Electrochemical Preparation of an Au Oxide Electrode and Its Application to Electro-Oxidation of Heterocycles Thiazole

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ABSTRACT

The growth and properties of Au oxide films formed on an Au electrode in a 0.1–1.0 M NaOH solution were investigated using potentiostatic and cyclic voltammetric techniques. Scanning electron microscopy images showed the structure of an Au oxide film on an Au electrode at various oxidation potentials: 1.5, 2.0, 2.5, and 3.0 V. The Au oxide electrode was used to determine oxidation potential of heterocycles thiazole in phosphate buffer (pH 2.21). The potential peaked at 0.54 V for rhodanine, 0.40 V for thiazolidine-2,4-dione, 0.47 V for thiazolidine, and 0.48 V for L(–)-thiazolidine-4-carboxylic acid. Compared with the results obtained from an Au oxide electrode, the peak potential of heterocycles thiazole was less positive and the peak current 3–15 times higher than that of the peak potential found using a bare gold electrode.

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Keywords : Electro-Synthesis, Au Oxide Electrode, Heterocycles Thiazole

1. Introduction

Heterocycles thiazole is a heterocyclic compound with five-membered rings containing nitrogen and sulfur; it has some biological and clinical significance. Thiazolidine-2,4-dione and 2-thioxo-4-thiazolidinone (rhodanine) derivatives, for example, appear in many drugs that have therapeutic potential for managing long-term diabetes complications.^{1–6} In addition, they are found in anti-inflammatory,^{7,8} antimicrobial,^{9,10} and antiviral drugs.¹¹ Rhodanine and substituted rhodanines have been extensively investigated by organic chemists because of their close association with various types of biological activities. They are also of particular interest because they are used as highly sensitive spectrophotometric reagents (complexing agents) for analyzing ions.^{12–15}

Metal oxide materials with microstructures or nanostructures are extensively used for anticorrosion coatings, electrochemical capacitors, electronic parts, magnetic nanostructures, photochemical energy conversion, lithium-ion batteries, and display technology.¹⁶ The microscale/nanoscale effects in the catalytic properties of gold particles are well-known to be chemically inert. Recently, some studies^{17–19} reported that the presence of oxidized Au species in the catalyst contributed to increased activity. The anodic oxidation of Au causes several types of Au oxide layers to form on electrode surfaces. There are studies of oxide growth on Au electrodes in alkaline and sulfuric acid solutions.^{20,21} The polarographic and electrolytic reduction of L(–)-thiazolidine-4-carboxylic acid^{22–24} and rhodanine derivatives^{25,26} in acetate and phosphate buffer at pHs from 3.8 to 8.0 were investigated using a dropping mercury electrode (DME) and a mercury pool, respectively. Electrochemical studies (cyclic voltammetry, impedance spectroscopy) were done of the synthesized complexes of thiazolidine-2,4-dione with δ and π acceptors.²⁷ Although the DME offers greater specificity, it is limited because mercury is highly toxic and causes environmental problems. One paper²⁸ dealing with the oxidation of thiazolidine-4-carboxylic acid on platinum and gold electrodes using chronopotentiometry and voltammetry does not describe the other thiazole heterocycles. Little attention has been paid to the electrochemical measurements of thiazole heterocycles. Our paper refers to the

electrochemical behavior of four 2,4-substituted derivatives of thiazolidine in various buffer solutions, and to the preparation of a Au oxide film on an Au electrode and then using it as a modified electrode to analyze the catalytic properties of heterocycles thiazole.

2. Experimental

2.1 Apparatus and materials

The electrolyte cell was designed with the following electrodes: a saturated calomel reference electrode (SCE), a stainless steel auxiliary electrode, and a gold (i.d.: 3 mm) working electrode, and operated using a potentiostat/galvanostat (263A; EG&G Princeton Applied Research, Princeton, NJ, USA)-controlled potentiostat. Cyclic and differential pulse voltammetric experiments were done using an electrochemical trace analyzer (Model 394; EG&G Princeton Applied Research, Princeton, NJ). The heterocycles thiazole (Scheme 1) were tested with rhodanine, thiazolidine-2,4-dione, thiazolidine (Acros Organics, Thermo Fisher Scientific, Geel, Belgium), and L(–)-thiazolidine-4-carboxylic acid (Alfa Aesar, Heysham, Lancashire, UK). Gold oxide was synthesized in our laboratory. All other reagents were locally purchased and of analytical grade.

