ELECTROSYNTHESIS AND ELECTROANALYTICAL STUDIES OF THE SELECTED DIHYDROXYBENZENE COMPOUNDS AT CARBON AND POLY (4–VINYLPYRIDINE) BASED NANOCOMPOSITE ELECTRODES

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UNIVERSITI SAINS MALAYSIA

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by

HANIEH GHADIMI

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This thesis is dedicated to my lovely parents

Mr. Mohammad Ebrahim

and

Mrs. Masoumeh (Azam)

For their endless love, support and encouragement

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A_1	Anodic peak
ACAP	Acetaminophen
AcO	Acetone
AA	Ascorbic acid
ASA	Aspirin
ºC	Degree centigrade
C_1	Cathodic peak
CT	Catechol
CHN	Elemental analyses of total carbon, hydrogen and nitrogen
CNTs	Carbon nanotubes
CV	Cyclic voltammetry
D	Dimensional
DCM	Dichloromethane
DHB	Dihydroxybenzenes
dl	Limit of detection
DMF	Dimethylformamide
DPV	Differential pulse voltammetry
DWCNTS	Double walled carbon nanotubes
δ	Chemical shift
ΔE_p	Peak separation
E_{pa}	Anodic peak potential
E_{pc}	Cathodic peak potential
EFTEM	Energy-filtering transmission electron microscope
EIS	Electrochemical impedance
EtOH	Ethanol
F–Test	Statistical hypothesis test
FT-IR	Fourier transform infrared
FESEM	Field emission scanning electron microscope
g	Gram
GCE	Glassy carbon electrode
GR	Graphene
GO	Graphene oxide
h	Hour
HOAc	Acetic acid
HQ	Hydroquinone
Hz	Hertz
I_{pa}	Anodic peak current
I_{pc}	Cathodic peak current
KHz	Kilohertz
MΩ cm	Megaohm centimeter
µA	Microampere
mA	Milliampere
mg	Milligram
mHz	megahertz
mL	Milliliter
mm	Millimeter

mmol	Millimole
mM	Millimolar
µL	Microliter
µM	Micromolar
MS	Mass spectrometry
mV	Millivolts
MWCNT	Multiwalled carbon nanotubes
nM	Nanomolar
NMR	Nuclear magnetic resonance
Ω	Ohm
PCT	Paracetamol
P4VP	Poly (4–vinylpyridine)
PNC	Polymer nanocomposites
R	Linear regression coefficients
R_{ct}	Charge transfer resistance
Rs	Solution resistance
RSD	Relative standard deviation
S_B	Standard deviation
SWCNT	Single walled carbon nanotubes
SWV	Square-wave voltammetry
THF	Tetrahydrofuran
TLC	Thin layer chromatography
TMS	Tetramethylsilane
TSC	Thiosemicarbazide
UA	Uric acid
V	Volt
$v^{1/2}$	Square root of the scan rate
v/v	Volume per volume
Z_w	Warburg element

KAJIAN ELEKTROSINTESIS DAN ELEKTROANALISIS SEBATIAN DIHIDROKSIBENZENA TERPILIH PADA ELEKTROD NANOKOMPOSIT BERASASKAN KARBON DAN POLI (4–VINILPIRIDINA)

ABSTRAK

Kajian ini telah dijalankan dengan menggunakan pelbagai elektrod berasaskan karbon iaitu karbon berkaca, komposit grafit, karbon tiub nano dan grafin sebagai elektrod substrat. Batang komposit grafit telah digunakan dalam sintesis elektro-organik melibatkan katekol (CT) dengan kehadiran tiosemikarbazida (TSC) pada pH 5.3. Mekanisma pengoksidaan kemudiannya dicadangkan. Penjanaan elektro *o*-kuinon mempunyai tindakbalas penambahan 1,4 dengan TSC. Peningkatan pada arus mangkin kerana pengoksidaan semula tiol-katekol yang digunakan bagi kuantifikasi thiol tersebut. Elektrod karbon berkaca terubahsuai dengan poli (4–vinilpiridina) (P4VP) dan gabungan nya dengan karbon tiub nano berbilang dinding (P4VP/MWCNT-GCE) dan juga dengan kepingan grafin (P4VP/GR-GCE) menggunakan kaedah titisan telah dikaji. Kesan penggabungan P4VP dan MWCNT pada peng-elektro oksidaan difenol dan parasetamol (PCT), aspirin (ASA) dan kafein dalam penimbal sulfat (pH 2.5) dan penimbal fosfat (pH 7) juga diperhatikan. Puncak pemisahan (ΔEp) yang lebih kecil bagi pengoksidaan hidrokuinon (HQ) dan CT menunjukkan bahawa proses berbalik elektrod telah dipertingkatkan. Penentuan serentak kedua-dua sebatian juga adalah mungkin. Kepekaan pengukuran HQ dan CT pada 15 nM dan 2.6 nM dan 8.1 dan 26 nM pada P4VP/MWCNT–GCE dan P4VP/GR–GCE, masing-masing telah diperoleh.

Tidak ada gangguan oleh fenol, nitrofenol, aminofenol, bisfenol A dan klorofenol. Hasil yang memuaskan telah diperoleh bagi pengesanan serentak pakuan HQ dan CT dalam air paip dan air tasik. Elektrod ini juga telah menunjukkan aktiviti elektrokimia yang lebih baik bagi pengoksidaan PCT berbanding GCE MWCNT–GCE dan GR–GCE. Arus PCT pada P4VP/MWCNT-GCE adalah 300 kali ganda lebih tinggi daripada elektrod lain. Pada keadaan optimum, had pengesanan sebanyak 1.7 nM dan 3.2 nM bagi PCT diperhatikan pada P4VP/MWCNT-GCE dan P4VP/GR-GCE. Tiada gangguan dari asid askorbik dan asid urik. Elektrod ini telah digunakan untuk menentukan PCT dalam tablet dan sampel urin. Kajian juga menunjukkan P4VP/MWCNT–GCE boleh digunakan sebagai penderia khusus bagi ASA dengan kehadiran kafein dan PCT. Had pengesanan bagi ASA dan kafein pada P4VP/MWCNT–GCE masing-masing adalah 4.4 dan 1.2 nM.

