



Electrodeposited indigotetrasulfonate film onto glutaraldehyde-cross-linked poly-L-lysine modified glassy carbon electrode for detection of dissolved oxygen

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ABSTRACT

The nano composited film of indigotetrasulfonate (ITS) electrodeposited onto poly-L-lysine (PLL)-glutaraldehyde (GA) (ITS/PLL-GA) was modified on glassy carbon electrode (GCE) by multiple scan cyclic voltammetry. Compositing of the proposed film was characterized by atomic force microscopy (AFM), scanning electron microscopy (SEM), electrochemical quartz crystal microbalance (EQCM), electrochemical impedance spectroscopy (EIS), and UV-vis spectrum for the absorption at λ_{\max} at 566 nm. For the electrocatalytic reduction of dissolved oxygen, ITS/PLL-GA film modified electrodes was determined in 0.1 M acetate buffer solution (pH 5.6) by cyclic voltammetry and rotating disk electrode voltammetry. This dissolved oxygen electrochemical sensor exhibited a linear response range (from 0 to 178.4 μM , $R^2 = 0.9949$), lowest detection limit (2.2 μM), lowest overpotential at -0.09 V, high sensitivity (906 $\mu\text{A mM}^{-1}$) and relative standard deviation (RSD) for determining dissolved oxygen ($n = 3$) was 4.2%. In addition, the ITS/PLL-GA/GCE was advantageous in terms of its simple preparation, specificity, stability and the ability of regeneration.

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1. Introduction

The use of poly-L-lysine (PLL) as synthetic polyelectrolyte has been subject of increasing interest as mimetic model of complex biological molecules, development of new system of drug delivery [1,2] and as versatile class of polyaminoacids used for coating several types of electrodes. Also, PLL can be used as cationic polyaminoacid ($\text{pK}_a = 10.4$) and used for anion detection [3–9]. Due to its versatility and easiness to preparation, PLL have been used recently for modification of several types of electrodes (glassy carbon, pyrolytic graphite, platinum, gold) and applied for electrochemical determination of biological molecules, pharmaceutical compounds, dyes and metals [5–9]. Glutaraldehyde is an aliphatic dialdehyde whose major uses are based on its highly reactive chemical properties. Its ability to effectively cross-link cellular proteins imparts a wide array of biocidal activities. For this reason, glutaraldehyde has been used in large quantities for many applications, such as sterilization, cross-linking biomolecules and chemical synthesis [10–12]. Previous scholars presented that the cross-linking of a proportion of the amino groups in PLL by means of GA might usefully produce a material that would adhere better to electrode surfaces than does PLL itself [13–15]. The ratio of PLL-GA could be used to adsorption of different anionic compounds, such as potassium ferricyanide [15], sodium

neodocromil [16], phosphotungstate [17], and silicomolybdate [18]. Indigotetrasulfonate (ITS) is an organic dye with redox active species bearing anionic sulfogroups and unstable in neutral or basic aqueous solution [19]. In the literatures, ITS always doped with different conducting polymers, such as polyaniline (PANI) [19,20] and 4-aminothiophenol (4-ATP) monolayer [21,22]. In many of the conducting polymers, PLL-GA is much more similar to the protein site of more complex biological molecules than those of other amines and amino acids [16,18]. Due to this fact, we design a ITS/PLL-GA film and modified on glassy carbon electrode (GCE) by cyclic voltammetry and describe the characteristics of strong interaction between the incorporating ions and the polymer.

Different methods and analytical techniques have been reported in the literature for the determination of oxygen, including nuclear magnetic resonance (NMR), thermogravimetry-Fourier transform infrared (TG-FTIR) and electrochemical methods [23–26]. Among these, the electrochemical method is an effective way for the determination of oxygen because of quick response, low cost, high sensitivity, simple of instrumentation, and possibility of miniaturization. This electrochemical technique had been considered very interesting for the determination of dissolved oxygen owing to their high sensitivity and lower over-potential.

In the present work, a novel and stable ITS/PLL-GA film was prepared by the electro-deposition of ITS on PLL-GA modified GCE. The surface morphology of ITS and ITS/PLL-GA films modified GCE had been examined by using SEM and AFM. Using ITS/PLL-GA

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film modified GCE had been successfully employed for the detection of dissolved oxygen in 0.1 M acetate buffer (pH 5.6) by cyclic voltammetry, EIS and RDE techniques.

2. Experimental

2.1. Reagents

Potassium indigotetrasulfonate (Dye content 85%) (ITS), poly-L-lysine hydrobromide (Mol wt. = 70,000–150,000) (PLL) and glutaraldehyde 25% (w/w) solution (GA) in water were obtained from Aldrich. All other chemicals used were of analytical grade (99%). Double distilled deionized water was used to prepare all the solutions. Acetate buffer solution of pH 5.6 was prepared using CH_3COOH (0.1 M). Pure nitrogen was passed through all the experimental solutions.

2.2. Apparatus

All electrochemical experiments were performed using CHI 1205a potentiostats (CH Instruments, USA). The BAS GCE ($\varphi = 0.3$ cm in diameter, exposed geometric surface area 0.07 cm², Bioanalytical Systems, Inc., USA) was used. A conventional three-electrode system was used which consists of an Ag/AgCl (saturated KCl) as a reference, bare or ITS/PLL-GA modified GCE as working and platinum wire as counter electrode. Electrochemical impedance studies (EIS) were performed using ZAHNER impedance analyzer (Germany). Scanning electron microscopy (SEM) images were obtained on a HITACHI S-3000H (Japan) scanning electron microscope. The AFM images were recorded with multimode scanning probe microscope (Being Nano-Instruments CSPM-4000, China). UV-visible spectra were obtained using Hitachi U-3300 spectrophotometer (Japan). The dissolved oxygen has been measured by using a commercial DO meter 323-A (WTW Wissenschaftlich-Technische Werkstätten GmbH, Germany). The buffer solution was entirely altered by de-aerating using nitrogen gas atmosphere. Further the oxygen gas was purged as required and the concentrations were measured using the commercial DO meter. The electrochemical cells were kept properly sealed with the continuous flow of nitrogen gas over the solution to avoid the oxygen interference from the atmosphere.

