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Optical and Electrochemical Combination Sensor with Poly-Aniline Film Modified Gold Surface and Its Application for Dissolved Oxygen Detection

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Abstract: Poly-aniline (PAn) film can be oxidized by contacting oxygen in an electron-transfer reaction and its redox state, for instance the open circuit potential and the dielectric constant, is quantitatively related to oxygen concentration. This feature may contribute to an improved application of dissolved oxygen (DO) detection with the combined optical and electrochemical sensor. In this paper, PAn is used as a sensing surface to detect DO by the combination sensor composed of electrochemistry and total internal reflection imaging ellipsometry (EC-TIRIE). Results demonstrate that both optical and electrical signals show a logarithmic correlation with DO concentration (0–20 ppm). Compared with the results obtained only with the gold surface, both the optical and electrical signals of the EC-TIRIE sensor for DO detection are amplified with the PAn modified gold surface.

Keywords: Combined optical and electrochemical sensor · Dissolved oxygen · Electrochemistry · Poly-aniline · Total internal reflection imaging ellipsometry

1 Introduction

Dissolved oxygen (DO) in surface water is used by all forms of aquatic life and it participates in a variety of chemical, biological and biochemical processes [1]. DO concentration is an indicator to monitor water quality. As a consequence, considerable efforts have been made into the development of DO measurement methods [2]. The widely studied method for DO measurement is Clark electrode and its modified forms [3–5], including the potentiometric DO sensors based on metal oxides electrodes [6–8]. Although electrochemical-based DO sensors can provide accurate measurement results, its drawbacks, such as the slow response time, a "static" reading and the aging of the electrodes, have limited its general application [9].Optical methods such as fiber optic sensors[10] offer attractive alternatives to the electrochemical-based DO sensors due to the fast response time, little oxygen consumption and no interference from exterior electromagnetic fields [9–11].Among these optical methods for DO detection, fluorescence-based and luminescence-based DO sensors have received special attention [11,12]. Such sensors exploit a decrease in fluorescence intensity of an excited indicator as a result of the quenching effect induced by the energy-transfer mechanism with oxygen molecule [12]. The key to these sensors is the oxygen-sensitive probe molecules. Mostly used probes are transition metal complexes, such as ruthenium or palladium compounds [12–15]. The main drawback of fluorescence-based or luminescence-based DO sensors is their irreversibility which influences the long-time use of these sensors [16]. Recently DO sensors based on the principle of total internal reflection have been reported and hold promise for use with high performance [16].

Total internal reflection imaging ellipsometry (TIRIE), based on imaging ellipsometry performed in a total internal reflection mode, is an automatic real-time analysis method with high sensitivity and less sample consumption [17]. In TIRIE, an evanescent wave appearing on the gold surface is employed as an optical probe to monitor interactions on the gold surface [17]. The sensitivity of the TIRIE is proved to be 10 times higher than that of the conventional surface plasma resonance (SPR) in principle [18]. TIRIE has been used to dynamically observe chemical and biochemical reactions on a solid surface and obtained several successful experiences [19–21]. Applying a gold film coated on a glass slide as the working electrode and the sensing surface, TIRIE and electrochemical systems can be combined to develop a novel sensor (EC-TIRIE) to detect a redox process.

Poly-aniline (PAn) is an oxygen sensitive polymer with special optical and electrical properties [22,23]. It is easily prepared on a solid surface with good stability under an ambient condition. With the reaction to oxygen, the "doping level" of PAn is changed with its redox state remarkably, resulting in its color variation in a wide range: a straw-yellow-colored fully reduced state, a bright

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green emeraldine state, a blue polaronic state and a dark blue quinoid state [24]. These features provide a possibility for PAn to be used as a signal amplifying medium for DO measurement in the EC-TIRIE sensor with good sensitivity and stability.