2.2 Procedures

2.2.1 Au oxide growth in alkaline solutions

The Au oxide films for voltammetric measurements were electrochemically prepared. The Au oxide films were formed on an Au wire (i.d.: 0.3 mm; length: 20 mm) by potential scans between 0.0 and 2.0–3.0 V (5 scans; scan rate: 10–100 mV/s) in 10 mL of a 0.1–1.0 M NaOH aqueous solution. The scan number for produced Au oxide was optimized in the range of 4–5 cycles, and the selected scan rate was 25 mV/s.

2.2.2 Voltammetric measurements

The two voltammetric techniques, cyclic and differential pulse voltammetric voltammetry, were all done on Au oxide and Au electrodes, respectively. Voltammograms of heterocycles thiazole were taken on an Au oxide electrode in an acetate buffer (pH 4.90),

Scheme 1. Structure of rhodanine, thiazolidine-2,4-dione, thiazolidine, and L(-)-thiazolidine-4-carboxylic acid.

Figure 1. Effect of NaOH concentration on the electro-synthesis of Au oxide film at a scan rate of 25 mV and on the fifth scan (a) 0.1 M; (b) 0.2 M; (c) 0.5 M; (d) 1.0 M NaOH. Substrate: 3 mm of Au.

phosphate buffer solutions (pH 2.21), and in Britton and Robinson buffer solutions (pH 2.06–6.71).

3. Results and Discussion

3.1 Optimization condition for the formation Au oxide films

Figure 1 shows the effect of the NaOH concentration for the electro-synthesis of Au oxide film at a scan rate 25 mV and on the fifth scan. We found that an elevated reaction concentration of NaOH was necessary to form Au oxide films. The peak height (current) increased with the concentration of NaOH (Fig. 1). The peak current (charge density) in 1 M NaOH was higher than that in 0.1 M NaOH (15.5 vs. 1.61 mC/cm²). An elevated reaction

Figure 2. Effect of scan order on the electro-synthesis of Au oxide film in 1.0 M NaOH solution at a scan rate of 25 mV/s. (a) first scan; (b) second scan; (c) third scan; (d) fourth scan; (e) fifth scan. Substrate: 3 mm of Au.

Figure 3. Scanning electron micrographs of Au oxide films prepared using electrochemically oxidized gold wire (0.3 mm) in 1.0 M NaOH solution under cyclic voltammetric potential conditions: (a) between 0 and 1.5 V; (b) between 0 and 2.0 V; (c) between 0 and 2.5 V; (d) between 0 and 3.0 V at 25 mV/s. Magnification: 50,000 $\times$.

concentration like this should be helpful for accelerating the formation rate of Au oxide films. The effect of scan order (from first to fifth scan) for the electro-synthesis of Au oxide film in 1.0 M NaOH solution at a scan rate 25 mV/s is shown in Fig. 2. It is also notable that the peak current increased with the scan number, and that the current difference from the first to the third scan was larger than that from the fourth to the fifth. The scans beyond the fifth scan have small current differences. The scan number of the charge density was calculated to be 3.41 and 12.1 mC/cm² from the first and fifth scans, respectively. A thin layer of Au oxide was produced on the surface of the Au electrode. To compare potential conditions (0–1.5, 0–2.0, 0–2.5, and 0–3.0 V), pictures of the four electrodes were taken using a scanning electron microscope (SEM) (JXA-840; JEOL Co., Tokyo, Japan) (Fig. 3). There was no significant change in the morphology of Au oxide particles [Fig. 3(a)]; a number of Au oxide particles with a diameter of 83–190 nm aggregated and became much larger throughout the Au substrate [Fig. 3(c)]. The Au

Figure 4. (Color online) Energy dispersion spectroscopy (EDS) of homemade Au oxide films in 1.0 M NaOH solution under cyclic voltammetric potential between 0 and 2.5 V at 25 mV/s.