ELECTROSYNTHESIS AND ELECTROANALYTICAL STUDIES OF THE SELECTED DIHYDROXYBENZENE COMPOUNDS AT CARBON AND POLY (4–VINYLPYRIDINE) BASED NANOCOMPOSITE ELECTRODES

ABSTRACT

This study has utilized various carbon based electrodes *viz.* glassy carbon, composite graphite, carbon nanotube and graphene as substrate electrodes. Composite graphite rods were utilised in electro-organic syntheses involving catechol (CT) in the presence of thiosemicarbazide (TSC) at pH 5.3. The oxidation mechanism of which was then suggested. The electro-generated *o*-quinone had a 1, 4-addition reaction with the TSC, such that an increase in current could be attributed to the re-oxidation of the thiol-catechol adduct and be used for quantification of the thiol. The glassy carbon electrode modified with a poly (4–vinylpyridine) (P4VP) and in combination with multiwalled carbon nanotubes (P4VP/MWCNT–GCE) and also with graphene sheets (P4VP/GR–GCE) using drop–casting method were investigated. The combined effect of P4VP and MWCNT on the electro-oxidation of diphenols and paracetamol (PCT), aspirin (ASA) and caffeine in the sulphate buffer (pH 2.5) and phosphate buffer (pH 7) solutions were observed. The smaller peak separation (ΔE_p) for the oxidation of hydroquinone (HQ) and CT indicates that the reversibility of the electrode process was enhanced. The simultaneous determination of both compounds was also possible. Sensitivities of measurement of HQ and CT at 15 nM, 2.6 nM, 8.1 nM and 26 nM on the P4VP/MWCNT–GCE and P4VP/GR–

GCE, respectively were obtained. There was no interference by phenol, nitrophenol, aminophenols, bisphenol A and chlorophenols. Encouraging results were obtained for simultaneous detection of spiked HQ and CT in tap water and lake water. The electrodes have also demonstrated excellent electrochemical activity toward PCT oxidation as compared to either GCE or MWCNT–GCE or GR–GCE. The currents of PCT on the P4VP/MWCNT–GCE were 300 fold higher than that of other electrodes. Under optimized conditions, limit of detection of 1.7 nM and 3.2 nM for PCT were observed on the P4VP/MWCNT–GCE and P4VP/GR–GCE, respectively. They were not interfered by ascorbic acid and uric acid. This electrode was applied for the determination of PCT in tablets and urine samples. The study also demonstrated that the P4VP/MWCNT–GCE can be used as a specific sensor for ASA in the presence of caffeine and PCT. Detection limit for ASA and caffeine on the P4VP/MWCNT–GCE were 4.4 nM and 1.2 nM, respectively.

CHAPTER 1

INTRODUCTION

1.1 Nanotechnology and Nanoscience

Nanoscience and nanotechnology has become a very dynamic and critical area of research, which is dramatically developing and spreading as a general-purpose technology in almost every field of technology domain as well as science and engineering disciplines due to its ability to create super-functional properties of materials at nano-scale [1, 2].

Nano-dimension transcends the conservative boundaries between scientific and engineering disciplines and technology segments. Apparently, nanotech is the foundation for gaining widespread benefits, consisting of smarter electronics, improved health, advanced agriculture and cleaner source of energy [3]. The tendency to understand how materials behave when sample sizes are close to atomic dimensions is one of the most important motivations in nanoscience.

Applying nanostructures for technology is also an opportunity in order to miniaturize and use new applications and devices as a result of unique properties of nanostructures. It should be noted that although many nanostructures such as large molecules and quantum dots are of great interest, the most active areas of study are related to nanotubes. Nanoscience and nanotechnology primarily deal with the synthesis, characterization, exploration, and exploitation of nanostructured materials which have received considerable attention. Another reason for the great popularity of this field is that the nanoscale phenomena are of great interest to chemists, physicists, biologists, electrical and mechanical engineers, and computer scientists.

1.1.1 Type and Properties of Nanostructures

Nanomaterials consist of various types of nanostructured materials including clusters, quantum dots, nanocrystals, nanowires, and nanotubes, while collections of nanostructures involve arrays, assemblies, and super lattices of the individual nanostructures [4, 5]. The properties of materials with nanometer dimensions significantly differ from those of atoms and bulk materials. This is mostly as a result of the nanometer size of the materials which causes (i) a large fraction of surface atoms; (ii) high surface energy; (iii) spatial confinement; (iv) reduced imperfections, which do not exist in the corresponding bulk materials [6]. The small dimensions of nanomaterials which provide them with an extremely large surface area to volume ratio will result in a large fraction of atoms of the materials to become the surface or interfacial atoms. However, when the sizes of nanomaterials are comparable to Debye length, surface properties of nanomaterials will affect the entire material [7, 8]. This consecutively may enhance or modify the properties of the bulk materials. For instance, metallic nanoparticles could be used as active catalysts and chemical sensors fabricated from nanoparticles and nanowires which also have higher sensitivities and selectivities.

1.1.2 Applications of Nanomaterials

Nanotechnology is being applied practically in all fields ranging from science, engineering, and health to medicine. Nanomaterials provide unique physical, chemical, and mechanical properties that could be used for a wide variety of applications in different areas. Nanomaterials are receiving considerable interest due to the potential of applications in a wide range of fields such as catalysis, sensors, semiconductors, fuel cells, drug delivery, and functional coatings. They can also be used in cosmetics, textiles, medical diagnosis and therapeutics, healthcare, water and air pollution treatment [9] .