2.3. Fabrication of ITS/PLL-GA film

Prior to the electrochemical deposition process, the GCE was well polished with the help of BAS polishing kit with aqueous slurries of alumina powder (0.05 μm), rinsed and ultrasonicated in double distilled deionized water. Solutions of product of poly-L-lysine and glutaraldehyde were prepared by mixing 97.5% PLL and 2.5% GA for 30 min. For this purpose, 1% (w/v) PLL and 0.05% (w/v) GA solutions were used [13–15,17,18]. Ten microliter of the product solution was placed on the polished GCE surface and allowed in room temperature to evaporate the solvent. The PLL-GA-coated electrode was successfully prepared after placing in oven at 80 °C for 15 min. The PLL-GA/GCE was electrodeposited with ITS film by performing in 10 ml, 0.1 M acetate buffer (pH 5.6) containing 0.5 mM ITS and the potential cycling between $+0.6$ and -0.5 V at the scan rate of 0.05 V s⁻¹ for 50 cycles.

3. Results and discussion

3.1. Electrodeposition of ITS Film on PLL-GA/GCE

As shown in the inset of Fig. 1A, the ITS film was successfully electrodeposited on PLL-GA/GCE between $+0.6$ and -0.5 V at scan

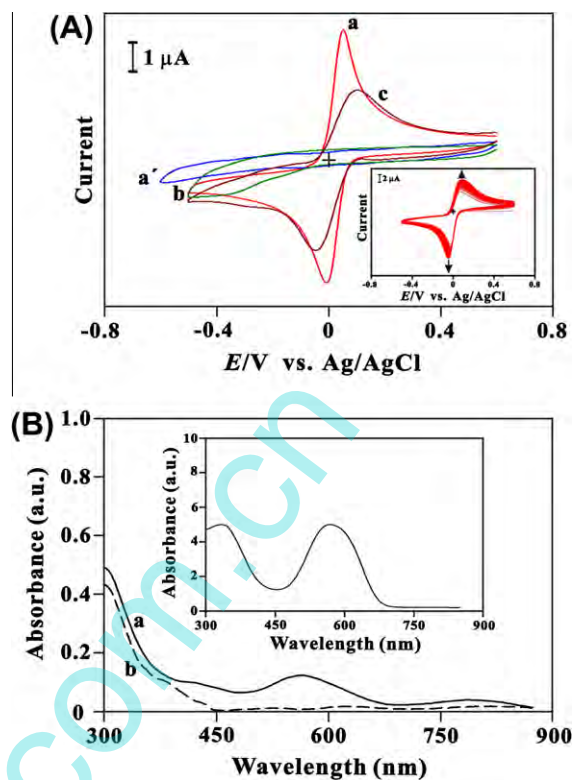


Fig. 1. (A) CVs of (a) ITS/PLL-GA/GCE, (b) PLL-GA/GCE and (a') bare GCE in 0.1 M acetate buffer solution (pH 5.6) in the absence of 0.5 mM ITS and presence (c) the bare GCE. Inset figure shows the CVs of the PLL-GA/GCE by consecutive sweeps in 0.1 M acetate buffer solution containing 0.5 mM ITS. Potential range $+0.6$ to -0.5 V, Scan rate = 0.05 V/s. (B) UV-vis spectrum of (a) ITS/PLL-GA/ITO, (b) PLL-GA/ITO and inset 0.1 M acetate buffer solution (pH 5.6) containing 0.5 mM ITS.

rate of 0.05 V s⁻¹ for 50 cycles. This might be the ion-exchange between ITS and PLL-GA films. The oxidation and reduction peaks of ITS/PLL-GA/GCE are separated as $+104$ and -45 mV. In Fig. 1A, curve (a) indicates the CV signals of ITS/PLL-GA/GCE, (b) PLL-GA/GCE, (a') bare GCE in the presence and (c) absence of 0.5 mM ITS in 0.1 M acetate buffer solution (pH 5.6). When comparing magnitude of current in 0.1 M acetate buffer solution (pH 5.6), ITS/PLL-GA/GCE was higher than bare GCE in the presence of 0.5 mM ITS. By the same way, the E^0 ($(E_{pa} + E_{pc})/2$) of ITS/PLL-GA/GCE (29.5 mV) was lower than bare GCE in the presence of 0.5 mM ITS (74.5 mV). In the same buffer solution, there was no obvious response at PLL-GA/GCE and bare GCE. Similarly, the ITS film cannot directly electrodeposit onto bare GC or Au electrodes (here not shown). All the above results indicated that ITS/PLL-GA film modified GCE showed a stable and higher current in 0.1 M acetate buffer solution.

UV-vis spectrum was used to confirm the ITS film electrodeposited on PLL-GA modified electrode. Fig. 1B showed the ITS/PLL-GA/ITO which compared with ITS dissolved in acetate buffer solution (pH 5.6). Compared with the curve (b) PLL-GA/ITO, the curve (a) ITS/PLL-GA/ITO shows an absorption peak around 561 nm and appear the ITS dissolved in acetate buffer solution (as shown in the inset of Fig. 1B). The above results confirm the successful electrodeposition of ITS on PLL-GA film.

