

# Electrochemical Sensor based on Carbon Paste Electrode Modified by TiO<sub>2</sub> nano-particles for the Voltammetric Determination of Resorcinol

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TiO<sub>2</sub> nano-particles were prepared and characterized by transmission electron microscope (TEM) and scanning electron microscope (SEM). A new carbon paste electrode modified by TiO<sub>2</sub> nano-particles was manufactured and characterized. The modified electrode was prepared by mixing TiO<sub>2</sub> nano-particles with graphite powder in presence of paraffin wax. The electrochemical activity of resorcinol (RS) was studied in Britton–Robinson (BR) buffer at different pH values using cyclic voltammetry (CV) and linear sweep (LSV). The results illustrated that the carbon paste modified electrode gave a good response for an electrocatalytic activity towards the electrochemical oxidation of RS. The electrochemical oxidation of RS at carbon paste electrode modified by TiO<sub>2</sub> nano-particles was diffusion-controlled and irreversible. By applying the optimum conditions for the determination of RS, a lower detection limit of  $1 \times 10^{-9}$  M was obtained. This method was applied for the determination of RS in tap water samples, and the recovery for RS from this study was 94% to 101.1%.

**Keywords:** Electrochemical Sensor; TiO<sub>2</sub> nano-particles; Voltammetry; Resorcinol

## 1. INTRODUCTION

Among the organic pollutants presented in water, phenol and its derivative compounds are important and a number of industrial processes contribute to it which have seriously dangerous to human's health [1,2]. Also these compounds are widely used in many fields, such as tanning, cosmetic, dye, chemical and pharmaceutical industries [1,3]. Phenol and its derivatives are important industrial products for a variety of organic wastewater contaminants discharged from many industries like paper, resin, textile, plastic, coking, tanning, rubber, pharmaceutical, herbicides, fungicides and petroleum [4-

6]. Resorcinol (RS) is one kind of phenolic compounds with high toxicity. It can be easily absorbed through the gastric tract and human skin, which can cause dermatitis, catarrh, convulsion, cyanopathy, and even death [1]. Also it has medicinal importance and widely used as antiseptic and disinfectant [7].

Due to the importance of this compound, Various methods have been employed for determination of RS, by fluorescence quenching, liquid chromatography, gas chromatography /mass, spectrometry and capillary electrophoresis methods [8]. These methods are time consuming, complex, have low precision and the equipment are expensive [9], Electrochemical technique considered an important analytical one, Which characterized by instrumental simplicity, lower cost, high sensitivity and portability [1, 4, 9,10-12].

As a common semiconductor materials  $\text{TiO}_2$ , with its non-toxicity, stability, unique electrochemical properties, high mechanical strength, oxygen ion conductivity, wide band gap (3.2 eV), better thermal stability, low cost of preparation and low temperature of processing. [13].  $\text{TiO}_2$  has been widely used in photocatalysis and electrocatalysis fields. The electrochemical performance for the determination of phenol and its derivatives was remarkably enhanced at  $\text{TiO}_2$ -modified electrode [14, 15]. So nanoparticles such as titanium oxide ( $\text{TiO}_2$ ) have recently been used for fabrication modified electrode [13].

This work aimed to prepare a hand-made nanostructured modified carbon paste electrode with low coast, high sensitivity, good reducibility, with highly stability with time, and optimization all condition such as type of supporting electrolyte such as sodium phosphate, sodium nitrate, Britton-Robison buffer, sodium sulphate, sodium chloride, potassium chloride, sodium acetate buffer. The effect of pH of BR as supporting electrolyte of the determination of RS was also examined and calculating the lower detection limit value (LOD) and comparing it to that obtained from other methods using the same technique.

## 2. MATERIALS AND METHODS

### 2.1. Reagents

0.01M RS (Sigma-Aldrich) was prepared by dissolving 94 mg from RS in absolute alcohol. Different concentrations from RS were prepared by suitable dilution from the stock solution. 0.1 M of BR buffer was prepared and sodium hydroxide (BDH) 1:1 solution was prepared and was used to prepare different pH values (from 3.0 to 11.0). Titaniumtetrachloride (Purity 99%) were procured from Sigma-Aldrich, USA. All other chemicals were used of analytical grade.

### 2.2. Preparation of nano- $\text{TiO}_2$

$\text{TiO}_2$  nanoparticles were prepared by addition 4.0 ml of  $\text{H}_2\text{O}_2$  with purity of 30% (wt/v) to 400 ml bidistilled water. The solution was stirred for 5 minutes and after that 5.0 ml of  $\text{TiCl}_4$  was added drop by drop at room temperature and solution was left to stir for 20 minutes and an intense yellow solution was formed. The solution was left to set for 2 days for complete precipitation. The yellow

precipitate was collected by decantation then the precipitate was let for dryness in an oven for 6 hrs. at 80° C. The dried precipitate was grind in a mill after ignition in the oven at (450° C) for 2 hrs. [16].

### 2.3. Characterization and Physical Measurements of TiO<sub>2</sub> nano particles.

The prepared TiO<sub>2</sub> nano-particles were characterized using a lot of techniques. X-ray diffraction spectra of the powders were recorded at room temperature using a powder diffractometer (Bruker axs D8 Advance, Germany with Cu K $\alpha$  radiation source,  $\lambda=1.5406\text{\AA}$  and  $2\theta$  in the range (10-80°). The average crystallite size of the catalyst was determined using the Scherrer equation

$$D = 0.9\lambda / (\beta \cos \theta)$$

Where D is the average crystallite size (nm),  $\lambda$  is the X-ray wavelength used ( $\lambda = 1.54056 \text{ \AA}$ ),  $\theta$  is the angle of diffraction and  $\beta$  is a full width at half the maximum of the diffraction line observed in radians. Particle size determination was carried out with a transmission electron microscope (TEM) and scanning electron microscope (SEM). Ultraviolet-Visible spectra were performed with a JASCO Corp.