1.2 Carbon Based Materials

Carbon is an essential constituent element of every living organism. We not only benefit from numerous carbon based products in our life, but also use it as a scientific tool. The physical and chemical properties of carbon are well documented, including the use of carbon in nanotechnology which is a great interest area of research and considerable funding is being allocated to the carbon nanotechnology research. Graphene (GR) (sp^2 bonded), graphite, diamond (sp^3 bonded), carbon nanotubes (sp^2 bonded), fullerenes and nanodiamonds are the well known forms of carbon (Figure 1.1) [10]. Nowadays, the applications of carbon nanotubes (CNTs), GR and carbon nanospheres in electrochemical sensors are the most interesting aspects of electrochemistry and they are going to be very important in the future of electrochemistry and related technologies in general.

Carbon based nanomaterials have received great attention regarding their electronic, mechanical, optical, and chemical characteristics. They can also be used for energy storage, molecular electronics, composite materials, bioengineering and environment. The unique and tunable properties of carbon-based nanomaterials which are most commonly cited in environmental applications are size, shape and surface area; molecular interactions and sorption properties; and electronic, optical, and thermal properties enable new technologies for identifying and addressing environmental challenges [11].

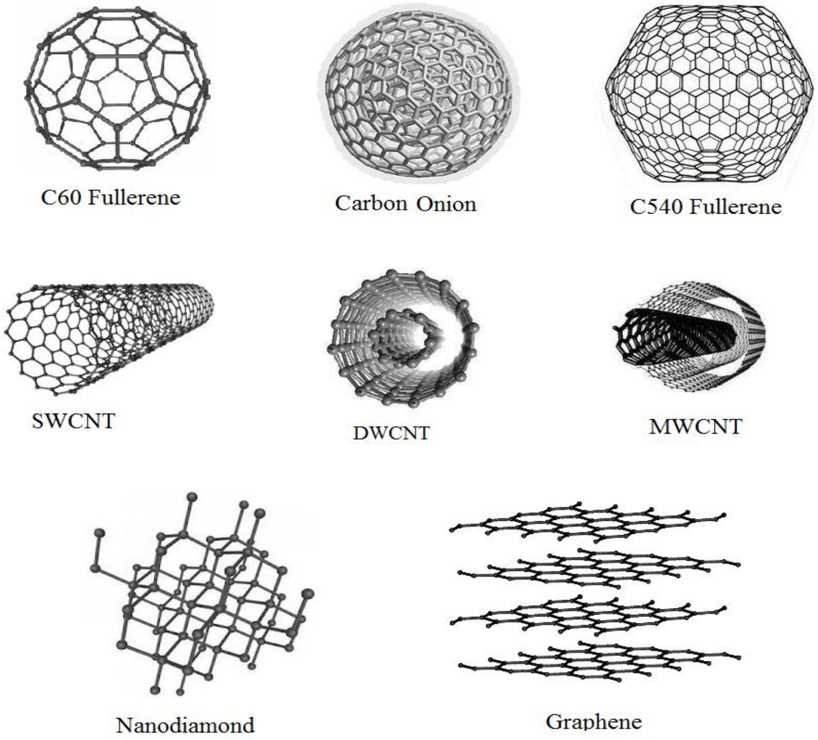


Figure 1.1; Various forms of carbon [12]

1.2.1 Carbon Based Materials in Electrochemistry

Carbon based materials such as glassy carbon, graphite, carbon fiber, graphite paste and composite graphite have been broadly applied in a variety of electrochemical devices due to their excellent conductivity and chemical inertness. Good crystallinity and micro structural order has been shown by the natural graphite (electron configuration $2s^2\ 2p^2$) which consists of multi-layers of GR. Therefore, it can be used as high-quality electrochemical devices with lower background current, wide potential window, fast electron-transfer rate and easily renewable surface. Thus, electrochemical devices fabricated from various based materials have become more important and their practical applications in electrochemistry have also been extensively studied with great success.

1.3 The Importance of Electrode Surface in Electrochemistry

In voltammetry, the most essential parameters include the electron-transfer rate, background current and accumulation of analytes. These parameters are significantly affected by the surface modification of the working electrode. Hence the sensitivity and selectivity could be optimized by improving the surface phenomena of electrodes.

The carbon electrode is broadly used due to its numerous advantages in contrast to the metal electrode. Firstly, it contains a majority of types which have been mentioned in section 1.2.1. Secondly, the carbon electrode forms an abundance of surface oxides, which not only results in a lower background current but also in an acceleration of the transfer of the electron [10]. Generally, there are two surface types of carbon, including pristine and monolayer oxides [10]. The pristine surface which can be gained by heat or polishing is a disordered surface without oxides or impurities. The monolayer oxides which can be achieved by modifying a thick film of oxides are a rich oxygen-containing surface. Hence, the voltammetric background can be increased due to the increasing of double-layer capacitance of interface, and the adsorption of cationic species can be also enhanced by the modifier. As a result, the sensitivity and selectivity of electroanalysis are a great deal enhanced by this process. There is a large variety of modifiers used for electrochemical pretreatment of the electrode surface in order to modify the electrochemical performance between the surface and the bulk solutions. The coating of the electrode surface with nanoparticles is one of the most important methods used.

1.3.1 Multi Walled Carbon Nanotube (MWCNT)

The carbon nanotubes have largely contributed in modern analytical sciences. As it is well documented, the basic composition of a CNT is GR and the structure of a CNT is like a sheet of GR rolled up into a tube (Figure 1.2). Besides their structural type, they are also classified as single walled carbon nanotubes (SWCNTs), double walled carbon nanotubes (DWCNTS) and multi walled carbon nanotubes according to the layer numbers (Figure 1.1). SWCNTs consist of only one layer of GR rolled to form a seamless cylinder with a few nanometers of diameter and a few hundred nanometers of length. DWCNTs consist of two GR cylinders with concentric arrangement and multi GR cylinders are termed as MWCNTs with diameters up to 100 nm [10].

