UNIVERSITI PUTRA MALAYSIA

ORGANIC LIGAND DEPENDENT OF COBALT-METAL-ORGANIC FRAMEWORK FABRICATED ELECTRODES FOR ELECTROCHEMICAL SENSING OF RUTIN

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By

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Chairperson : Prof. Lim Hong Ngee, PhD
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Rutin (RT) (vitamin P) is an electro-active flavanoid mainly found in plants. It is commonly utilize as drug and consumed as a supplement due to its physiological properties. However, consuming Rutin in excessive amount beyond the dose limit may cause health issues in human body. Hence in this research, a facile synthesis of Co-MOF was proposed by using 1,4- benzenedicarboxylic acid (BDC) and biphenyl-4,4-dicarboxylic acid (BPDC), respectively, as ligands (Co-BDC MOF and Co-BPDC MOF) through solvothermal method to effectively detect the presence of RT. The XRD result and FT-IR spectra confirm the formation of Co-BDC MOF and Co-BPDC MOF. Moreover, the SEM images revealed that the Co-BDC MOF possesses a stacked layer of MOF while Co-BPDC MOF shows a needle-like MOF which simply explains that CoDC MOF have larger surface area compare to the other. Further, the Co-BDC and Co-BPDC MOFs were constructed on glassy carbon electrode (GCE) to investigate the detection of RT. The experimental results shows that the organic ligands with different chain length of the synthesized MOF has influenced the interaction with RT. Besides that, Co-BPDC MOF/GCE also exhibited an excellent electrocatalytic activity than the Co-BDC MOF/GCE and bare GCE electrode. To explain this, the high conductivity and excellent interaction with RT are the main reason for Co-BPDC MOF/GCE to exhibit a good electrocatalytic activity. Furthermore, the real sample analysis proves that the Co-BPDC MOF/GCE is capable to determine the existence of RT in pharmaceutical samples with 99.54 to 103.93 % RT recovery. Hence the fabricated sensor in the research exhibited the lowest limit of detection of 0.03 µM (S/N = 3) and the superior sensitivity of 781.43 µA/µM/cm2 with excellent repeatability and reproducibility compare to other published works.

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

LIGAN ORGANIC YANG BERGANTUNG KEPADA FABRIKASI ELEKTROD KERANGKA ORGANIC LOGAM KOBALT UNTUK PENDERIAAN ELEKTROKIMIA RUTIN

Oleh

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Rutin (RT), yang juga dikenali sebagai vitamin P, adalah flavonoid elektro-aktif yang kebanyakannya ditemui di dalam tumbuh-tumbuhan. Secara umumnya, ia telah digunakan ubat dan juga turut diambil sebagai ubat suplimen. Hal ini kerana sifat fisiologinya yang sihat. Namun begitu, pengambilan RT dalam jumlah yang berlebihan sehingga melebihi had dos boleh menyebabkan masalah kesihatan pada tubuh manusia. Dengan itu, dalam penyelidikan ini, satu sintesis mudah Co-MOF telah dicadangkan dengan menggunakan 1,4-benzenedicarboxylic acid (BDC) dan biphenyl-4,4-dicarboxylic acid (BPDC), sebagai ligan (Co-BDC MOF dan Co-BPDC MOF) melalui cara solvothermal untuk mengesan kepekatan RT. Corak XRD dan spektrum FT-IR mengesahkan pembentukan Co-BDC MOF dan Co-BPDC MOF. Selain itu, gambar SEM mendedahkan bahawa Co-BDC MOF memiliki lapisan MOF yang bertumpuk, manakala Co-BPDC MOF pula memiliki MOF seperti jarum yang menjelaskan bahawa Co-BPDC MOF mempunyai luas permukaan yang besar berbanding dengan yang lain. Selanjutnya, Co-BDC dan Co-BPDC MOF telah difabrikasi pada elektrod karbon berkaca (GCE) untuk menyelidik pengesanan sensitif RT. Hasil eksperimen menunjukkan bahawa ligan organik dengan panjang rantai yang berbeza pada MOF yang disintesis telah mempengaruhi interaksinya dengan RT. Selain itu, Co-BPDC MOF/GCE juga mempamerkan aktiviti elektrokatalitik yang sangat baik daripada Co-BDC MOF/GCE dan elektrod GCE kosong. Untuk menerangkan perkara ini, kekonduksian yang tinggi dan interaksi yang cemerlang dengan RT ialah penyebab utama Co-BPDC MOF/GCE bagi menunjukkan aktiviti elektrokatalitik yang baik. Selanjutnya, analisis sampel sebenar telah membuktikan bahawa Co-BPDC MOF / GCE dapat mengesan kehadiran RT dalam sampel farmasi dengan kadar pemulihan RT sebanyak 99.54 hingga 103.93%. Dengan itu, sensor yang difabrikasi dalam penyelidikan ini menunjukkan had pengesanan terendah, 0.03 µM (S / N = 3) dan kepekaan

unggul sebanyak 781.43 μA/μM/cm^2 dengan kebolehulangan yang sangat baik berbanding dengan kerja lain yang telah diterbitkan.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