### 2.4 Preparation of carbon paste electrode modified by TiO<sub>2</sub> electrode

Carbon paste electrode was prepared by mixing 60% of pure graphite powder (99.9%) with 15% of TiO<sub>2</sub> nanoparticles in presence of 25% from paraffin wax as a binder. The mixture was mixed very will and heated till Paraffin oil milted and then packed into a Teflon tube with 3.0 mm inner diameter. Finally a copper wire was immersed in the paste as connector as a the working electrode in three electrochemical cell.

### 2.6. Instrumentation

A potentiostat model 263 (EG& G PARC) Princeton applied corporation (made in USA), was used in this work. The characteristic of modern stripping analyzer potentiostat control the working electrode, which minimize errors from the cell resistance. This was accomplished with a three-electrode system. The used working electrode was a carbon paste modified by TiO<sub>2</sub> nanoparticles, the reference electrode was (Ag/AgCl) and a Pt wire was used as a counter electrode.

## 3. RESULTS AND DISCUSSION

### 3.1. Characterization of TiO<sub>2</sub> nano-particles.

Figure 1 shows The XRD pattern of TiO<sub>2</sub> calcined at 450°C temperature. This figure indicates TiO<sub>2</sub> in nano- size and anatase was formed as the only phase at calcination temperature of 450°C. The mean crystal size of TiO<sub>2</sub> calcined at 450°C was calculated from the XRD results using Sherrer

equation to be 18.1nm. Also the particle size and morphology of the sample prepared that calcined at 450°C was further examined by its TEM and SEM image as shown in Fig (2,3) respectively. These images indicate that the spherical and uniform shape of the particles in the nano size, and in agreement with the Sherrer equation calculations.

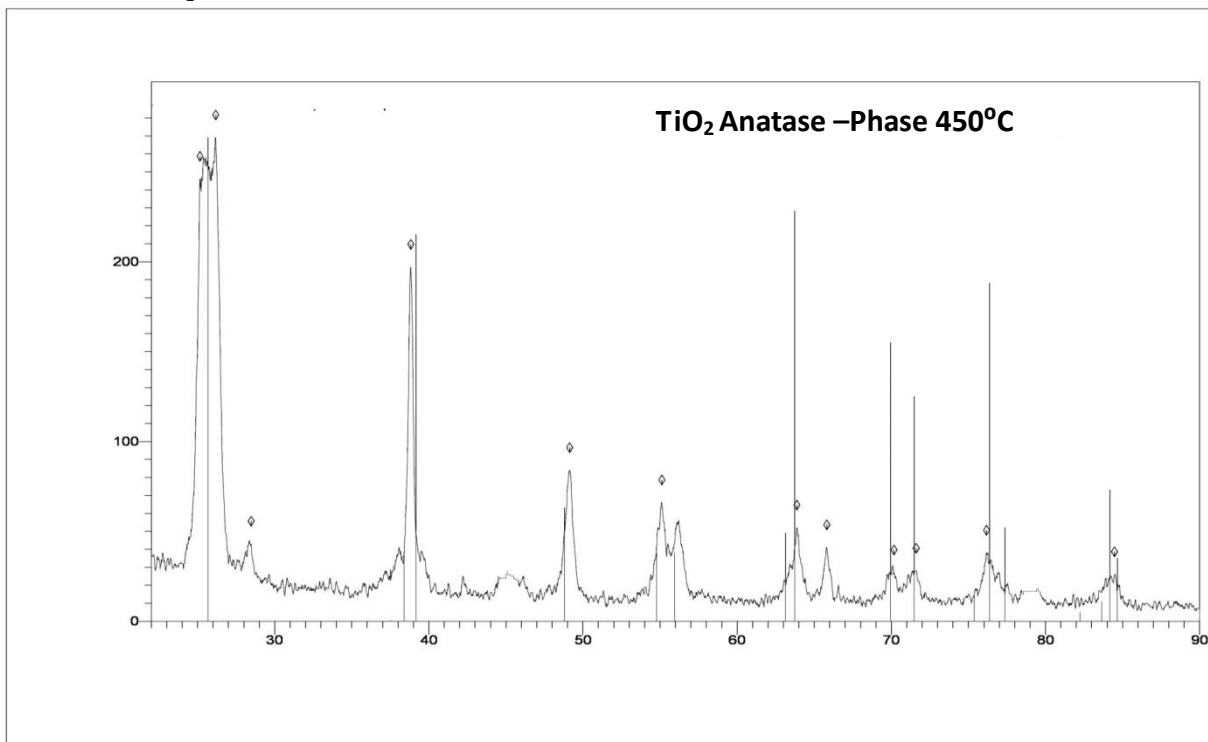


Figure 1. XRD pattern of TiO<sub>2</sub> calcined at 450 °C Anatase phase.