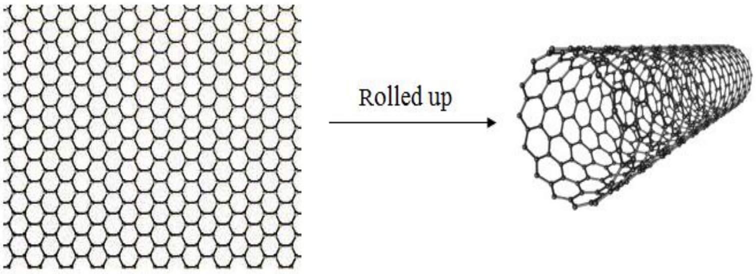


Figure 1.2; Graphene sheet rolled up to form CNT [13]

The unique properties of CNTs have led to significant applications in several fields, such as in the electronics and medicine aerospace industries, which have also encouraged the need of analytical methodologies to characterize and control the quality of these nanomaterials. Moreover, the use of CNTs as analytical tools, and the construction of nanodevices and nanosensor based on CNTs are considered as other areas of development for modern analytical science.

The wide-ranging role of CNTs in analytical chemistry has been reported by Valcaʾrcel et al. [14], Trojanowicz [15] and Merkoci [16]. Taking into consideration, in particular, the role of CNTs in electroanalytical chemistry, properties such as a high electronic conductivity and a high mechanical resistance have driven an impressive research effort in electroanalytical applications in recent years. Furthermore, an increased electrode active surface area, which gives rise to enhanced electrochemical responses, and a demonstrated anti-fouling capability of electrode surfaces upon modification with CNTs, are other key practical advantages that have promoted numerous noteworthy applications in electroanalytical chemistry, including electrochemical sensors [17-19].

The ability to promote electron transfer reaction when used as an electrode in electrochemical reaction has been suggested by the special electronic properties of CNTs, which provides a new application in the electrode surface modification to design new electrochemical sensors and novel electrocatalytic materials [20].

CNT modified electrode demonstrates the properties of electrocatalytic activity and electrosepration because CNT has unique electronic properties thus, it can promote electron transfer reaction which could be applied in the detection of analytes in a low concentration or in the complex matrix. The CNT modified electrodes generally consists of CNT paste electrode, CNT intercalated electrode, CNT coating electrode, and CNT embedded polymer electrode and are stated to give electrocatalytic activity towards a great variety of analytes, including dopamine [21], ascorbic acid [22], aspirin [23], acetaminophen [24] and various metal ions such as As^{3+}, Bi^{3+} , Pb^{2+} , Cd^{2+} [25, 26].

1.3.2 Graphene

GR as a novel carbon-based nanomaterial has aroused significant interest due to its potential applications in various fields [27-29]. GR is made from natural graphite which is found to be a new kind of nano-sized carbon based material besides CNTs. It is the mother element of some carbon allotropes, including graphite, carbon nanotubes, and fullerenes (Figure1.1). GR is a flat and sheet-like form of graphite [30] and it is the basic form of CNTs. Structurally, GR is a one-atom-thick planar sheet of sp^2-bonded carbon atoms densely packed in a honeycomb crystal lattice. GR is not only considered as the basic form of CNTs, but also many other kinds of carbon based materials. For instance, it has the ability to be rolled up to 1D CNTs, wrapped up to 0D fullerenes and stacked to 3D graphite [31, 32]. Due to its sp^2 structure, GR has numerous advantages having unique electronic, mechanical and optical properties. GR-based electrodes have demonstrated to have various applications such as transparent electrodes, ultrasensitive chemical sensors [33], supercapacitors (electric double layer capacitor) and nano electronics [34-36]. Among these mentioned properties exploring its application in the field of electrochemical sensor is of particular interest for the current studies [37-49].

GR is made from chemical reduction of graphene oxide (GO), which may present the advantage of being cheap. More recently, electrochemical reduction of GO to GR has received great attention because it is fast, inexpensive, green and nontoxic [50-52]. Figure 1.3 illustrates the scheme of the oxidation/reduction process of GR.

