

# Anthraquinonedisulfonate Doped Glutaraldehyde Cross-linked Poly-L-lysine Modified Electrode for $S_2O_8^{2-}$ , $IO_3^-$ and Oxygen Reduction

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The anthraquinone-2,6-disulfonate (AQDS) and poly-l-lysine (PLL) - glutaraldehyde (GA) film (AQDS/PLL-GA) was prepared on a glassy carbon electrode (GCE) by multiple scan cyclic voltammetry. This nanocomposite film was characterized using atomic force microscopy, scanning electron microscopy and electrochemical impedance spectroscopy. The advantages of the film were demonstrated for the determination of  $S_2O_8^{2-}$ ,  $IO_3^-$  and dissolved oxygen using cyclic voltammetry and rotating disk electrode voltammetry. The electrocatalytic reduction of  $S_2O_8^{2-}$ ,  $IO_3^-$  and dissolved oxygen at different electrode surfaces, such as bare GCE, PLL-GA/GCE and AQDS/PLL-GA/GCE modified electrodes, was determined in 0.1 M PBS (pH 7.0). The electrochemical sensor exhibited wide linear response range, low detection limit, high sensitivity and good stability.

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**Keywords:** Anthraquinone-2,6-disulfonate, poly-l-lysine, cyclic voltammetry, modified electrodes

## 1. INTRODUCTION

Quinone compounds are the electron accepting moieties of humic substances and play an important role not only as final electron acceptor for many recalcitrant organic compounds, but also facilitating electron transfer from an electron donor to an electron acceptor, like azo dyes [1-3]. Among them, anthraquinone-2, 6-disulfonate (AQDS) as a model quinone compound has received the greatest attention for its wide adaptability. It can not only accelerate the reduction of nitroaromatic compounds, but also improve the dechlorination of polyhalogenated hydrocarbon. AQDS also can function as redox mediator and have been proved to be effective one-electron-transfer mediators for oxygen reduction reaction (ORR) in aerated solution [4-14]. Some electrochemical researchers have found that

AQDS is a good catalyst for different modified electrode reactions [15, 16]. Quinone immobilized in a polymer matrix of its redox and transport properties has been extensively studied in the literature [17-23]. It has also been pointed out that the electrodes modified with conducting polymers doped by AQDS exhibits excellent electrocatalytic activities as well as remarkable stability compared with those modified with spontaneously adsorbed monolayer of AQDS [24, 25].

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 [26, 27] and as versatile class of polyaminoacids used for coating several types of electrodes. Also, PLL can be used as cationic polyaminoacid ( $pK_a=10.4$ ) and used for anion detection [28-34]. Due to its versatility and easiness to preparation, PLL have been used recently for modification of several types of electrodes (glassy carbon, platinum or gold etc...) and applied for electrochemical determination of biological molecules, pharmaceutical compounds, dyes and metals [30-34]. However, it has been shown that when a film composition of 97.5% PLL: 2.5% glutaraldehyde (GA) and then heated at about 80°C give good adhesion and retains the anionic exchange capability of PLL-GA film [35-37]. The PLL-GA film is much more similar to the protein site of more complex biological molecules than those of other polymers [35, 37]. Therefore, the PLL matrix with characteristics of harmlessness and high environmental stability could be used as a good carrier for immobilizing AQDS.

In the present work, a novel and stable AQDS films are prepared by electrodeposited on PLL-GA film coatings on glassy carbon electrode. The film growth and electrochemical properties of the modified electrodes are studied. The electrocatalytic activity of AQDS/PLL-GA film modified electrode toward reduction of  $IO_3^-$ ,  $S_2O_8^{2-}$  and dissolved oxygen were investigated. Different methods and analytical techniques have been reported in the literature for the determination of  $IO_3^-$ ,  $S_2O_8^{2-}$  and dissolved oxygen, including nuclear magnetic resonance (NMR), thermogravimetry–Fourier transform infrared (TG-FTIR) and electrochemical methods [38-41]. Among these, electrochemical methods have been considered to be an effective way of quick response, low cost, simple of instrumentation, high sensitivity and possibility of miniaturization. Finally, the surface morphology of AQDS film and AQDS/PLL-GA modified electrode has been examined by using SEM and AFM. The AQDS/PLL-GA film modified electrode successfully employed for the detection of dissolved oxygen in phosphate buffer solution (PBS, pH 7.0) using cyclic voltammetry (CV) and rotating disk electrode (RDE) techniques. The EIS technique also employed for the detection of dissolved oxygen using AQDS/PLL-GA modified GCE.

## 2. EXPERIMENTAL

### 2.1. Reagents

Anthraquinone-2, 6-disulfonic acid disodium salt, 90%, mixture of isomers (AQDS), poly-L-lysine hydrobromide (Mol wt = 70000 ~ 150000) (PLL) and glutaraldehyde 25% 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. A phosphate buffer solution (PBS, pH 7.0) was prepared using  $\text{Na}_2\text{HPO}_4$  (0.1 M) and  $\text{NaH}_2\text{PO}_4$  (0.1 M). Pure nitrogen was passed through all the experimental solutions.