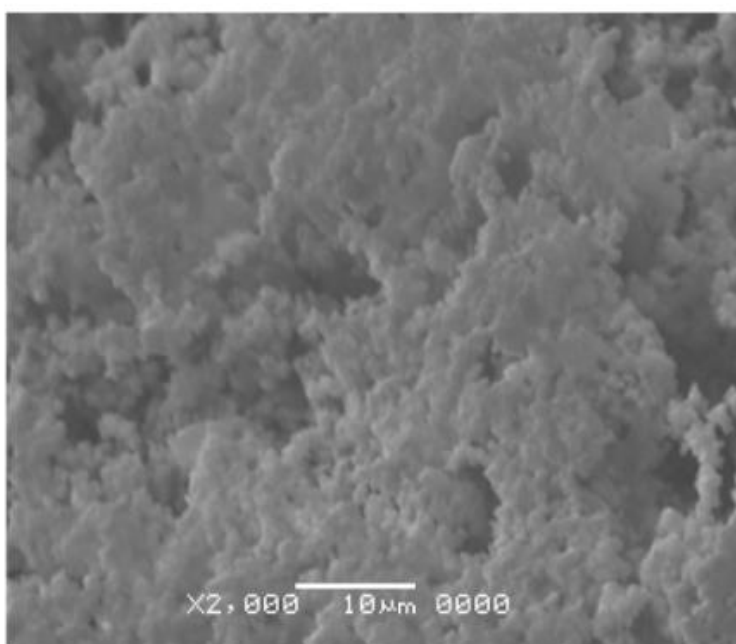
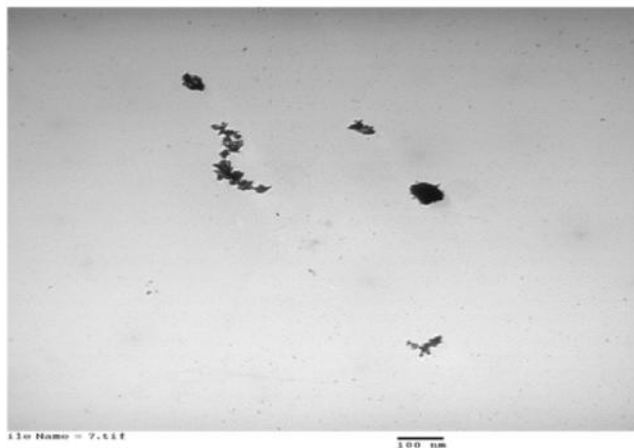
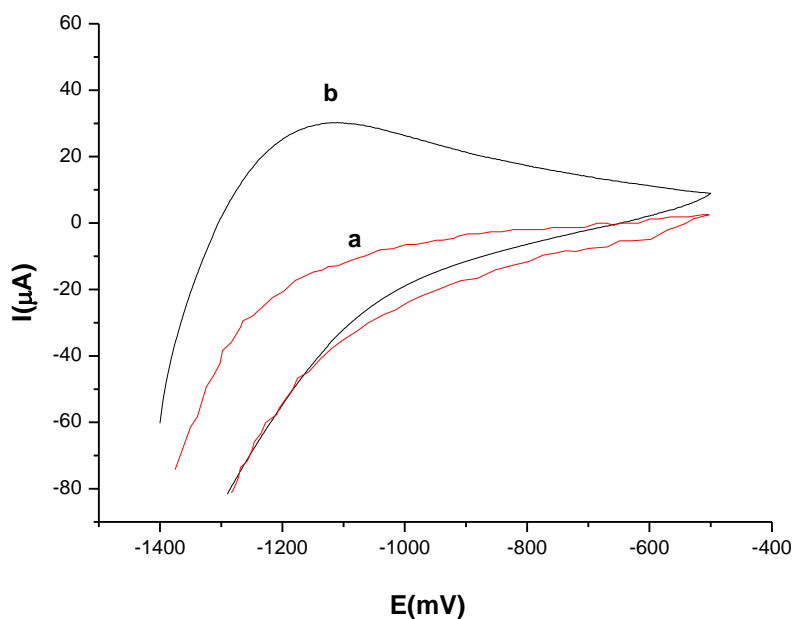


Figure 2. SEM of TiO<sub>2</sub> calcined at 450 °C



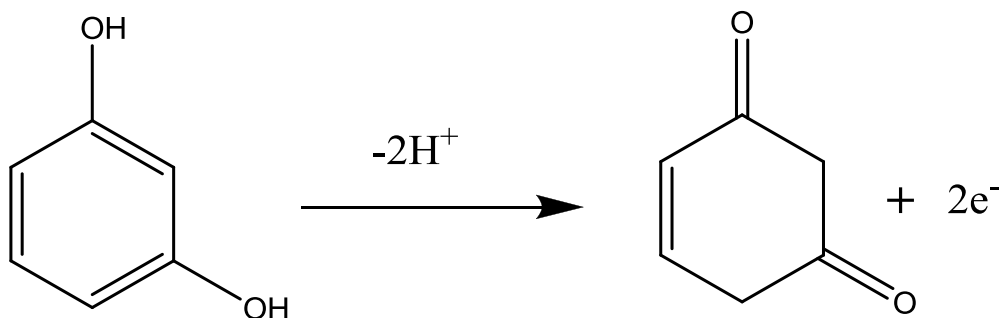
**Figure 3.** TEM image of  $\text{TiO}_2$  calcined at  $450\text{ }^\circ\text{C}$



**Figure 4.** Cyclic voltammogram (a)- in absence of  $3 \times 10^{-8}$  M RS (b)-in presence of  $3 \times 10^{-8}$  M RS in 0.1M B.R buffer, pH=2.0 at a scan rate 30mV/s using CPE modified by  $\text{TiO}_2$  nanoparticles

