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Recognition of glutathione based on its electrocatalytic oxidation on the bare fluorine doped tin oxide electrode

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ABSTRACT

We revealed that the bare fluorine doped tin oxide (FTO) exhibited the electrocatalytic ability towards the oxidation of glutathione (GSH) in a narrow pH region, which was examined using linear sweep voltammetry (LSV). LSV indicated that an oxidation peak of GSH at the FTO electrode occurs at 0.27 V (vs. SCE) that is 0.77 V negative of that at the bare Pt electrode, and GSH cannot be oxidized at the glassy carbon (GC) electrode in a potential region −0.40 to 1.20 V, at pH 4.4. On the basis of the electrocatalytic oxidation of GSH in a narrow pH region 4.0–5.5 and its lower oxidation peak potential, the bare FTO electrode can be used as a probe to recognize GSH from the 20 α-amino acids present in proteins, cystine, homocysteine, cysteamine, thiobenzoic acid, ascorbic acid, catechol, and dopamine. Its detection limit for the recognition of GSH is 5 nM.

1. Introduction

GSH is a tripeptide containing L-glutamic acid, L-cysteine and glycine, which exists in the living cells. It plays a critical role in the human metabolism including protection against oxidative stress and detoxification of xenobiotics [1]. Its level is directly related to many human diseases such as cancer, cardiovascular, neurodegenerative, Alzheimer's diseases and aging [2,3]. In addition, GSH levels in blood samples help in diagnosis of C-glutamyl cycle disorders [1]. Clearly, the determination of GSH is very significant in diagnostic purposes and many biological matrices. The determination of GSH has been carried out with various techniques such as spectrofluorometry [4], luminescence analysis [5], high performance liquid chromatography [6], and electrochemical methods [1,7–12]. Among these methods, the electrochemical technique has the inherent advantages of simplicity, rapid response, the high detection sensitivity and relatively low cost compared to other methods; which thus was used to investigate GSH oxidation at different modified electrodes [13–17]. The peak potentials of GSH oxidation at the modified electrodes are higher than 0.4 V (vs. Ag/AgCl) [1,10,11,17], which but are much lower than that of the bare Pt electrode due to the fact that the electrocatalytic oxidation of GSH took place at these modified electrodes. In addition, photoelectrochemical measurement is a newly developed technique for the detection of GSH [18–20], which possesses relatively low applied potentials and shows the high detection sensitivity.

Both GSH and cysteine containing the –SH group are present in human body, so they could be oxidized simultaneously at the electrodes. Thus the selective detection and recognition of GSH and cysteine is very significant in determination of GSH in physiological samples [21]. The selective detection of GSH has made great advancement using gold nanorods [22]. However, to our knowledge, little is known about the recognition of GSH from the 20 α-amino acids using the electrochemical methods and photoelectrochemical measurements.

The FTO electrode under the cathodic polarization over −0.7 V (vs.SCE)shows the novel photoelectric effect in a wide wavelength region 850–400 nm, in the aqueous solution free of a redox couple, which can effectively catalyze L-cysteine oxidation and also shows the photocatalytic ability towards cysteine oxidation at pH ≥ 7 [23]. This result reminds us that FTO could possess the electrocatalytic and photocatalytic ability to GSH oxidation because of containing –SH group in GSH. In this case, the photoelectrochemical experiment of GSH oxidation was carried out in our laboratory. Unfortunately, no photocatalytic response of GSH at the bare FTO electrode was observed at pH ≥ 7 because the electrochemical oxidation of GSH at the FTO electrode takes place in a very narrow pH region pH 4.0–5.5. In this pH region, FTO almost loses its photoelectric effect; but the bare FTO can pronouncedly catalyze the oxidation of GSH around pH 4.5. In this work, we report the electrocatalytic oxidation of GSH at the FTO electrode and provide a very novel strategy for the recognition of GSH.

