EFFECT OF CARBON PRETREATMENT AND PREPARATION METHOD ON ALCOHOL ELECTROOXIDATION OF Au/C CATALYST

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Abstract

For direct alcohol fuel cells, both anodic and cathodic reactions are equally important especially for high molecular weight alcohols like glycerol and ethylene glycol. In this research, the production of Au/C catalysts for alcohol electrooxidation in alkaline solution was focused by studying the effect of carbon pretreatment and catalyst preparation methods on the electrocatalytic activity of the prepared catalysts. Carbon pretreatment used in this work was heat treatment at 600 °C for 30 minutes, and loading of Au on the carbon support was prepared by polyvinyl alcohol (PVA) and citrate protection methods. The amount of Au on carbon was varied at 20, 30 and 40 wt%. The influence of carbon pretreatment was conducted with 20 wt% Au catalyst. The amount of Au adsorbed on carbon was determined from the amount of the Au left in the filtrate after immobilization step by using Atomic Absorption Spectroscopy (AAS). The average particle size and size distribution of Au on carbon were analyzed by Transmission Electron Microscopy Microscopy (TEM). The catalytic activity and stability of the prepared catalysts were characterized by conducting Cyclic Voltammetry (CV) and Chronoamperometry (CA), respectively. For 20 wt% Au/C, all Au metal was totally deposited on carbon for both PVA and citrate protection methods. However, at higher Au loading, there was some Au precursor left in the solution and the maximum Au loading obtained the PVA and the citrate protection methods was about 27 and 37 wt%, respectively. For the effect of carbon pretreatment, it was found from TEM images that the average Au particle size on treated carbon was smaller than that on untreated carbon. This is due to the enhancement of carbon surface area by heat-treatment. As a consequence, the catalytic activity of Au/treated C was higher for both catalyst preparation methods. When the amount of Au loading increased, the average Au particle size became bigger because of the agglomeration of Au particles. This led to a reduction of catalyst activity. In comparison between two methods of catalyst preparation, the Au/C catalysts prepared by the PVA protection method performed better in terms of activity and stability than that by the citrated one. The results of CA also confirmed that the carbon pretreatment not only enhanced the catalytic activity but also improved catalyst stability as observed from the lower decaying rate in the CV curves.

Keywords: Au/C Catalyst/ PVA Protection Method/ Citrate Protection Method/ Glycerol Oxidation/ Ethylene Glycol Oxidation

หัวข้อโครงการศึกษาวิจัย	ผลกระทบของการให้ความร้อนบนตัวรองรับ และ วิธีการเตรียมตัวเร่งปฏิกิริยา ที่มีต่อตัวเร่งปฏิกิริยา Au/C
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บทคัดย่อ

ปฏิกิริยาที่ขั้วแอโนดและขั้วแคโทดของเซลล์เชื้อเพลิงแอลกอฮอล์โดยตรงมีความสำคัญเท่ากัน โดยเฉพาะเมื่อใช้แอลกอฮอล์น้ำหนักโมเลกุลสูงเช่นกลีเซอรอลและเอทิลีนไกลคอลเป็นเชื้อเพลิง งานวิจัยนี้จะผลิต ตัวเร่งปฏิกิริยา Au/C สำหรับทำปฏิกิริยาอิเล็คโตรออกซิเดชันของแอลกอฮอล์ในสารละลายด่าง โดยมุ่งเน้นศึกษาผลกระทบของการปรับสภาพคาร์บอน และวิธีการเตรียมตัวเร่งปฏิกิริยาที่มีผลต่อความว่องไวของตัวเร่งปฏิกิริยานั้น การปรับสภาพคาร์บอนกระทำโดยการใช้ความร้อนที่อุณหภูมิ 600 องศาเซลเซียส นาน 30 นาที วิธีการเตรียมตัวเร่งที่ใช้ในงานวิจัยมีอยู่ 2 วิธีคือ การใช้โพลีไวนิลแอลกอฮอล์ (PVA) และซิเตรทเป็นตัวปกป้องซอล (sol) โดยมีการเปลี่ยนแปลงปริมาณตัวเร่งทอง (Au) ในปริมาณ 20%, 30% และ 40% โดยน้ำหนัก สำหรับการศึกษาของการปรับสภาพคาร์บอนจะทำการศึกษาโดยใช้ปริมาณ Au เท่ากับ 20% โดยน้ำหนักเท่านั้น

ในการหาปริมาณของ Au ที่ดูดซับบนคาร์บอนนั้นจะวิเคราะห์จากปริมาณ Au ที่เหลือในสารละลายหลังจากขั้นตอนการตรึง Au บนคาร์บอนโดยใช้เครื่อง Atomic Absorption Spectroscopy (AAS) ขนาดอนุภาคเฉลี่ยและการกระจายตัวของ Au บนคาร์บอนจะวิเคราะห์โดยใช้รูปถ่ายกำลังขยายสูงจากเครื่อง Transmission Electron Microscopy (TEM) ความว่องไวต่อการเร่งปฏิกิริยาและความเสถียรของตัวเร่งปฏิกิริยาจะถูกวัดโดยเทคนิค Cyclic Voltammetry (CV) และ Chronoamperometry (CA) ตามลำดับ ผลการทดลองพบว่า ในกรณีของ 20% โดยน้ำหนัก ตัวเร่งทอง (Au) ทั้งหมดสามารถตรึงอยู่บนคาร์บอน แต่เมื่อต้องการเพิ่มปริมาณ Au ให้สูงกว่านี้ พบว่าปริมาณ Au สูงสุดที่ตรึงบนคาร์บอน

โดยวิธีการเตรียมแบบใช้โพลีไวนิลแอลกอฮอล์ และซิเตรทมีค่าสูงสุด 27% และ 37% โดยน้ำหนักตามลำดับ

สำหรับอิทธิพลของการปรับสภาพคาร์บอน พบว่าคาร์บอนที่ผ่านการปรับสภาพให้ขนาดเฉลี่ยของ Au ที่เล็กกว่าคาร์บอนที่ไม่ผ่านการปรับสภาพ ที่เป็นเช่นนี้เป็นเพราะการเพิ่มขึ้นของพื้นที่ผิวของคาร์บอนภายหลังการให้ความร้อน ส่งผลให้ความว่องไวของตัวเร่งปฏิกิริยาที่เตรียมจากทั้ง 2 วิธีข้างต้นดีขึ้น เมื่อปริมาณของ Au เพิ่มขึ้น ค่าเฉลี่ยของขนาดอนุภาค Au จะใหญ่ขึ้น เป็นเพราะการรวมตัวกันของอนุภาค Au ซึ่งนำไปสู่การลดลงของค่าความว่องไวของตัวเร่งปฏิกิริยา ในการเปรียบเทียบระหว่างการเตรียมตัวเร่งปฏิกิริยาทั้ง 2 วิธี พบว่าตัวเร่งที่เตรียมจากวิธีการใช้โพลีไวนิลแอลกอฮอล์มีประสิทธิภาพสูงกว่า วิธีการใช้ซิเตรททั้งในด้านความว่องไวและความเสถียร การศึกษาของ Chronoamperometry ช่วยยืนยันถึงอิทธิพลการปรับสภาพคาร์บอนด้วยความร้อนว่าช่วยเพิ่มความว่องไวและความเสถียรให้กับตัวเร่งปฏิกิริยา Au/C

คำสำคัญ : ตัวเร่งปฏิกิริยา Au/C/ วิธีโพลีไวนิลแอลกอฮอล์โพรเทคชัน / วิธีซิเตรทโพรเทคชัน / กลีเซอรอล ออกซิเดชัน/ เอทีลีนไกคอล ออกซิเดชัน

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CHAPTER 1 INTRODUCTION

1.1 Introduction

At present, the renewable energy and environment is increasingly important. Consequently, the fuel cell technology and alternative fuels are produced such as ethanol, biodiesel. A fuel cell is an electrochemical cell that directly converts a source fuel into an electric current. The diagram of a simple fuel cell is shown in Figure 1.1. Fuel cell generates electricity inside a cell through electrochemical reactions between a fuel and an oxidant.

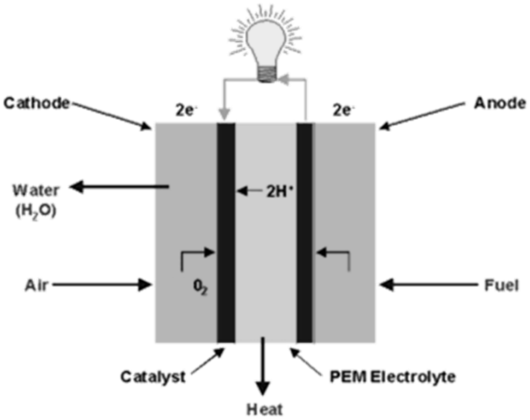


Figure 1.1 Schematic diagram of a simple fuel cell

The electrochemical reactions in fuel cell are important process including oxygen reduction at the cathode and fuel oxidation at the anode. The attractive alcohol fuels are methanol, ethanol, ethylene glycol and glycerol. Glycerol is a by-product of the biodiesel production, thus glycerol should be increased its value by using as fuel in fuel cell. The glycerol oxidation is catalyzed by many metals. In general, the classical oxidation catalyst is platinum. It is most widely used catalyst in fuel cells. However, because of platinum rareness on earth and consequent high cost, substitution of platinum by other catalysts has been widely studied. Gold based catalysts have been identified as candidate materials.

From the preliminary tests [1], gold on carbon appeared to be a great alternative with respect to classic systems. It has been found that a simple, monometallic catalyst was able to operate several times without showing deactivation and very selective when polyhydroxylated molecules were used as the substrates.

There are many previous works studying about oxidation reaction over carbon supported gold catalyst. Study of gold in catalysis has attracted a wide range of interest from laboratory research to industrial development aspects. N. Dimitratos et al. [2] reported that the effect of preparation method and different reduction method has a crucial effect on oxidation state of Au and on gold particle dimension in consequence on the catalytic behavior in the liquid phase oxidation of glycerol. S. Strbac et al. [3]

reported that the catalytic performance of the gold electrodes was markedly to depend markedly on the size of the gold particles.

For this work, the effects of carbon treatment and catalyst preparation methods including PVA protection and citrate protection were studied and investigated for improving the electrocatalyst properties.

1.2 Objectives

1. To study the effect of heat treatment of carbon on Au/C catalyst properties.
2. To study the effect of Au/C catalyst preparation methods (PVA protection and citrate protection) on Au/C property.

1.3 Scopes of work

1. The Au/C catalysts containing 20%, 30% and 40 % wt of Au were prepared by using the PVA protection method and citrate protection method.
2. For the catalyst characterization, three techniques were used including cyclic voltammetry (CV), chronoamperometry (CA), TEM and AAS.

1.4 Expected results

More uniform dispersion and high activity of Au/C catalyst could be obtained by using different catalyst preparation methods and the influence of heat treatment on carbon of Au/C catalyst was explored or was investigated.

CHAPTER 2 THEORY AND LITERATURE REVIEW

2.1 Catalyst Preparation

The method of preparation strongly influences catalyst particle size. Furthermore, the size of gold particles is a very important parameter in obtaining highly active catalysts for many reactions. There are many methods of catalyst preparation which are described as follows [4].

2.1.1 Impregnation

This method is the simplest method which can be used with any support. The precursors often used are chloroauric acid ($HAuCl_4$) and gold chloride ($AuCl_3$). The oxide supports are used including silica, alumina, magnesia, titania and ferric oxide. This preparation method lead to large gold particles (10-35 nm) even for low gold loading (1-2 wt%), and poor catalyst activity.

2.1.2 Coprecipitation

Gold catalysts prepared by coprecipitation could be loaded on various oxides namely α–Fe_2O_3, NiO and Co_3O_4. This method leads to high gold dispersion and larger oxide surface area than that in the absence of gold. It is a single step method and easy to carry out. However, some of Au particles can be embedded in the bulk of support. One of the most widely studied materials made by this method is gold on iron oxide.

2.1.3 Deposition-precipitation

The method is commonly referred to deposition-precipitation, because metal hydroxide is precipitated on oxide support. It has been widely used for preparing oxide-supported gold catalysts having small particle size. A typical preparation method is as follows, adding the support to an aqueous solution of $HAuCl_4$ hydroxide or carbonate, then stirring under heating for 1 hour. Next the product is washed with water, dried and calcined in air.

2.1.4 Preparation of Gold Catalysts on Specific Supports: Gold on Carbon Supports

The previous methods are not suitable for obtaining small gold particles on activated carbon because of reducing nature of the carbon. That limits the deposition of gold in a dispersed state. Carbon is a very suitable support for gold in liquid-phase oxidation of organic compounds. Immobilization of gold colloid on carbon has been developed by using polyvinylalcohol (PVA) and polyvinylpyrrolidone (PVP) as stabilizers, particles 6-8 nm in size being obtained. Other stabilizers have proved effective. For use in liquid-phase reactions, removal of the stabilizer is unnecessary.

Thus, the stabilization of gold colloid on carbon by using stabilizers is suitable for preparing Au/C catalyst. The stabilization of colloid is described below.

2.2 Stabilization of Colloidal Metal Particles

Metal particles cannot stabilize in dispersing medium since small metal particles tends to agglomerate to form a bulk. Due to short interparticle distances, the particles would be attracted to each other by van der Waals forces leading to a coagulation of metal particles. The counteraction can be provided by the stabilizer [5]. There are two main classes of stabilizers, which are electrostatic stabilizer and steric stabilizer [6]. These modes of stabilization will be discussed in separate sections below.

2.2.1 Electrostatic stabilizer

The theory of electrostatic colloidal stabilization is described by using Derjaugin, Landau, Verwey, and Overbeek theory (DLVO theory) [6]. Colloidal stabilization is based on a balance of interparticle forces between repulsive Coulombic forces and attractive van der Waals forces. This theory is used for the system with weak or no interactions between colloid and solvent that so called lyophobic colloids-colloids.

The electrostatic stabilizers are the anions which are added to the solution as shown in Figure 2.1. Colloidal particle will be bound by anion. Then anions form a layer adjacent to the particle that leading to Columbic repulsion between other particles, now anionically charged particles. This Columbic repulsion will prevent particle agglomeration. Cations are also present to provide charge balance and complete the electronic multilayer while monoanions such as halides ion sometimes are closet. The examples of electrostatic stabilizer are trisodium citrate, tetrakishydroxypropylphosphonium chloride (THPC) and tetrahydrofuran (THF) etc.

The limitations of DLVO theory are that it is not designed to account for counterions with multiple charges and it is not appear to work well in more concentrated system where dispersion force may dominate the electrostatic forces.

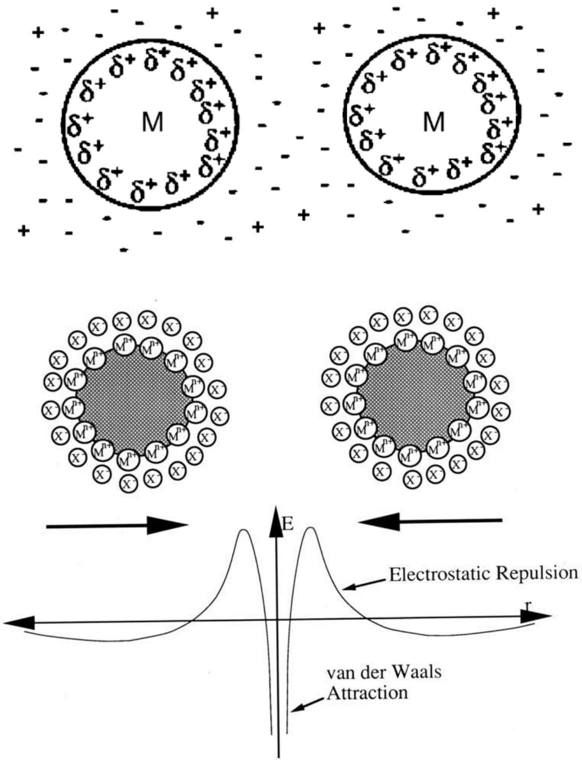


Figure 2.1 Electrostatic stabilization of metal colloid particles [5-6]

2.2.2 Steric stabilizer

There are many types of steric stabilizer namely polymer, siloxane polymers, dendrimers, microgels, alkanethiol (and other) surfactants, resorcinarenes, amines and phosphines and branched polymer [6]. For this work, the polymer was used as the steric stabilizer, thus only polymer type will be described below.

Polymers are mostly used as the steric stabilization. The molecules of polymer are adsorbed by the colloidal particles. The polymers stabilize not only at least in part by ligation of colloid surface, but also by occupying space around the colloid. These lead to discourage the contact between the colloids to prevent the agglomeration.

One model of polymer stabilization is written as if one polymer chain stabilizes one nanocluster as shown in Figure 2.2 (a) while Talylor dispersion indicates that one polymer chain can attach to multiple nanoclusters as displayed in Figrue 2.2 (b).

Colloids or nanocluster of transition metal have been prepared by a variety of polymer such as polyvinylpyrrolidone and polyvinyl alcohol. PVA polymers in nanocluster system have the potential to serve as both the reductant of the organometallic complex and the nanocluster stabilizer.

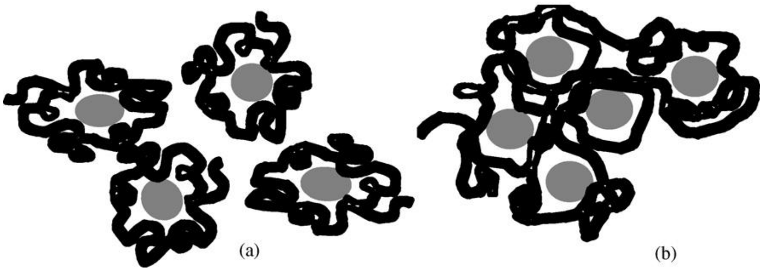


Figure 2.2 Two possible polymer stabilizer (a) colloid with individual polymer chains (b) multiple colloids with single polymer chain [6]

2.3 Catalyst Characterization

2.3.1 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectrometry (AAS) is a spectroanalytical procedure for the qualitative and quantitative determination of chemical elements. This method applies the absorption of light by free atoms in the gaseous state. This technique is used for determining the concentration of a particular element in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or in solid samples. The atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The analyte concentration is determined from the amount of absorption.

2.3.2 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a well known technique for imaging solid materials at atomic resolution. TEMs are a major analysis method in a range of scientific fields, in both physical and biological sciences. This technique uses a beam of electrons. It is transmitted through a thin specimen, interacting with the specimen as it passes through. An image is formed from the interaction of the electrons transmitted through the specimen. TEMs are capable of imaging at a significantly higher resolution than light microscopes because of the small de Broglie wavelength of electrons. For this work, TEM technique is used to determine particle size and size distribution of gold particles deposited on carbon support.

2.4 Electrooxidation of catalyst in alcohol

2.4.1 Cyclic voltammetry (CV)

Cyclic voltammetry (CV) is the most widely used to perform electrochemical technique. CV has been used for studying such as reaction analysis on an electrode surface and determining the electrochemical surface area (ESA) [7]. Generally, principle of the CV measurement is that the electrode undergoes a steady voltage potential sweep from low potential to high potential and resulting current generated at the electrode is measured. Normally, reference (RE), counter (CE) and working electrode (WE) are used in CV analysis. A typical CV of platinum electrode in an alkaline solution is shown in Figure 2.3.

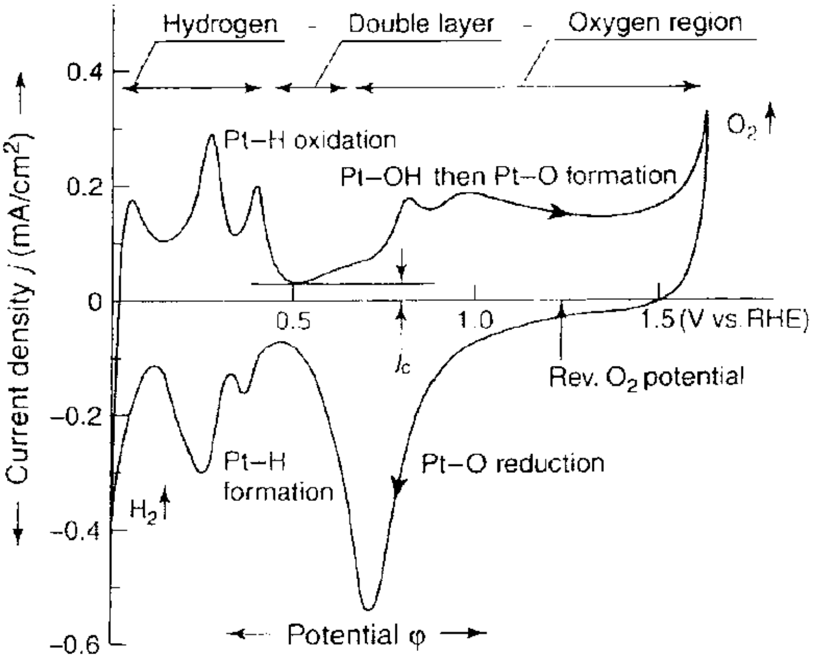


Figure 2.3 A typical CV of platinum electrode in alkaline solution [7]

At a low potential, it is the hydrogen oxidation region it contains several peaks which are the reaction flowers:

In alkaline solution:

$$Pt—H + OH^- \rightarrow Pt + H_2O + e^- \qquad (2.1)$$

While in acid solution:

$$Pt—H + H_2O \rightarrow Pt + H_3O^+ + e^- \qquad (2.2)$$

At higher potential, there is a double layer charging with no significant electrochemical reactions. Above ~800 mV the platinum oxidation takes place as the following reaction;

In alkaline solution:

$$\mathrm{Pt + OH^- \rightarrow \text{Pt—OH} + e^-} \tag{2.3}$$

$$\mathrm{\text{Pt—OH} + OH^- \rightarrow \text{Pt—O} + H_2O + e^-} \tag{2.4}$$

In acid solution:

$$\mathrm{Pt + H_2O \rightarrow \text{Pt—OH} + e^- + H^+} \tag{2.5}$$

$$\mathrm{\text{Pt—OH} + H_2O \rightarrow \text{Pt—O} + H_3O^+ + e^-} \tag{2.6}$$

At very high potential, the oxygen evolution reaction occurs as follows;

In alkaline solution:

$$\mathrm{4OH^- \rightarrow O_2 + 2H_2O + 4e^-} \tag{2.7}$$

In acid solution:

$$\mathrm{2H_2O \rightarrow O_2 + 4H^- + 4e^-} \tag{2.8}$$

After that the potential is then swept backward. The oxygen and Pt—O reduction reactions occur via the reversed reaction of (2.4) and (2.3) for alkaline solution and (2.6) and (2.5) for acid solution, respectively.

At the lower potential, hydrogen starts adsorbing on platinum via the following reactions;

In alkaline solution:

$$\mathrm{Pt + H_2O + e^- \rightarrow \text{Pt—H} + OH^-} \tag{2.9}$$

In acid solution:

$$\mathrm{Pt + H_3O^+ + e^- \rightarrow \text{Pt—H} + H_2O} \tag{2.10}$$

At very low potential, hydrogen evolution observed:

In alkaline solution:

$$\mathrm{2H_2O + 2e^- \rightarrow 2OH^- + H_2} \tag{2.11}$$

In acid solution:

$$\mathrm{2H_3O^+ + 2e^- \rightarrow 2H_2O + H_2} \tag{2.12}$$

These are the reactions of platinum electrode in CV. The main reactions in CV are the platinum oxidation (reaction of (2.3)-(2.4) or (2.5)-(2.6)) on the positive sweep, and the oxygen and Pt—O reduction (reversed reaction of (2.4)-(2.3) or (2.6)-(2.5)) on the negative sweep. For the reaction of gold in CV, it will be described in literature review.

Additionally, Electrochemical Surface area (ESA) can be determined by CV technique. ESA is used to describe the efficiency of catalyst on electrode. To calculate the ESA, the area of current versus time plot during the reduction peak in CV is used to determine the total charge per superficial electrode area. Then the value of charge is divided by the total catalyst loading and a proportionality constant for a given catalyst to obtain the ESA value.

$$\mathrm{ESA}=\frac{\int I(t)dt}{S\cdot C} \quad (m^2/g_{\mathrm{catalst}}) \qquad (2.13)$$

where S is a proportionality constant that used to convert the charge per area to effective catalyst active area, i.e., 386 µC/cm^2 for gold and 210 µC/cm^2 for platinum. C is the loading of the catalyst in grams.

2.4.2 Chronoamperometry (CA)

Chronoamperometry is a technique in which the electrode is held at constant potentials for a long time. For CA, the average current over the time can be determined while for CV, current is considered at individual time. Additionally, it can be used to determine the stability of catalyst on electrode on the length of time by calculating the slope of current versus time plot.

2.5 Literature review

J. Thepkaew, et al. [8] studied the effect of carbon support pretreatment on PtSn/C performance. Pretreatment of carbon support comprises of acid (HNO_3) and thermal treatments. The results show that after pretreatment, the specific surface area of carbon increases from 193 m^2/g to 202 m^2/g and 265 m^2/g for chemical treatment and thermal treatment, respetively. In addition, thermal treatment can generate more micro pores leading to a reduction of average pore radius. The reduction is attributed to the removal of inorganic matter and less stable oxygen complexes on the support surface at high temperature.

L. Prati, et al. 1999 [9] found that Au/C catalysts are a good catalyst for liquid-phase oxidation of ethane-1,2-diol (ethylene glycol). This catalyst resist to poisoning. They prepared the Au/C catalysts by deposition-precipitation and supported metallic sol methods. They found that deposition-precipitation method not suitable for Au/C preparation because it gives large aggregate of gold. For the supported metallic sol method, they used PVA as the protective agent. They prepared catalyst by using $HAuCl_4$ as the precursor, fixing the PVA/Au ratio at 0.62 (wt/wt) and $NaBH_4$/Au at 4 (mol/mol) to ensure the complete reduction of Au(III) to Au(0). The results show that gold particles well disperse on carbon support and high catalyst activity in liquid-phase oxidation of ethane-1,2-diol. They also found that the particles size about 7-8 nm gives the maximum activity, with larger and smaller particle sizes being less active and less selective.

F. Porta, et al. [10] studied about selective oxidation of glycerol to sodium glycerate with gold-on-carbon catalyst. They used different catalyst preparation methods (incipient wetness, impregnation, sol immobilization) and different supports (active carbon, graphite, and carbon black). The mean Au particle dimension was determined by using XRPD and HRTEM and the surface exposition for each catalyst was obtained from XPS. The catalysts prepared via sol immobilization (PVA, THPC), typically constituted by 4-5 nm of well-dispersed gold nanoparticles show the highest activity. These catalysts have small particle size and are characterized by good surface exposition, with corresponding higher activity.

DiScipio, et al. [11] prepared the colloidal gold particles by using PVA as the protective agent. They studied the effect of reducing agent type including sodium borohydride and sodium cyanoborohydride on Au particle size. They found that different reducing agent could generate different Au particle sizes. The results showed that the particle size of gold reduced by sodium borohydride could be either small size (20 A°) or large size (300 A°) depending on the initial concentration of tetrachloroauric acid. By using cyanoborohydride as the reducing agent, the medium size of gold particle (100 A°) was obtained. Additionally, they found that the temperature is not a major factor for producing gold particles of different size.

F. Porta, et al. [12] conducted experiment to synthesize sol by using different types of auric precursors ($AuCl_3$, $NaAuCl_4$ and $HAuCl_4$), the reducing agents ($H_2C_2O_4$, $SnCl_2$ and $NaBH_4$) and the stabilizing compounds (PVA and PDDA). Then the prepared catalysts were tested in the liquid-phase oxidation of ethylene glycol to glycolate. Firstly, they found that the type of gold precursors was not affect the final gold catalyst activity. The effect of reducing agent on the size and size distribution of particles was very high. $H_2C_2O_4$ and $SnCl_2$ were not useful for generating good catalysts for liquid-phase oxidation. The increasing molar ratio of the reducing agent ($NaBH_4$) to Au results in decreasing the Au particle size. Finally, the amount of the protective agent is also important for the immobilization on carbon The results show that a lower amount of protective agent produced more active catalysts which contradicts with the results of L. Pratt 1999 [9]. The increasing in catalytic activity appeared to be very high because of a decrease in mean size diameter and a lack of drawback of shielding the metal particle by the protective agent (PDDA).

S. Biella, et al. [13] found that the controlling factor of gold particle size on carbon support was not the total amount of $NaBH_4$ but the kinetics of metal sol formation which is depend on the $NaBH_4$ addition: in one step or in portions. The results show that the Au/C catalyst by dropwise $NaBH_4$ addition gives the highest activity although the particles size is the same with others. Thus they also concluded that the catalyst activity was not ruled only by the dimension and the exposure of gold.

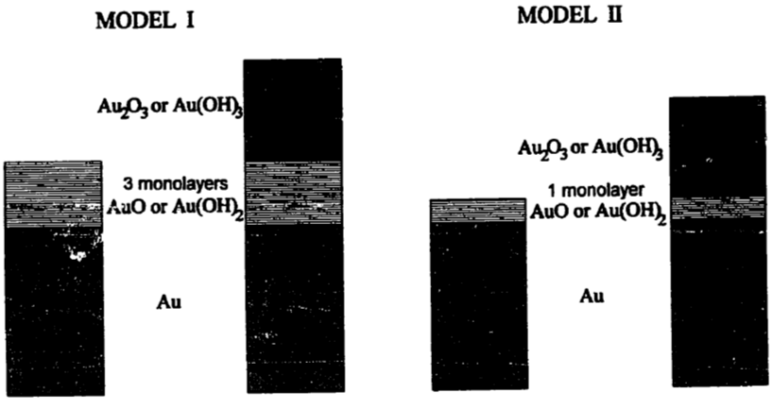
W. Chen, et al. [14] prepared the Au/C catalyst by PVA protection method and pre-precipitation method. Then, the electrochemical activities of these catalysts were measured. The results show that the catalyst prepared with the PVA protection method gives the current density of oxygen reduction more than that prepared with the pre-precipitation method, demonstrating the higher electrocatalytic activity of catalyst obtained from the PVA protection method. This is due to the small average size and low relative crystallinity of the Au particles in the Au/C catalyst prepared by the PVA protection method.

T. Inasaki, et al. [1] investigated the influence of cluster size of Au catalysts on the kinetics of oxygen reduction reaction (ORR) in acidic medium. They prepared gold nanoparticles by using triphenylphosphine-protected gold sol and citrate-protected gold sol. For the citrate protected gold sol, two different types of reducing agents, citrate itself and $NaBH_4$ were used with controlled solution temperature at 70°C and 0°C, respectively. Then the catalyst was characterized by TEM and measured the electrochemical activity by using CV technique in acid solution. It was found that the Au particle size and its size distribution depend on the catalyst preparation method. The triphynylphosphine-protected gold sol provided the smallest Au particle with nearly monodispersed size distribution, while the citrate-protected gold sol gives larger Au particles and broader size distribution. The particle size of the Au/C catalyst reduced by $NaBH_4$ was smaller than that reduced with citrate but both have same size distribution. For Au/C catalysts with smaller Au particle sizes, the cathodic peaks at 0.94 V, corresponding to Au oxide reduction reaction were larger than those for the Au/C catalysts with larger Au particle size, because of higher surface area of the smaller particles. In addition, the activity of the 2-step 4-electron reduction was higher when the size of Au particles was less than 3 nm.

N. Dimitratos, et al [2] studied about the effect of catalyst preparation method (deposition-precipitation versus sol immobilization) and reduction method (calcinations versus chemical reduction) on Au/TiO_2 catalysts for the liquid phase oxidation of glycerol. It was found that not only the choice of the reduction method but also the use of protective agents (PVA, THPC) for stabilization of the gold colloid could affect the activity of the prepared catalyst. It was found that the catalytic activity is shown to be dependent not only on the choice of the reduction method but also on the use of protective agent (PVA, THPC) for the stabilization of the gold colloids. When a low temperature chemical reduction was employed on a Au/TiO_2 sample synthesized by the deposition-precipitation method, the highest activity was obtained. The use of a higher pre-treatment temperature or a protective agent resulted in a lower activity.

G. Tremiliosi-Filho, et al. [15] proposes the possible model of gold oxide formation on electrode. They explained that thick oxide film which occurred by potentiostatic polarization of Au electrode comprise four oxide states namely OC1, OC2, OC3 and OC4. The OC1 state is the first feature in the oxide reduction profile and it slowly grows to a limiting thickness while the OC2, OC3 and OC4 states rapidly grow without the limitation thickness. OC1 state corresponds to development of quasi-2D state and very initial growth of the OC2 state, and the oxide growth is slow. Further growth of OC2 and formation of OC3 and OC4 state is significantly faster as shown in Figure 2.4. They defined the inner layer as α and outer layer as β. The α film corresponds to the

OC1 state while the β film corresponds to OC2, OC3 and OC4 state. The OC1 state (α film) reaches a limiting thickness of 3 monolayers of AuO or $Au(OH)_2$ in acid solution and 1 monolayer of AuO or $Au(OH)_2$ in base solution. For OC2, OC3 and OC4 states (β film) occur at outer oxide film having the Au_2O_3 or $Au(OH)_3$ without the thickness limit.



(a) (b)

Figure 2.4 (a) Model I: model of thin and thick Au oxide films formation in acid solution, (b) Model II: model of thin and thick Au oxide film formation in base solution [15]

L D Burke, et al. [16] explain the reactions of gold oxide formation/reduction which occur in electrode by CV technique. Commonly, feature of monolayer oxide formation/reduction is hysteresis. Hysteresis is the difference of potential range for monolayer oxide formation in the positive sweep as compared with that for monolayer oxide reduction in the negative sweep. Hysteresis in the monolayer oxide formation is attributed to gradual changes in the nature of the oxide film. The dipolar ($Au^{\delta+}$—$OH^{\delta-}$) species are produced which at appreciable coverage, repel one another. Repulsion energy raises the energy required to generate additional dipoles; thus there is an increase in potential with increasing coverage. These lead to an extended of plateau rather than a sharp peak in positive sweep in Figure 2.5. Then, rotation of some of the surface dipoles (referred to as place-exchange) occurs, and then relieves much of the lateral repulsion or stress in the surface layer as shown in Figure 2.6. Therefore no electrostatic cathodic peak is observed (see Figure 2.5).

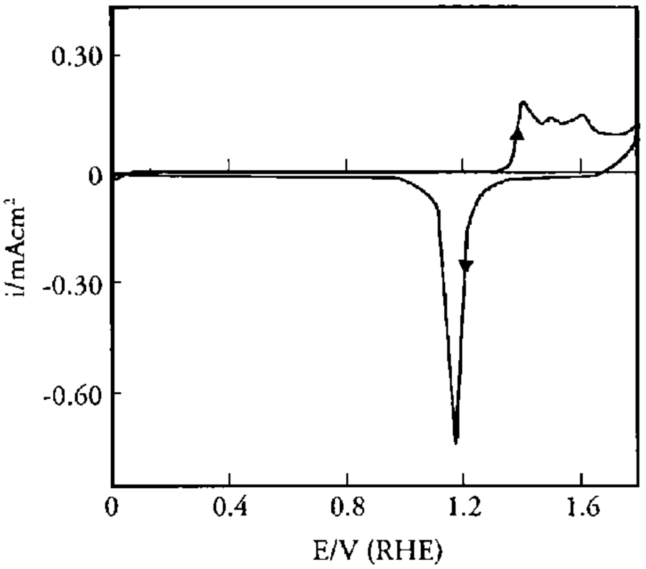


Figure 2.5 Typical CV for a poly crystalline gold disc electrode in acid solution [16]

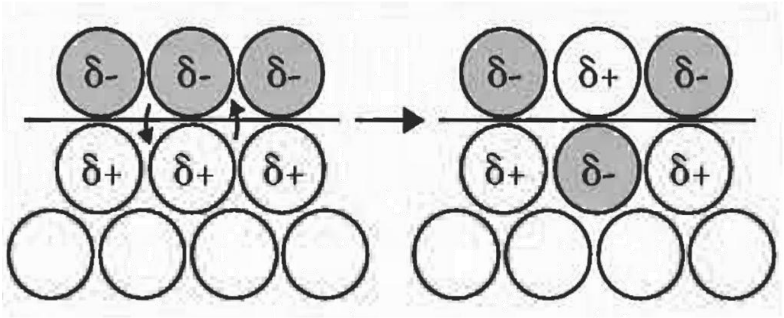


Figure 2.6 Place-exchange reaction involved in a monolayer oxide formation, unshaded circle defined as the metal atoms and shaded circles defined as adsorbed oxygen species [16]

Additionally they explain that there is another factor, related to change in the activity of surface metal atoms, that may contribute to the hysteresis effect. There are three state of gold atom including (i) bulk lattice atoms (Au^0) which have little relevance to the reaction at the surface, (ii) regular surface atoms (Au*) which are more active than those in the bulk atom and (iii) displaced surface atoms (Au**) which are in a state of higher activity as these are generated initially in a state of unusually low lattice coordination number on reduction of the partially place-exchanged surface oxide. The (iii) state of gold atoms is assumed to rapid change to the (ii) state.

According to the hysteresis, the Figure 2.6 can be used to describe in terms of the reaction. When considered the reaction in Figure 2.7, it can be seen that these reaction corresponds to the reaction of platinum oxidation and reduction in acid solution from reaction 2.5 and 2.6.

