H_2O_2 was associated with the modification of nonionic surfactants.

3.2. Analysis of surface properties of the nonionic surfactant-modified SPCE

The electrocatalytic activity of SPCE has been shown to be greatly enhanced by TX100 and TW20. The surface properties of nonionic surfactant-modified SPCE have not been studied. It is assumed that the surface of SPCE can be homogeneously coated by 2 μL of 7.5% surfactant solution. Thus, the average surface density of TX100 and TW20 on the working area of SPCE can be calculated as 5000 and 2542 nmol cm^{-2}, respectively, which is about 10,000- and 5084-fold more than that required for forming uniform monolayer coverage of the surfactant molecules on the SPCE [12]. This result indicates that the nonionic surfactant may form either multiple layers or micelles on the surface of SPCE [26]. This postulation was confirmed by monitoring the surface microstructures of $SPCE_{TX100}$ and $SPCE_{TW20}$ electrodes under the scanning electronic microscope (SEM). The SPCE without modification shows a rough surface with many partially exposed graphitic particles (Fig. 2A), which may be partially covered with organic oil, pasting binder and possibly other pollutants [27]. However, once covered with TX100 (Fig. 2B) and TW20 (Fig. 2C) the surface of SPCE becomes flat and smooth, forming multiple layers of nonionic surfactant on top of SPCE.

The surface of SPCE is normally hydrophobic due to a layer of excess organic oil, pasting binder and other pollutants [27,28]. This hydrophobic layer may form a barrier, preventing the access of electroactive substances to the graphite and blocking electrochemical reactions on the electrode. This may partially explain by the enhancing effect of the argon and oxygen plasma on the electrochemical responses of the SPCE [27,29]. The modification of surfactant may reduce the hydrophobicity of the surface of SPCE, facilitating the access of the analytes in the aqueous solution to the

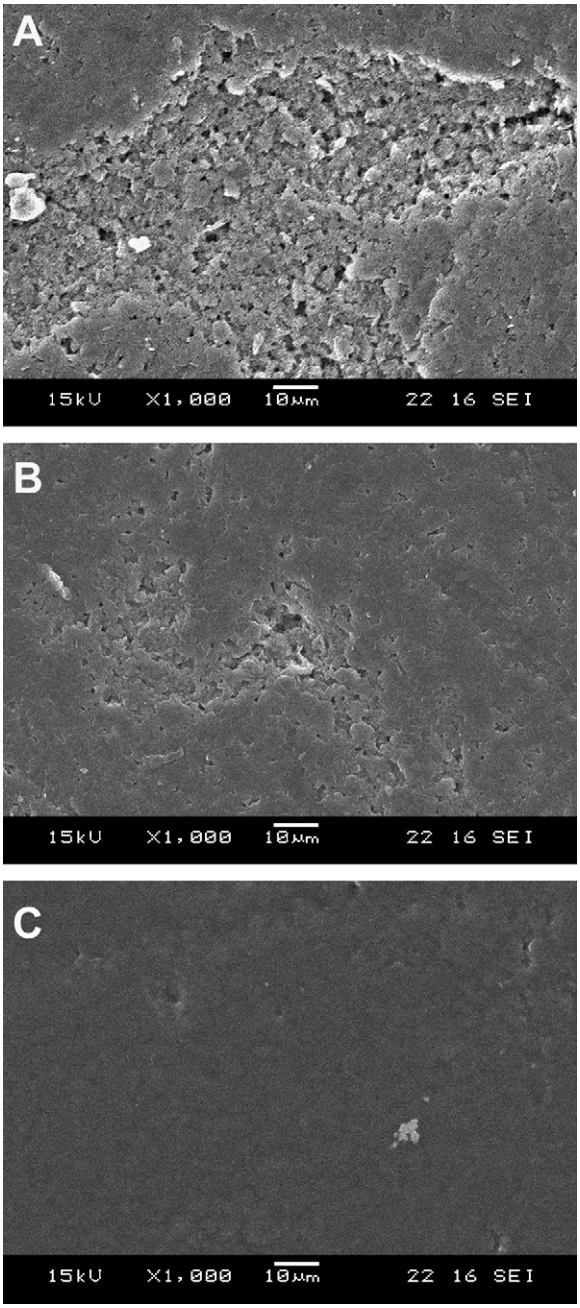
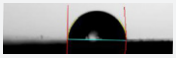


