DEVELOPMENT OF THREE DIMENSIONAL PLATINUM–RUTHENIUM/GRAPHENE FOAM BIMETALLIC NANOCATALYSTS FOR METHANOL AND ETHANOL OXIDATION REACTIONS IN ENERGY STORAGE AND HYDROGEN PEROXIDE DETECTION IN BIOSENSING

By

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Development of Three Dimensional Platinum–Ruthenium/Graphene Foam Bimetallic Nanocatalysts for Methanol and Ethanol Oxidation Reactions in Energy Storage and Hydrogen Peroxide Detection in Biosensing

Abstract

by

CHIH-CHIEN KUNG

Carbon materials have special electronic properties and are considered promising materials for batteries, biosensors, fuel cells, and optically transparent electrodes. A novel composite material of hierarchically structured PtRu nanoparticles incorporated with three dimensional graphene foam (3D GF) is reported. GF is a 3D porous architecture which holds extremely large surface and highly conductive pathways. In this study, the objective is to enhance the performance of PtRu nanocatalysts with carbon supporting materials as electrode materials for direct methanol fuel cells (DMFCs) and direct ethanol fuel cells (DEFCs) in anodic oxidation reaction for energy storage and for the detection of H₂O₂ in biosensing. This improvement is resulted from the enhanced surface area and the extended protection of the poisoning of the nanocatalyst. PtRu/3D GF nanocatalyst exhibits a remarkable performance toward electrochemical oxidation of H₂O₂ without any additional mediator or enzyme and has a high sensitivity (1023.1 µA mM⁻¹ cm⁻²) and a low detection limit (0.04 µM). PtRu/3D GF nanocatalyst also shows a higher tolerance to poisoning CO and exhibits a good catalytic activity for both the methanol oxidation reaction (MOR) and ethanol oxidation reaction (EOR). This new approach confirms that the nanocatalysts which have a small particle size and a high degree of the dispersion to
obtain large active surface area will provide the best performance in MOR and EOR reactions as well as for H$_2$O$_2$ detection in biosensing.
1. Background and introduction

Carbon materials have special electronic properties and are considered promising materials for field-effect devices, sensors and optically transparent electrodes. In this study, the objective is to enhance the performance of PtRu nanocatalysts with supporting carbon materials as electrode materials for direct ethanol fuel cells (DEFCs) and direct methanol fuel cells (DMFCs) in an anodic oxidation reaction and for the detection of H$_2$O$_2$ in biosensing.

1.1. Biosensors

The biosensor is based on the reaction of the analyte with the bioreceptor which can be quantified by a transducer. Transducers are devices which convert the biomolecular recognition signals into the other electrical signals. [1] The most common transducers are electrochemical, optical, and piezoelectric types which are applied toward the development of biosensor technology.

Measurements of analytes can be achieved by caregivers in non-hospital settings and patients at home using appropriate biosensors. Biosensors are devices consisting of a biological recognition system and a transducer which can be used to detect and quantify a particular analyte. [2] A specific biomarker is necessary because the biomarker can provides an effective pathway minimizing the operational time consuming required. Biomarkers are molecules performing as indicators of normal biological processes, pathogenic processes, or pharmacologic responses to a therapeutic intervention. [3]

Clark and Lyons reported the first biosensor to detect glucose in blood measurement.
The enzyme-based biosensor was the first generation and a variety of biosensors for detections of other analytes were developed in the subsequent years. Biosensors can be categorized according to the biological recognition element (e.g., enzyme and DNA) [4] or the signal transduction method (e.g., electrochemical, optical, thermal, and massed-based biosensors) [5]. (Fig. 1.1) The enzyme-based biosensor is based on the enzymatic reaction accompanying by the consumption or production of an electrochemically active species, such as \( \text{H}_2\text{O}_2 \). [1] The oxidation or reduction of \( \text{H}_2\text{O}_2 \) electrochemically will result in a current which can be transduced and used to quantify the analyte. This type of biosensor can also obtain the measuring results more directly reducing the time of the measurement, compared to the hours required of a typical ELISA test. [6]

![Fig. 1.1 Schematic of a biosensor.](image-url)

1.2. Fuel cells

The rapid industrial development and growing population increase the overall energy demand. The global energy consumption therefore has been accelerating at an alarming pace. The requirement of energy supply is estimated to be double by 2050. [8] In order to prevent the energy exhaustion, various energy sources have been sought and gained.
substantial research interest in recent years. Many of researchers concentrate on developing high performance, low cost, and environmental friendly energy storage systems. In particular, fuel cells are considered as an enabling technology for creating high performance energy conversion and storage devices. [9] Among different types of direct alcohol fuel cells (DAFCs), direct ethanol fuel cells (DEFCs) and direct methanol fuel cells (DMFCs) are excellent power sources due to the high energy density, low pollutant emission, low operating temperature, and easy fuel feeding. [10, 11] The low-loaded but active Pt nanocatalysts are essential for the DEFC and DMFC development. Practical approaches in the advancement of DEFC and DMFC include 1) decreasing particle size, 2) increasing active sites for ethanol and methanol, 3) a high resistance against CO poison. [12]

1.3. Bimetallic nanocatalysts

Transition metal nanoparticles are used in the development of electrochemical sensors and biosensors based on their catalytic activity. [13, 14] The large surface-to-volume ratio and special binding site on the surface of nanoparticles lead to a fast communication between an enzymatic process and a nanoparticle response for signal transduction in biosensing or for catalytic reactions. [15] Pt nanoparticles are used in electrochemical detections based on its activity for the oxidation of \( \text{H}_2\text{O}_2 \). [16–18] Electrodes modified with Pt nanoparticles enhance electron transfer and reduce the overpotential for \( \text{H}_2\text{O}_2 \) oxidation. [19, 20] The applications of Pt-based bimetallic catalysts in sensor development are reported by Wang and his coworkers. [21] They described biosensing of glucose using carbon-paste enzyme electrodes dispersed with PtRu-on-Vulcan XC-70 carbon and demonstrated enhanced sensitivity compared to the dispersion of pure metals.
A glucose biosensor with PtAu alloy nanoparticles electrodeposited on multi-walled carbon nanotubes (MWCNTs) solubilized in chitosan (CS) with glucose oxidase (GOD) cross-linked to CS through glutaraldehyde (GA) was designed by Kang et al. [22] Pt based bimetallic catalysts are recognized to be effective as amperometric biosensors for detection of $H_2O_2$. The comparison of different Pt nanoparticles-based $H_2O_2$ sensor is listed in Table 1.1 [23] including applied potential, linear range, sensitivity, detection limit and the pH value.

### Table 1.1 Comparison of the performances of the various types of Pt based bimetallic catalysts. [23]

<table>
<thead>
<tr>
<th>Support electrode</th>
<th>Sensing platform</th>
<th>Applied potential (vs Ag/AgCl)</th>
<th>Linear range (mM)</th>
<th>Sensitivity ($\mu$A/mM cm$^{-2}$)</th>
<th>LOD ($\mu$M)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>CPE</td>
<td>Pt metallized graphite</td>
<td>0.8 V</td>
<td>–</td>
<td>26.30$^p$</td>
<td>5</td>
<td>7.4</td>
</tr>
<tr>
<td>Pt micro</td>
<td>Mesoporous Pt</td>
<td>0.6 V (SCE)</td>
<td>0.02–40</td>
<td>28.00$^p$</td>
<td>4.5</td>
<td>7.0</td>
</tr>
<tr>
<td>Pt</td>
<td>Sputtered Pt NPs in graphite-like carbon film</td>
<td>0.6 V</td>
<td>0.005–2</td>
<td>55.59$^p$</td>
<td>0.0075</td>
<td>7.0</td>
</tr>
<tr>
<td>GCE or CNF micro</td>
<td>Pt NPs on Nafion solubilized SWCNTs</td>
<td>0.55 V</td>
<td>$2.5 \times 10^{-5}$ to 0.0100–2</td>
<td>3570 and 1850</td>
<td>0.025</td>
<td>7.2</td>
</tr>
<tr>
<td>Pt–Ir alloy micro</td>
<td>Electrodeposited nanoporous Pt</td>
<td>0.40 V</td>
<td>–</td>
<td>1975$^a$</td>
<td>–</td>
<td>7.4</td>
</tr>
<tr>
<td>GCE</td>
<td>Electrodeposited Pt NPs on MWCNTs</td>
<td>0.70 V</td>
<td>Up to 2.5</td>
<td>3847$^a$</td>
<td>0.025</td>
<td>6.0</td>
</tr>
<tr>
<td>Pt</td>
<td>Pt NPs assembled in PDDA polyelectrolyte matrix</td>
<td>0.8 V</td>
<td>$4.2 \times 10^{-3}$ to 0.16</td>
<td>500</td>
<td>0.042</td>
<td>7.0</td>
</tr>
<tr>
<td>GCE</td>
<td>Electrodeposited Pt NPs on MWCNTs</td>
<td>0.6 V</td>
<td>–</td>
<td>5 $\times 10^{-4}$ to 3</td>
<td>21.18$^a$</td>
<td>0.0005</td>
</tr>
<tr>
<td>GCE</td>
<td>Pt NP ensembles stabilized by PDDA</td>
<td>0.4 V</td>
<td>5 to 12</td>
<td>115.28</td>
<td>0.0006</td>
<td>7.2</td>
</tr>
<tr>
<td>GCE</td>
<td>Pt NPs immobilized on Nafion dispersed graphene</td>
<td>0.4 V</td>
<td>Upto 12</td>
<td>115.28</td>
<td>0.0006</td>
<td>7.2</td>
</tr>
</tbody>
</table>

However, electrodes modified with pure Pt nanoparticles require ca. +0.7 V versus Ag/AgCl to generate the oxidation current of $H_2O_2$. This high overpotential will oxidize ascorbic acid (AA) and uric acid (UA) in human blood resulting in an interference of the detection of the analyte. [23] Bimetallic nanoparticles create functional hybrid nanostructures, resulting in the modifications in electronic, catalytic, or photonic property. The addition of a second metal contributes to the alterations in particle size, shape, surface-morphology, composition, chemical and physical properties including the
catalytic activity and chemical selectivity of the material as compared to the single metallic nanocatalyst. [24] Pt based bimetallic nanoparticles are widely regarded also as the catalysts for the applications of fuel cell. Specifically, among platinum based bimetallic nanocatalysts, PtRu nanocatalysts exhibit a superior activity in $\text{H}_2\text{O}_2$ detection, ethanol oxidation reaction (EOR), and methanol oxidation reaction (MOR).