3.2. Electrochemical quartz crystal microbalance measurements

The consecutive cyclic voltammogram and quartz crystal microbalance results for the electrodeposition in 0.1 M acetate buffer (pH 5.6) containing 0.5 mM ITS were shown in Fig. 2A. It showed

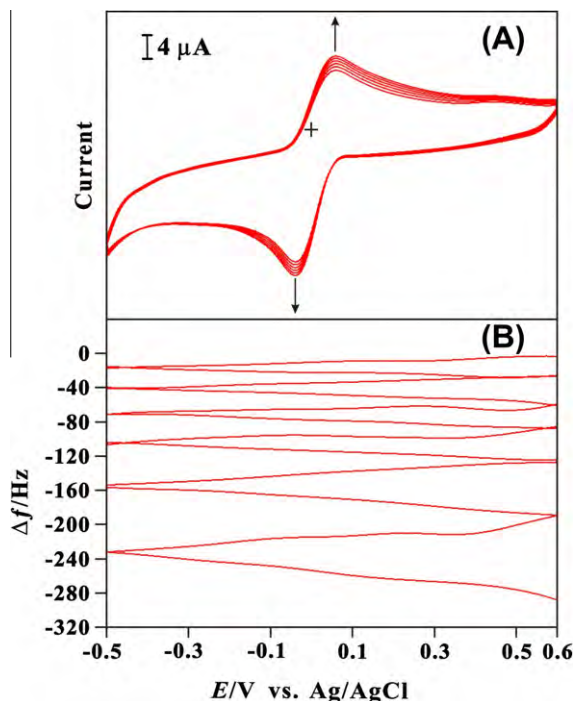


Fig. 2. (A) Consecutive cyclic voltammograms of the ITS film formation on a PLL-GA/gold electrode surface from 0.1 M acetate buffer solution (pH 5.6) containing 0.5 M ITS in the potential range of +0.6 to −0.5 V. (B) The frequency change responses recorded during the consecutive cyclic voltammograms.

a redox signal between the potentials of +0.6 and −0.5 V. Fig. 2B indicates the change in the EQCM frequency recorded during the first six cycles of the consecutive cyclic voltammetry. The increase in the voltammetric peak current of ITS redox couple in Fig. 2A and the frequency decrease (or mass increase) in Fig. 2B were found consistent with the growth of ITS film on the gold electrode. The PLL-GA film was doped by electrochemically driven anion exchange with redox active species bearing anionic sulfogroups of ITS [27–30]. The mass during ITS incorporation in PLL-GA film at the quartz crystal can be calculated by the Sauerbrey equation [30] from the frequency change.

$$\text{Mass change}(\Delta m) = -1/2(f_0^{-2})(\Delta f)A(K\rho)^{1/2}$$

where Δf is the frequency change; A , the area of gold disk; ρ , the density of the crystal and f_0 , the oscillation frequency of the crystal. A 1 Hz frequency change is, however, equivalent to a 1.4 ng change in mass. The mass change during ITS incorporation in PLL-GA film for the first six cycles was found 392 ng/cm².

3.3. AFM and SEM analysis

The surface morphology of PLL-GA and ITS/PLL-GA film modified at glassy carbon electrode were obtained on AFM and SEM. The AFM parameters have been evaluated for 5000 × 5000 nm surface area using the tapping mode. Fig. 3A and B shows the 2D magnified view of PLL-GA film and ITS/PLL-GA film modified on the GCE surface. Fig. 3C and D shows the SEM micrograph of PLL-GA film and ITS/PLL-GA film modified on the GCE surface. From Fig. 3A and C, we could observe the PLL-GA film with wide porous