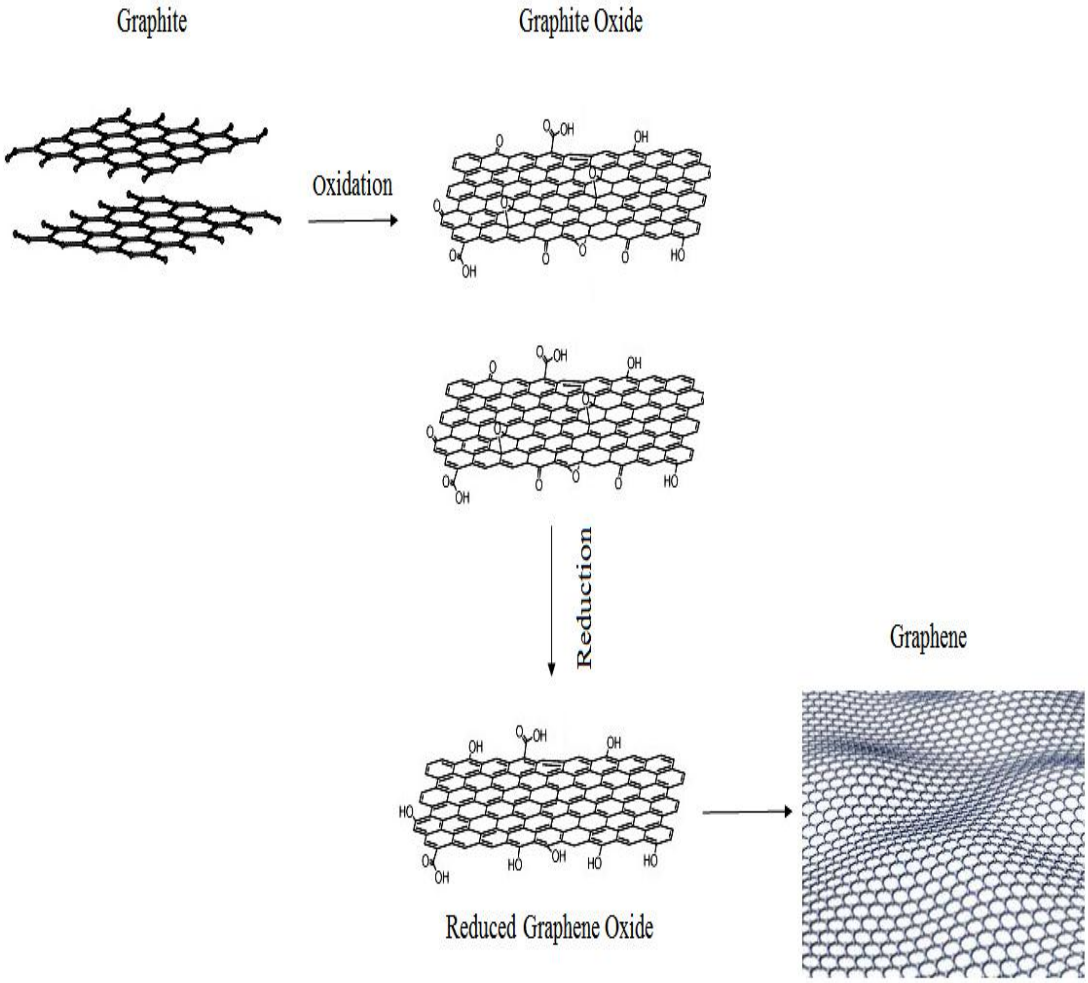


Figure 1.3; Production of GR via oxidation of graphite and reduction of graphite oxide to reduced graphene oxide (RGO) [53]

As can be seen from Figure 1.3, the resulting RGO from GO monolayers can be deposited in controllable density and many conductive substrates can be applied. Thus, the preparation of thin RGO film from GO can be achieved onto various solid and flexible substrates with conductivity increasing four times of the substrates [54-56]. Therefore, the GR produced from reduced GO, seems friendly in its application in electrochemical sensors. GR based electrodes have shown better advanced performance in terms of electrocatalytic activity compared to carbon nanotube based ones. These findings pointed out that the opportunities in electrochemistry encountered by carbon nanotubes might be also available for GR [57]. Studies on GR are likely to provide a fundamental insight into all carbon materials. In comparison with carbon nanotubes, GR demonstrates potential advantages of low cost, high surface area, ease of processing and safety [58].

Functionalization and dispersion of GR sheets are of critical importance in their applications. A large number of experiments focus on the insertion of additional chemical species between the basal planes of graphite [59, 60]. GR, the building block of graphite, was theoretically established in 1940 [61]. GR sheets with a high specific surface are hydrophobic and have a tendency to form agglomerates which may limit its further applications [62]. Aggregation can be reduced by the attachment of other small molecules or polymers to the GR sheets. Therefore, the material which has the ability to prevent GR from aggregating has received growing interest nowadays. The presence of hydrophilic or hydrophobic groups prevents the aggregation of GR sheets by stronger polar-polar interactions or by their bulky size [63, 64].

The functionalized GR sheets are more hydrophilic and can be easily dispersed in solvents with long-term stability [65, 66]. In addition, proper chemical functionalization of GR for instance by conventional acid treatment method, for formation of –COOH and –OH groups, prevents the agglomeration of single layer GR. The aggregation can also be reduced by the attachment of other small molecules or polymers to the GR sheets [65, 67, 68]. Meanwhile, non-covalent functionalization, such as co-dispersion with polymers has proved to be successful in solubilizing GR nanosheet [69]. The attachment of functional groups to GR also assists in its dispersion in a hydrophobic media as well as in the organic polymer. Therefore, an effective approach to the production of surface-functionalized GR sheets in large quantities has been a main focus of many researchers, with the goal of employing the majority of frequently proposed applications of GR in the areas of polymer nanocomposites, solar cells, drug delivery systems, super-capacitor devices, memory devices, transistor devices and biosensors [67] . As a novel and very capable material, it reveals fascinating applications in the fields of battery [70], supercapacitor [71], fuel cells [72] and ultrasensitive sensors [73]. In the area of electroanalytical chemistry, a great deal of attempts have been made to explore its electrocatalytic activity as electrode materials for the purpose of high sensitive analysis [39, 74].

1.3.3 Benefits of Applying Carbon Nanotubes (CNTs) and Graphene in Electrochemical Analysis

It is very important to develop simple, sensitive and accurate methods in order to identify pharmaceutical compounds and dihydroxybenzenes (DHB) by the electrochemical method. It has been found that due to the physical and chemical properties of CNTs and GR, it tends easily to absorb organic molecules through van der Waals and π–π stacking interactions or non-covalent interactions. Therefore, once the CNT or GR film is coated on the surface of a bare electrode, those organic molecules are easily accumulated on the surface of the modified electrode. The concept of chemically modified electrodes is one of the exciting developments in the field of electroanalytical chemistry. Several different strategies have been employed in the modification of electrode surface. The motivations for the modifications of the electrode surface area include improved electrocatalysis, freedom from surface fouling and prevention of undesirable reactions competing kinetically with the desired electrode process [75]. Some examples of the most ordinary methods are mentioned briefly in the following sections.

1.4 Polymer Nanocomposite (PNC) Based on Carbon Nanomaterial Electrode

Polymer nanocomposites (PNC) are of great interest for a variety of applications due to its numerous features such as low weight, low cost, ease of processing and shaping and corrosion resistant [76]. PNC are polymers that have been reinforced with small quantities (less than 5% by weight) of nano-sized particles having high aspect ratios [77] . The specific development of polymeric nanocomposite based on conventional polymers and conductive carbonaceous material has received a great deal of attention as a route to obtain the new materials with new structural and functional properties superior to those of the pure components and of previous nanocomposite systems with other fillers [78]. These properties could include increased modulus and strength, outstanding barrier properties, improved solvent and heat resistance and decreased flammability [79].

