



## Modification of the glassy carbon electrode with Multi-walled carbon nanotube/1, 4-dihydroxy anthraquinone/chitosan, As a potentiometric pH sensor

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**Abstract:** In this study, the electrochemical behavior of 1, 4-dihydroxy anthraquinone (Q) is investigated with cyclic voltammetry (CV) technique at glassy carbon electrode (GCE) in different pH. The results have been shown one redox wave in aqueous solution and the redox wave shifted to negative potential with increasing pH. The half potential ( $E_{1/2}$ ) for redox wave was linear in the pH range from 1.5 to 7.0. A modified glassy carbon electrode (GCE) is prepared using an appropriate mixture of Q/multi-walled carbon nanotubes/Chitosan. The electrochemical behaviors of sensor were studied in different pH. The half potential ( $E_{1/2}$ ) of the redox wave was shifted to negative potential with increasing pH. It is found the  $E_{1/2}$  for redox wave was linear over a range of 11 pH units in pH range between 1.0 and 12.0 the values of correlation coefficient and RSD are 0.997 and 1.99% respectively which is so better than previous method.

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**Keywords:** multi-walled carbon nanotubes, Chitosan, pH sensor, 1, 4-dihydroxy anthraquinone

### 1. Introduction

Chemical sensors provide direct, real-time information on the contents of certain chemical substance(s) present in their environment “(W. GoËpel and et al, 1989)”. Their practical importance continuously increases as they not only offer an advantageous alternative to time- and cost demanding laboratory analyses but, primarily, feed necessary input information to a great variety of automatic devices, regulating mechanisms and robots; therefore, humans often cease to be direct users of the information provided and can concentrate on the designing and operating larger scientific or technological systems. Sensor signals are handled by electronic circuits and it is advantageous, for financial, spatial and operational reasons, to integrate the sensor and its electronic circuitry into a single block; in this way it is further possible to construct integrated systems with sensor arrays and systems with some degree of artificial intelligence (smart sensors).

A significant group of chemical sensors is based on electrochemical principles “(W. GoËpel and et al, 1989)”, “(J. Janata and et al, 1994)”. The classical electrochemical sensors with liquid electrolytes are usually rather bulky and awkward; moreover, drying or leakage of the electrolyte may corrode various parts of the device and thus limit its

lifetime and impair its function. Therefore, the progress in the field is directed towards solid-state sensors, i.e., those that contain no macroscopic liquid phase. There exist several ways for preparation of solid-state electrochemical sensors and one of the important approaches is the replacement of a liquid electrolyte by a solid polymer exhibiting an ionic conductivity, called a solid polymer electrolyte (spe). On the other hand pH is one of the most common laboratory measurements because so many chemical, biological processes and practical applications such as clinical analysis, environmental analysis, process control and rate of chemical and biochemical reactions are dependent on pH “(E. Lindner and et al, 1998)”, “(H. Hisamoto and et al, 1996)”. In tradition, the measuring methods for pH values fall roughly into four categories: indicator reagents, pH test strips, glass electrode and metal electrode methods (hydrogen electrode, quinhydrone electrode and antimony electrode method). In past, the hydroquinone electrode used for determination of pH with potentiometric method but today this method is less used because not reproducible “(Z. Galback and et al, 2005)”. Obviously MWCNT as a magical material, because their uniqueness and have received excellent attention for the preparation of electrochemical sensor, as it was extensively reviewed. “(M. Trojanowicz and et al, 2005)”, “(J.

Wang, 2005)", "(N. Li, J. Wang and et al, 2003)", "(C.E. Banks and et al, 2006)", "(J. Wang, 2005)", "(M. Valcarcel and et al, 2005)"

## 2. Material and Methods

The chitosan solution (8%) was prepared by dissolving 0.8 g chitosan in 10 ml acetic acid. CNTs were functionalized by sonification treatment in a mixture of sulfuric acid and nitric acid (3:1) for 6 h at room temperature. Functionalized MCNTs (fMCNTs) were washed with double distilled water (DDW) and separated by centrifugation. "(S.Hoon Baek and et al, (2008))".

1,4-Dihydroxy anthra quinone(Q), Acetonitrile(AN) purchased.