Fig. 2. Scanning electron micrographs of SPCE with and without nonionic surfactant modification. SPCEs were either untreated (top panel), modified with 7.5% TX100 (middle panel) or 7.5% TW20 (bottom panel) prior to the SEM analysis. The magnification power of the images was 1000×.

electrode. The hydrophobicity of SPCE can be determined by contact angel (θ) of a water droplet, an angle between the tangential line of a hemispherical droplet at the surface contacting point and a line parallel to the surface [27]. Water droplet on a hydrophobic surface tends to exhibit a high contact angel. The shape of the water droplet was round on the untreated SPCE with a contact angle of 87.9° (Table 1). The contact angle was rapidly reduced to around 12.5° and 19.8° after modification with TX100 and TW20, respectively. The reduction of the contact angle of a water droplet on the nonionic surfactant-modified SPCEs confirms the postulation that the surface hydrophobicity of SPCE is reduced by the coverage of nonionic surfactants.

Table 1
The contact angle of water droplet on the surface of SPCE before and after nonionic surfactant modification.

Electrode	Unmodified SPCE	$SPCE_{TX100}$	$SPCE_{TW20}$
Contact angle	87.9° 	12.5° 	19.8° 

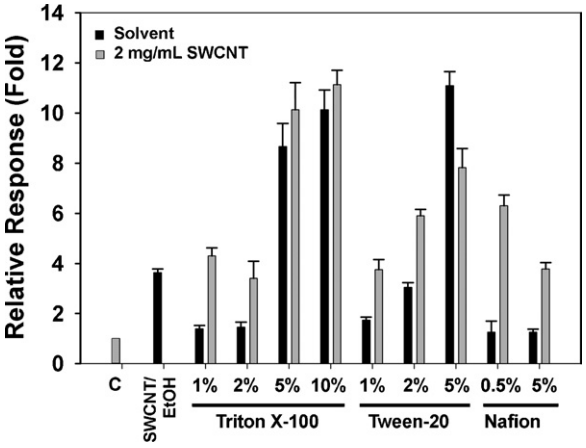


Fig. 3. Comparison of the responses of SPCEs modified with nonionic surfactants, SWCNT/nonionic surfactant and SWCNT/Nafion. SPCEs were coated with various concentrations of TX100 (0.5–10%), TW20 (1–5%) and Nafion (0.5 and 5%) in the absence (black bars) or the presence (gray bars) of SWCNT (2 mg mL^{-1}). Unmodified SPCE (C) and SPCE modified with 2 mg mL^{-1} SWCNT/ethanol were used as controls. Measurement of electrochemical responses was carried out at room temperature in 100 mM sodium phosphate buffer (pH 7.0) at a working potential of 0.5 V vs. Ag/AgCl.

3.3. Electrochemical characterization of nonionic surfactant-modified SPCE

The electrocatalytic activity of $SPCE_{TX100}$ and $SPCE_{TW20}$ electrodes was also compared with that of CNT-deposited electrodes. The SWCNT was solubilized in various concentrations of Nafion (0.5 and 5%), TX100 (1–10%) and TW20 (1–5%) and deposited on the working area of the SPCE. Compared with unmodified SPCE (C) and SPCEs modified with Nafion only (black bars), the SPCE modified with SWCNT dissolved in ethanol and Nafion (gray bars), exhibits a moderate enhancement (4–6-fold) in the response to H_2O_2 (Fig. 3). Similar enhancement effect was also observed in SPCEs modified with SWCNT dissolved in low concentrations (≤2%) of nonionic surfactants. Little or no enhancement in the electrocatalytic activity was observed when SPCEs were modified with Nafion or low concentrations (≤2%) of TX100 and TW20 alone. Interestingly, the electrocatalytic activity of SPCE to H_2O_2 was largely enhanced (8–10-fold) by high concentrations (≥5%) of nonionic surfactants either alone or with SWCNT. Apparently, SWCNT could not further improve the enhancing effect of high concentration nonionic surfactants in the electrocatalytic activity of SPCE (Fig. 3). Compared with SWCNT/Nafion, modification with nonionic surfactants provides an easy, economic and efficient way to improve the electrocatalytic activity of SPCE.