### 3.2. Cyclic Voltammetric and reparative cyclic measurements

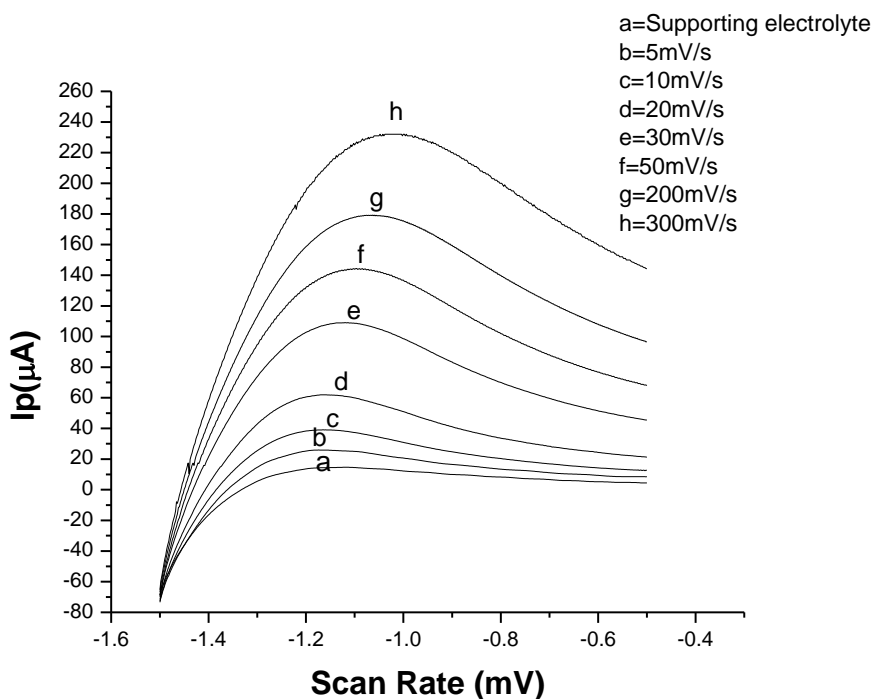
The electrochemical behavior for RS was studied using  $3 \times 10^{-8}$  M RS in 0.1 M BR buffer (pH 2.0) using CPE modified by  $\text{TiO}_2$  nano-particles. The obtained voltammograms, (Figure 4) showed only one oxidation peak at  $-0.84\text{ V}$  (vs.  $\text{Ag}/\text{AgCl}$ ). The oxidation peak may be due to oxidation of RS to phenoxy radical according to the following Scheme 1 [1].



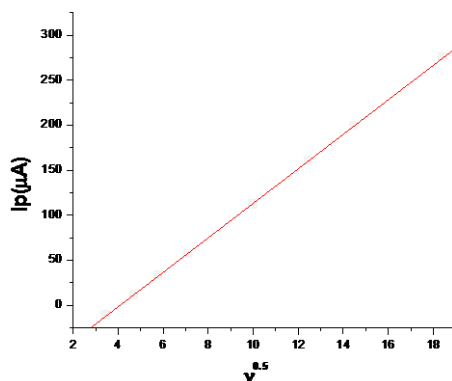
**Scheme 1.** The oxidation of RS

The electro-oxidation of RS is an irreversible process, because no corresponding reduction peak was observed on the cathodic scan. This may be attributed to the good adherence and adsorption of RS at the modified electrode surface, which prevent the reduction process [1]. Repetitive cyclic voltammogram for  $3 \times 10^{-8}$  M RS showed that the second cycle decreases comparing to the first scan. This may be due to the blocking of the electrode surface by the RS oxidation products. RS undergoes electro-oxidation possibly leading to the formation of m-benzoquinone

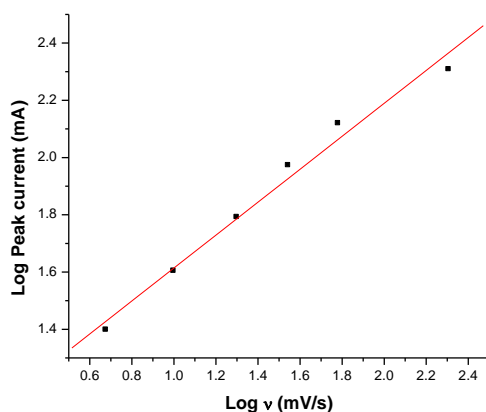
### 3.6. Effect of scan rate



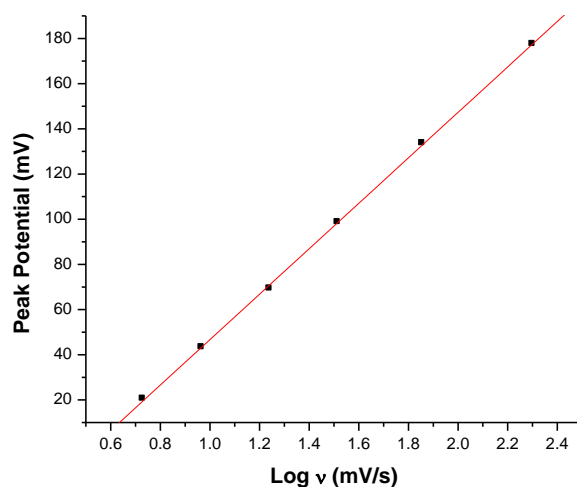
**Figure 5a.** The effect of scan rate (5 to 300 mV/s) on the peak current height of  $3 \times 10^{-7}$  M RS in B.R buffer at pH=10, using CPE modified by  $TiO_2$  nanoparticles.