1.4. Carbon supported materials

Carbon nanomaterials possess unusual size-/surface-dependent properties (e.g., morphological, electrical, optical, and mechanical) which are useful in enhancing energy conversion and storage capability. [8, 25–27] Specially, carbon materials enhance the availability electrochemical active surface area (ECSA) of electrocatalyst providing high mass transport of reactants to the electrocatalyst. Carbon materials come in many forms and are often categorized by their dimensionality, such as zero dimensional (0D) fullerene, one dimensional (1D) CNT, and two dimensional (2D) graphene, as shown in Table 1.2. Graphene possesses more novel properties compared with fullerene and CNT. [28–30] Graphene is a two dimensional monolayer of carbon atoms with high surface area, chemical stability, and thermal stability, making it as a useful growth substrate for energy conversion and electronics. [31, 32] Hybridisation of graphene with metal has been investigated in different applications such as lithium batteries[33], catalysts[34], fuel cells[35], biosensors[36], and photovoltaic devices[37].
Table 1.2 Properties of carbon materials. [9]

<table>
<thead>
<tr>
<th>Properties</th>
<th>Fullerenes</th>
<th>Carbon nanotubes</th>
<th>Activated carbon</th>
<th>Graphite</th>
<th>Graphene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal conductivity (W/m K)</td>
<td>0.4 [7]</td>
<td>&gt;3000 (multi-walled)</td>
<td>0.15-0.5 [9]</td>
<td>~3000 (in-plane)</td>
<td>~5000 [11]</td>
</tr>
<tr>
<td>Intrinsic mobility (cm³/yr)</td>
<td>0.56 [12]</td>
<td>~100,000 [13]</td>
<td>-</td>
<td>~13,000 (in-plane)</td>
<td>~15,000 (in-plane)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>values [11]</td>
<td>values on 3D surface</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>0.91 [17]</td>
<td>0.64 [18]</td>
<td>0.138 [19]</td>
<td>1.06 [20]</td>
<td>~1.0 [21]</td>
</tr>
<tr>
<td>Optical Transparency (%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>~0.7 [22]</td>
</tr>
</tbody>
</table>

However, graphene shows poor electrical conductivity and large resistance from structural defects, and the strong planar stacking of graphene sheets. [38, 39] In order to overcome these shortcomings, a new strategy is proposed to grow graphene on three dimensional (3D) skeletons (graphene foam/porous graphene) with a large surface area. [40, 41] Graphene foam (GF) is a 3D multilayer freestanding and monolithic electrochemical graphene film which is a promising material using in chemical sensing and energy storage. This porous architecture of GF holds extremely large surface and highly conductive pathways. [42, 43] GF also uses as the freestanding electrode with a low resistance enhancing the mobility of charge carries based on its mechanical strength and continuous skeleton. [44] Fig. 1.2 shows the different structures of allotropes of carbon.
Fig. 1.2 Molecular models of different types of sp2-like hybridized carbon nanostructures exhibiting different dimensionalities, 0D, 1D, 2D and 3D: (a) C60: Buckminsterfullerene; (b) nested giant fullerenes or graphitic onions; (c) carbon nanotube; (d) nanocones or nanohorns; (e) nanotoroids; (f) graphene surface; (g) 3D graphite crystal; (h) Haeckelite surface; (i) graphene nanoribbons; (j) graphene clusters; (k) helicoidal carbon nanotube; (l) short carbon chains; (m) 3D Schwarzite crystals; (n) carbon nanofoams (interconnected graphene surfaces with channels); (o) 3D nanotube networks, and (p) nanoribbons 2D networks. [45]

1.5. Relevant theory and principle

1.5.1. $\text{H}_2\text{O}_2$ detection
Electrochemical biosensors based on enzymatic activity receive significant interest in recent years. The advantages of the electrochemical biosensors include low cost, portability, a fast response time, and ease-of-usage by non-specialist personnel. [46] Hydrogen peroxide (H$_2$O$_2$) is an electrochemical active species produced by many oxidase enzymes. Thus, the measurement of H$_2$O$_2$ in various enzymatic reactions can quantify the analyte for biomarker detections as shown in Eq. (1). [47] The use of electrode or catalyst-modified electrode as a transducer is based on the Eq. (2) of H$_2$O$_2$ oxidation.

\[
\text{Analyte} + O_2 \xrightarrow{\text{Oxidase}} \text{Byproduct} + H_2O_2
\]  

(1)

\[
H_2O_2 \xrightarrow{\text{electrode}} O_2 + 2H^+ + 2e^-
\]  

(2)

The oxidation current of H$_2$O$_2$ is measured under a suitable applied potential between -0.1 V to +0.8 V. The changes in the concentration of the H$_2$O$_2$ can then relate to the analyte concentration as shown in Eq. (1).

Moreover, Ru requires less activation energy than Pt in adsorbing OH$_{\text{ads}}$ or O$_{\text{ads}}$. [48–52] Gsell et al reported that the oxygen adsorption preferably occurs onto the Ru (0001), hexagonal close-packed (hcp), surface. [53, 54] This allows the O$_{\text{ads}}$ inhibitor to adsorb on Pt surface, thereby minimizing the surface “poisons” on the Pt metal. Consequently, Pt active binding sites are able to interact with H$_2$O$_2$, enhancing the catalytic activity of the H$_2$O$_2$ detection. The addition of promoters, including of adding a metallic third element, adjustment of preparation parameters, using of alterative supports, and heat treatments on the bimetallic nanocatalyst, are proposed. [55–58] Carbon powder, carbon nanotube (CNT), and graphene as the supporting materials for bimetallic nanocatalysts are used
due to their unique structural, electrical, and mechanical properties. [55]

1.5.2. Ethanol oxidation reaction

Fuel cell currently is regarded as a potential power source. Both DEFC and DMFC were the DAFCs using aqueous ethanol and methanol solution as fuel, respectively. The detailed description of the ethanol oxidation mechanism on PtRu catalysts is described below. [59, 60] In Eq. 3, the reaction involves the ethanol adsorption and then oxidizes to acetaldehyde. The dissociation of water occurs by reacting with Ru as represented in step 2. [61] The acetaldehyde will then react with hydroxyl species (OH$_{ads}$) as represented by Eq. 4. In final step (Eq. 6), RuO$_x$H$_y$ species can help to remove the absorbed CO and enhance the EOR activity.

$$ Pt + C_2H_5OH \rightarrow Pt - C_2H_5OH_{ads} \rightarrow Pt - CH_3CHO_{ads} + 2H^+ + 2e^- $$  \hspace{1cm} (3)

$$ Ru + H_2O \rightarrow Ru - OH_{ads} + H^+ + e^- $$  \hspace{1cm} (4)

$$ Pt + Pt - (CO - CH_3)_{ads} \rightarrow Pt - (CO)_{ads} + Pt - (CH_3)_{ads} $$  \hspace{1cm} (5)

$$ Pt - CH_3CHO_{ads} + OH_{ads} \rightarrow Pt + CH_3COOH + H^+ + e^- $$  \hspace{1cm} (6)

$$ Pt - CO_{ads} + Ru - OH_{ads} \rightarrow Pt + Ru + CO_2 + H^+ + e^- $$  \hspace{1cm} (7)

1.5.3. Methanol oxidation reaction

The major step for methanol oxidation on Pt catalysts is primarily based on the balance between initial adsorptive dehydrogenation of methanol and subsequent oxidative removal of dehydrogenation fragments. [62, 63] The first step in this reaction is the methanol adsorption (Eq. 7). The second step is the methanol dehydrogenation and the formation of adsorbed methanolic residues (CO) on Pt surface (Eq. 7). When the pure
Pt surface is occupied by the monoxide, this situation is called surface “poisons”.

$$Pt + CH_3OH \longrightarrow Pt - CH_3OH_{ads} \longrightarrow Pt - (CO_{ads}) + 4H^+ + 4e^- \quad (8)$$

The dissociation of water occurs by reacting with Ru as represented in Eq. 8. [61]

$$Ru + H_2O \rightarrow Ru - OH_{ads} + H^+ + e^- \quad (9)$$

The reaction of chemisorbed CO with chemisorbed hydroxyl species (OH$_{ads}$) show that the CO$_{ads}$ can be removed from Pt active sites. In final step, OH$_{ads}$ groups and methanolic residues adsorbed on Pt sites can be reduced to pure Pt and pure Ru. [61]

$$Pt - CO_{ads} + Ru - OH_{ads} \rightarrow Pt + Ru + CO_2 + H^+ + e^- \quad (10)$$

On the other hand, according to the energy band theory of electrons in metal, transition metals such as those of Group VII possess d-bands whose are not completely occupied by electrons. PtRu alloys possess d-bands with fewer unoccupied states than pure Pt. The additional electrons introduced with the Ru lead to an alloy with a more completely filled d-band. This means the PtRu alloy requires less active energy to overcome the energy band. [64]

1.6. Rationale and approach

The rotating disk electrode (RDE) is intended for research and testing of materials, requiring the continuity of hydrodynamic conditions near the surface of the working electrode. The advantage of using a RDE is that, an accurate solution is available for convective diffusion and the current distribution is uniform under mass-transfer-limited conditions. This method provides therefore the possibility of continuous measurement of the increase or decrease in methanol, ethanol and hydrogen peroxide concentration.
1.6.1. Cyclic voltammetry and chronoamperometric techniques

Cyclic voltammetry is a technique commonly used to obtain qualitative information from electrochemical reactions. Cyclic voltammetry is often adopted to evaluate the performances of the thermodynamics of redox processes, the kinetics of heterogeneous electron transfer reactions, and chemical reactions or adsorption processes [65]. This method leads to rapidly identify and locate the oxidation or reduction potential of the electroactive species, such as H₂O₂. The cyclic voltammetric and amperometric experiments are therefore conducted using a CH Instrument 660C Electrochemical Workstation throughout this study (CH Instrument, Inc., Austin, TX, USA).

The response of a reversible redox using cyclic voltammetry is illustrated in Fig. 1.3. No redox process occurs at the starting point. A cathodic current begins to increase until the peak is reached as the applied potential approaches the E⁰⁺. The reduction process takes place in this region. With the same reasons, when the reverse current occurs, an anodic peak will appear during the oxidation process [65].

