Investigation and characterization of Pt-modified Au catalysts and polymer composites by electrochemistry, Raman and surface enhanced Raman spectroscopy (SERS)

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Investigation and Characterization of Pt-Modified Au Catalysts and Polymer Composites by Electrochemistry, Raman and Surface Enhanced Raman Spectroscopy (SERS)

by

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A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy
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Dedication

I dedicate this dissertation to Sri Sathya Sai Baba and my Devas for all their guidance at every moment of my life reminding me of my life’s real purpose. I would also dedicate to my father, late S.Muralidharan.
Acknowledgments

Firstly, I would thank my mother and sister for showing so much love for allowing me to come to the U.S.A and pursue my higher studies. Secondly I would thank my major professor Dr. Xiao Li, for constantly supporting me, and helping me throughout my projects, motivating me and showing the confidence in me. She would be available 24X7 to help me with my research questions. I am grateful for all the scientific learning received from her and above all for her guidance through my work. I am also grateful to my other committee members, Dr. Jon Antilla, Dr. Abdul Malik and Dr. Alberto A. Sagüés for giving me valuable advice throughout my program. Further, I would thank my group members Dr. Seongmin Hong, Micheal McIntosh, Sungyub Han, Dr. Rongfu Huang and Siqi Sun for being like my family away from home and supporting me in my research.

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Table of Contents

List of Tables ............................................................................................................................vi

List of Figures ..........................................................................................................................vii

Abstract ..................................................................................................................................xi

Chapter 1. Pt-modified Au surface as the potential catalyst for fuel cells .................. 1
  1.1 Introduction to Formic acid and Methanol Fuel cells ...................................... 1
     1.1.1 Methanol as the fuel ................................................................. 3
     1.1.2 Formic acid as the fuel ............................................................ 5
  1.2 Need for better anode catalysts in SOM fuel cells ................................. 6
     1.2.1 Current catalysts ........................................................................ 8
     1.2.2 Pt/Au catalysts ........................................................................... 10
     1.2.3 Deposition Methods .................................................................... 11
  1.3 Methods of Characterization ........................................................................... 12
     1.3.1 Electrochemical measurement Techniques .................................... 12
     1.3.2 Spectroscopic and microscopic Methods .................................... 16
     1.3.3 Raman Spectroscopic Methods .............................................. 18

Chapter 2. Experiments and Methods ................................................................. 25
  2.1 Chemicals and Materials ...................................................................................... 25
  2.2 Acid cleaning of the glassware ........................................................................ 25
  2.3 Electrochemical techniques .............................................................................. 26
     2.3.1 Preparation of an Ag/AgCl reference electrode ............................ 26
     2.3.2 Preparation of Pt-modified Au electrode using spontaneous 
         deposition ......................................................................................... 27
     2.3.3 Electrochemical measurement of BEDO-TTF/I film .............. 28
     2.3.4 Cyclic Voltammetry ................................................................... 28
     2.3.5 Commonly encountered mistakes during electrochemical 
         measurements .................................................................................. 28
  2.4 Spectroscopic and Microscopic Measurements ............................................... 29
     2.4.1 Normal Raman ............................................................................ 29
     2.4.2 Surface enhanced Raman spectroscopy (SERS) ................... 30
  2.5 Other Characterization Methods ................................................................... 34
     2.5.1 X-ray photon spectroscopy (XPS) .............................................. 34
     2.5.2 Scanning electron microscopy (SEM) ....................................... 34
     2.5.3 Energy Dispersive Spectroscopy (EDX) .............................. 35
     2.5.4 Transmission electron microscopy (TEM) ............................ 35
Chapter 3. In situ surface-enhanced Raman spectroscopic study of formic acid electrooxidation on spontaneously deposited platinum on gold ........................................ 36
  3.1 Abstract ........................................................................................................ 36
  3.2 Introduction ................................................................................................... 37
  3.3 Experimental .................................................................................................. 40
    3.3.1 Materials for electrochemistry ................................................................. 40
    3.3.2 Preparation of a Pt-modified gold electrode surface by spontaneous deposition ................................................................. 40
    3.3.3 Electrochemistry experiments ................................................................. 40
    3.3.4 SERS experiments .................................................................................. 41
  3.4 Results and analysis ..................................................................................... 42
    3.4.1 Spontaneous deposition of Pt on a Au surface ........................................ 42
    3.4.2 Formic acid electrooxidation on a Pt-modified gold electrode surface .................................................................................................. 44
    3.4.3 In situ surface enhanced Raman spectroscopy (SERS) studies .................. 52
  3.5 Discussion .................................................................................................... 55
  3.6 Conclusion .................................................................................................... 60
  3.7 Acknowledgements ...................................................................................... 61

Chapter 4. Effect of haloplattinate on the electrocatalytic activity of spontaneously deposited Pt-modified Au towards formic acid ......................................................... 62
  4.1 Abstract ........................................................................................................ 62
  4.2 Introduction ................................................................................................... 63
  4.3 Materials and Methods ................................................................................ 65
  4.4 Results and Analysis .................................................................................... 67
    4.4.1 Characterization of Pt-modified Au surfaces .......................................... 67
    4.4.2 Electrocatalytic activity of Pt-modified Au surfaces ............................... 70
    4.4.3 Effect of the concentration of the electrolyte ....................................... 72
    4.4.4 Effect of deposition time ...................................................................... 73
    4.4.5 Surface enhanced Raman spectroscopy ............................................. 74
  4.5 Discussion .................................................................................................... 77
  4.6 Conclusions .................................................................................................. 81
  4.7 Acknowledgements ...................................................................................... 82

Chapter 5: Electrochemical transformation and Raman spectroscopic study of iodine doped BEDO-TTF conductive films. ........................................................... 83
  5.1 Abstract ........................................................................................................ 83
  5.2 Introduction ................................................................................................... 83
  5.3 Experimental .................................................................................................. 85
    5.3.1 Materials and chemicals ......................................................................... 85
    5.3.2 Electrochemistry ..................................................................................... 85
    5.3.3 Raman spectroscopy ............................................................................ 85
  5.4 Results and Discussion ................................................................................ 86
  5.5 Conclusion .................................................................................................... 90
  5.6 Acknowledgements ...................................................................................... 91
List of Tables

Table 7-1. FWHM values and the intensity ratios of the D to G band of the as-received SWCNTs, S#3-5SWCNT and S#3-5SWCNT-20Ru. ......................................................... 100
List of Figures

Figure 1.1. A DMFC employing an acidic solid polymer electrolyte such as Du Point’s "Nafion" and finely dispersed platinum electro catalyst supported on porous carbon electrodes ................................................................................................................................. 4

Figure 1.2. The Scheme of formic acid electrooxidation pathways reproduced from reference 9 by Compton et al [9] ................................................................................................................................. 8

Figure 1.3: An overview of the research done in formic acid electrochemistry reproduced from reference [11]. ................................................................................................................................. 10

Figure 1-4. Theory behind Raman effect ........................................................................... 20

Figure 1.5. Normal Raman and SERS (on roughened Au electrode) spectra of 1 mM pyridine in 0.1 M KCl. ................................................................................................................................. 23

Figure 2.1. Oxidation reduction cycles procedure for preparing the SERS-active roughened surface of Au. ................................................................................................................................. 31

Figure 2.2. Best ORC cycle for preparing roughened Au (poly) with 1 mM pyridine in 0.1 M KCl .............................................................................................................................................. 32

Figure 2.3. Electrochemical workstation and the SERS setup for real time EC-SERS experiments .............................................................................................................................................. 33

Figure 3.1. a) Cyclic voltammograms on bare Au (blue), bare Pt electrode (black) and Pt@Au surface with different deposition time of 5 mins (red), 10 mins (green), 15 mins (purple) and 30 mins (pink) ................................................................................................................................. 43

Figure 3.2. a) Cyclic voltammograms of electrooxidation on plain Au (dotted line), poly Pt (thick line) and Pt-modified gold electrode surface (dashed line, 10 minutes deposition time) in a solution containing 0.45 M HCOOH ................................................................................................................................. 45

Figure 3.3. Electrooxidation of formic acid in a solution containing 0.45 M HCOOH + 0.125 M HClO₄ on plain Au (blue), Pt-modified gold electrode 5 mins (red), Pt-modified gold electrode 10 mins (green), Pt-modified gold electrode 15 mins (purple), Pt-modified gold electrode 30mins (pink) and Poly Pt (dashed black) ................................................................................................................................. 47
Figure 3.4. SERS spectra on Au (poly) in 0.125 M HClO₄ during a) anodic scan and b) cathodic scan. The spectra were taken at 0.2 V potential steps. 49

Figure 3.5. Potential dependent SERS spectra of electrooxidation formic acid on plain Au during a) anodic scan and b) cathodic scan between 200-1000 cm⁻¹ in a solution containing 0.45 M HCOOH in 0.125 M HClO₄. 50

Figure 3.6. SERS spectra on Pt-modified gold electrode (10 mins) in 0.125 M HClO₄ during a) anodic scan and b) cathodic scan. 53

Figure 3.7. Potential dependent SERS spectra of formic acid electrooxidation on Pt-modified gold electrode (10 mins) during a) anodic scan and b) cathodic scan in a solution containing 0.45 M HCOOH + 0.125 HClO₄. 54

Figure 4.1. Cyclic voltammograms on Au (black dashed line) and Pt-modified Au through spontaneous deposition for 5 minutes from PtI₆²⁻ (green), PtBr₄²⁻ (red) and PtCl₆²⁻ (blue) in 0.125 M HClO₄. Scan rate is 0.05 V/s. 66

Figure 4.2. The amount of electroactive Pt on the Pt-modified Au electrode obtained from the three precursors of 0.5 mM: PtI₆²⁻ (circle), PtBr₄²⁻ (triangle) and PtCl₆²⁻ (square) with different deposition times. 68

Figure 4.3. (A) XPS spectra of the Pt deposits obtained from the three surfaces from 0.5 mM PtBr₄²⁻ (5 minutes), PtCl₆²⁻ (15 minutes) and PtI₆²⁻ (30 minutes). 69

Figure 4.4. Cyclic voltammograms of the electrooxidation of 0.45 M HCOOH in 0.125 M HClO₄ on bare Au (blue line) and bare Pt (dash black line) and Pt-modified Au surfaces from 0.5 mM PtCl₆²⁻ (red line), PtBr₄²⁻ (purple line) and PtI₆²⁻ (green line). Scan rate is 0.05 V/s. 71

Figure 4.5. Effect of the concentration of the three deposition electrolyte PtCl₆²⁻ (black), PtBr₄²⁻ (grey) and PtI₆²⁻ (white) on the electrooxidation current density of 0.45 M HCOOH in 0.125 M HClO₄. 72

Figure 4.6. Plot of HCOOH oxidation (P-I; circles) and CO oxidation currents (P-II; triangles) with deposition time on Pt-modified Au surface from 0.5 mM (A) PtCl₆²⁻ (B) PtBr₄²⁻ and (C) PtI₆²⁻ in solution of 0.45 M HCOOH + 0.125 M HClO₄. 73

Figure 4.7. SERS spectra on Pt-modified Au surface from 0.5 mM PtCl₆²⁻ solution in 0.125 M HClO₄ A) without HCOOH and B) with 0.45 M HCOOH. 75

Figure 4.8. SERS spectra on Pt-modified Au surface from 0.5 mM PtBr₄²⁻ solution in 0.125 M HClO₄ A) without HCOOH and B) with 0.45 M HCOOH. 76
Figure 4.9. SERS spectra on Pt-modified Au surface from 0.5 mM PtI$_6^{2-}$ solution in 0.125 M HClO$_4$ A) without HCOOH and B) with 0.45 M HCOOH ........................................ 78

Figure 5.1. Cyclic Voltammograms of 0.063 mol/L iodine doped BEDO-TTF/I film (4 minutes) in 0.1 M KI at 5 mV/s................................................................. 86

Figure 5.2. Raman spectra 0.063 mol/L iodine doped BEDO-TTF (4 minutes) at different potentials in 0.1 M KI .............................................................. 87

Figure 5.3. Raman spectra of 0.033 mol/L iodine doped BEDO-TTF (10 minutes) (A) in the range of 50 – 250 cm$^{-1}$ and (B) the range of 1300-1700 cm$^{-1}$................. 89

Figure 6.1. Cyclic voltammogram of BEDO-TTF/Iodine film with 0.095 mol/L (2 mins) in 0.1 M KI aqueous solution......................................................... 95

Figure 7.1. Raman spectra of as-received SWCNT, S#3-5SWCNT and S#3-5SWCNT-20Ru.............................................................................................................. 100

Figure B1-S.1 Normal Raman spectra of 0.5 M and concentrated formic acid. Excitation wavelength at 647 nm from an Argon and Krypton laser (Coherent, Innova 70C series) with 35 mW of power, 5 s of exposure time and 1 accumulation. ........................................................................................................ 112

Figure B1-S.2. Energy dispersive X ray (EDX) spectrum of Pt-modified Au (10 minutes) surface. ......................................................................................... 113

Figure B1-S.3 a) Electrooxidation of formic acid on Pt-modified Au (10 mins) and Au surface (in blue) in a solution containing 0.09 M (red), 0.3 M (blue), 0.45 M (green), 0.90 M (purple) and 1.7 M (pink) HCOOH respectively, and on Au in solution containing 0.1 M HCOOH (brown)..................................................................................... 114

Figure B1 S.4. CO stripping curves of Pt-modified Au (10 minutes; dashed line) and poly Pt surface in 0.125 M HClO$_4$ at a scan rate of 50 mV/s............................................. 115

Figure C-S1: Raman spectrum of 0.063 mol/L BEDOTTF with iodine doped for 4 minutes (in red), The BEDOTTF in 1% polycarbonate matrix (in orange) and the polycarbonate matrix (in purple) ........................................................................................................................................ 116
Abstract

This dissertation thesis consists of six chapters. The main focus of this study is the need for understanding the reaction mechanism and intermediates formed on Pt-modified Au surface as anode catalysts in the formic acid fuel cells. Chapter 1 gives an introduction to formic acid and methanol fuel cells, an overview of the current catalysts employed at the anode of the fuel cells, specifically the Pt-modified Au electrodes as potential catalysts and the different deposition methods for preparing this catalytic surface. Information about different electrochemical methods used like cyclic voltammetry and potential step method along with other characterization methods and spectroscopic techniques has also been given. As one of the main methods to characterize the catalysts, Raman and surface enhanced Raman spectroscopy have been discussed in detail.

The electrooxidation of formic acid and the nature of the intermediates at a platinum-modified gold surface prepared through spontaneous deposition were characterized using a combination of electrochemistry and in situ surface enhanced Raman spectroscopy (SERS). Spontaneously deposited platinum on gold showed unique high catalytic activity for formic acid electrooxidation. The oxidation current of formic acid is more than five times higher on the Pt-modified gold electrode surface than on a bare Pt surface and about 72 times higher than on a bare Au surface. SERS results reveal the involvement of a novel HCOO\(^-\) adsorbate at 300 cm\(^{-1}\). Both electrochemical and spectroscopic results suggest that the formic acid electrooxidation takes place by the
dehydrogenation pathway involving a low frequency formate intermediate on the Pt-modified gold electrode catalyst. Next, the effect of the deposition solution employed in the spontaneous deposition process was explored and demonstrated to play an important role in catalytic activity of these surfaces. Electrochemical studies show that Pt-modified Au surfaces prepared from bromoplatinate solution are most active in oxidizing formic acid. The second most active surface for formic acid electrooxidation was that from chloroplatinate followed by that from the iodoplatinate solutions. Also, the optimal condition to prepare the most active surface is different for various haloplatinate solutions. In situ surface enhanced Raman spectroscopy (SERS) with potential control revealed the presence of formate at 300 cm$^{-1}$ as the reaction intermediate in the catalytic processes on all three Pt-modified Au surfaces, but with different potential-dependent behaviors.

A clear and transparent bis ethylenedioxy tetrathiafulvalene iodine doped polymer films (BEDO-TTF) was successfully prepared by electrochemical method of cyclic voltammetry. The formation of the transparent films has been linked to the reduction of the iodine species in the film to iodide species giving rise to colorless films. Furthermore, Raman studies have revealed the presence of different iodide species like triiodide, pentaiodide and iodine when anodic and cathodic potentials were applied to the films. Also, it was seen that the iodine was complexed with the BEDO-TTF polymer in a stoichiometry of 2.4: 3 [(BEDO-TTF)$_{2.4}$I$_3$] at certain concentration in the doping technique. Raman studies were also conducted on single walled carbon nanotubes (SWCNTs) to study the defects introduced during the ball milling procedure and Ru doping. The Raman results reveal that both ball milling procedure and Ru doping leads
to the formation of more defects and carbonaceous species in the SWCNTs. Thus, both electrochemical and Raman method were demonstrated to characterize the composition and properties of various materials including conducting polymer and carbon nanotubes.
Chapter 1. Pt-Modified Au Surface as the Potential Catalyst for Fuel Cells

1.1 Introduction to Formic acid and Methanol Fuel cells.

In the world today, the need for endurable and clean energy reserve has become our driving thrust in the current economic conditions. The awareness about the influence of green-house gases effect (global warming) and all the other harmful emissions from the fuels have raised worldwide concern about the abundant use of fossil fuels for electricity production and running vehicles in the last decade. Fuel cells being a relatively clean energy source have lured much interest. Fuel cells offer the advantages of high energy density, high efficiency conversion (since no combustion process is involved) and less noise pollution.[1] Although batteries, which are a good alternative, give us zero emission, they also suffer from environmental and engineering problems and the total working potential before it needs to be recharged is quite low.[1] So while batteries provide a short-term alternative, fuel cells constitute a better long-term option. A fuel cell is an electrochemical device that converts chemical energy obtained from fuel and oxidant externally into electrical energy. Fuel cells generate electricity directly from fuel and do not store them. Thus they have a number of advantages over batteries such as easily rechargeable and extended operating times. The major advantage is they are environment friendly. [2]
There are different types of fuel cells, which are classified mainly by the type of electrolyte employed in the cell like polymer electrolyte membrane fuel cell, alkaline fuel cells, phosphoric acid fuel cell, molten carbonate fuel cell and solid oxide fuel cell.[3] Though attractive, in principle the fuel cell has to overcome a number of problems before it can be really affordable. For example, it should be able to start immediately and must be able to meet the power requirements in the limited space of a particular vehicle. Since Solid oxide fuel cells and molten carbonate fuel cells operate at higher temperatures, they are not competent enough. Thus the proton exchange membrane cells (PEM) seem to have a great potential to be used as a substitute in vehicles and other applications[4, 5] As described earlier, the PEM cells employ a proton conducting membrane polymer as the electrolyte. Nafion is the most widely employed electrolyte in PEMs. It consists of poly-(tetrafluoroethylene) based (PTFE) backbone with sulphate ions which are involved in the transport of $\text{H}^+$. Other membranes such as Dow, Aciplex, Gore, and Asahi chemical are also used in the PEM fuel cells.[3] In a hydrogen fuel cell, the hydrogen gas is oxidized at the anode to protons which generates electrons. The electrons travel and carry out external work and return back to the circuit. In the mean time, the protons pass through this membrane and combine with the used electrons to reduce oxygen at the cathode and give water. Both the reactions at the anode and cathode take place on the respective catalyst layer. Thus, the catalyst layer plays a very important role in the operation of fuel cells. Most of the current PEMFC fueled vehicles employ hydrogen as the fuel source. But they suffer from handling and storage problems as well as weight and space limitations. Small organic molecules (SOM) such as formic acid, methanol, ethanol and formaldehyde have drawn attention for use as
possible fuels in direct small organic fuel cells.[5-7] There are basically three types of application of SOM fuel cells.[2]

a) Stationary applications where the electricity is directly generated from the fuel. They can be employed for commercial, residential and industrial applications.

b) Transportation applications since the fuel in the fuel cells like methanol fuel cells and formic acid fuel cells can be easily stored and handled. Moreover they do not require any humidification or reformer system but only a compact space in the vehicle.

c) Portable Applications such as laptop computers, cell phones and electronic game applications. The low operating temperature offers an added advantage for its portability. In micro fuel cells, the minimized size and reduced weight is a great advantage for its applications to portable electronic devices. [8] For example BASF and Tekion are developing an commercial direct formic acid cell by the trade name Formira (http://www.tekion.com; http://www.basf.de/en/intermed/products/formic_acid/tekion).

