NICKEL-BASED METAL-ORGANIC FRAMEWORK FOR NON-ENZYMATIC ELECTROCHEMICAL SENSING OF GLUCOSE

By

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Chair : Professor Chm Janet Lim Hong Ngee, Phd
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Glucose biosensors have grown in popularity due to their importance in managing diabetes patients' blood glucose levels. Elevated blood glucose levels have the potential to cause acute conditions like diabetes, obesity, and hypertension. These conditions can lead to a substantial financial burden and a diminished quality of life. Consequently, there is a great need for an accurate, quick, and dependable quantitative method of determining glucose concentration. Herein, we report a non-enzymatic glucose sensor based on a metal-organic framework (MOF) as an alternative approach for long-term glucose monitoring. Specifically, nickel-based MOFs were solvothermally synthesized using either 2-amino-1,4- benzenedicarboxylic acid (BDC-NH_2) or 2-hydroxy-1,4-benzenedicarboxylic acid (BDC-OH), both of which were characterized by different physicochemical techniques. The electrochemical performance of three electrodes towards glucose sensing was investigated, and Ni-BDC-NH_2 exhibited significantly better electrocatalytic behaviour towards the oxidation of glucose than Ni-BDC or Ni-BDC-OH in an alkaline media. This was attributed to a favourable multi-layered sheet-like structure that allowed diffusion for entrapment of glucose and the incorporation of -NH_2 functional groups attached to the BDC linker, which were responsible for electrochemical adsorption of glucose molecules. Ni-BDC-NH_2 displayed a lower detection limit (3.82 μM), higher stability (>180 days), and remarkable sensitivity (308 μA mM^{-1} cm^{-2}). Additionally, a molecular sieve effect for Ni-BDC-NH_2 led to a noteworthy anti-interference ability, and the sensor displays a fast response time of 5.4 s towards glucose detection. These results indicate that the as-synthesized non-enzymatic glucose sensor operates with a longer lifetime and is viable for use as an intensive monitoring system.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains

PENGESAN GLUKOSA BERASASKAN BUKAN-ENZIMATIK ELEKTROKIMIA DIDALAM KERANGKA NIKEL LOGAM-ORGANIK

Oleh

NUR AINA DIANA BINTI CHE DAUD

Oktober 2023

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Biosensor glukosa telah berkembang dalam populariti kerana kepentingan mereka dalam menguruskan tahap glukosa darah pesakit diabetes. Tahap glukosa darah yang tinggi berpotensi menyebabkan keadaan penyakit seperti kencing manis, obesiti, dan hipertensi. Keadaan ini boleh membawa kepada beban kewangan yang besar dan kualiti hidup yang berkurangan. Oleh itu, terdapat keperluan besar untuk kaedah kuantitatif yang tepat, cepat, dan boleh dipercayai untuk menentukan kepekatan glukosa. Di sini kami melaporkan pengesan glukosa bukan-enzimatik berdasarkan rangka kerja logam organik (MOF) sebagai pendekatan alternatif pengawalan paras glukosa secara jangka panjang. Secara spesifik, MOF berasaskan nikel disintesis secara solvo-thermal menggunakan asid amino-1,4-benzenedicarboxylic (BDC-NH_2) atau asid 2-hydroxyl-1,4- benzenedicarboxylic (BDC-OH), iaitu keduanya telah di dicirikan dengan teknik fisiokimia yang berbeza. Prestasi elektrokimia bagi ketiga elektrod terhadap pengesanan glukosa telah dikaji dan Ni-BDC-NH_2 menunjukkan perilaku elektro-katalitik yang lebih signifikan terhadap oksidasi glukosa berbanding Ni-BDC atau Ni-BDC-OH di dalam medium alkali. Bahan-bahan ini juga telah disusun di dalam bentuk pelbagai helaian lapisan struktur yang membolehkan penyerapan glukosa dan tindakbalas kumpulan -NH_2 yang menempel pada jaringan BDC, iaitu yang bertanggungjawab terhadap pelekatan elektrokimkia molekul glukosa. Ni-BDC-NH_2 telah memaparkan had pengesanan yang lebih rendah (3.82 uM, kestabilan yang lebih lama (>180 hari), dan sensitivity yang lebih memuaskan (308 uA $mM^{-1}cm^{-2}$). Tambahan lagi, kesan tapisan molekul terhadap Ni-BDC-NH_2 telah membawa kepada kemampuan anti-gangguan yang lebih berbaloi dan pengesanan yang lebih pantas, iaitu seawal 5.4 saat memaparkan pengesanan glukosa. Keputusan ini memberikan gambaran bahawa penghasilan pengesan glukosa secara bukan enzimatik boleh beroperasi dengan lebih lama dan berupaya untuk digunakan sebaagai sistem pemantauan yang lebih intensif.