**Figure 5b.** The relationship between anodic current and the square root of scan rates for  $3 \times 10^{-7}$  M RS in B.R buffer at pH=10 using CPE modified by  $TiO_2$  nanoparticles..



**Figure 5c.** A linear relationship between [log peak current] versus [log v] was found for RS ranging from 10 to 300 mV/s. A linear relationship was found with ( correlation coefficient  $R=0.998$  and stander deviation (SD)= 0.04).



**Figure 5d.** A linear relationship of [peak potential] Of  $3 \times 10^{-7}$  M of RS versus [log v] was found with ( correlation coefficient  $R=0.9997$  and stander deviation (SD)= 0.0016).

The effect of the scan rate on the oxidation peak current of the RS was investigated from 10 to 300 mV/s. By increasing scan rate values, the oxidation peak heights of  $3 \times 10^{-7}$  M in 0.1M BR buffer solution (pH 10.0) on the CPE modified by  $\text{TiO}_2$  were increased (Figure 5a). Also, peak potential was shifted towards more positive values. For further work, scan rate 100 mv/s was selected to further work to avoid the distortion on the peak at scan rate values higher than 100mV/s in high concentration [1]. The oxidation peak current varied with the square root of the scan and a linear relationship was obtained with correlation coefficient of 0.99. Which indicate that diffusion-controlled process occurring on the surface of CPE modified by  $\text{TiO}_2$  as demonstrated in Figure 5b [7]. The linear regression was represented in the following equation:

$$I_{pa} = 0.9647 + 0.0038 v^{0.5}$$

With correlation coefficient (R) of 0.999 and standard deviation (SD)= 0.8. Plotting the log oxidation peak current (log  $I_{pa}$ ) and log scan rate (log  $v$ ) for RS a linear relation was obtained (Figure 5c) over the rang from 10 to 300 mV/s, with a correlation coefficient  $R=0.998$  and standard deviation (SD) = 0.04). The linear relationship was given by the following equation.

$$\text{Log } I_{pa} = 1.038 + 0.57 \text{ Log } v$$

The obtained slope (0.57) is closed to the theoretical slope of 0.5 for diffusion controlled process [18,19]. According to the Laviron theory [20] the number of electron transfer can be determined by plotting the variation of peak potential versus log  $v$  (Figure 5d). A linear relationship was found with (correlation coefficient  $R=0.9997$  and standard deviation (SD) = 0.0016). The linear relationship was given by the following equation:

$$E_p = -51.4 + 0.99 \log v$$

By using the following equation:

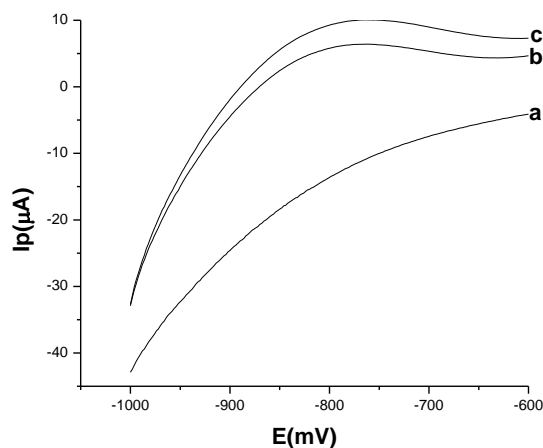
$$\Delta E_p = K - 2.3030 (RT/αnF) \log v$$

The number of electron transferred electrons  $n$  was found to be =1.75 that is mean that two electrons was contributed in the oxidation of RS to phenoxy radical.

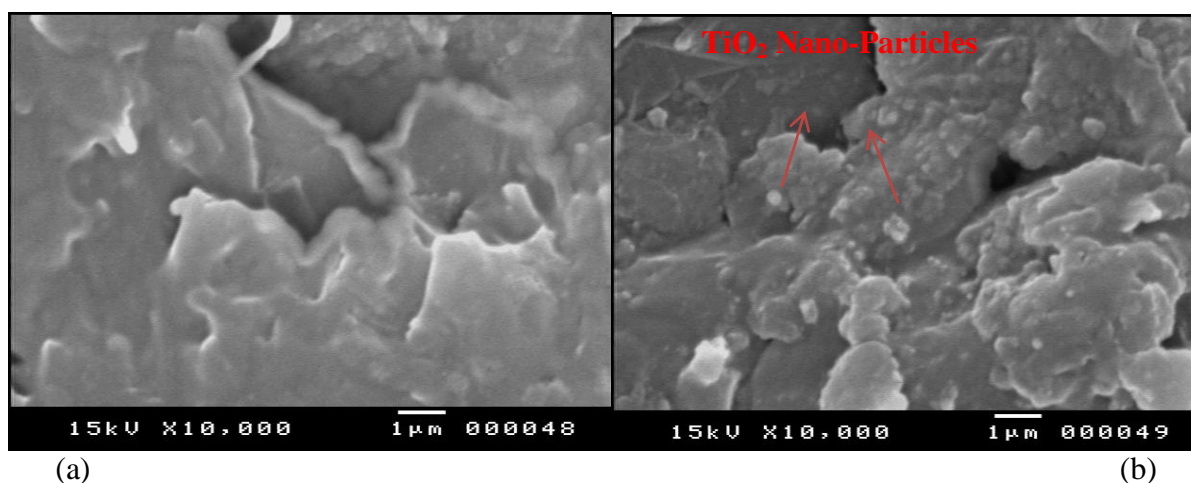
### 3.3. Voltammetric behavior of RS at modified and unmodified electrode.

