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Formation of platinum black film *via* Marangoni flow

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Formation of platinum black film *via* Marangoni flow

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In Partial Fulfillment for the
Degree of Bachelor of Science in Chemistry
Department of Chemistry, Faculty of Science
Chulalongkorn University
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Project Formation of platinum black film *via* Marangoni flow

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Accepted by Department of Chemistry, Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Degree of Bachelor of Science Program in Chemistry

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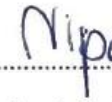

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Date ..... May, 2018

Quality of the following work is rated: ☑ Excellent ☐ Good ☐ Average

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บทคัดย่อ

เราได้พัฒนาวิธีการใหม่สำหรับสร้างฟิล์มแพลทินัมบนผิวของวัสดุรองรับพอลิไดเมทิลไซลอกเซน (PDMS) โดยอาศัยการเคลื่อนที่แบบมารางโกนิ โดยเริ่มจากหยดสารผสมสีเหลืองระหว่างกรดเฮกซะคลอโรแพลทินิก (H_2PtCl_6) กับโซเดียมฟอร์เมต (HCOONa) ลงบนผิววงกลมขนาด 5 มม. ของวัตถุรองรับพีดีเอ็มเอส สีของหยดสารจะเปลี่ยนจากเหลืองเป็นดำหลังจากแพลทินัมไอออน ถูกรีดิวซ์กลายเป็นอนุภาคแพลทินัมแบล็ก หลังจากนั้นจึงเปลี่ยนเป็นไม่มีสี เนื่องจากว่าอนุภาคแพลทินัมที่แขวนลอยอยู่ได้ตกลงไปเกาะบนผิววัสดุรองรับพีดีเอ็มเอส ผ่านการเหนี่ยวนำจากการเคลื่อนที่แบบมารางโกนิแล้ว การศึกษาพื้นผิวของฟิล์มแพลทินัมแบล็กด้วยกล้องจุลทรรศน์แบบใช้แสงและกล้องจุลทรรศน์อิเล็กตรอนแบบส่องกราดพบว่าฟิล์มมีการจัดเรียงอย่างสม่ำเสมอบนผิวของวัสดุรองรับ ฟิล์มที่ขึ้นรูปได้ถูกนำมาใช้เป็นตัวเร่งปฏิกิริยาการสลายตัวของไฮโดรเจนเปอร์ออกไซด์ (H_2O_2)

คำสำคัญ: อนุภาคแพลทินัมแบล็ก, ฟิล์มแพลทินัมแบล็ก, การเคลื่อนที่แบบมารางโกนิ

Project Title Formation of platinum black film *via* Marangoni flow
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Advisor Name Professor Sanong Ekgasit, Ph.D.
Department of Chemistry, Faculty of Science, Chulalongkorn University, Academic Year 2017

Abstract

We have developed a new fabrication process for making platinum black films on the surface of polydimethylsiloxane (PDMS) substrates using Marangoni flow. A yellowish droplet containing hexachloroplatinic acid (H_2PtCl_6) and sodium formate (HCOONa) was deposited on a 5-mm circular PDMS substrate. The droplet changed from yellow-wish to black after platinum (IV) ions were reduced to platinum black particles and subsequently turned colorless because the suspension particles were deposited uniformly on PDMS via Marangoni flow induction. The investigation of film morphology using optical microscopy and scanning electron microscopy revealed that Marangoni flow dispersed platinum black particles uniformly on the substrate. In addition, the fabricated film was employed as a catalyst for hydrogen peroxide (H_2O_2) decomposition.

Keywords: Platinum black particles, Platinum black film, Marangoni flow

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Chapter 1

Introduction

1.1 Background and motivation

Platinum black is a specific name of platinum nanoparticle. The name is derived from its black color, unlike from shiny silver-gray color of its corresponding bulk material. The particle has attracted much attention in science research because of its catalytic activities such as production of hydrogen from water [1] and reduction of many organic compounds [2,3]. Platinum black catalyst is mostly used as a form with many platinum black particles depositing on substrate or electrode, e.g., fuel cell or thin film electrode [4,5]. The conventional process for platinum black deposition is an electrodeposition [6,7], providing electric current to reduce dissolved metal cations and form a thin film coating on an electrode. However, this mentioned process has disadvantages of being complicated to control voltage and leaving toxic wastes.

Nowadays, there are many experiments offering innovative approaches of platinum black film fabrication using non-toxic chemical substances and easy to control. As well as this project work, we introduced a simple method of platinum black nanoporous film depositing on a polydimethylsiloxane (PDMS) substrate. Platinum black reagents, containing chloroplatinic acid precursor, sodium formate reducing agent, and water, deposited as a suspended droplet on a confined PDMS circular and left in a close chamber for 4 hours. Platinum (IV) ions from chloroplatinic acid were reduced by sodium formate spontaneously and became Pt^0 (platinum black particles), suspending inside the droplet. At the same time of reduction, the droplet also evaporated while altering surface tension of the droplet. These phenomena induced the movements inside the droplet, called Marangoni flow [8,9]. This flow influenced the deposition of platinum black particles on the substrate and formed the film structure. Thus, we can fabricate the platinum black film deposited on polymer substrate, PDMS, for catalytic purpose with environmental friendly process, no electricity required, and simple.

1.2 Objectives and scope

This work aims to develop a simple synthesis protocol for fabricating platinum black film using Marangoni flow. The structure and morphology of fabricated film are studied. Moreover, the potential of the film for catalytic application will be explored.

1.3 Theory and related researches

1.3.1 Platinum black film

Platinum black particle is a fine particle of platinum metal. It is widely used as a catalyst for chemical reactions such as the reduction of oxygen [10]. Synthesized platinum black particles are colloidal suspension, but for typical usages, they would be modified as a thin film. The typical technique for film fabrication is electrochemical deposition or electrodeposition. This technique provides an electric current to reduce platinum cations and forms the film structure coating on the conductive substrate or electrode.