In this paper, a novel EC-TIRIE sensor is proposed and PAn film is tried to fabricate on gold electrode surface as a sensing surface to amplify both the optical and electrochemical signals for DO detection with the EC-TIRIE sensor. Firstly, a PAn film is potentiodynamically deposited on the gold electrode surface to form the DO sensing surface and the electrochemical growth process of the PAn film is recorded by TIRIE with cyclic voltammetry. Then, the electrochemical and optical properties of the PAn film are studied in acidic solution to determine the conditions for DO measurement. Finally, the response curves of the EC-TIRIE sensor with the PAn film modified gold surface to different DO concentrations are presented to show that both the optical and electrical signals of the EC-TIRIE sensor are enhanced compared with the signals obtained only with the gold surface.

2 Experimental

2.1 Chemicals

Aniline was vacuum distilled and kept under nitrogen atmosphere. Sulfuric acid (98%), hydrogen peroxide (30%) (Beijing Chemical Works), and aniline (99.7%) (http://www.jkchemical.com/) were used without any further purification. All solutions were prepared using Millipore Milli-Q water. The aniline aqueous solution was stored in the dark at a low temperature. Nitrogen (99.9%) and oxygen (99.9%) gas were acquired from Beijing oxygen factory. All test solutions were de-aerated with high purity nitrogen gas for at least 15 min before electrochemical experiments. To obtain different dissolved oxygen concentration, oxygen and nitrogen were bubbled into water samples.

2.2 Electrode Preparation

A 29 mm × 17 mm × 2.8 mm SF10 glass slide coated with a 30-nm thick gold film and a 3-nm thick Cr adhesive under-layer served as both TIRIE sensing surface and the working electrode.

Prior to each experiment, the gold substrate was treated in piranha solution (3 : 1 mixture of concentrated H_2SO_4 and 30% H_2O_2) for 5 min, followed by rinsing with deionized water and high purity ethanol several times. (Caution: piranha solution is an extremely strong oxidant and is potentially explosive, so it should be handled with extreme caution).

2.3 Electrochemistry

Electrochemical experiments were performed using a VersaSTAT 3 electrochemical system (USA). A wound Pt wire counter electrode and a saturated calomel reference electrode were used in the custom-built compartment cell during electrochemical experiments. All the potentials are given with respect to this reference electrode.