This formira power pack claims to have a power up to 50 W and gives energy up to about 100 Wh.[9]

1.1.1 Methanol as the fuel

Methanol fuel cells are a sub category of the PEM cells, where the fuel is methanol. Methanol has lured interest because of its higher energy density. The direct methanol fuel cells (DMFC) have opened a panoramic view in the current field of fuel cells, especially for portable appliances since they do not require a separate system for generation of hydrogen, thus offering a prospective for compact systems in the power
range of watts to kilowatts. Moreover, methanol is a safe, inexpensive and widely available fuel, has low operating temperatures, and can be handled and distributed to the consumer very easily. However, these fuel cells although environment friendly are not fully free of emissions. They produce the green-house gas, carbondioxide (CO₂). On the other hand, hydrogen as fuel also produces CO₂ during the reforming step in the gas shift reaction. The important point is if generated from biomass the CO₂ formed can be balanced with that used up for photosynthesis.[2]

A schematic representation of DMFC is given in figure 1.

![Figure 1.1](image1.png)

**Figure 1.1.** A DMFC employing an acidic solid polymer electrolyte such as Du Point’s “Nafion” and finely dispersed platinum electro catalyst supported on porous carbon electrodes. The figure is reproduced from reference [4]

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Equation</th>
<th>Energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode Reaction</td>
<td>CH₃OH + H₂O → CO₂⁺ 6H⁺ +6e⁻</td>
<td>E_{anode} = 0.046V</td>
</tr>
<tr>
<td>Cathode Reaction</td>
<td>3/2O₂ + 6H⁺ + 6e⁻ → 3H₂O</td>
<td>E_{cathode} = 1.23V</td>
</tr>
<tr>
<td>Overall Cell Reaction</td>
<td>CH₃OH+3/2O₂ → CO₂+2H₂O</td>
<td>E_{cell} = 1.18V</td>
</tr>
</tbody>
</table>
1. Methanol is oxidized at the anode where carbon dioxide, protons and electrons are released.

2. The proton passes through the membrane to the cathode

3. The electron passes through the external circuit where it does the work

4. The used electron and the proton combine with the reduced oxygen to form water.

The DMFCs suffer from a major problem of methanol cross over. Methanol has similar characteristics, like dipole moment, which causes it to be carried to the cathode due to electro osmotic drag. It leads to a mixed potential oxidation resulting in the decreased cell performance. Some developments like Cesium doped nafion membrane helps to reduce the methanol permeability through the membrane. Also the design of a catalyst that would permit the use of lower concentrations of methanol may also help to alleviate this problem to large extent.[10] Furthermore, there are various intermediates formed during the methanol electrooxidation that tend to get adsorbed onto the catalyst surface thus slow down the electrooxidation kinetics. Principal by products in methanol electrooxidation are formaldehyde, formic acid and carbon monoxide. The goal is that the methanol is oxidized to carbon dioxide through these intermediates. However due to the poisoning of the catalyst surface by those by products, this process is hindered. The vital challenge is to develop new electrocatalysts that can augment the rate of the reaction without the formation of poisoning intermediates.[2]

1.1.2 Formic acid as the fuel

The potential danger for storage and transport and the fuel crossover problems with methanol resulted in research for other fuels as substitutes in fuel cell systems. Formic
acid has a higher EMF and excellent electro catalytic oxidation activity in comparison to methanol and hydrogen PEMFCs. [6]

Formic acid fuel cells (FAFC) are a sub category of PEM cells, where the fuel is formic acid. Although its energy density is generally lower than methanol, formic acid has a higher power density than methanol because the fuel crossover rate is lower as compared to methanol and also because of its faster oxidation kinetics at the anode. The lower fuel cross over rate is attributed to the repulsion between the formate ions (dissociated form of formic acid) and Nafion at the anode catalysts. Formic acid possesses a number of other advantages too:

1. It is liquid at room temperature and a strong electrolyte.
2. It is approved by the US FDA as a food additive.
3. Its storage and transport is safer than hydrogen.
4. It is readily available as insects and bacteria produce it naturally.

Reaction at FAFC:

Anode: \( \text{HCOOH} \rightarrow \text{CO}_2 + 2 \text{H}^+ + 2 \text{e}^- \quad \text{E}_{\text{anode}} = -0.25 \text{ V (vs. SHE)} \)

Cathode: \( \frac{1}{2} \text{O}_2 + 2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2\text{O} \quad \text{E}_{\text{cathode}} = 1.23 \text{ V (vs. SHE)} \)

Net reaction: \( \text{HCOOH} + \frac{1}{2} \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{E}_{\text{cell}} = 1.48 \text{ V (vs. SHE)} \).

1.2 Need for better anode catalysts in SOM fuel cells

Since most of the reactions of the fuel cells take place on catalysts, they constitute a very important area of fuel cell technology research and development.
The electrode kinetics at the cathode and anode are quite slow and the chemical reactions are more complex than they appear. The oxygen reduction or the formic acid or methanol oxidation takes place through a number of intermediates before the final product of carbon dioxide or water is formed. Hence, there is the need for development of an effective catalyst that will help in the electro oxidation/reduction process, as well as avoid any undesirable intermediates to be formed.

On a metal catalyst surface, the oxidation of formic acid proceeds via the two pathways: the direct pathway or the indirect pathway through the formation of weakly adsorbed intermediates. The direct pathway is also called the dehydrogenation pathway as shown in equation (1-1) which directly produces CO$_2$ as the product. The indirect pathway is the dehydration pathway as detailed in Eqn (1-2-4) with the formation of CO$_{ads}$ as a reactive intermediate at high potentials or a poison at low potentials.[11-14]

$$\text{HCOOH} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \quad (1-1)$$
$$\text{HCOOH} + \text{Pt}^0 \rightarrow \text{CO-Pt} + \text{H}_2\text{O} \quad (1-2)$$
$$\text{Pt}^0 + \text{H}_2\text{O} \rightarrow \text{Pt-OH} + \text{H}^+ + \text{e}^- \quad (1-3)$$
$$\text{Pt-CO} + \text{Pt-OH} \rightarrow 2\text{Pt}^0 + \text{CO}_2 + \text{H}^+ + \text{e}^- \quad (1-4)$$

Recently, the formation of bridge bonded formate has also been suggested to be the third pathway for formic acid oxidation. The following figure illustrates the different pathways for formic acid oxidation reproduced from reference 9.[9]
In the last few years, a number of preliminary studies have been carried out in half cell configuration to figure out the optimal composition of electro catalysts. In general, it is believed that most of these oxidation reactions require the presence of a platinum-based catalyst. Thus; the goal is to design a stable, less expensive and durable catalyst.

1.2.1 Current catalysts

Much research has aimed to study the electro oxidation of formic acid and methanol on Pt catalyst. Platinum possesses a number of advantages:

- It is the best active catalyst at low temperatures among all catalytic materials.
- It has the exceptional ability to maintain high kinetic rates of reaction at normal temperatures.

Figure 1.2. The Scheme of formic acid electrooxidation pathways reproduced from reference 9 by Compton et al [9]
• It is highly noble and thus resistant to corrosion even in concentrated solutions at ambient temperatures.
• It is able to directly oxidize saturated aliphatic hydrocarbons at lower temperatures. The innate ability of rhodium, iridium and platinum can take up hydrocarbons dissociatively.

However, a platinum catalyst suffer from the drawback of being very expensive, and also suffers from the problem of the formation of CO poison that becomes irreversibly adsorbed onto the catalyst, thus reducing fuel cell performance. For these reasons, the use of bimetallic catalysts has been under development.

There have been a number of studies focusing on alternative platinum-based catalysts in the last decade. Different combinations of bimetallic catalysts were explored by Pickup and coworkers, including Pt/Ru, Pt/Pd, Pt/Bi, Pt/Sb, Pt/Sn, Pt/Au and Pt/Pb, as potential anode catalysts in direct formic acid fuel cells (DFAFCs).[7, 9, 11, 12, 16-18] An overview of the different catalysts used in DFAFC’s has been reviewed by Compton et al [9]. The inclusion of a second metal not only reduces the consumption of platinum materials, but also enhances the activities of these catalysts. It tends to interrupt the large Pt surface to favor the dehydrogenation path; known as the third-body or the ensemble effect.[19] This is due to the fact that the dehydration path requires at least three adjacent Pt atoms while dehydrogenation needs at most two consecutive Pt atoms, thus reducing the available adsorption sites for CO.[20] Also, the presence of the second metal might affect the electronic structure of Pt known as electronic effect or induce formation of oxygen containing species at low potentials that result in the oxidative removal of CO$_{ads}$ known as the bifunctional effect.[19, 21]
Currently formic acid fuel cells use a palladium as catalyst.[27] However they suffer from the problem of low stability and acid dissolution. Furthermore there is formation of unknown intermediates that reduce the performance of the cell.[9]

### 1.2.2 Pt/Au catalysts

In this study, we have employed platinum-modified Au catalyst for its use as an anode catalyst in formic acid fuel cell. According to Choi and coworkers, the Pt/Au catalyst exhibited not only remarkably high oxidation currents and increased power density compared to Pt/Ru catalysts, but also prolonged durability.[24] It was also suggested by other authors that Au has inherent catalytic activity leading to the increased
enhancements. Furthermore, the use of Au as the second metal offers an additional critical advantage. It is oxidized at 1.2 V vs. RHE, a potential much higher when compared to other metals like Fe, Sb, Ti, and Bi. The consequence of surface oxidation at lower potentials in these metals is that it leads to material dissolution during the functioning of DFAFCs.

1.2.3 Deposition Methods

There are many ways to deposit platinum onto gold given in various literatures. Uosaki et al. described the layer by layer deposition of platinum on Au(111) from hexachloroplatinic acid. Waibel et al. have studied the initial stages of platinum deposition onto Au (100) and Au (111) from the observed difference in behavior when deposition is carried from [PtCl₄]²⁻ and [PtCl₆]²⁻. Friedrich et al. described how platinum deposits are first formed on defects on Au (111). Brankovic et al. deposited sub monolayer amount of Pt by replacing Cu-UPD (under potential deposition) on Au (111). Pt deposition can also be performed by electrochemical quartz crystal microbalance (EQCM).

There are different approaches for depositing a sub monolayer of platinum like spontaneous deposition method. The different approaches for preparing a bimetallic catalyst by deposition of a sub monolayer or multilayers of platinum through spontaneous deposition method have been summarized by Strbac and coworkers. Kim et al. have obtained Pt deposits by dipping in aqueous solution of 40 µM H₂PtCl₆ and 0.05 M H₂SO₄ for an appropriate amount of time. According to Tong et al., an Au electrode was first reduced by holding the potential at -0.25 V for about 10
min before spontaneous deposition of platinum by immersion in 0.5 mM deaerated
H$_2$PtCl$_6$ solution for about 5 s. Nagahara et al.[37] suggested the spontaneous
deposition of Pt on Au (111) from 50 μM Pt complex from all haloplatinate complexes
(K$_2$PtCl$_4$, K$_2$PtBr$_4$, and K$_2$PtI$_6$) in 0.1 M perchloric acid electrolyte. In the current work we
have employed the spontaneous deposition method following the work of Nagahara and
coworkers.[37] The activities of this spontaneously deposited Pt/Au catalyst was
examined toward formic acid electrooxidation. Then, in situ SERS was employed real
time during formic acid oxidation on Pt (Au) catalyst for elucidation of the intermediates
and nature of the chemisorbate-surface bonding at the metal surfaces.

1.3. Methods of Characterization

1.3.1 Electrochemical measurement Techniques[38]

Since a fuel cell is an electrochemical device, electrochemical techniques play a
pioneering role in the evaluation and characterization of the different fuel cell
components like the electrode, membrane, and catalyst. The most prevalent
electrochemical analytical techniques are potential step, cyclic voltammetry, rotating
disk electrode experiments and impedance measurements. An electrochemical reaction
involves the following steps:

- Transfer of reactants to the electrode surface,
- Reactants adsorption,
- Heterogeneous electron transfer between analyte molecules adjacent to the
electrode and surface of the electrode,
- Charge transfer due to oxidation/ reduction reactions on the surface,
Transfer of the products from the electrode to the solution.  

The purpose of electrochemical techniques is to elaborate these steps.

1.3.1.1 Cyclic Voltammetry

It refers to cycling the working potentials between low and high limits and recording the current in the mean time. [38, 39] The resulting potential versus current plot is called a voltammogram. The potential is usually swept linearly with time. If the reaction is reversible, the potential difference of the anodic or cathodic peaks equals 56.9/n mV and the peak height is proportional to square root of scan rate. Thus, qualitative information about the electrochemical processes in various conditions can be obtained. The peak currents in CV are directly proportional to analyte concentration. Electrochemically active intermediates formed during the process might exhibit characteristic peaks which help us to understand the reaction mechanism of the elementary oxidation/reduction steps. Quantitative information is obtained from Eqn. 1-5:

\[ i = (2.687 \times 10^5) n^{3/2} u^{1/2} D^{1/2} A C \]  

Equation 1-5

In this equation, \( n \) is the number of electrons appearing in half-reaction for the redox couple, \( u \) is the scan rate at which the potential is swept (V/sec), \( F \) is Faraday's constant (96485 C/mol), \( A \) is the electrode area (cm\(^2\)), \( C \) is the concentration of the analyte, and \( D \) is the analyte's diffusion coefficient (cm\(^2\)/sec) in the solution.
1.3.1.2 Potential Step method

Instead of cycling the potential, the potential can be changed from one value at which the potential is too low to cause a reaction to another level where the potential is high or low enough so that the reaction occurs at high rate and is controlled by mass transport rate. [38] The corresponding current versus time is analyzed and is known as chronoamperometry. The current is given by Cottrell equation, Eqn. 1-6:

\[ i = nFAC^O(D)^{1/2}\pi^{-1/2}t^{-1/2}, \]  

Equation 1-6

where \( i \) = current, in unit A

- \( n \) = number of electrons in the half cell reaction
- \( F \) = Faraday's constant, 96,500 coulombs/mole
- \( A \) = area of the (planar) electrode, \( \text{cm}^2 \)
- \( c^O \) = initial concentration of the analyte with units \( \text{mol/L} \)
- \( D \) = Diffusion coefficient for the analyte in units \( \text{cm}^2/\text{s} \)
- \( t \) = time, \( \text{s} \)

Potential step experiments are typically carried out for the duration of a few minutes. This is due to the following reasons:

- Diffusion zone depletes very fast and leads to over potential in the double layer.
- With longer time, problems due to convection and density gradients may arise.

Although charging currents may exist because of the short duration of the experiment, it can be nullified by subtracting the background current from the current obtained for the
active species. By integrating the current with time, we can obtain the charge due the electrochemical reaction.

1.3.1.3 Rotating Disc Electrode

In stagnant electrolyte, diffusion is the major process for the transfer of the analyte to the electrode. However, when a forced convection is introduced into the system by RDE, [38, 40] the mass transport is significantly increased. Convection is achieved by creating relative motion of the electrode by rotating the electrode. Thus, both diffusion and convection determine the mass transport of the analyte to the electrode surface. When the disk electrode is rotated rapidly the liquid flows rapidly from the center of the device which produces an axial flow replenishing the displaced liquid. This leads to the Levich equation:

\[ i = (0.620) n F A D^{2/3} v^{1/2} w^{-1/6} C, \text{ where} \]

where \( i \) is the current in A,

\( n \) is the number of electrons transferred in the half reaction

\( F \) is the Faraday's constant, 96,500 coulombs/mole

\( A \) is the electrode area in units/ cm\(^2\)

\( D \) is the diffusion coefficient in units cm\(^2\)/s

\( w \) is the angular rotation rate of the electrode in radians/sec

\( v \) is the kinematic velocity in cm\(^2\)/sec

\( C \) is the analyte concentration

Thus, the kinetics and the electrochemical reaction mechanisms can be studied.
Along with using the potential step method in some initial experiments, most of the work in this thesis involves the use of the cyclic voltammetry method. Reaction kinetics using the RDE is not carried out here since there are a plethora of studies using this technique already.

1.3.2. Spectroscopic and microscopic Methods

1.3.2.1 X-ray Photoelectron Spectroscopy (XPS)

It is a surface sensitive technique that helps to measure the elemental composition along with the chemical state of the elements at the surface of a material. [41, 42] When a sample is irradiated with X-rays, the number of electrons that escape from the surface of material along with their kinetic energy were measured. Usually in an XPS spectrum, the number of electrons is plotted against the binding energy of the electrons. The peaks obtained in the spectra can be related to the electronic configuration of the atoms.

