CHAPTER
I

INTRODUCTION

AND

LITERATURE SURVEY

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1. Introduction

In this chapter, a brief overview of electrochemistry fundamentals relevant to results presented in the present work will be overviewed. The main character of the thesis (glucose oxidation) is described by introducing some of its biological fundamental, chemistry, and utilization. Glucose electrooxidation will then be discussed starting from its history, classification and definitions emphasizing the most important applications involving this topic.

1.1. Scope of electrochemistry [1]

Electrochemistry is the branch of chemistry that deals with the chemical changes produced by electricity and the reverse. These changes occur in solutions in a homogeneous or heterogeneous manner on the electrode surface. The transshipment reaction causes two or more opposing events in opposite directions to ensure electroneutrality. In the case of homogeneous oxidation and reduction reactions, they often occur on electrodes immersed in the cell solution and separated into space. The

charges are transported between electrodes either ionically in solution or externally by electric wire. The products can be separated in the two electrode reactions if the cell configuration permits. For batteries energy, the sum of the free energy changes at both electrodes need to be negative. External electrical energy can be provided if the total free energy is positive, leading to the binding of electrode reactions and the conversion of chemicals.

1.2. The nature of electrode reactions [1]

1.2.1. Electrode reactions.

Heterogeneous electrode reactions occur in an area where the charge distribution differs from those phases between the electrode and the solution. The structure of the interlayer affects the electrode process. In the following section, the kinetics and thermodynamics of electrode processes are summarized.

1.2.2. Thermodynamics and kinetics of electrode reaction

For half-reactions at equilibrium, the potential, *E,* can be related to the standard electrode potential through the *Nernst equation:*

$$E = E^\theta - \frac{RT}{nF} \sum Vi \ \ln a_i \qquad (1.1)$$

where a_i are the activity of species and v_i, are the stoichiometric numbers, positive for products (reduced species) and negative for reagents (oxidized species). The tendency for the reduction to occur, relative to the NHE reference, is thus given by;

$$AG^{\theta} = -n\,FE^{\theta} \qquad (1.2)$$

In term of activity ($a_i = \gamma_i c_i$ with γ_i, the activity coefficient of species I and c is the concentration of this species) The Nernst equation (1.1) is rewritten as

$$E = E^{\theta} - \frac{RT}{nF}\sum Vi\,\ln c_i \qquad (1.3)$$

in which E^{θ} is the formal potential.

Nernst equation can be applied if the oxidized and reduced species are in equilibrium at the electrode surface. The electrode reaction is then known as a *reversible* reaction. Thus, Nernst equation, and therefore reversibility is considered in the term of the time allowed for the electrode reaction to reach equilibrium.

The concentrations of species at the interface depend on the mass transport of these species from bulk solution, often described by the mass transfer coefficient k_d. *A* reversible reaction corresponds to the case where

the kinetics of the electrode reaction is much faster than the transport. The kinetics is expressed by a standard rate constant, k_0, which is the rate constant when $E = E^{\theta}$. So, the criterion for a reversible reaction is $k_o \gg k_d$.

By contrast, an *irreversible* reaction is one where the electrode reaction cannot be reversed. A high kinetic barrier has to be overcome, which is achieved by application of an extra potential (extra energy) called the *overpotentially, η ,* and in this case $k_o \ll k_d$.

Quasi-reversible reactions exhibit behavior intermediate between reversible and irreversible reactions, the overpotential having a relatively small value, so that with this overpotential reactions can be reversed.

The potential-dependent expression for the rate constant of an electrode reaction is, for a reduction,

$$k_c = k_0 exp\left[-\alpha_c nF(E - E^{\theta})/RT\right] \qquad (1.4)$$

and for an oxidation

$$k_a = k_0 exp\left[\alpha_a nF(E - E^{\theta})/RT\right] \qquad (1.5)$$

In these equations α_c and α_a are the cathodic and anodic *charge transfer coefficients* and are a measure of the symmetry of the activation barrier, being close to 0.5 for a metallic electrode and a

simple electron transfer process. As mentioned above, the standard rate constant is the rate constant at $E = E^{\theta}$.

An alternative way used to express the rates of electrode reactions is through the *exchange current, I_0*. This is the magnitude of the anodic or cathodic partial current at the equilibrium potential, E_{eq}.

1.3. Applications of electrochemistry

There are a wide range of applications including: voltammetric, electroanalysis and potentiometric, electroplating, fuel cells, industrial electrolysis, electrochemical machining, as well as a lot of related applications, for example, suppression of corrosion; bioelectrochemistry and biosensors.

1.3.1. Electrocatalysis:

The *electrochemical* reaction is carried out in three basic steps as shown in Figure 1.1(I) the transfer of the reactive material in the electrolyte interface, (II) the transfer of the electron between the reactant and the electrode, and the adsorbent (III) which results in the formation of products. The main reason for the use of a catalyst in an electrochemical reaction is to either reduce the activation energy to a step limiting the rate or to look for an alternative reaction pathway [2] as

shown in Figure 1.2. *Electrocatalysis* includes either homogeneous or heterogeneous processes as in conventional chemical catalysis.
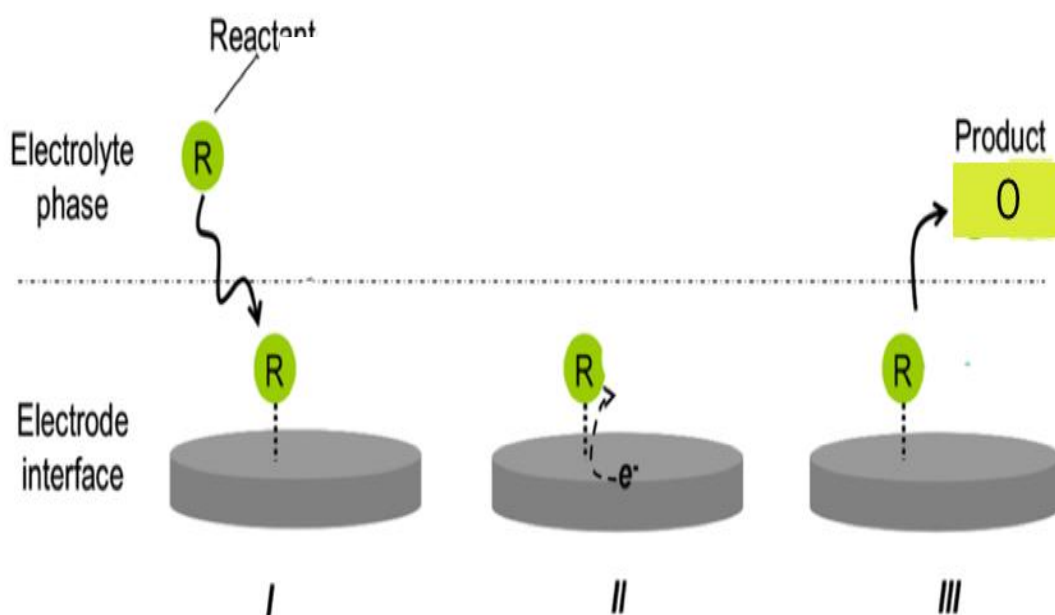

Figure 1.1. Main steps (I – III) of an electrochemical reaction with electron transfer from the electrode to an adsorbed species on its surface (a reduction reaction).
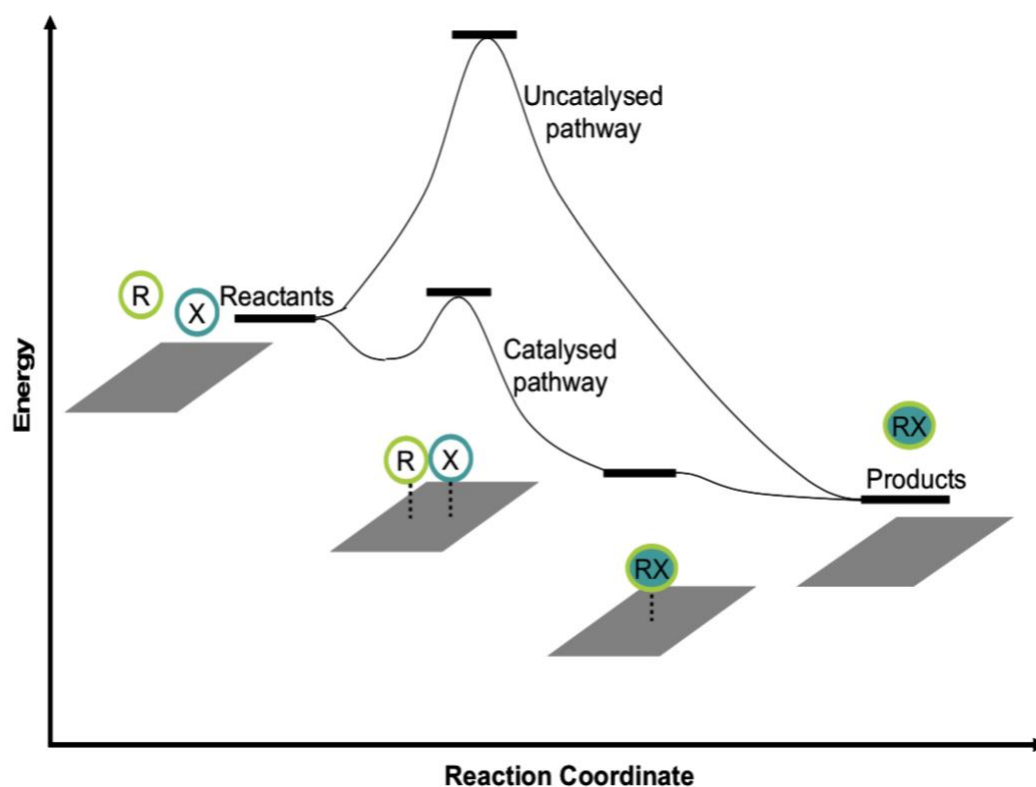
Figure 1.2. Schematic representation of catalysed and uncatalysed reaction pathways [3].

As represented in Fig. 1.2, the reaction activation barrier decreases and the reaction rate rises because the reaction rate is mainly controlled by the highest activation along the reaction coordinates. The reaction mechanism is called Langmuir-Hinshelwood when there is a reaction of adsorbed species on the catalyst surface. The mechanism is known as Eley-Rideal [4] if one of the reactants is obtained directly from the liquid or gas phase.

There are many applications of electrocatalysis as shown in Figure 1.3 for heterogeneous catalysts and the basis for development and research. The use of electrical catalysts has many advantages, including more efficient conversion of chemistry to electrical energy (in a fuel cell), more efficient use of energy (in an electrolysis cell), a more selective way of reacting (i.e., greater productivity than the desired product), and low cost of materials.
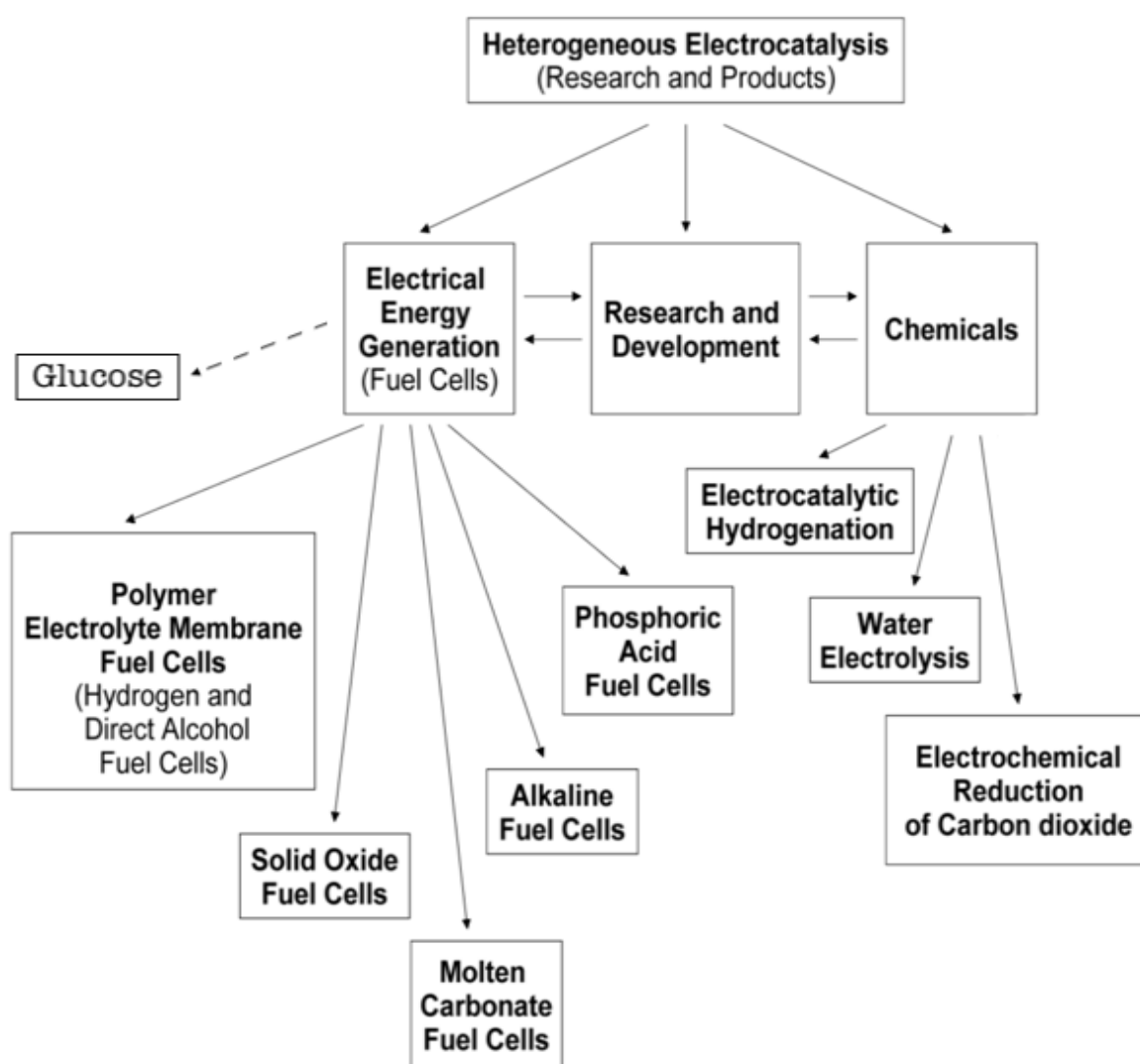

Figure 1.3. Various applications, research and development areas of heterogeneous electrocatalysis [5].