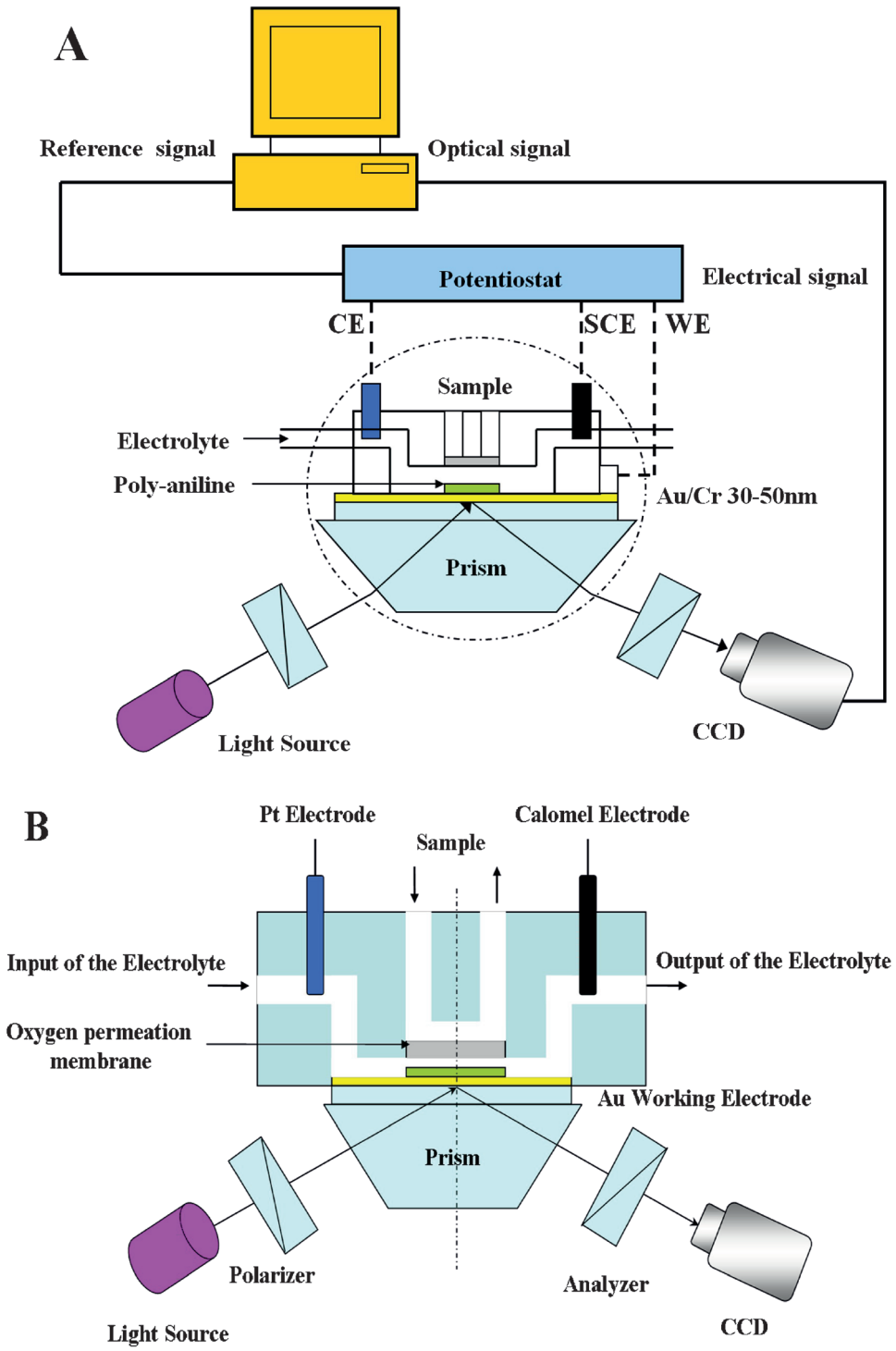
The electrochemical cell and the sample cell were two independent compartments separated by an oxygen permeable membrane. The electrolyte was filled in the space between the oxygen permeable membrane and the three-electrode system. Dissolved oxygen in water sample can diffuse into supporting electrolyte through this oxygen permeable membrane. In addition, a Viton O-ring was used to provide a liquid-tight seal for these two cells. A commercial dissolved oxygen meter (TP 351, Beijing Timepower Measurement and Control Equipment Co, Ltd) was used to determine oxygen concentration in the water samples.

Poly-aniline film was grown on the gold substrate from 0.5 M H_2SO_4 containing 0.1 M aniline. It was synthesised potentiodynamically by cycling the potential between −0.2 to 0.8 V vs. SCE for the first five cycles, then lowering the anodic limit to 0.75 V for the next three cycles in order to avoid over-oxidation of the poly-aniline film [25,26]. After electrosynthesis, the substrate modified by poly-aniline was washed with distilled water and blown to dry with nitrogen. During DO detection, 0.1 M H_2SO_4 deaerated with nitrogen as supporting electrolyte was pumped into the electrochemical cell. Before each measurement, 0mV potential (vs. SCE) was applied to the PAn film for 60 s to have the same initial conditions. Then DO was measured under open circuit potential.

2.4 Total Internal Reflection Imaging Ellipsometry

The prism-based TIRIE setup used for all experiments described in this paper is shown in Scheme 1. A SF10 trapezoidal prism was used with an expanded light beam at 633 nm wavelength as a light source and a high-speed CCD camera as detector. A gold-coated (about 30 nm) glass slice was placed on top of the prism using index-matching oil and used as the TIRIE sensing surface. An electrochemical cell was placed on top of the gold film for holding the electrolyte. The counter electrode and the reference electrode were inserted into the electrochemical cell from the top opening. The light from a Xe lamp was guided by an optical fiber and expanded by the collimating system. After passing the polarizer and compensator, the polarized collimated beam propagated perpendicularly to the prism and onto the sensing surface. When the incident angle was larger than the critical angle, the evanescent wave appeared sharply at the sensing surface to detect interaction in very shallow depth from the surface. The reflected light carrying surface information was then imaged by CCD camera after passing the analyzer.