Previously, surfactant aggregates was postulated to concentrate small electrochemical reactants on the surface of the electrode [6,7,26,30,31], presumably through the hydrophobic region of the micelles. Thus, compared with ionic compounds, the neutral species are more favorable to partition to the nonionic surfactant micelles [31]. Therefore, it is possible that the nonionic surfactant aggregates help to enhance the electrocatalytic activity of SPCE by concentrating H_2O_2, one of a neutral electroactive species, on the surface of SPCE. This postulation was partially confirmed by measuring the electrochemical response of ascorbic acid on SPCE, $SPCE_{TX100}$ and $SPCE_{TW20}$. Ascorbic acid is a potent antioxidant and an anionic electroactive substance in serum with a physiological concentration of around 50 μM. Ascorbic acid was known to cause a significant interference to the detection of analytes in blood. Unmodified SPCE exhibited a large electrochemical response to 500 μM ascorbic acid at working potentials higher than 0.3 V (Table 2). However, the modification of SPCE with 7.5% TX100 and TW20 resulted in a 41–65% and 33–38% reduction, respectively, in the response to 500 μM ascorbic acid (Table 2). This result suggests that the nonionic surfactants TX100 and TW20 exhibit a differential electrocatalytic effect to ascorbic acid and H_2O_2, presumably due to their preferential partition of neutral (e.g., H_2O_2) over ionic (e.g., ascorbic acid) electroactive species.

The responses and reproducibility of $SPCE_{TX100}$ and $SPCE_{TW20}$ electrodes were also studied by repetitively measuring their response to 1 mM H_2O_2 20 times within a few days. The $SPCE_{TX100}$ electrode exhibits an average electrochemical response to 1 mM H_2O_2 of 706.5 nA with a R.S.D. (relative standard deviation) of 4.42% (Fig. 4, solid circles). After 20 measurements, the average electrochemical response of the $SPCE_{TW20}$ electrode was 1744.7 nA with a R.S.D. of 2.88% (Fig. 4, open circles). This result demonstrates that the improvement of electrocatalytic activity of SPCE by modifying with nonionic surfactants is feasible and highly reproducible.

3.4. Characterization of an enzyme electrode fabricated by a surfactant-modified SPCE

The capability of nonionic surfactant-modified SPCE in the fabrication of biosensors was further investigated. The glucose biosensors were fabricated by placing the glucose oxidase on top of the nonionic surfactant that covers the surface of SPCE (Fig. 5A). In this experimental design the orientation as well as the activity of the glucose oxidase may not be affected by the nonionic surfactant. Therefore, the change of responses in glucose biosensors developed from modified SPCE may reflect the effect of the modification of nonionic surfactant. The chronoamperometric responses of successive increments of 200 μM glucose for glucose biosensors fabricated from the unmodified SPCE, $SPCE_{TX100}$ and $SPCE_{TW20}$ shown that the average amperometric response was 13.1, 84 and

Table 2
Electrochemical response of unmodified and nonionic surfactant-modified SPCEs to 500 μM ascorbic acid.

Types of SPCE	0.3 V		0.5 V		0.7 V	
	Net anodic current (μA)	% reduction	Net anodic current (μA)	% reduction	Net anodic current (μA)	% reduction
Unmodified	8.49	–	14.10	–	13.85	–
Modified with 7.5% TX100	3.00	64.7%	5.87	58.4%	8.08	41.7%
Modified with 7.5% TW20	5.61	33.9%	8.70	38.3%	8.60	37.9%

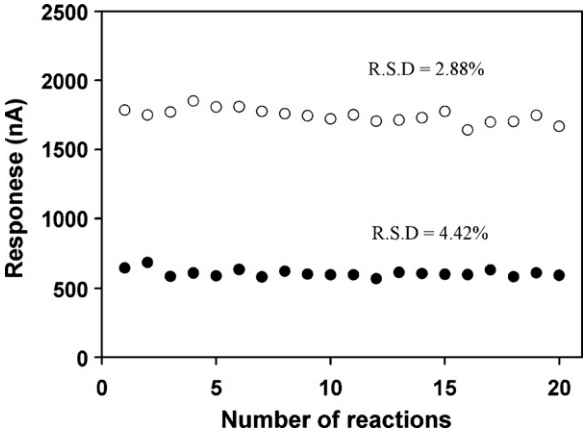


Fig. 4. Repetitive measurements of H_2O_2 by nonionic surfactant-modified SPCE. The ability of $SPCE_{TX100}$ (●) and $SPCE_{TW20}$ (○) electrodes to repetitively measure the electrochemical response of 1 mM H_2O_2 was studied and performed at room temperature in 100 mM phosphate buffer, pH 7.0. The working potential applied to the experiment was 0.5 V vs. Ag/AgCl.