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LIST OF ABBREVIATIONS

1D	One-Dimensional
$(Ni (NO_3)_2 . 6H_2O)$	Nitrate Hexahydrate
COOH	Carboxylic Acid
OH	Hydroxyl Group
SO_3H	Sulfonic Group
2θ	Diffraction Angle Range
AA	Ascorbic Acid
Ag	Silver
AgCl	Silver Chloride
Al	Aluminium
BDC	1,4-Benzenedicarboxylic Acid
$BDC-NH_2$	2-Amino-1,4-Benzenedicarboxylic Acid
BDC-OH	2-Hydroxy-1,4-Benzenedicarboxylic Acid
BTC	1,3,5-Trimesic Acid
CA	Chronoamperometry
CCDC	Cambridge Crystallographic Data Center
Co	Cobalt
Co_3O_4	Cobalt Tetraoxide
Cr	Chromium
Cu	Copper
CuO	Copperoxide
CV	Cyclic Voltammogram
DCM	Dichloromethane
DEG	Di-Ethylene Glycol
DMF	N-Dimethylacetamide
EDX	Energy Dispersive X-Ray
EIS	Electrochemical Impedance Spectroscopy
FAD	Flavin Adenine Dinucleotide
FE-SEM	Field Emission Scanning Electron Microscope
FT-IR	Fourier Transform Infrared
GCE	Glassy Carbon Electrode

GDH	Glucose Dehydrogenase
LOD	Limit Of Detection
MOFs	Metal–Organic Frameworks
NaOH	Sodium Hydroxide
Ni^{2+}/Ni^{3+}	Nickel Ion
PQQ	Pyrroloquinoline Quinone
RCA	Rolling Circle Amplification
Rct	Charge Transfer Resistant
UA	Uric Acid
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Metal Organic Frameworks

Metal–organic frameworks (MOFs) are a novel class of crystalline porous materials that tremendous promise for various application fields, including energy storage, drug delivery, catalysis adsorption, detection, separation, and conversion of gases (J. A. Cruz-Navarro et al., 2020; C. Sen Liu et al., 2020; Ma et al., 2019). Among various applications, electrochemical applications of MOFs have been paid extreme attention. MOFs derived porous materials have shown promising capabilities when used to detect glucose due to their abundant mass transportation channels and nanoscale grains (C. Sen Liu et al., 2020; Ma et al., 2019). These merits contribute to a broad active range and enabled the transport of ion through the electrode processes, which, when used as a sensor, would be ideally sensitive with good detection limit. (Amini et al., 2020a; Butova et al., 2016a; W. J. Li et al., 2016).