2. Experimental

GSH, cystine, the 20 α-amino acids, and other chemicals were received from Sinopharm Chemical Regent Company (Shanghai) and were of analytic reagent grade. Doubly distilled water was used to prepare all aqueous solutions. The pH values of 0.30 M Na_2SO_4 solution containing testing chemicals were determined with a PXD −12 pH

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meter, which were adjusted with NaOH or H_2SO_4 solutions. The blood serum was first diluted to 8% (v/v) with 0.20 M phosphate solution or 0.30 M Na_2SO_4 solution, and then filtered with filter paper. Finally, the pH of both solutions was adjusted to 4.4, which was used for the LSV experiments.

A conventional three-electrode cell, consisting of a transparent FTO glass working electrode, a platinum foil counter electrode and a saturated calomel reference electrode (SCE), was used for the electrochemical experiments that were performed on a CHI 407 workstation. The cell with a glass jacket allowing circulation of water from a thermostat was put in a GHX-3 photoelectrolytic reactor. A 150 W Xe lamp was used as a light source. The distance between the working electrode and the lamp is 10 cm. All experiments were performed at 25 ± 0.1 °C.

3. Results and discussion

3.1. Evidence for electrocatalytic oxidation of GSH and photoelectrochemical tests

Curves 1, 2, and 3 in Fig. 1 show the LSVs of the Pt, FTO, and GC electrodes in 0.30 M Na_2SO_4 solution of pH 4.4, respectively, at a scan rate of 60 mV s^{-1}. Curve 1 indicates that the oxidation current increases from about 0.3 to 1.2 V, which would be caused by the oxidation of Pt itself because no evident oxidation peak is observed and only a broad shoulder occurs in the potential region 0.6–0.9 V. To confirm it, the scan rate was set at 20 mV s^{-1}, its result is shown in the inset of Fig. 1. Its LSV is similar in shape to that of curve 1, i.e. no oxidation peak occurs at a scan rate of 20 mV s^{-1}. Curves 2 and 3 in Fig. 1 show the LSVs of the FTO and GC electrodes, respectively, no oxidation peak is detected in the solution without GSH.

Curves 1, 2, and 3 in Fig. 2A show the LSVs of GSH in a solution of 0.30 M Na_2SO_4 of pH 4.4 at the Pt, GC, and FTO electrodes, respectively. Curve 1 indicates that the oxidation current increases from about 0 to 1.2 V, and its electrochemical behavior is different from that of the Pt electrode in the solution without GSH shown in curve 1 of Fig. 1. The increase in the current in the positive-going scan indicates GSH oxidation, but no oxidation peak is observed on curve 1 at a scan rate of 60 mV s^{-1}. To confirm it, the scan rate was set at 20 mV s^{-1}, its LSV is put in the inset of Fig. 2A, in which a shoulder peak appears at 1.04 V. This result is different from that of the Pt electrode in the solution without GSH, which is shown in the inset of Fig. 1. Thus, the oxidation peak at 1.04 V is caused by GSH oxidation. Comparison of the inset and curve 1 in Fig. 2A shows that the charge transfer rate of GSH reaction at the Pt electrode is rather slow. Curve 2 in Fig. 2A is the LSV of GSH at the bare GC electrode; clearly GSH was not oxidized in a sweeping potential region −0.4 to 1.2 V. Curve 3 shows the LSV of GSH at the FTO electrode; an oxidation peak occurs at 0.27 V that is caused by GSH oxidation. Comparison of the inset and curve 3 in Fig. 2A shows that the oxidation peak potential of GSH at the FTO electrode is 0.77 V negative of that at the Pt electrode; furthermore, GSH cannot be oxidized at the GC electrode. This is strong evidence for the electrocatalytic oxidation of GSH at the FTO electrode.