1.3.2.2 Scanning Electron Microscopy (SEM) / Energy dispersive Spectrometer (EDS)

The SEM column comprises of an electron gun, two condenser lens, an electron detection system and a set of deflectors in vacuum. [43] The electrons are produced from the electron gun. They are accelerated to energies of 1 – 30 KeV. The deflection system then scans the electron probe in a raster like fashion on the specimen and this operates together with the computer display or the cathode ray tube. Electron detectors then detect the various signals. When the beam interacts with sample, various types of signals are generated like secondary electrons, backscattered electrons, X-rays,
transmitted electrons and absorbed electrons. The secondary electrons are low in energy and have energies less than 50 eV. Most of them are between 0.5 to 5 eV range. Back scattered electrons lie in the range around 50 eV. When the primary beams interactions with the specimen generates photons in the X-ray range this permits for the identification of elements present through the technique Energy dispersive Spectrometer (EDS). EDS is usually a standard attachment to any SEM.

1.3.2.3 Transmission electron microscope (TEM)

The transmission electron microscope (TEM) is an important tool in for characterizing the microstructural details of materials. [44, 45] When the electron beam is focused on the sample, the diffraction patterns can be studied. The intensity of electrons diffracted across a specimen can help to study defects, dislocations based on the diffraction contrast. Also, the intensity of the diffracted beam in high resolution known as HRTEM or high resolution TEM can be measured. The phase of the diffracted wave interferes constructively or destructively with the phase of the transmitted wave thus giving images of columns of atoms. Other than these phenomena, the high energy electrons can also give rise to electronic excitations in the atom. The electrons are emitted by a thermionic, Schottky, or field emission electron gun. The variation of illumination on the sample is controlled with the help of three or four stage condenser lens. The intensity distribution of the electrons behind the sample is images using about 3 - 8 lenses onto a fluorescent screen. The image is captured via a fluorescent screen coupled with a fiber optic plate to a CCD camera.
1.3.3 Raman Spectroscopic Methods

1.3.3.1 General Introduction for optical spectroscopic method

Many of the tools in analytical chemistry have been well used to study the electrochemistry in fuel cells like in situ FTIR (Fourier transform infrared spectroscopy), ellipsometry, differential electrochemical mass spectrometry (DEMS), infrared reflection-absorption (IRAS), sum frequency generation (SFG) and Electron Energy Loss Spectroscopy (EELS).

FTIR gives information about the surface groups and the intermediates/adsorbates on the catalyst surface.\[46]\ Thus it provides vibrational information about the analyte. However it cannot be used for aqueous samples because water absorbs IR light strongly thus affecting the resulting IR spectrum. Other methods like X-ray diffraction (XRD) and X-ray photo electron spectroscopy (XPS) employ X-ray radiation for characterizing the catalysts.\[46]\ Energy dispersive X-ray spectroscopy can also be employed to study the catalyst surfaces. \[47]\ It helps to characterize the sample due to the interaction of focused beam of electrons like X rays and sample. It gives a qualitative measurement of the elements present in the sample in case of the Au and Pt measurements, since the characteristic X rays of Au and Pt are very similar in energy values. The widely used method TEM (transmission electron microscope) helps to provide information about surface area, shape and particle size of metal crystals. However it is operated in vacuum conditions and it is difficult to distinguish certain metals like Au and Pt since the distance between the atomic lines are similar for these atoms. Scanning tunneling microscope (STM) along with electrochemical methods like
voltammetry has served to be invaluable to study the surface chemistry. [35, 37] Information has been obtained about the composition, crystallite size, oxidation state of the species and interaction of the catalyst with substrate.[46, 48] However, STM can only be applied on highly smooth or single crystalline surface. Many vibrational spectroscopy techniques have been employed to characterize the surface chemical bonding, such as Infrared Reflection- Absorption Spectroscopy (IRAS), Sum Frequency Generation (SFG), and Electron Energy Loss Spectroscopy (EELS). While the IRAS and SFG suffer from the limitation of the vibrational modes not within their available frequency range, EELS is limited to UHV interfaces.[49, 50]

1.3.3.2 Normal Raman Spectroscopy
The phenomenon of Raman scattering was first described by Raman & Krishnan in 1928. When electromagnetic radiation interacts with the molecule, most of the times it is scattered since the incoming radiation does not match any molecular transition. This elastic scattering is known as Rayleigh scattering. When the scattered radiation is of a lower frequency than the excited radiation it is called Stokes scattering. When the scattered radiation is of a higher frequency than the source radiation it is antistokes scattering (See Figure below). In the Raman spectra, the abscissa depicts the wavenumber shift ie. the difference in the wavenumbers (cm\(^{-1}\)) between the observed and the source radiation. The magnitude of Raman shift is independent of the wavelength of light used.
Although IR and Raman are dependant on similar vibrational modes they arise from different processes. Infrared absorption requires a change in dipole moment however scattering involves momentary distortion of the electrons distributed around the bond in a molecule followed by remission of radiation as the bond returns to its normal state. Thus this distortion results in molecule becoming polarized and developing an temporary induced dipole which disappears upon relaxation and remission. The Raman technique is superior over IR since we can use water as solvent and the vibrational energies in the range of 100-700 cm\(^{-1}\) can be easily studied. [51]

1.3.3.3 Surface-enhanced Raman Spectroscopy

1.3.3.3.1 Introduction and History

Surface enhanced Raman spectroscopy (SERS) has become a versatile technique for understanding the adsorbates/intermediates formed in electrochemical environments for
its unique properties.[52-55] SERS is a phenomenon in which the intensity of Raman scattering from molecules close to certain metal surface is enhanced by a factor of $10^6$. The low sensitivity from normal Raman has resulted in widespread application of SERS.

The main reason for enhancement is electromagnetic enhancement (EM) which is due to generation of localized surface plasmon (collective electron oscillations) at rough metal surfaces by laser excitation. There is a field enhancement, which is influenced by both the incident and scattered light and thus results in the enhancement of the Raman signal. The EM depends on the optical property of the substrate (the metal), the surface morphology and the excitation wavelength of the laser.[56] On the other hand, chemical enhancement mechanism like the charge transfer mechanism also helps in the SERS enhancements when adsorbed molecules with certain acceptor or donor orbitals interact with metal substrate and the coupling effect between the adsorbed molecules and electron-hole pair.[56] [57] Thus SERS is a vital technique that exhibits interfacial selectivity and sensitivity. Van Duyne and Jeannaire first reported the large enhancements in the Raman cross section of the species located on noble metal surfaces.[58]

Surface-enhanced Raman spectroscopy (SERS) is a versatile as well as sensitive means of obtaining adsorbate vibrational spectra at catalytic, especially Au, Ag or Cu, surfaces in an electrochemical environment. The large surface enhancements, which are distinctive of SERS, give information of the vibrational state of the different molecules adsorbed on the surface over a wide frequency range. Mainly, the noble metals like silver and gold have a very strong Raman signal enhancement up to 6
orders of magnitude. Moreover, the excitation wavelengths are not dependent upon the adsorbed molecule but on the substrate, thus allowing the use of a single wavelength for the detection of multiple species. The main advantages of SERS with respect to surface infrared spectroscopy is the ability to run in aqueous sample conditions and the adeptness to obtain exquisite spectral information even down to 100-700 cm\(^{-1}\), the region where the interaction between the surface and the adsorbates are situated. The major advantage in comparison with fluorescence technique is that there will be no photo bleaching, a major drawback of the fluorescence technique. Also, certain excitations in Raman are in the near infrared region, which reduce the interference from fluorescence background from biological materials (laser wavelength 785 nm is closer to infrared region). [52] Of particular interest is the presence of charge coupled device (CCD) detectors that enabled real time SER spectrum acquisition during the voltammetric and electrochemical reactions, thus explaining complicated electrode processes. When applied in combination with electrochemical methods, SERS can provide a very good understanding of the surface processes, which is very important in the field of electro catalysis.

1.3.3.2.2 Electrochemical SERS (EC-SERS):

SERS also helps to obtain intramolecular adsorbate vibrational modes in electrochemical environment.[54] Upto mid 1970’s the biggest obstacle to the development of the EC-SERS was to obtain SERS on transition metals, since it was believed that the transition metals are not SERS active. In the next few decades, researchers have developed various methods to meet this challenge. Weaver etal. and
Fleischmann et al. developed the method in which we deposit ultrathin transition metal layer on SERS active surface. With the help of the electromagnetic enhancement, SERS spectra were obtained of adsorbates on a number of transition metals.[59] It is well known that in order to obtain significant surface enhancement the surface needs to be roughened. There are five SERS activation methods for obtaining Au, Ag and Cu surfaces. These are current and potential controlled ORC, template synthesis, electrodeposition and chemical etching.[59] Figure 1-4 shows the SERS signal obtained from 1 mM pyridine on roughened Au surface. The peaks are due to the ring stretching of pyridine.

![Figure 1.5. Normal Raman and SERS (on roughened Au electrode) spectra of 1 mM pyridine in 0.1 M KCl.](image)

The EC-SERS usually comprises of the electrode with nanocatalyst and the electrolyte. EC-SERS has been employed to identification of target molecules with good sensitivity and selectivity and for characterization in terms of evaluating the contributions from the enhancement mechanisms. It has been also used to provide important information
regarding adsorbates at the surface and the to decipher reaction mechanisms in electrochemical systems.[56] Both the chemical and electromagnetic enhancements are affected to some extent by the change in electrode potential. Thus as the potential is changed it will result in the change of the adsorption orientation of the molecule or coverage both of these will lead to change in SERS intensity. There are other factors like the photo-driven charge transfer mechanism and the change in the bonding strength between the molecule and the surface which can affect the SERS intensity with change in potential.[56] By changing the potential, the surface density of the metal electrodes can be tuned. When a positive potential is applied there is red shift in the plasmon resonance band. However, application of a negative potential results in the increase and blue shift of the plasmon resonance band.[56] Many different systems have been investigated by EC-SERS as outlined in reference [56].

According to Koper et al [25], further density functional theory (DFT) calculations can be performed too with SERS, which helps to assess the relative stability, nature of surface bond and the geometry of the intermediates formed in the electro oxidation process.
Chapter 2. Experiments and Methods

2.1 Chemicals and Materials

Analytical grade formic acid (85 % w/w), perchloric acid (70 % w/w) and KCl (Fisher Scientific) solutions were prepared from doubly distilled water (18.2 MΩ·cm) obtained from a Cascada BIO and AN Lab Water System. Potassium tetrabromoplatinate (II) (99 %), dihydrogen hexachloroplatinate (IV) (99.9 %) and Potassium hexaiodoplatinate (IV) (99.9 %) were purchased from Alfa Aesar. Potassium iodide (Sigma Aldrich), Potassium bromide (Sigma Aldrich) were used in 0.1 M concentration in water.

2.2 Acid cleaning of the glassware

All the glassware used for experiments were acid washed. Firstly they were kept in solution of about 10 M sulphuric acid for 4 hours. Then, they were removed from acid solution and rinsed with lots of deionized water. While washing, it is recommended to add sodium bicarbonate to neutralize any acid remains in the sink before it goes to the drain. Further the glassware is dipped into a solution of 8 M nitric acid for 2 hours. Later the glassware are washed with boiling water to remove any remains of acid and left for drying before use. Again we add sodium bicarbonate to neutralize any acid remains in the sink before it goes to the drain.
2.3 Electrochemical techniques

For all electrochemical experiments, the working electrode was a gold rod (3 mm and 4 mm) sheathed in Teflon (Goodfellow Cambridge Ltd.) or a 2 mm polycrystalline disc platinum electrode (CH instruments). The electrical contact of the working electrode was established with the help of a copper wire with 3 mm diameter at the back of the polycrystalline gold. The Teflon insulated electrode was polished with 1.0, 0.3 and 0.05 micron alumina powder (EMS Technologies) consecutively on a microcloth (Buehler), with intermittent sonication of 5 minutes. The reference electrode was an Ag/AgCl electrode (BASi) and a platinum wire was used as the counter electrode (CH instruments). A CH760 electrochemistry workstation (CH Instrument, TX, USA) was used for the measurements. An in-house made electrochemical cell was used to hold the electrodes. High purity nitrogen was bubbled into the electrolyte solutions for 5 minutes before experiments and all experiments were carried out in a nitrogen atmosphere.

2.3.1 Preparation of an Ag/AgCl reference electrode

The Ag/AgCl reference electrode can be made in the lab using the following procedure. An Ag wire of 6 cm in length was cleaned with a reagent of alcohol and attached to a Copper metal piece by epoxy (Epoxy Inc.). The Cu metal needs to heated/oxidized and rubbed and cleaned on sand paper before attaching it to the Ag wire. Then the Ag wire is chloridised in a solution of 0.1 M HCl containing 1 M KCl. (Ag wire is the working electrode, Ag/AgCl as the reference electrode and platinum as the counter electrode). An amperometric It curve program is used through the EC software at 1 V with highest
sensitivity of $10^{-1}$ for 10 minutes. If two or three silver wires are chloridized at the same time, they should be kept away from each other as they tend to stick to each other. The chloridised Ag wire is put into the glass body of with the vycor frit heat sealed (using a heat gun) at the end. A saturated solution of KCl is added into the glass body and sealed at the end. Now the potential of the prepared electrode is measured with respect to a commercially available electrode occasionally to check the potentials.

2.3.2 Preparation of Pt-modified Au electrode using spontaneous deposition

Platinum was deposited on polycrystalline gold electrode (Au (poly) by the spontaneous deposition procedure. In this method, after polishing, the Au (poly) disc was dipped in a 0.5 mM hexachloroplatinate, tetrabromoplatinate or hexaiodoplatinate solutions for 15, 5 and 30 minutes, respectively. These deposition times were chosen since they give the highest formic acid oxidation currents. The electrode was rinsed with water, followed by a cathodic scan to deposit the platinum in the solution of 0.125 M HClO$_4$.

After preparation of the Au (poly) by previously described polishing procedure, the disk was dipped in different concentrations of potassium tetrabromoplatinate (II) (99 %), dihydrogen hexachloroplatinate (IV) (99.9 %) and potassium hexaiodoplatinate (IV) (99.9 %, Alfa Aesar) in 0.125 M HClO$_4$ for the appropriate amount of time. After cleaning with deionized water, platinum was deposited spontaneously by a cyclic voltammetric cathodic scan immediately in 0.125 M HClO$_4$. The deposited platinum was removed easily from the gold surface by successive polishing with 1, 0.3 and 0.05 micro alumina for 5 minutes each with intermittent sonication, allowing the polished Au surface to be reused for further measurements.
2.3.3 Electrochemical measurement of BEDO-TTF/I film

The doping of the BEDO-TTF/I films with two different concentrations of iodine of 0.063 mol/L and 0.033 mol/L respectively was performed using procedures as given in the paper.[60] This iodine doped film was used as the working electrode. Ag/AgCl was employed as the reference electrode (BAsi Inc.) along with platinum wire (CHI, TX, USA) as the counter electrode. An in-house electrochemical glass cell was used to hold the working, reference and counter electrodes together. Electrochemical measurements were performed with a CHI800 electrochemistry workstation (CHI, TX, USA).

2.3.4 Cyclic Voltammetry

Most of the CV voltammograms were performed between -0.4 V and 1.4 V except for the experiments with platinum where in lower potentials were maintained in order to avoid the oxidation of platinum on the surface. A scan rate of 50 mV/s was used along with sensitivity of $10^{-3}$.

2.3.5 Commonly encountered mistakes during electrochemical measurements

If overflow of the current is observed, a standard solution of 10 mM potassium ferricyanide in 0.5 M sodium sulphate needs to be prepared to check the performance of the system with the common-know stable standard. The inhouse Ag/AgCl reference electrode’s potential was checked with the commercially bought reference electrode for any potential shift. If any change in potential was observed the experimental observations were corrected for that change accordingly. Otherwise the resistance was
measured between the reference electrodes to make sure current is flowing in the system.

### 2.4 Spectroscopic and Microscopic Measurements

All the Raman experiments on the BEDO-TTF/I films were carried out using a Confocal Raman microscope (Olympus, IX71) purchased from Horiba Jovin Yvon, equipped with Argon and Krypton laser (Coherent, Innova 70C series) producing 514 nm or 647 nm of wavelength. If the excitation wavelength at 514 nm from argon and Krypton laser was applied, a power of 30 mW, 5 s of exposure time and 1 accumulation was used. The spectrograph grating was 300 grooves/mm and the 20X objective was used throughout the experiments. Spectra were obtained between 200 and 3000 cm\(^{-1}\). Before taking the Raman spectrum the sample position was adjusted with white light then the laser light was turned on to the sample.

#### 2.4.1 Normal Raman

Each time, Raman was obtained at different spots around the sample to confirm for the uniformity of the sample. Also, the z-axis was adjusted to obtain the best intensity of the peaks. For example, for BEDO/TTF I samples, a z axis distance of about negative 100 from the base (0 axis) was seen to give the highest intensity of the Raman peaks. If the used sample was in liquid form then firstly the normal Raman was obtained at 0 axis then the z axis was moved forward and backward to check for the best position which gives the highest intensity of the peaks. Also the accumulation time and exposure times were changed to obtain the best spectrum. As far as the power of the laser goes the
optimal setting were for 514 nm laser a power of 13.2 mA and for 647 nm, a power of 35 mW with the current being 17.2 mA.

2.4.2 Surface enhanced Raman spectroscopy (SERS)

All the SERS experiments in this thesis, a laser of 647 nm wavelength was employed. The laser power delivered to the sample was 35 mW. A 600 grooves/mm grating and a 20X objective was used. The sample position was adjusted with white light before the laser was applied to the sample. It was seen that for the EC-SERS experiments, the best z position giving the best SERS intensity was that of 105 from the base.

2.4.2.1 Preparation of SERS active Au surface

SERS has to be studied on roughened electrode surfaces. Although there are a number of procedures for roughening the electrode, the method employed here was obtained from Stolberg et al. [61] This approach as shown in Figure 2-1, involves many oxidation and reduction cycles, which are carried out in 0.1 M KCl solution. Prior to the first cycle, the freshly polished gold electrode is cathodically cleansed at a potential of -1.4 V (vs. Ag/AgCl) for 600 seconds. Then, the potential is increased to -0.3 V for 120 seconds so that the hydrogen bubbles generated in the cathodic cleaning are removed. Then the oxidation reduction cycle is followed as depicted in figure below. The potential is swept between -0.3 V to 1.2 V at scan rate of 1.0V/s. Further potential is held at +1.2 V for 1.3 seconds. The direction of sweep is reversed and potential is swept between 1.2 V to -0.3 V at scan rate of 0.5 V/s. This ORC cycle was carried out for optimum number of cycles.
A number of literatures suggest that 15 ORCs give the maximum enhancement while others suggest about 20-25 ORCs for obtaining the highest SERS enhancement as compared to normal Raman. [61, 62] However, in this study, an experiment was carried out in order to determine the maximum number of ORCs needed to obtain the highest enhancement by SERS. Pyridine (1 mM) in 0.1 M KCl was used as the standard for this study. As shown by the plot in Figure 2-2, it was seen that as the number of ORCs were increased, the SERS enhancement increased until 20 ORCs, but after that it started decreasing. This indicates for the present study that 20 ORCs gave the most intense SERS signal.
Figure 2.2. Best ORC cycle for preparing roughened Au (poly) with 1 mM pyridine in 0.1 M KCl.