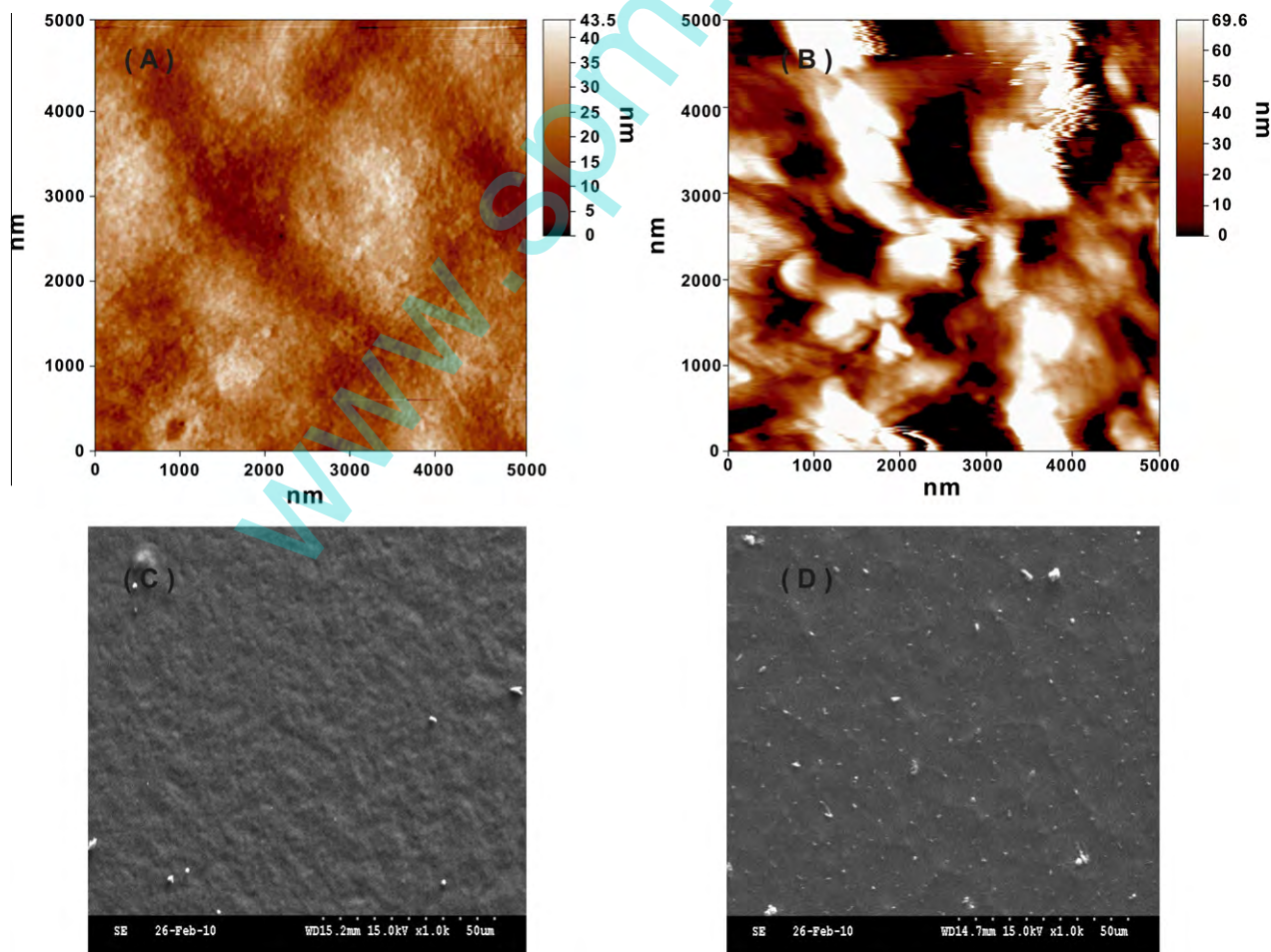


Fig. 3. Results of different scan rate studies of a ITS/PLL-GA film modified GCE in 0.1 M acetate buffer solution (pH 5.6). Scan rate in the range of a-l: 0.01–1 V/s.

surface. It provides a network porous structure to embed nanoparticles and enhance the stability of composited film. The average particle size of PLL-GA was 41 nm. Fig. 3B and D shows the AFM and SEM images of ITS/PLL-GA film surface. The average particle size of ITS/PLL-GA was in the ranges of 50–82 nm and average height of 23 nm. As expected, the PLL-GA network structure provided a substrate for successful deposition of ITS nano particles on the GCE surface.

3.4. EIS analysis

The electrochemical activity of ITS/PLL-GA modified GCE has been examined using electrochemistry impedance spectroscopy

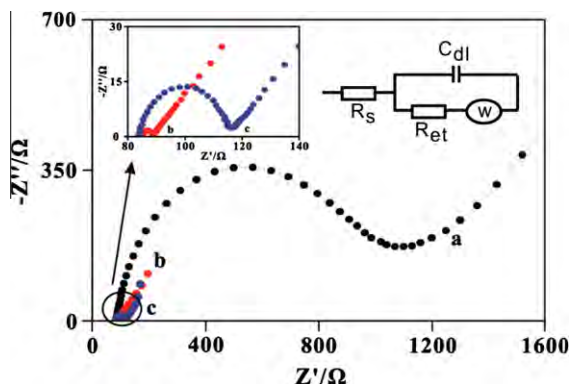


Fig. 4. CVs of ITS/PLL-GA film modified GCE at pH 1, 5.6, 9, 11 and 13 solutions. Scan rate = 0.05 V/s.