Scheme 1A depicts a schematic of a sample configuration that combines the TIRIE system with an electrochemical cell and a substrate consisting of Au film as the sensing surface. The substrate is mounted to an organic glass cell, which can be filled with electrolyte and con-



Scheme 1. (A) Schematic of the whole combined electrochemical TIRIE system. (B) Schematic illustration of the TIRIE setup used for total internal reflection imaging ellipsometry and electrochemistry measurements. Poly-aniline (the green part) modified gold layer (30 nm) on the base of SF10 glass slide as working electrode for simultaneous electrochemical and optical measurements. Oxygen permeable membrane (the gray part) separates the electrochemical cell from the sample cell.

tains the counter and the reference electrodes. Combined with an external electrochemical working station, this configuration allows for simultaneous TIRIE imaging of the change on the gold surface.

3 Results and Discussion

3.1 TIRIE Studies of the PAn Electropolymerization

PAn film has been grown on a gold electrode by employing repeated cyclic voltammetry scans. The cyclic voltam-

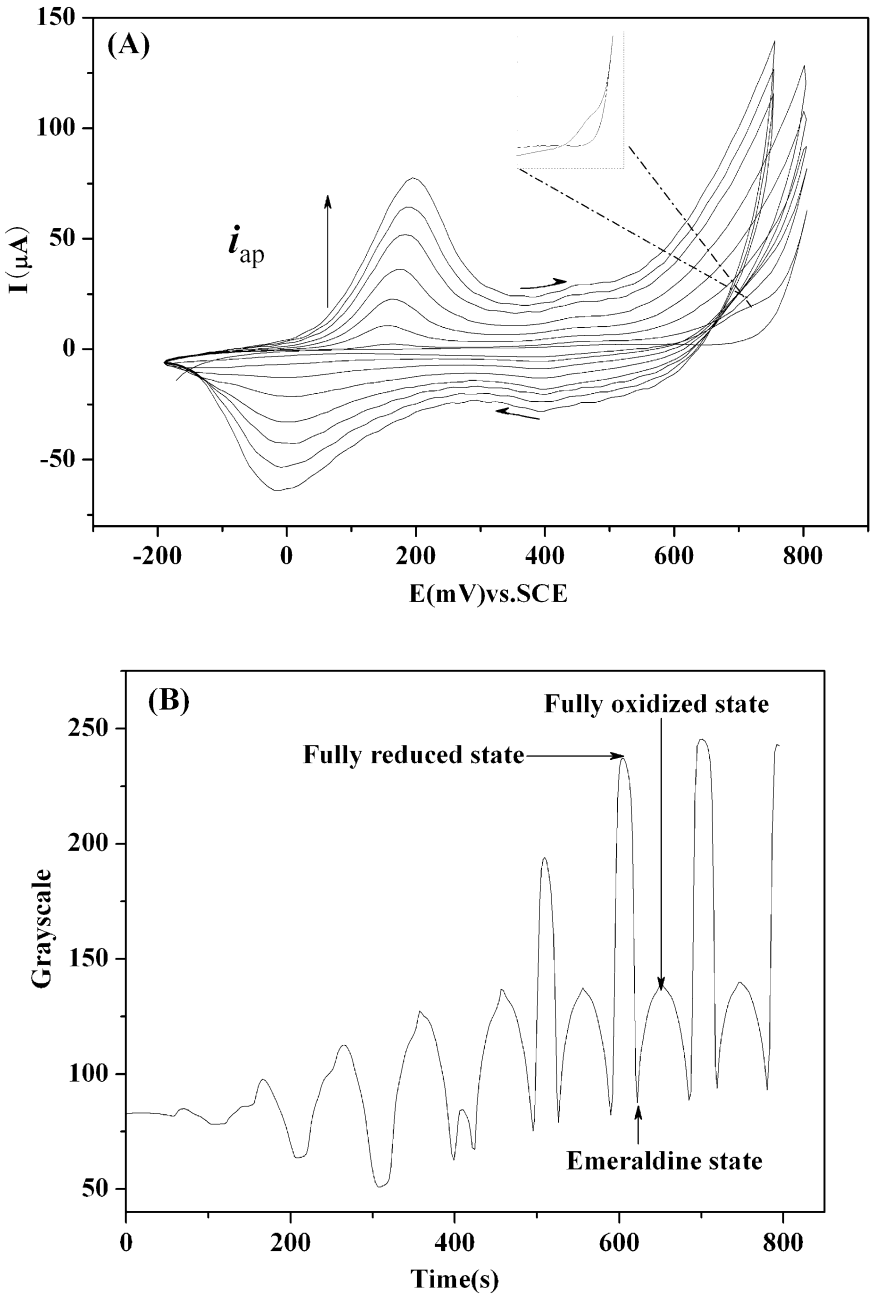


Fig. 1. (A) Cyclic voltammograms (CVs) recorded during the growth of poly-aniline film on a gold coated glass substrate in 0.5 M H_2SO_4 containing 0.1 M aniline monomers at a scan rate of 20 mV/s from −200 to 800 mV. Inset: detailed view of the first polymerization cycle in the potential range of 400 to 800 mV (The arrows in CVs show the directions of scan). (B) The corresponding TIRIE grayscale change recorded simultaneously to the CVs during the polymer growth.

mograms (CV) (Figure 1A) and its corresponding TIRIE signal in grayscale curves (Figure 1B) during the potentiodynamic growth of PAn on the gold electrode are presented in Figure 1. An increase in the anodic current occurs at more positive potentials (higher than 700 mV). It indicates that the monomer species is oxidized and consequently results in nucleation