Then the electrode is held at -0.36 V to remove any residual Cl⁻.[63] Following the roughening the electrode, it is rinsed with copious amounts of distilled water and then transferred to a quartz SERS cell.

2.4.2.2 In situ SERS setup

For performing real time in situ SERS, we need to have the EC workstation and the SERS running simultaneously. Figure 2-3 below shows the setup with the electrochemical cell on the center stage. For EC-SERS, before SERS measurements, the Au surface was roughened and rinsed with distilled water.[61, 62] In order to obtain the real time SERS measurements, the spectrum was taken once a particular potential was applied to the system. The potential was scanned from 0 V to 1.1 V (anodically and cathodically). Once a particular potential was applied, the SERS spectrum was obtained after waiting for a equilibration time of 5 minutes.
It was seen that a minimum equilibration time of 5 minutes was mandatory for the formate peak to be seen at 300 cm$^{-1}$. Before the experiments, the potential dependent SERS was carried out in the blank solution to confirm the absence of interference from the ions in the platinum deposition process and the chloride ion from the Au roughening procedure. This was necessary, as the chloride tends to adsorb onto the electrode from the roughening procedure. If so, the electrode was polished again and the roughening procedure was repeated till a surface free of interference from Cl$^-$ ions was obtained. Although SERS spectra were obtained from 200 - 3000 cm$^{-1}$, only spectral region with peaks are discussed here. The solution for SERS and electrochemical experiments was bubbled and kept in the nitrogen environment during the experiments. The catalyst
electrode surface for SERS was prepared by spontaneous deposition method as described in 2.2.2.

2.5 Other Characterization Methods

2.5.1 X-ray photon spectroscopy (XPS)

A commercial ultrahigh vacuum system (SPECS GmbH, Berlin) equipped with X-ray photoemission spectroscopy (XPS) was used to perform XPS measurements on the samples. All samples were conglutinated on customized sample holders with double side copper tape providing electrical contact between the sample holder and sample surface. The surface of prepared samples was characterized using standard XPS (Mg Kα, 1253.6 eV, 20 mA emission current). The platinum was deposited using the procedures described above and used as it is for the XPS measurements.

2.5.2 Scanning electron microscopy (SEM)

The Hitachi Scanning Electrochemical Microscope (HS-800) was used for SEM measurements. The image is generated by scanning a small diameter electron beam over the specimen. These electrons are scattered from the surface, and are then collected to generate an image. The electron beam source is a cold cathode field emission source with 300,000 X magnification and 2nm resolution. Depending on the Z and the acceleration voltage we can go from 1-3 μm. Usually for SEM the acceleration voltage is kept above 27 kV. The condenser lens current is kept large. The aperture opening diameter is less than 100 μm. Secondary electrons mainly indicate information about the surface of as specimen under the beam. Since they do not diffuse much into the sample they are best suitable for observing fine structures.
2.5.3 Energy Dispersive Spectroscopy (EDX)

The electron beam is also used to perform chemical analysis using an x-ray spectrometer. The spectrometer collects x-rays that are also generated by the electron beam. The x-rays are characteristic of the quantity of each element present in the area scanned by the electron beam. The EDAX detector is connected to the SEM instrument. When we need EDAX image, the EDAX detector is set above 6cm and images are obtained. The acceleration voltage is kept between 5-27 kV. The condenser lens current is kept small for best image quality. The aperture opening diameter is about 300 μm.

2.5.4 Transmission electron microscopy (TEM)

The Transmission Electron microscope equipped with energy dispersive X-rays (EDX) attachment (TECHNAI F 20 was used from NREC, USF. The TEM sample of the platinum deposited Au was prepared by focused ion beam Quanta 200 3D. The 5-30 kV Gallium liquid metal ion source is used to thin slice from bulk samples, which is removed with the help of Omniprobe micromanipulator. Then beam is used to attach this sample to 3mm grid for detailed analysis. The electron source in TEM is Schottky Field emitter and magnification of 25x to 1030 Kx. It has point resolution of 0.24nm and can give information upto 0.14nm.
Chapter 3. In Situ Surface-Enhanced Raman Spectroscopic Study of Formic Acid Electrooxidation on Spontaneously Deposited Platinum on Gold

Note to Reader

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3.1 Abstract

Present formic acid fuel cell efficiency is limited by low kinetics at the anode, indicating the need for effective catalysts to improve the formic acid oxidation. As a prerequisite, the nature of adsorbed species and specifically the reaction intermediates formed in this process needs to be examined. This work focuses on the electrooxidation of formic acid and the nature of the intermediates at a platinum-modified gold surface prepared through spontaneous deposition using a combination of electrochemistry and in situ surface enhanced Raman spectroscopy (SERS). This Pt-modified gold electrode surface assists in oxidizing formic acid at potentials as low as 0.0 V vs. Ag/AgCl which is 0.15 V more negative than a bare Pt surface. The oxidation current obtained on the Pt-modified gold electrode is 72 times higher than on a bare Au surface and 5 times
higher than on a bare Pt surface at the same potential. In situ SERS has revealed the involvement of formate at a low frequency as the primary intermediate in this electrooxidation process. While previous studies mainly focused on the formate mode at ca. 1322 cm\(^{-1}\), it is the first time that a formate peak at ca. 300 cm\(^{-1}\) was observed on a Pt or Pt-associated surface. A unique relationship has been observed between the formic acid oxidation currents and the SERS intensity of this formate adsorbate. Furthermore, the characteristic Stark effect of the formate proves the strong interaction between the adsorbate and the catalyst. Both electrochemical and spectroscopic results suggest that the formic acid electrooxidation takes place by the dehydrogenation pathway involving a low frequency formate intermediate on the Pt-modified gold electrode catalyst.

3.2 Introduction

Among the liquid fuels in fuel cell technology, formic acid has been propitious due to its high thermodynamic cell potential and high electromotive force as calculated from its Gibbs free energy. [17] Extensive studies have been reported on the electrooxidation of formic acid using platinum-based catalysts, and compared to other fuels (e.g. methanol) it is “Generally Regarded As Safe” (GRAS) to handle, easily transported, stored, and exhibits small crossover flux through the membrane. [11-13, 17] The central focus of these studies is on designing a better catalyst which is highly efficient, durable and less expensive than platinum by itself.

For the last few years, various Pt/Au catalysts have been tested for the electrooxidation of formic acid, including Pt-decorated Au nanoparticles, Pt-electrodeposited on Au, and
Pt–Au alloy nanoparticles. According to Choi and coworkers, the Pt/Au catalyst exhibited not only remarkably high oxidation currents and prolonged durability, but also increased power density compared to Pt/Ru catalysts. It was suggested that the enhanced catalytic effect observed from Pt/Au for the formic acid oxidation is due to their ensemble effect or third body effect, wherein the second metal tends to interrupt the large Pt surface thus favoring the dehydrogenation path. Since gold does not possess any catalytic activity at low potentials, it was considered to decrease the surface sites available for CO/(COH)ads. The presence of Au along with Pt reduces consecutive platinum sequences, thus favoring the dehydrogenation process. It was also suggested by other authors that Au has inherent catalytic activity leading to the increased enhancements. Furthermore, the use of Au as the second metal offers an additional critical advantage. It is oxidized at 1.2 V vs. RHE, a potential much higher when compared to other metals like Fe, Sb, Ti, and Bi. The consequence of surface oxidation at lower potentials in these metals is that it leads to material dissolution during the functioning of DFAFCs.

The different approaches for preparing a bimetallic Pt/Au catalyst, by deposition of a submonolayer or multilayers of platinum, have been summarized previously. In this paper, platinum was spontaneously deposited onto a gold electrode from PtBr₄²⁻ solution. By the careful control of the surface composition of Pt/Au bimetallic catalysts, the activity of the catalysts can be significantly enhanced. Many vibrational spectroscopy techniques have been employed to characterize the surface chemical bonding, such as Infrared Reflection-Absorption Spectroscopy (IRAS), Sum Frequency Generation (SFG), and Electron Energy Loss Spectroscopy (EELS). While the former
two suffer from the limitation of the vibrational modes not within their available frequency range, the latter is limited to ultrahigh vacuum (UHV) interfaces.\textsuperscript{[49, 50]} The unique properties of Surface Enhanced Raman Spectroscopy (SERS) have made it a versatile technique for understanding the adsorbates/intermediates formed in electrochemical environments.\textsuperscript{[52-55, 69]} The advantages of SERS over spectroscopic techniques (e.g. IR) are the absence of bulk phase interference and its ability to extract acute spectral information in the lower frequencies of 100–700 cm\textsuperscript{−1} where the surface adsorbate vibrations are present. It also helps to obtain intramolecular adsorbate vibrational modes in an electrochemical environment.\textsuperscript{[52-55, 70]} The approach is to obtain in situ SERS spectra with potential control, so as to correlate the SERS vibrational information with the electrochemical behavior.

Previous SERS studies on a plain gold surface suggested the prevalence of a dehydrogenation pathway with low frequency formate being the intermediate for formic acid oxidation.\textsuperscript{[25]} Although formate is thought to be the intermediate in electrooxidation of formic acid on gold at high potentials, no information has been reported yet about the effect of this adsorbate on a Pt-modified gold electrode surface. Further it would be interesting to compare the behavior of the intermediate on Au and Pt-modified gold electrode surfaces. Therefore, in situ SERS was employed in real time during formic acid oxidation on Pt-modified gold electrode catalysts for elucidation of the intermediates and the nature of the chemisorbate-surface bonding at the metal surfaces. The potential dependent behavior of the HCOO\textsuperscript{−} stretching mode, including the Stark effect, is also studied.\textsuperscript{[71-73]} The results provide a new insight into the behavior of this low frequency formate adsorbate generated in the electrooxidation
process on the Pt-modified gold electrode catalyst surface. This is the first time that this reaction intermediate for formic acid oxidation has been explored on the Pt-modified gold electrode surface using in situ SERS with potential control.

3.3 Experimental

3.3.1 Materials for electrochemistry

All solutions were prepared from doubly distilled water (18.2 MΩ cm) from a Cascada BIO and AN Lab Water System. Analytical grade sulfuric acid, formic acid (85% w/w), perchloric acid (70% w/w) and KCl were purchased from Fisher, KOH was purchased from Merck. Potassium tetrabromo platinate(II) (99%) was purchased from Alfa Aesar. All chemicals were used as received without further purification. All glassware was acid washed using concentrated sulfuric acid followed by nitric acid : water (1 : 1).

3.3.2 Preparation of a Pt-modified gold electrode surface by spontaneous deposition

After preparation of the Au (poly) using the previously described polishing procedure, the disk was dipped in 50 μM tetrabromoplatinate in 0.125 M HClO₄ for the appropriate amount of time.[37] After cleaning with deionized water, platinum was deposited spontaneously followed by a cathodic scan immediately. The deposited platinum was removed easily from the gold surface by successive polishing with intermittent sonication, allowing the polished Au surface to be reused for further measurements.

3.3.2 Electrochemistry experiments

The working electrode was a 3 mm diameter polycrystalline gold disk obtained from Goodfellow Cambridge Ltd., insulated in Teflon, which was mechanically polished with
1, 0.3 and 0.05 micron alumina powder (EMS Technologies) successively on a microcloth (Buehler), with intermittent sonication. A commercially available Ag/AgCl electrode (BASi) was used as the reference electrode and a platinum wire was used as the counter electrode. The polycrystalline platinum disc electrode was obtained from CH instruments (diameter of 2 mm). The electrolyte solutions were deaerated by bubbling with high-purity nitrogen gas for 10 minutes before all the experiments. The nitrogen atmosphere was maintained throughout the experiments. All electrochemical measurements were carried out using a CH 760 electrochemistry workstation (CH Instrument, TX, USA). All reported results are based on at least three repeated measurements to check the reproducibility.

### 3.3.4 SERS experiments

The same electrodes were used for both the electrochemical and SERS measurements. A quartz electrochemical cell was used to hold the working, reference and counter electrodes during the in situ SERS experiments. To obtain high SERS enhancement, the Au surface was roughened following the procedure of Stolberg et al.[61] At the end of the procedure, the potential was held at −0.36 V for 2 min to desorb chloride.[63] Then, the roughened disk was rinsed with large amounts of distilled water and transferred to a SERS cell. While some literature studies suggest 15 oxidation–reduction cycles (ORCs), others suggest 20–25 ORCs to achieve the maximum enhancement. For these experiments, 20 ORCs gave us the most intense SERS signal.[61, 62] Pyridine (1 mM, Fisher) in 0.1 M KCl was used as the standard molecule to examine the SERS enhancement of the surface. SERS measurements were carried out in a solution containing 0.45 M HCOOH on the Pt-modified gold electrode surface,
which was prepared using a deposition time of 10 minutes. These conditions proved to give the highest oxidation currents from the electrochemical experiments.

SERS experiments were carried out using a Confocal Raman Microscope (Olympus, IX71) purchased from Horiba Jovin Yvon. For all experiments, an excitation wavelength of 647 nm from an Argon and Krypton laser (Coherent, Innova 70C series) has been used with 35 mW of power, 5 s of exposure time and 1 accumulation. The spectrograph grating was 600 grooves per mm and the 20× objective was used throughout the experiments. Spectra were obtained between 200 and 3000 cm$^{-1}$ at 0.1 V or 0.2 V intervals. The system was allowed to equilibrate for 5 min at each potential before spectra were acquired. All the reported results were calculated from at least three repeated trials. Only the spectral regions with peaks are shown in this paper.

3.4 Results and analysis

3.4.1 Spontaneous deposition of Pt on a Au surface

Figure 3.1(a) shows the CVs of Pt-modified gold electrode surfaces with various deposition times (0 to 30 minutes) in comparison to the bare Pt electrode and the bare Au electrode in the blank solution. The inset shows the magnified cathodic scan. Clearly, the increase in the Pt deposition time leads to the decrease in the gold oxide reduction peak at ca. 0.85 V accompanied by the increase in the platinum oxide reduction peak at ca. 0.3 V. The observed behavior is typical of the Pt modified gold surface.[21, 36, 65] As more platinum is deposited on the Au surface, there is a negative shift in the peak potential for reduction of gold oxide and less gold oxide is formed on the surface leading to the decrease in the current for gold oxide reduction at
ca. 0.85 V. There was also an increase of the current in the hydrogen adsorption–desorption region indicating the presence and reconstruction of the Pt deposits on the surface at these potentials. Interestingly, as the deposition time increases from 15 to 30 minutes, the current for the hydrogen absorption–desorption region along with the platinum oxide reduction current decreases. This can be explained in conjunction with the amount of electroactive Pt on the surface as discussed below.

Figure 3.1. a) Cyclic voltammograms on bare Au (blue), bare Pt electrode (black) and Pt@Au surface with different deposition time of 5 mins (red), 10 mins (green), 15 mins (purple) and 30 mins (pink). The voltammograms were recorded in 0.125 M HClO₄ with a scan rate of 50 mV/s. The inset shows the magnified cathodic scan (see text for details). b) The amount of electroactive Pt on the Pt@Au electrode with deposition time. Data obtained from three trials.

To examine the composition of the Pt-modified gold electrode surface, the amount of moles of electroactive Pt surface coverage was estimated from the hydrogen adsorption–desorption charge in voltammograms after subtraction of the background current following the work of Kim et al.[35] Figure 3.1(b) shows the dependence of the
amount of electroactive Pt on the surface on the deposition time. As the deposition time increases, an increase in the amount of electroactive Pt was observed which reaches a maximum value at 10 minutes. At 15 minutes, there is a sharp decrease in the amount of electroactive Pt. Similar phenomena were observed previously using STM, which are attributed to the vertical growth of multiple layers of platinum at the expense of the small Pt deposits thus accompanied by the apparent decrease of the Pt coverage.[35, 37] The presence of platinum was further affirmed by EDX analysis[62] (data are shown in B1-S2).

3.4.2 Formic acid electrooxidation on a Pt-modified gold electrode surface

3.4.2.1. Electrooxidation

Figure 3.2 shows the CVs of formic acid oxidation on bare Au, a Pt-modified gold electrode surface with ten minutes deposition time and a bare platinum electrode. The concentration of formic acid for this study is 0.45 M HCOOH. The effect of concentration of formic acid in the range of 0.09–2.0 M was examined (data shown in B1-S3). The concentration of 0.45 M formic acid generates the highest oxidation currents at the Pt-modified gold electrode surface with the optimal deposition time of 10 minutes. Therefore, all further experiments were conducted using this concentration. Since the bare Au surface is not active for formic acid electrooxidation in the potential range below 0.3 V vs. Ag/AgCl (Figure 3.2 inset), it is safe to assert that the observed currents on the Pt-modified gold electrode surface are due to the catalytic activity of platinum on gold.[21]
Figure 3.2. a) Cyclic voltammograms of electrooxidation on plain Au (dotted line), poly Pt (thick line) and Pt-modified gold electrode surface (dashed line, 10 minutes deposition time) in a solution containing 0.45 M HCOOH. The inset shows the cyclic voltammograms of plain Au without (dashed) and with (black line) 0.45 M HCOOH. The electrolyte is 0.125M HClO₄ with a scan rate of 50 mV/s.

On the Pt-modified gold electrode surface, the oxidation peak starts at ca. 0 V in the anodic scan and reaches a maximum at 0.4 V. This is due to the direct oxidation of formic acid to carbon dioxide through the dehydrogenation path on the exposed sites where CO is not adsorbed; process I (P-I). It is remarkable to note that the oxidation currents obtained on the Pt-modified gold electrode catalyst at ca. 0.30 V are 72 times higher than on plain Au. Formic acid oxidation on the Pt-modified gold electrode surface exhibits a different behavior than the bare Pt electrode. First, a negative shift for the onset potential for formic acid oxidation was observed from 0.15 V on bare Pt to 0.0 V
on the Pt-modified gold electrode surface, as indicated by the arrows in Figure 3.2, which signifies a lower oxidation potential for formic acid on the Pt-modified gold electrode surface. Secondly, the current for direct formic acid oxidation (P-I) in the potential range of 0.2 V to 0.4 V is about five times higher on the Pt-modified gold electrode surface as compared to the bare Pt surface. In summary, the Pt-modified gold electrode exhibits superior performance for formic acid oxidation through the direct pathway compared to pure platinum by itself.