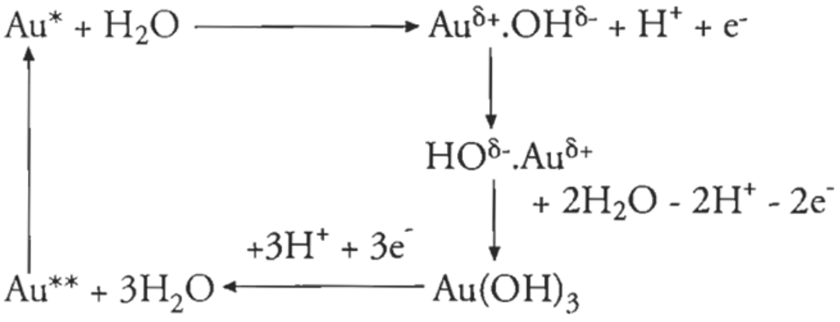


Figure2.7 Schematic of reaction of gold electrode [16]

T. C. Wen, et al. [17] compared the pure gold and gold deposited on titanium electrode by using CV techniques. They found that gold deposited on titanium gives higher current than pure gold because of crystalline structure. Pure gold had a perfect crystalline structure than the gold deposited on titanium which has the porous structure so that OH/H_2O can easily penetrate to the inner layer. Additionally, they found that the gold state (Au^{III}; after one monolayer) was not helpful in the oxidation because the surface saturations of OH/H_2O on gold resists the movement of alcohol molecules into the reactive region.

H. Erikson, et al. [18] studied the electrochemical reduction of oxygen on Au/C catalyst by varying amount of Au (20 wt% and 30 wt%). The results showed that the 20wt% Au of Au/C catalyst gives higher activity for oxygen reduction activity than 30wt% Au that corresponds to the particle size of catalyst. The 20wt% Au of Au/C catalyst had smaller Au size than the other.

CHAPTER 3 METHODOLOGY

There are three main steps that were to executed to accomplish this work which are catalyst preparation, catalyst characterization and electrooxidation activity test of the prepared catalysts in two types of alcohol (glycerol and ethylene glycol). The steps of each catalyst preparation were started with carbon heat treatment and metal loading on carbon by PVA protected and citrate protected gold sol preparation. After that the catalysts were characterized to determine the metal particle size. Then the catalysts were tested for activity by performing electrooxidation of the alcohol. This chapter presents the detail of each step.

3.1 Catalyst Preparation

First, the effect of heat treatment on carbon support was studied by comparing the 20 wt% of Au on untreated carbon with that on heat treated one. Secondly, a series of Au/C catalysts were prepared by varying Au loading at 20%, 30% and 40% wt for both protected gold sol preparation methods. The steps of each catalyst preparation were described below.

3.1.1 Pretreatment of Carbon support

Approximately 1 g of Vulcan XC-72R carbon black was transferred into ½″ stainless steel tube which had been packed with a small amount of quartz wool at the bottom. Then N_2 gas was flowed through the tube at a flow rate of 30 ml/min. The reactor temperature was set at 600°C and hold at this temperature for 30 min. After the reactor was cooled down to room temperature, the heat treated Vulcan XC-72R carbon black was collected.

3.1.2 PVA Protection Method

The solution of 110 µg/ml of $HAuCl_4$ and 2% wt PVA with respect to gold weight were prepared [9]. The 0.1 M of $NaBH_4$ solution was dropped dropwise very slowly under vigorous stirring. After 15 minutes, an ethanol dispersion of the heat treated or untreated Vulcan XC-72R carbon black was added with the required proportion (60%, 70% and 80% wt) and kept stirring for 3 hours. Then the mixture was filtered. The catalyst was washed thoroughly with deionized water for several times and then washed with ethanol. Lastly it was dried in vacuum oven at 70 °C for 30 minutes to give Au/C catalyst by PVA protection method.

3.1.3 Citrate Protection Method

An aqueous $HAuCl_4$ solution of 55 µg/ml cooled to 0 °C was added with an aqueous tripotassium citrate of 11 mg/ml. After 5 minutes, a mixture of triprotassium citrate (44 mg) and $NaBH_4$ (0.0189 mg) in H_2O (4 ml) was slowly dropped to the solution under vigorous stirring[1]. Then the mixture was kept stirring for 15 minutes. The heat treated or untreated Vulcan XC-72R carbon black in ethanol was added into the mixture and stirred for 3 hours. Next the mixture was filtered, washed with deionized water for several times and then washed with ethanol. Finally, it was dried in vacuum oven at 70 °C for 30 minutes to give Au/C catalyst by citrated protection method.

3.2 Catalyst Characterization

After Au/C catalysts were obtained, they were checked by Atomic Absorption Spectroscopy (AAS) and Transmission Electron Microscopy (TEM).

3.2.1 Atomic Absorption Spectroscopy (AAS)

AAS was used to measure the amount of Au that was left in the filtrate (mg/l) after immobilization step. This information was then utilized to determine the amount of Au deposited on carbon support. AAS was performed at the Department of Science Service (DSS), Ministry of Science and Technology.

After the concentration of Au in the filtrate from AAS analysis ($AAS_{results}$;mg/l) was obtain, the amount of Au remained in the filtrate ($Au_{filtrate}$;mg) was determined by using equation of 3.1.

$$\mathrm{Au_{filtrate}} = \mathrm{AAS_{result}} \times (\mathrm{Total\ filtrate\ volume\ ;\ ml}) \quad (3.1)$$

After $Au_{filtrate}$ was known, the amount of Au deposited on carbon support ($Au_{support}$;mg) was estimated by using equation 3.2. In equation 3.2, Au_{total} is the total amount of Au used in the catalyst preparation (mg).

$$\mathrm{Au_{total}} = \mathrm{Au_{support}} + \mathrm{Au_{filtrate}} \qquad (3.2)$$

$Au_{support}$ was then used to calculate the percentage of Au deposited on carbon support by using equation 3.3. In equation 3.3, S is the weight of carbon support (mg).

$$\%\mathrm{Au_{deposited}} = \frac{\mathrm{Au_{support}}}{(\mathrm{Au_{support}} + \mathrm{S})} \times 100 \qquad (3.3)$$

3.2.2 Transmission electron microscopy (TEM)

TEM is a technique to determine particle size and size distribution of Au on carbon support. Images of TEM technique were captured at the National Metal and Materials Technology Center (MTEC). The average size and particle size distribution were obtained by counting onto the micrographs at least 500 particles. The source of electron beam was used at 200KeV and the size of Au was measured from TEM image at magnification of 100,000x.

3.3 Electrooxidation experiments

The catalyst activity was measured by performing electrooxidation of two types of alcohols, glycerol and ethylene glycol in basic solution. Cyclic Voltammetry (CV) and Chronoamperometry (CA) techniques have been used in this investigation. Since we aimed to investigate the suitable catalyst for electrooxidation of high molecular wight alcohols, glycerol and ethylene glycol were used to test the catalytic activity.

3.3.1 Cyclic Voltammetry (CV*)*

This technique was used to determine the electrochemical surface area (ESA) and catalyst activity of Au/C catalyst in alcohol oxidation. The procedure of alcohol oxidation was divided into two main sections, glycerol and ethylene glycol oxidation. However, for both alcohols oxidation, the first step was the ESA determination as described below.

3.3.1.1 Electrochemical Surface Area (ESA)

Electrolyte was prepared by 40 ml of 0.1 M KOH which was saturated with nitrogen gas for 30 minutes to remove dissolved oxygen. Then working electrodes were prepared by ultrasonically dispersing the synthesized catalyst in a solution of 5 wt% Nafion ionomer and isopropanol for 1 hour. Then a 2.85 µL of the suspension was dropped on a 6 mm glassy carbon for 4 times. A gold gauze and a mercury/mercury oxide were used as counter and reference electrodes, respectively. All three electrodes were immerged into the electrolyte solution. The potential was scanned between -0.8 V and 0.8 V at a scan rate of 20 mV/sec. The temperature of solution was controlled at 25 °C. The reduction peak of cyclic votammogram was used to determine the electrochemical surface area. Prior to the electrochemical measurement, the pretreatment of the Au/C electrodes was performed by repeating the potential scan in the range of -0.8 to 0.8 V VS Hg/HgO electrode until a reproducible constant CV characteristic was obtained.

3.3.1.2 Glycerol oxidation

The experimental work was performed with Au/C catalysts as working electrodes by loading the catalyst as mentioned above. The 40 ml of 0.1 M glycerol and 0.1M KOH solution was used as the electrolyte. This solution was purged with nitrogen gas for 30 minutes. The mercury/mercury oxide was used as the reference electrode while gold gauze was used as the counter electrode. The potential was scanned between -0.8 V and 0.8 V with a scan rate of 20 mV/sec. The working electrode was then electrochemically pretreated with the same manner as mentioned above.

3.3.1.2 Ethylene glycol oxidation

This step was the same as the step of glycerol oxidation but the electrolyte was replaced with the mixture of 0.1 M ethylene glycol and 0.1M KOH.

3.3.2 Chronoamperometry (CA)

Chronoamperometry technique was used to investigate the stability of the catalysts in different type of alcohol that was indicated by a decaying rate.

3.3.2.1 Chronoamperometry in glycerol

The working, reference and counter electrodes used in this experiment were the same as those in the CV technique. Chronoamperometric experiment was performed by holding the potential at either 0.2 V or 0.4 V for 45 minutes in the mixed solution of 0.1 M glycerol and 0.1M KOH.

3.3.2.2 Chronoamperometry in ethylene glycol

The procedure of chronoamperometry in ethylene glycol was the same as that in glycerol but the electrolyte was used was 0.1 M ethylene glycol and 0.1M KOH solutions instead.

CHAPTER 4 RESULTS AND DISCUSSIONS

4.1 Au deposition

In preparing 20 wt% of Au/C, the filtrate obtained after the immobilization step was cleared. On the other hand, for the case of 30 and 40 wt% of Au/C, the filtrate still had ruby-red color indicating that there was Au sol left in the solution. The adsorption of gold on carbon was then checked by AAs analysis of the filtrate.

Therefore, these filtrates were checked by AAs to determine the amount of Au which was deposited on carbon. The results of AAs are shown in Table 4.1. After obtaining the AAs results, the percentage of Au deposited on carbon support was calculated by using equation (3.1) to (3.3) in Chapter 3.

Table 4.1 Results of AAs and the percentage of Au deposition on carbon

Sample	AAs$_{\text{result}}$ (mg/L)	% Au$_{\text{deposited}}$
PVA method		
20% Au/ untreated C	n.d.	20.00
20% Au/ treated C	n.d.	20.00
30% Au/ treated C	11	27.81
40% Au/ treated C	48.2	27.35
Citrate method		
20% Au/ untreated C	n.d.	20.00
20% Au/ treated C	n.d.	20.00
30% Au/ treated C	0.47	29.80
40% Au/ treated C	5.9	37.11

n.d. = not detected at the detection limit of 2.0 ppm.

For 20 wt% Au/C catalyst, all of Au sol was adsorbed on carbon. However for 30 wt% and 40 wt% Au/C catalysts from both PVA and citrate methods, Au sol was not totally adsorbed on carbon. These results corresponded to the color intensity of solution observed in the catalyst preparation step.

For PVA protection method, at 30 wt% and 40 wt% Au, the percentage of Au deposition was approximately 27%. This indicated the maximum Au that could be adsorbed on carbon support. The reasons why Au sol remained in the solution were either the excessive amount of PVA or the saturation of Au adsorption on the carbon. In principle, PVA anchored with Au sol as organo-shell could prevent the agglomeration of Au particles. Since we controlled the PVA:Au ratio, the amount of PVA increased with increasing % Au. As a result of a large amount of PVA prevent in solution, active carbon could not adsorb these sol. Au sol still remained in the solution was probably caused either by the excessive amount of PVA or by the saturation of Au adsorbed on carbon. In other words, big organo-shell could interface with each other as well as with the support and inhibit the adsorption of sol on carbon surface.

For citrate protection method, at 30 wt% and 40 wt% Au, the percentage of Au deposition was more than 27 %. It shows that the Au deposition by the citrate protection method was higher than that of the PVA protection method.

4.2 Particle Size and Size Distribution from TEM image

The particle size and size distribution was evaluated from TEM image. TEM images of catalysts by PVA protection method are shown in Figure 4.1-4.4. Figure 4.1(a) shows TEM image of 20 wt% Au catalyst by PVA protection method on untreated carbon. From Figure 4.1(b), the average Au particle size of this catalyst was approximately 3.1 ± 0.8 nm. There is a few number of Au particles with a diameter larger than 3.5 nm that are bigger than 3.5 nm. That was about 10.25%.

TEM image of the 20 wt% Au catalyst by PVA protection method on treated carbon is shown in Figure 4.2(a). From Figure 4.2(b), it was found that the average Au particle size of this catalyst was about 2.7 ± 0.5 nm. The Au particle size of this catalyst was the smallest among the prepared catalysts. Most Au particle size of this catalyst was 2.5 nm. The number of Au particles with D_p > 3.5 nm was very small accounted for 1.87 %. By comparing this catalyst with the previous one, the treated carbon provided smaller Au particle size.

Figure 4.3(a) shows TEM image of 30 wt% Au catalyst on treated carbon. For Figure 4.3(b), the average Au particle size of this catalyst was about 3.2 ± 0.6 nm. Maximum population of Au particles of this catalyst had a diameter of 3.5 nm and there was about 10.42% of Au particle with a size over 3.5 nm. At 20 wt% Au, the number of Au particles with a diameter of 3.5 nm on the treated carbon was higher than that on the untreated carbon.

Lastly, Figure 4.4(a) shows TEM image of 40 wt% Au on treated carbon. From Figure 4.4(b), the average Au particle size of this catalyst was about 3.4 ± 0.7 nm. The Au particle size and distribution of 40 wt% /treated C was similar to that of 30 wt% Au /treated C, except that the number of Au particle with a size over 3.5 nm of 40 wt% /treated C became relatively greater than that of 30 wt% Au /treated C (23.45% compared to 10.42%, respectively). It indicated that the increase of Au loading promoted the catalyst agglomeration.

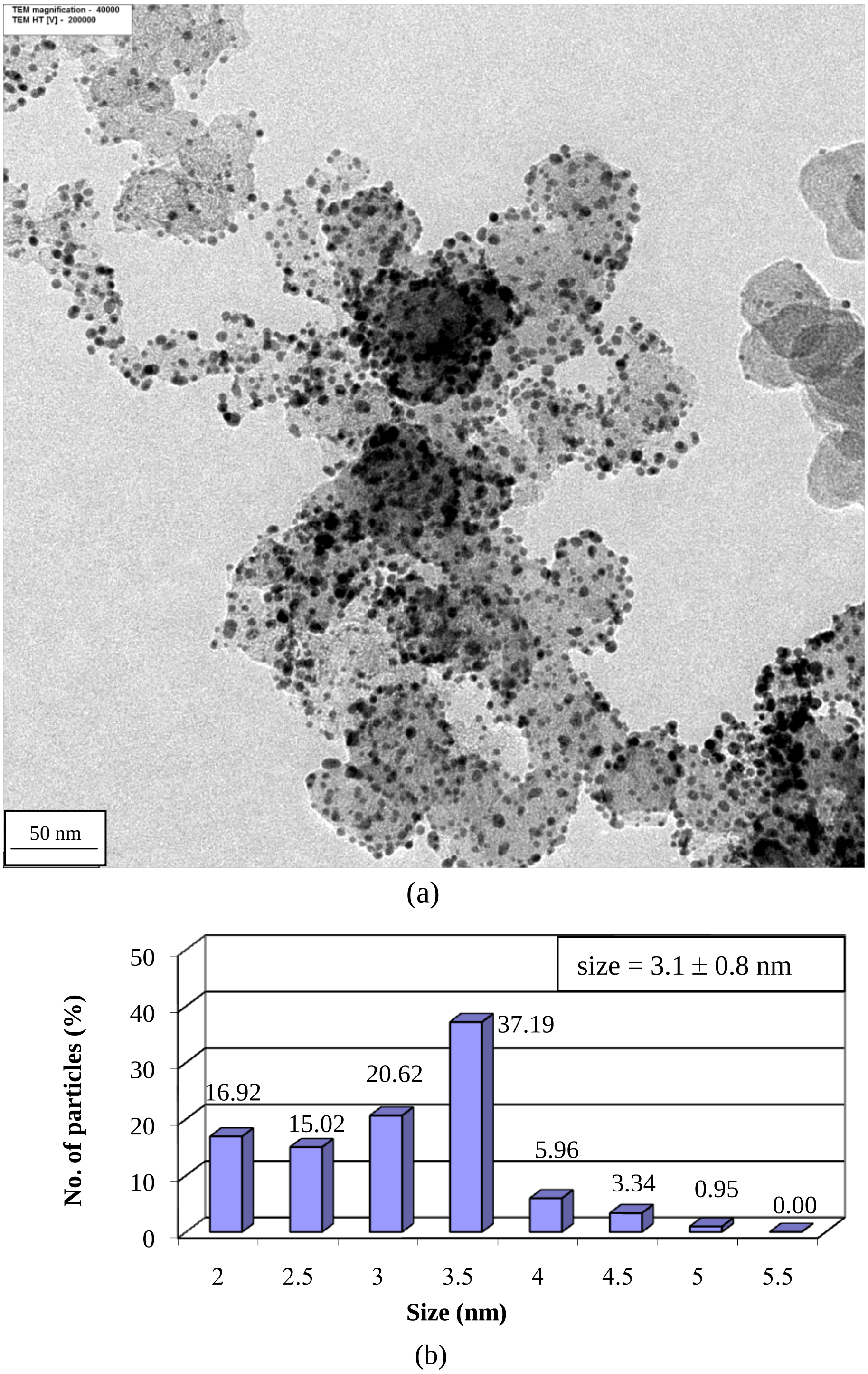


Figure 4.1 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 20% Au prepared by PVA protection method on untreated Vulcan XC-72R carbon

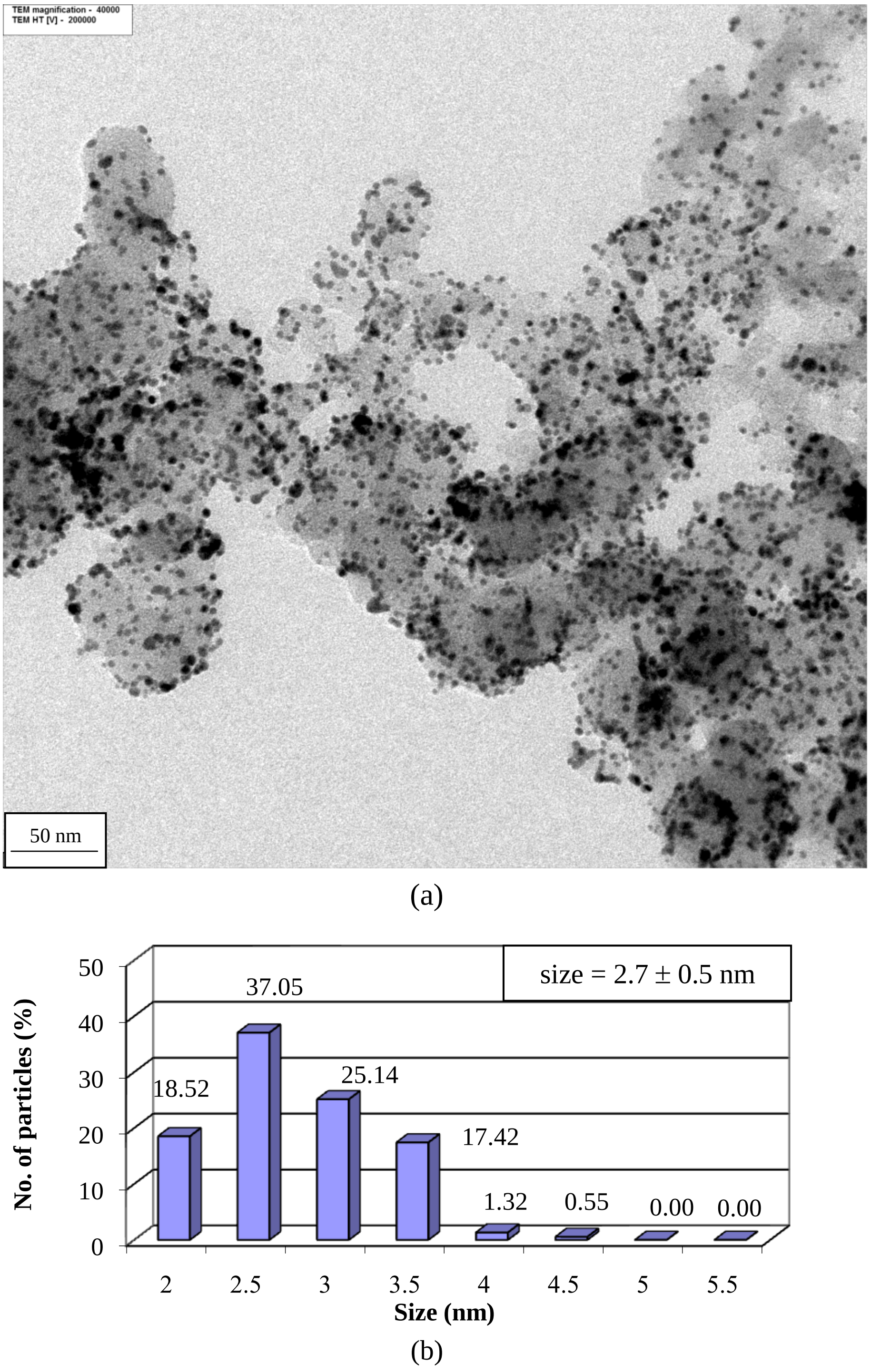
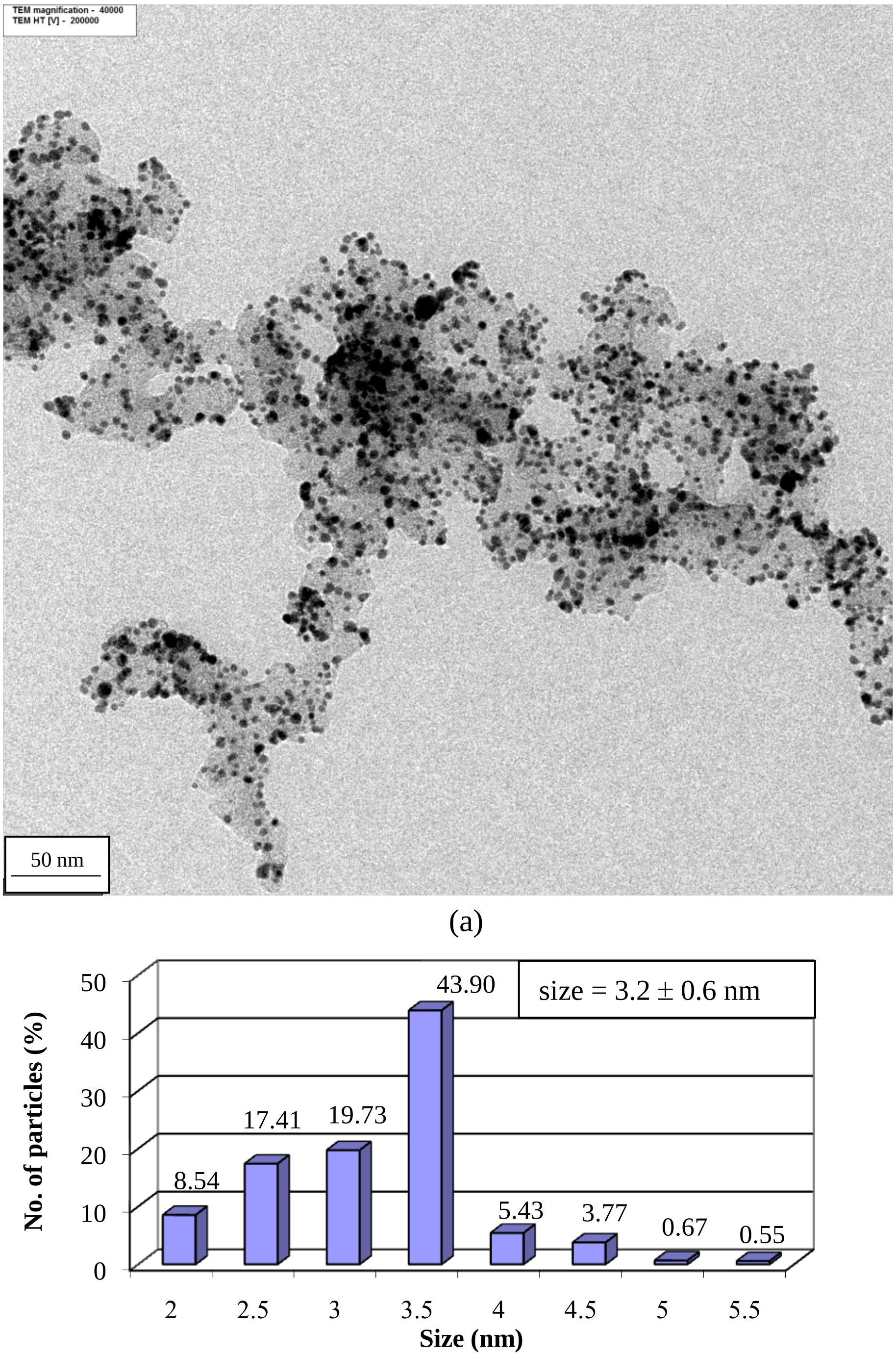


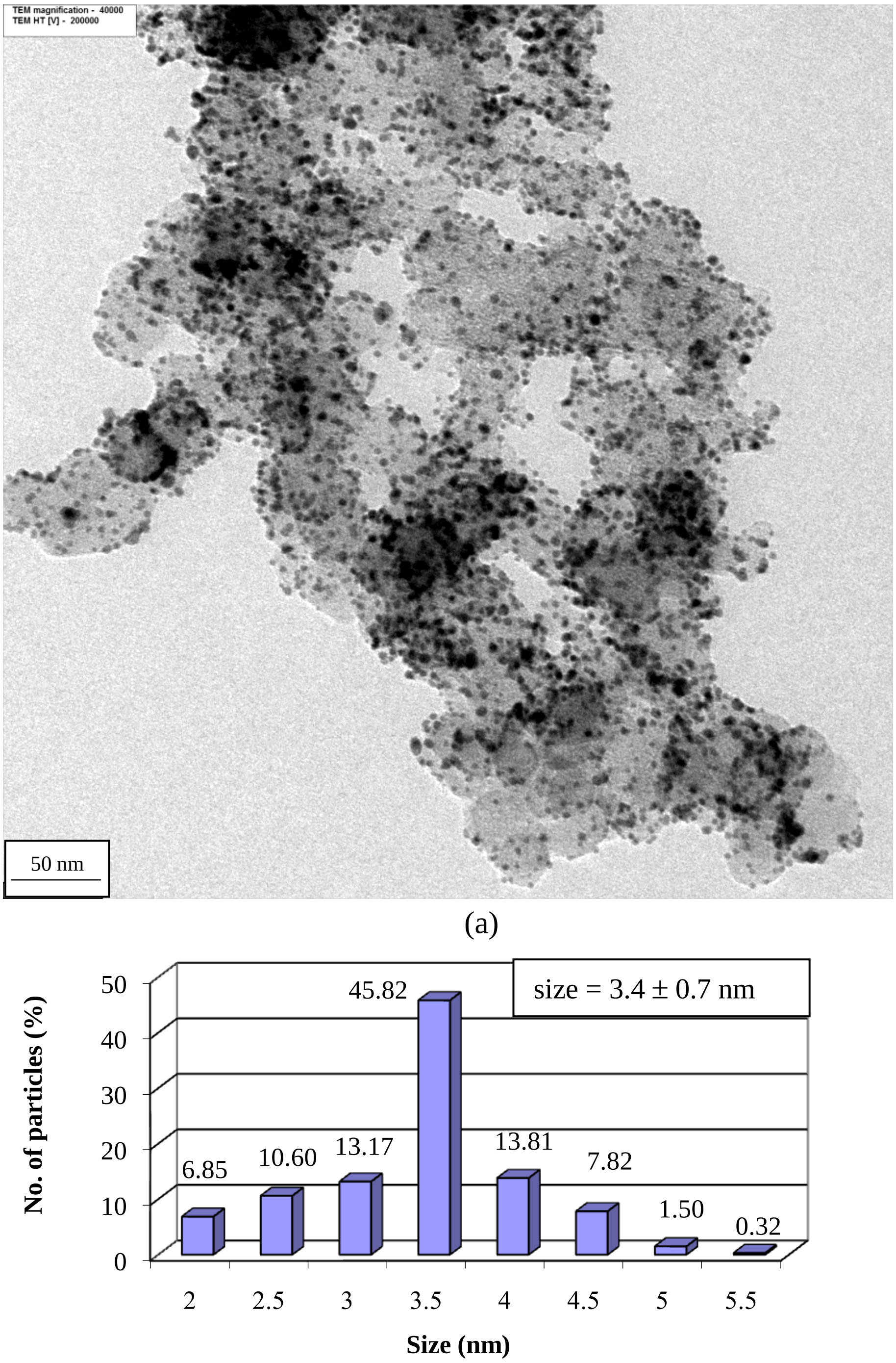
Figure 4.2 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 20% Au prepared by PVA protection method on treated Vulcan XC-72R carbon



(a)

(b)

Figure 4.3 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 30% Au prepared by PVA protection method on treated Vulcan XC-72R carbon



(a)

(b)

Figure 4.4 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 40% Au prepared by PVA protection method on treated Vulcan XC-72R carbon

For citrate protection method, TEM images are shown in Figures 4.5-4.8. Figure 4.5(a) shows TEM image of 20 wt% Au on untreated carbon. From Figure 4.5(b), the average Au particle size of this catalyst was approximately 3.4 ± 0.7 nm. Most of the Au size of this catalyst was 3.5 nm.

Figure 4.6(a) and (b) show TEM image and histogram of particle size distribution of the 20 wt% Au on treated carbon, respectively. The average Au particle size of this catalyst was approximately 3.3 ± 0.8 nm. The average Au particle size of this catalyst was the smallest when it was compared with the others. However, the number of the particle with the particle size < 3.5 nm was greater than that on untreated carbon. It indicated that the pretreatment of carbon support generated smaller particles. The same results was also observed in the case of PVA protection method.

Figure 4.7(a) shows TEM image of the 30 wt% /treated carbon catalyst. The particle size distribution of this catalyst as displayed in Figure 4.8(b) was then used to estimate the average Au particle size which was found to be equal to 3.4 ± 0.8 nm. Most Au particle had a diameter about 3.5 nm.

Figure 4.8(a) shows TEM image of the 40 wt% Au catalyst with treated carbon. Figure 4.8(b) shows that the average Au particle size of this catalyst was about 3.6 ± 0.9 nm. The average Au particle size of this catalyst was the biggest among all catalysts prepared by the citrate protection method. Furthermore the number of Au particles that bigger than 3.5 nm was the highest. In agreement with the PVA protection method, the number of higher particle size was increased, when the amount of Au was increased.

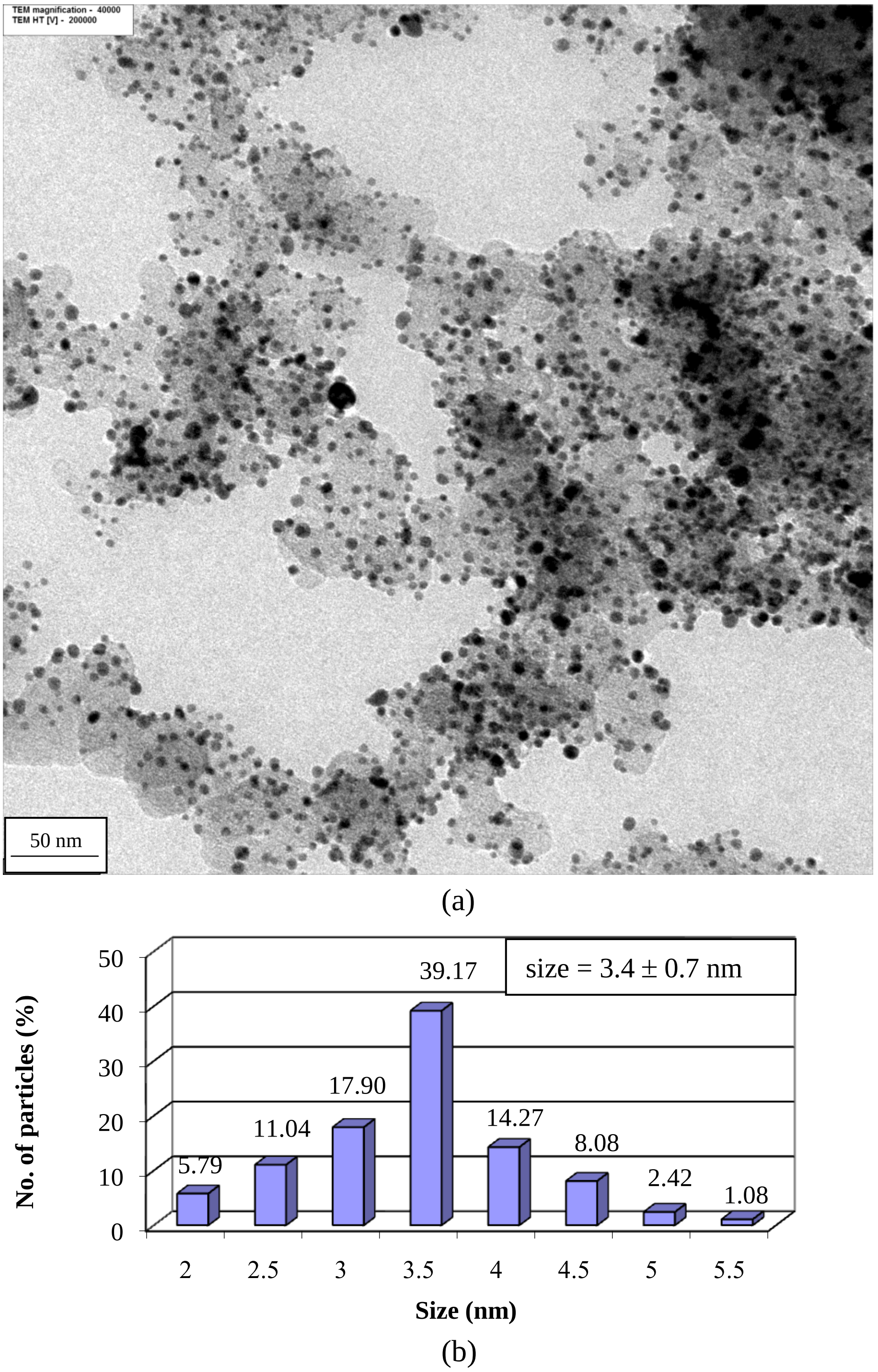
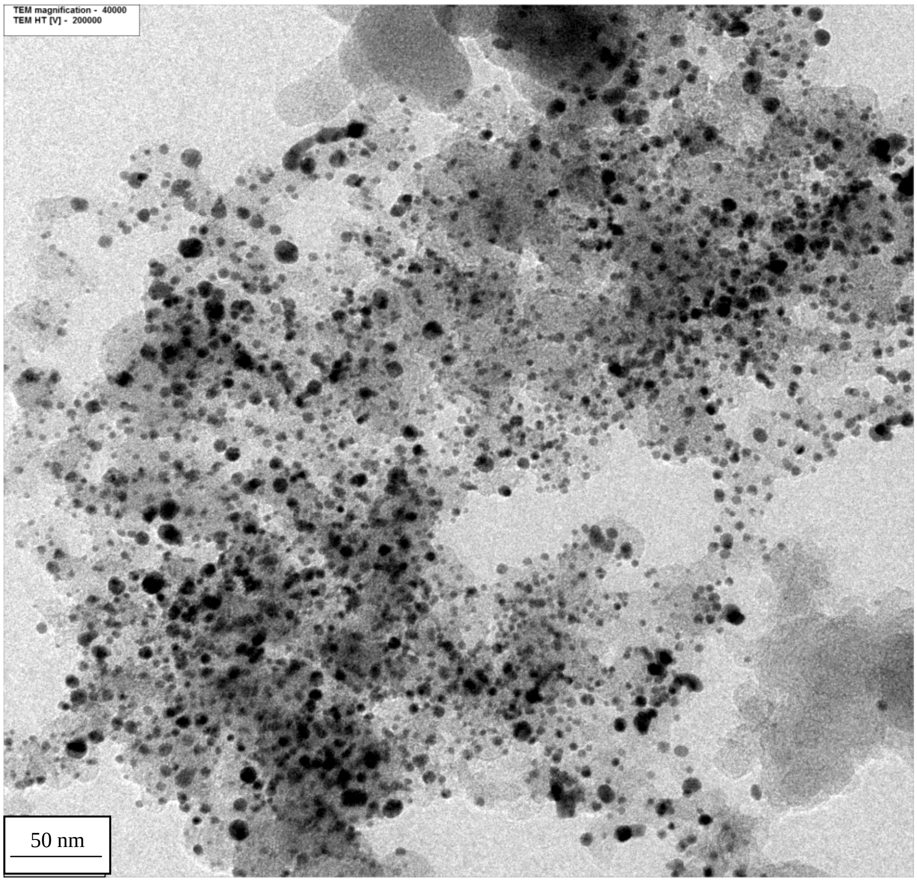
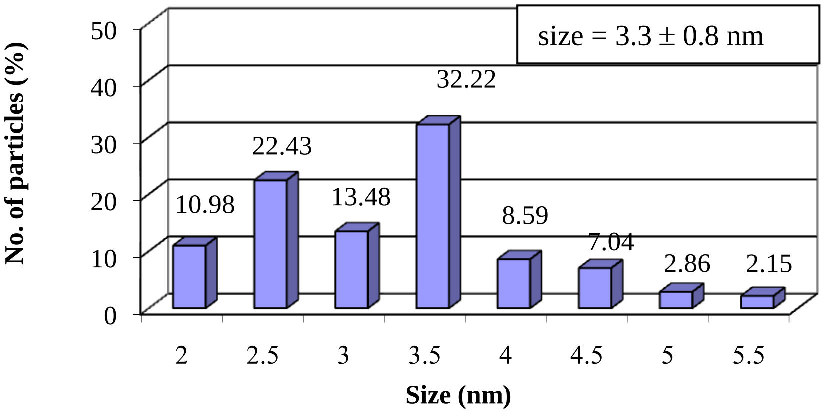