oxide particles were distributed more uniformly when aggregated on the gold electrode [Fig. 3(c)] than on the other three [Figs. 3(a), 3(b), and 3(d)]. Energy dispersion spectroscopy (EDS) is an analytical technique used for the elemental analysis or chemical characterization of a sample. In the scanning mode, SEM/EDS instruments can be used to produce maps of element location, concentration, and distribution. Figure 4 shows a SEM image as well as the EDS pattern of Au oxide. The EDS spectrum is portrayed as a plot of X-ray counts vs. energy (in keV). Two energy peaks of the AuM (At%: 44.49) and OK (At%: 55.51) elements appeared in the Au oxide.

3.2 Electrochemical behavior of heterocycles thiazole on the Au oxide electrode

The cyclic voltammogram of rhodanine shows the irreversibility of the process. A single, anodic peak is obtained, and the cathodic peak observed in the reverse scan is due to the reduction of the Au oxide. Cyclic voltammograms from a 138- $\mu\text{g mL}^{-1}$ rhodanine solution recorded at Au oxide and Au electrodes in phosphate buffer (pH 2.21) show that one well-defined oxidation peak appeared at the Au oxide electrode at +0.875 V and that one appeared at the Au electrode at +0.981 V (Fig. 5). The potential was lower and the current higher at the Au oxide electrode than at the Au electrode. We found that the Au oxide electrode performed better than did the Au; therefore, we chose the Au oxide electrode to determine heterocycles thiazole using differential pulse voltammograms in phosphate buffer (pH 2.21) (Fig. 6). There is an electron-rich thiazolidine-2,4-dione (peak at 0.387 V) backbone because of its two oxygen-molecule-containing group in the five-membered ring structure; the potential of this compound is less positive than that of other heterocycles thiazole.

Table 1 summarizes data obtained from differential pulse voltammetric studies of 4.0 $\mu\text{g mL}^{-1}$ of heterocycles thiazole solution in various other solutions. Our analyses of the effect of pH and supporting electrolytes on the oxidation peak current and peak potential of heterocycles thiazole in Britton-Robinson buffered solution in the pH range of 2.06–6.71, phosphate buffer (pH 6.62), and acetate buffer (pH 4.90) showed that peaks shifted more to positive potential in phosphate buffer (pH 2.21) and that the peak current in phosphate buffer was higher than in the others (Fig. 7). This indicates that the oxidation of heterocycles thiazole is strongly pH-dependent.

Figure 5. Cyclic voltammograms of rhodanine (138 $\mu\text{g mL}^{-1}$) in phosphate buffer (pH 2.21). The solid line (—) is for an Au oxide electrode (peak at 0.875 V, 694 μA); the dashed line (---) is for an Au electrode (peak at 0.981 V, 268 μA).

Figure 6. Differential pulse voltammograms of five-membered heterocyclic compounds (nitrogen, sulfur) (60 $\mu\text{g mL}^{-1}$) in phosphate buffer (pH 2.21). The solid line is for a thiazolidine-2,4-dione (peak at 0.387 V, 64.6 μA); the dotted line is for a rhodanine (peak at 0.676 V, 264 μA); the medium dashed line is for a thiazoline peak at (0.515 V, 190 μA); the dash-dot-dot (— · — · —) line is for an L-thiazolidine-4-carboxylic acid (peak at 0.613 V, 99.4 μA).

3.3 Catalysis of the oxidation of rhodanine by the Au oxide electrode

Cyclic voltammograms were obtained using the standard addition method at the Au oxide electrode (Fig. 8) (regression equation: $y = 3.26x - 53$; correlation coefficient: $r = 0.9976$). The oxidative peak current increases linearly with the concentration of rhodanine, which indicates that the process is diffusion-controlled. The linear relationship found for low concentrations (5–140 $\mu\text{g mL}^{-1}$) offers notable advantages in the analysis of small amounts of rhodanine in aqueous solution. Cyclic voltammograms were recorded at different scan rates (Fig. 9). The effect of the scan rate (5–800 mV/s) on the electro-oxidation of rhodanine was examined in aqueous methanol. There was good linearity between the peak height (current) and the square root of the scan rate [Fig. 10(A)]. The relationship between peak potential and the logarithm of the scan rate [Fig. 10(B)] can be used to roughly estimate the number of electrons involved in the catalytic oxidation. For a totally irreversible electrochemical

Table 1. Effect of pH and supporting electrolytes on the differential pulse voltammetric peak potential and peak current of thiazole heterocycles at Au oxide and Au electrodes.