It is of great interest to further compare the electrooxidation of formic acid on the Pt-modified gold electrode to that on the bare Pt electrode. As observed previously, formic acid oxidation on platinum goes through the indirect pathway (P-II) via the CO intermediate as seen by a distinctive oxidation peak at higher potentials (about 0.7 V).[13, 74] In contrast, no distinguishable peak was observed at potentials between 0.6 V and 0.8 V on the Pt-modified gold electrode surface. Furthermore, unlike the bare Pt electrode, where the cathodic formic acid oxidation current (P-III) is higher than the anodic scan, the current on the Pt-modified gold electrode surface is more reversible. These differences undoubtedly indicate that the CO oxidation is significantly prominent on the bare Pt electrode and that the amount of poison formed on the Pt-modified gold electrode is minimal.[35]

3.4.2.2 Effect of deposition time.

Figure 3.3 shows the CVs of 0.45 M formic acid on bare Pt electrode, bare Au electrode, and Pt-modified gold electrode surfaces with different deposition times. The
oxidation current for all three peaks (P-I–P-III) reaches the maximum at the Pt-modified gold electrode surface with 10 minutes deposition time.

Interestingly, this observation coincides with the amount of electroactive platinum on the surface shown in Figure 3.1(b). At the deposition time of 5 minutes, peak P-I is clearly observed while P-II is absent. This is because the amount of electroactive platinum is only about 5 nanomoles giving rise to comparatively lower formic acid oxidation current with no significant peak for CO poison. As the deposition time is increased to 10 minutes, all peak current increases while the amount of electroactive Pt rises to its maximum.

Figure 3.3. Electrooxidation of formic acid in a solution containing 0.45 M HCOOH + 0.125 M HClO₄ on plain Au (blue), Pt-modified gold electrode 5 mins (red), Pt-modified gold electrode 10 mins (green), Pt-modified gold electrode 15 mins (purple), Pt-modified gold electrode 30mins (pink) and Poly Pt (dashed black). The voltammograms were recorded with a scan rate of 50 mV/s.

As the deposition time is further increased, all current decreases and P-II becomes obvious which resembles that of pure platinum.[13] Hence a deposition time of ten
minutes was used to prepare the Pt-modified gold electrode surface for all experiments since it generated the highest oxidation currents for formic acid.

3.4.3.1 SERS on a plain gold surface in blank solution.

Figure 3.4 shows the SERS spectra on a bare Au electrode in 0.125 M HClO$_4$ during (a) anodic scan and (b) cathodic scan. The electrode potentials are specified near each spectrum at 0.2 V intervals between 0 V and 1.4 V. Three peaks were observed and their behaviors are similar to previous reports.[25, 53] Two peaks were observed only at high potentials. Peak 2 at 335–345 cm$^{-1}$ appears only at 1.4 V in the anodic scan and disappears when the potential is scanned negatively below 1.0 V. The appearance of peak 2 coincides with the onset of gold oxide formation. Therefore, peak 2 is attributed to bending modes of terminal/bridging oxygen-containing species like surface hydroxide.[53] Peak 3 is a broad band at 550–600 cm$^{-1}$, and only observed at 1.4 V in both scans. This peak occurs at potentials when gold is oxidized and is assigned to the surface oxide.[25, 53] This peak assignment is further affirmed as the intensities of both peaks 2 and 3 gradually increase with time when the potential is held constantly at high potentials (ca. 1.4 V). Peak 1 at 935 cm$^{-1}$ is well understood to be the symmetric stretching mode of perchlorate ions.[63] The intensity of this peak increases as the potential increases due to the increase in the electrostatic force at the Au surface, which causes higher adsorption of the anion on the surface.[38] However, the intensity of this peak drops as the potential is scanned positively above 1.2 V. This can be explained by the formation of oxide on the gold surface at high potentials as seen in the CV, which limits the sites available for the adsorption of perchlorate ions on the surface.
3.4.3.2 SERS of formic acid oxidation on a plain gold surface.

Before every SERS experiment for formic acid oxidation on a Au surface, the potential dependent SERS was obtained in blank solution to verify that there is no interference of the chloride ion in the roughening procedure. Figure 3.5a and 3.5b shows the SERS spectra of formic acid electrooxidation on a bare Au surface. With the addition of formic acid in the solution, a new peak (peak 4) appears along with the previously described peaks. The intensity of peak 1 for perchlorate ions is much lower than that in the blank solution. This indicates that the presence of formic acid molecules limits the adsorption of perchlorate ions on the surface. The intensity of peak 3 of the surface oxide is also lowered during the electrooxidation process, which is not unexpected since the potential does not go beyond 1.1 V. Interestingly, in the presence of formic acid, peak 2 for the surface oxygen-containing species appears at 1.0 V in the anodic scan with its intensity
Figure 3.5. Potential dependent SERS spectra of electrooxidation formic acid on plain Au during a) anodic scan and b) cathodic scan between 200-1000 cm$^{-1}$ in a solution containing 0.45 M HCOOH in 0.125 M HClO$_4$. c) Comparison of the SERS intensity of peak 4 (black dots for cathodic scan and grey triangles for anodic scan, Y-axis on the left) overlapped with the cyclic voltammogram (dotted line, Y-axis on the right) for formic acid electrooxidation on Au. d) The Stark effect of the peak 4 on Au (black dots for cathodic scan and grey triangles for anodic scan). The standard deviation is obtained from minimum of three experiments.

gradually decreasing as the potential is scanned negatively and it eventually disappears below 0.9 V. The potentials where peak 2 is observed (0.9–1.1 V) during the formic acid electrooxidation are much lower than that in the blank solution (1.2–1.4 V). Contrary to that, the intensity of peak 2 during the anodic scan is much higher than that of the blank solution. These observations strongly suggest that more oxygen-containing species like the surface hydroxide are generated on the Au surface during the formic acid oxidation.
Because the concentration of formic acid is 0.45 M during the SERS measurements, no interference is expected from formic acid in the bulk solution. Since peak 4 is absent in the Raman spectrum of concentrated formic acid and at 0.45 M, it definitely does not belong to free formic acid molecules (data shown in the B1-S1).[76] Thus, this feature is characteristic of formate on the surface. It has been reported that peak 4 is the characteristic vibrational mode of the metal surface formate bond.[25, 52] Figure 3.5c shows overlaps of the SERS intensity of peak 4 with the cyclic voltammogram on the Au surface. Peak 4 is present in the anodic scan through the potential range till 1.1 V. As the potential is reversed for the cathodic scan, the intensity of the SERS formate peak increases dramatically, reaching its maximum at 0.7 V and begins to decline below 0.6 V. The intensity of peak 4 gradually decreases at lower potentials and eventually disappears.

More interestingly, as indicated by the dotted line in 3.5a and b, the peak energy of the formate vibrational mode changes as the potential changes. Figure 3.5d shows the Stark effect of peak 4 on the bare Au surface, the shift in the frequency of the formate adsorbate because of the influence of electrochemical potential.[72, 73] This low frequency formate adsorbate exhibits a Stark tuning slope of 27 cm$^{-1}$ V$^{-1}$ in the potential range where formic acid electrooxidation takes place on the plain Au surface (ca. 0.3 V to 0.6 V).[25] The positive Stark effect value shows that the adsorbate is anionic.[25, 77]

3.4.3.3 SERS on a Pt-modified gold electrode surface in blank solution.

Figure 3.6a and b shows the potential dependent SERS spectra on a Pt-modified gold
electrode surface with 0.125 M HClO₄ between 0.0 V and 1.1 V. The upper limiting potential is set to 1.1 V so that the deposited Pt adlayers on the Au surface were not removed during the SERS measurements. The presence of platinum on the gold surface was also confirmed by the electrochemical measurements after each SERS experiment. Interestingly, all three peaks (peaks 1–3) are observed. The peak 1 at 935 cm⁻¹ is observed at all potentials, though its intensity is weaker than on the bare Au surface. This is expected since the presence of Pt adlayers on the Au surface obscures part of the enhancement from the underlying Au substrate. Peak 2 at 335–345 cm⁻¹ appears at 1.0 V and disappears at the same potential in the cathodic scan. Peak 3 at 550–600 cm⁻¹ is only observed between 1.0–1.1 V. Interestingly, the potentials where peak 2 and peak 3 were observed are 0.4 V more negative than those on the bare Au surface. This difference arises from the presence of Pt adlayers since the formation of platinum oxide occurs at lower potentials than gold oxide.[53, 75, 78]

3.4.3.4 SERS of formic acid oxidation on a Pt-modified gold electrode surface.

Figure 3.7a and b shows the SERS spectra of formic acid electrooxidation on the Pt-modified gold electrode. Before the experiments, the potential dependent SERS was obtained in blank solution to confirm the absence of interference from the bromide ion in the platinum deposition process and the chloride ion in the Au roughening procedure.
Figure 3.6. SERS spectra on Pt-modified gold electrode (10 mins) in 0.125 M HClO$_4$ during a) anodic scan and b) cathodic scan.

All four spectral peaks are observed. Surprisingly, SERS peak intensities are much stronger on the Pt-modified gold electrode surface during the electrooxidation process than on the bare Au surface despite the fact that the Pt-modified gold electrode surface exhibits lower SERS enhancement than the bare Au surface. The intensity of peak 1 at 935 cm$^{-1}$ for perchlorate ions increases in the anodic scan and disappears as the potential is reversed. Peak 2 for the surface oxygen-containing species appears at 1.1 V in the anodic scan and disappears at 1.0 V in the cathodic scan. As in the blank solution, peak 3 for the surface oxide is only observed at the highest potential 1.1 V.

Interestingly, unlike that on the bare Au surface, the surface metal-formate bonded vibrational mode (peak 4) is not observed in the anodic scan. In the reverse scan, its SERS intensity increases at 0.9 V and the peak seems to disappear at potentials below 0.2 V.
Figure 3.7. Potential dependent SERS spectra of formic acid electrooxidation on Pt-modified gold electrode (10 mins) during a) anodic scan and b) cathodic scan in a solution containing 0.45 M HCOOH + 0.125 HClO4. c) Comparison of the SERS intensity (dots, left Y-axis) of peak 4 overlapped with the cyclic voltammogram (black line, right Y-axis) of formic acid electrooxidation on Pt-modified gold electrode. D) Vibrational Stark effect of peak 4 on Pt-modified gold electrode surface. The standard deviation is obtained from minimum of three experiments.

This hints that the adsorbate is short lived on the Pt-modified gold electrode surface. Figure 3.7c shows overlaps of the SERS intensity of peak 4 with the cyclic voltammogram on the Pt-modified gold electrode surface. Peak 4 appears in the cathodic scan, reaches its maximum at 0.9 V and gradually diminished down and disappears at 0.2 V. Figure 3.7d shows the Stark effect of peak 4 on the Pt-modified gold electrode surface. The Stark tuning slope is calculated to be 73 cm$^{-1}$ V$^{-1}$ in the potential range of formic acid oxidation between 0.2 and 0.5 V. This Stark slope is much
larger than that on the bare Au surface indicating the stronger influence of the electric potentials on the surface-formate vibrational mode.

3.5 Discussion

Many spectroscopic studies, including Infrared Reflection Absorption Spectroscopy (IRRAS) and surface-enhanced IR absorption spectroscopy (SEIRAS), have shown the presence of formate as an intermediate on the Pt surface. However, this formate band is seen in the range 1322–1325 cm$^{-1}$ which is attributed to the symmetric COO$^-$ stretching mode of adsorbed formate on the Pt with a bridging configuration.[79-83] It is interesting to note that no peak in that frequency range was observed on this Pt-modified gold electrode surface. Instead, a surface formate band at ca. 300 cm$^{-1}$ is observed. This is the first time that such a low frequency formate band was observed on a Pt-modified surface. Moreover, most of the previous spectroscopic studies have been carried out at millimolar concentrations of formic acid; this is the first time that in situ spectroscopic data have been obtained at molar concentrations on a Pt-modified gold electrode surface.

This 300 cm$^{-1}$ mode is also observed on a bare Au surface however with different potential dependent SERS behaviors. We believe this peak at 300 cm$^{-1}$ might be due to the formate adsorbate on the surface through an orientation other than the bridging configuration, for example the one end absorption through single bonded oxygen. Because the band at ca. 1322 cm$^{-1}$ is specific to formic acid oxidation on Pt through the dehydration pathway, the absence of this peak indicates that the dehydration pathway might not be the dominant pathway for formic acid electrooxidation on the Pt-modified
gold electrode surface.[79-82] The observation of the formate peak at 300 cm\(^{-1}\), on both the Pt-modified gold electrode and the bare Au surface, suggests that similar reaction mechanisms may be prevalent on both these surfaces. As this formate peak is characteristic of the dehydrogenation pathway on the Au surface,[25] it is more likely that the formic acid oxidation on the Pt-modified gold electrode surface goes through the same pathway.

There have been plenty of spectroscopic studies of CO oxidation on platinum and platinum modified catalysts.[52, 55, 70, 75, 84-86] Among those, the behaviors of the different vibrations for CO oxidation are discussed in the higher frequency range of 2000–2100 cm\(^{-1}\) and the lower range of 450–500 cm\(^{-1}\).[87] It is remarkable to note that no such peaks were observed on our Pt-modified gold electrode catalyst in these frequency ranges during the formic acid electrooxidation process. The absence of CO peaks on the Pt-modified gold electrode indicated that either only a low amount of CO is present on the surface during the reaction, or the kinetics of the reaction are fast, resulting in the immediate oxidation of CO formed to CO\(_2\), thus undetectable in the spectra.

Electrochemical results suggest that the electrooxidation of formic acid on a plain Au surface takes place at three potential regions O-I, O-II and O-III.[88-90] SERS results confirm the involvement of formate as an intermediate during the electrooxidation process on Au.[25, 77] When both results are correlated to each other, the study leads to edifying results. The unobservable intensity of formate in the anodic scan is due to the negligible catalytic activity of the bare Au surface toward formic acid oxidation at low
potentials and the removal of formic acid by surface gold oxide at high potentials above 1.0 V. As the potential is scanned negatively, surface oxide is removed which leaves vacant sites for the adsorption of formate on the bare Au surface. As a result, the peak intensity for formate adsorbed on the surface reaches its maximum at 0.7 V, where the limiting current is achieved. As the potential is swept negative of 0.7 V, formic acid oxidation is permitted to occur, as depicted in the CV, resulting in lowered intensity of the SERS formate peak. Thus an important relationship between the oxidation currents and the surface coverage of the formate was observed: the potential regions at which formic acid was oxidized coincide with lower formate coverage. A Stark slope of 27 cm$^{-1}$ V$^{-1}$ was observed for the 300 cm$^{-1}$ formate peak which is low compared to that observed by Beltramo and co-workers because the potential range of the study is different.[25] Furthermore, no peak for CO was observed on Au by SERS during the electrooxidation process of formic acid. The observation of the formate adsorbate and the absence of a CO peak agree well with a previous study that formic acid oxidation on a plain Au surface follows mainly the dehydrogenation route.[25]

The electrochemical results for the Pt-modified gold electrode catalyst prove that this catalyst has a remarkable catalytic activity towards formic acid electrooxidation using the optimal spontaneous deposition time of 10 minutes. The oxidation current density on the Pt-modified gold electrode ca. 0.3 V is five times higher than on the bare Pt surface and over 70 times higher than on the plain Au surface. In addition, the onset potential for formic acid oxidation on the Pt-modified gold electrode surface is 0.3 V more negative than on the bare Au surface and 0.15 V more negative than on the bare Pt
surface. In summary, spontaneous deposition of platinum on Au leads to higher oxidation currents at lower potentials.

A unique behavior was observed for the formate adsorbate on the Pt-modified gold electrode surface using SERS. In the anodic cycle, the formate adsorbate was absent owing to the inherent catalytic activity of the surface, which oxidizes any formic acid on the surface. In the cathodic scan as the potential reaches 1.0 V, due to the presence of platinum oxide, the surface becomes inactive for formic acid oxidation. At 0.9 V, once all the platinum surface oxides are reduced, formate is adsorbed on the vacant Pt sites, leading to the increase of the formate peak. Once the surface oxide is removed at lower potentials, formic acid electrooxidation is permitted to occur on the surface. Due to the fast kinetics of the reaction, the peak intensity for formate decreases during the cathodic scan and eventually disappears below 0.2 V. Thus, as observed on plain Au, the formate adsorbate coverage is inversely related to the formic acid oxidation currents on the Pt-modified gold electrode surface.

More importantly, despite the lower enhancement from the Pt-modified gold electrode compared to the Au surface, the intensity of the formate peak is nearly three times higher on the Pt-modified gold electrode surface than on the Au surface. Such a difference can be caused by two possibilities: stronger interaction between the formate and the surface or higher surface coverage of formate. This former possibility is supported by a substantial increase in the Stark slope for this potential dependent adsorbate from 27 cm$^{-1}$ V$^{-1}$ on the bare Au surface to 72 cm$^{-1}$ V$^{-1}$ on the Pt-modified gold electrode surface. Clearly, the formate adsorbate is more strongly influenced by
the electric fields and it has stronger interaction with the Pt-modified gold electrode than with the bare Au surface. [50] On the other hand, the latter possibility can be supported by the electrochemical results where the Pt-modified gold electrode surface generates much higher oxidation current for formic acid than the bare Au surface, resulting in formation of more formate adsorbates during the oxidation process on the Pt-modified gold electrode surface than on the bare Au surface.