Figure 4.5 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 20% Au prepared by citrate protection method on untreated carbon

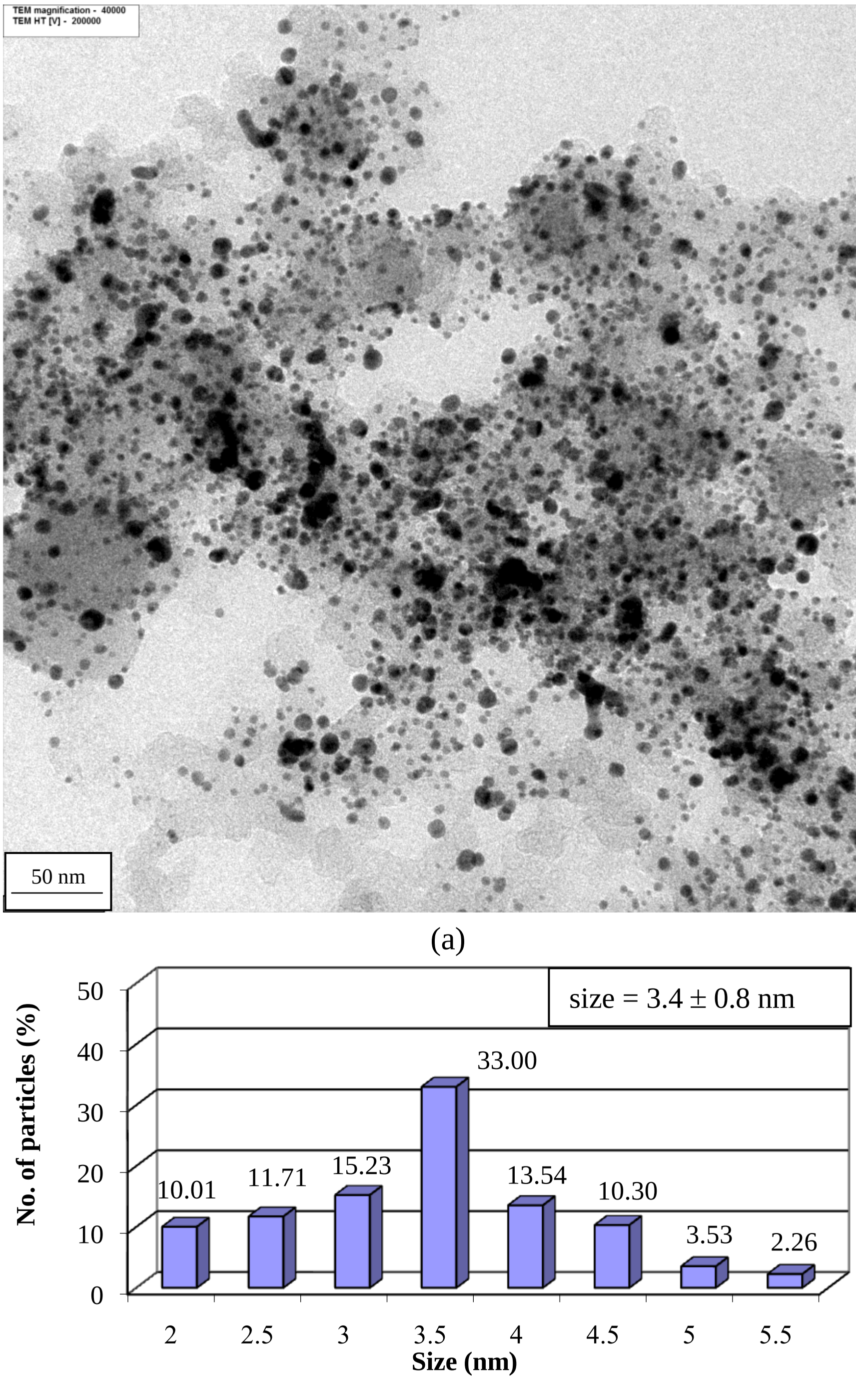


(a)



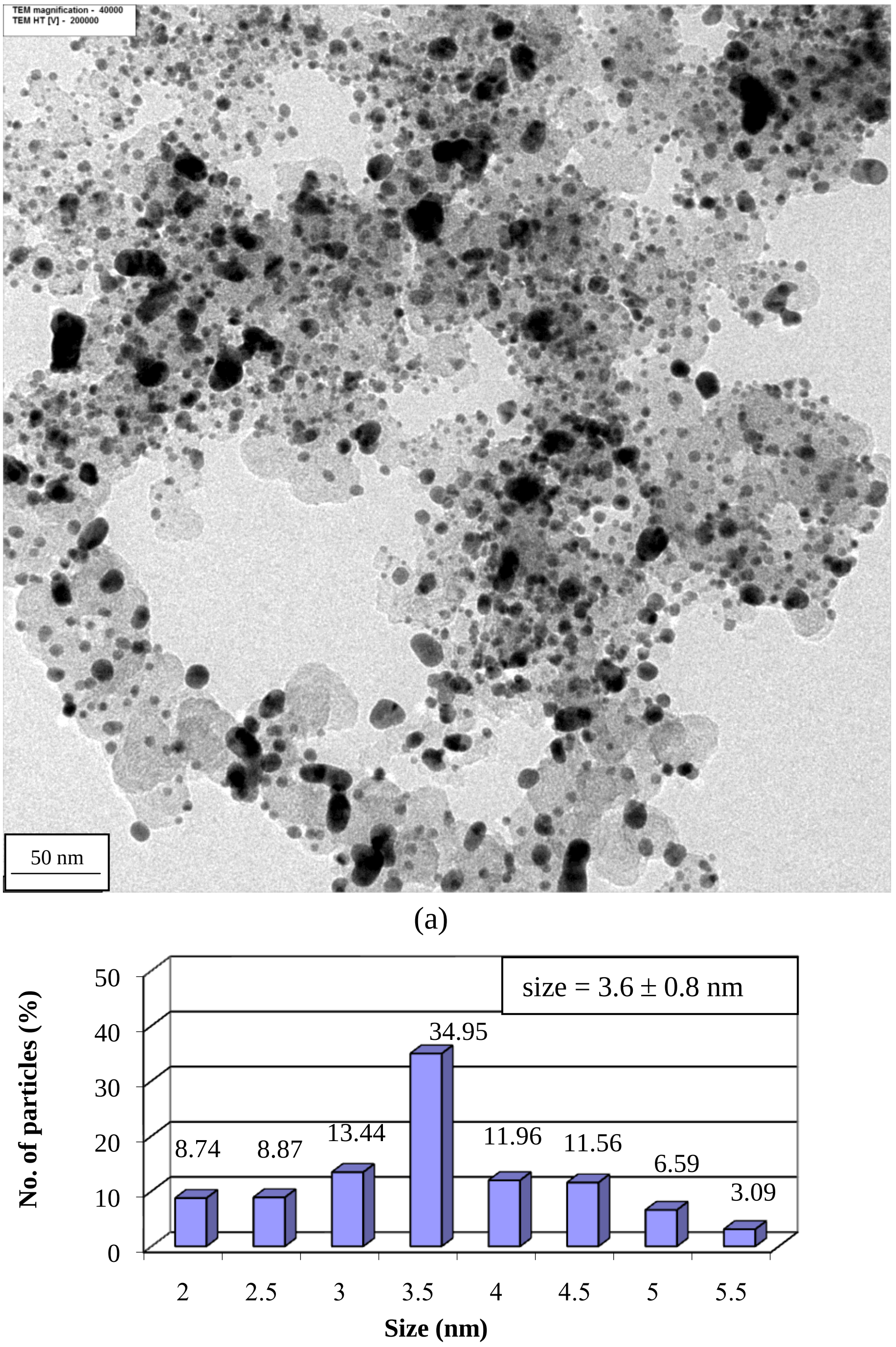
(b)

Figure 4.6 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 20% Au prepared by citrate protection method on treated carbon



(b)

Figure 4.7 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 30% Au prepared by citrate protection method on treated carbon



(a)

(b)

Figure 4.8 (a) TEM image at magnification of 40,000 and (b) Histogram of size distribution of 40% Au prepared by citrate protection method on treated carbon

Table 4.2 summarizes the average particle size and size distribution of each catalyst obtained from Figures 4.1-4.8. By comparing between the 20 wt% Au on treated carbon and than that on untreated carbon prepared by the same method, the treated carbon provided smaller particle than the other. From previous study [8] it was found that heat treatment of carbon support could enhance specific surface area of carbon by generating more micropores and produced less stable oxygen complexes on carbon surface. Thus, the treated carbon supports reduce the Au particle size.

For each catalyst preparation method, when amount of Au loaded was increased, Au particle size was increased. Because of increasing amount of Au, Au particles have short interparticle distances and could easily aggregate. Furthermore, from Table 4.2, it is seen that almost all Au particle sizes and size distributions of the catalyst prepared by citrate protection method was higher than that was prepared catalyst by PVA protection method.

Table 4.2 Summary of average particle size and size distribution of each catalyst

Catalyst	**Average Particle Size (nm)**
PVA method	
20% Au/ untreated C	3.0 ± 0.8
20% Au/ treated C	2.7 ± 0.5
30% Au/ treated C	3.2 ± 0.6
40% Au/ treated C	3.4 ± 0.7
Citrate method	
20% Au/ untreated C	3.4 ± 0.7
20% Au/ treated C	3.3 ± 0.8
30% Au/ treated C	3.4 ± 0.8
40% Au/ treated C	3.6 ± 0.9

4.3 Cyclic Voltammetry (CV)

In order to study the electrochemical properties of catalyst, all of Au catalyst was tested by cyclic voltammetry. Three solutions were used as the electrolytes namely 0.1M KOH, 0.1M KOH with 0.1M glycerol and 0.1M KOH with 0.1M ethylene glycol.

4.3.1 Cyclic Voltammetry (CV) in 0.1M KOH

Before testing with alcohol, each electrode was tested in 0.1M KOH to determine its electrochemical surface area (ESA). Thus there were two sets of cyclic voltammograms in 0.1M KOH which were cyclic voltammograms of all catalysts before testing with glycerol (denoted by set No. 1) and cyclic voltammograms of all catalysts before testing with ethylene glycol (denoted by set No. 2).

Figures 4.9-4.12 show the cyclic voltammograms of both Au/C catalysts prepared by PVA protection method and citrate protection method of set 1. The formations of the oxide monolayer of most catalysts commenced at about -1.7 V. At higher potential (> 0.25 V) the gold oxidation was formed according to the following reactions [7, 16];

$$Au + OH^- \rightarrow Au—OH + e^- \qquad (4.1)$$

$$Au—OH + 2OH^- \rightarrow Au(OH)_3 + 2e^- \qquad (4.2)$$

On the negative sweep, Au oxide begins to reduce at 0.3 V for the first reduction peak in which is mainly reduced from monolayer of outer surface and at about 0.01-0.02 V for the second peak which is from inner layer. The reactions on the negative sweep which are oxygen and $Au(OH)_3$ reduction are the reverse reaction of equations (4.2) and (4.1) as following [7, 16];

$$Au(OH)_3 + 2e^- \rightarrow Au—OH + 2OH^- \qquad (4.3)$$

$$Au—OH + e^- \rightarrow Au + OH^- \qquad (4.4)$$

However, the first peak of negative sweep was used to determine ESA of the catalysts because it represents the oxygen reduction. From Figures 4.9 and 4.10, the reduction peak areas of catalysts with treated and untreated carbon were close although Au/C catalyst with untreated carbon had bigger particle size. It means that the activity of the catalyst with untreated carbon in alkaline solution was nearly the same as that with treated carbon. The heat treatment on carbon support had no influence on oxygen reduction on catalyst surface in alkaline solution.

Figures 4.11 and 4.12 show cyclic voltammograms of 20 wt%, 30 wt% and 40 wt% on treated carbon prepared by the PVA protection method and the citrate protection method (set 1), respectively. The Figures show that when the amount of gold was increased, the reduction peak decreased. It may explain in terms of particle size. When the amount of gold was increased, the particle size increased resulting in less catalytic activity in alkaline solution.

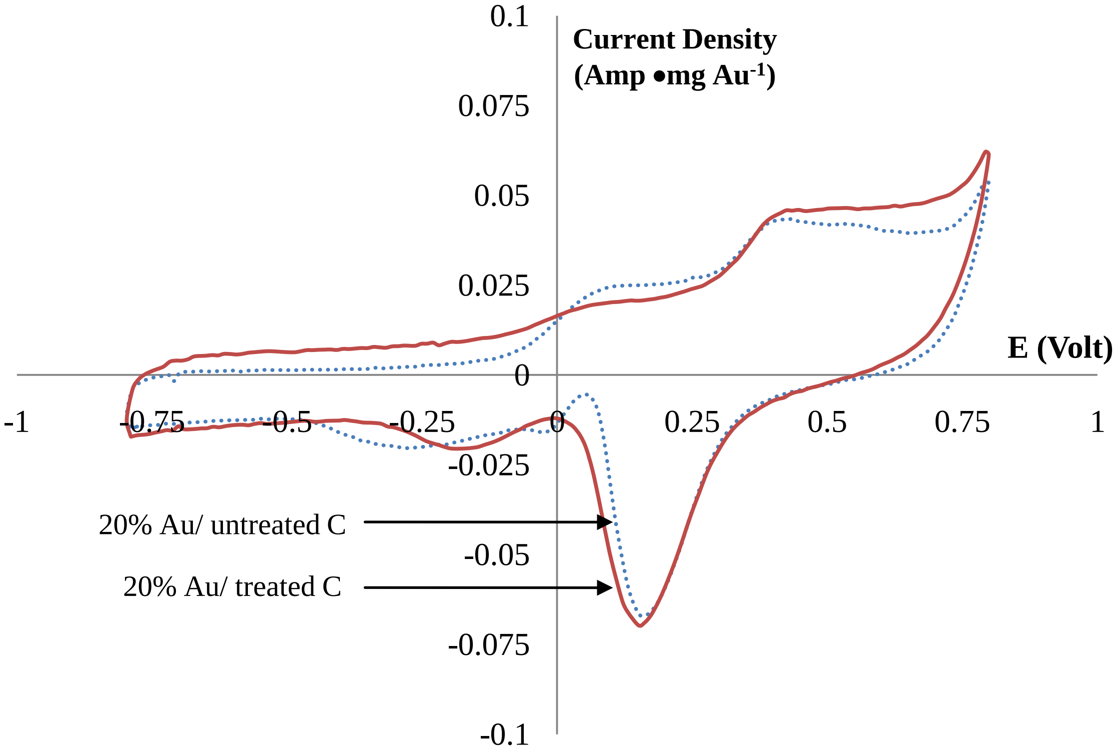


Figure 4.9 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 1)

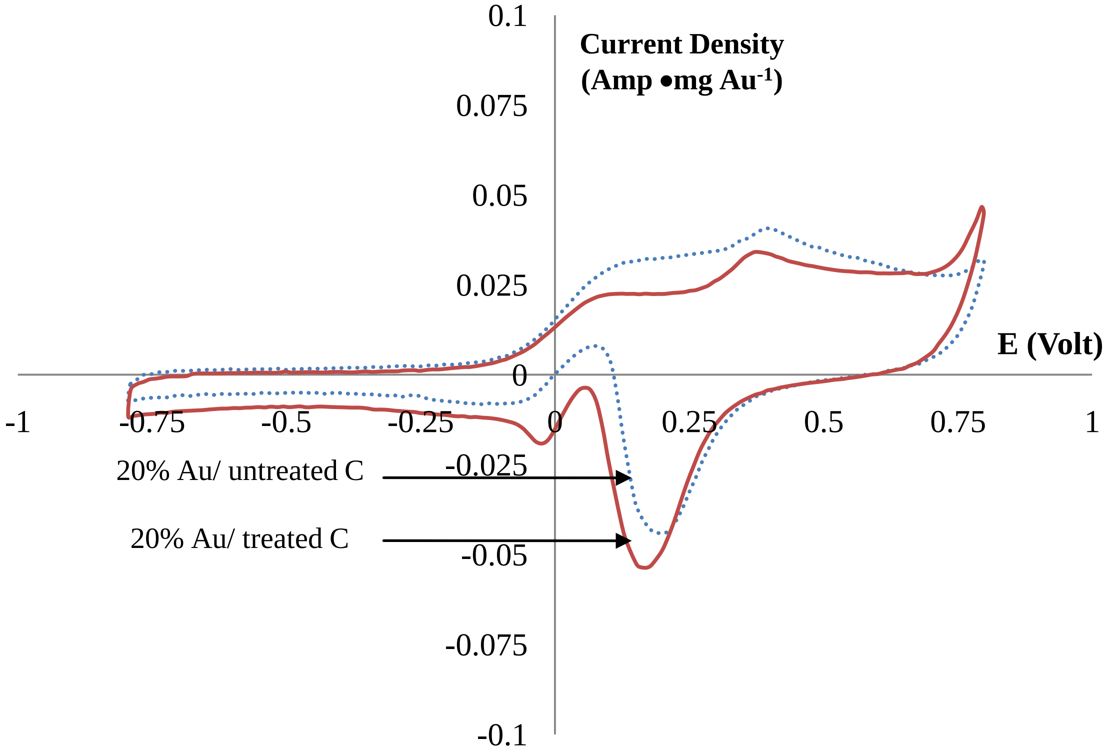


Figure 4.10 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 1)

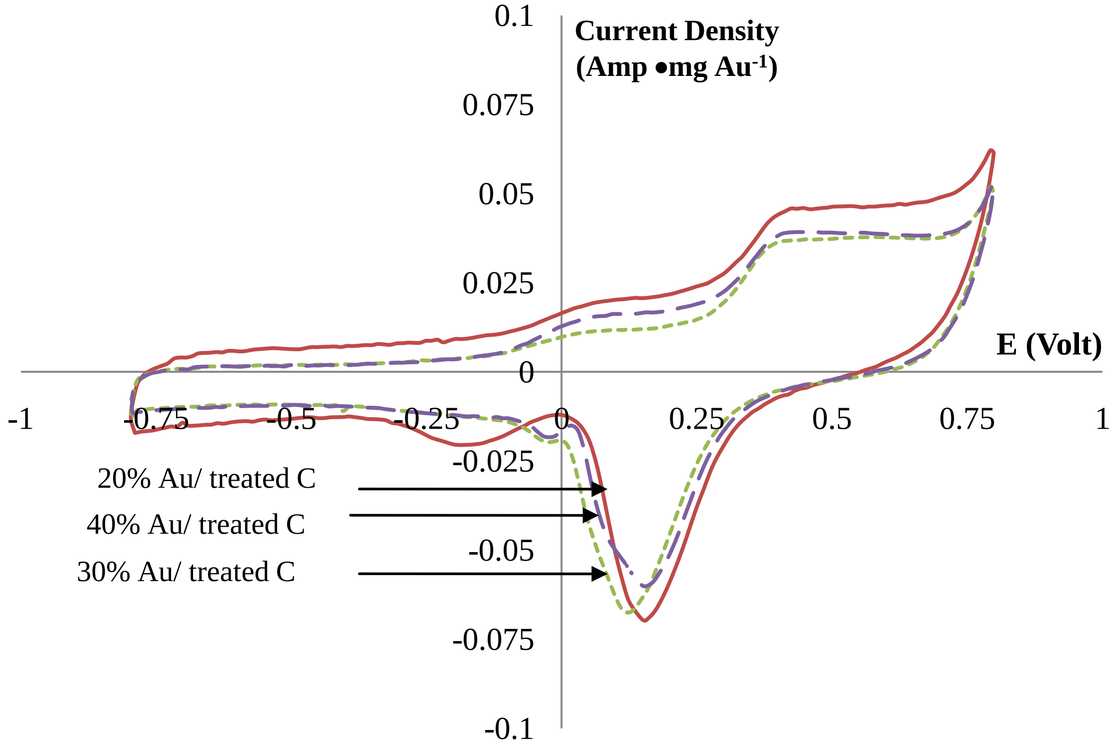


Figure 4.11 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 1)

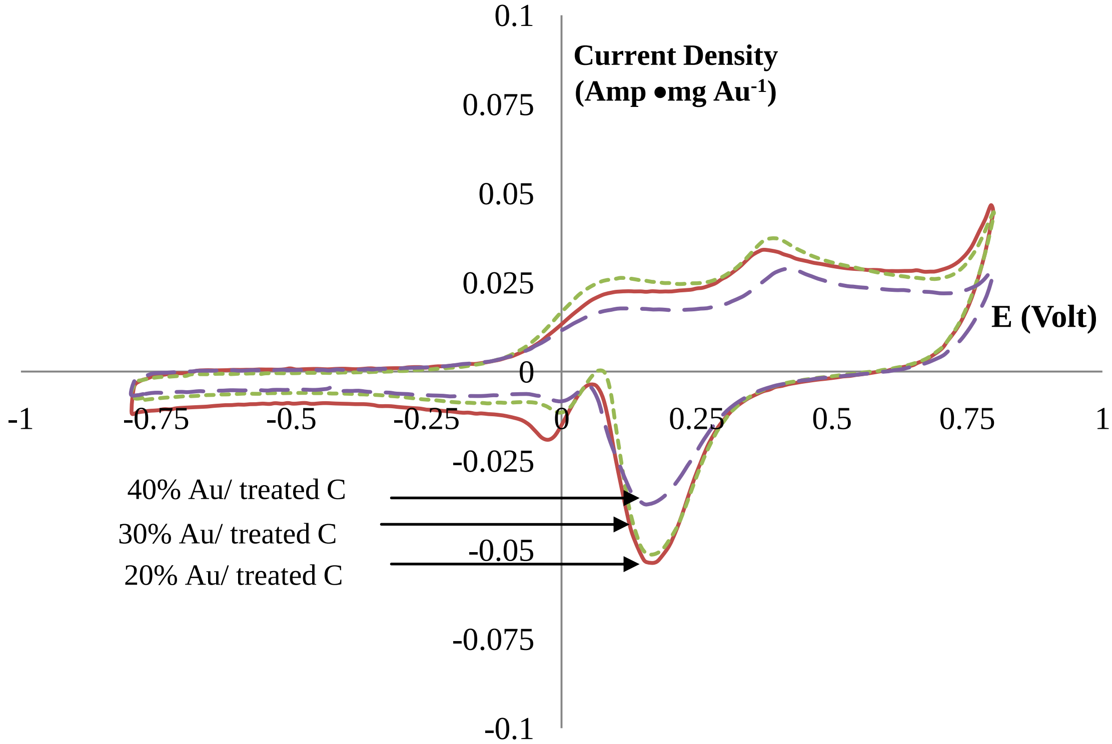


Figure 4.12 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 1)

Figures 4.13-4.16 show the cyclic voltammograms of Au/C catalysts prepared by the PVA protection method and the citrate protection method. The formation of the oxide monolayer and reduction of Au oxides commences nearly the same as that of experimental set No.1. The reactions on the positive and negative sweep were described as the above reactions. The results in Figure 4.13 and 4.14 show the same trend as that in Figure 4.9 and 4.10. The reduction peak areas of catalyst with treated carbon support and untreated carbon support were similar. It was confirmed that the oxide reduction of Au/C catalyst in alkaline solution was not affected by the pre-heat treatment of carbon support.

The results in Figures 4.15 -4.16 were similar to those in Figures 4.11-4.12. The decrease of catalytic activity of Au/C as the amount of Au loading increased resulted from the agglomeration of Au particles to form bigger particle size.

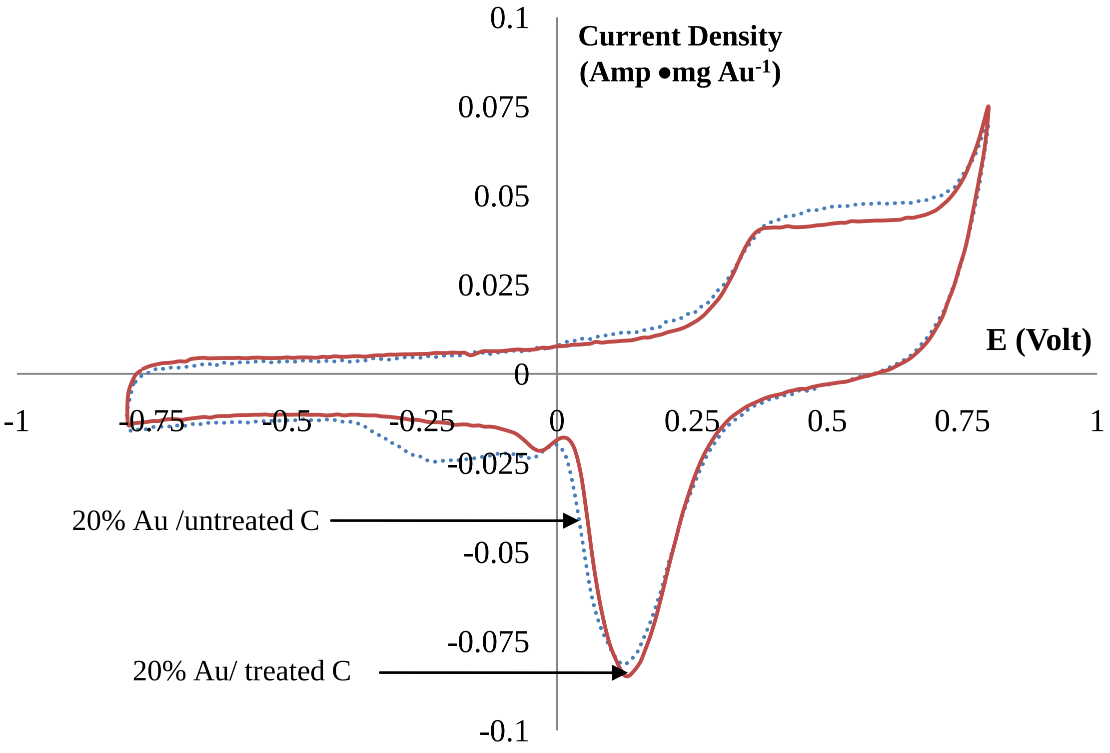


Figure 4.13 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 2)

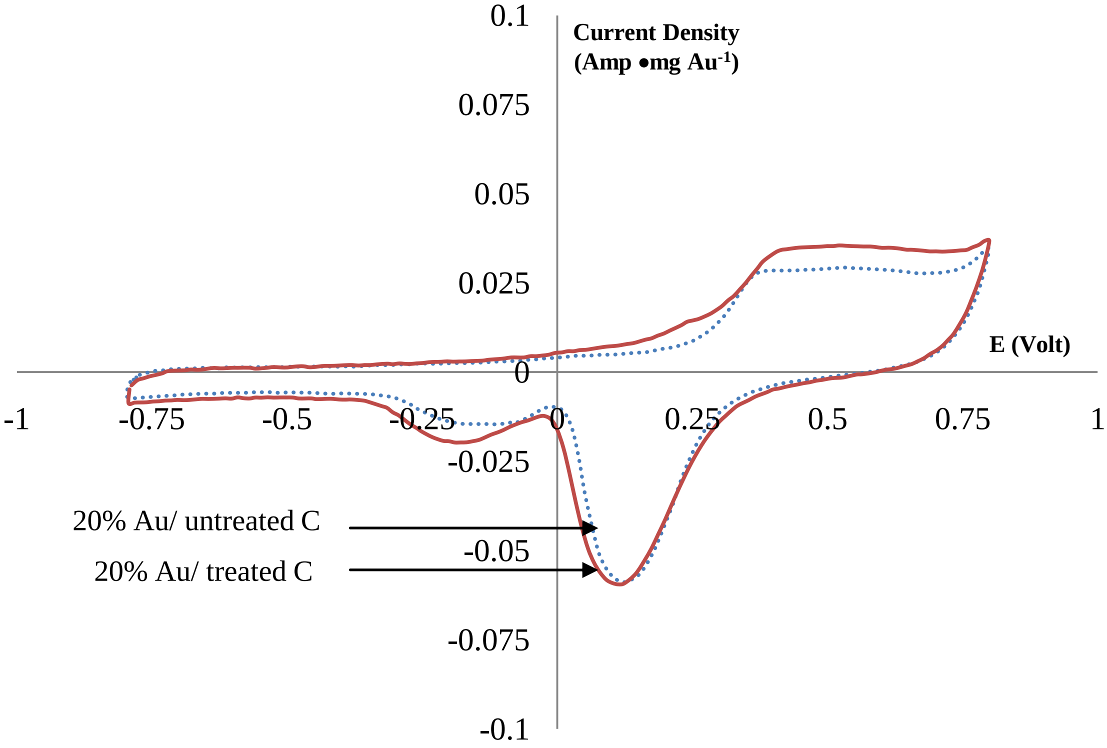


Figure 4.14 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 2)

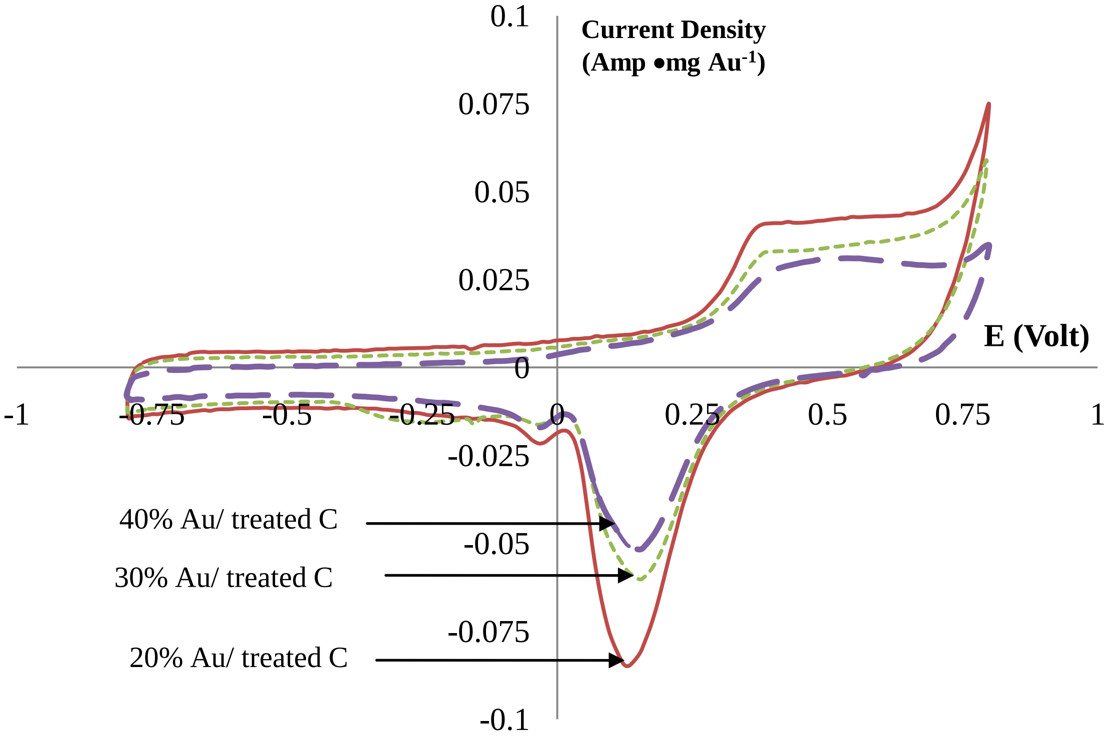


Figure 4.15 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 2)

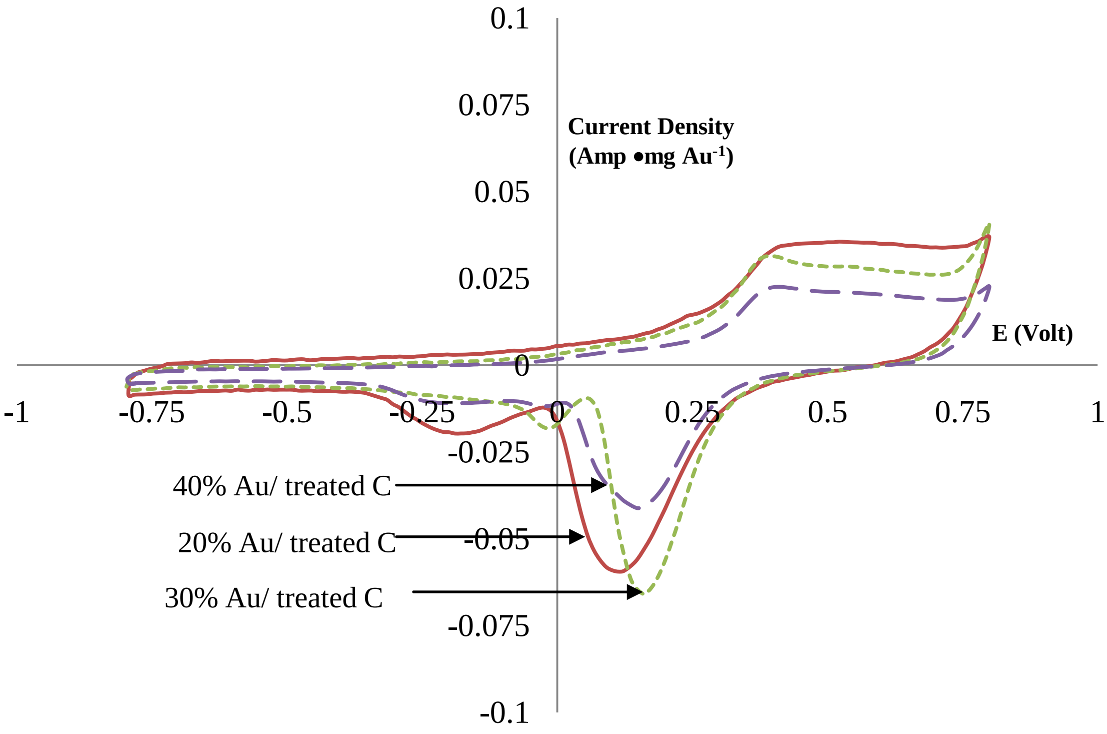


Figure 4.16 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with scan rate 20 mVs^{-1} at 25 °C (set 2)

Table 4.3 shows the ESA and average ESA which were calculated by integrating the first reduction peak of all catalysts from the experimental sets No.1 and No.2. For both PVA and citrate protection methods, the average ESAs of 20 wt% Au on treated carbon and untreated carbon were very close. Thus, as mentioned before, it can be concluded that heat treatment on carbon support did not affect oxygen reduction of the catalyst surface in alkaline solution.

For 20 wt%, 30 wt% and 40 wt% Au of Au/C catalysts prepared from both PVA and citrate protection methods, the increase of Au amount led to a decrease of ESA. The reasons were the same as described with Figures 4.11-4.12 and 4.15-4.16. Thus it can be concluded that due to the increase of particle size in accordance with the amount of Au, the bigger particle size, the lesser will be the catalytic activity in alkaline solution.

Furthermore the average ESA of the catalyst prepared by the PVA protection method is higher than that prepared by the citrate protection method. These results are in agreement with the results of TEM. The Au/C catalysts prepared by the PVA protection method had higher ESA than those prepared by the citrate protection method since the former contained smaller Au particle sizes.

Table 4.3 ESA and average ESA of Au/C catalysts prepared from both the PVA and citrate protection methods

	ESA (set 1) (m^2-Au/g-Au.)	ESA (set 2) (m^2-Au/g-Au.)	ESA_{ave} (m^2-Au/g-Au.)
PVA method			
20% Au/ untreated C	35.81	37.45	36.63
20% Au/ treated C	33.75	36.62	35.18
30% Au/ treated C	28.01	27.07	27.54
40% Au/ treated C	26.69	21.87	24.28
Citrate method			
20% Au/ untreated C	27.88	30.87	29.37
20% Au/ treated C	27.40	31.80	29.60
30% Au/ treated C	26.92	28.76	27.84
40% Au/ treated C	19.75	18.57	19.16

4.3.2 Cyclic Voltammetry (CV) in 0.1M KOH with 0.1M glycerol

As shown in Figures 4.17 to 4.20, the cyclic voltammograms of all Au/C catalysts in glycerol with alkaline solution demonstrates that there were two oxidation peaks; i.e. forward oxidation peak and reverse oxidation peak. The forward oxidation peak commenced at the potential about -0.3 V and reached the highest peak at the potential about 0.4 V. Then oxidation occurs again in the backward sweep at the potential about 0.2 V. It can be explained that the electrooxidation of glycerol commences in the potential lower than Au oxide forming region during the positive sweep (see Figure 4.9 to 4.12). When monolayer of oxide film begins, oxidation of glycerol was inhibited from the potential of 0.4 to 0.8 V. During the negative sweep, glycerol began again at the potential that the monolayer of oxide had reduced starting from 0.45 V (also see Figure 4.9 to 4.12). Generally, organic compounds are oxidesed in the presence of AuOH formed in the premonolayer region.