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CHAPTER 1

INTRODUCTION

1.1 Overview

Flavonoids are phenolic compounds that are commonly found in plants. The main function of flavonoids is to prompt the growth of vegetables and to shield the vegetable against the opaque layer of bacteria or cell culture (Havsteen, 2002). Rutin (RT) also known as vitamin P, is a class of flavonoid (Cheng, et al., 2013) that extensively found as an active constituent in leaves and fruits. The chemical structure of RT comprise of aglycone quercetin and a disaccharide rutinose bound to quercetin. Apples, green tea, apricot, and buckwheat are few examples of sources of RT. RT possesses a varieties of medical properties such as anti-tumor, anti- inflammatory, anti-oxidant, anti-bacteria, and anti-diabetic (Atanassova, et al., 2009). RT also maintains healthy collagens that enable human skin to stay firm and healthy. Besides, it is also beneficial for hemorrhoids, atherosclerosis, osteoarthritis, and hypertension (Sattanathan, et al., 2011, Kumar, et al., 2012).

Owing to its broad range of physiological functions, RT is often used in Chinese traditional medicine, prescribed as therapeutical medicine by the clinic, and also consumed in the form of a supplement (Wang, et al., 2003, Vetrugno, et al., 2012). Besides that health-related problems is associated if RT is taken in excessive amount. Hence, accurate sensing of RT's concentration in the body is essential to avoid the disease. Spectrometry, high-performance liquid chromatography, and chemiluminescence are few common analytical methods used to detect RT. But, all this analysis requires an expensive apparatus and has a tedious and complex experimental setup and procedure. Electroanalytical techniques offer a fast and accurate detection at an economically viable approach with a simple experimental operation (He, et al., 2019). Currently, more studies are being carried out for employing different types of chemical compounds as an electrode material to detect RT (Liu, et al., 2017)). Material like graphene, multi-walled carbon nanotube composite, and other types of carbon-based material doped with other chemicals are widely used as an electrode material to detect RT.

But to the best of our knowledge, no work has been published solely using the metal-organic framework (MOF) as a modified electrode to detect the presence of RT. Metal-organic frameworks (MOFs) are an rising class of porous material that evolved from the fields of coordination chemistry and zeolite chemistry (Stock, et al., 2011). MOF is a porous crystalline structure consisting of metal ions linked together by organic ligands (Paz, et al., 2012)). MOF's structure and property can be always tune according to the research and function by varying the ligands and metal ions (Lu, et al., 2014).

1.2 Problem Statement

To the best of our knowledge, no work has been published using primary metal-organic framework (MOF) or in the other words MOFs without any added external additive as a modified electrode to detect the presence of RT. Jin, Y., et al, proven from their results that Zeolitic Imidazolate Frameworks (ZIFs) able to detect the presence of Rutin with small redox current when compare with ZIF-Acetylene black composite (Jin, Y., et al, 2018). ZIF is a special class of MOFs that consist of imidazole as fixed metal node. Hence, MOFs can be a potential electrode material for the detection of RT. Moreover, investigating the possible interaction sites of MOF is important to understand the detection of RT using MOF as electrode material. However as this is a novel research idea, the possible interaction sites of RT in MOFs are still undiscovered.Apart from that, although MOFs are reported as potential electrode material in sensing, but the low energy transport pathways of Co-MOFs classified as a huge disadvantage in the electrochemical sensing. Thus, to solve this problem, incorporation of other conducting materials in Co-MOFs were frequently reported in published research rather than, application of primary Co-MOF utilizing the organic ligand to increase energy transport pathways in electrochemical sensing. (Sun, et al., 2016).

1.3 Objective

The objectives of this research are as follows:

1. To utilize primary MOF as novel electrode material for electrochemical sensing of RT,
2. To investigate, the relationship of molecular length and functional group of organic ligands of MOF with interaction sites of RT
3. To study, the performance of Rutin sensor using Co-MOF as electrode material by varying molecular length of organic ligands that have same functional groups.

1.4 Scope of Work

In this work, we have synthesized two types of MOFs varying the molecular length of organic ligand that has a similar functional groups which are then named as Co-BDC MOF and Co-BPDC MOF through solvothermal method. The as-synthesized MOFs are characterized via XRD, FTIR and SEM to study the properties and structural differences caused by changing molecular length of organic compounds. The produced MOFs crystals are then mixed with water and PVDF as binder to form a homogenous dispersion which are then fabricated on glassy carbon electrode (GCE) to perform further electrochemical analysis. Both the modified electrodes have displayed a positive response towards RT. Yet, Co-BPDC MOF modified electrode exhibit an excellent sensitivity and great interaction with RT which provides a highly sensitive detection of RT

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