شبكة المعلومات الجامعية

بسم الله الرحمن الرحيم

# شبكة المعلومـــــات الجامعية

# التوثيق الالكتروني والميكروفيلم

شبكة المعلومات الجامعية

# جامعة عين شمس

## التوثيق الالكتروني والميكروفيلم

## قَســم

**نقسم بالله العظيم أن المادة التي تم توثيقها وتسجيلها**
**علي هذه الأفلام قد اعدت دون آية تغيرات**

## يجب أن

تحفظ هذه الأفلام بعيداً عن الغبار

في درجة حرارة من 15 – 20 مئوية ورطوبة نسبية من 20-40 %

**To be kept away from dust in dry cool place of**
**15 – 25c and relative humidity 20-40 %**

# بعض الوثائق

# الأصلية تالفة

# بالرسالة صفحات

# لم ترد بالأصــــل

# CHARACTERIZATION AND INVESTIGATION OF THE ELECTROCATALYTIC PROPERTIES OF SOME NEW MODIFIED ELECTRODES AS MEDIATORS FOR SOME ELECTROORGANIC SYNTHESIS.

A Thesis
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A B C D E F

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***Mohamed EL-Bagoury***

# CONTENTS

# *Aim of the present work*

The activity in the electrochemically modified electrodes has been growing over the last twenty years and is motivated by the need to develop exchange processes and for controlling electrochemical reactions. The interest in electrochemically modified electrodes stems from the fact that these electrodes may impact on many different technology areas such as electrocatalysis , electroorganic synthesis, etc.

In this work, we will present new modified electrodes which obtained by the anodic polymerization of the Schiff base resulting from the condensation reaction between 1,8- diaminonaphthalene (1,8-DAN) and dehydroacetic acid (dha) on the platinum and glassy carbon electrodes in acetonitrile solution.

The work will put into consideration the following.

1- Formation of electrochemically modified electrodes by two techniques, cyclic voltametery (CV) and controlled potential electrolysis (CPE).

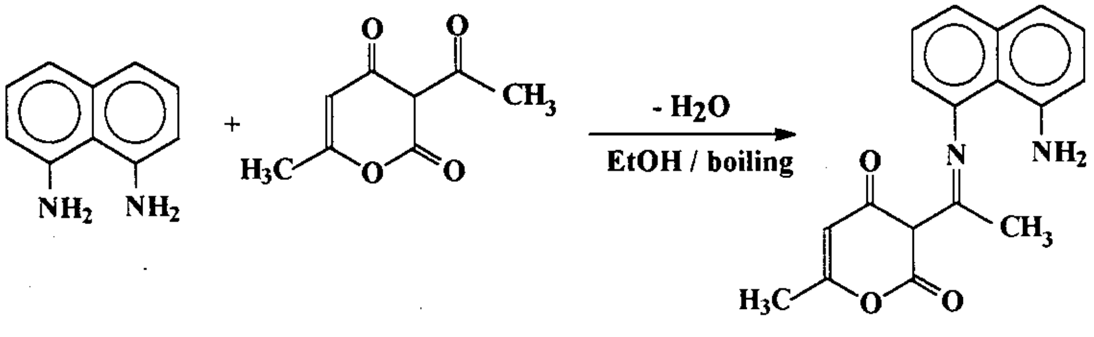
2- Study the activity of the formed films in aqueous and non-aqueous solutions.

3- Study the application of the prepared modified electrodes in the electroorganic reactions as a mediators.

# SUMMARY

# *SUMMARY*

The condensation reaction between 1,8- diaminonaphthalene and dehydroacetic acid gave the corresponding schiff base namely 8-[3-acetylimino-6-methyl-2,4-dioxopyran] 1-aminonaphthaline (I) according to the following scheme.