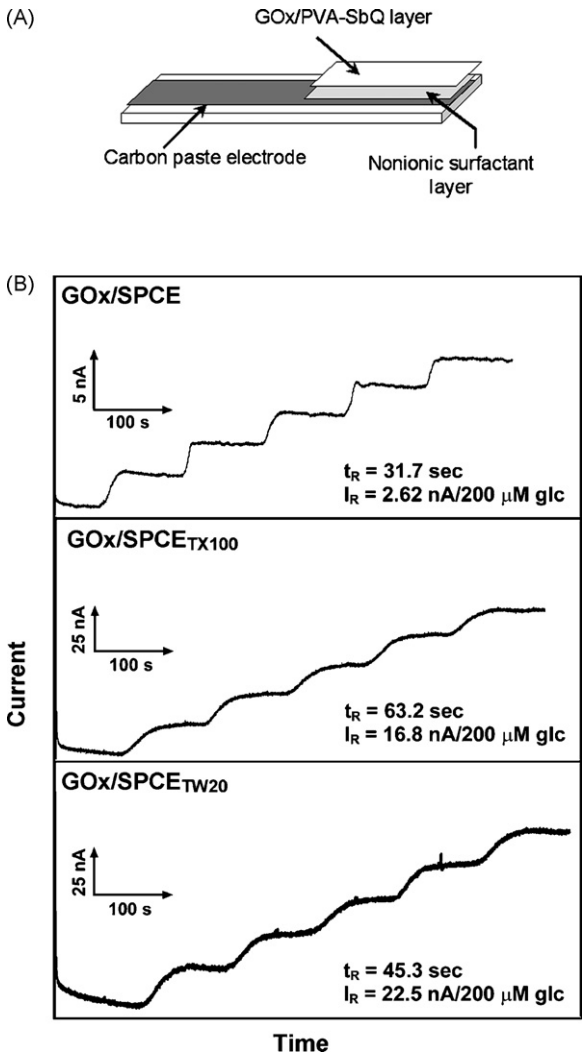


Fig. 5. Time–current response curves of glucose biosensors. (A) A simple diagram of the glucose biosensor fabricated from nonionic surfactant-modified SPCE. The glucose biosensors were fabricated by immobilizing GOx (9.75 U) on top of unmodified SPCE, $SPCE_{TX100}$ or $SPCE_{TW20}$ electrode by PVA-SbQ. (B) The step responses of biosensors GOx/SPCE (top panel), GOx/$SPCE_{TX100}$ (middle panel) and GOx/$SPCE_{TW20}$ (bottom panel) to 200 μM glucose were performed in 100 mM phosphate buffer, pH 7.0. The working potential was 0.5 V vs. Ag/AgCl.

112.5 nA mM^{-1} glucose, respectively (Fig. 5B). These results suggest that modification using a nonionic surfactant is capable of improving the electrocatalytic activity of SPCE 6.4–8.6-fold. However, the response times of glucose biosensors fabricated from $SPCE_{TX100}$ and $SPCE_{TW20}$ were 63.2 and 45.3 s, respectively, which are slightly longer than that of biosensors fabricated from unmodified SPCE (31.7 s). The long response time of SPCEs with nonionic surfactant modification may be due to the mass transfer limitation of H_2O_2 within multiple layers of nonionic surfactant. An analyte has to be in a close proximity of electrode to allow a successful electron transfer to occur between an analyte and electrode. On