1.3.2. Potential step and sweep techniques [2]

1.3.2.1. Chronoamperometry

Chronoamperomety is where the current from an electrochemical procedure is estimated carefully as a function of time [6,7]. The potential of the working electrode is stepped to a certain potential and the resulting current from faradaic processes occurring at the electrode (caused by the potential step) is monitored as a function of time. A single (Figure 1.4) or double potential step to the working electrode of the electrochemical system is applied.
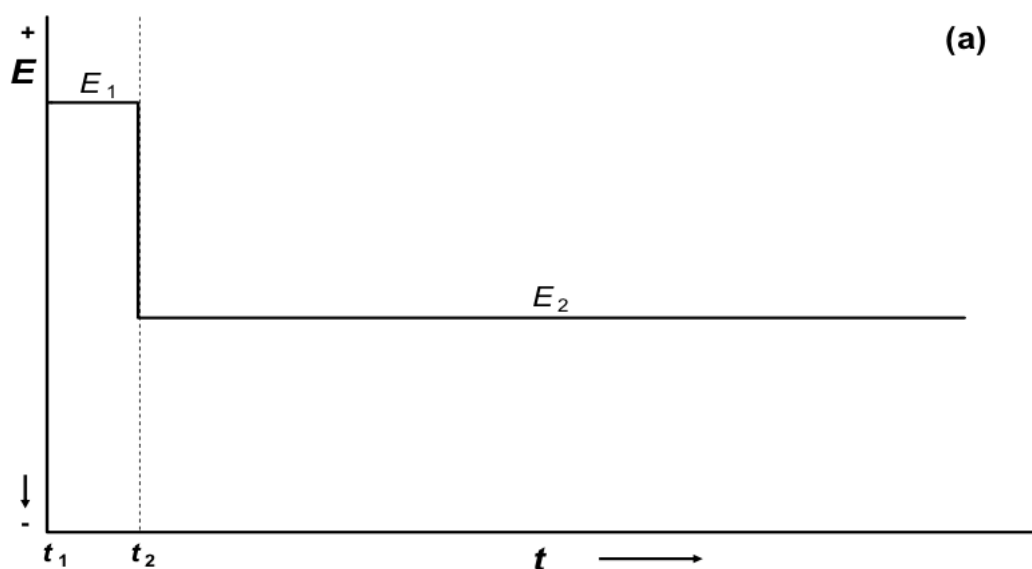

Figure 1.4. (a) Potential stepping waveform in a typical experiment in which a species of interest is electro inactive at E_1, but is reduced at a diffusion-controlled rate at E_2 [2].
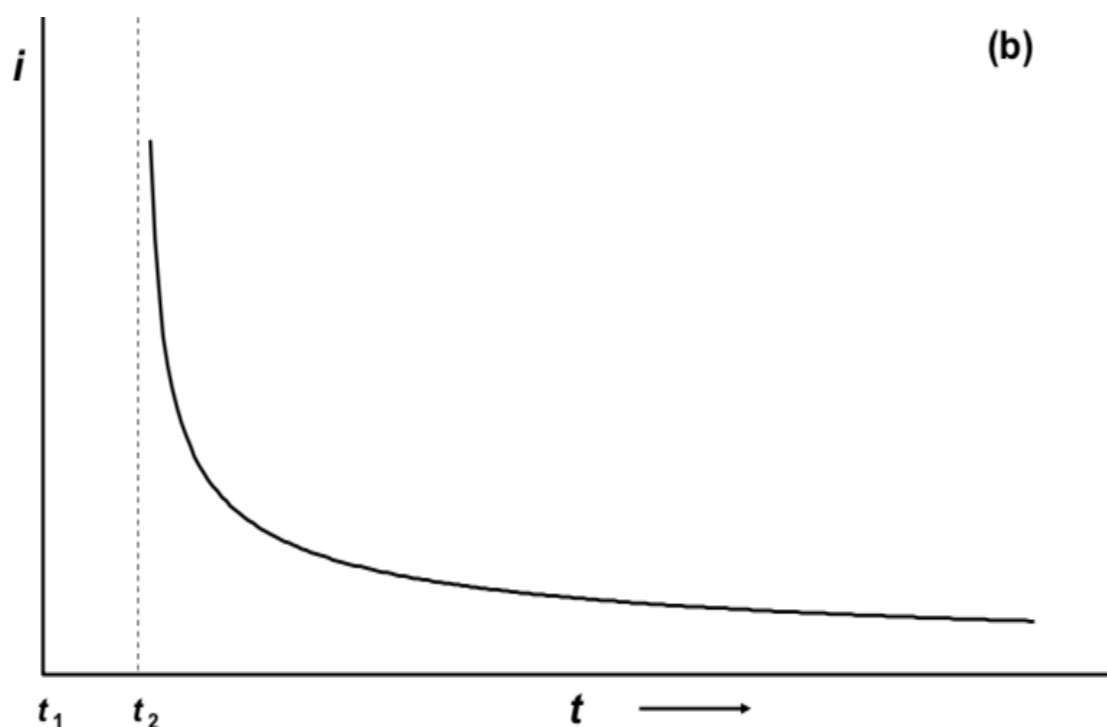
Figure 1.4. (b) Chronoamperometric response as a result of the waveform perturbation described in (a) [2].

1.3.2.2. Voltammetry

Voltammetry (*volt-amperometry*) contains a unique gathering of chronoamperometric electrochemical techniques in which data about an electrochemically-active species is gotten from the measurement of current through a working electrode as a function of time, while the applied potential to the electrode is controlled as a linear function of time [8]. The utilization of the three electrodes (working, counter, and reference), alongside the potentiostat instrument, allows accurate

application from the electrochemical cell of a perturbation potential waveform and the measurement of the resultant signal. Usually, a voltammogram is acquired during the potential sweep by measuring the current at the working electrode. The primary event is the oxidation or reduction of a chemical species at a working electrode and the *i-E* response measured can be considered as an 'electrochemical spectrum' in particular, information is obtained as if oxidation and reduction occurs [6, 9,10].

The technique can provide thermodynamic information as well as kinetic parameters related to electron transfer reactions at an electrode-solution interface. In addition, voltammetry can provide information related to the kinetics and mechanisms of chemical reactions subsequent to an electron transfer step. Some of the main advantages of sweep voltammetry are based on the fact that a wide potential range can be scanned rapidly for reducible and oxidizable species. These experiments can also be performed with variable time scales by applying different potential scan rates [6, 9,10].

Cyclic voltammetry (CV)

Cyclic voltammetry is a method for investigating the electrochemical behavior of a system. It was first reported in 1938 and

described theoretically by Randies [11]. Cyclic voltammetry is the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of cyclic voltammetry results from its ability to rapidly provide considerable information on the thermodynamics of redox processes, on the kinetics of heterogeneous electron-transfer reactions, and on coupled chemical reactions or adsorption processes. Cyclic voltammetry is often the first experimental approach performed in an electroanalytical study, since it offers rapid location of redox potentials of the electroactive species and convenient evaluation of the effect of media upon the redox process [12-14].

Basic principles of Cyclic Voltammetry

A cyclic voltammogram is obtained by applying a linear potential sweep (that is, a potential that increases or decreases linearly with time) to the working electrode. As the potential is swept back and forth past the formal potential, E°, of an analyte, a current flow through the electrode that either oxidizes or reduces the analyte. The magnitude of this current is proportional to the concentration of the analyte in solution, which allows cyclic voltammetry to be used in an analytical determination of concentration.

The equipment required to perform cyclic voltammetry consists of a conventional three-electrode potentiostat connected to three electrodes (working, reference and auxiliary) immersed in a test solution. The potentiostat applies and maintains the potential between the working and reference electrode while at the same time measuring the current at the working electrode.

Voltammetry is a collection of electroanalytical techniques in which the current is measured as a function of applied potential of certain waveform (Fig. 1.5). The excitation signal for CV is a linear potential scan with triangular waveform as shown in Fig. 1.5. This triangular potential excitation signal sweeps the potential of an electrode between two values, sometimes called the switching potential. It is widely used by chemists for non-analytical purposes including fundamental studies on redox processes, adsorption processes on surfaces, electron transfer mechanisms and electrode kinetics. Oxidation potentials, diffusion coefficients and electron transfer rates are readily obtained using electroanalytical methods.
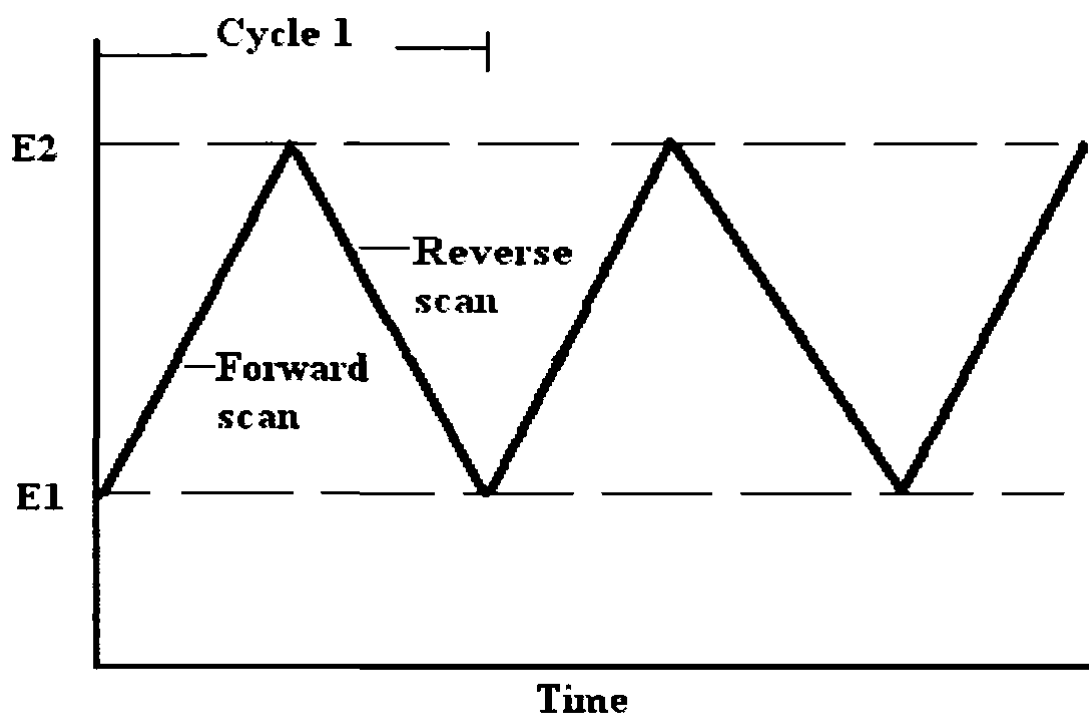
Figure 1.5. Variation of the applied as a function of time in a cyclic voltammetry experiment [11].

In CV the electrode potential between potential limits E1 and E2 at a known sweep rate (also called scan rate) is scanned. On reaching limit E2 the sweep is reversed to E1 to obtain a cyclic scan. The CV scan is a plot of current verses potential and indicates the potential at which redox process occur, and the result is referred to as a cyclic voltammogram. A peak in the measured current is seen at a potential that is characteristic of any electrode reaction taking place. The peak width and height for a particular process may depend on the sweep rate, electrolyte concentration and the electrode material [15,16].

The CV is usually initiated at a potential where species are not electroactive. The important parameters of a cyclic voltammogram are the magnitudes of anodic peak current (i_{pa}), the cathodic peak current (i_{pc}), the anodic peak potential (E_{pa}) and cathodic peak potential (E_{pc}). The basic shape of the current versus potential response for a cyclic voltammetry experiment is shown below (Fig. 1.6).
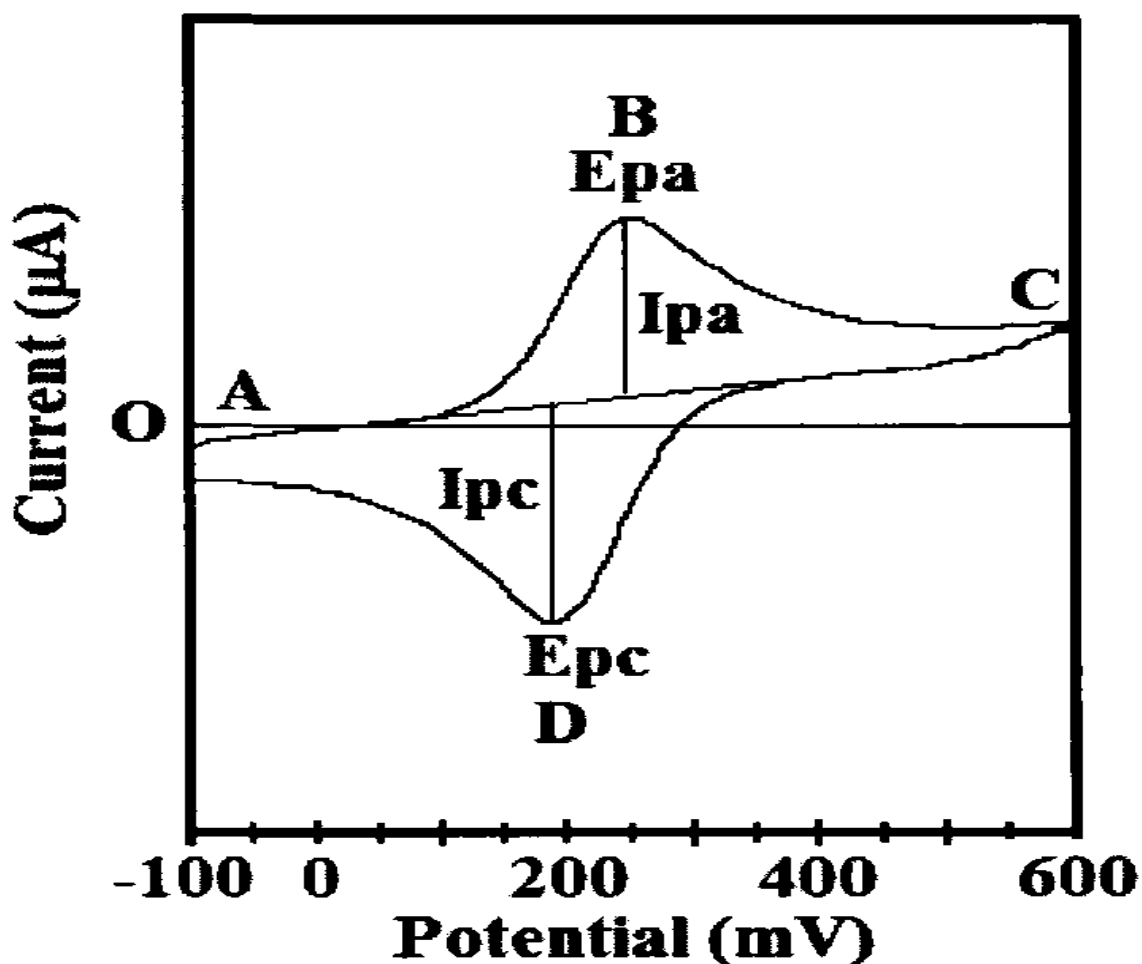

Figure 1.6. A typical cyclic voltammogram of current potential [11].

At the start of the experiment, the bulk solution contains only the reduced form of the redox couple (R) so that at potentials lower than the redox potential, i.e. the initial potential, there is no net conversion of R into O, the oxidized form (point A). As the redox potential is approached, there is a net anodic current which increases exponentially with potential. As R is converted into O, concentration gradients are set up for both R and O, and diffusion occurs down these concentration gradients. At the anodic peak (point B), the redox potential is sufficiently positive that any R that reaches the electrode surface is instantaneously oxidised to O. Therefore, the current now depends upon the rate of mass transfer to the electrode surface. Upon reversal of the scan (point C), the current continues to decay and a peak shaped response (point D). If a redox system remains in equilibrium throughout the potential scan, the electrochemical reaction is said to be reversible. In other words, equilibrium requires that the surface concentrations of O and R are maintained at the values required by the Nernst Equation.