Previous studies have suggested that formic acid oxidation on a bare Pt surface takes place through both pathways but mainly through the indirect pathway. [13] Both the electrochemical and SERS results indicate that the reaction mechanism on the Pt-modified gold electrode catalyst is quite different from either bare Au or Pt surfaces. While most of the formic acid is oxidized by pathway I on the Pt-modified gold electrode surface, there is formation of CO poison too which happens at higher concentrations of formic acid and longer deposition times. The oxidation of CO by pathway II on the Pt-modified gold electrode is quite different from that on the bare Pt surface. This is also confirmed by the CO stripping experiments (data shown in B1-S4), which prove that the Pt-modified Au surface is active for CO oxidation and its activity is highly sensitive to the structure of Pt deposits. [68, 91] Furthermore, electrochemical results show no distinguishable peak for CO oxidation on the Pt-modified Au surface during formic acid electrooxidation while a clear peak was observed on bare Pt surface. Besides, a more reversible redox behavior was observed on the Pt-modified gold electrode surface than the bare Pt surface where the oxidation current for formic acid is higher cathodic oxidation current than the anodic oxidation current. All these observations suggest that the dehydrogenation pathway is more dominant on the Pt-modified Au surface.
Both the electrochemical and SERS results indicate that the Pt-modified gold electrode is a more effective surface for oxidizing formic acid than either bare Pt or bare Au, as it mitigates each of their major drawbacks. This was suggested to be due to the third body or the ensemble effect, wherein the presence of Au and Pt together favors the dehydrogenation instead of the dehydration pathway which requires continuous Pt atoms.[21, 64, 66] The inherent catalytic activity of Au along with Pt atoms interspersed between Au atoms leads to formation of carbon dioxide, since adsorption of the CO poison relies on large Pt clusters.[67] It was also suggested that Au may involve in the conversion of HCOOH to HCOO$_{ads}$ followed by its conversion to CO$_2$ by the Pt on the surface.[91]

### 3.6 Conclusion

This study is to explore the electrooxidation of formic acid on a spontaneously deposited Pt-modified gold electrode surface employing both electrochemical methods and in situ surface enhanced Raman spectroscopy. Understanding the behavior of reaction intermediates like formate gives us better insight into the mechanism of oxidation. Spontaneously deposited platinum on gold showed unique high catalytic activity for formic acid electrooxidation. The starting potential of formic acid on the Pt-modified gold electrode surface is 0.15 V more negative than on a Pt surface. The oxidation current of formic acid is more than five times higher on the Pt-modified gold electrode surface than on a bare Pt surface and about 72 times higher than on a bare Au surface. Unlike previous studies, the electrooxidation process of formic acid at a high concentration of 0.45 M was examined using the in situ spectroscopic method. SERS results reveal the involvement of the HCOO$^{-}$ adsorbate at 300 cm$^{-1}$. This formate peak, which has not
been detected on any Pt or Pt-modified surface yet, was observed for the first time on the Pt-modified gold electrode surface. This surface formate is seen on both the Au and Pt-modified gold electrode surfaces but with different potential dependent behaviors. In addition, the Stark effect of this formate vibrational mode is larger on the Pt-modified gold electrode surface than on the Au surface, which suggests a stronger interaction of formate on the Pt-modified gold electrode surface than on the Au surface. Both the electrochemical and SERS results corroborate that the dehydrogenation pathway is the dominant mechanism for formic acid electrooxidation on the spontaneously deposited Pt-modified gold electrode surface. Research focusing on the surface structure and composition of the Pt-modified gold electrode catalysts is currently being carried out which will help to further understand the relationship between these surfaces and their activities.

3.7 Acknowledgements

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Chapter 4. Effect of Haloplatinate on the Electrocatalytic Activity of Spontaneously Deposited Pt-Modified Au Towards Formic Acid

4.1 Abstract

Spontaneous deposition is a promising method for creating a platinum-modified gold surface for application in the anode of fuel cells. The effect of the deposition solution employed in the spontaneous deposition process was explored and demonstrated to play an important role in catalytic activity of these surfaces. This work focuses on the study of the catalytic activity and the reaction mechanism of the Pt-modified Au surface prepared through spontaneous deposition from different haloplatinate solutions towards formic acid electrooxidation. Electrochemical studies show that Pt-modified Au surfaces prepared from bromoplatinate solution are most active in oxidizing formic acid. The second most active surface for formic acid electrooxidation was that from chloroplatinate followed by that from the iodoplatinate solutions. Also, the optimal condition to prepare the most active surface is different for various haloplatinate solutions. The platinum deposits obtained from the chloroplatinate solution exhibit the maximum catalytic activity at a concentration of 0.5 mM with deposition time of 15 minutes, while the optimal condition for bromoplatinate solution is at a concentration of 0.05 mM with deposition times of 5 minutes. In situ surface enhanced Raman spectroscopy (SERS) with potential control revealed the presence of formate at 300 cm$^{-1}$ as the reaction intermediate in the catalytic processes on all three Pt-modified Au surfaces, but with different potential-dependent behaviors.
4.2 Introduction

The use of bimetallic catalysts is attractive due to their activity towards electrooxidation of formic acid, which is higher than pure single metal catalysts. [7, 18, 92-94] Especially Pt/Au catalysts give high currents for electrooxidation of formic acid and thus have been favorable in their use in formic acid fuel cell anodes.[65, 95-97] There are various ways to generate such electrode surfaces including electrodeposition [31, 96] at a fixed potential[68, 75], overpotential method[30] or spontaneous deposition method.[36, 37, 75] Spontaneous deposition was shown to yield consistent distribution of metal ions on the surface with an enhanced catalytic activity.[37] It is a simple method, which generates good coverage of platinum on a gold surface. Another important aspect of this approach is that formic acid electrooxidation on Pt-modified Au surfaces obtained by this method appear to mainly take the dehydrogenation pathway. [98]

The spontaneous deposition method involves the dipping of an electrode in a platinum containing electrolyte solution, followed by a cathodic potential sweep for the reduction of platinum on the surface.[99] The size, coverage and the geometric structure of such deposits have been investigated previously on single crystalline systems.[29, 35, 37, 100] With a short deposition time of about 1 minute on single crystalline gold, the platinum deposits appeared to be of monolayer height and had a diameter of. 2 - 4 nm.[35] Atomic resolution STM analysis revealed pinwheel structures of the Pt deposits on the surface.[37] Nagahara and coworkers have reported that the surface morphology of Pt deposits strongly depended on the composition of the
electrolytes. Moreover, the activity of the platinum deposits towards oxygen reduction also varied, depending on the electrolyte used. The platinum deposits obtained via the chloro- and bromoplatinate electrolytes are active while the use of iodoplatinate results in deposits that are almost inert towards oxygen reduction.[37] To the knowledge of the authors, no study has been reported about the effect of electrolytes towards formic acid electrooxidation. Previous studies on the halide adsorption on a platinum surface in the presence of excess electrolytes (1 N HClO4 and 1 N H2SO4) in KBr, KCl and KI solution have shown that the adsorption of I⁻ is stronger than Br⁻ and Cl⁻.[100, 101] Furthermore, Hiralal and coworkers have reported that iodide layers adsorbed on platinized platinum surfaces showed considerable catalytic activity for formic acid oxidation.[102] Motivated by these studies, the effect of these halides in the deposition solution on formic acid oxidation is investigated in this work.

The goal was to explore the catalytic activity of Pt-modified polycrystalline Au surfaces prepared from different haloplatinate solutions towards formic acid oxidation. The effect of the haloplatinate as well as its concentration and deposition time on the surface structure of the Pt-modified Au has been studied. Additionally, adsorbates or reaction intermediates formed in the oxidation process were investigated using in situ surface-enhanced Raman spectroscopy with potential control. Low frequency formate was seen as an intermediate when deposited from low concentration (0.05 mM) of bromoplatinate solution.[98] However, there is no information about the role of this intermediate along with any other intermediates on Pt-modified Au surface when deposited from chloro- or iodoplatinate solutions and at higher concentration of bromoplatinate solutions.
4.3. Materials and Methods

3 mm diameter polycrystalline gold electrode was used as working electrode. (Goodfellow Cambridge Ltd.) This electrode was Teflon insulated and polished with 1.0, 0.3 and 0.05 micron alumina powder (EMS Technologies) consecutively on a microcloth (Buehler), with intermittent sonication. The reference electrode was an Ag/AgCl electrode (BASi) and a platinum wire was used as the counter electrode. A 2 mm polycrystalline disc platinum electrode (CH instruments) and a CH760 electrochemistry workstation (CH Instrument, TX, USA) were used for the measurements. The in-house made electrochemical cell was used to hold the electrodes. High purity nitrogen was bubbled into the electrolyte solutions for 5 minutes before experiments and all experiments were carried out in nitrogen atmosphere.

Analytical grade formic acid (85 % w/w), perchloric acid (70 % w/w) and KCl (Fisher Scientific) solutions were prepared from doubly distilled water (18.2 MΩ·cm) obtained from a Cascada BIO and AN Lab Water System. Potassium tetrabromoplatinate (II) (99 %), dihydrogen hexachloroplatinate (IV) (99.9 %) and Potassium hexaiodoplatinate (IV) (99.9 %) were purchased from Alfa Aesar. Platinum was deposited on polycrystalline gold electrode (Au (poly) by the spontaneous deposition procedure. In this method, after polishing, the Au (poly) disc was dipped in a 0.5 mM hexachloroplatinate, tetrabromoplatinate or hexaiodoplatinate solutions for 15, 5 and 30 minutes, respectively. These deposition times were chosen since they give the highest formic acid oxidation currents. The electrode was rinsed with water, followed by a cathodic scan to deposit the platinum.
Figure 4.1. Cyclic voltammograms on Au (black dashed line) and Pt-modified Au through spontaneous deposition for 5 minutes from PtI$_6^{2-}$ (green), PtBr$_4^{2-}$ (red) and PtCl$_6^{2-}$ (blue) in 0.125 M HClO$_4$. Scan rate is 0.05 V/s.

Before SERS measurements, the Au surface was roughened and rinsed with distilled water.[62, 63, 103] Before the experiments, the potential dependent SERS was carried out in the blank solution to confirm the absence of interference from the ions in the platinum deposition process and the chloride ion from the Au roughening procedure. SERS measurements were carried out with a confocal Raman microscope (Olympus, IX 71, Horiba Jovin yvon) using air cooled CCD and Ar-Kr laser (Coherent, Innova 70C series). The laser power delivered to the sample was 35 mW. A 600 grooves/mm grating and a 20X objective was used. Although SERS spectra were obtained from 200 - 3000 cm$^{-1}$, only spectral region with peaks are discussed here. A minimum equilibration time of 5 minutes was given before each spectrum was taken. The solution for SERS and electrochemical experiments was bubbled and kept in the nitrogen environment during the experiments.
A commercial ultrahigh vacuum system (SPECS GmbH, Berlin) equipped with X-ray photoemission spectroscopy (XPS) was used to perform XPS measurements on the samples. All samples were conglutinated on customized sample holders with double side copper tape providing electrical contact between the sample holder and sample surface. The surface of prepared samples was characterized using standard XPS (Mg Kα, 1253.6 eV, 20 mA emission current).

4.4 Results and Analysis

4.4.1 Characterization of Pt-modified Au surfaces

4.4.1.1 Electrochemical Behavior of the Pt Deposits

The Pt-modified Au surfaces obtained from the three electrolytes show quite different behaviors, as shown in 4.1. The platinum deposits from PtCl₆²⁻ and PtBr₄²⁻ exhibit the characteristic platinum oxide reduction peak in the cathodic scan at 0.31 V for PtCl₆²⁻ and at 0.37 V for PtBr₄²⁻ and the lowering of the gold oxide reduction peak due to the presence of platinum on the surface. The usual hydrogen adsorption/desorption region is also observed at potentials below -0.2 V on both surfaces.[36, 98] These phenomena suggest that Pt has been successfully deposited on the Au surface from both deposition solutions. Interestingly, the Pt-modified Au surface from PtI₆²⁻ deposition solution shows only a minor platinum oxide reduction peak at 0.5 V, with the absence of distinguishable current in the hydrogen adsorption/desorption region. The small reduction peak of platinum oxide indicates that
Figure 4.2. The amount of electroactive Pt on the Pt-modified Au electrode obtained from the three precursors of 0.5 mM: PtI$_6^{2-}$ (circle), PtBr$_4^{2-}$ (triangle) and PtCl$_6^{2-}$ (square) with different deposition times.

only a small amount of Pt was deposited on the Au surface from this solution. It is important to note that this reduction occurs at a potential of about 200 mV higher on the Pt-modified Au surface from PtI$_6^{2-}$ than from the other two electrolytes, hinting that the Pt deposits obtained from PtI$_6^{2-}$ solution are different.

4.4.1.2 Electrochemical coverage of the platinum deposits

The amount of the electroactive platinum can be calculated by integrating the current in the region between -0.4 V and 0.03 V in the hydrogen adsorption/desorption region after subtracting the background current following the established method.[98]

4.2 shows the amount of electroactive platinum on the surface prepared from the three haloplatinate solutions. As the deposition time increases, the amount of electroactive platinum from the PtCl$_6^{2-}$ deposition solution increases and reaches the
maximum ca. 3.8 nanomoles at 15 minutes. Furthermore, as the deposition time increases, the amount of electroactive platinum from PtBr₄²⁻ deposition solution decreases, with the highest amount of ca. 3.5 nanomoles obtained at a deposition time of 5 minutes.[35] On the other hand, the amount of platinum from PtI₆²⁻ solution is much lower and does not go beyond 1.8 nmol, even after 30 minutes of deposition. Therefore, the deposition time of 15 minutes, 5 minutes and 30 minutes are optimal for obtaining the maximum amount of electroactive Pt from PtCl₆²⁻, PtBr₄²⁻ and PtI₆²⁻, respectively.

4.4.1.3 XPS results of the Pt deposits

X-Ray photoelectron spectroscopy (XPS) measurements were performed to prove the successful deposition of platinum and compare the amount of platinum of different samples qualitatively. The Pt 4f core level lines with a spin-orbit-split doublet
for three samples are shown in 4.3(A), which confirm the successful deposition of platinum. [104] By comparing the intensity of Pt 4f\(_{7/2}\) of three samples, the total amount of platinum deposited from PtBr\(_4^{2-}\) (5 minutes), is the highest followed by that from PtCl\(_6^{2-}\) (15 minutes) and that from PtI\(_6^{2-}\) (30 minutes) being the lowest. It is vital to note that strong iodine emissions were seen in the Pt deposits obtained from PtI\(_6^{2-}\) as shown in 4.3(B). On the other hand, there were no halide emissions observed on surfaces obtained from both PtCl\(_6^{2-}\) and PtBr\(_4^{2-}\) depositions. These results prove the irreversible adsorption of the iodide and removable adsorption of chloride and bromide onto the surface during the deposition process.[100] The weak absorption of chloride and bromide to the surface as compared to the iodide ions can be also be related to their decreasing solvation energy.[105]

### 4.4.2 Electrocatalytic activity of Pt-modified Au surfaces

Figure 4.4 shows the CVs of the electrooxidation of 0.45 M formic acid on a Pt-modified Au surface, prepared from all three precursors, at 0.5 mM at their optimal deposition times, overlapped with the CV obtained from pure platinum surface. The characteristic three features were observed during the formic acid electrooxidation between 0.2 - 0.4 V (P-I in Figure 4.4) in the anodic scan, followed by CO oxidation between 0.6 - 0.8 V (P-II) and the subsequent formic acid oxidation on the now free sites in the cathodic scan (P-III). [98, 106] The peak current density of P-I obtained on the Pt deposits from PtCl\(_6^{2-}\) is 60 times higher than the pure Au surface and 2 times higher than a bare Pt surface. For PtBr\(_4^{2-}\) depositions, the current for formic acid oxidation is only about 50 times higher than Au and again almost twice as high as on bare Pt surface.
Figure 4.4. Cyclic voltammograms of the electrooxidation of 0.45 M HCOOH in 0.125 M HClO$_4$ on bare Au (blue line) and bare Pt (dash black line) and Pt-modified Au surfaces from 0.5 mM PtCl$_6^{2-}$ (red line), PtBr$_4^{2-}$ (purple line) and PtI$_6^{2-}$ (green line). Scan rate is 0.05 V/s.

Previous studies with a lower concentration of the PtBr$_4^{2-}$ electrolyte (0.05 mM), have shown that the oxidation currents are 72 times higher than on the plain Au surface.[98] In comparison to pure platinum, the current is only half of that observed in previous studies, suggesting that the concentration of the bromoplatinate solution plays an important role towards the catalytic activity of these surfaces. The Pt deposits from the PtI$_6^{2-}$ depositions in comparison can oxidize formic acid with the currents being 40 times higher, compared to the Au surface, but considerably lower than on a pure platinum surface. This observation suggests that the surface obtained from PtI$_6^{2-}$ has limited catalytic activity towards formic acid.
For all Pt-modified Au surfaces, no distinguishable peak can be observed for the CO oxidation (P-II). Also, the cathodic current in P-III regions is smaller than that in the anodic scan which is quite opposite to what is observed on the pure Pt surface. Thus, both these observations suggest that the amount of CO poison generated is minimal.[98] The potentials at which the formic acid is oxidized is critical for application of this surface as anode catalysts. On the Pt deposits from PtCl$_6^{2-}$ and PtBr$_4^{2-}$, formic acid begins to be oxidized at ca. 0 V (P-I), which is 0.3 V lower than on Au, and about 0.15 V lower than that on a bare Pt surface. This clearly indicates the stronger catalytic activity of these surfaces. Since the depositions from PtI$_6^{2-}$ did not yield any clear peak shapes for the P-I region, it is difficult to make similar observations on the PtI$_6^{2-}$ deposits.

### 4.4.3. Effect of the concentration of the electrolyte

![Figure 4.5. Effect of the concentration of the three deposition electrolyte PtCl$_6^{2-}$ (black), PtBr$_4^{2-}$ (grey) and PtI$_6^{2-}$ (white) on the electrooxidation current density of 0.45 M HCOOH in 0.125 M HClO$_4$.](image)

The concentration of the three electrolytes also had a prominent effect on the catalytic activity of the Pt-modified Au surface. A wide concentration range from 5 µM to 5 mM of...
all the three haloplatinate solutions were investigated and their effect on the catalytic activity has been shown in 4.5. For the PtCl₆²⁻ solutions, the optimal concentration of the electrolyte resulting in the highest oxidation current for formic acid is 0.5 mM, while for PtBr₄²⁻ is about 0.05 mM. In case of PtI₆²⁻, it was observed that the highest concentrations of 5 mM or more yields the largest formic acid oxidation currents.

4.4.4 Effect of deposition time

Figure 4.6 shows the plot of oxidation currents from P-I and P-II as the function of the deposition time. This plot allows the determination of the optimal deposition times resulting in the highest oxidation current for formic acid and the lowest amount of CO formed on the 3 surfaces. For the Pt deposits from PtCl₆²⁻, a deposition time of 15 minutes gives the highest oxidation current, with the absence of distinguishable currents for CO oxidation.

![Figure 4.6](image)

Figure 4.6. Plot of HCOOH oxidation (P-I; circles) and CO oxidation currents (P-II; triangles) with deposition time on Pt-modified Au surface from 0.5 mM (A) PtCl₆²⁻ (B) PtBr₄²⁻ and (C) PtI₆²⁻ in solution of 0.45 M HCOOH + 0.125 M HClO₄. The error bar is from three replicate experiments.