## 2.2. Apparatus

All electrochemical experiments were performed using CHI 750a potentiostats (CH Instruments, USA). The BAS GCE ( $\phi = 0.3$  cm in diameter, exposed geometric surface area  $0.07$  cm<sup>2</sup>, 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 AQDS/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 microscope (SEM) images were performed using HITACHI S-3000H (Japan). The AFM images were recorded with multimode scanning probe microscope (Being Nano-Instruments CSPM-4000, China). 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 AQDS/PLL-GA film

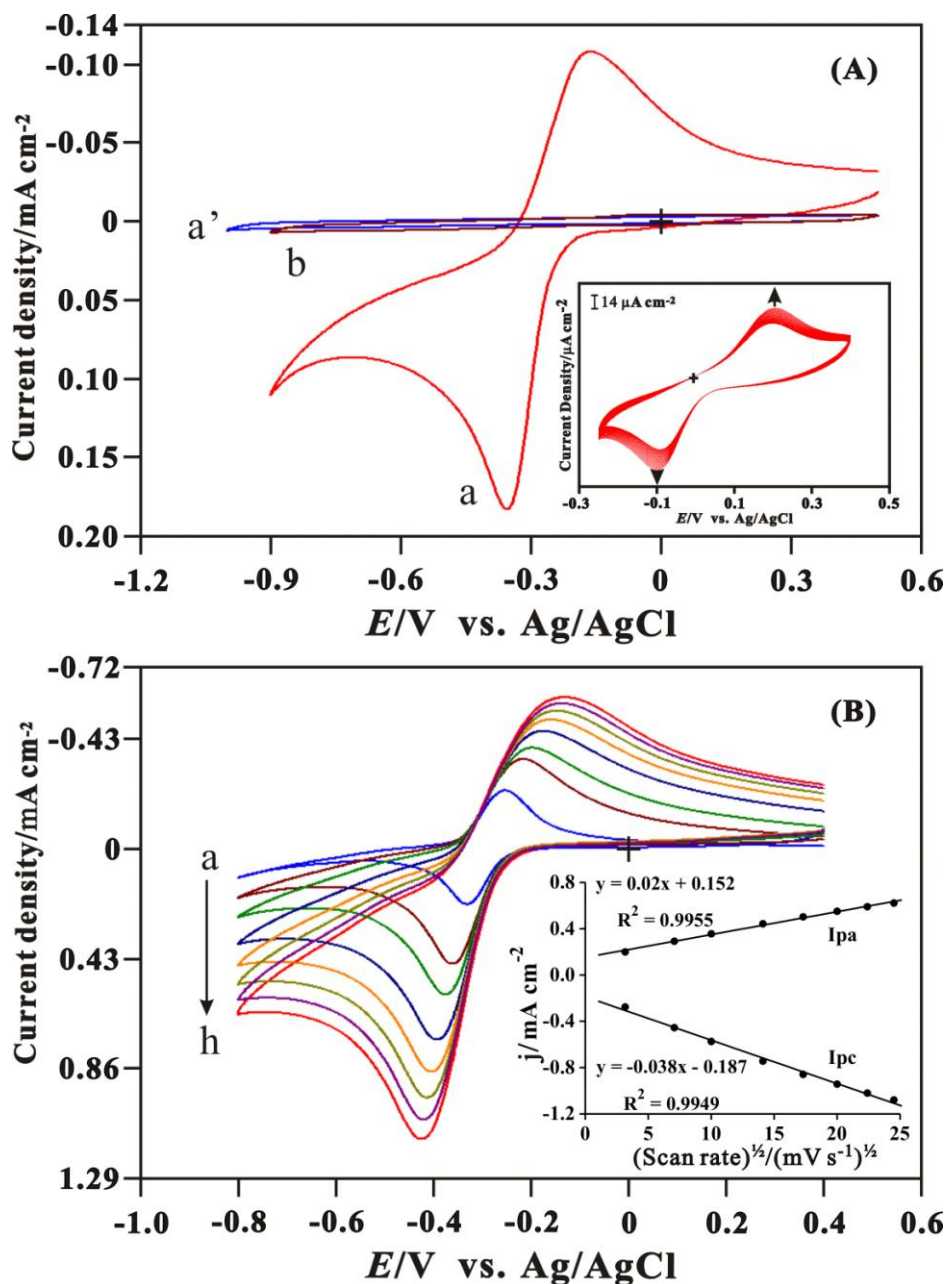
Prior to the electrochemical deposition process, the GCE was well polished with the help of BAS polishing kit with aqueous slurries of alumina powder ( $0.05$   $\mu\text{m}$ ), rinsed and ultrasonicated in double distilled deionized water. Solutions of product of poly-L-lysine and glutaraldehyde were 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 [35-37].  $10$   $\mu\text{L}$  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  $80^\circ\text{C}$  for 15 min. The PLL-GA/GCE was electrodeposited with AQDS film by performing in  $10$  ml  $0.1$  M  $\text{H}_2\text{SO}_4$  (pH 1.0) containing  $5$  mM AQDS and the potential cycling between  $+0.4$  and  $-0.25$  V at the scan rate of  $0.05$  V/s for 50 cycles.

## 3. RESULTS AND DISCUSSION

### 3.1. Electrodeposition of AQDS Film on PLL-GA/GCE

As shown in the inset figure of Fig. 1A, AQDS film was successfully electrodeposited on PLL-GA/GCE between  $+0.4$  and  $-0.25$  V at the scan rate of  $0.05$  V/s for 50 cycles between AQDS and PLL-GA film. In Fig. 1, curve (a) indicates the CV signals of AQDS/PLL-GA/GCE, the oxidation and

reduction peaks of AQDS/PLL-GA/GCE are separated as -0.16 and -0.35 V in 0.1 M PBS (pH 7.0). In the same buffer solution, there was no obvious response at the curve of (b) PLL-GA/GCE and (a') bare GCE. Also mentioned, AQDS film cannot be directly deposited on plate electrode (GCE, ITO, Au electrode, etc...). All the above results indicate that the AQDS/PLL-GA film modified GCE shows a stable and higher current in 0.1 M PBS (pH 7.0).