The transfer of electrons to or from the substrate is an activated process. The electron transfer process can be

  i.   Reversible process

 ii.   Irreversible process and

iii.   Quasi-reversible process

Reversible Electron Transfer Process
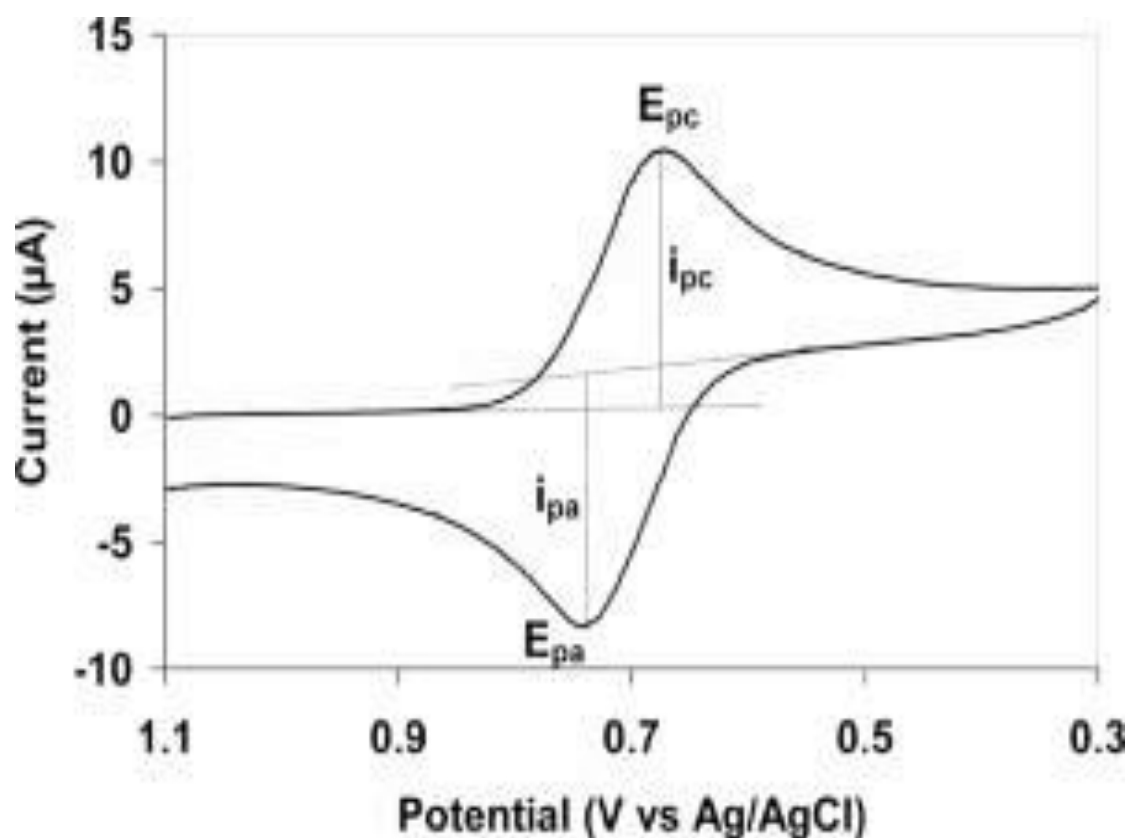
Figure 1.7. Typical voltammogram for a reversible process.

For a reversible process, oxidation and reduction peak is observed as shown in Fig. 1.7 in which E_{pa} and E_{pc} are potentials of anodic and cathodic peaks, respectively, and i_{pa} and i_{pc} are the corresponding currents. Reversibility can be defined as chemical or electrochemical. In an electrochemically reversible process the electron transfer is not rate limiting. For a chemically reversible process, both forms of redox couple (O for oxidized form and R for reduced form) are stable in the time scale

of measurement. The rate of electron transfer is fast compared to the rate of mass transport and does not control the overall rate. In this process the rate of the reaction is fast enough to maintain equal concentration of the oxidized and reduced species at the surface of electrode. The concentration C_{ox} and C_{red} of oxidized and reduced forms of the redox couple respectively follow the Nernst equation

$$E = E^\circ + \frac{RT}{nF} Ln \frac{C_{ox}}{C_{red}} \qquad (1.6)$$

where, n= number of electrons transferred, F= Faraday constant, R= gas constant and T= temperature. If the system is diffusion controlled then the Fick's law of diffusion holds for both oxidation and reduction. Under these conditions, peak current is given by Randies Sevcik equation;

$$i_p = (2.69 \times 10^5) n^{3/2} A D_o^{1/2} C_o v^{1/2} \qquad (1.7)$$

where n is the stoichiometric number of electrons involved in the electrode reaction, A is the area of electrode in cm2. D_o is the diffusion coefficient of the species O in $cm^2 s^{-1}$, C_o is the concentration of the species O in mol/cm^3 and υ is the scan rate in $V s^{-1}$.

Irreversible Electron Transfer Process
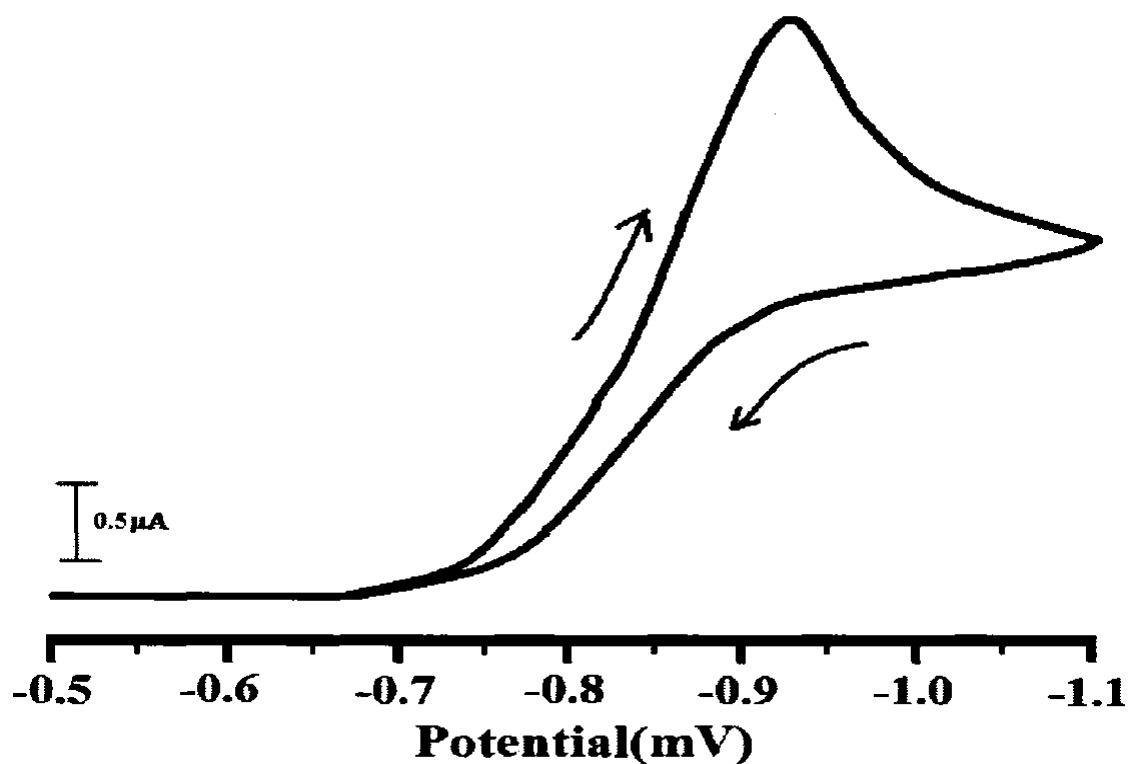

Figure 1.8. Typical voltammogram for an irreversible process [11].

For an irreversible process, only forward oxidation or reduction peak is observed (Fig. 1.8). This process is usually due to slow electron exchange or slow chemical reactions at the electrode surface [17]. In an irreversible electrode process, the mass transfer step is very fast as compared to the charge transfer step.

For an Irreversible reaction, the peak current is given by [18]

$$i_p = (2.99 \times 10^5)n\,(\alpha n)^{1/2} A\,D_o^{1/2}\,v^{1/2}\,C_o^* \qquad (1.8)$$

$$(\alpha n_a) = \frac{47.7}{E_p - E_{p/2}} \qquad (1.9)$$

The value of E_p, the difference between the cathodic and anodic peak is given by equation 1.9. The peak separation E_p is a factor determining the reversibility or irreversibility of an electrode reaction.

Quasi Reversible Electron Transfer process

Quasi-reversible process is intermediate between reversible and irreversible systems (Fig. 1.9). The current due to quasi-reversible processes is controlled by both mass transport and charge transfer kinetics [19]. The process occurs when the relative rate of electron transfer with respect to that of mass transport is insufficient to maintain Nernst equilibrium at the electrode surface. In the quasi-reversible region both forward and backward reactions contribute to the observed current. The equation by Nicholson is normally used to calculate electron transfer rate constants [20].
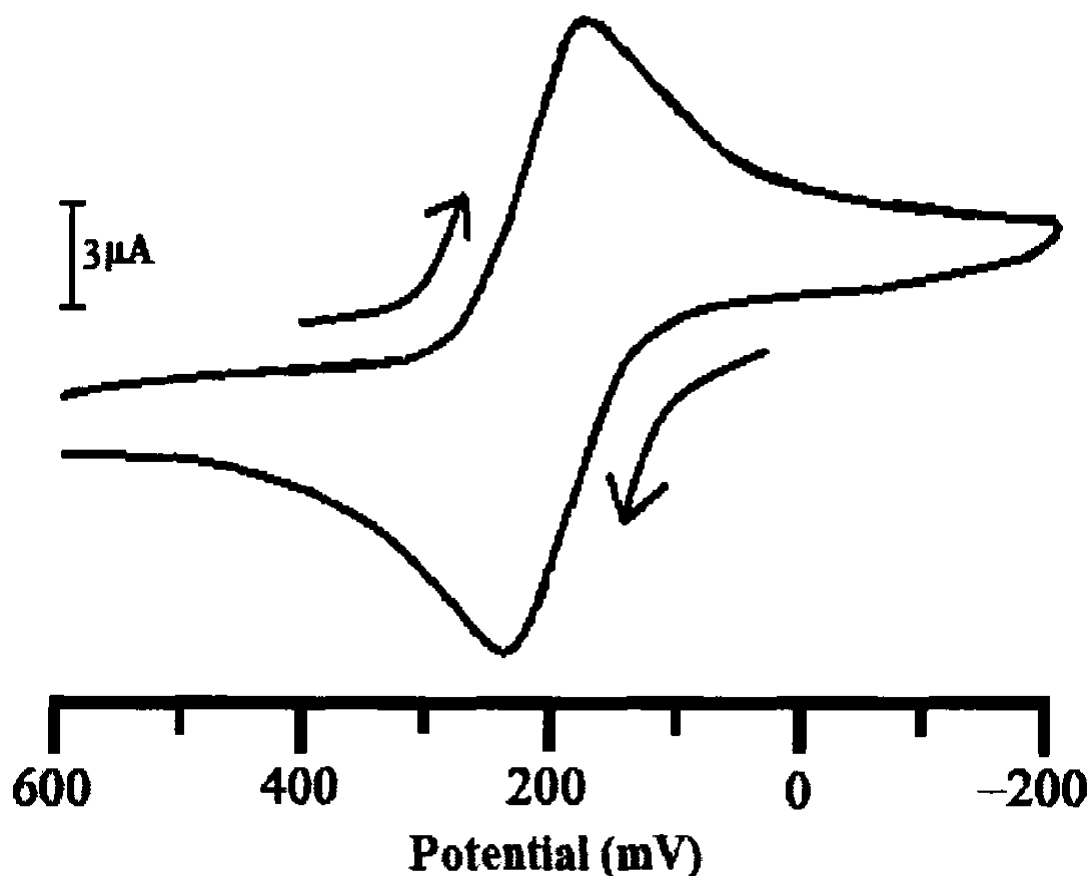
Figure 1.9. Typical voltammogram for a quasi-reversible process [11].

1.4. Electrocatalysis at nanomaterials

Nanomaterials are solid materials that have dimensions at the nanoscale. In general, nanomaterials are fabricated either by size reduction of bulk materials, the so called top-down, or, starting from the atomic level and build up the nanomaterials, the so-called bottom-up approach. The former one is based on physical processes like crushing or grinding, and usually adopted by Engineers. Bulk material is ventured into the nanometer range via miniaturization. Using this approach, it is

difficult to prepare nanomaterials of uniform shapes. In addition, nanomaterials prepared by this approach suffers from imperfections and significant damage of the crystallographic orientation of the surface [21]. Synthesis of nanomaterials considering the route can be subdivided into top-down and bottom up, and in view of routes, it can be subdivided into physical and chemical methods. It can also be subdivided in terms of phase of medium for preparation into gas phase/ liquid phase/ aerosol phase and Solid phase. Selection of the route, of course, depends on the purpose of preparing the nanomaterials.

In the other hand, bottom –up approach includes the build-up of a material from the bottom: atom-by-atom, molecule-by-molecule or cluster-by-cluster. It utilizes the chemical and/or physical forces in assembling basic units into larger structures in the nano range. This approach avoids most of the problems encountered by the previous approach. In addition, it provides several alternative ways to control onto scale dimension. Thus, it is often used for fabricating nano-scale materials characterized by a uniform size, shape and distribution. This route is approached by chemical synthesis by which a tailored nanomaterial can be assembled.

1.5.   Nanomaterials for the direct oxidation of glucose

Detection of glucose oxidation directly at an electrode is one of the most important research in non-enzymatic glucose sensors. However, there are several limitations in it such as the need for a large applied potential and slow reaction kinetics, which decreases specificity [22]. Nanomaterials have helped to overcome these limitations and thereby have allowed the development of direct-oxidation glucose sensors as replacements for biological recognition sensors.

1.6.   Glucose

It is a simple sugar with the molecular formula $C_6H_{12}O_6$. Glucose is the most abundant monosaccharide, a subcategory of carbohydrates. Glucose is mainly made by plants and most algae during photosynthesis from water and carbon dioxide, using energy from sunlight. In energy metabolism, glucose is the most important source of energy in all organisms. Glucose for metabolism is partially stored as a polymer, in plants mainly as starch and amylopectin and in animals as glycogen. Glucose circulates in the blood of animals as blood sugar. The naturally occurring form of glucose is D-glucose, while L- glucose is produced synthetically in comparatively small amounts and is of lesser importance. Glucose is a monosaccharide containing six carbon atoms and an

aldehyde group and is therefore referred to as an aldohexose. The glucose molecule can exist in an open-chain (acyclic) and ring (cyclic) form, the latter being the result of an intramolecular interaction between the aldehyde C atom and the C-5 hydroxyl group to form an intramolecular hemiacetal [23].