![Fig. 1.3 Typical voltammogram for a reversible redox process. [66]](image-url)
The basic of the controlled-potential technique is the measurement of the current response to an applied potential. The mass transport involves a gradual expansion of the diffusion layer with the depletion of the reactant and decreased slope of the concentration profile as time progresses and decreased current as time progresses, as shown in Fig. 1.4. [65] Therefore, the concentration of the targeted species can be directly and quickly analyzed by the oxidation or reduction current generated through the conversion of biological changes.

1.6.2. Rotating disk electrode

**Fig. 1.4** (A) change in concentration profiles as time progresses, (B) the resulting current over time response. [65]
RDE is a common convective electrode system using for the measurement under the steady state. The RDE reduces the thickness of the diffusion layer maintaining the bulk concentration (control kinetic effect) and therefore enhances the transport of components to the electrode surface. This means that the RDE system can approach the steady state in a relatively short response time. Based on the flow profile at a RDE, the solution is forced to the rotating surface results in a vortex as shown in Fig. 1.5.

![Fig. 1.5 Flow profile at a rotating disk electrode. [67]](image)

The thickness of the diffusion layer decreases with increasing electrode angular velocity under laminar flow conditions. [68] The diffusion layer thickness is

\[
\delta = 1.61 D^{1/3} \omega^{-1/2} \nu^{1/6}
\]

where $D$ is the diffusion coefficient (cm$^2$/s), $\omega$ is the angular velocity (rad/s) and $\nu$ is the kinematic viscosity (cm$^2$/s). [68] As described by the Levich equation [68], the limiting current is given by
\[ i = 0.62nFAD^{2/3} \omega^{1/2}v^{-1/6}C \]  

where \( n \) is the number of electrons for the reaction, \( F \) is faraday constant 96,485 (C/mol), \( A \) is the electrode surface area (cm\(^2\)/s) and \( C \) is the concentration (mol/cm\(^3\)). [68] Levich equation is used to describe the totally mass-transfer-limited condition at RDE. The RDE system using for anodic oxidation of EOR and MOR and for \( \text{H}_2\text{O}_2 \) detecting in biosensing are investigated throughout this study.

1.6.3. Methods of estimating limit of detection (LOD)

LOD is taken as the lowest concentration of an analyte in a test sample that can be detected. A signal-to-noise ratio (S/N) of three is generally accepted for estimating LOD. This method is commonly applied to analytical methods that exhibit baseline noise. The blank determination is applied when the blank analysis provides results with a non-zero standard deviation. LOD is expressed as the analyte concentration corresponding to the sample blank value plus three standard deviation as shown in the following equation:

\[ LOD \cong \bar{X}_b + 3S_b (S / N = 3) \]  

where \( \bar{X}_b \) is the mean concentration of the blank and \( S_b \) is the standard deviation of the blank.

1.6.4. The estimation of the catalyst surface area

1.6.4.1. \( \text{CO} \) stripping

The poor kinetics of EOR and MOR at the anode are possibly causing by self-poisoning of the surface by CO which is formed during dehydrogenation of the ethanol and the methanol. The evaluation of PtRu nanocatalysts surface area is based on the
measurements of CO tolerance by CO anodic stripping voltammetry. A method for an estimation of the PtRu nanocatalyst surface area in a fuel cell is based on the calculation of experimental CO oxidation data using a mathematical model. The calculation integrates the area between the peak of CO oxidation and the removal of CO adsorbed.

The CO stripping technique is used to determine the ECSA. The CO stripping measurement is conducted with a three electrode cell using 0.5 M H₂SO₄ as electrolyte throughout this study. Pure CO (99.5%) is pre-adsorbed onto the nanocatalyst surface at −0.15 V versus SCE for 1 h. Two cyclic voltammograms are recorded between −0.2 V and +1.2 V versus SCE at a scan rate of 0.5 V/s. The first potential sweep is conducted to electro-oxidize the adsorbed CO and the second potential sweep is to verify the completeness of the CO oxidation.

1.6.4.2. Brunauer, Emmett and Teller (BET) measurement

BET is based on physical adsorption of a monolayer of gas molecules on the surface of a material. The data are then treated according to the Brunauer, Emmett and Teller adsorption isotherm equation. [69] This technique is used to measure the surface area, pore size and pore size distribution of a powder. The surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbed gas corresponding to a monomolecular layer on the surface. Physical adsorption occurs based on relatively weak forces (van der Waals forces) between the adsorbed gas molecules and the adsorbent surface area of the test powder. The determination is usually carried out of the liquid nitrogen. The amount of adsorbed gas is measured by a volumetric or continuous flow procedure. The evaluation of surface
area for PtRu nanocatalysts with different carbon supported materials therefore can be carried out by the BET measurement.
1.7. Bibliography


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2. Preparation and characterization of three dimensional graphene foam supported platinum-ruthenium bimetallic nanocatalysts for hydrogen peroxide based electrochemical biosensors

Thick film screen-printing and ink-jet printing are commonly used for the electrochemical based biosensors. Generally, a paste or ink is pressed onto the flat surface of a substrate by a mechanical squeegee through the openings on a stainless steel or polymeric screen transferring a desired pattern onto the substrate. A biosensor generally contains three electrodes: working, counter and reference electrodes. An electrochemical potential can be applied between the working and the reference electrode. H₂O₂ is an electrochemical active product produced by various enzymatic reactions. The produced oxidize current can then be used to quantify the concentration of the analyte. Consequently, H₂O₂ can lead to the advancement of biomedical sensors for the detection of biomarkers in various diseases. In order to enhance the sensitivity and selectivity of these thick-film printed, single use, disposable biosensors, the incorporation of metallic catalyst into the thick film printing ink (or paste) has been proposed and attempted. Metallic nanoparticles deposited onto the surface of the various carbons will serve as excellent nanocatalysts for reactions including the enzymatic produced H₂O₂ reaction and others. Our research objective is therefore to design and synthesize bimetallic nanocatalysts specifically for the oxidation of H₂O₂ through an enzymatic reaction mechanism for biosensing applications.

2.1. Introduction

The large surface, the excellent dispersion and the high degrees of sensitivity of
bimetallic nanocatalysts are very attractive features. Graphene foam (GF) is a three dimensional (3D) porous architecture consisting of extremely large surface and high conductive pathways. In this study, the preparation of novel 3D GF using Ni foam as a sacrificial template in a facile process was described. 3D GF was then used incorporating platinum-ruthenium (PtRu) bimetallic nanoparticles as an electrochemical nanocatalyst for the detection of hydrogen peroxide (H₂O₂). The results of PtRu bimetallic nanocatalysts with various carbon substrate materials, such as Vulcan XC-72 carbon, graphene, and GF as the supporting materials toward the H₂O₂ detection were investigated. The atomic structures of different carbon supports and the electroactivity of PtRu nanocatalysts were characterized by X-ray diffractometer (XRD), scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM), and cyclic voltammetry (CV). The electrochemical measurements showed that the GF supported PtRu exhibited an excellent electrocatalytic activity toward the H₂O₂ detection. PtRu/3D GF nanocatalyst exhibited a remarkable performance toward electrochemical oxidation of H₂O₂ without any additional mediator showing a high sensitivity (1023.1 µA mM⁻¹ cm⁻²) and a low detection limit (0.04 µM) for H₂O₂. Amperometric results demonstrated that GF provided a promising platform for the development of electrochemical sensors in biosensing and PtRu/3D GF nanocatalyst possessed the excellent catalytic activity toward the H₂O₂ detection. A small particle size and a high degree of the dispersion in obtaining of large active surface area were important for the nanocatalyst for best H₂O₂ detection in biosensing. Moreover, potential interference by ascorbic acid and uric acid appeared to be negligible. 3D PtRu/GF nanocatalyst also exhibited a superior conductivity, low detection limit and high sensitivity, providing a new opportunity for the design and application of
electrode materials with enhanced performance in biosensing.

2.2. Experimental

2.2.1. Materials

Hydrogen hexachloroplatinate (IV) hexahydrate (H₂PtCl₆ • 6H₂O, 37.5% Pt basis), ruthenium (III) chloride hydrate (RuCl₃ • nH₂O, 99.8% purity), citric acid (99.5 wt.%) and sodium borohydride (NaBH₄, 99 wt.%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Nafion solution (LIQUION) was obtained from Ion Power Inc (New Castle, DE, USA). Vulcan XC-72R carbon and graphene nanopowder (12 nm flakes) were received from Cabot corporation (Boston, MA, USA) and Graphene Supermarket (Calverton, NY, USA), respectively. Phosphate buffer solution (PBS) (0.1 M) of pH 7.4 solution was prepared with 0.15 M KCl as the supporting electrolyte, KH₂PO₄, K₂HPO₄, and de-ionized water in appropriate portions.

2.2.2. Growth of the 3D graphene foam

Fig. 2.1 shows photodigital images of a nickel foam (Fig 2.1 (a)) and graphene foam (Fig 2.1 (b)). [1] 3D GF was prepared as follow. A nickel foam (INCO, Alantum Advanced Technology Materials (Dalian) Co., Ltd., Dalian, Liaoning, China; Pore size: 590µm) was first heated up to 1000 °C in a horizontal quartz tube under Ar (500 sccm) and H₂ (200 sccm) and kept in-situ for 5 min in order to clean its surface and remove any thin surface oxide layer. CH₄ (5 sccm) was then introduced into the furnace tube for 5 min. At this stage, graphene coated nickel foam was formed. Upon cooling to room temperature (20 °C), the Ni foam covered with graphene was removed from the furnace
tube and dip-coated with poly(methyl methacrylate) (PMMA) solution (6 M in toluene), and then dried at 180 °C for 30 min forming a thin PMMA film on graphene surface (PMMA/GF@Ni) preventing structural failure of the resultant GFs when the nickel template was etched and removed. The nickel foam was removed by immersing the whole structure in a HCl (3 M) solution at 70 °C for 5 h in order to obtain PMMA/GF. Finally, free-standing GF was obtained by dissolving the PMMA protection layer in hot acetone at 55 °C. The 3D GF then was used as the substrate for the adsorption of PtRu nanoparticles to synthesize PtRu/3D GF nanocatalyst.