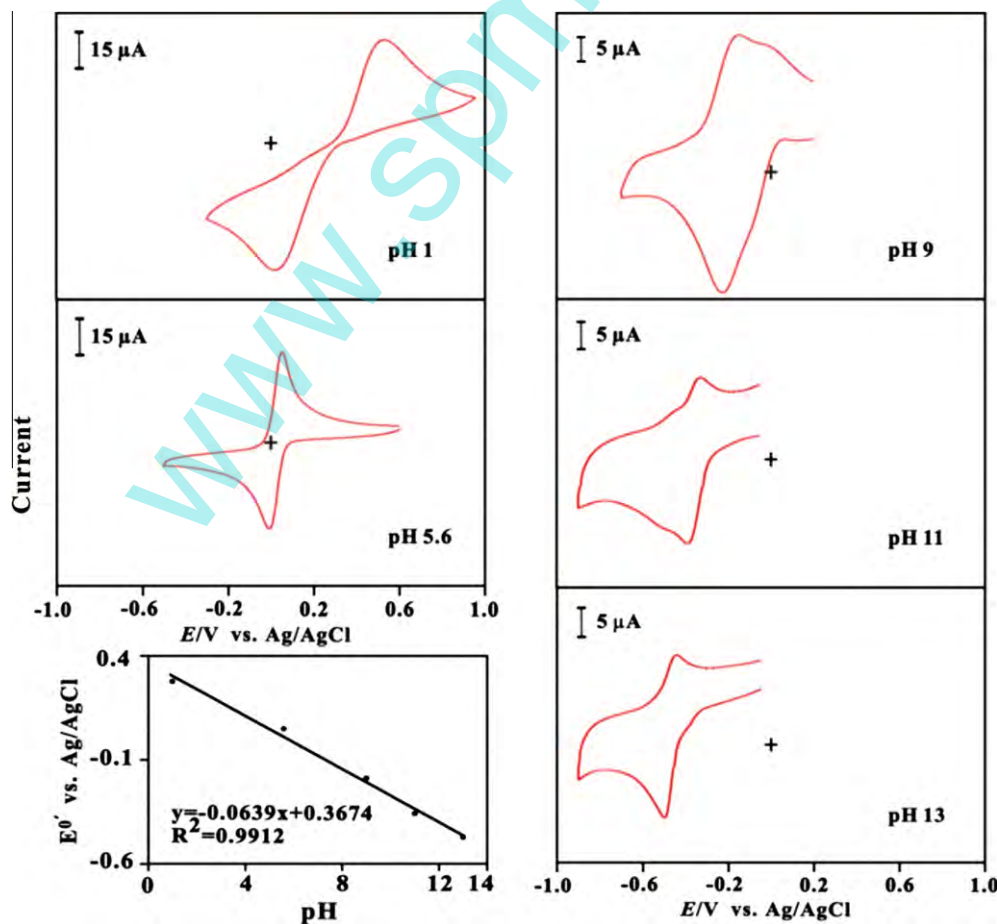


Fig. 6. Tapping mode AFM image (2D) of (A) PLL-GA film on a GCE, (B) ITS/PLL-GA film on a GCE and SEM image of a (C) PLL-GA film on a GCE, (D) ITS/PLL-GA film on a GCE.

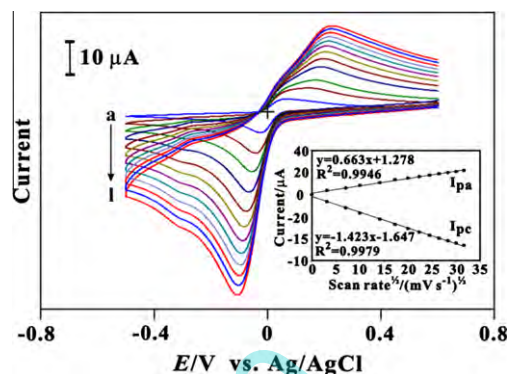


Fig. 5. EIS curves of (a) bare GCE, (b) PLL-GA, and (c) ITS/PLL-GA film modified GCE in 0.1 M acetate buffer solution (pH 5.6) containing 5×10^{-3} M $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1).

(EIS) technique. EIS is an effective method to probe the features of surface modified electrodes. This study was employed to analyze detailed electrochemical activities of different modified electrodes with same condition. The complex impedance can be presented as a sum of the real impedance ($Z'(w)$) and imaginary impedance ($Z''(w)$), which are components that originate mainly from the resistance and capacitance of the cell. From the shape of an impedance spectrum, the electron-transfer kinetics and diffusion characteristics can be extracted. The respective semicircle parameters correspond to the electron transfer resistance (R_{et}) and the double

layer capacity (C_{dl}) nature of the modified electrodes. As shown in Fig. 4 and the inset figure, curve (a) indicates the Nyquist plot of bare GCE, (b) PLL-GA/GCE and (c) ITS/PLL-GA/GCE in 0.1 M acetate buffer (pH 5.6) containing 5 mM $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (molar ratio = 1:1), which were performed at the open circuit potential (E^0 around 0.63 V). The depressed semi circle arc of PLL-GA/GCE was 89.1 (Z'/Ω). Compared with bare GCE ($R_{et} = 1070$ (Z'/Ω)) and ITS/PLL-GA/GCE ($R_{et} = 117$ (Z'/Ω)), PLL-GA film provide a faster electron transfer and diffusion limited electron-transfer behavior [15,35,36]. These results clearly illustrate the electrochemical activities of ITS/PLL-GA, PLL-GA film modified GCEs and bare GCE, respectively.

3.5. Electrochemical properties of ITS/PLL-GA film modified GCE

ITS/PLL-GA film modified GCE was employed for different scan rate studies in 0.1 M acetate buffer (pH 5.6). Fig. 5 showed the different scan rate studies of ITS/PLL-GA film modified GCE in the range of (a) 10, (b) 50, (c) 100, (d) 200, (e) 300, (f) 400, (g) 500, (h) 600, (i) 700, (j) 800, (k) 900 (l) 1000 $mV s^{-1}$. As expected, the cyclic voltammograms of ITS/PLL-GA modified GCE exhibited a redox couple with anodic peak at +0.458 V and cathodic peak at +0.381 V vs. Ag/AgCl/KCl_{sat}. The inset of Fig. 5 showed the redox peak current of ITS/PLL-GA film vs. the square root of scan rate. The corresponding linear regression equations were found as I_{pa} (μA) = $0.663v$ (V/s) + 1.278, $R^2 = 0.9946$ and I_{pc} (μA) = $-1.423v$ (V/s) - 1.647, $R^2 = 0.9979$. This demonstrates that the electrochemical process of ITS/PLL-GA film is diffusion control behavior [31,32].

Fig. 6 showed the cyclic voltammograms of ITS/PLL-GA film modified electrode with different pH values (pH 1, 5.6, 9, 11, 13). It can be noticed that the peak potential shift to more negative potential direction and peak currents decreases with the increase of pH value. Also, with the increase of pH value, the oxidation and reduction peaks are closer. This behavior might be the PLL film in aqueous solutions below pH 10.5, the NH_2 groups in PLL are in the protonated state, and PLL exists in a random coil conformation. On the contrary of pH > 10.5, the NH_2 groups are deprotonated and PLL in solution acquires α -helical conformation [13,15,33,34]. Another possible explanation could be that the amino groups of monolayers controlling the pH dependence of electrochemical reversibility of ITS. The E^0 of ITS redox couples were pH dependent with a slope of -64 mV per pH for ITS/PLL-GA redox couple (Inset, Fig. 6), which were close to the anticipated Nernstian value of -59 mV/pH for electrochemical processes involving the same number of protons and electrons. For the above results, pH 5.6 was chosen as the appropriate pH value for determination of oxygen since larger currents and the best voltammograms were obtained.