1.6.1. Chemical properties

With six carbon atoms, it is classed as a hexose, a subcategory of the monosaccharides. D-Glucose is one of the sixteen aldohexose stereoisomers. The D-isomer, D-glucose, also known as dextrose, occurs widely in nature, but the L-isomer, L- glucose, does not. Glucose can be obtained by hydrolysis of carbohydrates such as milk sugar (lactose), cane sugar (sucrose), maltose, cellulose, glycogen, etc. All forms of glucose are colorless and easily soluble in water, acetic acid, and several other solvents. They are only sparingly soluble in methanol and ethanol.

1.6.2. Practical applications

Electrochemical oxidation of glucose has generated much interest over the years. It has been extensively studied for applications in glucose sensors, [23] whose optimization (in terms of response time, lifetime, sensitivity and selectivity) is required to improve the treatment of Diabetes Mellitus, a chronic disease affecting millions of people around

the world [24]. Most studies on this subject have involved the use of the enzymes to catalyze the oxidation of glucose to δ-gluconolactone [23]. Although enzymatic detection usually shows good selectivity and high sensitivity, the enzyme is easily denatured during its immobilization process. The most serious problem of such sensors is the inherent lack of stability due to the sensitive nature of enzymes, especially in implantable devices that represent the new frontier in diabetes management. Non-enzymatic glucose sensors have been studied in order to develop effective enzyme-free sensors. Much attention has also been paid to the electrocatalytic oxidation of glucose for the construction of glucose-air biofuel cells and abiotically catalyzed fuel cells. In comparison with other fuel cells, this new type is powered with glucose derived from degradable biomass. Moreover, the direct glucose fuel cell is of high energy-density. Theoretically, glucose can be completely oxidized to CO_2 and H_2O, releasing 24 electrons per glucose molecule [25].

1.7. Mechanism of glucose oxidation on electrode surface

The glucose oxidation rate and its detection are mainly influenced by the electrochemical factors on the surface of the electrode. The glucose oxidation mechanism on the surface of the electrode is unclear, but two main models have been proposed to explain them [26-28].

The first model, discovered by the researcher Pletecher [29]. This model is known as chemisorption activator. The mechanism occurs by forming a part of the glucose bond with the surface of the electrode through the process of adsorption with the help of electric balls. At the same time, the hydrogen atom is extracted in the part of the glucose (see Figure 1.10), which is attached to hemiacetal carbon [26,27,30].
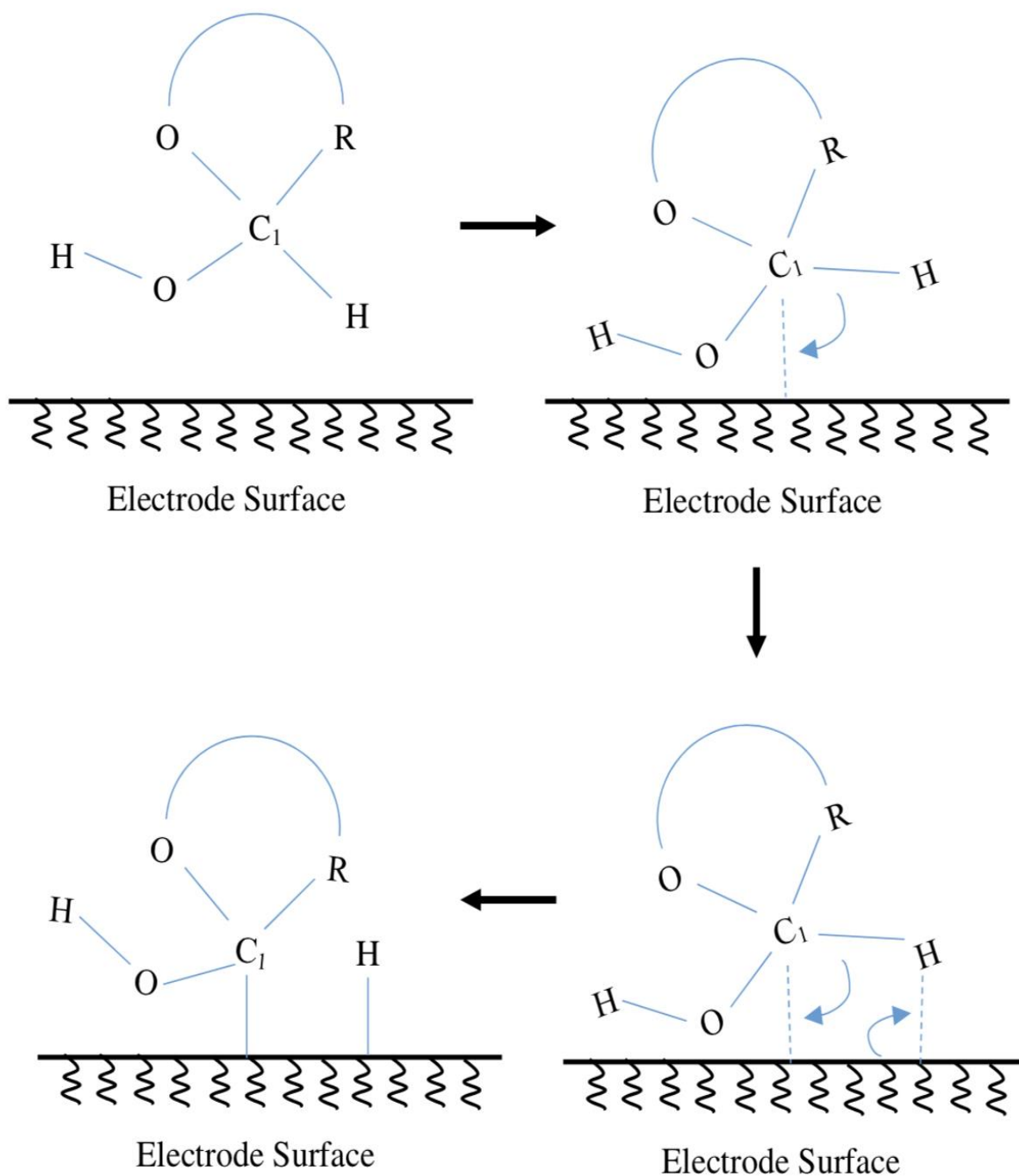
Figure 1.10. An example of the concentric adsorption theory with adjacent adsorption sites proposed by Pletcher. C1: hemiacetalic carbon atom. R: the other parts of the glucose molecule [31]

After extraction the hydrogen atom is associated with the electrode surface and the link is near the selected glucose. There is a change in the interaction of the glucose with the metal because of the change in the case of oxidation of the part of the glucose at the metal electrode. So, the effect of the strength of the link between the glucose and the metal occurs, which leads to the adsorption of the part of the glucose on the surface of the electrode. A strong intermediate bond is needed in the electro-catalytic process to form and break the bonds on the surface of the electrode and on the glucose molecules. Therefore, a strong, intermediate bonding force must be available in this method, and this association helps to adsorption (Formation of the bonds) and operations of desorption (break the bonds).

The second model, discovered by the researcher Burke and named "incipient hydrous oxide adatom mediator" (IHOAM) [28,32]. This model was originally suggested based on the observation that there are active metallic atoms on the electrode surface that have low lattice stability and improved interaction [26,32,33]. Where the metal atoms are subjected to premonolayer oxidation step through which the formation of the primary water oxide, OH_{ads} is formed. This layer is believed to mediate the oxidation of glucose on the electrode surface [33]. Figure 1.11 shows a schematic illustration of the IHOAM model.
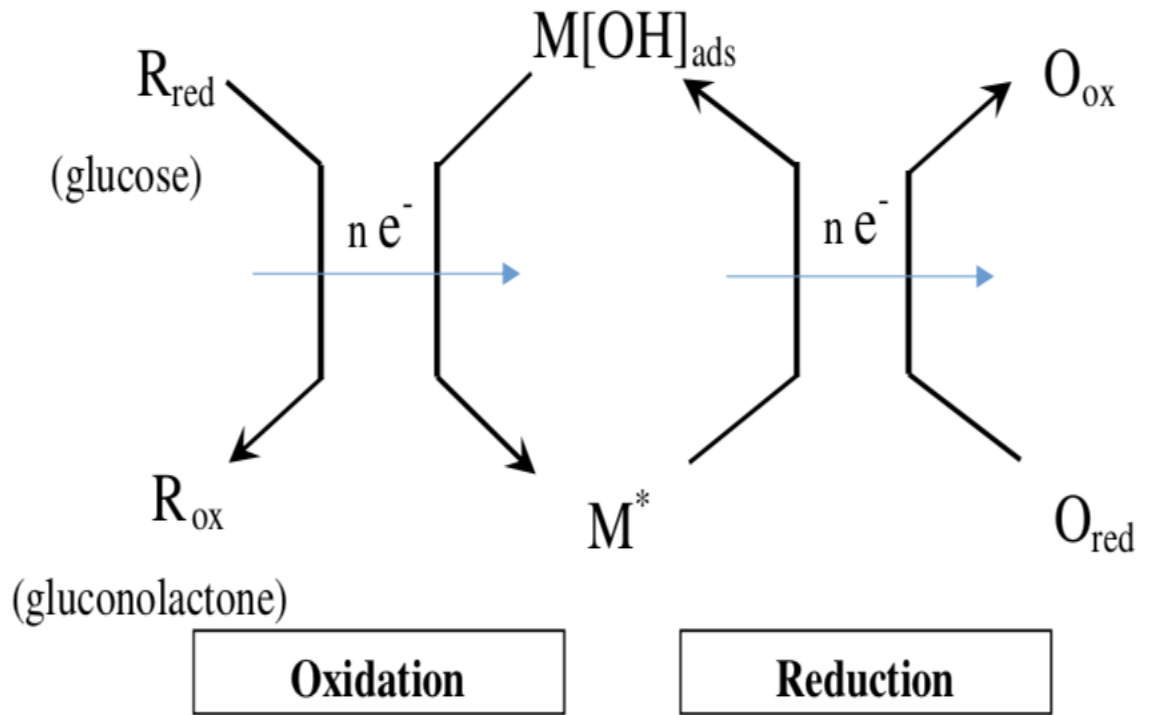
Figure1.11. A schematic illustration of the IHOAM model [31].

1.8.   Literature survey

Glucose electro-oxidation is of potential importance in many fields including for example the diagnosis of diabetes mellitus, food preparation and for the development of a category of fuel cells [34-38]. Glucose electrooxidation is realized by catalysis either enzymatically (enzyme-based) or non-enzymatically (enzymeless-based) methods. In the enzymatically based methods, the used enzyme can be utilized in a free state or in an immobilized one.

Enzyme-based electrooxidation is characterized by;

   i.   High selectivity

   ii.   It is the widely accepted approach since 1967 [39].

   iii.   Most of enzymatic sensing electrodes need electron shuttle, i.e., mediators or catalysts [40,41].

In this case, the enzyme converts analyte into electroactive species. However, enzymatic detection of glucose suffers from some restrictions;

   i.   The prerequisite of a biocompatible matrix as support

   ii.   Limited stability.

   iii.   Oxygen deficit under low oxygen pressure.

   iv.   The difficult immobilization of the enzyme [42,43].

Glucose oxidase (GOD)-based sensor depends on reaction conversion of glucose to gluconic acid, liberating hydrogen peroxide

(H₂O₂). Thus, the glucose was sensed either by measuring the consumption of oxygen or the liberated H₂O₂ [43].

$$Glucose + O_2 + H_2O \xrightarrow{GOD} gluconic\ acid + H_2O_2 \qquad (1.10)$$
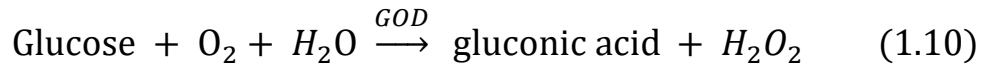
Enzyme-based electrodes have been fabricated by several approaches including reversible and irreversible immobilization (Fig.1. 12)

Figure1.12. Classification and representation of different enzyme immobilization techniques.

Reversible immobilization occurs via adsorption which includes the enzyme molecule bounding to the carrier matrix either by hydrogen bonding, van der Waals forces, electrostatic and hydrophobic interactions. This strategy of adsorption fulfills several advantages as for instance simplicity, cost effective and is generally non-destructive toward enzyme activity. However, it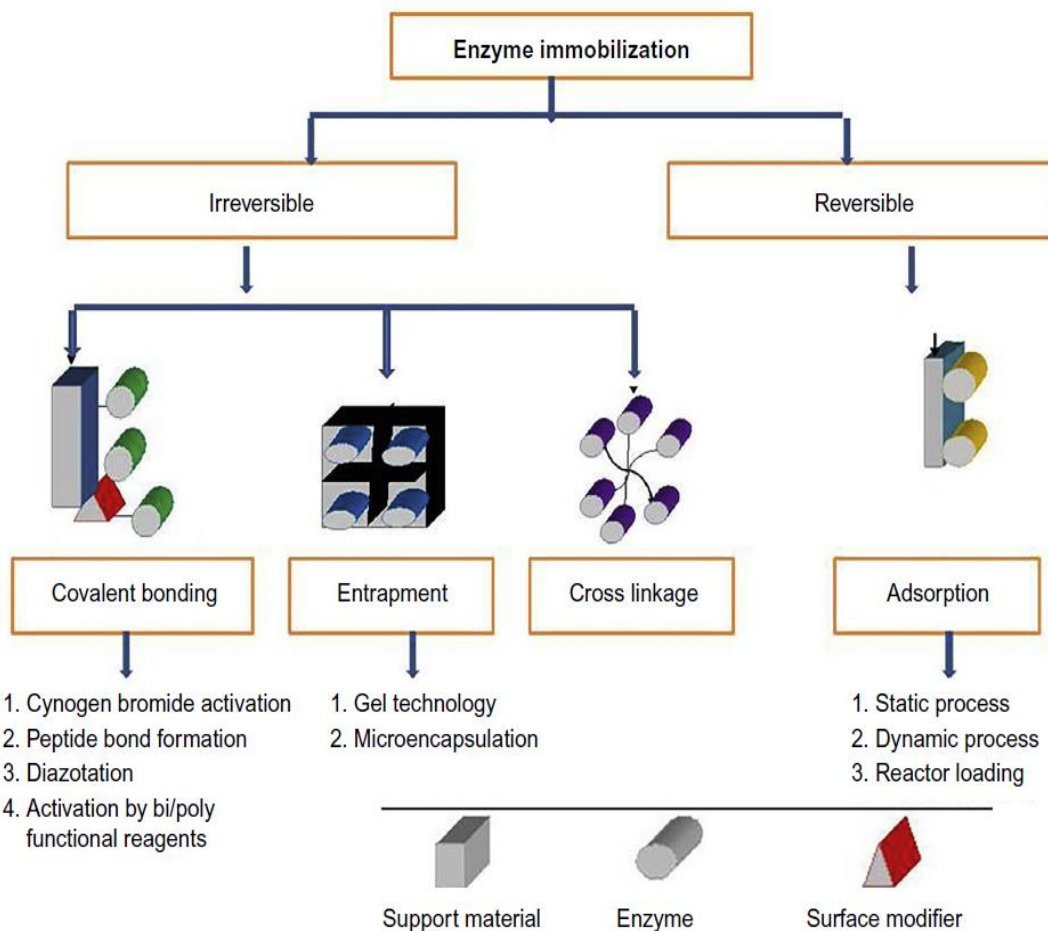 suffers several drawbacks as the bound of the enzyme to the carrier matrix is loose. Changes in temperature, pH or ionic strength may result in enzyme desorption. Enzyme leaching from the carrier can be prevented by compounds such as silicone [44].