![Fig. 2.1](image)

**Fig. 2.1** Photographs of (A) nickel foam, (B) graphene foam. [1]

### 2.2.3. Synthesis and modification of PtRu nanoparticle catalyst

The PtRu was synthesized using the borohydride reduction. Typically, in an experimental trial, the Pt and Ru precursors were first dissolved in deionized (DI) water achieving a 1.8mM metal solution, respectively. Citric acid was used as the capping agent adding into the metal solution preventing nanoparticles agglomeration at a molar ratio of 0.42 between citric acid and the metal solution. The bimetallic PtRu solution was then adjusted to pH = 7.0 using 0.1 M NaOH solution and NaBH₄ was used as reducing agent
and added dropwise into the metal solution. The amount of NaBH$_4$ was 1.4-times the molarity of PtRu which reduced the PtRu metal in the solution. The solution was stirred for 12 h at room temperature for the completion of the chemical reduction. For the preparation of PtRu nanocatalysts with carbon supported materials, the PtRu solution was first sonicated for 2 h and then mixed with 47.7 mg of various carbon supported materials, respectively. The nanocatalyst solution was stirred for 12 h at room temperature again. The nanocatalyst solution was thereafter washed with acetone three times and collected by centrifugation at 18,000 rpm (Sorval RC-5C Centrifuge, Thermo Scientific, Asheville, NC, USA) for 20 min. Finally, the slurry was placed into a vacuum oven at 70 °C for 24 h. Then, the nanocatalyst with 20 wt% loading of PtRu mixed with carbon supported materials was obtained.

2.2.4. Characterization of PtRu nanocatalysts with different carbon supported materials

Phase structures and compositions of the PtRu nanocatalysts with different carbon supported materials were examined by XRD (Rigaku Corporation, Tokyo, Japan) using Cu K$_\alpha$ radiation ($\lambda = 1.54$ Å) and operating at 30 kV and 15 mA with a scan rate of 3°/min for 2θ in a range from 15° to 85°. The particle size of alloy nanoparticles was estimated using Debye–Scherrer’s equation. SEM images were obtained at 5.0 keV on a Quanta 3D SEM (FEI, Hillsboro, OR, USA). The morphologies of the nanocatalysts were studied using a Tecnai F30 STEM (FEI, Hillsboro, OR, USA) and operated at 300 keV. The specimens for STEM analysis were prepared by ultrasonically suspending the nanocatalyst powders in ethanol. The suspension was then immediately dropped and dried on an ultrathin carbon supported 400 mesh copper grid (Ted Pella, Inc., Redding, CA, USA) which was used for STEM examination.
2.2.5. Electrochemical measurements

2.2.5.1. H$_2$O$_2$ detection

Literatures suggest that metal nanoparticles-based sensor electrodes often give increased current response and higher sensitivity and selectivity for H$_2$O$_2$ sensing. [2, 3] Prior to experiments, phosphate buffer solution (PBS) was deoxygenated with nitrogen gas. A glassy carbon electrode (GCE) was cleaned with acetone and ethanol in sequence, and then polished with 0.05 µm alumina powder. The GCE was then rinsed with DI water and sonicated for 10 min. In a typical H$_2$O$_2$ detection run, the bimetallic nanocatalyst with the carbon based substrate was placed on the surface of a rotating disk electrode for evaluation. 1.0 mg of metal/carbon powder was dispersed in a 45 µL of ethanol and 5 µL of Nafion solution (15 wt%), and then sonicated for 10 minutes to prepare the electrocatalyst. After sonication, 8.0 µL of the mixture was deposited onto the glassy carbon working electrode with a surface area of 0.196 cm$^2$ (Part no. AFE2M050GC, PINE Instrument Company, Grove City, Pennsylvania, USA). This thick film ink-coated electrode was dried under ambient condition for 3 minutes. A saturated calomel electrode (SCE) and a Pt mesh electrode (1 cm$^2$) were served as a reference and a counter electrode, respectively. The working electrode was operated at the rotational speed of 1,000 rpm. The electrochemical titrations of various H$_2$O$_2$ in a PBS at pH = 7.4 with 0.15 M KCl as supporting electrolyte were carried out. An Electrochemical Workstation (CHI 660C, CH Instrument, Inc., Austin, TX, USA) was used for cyclic voltammetry and amperometry. Cyclic voltammetric studies were arranged over a voltage range of -0.2 V – +1.2 V versus the SCE with a voltage scan rate of 0.1 V/s.
2.2.5.2. CO stripping

In order to evaluate the ECSA of the nanocatalyst, the CO stripping measurement was conducted in a solution of 0.5 M H₂SO₄. The prepared process of nanocatalysts for the CO stripping measurement was identical to that for H₂O₂ detection as described above. Pure CO (99.5%) was then purged closed to the working electrode for 1 h with the electrode polarized at -0.15 V versus SCE. The CO adsorption time was found to be sufficient to reach the steady state. Afterwards, the dissolved CO was removed by bubbling Ar into the solution for 20 min, and the stripping voltammograms were collected at a scan rate of 0.5 V/s. Two cyclic voltammometries were recorded from -0.2 V to +1.2 V versus SCE. The first potential sweep was conducted to electro-oxidize the adsorbed CO and the second potential sweep was to verify the completeness of the CO oxidation.

2.3. Results and discussion

2.3.1. Physicochemical characterization of PtRu nanocatalysts with different carbon supported materials

The morphologies of the pure commercial graphene and 3D GF were characterized by SEM as shown in Fig. 2.2 (A) and Fig. 2.2 (B), respectively. The morphology was totally different between these two samples. Pure commercial graphene possessed a wrinkled and sheetlike structure. However, GF exhibited a macroporous structure with the pore diameter 50-250 µm. 3D GF showed a larger surface area comparing with the commercial graphene based on its macroporous structure. Moreover, 3D GF supplied a large number of active sites for adsorption of PtRu nanoparticles, and PtRu nanoparticles dispersed homogenously on the surface. [4] GF also revealed an ultra-hollow internal
structure with a high porosity based on the cross section of SEM (Fig. 2.2 (C)). Fig. 2.2 (D)–(G) show the STEM images for the PtRu, PtRu/C, PtRu/Graphene and PtRu/3D GF nanocatalysts, respectively. PtRu nanoparticles with relatively uniform dispersions were formed on the different carbon supported materials. In the STEM images of pure PtRu (Fig. 2.2 (D)), an aggregation of nanoparticles was observed, because pure PtRu nanoparticles were not separated without carbon supported materials. Additionally, the PtRu nanoparticles were uniformly well-dispersed with Vulcan XC-72 carbon (Fig. 2.2 (E)), and graphene (Fig. 2.2 (F)) especially for the 3D GF (Fig. 2.2 (G)) based on the STEM images. This was due to the availability of more surface area of the carbon supported materials, facilitating better dispersion of the PtRu nanoparticles. For Fig. 2.2 (F) and Fig. 2.2 (G), PtRu nanoparticles were dispersed onto the graphene sheets and GF, respectively. Both images displayed that a slightly wrinkled morphology. Aksay et al. state that this wrinkle is an important factor to prevent the aggregation of graphene and maintain high active surface area. [5, 6] The STEM image of Fig. 2.2 (G) shows a nanoporous structure providing the substrate for PtRu nanoparticles to adsorb on the flat layer and the scaffold. The average nanoparticle size of PtRu/3D GF nanocatalyst was smaller than with other carbon supported materials. The size difference and nanoparticle dispersion could be explained by the different specific surface areas of carbon supported materials and calculated based on the results of XRD.
**Fig. 2.2** SEM images of (A) pure commercial graphene, (B) pure graphene foam (plane view), (C) pure graphene foam (cross section). STEM images of (D) pure PtRu nanoparticles, (E) PtRu/Vulcan XC-72R carbon, (F) PtRu/Graphene, (G) PtRu/3D GF.

**Fig. 2.3** shows the XRD patterns of PtRu, PtRu/C, PtRu/Graphene and PtRu/3D GF nanocatalysts. For pure Pt crystal, the peaks at 39.76°, 46.24°, 67.45°, and 81.28° were correspond to the (111), (200), (220) and (311) planes, respectively. These peaks indicated that Pt was presented in the face-centered cubic (fcc) structure. [7] The 2θ values of the (220) peaks for the PtRu, PtRu/C, PtRu/Graphene and PtRu/3D GF nanocatalysts were observed at 67.92°, 67.52°, 67.96° and 67.48°, respectively. All of the peaks were slightly shifted to higher angles from pure Pt crystal, indicating as the evidence of alloying. [8] The absence of the peaks associated with a typical hcp structure of pure Ru or RuO₂ in the XRD pattern suggested that Ru either formed alloys with Pt atoms or existed as oxides in the amorphous state. [9] The elemental mapping results from the energy dispersive spectroscopy (EDS) of PtRu nanocatalyst also confirmed that Pt and Ru elements themselves had formed PtRu alloys. **(Fig. 2.4)** The diffraction peak at
54.7° indicated the (004) plane of carbon support. This peak appeared when only high graphitization was achieved. [10] Also, the diffraction peak at around 26° observed in all the XRD patterns of the carbon supported nanocatalysts was due to the (002) plane of the hexagonal structure of carbon support. The existence of sharp diffraction peaks (002) demonstrated the crystalline nature of carbon support material. Carbon support material therefore acted as a good conductive substrate and influenced the crystalline nature of the Pt and PtRu nanoparticles being dispersed over the carbon material. In the case of PtRu/3D GF nanocatalyst, a very sharp peak appeared at the same 2θ value indicating the good crystalline nature and excellent conductivity of the GF.

**Fig. 2.3** X-ray diffraction patterns of PtRu-based nanocatalysts with different carbon supported materials.
**Fig. 2.4** The chemical composition of PtRu nanocatalyst examined by the energy dispersive spectroscopy (EDS).

The average particle size of the nanocatalyst was calculated from the Pt (220) diffraction peaks (**Fig. 2.5**) using Debye–Scherrer equation.

\[
d = \frac{k \lambda}{\beta \cos \theta_{\text{max}}}
\]

(1)

where \(k\) is a coefficient (0.9), \(\lambda\) is the wavelength of the X-ray (1.54 Å), \(\beta\) is the full width at half-maximum (FWHM) of the respective diffraction peak (rad), \(\theta\) is the angle at the position of peak maximum (º).