3.6. Electrocatalytic reduction of dissolved oxygen at ITS/PLL-GA modified GCE

The electrocatalytic reduction of dissolved oxygen was investigated using CV and RDE (Fig. 7A and B). The amount of dissolved oxygen was measured by using commercially available oxygen meter. As shown in Fig. 7A, curve (a) indicated the reduction peak of ITS/PLL-GA/GCE, (b) PLL-GA/GCE modified electrode and (a') bare GCE in 0.1 M acetate buffer solution (pH 5.6) containing 3.1 μM dissolved oxygen. The catalytic peak potential for oxygen reduction is found at -0.09 V for ITS/PLL-GA film modified GCE, whereas PLL-GA/GCE and bare GCE exhibit reduction peak at around -0.48 and -0.58 V. Therefore, a decrease of about 0.39 and 0.49 V in over potential and the significant enhancement of the reduction peak current were achieved with ITS/PLL-GA film modified GCE. This result indicated that using the ITS/PLL-GA film

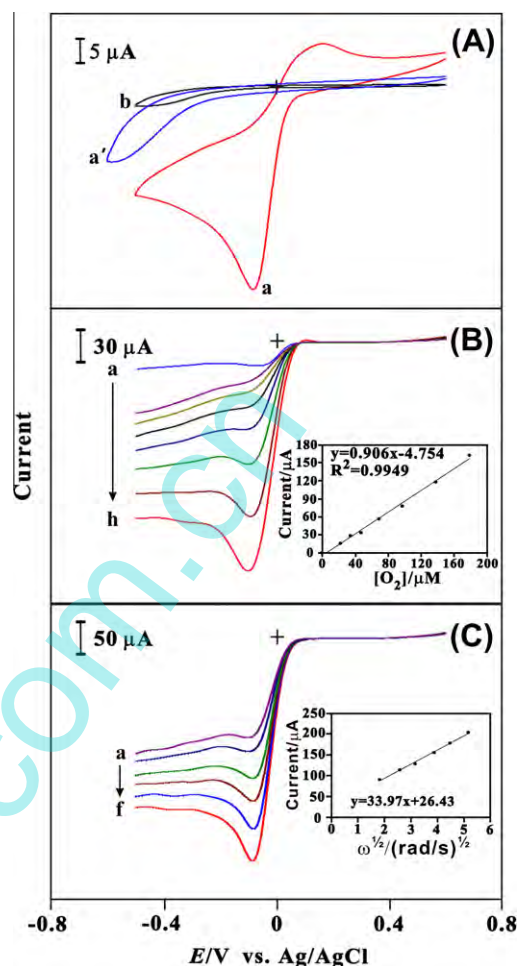


Fig. 7. (A) CVs of (a) ITS/PLL-GA/GCE, (b) PLL-GA/GCE and (a') bare GCE in 0.1 M acetate buffer solution (pH 5.6) containing 3.1 μM dissolved oxygen. (B) RDE voltammograms of ITS/PLL-GA film for the detection of dissolved oxygen in 0.1 M acetate buffer solution (pH 5.6). Dissolved oxygen concentrations were in the range of (a-h): 0, 22.2, 34.4, 47.0, 68.9, 97.1, 137.7, and 178.4 μM . Rotating speed: 1000 rpm. Inset: calibration plot of reduction current vs. concentration of dissolved oxygen. (C) RDE voltammograms of ITS/PLL-GA film in 0.1 M acetate buffer solution (pH 5.6) containing 178.4 μM dissolved oxygen at different electrode rotation rate speed: (a) 200, (b) 400, (c) 600, (d) 900, (e) 1200, and (f) 1600 rpm.

modified electrode can help to enhance the electro catalytic reduction of dissolved oxygen.

The RDE technique was employed for the detection of dissolved oxygen in 0.1 M acetate buffer solution. The rotation speed of ITS/PLL-GA film modified GCE was set to be as 1000 rpm and the reduction progress has been examined within the potential of +0.6 to -0.5 V, scan rate = 0.1 V/s. Curve (a)–(h) of Fig. 7B showed that there is a great increase in the cathodic peak current at ITS/PLL-GA/GCE for the increasing concentrations of dissolved oxygen (0, 22.2, 34.4, 47.0, 68.9, 97.1, 137.7 and 178.4 μM) in 0.1 M acetate buffer solution. The reduction peak current vs. concentration of the dissolved oxygen has been plotted and shown in the inset of Fig. 7B. The calibration plot is linear in the entire range (0–178.4 μM , $R^2 = 0.9949$) of dissolved oxygen concentration studied with a sensitivity of $906 \mu A mM^{-1}$. The detection limit was found to be 2.2 μM and the relative standard deviation (RSD) for determining dissolved oxygen ($n = 3$) was 4.2%, respectively. These results showed the electro-catalytic oxygen reduction occurs at ITS/PLL-GA film modified GCE. Fig. 7C showed the RDE voltammograms in the presence of 178.4 μM dissolved oxygen on ITS/PLL-GA modified electrode at different rotation rates. The catalytic current of oxygen reduction

Table 1

Comparison of the determination of dissolved oxygen by various electrochemical modified electrodes. Linear concentration range (LCR). Limit of detection (LOD).