1.4.1 PNC Based on Multi Walled Carbon Nanotube (MWCNT)

Carbon nanotubes (CNTs) with exceptional structural properties and the presence of edge plane like sites located at the end and in the defect areas of their tubules possess high electrical conductivity, high chemical stability and extremely high mechanical strength. Due to its excellent properties, CNTs can be used as ideal reinforcing agents for high performance polymer composites. They have been applied broadly in the fabrication of ion sensors and biosensors with the least fouling, reduced overvoltage effects, faster electron transfer kinetics and higher sensitivities than the traditional carbon electrodes [80, 81]. However, poor solubility and process ability of CNTs have been the key technical obstacles, hindering their biomedical and other promising applications. It is extremely hard to disperse MWCNT in liquid. There are several methods for the dispersion of nanotubes in the polymer matrix consisting of solution mixing, melt mixing, electrospinning, in situ polymerization and chemical functionalization of the carbon nanotube. Also several types of CNT modified electrodes have been studied *viz.* CNT paste electrode [82], CNT film-coated electrode [83, 84], CNT power microelectrode, and conducting polymer/CNT modified electrode [85, 86]. The latest is of special interest because they have three-dimensional structures due to the incorporation of CNT into conducting polymers.

The non-covalent and covalent modifications of the CNTs with polymers are generally applied to improve their dispersion and orientation in aqueous solutions

[87-89]. The non-covalent approach mostly includes surfactant modification [90, 91], polymer wrapping [92], and polymer absorption [93, 94]. The interaction between the aromatic moieties of the polymers and the CNT surface were proposed to be responsible for the introduction of polymers into the CNT samples [95]. Among the non-covalent methods, polymer wrapping is the simplest route. Polymer/ CNT nanocomposite is one of the most promising field for CNT [96, 97]. These PNC have remarkable enhanced properties in electrical, thermal, physical, chemical, conductive and other smart functionalities which have attracted great attention worldwide from both academic and industrial points of view.

1.4.2 PNC Based on Graphene

Material scientists are examining materials with improved physicochemical properties that are dimensionally more appropriate in the field of nanoscience and technology. In this respect, the discovery of GR and GR-based polymer nanocomposites is an essential addition in the nanoscience area having a key role in modern science and technology [98]. The discovery of polymer nanocomposites by the Toyota research group has created a new dimension in the field of material science.

GR is expected to have significant properties such as outstanding conductivity, high specific surface area; high mechanical, thermal and chemical stabilities compared to CNTs and electrically conducting reinforced nanocomposites [99-103]. Mentioned properties provide GR as a promising material that could be employed in many applications such as in photovoltaic devices, transparent electrodes, sensors, super capacitors and conducting composites [98, 104-109]. The inherent properties of GR have created great interest in its possible implementation in innumerable devices [110] leading to future generations of high speed and radio frequency logic devices, thermally and electrically conducting reinforced nanocomposites, ultra-thin carbon films, sensors, electronic circuits, and transparent and flexible electrodes used for displays and solar cells [110].

It should be noted that the tensile strength of GR is similar or slightly higher than that CNT and the thermal and electrical conductivity of GR is also higher than those of CNT. The superior properties of GR compared to polymers are also reflected in polymer/GR nanocomposites. Polymer/GR nanocomposites present better mechanical, thermal, gas barrier and electrical properties compared to the neat polymer. Various polymer matrices have been employed for composites, including thermoplastics [111-113], liquid crystalline polymers [114, 115], water soluble polymer [116] and conductive polymers [117] among others.

1.5 Conductive Polymer

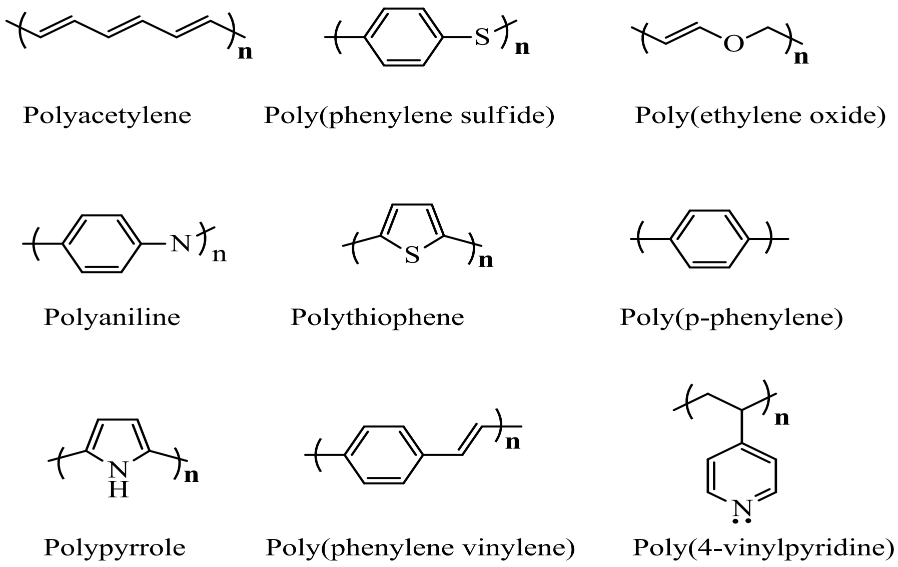
Conductive polymers are a new category of materials which demonstrate highly reversible redox behavior. Electrically conducting polyacetylene was discovered by scientists in 1977 [118, 119] and the Chemistry Nobel Prize was awarded to the scientists in 2000 [120]. The forthcoming utility of conductive polymers with an effective application in the growing technologies in bimolecular electronics display devices and electrochemical storage system. The most important conductive polymers is polyenes or polyaromatics such as polyaniline [121], poly pyrrole [122], and polythiophene [123]. These compounds have many potential applications as well as their derivatives, including sensors, biosensors, electrochromic devices [124] electromagnetic shielding [125, 126], corrosion inhibitor [127, 128], super capacitors [129, 130], polymeric batteries [131], and polymeric actuators [132, 133]. Intrinsically these conducting polymers are important owing to their relatively high thermal stability, low costs, ease of synthesis and good environmental behavior among the polymer modified electrodes. Conducting polymer based drug delivery systems which is used as a therapeutic electrode material for micro fabricated neural devices have developed much and dramatically during the past few decades [128].