Since alcohol oxidation the main is reaction in fuel cell, the current density at the peak of positive sweep was used to evaluate the activity of Au/C catalyst. Form Figures 4.17 and 4.18, the catalysts with treated carbon gave higher current density than these with untreated carbon although their ESA were similar. It is possible that the gold oxide was not responsible for glycerol oxidation. Instead, the major factor was the gold particle size. The smaller particle size of catalyst yielded higher current density of glycerol oxidation. Thus, it can be concluded that the influence of particle size was higher than the presence of gold oxide (AuOH) formed on gold electrode surface.

Figures 4.19 and 4.20 show cyclic voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon prepared by the PVA and the citrate protection method. When the amount of Au increased, the current density (Amp/mgAu) was reduced. These results correspond to the previous studies [18]. The average particle sizes of 30 and 40 wt% Au catalyst prepared by the PVA protection method were about 3.2 ± 0.6 and 3.4 ± 0.7 nm, respectively, whereas they were about 3.4 ± 0.8 and 3.6 ± 0.9 nm for case of the citrate protection method. The higher of current density obtained from the 30 wt% Au/C than that from the 40 wt% Au/C corresponded to the Au particle size instead of ESA. These results confirm that the main influence of glycerol oxidation was particle size of the catalysts. However, for 20 wt% Au catalyst, both particle size and the presence of gold oxide on gold electrode surface from ESA yielded higher current density than the other catalysts.

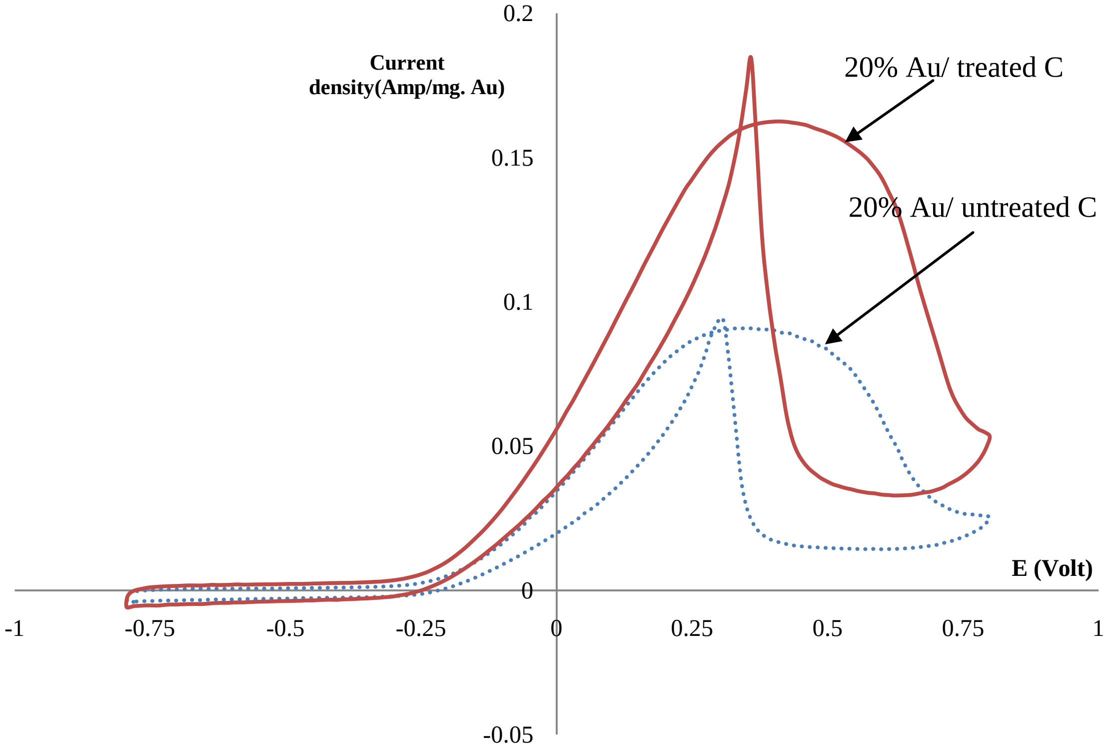


Figure 4.17 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M glycerol, scan rate 20 mVs^{-1} at 25 °C

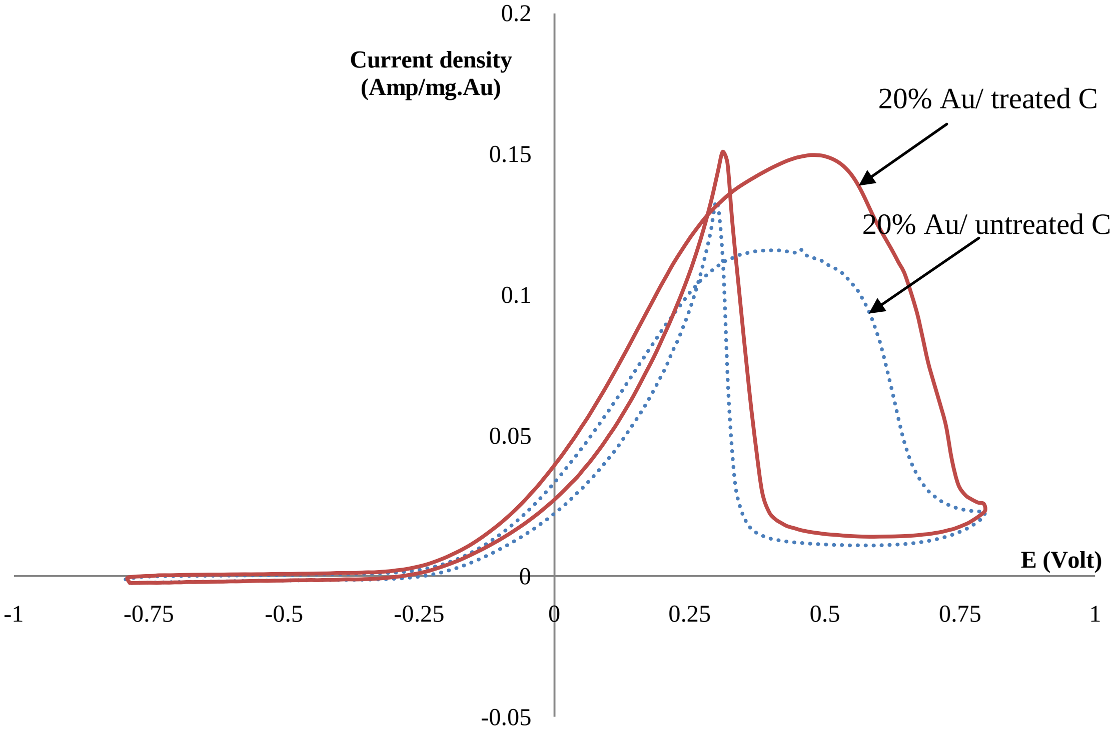


Figure 4.18 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M glycerol, scan rate 20 mVs^{-1} at 25 °C

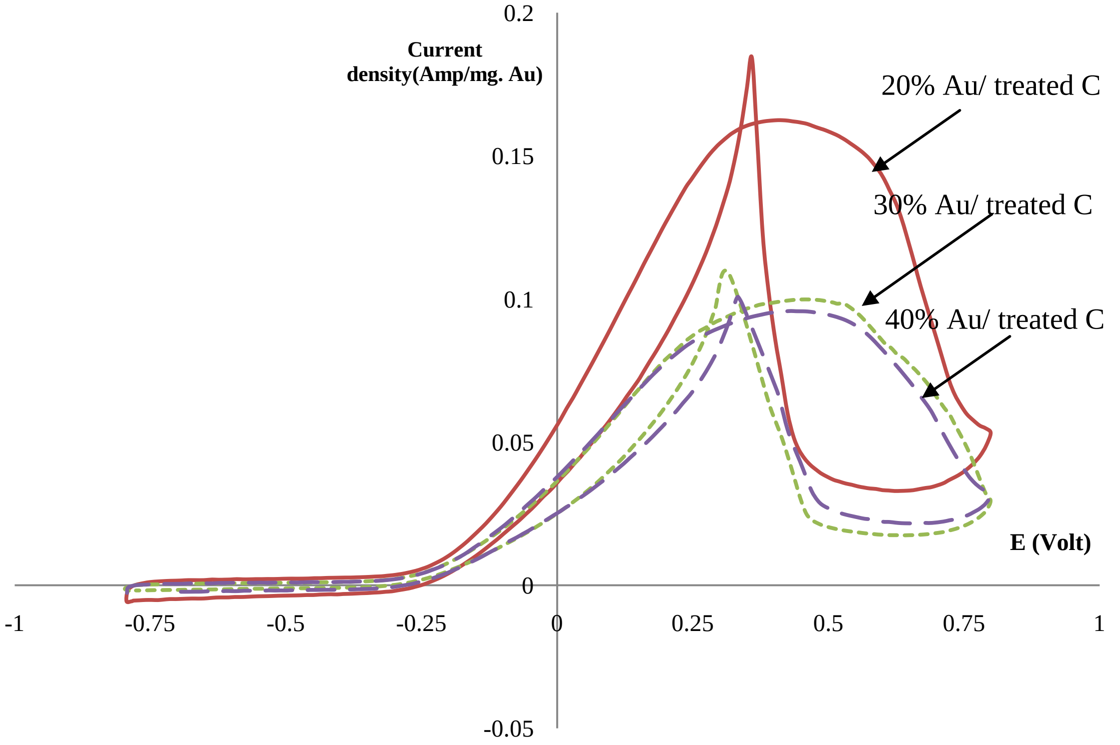


Figure 4.19 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M glycerol, scan rate 20 mVs^{-1} at 25 °C

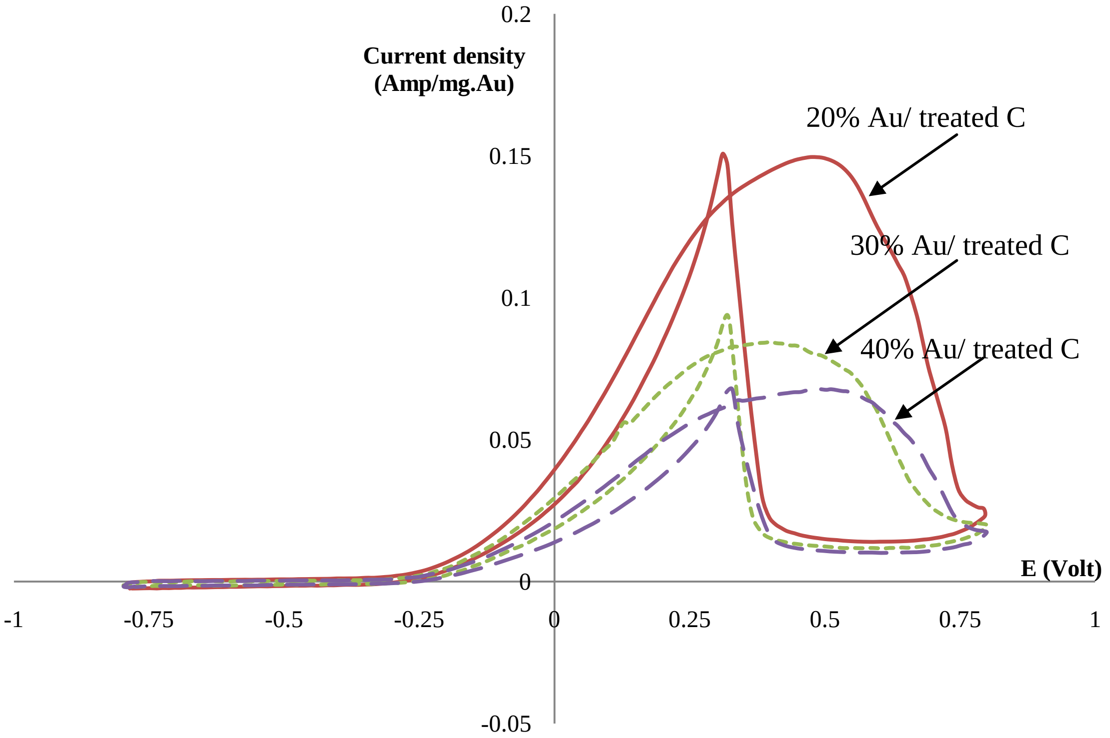


Figure 4.20 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M glycerol, scan rate 20 mVs^{-1} at 25 °C

Table 4.4 shows the current density of positive sweep oxidation in 0.1M KOH with 0.1M glycerol of different catalysts. In comparing between the catalysts prepared by the PVA and the citrate protection method, most of the catalysts by PVA method give higher current density than those by citrate protection method because of the size effect as previously discussed.

Table 4.4 Current density of positive sweep oxidation in 0.1M KOH with 0.1M glycerol

Catalyst	**Current Density Amp·mg Au^{-1}**
PVA method	
20% Au/ untreated C	0.0908
20% Au/ treated C	0.1625
30% Au/ treated C	0.1000
40% Au/ treated C	0.0958
Citrate method	
20% Au/ untreated C	0.1158
20% Au/ treated C	0.1496
30% Au/ treated C	0.0844
40% Au/ treated C	0.0678

4.3.3 Cyclic Voltammetry (CV) in 0.1M KOH with 0.1M ethylene glycol

Cyclic voltammograms of the ethylene glycol electrooxidation with all Au/C catalysts in a base solution are shown in Figure 4.21 to 4.24. Two oxidation peaks, forward and reverse oxidation peaks were observed which is similar to the glycerol cyclicvoltammograms. It can be seen that ethylene glycol elecrooxidation commences during the positive sweep at a potential of -0.25 V. This is the potential region before the surface oxide was formed on gold (see Figure 4.13 to 4.16), then ethylene glycol electrooxidation was inhibited by the surface oxide on the gold electrode from the potential of 0.4 V to 0.8 V. During the negative sweep, oxidation of ethylene glycol recurrented after the surface gold oxide has been reduced (see also Figures 4.31 to 4.16).

Figures 4.21 and 4.22 show cyclic voltammograms of the ethylene glycol electrooxidation by catalysts with treated and untreated carbon prepared by the PVA method and the citrate methods. From Figure 4.21, the peak current density obtained from ethylene glycol oxidation of all catalysts was very close and the effect of pretreatment of carbon support was less pronounced. It was also observed that with the same catalyst, the peak current densities obtained from ethylene glycol oxidation was less than those from glycerol oxidation. It was possibly that ethylene glycol was more difficult to oxidize than glycerol. Although the 20 wt% Au/ treated carbon had smaller Au particle size than that with untreated carbon, the peak current density obtained from both catalysts was about the same for the case of PVA method (see Figure 4.21) and slightly different for the case of citrate method (see Figure 4.22). For Figure 4.22, the result was in accord with glycerol oxidation.

Cyclic voltamograms of 20 wt%, 30 wt% and 40 wt% Au with treated carbon are shown in Figure 4.23 and 4.24. The reduction of peak current density with the increase in Au loading could be explained by the particle effect as described in section 4.3.2. Thus it can be ensured that influence of particle size, which was greater than the presence of gold oxide (AuOH) formed on gold electrode surface.

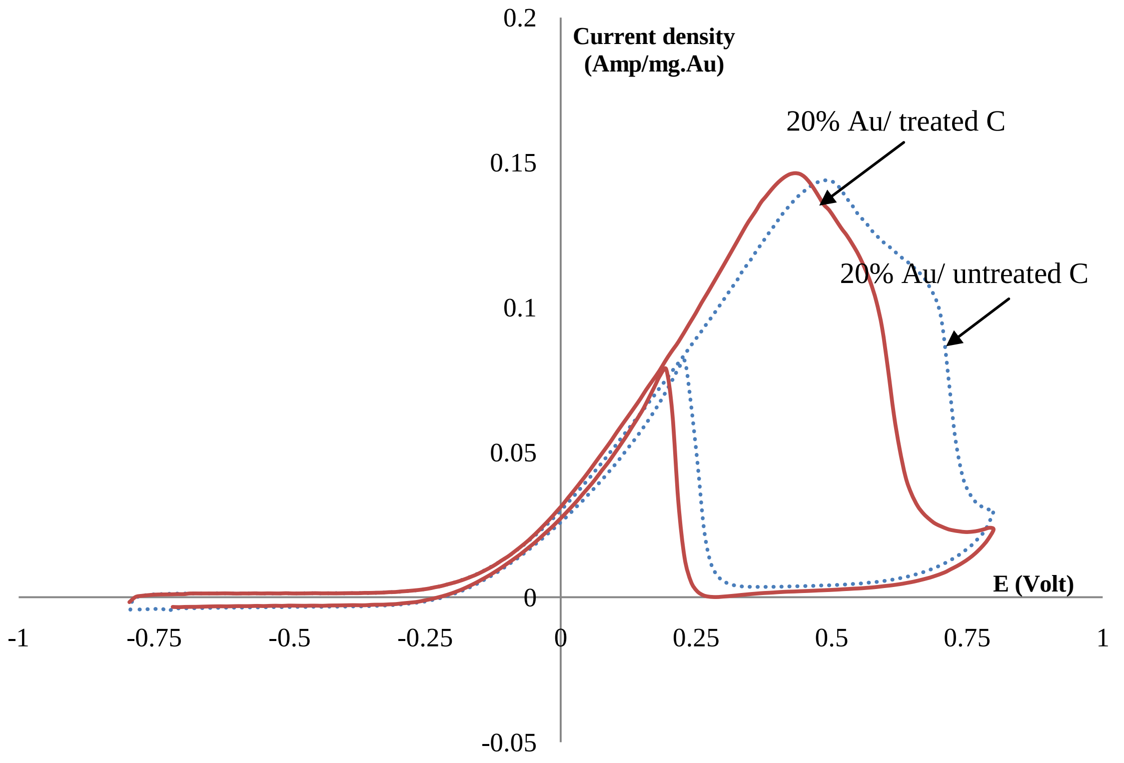


Figure 4.21 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M ethylene glycol, scan rate 20 mVs^{-1} at 25 °C

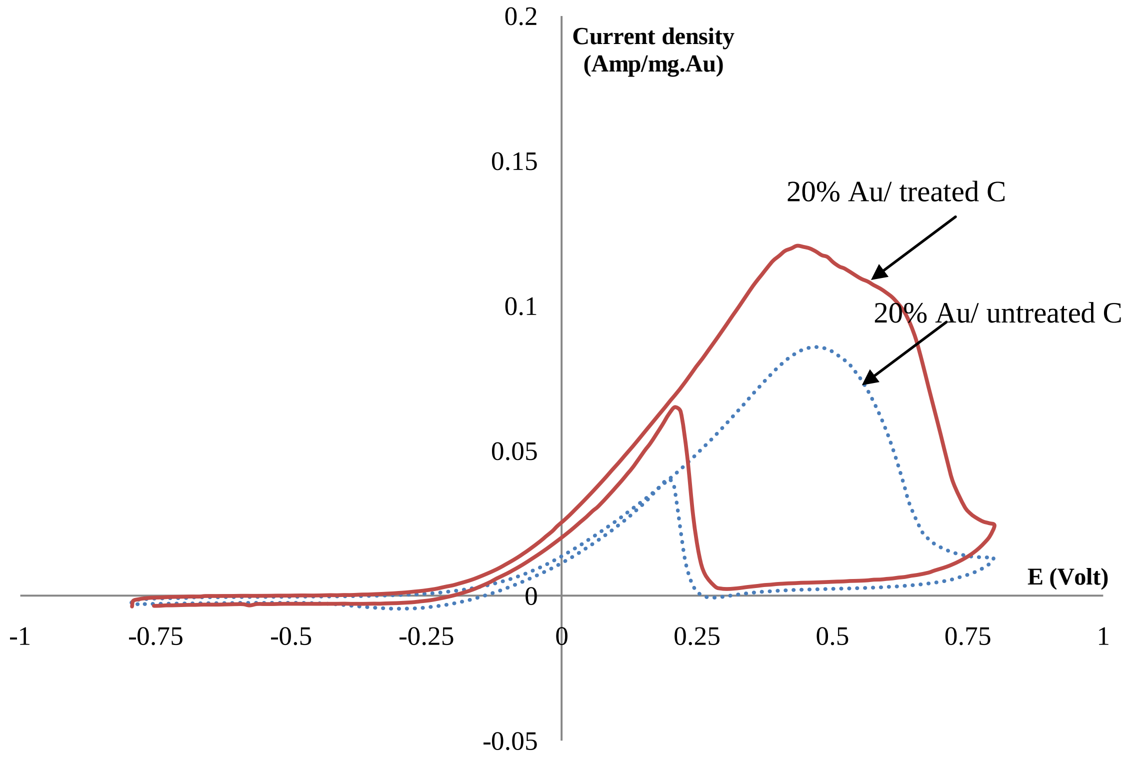


Figure 4.22 Cyclic Voltammograms of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M ethylene glycol, scan rate 20 mVs^{-1} at 25 °C

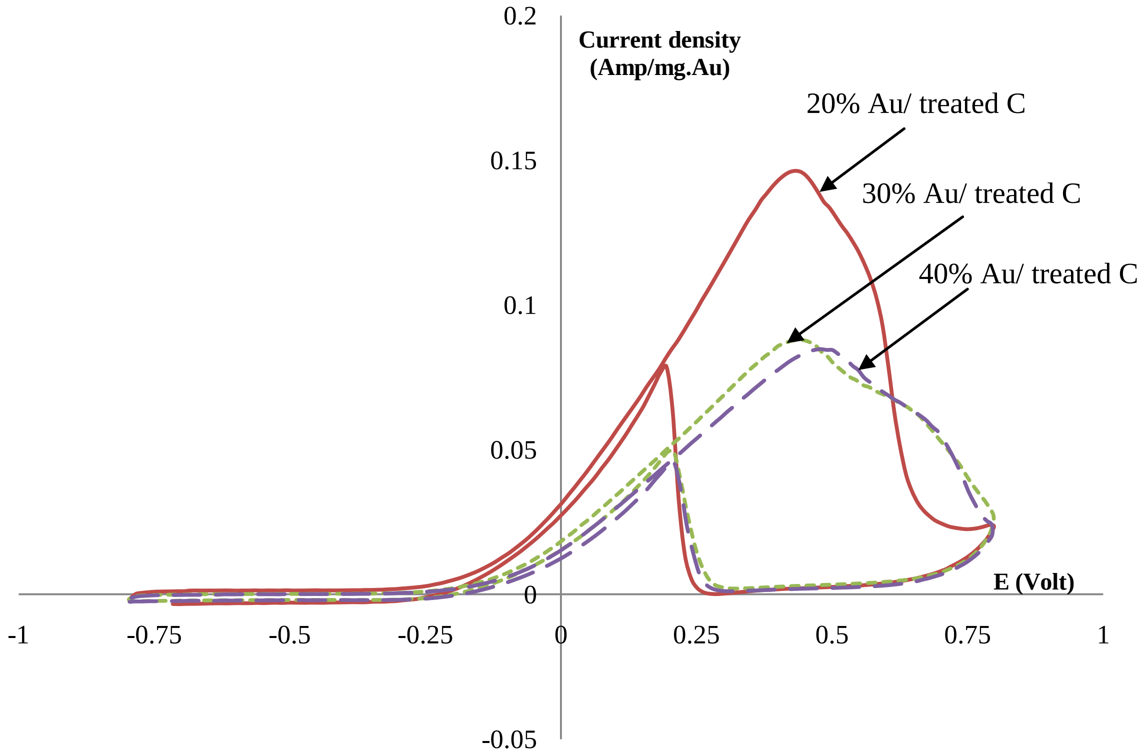


Figure 4.23 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M ethylene glycol, scan rate 20 mVs^{-1} at 25 °C

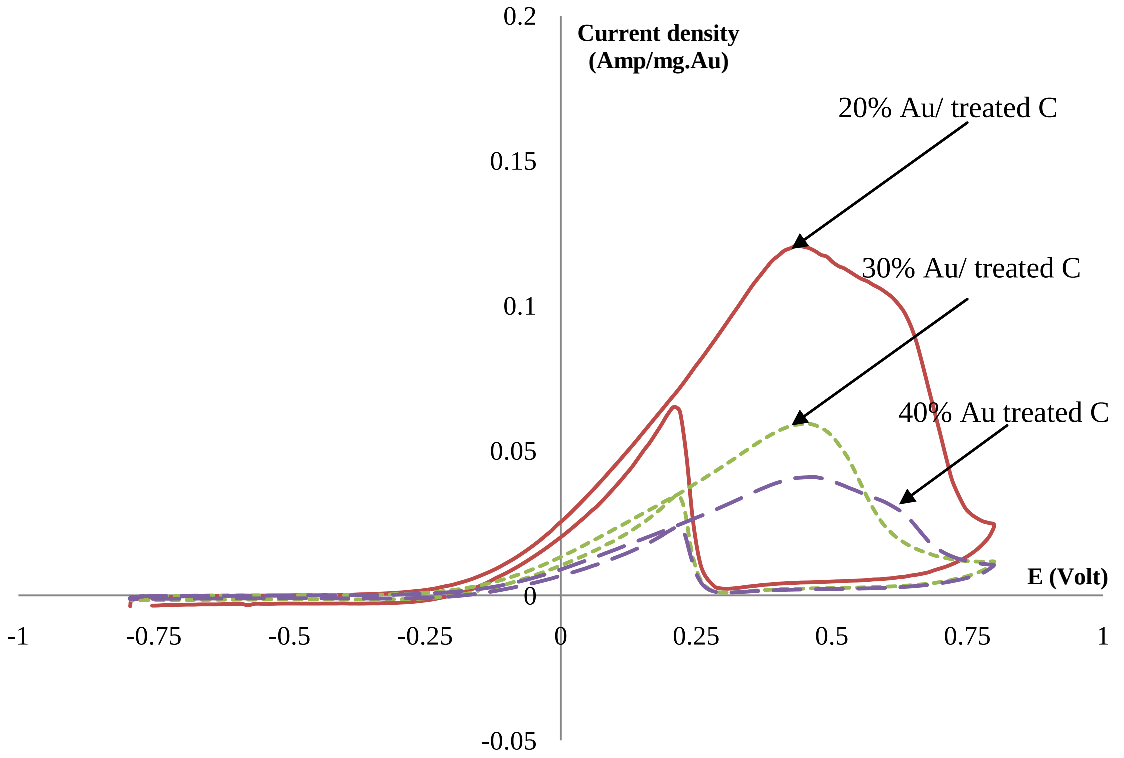


Figure 4.24 Cyclic Voltammograms of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M ethylene glycol, scan rate 20 mVs^{-1} at 25 °C

Table 4.5 shows the peak current density of the positive sweep oxidation in 0.1M KOH with 0.1M ethylene glycol of all catalysts. It can be seen that all catalysts prepared by the PVA method gave higher current density than these by citrate protection method. This tendency was also found in the case of glycerol oxidation.

Table 4.5 The peak current densities of the positive sweep oxidation in 0.1M KOH with 0.1M ethylene glycol for all prepared catalysts

Catalyst	**Current Density Amp·mg Au^{-1}**
PVA method	
20% Au/ untreated C	0.1439
20% Au/ treated C	0.1463
30% Au/ treated C	0.0879
40% Au/ treated C	0.0844
Citrate method	
20% Au/ untreated C	0.0858
20% Au/ treated C	0.1207
30% Au/ treated C	0.0592
40% Au/ treated C	0.0409

4.4 Chronoamperometry (CA)

Chronoamperometry (CA) was tested to ensure the results from CV. The catalyst was tested by holding the potential constant at 0.2 V and 0.4 V because alcohol could be significantly oxidized at those potentials. This technique was also used to determine the stability of catalyst by considering the decaying rate of each catalyst.

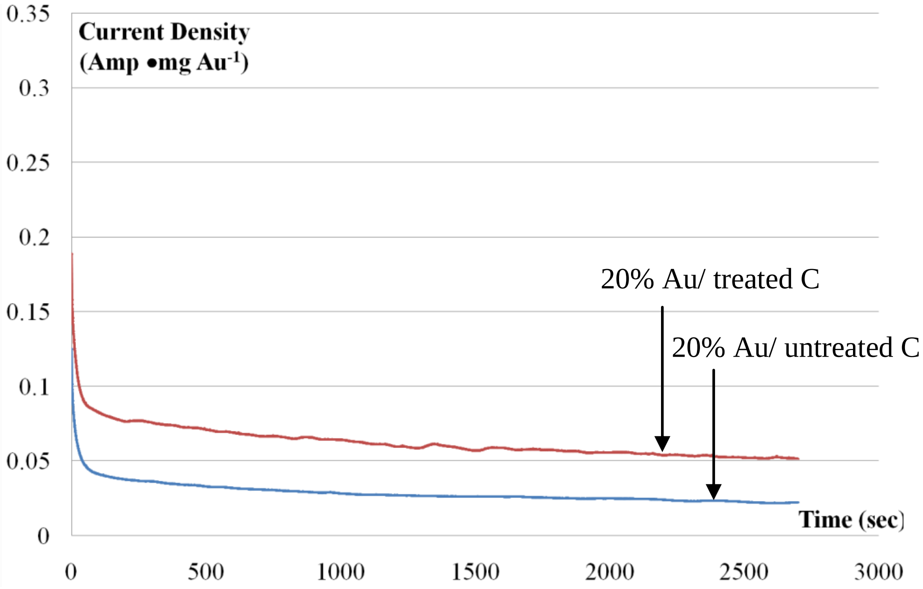
4.4.1 Chronoamperometry (CA) in 0.1M KOH with 0.1M glycerol

Chronoamperometry (CA) of Au/C catalysts prepared by PVA and citrate method in glycerol with alkaline solution at 0.2 V and 0.4 V were shown in Figure 4.25 to 4.28. After holding potential at 0.2 V and 0.4 V, the current generated from each catalyst drop rapidly at the initial, and then gradually decrease to approach a stable current density during 45 minutes of testing time.

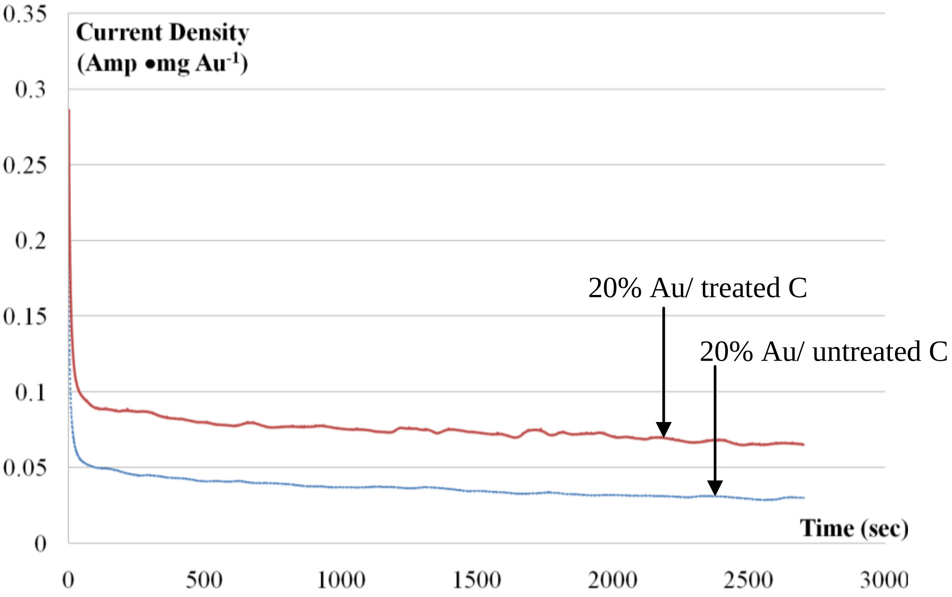
The average current from 10-45 minutes and a final stable current of these catalysts are concluded in Table 4.6. Furthermore, the slope of chronoamperometry can be used to determine the decaying rate of catalysts as shown in Table 4.7. In comparison to catalysts 20 wt% Au on treated carbon and untreated carbon of both catalyst preparation, the decaying rate of 20 wt% Au with treated carbon catalyst was lesser while the obtained current density was higher than that of 20 wt% Au on untreated carbon indicating that 20 wt% Au/ treated C was more tolerant to poison in glycerol oxidation. Therefore, it can be concluded that catalyst with treated carbon showed better performance than that with untreated carbon.

By increasing the amount of Au, the decaying rate was decreased. It can be explained that the catalyst with higher amount of Au was less active in glycerol oxidation producing less current density and less poisoning, thus decaying rate was low. Although 20 wt% Au catalysts with treated carbon had higher decaying rate, this catalyst generated current density higher than 30 wt% and 40 wt% Au catalysts with treated carbon in glycerol oxidation. Thus, 20 wt% Au catalyst with treated carbon was better than 30 wt% and 40 wt% Au of Au/C catalyst.

Furthermore, for considering the effect of catalyst preparation method, most of catalysts by prepared by PVA protection method provided higher current density and lower decaying rate thus; these confirm that Au/C catalysts prepared by PVA protection were more active than those by citrate protection method.