In 1999, Elliott, *et al.* used electrodeposition to prepare high surface area platinum films by deposition from H_2PtCl_6 in a lyotropic liquid crystalline phase. The study varied temperature and deposition potential to find the best condition of film electrodeposition [11]. In 2005, Lu, *et al.* employed cyclic voltammetry and chronoamperometry to evaluate appropriate conditions for the electrodeposition of platinum nanoparticles on highly oriented pyrolytic graphite (HOPG) [12]. In 2012, Yihua, *et al.* developed a self-terminating rapid electrodeposition process for controlled growth solution of platinum monolayer films from a K_2PtCl_4-NaCl electrolyte. This process provided the potential periodically to control film thickness [13].

The fabrication of platinum black film by electrodeposition technique has been developed for long time to assess the proper condition that can control the film fabrication. Alternatively, there are other protocols to synthesis platinum black particles and fabricate the film using chemicals instead of electric current.

In 2009, Goyal, *et al*. tried embedding platinum nanoparticles inside PDMS polymer. A homogeneous mixture of chloroplatinic acid, PDMS base, and curing agent was prepared. The curing agent reduced the chloroplatinic acid to platinum nanoparticles and concurrently crosslinked the silicone elastomer, forming to the nanoparticle-PDMS film. The film could be applied for catalysis, optical and biomedical devices and gas separation membranes [14].

In 2010, Sun, *et al.* synthesized platinum black by dropping a solution of H_2PtCl_6 in ethylene glycol to deposit on substrates; glass, fluorine-doped tin-oxide (FTO) glass, and indium tin oxide coated polyethylene terephthalate (ITO/PET) under 180°C thermal treatment. The synthesized platinum film by this method could be used as the counter electrode of high-performance dye sensitized solar cells (DSCs) [15]. Lina, *et al.* fabricated Pt/MWCNTs nanocatalyst for using as proton exchange membrane fuel cells. The multi-walled carbon nanotubes (MWCNTs) were added into H_2PtCl_6, dissolved in organic phase. Aqueous sodium formate was used to reduce $PtCl_6^{2-}$ to Pt nanoparticles, deposited on MWCNTs (Figure 1.1). The Pt/MWCNTs nanocatalyst was used for proton exchange membrane fuel cells [5].

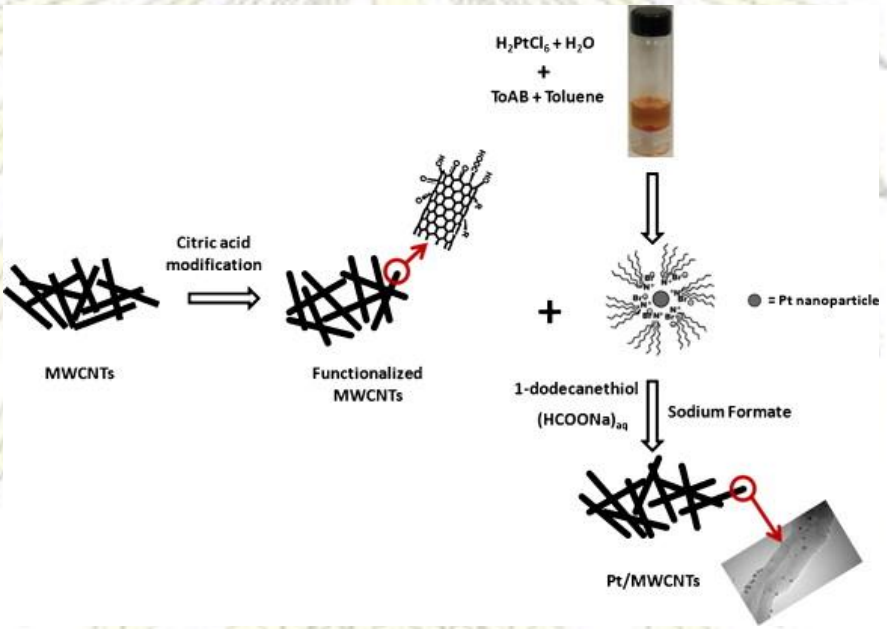

Figure 1.1 Schematic representation of surface modification of MWCNTs and Pt nanoparticles deposition [5]

In 2014, Aritonang, *et al.* synthesized platinum black using method similar to Lina, *et al.'*s. The bacterial cellulose (BC) hydrogels were soaked in the K_2PtCl_4 solution. Platinum nanoparticles developed after reducing by hydrogen gas and occupied thoroughly in BC membrane. The Pt-BC membrane can be used as a fuel cell [16].

This project also used chemicals, H_2PtCl_6 and HCOONa, to synthesize platinum black particles. $PtCl_6^{2-}$ ions from H_2PtCl_6 were reduced by $HCOO^-$ as describe by the following equations [17,18].

$$PtCl_6^{2-} + HCOO^- + H_2O \longrightarrow PtCl_4^{2-} + 2Cl^- + HCO_3^- + 2H^+ \quad \text{Eq. 1.1}$$

$$PtCl_4^{2-} + HCOO^- + H_2O \longrightarrow Pt^0 + 4Cl^- + HCO_3^- + 2H^+ \quad \text{Eq. 1.2}$$

According to equations 1.1 and 1.2, the reaction potential, E^0_{rxn}, can be calculated using E^0 values from the Table 1.1.