The nanoparticle sizes of Pt calculated by the Debye–Scherrer equation were 7.07, 5.39, 4.24, and 3.51 nm for the PtRu, PtRu/C, PtRu/Graphene and PtRu/3D GF nanocatalysts, respectively. In general, the nanoparticle size of Pt decreased when adding the carbon supported material during the preparation process, suggesting that the nanoparticle size of PtRu alloy in the nanocatalysts decreased with the addition of carbon.
supported material. Among the four nanocatalysts, the nanoparticle size for PtRu/3D GF nanocatalyst was the smallest, while that for PtRu nanocatalyst was the biggest. This large nanoparticle size of PtRu was probably due to agglomeration. This result indicated that PtRu/3D GF nanocatalyst had the largest surface area due to its smallest nanoparticle size among the four nanocatalysts. Thus, homogeneous distribution of PtRu nanoparticles were obtained by adding the carbon supported materials which provided the large surface area. PtRu nanocatalysts with small nanoparticle sizes and a uniform distribution indicated that the active binding sites of itself increased enhancing the possibility to interact with H$_2$O$_2$.

![X-ray diffraction patterns of PtRu-based nanocatalysts with different carbon supported materials at the Pt (220) and (311) diffraction peaks.]

**Fig. 2.5** X-ray diffraction patterns of PtRu-based nanocatalysts with different carbon supported materials at the Pt (220) and (311) diffraction peaks.
2.3.2. Electrochemical characterization and performance

The electrochemical performances of PtRu nanocatalyst with different carbon supported materials were investigated by cyclic voltammetry (CV) using potassium ferricyanide (15 mM) and potassium ferrocyanide (15 mM) as the benchmark redox reactions for various modified electrodes. As shown in Fig. 2.6 (A), the intensity of redox peak for pure PtRu nanocatalyst was low and the peak-to-peak potential separation (\( \Delta E_p = E_{pa} - E_{pc} \)) was 172 mV. In addition, the peak separations of the PtRu/C, PtRu/Graphene and PtRu/3D GF nanocatalysts were 152, 155 and 166 mV, respectively. When glassy carbon electrode (GCE) was deposited with different carbon supported materials, the peak separation decreased and the redox peak current of [Fe(CN)₆]³⁻/⁴⁻ increased substantially. The smaller peak-to-peak potential separation and the existence of sharp redox peaks current of [Fe(CN)₆]³⁻/⁴⁻ demonstrated that the carbon supported materials improved the electron and mass transfer due to the increased surface area and lower electric resistance of nanosized PtRu particles. The smaller nanosized PtRu particles accelerated the electron-transfer kinetics. PtRu/3D GF specimen showed the best improvement in the anodic peak current (\( i_{pa} \)) and cathodic peak current (\( i_{pc} \)) by extending the three dimensional structure of GF. The result indicated that the carbon supported material provided the larger surface area, the electron and mass transfer rate would be accelerated due to the finer nanoparticle size and more uniform dispersion of PtRu nanocatalysts. [3] This performance also carried out by the STEM images and XRD results.
Enzymatic produced H$_2$O$_2$ shown in Eq. (1) of Chapter 1 is oxidized at an appropriate electrochemical potential. The oxidation current of the generated H$_2$O$_2$ quantifies the concentration of analyte stoichiometrically. In order to verify the capability of this PtRu nanocatalyst for the detection of H$_2$O$_2$, experiment was firstly conducted measuring H$_2$O$_2$ in 0.1 M pH 7.4 PBS with 0.15 M KCl as a supporting electrolyte. The range of scanned potential was set between -0.2 V to +1.2 V versus SCE for six cycles with a voltage scan rate of 0.1 V/s. **Fig. 2.6 (B)** compares the measured cyclic voltammogram of the 3rd and 4th cycles in PBS with and without 2 mM H$_2$O$_2$. A separable current
appeared at +0.2 V versus the SCE reference electrode demonstrating the ability of this PtRu nanocatalyst for the detection of \( \text{H}_2\text{O}_2 \) at that oxidation potential.

**Fig. 2.6 (B)** Cyclic voltammogram of pH 7.4 PBS containing 0.15 M KCl supporting electrolyte with and without \( \text{H}_2\text{O}_2 \).

2.3.3. Electrochemical active surface area measurement

CO stripping voltammetry is applied to evaluate the ECSA of the nanocatalyst. [11, 12] **Fig. 2.7** shows the CO stripping voltammograms and the subsequent CV for the PtRu (Fig. 2.7 (A)), PtRu/C (Fig. 2.7 (B)), PtRu/Graphene (Fig. 2.7 (C)) and PtRu/3D GF (Fig. 2.7 (D)) nanocatalysts in 0.5 M H\(_2\)SO\(_4\) at a scan rate of 0.5 V/s. For all of the nanocatalysts, the first scan showed that the CO oxidation peaks were present at E\(\approx\)0.5 V
and no CO oxidation was observed in the second scan confirming the complete removal of the CO\textsubscript{ads} species. The ECSA was estimated by using the following equation:

\[
ECSA = \frac{Q_{co}}{[Pt] \times 420 \ \mu C \ cm^{-2}}
\]

(2)

where \( Q_{co} \) represented the charge for the CO stripping (mC cm\(^{-2}\)), [Pt] is the platinum loading (mg cm\(^{-2}\)) in the electrode, and 420 \( \mu C \ cm^{-2} \) was the charge density which is required to oxidize a monolayer of CO. The relevant results were calculated to be 31.2 m\(^2\) g\(^{-1}\), 54.2 m\(^2\) g\(^{-1}\), 121.8 m\(^2\) g\(^{-1}\) and 186.2 m\(^2\) g\(^{-1}\) for the PtRu, PtRu/C, PtRu/Graphene and PtRu/3D GF, respectively. The ECSA of the PtRu/3D GF nanocatalyst was higher than those of the other three nanocatalysts. The higher ECSA of PtRu/3D GF was due to the smaller size and better dispersion of the PtRu nanoparticles on GF. This observation was in agreement with the experimental results stated by XRD that PtRu/3D GF nanocatalyst had the largest surface area.
Fig. 2.7 CO stripping voltammograms of (A) PtRu, (B) PtRu/C, (C) PtRu/Graphene and (D) PtRu/3D GF nanocatalysts in 0.5 M H₂SO₄ at room temperature and 0.5 V/s scan rate. The soild line voltammogram and dash line voltammogram referred to the first cycle and second cycle, respectively.

2.3.4. Amperometric measurement of H₂O₂

The performances of the PtRu nanocatalysts with different carbon supported materials were evaluated by the amperometric detections of H₂O₂. Fig. 2.8 (A) shows the typical amperometric responses of the PtRu, PtRu/C, PtRu/Graphene, and PtRu/3D GF nanocatalysts for continual additions of H₂O₂ to a stirred supporting electrolyte solution at an applied potential of +0.32 V versus SCE. This applied potential of +0.32 V versus SCE was selected to minimize the interference from AA and UA. The stable amperometric response was obtained and the responsive time was less than 10 s achieving 95% steady state current for the nanocatalyst with carbon supported materials.
The fast response was the result of the high electronic conductivity and good catalytic activity of PtRu nanoparticles with different carbon supported materials facilitated the electron transfer in the nanocomposite film. Moreover, the PtRu/3D GF nanocatalyst exhibited a larger current output (corresponding to time) than PtRu, PtRu/C and PtRu/Graphene.

Fig. 2.8 (A) Amperometric responses of PtRu nanocatalysts with different carbon supported materials obtained from successive additions of H₂O₂.

Fig. 2.8 (B) the amperometric currents versus H₂O₂ concentrations were compared for the four nanocatalysts. The experimentally measured maximum detectable H₂O₂ concentration was found to be 5 mM with a signal-to-noise ratio of 3. This was the average of three successive measurements, corresponding to the same H₂O₂
concentration. PtRu/3D GF nanocatalyst showed the best performance when the concentration of H$_2$O$_2$ reached 5 mM. This result suggested that PtRu/3D GF nanocatalyst maintained good diffusion property because of the large surface area and high catalytic activity.

**Fig. 2.8 (B)** Currents versus H$_2$O$_2$ concentrations of chronoamperometric curve for different PtRu-based nanocatalysts with different carbon supported materials. (Repetition: $n = 3$).

**Fig. 2.9 (A)** shows time-dependent current of the PtRu/3D GF nanocatalyst for additions of H$_2$O$_2$ over a concentration range of 0.005–0.04 mM. The PtRu/3D GF amperometric sensor responded rapidly achieving 95% of the steady-state current within 10 s. **Fig. 2.9 (B)**, the calibration was linear over a H$_2$O$_2$ concentration range 0.005–0.02
mM: the linear regression equation was $I (\mu A \text{ cm}^{-2}) = 1023.1 (\mu A \text{ mM}^{-1} \text{ cm}^{-2}) C (\text{mM}) + 1.14 (\mu A \text{ cm}^{-2})$ with a coefficient of determination ($R^2 = 0.999$). The sensitivity and the detection limit were $1023.1 \mu A \text{ mM}^{-1} \text{ cm}^{-2}$ and $0.04 \mu M$, respectively. The detection limit was calculated based on signal to noise ratio ($S/N = 3$). PtRu/3D GF nanocatalyst showed the highest sensitivity and the best of limit of detection (LOD) among four samples, following by PtRu/Graphene, PtRu/C, and PtRu in order. The high LOD of the PtRu/3D GF nanocatalyst was attributed to the nanocatalyst having a high electrocatalytic activity. Additionally, the stability of this nanocatalyst reduced the interference of background current achieving the higher LOD.

Fig. 2.9 (A) Current versus time curve of the PtRu/3D GF for successive additions of $H_2O_2$.
Fig. 2.9 (B) Calibration curve of the PtRu/3D GF for H$_2$O$_2$ detection. (Repetition: $n = 3$).