Figure 6 shows the linear sweep voltammograms for  $5.0 \times 10^{-5}$  M RS on carbon paste electrode and carbon paste electrode modified by  $\text{TiO}_2$  nano-particles in 0.1 M BR buffer solution (pH 2.0) at scan rate 30mV/s. As shown from Figure 6 RS showed a higher oxidation peak current in carbon paste electrode modified by  $\text{TiO}_2$  nano-particles than in carbon paste electrode only. That is may be due to the unique nanostructures of the  $\text{TiO}_2$ . Nano structures have been found to enhance the electro-catalytic activity of the sensor for RS determination. Nanostructure can act as a provider to enhance the electrochemical reaction. Also the huge specific surface area of nanoparticles can also increase the effective area of the electrode. Leading to increase the adsorption of RS on the surface of modified electrode. In this work, modification of carbon paste electrode by  $\text{TiO}_2$  nano-particles adherence of RS. Figure 7 illustrates the difference between SEM image of unmodified CPE surface (a) and SEM image of a modified CPE by  $\text{TiO}_2$  surface (b). The SEM for carbon paste electrode showed a smooth surface while modified CPE by  $\text{TiO}_2$  Figure 7b, spherical nanoparticles were obtained.





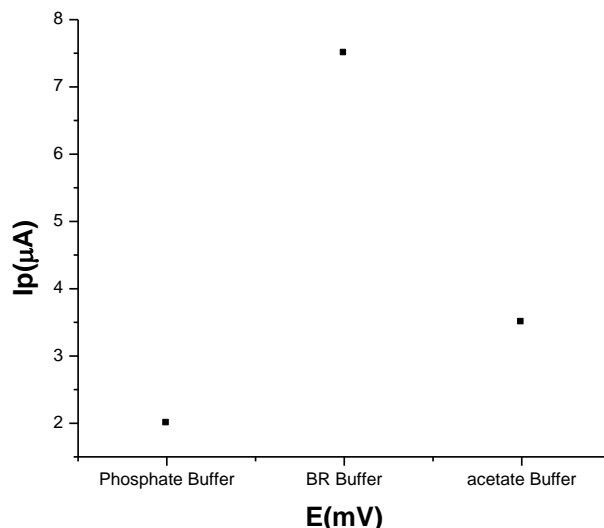
**Figure 6.** Linear sweep voltammograms for (a) CPE in the absence of (RS) and (b) CPE presence of  $5.0 \times 10^{-5}$  M (RS) and (c) CPE modified by  $\text{TiO}_2$  nanoparticles in the presence of  $5.0 \times 10^{-5}$  M of (RS) in 0.1 M BR buffer solution (pH 2.0) at scan rate 30mV/s.



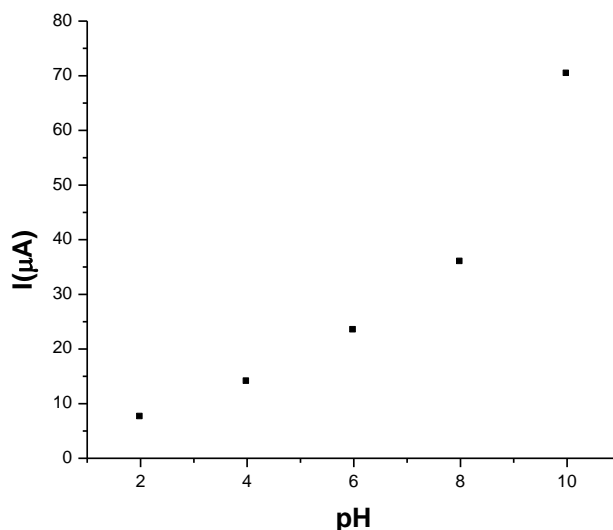
**Figure 7.** Illustrates the difference between a- SEM image of unmodified CPE surface , b– SEM image of a modified CPE by  $\text{TiO}_2$  surface.

### 3.4. Effect of the Supporting Electrolyte

The effect of supporting electrolyte were examined on the oxidation peak of RS at the same conditions such as: sodium phosphate, sodium nitrate, Britton-Robison buffer, sodium sulphate, sodium chloride, potassium chloride, sodium acetate buffer. In BR buffer, sodium phosphate and sodium acetate buffer RS showed an oxidation peak. The shape and the height of the oxidation peak of RS were taken into consideration on choosing the suitable supporting electrolyte. Figure 8a showed the effect of supporting electrolyte of  $5 \times 10^{-5}$  M of RS on CPE modified by  $\text{TiO}_2$  electrode at pH=2.0 using scan rate 30mV/s. The highest oxidation peak current was appeared using in BR buffer.



**Figure 8a.** The effect of supporting electrolyte on the peak current signals for  $3 \times 10^{-5}$  M of RS on CPE modified by  $\text{TiO}_2$  at  $\text{pH}=2.0$ .