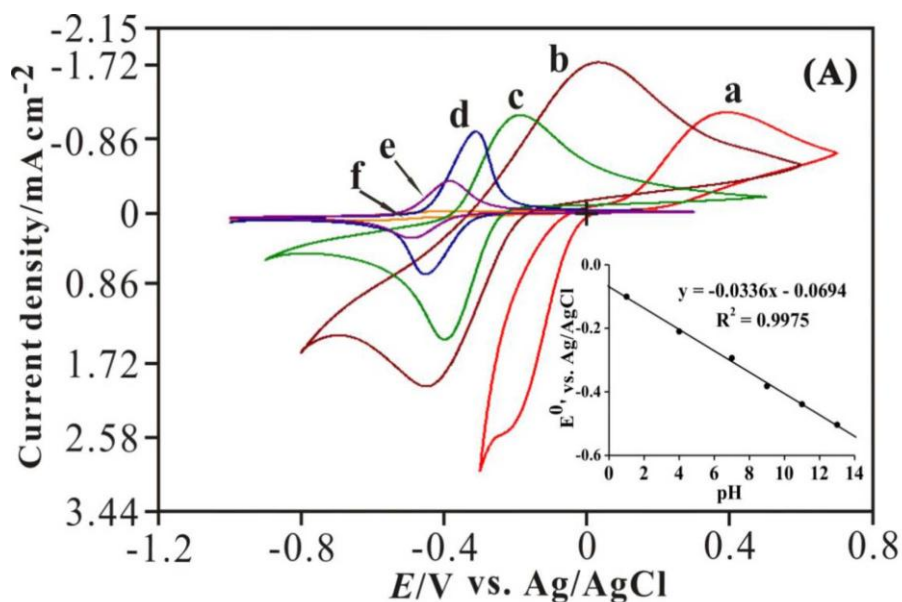
**Figure 1.** (A) CVs of (a) AQDS/PLL-GA/GCE, (b) PLL-GA/GCE and (a') bare GCE in 0.1 M PBS (pH 7.0) Inset figure shows the CVs of the PLL-GA/GCE by consecutive sweeps in 0.1 M H<sub>2</sub>SO<sub>4</sub> (pH 1.0) containing 5 mM AQDS. Potential range +0.4 to -0.25 V, Scan rate = 50 mV s<sup>-1</sup>. (B) Results of different scan rate studies of AQDS/PLL-GA film modified GCE in 0.1 M PBS (pH 7.0). Potential range +0.4 to -0.8 V, scan rate in the range of a-h: 10 - 600 mV s<sup>-1</sup>. Inset shows dependence of both anodic and cathodic peak currents on the scan rates.

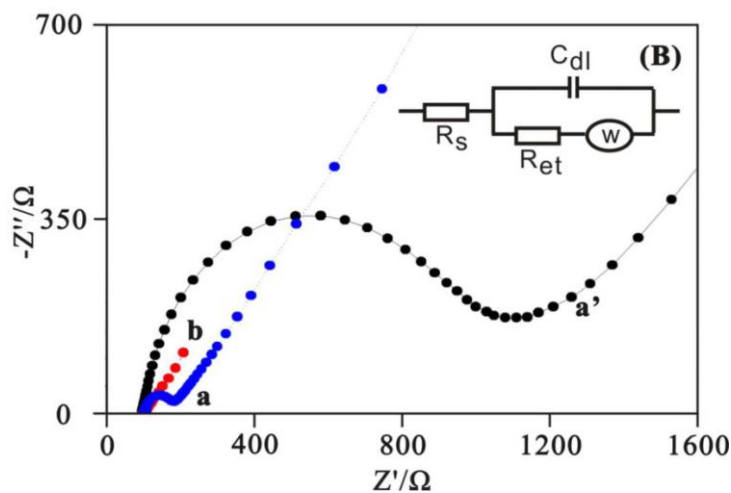
In order to confirm the AQDS/PLL-GA film was successfully immobilized on the electrode surface, it was transferred to pH 7.0 PBS for CV studies. By the way, the influence of scan rate on the electrochemical response of AQDS/PLL-GA film modified GCE was also investigated. Fig. 1B shows cyclic voltammograms of AQDS/PLL-GA/GCE were performed for the different scan rate studies. According to the obvious redox couple, it represents AQDS/PLL-GA can be modified on GCE in 0.1 M PBS (pH 7) at different scan rate in the range of (a) 10, (b) 50, (c) 100, (d) 200, (e) 300, (f) 400, (g) 500, (h) 600 mV/s. In the potential range of +0.4 to -0.8 V, the AQDS/PLL-GA film exhibits anodic peak and cathodic peak at the range of -0.26 to -0.15 V and -0.33 to -0.43 V versus Ag/AgCl/KCl<sub>sat</sub>. The inset of Fig. 1B shows the plot of AQDS/PLL-GA film signal of anodic and cathodic peak current vs. the square root of scan rate. The corresponding linear regression equations were found as  $I_{pa} (\mu A) = 0.02v (V/s) + 0.152$ ,  $R^2 = 0.9955$  and  $I_{pc} (\mu A) = -0.038v (V/s) - 0.187$ ,  $R^2 = 0.9949$ . Here the linear increase in the anodic and cathodic peak currents of AQDS/PLL-GA film modified GCE according to the scan rate illustrates that the film may be very thick since there is a bulk diffusion behavior. It was a typical characteristic of diffusion controlled electrochemical behavior [42, 43].

### 3.2. Electrochemical properties of AQDS/PLL-GA film modified GCE

#### 3.2.1 pH effect

Fig. 2A shows cyclic voltammograms of AQDS/PLL-GA film modified electrode of different pH values (pH 1, 4, 7, 9, 11, 13). The  $E^{0'}$  of the redox couple ( $E_{pa} + E_{pc}$ )/2 was found to shift to more negative potential direction and peak currents decreases with increasing pH value. This behavior might be when the PLL film in aqueous solutions below pH 10.5, NH<sub>2</sub> groups in PLL are in the protonated state, and PLL exists in a random coil conformation.





**Figure 2.** (A) CVs of AQDS/PLL-GA film modified GCE at pH 1, 4, 7, 9, 11 and 13 solutions. Scan rate =  $50 \text{ mV s}^{-1}$ . Inset: Plots of formal potentials of redox couples versus pH. (B) EIS curves of (a') bare GCE, (b) PLL-GA, and (a) AQDS/PLL-GA film modified GCE in 0.1 M PBS (pH 7.0) containing  $5 \times 10^{-3} \text{ M K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  (molar ratio = 1:1).