Irreversible immobilization includes covalent bonding, entrapment and cross- inking. In immobilization via covalent bonding, stable complexes between functional groups on enzyme molecules and a support matrix are formed, taking in consideration that the included functional group of the enzyme in the covalent bond is not essential for enzymatic activity. The enzyme functional groups that could be utilized in covalent coupling include: amino group, carboxylic group, phenolic group, sulfhydryl group, thiol group, imidazole group, indole group and hydroxyl group [45].

In entrapment immobilization, enzyme is entrapped within a polymeric network. Entrapment immobilization process is conducted via mixing the enzyme with a monomer solution, and the subsequent

polymerization of monomer solution either chemically or electrochemically. This method improves enzyme stability and minimize enzyme leaching and denaturation. However, a limitation of the method is the mass transfer resistance occurred as polymerization extension tends to increase the gel matrix thickness [46].

In cross linking immobilization, a bifunctional chemical cross-linker is used. This had several drawbacks such as low activity retention, low mechanical stability, poor reproducibility, and difficulties in handling the gelatinous cross-linked enzymes [47].

Immobilized enzymes, compared with free enzymes, can be operated in a continuous manner and present good stability and wider working concentration range of analytes [48-50], but the lifetime of the enzyme-based sensors is limited [51,52]. Immobilization of the enzymes onto metallic substrates through a thin film of self-assembled monolayer and conducting polymers [53-57] were introduced to increase the life time of enzyme- based sensors. Also, nanostructured materials have been used as an underlying platform for enzymes immobilization because of their large surface-to-volume ratio and high catalytic and surface reaction activity. Using nanomaterials as substrates require some strategies to prevent enzyme leaching from electrode surface [58].

1.8.1. Enzymeless glucose sensors

Enzymeless glucose sensors can overcome the above-mentioned problems, and thus have been uses as a promising alternative for enzyme-based analysis [59]. Electrocatalysts designed for sensing or electrocatalysis of glucose oxidation usually use a single or binary catalyst of metal and/or metal oxides. Noble metals have been extensively used for the purpose of enzymeless electroanalysis of glucose owing to their biocompatibility, good electrocatalytic activity and strong stability [60,61].

Platinum was the first discovered material that demonstrated electrocatalytic activity for glucose oxidation [62]. However, Pt electrode suffer from required large polarization as well as the poisoning by adsorbed intermediates and interfering species. As a result, the sensitivity is low and selectivity is very poor [63-67]. To solve these problems, researchers used another metal as a co-catalyst with Pt with the aim to decrease poisoning. It has been reported that using a sacrificial metal with Pt increase the life time of Pt [68,69]. Pt-based electrocatalysts, PtM (M = Ru, Pd, Au, Ni, Ag, Bi, Pb) received much attention regarding glucose oxidation. They provide rapid response, good stability, and high catalytic efficiency [70-88].

Gold electrode is characterized by oxidizing glucose at relatively low anodic potential, both in neutral and alkaline media, and so shows high selectivity as well as sensitivity towards glucose oxidation. However, the electro-oxidation of glucose at Au electrodes has been faced with two main problems. First is the interference from ascorbic acid (AA), and the other one is the deactivation of the electrode activity by Cl– ions [89,90]. Chlorides, getting adsorbed at gold active sites inhibit the glucose oxidative-adsorption, which is the first and key step of the failure of the oxidation mechanism [91]. Toghill and Compton reported this problem earlier in 2010 [59]. After that, a number of approaches have been reported including that of gold-modified electrodes [92-96]. Au electrode surfaces with porous structures have been successfully used to eliminate interference from AA [97-102]. Several strategies have been explored for the preparation of nanostructured Au-modified electrodes in recent years. Nanoporous gold electrodes have been prepared mainly by de-alloying [102,103] and anodization [104-107]. Pd coated nanoporous gold films [108] enhanced the catalytic activity and stability of gold electrode for glucose oxidation [109,110]. Pd nanoparticles have been dispersed on a variety of substrates such as indium tin oxide, carbon nanotubes [111,112], epoxy-silver [113], graphene nanohybrids [114], boron-doped diamond [115], and polymers [116-118]. In this correspondence, Au-based bimetallic catalysts, AuM (M = Pt, Pd, Ag)

have been reported [119,120]. Other bimetallic catalysts have been reported albeit not extensively as those of the combination of either Pt or Au with other metals [121].

Cu-modified electrodes, characterized by their low cost and ease of fabrication, have received considerable attention due to their electrocatalytic activity for glucose oxidation [122]. The effect of the underlying substrate on the electrocatalytic properties of copper-modified electrodes has also been reported [123,124]. Recently, combining copper-based materials with carbon nanotubes for glucose detection has been widely investigated. This has been achieved by sputtering cupric oxide on multi-walled carbon nanotubes (MWCNTs) [125,126], electrodepositing copper nanocubes onto vertically-well-aligned MWCNTs [127], electrochemical deposition of copper oxide nanoparticles on horizontally-aligned single-walled carbon nanotubes (SWCNTs) [128], seed-mediated growth synthesis of copper nanoparticles on carbon nanotubes (CNTs) [129], copper oxide nanoleaves decorated CNTs [130] and nanospindle-like cuprous oxide/straight CNT nanohybrids [131].

1.8.2. Metal oxides

Recently, large numbers of transition metal oxides replaced costly noble metals as non-enzymatic electrocatalysts for glucose

electrooxidation [132-142]. Among these oxides, NiOx and CuOx received substantial attention because of their low cost and environmental safety [143-158].

Copper oxides (CuO, Cu_2O), as an important class of p-type semiconductor metal oxides, have attracted considerable attention for use in enzyme free glucose sensors due to their high electrocatalytic activity resulting from the multi-electron oxidation mediated by surface metal oxide layers [159-160]. Since the catalytic activities of the nanoscale materials are shapes dependent, the electrochemical behavior of glucose at nanostructured copper oxides with various morphologies have been studied [161-167].

Electrocatalytic materials containing nickel redox couple Ni(II)/Ni(III) received much interest devoted to investigations of the electrochemistry of a nickel hydroxide/oxyhydroxide couple [168-171]. Nickel oxyhydroxide has high affinity for the adsorption of some organic substances and electrocatalyze their oxidation via mediation electron-transfer processes in alkaline solutions. The electrocatalytic activity of Ni-based nanomaterials originating from the redox couple of Ni(II)/Ni(III) formed on the electrode surface in alkaline medium [172-176].

1.8.3. Details regarding nickel

- *Electrocatalytic oxidation of glucose at Nicke.*

Nickel-modified glassy carbon electrode prepared by galvanostatic deposition has been used for the electrocatalytic oxidation of glucose in alkaline solutions utilized several electrochemical techniques. In cyclic voltammetry studies, in the presence of glucose an increase in the peak current of the oxidation of nickel hydroxide is followed by a decrease in the corresponding cathodic current. The oxidation of glucose has been reported to follow mediated electron transfer in which the nickel hydroxide layer comprising nickel ions of various valence states play the role of a mediator. The reaction followed a Cottrellian behavior and the diffusion coefficient of glucose was found to be $8 \times 10^{-6} cm^2 s^{-1}$ and was in consistency with the value determined hydrodynamic voltammetry [177].

Also, Nickel based materials such as nickel, its oxides, hydroxides as well as oxyhydroxides exhibited excellent electrocatalysis performances toward many small molecules. Electrocatalyis by these modifiers are proposed from three aspects such as $Ni(OH)_2$/NiOOH mediated electrolysis, direct electrocatalysis of $Ni(OH)_2$ or NiOOH. The transformation from nickel or its oxides to hydroxides or oxyhydroxides enhanced in the strong alkaline solution under the

cyclic scanning at relatively high positive potential. The redox transition between Ni(OH)$_2$ and NiOOH is also contributed to the electrocatalytic oxidation of Ni and its oxides toward small molecules in alkaline media [178].

Nickel based modified electrodes have been utilized for highly sensitive and selective non-enzymatic detection of glucose. A novel disposable electrochemical sensor based on three-dimensional (3D) porous nickel nanostructures. The enzyme-free sensor was fabricated through in situ growing porous nickel networks on a homemade screen-printed carbon electrode substrate via electrochemically reducing the Ni^{+2} precursor, along with continuously liberating hydrogen bubbles. The resulting nickel-modified electrode was morphologically and electrochemically characterized Under optimized condition. The enzymeless sensor exhibited excellent performance for glucose analysis selectively, offering a much wider linear range (from 0.5 μM to 4 mM), an extremely low detection limit (0.07 μM, signal-to-noise ratio (S/N) of 3), and an ultrahigh sensitivity of 2.9 mA/(cm^2 mM). Application of the proposed sensor in monitoring blood glucose was also demonstrated [179].

Modification of nickel in the form of foam by low-cost methods has been also reported and applied for non-enzymatic glucose sensing.

The Ni nanofoam was converted to the catalytic Ni(OH)$_2$/NiOOH – necessary for non-enzymatic glucose oxidation – by cyclic voltammetry (CV) in NaOH electrolyte. The electrode fabricated on conducting glass substrate showed a glucose sensitivity of 2.37 mA/cm^2 mM, a linear range of 0.01–0.7 mM, a limit of detection (LOD) of 5 μM, a fast response time (1 s), and resistance to chloride poisoning. The glucose sensor also exhibited an excellent long-term stability (4% decrease in sensitivity after 64 days) and selectivity in the presence of common interfering species. The versatility of the preparation method was demonstrated in the fabrication of a flexible (plastic substrate) sensor with a sensitivity of 1.43 mA/cm^2 mM. The ease of fabrication and the excellent properties of Ni nanofoam in glucose sensing make it promising for low-cost and wearable sensing applications [180].

Nickel nanoparticles (NPs) modified glassy carbon electrode, characterized morphologically and electrochemically, prepared by potentiostatic electrodeposition has been also reported and applied for glucose electro-oxidation in alkaline medium. Amperometric response of the electrocatalytic oxidation to glucose at the potential of 500 mV presents a linear dependence in the glucose concentration range of 5 μM-1.155 mM, with a 1 μM detection limit. The biologic compounds

probably existed in human serum sample, such as ascorbic acid, uric acid, and dopamine, do not disturb the determination of glucose. The relative standard deviation (RSD) of the determination of practical serum samples is less than 7 % compared with the results obtained from clinical examination. The proposed sensor exhibits excellent electrocatalytic activity toward the oxidation of glucose, which is a good candidate for glucose quantification [181].

- *Electrocatalytic oxidation of glucose at Nickel oxide*

The electrochemical pretreatment of the glassy carbon prior to the electrodeposition of nickel largely affected the response of the modified electrode as has been reported. Different shape and size of NiO_X nanoparticles were reported when NiO_X is deposited on anodically oxidized GC electrode. Glucose electrooxidation is conducted in alkaline medium at GC/NiO_X (GC is untreated) and GC_{OX}/NiO_X (GC is treated) electrodes. The GC_{OX}/NiO_X shows an excellent electrocatalytic activity toward glucose oxidation compared to GC/NiO_X. The enhancement of the electrocatalytic activity obtained at the GC_{OX}/NiO_X is discussed in the light of the obtained differences

in characteristics of GC_{OX} /NiO_X and increase in the surface concentration of C–O functional groups [182].

Preparation method has been reported to largely affect the electrocatalytic activity. Nickel oxide nanoparticles (nano-NiO_X) of peculiar shape were prepared by sole gel technique and its electrocatalytic activity was evaluated at different conditions. The prepared nanoparticles were annealed at three different temperatures, i.e., 200, 400 and 600 C and anchored on glassy carbon (GC) electrode. Nano-NiO_X modified GG (nano-NiO_X/GC) electrodes are subjected to surface analysis techniques such as field emission scanning electron microscopy (FE-SEM) high resolution transmission electron micrograph (TEM) and X-ray diffraction (XRD). Electrochemical characterizations were performed using cyclic voltammetry and chronoamperometric techniques. The effects of annealing temperature on the morphological structure, surface concentration and subsequently on the electrochemical properties of nano-NiO_X/GC were examined. Experimental results indicated that the grain size and electrochemical characteristics of the nano-NiO_X/GC are significantly affected by the annealing temperature. The electrocatalytic oxidation of glucose at nano-NiO_X/GC electrode is

significantly enhanced especially with nano-NiO$_X$ annealed at 200 C compared to those annealed at 400 and 600 C. Nano-NiO$_X$ is applied for the electrocatalytic oxidation of glucose [183].

Impacts of the synthesis route on the structural and electrochemical properties of NiO$_X$ nanoparticles modified glassy carbon electrode (nano-NiO$_X$/GC) have been reported. Nanoparticles of nickel oxide (nano-NiO$_X$) have been synthesized using electrochemical and sol-gel routes. Cyclic voltammetry (CV), field emission scanning electron microscopy (FE-SEM), X-ray diffraction and transmission electron microscopy (TEM) were used for the characterization of nano-NiO$_X$/GC. The size of the particles using the sol-gel technique (NiO$_X$-SG) is uniform and have smaller particle size (~20 nm) than that obtained using the electrochemical route (NiO$_X$-El, ~80 nm). The specific activity (given in mA per mg of the NiO$_X$) of the Ni(OH)$_2$/NiOOH redox couple of the NiO$_X$-SG is higher with higher reversibility compared with the NiO$_X$-EL. Impacts of the synthesis route on the electrocatalytic properties of the NiO$_X$-SG and NiO$_X$-El are tested by the glucose oxidation in alkaline solution as a probing reaction for the electrocatalytic activity [184].

Assembled NiO nanosheets have been successfully prepared using graphene oxide (GO) film as template, where the Ni^{2+} ion was firstly adsorbed in GO film, followed by calcination in N_2 to form NiO-based materials and calcination in air to remove carbon-based template. The morphology, structure, and electrochemical activities of these NiO nanosheets were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM) and electrochemical techniques, respectively. It has been found that the NiO nanosheets thus obtained electrochemically catalyzed glucose oxidation in 0.1 M NaOH, leading to fabrication of non-enzymatic glucose sensor. The glucose sensor based on NiO nanosheets exhibits detection limit of 0.18 μM, and linear range from 1 μM to 0.4 mM with the sensitivity of 1138 μA mM^{-2} cm^{-2}. Furthermore, such glucose sensor also shows excellent selectivity for detection of glucose, compared to the commonly interfering species, such as ascorbic acid, dopamine, and uric acid [185].