All experiments were carried out at room temperature (about 15 °C).

All the electrochemical measurements were carried out with a Electroanalyser.

The three-electrode system consisted of a modified GCE, a SCE reference electrode, and a platinum auxiliary electrode. All potentials were referred to the SCE.

First make a solution of Q (0.05mg) in 2.5ml acetonitril and then added 25mg of MWCNT and agitation with ultrasonic to give a black suspension, now 0.5ml of this suspension mixed with 0.1ml of chitosan solution (0.5%).

Before being modified, the GCE was polished with 0.3 and 0.05  $\mu\text{m}$  aluminum slurry, rinsed thoroughly with DDW, then ultrasonically cleaned with H<sub>2</sub>SO<sub>4</sub>(1M) for 5 min, finally rinsed with DDW, and dried under an infrared lamp. After the GCE was cooled, it was smeared evenly with 6  $\mu\text{L}$  of a MWCNT–chitosan–anthraquinone (0.5%) solution by a micro-syringe, and then dried under an infrared lamp for 10 min. After cooling, the MCQ/GCE could be used.

A phosphate buffer solution (PB) 0.3 M (pH= 1-12) was used as the supporting electrolyte. The solution was purged with nitrogen for 2 minutes. In the differential pulse voltammetric (DPV) study, the electrode was scanned between 0 and -1V.

## 3. Results

the electrochemical behavior of 1, 4-dihydroxy anthraquinone (Q) is investigated with cyclic voltammetry (CV) technique at glassy carbon electrode (GCE) in different pH. The results have been shown (Figure 1) one redox wave in aqueous solution and the redox wave shifted to negative potential with increasing pH. The cathodic potential (Epc) for redox wave was linear in the pH range form 1.5 to 7.0 with a correlation coefficient of  $r = 0.97$ .

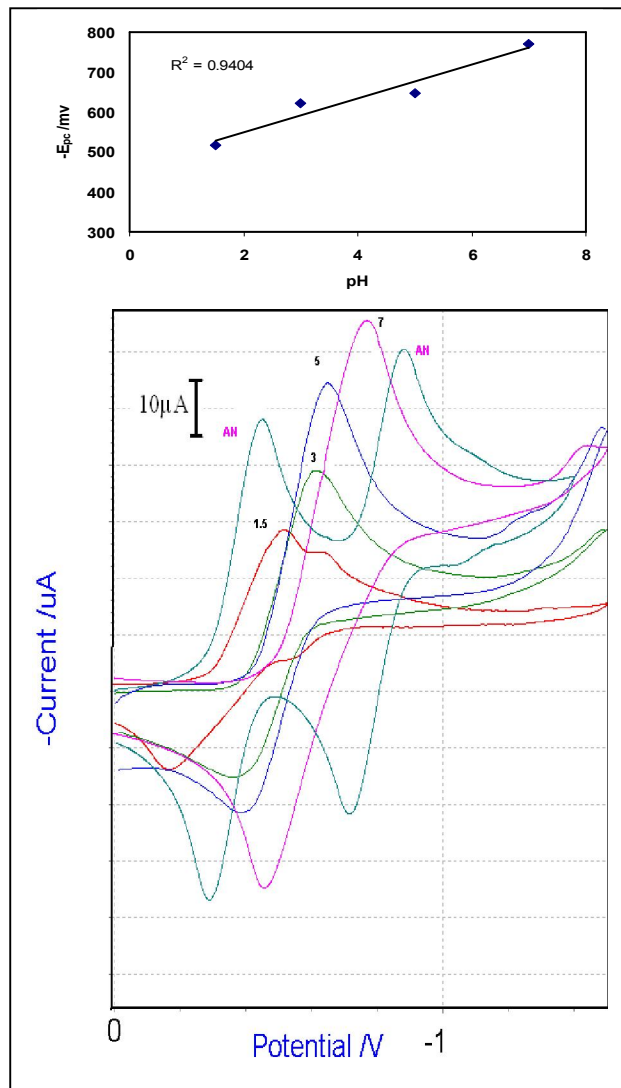


Figure 1. Cyclic voltammogram for  $5.0 \times 10^{-3}$  mol L<sup>-1</sup> Q in mixture (3:1) acetonitril and PB solution (PH=1.5-7) + 0.1 M TBAP on GCE in the, Scan rate: 100 mVs-1. Inset, plot of E1/2 vs. pH values

The CV former component of electrode shown in fig.2 at the QMC/GCE the CV demonstrated two reversible waves with half peaks potential (E1/2) respectively at -0.032 and -0.327 V.