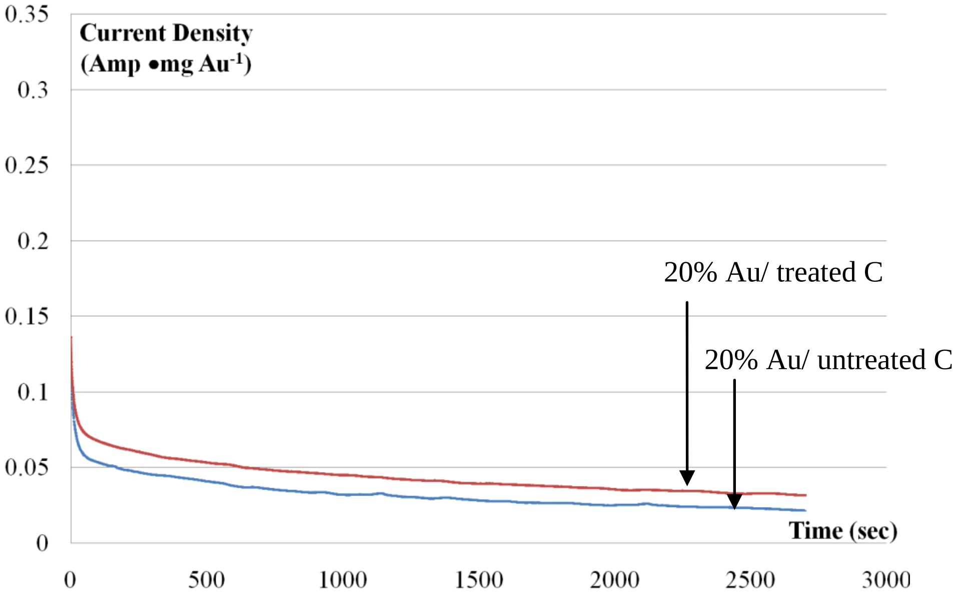


(a)

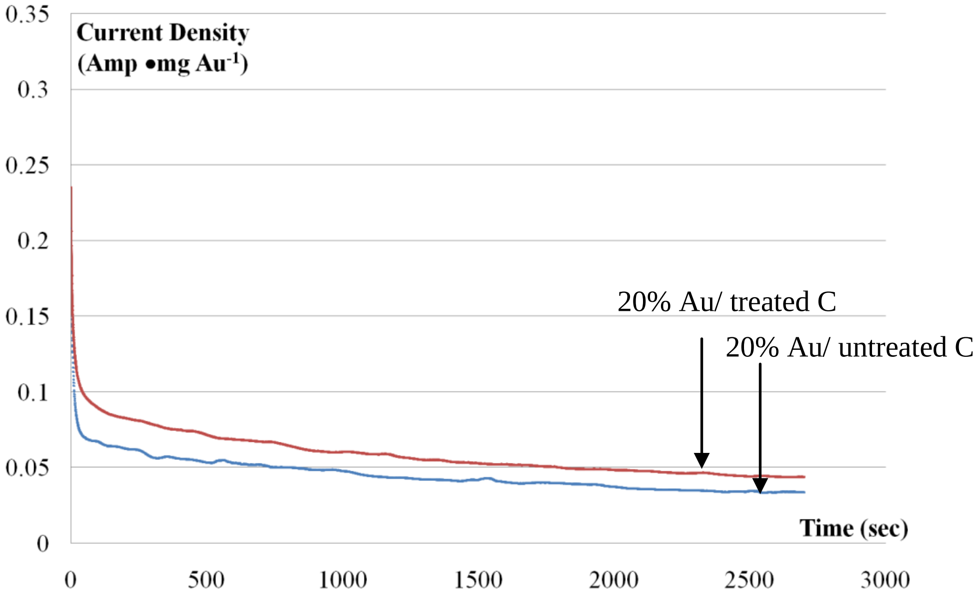


(b)

Figure 4.25 Chronoamperometric curves of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M glycerol at (a) 0.2 V (b) 0.4 V for 45 min



(a)



(b)

Figure 4.26 Chronoamperometric curves of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M glycerol at (a) 0.2 V (b) 0.4 V for 45 min

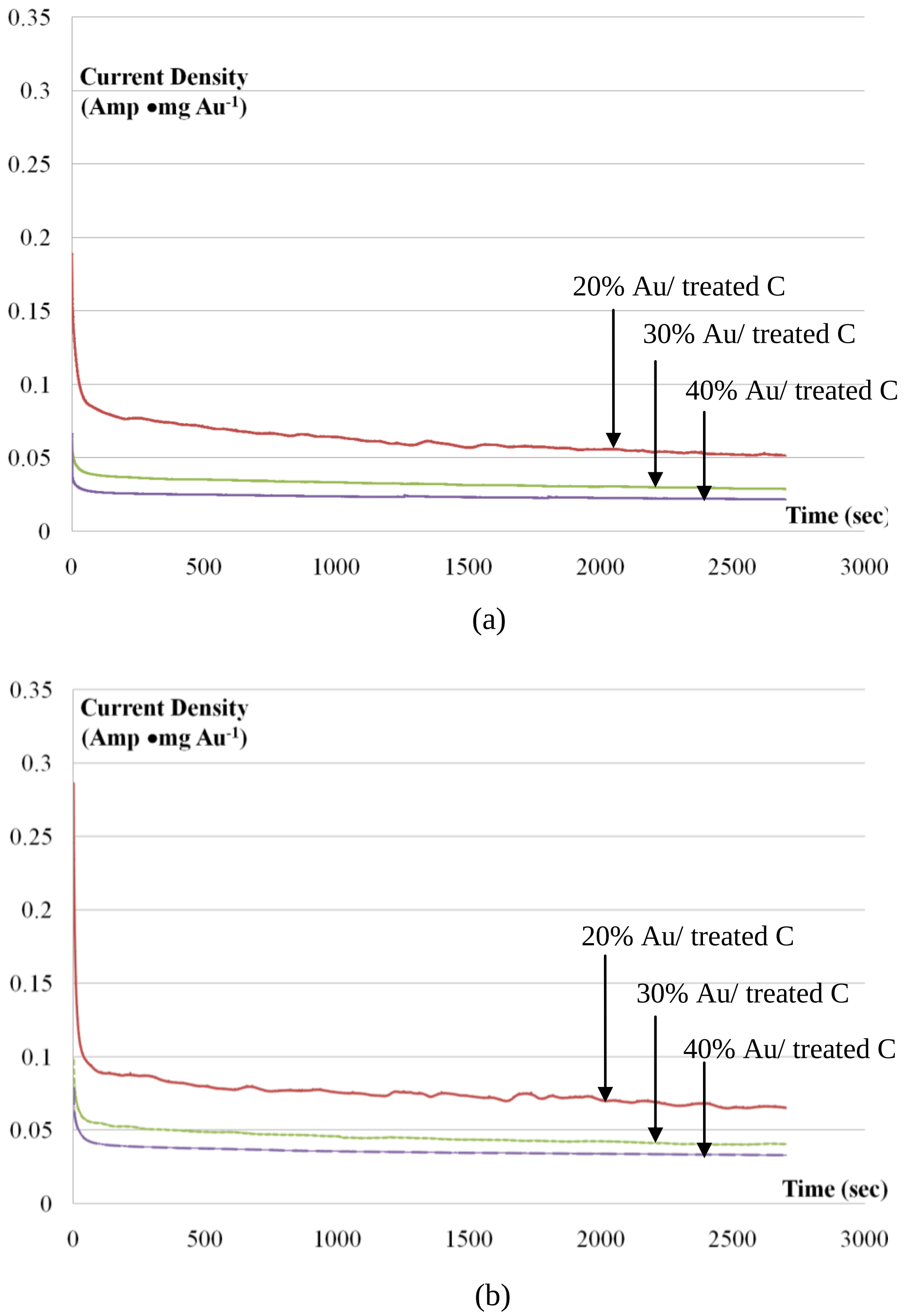
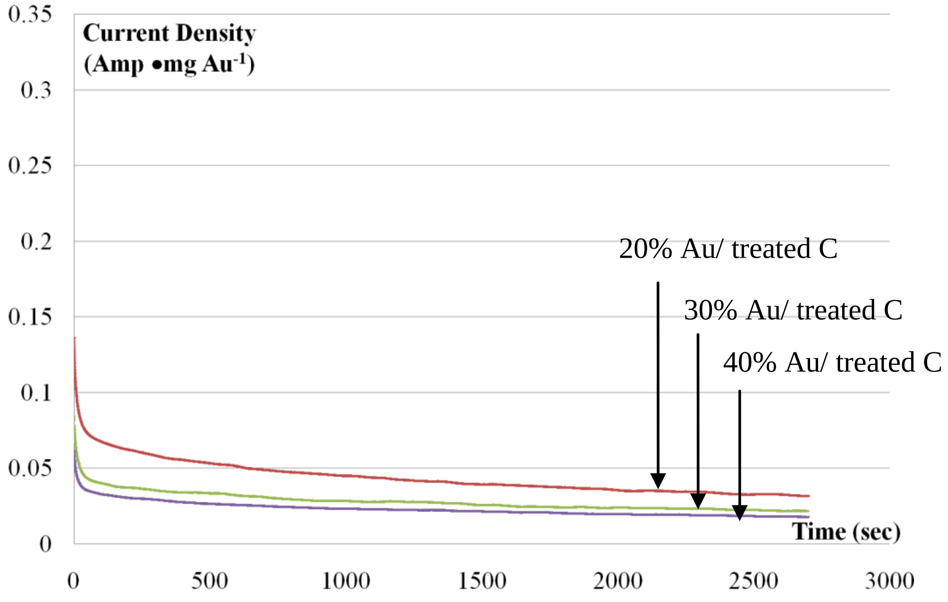
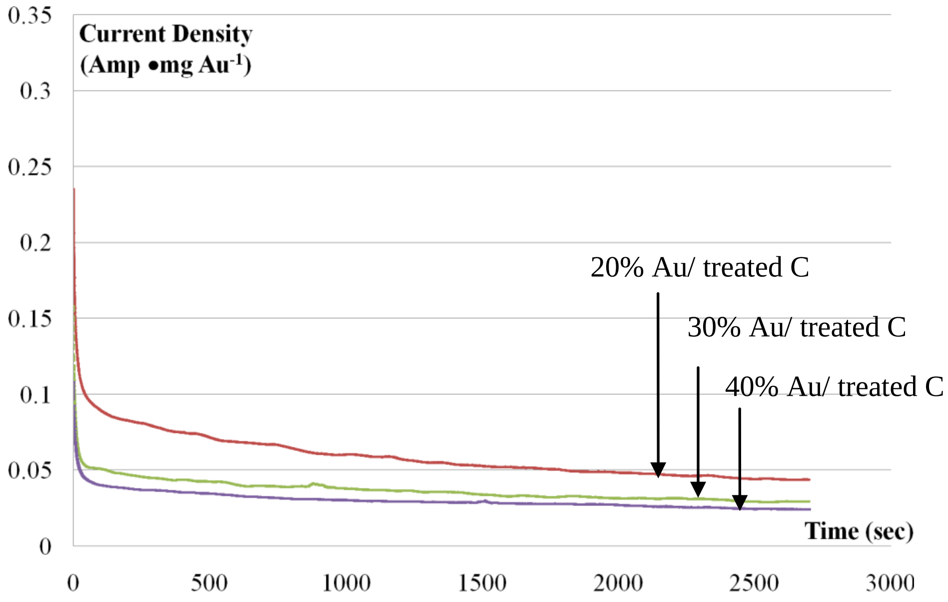


Figure 4.27 Chronoamperometric curves of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M glycerol at (a) 0.2 V (b) 0.4 V for 45 min



(a)



(b)

Figure 4.28 Chronoamperometric curves of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M glycerol at (a) 0.2 V (b) 0.4 V for 45 min

Table 4.6 Average current density and final stable current density from CA of Au/C catalysts in glycerol with alkaline solution by holding the potential constant at 0.2 V and 0.4 V

	At 0.2 V		At 0.4 V	
	Current $density_{ave}$ (Amp·mg Au^{-1})	Current $density_{final}$ (Amp·mg Au^{-1})	Current $density_{ave}$ (Amp·mg Au-^{1})	Current $density_{final}$ (Amp·mg Au^{-1})
PVA method				
20%Au/ untreated C	0.0250	0.0223	0.0331	0.0301
20%Au/ treated C	0.0566	0.0517	0.0711	0.0652
30%Au/ treated C	0.0308	0.0287	0.0424	0.0403
40%Au/ treated C	0.0228	0.0217	0.0340	0.0000
Citrate method				
20%Au/ untreated C	0.0265	0.0215	0.0387	0.0335
20%Au/ treated C	0.0372	0.0315	0.0503	0.0438
30%Au/ treated C	0.0246	0.0217	0.0328	0.0295
40%Au/ treated C	0.0202	0.0177	0.0272	0.0242

Table 4.7 Decaying rate of Au/C catalysts in glycerol with alkaline solution by holding the potential constant at 0.2 V and 0.4 V

	Decaying rate (% s^{-1})	
	at 0.2V	at 0.4V
PVA method		
20% Au / untreated C	0.0125	0.0125
20% Au / treated C	0.0108	0.0076
30% Au / treated C	0.0076	0.0075
40% Au / treated C	0.0050	0.0047
Citrate method		
20% Au / untreated C	0.0176	0.0163
20% Au / treated C	0.0161	0.0159
30% Au / treated C	0.0134	0.0129
40% Au / treated C	0.0131	0.0099

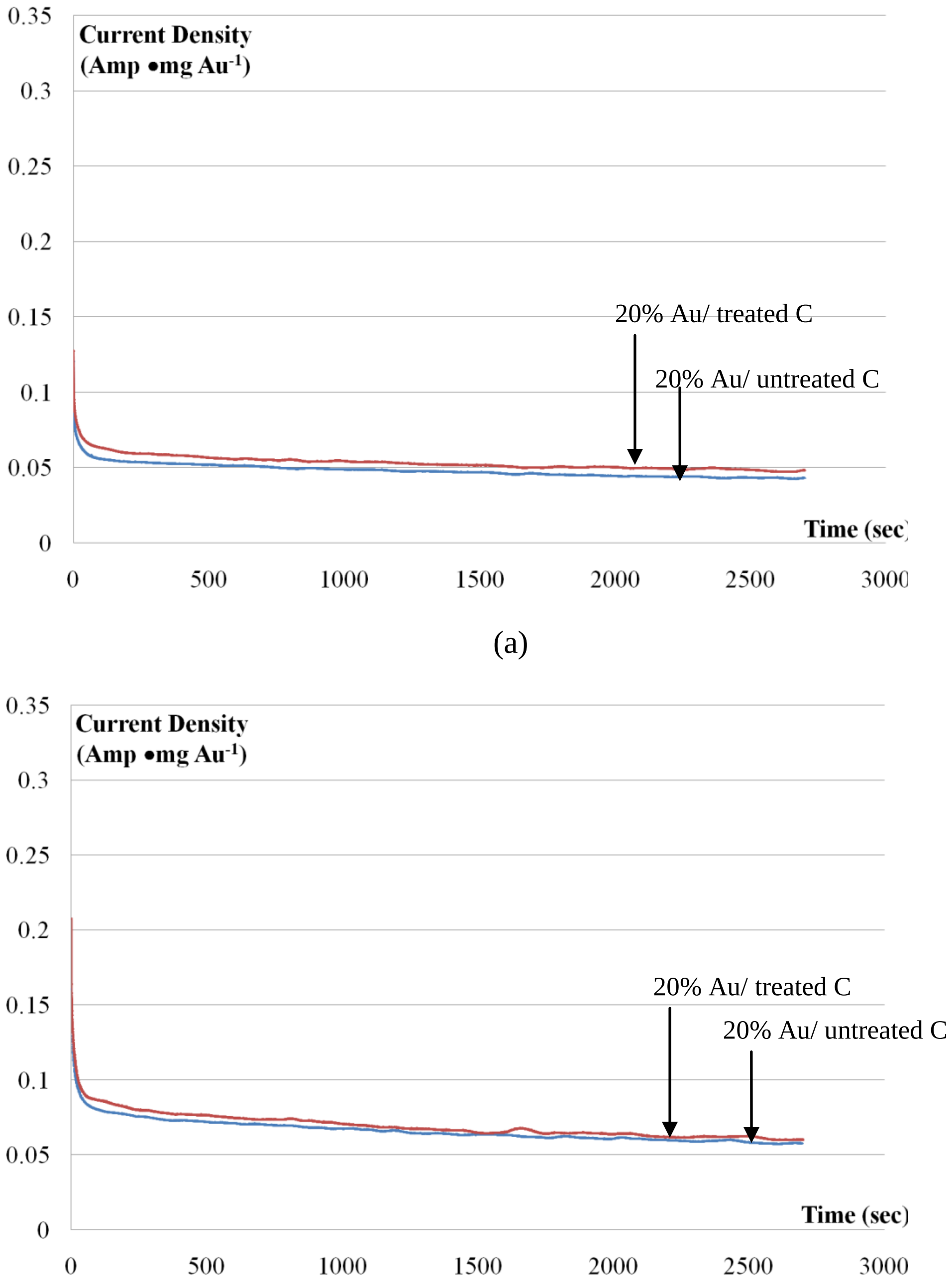
4.4.2 Chronoamperometry (CA) in 0.1M KOH with 0.1M ethylene glycol

Figure 4.29 to 4.32 show chronoamperometry (CA) of Au/C catalysts prepared by PVA and citrate method in ethylene glycol with alkaline solution at a potential of 0.2 V and 0.4 V. The current of catalysts drop rapidly at initial, and then decay slowly until 45 minutes.

The average current density from 10 minutes to 45 minutes and final stable density current of these catalysts are summarized in Table 4.8 while the decaying rates of all catalysts are shown in Table 4.9. These results are in agreement with those in glycerol with alkaline solution. When the 20 wt% Au on treated carbon and untreated carbon catalysts of both catalyst preparation were compared, the decaying rate (from Table 4.9) of catalyst with treated carbon was smaller and current density (from Table 4.8) was also higher than that with untreated carbon especially at 0.4 V, thus it can be concluded that catalysts with treated carbon were better than those with untreated carbon in ethylene glycol oxidation.

Decaying rate was decreased as the amount of Au increased. The reason was already explained in section 4.4.1. However, although 20 wt% Au catalyst with treated carbon showed higher decaying rate, this catalysts still gave higher current density than 30 wt% and 40 wt% Au catalysts with treated carbon in ethylene glycol oxidation. Thus, 20 wt% Au catalysts with treated carbon were better than 30 wt% and 40 wt% Au catalysts.

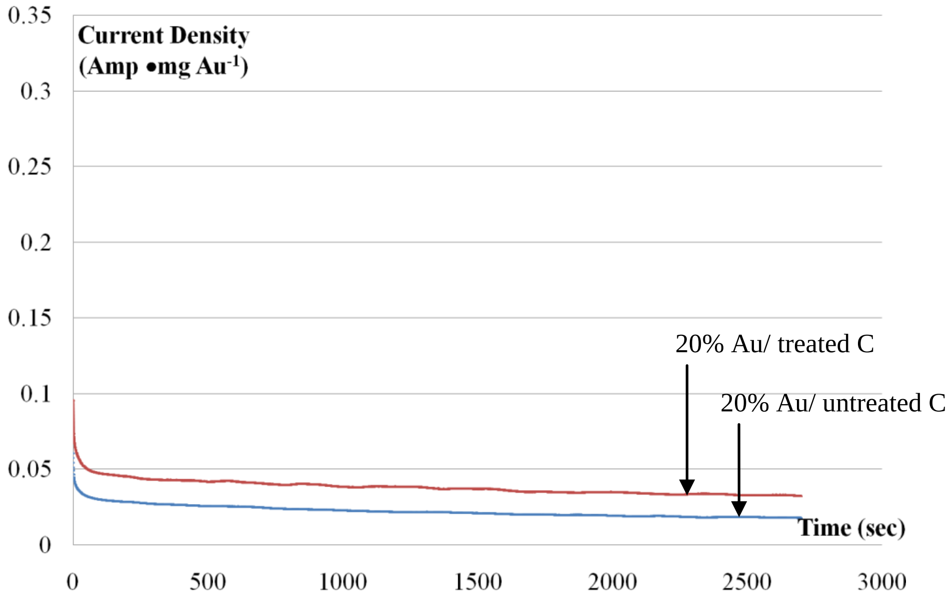
For the effect of catalyst preparation method, most of catalysts prepared by PVA protection method have higher current density and lower decaying rate, suggesting that the Au/C catalyst prepared by PVA protection was more attractive than that prepared by citrate protection method.



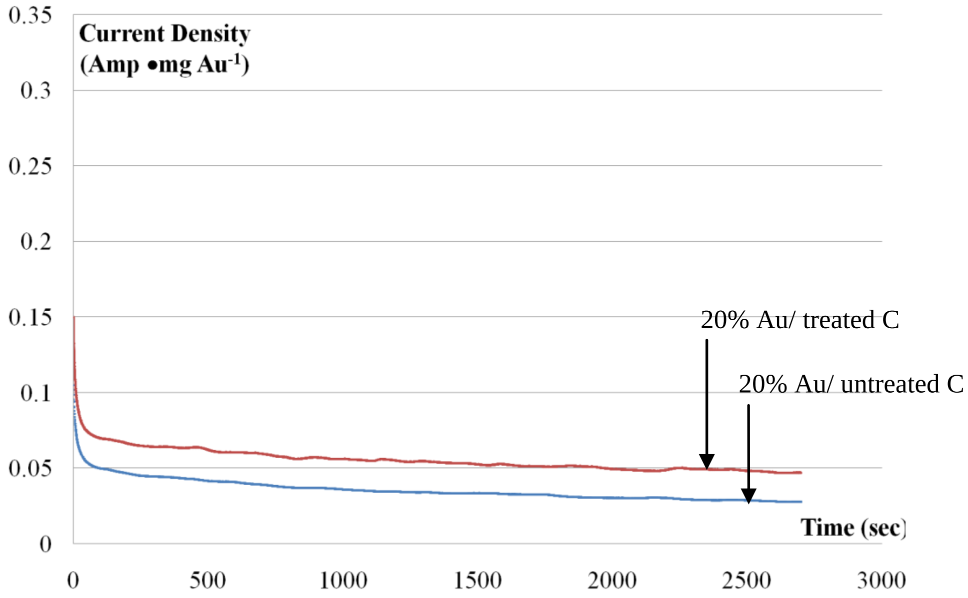
(a)

(b)

Figure 4.29 Chronoamperometric curves of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M ethylene glycol at (a) 0.2 V (b) 0.4 V for 45 min

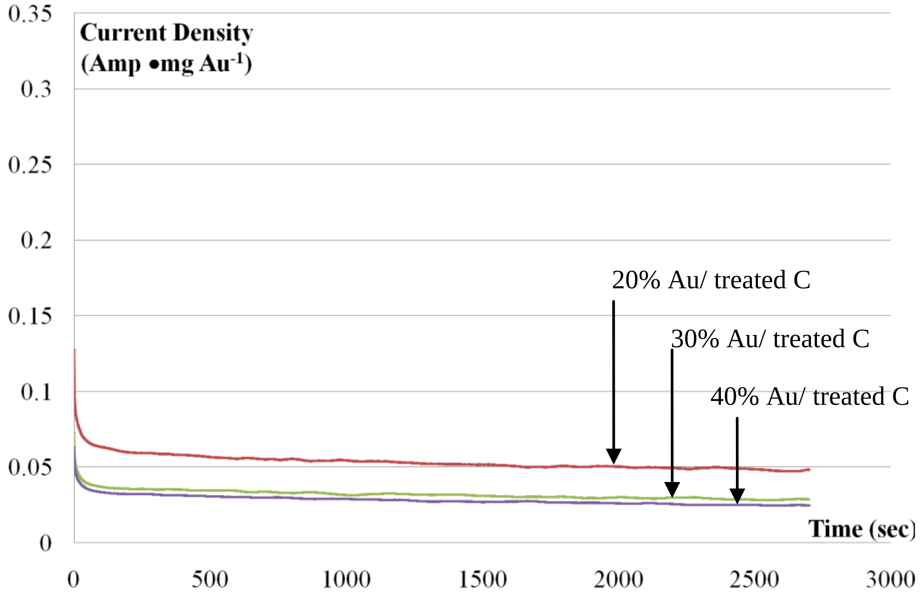


(a)

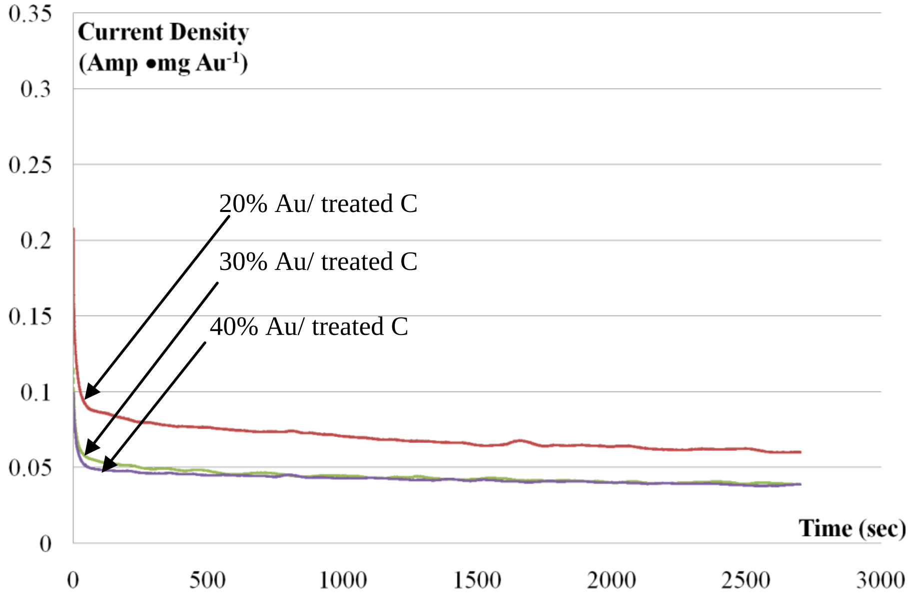


(b)

Figure 4.30 Chronoamperometric curves of 20 wt% Au on treated and untreated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M ethylene glycol at (a) 0.2 V (b) 0.4 V for 45 min

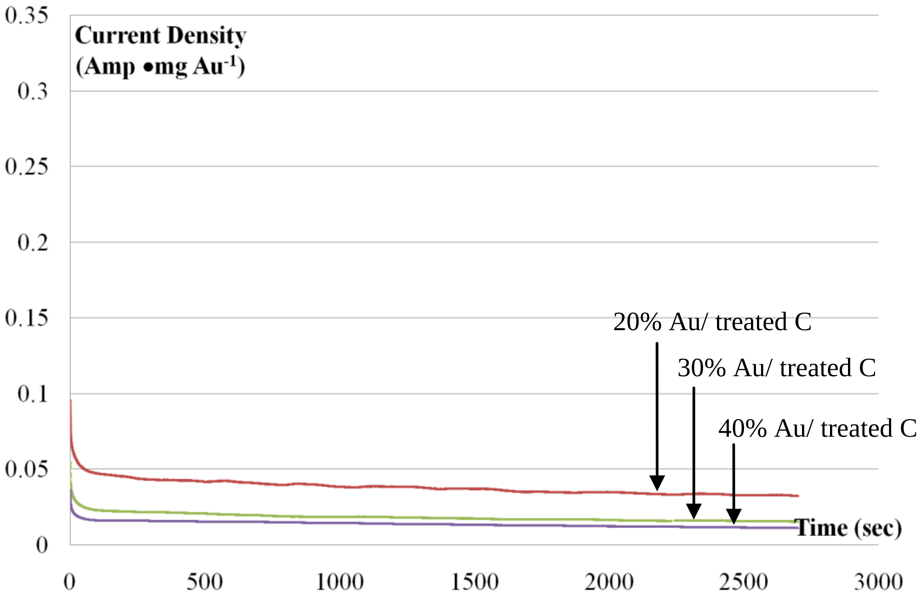


(a)

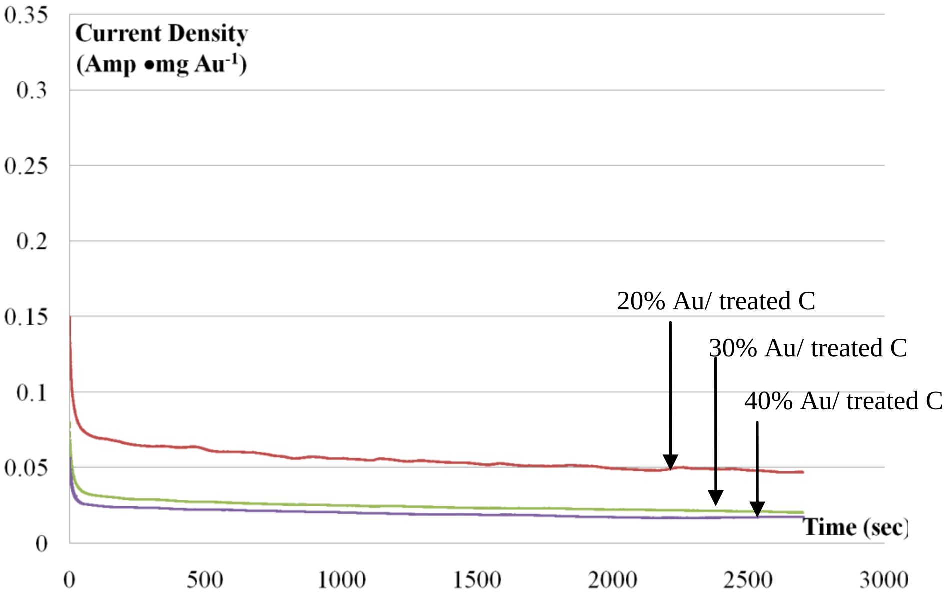


(b)

Figure 4.31 Chronoamperometric curves of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the PVA protection method in 0.1M KOH with 0.1M ethylene glycol at (a) 0.2 V (b) 0.4 V for 45 min



(a)



(b)

Figure 4.32 Chronoamperometric curves of 20 wt%, 30 wt% and 40 wt% Au on treated carbon of Au/C catalyst prepared by the citrate protection method in 0.1M KOH with 0.1M ethylene glycol at (a) 0.2 V (b) 0.4 V for 45 min

Table 4.8 Average current density and final stable current density from CA of Au/C catalysts in ethylene glycol with alkaline solution by holding the potential constant at 0.2 V and 0.4 V

	At 0.2 V		At 0.4 V	
	Current density$_{ave}$ (Amp·mg Au^{-1})	Current density$_{final}$ (Amp·mg Au^{-1})	Current density$_{ave}$ (Amp·mg Au-^{1})	Current density$_{final}$ (Amp·mg Au^{-1})
PVA method				
20%Au/ untreated C	0.0454	0.0432	0.0619	0.0577
20%Au/ treated C	0.0505	0.0483	0.0646	0.0602
30%Au/ treated C	0.0302	0.0287	0.0414	0.0391
40%Au/ treated C	0.0264	0.0246	0.0405	0.0388
Citrate method				
20%Au/ untreated C	0.0198	0.0178	0.0315	0.0278
20%Au/ treated C	0.0352	0.0322	0.0511	0.0471
30%Au/ treated C	0.0167	0.0153	0.0226	0.0204
40%Au/ treated C	0.0126	0.0110	0.0180	0.0174

Table 4.9 Decaying rate of Au/C catalysts in ethylene glycol with alkaline solution by holding the potential constant at 0.2 V and 0.4 V

	Decaying rate (% s^{-1})	
	at 0.2V	at 0.4V
PVA method		
20% Au / untreated C	0.0075	0.0085
20% Au / treated C	0.0066	0.0086
30% Au / treated C	0.0073	0.0069
40% Au / treated C	0.0085	0.0068
Citrate method		
20% Au / untreated C	0.0128	0.0129
20% Au / treated C	0.0098	0.0093
30% Au / treated C	0.0096	0.0098
40% Au / treated C	0.0122	0.0109

CHAPTER 5 CONCLUSIONS AND RECCOMENDATIONS

5.1 Conclusions

Heat treatment on carbon support of Au/C catalyst could improve the catalytic activity of Au/C catalyst for high molecular weight alcohol electrooxidation. Au particle size on heat treated carbon was smaller than those on untreated carbon leading to more active Au catalyst for glycerol and ethylene glycol oxidation. It was also found that particle size effect was more important than the capacity of gold oxide formation on electrode surface. Furthermore, the tolerance to poisoning of Au/ treated carbon was higher than Au/ untreated carbon. Therefore it can be concluded that the heat treatment on carbon support can improve the performance of Au/C catalyst.

Increasing the amount of Au in Au/C catalyst led to particle size agglomeration resulting in a reduction of catalytic activity in alcohol oxidation. Although 20 wt% Au/C had higher decaying rate than 30 wt% and 40 wt% Au/C, it can produce higher current density. Since the increase of Au loading could cause Au particle agglomeration resulting in a reduction of Au catalytic activity, the suitable Au loading for Au/C catalyst was 20 wt%.

Catalyst preparation methods could also affect the performance of Au/C catalyst in alcohol electrooxidation. In overall, the particle size of Au/C catalyst prepared by PVA protection method was smaller than that from citrate protection method. Consequently, the catalytic activity of the Au/C catalysts prepared by the PVA protection method was higher than those prepared by the citrate protection method. In addition, PVA protection method provided higher tolerant catalyst. Therefore the suitable Au/C catalyst preparation method was the PVA protection technique.

5.2 Recommendations

To ensure the effect of heat treatment 30 wt% and 40 wt% Au of Au/C catalysts with untreated carbon should be studied. Furthermore the suitable amount of Au in Au/C catalyst should be investigated by varying Au loading in the narrow range.

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APENDIX A

Experimental Data

A.1 Catalyst Preparation

PVA Protection Method

Example of 20% Au of Au/C catalyst preparation was discussed below;

Catalysts 100 mg contain → 20 mg of Au
→ 80 mg of carbon

Au 0.5 mg was obtained from $HAuCl_4$ 1 mg

Thus, Au 20 mg was obtained from $HAuCl_4$ 40 mg

40 mg of $HAuCl_4$ was weighed out and dissolved in 181.8 ml of water to obtain 110 µg/ml .

Next, 100 mg of PVA was weighed out and dissolved in 5 ml of water, and then about 0.2 ml was dropped into $HAuCl_4$ solution (2 %wt of PVA).

$NaBH_4$ were used with the mole ratio of $NaBH_4$:Au (4:1);$NaBH_4$ 0.1M was prepared by weighed out 0.0189 g and then dissolved in 5 ml of water. After that 4.7 ml of $NaBH_4$ was added dropwise in $HAuCl_4$ solution. The amounts of every component for preparing 20, 30 and 40 wt% Au/C were summarized in Table A.1, A.2 and A.3, respectively.

Table A.1 The amount of substances used in preparing 20 wt% Au/C catalyst by PVA method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	40	181.8	-
2. Carbon	80	-	-
3. PVA	100	5	0.2
4. $NaBH_4$	0.0189	5	4.7

Table A.2 The amount of substances used in preparing 30 wt% Au/C catalyst by PVA method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	60	272.7	-
2. Carbon	70	-	-
3. PVA	100	5	0.3
4. $NaBH_4$	0.0378	10	7.05

Table A.3 The amount of substances used in preparing 40 wt% Au/C catalyst by PVA method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	80	363.6	-
2. Carbon	60	-	-
3. PVA	100	5	0.4
4. $NaBH_4$	0.0378	10	9.4

Citrate Protection Method

Table A.4 The amount of substances used in preparing 20 wt% Au/C catalyst by citrate method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	40	381	-
2. Carbon	80	-	-
3. tri-potassium citrate	44	4	4
4. tri-potassium citrate $NaBH_4$	0.0189 44	5	4.7

Table A.5 The amount of substances used in preparing 30 wt% Au/C catalyst by citrate method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	60	571.43	-
2. Carbon	70	-	-
3. tri-potassium citrate	66	6	6
4. tri-potassium citrate $NaBH_4$	0.0378 132	10	7.05

Table A.6 The amount of substances used in preparing 40 wt% Au/C catalyst by citrate method

	Weigh (mg)	**Dissolving in Water (ml)**	**Adding in $HAuCl_4$ solution (ml)**
1. $HAuCl_4$	80	762	-
2. Carbon	60	-	-
3. tri-potassium citrate	88	8	8
4. tri-potassium citrate $NaBH_4$	0.0378 176	10	9.4

A.2 Results of Atomic Absorption Spectroscopy

Table A.7 Results of AAS and calculation of Au deposition on carbon support

Catalyst	AAS_{result} (mg/L)	filtrate volume (ml)	Au_{Total} (g)	Au_s (g)	Support (g)	$\%Au_{deposited}$
PVA method						
20% Au/untreated C	n.d.	197	0.02	0.0200	0.08	20.00
20% Au/treated C	n.d.	186	0.02	0.0200	0.08	20.00
30% Au/treated C	11	280	0.030	0.0270	0.07	27.81
40% Au/treated C	48.2	408	0.042	0.0226	0.06	27.35
Citrate method						
20% Au/untreated C	n.d.	387	0.02	0.0200	0.08	20.00
20% Au/treated C	n.d.	407	0.02	0.0200	0.08	20.00
30% Au/treated C	0.47	575	0.03	0.0296	0.0698	29.80
40% Au/treated C	5.9	780	0.04	0.0354	0.06	37.11

A.3 Transmission Electron Microscopy (TEM) image

There are many TEM images of each catalyst captured by National Metal and Materials Technology Center (MTEC). TEM images of each catalyst were taken at three magnifications, 40,000x, 100,00x and 200,000x.