The performance of PtRu nanocatalysts with different carbon supported materials were compared with other nanocatalysts as shown in Table 2.1, including applied potential, linear range, sensitivity and detection limit. PtRu/3D GF nanocatalyst showed the excellent performance which was contributed to the large surface area and excellent electrical conductivity of GF.
Table 2.1 A comparison of the performance using Pt based nanoparticles toward the H$_2$O$_2$ detection.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Applied potential (V)</th>
<th>Linear range (mM)</th>
<th>Sensitivity (µA mM$^{-1}$cm$^{-2}$)</th>
<th>LOD (µM)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/CNT</td>
<td>-0.1 (Ag/AgCl)</td>
<td>5×10$^{-3}$ to 25</td>
<td>140</td>
<td>1.5</td>
<td>[13]</td>
</tr>
<tr>
<td>Pt/MWCNT</td>
<td>+0.7 (Ag/AgCl)</td>
<td>Up to 2.5</td>
<td>3847</td>
<td>0.025</td>
<td>[14]</td>
</tr>
<tr>
<td>Pt/t-MWCNT/PDDA$^a$</td>
<td>-0.1 (Ag/AgCl)</td>
<td>1×10$^{-3}$ to 8</td>
<td>481.3</td>
<td>0.27</td>
<td>[15]</td>
</tr>
<tr>
<td>Pt/t-GO/PDDA$^b$</td>
<td>-0.1 (Ag/AgCl)</td>
<td>1×10$^{-3}$ to 5</td>
<td>353.9</td>
<td>0.65</td>
<td>[15]</td>
</tr>
<tr>
<td>PdIr/MWCNT</td>
<td>+0.25 (SCE)</td>
<td>2.5×10$^{-3}$ to 0.075</td>
<td>58.8</td>
<td>2.5</td>
<td>[3]</td>
</tr>
<tr>
<td>PtPd/MWCNT</td>
<td>+0.3 (SCE)</td>
<td>2.5×10$^{-4}$ to 0.125</td>
<td>414.8</td>
<td>1.2</td>
<td>[3]</td>
</tr>
<tr>
<td>Nanoporous PtCu/C</td>
<td>+0.3 (Ag/AgCl)</td>
<td>0 to 4</td>
<td>69.4</td>
<td>12.2</td>
<td>[16]</td>
</tr>
<tr>
<td>Nanoporous PtNi/C</td>
<td>+0.3 (Ag/AgCl)</td>
<td>0 to 2</td>
<td>208.5</td>
<td>31.5</td>
<td>[16]</td>
</tr>
<tr>
<td>Nanoporous PtPd/C</td>
<td>+0.3 (Ag/AgCl)</td>
<td>0 to 3</td>
<td>239.8</td>
<td>114.0</td>
<td>[16]</td>
</tr>
<tr>
<td>Nanoporous PtRh/C</td>
<td>+0.3 (Ag/AgCl)</td>
<td>0 to 2</td>
<td>839.9</td>
<td>34.8</td>
<td>[16]</td>
</tr>
<tr>
<td>PtRu/C</td>
<td>+0.32 (SCE)</td>
<td>0 to 0.02</td>
<td>22.2</td>
<td>0.817</td>
<td>This work</td>
</tr>
<tr>
<td>PtRu/Graphene</td>
<td>+0.32 (SCE)</td>
<td>0 to 0.02</td>
<td>791.5</td>
<td>0.379</td>
<td>This work</td>
</tr>
<tr>
<td>PtRu/3D GF</td>
<td>+0.32 (SCE)</td>
<td>0 to 0.02</td>
<td>795.4</td>
<td>0.355</td>
<td>This work</td>
</tr>
</tbody>
</table>

$^a$ Pt/t-MWCNT/PDDA represented a Pt/thiolated-MWCNT/poly-(diallyldimethylammonium chloride).
$^b$ Pt/t-GO/PDDA represented a Pt/thiolated-graphene oxide/poly-(diallyldimethylammonium chloride).

2.3.5. Interference tests

The interference from physiological species such as ascorbic acid (AA) and uric acid (UA) is always a concern for H$_2$O$_2$ based electrochemical biosensor. The concentrations of AA and UA in human blood are 0.125 mM and 0.33 mM, respectively. [14] Responses to the successive addition of 1.0 mM H$_2$O$_2$, 0.15 mM AA, and 0.5 mM UA were measured at +0.32 V versus SCE, as shown Fig. 2.10. The negligible effects of the interferences on the H$_2$O$_2$ response indicated the high selectivity of the PtRu/3D GF nanocatalyst. The high selectivity could be attributed to a relative low potential applying for H$_2$O$_2$ detection minimizing the responses of common interfering species.
2.3.6. Stability and durability of the PtRu/3D GF nanocatalyst

The stability of the PtRu/3D GF nanocatalyst was investigated through the amperometric response to 0.04 mM H₂O₂ at +0.32 V versus SCE in 0.1 M PBS (pH = 7.4) with 0.15 M KCl. In a series of 8 successive measurements, 0.005 mM H₂O₂ was measured continuously, and a good stability with a relative standard deviation (RSD) of 1.54% was obtained from three different electrodes prepared under the same conditions. The results showed that the PtRu/3D GF nanocatalyst had satisfactory stability as shown in Fig. 2.11.
Fig. 2.11 Current response of three different PtRu/3D GF nanocatalysts to 0.04 mM H$_2$O$_2$ in PBS (pH = 7.4) with 0.15 M KCl at an applied potential of +0.32 V versus SCE.

For durability evaluation, the PtRu/3D GF electrode was stored in 0.1 M PBS (pH = 7.4) with 0.15 M KCl at room temperature (25 °C) when not in use. The PtRu/3D GF electrode was then investigated through the amperometric response to 5 mM H$_2$O$_2$ at +0.32 V versus SCE in 0.1 M PBS (pH = 7.4) with 0.15 M KCl. The results showed that the PtRu/3D GF electrode remained at 96.5% of its original response after 7 days, 94.1% after 14 days, and 93.4% after 21 days, suggesting that the good stability and durability of the PtRu/3D GF nanocatalyst for H$_2$O$_2$ detection. This result demonstrated that the three dimensional structure facilitated the electron and mass transfer due to the increased surface area and high conductivity of nanosized PtRu particles.

2.4. Conclusion for H$_2$O$_2$ detection in biosensing
The measurement of H$_2$O$_2$ based amperometric biosensors are often inaccurately due to the low sensitivity and low LOD toward the H$_2$O$_2$ detection. Converting bimetallic nanoparticles into 3D porous structure enhance the active surface area and increase the effective transport in the reaction. In this study, PtRu bimetallic nanoparticles with 3D GF nanocatalyst for H$_2$O$_2$ detection was designed. 3D GF demonstrated to be as a good platform to incorporate with PtRu bimetallic nanoparticles for biosensing. PtRu/3D GF nanocatalyst exhibited a good performance toward electrochemical oxidation of H$_2$O$_2$ without any additional mediator or enzyme possessing a high sensitivity (1023.1 µA mM$^{-1}$ cm$^{-2}$) and a low detection limit (0.04 µM). 3D GF improved the availability ECSA of nanocatalyst for electron transfer and also provided high mass transport of reactants to the nanocatalyst. The increased active binding sites of PtRu/3D GF nanocatalyst showed a higher possibility to interact with H$_2$O$_2$, enhancing the catalytic activity of the H$_2$O$_2$ detection.
2.5. Bibliography


7. X. Zhang and K. Y. Chan, “Water-in-oil microemulsion synthesis of platinum–ruthenium nanoparticles, their characterization and electrocatalytic


3. Three dimensional graphene foam supported platinum–ruthenium bimetallic nanocatalysts for direct methanol and direct ethanol fuel cell applications

Pt-Metal (Pt-M) bimetallic nanocatalysts are important in the direct methanol and direct ethanol fuel cell applications. However, easily agglomerated nanoparticles over time may occur during the testing process. Therefore, an improvement to produce highly ordered, size controllable and morphological nanoparticles is desirable. A simple method to create a nanocatalyst with atomically dispersed PtRu nanoparticles on various carbon supporting materials is developed, especially for three dimensional graphene foam (3D GF). The morphology of deposits varies by changing the carbon supporting materials. 3D GF provides more active sites for the adsorption of PtRu nanoparticles than the other carbon supporting materials, facilitating better dispersion of the PtRu nanoparticles on 3D GF. Metallic nanocatalysts can be therefore directly adsorbed on carbon supporting materials through a single step process. This new composite material of hierarchically structured recently gains its attention to the study of bimetallic nanocatalysts because it offers the potential of increased activities and selectivities combined with enhanced stability as compared to their monometallic counterparts.

3.1. Introduction

Hu and co-workers have reported on the development of 3D GF with Pt/PdCu nanocatalyst for its application in ethanol fuel cell. [1] The results show that 3D GF can assist nanocatalysts to have better catalytic activity. In the present work, the preparation of novel 3D GF using Ni foam as a sacrificial template in a facile process is reported. Furthermore, platinum–ruthenium (PtRu) nanoparticles anchored onto the 3D GF as a
new composite material of hierarchically structured PtRu/3D GF for anodic electrocatalysis is also described. 3D porous graphene structure as a support for PtRu nanoparticles provided enhanced surface area for electron transfer for methanol and ethanol oxidation. PtRu/3D GF nanocatalyst showed a higher tolerance to poisoning by CO and exhibited improved catalytic activity for both methanol oxidation reaction (MOR) and ethanol oxidation reaction (EOR). PtRu/3D GF nanocatalyst exhibited catalytic activity for MOR (109.3 mA cm$^{-2}$) and EOR (78.6 mA cm$^{-2}$) which was about 2 times higher than that of PtRu/Graphene, respectively. After cyclic voltammetry (CV) for 900 cycles, the catalytic activity of PtRu/3D GF nanocatalyst retained a higher tolerance to CO poisoning. Cyclic voltammetry (CV) results and long-term cycle stability tests demonstrated that GF provided a promising platform for the development of electrochemical nanocatalysts. Specifically, PtRu/3D GF nanocatalyst showed excellent catalytic activity toward MOR and EOR compared with PtRu/Graphene (Commercial graphene), PtRu/C (Vulcan XC-72R carbon), and PtRu alone. The particle size of PtRu on 3D GF was reduced to 3.5 nm and its active surface area was enhanced to 186.2 m$^2$g$^{-1}$. Consequently, the MOR and EOR rates were nearly doubled on PtRu/3D GF compared to those on PtRu/Graphene. The good conductivity of 3D GF, large active surface area of the composite material led to the enhanced catalytic activity. 3D PtRu/GF nanocatalyst provided new avenues for design of high performance electrode materials for direct methanol fuel cells (DMFCs) and direct ethanol fuel cells (DEFCs).

3.2. Experimental

3.2.1. Materials
Ruthenium (III) chloride hydrate (RuCl$_3$ $\cdot$ nH$_2$O, 99.8% purity), hexachloroplatinic acid (IV) hexahydrate (H$_2$PtCl$_6$ $\cdot$ 6H$_2$O, 37.5% Pt basis), citric acid (99.5 wt.%) and sodium borohydride (NaBH$_4$, 99 wt.%) were purchased from Sigma Aldrich (St. Louis, MO). Nafion solution (LIQUION) was purchased from Ion Power Inc (New Castle, DE). Vulcan XC-72R carbon (Cabot corporation, Boston, MA) and 12 nm flakes graphene (Graphene Supermarket, Calverton, NY) were used as received.