**Figure 8b.** The effect of pH values (from 2 until 10) on the peak current signals of  $5 \times 10^{-5}$  M of RS using on CPE modified by  $\text{TiO}_2$

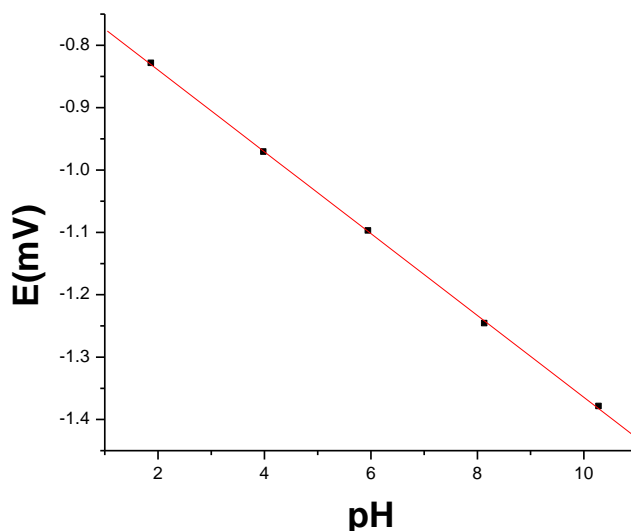
### 3.5. Effect of pH

The oxidation peak of RS was examined over pH range from 2 to 10 in 0.1M BR supporting electrolyte. The results showed that the oxidation peak currents of  $3.0 \times 10^{-5}$  M of RS depends of the pH values. By increasing the pH values for BR for 2.0 to 10.0 the peak current height increased. The best peak shape and highest peak current of  $3.0 \times 10^{-5}$  M of RS was obtained at pH 10 by using 30mV/s at CPE modified by  $\text{TiO}_2$  nanoparticles (Figure 8b). The peak potential was shifted to more negative

values by increasing the pH values from 2.0 to 10.0 (Figure 8c) according to the following equation with standard deviation (SD)= 0.003 and correlation coefficient (R)=0.999

$$E_{ox} = -0.70 - 0.06 \text{ pH}$$

The slope of this is close to the theoretical value of  $0.058 \text{ V pH}^{-1}$  for two electrons and two protons process [1, 17], indicating that pH 10.0 is the optimum pH for electrochemical oxidation of RS at CPE modified by  $\text{TiO}_2$  nanoparticles.



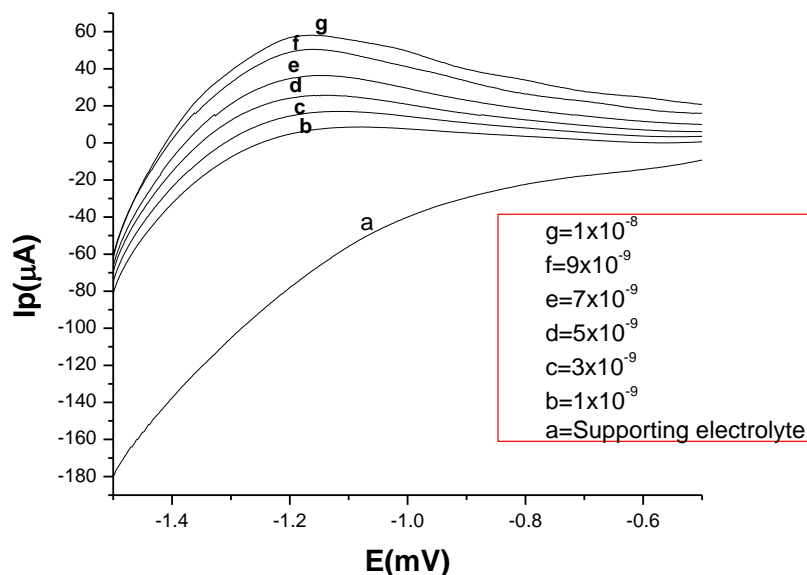
**Figure 8c .** The effect of pH values (from 2 until 10) on the oxidation peak potentials for RS using LSV at scan rate of 30 mV/s.

### 3.7. Effect of concentration and calibration curve.

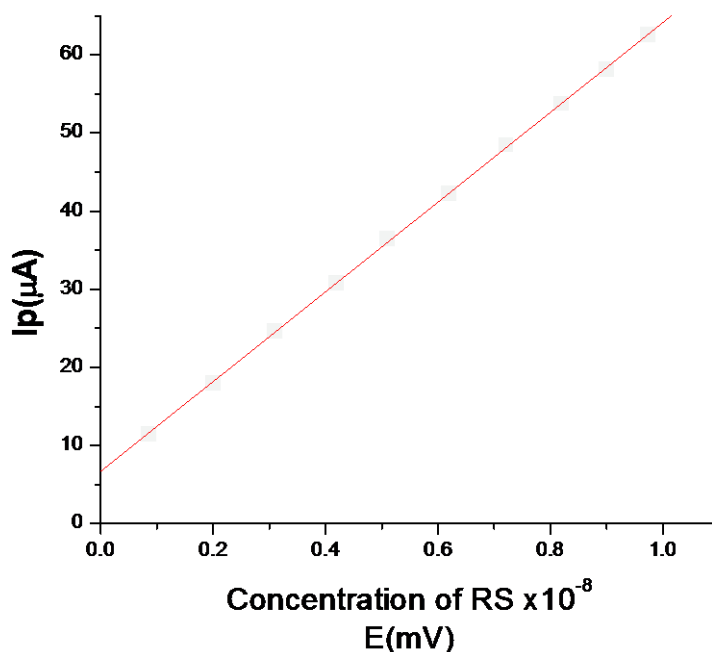
**Table 1.** Comparison between the our work and other work with the same technique.