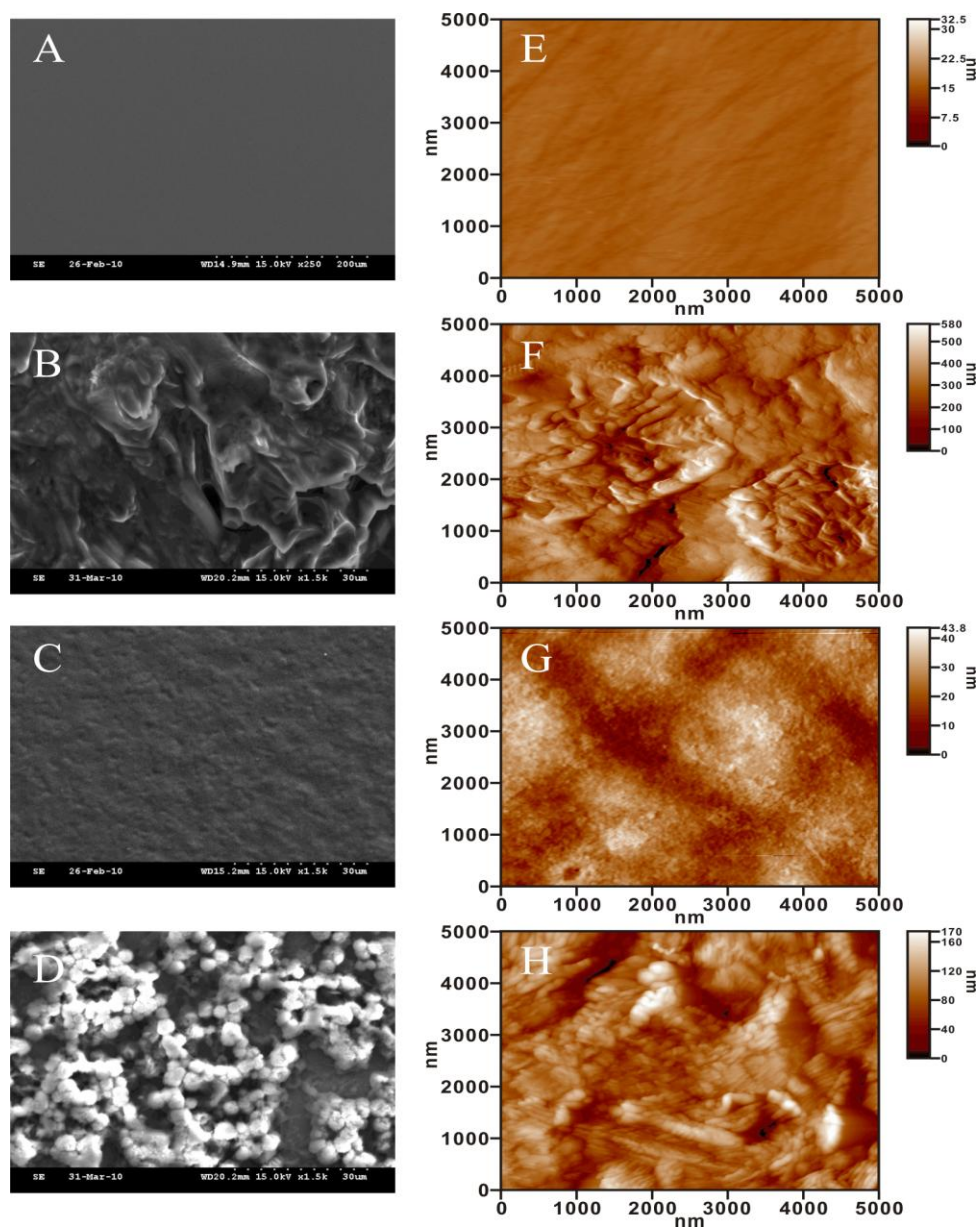
On the contrary, at  $\text{pH} > 10.5$ ,  $\text{NH}_2$  groups are deprotonated and PLL in solution acquires  $\alpha$ -helical conformation [35, 37, 46, 50]. For this reason, pH 7.0 was chosen as the appropriate pH value for determination of oxygen since larger currents and the best voltammograms were obtained.

### 3.2.2 EIS analysis

The electrochemical activity of AQDS/PLL-GA film modified GCE has been examined using EIS technique. Here the complex impedance can be presented as a sum of the real  $Z'$  ( $\omega$ ), and imaginary  $Z''$  ( $\omega$ ), 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 ( $R_{\text{et}}$ ) and the double layer capacity ( $C_{\text{dl}}$ ) nature of the modified electrode. As shown in Fig. 2B, curve (a') indicates the Nyquist plot of bare GCE, (b) PLL-GA/GCE and (a) AQDS/PLL-GA/GCE in the presence of 5 mM  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  (1:1) in 0.1 M PBS (pH 7.0). The PLL-GA/GCE shows a very small depressed semi circle arc with an interfacial resistance due to its effectively in facilitating electron transfer in negatively molecules,  $\text{Fe}(\text{CN})_6^{3-/4-}$  [37, 46, 47]. This depressed semi circle arc ( $R_{\text{et}} = 96.2 \text{ (Z}'/\Omega)$ ) of PLL-GA/GCE clearly indicates the higher electron transfer resistance behavior comparing with bare GCE ( $R_{\text{et}} = 1030 \text{ (Z}'/\Omega)$ ) and AQDS/PLL-GA/GCE ( $R_{\text{et}} = 166 \text{ (Z}'/\Omega)$ ). These results clearly illustrate the electrochemical activities of AQDS/PLL-GA, PLL-GA film modified GCE and bare GCE, respectively.

### 3.3. AFM & SEM analysis

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were utilized to image the morphology of (A) (E) bare GCE, (B) (F) AQDS, (C) (G) PLL-GA and (D) (H) AQDS/PLL-GA film modified at glassy carbon electrode, as shown in Fig. 3.