Table 1.1 Standard reduction potentials of the reagents [16,17]

Reduction equation	E^0 (V)
$PtCl_6^{2-} + 2e^- \rightleftharpoons PtCl_4^{2-} + 2Cl^-$	+0.68
$PtCl_4^{2-} + 2e^- \rightleftharpoons Pt + 4Cl^-$	+0.755
$HCO_3^- + 2H^+ + 2e^- \rightleftharpoons HCOO^- + H_2O$	−0.389

$$E^0_{rxn} = E^0_{cathode} - E^0_{anode} \quad \text{Eq. 1.3}$$

Using the relation of standard Gibbs free energy and standard reduction potential to calculate $E^0_{cathode}$; $\Delta G^0_{cathode} = n_{cathode} F E^0_{cathode}$ Eq. 1.4

$PtCl_6^{2-}$; $\Delta G^0_{Pt(4+)} = n_{Pt(4+)} F E^0_{Pt(4+)}$

$PtCl_4^{2-}$; $\Delta G^0_{Pt(2+)} = n_{Pt(2+)} F E^0_{Pt(2+)}$

Due to; $\Delta G^0_{cathode} = \Delta G^0_{Pt(4+)} + \Delta G^0_{Pt(2+)}$

$$n_{cathode} F E^0_{cathode} = n_{Pt(4+)} F E^0_{Pt(4+)} + n_{Pt(2+)} F E^0_{Pt(2+)}$$

$$E^0_{cathode} = \frac{n_{Pt(4+)} E^0_{Pt(4+)} + n_{Pt(2+)} E^0_{Pt(2+)}}{n_{cathode}}$$

$$= \frac{2(+0.68) + 2(+0.755)}{4} = = 0.72 \text{ V}$$

Then; $E^0_{rxn} = 0.72 - (-0.389) = +1.11$ v

From the equation 1.3, the calculated reaction potential, E^0_{rxn}, is +1.11 V. Hence, the reduction of $PtCl_6^{2-}$ to Pt^0 using HCOONa reducing agent is a spontaneous reaction.

1.3.2 Marangoni flow

The fabrication of platinum black film of this work was achieved by dropping the growth solutions on the PDMS surface. Due to the hemisphere-like shape of the droplet, it causes the different of the evaporation rate at each region on the surface. This nonuniform evaporation creates surface tension gradients and generates the loop flow inside the droplet called Marangoni flow. This flow can stir the particles inside the droplet and induce the uniform deposition of the particles on the substrate surface [19, 20].

The evaporation order of each region on the droplet surface depends on its shape. Manukyan, *et al.* presented the evaporation profile of liquid droplet on hydrophilic substrate and hydrophobic substrate. The wetting contact angle (θ_{CA}) of substrate affected to the droplet shape and the evaporation order as well (Figure 1.2) [21].

The length arrows, pointing out from blue area, indicates the strength of evaporation. Figure 1.2A, the droplet on hydrophilic substrate ($\theta_{CA} < 45°$) has the highest evaporation rate at the contact line, the zone that liquid surface contacts with solid surface and air. This zone evaporates faster than the other and has the lowest temperature. Whereas Figure 1.2B, the droplet on hydrophobic substrate ($\theta_{CA} > 90°$) has the lowest temperature at the apex.

The different of temperature gradients between two substrates created the different of surface tension (σ) *as described by the dash arrow in Figure 1.2.*

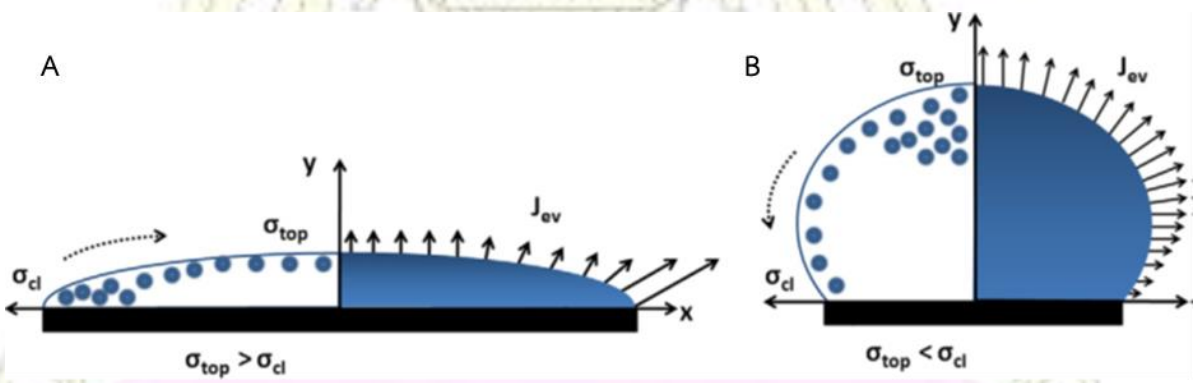

Figure 1.2 The evaporation profile of sessile droplet on A: hydrophilic substrate and B: hydrophobic substrate [21]

Manukyan, *et al.* used spectral radar optical coherence tomography technique (SR-OCT) to observe that the Marangoni flow direction depended on the substrate as shown in Figure 1.3.

Figure 1.3A shows that the Marangoni flow inside the droplet on the hydrophilic surface flows from the center to the edges and Figure 1.3B shows that the Marangoni flow inside the droplet on the hydrophobic surface flows from the edges to the center.

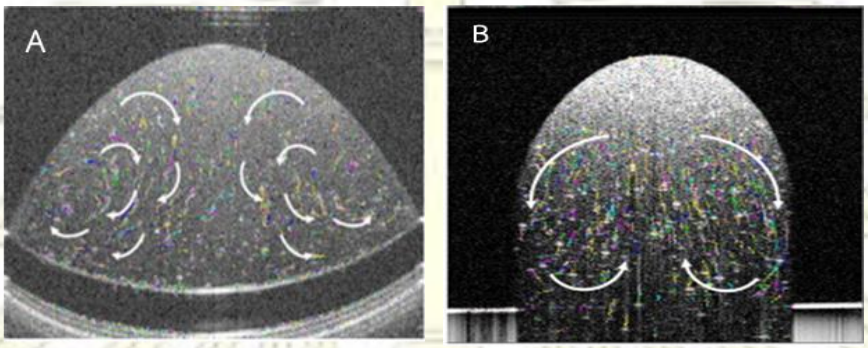

Figure 1.3 Direction of Marangoni flow inside the droplet on A: hydrophilic substrate and B: hydrophobic substrate [21]

In addition, Ristenpart, *et al.* investigated that the flow direction also depends on the relative thermal conductivity of the solid substrate and the solution as described in the following equation [22].

$$k_R = k_S/k_L$$

k_S is the thermal conductivity of solid (W $m^{-1}K^{-1}$)

k_L is the thermal conductivity of liquid (W $m^{-1}K^{-1}$)

k_R is the relative thermal conductivity of solid and liquid

If $k_R > 2$, the Marangoni flow is directed radially outward along the substrate. But if the value is in the range between 1.45 and 2, the flow is inward along the substrate. This project protocol selected the PDMS substrate for depositing of platinum black film. The PDMS thermal conductivity, $k_S = 0.23$ [22] and the platinum black growth solution is composed mostly with water, $k_L = 0.615$ [23]. Thus, the relative thermal conductivity, $k_R = 0.37$. Moreover, PDMS contact angle, θ_{CA}, is in the range of 99 ± 3° and 138 ± 3° [24]. It means that PDMS is a hydrophobic surface.