For the Pt-modified Au surface from PtBr₄²⁻, a deposition time of 5 minutes yields the highest oxidation current for formic acid while a CO oxidation currents of 1 - 2 µA was
observed. Finally, the Pt deposits obtained from PtI$_6^{2-}$, showed gradually increasing oxidation currents for formic acid with the deposition time with no significant current for CO oxidation. Therefore, the optimal deposition time is about 30 minutes for PtI$_6^{2-}$. These conclusions are similar to those based on the amount of electroactive Pt on the surface in Figure 4.2. This suggests that the electrocatalytic activity of the Pt-modified Au surface is directly related to the amount of electroactive Pt present.

4.4.5 Surface enhanced Raman spectroscopy

4.4.5.1 SERS on Pt-modified Au surface from PtCl$_6^{2-}$

Figure 4.7A shows the SERS spectra on Pt deposits obtained from PtCl$_6^{2-}$ with potential control between 0 V and 1.1 V in the blank solution of HClO$_4$. Peak 1 at 934 cm$^{-1}$ belongs to the symmetric vibration mode of perchlorate adsorbate. Peak 2 at 550 cm$^{-1}$ is assigned to platinum oxide and occurs at 1.1 V. It disappears as the potential is swept negatively. [98] An additional peak at ca. 790 cm$^{-1}$ is observed during the anodic scan at potentials above 0.8 V. [63] This peak can be assigned to the bending vibration of OH$^-$ adsorbed on Au. In the cathodic scan a peak at 850 cm$^{-1}$ is observed at 0.2 V, which is the twisting mode of water in the clathrate structure generated by the perchlorate above the Au surface. [63] With the presence of formic acid (Figure 4.7B), an appearance of a band at 350 cm$^{-1}$ (Peak 3) is observed at 1.1 V. This band is typically related to terminal/bridging oxygen-containing species like surface oxide/hydroxide. [98] Since this band is absent in the blank solution on the Pt-modified Au surface without formic acid, its presence suggests that this band is from surface oxides/hydroxides formed as reaction intermediates during the formic acid oxidation
Figure 4.7. SERS spectra on Pt-modified Au surface from 0.5 mM PtCl$_6^{2-}$ solution in 0.125 M HClO$_4$ A) without HCOOH and B) with 0.45 M HCOOH. The left panels are spectra during anodic scan while the right ones are for cathodic scans.

The surface oxide peak disappears at potentials lower than 1.0 V in the cathodic scan. In the cathodic scan at 1.0 V, a new and broad band belonging to the low frequency formate intermediate at 260 cm$^{-1}$ (Peak 4) appears along with the peak at 350 cm$^{-1}$.[98] The peak for the formate adsorbate decreases as the potential is reduced to about 0.6 V. No SERS peak for CO was seen in the Pt deposits obtained from PtCl$_6^{2-}$.[98]

4.4.5.2 SERS on Pt-modified Au surface from PtBr$_4^{2-}$

Figure 4.8A shows the real time SERS spectra obtained at potentials between 0 - 1.1 V in the blank electrolyte for the Pt-modified Au surface obtained from PtBr$_4^{2-}$. The surface shows the Peak 1 at 934 cm$^{-1}$ which is from the perchlorate ions. Peak 2 at 550 cm$^{-1}$ was only observed at high potentials which agrees well with start of surface
oxidation. In addition, the peak 3 at 350 cm\(^{-1}\) is not seen on the Pt-modified Au surface obtained from PtBr\(_4^{2-}\). Previous studies have shown the presence of this peak on surfaces prepared from a ten times lower concentration of PtBr\(_4^{2-}\) electrolyte. This difference is likely caused by the larger amount of platinum deposited from our solution compared to the amount deposited in reference[98], which blocks the formation of oxide on Au surface; causing a low intensity of peak 3.

Figure 4.8. SERS spectra on Pt-modified Au surface from 0.5 mM PtBr\(_4^{2-}\) solution in 0.125 M HClO\(_4\) A) without HCOOH and B) with 0.45 M HCOOH. The left panels are spectra during anodic scan while the right ones are for cathodic scans

With addition of formic acid (Figure 4.8B), peak 3 at 350 cm\(^{-1}\) is observed in a similar way as in the PtCl\(_6^{2-}\) depositions. Besides, the low frequency formate adsorbate, peak at 260 cm\(^{-1}\) is not observed.[98] There was no CO related peak observed on this surface even at this high concentration of PtBr\(_4^{2-}\) precursor electrolyte.[52, 68, 98]
4.4.5.3 SERS on Pt-modified gold from PtI$_6^{2-}$

Figure 4.9A shows the SERS spectra of Pt-modified gold from PtI$_6^{2-}$ in blank electrolyte. There is a strong increase in the intensity of all SERS peaks in the spectra. Peak 1 is observed at 934 cm$^{-1}$. Both Peak 2 at 550 cm$^{-1}$ and peak 3 at 350 cm$^{-1}$ appear only at higher potentials corresponding to the formation of surface oxide or hydroxide. With the addition of formic acid, (Figure 4.9B) there is a substantial increase in the intensity of all the peaks in the spectra. The peak 4 at 260 cm$^{-1}$ starts appearing at 1.0 V in the anodic scan and its intensity increases as potentials increases. In the cathodic scan, the intensity of formate reaches the maximum at 0.8 V and finally disappearing at 0.4 V. There is an upsurge in the intensity of peak 3 too at high potentials, which again hints involvement of oxides/hydroxides as intermediates in the oxidation process.

4.5 Discussion

Different haloplatinate solutions have been employed to create catalytic active surfaces by spontaneous deposition for effective oxidation of formic acid. [36, 52, 98] In this study, we have deposited platinum from different haloplatinate solutions on Au by spontaneous deposition and have studied their impact on the surface structure and the catalytic activity for formic acid. Since Pt deposits from the bromoplatinate solution have previously been demonstrated to show remarkable catalytic activity for formic acid, it would be interesting to understand if the change in the halide composition in the deposition solution will have an impact in the catalytic activity of these bimetallic surfaces. [98]
Firstly, XPS measurements have revealed that the amount of platinum deposited is highest from the PtBr$_4^{2-}$ solutions followed by those obtained from PtCl$_6^{2-}$ at the optimal deposition times. But, the amount of electroactive Pt from both depositions is only about 3-4 nanomoles. The amount of electroactive Pt from PtI$_6^{2-}$ solution was less than 1 nanomole. This low amount of electroactive Pt deposited from PtI$_6^{2-}$ is also confirmed by the minor Pt oxide reduction peak and the almost identical Au oxide reduction peak, as seen in the CV and also by the low intensity of the peaks in XPS measurements. Furthermore, XPS had also revealed the high interference from iodide ions that adsorbs and blocks the Pt surface. Thus, the low catalytic activity of the Pt
deposits obtained from PtI$_6^{2-}$ can be linked to the competition of the iodide ions to get onto the surface along with platinum during deposition.

The chloroplatinate solution shows the highest activity for formic acid oxidation at a 0.5 mM concentration of the deposition solution at a deposition time of 15 minutes. A concentration of 0.05 mM gives the highest oxidation currents from the bromoplatinate solutions at an optimum deposition time of 10 minutes, as revealed by previous studies.[98] In contrast, the best condition for iodoplatinate is at the highest concentration of 5 mM and longest deposition time of 30 minutes. Thus, both the concentration and the deposition time of the precursor solution have a significant impact on the catalytic activity of the Pt-modified Au surface.

Electrochemical studies for the catalytic activity of these surfaces have shown that Pt deposits obtained from PtCl$_6^{2-}$ oxidize formic acid with currents 60 times higher compared to plain Au and two times higher than pure platinum. Real time in situ SERS has shown the prevalence of a low frequency intermediate ca. 260 cm$^{-1}$. This formate intermediate was observed for the first time on the Pt-modified Au surface obtained from PtCl$_6^{2-}$. Furthermore, the involvement of oxide/hydroxides as intermediates was observed by SERS. The presented results also show an absence of any CO oxidation currents on this surface.

The deposits obtained from PtBr$_4^{2-}$ oxidize formic acid at an optimal deposition time of 5 minutes. The formic acid oxidation currents obtained from this surface were about 50 times higher than Au and twice as much as the platinum surface. Besides, short deposition time for this surface leads to not only high activity for formic acid oxidation but also low formation of CO. Besides, no CO peak was observed by in situ
SERS which hints the dominance of the dehydrogenation pathway for the formic acid electrooxidation. Moreover, SERS did not reveal the presence of formate intermediate, which can be owed to the non-optimal concentration of the deposition solution of PtBr$_4^{2-}$. Lowering the concentration of PtBr$_4^{2-}$ by ten times to 0.05 mM during the deposition procedure has been demonstrated to generate the best catalytic Pt-modified Au surface which results in an improvement by 150% in the current density along with the presence of the formate intermediate as seen by in situ SERS.[98] Therefore, the absence of formate vibrational information on this surface during SERS measurements might be due to the short lifetime and low surface coverage of the formate during the reaction. The Pt deposits from PtI$_6^{2-}$ were least active in oxidizing formic acid. The current density for formic acid oxidation is only 16% of that from the bare platinum surface. It is of great interest to understand the reason behind the catalytic inability of this surface. As mentioned before, XPS has revealed strong iodine emissions from the surface, hinting the presence of large amount of iodide on the surface, which might block the surface active sites. Moreover, this is also confirmed by the absence of the hydrogen adsorption/desorption region, characteristic to platinum deposits on Au. There is a remarkable increase in the intensity of the formate intermediate, which is seen for the first time by in situ SERS from PtI$_6^{2-}$ deposits. In detail, the formate intermediate appears in the anodic scan with its intensity increasing with potential. In the cathodic scan, formate intensity is almost doubled. This observation hints that the formate adsorbate has a long lifetime on the surface that is also confirmed by the low catalytic activity of the surface towards formic acid electrooxidation. The long lifetime of the
formate leads to high surface coverage and an increase in the SERS intensity of this intermediate.

The Pt-modified Au surface through spontaneous deposition from all three haloplatinate solutions exhibits catalytic activity for formic acid electrooxidation. More importantly, formate was observed during the process on all surfaces under suitable condition and is an active reaction intermediate. Minimal or no CO was observed both electrochemically and by SERS. At the optimal deposition times and optimal concentration of the precursor solution, the Pt deposits obtained from PtBr$_4^{2-}$ are most active for oxidizing formic acid followed by the PtCl$_6^{2-}$. Due to the strong adsorption and interference of iodide, the Pt-modified Au surface from PtI$_6^{2-}$ solution is least active towards the formic electrooxidation. This conclusion is important when we want to choose a suitable electrolyte to study an electrochemical process.

4.6 Conclusions

Spontaneously deposited Pt-modified gold surface from the three haloplatinate solutions showed distinguishable behavior for formic acid oxidation. Both the electrochemical and SERS results show that the deposition time, concentration and the halide in the precursor solution exhibit significant effect on the surface structure and thus the catalytic activity of the surface towards formic acid oxidation. The Pt deposits obtained from the deposition solution were active in the order PtBr$_4^{2-}$ > PtCl$_6^{2-}$ >> PtI$_6^{2-}$ towards electrooxidation of formic acid. The diminished catalytic activity of PtI$_6^{2-}$ was partly due to the strong adsorption of iodide ions along with the platinum atoms onto the surface as confirmed by XPS. Besides, in situ SERS with potential control has revealed the presence of low frequency formate and oxides/hydroxides as the reaction
intermediates during the oxidation process. Interestingly, the dehydrogenation pathway is prominent on all three surfaces.

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Chapter 5: Electrochemical Transformation and Raman Spectroscopic Study of Iodine Doped BEDO-TTF Conductive Films.

5.1 Abstract
Clear and transparent bis ethylenedioxy tetrathiafulvalene iodine doped polymer films were created by the electrochemical method of cyclic voltammetry. The formation of the transparent films at low potentials ca. - 0.22 V (vs. Ag.AgCl) has been linked to the reduction of the iodine in the film to iodide species giving rise to colorless films. Furthermore, Raman studies have revealed the presence of different iodide species like triiodide, pentaiodide and iodine when potentials were applied to the films. Also, the formation of complex between the iodine and the BEDO-TTF polymer in a stoichiometry of 2.4: 3 [(BEDO-TTF) \textsubscript{2.4}I\textsubscript{3}] was observed at certain concentration using the electrochemical doping method. Thus, by a combination of electrochemical method and Raman studies we were able to study the composition and properties these conducting polymer materials prepared by the doping technique for their varied applications.

5.2 Introduction
Bis ethylenedioxy tetrathiafulvalene (BEDO-TTF) material has lot of various applications in Langmuir-Blodgett films, crystalline organic metals, metal-like composites, biosensors, soft electrodes, design of organic superconductors and semiconductors.[60] BEDO-TTF can be prepared in polycarbonate (1%) and complexed with iodine giving rise to dark colored films with very high conductivity. [60] On further modification with
gold nanoparticles and addition of functional groups, these films become sensitive to nitro compounds. Nitro compounds are the primary constituents in detection of explosives.[107] Although high in conductivity, the BEDO-TTF films are opaque and reflect light. [108] Interestingly, these BEDO-TTF iodine films (BEDO-TTF/I) can be electrochemically modified and transformed to transparent films while retaining their high conductivity. [60] Tracz and coworkers first reported the possibility of creating transparent films by electrochemical method, although it is not clear about the possible chemical identity of iodide species and their concentration in those BEDO TTF films.[109] The electrochemical behavior of these films has been reported earlier in a non-aqueous media.[110] To the best knowledge of the authors, there has been no other study about the electrochemical transformation of the BEDO-TTF/I in an aqueous environment. In this paper we intend to study the electrochemical transformation of iodine doped BEDO-TTF films in aqueous solution using both electrochemical method and Raman spectroscopy.

Raman Spectroscopy has been widely used to study BEDO TTF polymers.[111-113] So far, there has been no Raman spectroscopic study on BEDO-TTF/I samples prepared by the doping method. Since the method of preparation of the films might affect the crystal structure of the BEDO-TTF / I complex, the spectroscopic study will help us understand the structure of the iodine in the films and the effect of the doping methods. Here, we intend to identify the different forms of iodine or iodide in the films and examine the effect of potential on the chemical state of the iodine species. Raman spectroscopy along with the electrochemical technique will give us new insights into the
structure of the iodine in these electrochemically modified films which have great potential applications.

5.3 Experimental

5.3.1 Materials and chemicals

All solutions were prepared from doubly distilled water (18.2 MΩcm, Cascada BIO and AN Lab Water System). Potassium iodide (Sigma Aldrich), Potassium bromide (Sigma Aldrich) was used in 0.1 M concentration in water. The doping of the BEDOTTF/I films with two different concentrations of iodine of 0.063 mol/L and 0.033 mol/L respectively was performed using procedures as given in the paper.[60]

5.3.2 Electrochemistry

This BEDOTTF/I film was used as the working electrode, which was prepared using the procedure in reference 59.[60] Ag/AgCl was employed as the reference electrode (BAsi Inc.) along with platinum wire (CHI, TX, USA) as the counter electrode. An in-house electrochemical glass cell was used to hold the working, reference and counter electrodes together. Electrochemical measurements were performed with a CHI800 electrochemistry workstation (CHI, TX, USA).

5.3.3 Raman spectroscopy

All the Raman experiments were carried out using Confocal Raman Microscopy (Olympus, IX71) purchased from Horiba Jovin Yvon, equipped with Argon and Krypton laser (Coherent, Innova 70C series) producing 514 nm of wavelength. For all experiments, the excitation wavelength at 514 nm from argon and Krypton laser was
applied with a power of 30mW while 5 s of exposure time and 1 accumulation was used. The spectrograph grating was 300 grooves/mm and the 20X objective was used throughout the experiments. Spectra were obtained between 200 and 3000 cm⁻¹ (See supporting information), but the regions with interesting peaks are being discussed in the paper. All the results that are reported have been repeated three times for the reproducibility.

5.4 Results and Discussion

Figure 5.1 shows the typical cyclic voltammograms (CV) of the iodine doped BEDO-TTF film in 0.1 M KI solution. The starting potential is -0.22 V. As expected, formation of a transparent film by the end of the cathodic scan at -0.22 V was observed. There are 2 oxidation peaks in the initial anodic scan at 0.46 and 0.62 V respectively, followed by 2 reduction peaks in the cathodic scan at 0.19 and 0.04 V. Based on previous studies on oxidation of iodide ions on gold, platinum and polymer graphite electrodes,[114-118] the following reactions (I - IV) might be prevalent on the surface. The two oxidation peak at
0.46 and 0.62 V was observed previously and can be assigned to the oxidation of iodide to triiodide and to iodine respectively. [114, 115] The peaks at 0.04 and 0.19 V are assigned to the reduction of the iodine or triiodide back to iodide. [117]

Anodic scan:

\[ 3 \text{I}^- \longrightarrow \text{I}_3^- + 2\text{e}^- \text{ at } 0.46 \text{ V vs. Ag/AgCl} \quad (I) \]

\[ 2 \text{I}^- \longrightarrow \text{I}_2 + 2\text{e}^- \text{ at } 0.62 \text{ V} \quad (II) \]

Cathodic scan:

\[ \text{I}_2 + 2\text{e}^- \longrightarrow 2 \text{I}^- \text{ at } 0.038 \text{ V vs. Ag/AgCl} \quad (III) \]

\[ \text{I}_3^- + 2\text{e}^- \longrightarrow 3 \text{I}^- \text{ at } 0.19 \text{ V} \quad (IV) \]

Figure 5.2. Raman spectra 0.063 mol/L iodine doped BEDO-TTF (4 minutes) at different potentials in 0.1 M KI.
In general, in the anodic scan the iodide ions are oxidized to triiodide or iodine species followed by the cathodic scan where it is reduced from the triiodide/iodine back to polyiodide species giving rise to transparent BEDOTTF/I films. Tracz and coworkers had reported the presence of reversible peak for BEDO-TTF at 0.5 V. However, no such reversible peak was observed in our cyclic voltammograms. This can be attributed to a different concentration of the BEDO-TTF species used in the films. Since the concentration of BEDO-TTF is not revealed in the previous studies it is difficult to further interpret the absence of such peaks.[109]

Raman spectroscopy was employed to examine and identify the different vibrations and various iodine species present in these films. The whole Raman spectrum with the characteristic vibrational peaks was observed. (Figure BS-1 in the supporting information). To focus on the iodine/iodide species, only region of 100 – 250 cm$^{-1}$ is shown in Figure 5.2 and discussed here. Figure 5.2 shows the Raman spectra of the films at different potentials in potassium iodide solution. Before the application of any potential, no distinguishable peaks belonging to the iodine species were observed. As the potential was scanned positively to 0.8 V two Raman peaks at 207 cm$^{-1}$ and 103 cm$^{-1}$ were observed. The broad peak at 207 cm$^{-1}$ belongs to the iodine while the strong peak at 103 cm$^{-1}$ is assigned to the linear asymmetric stretching of I$_3^-$. [119, 120] As the potential was scanned negatively to - 0.4V, two peaks at 214 cm$^{-1}$ and 103 cm$^{-1}$ were observed belonging to the iodine and iodide species respectively.[119] While the intensity of I$_2$ peak remains the same, the intensity of I$_3^-$ peak nearly doubles. Such increase in Raman intensity strongly indicates that more I$_3^-$ is present at such low
potentials. This agrees well with our conclusions from electrochemical measurements that more iodide in the reduced form after cathodic scan.