Metal clusters in MOFs form a framework that facilitates intermolecular interaction as a linker and organic bond and are designed as active sites for catalytic reactions (Duan et al., 2019; Lopa et al., 2018a; Zhu et al., 2016). Metallic ions in the MOF structure offer a redox-active material with electrocatalytic properties towards diverse biomolecules, organic compounds, and heavy metals. Noble (e.g., Au, Pt, Pd) and transition metals (e.g., Ni, Cu, Co) are used in glucose detection since they can facilitate glucose oxidation in electrocatalytic manner (Sehit & Altintas, 2020). Nickel-based metal-organic frameworks (Ni-MOFs), such as nickel metal, nickel oxide and nickel hydroxide, have attracted increasing attention in non-enzymatic glucose sensing with good catalytic performance. Ni have been explored as an efficient electrocatalytic activity from their redox couple (Ni^{2+}/Ni^{3+}), low toxicity, abundance, low cost, strong oxidizing power of high valent Ni, and exceptional stability and activity at high pH.

The structures and characteristics of MOFs can be modified with the assistance of organic ligands. In recognition of their functional characteristics, carboxylic acid ligands have a wide range of potential uses and research in coordination chemistry. The aromatic carboxylate-based MOFs exhibit distinct flexibility in the formation of multi-dimensional nanostructures due to the variety of coordination modes and robust coordination ability, in contrast to the aliphatic carboxylate-based MOFs, which typically own advantages of good water stability and simple synthesis. Plenty of literature suggested that adding specific functional groups into MOF can boost the sensor's overall performance in terms of sensitivity and specificity towards the interest target. Aromatic di- and tri-carboxylate ligands, such as 1,4-benzene dicarboxylic acid (BDC) and 1,3,5- trimesic acid (BTC), are sensible choices of organic linkers to form organic frameworks with transition metal ions for energy and environmental applications (D. Yang et al., 2021).

1.2 Electrochemical Sensing Applications

The electrochemical sensor is a novel detection technique with simplicity, speed, portability, and highly selective and sensitive devices (Ferrag & Kerman, 2020; Ghimire et al., 2019). With promising uses in point-of-care diagnostics and on-site monitoring, electrochemistry is a technique for the quantitative or semi-quantitative screening of biomarkers, neurotransmitters, medications, environmental toxins, or hazardous food components or additives (Moro et al., 2020). Extensive signal amplification techniques have been investigated and developed to enhance the performance of electrochemical sensors in response to the rising need for ultrasensitive detection. In both environmental and industrial applications, MOFs have been used as one of the top candidates for chemical sensing (Amini et al., 2020b; Ferrag & Kerman, 2020). Electrochemical sensors use current as the detecting response for the targeted analyte, and the sensitivity is directly influenced by the rate of the electrochemical process that includes the analyte. Typically, it is necessary to use electro-catalysts with fast reaction rates that can react selectively with the desired analyte. Because electrochemical reactions can only occur on the electrode surface, improved electrodes constructed of MOFs combined with active species for electrochemical sensors are anticipated to be great options for electroanalytical applications (Chuang & Kung, 2020).

In recent decades, numerous micro materials and nanomaterials with diverse features have been applied to electrochemical sensing (S. Liu et al., 2020). Nanomaterials have been proven to be remarkably valuable in sensors. Nanomaterials modified on sensor surfaces have increased interface adsorption, catalytic performance, biocompatibility, and charge transport kinetics (Ferrag & Kerman, 2020; G. Li & Wen, 2020). The sensor performs notably better and has improved selectivity and sensitivity toward detecting specific analytes owing to all these benefits. The limit of detection (LOD) is a special feature to look into while constructing an electrochemical sensor. The lowest concentration or amount of a certain analyte that can be consistently identified with a respectable signal-to-noise ratio is represented by this number. Developing a sensor with a reduced LOD is necessary since analytes frequently occur in real-world samples at trace amounts.

Seeing as MOFs have much higher specific surface areas than other traditional materials, they can be used to support catalytically active sites at a higher density, and their interconnected porosity makes it simple for the targeted analyte to diffuse into these active sites, modified electrodes made of MOFs combined with active species for electrochemical sensors are expected to be ideal candidates for electroanalytical purposes (Chuang & Kung, 2020). The relevance of electrochemical sensors can be attributed to the ease with which a chemical reaction can be transformed into an electrical signal, as well as the ability to obtain rapid and sensitive responses promptly using portable, energy efficient, and consumer devices (Moro et al., 2020).