As a result, the Marangoni flow direction of this work turns from the edges to the center (Figure 1.4).

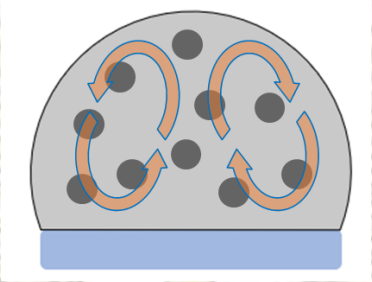

Figure 1.4 The model of Marangoni flow direction in this project

Chapter 2

Experimental section

2.1 Instruments & equipment

1. Petri dish
2. 5 mm diameter hollow puncher
3. Micropipettes
4. Beaker
5. Magnetic stirrer
6. Hot plate
7. Optical microscope (Carl Zeiss AxioCam HRc)
8. Electron microscope (JEOL JSM-6510A)

2.2 Chemicals

1. Platinum metals (99.99%, purchased from Umicore Precious Metal)
2. Hydrochloric fuming acid (HCl, purchased from Merck)
3. Nitric acid (HNO_3, purchased from Merck)
4. Formic acid (HCOOH)
5. Sodium hydroxide (NaOH, purchased from Merck)
6. Hydrogen peroxide (H_2O_2, purchased from Merck)
7. 3,3',5,5'-Tetramethylbezidine (TMB, ≥99%, purchased from Sigma-Aldrich)
8. Sylgard 184 PDMS elastomer (purchased from Dow Corning Corporation)

2.3 Experimental section

2.3.1 Preparation of hexachloroplatinic acid (H_2PtCl_6) precursor

H_2PtCl_6 was prepared by dissolving 10.0687 g of platinum granules in 40 mL of aqua regia (the mixture of fuming hydrochloric acid and nitric acid with 4:1 volume proportion). The solution was stirred with magnetic stirrer under heating. After all of platinum granules completely dissolved, the solution was further heated until almost dry, adding 40 mL of water and repeating the processes of heating for 7 times to eliminate NO_2 gas from the solution. The volume of the solution was adjusted to 100 mL with adding deionized water. The 0.5161 M H_2PtCl_6 stock solution was employed for further experiments.

2.3.2 Preparation of sodium formate reducing agent (HCOONa)

NaOH (5 M) was *dropped wise* to HCOOH (2 M, 50 mL) slowly until the pH of HCOOH was steady at pH 7. the volume of solution was adjusted to 100 mL with deionized water. Finally, a 1 M HCOONa was prepared in the HCOOH/HCOONa buffer solution form.

2.3.3 Preparation of polydimethylsiloxane substrate (PDMS substrate)

Polydimethylsiloxane (PDMS) substrate was prepared by mixing PDMS base with curing agent (10:1 weight proportion) and stirring for 10 min. The homogeneous mixture was kept in a petri dish to degas and cure for 1 day. Then, the cured PDMS was cut to circular shapes with 5 mm diameter and 1 mm thickness. The 5-mm PDMS disks were employed as film substrates.

2.3.4 Fabrication of platinum black film on PDMS substrate

The reagents, water (2 mL), HCOONa (1 M, 7.8 mL), and H_2PtCl_6 (0.5161 M, 192 µL), were mixed in a beaker and stirred with magnetic stirrer. A 50 µL droplet of homogeneous solution was deposited on a PDMS substrate and left in a closed chamber petri dish for 4 hours to produce a platinum black film. After that, the film was rinsed with deionized water and dried in a vacuum chamber. The platinum black film was fabricated for characterization and catalytic application.

2.3.5 Characterization of platinum black film

An optical microscope (OM), Carl Zeiss AxioCam HRc, was employed to investigate the structure morphology of the platinum black film using bright field mode with 50x magnification. The film was also characterized using scanning electron microscope (SEM), JEOL JSM-6510 at an accelerating voltage of 25 kV. The sample was attached an aluminum stub by a conductive carbon tape and dried in a closed chamber vacuum before characterization. An imaging software (ImageJ 1.43r, Rasband, W. National institutes of health, USA) was used to measure the sizes of platinum black particles.

2.3.6 Catalytic test

Hydrogen peroxide (H_2O_2: 10 M, 1.2 mL) was mixed homogeneously with 3, 3', 5, 5'-Tetramethylbenzidine (TMB: 3.5 mM, 1.2 mL). The mixture was dropped on a platinum black film and a bare PDMS, each droplet containing 50 µL of mixture. The change of droplet color from colorless to light blue was observed for the catalytic activity of the film.

Chapter 3

Results and discussion

3.1 Synthesis of platinum black particle

Platinum black particle can be synthesized from the reduction of H_2PtCl_6 or K_2PtCl_4, with several reducing agents [5,14,15]. This work offered to produce the particles from the reduction of H_2PtCl_6 by HCOONa. The H_2PtCl_6 was prepare form platinum granules and HCOONa was prepared from HCOOH.