The behavior of Q at a bare GCE and QMC/GCE was studied by cyclic voltammetry. As shown in fig.2 the values of  $i_{pa}$ ,  $i_{pc}$  for QMC/GCE is more than of this values for Q/ GCE respectively because chitosan promote electron transfer in the matrix. "(Zhang M and et al, 2005)", "(Zhang M and et al, 2005)", "(Zhang M and et al, 2004)".

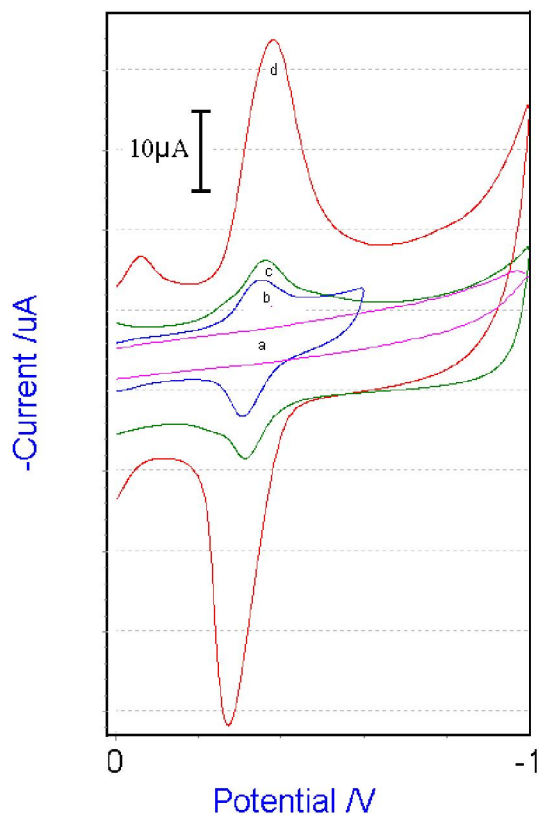


Fig 2. The CV former component of electrode in 0.3M PB (PH=1.5), Scan rate=100mv/sec,a)modified GCE with chitosan (C/ GCE) b) Q/ GCE c) QC/ GCE d) QMC/ GCE

The electrochemical behaviors of sensor were studied in different pH in DPV mode. The half potential ( $E_{1/2}$ ) of the redox wave was shifted to negative potential with increasing pH. It is found the  $E_{1/2}$  for redox wave was linear over a range of 11 pH units in pH range between 1.0 and 12.0 with a correlation coefficient of 0.997, which is so better than previous method. "(S. Rosini and et al, 2004)" Because this electrode is stable at this range of pH and on the other hand Better performance for detection of pH on MWCNT-GCE was attributed to the MWCNTs potential porous leading to the larger electroactive surface area and thus greater response of pH "(C.E. Banks and et al, 2005)" "(C.E. Banks and et al, 2004)". This result are given in fig.3