Modified electrode	Method	E_{pc} (mV)	Electrolyte	LCR (μM)	LOD (μM)	Sensitivity ($\mu\text{A mM}^{-1}$)	Reference
Au–Ag alloy nanoparticles/GCE	CV	–550 (–)	PBS (pH 7.2)	–	–	–	[34]
Ag-deposited microelectrode	CV	–400 (Ag/AgCl, 3 M KCl)	0.01 M KCl (pH 7.0)	1.7–24.9	1.72	–	[35]
BMT ^a –Nafion/nano–Ag/GCE	CV, RDE	–440 (Ag/AgCl, sat. KCl)	PBS (pH 7.0)	9.4–10.6 (CV) 0.6–3.4 (RDE)	–	–	[23]
Sn-اداتoms-modified PAE ^b	CV, RDE	–209 (Ag/AgCl, sat. NaCl)	0.5 M H ₂ SO ₄ (pH 1.0)	–	–	–	[36]
Nafion/MV ^c /GDME ^d	CV	–450 (Ag/AgCl, sat. KCl)	PBS (pH 7.4)	0.3–29.2	0.19	0.17	[37]
MWCNTs–Nafion–Hb ^e /GCE	CV, RDE	–200 (Ag/AgCl, sat. KCl)	H ₂ SO ₄ (pH 2.5)	6.9–2.8 (CV) 6.9–27.5 (RDE)	–	36.4	[38]
ITS/PLL–GA/GCE	CV, RDE	–90 (Ag/AgCl, sat. KCl)	Acetate buffer (pH 5.6)	0–178.4	2.2	906	This work

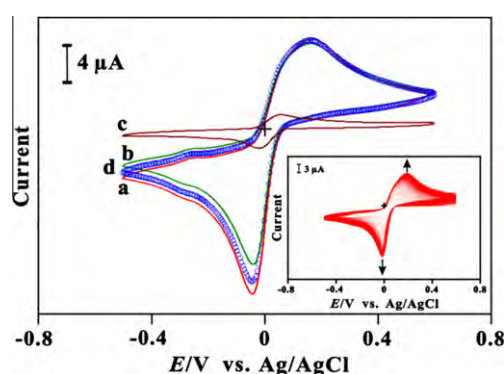
^a 1-Butyl-3-methylimidazolium tetrafluoroborate.^b Poly Au electrode.^c Methyl viologen.^d Gold disk microelectrode.^e Haemoglobin.

Fig. 8. CVs of ITS/PLL–GA/GCE at (a) initial, (b) after 1 week, (c) after 1 month and (d) regeneration situation in 0.1 M acetate buffer solution. Inset figure shows the CVs of the PLL–GA/GCE by consecutive sweeps in 0.1 M acetate buffer solution containing 0.5 M ITS. Potential range +0.6 to –0.5 V, Scan rate = 0.05 V/s.

was increased with the electrode rotation speed in the range of ((a) 200, (b) 400, (c) 600, (d) 900, (e) 1200, and (f) 1600 rpm) as shown in Levich plot (inset of Fig. 7C). This indicated that the oxygen reduction reaction was diffusion controlled process on modified electrode. The I_{pa} was found increased linearly with the rotation rate with slope 33.97 $\mu\text{A}/\text{rpm}$ and the diffusion coefficient for oxygen calculated from the Levich plot was $3.398 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Table 1 showed the comparison of the determination of dissolved oxygen by various electrochemical modified electrodes [26,37–41]. Compared with other modified electrodes in buffer solution, ITS/PLL–GA film modified GCE has the lowest over-potential at the determination of dissolved oxygen. Similarly, ITS/PLL–GA film modified GCE for the detection of dissolved oxygen also had a higher linear concentration range (LCR) in 0.1 M acetate buffer solution.

3.7. Stability and regeneration of ITS/PLL–GA film modified GCE

The stability of ITS/PLL–GA film modified electrode was then investigated by storing it at room temperature in the presence of 0.1 M acetate buffer solution (pH 5.6). It was stable for 1 week (curve (b) of Fig. 8, current values decrease 15%) but thereafter there was a decrease (80%) in the current values after 1 month (curve (c) of Fig. 8). Curve (d) of Fig. 8 indicated the background CV signal of ITS/PLL–GA film modified GCE. When ITS/PLL–GA film modified electrode store for a month in pure 0.1 M acetate buffer solution (pH 5.6), the voltammetric response current of dissolved oxygen decreased by 85% of the initial current. This may be the diffusion of the ITS from the PLL–GA film to the buffer, and therefore of limited binding of the ITS to the membrane. In order to restore

the background peak current and electro-catalytic activity of the electrode, ITS film was electrodeposited again onto the electrode surface following the same procedure mentioned earlier (inset of Fig. 8). The re-modified electrode exhibited almost the same redox peak current (curve (d) of Fig. 8) and electro-catalytic activities towards the determination of dissolved oxygen. The reason is that the weak response of modified electrode still consist PLL–GA, ITS/PLL–GA film modified electrode can be regenerated. These results suggest that ITS/PLL–GA film modified GCE had high stability and the ability of regeneration.

4. Conclusion

ITS/PLL–GA film was successfully electrodeposited on GCE and characterized using AFM, SEM, UV–vis spectrum, EQCM and EIS. The advantages of the ITS/PLL–GA film were demonstrated for the determination of dissolved oxygen in 0.1 M acetate buffer solution (pH 5.6) with a correlation coefficient of 0.9949 and a sensitivity of $906 \mu\text{A mM}^{-1}$. The detection limit was found to be $2.2 \mu\text{M}$. For the determination of dissolved oxygen, ITS/PLL–GA film modified GCE had the lowest over-potential at –0.09 V. Also, ITS/PLL–GA film modified GCE had high stability and the ability of regeneration.