Platinum granules were dissolved in the mixture of HCl and HNO_3 which is called aqua regia. Heterogeneous mixture of shiny silver-gray color platinum and colorless aqua regia turned to the orange solution of H_2PtCl_6 following this equation.

$$Pt_{(s)} + 4HNO_{3\,(aq)} + 6HCl_{(aq)} \longrightarrow H_2PtCl_{6\,(aq)} + 4NO_{2\,(g)} + 4H_2O_{(l)} \qquad \text{Eq. 3.1}$$

The orange solution of H_2PtCl_6 (Figure 3.1) was not pure yet because there was NO_2 gas, contaminating in the solution. The brownish NO_2 gas would be eliminated by further heating and adding water to dilute. After elimination of NO_2 gas, the volume of solution was adjusted to 100 mL by adding deionized water. The prepared 0.5161 M H_2PtCl_6 has orange color but its diluted concentration is yellow.

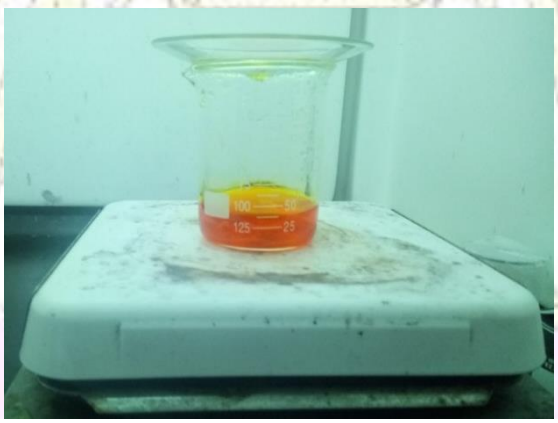

Figure 3.1 The dissolving of platinum granules in aqua regia

To prepare HCOONa, 5 M NaOH was added to neutralize HCOOH (2M, 50 mL). The reaction is described by this equation.

$$HCOOH_{(aq)} + NaOH_{(aq)} \rightleftharpoons HCOONa_{(aq)} + H_2O_{(l)} \qquad \text{Eq. 3.2}$$

This neutralization required 15.6 mL of NaOH to produce HCOONa in a form of HCOONa/HCOOH buffer solution which can retained its pH consistently at pH 7. The volume of HCOONa solution were adjusted to 100 mL by adding deionized water.

Both reagents, H_2PtCl_6 and HCOONa, were mixed homogeneously in a vial and the reaction was observed as shown in Figure 3.2. The yellow mixture (Figure 3.2A) turned to black (Figure 3.2C) within 2 hours and 40 minutes. The revealing of black solution agrees with that reported by Stanca, *et al.* [25], indicating that the platinum black particles were successfully prepared.

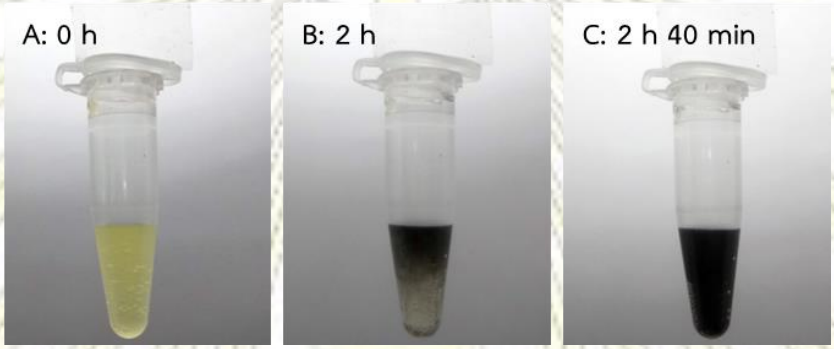

Figure 3.2 Color of H_2PtCl_6 and HCOONa mixture at A: 0 h, B: 2 h, and C: 2 h 40 min

3.2 Fabrication of platinum black film

Platinum black film generally prepared from the electrodeposition technique which is a piece-by-piece production on conductive electrode. While, this work developed a high-throughput fabrication by depositing the mixture, containing H_2PtCl_6, HCOONa, and water, on non-conductive PDMS substrates as shown in Figure 3.3.

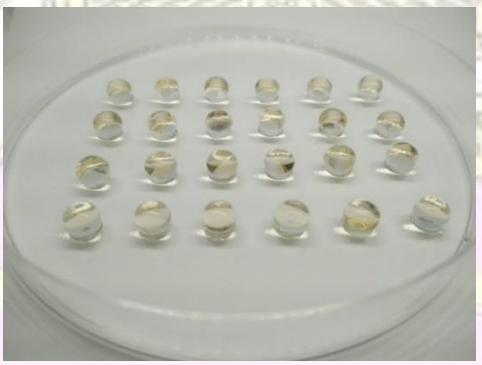

Figure 3.3 Droplets of the mixture, containing H_2PtCl_6, HCOONa, and water, on PDMS substrates

The fabrication method started with mixing water (2 mL), HCOONa (1 M, 7.8 mL), and H_2PtCl_6 (0.5 M, 192 µL) in a beaker. The mixture was dropped on the substrates with 50 µL of droplet size per substrate and left in a closed chamber petri dishes for 4 hours to produce the platinum black films. After rinsing with deionized water and drying in a vacuum chamber, the films would be fabricated on the substrates.

The development of platinum nanoparticle film on PDMS substrate was observed to explain the process of platinum black film formation. Figure 3.4 presented the change of droplet color. From Figure 3.4A to 3.4C, the droplet changed from yellow to deep black. It indicated that $PtCl_6^{2-}$ had been reduced to Pt^0 already. It should be noted that the color change of the droplet occurred slower than those in the vial (Figure 3.2) probably due to the characteristic of the reaction. However, the appearance of synthesized platinum black is not significantly different.

After 30 minutes (Figure 3.4D to 3.4F), the droplet turned colorless. Interestingly, the particles could deposit on the PDMS substrate though the substrate surface was not modified. This indicated that the platinum black film on unmodified PDMS surface can be fabricated by this method.