Substitution of carbon substrate reflected on the electrocatalytic activity of deposited nickel. Nickel oxide (NiO) nanofilm electrodeposited on a bare Cu electrode for glucose oxidation has been reported. Electrochemical deposition was assisted with cetyl

trimethylammonium bromide (CTAB) as a template. Scanning electron microscopy (SEM) was applied to observe the surface morphology of the modified electrode. Cyclic voltammetry (CV) and amperometry techniques were used to study the electrocatalytic behavior of NiO porous film in glucose and methanol detection. The electrode showed a linear relationship in the concentration range of 0.01-2.14 mM with a low limit of detection (LOD) 1.7 µM. Moreover, high sensitivities of 4.02 mA mM^{-1} cm^{-2} and 0.38 mA mM^{-1} cm^{-2} respectively in glucose and methanol monitoring suggested the modified electrode as an excellent sensor. The NiO-Cu modified electrode was relatively insensitive to common biological interferers. The sensor possessed good poison resistance towards chloride ions, and long-term stability and significant selectivity towards glucose and methanol. The proposed sensor was successfully applied for determination of glucose in human blood serum samples [186].

The aqueous NiOOH nanosheets were also synthesized using a hydrothermal method via a surfactant template under mild reaction conditions. The as-prepared products were characterized by atomic force microscopy (AFM), X-ray diffraction (XRD) and scanning electron microscopy (SEM), the results of which indicated that ultrathin and porous NiOOH nanosheets with a thickness of only

several nanometers have been obtained. The obtained NiOOH nanosheets were subsequently assembled on electrochemically pretreated glassy carbon (EPGC) electrode through a simple physical bath deposition method to form NiOOH/EPGC electrode. SEM, energy dispersive X-ray spectroscopy (EDX) and electrochemical impedance spectroscopy (EIS) proved the successful assembly of NiOOH on EPGC surface. They explained the effective deposition of NiOOH electrocatalyst based the higher surface area and higher surface concentration of C-O functional groups existing on EPGC surface. The modified electrode was applied for glucose and methanol oxidation [187].

- *Electrocatalytic oxidation of glucose at Nickel composite*

A non-enzymatic potentiometric glucose sensor was developed by modifying a glass carbon electrode with Ni/NiO decorated nitrogen doped carbon spheres (Ni/NiO/NCSs). The Ni/NiO/NCSs were prepared with in situ growth of Ni/NiO on the nitrogen doped carbon spheres. The amperometric measurement revealed that the sensor had wide linear regions of 2 mM-600 mM and 800 mM-2500 mM with a sensitivity of 219.19 mA $mM^{-1}cm^2$ and 87.88 mA $mM^{-1}cm^2$ respectively. Moreover, the Ni/NiO/NCS composites also exhibited

good selectivity by adding certain amount of urea, NaCl, L-proline, L-valine, L-Leucine and ascorbic acid into 0.1 M NaOH solution. The excellent electro- catalytic performance was attributed to the synergistic effect of nitrogen doping and Ni loading, which may result in the increase of electron density and the enhancement of surface conductivity of the composite electrode materials [188].

- *Electrocatalytic oxidation of glucose by nickel oxides composite*

A novel binary electrocatalyst fabricated from manganese and nickel oxides nanoparticles (MnO_X and NiO_X), prepared by electrodeposition, has neen proposed as an anode for an amplified electrochemical oxidation of glucose in NaOH solutions. Cyclic voltammetry and scanning electron microscopy images were used to characterize these electrocatalysts. It has been found that the electrocatalytic activity critically depends on the order of the deposition of the two oxides. The $NiO_X/MnO_X/GC$ electrode (MnO_X deposited first) showed a superior electrocatalytic activity towards glucose oxidation compared to NiO_X/GC, MnO_X/GC or $MnO_X/NiO_X/GC$ electrodes (NiO_X deposited first). The extraordinary activity obtained at the $NiO_X/MnO_X/$ GC electrode is attributed to the compilation of the better adsorption of glucose molecules on the

MnO_X sites and the increase of conductivity of the NiO_X due to the increase of Ni^{3+} content. A synergism between the two oxides towards the electrooxidation of glucose was proposed for explaining the extraordinary electroactivity [189].

Modification of glassy carbon electrode (GCE) with graphene oxide (GO), NiO nanofibers (NiONFs) and Nafion (NA) were also reported for the oxidation of glucose. NiONFs were prepared by the facile electrospinning technique followed by calcination. The modified electrode was pretreated by the electrochemical reduction. The sensor was characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS). The sensor exhibited high sensitivity (1100 μ A mM^{-1} cm^{-2}), fast response time (less than 5 s), low detection limit of 0.77 μM (S/N = 3), long term stability, and excellent anti-fouling ability for glucose determination. The sensor was further applied to detection of glucose in human blood serum sample, and the results accorded with those of commercial test [190].

1.9. REFERENCES

1. Brett CM and Brett O (1993). Electrochemistry, A. M., *Principles, methods and applications.*

2. JO'M B and Minevski ZS (1994). Electrocatalysis: past, present and future. *Electrochim. Acta*, 39(11-12), 1471-1479.

3. Mkwizu and Samwel Peter (2015). Electrochemical Synthesis and Characterization of Multi metallic Nanostructured Electrocatalysts. *Diss. University of Pretoria.*

4. Chorkendorff I and Niemantsverdriet JW (2003). Concepts of modern catalysis and kinetics. *Weinheim: Wiley-VCH.*

5. Lu GQ and Wieckowski A (2000). Heterogeneous electrocatalysis: a core field of interfacial science. *Curr. Opin. Colloid Interface Sci.*,5(1-2), 95–100.

6. Bard A and Faulkner LR, (2001). Electrochemical methods: Fundamentals and Applications. *John-Wiley & Sons*, New York.

7. Girault HH (2004). *Analytical and physical electrochemistry*. CRC Press.

8. Speiser B, Bard AJ, Stratmann M, Unwin PR (2003). Encyclopedia of Electrochemistry. *Wiley-VCH: Weinheim*, p. 81-104.

9. Fischer AC (1996). Electrode Dynamics, *Oxford University Press*, NewYork.

10. Christensenand PA and Hamnett A (1994). Techniques and Mechanismsin Electrochemistry, *Chapman & Hall, London*.

11. Hibbert DB (1993), Introduction to Electrochemistry, *Macmillan, London Eds*.

12. Randles JE (1948). A cathode ray polarograph. Part II.—The current-voltage curves. *Trans. Faraday Soc*., 44, 327-338.

13. Kaifer AE and Kaifer MG, (1999). Supramolecular Electrochemistry. *Willey, VCH, New York Eds*.

14. Bard AJ and Faulkner LR (1996). Electrochemical Methods: Fundamentals and Applications. *John Willey & Sons Eds*.

15. Brown ER and Large RF (1971). Techniques of Chemistry, Vol. 1, Part II A," *Electrochemical Methods*", chapter 6.

16. Renault JP, Bernard A, Bietsch A, Michel B, Bosshard HR, Delamarche E, Wild UP (2003). Fabricating arrays of single protein molecules on glass using microcontact printing. *J. Phys. Chem. B*, *107*(3), 703-711.

17. Bockris J.O.M and Shaded U. M. K. (1993). Surface Electrochemistry: *a Molecular Level Approach Plenum Press*. New York, *78*.

18. Van Benschoten JJ, Lewis JY, Heineman WR, Roston DA, Kissinger PT (1983). Cyclic voltammetry experiment. *J. Chem. Educ.*, *60*(9), 772.

19. Domb AJ, Kost J, Wiseman D (1998). *Handbook of biodegradable polymers*. CRC press.

20. Nicholson RS and Shain I (1964). Theory of stationary electrode polarography. Single scan and cyclic methods applied to reversible, irreversible, and kinetic systems. *Anal. Chem.*, *36*(4), 706-723.

21. Kulkarni and Sulabha K. (2015). Nanotechnology: Principles and Practices. *Springer*.

22. Shamsipur M, Najafi M, Hosseini M. R. M (2010). Highly improved electrooxidation of glucose at a nickel(II) oxide/multi-walled carbon nanotube modified glassy carbon electrode. *Bioelectrochem.*, 77(2), 120–124.

23. Heller A and Feldman B (2008). Electrochemical glucose sensors and their applications in diabetes management. *Chem. Rev.*, *108*(7), 2482-2505.

24. Ekoé JM, Rewers M, Williams R, Zimmet P (Eds.) (2008). *The epidemiology of diabetes mellitus*. John Wiley & Sons.

25. Kerzenmacher S, Ducrée J, Zengerle R, Von Stetten F (2008). Energy harvesting by implantable abiotically catalyzed glucose fuel cells. *J. Power Sources*, *182*(1), 1-17.

26. Nikolaeva NN, Khazova OA, Vasilev YB (1983). Main principles of the electrooxidation of glucose on a gold electrode. *Soviet. Electrochem.*, *19*(8), 934-940.

27. Wang J (1999). Amperometric biosensors for clinical and therapeutic drug monitoring: a review. *J. pharm. Biomed. Anal.,* 19(1-2), 47-53.

28. Rahman M, Ahammad AJ, Jin JH, Ahn SJ, Lee JJ (2010). A comprehensive review of glucose biosensors based on nanostructured metal -oxides. *Sensors*, 10(5), 4855-4886.

29. Si P, Huang Y, Wang T, Ma J (2013). Nanomaterials for electrochemical non-enzymatic glucose biosensors. *RSC Adv.*, 3(11), 3487-3502.

30. Pletcher D (1984). Electrocatalysis: present and future. *J. Appl. Electrochem.*, 14(4):403-15.

31. Tian K, Prestgard M, Tiwari A (2014). A review of recent advances in nonenzymatic glucose sensors. *Mater. Sci. Eng.*, *C*, 41:100-18.

32. Burke LD (1994). Premonolayer oxidation and its role in electrocatalysis. *Electrochim. Act*a, 39(11-12):1841-8.

33. Ernst S, Heitbaum J, Hamann CH (1980). The electrooxidation of glucose in phosphate buffer solutions: kinetics and reaction mechanism. *Berichte der Bunsengesellschaft für physikalische Chemie*. ,84(1):50-5.

34. Bankar SB, Bule MV, Singhal RS, Ananthanarayan L (2009). Glucose oxidase—an overview. *Biotechnol. Adv.*, 27, 489.

35. Quan H, Park SU, Park J (2010). Electrochemical oxidation of glucose on silver nanoparticle-modified composite electrodes. *Electrochim. Acta*, *55*(7), 2232-2237.

36. Newman JD and Turner AP (2005). Home blood glucose biosensors: a commercial perspective. *Biosens. Bioelectron.*, *20*(12), 2435-2453.

37. Wilson GS and Gifford R (2005). Biosensors for real-time in vivo measurements. *Biosens. Bioelectron.*, *20*(12), 2388-2403.

38. Ramanavicius A, Kausaite A, Ramanaviciene A (2005). Biofuel cell based on direct bioelectrocatalysis. *Biosens. Bioelectron.*, *20*(10), 1962-1967.

39. Updike SJ and Hicks GP (1967). The enzyme electrode. *Nature*, *214*(5092), 986-988.

40. Wang J and Pamidi PV (1997). Sol− gel-derived gold composite electrodes. *Anal. Chem., 69*(21), 4490-4494.

41. Patolsky F, Weizmann Y, Willner I (2004). Long-range electrical contacting of redox enzymes by SWCNT connectors. *Angew. Chem. Int. Ed.*, *43*(16), 2113-2117.

42. Wang J (2008). Electrochemical glucose biosensors. *Chem. Rev.*, *108*(2), 814-825.

43. Park S, Boo H, Chung TD (2006). Electrochemical non-enzymatic glucose sensors. *Anal. Chim. Acta*, *556*(1), 46-57.

44. Zhang Y, Chang G, Liu S, Lu W, Tian J, Sun X (2011). A new preparation of Au nanoplates and their application for glucose sensing. *Biosens. Bioelectron.*, *28*(1), 344-348.

45. Hanachi P, Jafary F, Motamedi S (2015). Immobilization of the alkaline phosphatase on collagen surface via cross-linking method. *Iran. J. Biotechnol*. 13 (2), 31–38.

46. Nawaz MA, Rehman HU, Bibi Z, Aman A, Qader S.A.U (2015). Continuous degradation of maltose by enzyme entrapment technology using calcium alginate beads as a matrix. *Biochem. Biophys*. *Rep.,* 4, 250–256.

47. Dwevedi A (2016). Enzyme Immobilization Advances in Industry, Agriculture, Medicine, and the Environment. *Springer*.

48. Chen T, Friedman KA, Lei I, Heller A (2000). In situ assembled mass-transport controlling micromembranes and their application in implanted amperometric glucose sensors. *Anal. Chem.*, *72*(16), 3757-3763.

49. Guo G, Chen Q, Chen X (2011). Electrochemiluminescence glucose biosensor based on glucose dehydrogenase functionalized Ru (bpy) 3 2+ doped silica nanoparticles. *Sci. China Chem.*, *54*(11), 1777-1781.

50. Guo G, Wang X, Zhou T, Chen X (2010). Extended detection range for an optical enzymatic glucose sensor coupling with a novel data-processing method. *Sci. China Chem.*, *53*(6), 1385-1390.

51. Kausaite-Minkstimiene A, Mazeiko V, Ramanaviciene A, Ramanavicius A (2010). Enzymatically synthesized polyaniline layer for extension of linear detection region of amperometric glucose biosensor. *Biosens. Bioelectron.*, 26, 790.

52. Cosnier S (1999). Biomolecule immobilization on electrode surfaces by entrapment or attachment to electrochemically polymerized films. A review. *Biosens. Bioelectron.*, *14*(5), 443-456.

53. Heller J and Heller A (1998). Loss of activity or gain in stability of oxidases upon their immobilization in hydrated silica: significance of the electrostatic interactions of surface arginine residues at the entrances of the reaction channels. *J. Ame. Chem. Soc.*, *120*(19), 4586-4590.

54. Ratner BD (1995). Surface modification of polymers: chemical, biological and surface analytical challenges. *Biosens. Bioelectron.*, *10*(9-10), 797-804.

55. Chaudhury MK (1995). Self-assembled monolayers on polymer surfaces. *Biosens. Bioelectron.*, *10*(9-10), 785-788.

56. Gooding JJ and Hibbert DB (1999). The application of alkanethiol self-assembled monolayers to enzyme electrodes. *TrAC Trends Anal. Chem.*, *18*(8), 525-533.

57. Willner I, Katz E, Willner B (1997). Electrical contact of redox enzyme layers associated with electrodes: routes to amperometric biosensors. *Electroanalysis*, *9*(13), 965-977.

58. Ferretti S, Paynter S, Russell DA, Sapsford KE, Richardson DJ (2000). Self-assembled monolayers: a versatile tool for the formulation of bio-surfaces. *TrAC Trends Anal. Chem.*, *19*(9), 530-540.

59. Toghill KE and Compton RG (2010). Electrochemical non-enzymatic glucose sensors: a perspective and an evaluation. *Int. J. Electrochem. Sci.*, *5*(9), 1246-1301.

60. Hu Y, Song Y, Wang Y, Di J (2011). Electrochemical synthesis of gold nanoparticles onto indium tin oxide glass and application in biosensors. *Thin Solid Films*, *519*(19), 6605-6609.