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References

- [1] H. Maeda, Adv. Drug Deliv. Rev. 6 (1991) 181–202.
- [2] C. Li, Adv. Drug Deliv. Rev. 54 (2002) 695–713.
- [3] F.C. Pereira, A.G. Fogg, M.V.B. Zanoni, Talanta 60 (2003) 1023–1032.
- [4] F.C. Pereira, A.G. Fogg, P. Ugo, E.P. Bergamo, N.R. Stradiotto, M.V.B. Zanoni, Electroanalysis 17 (2005) 1309–1316.
- [5] R. De Cassia Silva Luz, F. Santos Damos, A. Bof de Oliveira, J. Beck, L.T. Kubota, Electrochim. Acta 50 (2005) 2675–2683.
- [6] C.O. Costa, P.R.B. Miranda, B. Hazra, M.D. Sarma, R.C.S. Luz, L.T. Kubota, M.O.F. Goulart, Talanta 68 (2006) 1378–1383.
- [7] R.C.S. Luz, F.S. Damos, A.A. Tanaka, L.T. Kubota, Sens. Actuators B 114 (2006) 1019–1027.
- [8] S.C.C. Monterroso, H.M. CarapuAa, A.C. Duarte, Talanta 68 (2006) 1655–1662.
- [9] E.R.C. Viana, F.C. Pereira, M.V.B. Zanoni, Dyes Pigm. 71 (2006) 145–152.
- [10] L. Duan, Q. He, X. Yan, Y. Cui, K. Wang, J. Li, Biochem. Biophys. Res. Commun. 354 (2007) 357–362.
- [11] W.J. Tong, C.Y. Gao, H. Mohwald, Macromolecules 39 (2006) 335–340.
- [12] M.M.A. Sekar, P.D. Hampton, T. Buranda, G. Lopez, J. Am. Chem. Soc. 121 (1999) 5135–5141.
- [13] F.C. Pereira, E.P. Bergamo, N.R. Stradiotto, M.V.B. Zanoni, A.G. Fogg, Electroanalysis 16 (2004) 1439–1443.
- [14] F.C. Anson, J.M. Saveant, K. Shigehara, J. Am. Chem. Soc. 105 (1983) 1096–1106.

- [15] Y.-C. Wu, R. Thangamuthu, S.-M. Chen, *Electroanalysis* 21 (2009) 953–958.
- [16] R. Pirezad, J.C. Moreira, A.E. Davies, A.G. Fogg, *Analyst* 119 (1994) 2439–2442.
- [17] R. Thangamuthu, Y.-C. Pan, S.-M. Chen, *Electroanalysis* 22 (2010) 1812–1816.
- [18] Y.-C. Pan, R. Thangamuthu, S.-M. Chen, *Electroanalysis* 22 (2010) 1115–1122.
- [19] R. Mazeikiene, A. Malinauskas, *Eur. Polym. J.* 36 (2000) 1347–1353.
- [20] R. Mazeikiene, A. Malinauskas, *Eur. Polym. J.* 38 (2002) 1947–1952.
- [21] T. Komura, T. Yamaguchi, K. Takahashi, H. Terasawa, *J. Electroanal. Chem.* 481 (2000) 183–191.
- [22] T. Komura, T. Yamaguchi, H. Shimatani, R. Okushio, *Electrochim. Acta* 49 (2004) 597–606.
- [23] N. Nestle, T. Baumann, R. Niessner, *Water Res.* 37 (2003) 3361–3366.
- [24] J.A. MacPhee, J.-P. Charland, L. Giroux, *Fuel Process. Technol.* 87 (2006) 335–341.
- [25] J.-P. Charland, J.A. MacPhee, L. Giroux, J.T. Price, M.A. Khan, *Fuel Process. Technol.* 81 (2003) 211–221.
- [26] T.-H. Tsai, S. Thiagarajan, S.-M. Chen, *Electroanalysis* 22 (2010) 680–687.
- [27] A. Chandra, S. Chandra, *J. Phys. D: Appl. Phys.* 27 (1994) 2171–2179.
- [28] L.M. Abrantes, C.M. Cordas, E. Vieil, *Electrochim. Acta* 47 (2002) 1481–1487.
- [29] V.S. Vasantha, S.-M. Chen, *Electrochim. Acta* 51 (2005) 347–355.
- [30] C.G. Zoski, *Handbook of Electrochemistry*, first ed., Elsevier, Boston, 2007.
- [31] R.W. Murray, In *Electroanalytical Chemistry*, in: A.J. Bard (Ed.), Marcel Dekker, Inc, New York, 1983, pp. 191–192.
- [32] A.J. Bard, L.R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, second ed., Wiley, New York, 1980.
- [33] S. Sinha, B.D. Humphrey, A.B. Bocarsly, *Inorg. Chem.* 23 (1984) 203–212.
- [34] F.C. Pereira, M.V.B. Zanoni, *Electroanalysis* 19 (2007) 993–998.
- [35] J. Haladjian, I.T. Chef, P. Bianco, *Talanta* 43 (1996) 1125–1130.
- [36] R. Thangamuthu, Y.-C. Wu, S.-M. Chen, *Electroanalysis* 21 (2009) 994–998.
- [37] S. Devarajan, P. Bera, S. Sampath, *J. Colloid, Interf. Sci.* 290 (2005) 117–129.
- [38] Y.-P. Chen, S.-Y. Liu, F. Fang, S.-H. Li, G. Liu, Y.-C. Tian, Y. Xiong, H.-Q. Yu, *Environ. Sci. Technol.* 42 (2008) 8465–8470.
- [39] Md.R. Miah, T. Ohsaka, *Electrochim. Acta* 54 (2009) 5871–5876.
- [40] W. Sun, J. Xue, J. Chen, L. Mao, L. Jin, K. Yamamoto, S. Tao, J. Jin, *Talanta* 49 (1999) 345–356.
- [41] J.-W. Shie, U. Yogeswaran, S.-M. Chen, *Talanta* 78 (2009) 896–902.