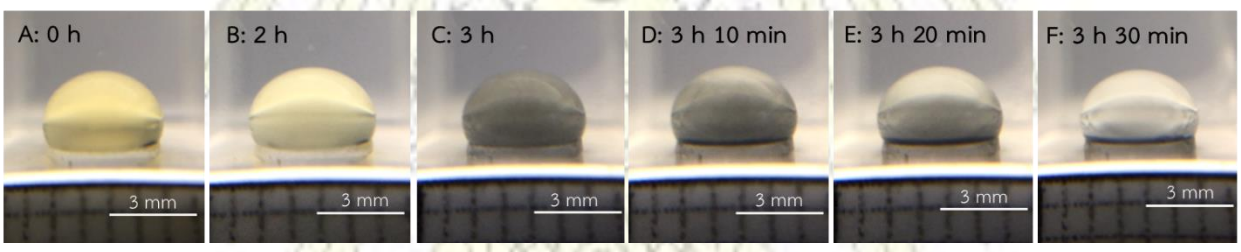

Figure 3.4 A droplet of platinum black growth solution at A: 0 h, B: 2 h, C: 3 h, D: 3 h 10 min, E: 3 h 20 min, and F: 3 h 30 min

3.3 Structure of platinum black film on PDMS

An optical microscopy (OM) image of the fabricated film (Figure 3.5) presents that the platinum black particles formed the film structure with different patterns at 3 regions; the edge (A), the middle (B), and the center (C). The result of this formation structure was probably from the induction of Marangoni flow. The influence of Marangoni flow will be discussed further by varying the film deposition time.

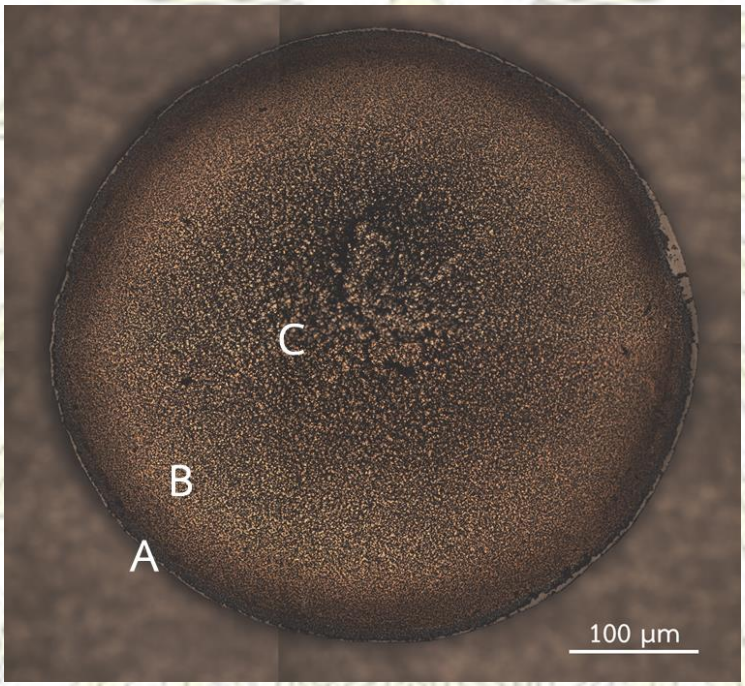

Figure 3.5 OM image (bright field mode, 50x) shows fabricated platinum black particles deposited on the substrate A: at the edge, B: at the middle, and C: at the center.

The time-dependent change of the film was studied. A 50 µL droplets of synthesized platinum black particles were deposited on PDMS substrates at various time: 0 min, 3 min, 6 min, 10 min, 15 min, 20 min, 25 min, and 30 min. The OM images showed the film structure of different deposition time comparing with virgin PDMS as shown in Figure 3.6.

At the first 10 minutes (Figure 3.6B to 3.6E), the particles distributed on the substrate uniformly but after that (Figure 3.6F to 3.6I) the different of particles deposition at each region were appeared due to the induction of Marangoni flow because platinum particles accumulated densely at the center of the substrate [26].