### 3.2.2. Growth of the 3D graphene foam

The heteroatom-free pure carbon 3D graphene foams (GFs) were grown by conventional chemical vapor deposition (CVD). Detailed procedures for preparing the 3D GFs were reported elsewhere. [2] Specifically, a nickel foam with pore size 590µm was used and heated in Ar (500 sccm) and H$_2$ (200 sccm) for 5 min sequentially. Graphene coated nickel foam was formed by introducing CH$_4$ (5 sccm). The 3D GF was then dip-coated with a poly(methyl methacrylate) (PMMA) solution (6 M in toluene) preventing structural failure of the resultant GFs. The PMMA covered GF in nickel substrate was then placed in a 3M HCl solution removing the nickel template and dissolving the PMMA by acetone to obtain 3D GF.

### 3.2.3. Synthesis and modification of PtRu nanoparticle catalyst

Various Pt based bimetallic catalysts were studied [3], and PtRu appeared to be attractive as nanocatalyst for methanol and ethanol oxidation applications. Thus, the PtRu nanoparticles were synthesized via the borohydride reduction. The details of the preparation of PtRu nanoparticles were described elsewhere. [2] In brief, aqueous
solutions of the H$_2$PtCl$_6$ (1.8mM) and RuCl$_3$ (1.8mM) were used as the precursors of this preparation. The quantity of RuCl$_3$ was added based on Pt to Ru atomic ratio 1:1. The prepared PtRu nanoparticles were then mixed with various carbon supporting materials: 0D active carbon particles (Vulcan XC-72R carbon), 2D commercial graphene and 3D GF. For the each testing of DMFC or DEFC testing, the loading of Pt nanocatalyst at the electrode (surface area: 0.196 cm$^2$) was calculated as 0.68 m$^2$ g$^{-1}$. 20 wt.% loading of PtRu nanoparticles was used in this study.

3.2.4. Characterization of PtRu nanocatalysts

Phase structures and compositions of the PtRu nanocatalysts with different carbon supported materials were characterized by XRD. The particle size was calculated using Debye–Scherrer’s equation. The morphologies of the PtRu nanoparticles were examined by SEM and STEM, and details were presented elsewhere. [2] N$_2$ adsorption/desorption (BET) analysis was performed at 77 K using a NOVA 4200e (Quantachrome®, Boynton Beach, FL). Before the BET analysis, samples were degassed at 120 °C for 5 h.

3.2.5. Electrochemical measurements

3.2.5.1. Methanol and ethanol oxidation measurements

CV studies of MOR and EOR were performed using an Electrochemical Workstation (CHI 660C, CH Instrument, Inc., Austin, TX). Typically, one milligram of the bimetallic nanocatalyst with the carbon based substrate was dispersed in a 45 μL of ethanol and 5 μL of Nafion solution (15 wt.%), and then sonicated for 10 min to prepare the ink. After sonication, 8.0 μL of the mixture was deposited onto a glassy carbon working electrode
with a surface area of 0.196 cm$^2$ (Part no. AFE2M050GC, PINE Instrument Company, Grove City, PA). A Pt mesh electrode (1 cm$^2$) and a saturated calomel electrode (SCE) were used as a counter and a reference electrode, respectively. The solutions consisted of 0.5 M H$_2$SO$_4$ + 1.0 M methanol or 1.0 M ethanol and were purged with N$_2$ before each experiment. Before data collection, the electrocatalyst electrode was cleaned with 15 CV scans in the voltage range of $-0.241$ V to $+1.2$ V versus SCE at 0.1 V/s. CV studies were then conducted between $-0.241$ V and $+1.2$ V at a CV rate of 0.05 V/s for 900 cycles.

3.2.5.2. CO stripping

The CO stripping technique was used to determine the electrochemical active surface area (ECSA). The CO stripping voltammograms were conducted with a three electrode cell using 0.5 M H$_2$SO$_4$ as electrolyte. Pure CO (99.5%) was pre-adsorbed onto the nanocatalyst surface at $-0.15$ V versus SCE for 1 h. The dissolved CO was then removed by bubbling N$_2$ into the solution for 30 min, and the stripping voltammograms were collected at a scan rate of 0.5 V/s. Two cyclic voltammograms were recorded between $-0.2$ V and $+1.2$ V versus SCE. The first potential sweep was conducted to electro-oxidize the adsorbed CO and the second potential sweep was to verify the completeness of the CO oxidation.

3.3. Results and discussion

3.3.1. Physicochemical characterization of PtRu nanocatalysts with different carbon supported materials

3D GF revealed a macroporous structure with a pore diameter of 50–250 µm and
extremely thin interconnected sheets of graphene providing sufficient binding sites for PtRu nanoparticles, as shown in Fig. 3.1 (a). The STEM image of Fig. 3.1 (b) shows PtRu nanoparticles covering the entire surface of the 3D GF nanoporous structure uniformly. Details of this assessment were reported elsewhere. [2] The particle size of each sample also could be verified by the XRD results.

![Fig. 3.1](image)

**Fig. 3.1** (a) The SEM image of pure graphene foam, (b) The STEM image of PtRu/3D GF.

XRD patterns of PtRu nanoparticles with different carbon supporting materials were reported. [2] The diffraction patterns from the (111), (200), (220) and (311) planes of the Pt crystal were given. The nanoparticle sizes of the PtRu, PtRu/C, PtRu/Graphene were 7.07, 5.39 and 4.24 nm, respectively. In summary, the PtRu/3D GF nanocatalyst showed the smallest nanoparticle size of 3.51 nm, indicating it had the largest surface area per unit volume among the four nanocatalysts. Consequently, the PtRu/3D GF nanocatalyst would be attractive to catalyze the methanol or ethanol oxidation reactions.
3.3.2. Surface area measurements

3.3.2.1. Electrochemical active surface area measurement

CO stripping voltammetry is a reliable method applied to evaluate the ECSA of the nanocatalyst. [4, 5] The ECSA is calculated by

\[
ECSA = \frac{Q_{co}}{[Pt] \times 420 \ \mu C \ cm^{-2}}
\]

where \(Q_{co}\) is the charge for the CO stripping (mC cm\(^{-2}\)), [Pt] is the platinum loading (mg cm\(^{-2}\)) in the electrode, and 420 \(\mu C \ cm^{-2}\) represents the charge density which is required to oxidize a monolayer of CO on the Pt site. In this study, the ECSA values were 37.2 m\(^2\)/g, 54.2 m\(^2\)/g, 121.8 m\(^2\)/g and 186.2 m\(^2\)/g for the PtRu, PtRu/C, PtRu/Graphene and PtRu/3D GF, respectively. The PtRu/3D GF nanocatalyst showed higher ECSA compared to the other three nanocatalysts. This observation was in agreement with the experimental results obtained by XRD that PtRu/3D GF nanocatalyst had the largest surface area based on particle size.

3.3.2.2. Brunauer, Emmett and Teller (BET) measurement

BET was used to measure the total specific surface area by evaluating the external area and the pore area of a material. This technique is based on physical adsorption of a monolayer of gas molecules on the surface of a material. The data are then treated according to the Brunauer, Emmett and Teller adsorption isotherm equation. [6] In this study, the BET surface area values of the PtRu, PtRu/C, PtRu/Graphene and PtRu/3D GF were measured by the N\(_2\) adsorption/desorption and were 44.9 m\(^2\)/g, 52.9 m\(^2\)/g, 135.7
$158.6 \text{ m}^2 \text{ g}^{-1}$ and $158.6 \text{ m}^2 \text{ g}^{-1}$, respectively. PtRu/3D GF was more than triple that of the commercial carbon support, Vulcan XC-72R carbon powder. The difference between CO stripping measurement and BET measurement is that CO stripping method is an electrochemical measurement which estimates the surface area of PtRu nanoparticles, but BET method is a physical measurement which estimates the surface area including PtRu nanoparticles and carbon supporting materials. It was also expected that not all of the surface area of the nanocatalysts for processes of electro-oxidation could be measured by BET due to the fineness of the porosity defined by such small nanoparticle size. However, the trend of CO stripping voltammetry was consistent with the trend of BET measurement.