PVA protection method

1. 20% Au/ untreated Carbon

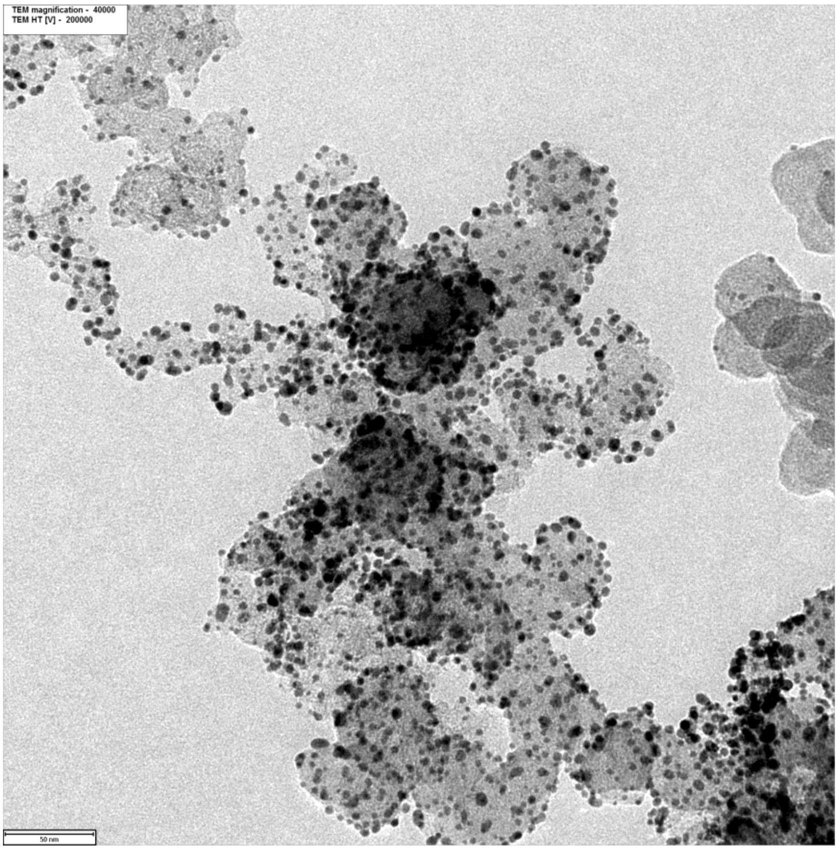
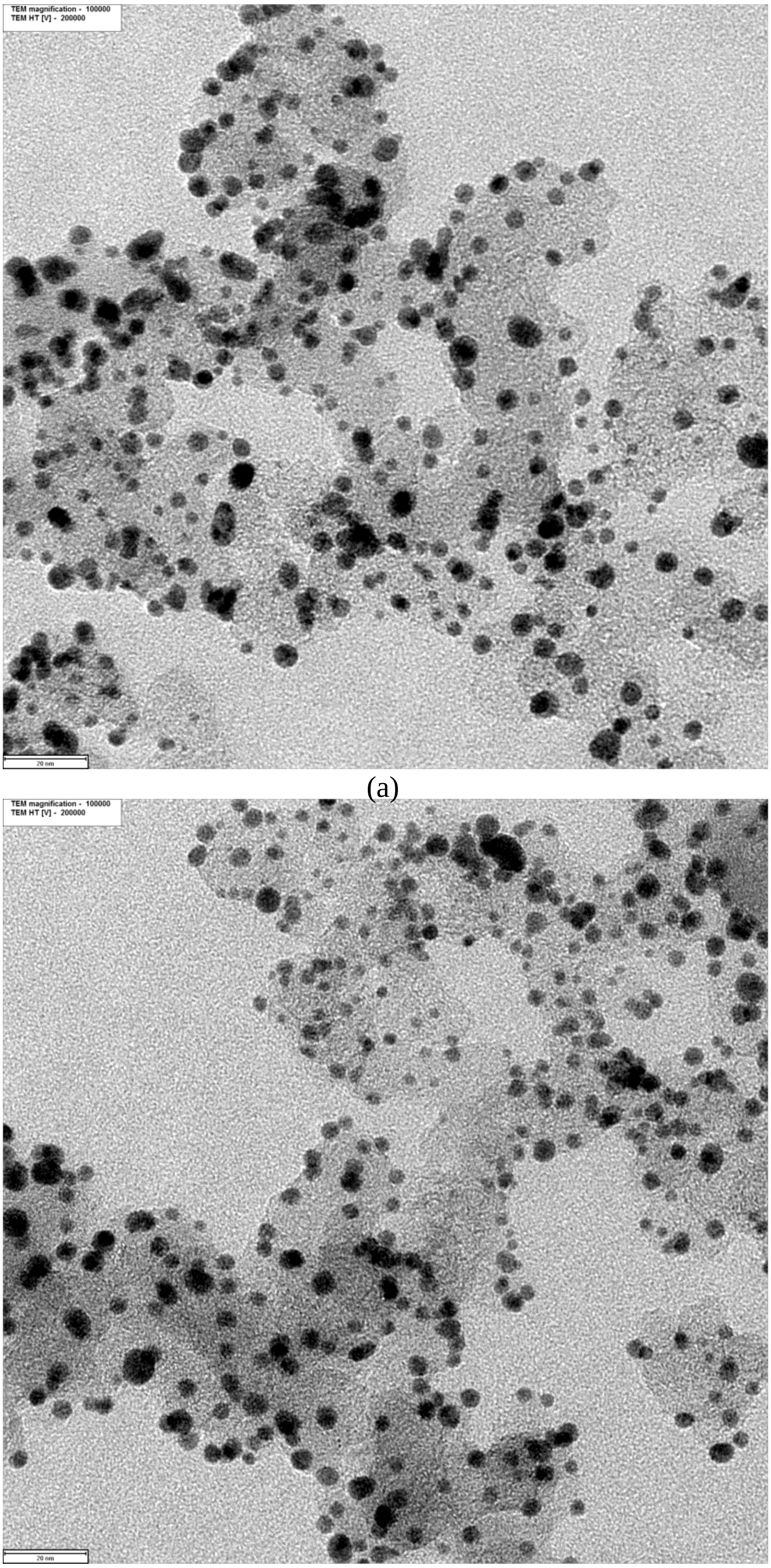


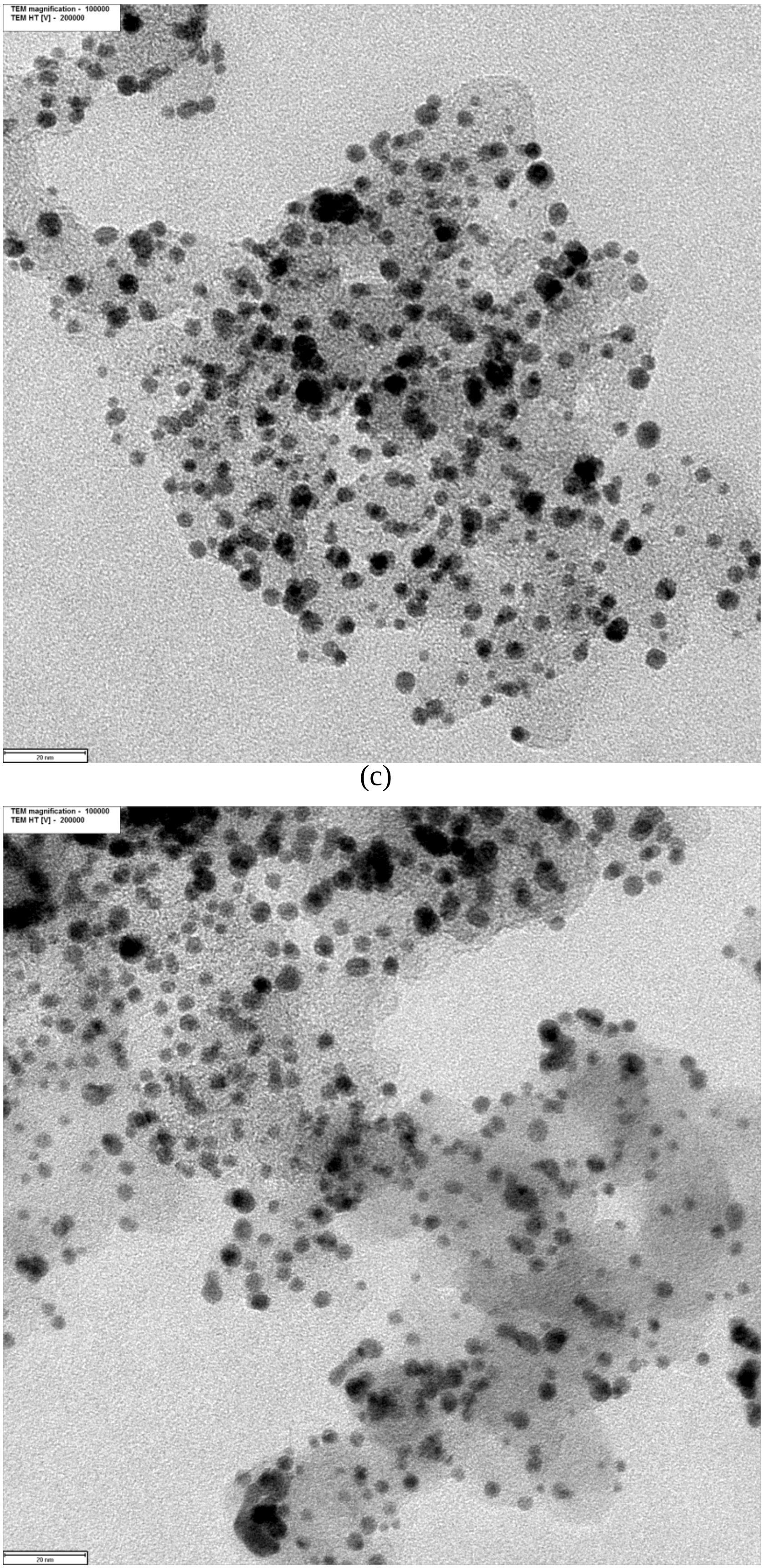
Figure A.1 TEM image at magnification of 40,000x. of 20 wt% Au on untreated carbon



(a)

(b)

Figure A.2 (a)-(d) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon



(c)

(d)

Figure A.2 (a)-(d) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon (continue)

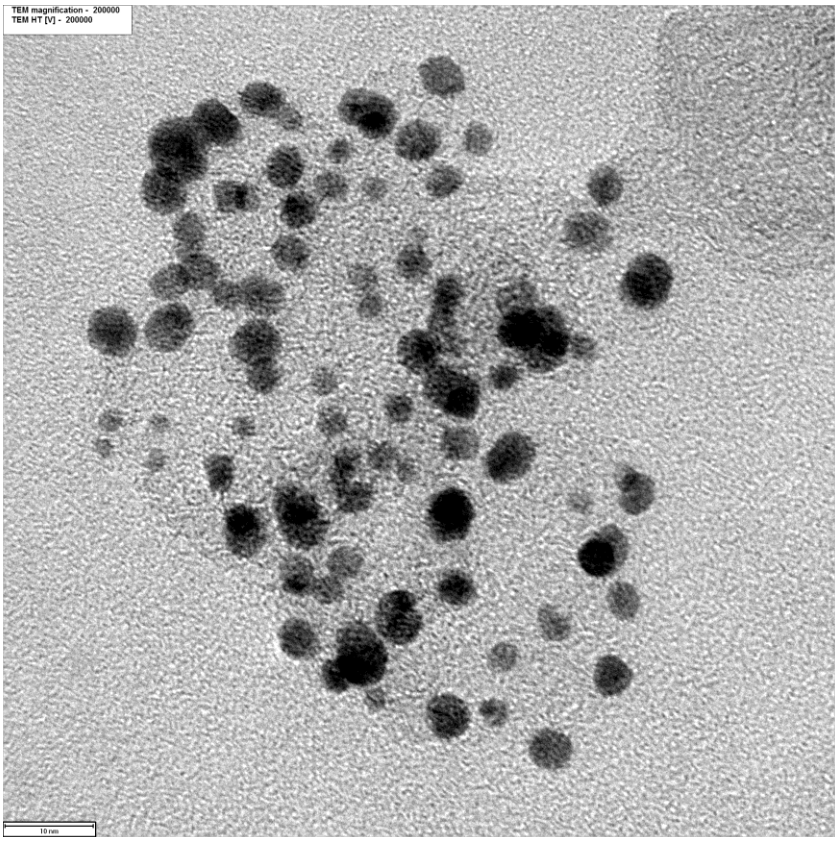
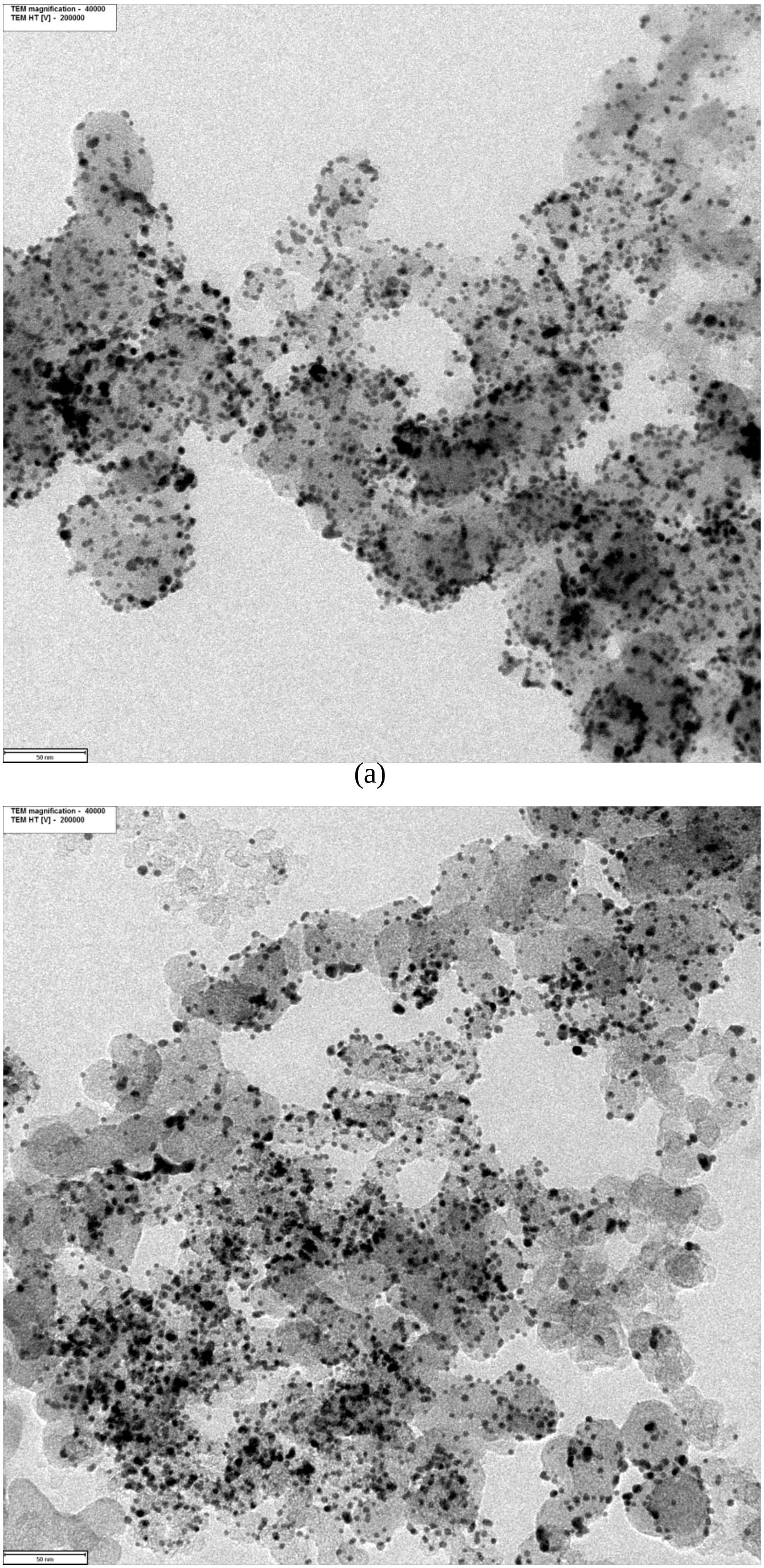


Figure A.3 TEM image at magnification of 200,000x. of 20 wt% Au on untreated carbon

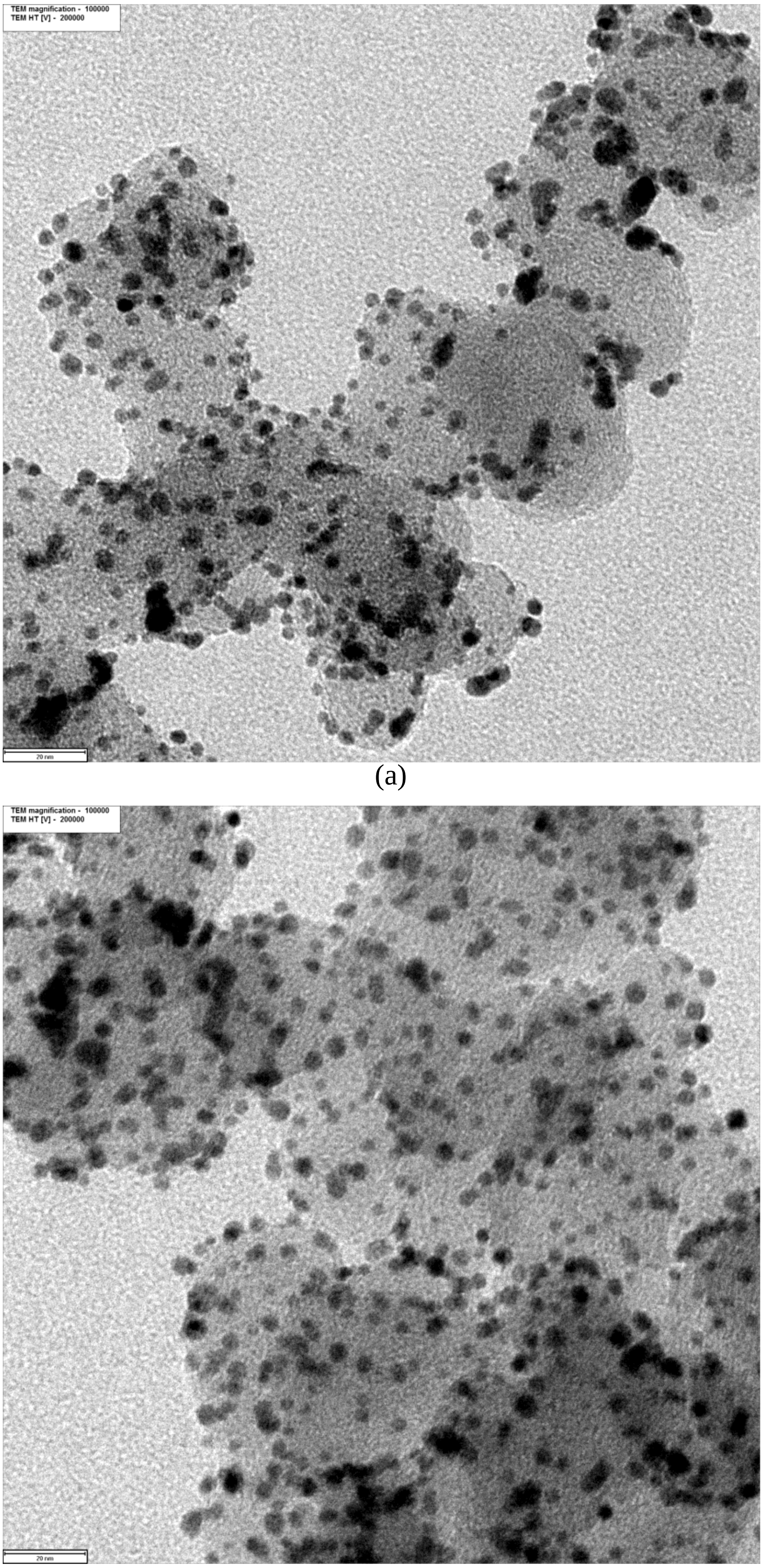
2. 20% Au/ treated Carbon



(a)

(b)

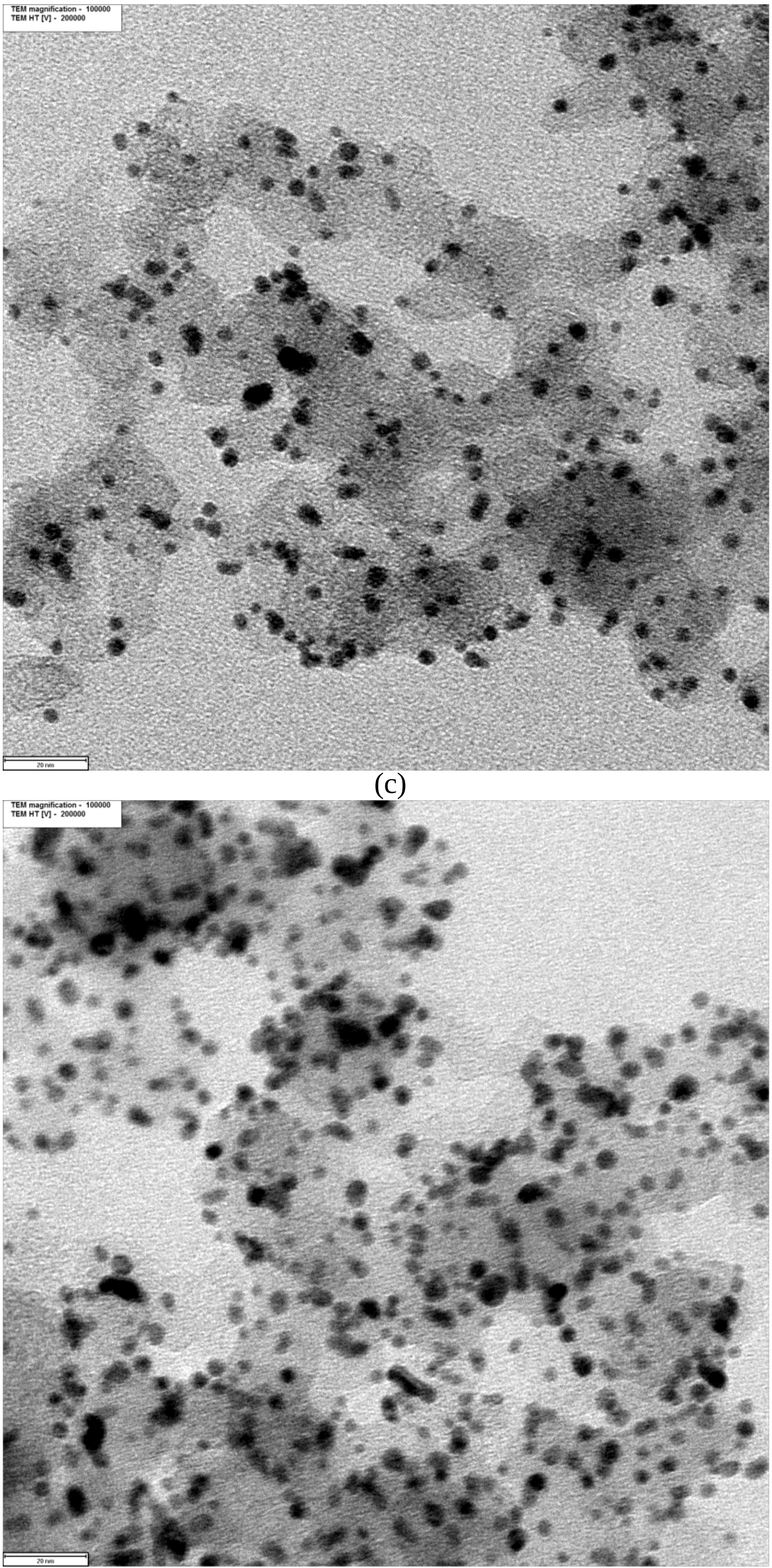
Figure A.4 (a)-(b) TEM image at magnification of 40,000x. of 20 wt% Au on treated carbon



(a)

(b)

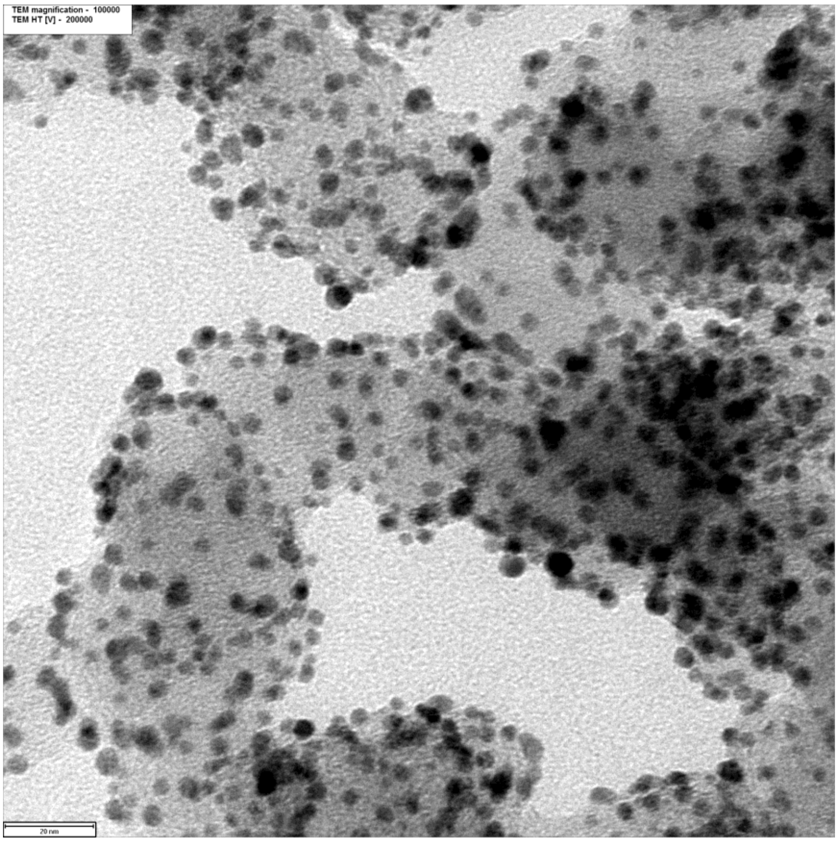
Figure A.5 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on treated carbon



(c)

(d)

Figure A.5 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on treated carbon (continue)



(e)

Figure A.5 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on treated carbon (continue)

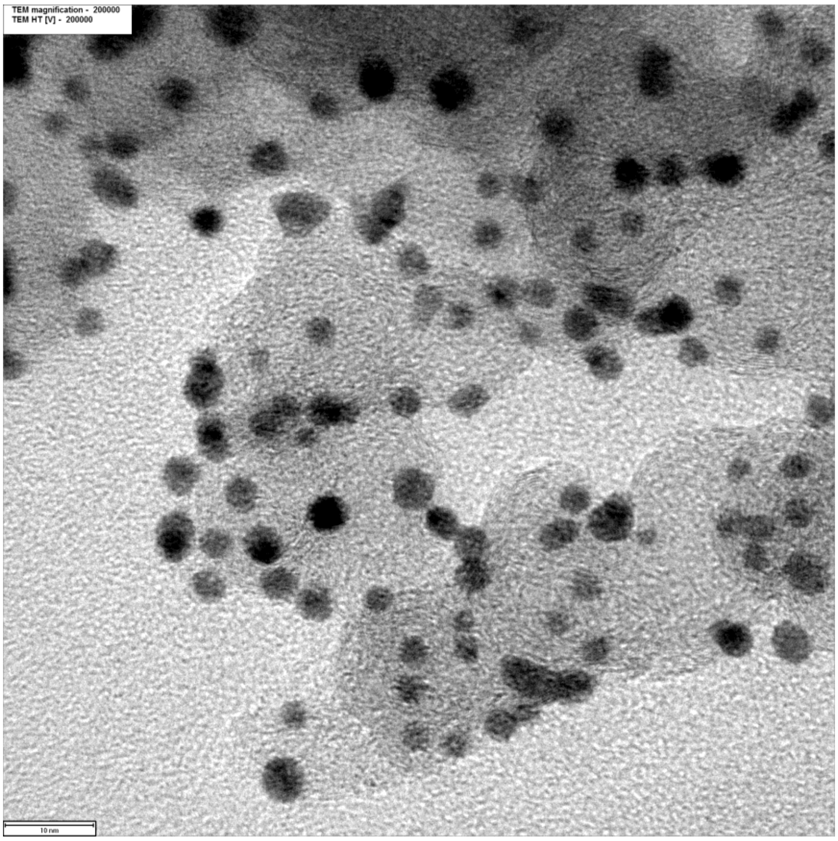
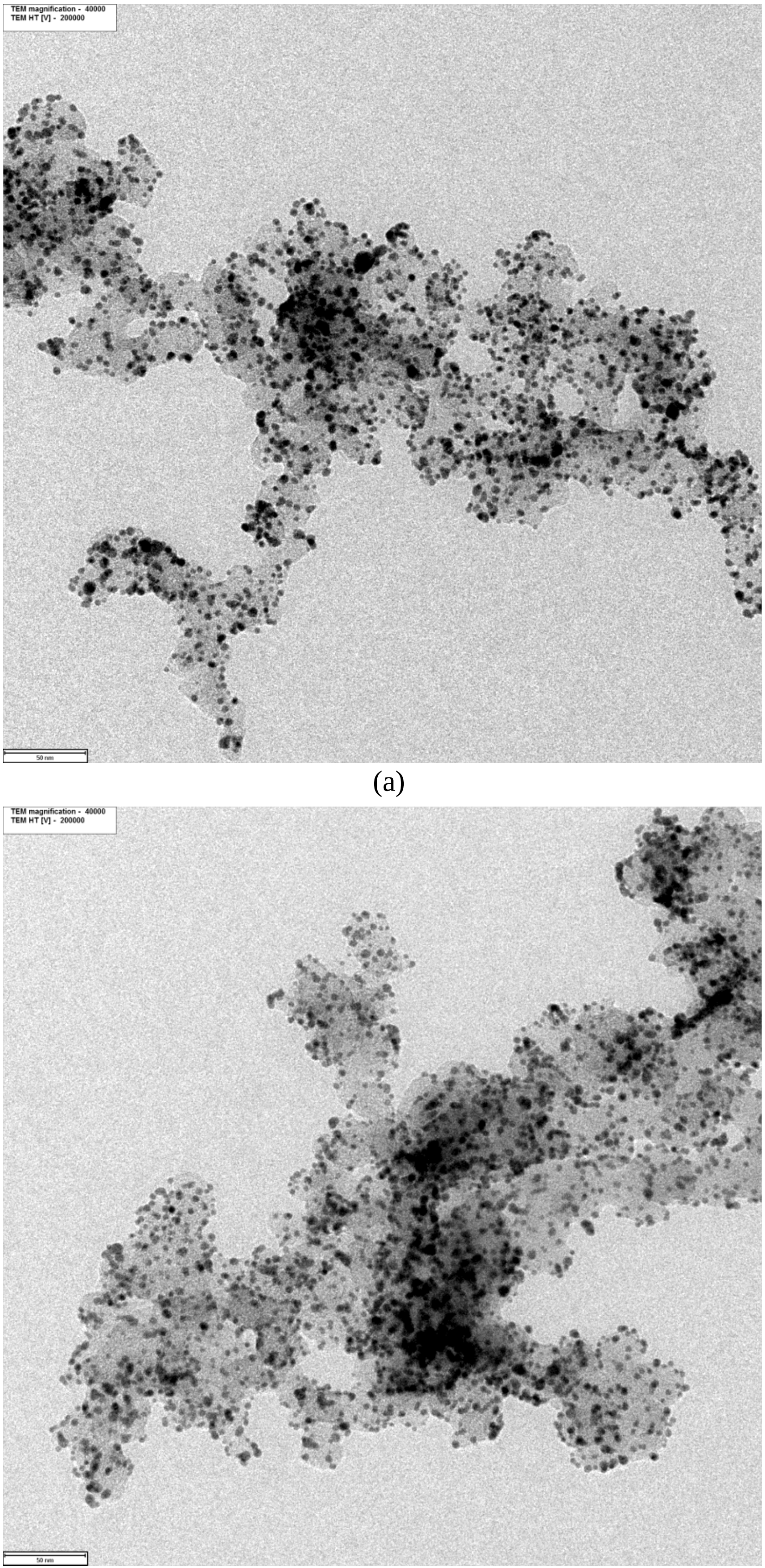


Figure A.6 TEM image at magnification of 200,000x. of 20 wt% Au on treated carbon

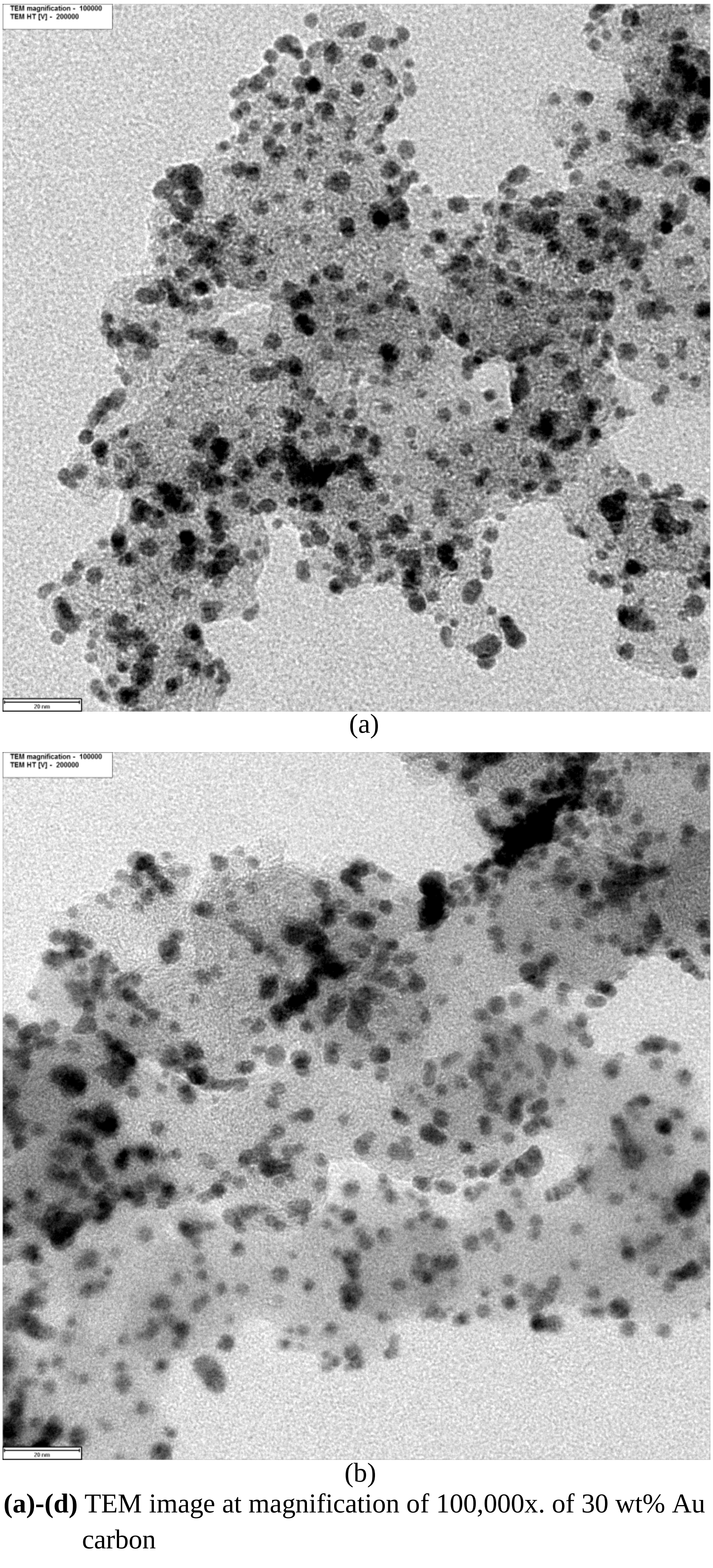
3. 30% Au/ treated Carbon



(a)

(b)

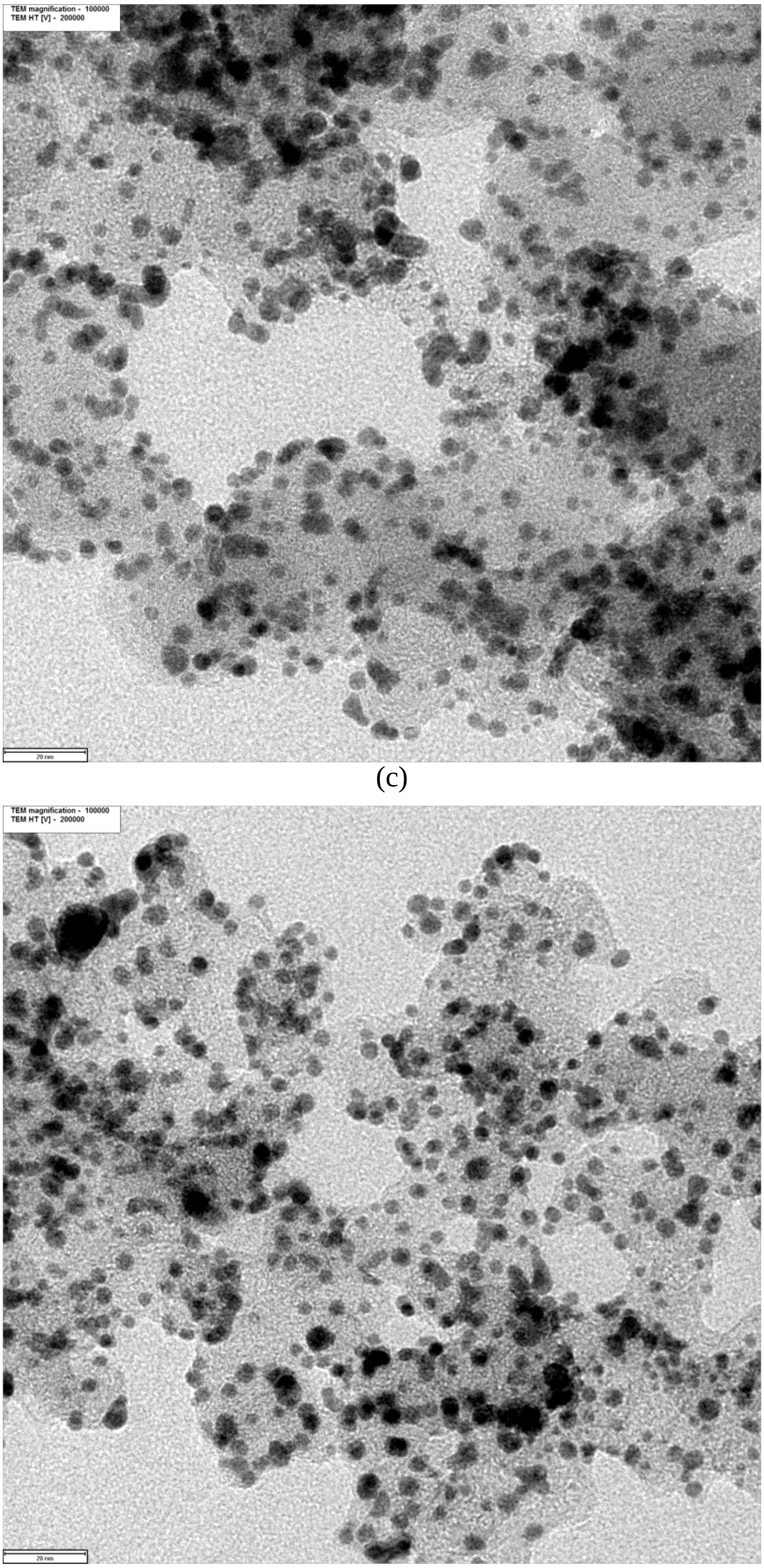
Figure A.7 (a)-(b) TEM image at magnification of 40,000x. of 30 %wt Au on treated carbon



(a)

(b)

Figure A.8 (a)-(d) TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon



(c)

(d)

Figure A.8 (a)-(d) TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon (continue)