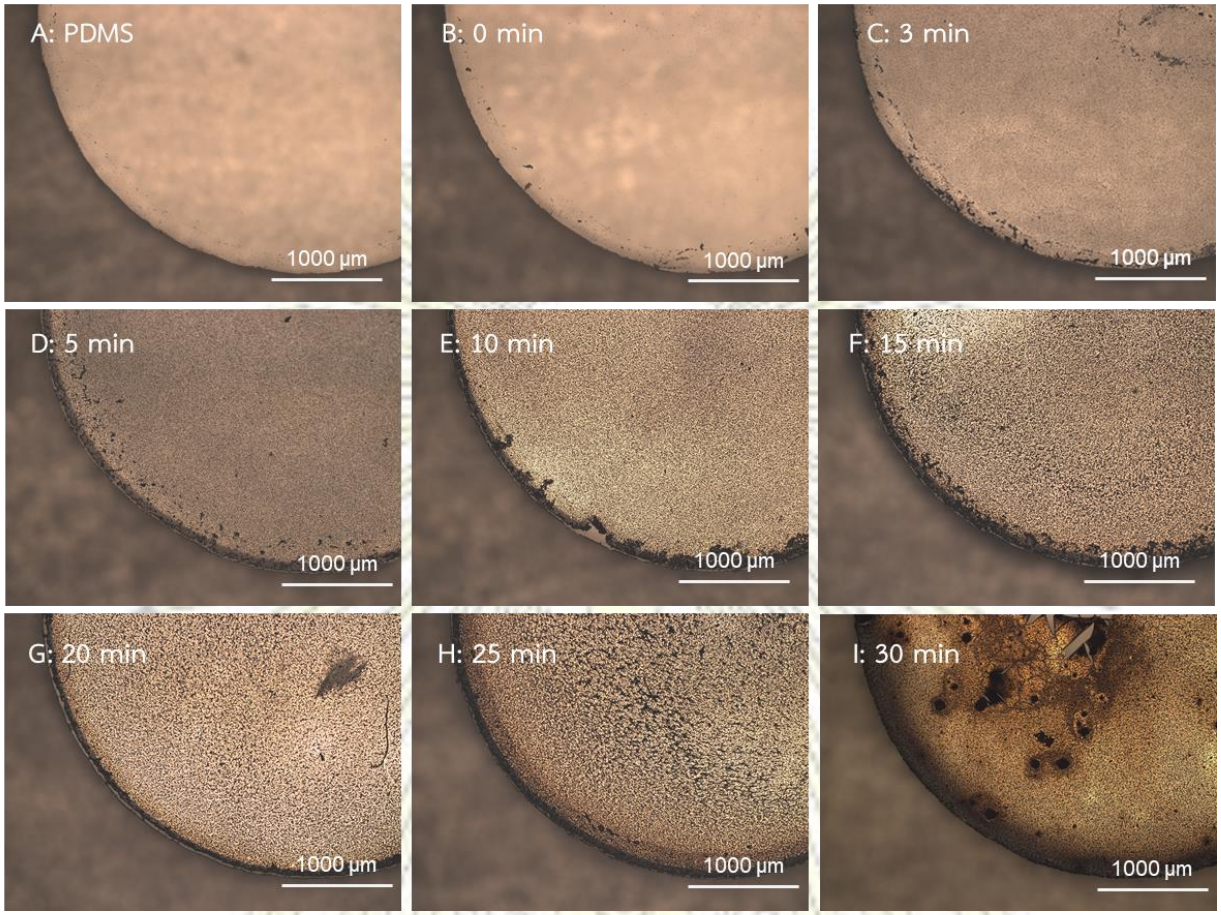

Figure 3.6 OM images (bright field mode, 50x) of A: virgin PDMS substrate and platinum black film at B: 0 min, C: 3 min, D: 6 min, E: 10 min, F: 15 min, G: 20 min, H: 25 min, and I: 30 min of deposition time

The difference of film morphology at the edge, the middle, and the center in Figure 3.5 was hypothesized that all three regions had the same size of the particle but various structure arrangement. The particle sizes and structure arrangement of the film were studied with scanning electron microscopy (SEM).

The SEM images (Figure 3.7) shows that the particle size at the edge (Figure 3.7A), the middle (Figure 3.7B), and the center (Figure 3.7C) were different. The average size of platinum black particles at the edge is 612 ± 343 nm (Figure 3.8) while those at the middle and the center were too small to measure.

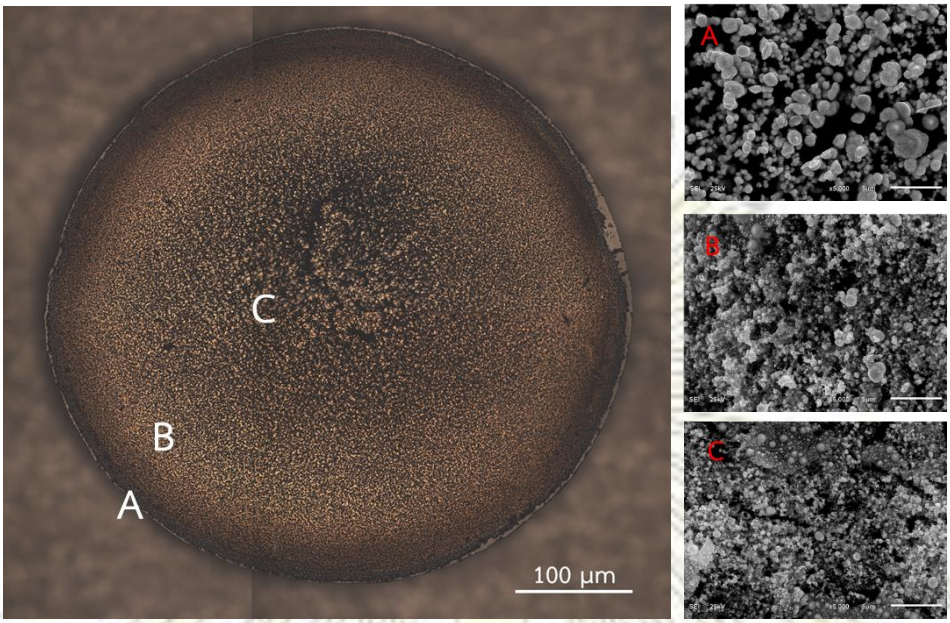

Figure 3.7 SEM images (25 kV, 5000x) of particles at A: the edge, B: the middle, and C: the center

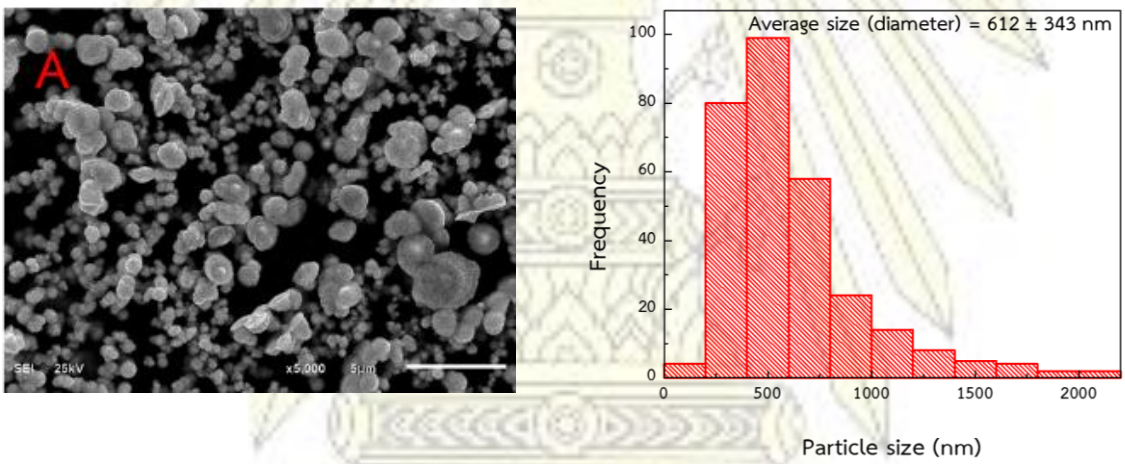

Figure 3.8 Histogram of particle size distribution at the edge region

3.4 Catalyst characteristic test of platinum black film

The fabricated platinum black film can be used as a catalyst for chemical reactions. To confirm the success of this film fabrication process, platinum black film was employed as peroxidase-like catalyst for the decomposition of H_2O_2, detecting by TMB [27,28].