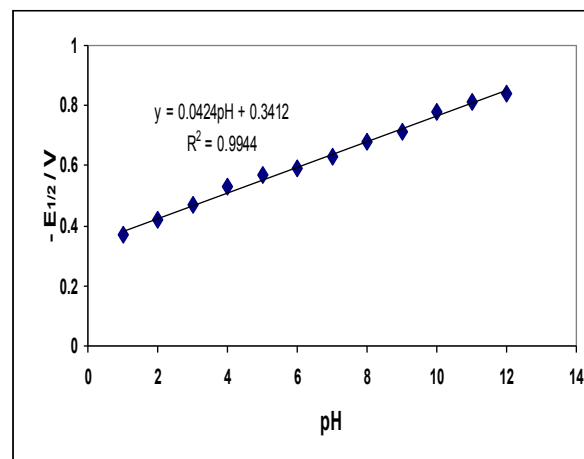
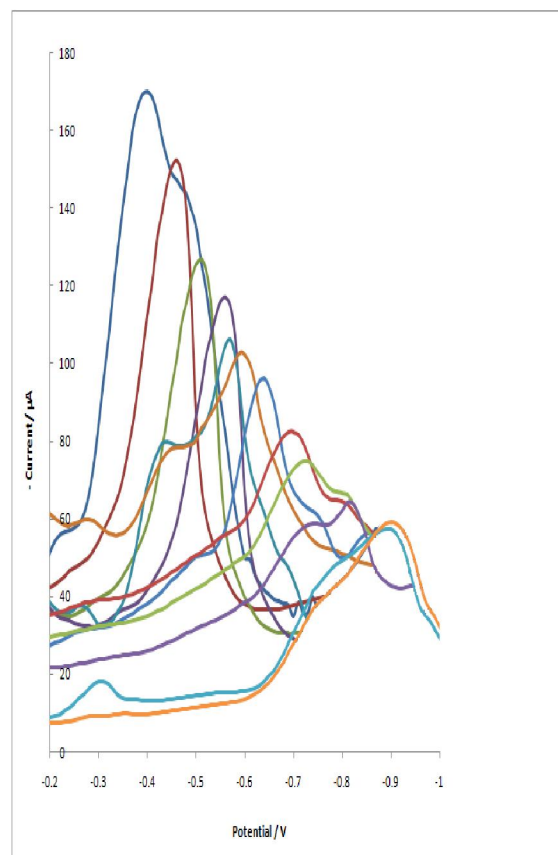


Fig 3. Differential pulse voltammograms of QMC/GCE, at scan rate 100 mVs-1 with increasing pH values (from 1 to 12) 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0, 9.0, 10.0, 11.0, 12.0 in phosphate buffer solution. Inset, plot of  $E_{1/2}$  vs. pH values.

The amount of modifier on the surface of electrode affected the ipa and ipc. Fig 4. Showed that the ipa, ipc enhanced when the amount of MWCNT increased, which probably because of the presence of electro-reactive sites which increased with the amount of MWCNTs "(C.E. Banks and et al,2005)" "(C.E. Banks and et al,2004)".

When the concentration of MWCNTs in the modifier surpassed 0.5ml, the ipa, ipc of pH fell. These because the film on the electrode surface was too thick, which prevented the electron transfer between Hydrogen ions and electrode.

In this paper, 0.5ml MWCNTs in the Q-chitosan-MWCNT modifier was used as optimum amount for voltammetric determination of pH.

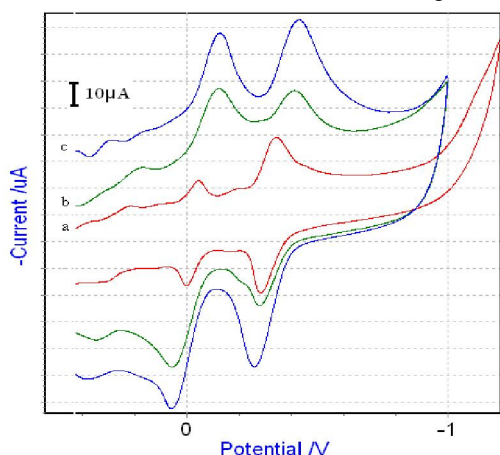


Fig 4. The cyclic voltammogram of QMC/GCE prepared with ratios contains a) 0.1 ml of mix (MWCNT, Q) b) 0.3 ml of mix (MWCNT, Q), c)0.5 ml of mix (MWCNT, Q) with 0.1 ml chitosan in 0.3M PB (PH=1.5),Scan rate=100mv/sec

#### 4. Discussions

We describe a highly sensitive pH sensor in wide range of pH, although in high values of pH the quinine compounds are not stable at the surface of electrode but as mentioned this modified electrode stable and reproducible in different pH and scan rates.

On the other hand the electrochemical behavior of Q investigated in different medium and pH at BGC and M-GC.

Obviously we found that the chitosan is good compound for immobilization of Q at the surface of electrode.

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