1.3 Non-Enzymatic Glucose Sensor

The essential human biomarker is glucose, a low-molecular biomarker because most diseases correlate with blood glucose level alterations (Ghimire et al., 2019; G. Li & Wen, 2020). Traditional enzymatic glucose sensors suffer from the thermal and chemical instability of glucose oxidase and the complex enzyme immobilization processes. Most commercial blood glucose monitors use an enzyme-based electrochemical method. There are many reports on the evolution of blood glucose sensors. Glucose oxidase (GOx) and glucose dehydrogenase (GDH) are the most commonly used enzymes in this technology (Hwang et al., 2018). Regardless of the type of enzymes used, sophisticated enzyme fixation is required for all enzyme-based sensors, which means they all unavoidably suffer from the unpredictability of biologically constructed substances. Non-enzymatic glucose sensors can, however, be developed or used due to stability problems that surround enzymatic systems in all branches of science (Sehit & Altintas, 2020a).

On the other hand, most non-enzymatic sensors that lack biological functional units can be advantageous in terms of structural simplicity and quality control for mass production. Oxygen deficiency results in a nonlinear and far less responsive response to glucose concentration without a mediator. These limitations are overcome by non- enzymatic sensing platforms that use direct electro-catalytic glucose oxidation on an anode surface (Ma. MZhu 2019). Novel nanoparticles that can be used in enzyme-free systems to detect glucose have been developed due to advances in nanoscience and nanotechnology (Adeel et al., 2020). The development of non-enzymatic glucose sensors has advanced significantly during the past 20 years (Dhara & Mahapatra, 2018). Therefore, the advancement of electrochemical non-enzymatic glucose sensors that are commonly rely on the current response of directly oxidizing glucose molecules is crucial and considered the most effectual and favourable approach for glucose detection.

1.4 Problem Statements

High blood glucose may lead to an acute disease such as diabetes, obesity and hypertension, which subsequently results in significant financial burden associated with reduced quality of life (Afroz et al., 2018). Consequently, a high demand for cost-effective, rapid, and reliable quantitative determination of glucose concentration leads to continuing industry interest in developing new sensors for clinical diagnostics, food industry and biotechnology.

To date, commercially available glucose biosensors are predominantly based on the catalytic activity of an immobilized enzyme, which offers a high sensitivity and satisfactory selectivity. However, enzyme-based glucose sensors mainly experience instability, are expensive to produce and are associated with sophisticated immobilization procedures, which are badly affected by the surrounding circumstances (Arif et al., 2020).

Metal-organic frameworks (MOFs), which are composed of metal clusters connected by organic linkers, are an attractive porous material with exceptional specific surface area, tuneable pore size, and abundant active sites that can be exploited as catalysts for glucose detection (Xuan et al., 2020). The distinctive framework and porous structure of MOFs created an abundance of exposure for a functional element that may perform as catalytic centres for glucose sensing. Ample exposed active sites lead to interesting catalytic properties in MOF, including exceptional sensitivity and lowest limit of detection (LOD). More significantly, the molecular sieve effect of MOF (due to compatible pore sizes of the MOF and glucose molecules) during sensing has surmounted the problem of poor selectivity of non-enzymatic catalysts (L. Zhang et al., 2019).

From its very powerful catalytic activity of redox process of Ni^{2+}/Ni^{3+} couple for the transformation of glucose to gluconate, glucose has attracted much more attention for the nickel-based materials (J. A. Cruz-Navarro et al., 2020). New Ni-based materials need yet to be discovered to enhance their practical use in glucose sensing analysis, particularly in actual blood samples (F. Wang et al., 2019a). Various strategies have been employed to tune the size, morphology and sensitivity of MOFs towards glucose detection, including the use of functionalized linkers bearing $-NH_2$, -COOH and $-SO_3H$ functional groups (L. Wang et al., 2019). This approach cannot only control the surface morphology but impart the conductivity in MOFs due to the highly conjugated and delocalized π-bond in the linker, as well as enhance the electrochemical adsorption of the glucose molecule. Hence, this architecture facilitates electron transport and promotes the system's excellent conductivity and electrochemical adsorption (Qiao et al., 2020).