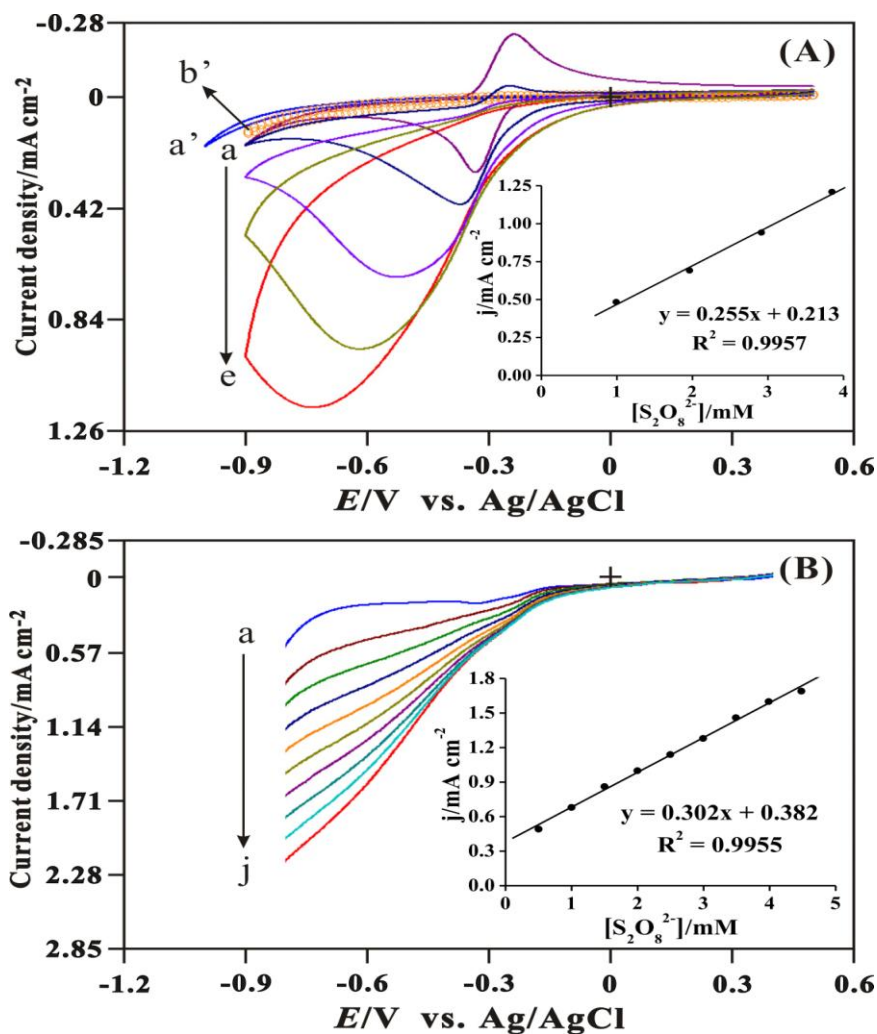


**Figure 3.** SEM images of (A) bare GCE, (B) AQDS/GCE, (C) PLL-GA/GCE and (D) AQDS/PLL-GA/GCE; tapping mode AFM images of (E) bare GCE, (F) AQDS/GCE, (G) PLL-GA/GCE and (H) AQDS/PLL-GA/GCE.

The AQDS/GCE was formed by dropping on GCE. The AFM images of these films showed average diameter of 90 nm, 41 nm, and 66 nm for AQDS, PLL-GA, and AQDS/PLL-GA in  $5000 \times 5000$  nm surface area by using the tapping mode, respectively. And the height of nano-grains was found in 89 nm, 7.5 nm, and 29 nm. By comparison, the PLL-GA layer has wide porous surface and provides a large porous electrode structure to enhance the stability and modification of thin film materials in SEM and AFM images. Moreover, it is found that AQDS/PLL-GA shows the average diameter size between AQDS and PLL-GA. It might be caused by the static adsorption between positive charge of PLL-GA and AQDS. As expected, the polymer (PLL-GA) network with a highly porous structure can be seen, which might easily entrap AQDS nano particles.

3.4. Electrocatalytic Reduction of  $S_2O_8^{2-}$ ,  $IO_3^-$  and Dissolved Oxygen at AQDS/PLL-GA Modified GCE3.4.1. Mediated Reduction of  $S_2O_8^{2-}$ 

Fig. 4A shows cyclic voltammograms of AQDS/PLL-GA film modified electrode in pH 7 PBS (curve a) and in the presence of different concentration of  $S_2O_8^{2-}$  in the range of 0 to  $3.8 \times 10^{-3}$  M (curve a-e).



**Figure 4.** (A) CVs of AQDS/PLL-GA modified GCE in 0.1 M PBS (pH 7.0) containing  $S_2O_8^{2-}$  (a) 0.0 mM, (b) 1.0 mM, (c) 2.0 mM, (d) 3.0 mM, (e) 4.0 mM, and (a') bare GCE (b') PLL-GA/GCE with 4.0 mM  $S_2O_8^{2-}$ . (B) RDE voltammograms of AQDS/PLL-GA modified GCE in 0.1 M PBS (pH 7.0) containing  $S_2O_8^{2-}$  (a) 0.0 mM, (b) 0.5 mM, (c) 1.0 mM, (d) 1.5 mM, (e) 2.0 mM, (f) 2.5 mM, (g) 3 mM, (h) 3.5 mM, (i) 4 mM, (j) 4.5 mM.