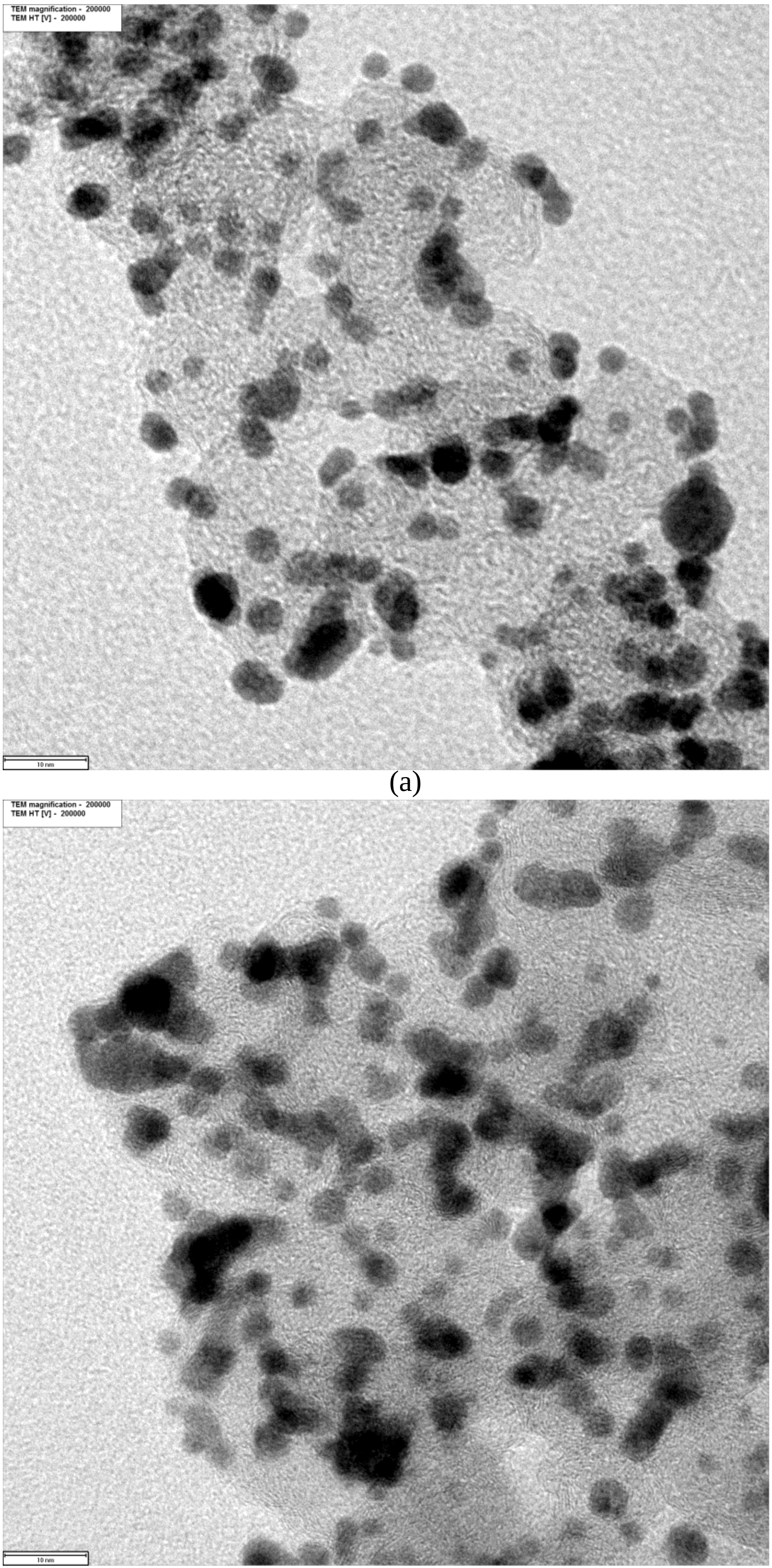


Figure A.9 (a)-(b) TEM image at magnification of 200,000x. of 30 wt% Au on treated carbon

4. 40% Au/ treated Carbon

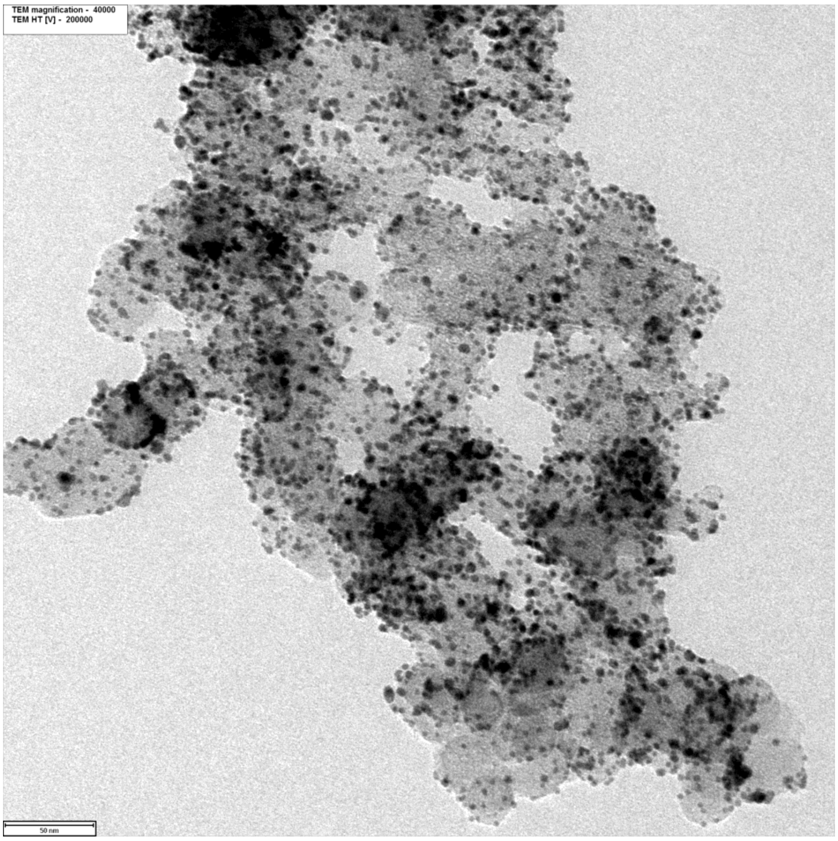
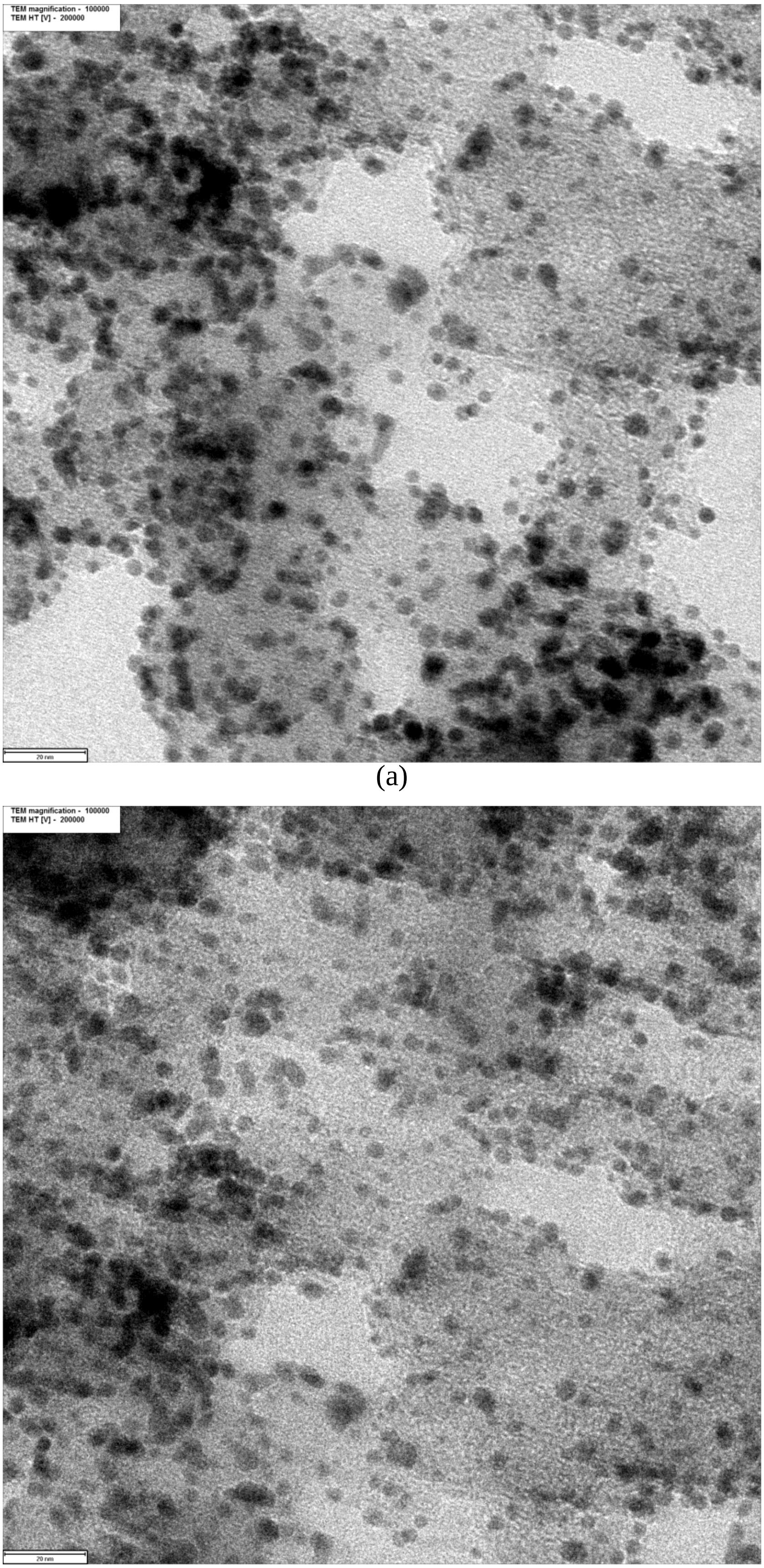


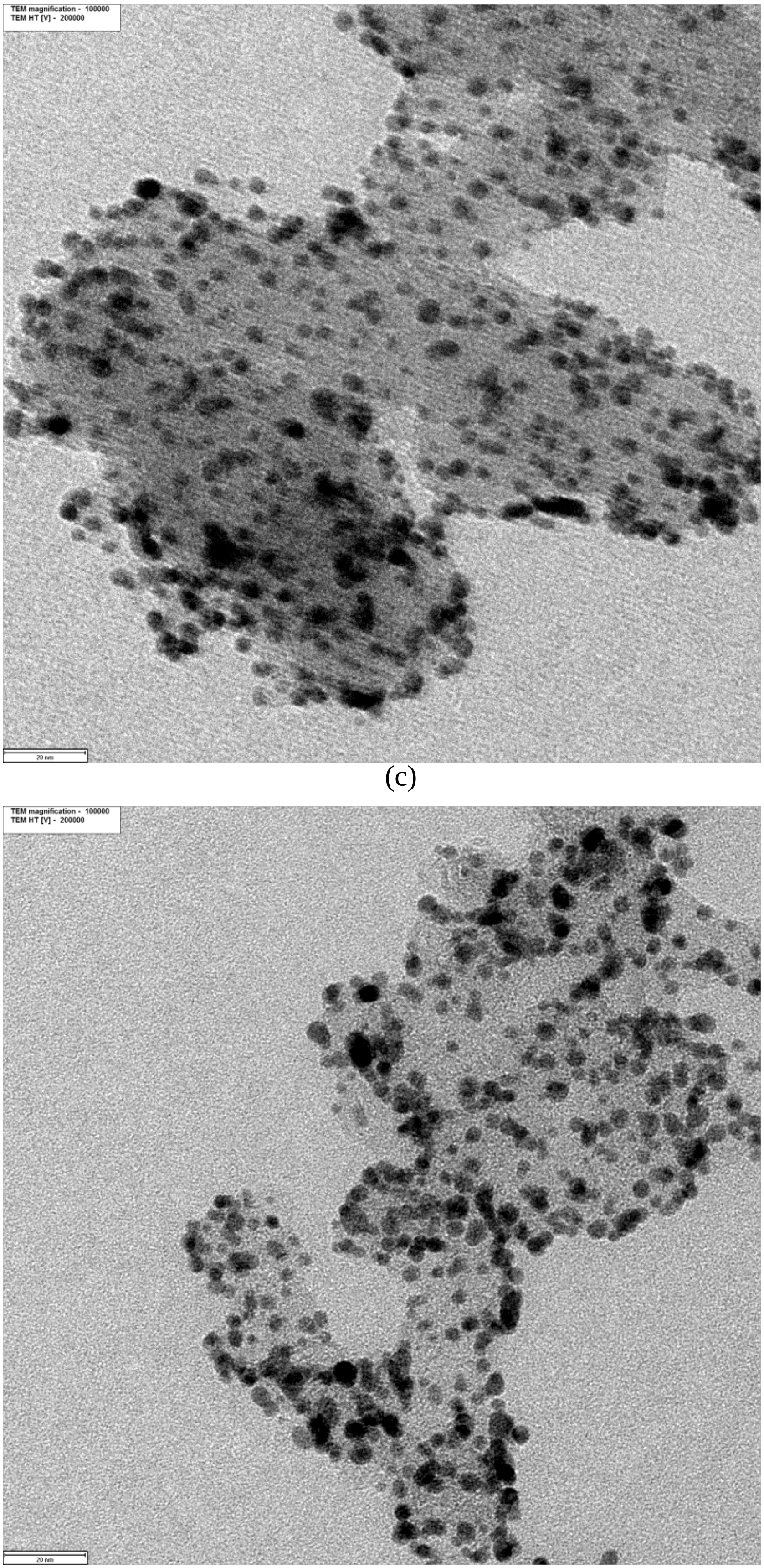
Figure A.10 TEM image at magnification of 40,000x. of 40 %wt Au on treated carbon



(a)

(b)

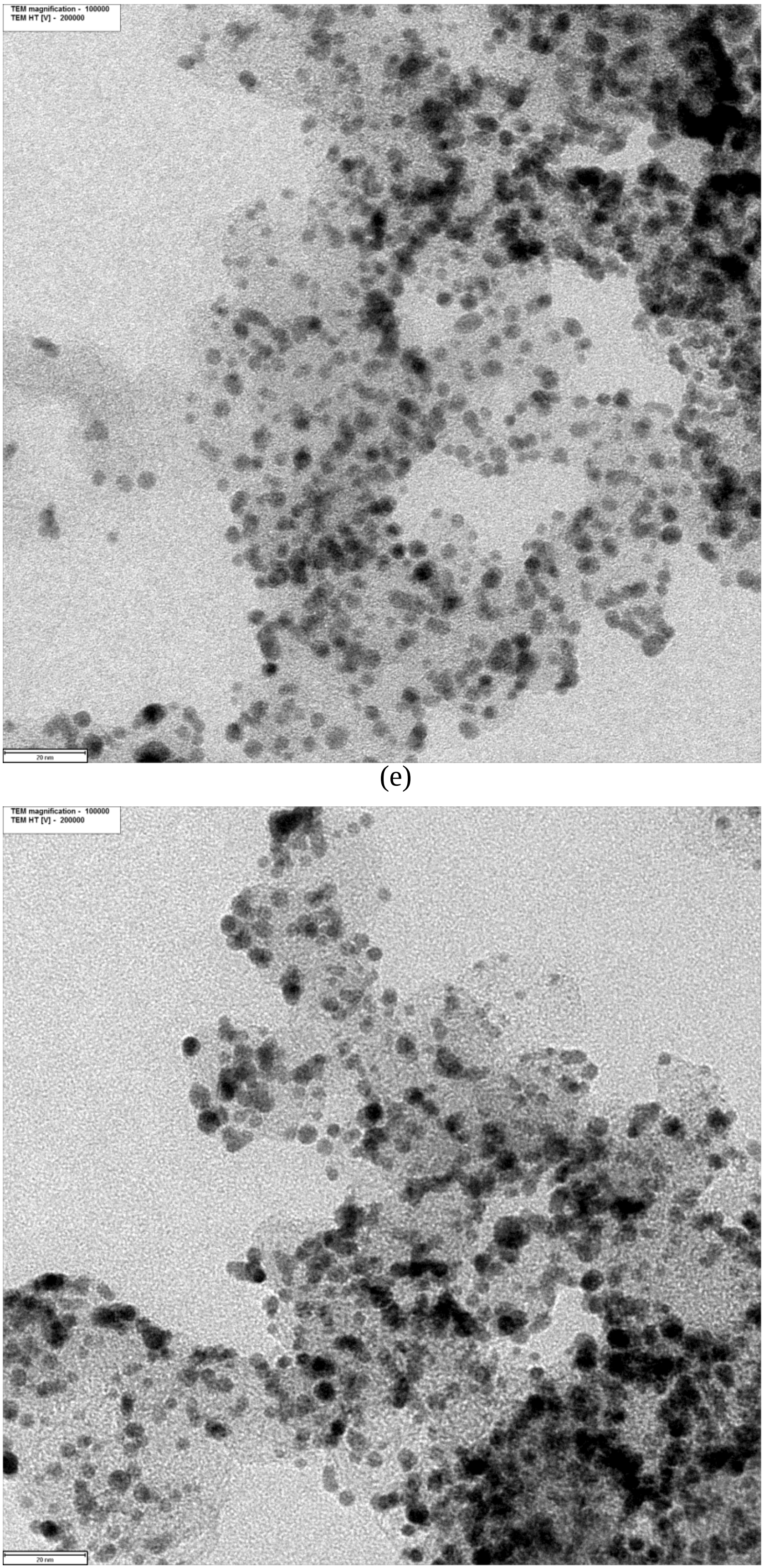
Figure A.11 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon



(c)

(d)

Figure A.11 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon (continue)



(e)

(f)

Figure A.11 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon (continue)

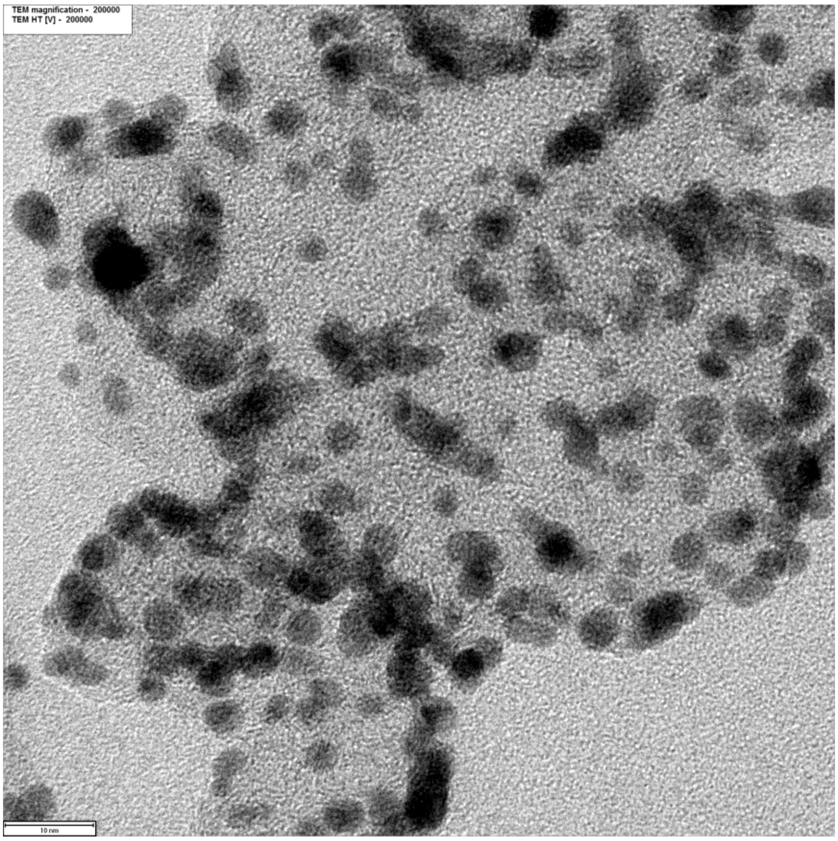


Figure A.12 TEM image at magnification of 200,000x. of 40 wt% Au on treated carbon

Citrate protection method

1. 20% Au/ untreated Carbon

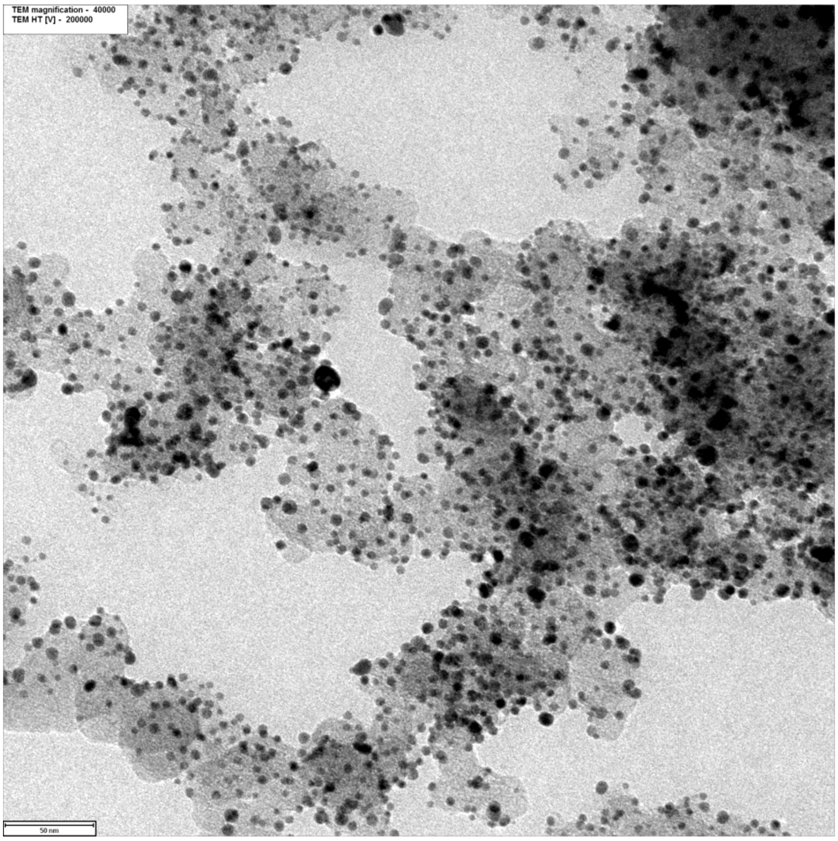
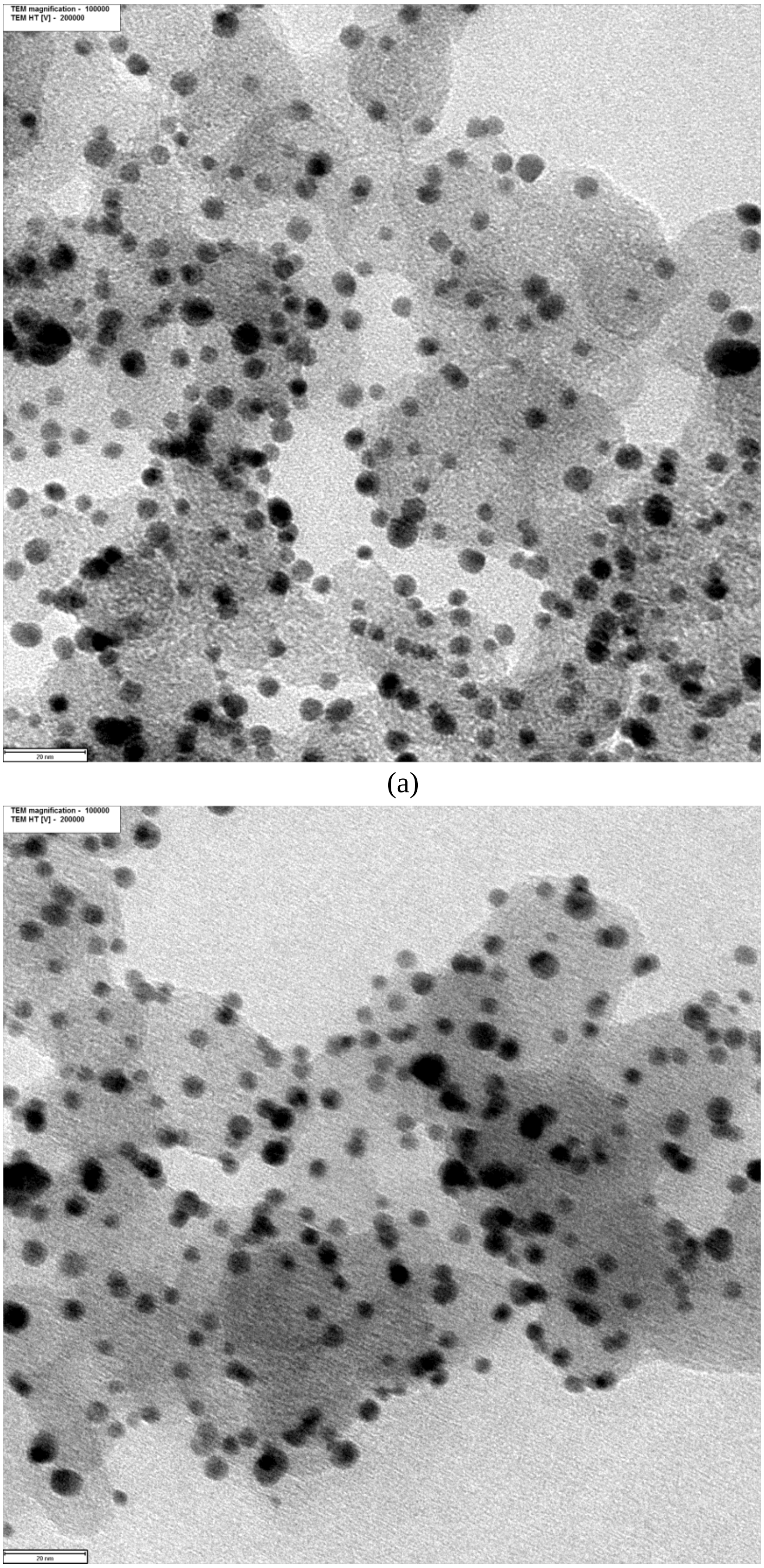


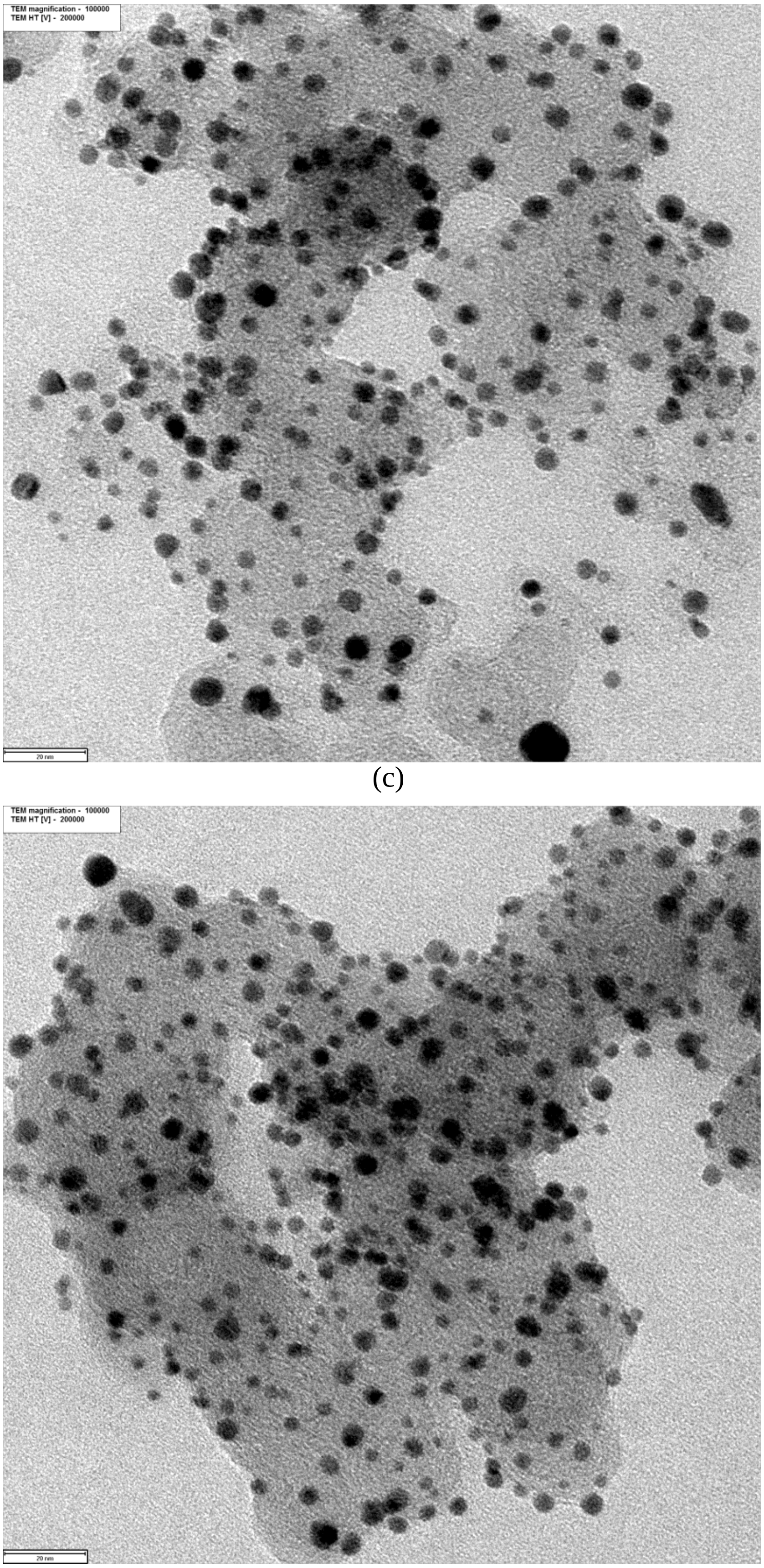
Figure A.13 TEM image at magnification of 40,000x. of 20 wt% Au on untreated carbon



(a)

(b)

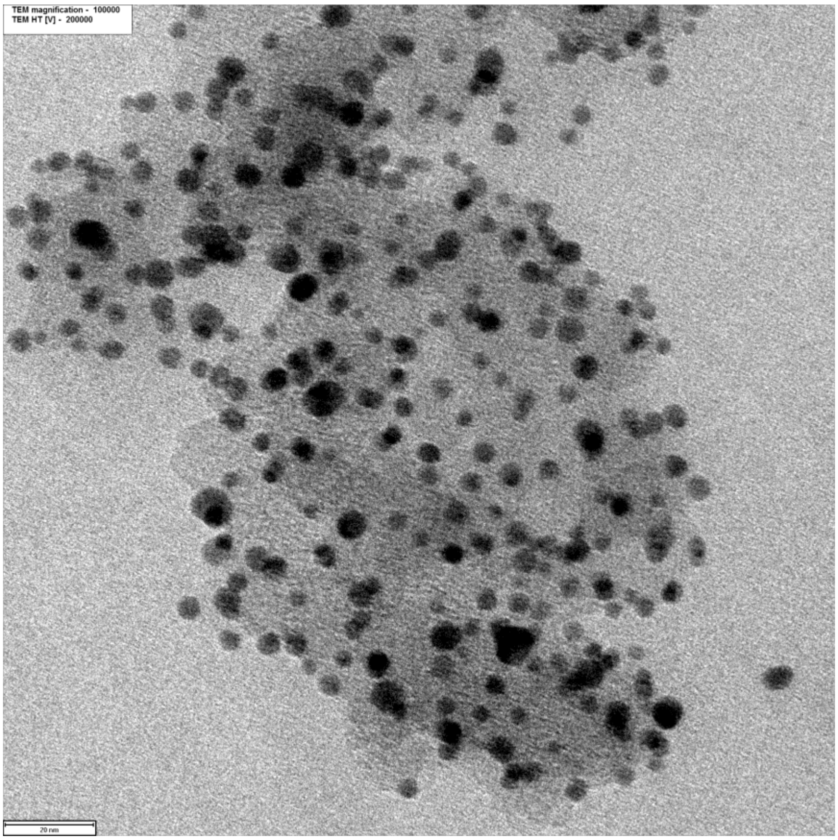
Figure A.14 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon



(c)

(d)

Figure A.14 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon (continue)



(e)

Figure A.14 (a)-(e) TEM image at magnification of 100,000x. of 20 wt% Au on untreated carbon (continue)

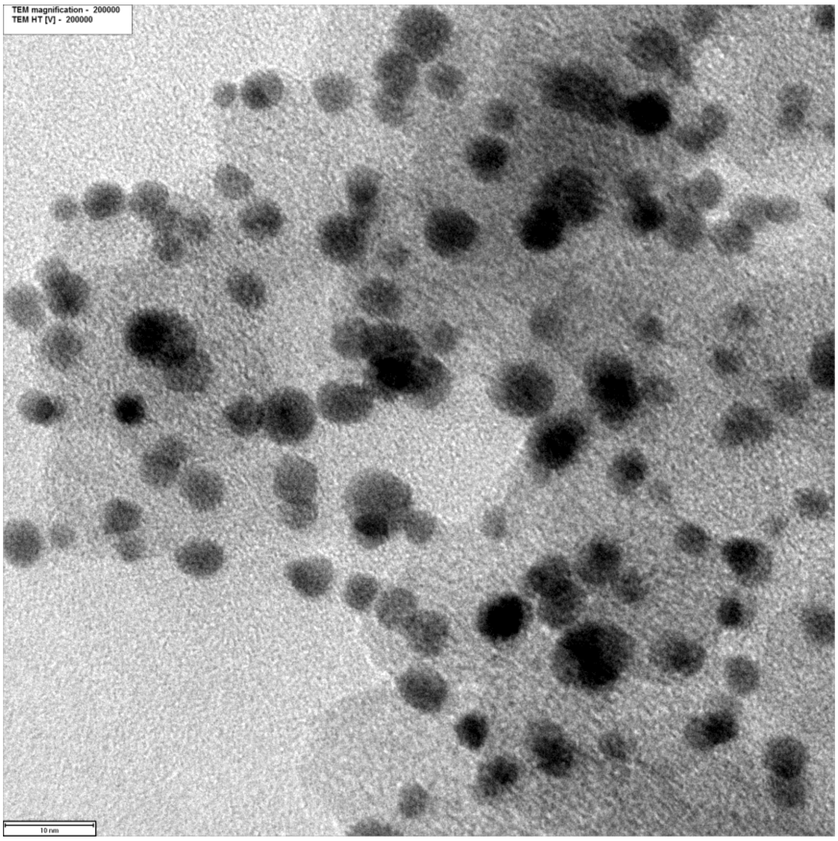


Figure A.15 TEM image at magnification of 200,000x. of 20 wt% Au on untreated carbon

2. 20% Au/ treated Carbon

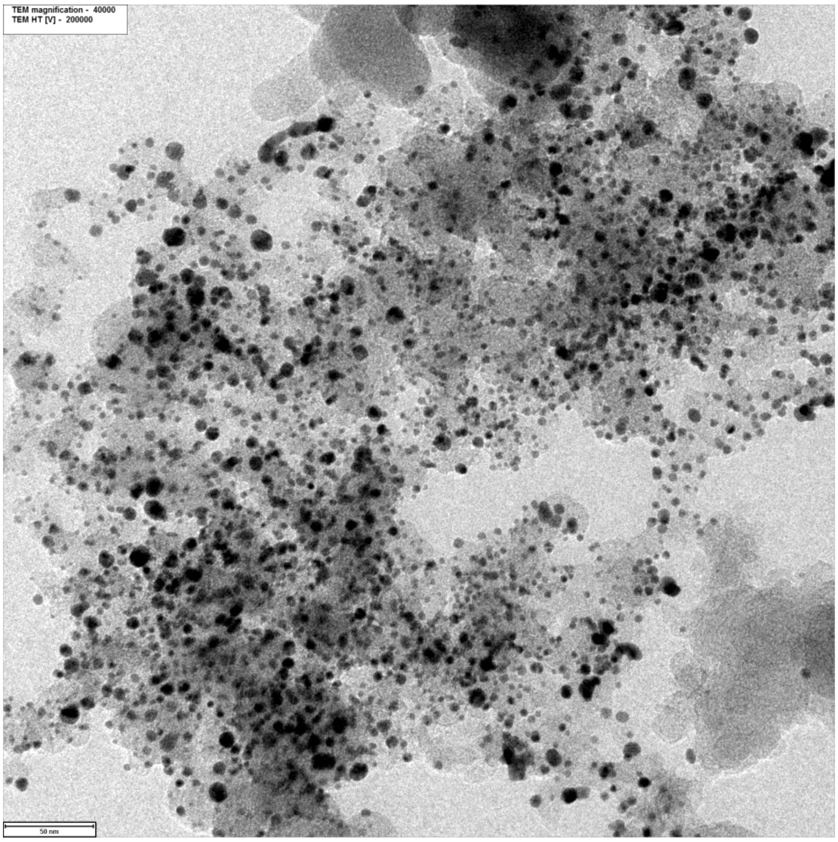
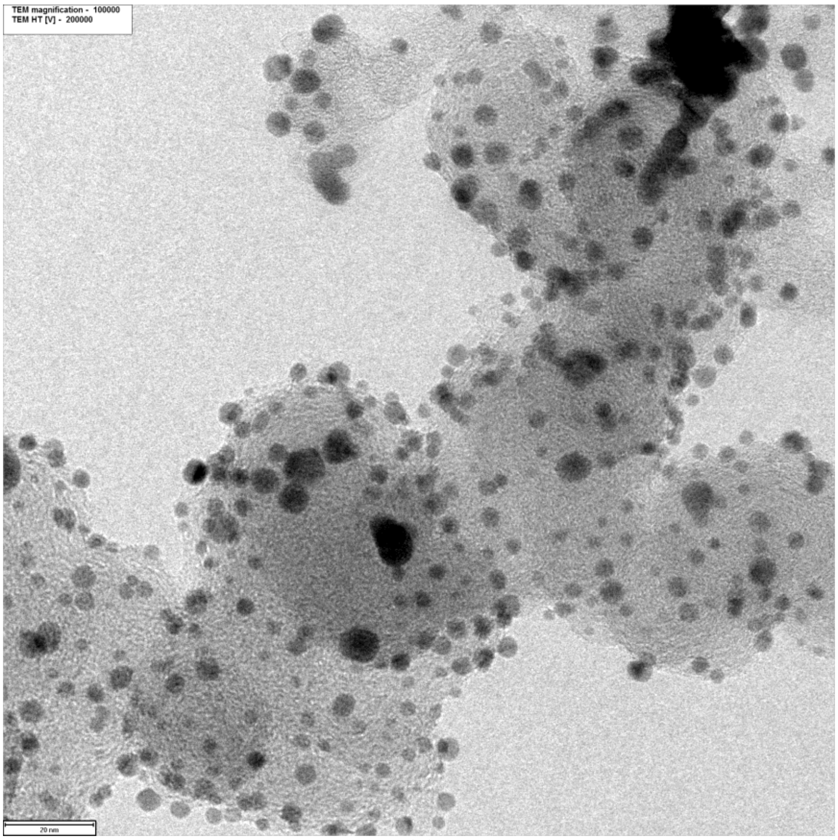
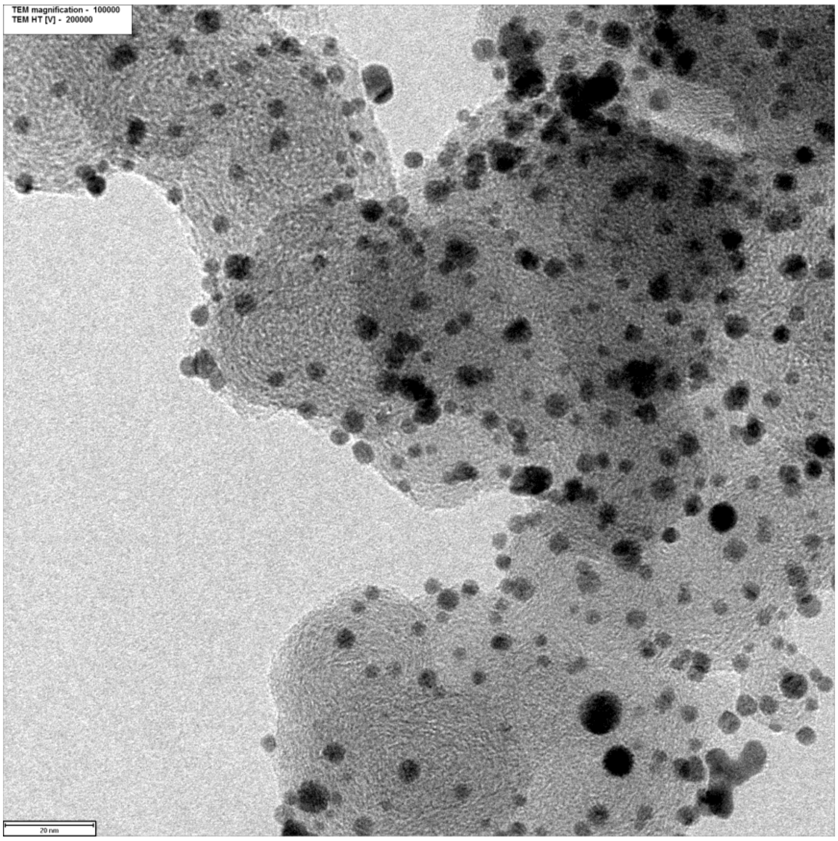