Analytes 4.0 (μg mL ⁻¹)	Phosphate buffer						Acetate buffer		Britton-Robison buffer							
	pH 2.21		pH 2.21		pH 6.62		pH 4.90		pH 2.06		pH 4.68		pH 5.42		pH 6.71	
	Peak potential (V); Current (μA)								Peak potential (V); Current (μA)							
	Au (i.d.: 3 mm)		Au oxide		Au oxide		Au oxide		Au oxide							
	(V)	(μA)	(V)	(μA)	(V)	(μA)	(V)	(μA)	(V)	(μA)	(V)	(μA)	(V)	(μA)	(V)	(μA)
Rhodanine	1.03	29.8	0.54	205	0.49	47.7	0.60	97.1	0.51	43.0	0.53	36.3	0.51	47.6	0.50	46.3
Thiazolidine-2,4-dione	1.00	18.5	0.40	62.8	0.42	26.6	0.55	63.6	0.47	31.5	0.44	31.0	0.48	36.7	0.48	39.7
Thiazolidine	1.14	9.27	0.47	141	0.55	41.8	0.67	135	0.45	25.9	0.50	34.7	0.56	41.7	0.55	49.1
L(−)-Thiazolidine-4-carboxylic acid	0.86	15.1	0.48	79.4	0.52	31.6	0.36	54.6	0.57	40.3	0.54	27.9	0.52	37.2	0.52	23.9

Figure 7. Differential pulse voltammograms of rhodanine ($8 \mu\text{g mL}^{-1}$) in various electrolytes at an Au oxide electrode. The solid line (–) is phosphate buffer (pH 2.21) (peak at 0.567 V, 212 μA); the medium dashed line (– –) is acetate buffer (pH 4.90) (peak at 0.630 V, 133 μA); the dotted line (···) is Britton-Robison buffer (pH 5.42) (peak at 0.571 V, 49.8 μA). **Figure 9.** Cyclic voltammograms of rhodanine ($48 \mu\text{g mL}^{-1}$) in phosphate buffer (pH 2.21) on Au oxide electrode at different scan rates: (a) 5 mV/s (0.786 V, 56.1 μA); (b) 10 mV/s (0.799 V, 86.0 μA); (c) 12.5 mV/s (0.802 V, 91.3 μA); (d) 25 mV/s (0.833 V, 166 μA); (e) 50 mV/s (0.868 V, 265 μA); (f) 100 mV/s (0.912 V, 429 μA); (g) 200 mV/s (0.983 V, 690 μA); (h) 400 mV/s (1.10 V, 1191 μA); (i) 800 mV/s (1.21 V, 1789 μA). **Figure 8.** Cyclic voltammograms of rhodanine in different concentrations at an Au oxide electrode and a related current-concentration curve: (a) $5 \mu\text{g mL}^{-1}$ (0.799 V, 270 μA); (b) $20 \mu\text{g mL}^{-1}$ (0.799 V, 306 μA); (c) $40 \mu\text{g mL}^{-1}$ (0.804 V, 379 μA); (d) $80 \mu\text{g mL}^{-1}$ (0.839 V, 514 μA); (e) $140 \mu\text{g mL}^{-1}$ (0.875 V, 694 μA); in phosphate buffer solution at a scan rate of 25 mV/s.