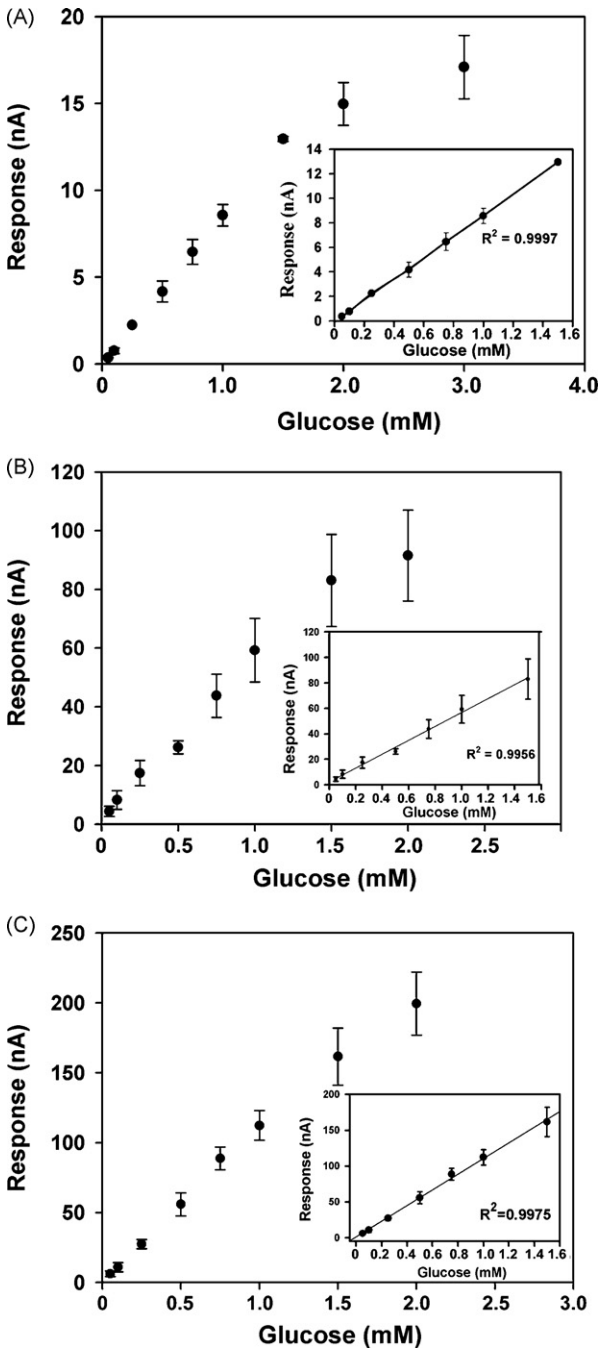


Fig. 6. Linear dynamic range of glucose on the fabricated glucose biosensors. The oxidative currents of GOx/SPCE (A), GOx/$SPCE_{TX100}$ (B) and GOx/$SPCE_{TW20}$ (C) biosensors to glucose were determined in 100 mM phosphate buffer, pH 7.0. The working potential was 0.5 V vs. Ag/AgCl. Data is presented as the mean ± S.D. from three independent measurements.

a surfactant-modified electrode, an analyte must replace surfactant at a site on the electrode to allow it to approach the electrode closely [7,26]. Therefore, compared to unmodified SPCE, the access of H_2O_2 to the surface of electrode may be slowed down by the nonionic surfactant layer on the electrode. The typical calibration graph (the steady-state current vs. concentrations of glucose) of biosensors fabricated from $SPCE_{TX100}$ and $SPCE_{TW20}$ was also determined (Fig. 6). Both $GOx/SPCE_{TX100}$ and $GOx/SPCE_{TW20}$ electrodes exhibit a linear range of 0.05–1.5 mM glucose (r^2 = 0.995–0.997) with the lowest detection limit being 50 μM for glucose.

4. Conclusion

In this study, data is presented to demonstrate that nonionic surfactants, such as TX100 and TW20, exhibit a potential in improving the electrochemical catalytic activity of SPCE to H_2O_2. A 10 folds enhancement in the response to H_2O_2 can be reached by simply modifying with nonionic surfactants, such as TX100 and TW20. A concentration effect of nonionic surfactant to neutral electroactive species was postulated to explain the enhancement of electrocatalytic activity to H_2O_2. Ascorbic acid, a common electroactive species, usually causing interference in clinical diagnosis, exhibits a lower electrochemical response on the nonionic surfactant-modified SPCE than on the unmodified SPCE. Moreover, the access of analytes to the electrode surface may also facilitated by the modification of SPCE with nonionic surfactants due to their amphiphilic property. The nonionic surfactant-modified SPCE exhibits a good reproducibility (R.S.D. ≤ 5%) in the electrochemical measurement of H_2O_2 and feasibility for fabrication of a biosensor.

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