1.5.1 Types of Conducting Polymers

Types of conducting polymers fall under three headings [134]:

(a). Intrinsically/inherently conducting polymers.
(b). Conducting polymer composites.
(c). Ionically conducting polymers.

Polyacetylene, polypyrrole, polythiophene, polyaniline, poly (*p*-phenylene) and poly (phenylene vinylene) are the most common examples of intrinsically/inherently conducting polymers. Figure 1.4 illustrates some of the conjugated polymers studied as intrinsically conducting polymers. Simplicity of synthesis, low cost, good environmental stability and high conductivity are some properties which makes conducting polymer desirable for use.



Polyacetylene Poly(phenylene sulfide) Poly(ethylene oxide)

Polyaniline Polythiophene Poly(p-phenylene)

Polypyrrole Poly(phenylene vinylene) Poly(4-vinylpyridine)

Figure 1.4; Examples of inherently conducting polymers

The two main groups of applications for organic conducting polymers are briefly described in the following section:

Group I: This group utilizes polymers conductivity as its main property including its light weight, biological compatibility for ease of manufacturing or cost, electrostatic materials, conducting adhesives, printed circuit boards, electromagnetic shielding, artificial nerves, antistatic clothing, active electronics (diodes, transistors), piezoceramics, and aircraft structures. Conducting polymer is also incorporated in the construction of super capacitors with efficient charge propagation [135]. Efficient super capacitors can be applied as power conditioners in cameras, in power generators and also as excellent power supplies.

Group II: This group uses the electroactivity character property of the materials consisting of molecular electronics, electrical displays, optical computers, ion exchange membranes, and electromechanical actuators. Moreover, one of the other important applications of these polymers is in the field of sensors such as chemical sensors, ion and biochemical sensors [136] and in the medical field owing to the fact that several tissues in the human body are responsive to electrical fields [120]. Most conducting polymers have high biocompatibility and the ability to trap and release biological molecules. Hence, this makes them useful as tissue-engineering scaffolds, neural probes, bio-actuators and also drug delivery devices [137]. Among the mentioned conducting polymers in Figure 1.4, Poly (4–vinylpyridine) (P4VP) is of interest in this research due to its electrical conductive properties and good redox polymer.

1.5.2 Poly (4–vinylpyridine) (P4VP) as a Conducting Polymer

The use of conducting polymers such as P4VP and polypyrrole to improve the electrocatalytic activity, electron transfer kinetics and stability of the modified electrodes have been reported [138-142]. P4VP is a hydrophobic polymer in a polar solvent and is a cationic (protonated) polyelectrolyte at low pH [142]. It has been reported that non-covalent and covalent modifications of the carbon-based nanomaterials, such as CNTs and GR, with polymers or biomolecules are aimed at improving their dispersions and orientations in aqueous solutions. The flexible chains of P4VP may act as a stabilizing agent when wrapped around the MWCNT or GR, preserving its intrinsic electrical and mechanical properties and also rendering their solubility in water, ethanol and dimethylformamide (DMF). Furthermore, P4VP can easily be processed and fabricated to form free-standing films which are desired in most applications [143]. This is an important feature for assembling CNT and other materials applying the layer by layer assembly approach [144]. Besides that, the high electrical conductivity and good redox mediator are among the analytical advantage of P4VP in polymer nanocomposite electrodes [138, 145, 146].

1.6 Electro-Organic Synthesis

Among the most interesting and innovative chemical technologies, the electro-chemical method provides a very appealing and potent means for the small-scale and high purity production of compounds. From the point of view of green chemistry, using electrosynthesis is considered as a method having significant advantages. The electrochemistry of organic compounds was being studied for more than 150 years with the first one suggesting applicability of the development of green methods organic synthesis [147]. The benefit of applying the electro-organic synthesis method is well documented in previous research by Nematollahi group [148-150] and others [151-153], which confirmed that the emergence of organo-synthesis *via* electrochemical procedures, were especially advantages of the electrochemistry. These include energy specificity, clean synthesis, absence of toxic reagents and solvents, operation at room temperature and pressure, chemical selectivity and specific activation of small molecules [152].

Electrosynthesis can result in efficient and occasionally unexpected synthesis of compounds, which cannot be easily prepared by conventional organic synthesis [154]. The top green advantages of the electro-organic synthesis are listed as follows:

1) The electro-organic reaction is effectively achievable at room temperature.

2) Since the electrode potential has the ability of being controlled over a wide range, a wide variety of electro-organic reactions are able to be designed.
3) Since the structures and reactivities of the active species are different from those formed in usual chemical reactions, a diversity of novel reactions can be realized.
4) The electro-organic reaction is fundamentally non-polluting.
5) The reaction scale is controlled easily.
6) The energy efficiency is usually high.

1.7 Dihydroxybenzenes and Its Derivatives

Ortho- and *para*-dihydroxybenzenes are well known in biological systems. 1,2- and 1,4-naphthalenediols are often used as metabolites of simpler aromatic hydrocarbons such as benzene or naphthalene. Due to the existence of two exchangeable hydrogen atoms, the aromatic diols is likely to be biologically reactive molecules, capable of demonstrating both anti- and pro-oxidant behavior. These compounds have antioxidant and antimicrobial activity and they are usually important elements of plant extracts used in medicinal chemistry for their various biological activities [155]. Some examples of the dihydroxybenzenes compound are described briefly in the following section.

1.7.1 Catechol (CT)

Catechols such as DHB are antioxidants (Figure 1.5). They have mixed effects on normal and cancer cells at *in vitro* and *in vivo*. Depending on the amount of DHB used and the time before its application, DHB could reduce tumor growth [156].