formation. The current trace across the forward sweep (Inset in Figure 1A) observed upon scan reversal is a typical feature of nucleation formation and it shows the monomer oxidation is followed by polymer film formation process [27]. During the repeated cyclic voltammetry scans, a couple of redox peaks ($E_a = 194$ mV, $E_c = 0$ mV) are observed. With the increase of scan cycles, the continuous rise of these anodic and cathodic current peaks reflects the polymer film growth. However, the peak potentials retain almost constant, suggesting PAn film retains a similar property regardless of the film thickness. Many works in the literature demonstrate that these two peaks are attributed to the transformation between leucoemeraldine and emeraldine [28–30].

Corresponding to the cyclic voltammetry scans, the TIRIE signal in grayscale curves shows sequential oscillations with a periodicity. With the growth of the PAn film, the grayscale value at a given potential increases continually in the whole electropolymerization process. At different potentials, PAn presents different oxidation states with different refractive index, which are corresponding to different grayscale values at different potentials [28]. Three special oxidation states that are fully reduced state, emeraldine state and fully oxidized state at the voltage values of −200 mV, 194 mV and 750 mV respectively are marked in Figure 1B. At the last cycle a grayscale change of nearly 150 is observed between fully reduced state and emeraldine state. Compared with the EC-SPR, this EC-TIRIE system can provide continuous information concerning the electropolymerization process of poly-aniline [31,32].

3.2 Voltammetric Behavior of PAn in Sulfuric Acid Solution

As DO detection is carried out in sulfuric acid solution, it is essential to study both the electrochemical and optical behavior of the PAn film in sulfuric acid solution to determine the conditions for DO detection. Figure 2 shows the CV (2A) and TIRIE curves (2B) for the bare gold and