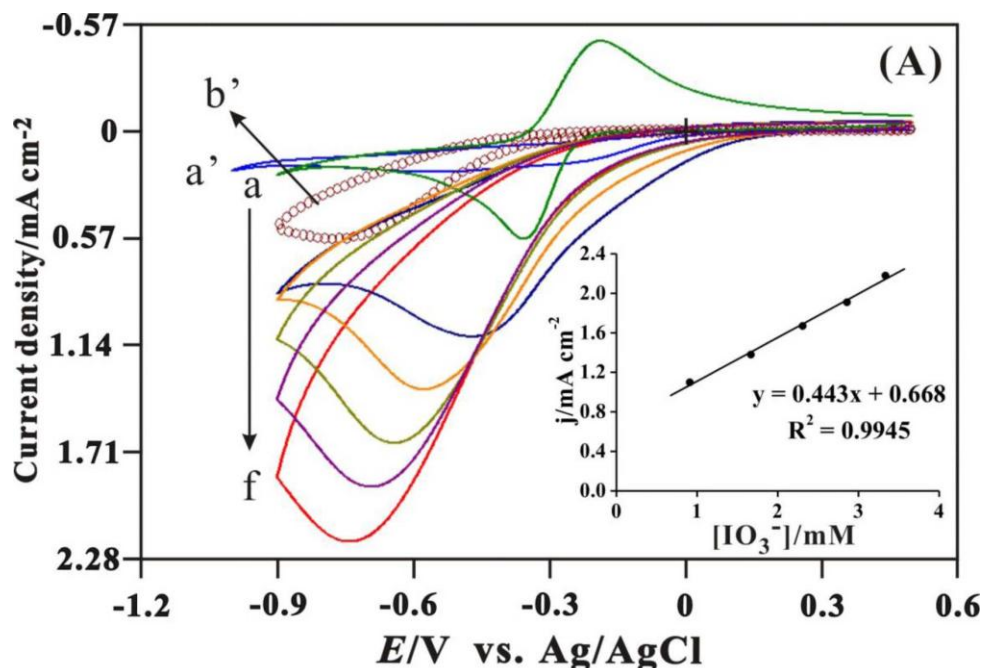
Curve a' and b' represents reduction of  $3.8 \times 10^{-3}$  M  $S_2O_8^{2-}$  on bare GCE and PLL-GA/GCE. It can be seen that there is no appreciable direct reduction of  $S_2O_8^{2-}$  occurred on bare electrode and PLL-GA/GCE. On the other hand, the cathodic peak currents of AQDS/PLL-GA film electrode increases noticeably with increasing concentration of  $S_2O_8^{2-}$ , while the anodic peak currents decreased. These

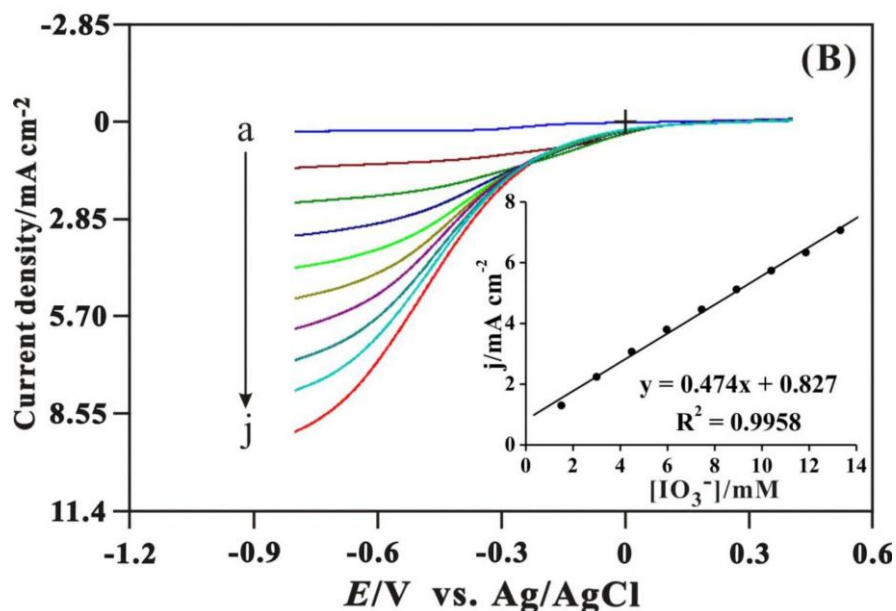


results indicate that the AQDS/PLL-GA film mediated the reduction of  $S_2O_8^{2-}$ . The RDE technique was employed for the detection of  $S_2O_8^{2-}$  in 0.1 M PBS (pH = 7.0) in Fig. 4B. The rotation speed of AQDS/PLL-GA film modified GCE was set to be as 1000 rpm and the reduction progress has been examined within the potential of +0.45 to -0.8 V, scan rate = 0.1 V/s. Curve a–j of Fig. 4B show that there is a great increase in the cathodic peak current at AQDS/PLL-GA/GCE for the increasing concentrations of  $S_2O_8^{2-}$  (0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, 4.0 and 4.5 mM) in 0.1 M PBS (pH 7.0). The reduction peak current vs. concentration of  $S_2O_8^{2-}$  has been plotted and shown in the Inset of Fig. 4B. The calibration plot is linear in the entire range (0.5 to 4.5 mM,  $R^2=0.9955$ ,  $n=3$ ) of  $S_2O_8^{2-}$  concentration studied with a sensitivity of  $0.24 \text{ mA mM}^{-1} \text{ cm}^{-2}$ . The detection limit was found to be 0.1 mM.

### 3.4.2. Mediated Reduction of $IO_3^-$

In Fig. 5A, it can be inferred from curve a' and b' that iodate is electrochemically inactive on bare GCE and PLL-GA/GC. In the case of modified electrode, only cathodic waves corresponding to the reduction of the AQDS anion products have the catalytic activity toward  $IO_3^-$  reduction. Fig. 5B shows RDE obtained by potential range of +0.45 to -0.8 V of AQDS/PLL-GA film modified electrode and injecting different concentrations of  $KIO_3$  into 0.1 M  $H_2SO_4$ . For each addition, a well reduction current response was obtained. As shown in the calibration curve in Fig. 5B, the current increases with increasing  $KIO_3$  concentration. As shown in the Figure, linear relationship between concentration and current was observed between 1.5 to 13.5 mM with sensitivity of  $0.52 \text{ mA mM}^{-1} \text{ cm}^{-2}$  and detection limit of 0.5 mM.