Figure 5.3. Raman spectra of 0.033 mol/L iodine doped BEDO-TTF (10 minutes) (A) in the range of 50 – 250 cm\(^{-1}\) and (B) the range of 1300-1700 cm\(^{-1}\).

The effect of doping concentration of iodine on these films was also studied by Raman spectroscopy. Figure 5.3A shows the Raman spectra of the BEDO-TTF before and after doping of I\(_2\) with different doping concentration and time. Before doping, no peak was observed from either the polymer matrix or the BEDO-TTF complex. When iodine was doped with the concentration of 0.063 mol/L and 4 minutes deposition time, one peak was observed at 103 cm\(^{-1}\), that belongs to the triiodide species. When iodine with the concentration of 0.033 mol/L and 10 minutes deposition time was doped to the film, a broad peak at 216 cm\(^{-1}\) is observed. The appearance of iodine peak (216 cm\(^{-1}\)) indicates
the high concentration of iodine in these films. This is an important observation as it confirm our previous observation that the absence of this peak in the Raman spectrum of 0.063 mol/L doped BEDO-TTF/I films was due to the lower concentration of iodine at this concentration, which was not seen even when anodic potentials were applied to the system.

Figure 5.3B show the Raman spectra of the BEDO-TTF film with and without I₂ doping in the range at higher wavenumbers. In the PC matrix, a strong peak at 1606 cm⁻¹ and a doublet peaks at 1462 cm⁻¹ have been observed and are assigned to the phenyl ring stretching/breathing of the PC.[121] [122]. These characteristic peaks of the PC matrix were observed in all films with and without the doping. Interestingly, the Raman spectra of the film from 0.033 mol/L iodine doped for 10 minutes shows two new peaks at 1474 and 1630 cm⁻¹. Those two peaks have been observed before and are assigned to one phase of iodine, corresponding to a crystal stoichiometry of 2.4: 3 [(BEDO-TTF)₂₄I₃].[112] No such peaks was observed in the BEDO-TTF/I film at 0.063 mol/L doped with 4 minutes. This difference is important since it demonstrated that the type of complex formed between the iodine and BEDO-TTF can be strongly influenced by the doping technique and conditions.

5.5 Conclusion

Clear and transparent BEDO-TTF/I₂ films can be generated electrochemically with only a 10% loss in conductivity, which is due to the formation of different iodine/iodide species in the film at different potentials and possible electrochemical reactions taking place on these films have been proposed. Both electrochemical and Raman data
confirm the presence of iodine and triiodide at high potentials when the film is dark and opaque, while pentaiodide and triiodide dominate at low potentials when the film is clear and transparent. Also, possible formation of crystal between BEDO-TTF and I₃ was also observed by Raman studies, which is highly dependent on the doping conditions.

5.6 Acknowledgements

The authors would like to acknowledge and thank Parul Jain for preparing the films. Also, J. P. Harmon and Norma A. Alcantar for the collaboration.
Chapter 6 Processing and Performance of Polymeric Transparent Conductive Composites

Note to the Reader

 Portions of this chapter comprising of electrochemical experiments has been previously published as Parul Jain, Ranjani Muralidharan, Jennifer Sedloff, Xiao Li, Norma A. Alcantar, and Julie P. Harmon Processing and Performance of Polymeric Transparent Conductive Composites International Journal of Polymer Science Volume 2013 (2013), Article ID 845432, 13 pages

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Author contributions. PJ, NAA and JPH came up with project. RM and XL designed the experimental research for the electrochemical experiments; RM performed research, analyzed data and wrote the initial draft for the electrochemical experiments; XL improvised the draft.


6.1 Introduction

This work aims to investigate the use of polycarbonate films doped with BEDOTTF/halogen complexes for their application in sensors, which help in detection of nitroaromatic compounds. Detailed studies on the films have been carried out. The films were characterized using differential scanning calorimetry, dielectric analysis, UV-Vis Spectroscopy, cyclic voltammetry and four point probe method. Furthermore, dielectric spectroscopy was employed to study the conductive nature of BEDOF-TTF in polycarbonate matrix and relaxation behavior of the polycarbonate in presence of BEDO-TTF. The four point probe was used to study the conductivity and resistivity of the iodine doped BEDO-TTF/PC films. Dielectric analysis has been employed to study the primary, secondary and ionic conductivity relaxation. Although high in conductivity, the BEDO-TTF films are opaque and reflect light. [108] Interestingly, these BEDO-TTF iodine films (BEDO-TTF/I) can be electrochemically modified and transformed to transparent films while retaining their high conductivity. [60] Tracz and coworkers first reported the possibility of creating transparent films by electrochemical method, although it is not clear about the possible chemical identity of iodide species and their concentration in those BEDO TTF films.[109] The electrochemical behavior of these films has been reported earlier in a non-aqueous media.[110] But there has been no other study about the electrochemical transformation of the BEDO-TTF/I in an aqueous environment. In this paper we intend to study the electrochemical transformation of
iodine doped BEDO-TTF films in aqueous solution using both electrochemical method of cycliv voltammetry. Cyclic voltammetry is a vital electrochemical technique since it opens the possibility of reducing the coloured films into transparent films. Infact, using the electrochemical method the oxidation state of iodine in the films was controlled thus inducing transparency in the films with only a 10% loss of conductivity. [109]

6.2 Electrochemistry Experimental
The electrochemical modifications on BEDO-TTF/PC-Iodine film (0.095 mol·L⁻¹, exposed for 2 minutes) were carried out using a CH 760 electrochemistry workstation (CH Instrument, TX, USA). An Ag/AgCl electrode (BASi) was used as the reference electrode, and a platinum wire was used as the counter electrode. The electrolyte was 0.1 M KI solution in water.

6.3 Results and Discussion

6.3.1 Electrochemical Properties
Figure 6.1 shows the cyclic voltammogram of BEDO-TTF/PC-Iodine film in 0.1 M KI solution. The oxidation peak at 0.5 V in the anodic scan corresponds to the oxidation of iodide to iodine, and the reduction peak at −0.15 V in the reverse scan is due to reduction of iodine to iodide. [115, 117] The oxidation and reduction of iodine at these potentials is also confirmed by the visual observation of the coloration of the film at high potentials and discoloration at low potentials. It is interesting to note that while the reversible oxidation/reduction peak of BEDO or TTF was reported ca. 0.4–0.6 V in organic solvents [110, 123], no distinguishable peak for BEDO-TTF was observed on the film in aqueous solution. This is due to the presence of iodine in the film which can
react with BEDO-TTF.[124] Furthermore, the electrochemical method can be used to control the oxidation state of iodine species in the film. For instance, by holding the potential at −0.4 V, the iodine species in the film was reduced to iodide. Then, the conductivity of the reduced film was measured to ascertain the effect of iodine on the conductivity of the film. The discoloration gives rise to transparent film with 10% loss in conductivity. This finding encourages further studies on optimizing these systems.

Figure 6.1. Cyclic voltammogram of BEDO-TTF/Iodine film with 0.095 mol/L (2 mins) in 0.1 M KI aqueous solution. Starting potential is 0.2 V, and scan rate is 5 mV/s.
6.4 Conclusions
The work reveals that films processed via the reticulate doped polymer method can be reduced by cyclic voltammetry to yield conductive, colorless, transparent films. These features make it very attractive for design of optimum sensors.

6.5 Acknowledgements
I would like to thank Dr. Parul Jain, Jennifer Sedloff, and Dr. Julie P. Harmon at Chemistry Department, and Dr. Norma A. Alcantar, at Department of Chemical engineering, University of south Florida for initiating and collaborating this work with us.
Chapter 7: Reversible Hydrogen Storage in the Li–Mg–N–H System – The Effects Of Ru Doped Single Walled Carbon Nanotubes on NH₃ Emission and Kinetics

Note to the Reader:

Portions of this chapter consisting of Raman experiments has been previously published (Derviş Emre Demirocak, Sesha S. Srinivasan, Manoj K. Ram, John N. Kuhn, Ranjani Muralidharan, Xiao Li, D. Yogi Goswami, Elias K. Stefanakos


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Author contributions: RM and XL designed the experimental research for the Raman experiments; RM performed research, analyzed data and wrote the initial draft; XL improvised the draft.

7.1 Introduction

In this study, the hydrogen ab/desorption kinetics and the ammonia emission characteristics of the Li-Mg-N-H system in different conditions has been elucidated due to the effects of the ball milling parameters. Moreover the kinetics and the ammonia
emission characteristics of single walled carbon nanotubes (SWCNTs) and Ru doped SWCNTs in the Li-Mg-N-H system has been studied. Of these an important parameter studied is the introduction of structural defects in the SWCNTs to make them effective catalysts in the Li-Mg-N-H system. This was done by ball milling process. The optimal ball milling duration should be long enough to ensure homogenous dispersion of the SWCNTs and to introduce structural defects, but should not be very long to ensure that the majority of the SWCNTs are still present (i.e., not converted to amorphous carbon or graphite) after ball milling. Therefore, we selected a ball milling duration of 60 min due to SWCNT’s moderate surface area. We further validated our decision via Raman spectroscopy, which is a powerful tool for studying the structural characteristics of CNTs.[125] Raman is a useful and widely employed tool for characterization of the CNT’s. The presence of the D peak (around 1350cm⁻¹) suggests that defects have been introduced into the sample. The G band (around 1585 cm⁻¹) is due to the inplane tangential stretching of C-C bonds. Thus the G/D ratio is considered as the index of purity for SWCNT’s and helps in quantifying the disorder by analyzing the intensity ratio of I_D/I_G.[125, 126]

7.2 Experimental

Raman experiments were carried out using a Confocal Raman Microscope (Olympus, IX71) purchased from Horiba Jovin Yvon. For all experiments, an excitation wavelength at 647 nm from an Argon and Krypton laser (Coherent, Innova 70C series) has been used with 5 mW of power, 10 s of exposure time and 3-5 accumulations. The spectrograph grating was 600 grooves/mm and the 20X objective was used throughout
the experiments. Raman measurements were taken at various locations on the samples to account for the heterogeneity of the solid samples.

### 7.3 Results and Discussion

Figure 6-2-1 shows the Raman spectra of the as-received SWCNTs, S#3-5SWCNT and S#3-5SWCNT-20Ru (i.e., 5 wt. % SWCNT-20Ru doped S#3). The peaks at 1317 cm\(^{-1}\) and 1585 cm\(^{-1}\) are the characteristic D (disorder mode) and G (tangential mode) bands of the SWCNTs, respectively. The full width at half maximum (FWHM) value of D band can be used to indicate the presence of non-SWCNT carbonaceous impurities; in addition, the intensity ratio of D band to G band (I\(_D\)/I\(_G\)) is related to the defects introduced into the SWCNTs.\[127\]

Table 7-1 shows the mean values of I\(_D\)/I\(_G\) and the FWHM of the D band. Upon ball milling of SWCNTs and SWCNT-20Ru with S#3, the value of I\(_D\)/I\(_G\) increased more than three times from 0.26 for the as-received SWCNTs to 0.87 and 0.81 for S#3-5SWCNT and S#3-5SWCNT-20Ru, respectively, which indicates that structural defects were successfully introduced after 60 min of ball milling. Moreover, the D band is narrower in the starting material (FWHM \(\approx 52\) cm\(^{-1}\)) as compared to S#3-5SWCNT (FWHM \(\approx 65\) cm\(^{-1}\)) and S#3-5SWCNT-20Ru (FWHM \(\approx 127\) cm\(^{-1}\)). This further supports our previous conclusion that amorphous and nano-crystalline carbon were introduced during the ball milling process due to the decomposition of the SWCNTs. One interesting observation is that the FWHM of the D band for the S#3-5SWCNT-20Ru is almost double that of S#3-5SWCNT. This broadness most likely originates from the Ru doping steps in preparation of the SWCNT-20Ru catalyst. In addition, a closer look into the G band, given in Fig. 7-1, shows that the frequency of G band downshifts by 3 cm\(^{-1}\) after Ru doping into the
SWCNTs. It has been reported that doping with either electron donors or acceptors can change the shape and energy of some of the vibrational modes of SWCNTs. [128] The red shift of G band suggests that there is charge transfer from Ru to the SWCNTs. The higher electron density in the reduced SWCNTs results in weaker net bonding thus lowering the G band frequency.

**Table 7-1.** FWHM values and the intensity ratios of the D to G band of the as-received SWCNTs, S#3-5SWCNT and S#3-5SWCNT-20Ru.

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<td>I_D / I_G</td>
<td>0.26</td>
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Figure 7.1. Raman spectra of as-received SWCNT, S#3-5SWCNT and S#3-5SWCNT-20Ru.
7.4 Conclusions

Raman results prove that both ball milling procedure and Ru doping leads to the formation of more defects and carbonaceous species in the SWCNTs. More importantly, doping of Ru in the SWCNTs affects their structure and electron density, which might be related to the catalytic activity of this catalyst.

7.5: Acknowledgements

I would like to thank our collaborators, Derviş Emre Demirocak, Sesha S. Srinivasan, Manoj K. Ram, John N. Kuhn, D. Yogi Goswami, Elias K. Stefanakos, from the department of Clean Energy Research Center, College of Engineering, University of South Florida, Tampa, FL 33620, USA, Department of Physics, College of Arts and Sciences, Tuskegee University, Tuskegee, AL 36088, USA and Department of Chemical and Biomedical Engineering, College of Engineering, University of South Florida, Tampa, FL 33620, USA.
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Appendices
Appendix A: Chapter 1

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Figure B1-S.1 Normal Raman spectra of 0.5 M and concentrated formic acid. Excitation wavelength at 647 nm from an Argon and Krypton laser (Coherent, Innova 70C series) with 35 mW of power, 5 s of exposure time and 1 accumulation.

Figure B1-S.1 shows the normal Raman spectra of 0.5 M formic acid and concentrated solution of formic acid. Peak at about 205 cm\(^{-1}\) is due to OH…H out of plane bend and peak at belong to OCO bend.\(^1\) No clear peak was observed in the range of 250 - 300 cm\(^{-1}\) which indicates that there is no interference from the formic acid in aqueous solution during the SERS measurements.

Figure B1-S2 shows the EDX spectrum of the Pt@Au surface with a deposition time of 10 minutes. The presence of both the gold and platinum peaks was confirmed.
Figure B1-S.2. Energy dispersive X ray (EDX) spectrum of Pt-modified Au (10 minutes) surface.

Figure B1-S.3 (a) shows the CVs for the electrooxidation of formic acid at concentrations of 0.09 M, 0.30 M, 0.45 M, 0.90 M, 1.7 M and 2.0 M in 0.125 M perchloric acid on the Pt@Au electrode. The characteristic oxidation peaks/processes P-I, II, III can be clearly seen in all voltammograms. However, the peak shapes observed at lower concentrations are different from that obtained at higher concentrations. At 0.09 M, though it is evident that formic acid is oxidized, there is no distinguishable peak (P-II) for CO. At concentrations of 0.30 M and higher, a distinctive peak for CO oxidation is observed between 0.6 - 0.8V. This can be explained by the increase in overall poison present in the system. Therefore, at lower concentrations, formic acid is mostly oxidized by the dehydrogenation pathway.
Figure B1-S.3 a) Electrooxidation of formic acid on Pt-modified Au (10 mins) and Au surface (in blue) in a solution containing 0.09 M (red), 0.3 M (blue), 0.45 M (green), 0.90 M (purple) and 1.7 M (pink) HCOOH respectively, and on Au in solution containing 0.1 M HCOOH (brown) The voltammograms were collected with a scan rate of 50 mV/s. b) Plot of the oxidation current of HCOOH vs. the concentration, peak I (circles) and CO peak II (triangles). The standard error is obtained from minimum of 3 experiments.

As the concentration increases, more formic acid molecules take the dehydration pathway. Figure S.3 (b) shows the relationship between peak current and formic acid concentration. As the formic acid concentration increases, peak current of P-I (circles) for the direct oxidation of formic acid increases and reaches a maximum of 180 μA at 0.45 M, then drops to about 100 μA at 1.7 M. On the other hand, as the concentration of formic acid increases, the peak current of P-II for the CO oxidation (triangles) increases initially. However when the concentration of formic acid is above 0.3 M, the P-II current hovers around 60 μA. Interestingly, the oxidation current of both peaks decreases as the concentration of formic acid is further increased above 1.7 M. These phenomena suggest that the dehydrogenation pathway is more predominant on Pt@Au surface when the formic acid concentration is below 0.45 M.
CO stripping measurements were done following previous procedure. Briefly, CO was bubbled in to the electrochemical cell for 15 minutes followed by holding at 0.05 V for 15 minutes. Then, nitrogen was purged in for 30 minutes to remove any CO in the solution before taking the measurements. As reported previously, plain Au does not absorb any CO. Therefore, the voltammogram is not shown here. Figure B1-S.4 shows the CO stripping curves obtained on Pt-modified Au and polycrystalline Pt surface. CO is oxidized at 0.61 V on plain Pt surface as reported. Interestingly, on the Pt-modified Au surface, CO is oxidized at two potentials 0.53 and 0.67 V. This phenomenon was observed on Pt spontaneously deposited Au(111) surface. The peak at 0.53 V is due to CO oxidation on Pt islands larger than 10 nm while the one at 0.67 V is ascribed to CO oxidation on Pt islands less than 10 nm. Clearly, Pt-modified Au surface is active for CO oxidation and its activity highly depends on the structure of the Pt deposits.
Figure C-S1: Raman spectrum of 0.063 mol/L BEDOTTF with iodine doped for 4 minutes (in red), The BEDOTTF in 1% polycarbonate matrix (in orange) and the polycarbonate matrix (in purple)
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