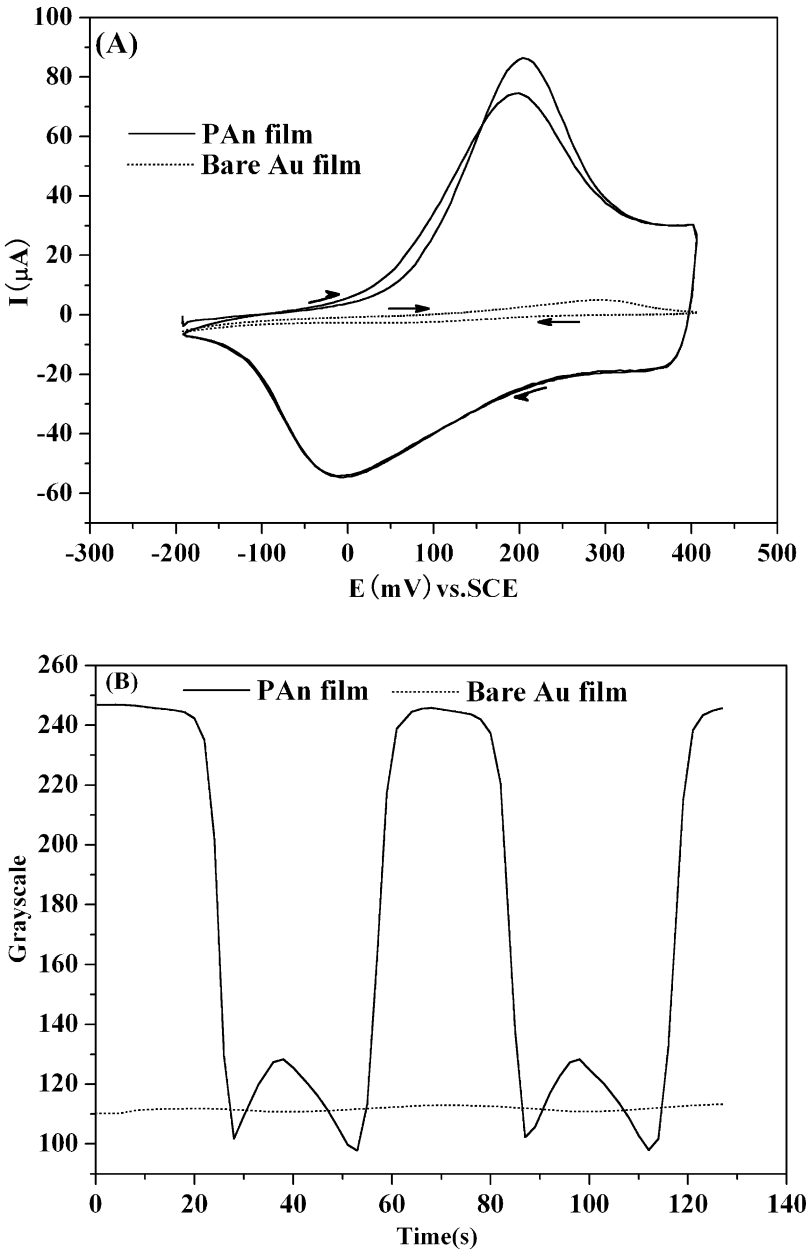


Fig. 2. (A) Cyclic voltammograms (the first and second scans) of the redox behaviour of PAn film recorded with a scan rate of 20 mV/s from −200 to 400 mV in 0.1 M H_2SO_4 (The arrows in CVs show the scan directions). (B) The TIRIE grayscale changes recorded simultaneously to the CVs.

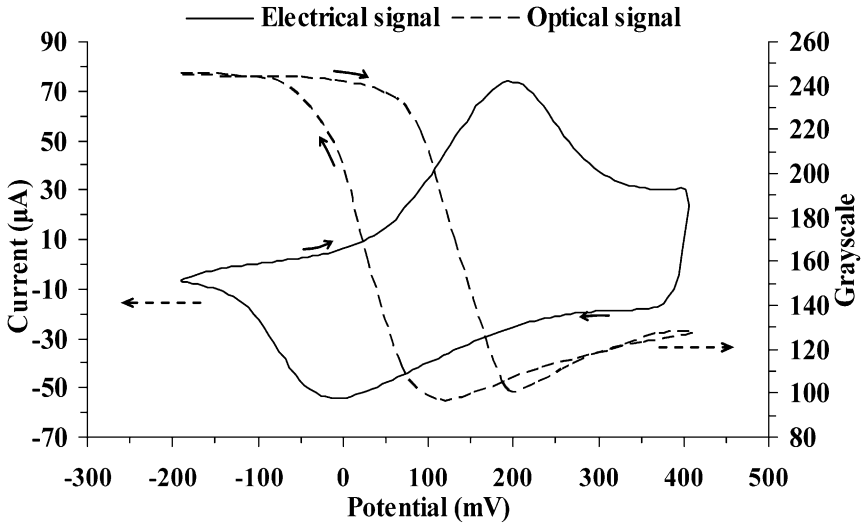


Fig. 3. Typical cyclic voltammogram curve (solid line) and its corresponding TIRIE curve (dashed line). The TIRIE curve was taken by real time monitoring the change of grayscale with the potential in 0.1 M H_2SO_4.The potential scan rate is 20 mV/s (The two dashed arrows indicate the *Y*-axis in the curves, and the short solid arrows show the direction of scan).