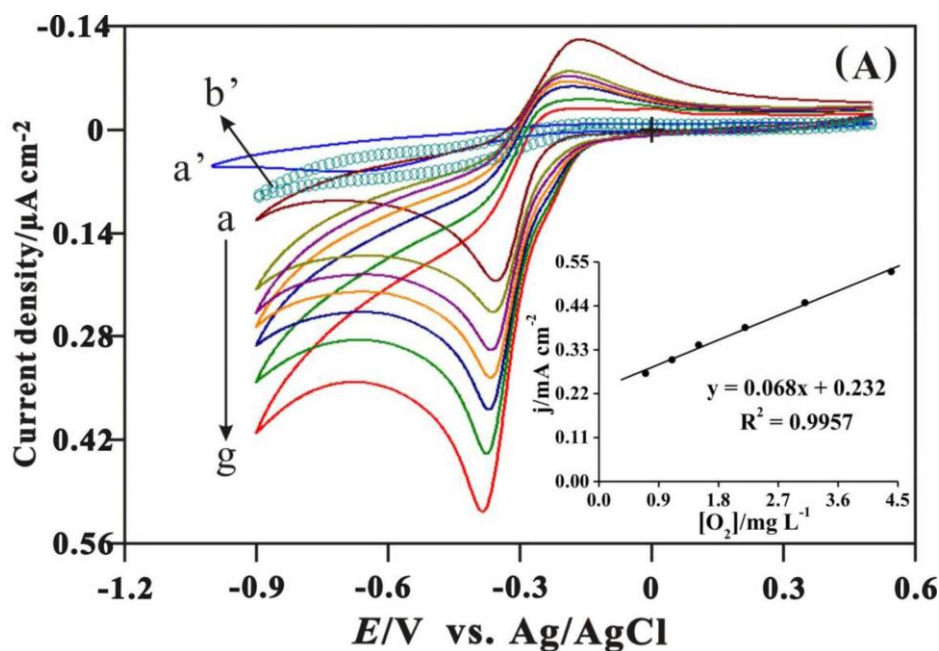


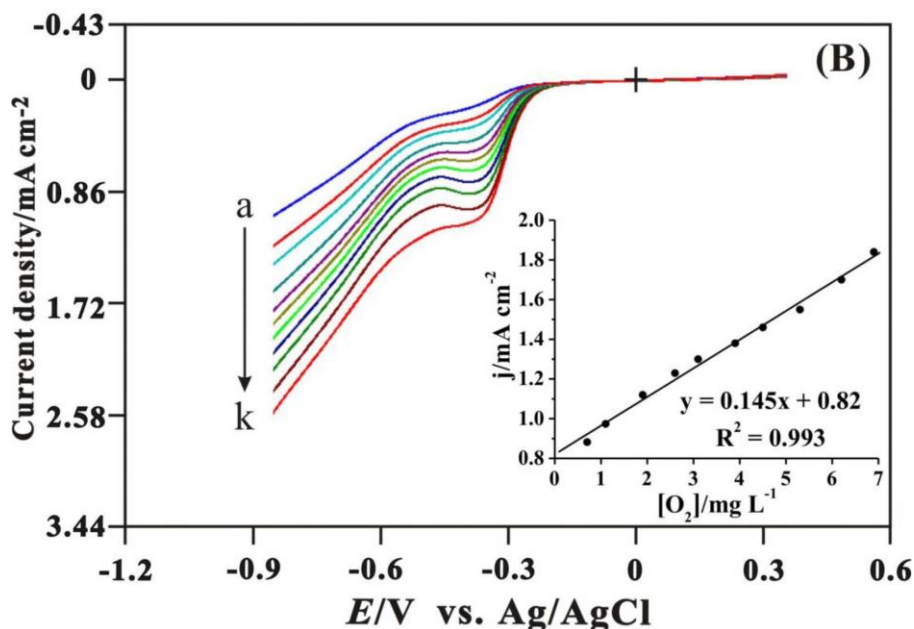


**Figure 5.** (A) CVs of AQDS/PLL-GA modified GCE in 0.1 M PBS (pH 7.0) containing  $\text{IO}_3^-$  (a) 0.0 mM, (b) 0.9 mM, (c) 1.7 mM, (d) 2.3 mM, (e) 2.9 mM, (f) 3.5 mM, and (a') bare GCE (b') PLL-GA/GCE with 3.5 mM  $\text{IO}_3^-$ . (B) RDE voltammograms of AQDS/PLL-GA modified GCE in 0.1 M PBS (pH 7.0) containing  $\text{IO}_3^-$  (a) 0.0 mM, (b) 1.5 mM, (c) 3.0 mM, (d) 4.5 mM, (e) 6.0 mM, (f) 7.5 mM, (g) 9.0 mM, (h) 10.5 mM, (i) 12.0 mM, (j) 13.5 mM.

### 3.4.3. Mediated Reduction of dissolved oxygen

The electrocatalytic reduction of dissolved oxygen was investigated using CV in Fig. 6A.