Due to their mechanisms [157-162], synthesis [148, 149, 151, 152, 155, 163-166] and the importance of interest, the study of reaction between quinones and nucleophiles is increasing. Selection of solvents, pH, nature of nucleophiles and electrophiles and type of DHB will affect the mechanism. CT is also an important material which is widespread in the environment, and especially as constituents of edible plants [167] it is also widely used in tanning, cosmetic, chemical materials and in pharmaceutical industries. CT is hazardous to human health occurring frequently in the environment [168]. In addition, CT is one of the most important phenolic compounds which occur naturally in fruits and vegetables and which could be released in the environment with its manufacture and use. It is also detected at low levels in ground water, soil samples and in wastewater from coal conversion [169]. CT and their quinone derivatives have received significant attention due to their abundance in nature and key roles in many biological systems. Furthermore, most of the compounds incorporating CT moiety exhibit antioxidant, anti- carcinogenic anti-fungus and anti-bacterial activities are applied as HIV integrase inhibitors.

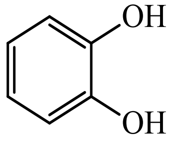


Figure 1.5; The structural formula of CT

1.7.2 Hydroquinone (HQ)

HQ, (1, 4- dihydroxybenzene), which is one of the isomers of diphenol (Figure 1.6), is very vital in a large number of biological and industrial processes such as paper manufacturing, coal-tar production and photography [170]. HQ has been widely used in dye production for skin whitening, cosmetic products, antioxidant, polymer, pharmaceutical industries and as an anticancer agent. HQ is a potentially carcinogenic substance, causing severe effects on the central nervous system [171]. Indeed, HQ is a serious environmental pollutant for instance exposure to HQ can cause irritation to the eyes, nose, throat, skin and nail discoloration [172]. Therefore, the determination and quantification of HQ is necessary to estimate its possible effect. Recently, utilizing HQ for substitution of unstable oxygen is such growing interests in order to act as electron transfer media in construction of enzyme-based glucose biosensor [173].

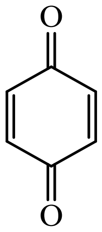


Figure 1.6; The structural formula of HQ

1.8 Electrochemical Synthesis of CT in the Presence of Nucleophile

CT as one of the most well-known compounds in biological systems frequently performs as the reactive center of electron transfer in the structure of numerous natural compounds. An enormous number of quinones with various structures are provided by nature and have a very important role in the redox electron-transport chain of living systems [174]. It is well documented that CT could be oxidized electrochemically to *o*-quinone and since the quinones formed are quite reactive they could be attacked by a variety of nucleophiles such as methanol [175], 4-hydroxycoumarin, 4-hydroxy-6-methyl-2-pyrone [176], sulfinic acids [159, 177, 178], barbituric acids [179] and were converted to the corresponding methoxyquinone [175], coumestan [176], spiro [180] dispiropyrimidine benzofuran [179], and arylsulfonylbenzendiol [177, 178] derivatives, respectively. Moreover, since electrochemical oxidation is often similar to the oxidation of CT in the mammalian and human body's central nervous system, this appealing incident leads to the study of anodic oxidation of CT in the presence of different nucleophile [175]. Some examples of the most important electro-organic synthesis methods which have been investigated in the previous research [167, 181] are discussed in the following discussion.

The electrooxidation of 4-methylcatechol in the presence of 1, 3-dimethylbarbituric acid and 1, 3-dimethylthiobarbituric acid as nucleophiles has been studied in depth by CV and controlled-potential coulometry. The results reveal that 4-methylcatechol would be oxidized to *o*-benzoquinone with no conversions to its quinone methide tautomeric form, under ECEC [182, 183] mechanism. The electrochemical synthesis of the final product has been successfully performed in one pot in an undivided cell [167].

Fotouhi *et al.* [184] have worked on the electrochemical oxidation of CT in the presence of 6-methyl-1,2,4-triazine-3-thion-5-one in aqueous sodium acetate, using CV and controlled-potential coulometry. They suggested a mechanism for the oxidation of CT and their reaction with 6-methyl-1,2,4-triazine-3-thion-5-one. The results show that CT derivatives were converted into 7H-thiazolo [3,2-b]-1,2,4-triazin-7-one derivatives under a Michael-type addition reaction of 6-methyl-1,2,4-triazine-3-thion-5-one to anodically generated *o*-quinones. The results also confirmed the successful performance of electrochemical synthesis of some new 6-methyl-1, 2, 4-triazine-3-thion-5-one derivatives in an undivided cell.

Electrochemical oxidation of CT in the presence of cyanoacetone and methyl cyanoacetone as nucleophiles in aqueous solutions has been investigated using CV and controlled-potential coulometry under ECEC mechanism. New nitrile containing benzofurans has been found as the final products [185].

The electrochemical oxidation of CT in the presence of sulfanilic acid was investigated using CV and controlled-potential coulometry [159]. The results illustrate that the *o*-quinone drived from CT take part in a Michael addition reaction with the sulfanilic acid.

Electrochemical oxidation of quercetin which is a flavonoid broadly spread in nature has been studied in the presence of benzensulfinic acids as nucleophiles in an acetonitrile water mixture, using CV and controlled-potential coulometry. The results revealed that the *o*-quinone derived from quercetin was involved in a Michael addition reaction with the benzenesulfinic acids in order to form the corresponding sulfonyl derivatives, consequently the electrochemical synthesis of these derivatives has been effectively performed at carbon rod electrode in an undivided cell in good yield (74%) and purity [186].

Electrochemical oxidation of 4-aminocatechol has been examined in the presence of 4-toluensulfinic acid and benzensulfinic acid as nucleophiles in aqueous solutions, via CV and controlled-potential coulometry. The results show that the *o*-quinone derived from 4-aminocatechol takes part in Michael addition with these nucleophiles in order to form the corresponding new organosulfone derivatives [181]. The electrochemical behavior of CT and 4-methyl catechol in