PAn modification surface in 0.1 M H_2SO_4 solution. A redox couple at about 100 mV indicates the conversion of the polyleucoemeraldine to the polyemeraldine state [33,34]. However the oxidation current peaks in the first cycle are different from the following ones, because of different doping states of the PAn film that are undoped state in the first cycle and partly doped state in the following cycles. A very similar CV of PAn has been obtained on polycrystalline Au electrodes [35].

Corresponding to the CV, the TIRIE curve shows periodic variation with a great grayscale change between the reduced state and the oxidized state. Meanwhile, the TIRIE response on the bare gold surface shows that the grayscale change in Figure 2B could be attributed to the change of the optical property of the PAn film which results from the change of the oxidation states of the PAn film during its oxidation or reduction process. The redox processes of the PAn film are also accompanied by structural transformation due to the doping and undoping processes involving protons and anions [36,37].

To better understand the CV process of poly-aniline in sulfuric acid solution, the second cycle of the CV that is partly doped PAn film and its corresponding TIRIE curve with potential are compared in Figure 3. It is obvious that continuous changes in contrast come out in PAn film oxidized state (between the electrodes at −200 mV in the reduced state and the electrode at 400 mV) [34]. In the potential range from −200 to 0 mV both the current and grayscale remain almost constant, indicating the poly-aniline is in the same reduced state. Clear current change is obtained from 0 mV, reflecting the ready oxidation of the polymer film. The redox couple in the CV is corresponding to the transformation between the reduced state and the oxidized state of poly-aniline [35–37]. The TIRIE curve also yields a similar couple of peaks at the redox potential of the PAn film. However the potential of the reduction peak in optical signal is different from that in electrochemical signal, which may be caused by the thickness of the PAn film on the gold surface. With increasing applied potential the grayscale change occurs reflecting the clear difference in the dielectric properties of the reduced and oxidized poly-aniline.

3.3 Amplification of PAn for DO Detection

Our previous results have shown the signal response of the EC-TIRIE sensor with only gold surface to DO(Figure 4B). The optical signal change is only about 2 grayscale from 0 to saturated DO, which is so small that it limits the further application of the EC-TIRIE sensor. As PAn is oxygen sensitive polymer, with this PAn modified gold surface the performance of the EC-TIRIE sensor for DO detection has been improved significantly. To examine the response of the PAn modified sensor to DO, different DO concentration samples which have been determined by a commercial oxygen electrode are detected by the EC-TIRIE sensor.

Figure 4A shows both the electrical and optical signal response of the EC-TIRIE sensor with PAn film modified gold surface to different DO concentrations. The optical signals are in good accordance with the electrical signals, demonstrating the TIRIE method is in synchronization with the electrochemical method. The open circuit potential of the PAn modified electrode increases gradually as the grayscale decreases, which is similar to the CV diagrams in Figure 3. The electrochemical response of the PAn modified gold electrode to DO shows a logarithmic correlation ($y = 15.001 \ln x + 54.30$, $R^2 = 0.9706$) with DO concentrations in the range from 0 to 20 ppm, formally keeping with the Nernst equation. Compared with the results obtained by only bare gold electrode (Figure 4B), both the optical and electrical signals of the EC-TIRIE