**Figure 6.** (A) CVs of AQDS/PLL-GA modified GCE in 0.1 M PBS (pH 7.0) containing dissolved oxygen (a) 0.0 mg L<sup>-1</sup>, (b) 0.7 mg L<sup>-1</sup>, (c) 1.1 mg L<sup>-1</sup>, (d) 1.5 mg L<sup>-1</sup>, (e) 2.2 mg L<sup>-1</sup>, (f) 3.1 mg L<sup>-1</sup>, (g) 4.4 mg L<sup>-1</sup>, and (a') bare GCE (b') PLL-GA/GCE with 4.4 mg L<sup>-1</sup> dissolved oxygen. Scan rate = 50 mV s<sup>-1</sup>. (B) RDE voltammograms of AQDS/PLL-GA modified GCE in 0.1 M PBS (pH 7.0) containing dissolved oxygen (a) 0.0 mg L<sup>-1</sup>, (b) 0.7 mg L<sup>-1</sup>, (c) 1.1 mg L<sup>-1</sup>, (d) 1.9 mg L<sup>-1</sup>, (e) 2.6 mg L<sup>-1</sup>, (f) 3.1 mg L<sup>-1</sup>, (g) 3.9 mg L<sup>-1</sup>, (h) 4.5 mg L<sup>-1</sup>, (i) 5.3 mg L<sup>-1</sup>, (j) 6.2 mg L<sup>-1</sup> and (k) 6.9 mg L<sup>-1</sup>. Scan rate = 50 mV s<sup>-1</sup>. Rotating speed: 1000 rpm.

The amount of dissolved oxygen was measured by using commercially available oxygen meter. As shown in Fig. 6A, curve a to g indicate the reduction peak of dissolved oxygen in the range of 0.7 to 4.4 mg/L of AQDS/PLL-GA/GCE. Curve (a') bare GCE and (b') PLL-GA/GCE modified electrode in 0.1 M PBS (pH 7.0) containing 4.4 mg/L dissolved oxygen. The catalytic peak potential for the oxygen reduction is found at -360 mV for AQDS/PLL-GA film modified GCE, whereas for PLL-GA/GCE and bare GCE they fail to exhibit reduction peak for the dissolved oxygen and show the peaks at around -480 and -683 mV. Therefore, a decrease of about 120 and 323 mV in overpotential and the significant enhancement of the reduction peak current are achieved with AQDS/PLL-GA film modified GCE. The RDE technique was employed for the detection of dissolved oxygen in 0.1 M PBS (pH = 7.0). The rotation speed of AQDS/PLL-GA film modified GCE was set to be as 1000 rpm and the reduction progress has been examined within the potential of +0.4 to -0.8 V, scan rate = 0.1 V/s. Curve a–k of Fig. 6B show that there is a great increase in the cathodic peak current at AQDS/PLL-GA/GCE for the increasing concentrations of dissolved oxygen (0.7, 1.1, 1.5, 2.2, 3.1 and 4.4 mg L<sup>-1</sup>) in 0.1 M PBS (pH 7.0). The reduction peak current vs. concentration of the dissolved oxygen has been plotted and shown in the Inset of Fig. 6B. The calibration plot is linear in the entire range (0.7 to 4.4 mg/L, R<sup>2</sup>=0.993, n=3) of dissolved oxygen concentration studied with a sensitivity of per mg/L for 0.07 mA cm<sup>-2</sup>. The detection limit was found to be 0.3 mg/L. This above result clearly indicates the occurrence of electrocatalytic reduction of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, IO<sub>3</sub><sup>-</sup> and dissolved oxygen at AQDS/PLL-GA film modified GCE.

Table 1 shows the comparison of AQDS with different polymer composites film modified electrodes [13-14, 20, 48-49]. Compared with other modified electrodes in buffer solution, the AQDS/PLL-GA film modified GCE has the lowest overpotential at the determination of  $S_2O_8^{2-}$ ,  $IO_3^-$  and dissolved oxygen. Similarly, the AQDS/PLL-GA film modified GCE also has a higher linear concentration range (LCR) in 0.1 M PBS (pH 7.0).

**Table 1.** Experimental conditions and analytical parameters for different modified electrodes. Linear concentration range (LCR).

Modified Electrode	$\Delta E_p$ (mV)	Analyte	$E_{app.}$ (mV)	LCR (mM)	Ref.
AQDS/Ppy/GCE	152 (pH 2.0)	Oxygen	-468	---	[48]
AQDS/PANI/GCE	144 (pH < 3.0)	Oxygen	-200	---	[13]
AQDS/PEDOT/GCE	20 (pH 1.0)	---	---	---	[49]
AQDS/Ppy/GCRDE	---	Oxygen, Azo dye	-650 (pH 3.0) -600 (pH 4.0) -520 (pH 6.0)	---	[20]
AQDS/HOPG <sup>[a]</sup>	75	Oxygen	-650	---	[14]
AQDS/PLL-GA/GCE	110 (pH 7.0)	$S_2O_8^{2-}$ $IO_3^-$ Oxygen	-370 -450 -360	0.5 ~ 4.5 1.5 ~ 130 0.7 ~ 6.9 (mg L <sup>-1</sup> )	This work

[a] Highly oriented pyrolytic graphite

### 3.5. Stability and Regeneration of AQDS/PLL-GA film modified GCE

The stability of AQDS/PLL-GA film modified electrode was then investigated by storing it at room temperature in the presence of 0.1 M PBS (pH 7.0). It was stable for one week (current values decrease 11%). In addition, the stability of these modified electrodes was also tested by scanning the electrode potential continuously 50 cycles in pure supporting electrolyte. After continuous cycling, the decrease in peak current of modified electrodes was less than 10%, indicating high stability of modified films and promising for sensor applications. These results suggest that the AQDS/PLL-GA film modified GCE has high stability.

## 4. CONCLUSION

In the present study, stable electrochemically active hybrid coatings were obtained by cycling the cationic coating covered electrode repetitively in pH 7 PBS containing PLL-GA polymers and AQDS anionic complexes. The AQDS film was successfully electrodeposited on PLL-GA/GCE and characterized using AFM, SEM, and EIS. The advantages of AQDS/PLL-GA film were demonstrated for the determination of  $S_2O_8^{2-}$ ,  $IO_3^-$  and dissolved oxygen in 0.1 M PBS with pH 7.0. The experimental methods of CV and RDE with nanocomposite film sensor integrated into the GCE which

is presented in this paper provide an opportunity for a qualitative and quantitative characterization. Therefore, this work establishes and illustrates, in principle and potential, a simple and novel approach for the development of voltammetric and amperometric sensor based on modified electrodes.

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