Working Electrode	Linearity range [ $\mu\text{M}$ ]	Detection limit [M]	Reference
Glassy carbon electrode modified with multi-walled carbon nanotube	1.2 - 0.019	$4.9 \times 10^{-7}$	1
RGO/Au-NPs Composite modified electrode.	1.0 - 0.01	$7.8 \times 10^{-7}$	3
C-nanotube-modified electrodes	1.0 - 0.03	$3.8 \times 10^{-7}$	6
Nitrogen doped porous carbon nanopolyhedrons-multiwall carbon/nanotubes hybrid materials modified Glassy carbon electrode	2.0 - 0.01	$1.0 \times 10^{-6}$	8
Graphene-chitosan composite film modified glassy carbon electrode	20 - 140	$7.5 \times 10^{-7}$	21
Carbon dot/reduced grapheme oxide composite modified electrodes	0.5 - 1000	$1.0 \times 10^{-6}$	22
Carbon paste electrode modified by $\text{TiO}_2$ nanoparticles.	1000 - 10	$1 \times 10^{-9}$	Present Work

Influence of RS concentration on the oxidation peak current was studied over the range from  $1 \times 10^{-9}$  –  $1 \times 10^{-7}$  M RS in B.R pH= 10.0. The oxidation peak currents of RS were increased by increasing of RS concentration. Figure 9a showed a typical linear sweep voltammograms for different RS concentrations ranged from  $1 \times 10^{-9}$  to  $4 \times 10^{-8}$  M.



**Figure 9a.** Linear sweep Voltammograms for different concentrations of RS under the conditions of B.R buffer pH=10 using CPE modified by TiO<sub>2</sub> nanoparticles at scan rate 50 mV/s.



**Figure 9b.** Calibration curve for RS in B.R buffer (pH=10) using scan rate 50 mV/s at CPE modified by TiO<sub>2</sub> nanoparticles.

By plotting RS concentrations versus the obtained peak currents, a linear dependence was observed. The oxidation peak current was found to be proportional to RS concentration from  $1.0 \times 10^{-9}$  M to  $1 \times 10^{-8}$  M, with correlation coefficient of  $R = 0.999$  and standard deviation of  $SD = 0.20$  as illustrated in (Figure 9b). A  $1.0 \times 10^{-9}$  M detection limit was obtained. The detection limit and linearity range of this work is compared to other works used the same techniques with a different and same electrode. The collected results are compared with the previously published data as illustrated in Table 1. Table 1 represent the lower detection limit and linearity range was obtained in our work.

### 3.9. Reproducibility and Stability of $TiO_2$ modified electrode.

The stability of CPE modified by  $TiO_2$  nano-particles was examined by repeating eight successive measurement for  $3 \times 10^{-6}$  M in 0.1M BR buffer solution of pH 10.0 at scan rate 100mV/S of RS using CPE modified by  $TiO_2$  nano-particles. No obvious change in peak current was observed, which confirms that CPE modified by  $TiO_2$  nano-particles is highly stable. The relative standard deviation RSD for six measurements was found to be 1.9% indicating an acceptable reproducibility. After CPE modified by  $TiO_2$  nano-particles was stored for ten days, an increase by 5.3% in the oxidation peak of  $3 \times 10^{-6}$  M RS was found. Which could be attributed to the excellent stability comparing to other research with other modified electrode [17].

### 3.10. Interferences study

One of the most important advantages of modified electrode is having good selectivity. To test the selectivity of CPE modified by  $TiO_2$  nano-particles upon the determination of RS using linear sweep voltammetry technique, and applying the optimum conditions, some interferents were investigated by the addition of interference species with the same concentration of RS to 0.1 M BR in the presence of  $5.0 \mu\text{M}$  of RS. The results indicate that the common ions such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  did not show interference with RS detection. Phosphoric acid, Acetic acid and boric acid have no obviously interference in RS.

### 3.11. Analytical applications and recovery test

Using tap water as an analytical samples, the experiment was carried out by the spike and recovery method, by adding 10 ml of standard solution of RS to 10 ml of 0.1M BR buffer under the optimum conditions. By adding different concentrations of the RS to tap water and determination the contents and calculated their recoveries. The recovery was founded from 99.8-100% as seen in (Table 2).

**Table 2.** Determination of the content of RS in the tap water sample.

Added ( $\mu\text{M}$ )	Found ( $\mu\text{M}$ )	Recovery (%)
1.0	0.9	90.0 %
3.0	3.1	103.0%
4.0	4.1	102.5%
5.0	5.0	100.0%
0.1	0.1	100.0%
0.3	0.3	100.0%
0.4	0.4	100.0%
0.5	0.5	100.0%

## 6. CONCLUSION

- Preparation of new handmade nano modified electrode with special properties such as catalysis, the large specific surface area and more adsorption sites comparing to unmodified electrode
- From obvious results obtained during electrooxidation process of RS we can reach to the ideal conditions to detect and determine RS in lower concentration such as: B.R buffer at pH=10 and with scan rate 50mV/s.
- Our work has a great importance for determination RS as pollutant from the good obtained results of reproducibility, Beside the Lower detection limit that obtained comparing to other published work as we seen before.
- The suggested procedures can be used to detect the studied compounds with accurate, easily, rapidly, simple, cheap good reproducibility and low detection limit.

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