3.3.3. Methanol and ethanol oxidation measurements

Fig. 3.2 (a) and (b) shows the cyclic voltammograms for methanol and ethanol oxidation in a solution of $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M CH}_3\text{OH}$ and $0.5 \text{ M H}_2\text{SO}_4 + 1 \text{ M C}_2\text{H}_5\text{OH}$ over PtRu nanocatalysts with different carbon supporting materials, respectively. The potential was swept between $-0.2$ and $+1.2 \text{ V}$ versus saturated calomel electrode (SCE) at a voltage scan rate of $0.05 \text{ V/s}$. For the methanol and ethanol oxidation, PtRu catalysts with different carbon supporting materials showed similar trends. The addition of methanol or ethanol to the electrolyte resulted in a significant change in the appearance of voltammograms due to MOR or EOR taking place on the surface of the nanocatalysts as shown in Fig. 3.2 (a) and (b). Methanol and ethanol oxidation were characterized by well-separated anodic peaks in the forward ($I_f$) and reverse ($I_b$) scans. The magnitude of peak in forward scan was directly proportional to the amount of methanol or ethanol oxidized at the nanocatalyst electrode. The reverse scan
was attributed to the removal of carbon monoxide (CO) and other residual carbonaceous species formed in the forward scan. PtRu/3D GF showed the highest current density \( (I_f) \) of oxidation reaction for both methanol (109.3 mA cm\(^{-2}\)) and ethanol (78.6 mA cm\(^{-2}\)) compared to the other carbon supported materials. The current density \( (I_f) \) of the PtRu/3D GF was 4.35 and 2.13 times higher than that of PtRu/C and PtRu/Graphene for MOR, respectively. In EOR, the current density \( (I_f) \) of the PtRu/3D GF was 2.32 and 1.86 times higher than that of PtRu/C and PtRu/Graphene, respectively. The increased number of active adsorption sites and the larger surface area accelerated the reaction rate resulting in the enhanced catalytic activity. The resistance to CO poisoning was also an important concern for nanocatalysts. The ratio of peak currents associated with the anodic peaks in forward \( (I_f) \) and reverse \( (I_b) \) was used to describe the tolerance of a catalyst to intermediates generated during the oxidation of methanol. [7] A low \( I_f/I_b \) ratio indicated poor electro-oxidation of methanol to CO during the forward scan, suggesting excessive accumulation of carbonaceous intermediates on the catalyst surface. [8] For PtRu/3D GF nanocatalyst, the value of \( I_f/I_b \) was 1.14 which was larger than that of PtRu/C (0.99) and PtRu/Graphene (0.91) for MOR. In EOR, the \( I_f/I_b \) value of PtRu/3D GF nanocatalyst was 1.00 which was also larger than that of PtRu/C (0.66) and PtRu/Graphene (0.84). This result suggested that PtRu/3D GF nanocatalyst possessed a relatively higher tolerance to the CO poisoning and the carbonaceous intermediates. The onset potential of the methanol and ethanol oxidation reaction for the PtRu/3D GF were shifted towards more negative potentials than the PtRu/C and PtRu/Graphene. Thus, the reduction in the overpotential for PtRu/3D GF suggested that PtRu/3D GF nanocatalyst could be used to lower the kinetic resistance to dissociate methanol or ethanol.
Fig. 3.2 The cyclic voltammograms of PtRu nanocatalysts with different carbon supported materials (a) in a solution of 0.5 M H₂SO₄ and 1 M CH₃OH, (b) in a solution of 0.5 M H₂SO₄ and 1 M C₂H₅OH.
The catalytic activity and stability of the PtRu/3D GF nanocatalyst were also demonstrated in Fig. 3.3 for MOR and Fig. 3.4 for EOR in comparison with PtRu/Graphene nanocatalyst, respectively. The cyclic voltammograms of PtRu/3D GF and PtRu/Graphene nanocatalysts in a solution of 0.5 M H₂SO₄ and 1 M CH₃OH at a voltage scan rate of 0.05 V/s for 100 cycles were shown in Fig. 3.3. For PtRu/3D GF nanocatalyst, the current density of the first scan at both forward and reverse scan peaks increased from 109.3 and 96.2 mA cm⁻² to 146.2 and 114.8 mA cm⁻² in the 30 cycles, and then continuously increased to 151.3 mA cm⁻² and 118.4 mA cm⁻² in the 50th cycle, respectively. In 100th cycle, the current density at both forward and reverse scan peaks were enhanced to 157.2 and 126.9 mA cm⁻², as shown in Fig. 3.3 (a). For PtRu/Graphene nanocatalyst, a decrease in current density at both forward and reverse scan peaks were observed in 30 cycles. After 30 cycles, the current density at both forward and reverse scan peaks gradually decreased from 46.0 and 45.3 mA cm⁻² in the 30th cycle to 38.3 and 41.5 mA cm⁻² in the 100th cycle, as shown in Fig. 3.3 (b).
Fig. 3.3 The cyclic voltammograms of two PtRu nanocatalysts for 100 cycles in a solution of 0.5 M H₂SO₄ and 1 M CH₃OH (a) PtRu/3D GF, (b) PtRu/Graphene.
The cyclic voltammograms of PtRu/3D GF and PtRu/Graphene nanocatalysts in a solution of 0.5 M H₂SO₄ and 1 M C₂H₅OH at a voltage scan rate of 0.05 V/s for 100 cycles were shown in Fig. 3.4. For PtRu/3D GF nanocatalyst (Fig. 3.4 (a)), the current density in the first forward scan decreased from 78.6 mA cm⁻² to 58.5 mA cm⁻² in the 30 cycles, and then continuously decreased to 54.8 mA cm⁻² and 48.0 mA cm⁻² in the 50th and 100th cycle, respectively. For PtRu/Graphene nanocatalyst (Fig. 3.4 (b)), a decrease in current density at forward scan peak was observed, following by 42.3 mA cm⁻² in the 1st cycle, 31.9 mA cm⁻² in the 30th cycle, 29.6 mA cm⁻² in the 50th cycle, and 26.3 mA cm⁻² in the 100th cycle. Both of the anodic peaks in forward scan \( (I_p) \) in MOR (Fig. 3.3) and EOR (Fig. 3.4) shifted towards positive potential as the cycle’s number increased. This higher potential of MOR and EOR suggested that the Pt surface was poisoned by CO continuously and nanocatalyst itself therefore had to overcome the higher overpotential to dissociate of methanol or ethanol. It was clear that 3D GF used as the supporting materials exhibited a higher and more stable catalytic activity than commercial graphene and vulcan XC-72R carbon in MOR and EOR. Hu and Zhang state that the agglomeration of nanoparticles appear after the potential cycling which is due to the Ostwald ripening process. [1, 9] However, PtRu nanoparticles on 3D GF have the finer dispersion and stronger attachment than on Vulcan XC-72R carbon and commercial graphene keeping itself from agglomeration and Ostwald ripening. PtRu nanoparticles with relatively uniform dispersions on 3D GF would reduce and prevent the agglomeration phenomenon and therefore maintain the superior catalytic activity and stability during the potential cycling.
Fig. 3.4 The cyclic voltammograms of two PtRu nanocatalysts for 100 cycles in a solution of 0.5 M H$_2$SO$_4$ and 1 M C$_2$H$_5$OH (a) PtRu/3D GF, (b) PtRu/Graphene.
In order to investigate the long-term cycle stability of the nanocatalysts, CV measurements were performed for 900 cycles. Fig. 3.5 (a) and (b) show the durability performance of PtRu nanocatalyst with different carbon supported materials for MOR and EOR, respectively. The current density for both MOR and EOR showed a rapid decay in the initial period for PtRu/C and PtRu/Graphene nanocatalysts. The result showed that after 900 cycles the current density of PtRu/C, PtRu/Graphene, PtRu/3D GF nanocatalysts were reduced by 78.8%, 54.6%, and 0.7% of their initial current density for MOR and decreased by 98.1%, 92.3%, and 67.5% of their initial current density for EOR, respectively. The current density of PtRu/3D GF nanocatalyst remained around 110 mA cm\(^{-2}\) after 900 cycles for MOR which was 20.5 and 4.7 times higher than PtRu/C and PtRu/Graphene, respectively. In EOR, the current density of PtRu/3D GF nanocatalyst was around 25 mA cm\(^{-2}\) after 900 cycles which was 40.5 and 7.7 times higher than PtRu/C and PtRu/Graphene, respectively. All physical and electrochemical characteristics of PtRu bimetallic catalysts on the various carbon supports are summarized in Table 3.1. PtRu/3D GF nanocatalyst showed superior performance compared to the other catalysts studied, which was due to the large surface area and high catalytic activity of PtRu/3D GF. Figures 2 to 5 illustrate the details of the oxidation reactions of methanol and ethanol, the profiles of the MOR and EOR were similar, but the magnitudes of current density were different.
Fig. 3.5 The durability performance of PtRu nanocatalysts with different carbon supported materials (a) for methanol oxidation reaction, (b) for ethanol oxidation reaction.
Table 3.1 A comparison of the performance of the PtRu/3D GF, PtRu/Graphene and PtRu/C nanocatalysts for methanol and ethanol oxidation reactions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Particle size (nm)</th>
<th>ECSA (m² g⁻¹)</th>
<th>BET (m² g⁻¹)</th>
<th>Methanol oxidation</th>
<th>Ethanol oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>( I_f ) (mA cm⁻²)</td>
<td>( I_f/I_b ) ratio</td>
</tr>
<tr>
<td>PtRu/3D GF</td>
<td>3.51</td>
<td>186.2</td>
<td>158.6</td>
<td>109.3</td>
<td>1.14</td>
</tr>
<tr>
<td>PtRu/Graphene</td>
<td>4.24</td>
<td>121.8</td>
<td>135.7</td>
<td>51.3</td>
<td>0.91</td>
</tr>
<tr>
<td>PtRu/C</td>
<td>5.39</td>
<td>54.2</td>
<td>52.9</td>
<td>25.1</td>
<td>0.99</td>
</tr>
</tbody>
</table>

3.4. Conclusion for methanol and ethanol oxidation reactions in energy storage

In summary, a new nanocatalyst system of PtRu bimetallic nanoparticles decorated on 3D GF was fabricated. Anchoring bimetallic nanocatalysts onto 3D porous structure enhanced the active surface area and increased the effective transport of the reactants. The MOR and EOR activities of PtRu/3D GF were not only better than those of PtRu and PtRu/C, but also showed substantial improvement over PtRu/Graphene after prolonged cycling. 3D GF provided the uniform distribution of PtRu nanoparticles, improved the availability ECSA of nanocatalyst for electron transfer, and enhanced the tolerance to CO poisoning. The PtRu/3D GF nanocatalyst thus enhanced the rates of methanol and ethanol oxidation reactions.
3.5. Bibliography


4. Conclusions

PtRu bimetallic nanoparticle catalyst was synthesized using borohydride reduction and then physically mixed with three different carbon supported materials. A new nanocatalyst system of PtRu bimetallic nanoparticles decorated on 3D GF was designed. Characterization of the PtRu nanocatalyst on various carbon supporting materials and their activities towards the methanol and ethanol oxidation reactions and for H$_2$O$_2$ detection were determined. Electrochemical titration of the PtRu bimetallic nanoparticles by H$_2$O$_2$ was undertaken. PtRu/3D GF nanocatalyst exhibited a good performance toward electrochemical oxidation of H$_2$O$_2$ without any additional mediator or enzyme possessing a high sensitivity ($10^{23.1}$ µA mM$^{-1}$ cm$^{-2}$) and a low detection limit (0.04 µM).

PtRu/3D GF possessed superior performances compared to the other carbon supporting nanocatalysts, in terms of the catalytic activity and the durability for MOR and EOR. The MOR and EOR activities of PtRu/3D GF were not only better than that of PtRu and PtRu/C, but also possessed a 4.7 and 7.8 times improvement over the PtRu/Graphene after 900 cycles, respectively. It displayed the lowest onset potential and the highest current density among the four differently prepared carbon supported materials for both methanol and ethanol oxidations at room temperature.

For both measurements in biosensing and energy storage, the key advancements of the development of bimetallic electrocatalyst were the large surface, the excellent dispersion and the high degrees of sensitivity. Therefore, incorporating the bimetallic nanoparticles into 3D porous structure, enhanced the active surface area, and increased the effective
transport in the reaction were our goals. 3D GF demonstrated to be as a good platform to incorporate with PtRu bimetallic nanoparticles for biosensing and energy storage. 3D GF provided the uniform distribution of PtRu nanoparticles and improved the availability ECSA of nanocatalyst for electron transfer of reactants to the nanocatalyst.