61. Atta NF, Galal A, Ekram H (2012). Gold nanoparticles-coated poly (3, 4-ethylene-dioxythiophene) for the selective determination of sub-nano concentrations of dopamine in presence of sodium dodecyl sulfate. *Electrochim. Acta*, *69*, 102-111.

62. Park S, Chung TD, Kim HC (2003). Nonenzymatic glucose detection using mesoporous platinum. *Anal. Chem.*, *75*(13), 3046-3049.

63. Yuan JH, Wang K, Xia XH (2005). Highly ordered platinum-nanotubule arrays for amperometric glucose sensing. *Adv. Funct. Mater.*, *15*(5), 803-809.

64. Guo MQ, Hong HS, Tang XN, Fang HD, Xu XH (2012). Ultrasonic electrodeposition of platinum nanoflowers and their application in nonenzymatic glucose sensors. *Electrochim. Acta*, *63*, 1-8.

65. Wang J, Thomas DF, Chen A (2008). Nonenzymatic electrochemical glucose sensor based on nanoporous PtPb networks. *Anal. Chem.*, *80*(4), 997-1004.

66. Song YY, Zhang D, Gao W, Xia XH (2005). Nonenzymatic glucose detection by using a three-dimensionally ordered, macroporous platinum template. *Chem. –A Euro. J.*, *11*(7), 2177-2182.

67. Shen Q, Jiang L, Zhang H, Min Q, Hou W, Zhu JJ (2008). Three-dimensional dendritic Pt nanostructures: sonoelectrochemical synthesis and electrochemical applications. *J. Phys. Chem. C*, *112*(42), 16385-16392.

68. Ryu J, Kim K, Kim HS, Hahn HT, Lashmore D (2010). Intense pulsed light induced platinum–gold alloy formation on carbon nanotubes for non-enzymatic glucose detection. *Biosens. Bioelectron.*, *26*(2), 602-607.

69. Safavi A and Farjami F (2011). Electrodeposition of gold–platinum alloy nanoparticles on ionic liquid–chitosan composite film and its application in fabricating an amperometric cholesterol biosensor. *Biosens. Bioelectron.*, *26*(5), 2547-2552.

70. Bai Y, Sun Y, Sun C (2008). Pt–Pb nanowire array electrode for enzyme-free glucose detection. *Biosens. Bioelectron.*, *24*(4), 579-585.

71. Bo X, Bai J, Qi B, Guo L (2011). Ultra-fine Pt nanoparticles supported on ionic liquid polymer-functionalized ordered mesoporous carbons for nonenzymatic hydrogen peroxide detection. *Biosens. Bioelectron.*, *28*(1), 77-83.

72. Ding Y, Liu Y, Parisi J, Zhang L, Lei Y (2011). A novel NiO–Au hybrid nanobelts based sensor for sensitive and selective glucose detection. *Biosens. Bioelectron.*, *28*(1), 393-398.

73. Li LH, Zhang WD, Ye JS (2008). Electrocatalytic oxidation of glucose at carbon nanotubes supported PtRu nanoparticles and its detection. *Electroanalysis*, *20*(20), 2212-2216.

74. Xiao F, Li Y, Gao H, Ge S, Duan H (2013). Growth of coral-like PtAu–MnO2 binary nanocomposites on free-standing graphene paper for flexible nonenzymatic glucose sensors. *Biosens. Bioelectron. 41*, 417-423.

75. Liu Y, Ding Y, Zhang Y, Lei Y (2012). Pt–Au nanocorals, Pt nanofibers and Au microparticles prepared by electrospinning and calcination for nonenzymatic glucose sensing in neutral and alkaline environment. *Sens. Actuators, B*, *171*, 954-961.

76. Chen J, Wiley B, McLellan J, Xiong Y, Li ZY, Xia Y (2005). Optical properties of Pd− Ag and Pt− Ag nanoboxes synthesized via galvanic replacement reactions. *Nano lett.*, *5*(10), 2058-2062.

77. Guo S, Dong S, Wang E (2010). Ultralong Pt-on-Pd bimetallic nanowires with nanoporous surface: nanodendritic structure for enhanced electrocatalytic activity. *Chem. Commun.*, *46*(11),1869-1871.

78. Basu D and Basu S (2011). Synthesis, characterization and application of platinum based bi-metallic catalysts for direct glucose alkaline fuel cell. *Electrochim. Acta*, *56*(17), 6106-6113.

79. Basu D, and Basu S (2010). A study on direct glucose and fructose alkaline fuel cell. *Electrochim. Acta*, *55*(20), 5775-5779.

80. Liu Z, Huang L, Zhang L, Ma H, Ding Y (2009). Electrocatalytic oxidation of d-glucose at nanoporous Au and Au–Ag alloy electrodes in alkaline aqueous solutions. *Electrochim. Acta*, *54*(28), 7286-7293.

81. Jin C and Taniguchi I (2007). Electrocatalytic activity of silver modified gold film for glucose oxidation and its potential application to fuel cells. *Mater. Lett.*, *61*(11-12), 2365-2367.

82. Cuevas-Muñiz FM, Guerra-Balcázar M, Castaneda F, Ledesma-García J, Arriaga LG (2011). Performance of Au and AuAg nanoparticles supported on Vulcan in a glucose laminar membraneless microfuel cell. *J. Power Sources*, *196*(14), 5853-5857.

83. Zhu C, Guo S, Dong S (2012). PdM (M= Pt, Au) Bimetallic Alloy Nanowires with Enhanced Electrocatalytic Activity for Electro-oxidation of Small Molecules. *Adv. Mater.*, *24*(17), 2326-2331.

84. Cui HF, Ye JS, Liu X, Zhang WD, Sheu, FS (2006). Pt–Pb alloy nanoparticle/carbon nanotube nanocomposite: a strong electrocatalyst for glucose oxidation. *Nanotechnol.*, *17*(9), 2334.

85. Sun Y, Buck H, Mallouk TE (2001). Combinatorial discovery of alloy electrocatalysts for amperometric glucose sensors. *Anal. Chem.*, *73*(7), 1599-1604.

86. Tonda-Mikiela P, Napporn TW, Morais C, Servat K, Chen A, Kokoh KB (2012). Synthesis of gold-platinum nanomaterials using bromide anion exchange-synergistic electroactivity toward CO and glucose oxidation. *J. Electrochem. Soc.*, *159*(11), H828.

87. Gao H, Xiao F, Ching CB, Duan H (2011). One-step electrochemical synthesis of PtNi nanoparticle-graphene nanocomposites for nonenzymatic amperometric glucose detection. *ACS Appl. Mater. Interfaces*, *3*(8), 3049-3057.

88. Hermans S, Deffernez A, Devillers M (2011). Au–Pd/C catalysts for glyoxal and glucose selective oxidations. *Appl. Catal., A*, *395*(1-2), 19-27.

89. Cho S, Shin H, Kang C (2006). Catalytic glucose oxidation on a polycrystalline gold electrode with an amalgamation treatment (TM 05092). *Electrochim. Acta*, *51*(18), 3781-3786.

90. Seo B, Choi S, Kim J (2011). Simple electrochemical deposition of Au nanoplates from Au (I) cyanide complexes and their electrocatalytic activities. *ACS Appl. Mater. Interfaces*, *3*(2), 441-446.

91. Pasta M, La Mantia F, Cui Y (2010). A new approach to glucose sensing at gold electrodes. *Electrochem. Commun.*, *12*(10), 1407-1410.

92. Habrioux A, Servat K, Girardeau T, Guérin P, Napporn TW, Kokoh KB (2011). Activity of sputtered gold particles layers towards glucose electrochemical oxidation in alkaline medium. *Curr. Appl. Phys.*, *11*(5), 1149-1152.

93. Oztekin Y, Yazicigil Z, Ramanaviciene A, Ramanavicius A (2011). Polyphenol-modified glassy carbon electrodes for copper detection. *Sens. Actuators, B*, *152*(1), 37-48.

94. Jeong H and Kim J (2012). Electrochemical oxidation of glucose at nanoporous black gold surfaces in the presence of high concentration of chloride ions and application to amperometric detection. *Electrochim. Acta*, *80*, 383-389.

95. Liu A, Ren Q, Xu T, Yuan M, Tang W (2012). Morphology-controllable gold nanostructures on phosphorus doped diamond-like

carbon surfaces and their electrocatalysis for glucose oxidation. *Sens. Actuatros, B*, *162*(1), 135-142.

96. Wang Q, Min F, Zhu J (2013). Preparation of gold nanowires and its application in glucose biosensing. *Mater. Lett.*, *91*, 9-11.

97. Li Y, Song YY, Yang C, Xia XH (2007). Hydrogen bubble dynamic template synthesis of porous gold for nonenzymatic electrochemical detection of glucose. *Electrochem. Commun.*, *9*(5), 981-988.

98. Cho S and Kang C (2007). Nonenzymatic glucose detection with good selectivity against ascorbic acid on a highly porous gold electrode subjected to amalgamation treatment. *Electroanalysis*, *19*(22), 2315-2320.

99. Bai Y, Yang W, Sun Y, Sun C (2008). Enzyme-free glucose sensor based on a three-dimensional gold film electrode. *Sens. Actuators, B*, *134*(2), 471-476.

100. Xia Y, Huang W, Zheng J, Niu Z, Li Z (2011). Nonenzymatic amperometric response of glucose on a nanoporous gold film electrode fabricated by a rapid and simple electrochemical method. *Biosens. Bioelectron.*, *26*(8), 3555-3561.

101. Hyun M, Choi S, Kim J (2010). Simple Fabrication of Porous Gold-Film Electrodes and Their Electroanalytical Applications. *Anal. Sci.*, *26*(1), 129-132.

102. Liu Z, Du J, Qiu C, Huang L, Ma H, Shen D, Ding Y (2009). Electrochemical sensor for detection of p-nitrophenol based on nanoporous gold. *Electrochem. Commun.*, *11*(7), 1365-1368.

103. Seo B and Kim J (2010). Electrooxidation of glucose at nanoporous gold surfaces: structure dependent electrocatalysis and its application to amperometric detection. *Electroanalysis*, *22*(9), 939-945.

104. Deng Y, Huang W, Chen X, Li Z (2008). Facile fabrication of nanoporous gold film electrodes. *Electrochem. Commun.*, *10*(5), 810-813.

105. Nishio K and Masuda H (2011). Anodization of gold in oxalate solution to form a nanoporous black film. *Angew. Chem. Int. Ed.*, *50*(7), 1603-1607.

106. Zhao W, Xu JJ, Shi CG, Chen HY (2006). Fabrication, characterization and application of gold nano-structured film. *Electrochem. Commun.*, *8*(5), 773-778.

107. Qiu H and Huang X (2010). Effects of Pt decoration on the electrocatalytic activity of nanoporous gold electrode toward glucose and its potential application for constructing a nonenzymatic glucose sensor. *J. Electroanal. Chem.*, *643*(1-2), 39-45.

108. Tavakkoli N and Nasrollahi S (2013). Non-enzymatic glucose sensor based on palladium coated nanoporous gold film electrode. *Aust. J. Chem.*, *66*(9), 1097-1104.

109. Bai H, Han M, Du Y, Bao J, Dai Z (2010). Facile synthesis of porous tubular palladium nanostructures and their application in a nonenzymatic glucose sensor. *Chem. Commun.*, *46*(10), 1739-1741.

110. Chen XM, Cai ZM, Lin ZJ, Jia TT, Liu HZ, Jiang YQ, Chen X (2009). A novel non-enzymatic ECL sensor for glucose using palladium nanoparticles supported on functional carbon nanotubes. *Biosens. Bioelectron.*, *24*(12), 3475-3480.

111. Meng L, Jin J, Yang G, Lu T, Zhang H, Cai C (2009). Nonenzymatic electrochemical detection of glucose based on palladium− single-walled carbon nanotube hybrid nanostructures. *Anal. Chem.*, *81*(17), 7271-7280.

112. Zhang WJ, Bai L, Lu LM, Chen Z (2012). A novel and simple approach for synthesis of palladium nanoparticles on carbon nanotubes for sensitive hydrogen peroxide detection. *Colloids. Surf., B*, *97*, 145-149.

113. Gutes A, Carraro C, Maboudian R (2011). Nonenzymatic glucose sensing based on deposited palladium nanoparticles on epoxy-silver electrodes. *Electrochim. Acta*, *56*(17), 5855-5859.

114.   Lu LM, Li HB, Qu F, Zhang XB, Shen GL, Yu RQ (2011). In situ synthesis of palladium nanoparticle–graphene nanohybrids and their application in nonenzymatic glucose biosensors. *Biosens. Bioelectron.*, *26*(8), 3500-3504.

115. Szunerits S and Boukherroub R (2008). Investigation of the electrocatalytic activity of boron-doped diamond electrodes modified with palladium or gold nanoparticles for oxygen reduction reaction in basic medium. *CR CHIM*, *11*(9), 1004-1009.

116. Atta NF and El-Kady MF (2009). Poly (3-methylthiophene) /palladium sub-micro-modified sensor electrode. Part II: Voltammetric and EIS studies, and analysis of catecholamine neurotransmitters, ascorbic acid and acetaminophen. *Talanta*, *79*(3), 639-647.

117. Liao F, Wang Z, Guo T, Zhang T, Wu Z (2012). Synthesis of well dispersed palladium nanoparticles-decorated poly (o-phenylenediamine) colloids with excellent performance for hydrazine oxidation. *J. Electroanal. Chem.*, *673*, 38-42.

118. Santhosh P, Manesh KM, Uthayakumar S, Komathi S, Gopalan AI, Lee KP (2009). Fabrication of enzymatic glucose biosensor based on palladium nanoparticles dispersed onto poly (3, 4-ethylenedioxythiophene) nanofibers. *Bioelectrochem.*, *75*(1), 61-66.

119. Reyter D, Odziemkowski M, Bélanger D, Roué L (2007). Electrochemically Activated Copper Electrodes Surface

Characterization, Electrochemical Behavior, and Properties for the Electroreduction of Nitrate. *J. Electrochem. Soc.*, *154*(8), K36-K44.

120. Jin C and Taniguchi I (2007). Electrocatalytic activity of silver modified gold film for glucose oxidation and its potential application to fuel cells. *Mater. Lett.*, *61*(11-12), 2365-2367.

121. Cuevas-Muñiz FM, Guerra-Balcázar M, Castaneda F, Ledesma-García J, Arriaga LG (2011). Performance of Au and AuAg nanoparticles supported on Vulcan in a glucose laminar membraneless microfuel cell. *J. Power Sources*, *196*(14), 5853-5857.

122. Zhu C, Guo S, Dong S (2012). PdM (M= Pt, Au) Bimetallic Alloy Nanowires with Enhanced Electrocatalytic Activity for Electro-oxidation of Small Molecules. *Adv. Mater.*, *24*(17), 2326-2331.

123. Zhao J, Wei LM, Peng CH, Su YJ, Yang Z, Zhang LY, Wei H, Zhang YF (2013). A non-enzymatic glucose sensor based on the composite of cubic Cu nanoparticles and arc-synthesized multi-walled carbon nanotubes. *Biosens. Bioelectron.*, 47, 86.