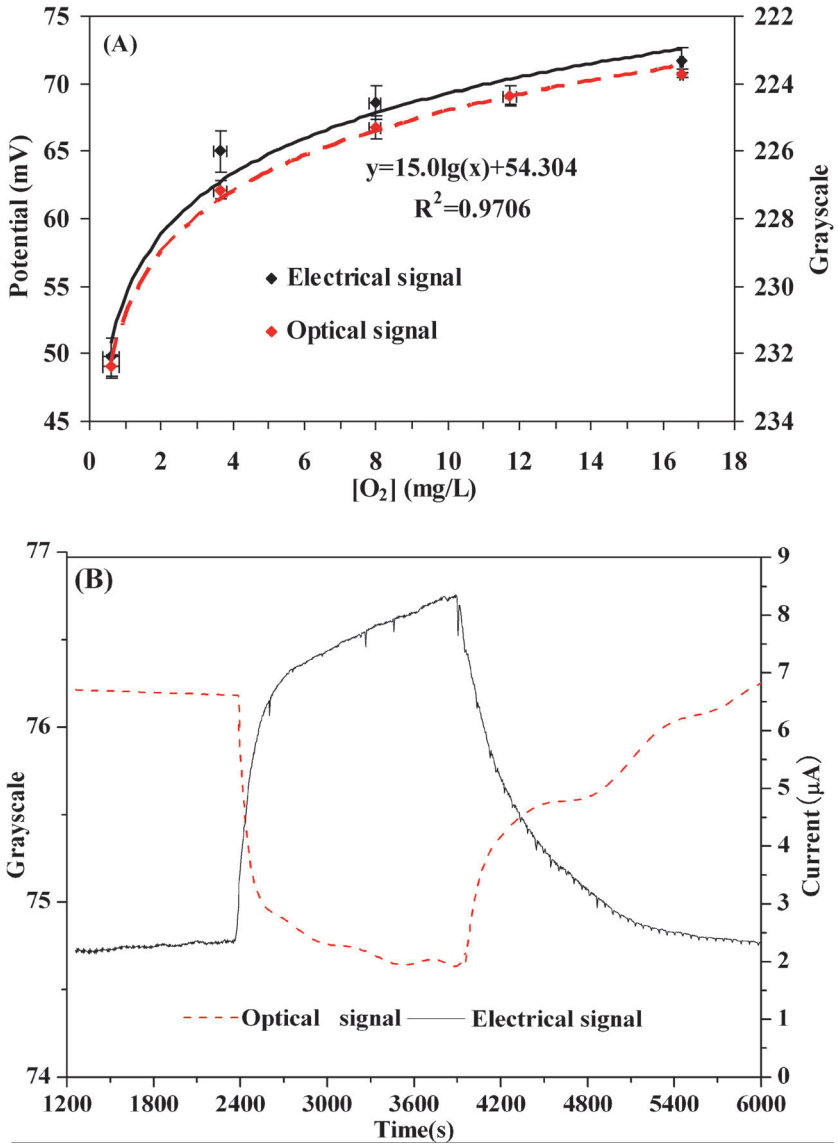


Fig. 4. (A) Responses in both open circuit potential (black solid line) and gray-scale (red dashed line) by EC-TIRIE sensor with poly-aniline modified gold surface upon various oxygen concentrations (Error bars represent three repeated experiments). (B) The signal changes obtained by only bare gold electrode (The black solid line is the electrical signal and the red dashed line is the optical signal).

sensor with PAn modified gold surface are amplified significantly. The grayscale change of the TIRIE signal is about 10, nearly five times than that of the bare gold electrode, making it possible for DO detection applications with this EC-TIRIE sensor and bringing better detection performance, for instance detection sensitivity and limit of detection in DO detection applications.

4 Conclusions

An EC-TIRIE sensor with PAn modified gold surface has been developed and successfully applied for DO detection. The gold surface modified by the PAn film has been proven to enhance DO detection performance with the EC-TIRIE sensor. The main advantage of this specific design is that the data obtained by optical signal and electrochemical signal highly corroborate each other, providing a potential to adjust the sensor automatically and simply. In addition, DO detection can be performed repeatedly with this EC-TIRIE sensor just by reducing the PAn film electrochemically at a negative potential to its reduced state. It can be foreseen that this EC-TIRIE sensor may be further developed as a platform for detection of water pollutants in practice, such as biological oxygen demand (BOD), or even heavy metal ions.

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