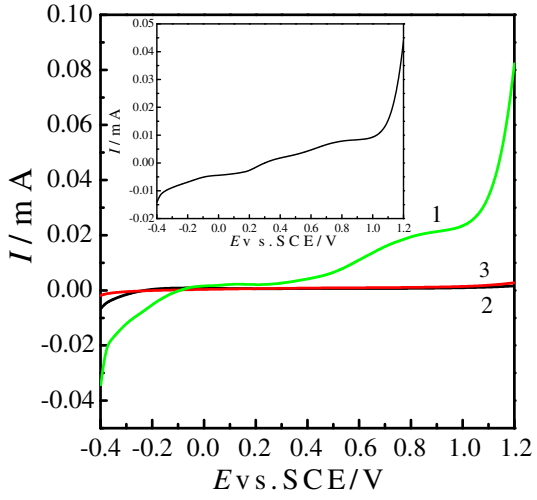

Fig. 1. Voltammograms of 0.30 M Na_2SO_4 solution with pH 4.4, at different electrodes, curves: (1) Pt, (2) FTO, (3) GC, at a scan rate of 60 mV s^{-1}; inset is Pt, at a scan rate of 20 mV s^{-1}.

The cyclic voltammograms (CV) of GSH at the FTO electrode are shown in Fig. 2B, in which curve 1 was recorded in the dark and curve 2 was recorded in the light illumination. Two oxidation peaks at 0.26 V are almost completely overlapped together, indicating that no photocatalytic oxidation takes place for GSH oxidation at the FTO electrode. This result is quite different from the oxidation of cysteine at the FTO electrode in the light illumination [23]. This is because the FTO electrode under the cathodic polarization shows an *n*-type semiconductor at pH ≥ 7; evidence is a reduction peak of FTO occurring around −0.62 V that is indicative of *n*-type semiconductor [23]. However, no reduction peak is detected in Fig. 2B because the pH of the GSH solution is 4.4. In this case, FTO cannot be converted to *n*-type semiconductor; thus it loses photocatalytic ability towards GSH oxidation.

3.2. Effect of pH on GSH oxidation

The electrochemical oxidation of the reduced GSH produces the oxidized GSH and proton, which is suggested as follows [24,25]:

$$2GSH - e^- \rightarrow GSSG + 2H^+$$

Thus the oxidation of reduced GSH would be affected by pH. Fig. 3A shows the effect of pH on the LSVs for the oxidation of reduced GSH. As can be seen in Fig. 3A, a weak anodic peak occurs at 0.27 V on curve 1, indicating that GSH at FTO electrode can be oxidized at pH 4.0. A maximum peak current occurs on curve 2 at pH 4.4 and however, the oxidation peak almost disappears on curve 4 at pH 5.5. The result in Fig. 3A demonstrates that the oxidation of GSH at the FTO electrode is strongly affected by pH, and its oxidation is in a very narrow pH region, indicating that GSH cannot be oxidized at the FTO electrode at pH > 5.5. This phenomenon is similar to the oxidation of GSH at the porous TiO_2-Pt nanowhisker electrode, in which its oxidation also occurs in a narrow pH region 5–8 with the maximum response current at pH 7.0 and its oxidation current almost disappears at pH ≥ 8 [19]. However, the pH region for the oxidation of GSH at the FTO electrode is different from that at the TiO_2-Pt electrode, this discrepancy is caused by the different electrode materials.

GSH consists of L-glutamic acid, L-cysteine and glycine with different functional groups of pK_a, which is found to be 2.1 (COOH on glutamyl), 3.5 (COOH on glycine), 8.7 (NH_2), and 9.6 (SH) [9,19]. It was found that L-cysteine at pH > 7.0 can be oxidized on the FTO electrode [23]. However, Fig. 3A indicates that the oxidation of GSH on the FTO electrode occurs in a narrow pH region 4.0–5.5. This difference is attributed to the different pK_a values between cysteine and GSH, since cysteine contains different functional groups of pK_a, which is 1.96 (COOH), 8.18 (thiol) and 10.28 (NH_3^+) [26]. There are two —COOH groups with low pK_a values in GSH, and the pK_a of —SH group in GSH is different from that of —SH group in cysteine, which makes the oxidation of GSH on the FTO electrode shift towards lower pH value compared to that of cysteine.

A possible catalytic reaction mechanism is proposed as follows [9,27,28]:

$$GSH \leftrightarrow GS^- + H^+ \quad (1)$$

$$GS^- \xrightarrow{AtFTO} GS^{\cdot} + e^- \quad (2)$$