Figure 3.9 described the mechanism of TMB detection on H_2O_2 decomposition. Under the catalyzation, H_2O_2 was able to decompose to the reactive oxygen species. This derivative would withdraw an electron from the colorless TMB. Then, the cation free radical TMB formed the charge-transfer complex, which expresses light blue color.

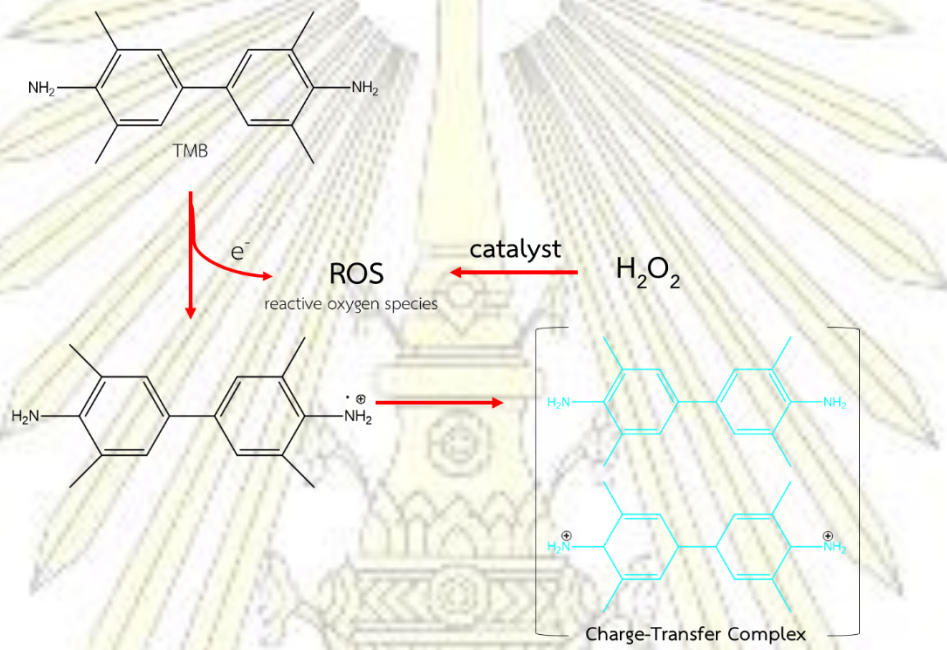

Figure 3.9 the mechanism of TMB detection on the decomposition of H_2O_2

The experiment was designed by mixing H_2O_2 (10 M, 1.2 mL) and TMB (3.5 mM, 1.2 mL). Then, a 50 µL of the mixture was dropped on the platinum black film and the virgin PDMS and observed the change of droplet color immediately. The change of droplet color from colorless to light blue indicated the catalytic activity of the material.

The droplet on the virgin PDMS substrate (Figure 3.10) expressed that the decomposition of H_2O_2 was not occurred. Compared with the droplet on the platinum black film (Figure 3.11), colorless droplet turned light blue within 4 minutes as shown in Figure 3.11C. Hence, the fabricated platinum black film showed catalytic activity.

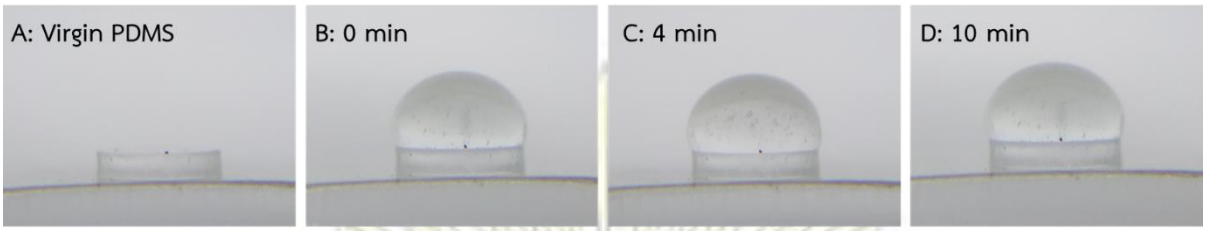

Figure 3.10 A: the virgin PDMS substrate and the droplet of H_2O_2 and TMB mixture on the substrate at B: 0 min, C: 4 min, and D: 10 min

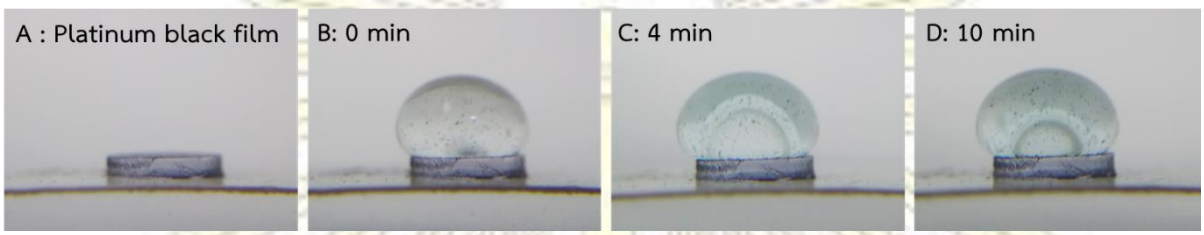

Figure 3.11 A: the platinum black film and the droplet of H_2O_2 and TMB mixture on the film surface at B: 0 min, C: 4 min, and D: 10 min

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Chapter 4

Conclusions

The platinum black film was fabricated from depositing the mixture of H_2PtCl_6, HCOONa in water, as a suspended droplet on the PDMS substrate. The reduction of $PtCl_6^{2-}$ produced platinum black particles and sequentially form a film structure on the PDMS surface. The platinum black particles formed the film structure with different patterns at 3 regions; the edge, the middle, and the center due to the induction of Marangoni flow. The average particle size is less than 620 nm. In addition, the fabricated film showed a catalyst activity with the decomposition of H_2O_2.

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Vitae

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