Therefore, it is essential to investigate the influence of functional organic linkers on the properties and the electrochemical applications of the non-enzymatic glucose sensors. New MOF composites that outperform the performance of the original components can be created by combining MOF with functional materials.

1.5 Scope of Research

Herein, we focus to investigate the relationship between functional group tuning of Nickel-based metal-organic frameworks (Ni-MOFs) using 1,4-benzene dicarboxylic acid (BDC) organic linker with an electrochemical response. Accordingly, we fabricated 3D π-conjugated MOFs composed of nickel and a functionalized linker [2- amino-1,4-benzenedicarboxylic acid (BDC-NH_2) or 2-hydroxy-1,4-benzenedicarboxylic acid (H_2BDC-OH)] via a simple solvothermal approach. The as-synthesized MOFs were then drop-casted on a glassy carbon electrode (GCE) and acted as working electrodes for a non-enzymatic glucose sensor. The MOF materials were examined as glucose sensors using various of physicochemical techniques to evaluate their catalytic activity. Amperometry studies indicated that Ni-BDC-NH_2 MOF exhibited excellent electrocatalytic activity towards glucose oxidation with a lower detection limit, higher sensitivity and remarkable stability. Additionally, the performance of the as-synthesized modified sensor was studied using real-sample data to justify the solid evidence analysis.

1.6 Research Objectives

The primary goal of the current research is to construct a non-enzymatic glucose sensor that uses Ni metal and functional group tuning of MOFs. Therefore, analysis of the low cost, new electrolyte configurations, and strong alkaline conductivity, electrocatalysis-based Ni^{2+}/Ni^{3+} redox pairs, and a precursor of functionalised BDC linker has been suggested. The specific objectives of the study are outlined below:

1. To synthesize and characterize Ni-(M-BDC) metal-organic frameworks (MOF)s, where M = -(NH_2), -(OH) and BDC = benzene-1,4-dicarboxylic acid for overall performance of non-enzymatic electrochemical glucose sensor study.
2. To fabricate the synthesized Ni-(M-BDC) MOFs on the electrode surface for the construction of an electrochemical glucose sensor.
3. To analyse the performance Ni-(M-BDC) modified electrode using electrochemical approaches.

1.7 Thesis Outline

This thesis will investigate Ni-(M-BDC) MOFs containing Ni metal centres and -NH_2 and -OH replacements on benzene rings of benzene-1,4-dicarboxylic acid-derived linkers.

Chapter 1 gives a general introduction to the Metal-organic Framework (MOF), electrochemical sensing applications, non-enzymatic glucose sensors, and problem statements and highlights the primary objectives of this study.

Chapter 2 presents a comprehensive literature review on the significant composition design of MOF and electrochemical sensing of glucose. It concludes that a precursor of functionalised BDC linker with Ni^{2+} was used to effectively implement non-enzymatic glucose sensation under an alkaline condition. Donor ligands are a good site for introducing unique types of Metal Organic Framework (MOF), as the MOF properties can be modified by selecting linkers.

Chapter 3 discusses the materials and research methods of sample preparation, and the various characterization techniques used in Ni-based MOF experiments (M-BDC).

Chapter 4 presents the results and discussion of the modified electrode of novel Ni-(M-BDC) using various electrochemical approaches. The electroanalysis can also be extended to the determination of the analytes from commercial beverage, (Coca-Cola®) samples to prove the practicability of the sensor.

Chapter 5, summarise a conclusion and several future recommendations. The post of Chapter 5 contains a list of the references cited in this thesis, student biographies, and a list of publications.

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