124. Zhao Y, Zhao JZ, Ma DC, Li. YL, Hao XL, Li LZ, Yu CZ, Zhang L, Lu Y, Wang ZC (2012). Synthesis, growth mechanism of different Cu nanostructures and their application for non-enzymatic glucose sensing. *Colloids Surf., A,* 409, 105.

125. Jiang LC and Zhang WD (2010). A highly sensitive nonenzymatic glucose sensor based on CuO nanoparticles-modified carbon nanotube electrode. *Biosens. Bioelectron.*, 25, 1402.

126. Wu, H. X., Cao, W. M., Li, Y., Liu, G.,Wen, Y., Yang, H. F. and Yang, S-P. (2010). In situ growth of copper nanoparticles on multiwalled carbon nanotubes and their application as non-enzymatic glucose sensor materials. *Electrochim. Act*a, 55, 3734.

127. Yang JA, Zhang WD, Gunasekaran S (2010). An amperometric non-enzymatic glucose sensor by electrodepositing copper nanocubes onto vertically well-aligned multi-walled carbon nanotube arrays. *Biosens. Bioelectron.*, 26, 279.

128. Jiang F, Wang S, Lin JJ, Jin HL, Zhang LJ, Huang SM, Wang J (2011). Aligned SWCNT-copper oxide array as a nonenzymatic electrochemical probe of glucose. *Electrochem. Commun.,* 13, 363-365, 2011.

129. Lu LM, Zhang XB, Shen GL, Yu RQ (2012). Seed-mediated synthesis of copper nanoparticles on carbon nanotubes and their application in nonenzymatic glucose biosensors. *Anal. Chim. Act*a, 715, 99.

130. Yang Z, Feng J, Qiao J, Yan Y, Yu Q, Sun K (2012). Copper oxide nanoleaves decorated multi-walled carbon nanotube as platform for glucose sensing. *Anal. Methods*, 4, 1924.

131. Zhou X, Nie H, Yao Z, Dong Y, Yang Z, Huang S (2012). Facile synthesis of nanospindle-like Cu2O/straight multi-walled carbon nanotube hybrid nanostructures and their application in enzyme-free glucose sensing. *Sens. Actuators, B,* 168, 1.

132. Yang GC, Liu   EJ, Khun NW, Jiang SP (2009). Copper oxide nanoleaves decorated multi-walled carbon nanotube as platform for glucose sensing. *J. Electroanal. Chem*., 627, 51.

133. Li C, Liu Y, Li L, Du Z, Xu S, Zhang M, Yin X, Wang T (2008). A novel amperometric biosensor based on NiO hollow nanospheres for biosensing glucose, *Talanta*, 77, 455.

134. Xia C and Ning W (2010). A novel non-enzymatic electrochemical glucose sensor modified with FeOOH nanowire. *Electrochem. Commun*., 12, 1581.

135. Das D, Sen P, Das K (2006). Electrodeposited MnO 2 as electrocatalyst for carbohydrate oxidation. *J. Appl. Electrochem*., 36, 685.

136. Shim J, Kang M, Lee Y, Lee C (2012). A nanoporous ruthenium oxide framework for amperometric sensing of glucose and potentiometric sensing of pH. *Microchim. Act*a, 177, 211.

137. Zhang L, Li H, Ni Y, Li J, Liao K, Zhao G (2009). Porous cuprous oxide microcubes for non-enzymatic amperometric hydrogen peroxide and glucose sensing. *Electrochem. Commun*.,11, 812.

138.   Ding Y, Wang Y, Su L, Bellagamba M, Zhang H, Lei Y (2010). Electrospun Co3O4 nanofibers for sensitive and selective glucose detection. *Biosens. Bioelectron.*, 26, 542.

139.   Bai Y, Sun Y, Sun C (2008). Pt–Pb nanowire array electrode for enzyme-free glucose detection. *Biosens. Bioelectron.*, 24, 579.

140. Lei Y, Yan X, Zhao J, Liu X, Song Y, Luo N, Zhang Y (2011). Improved glucose electrochemical biosensor by appropriate immobilization of nano-ZnO. *Colloids Surf., B*, 82, 168.

141. Berchmans S, Gomathi H, Rao GP (1995). Electrooxidation of alcohols and sugars catalysed on a nickel oxide modified glassy carbon electrode. *J. Electroanal. Chem.*, 394, 267.

142. Lyons ME, Fitzgerald CA, Smyth MR (1994). Glucose oxidation at ruthenium dioxide-based electrodes, *Anal.*, 119, 855.

143. Chen JW, Zhang D, Ye JS (2008). Nonenzymatic electrochemical glucose sensor based on MnO2/MWNTs nanocomposite. *Electrochem. Commun.*, 10, 1268.

144. Noorbakhsh A and Salimi A (2009). Amperometric detection of hydrogen peroxide at nano-nickel oxide/thionine and celestine blue nanocomposite-modified glassy carbon electrodes. *Electrochim. Acta*, 54, 6312.

145. Nam, K. W. and Kim, K. B. (2002). A study of the preparation of NiO x electrode via electrochemical route for supercapacitor

applications and their charge storage mechanism. *J. Electrochem. Soc.*, 149, A346.

146. Zhang Y, Xu FG, Sun YJ, Shi Y, Wen ZW, Li Z (2011). Assembly of Ni (OH) 2 nanoplates on reduced graphene oxide: a two-dimensional nanocomposite for enzyme-free glucose sensing. *J. Mater Chem.*,21, 16949.

147. Li X, Liu J, Ji X, Jiang J, Ding R, Hu Y, Huang X (2010). Ni/Al layered double hydroxide nanosheet film grown directly on Ti substrate and its application for a nonenzymatic glucose sensor. *Sens. Actuators, B*, *147*(1), 241-247.

148. Zhang YC, Su L, Manuzzi D, Jia WJ, Huo DQ, Hou CJ, Lei Y (2012). Ultrasensitive and selective non-enzymatic glucose detection using copper nanowires. *Biosens. Bioelectron.*, 31, 426.

149. Li S, Zheng YJ, Qin GW, Ren YP, Pei WL, Zuo L (2011). Enzyme-free amperometric sensing of hydrogen peroxide and glucose at a hierarchical Cu2O modified electrode. *Talanta*, 85,1260.

150. Cherevko S and Chung CH (2010). The porous CuO electrode fabricated by hydrogen bubble evolution and its application to highly sensitive non-enzymatic glucose detection. *Talanta*, 80, 1371.

151. Tong SF, Jin HY, Zheng DF, Wang W, Li X, Xu YH, Song WB (2009). Investigations on copper–titanate intercalation materials for amperometric sensor. *Biosens. Bioelectron.*, 24, 2404.

152. Luo J, Jiang SS, Zhang HY, Jiang JQ, Liu XY (2012). A novel non-enzymatic glucose sensor based on Cu nanoparticle modified graphene sheets electrode. *Anal. Chim. Acta*,709. 47.

153. Li X, Zhu Q, Tong S, Wang W, Song W (2009). Self-assembled microstructure of carbon nanotubes for enzymeless glucose sensor. *Sens. Actuators, B,* 136, 444.

154. Luque G, Rodríguez M, Rivas G (2005). Glucose biosensors based on the immobilization of copper oxide and glucose oxidase within a carbon paste matrix. *Talanta*, 15, 467.

155. Tong S, Xu Y, Zhang Z, Song W (2010). Dendritic bimetallic nanostructures supported on self-assembled titanate films for sensor application. *J. Phys. Chem. C*, 114, 20925.

156. Luo P, Prabhu SV, Baldwin RP (1990). Constant potential amperometric detection at a copper-based electrode: electrode formation and operation. *Anal. Chem*., 62, 752.

157. Luo PF and Kuwana T (1994). Nickel-titanium alloy electrode as a sensitive and stable LCEC detector for carbohydrates. *Anal. Chem*., 66, 2775.

158. Casella IG, Desimoni E, Cataldi TR (1991). Study of a nickel-catalysed glassy carbon electrode for detection of carbohydrates in liquid chromatography and flow injection analysis. *Anal. Chim. Acta*, 248, 117.

159. Lu B, Bai J, Bo X, Zhu L, Guo L (2010). A simple hydrothermal synthesis of nickel hydroxide–ordered mesoporous carbons nanocomposites and its electrocatalytic application. *Electrochim. Acta*, 55, 8724.

160. El Khatib KM, Hameed RA (2011). Development of Cu2O/Carbon Vulcan XC-72 as non-enzymatic sensor for glucose determination. *Biosens. Bioelectron.*, 26, 3542.

161. Wang W, Zhang L, Tong S, Li X, Song W (2009). Three-dimensional network films of electrospun copper oxide nanofibers for glucose determination. *Biosens. Bioelectron.*, 25, 708.

162. Zhang X, Wang G, Liu X, Wu J, Li M, Gu J, Liu H, Fang B (2008). Different CuO nanostructures: synthesis, characterization, and applications for glucose sensors. *J. Phys. Chem., A*, 112, 16845.

163. Wang X, Hu C, Liu H, Du G, He X, Xi Y (2010). Synthesis of CuO nanostructures and their application for nonenzymatic glucose sensing. *Sens. Actuators, B*, 144, 220.

164. Li C, Su Y, Zhang S, Lv X, Xia H, Wang Y (2010). An improved sensitivity nonenzymatic glucose biosensor based on a CuxO modified electrode. *Biosens. Bioelectron.*, 26, 903.

165. Zhuang Z, Su X, Yuan H, Sun Q, Xiao D, Choi MM (2008). An improved sensitivity non-enzymatic glucose sensor based on a CuO nanowire modified Cu electrode. *Anal.*,133, 126.

166. Li JY, Xiong S, Pan J, Qian Y (2010). Hydrothermal Synthesis and Electrochemical Properties of Urchin-Like Core− Shell Copper Oxide Nanostructures. *J. Phys. Chem. C*, 114, 9645.

167. Reitz E, Jia W, Gentile M, Wang Y, Lei Y (2008). CuO nanospheres based nonenzymatic glucose sensor. *Electroanal*ysis, 20, 2482.

168. Fleischmann M, Korinek K, Pletcher D (1971). The oxidation of organic compounds at a nickel anode in alkaline solution. *J. Electroanal. Chem.*,31, 39.

169. Vertes G and Horanyi G (1974). Some problems of the kinetics of the oxidation of organic compounds at oxide-covered nickel electrodes. *J. Electroanal. Chem.*, 52, 47.

170. Robertson PM (1980). On the oxidation of alcohols and amines at nickel oxide electrodes: mechanistic aspects. *J. Electroanal. Chem.*, 111, 97.

171. Wolf JF, Yeh LR, Damjanovic A (1981). Anodic oxide films at nickel electrodes in alkaline solutions—I. Kinetics of growth of the β-Ni (OH) 2 phase. *Electrochim. Acta*, 26, 4.

172. Nie H, Yao Z, Zhou X, Yang Z, Huang S (2011). Nonenzymatic electrochemical detection of glucose using well-distributed nickel nanoparticles on straight multi-walled carbon nanotubes. *Biosens. Bioelectron.*, 30, 28.

173. You T, Niwa O, Chen Z, Hayashi K, Tomita M, Hirono S (2003). An amperometric detector formed of highly dispersed Ni nanoparticles embedded in a graphite-like carbon film electrode for sugar determination. *Anal.Chem.*, 75, 5191.

174. Mu Y, Jia D, He Y, Miao Y, Wu HL (2011). Nano nickel oxide modified non-enzymatic glucose sensors with enhanced sensitivity through an electrochemical process strategy at high potential. *Biosens. Bioelectron.*, 26, 2948.

175. Safavi A, Maleki N, Farjami E (2009). Fabrication of a glucose sensor based on a novel nanocomposite electrode. *Biosens. Bioelectron.*, 24, 1655.

176. De Mele MF, Videla HA, Arvia AJ (1983). The electrooxidation of glucose on platinum electrodes in buffered media. *J. Electroanal. Chem. Interfacial Electrochem.*,155:239-49.

177. Danaee I, Jafarian M, Forouzandeh F, Gobal F (2012). Kinetic studies of glucose electrocatalytic oxidation on GC/Ni electrode. *Int. J. Chem. Kinet.*, *44*(11), 712-721.

178. Miao Y, Ouyang L, Zhou S, Xu L, Yang Z, Xiao M, Ouyang R (2014). Electrocatalysis and electroanalysis of nickel, its oxides, hydroxides and oxyhydroxides toward small molecules. *Biosens. Bioelectron.*, *53*, 428-439

179. Niu X, Lan M, Zhao H, Chen C (2013). Highly sensitive and selective nonenzymatic detection of glucose using three-dimensional porous nickel nanostructures. *Anal. Chem.*, *85*(7), 3561-3569

180. Iwu KO, Lombardo A, Sanz R, Scirè S, Mirabella S (2016). Facile synthesis of Ni nanofoam for flexible and low-cost non-enzymatic glucose sensing. *Sens. Actuators, B*, *224*, 764-771.

181. Guo H, Huang Z, Zheng Y, Weng S (2015). Electrodeposition of nickel nanoparticles modified glassy carbon electrode for nonenzymatic glucose biosensing. *Int. J. Electrochem. Sci.*, *10*, 10703-10712.

182. Ghonim AM, El-Anadouli BE, Saleh MM (2013). Electrocatalytic glucose oxidation on electrochemically oxidized glassy carbon modified with nickel oxide nanoparticles. *Electrochim. Acta*, *114*, 713-719.

183. Danial AS, Saleh MM, Salih SA, Awad MI (2015). On the synthesis of nickel oxide nanoparticles by sol–gel technique and its electrocatalytic oxidation of glucose. *J. Power Sources*, *293*, 101-108.

184. Danial AS, Awad MI, Al-Odail FA, Saleh MM (2017). Effect of different synthesis routes on the electrocatalytic properties of NiOX nanoparticles. *J. Mol. Liq.*, *225*, 919-925.

185. Zhang H and Liu S (2017). Nanoparticles-assembled NiO nanosheets templated by graphene oxide film for highly sensitive non-enzymatic glucose sensing. *Sens. Actuators, B*, *238*, 788-794.

186. Hasanzadeh M and Sabzi R (2015). Preparation and characterization of nickel oxide nanoparticles and their application in glucose and methanol sensing. *Curr. Chem. Lett.*, *4*(2), 45-54.

187. Qiao N and Zheng J (2012). Nonenzymatic glucose sensor based on glassy carbon electrode modified with a nanocomposite composed of nickel hydroxide and graphene. *Microchim. Acta*, *177*(1-2), 103-109.

188. El-Refaei SM, Saleh MM, Awad MI (2013). Enhanced glucose electrooxidation at a binary catalyst of manganese and nickel oxides modified glassy carbon electrode. *J. power sources*, *223*, 125-128.

189. Zhang Y, Wang Y, Jia J, Wang J (2012). Nonenzymatic glucose sensor based on graphene oxide and electrospun NiO nanofibers, *Sens. Actuators, B.*, *171*, 580-587.

190. El-Refaei SM, Awad MI, El-Anadouli BE, Saleh MM (2013). Electrocatalytic glucose oxidation at binary catalyst of nickel and manganese oxides nanoparticles modified glassy carbon electrode: Optimization of the loading level and order of deposition. *Electrochim. Acta*, *92*, 460-467.