oxidation, the peak current in cyclic voltammograms can be expressed as:

$$I_p = (2.99 \times 10^5) n(\alpha n_a)^{1/2} A C_0 D_0^{1/2} \nu^{1/2}$$

where I_p is the peak current, n is the number of electrons involved in the oxidation, αn_a is a parameter reflecting the irreversibility of the oxidation, A is the area of the electrode (cm^2), C_0 is the concentration of substrate, ν is the potential scan rate, and D_0 is the diffusion coefficient of the substrate. The value of $n(\alpha n_a)$ can be calculated from the slope of the line shown in Fig. 10A: $n_a = 0.8$ (approximately) for an irreversible process. On the other hand, the peak potential in cyclic voltammograms can be expressed as a function of the logarithm of the scan rate: $E_p = \text{constant} + 2.3 RT / 2\alpha n_a F \log \nu$; it can be used to roughly estimate the number of electrons involved in the catalytic oxidation. The controlled-potential coulometry was done in buffered solution (phosphate: pH 2.21) containing $6.45 \times 10^{-4} \text{ M}$ rhodanine at the constant anodic potentials of 1.0 and 1.5 V (vs. Ag/AgCl). The progression of the electrolysis process, monitored using cyclic voltammetry, shows that the peak current for rhodanine (1.37 V) decreased and that the peak current for the newly appeared anodic wave (1.09 V) in less-positive potential increased. Rhodanine and the electrolyzed

Figure 10. (A) Magnitude of the peak current, I_p , for rhodanine oxidation as a function of the square root of the scan rate and (B) peak potentials.

solution (sulfoxides) were analyzed using gas chromatography (GC) (GC-2014 with FID (flame ionization detection); Shimadzu Taiwan Industrial Machinery, Hsinchu City, Taiwan) and an HP-5 column (60 m $\times$ 0.32 mm; film thickness: 0.25 μm) (Agilent Technologies, Santa Clara, CA) and GC/MS (gas chromatography/mass spectrometry) (QP-2010 mass spectrometer; Shimadzu Taiwan) and a

DB-5 (5% phenyl-methylpolysiloxane) fused silica capillary column (30 m $\times$ 0.25 mm, film thickness 0.25 μm). Because rhodanine is thermally unstable, it does not yield stable chromatograms: it has no boiling point and easily decomposes at temperatures $>171^\circ C$. Therefore, high-performance liquid chromatography (HPLC) and Fourier transform infrared (FT-IR) spectrophotometry were used to characterize the products of the oxidation process in the electrolyzed solution for rhodanine. The electrolyzed solution was extracted with ethyl acetate:hexane (3:2, v/v) and then concentrated for HPLC and FT-IR analysis. Elution and HPLC analysis of the electrolyzed solution were done using a Luna C_{18} column (250 mm $\times$ 4.6 mm) (Phenomenex, Torrance, CA) during the mobile phase with methanol-phosphate buffer ratios (10:90, v/v) containing 1.0 mM dihydrogen potassium phosphate (pH 6.85) at a flow rate of 1 mL/min, and at a detection wavelength of 290 nm. The retention time of the new peak was 7.63 min and of rhodanine was 8.51 min. The sulfoxide group (S=O) stretching frequency is usually at 1070–1030 cm^{-1} . The IR spectra of electrolyzed residue in KBr had an S=O stretching bond at $\sim 1074 cm^{-1}$ and an N-H rocking band at 682 cm^{-1} . The total number of electrons was determined using controlled-potential coulometry with a gold electrode. The accumulated charge (Q) was taken from the digital coulometer at a curve (potential corresponding to peak current) of the oxidation wave. Applying the equation:

$$Q = nFw/M$$

where w is the weight of the sample in grams and M its molecular weight, the value of n for rhodanine was two electrons. The anodic oxidation of organic sulfides in the presence of water clearly proceeds by successive two-electron steps to afford sulfoxides and sulfones.^{28,29} Therefore, a possible mechanism is given in Scheme 2.

4. Conclusions

Au oxide film on Au electrode and its supported Au catalysts was fabricated using potentiostatic and potential cycling conditions. The present work shows that the anodic oxidation of heterocycles thiazole on an Au oxide electrode in the pH range 2.06–6.71 was investigated. The presented DPV method is simple and can be directly used for precisely and accurately monitoring sub-micromolar amounts of the heterocycles thiazole in aqueous buffered solutions.

Acknowledgments

This work was financially supported by grant National Science Council of the Republic of China (NSC 99-2113-M-041-001-MY3).

Scheme 2. Possible mechanism.

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