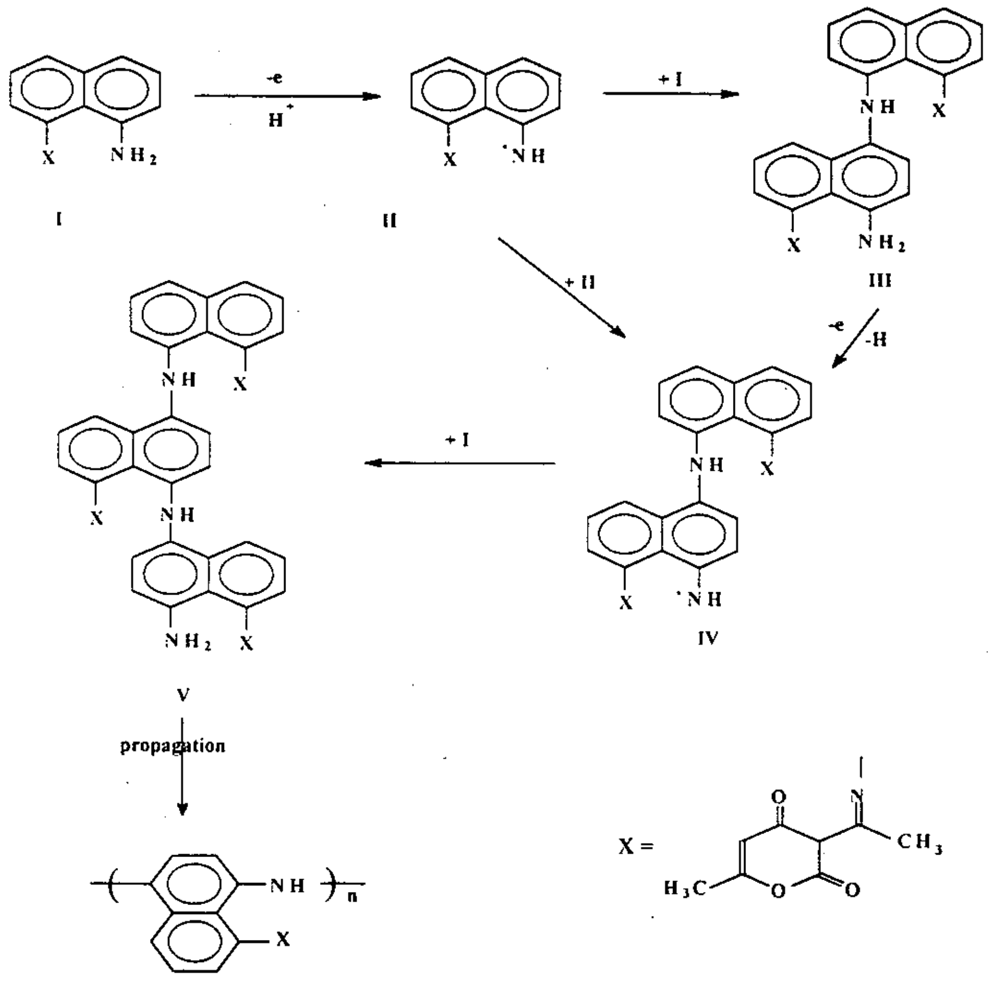


(I)

The resulting schiff base was identified and characterized using analytical spectra. Anodic polymerization of the schiff base (I) on the platinum and glassy carbon electrodes in acetonitrile solution was found to yield thin electroactive polymeric films. The effect of different experimental conditions ( mononmer concentration, type of electroyte, polymerization media, type of the working electrode, scan rate, number of cycles, potential range) on the prepared modified electrode was studied. The best response of the polymer film was obtained if the electrode potential was sweept continuously at rate of 100mV/s between -0.5 and 1.4V for 30 cycles on plutinum eletrode in $10^{-3}$M of monomer in 0.1M $LiClO_4$ acetonitrile solution.

A mechanism of electropolymerization is suggested as shown in the following scheme

The films were found electroactive in acetonitrile and aqueous $H_2SO_4$ solutions and the electroactivity is attributed to the electrotransformation of the amino/imino sites in the polymer film as in aromatic amines polymers. Electron transfere reactions on the polymer-covered Pt electrodes indicated that the polymer films are highly portous and semiconducting. Electrocatalytic properties for this new modified electrodes was studied as mediators for some organic reactions as the electrooxidation of hydroquinone, catechol, o-aminophenol, 5- amino uracil and benzaldehyde.



Polymer I

# INTRODUCTION

# *I. Introduction*

The activity in chemically modified electrodes has been growing over the last twenty years and is motivated by the need to develop will defined surfaces for studying electron exchange processes and for controlling electrochemical reactions. This area has grown very rapidly, and a large number of materials can now be used to modify an electrode. The preparative methods used to produce the electrode coatings are limited, and most procedures can be classified in three general categories. One category involves placement of a covalently bonded layer of small molecules on the electrode. The most commonly used reagents for this modification are organosilanes in which the silyl functionality bonds to the surface oxide of the electrode. The other category involves coating the electrode with a relatively thick layer of a polymer. In one approach, electroactive conductive polymer film coatings can be generated in situ by the electrooxidation of aromatic compounds. These films are prepared from benzenoid, nonbenzenoid, and heterocyclic aromatics, in particulr from the derivatives of pyrrole, thiophene, carbazole, azulene, pyrene, triphenylene, and aniline. Alternatively, a fully formed polymer with the desired chemical structure can be applied to the electrode by dip or spin coating using a dilute solution of the polymer. Finally, modifications can be accomplished by the irreversible adsorption of large aromatic compounds and polymers.

The interest in the chemically modified electrodes stems from the fact that, these electrodes may be impact on many different technology areas, such as electrocataysis, electrosensores, electrophotosensitization electrosynthesis, energy storage, electrorelease of reagents, membrane barriers, display devices, and optical shutters[1-15].

If we compere between all the types of modifications, we can see that, polymer films have fundamental advantages over monolayers of active species covalently bonded or adsorbed. They show greater chemical and electrochemical stability, since thickness equivalant to upto $10^5$ monolayers are possible. They also possess a high active-center concentration, often as high as 0.1 to 5M. Furthermore, they allow a greater diversity and complexity of immobilized chemical microstructures. In other words, polymer modified electrodes can be seen as truly molecular electrode materials, with numerous applications in many areas. Also, the electrochemical polymerization and precipitation of polymer films directly on the electrode offer some advantages, as compared with the deposition of chemically performed polymers. Electropolymerization allows the deposition of insoluble polymers, a uniform coating of irregular surfaces, and easy electrochemical control of the film thickness.

## I. Preparation of modified electrodes using diaminonaphthalene compounds.

Aromatic polyamines became a new candidate for electro polymerization e.g. 2,3-diaminonaphthalene(2,3-DAN) and 1,8-diaminonaphthalene(1,8-DAN.) N. Oyama et al [16] studied the electrooxidative polymerization of 2,3 DAN and 1,8 DAN by cyclic voltammetry in aqueous solutions containing 0.2M $NaClO_4$ and 20mM 2,3 DAN or 1,8 DAN. The oxidation of the two monomers showed a