Figure A.16 TEM image at magnification of 40,000x. of 20 %wt Au on treated carbon

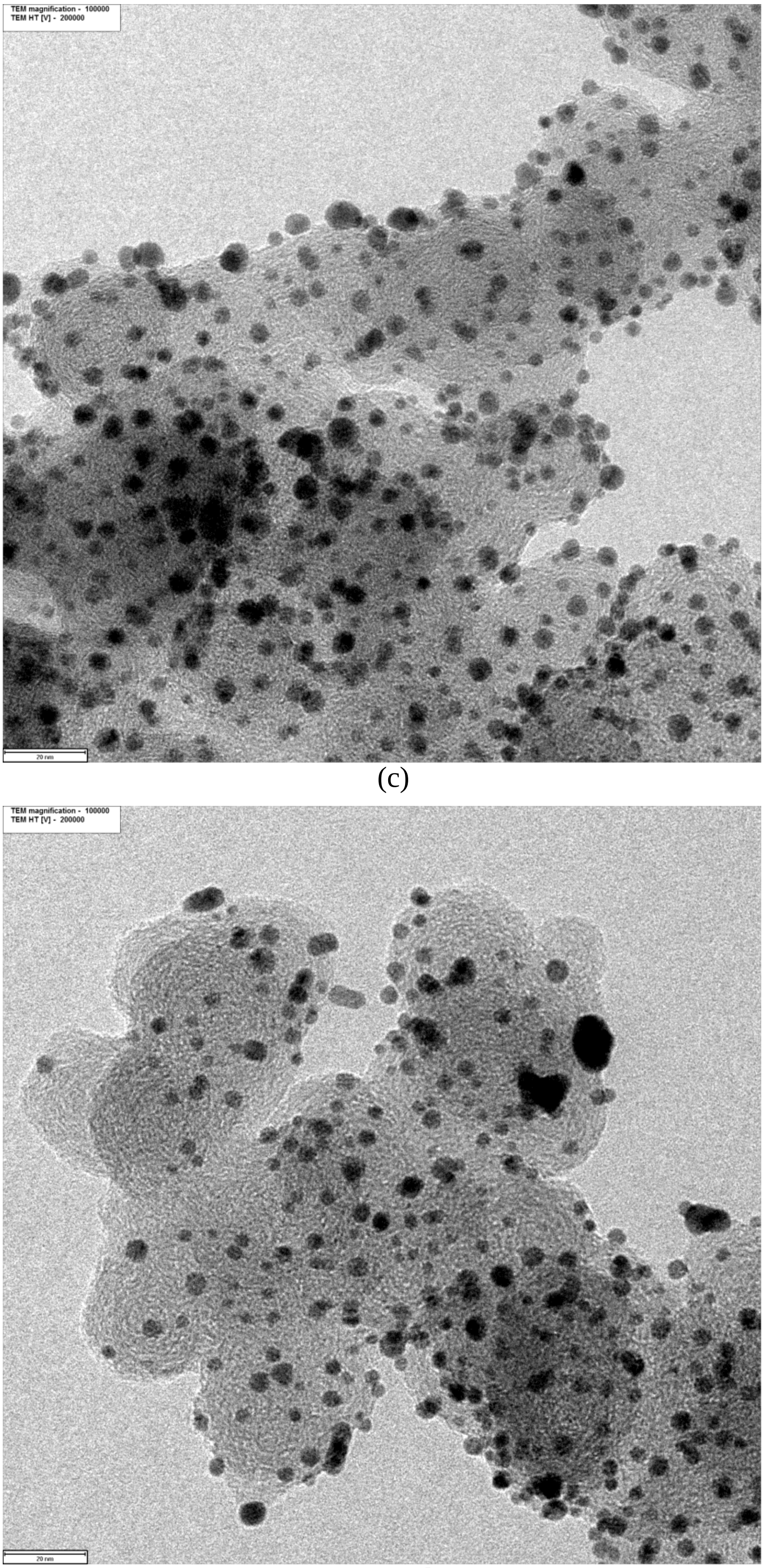


(a)



(b)

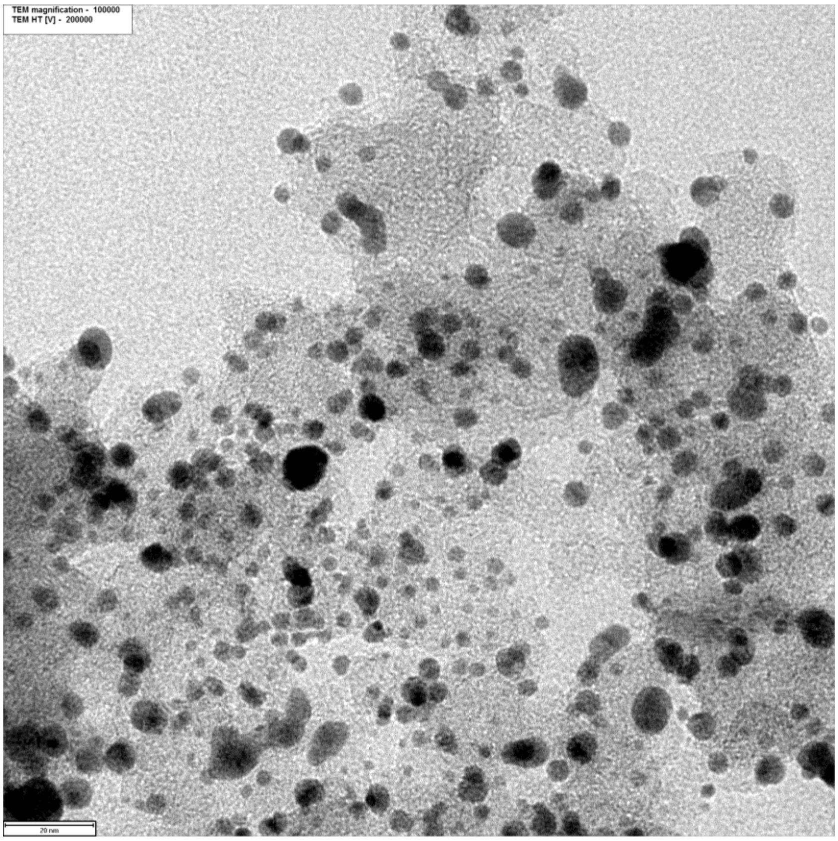
Figure A.17 (a)-(e) TEM image at magnification of 100,000x. of 20 %wt Au of Au/C by citrate protection method on treated carbon



(c)

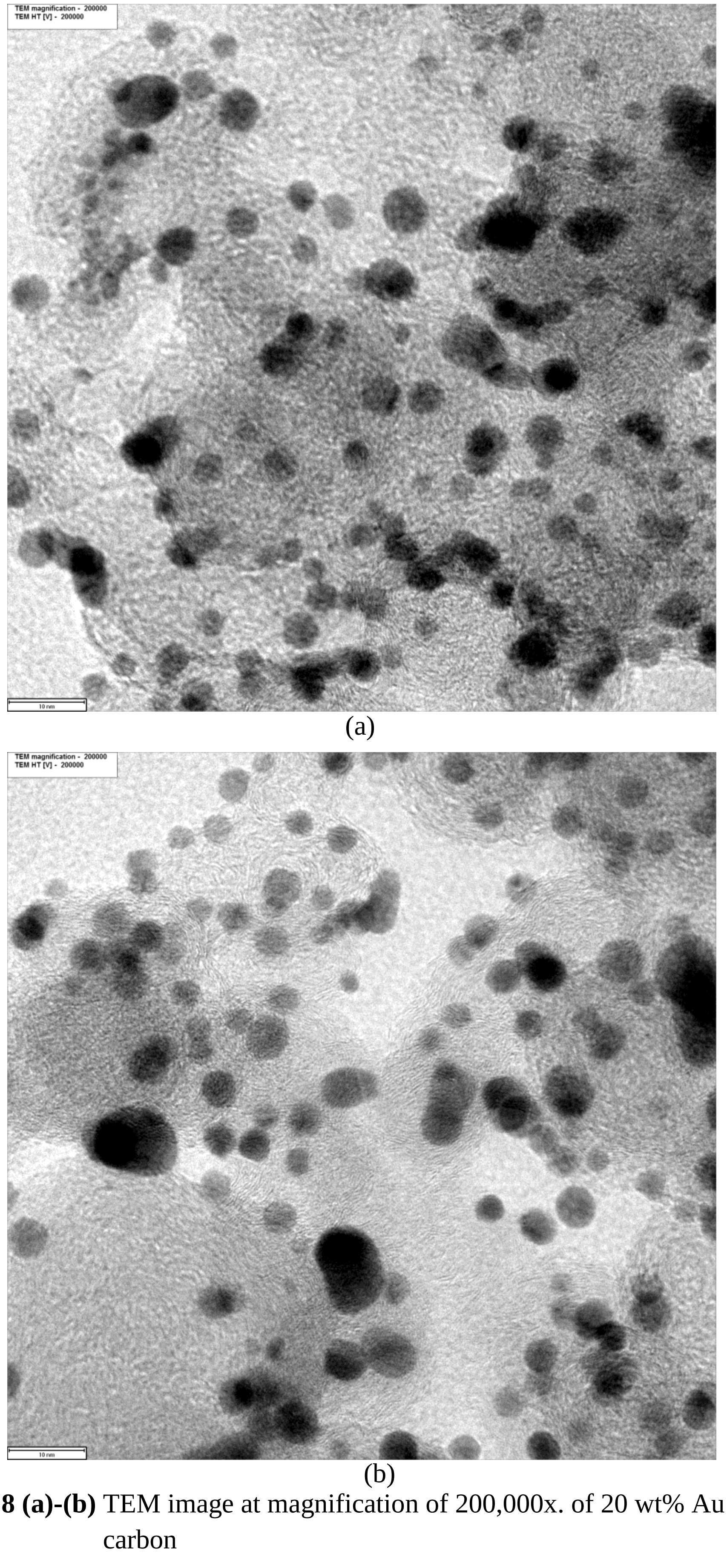
(d)

Figure A.17 (a)-(e) TEM image at magnification of 100,000x. of 20 %wt Au of Au/C by citrate protection method on treated carbon (continue)



(e)

Figure A.17 (a)-(e) TEM image at magnification of 100,000x. of 20 %wt Au of Au/C by citrate protection method on treated carbon (continue)



(a)

(b)

Figure A.18 (a)-(b) TEM image at magnification of 200,000x. of 20 wt% Au on treated carbon

3. 30% Au/ treated Carbon

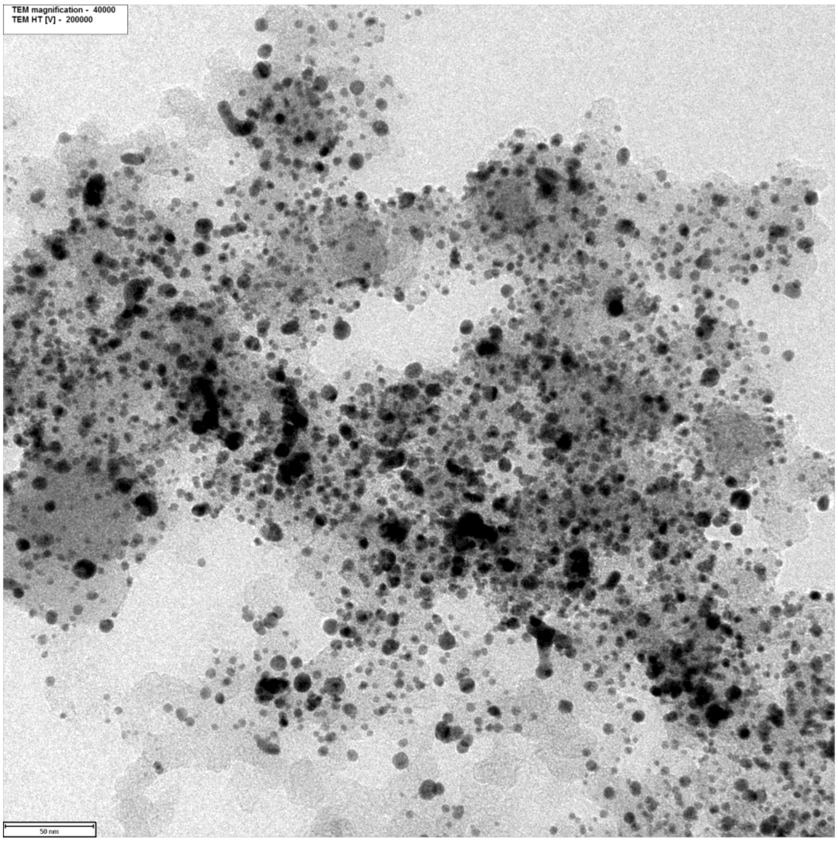
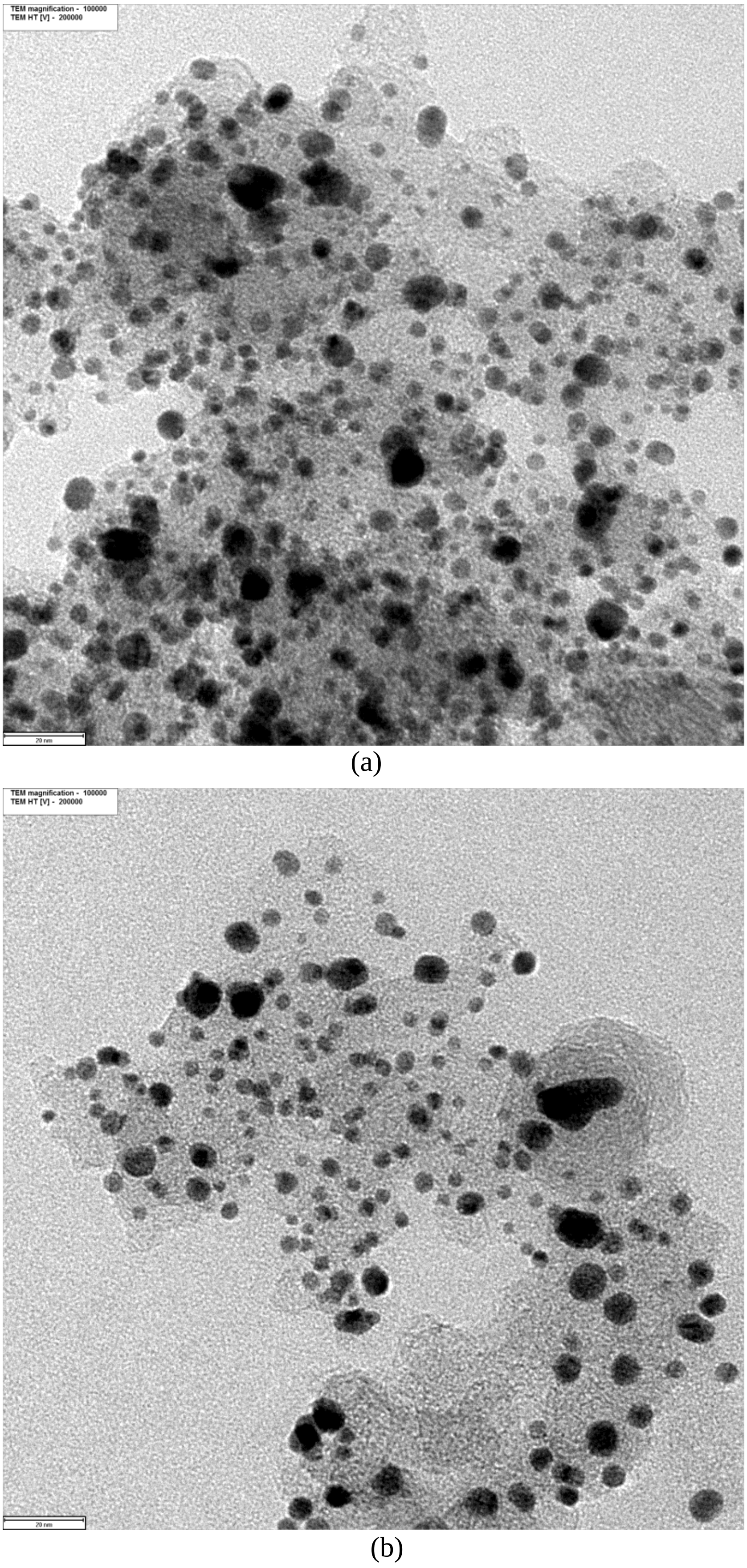


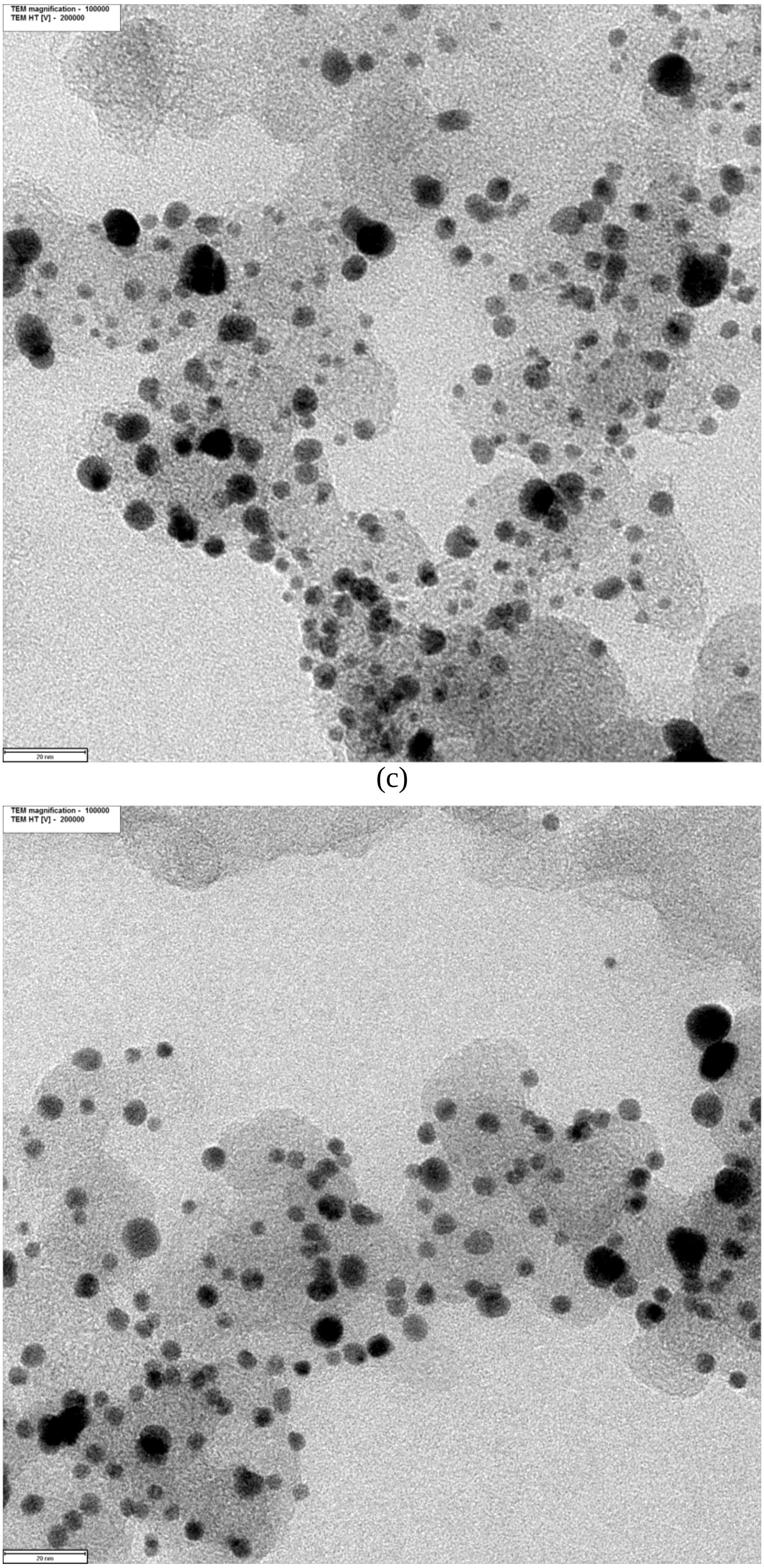
Figure A.19 TEM image at magnification of 40,000x. of 30 %wt Au on treated carbon



(a)

(b)

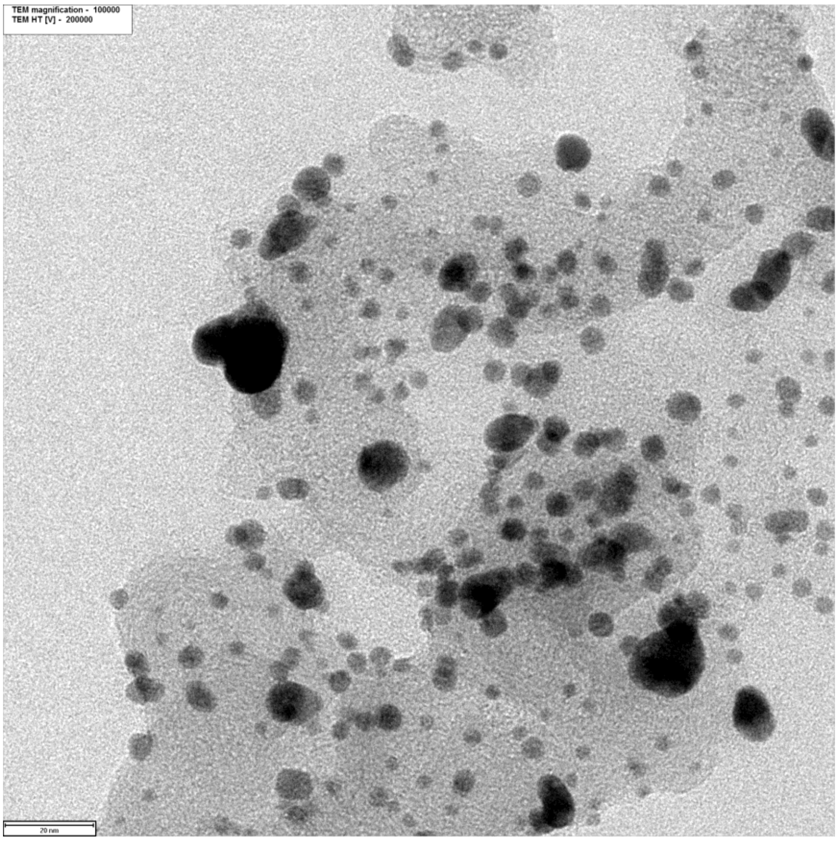
Figure A.20 TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon



(c)

(d)

Figure A.20 TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon (continue)



(e)

Figure A.20 TEM image at magnification of 100,000x. of 30 wt% Au on treated carbon (continue)

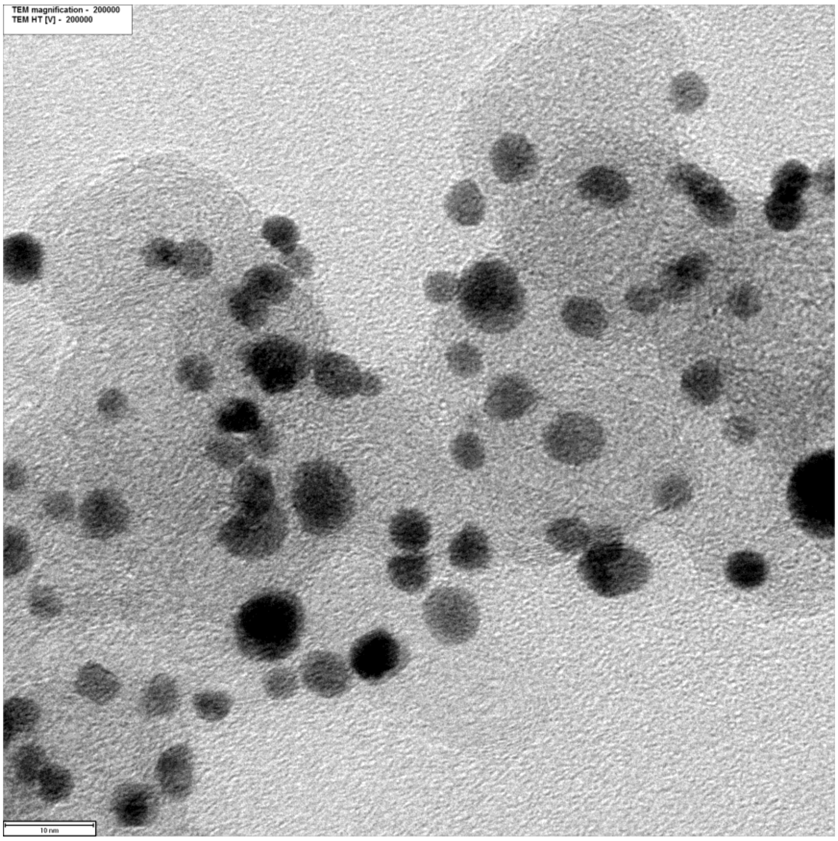


Figure A.21 TEM image at magnification of 200,000x. of 30 wt% Au on treated carbon.

4. 40% Au/ treated C

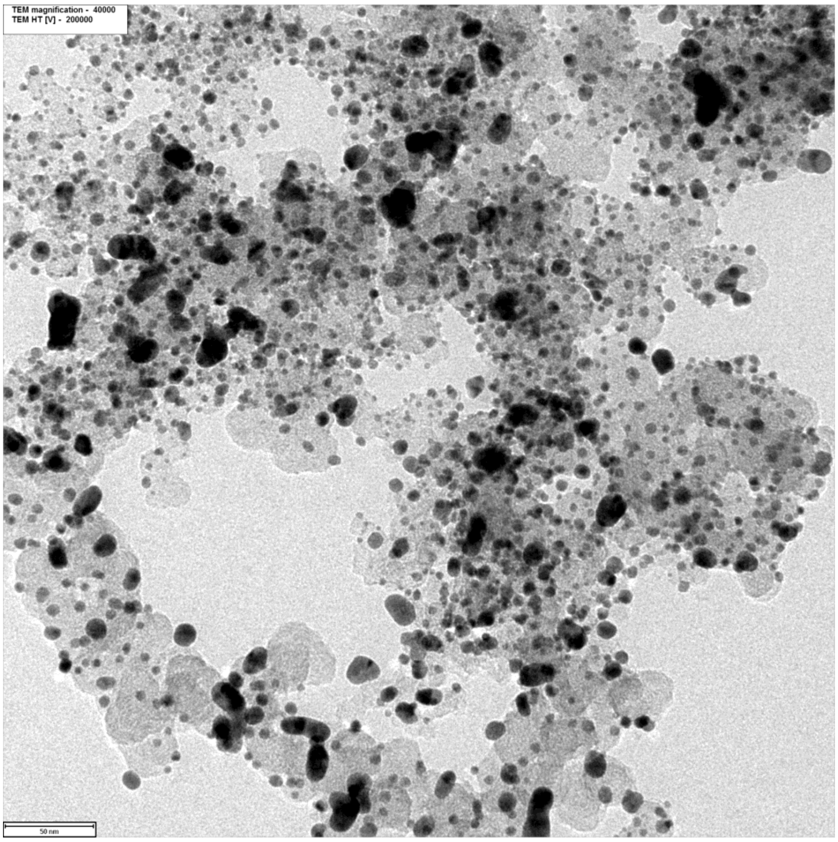


Figure A.22 TEM image at magnification of 40,000x. of 40 wt% Au on treated carbon.

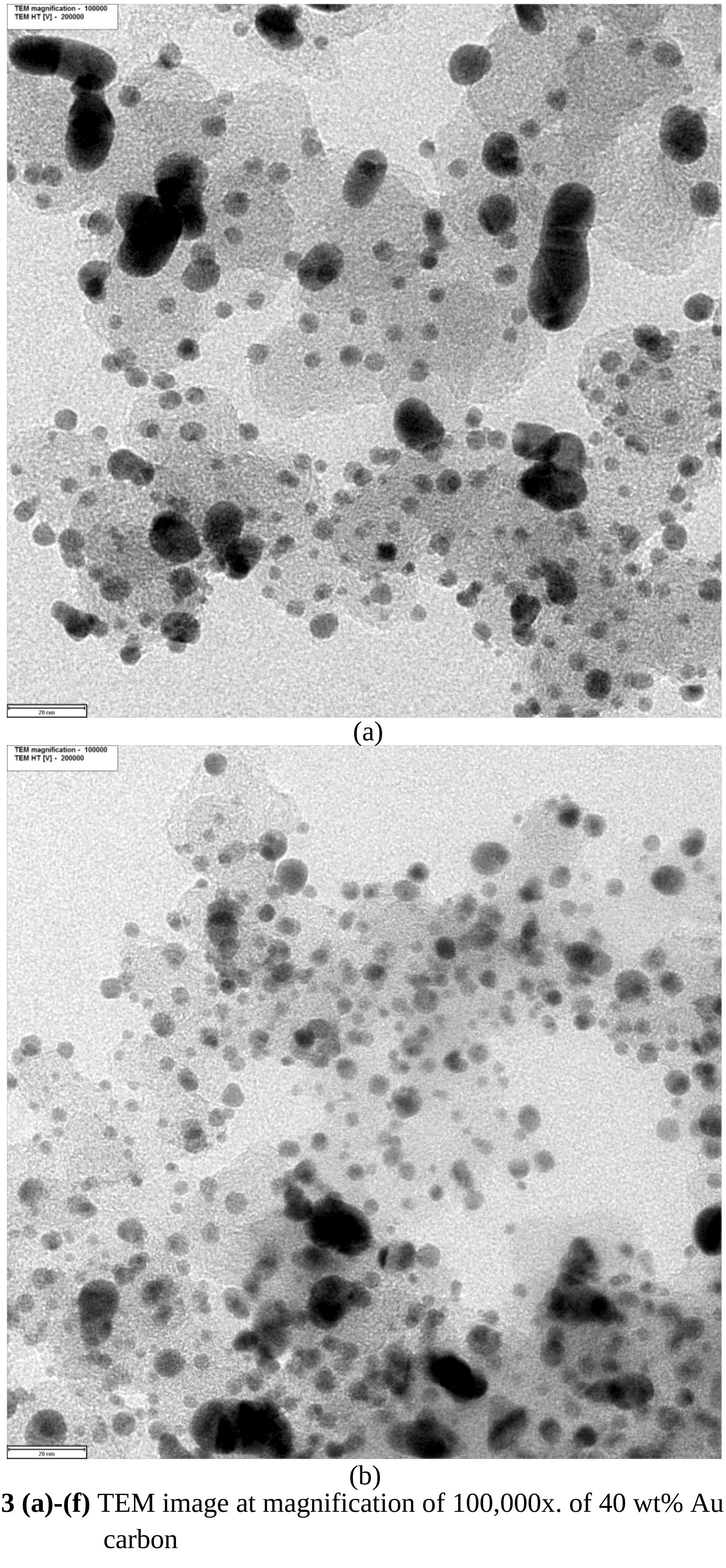
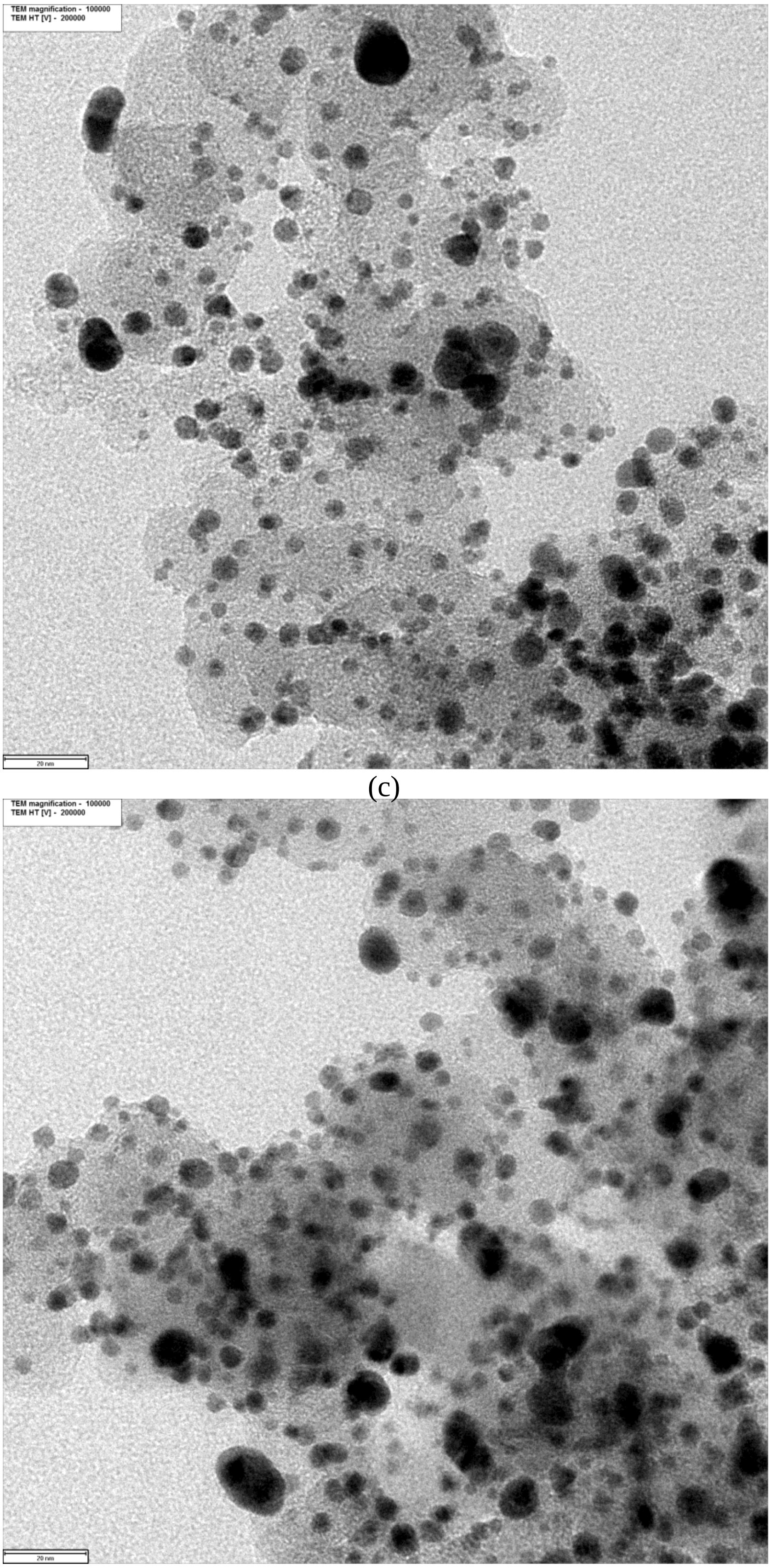


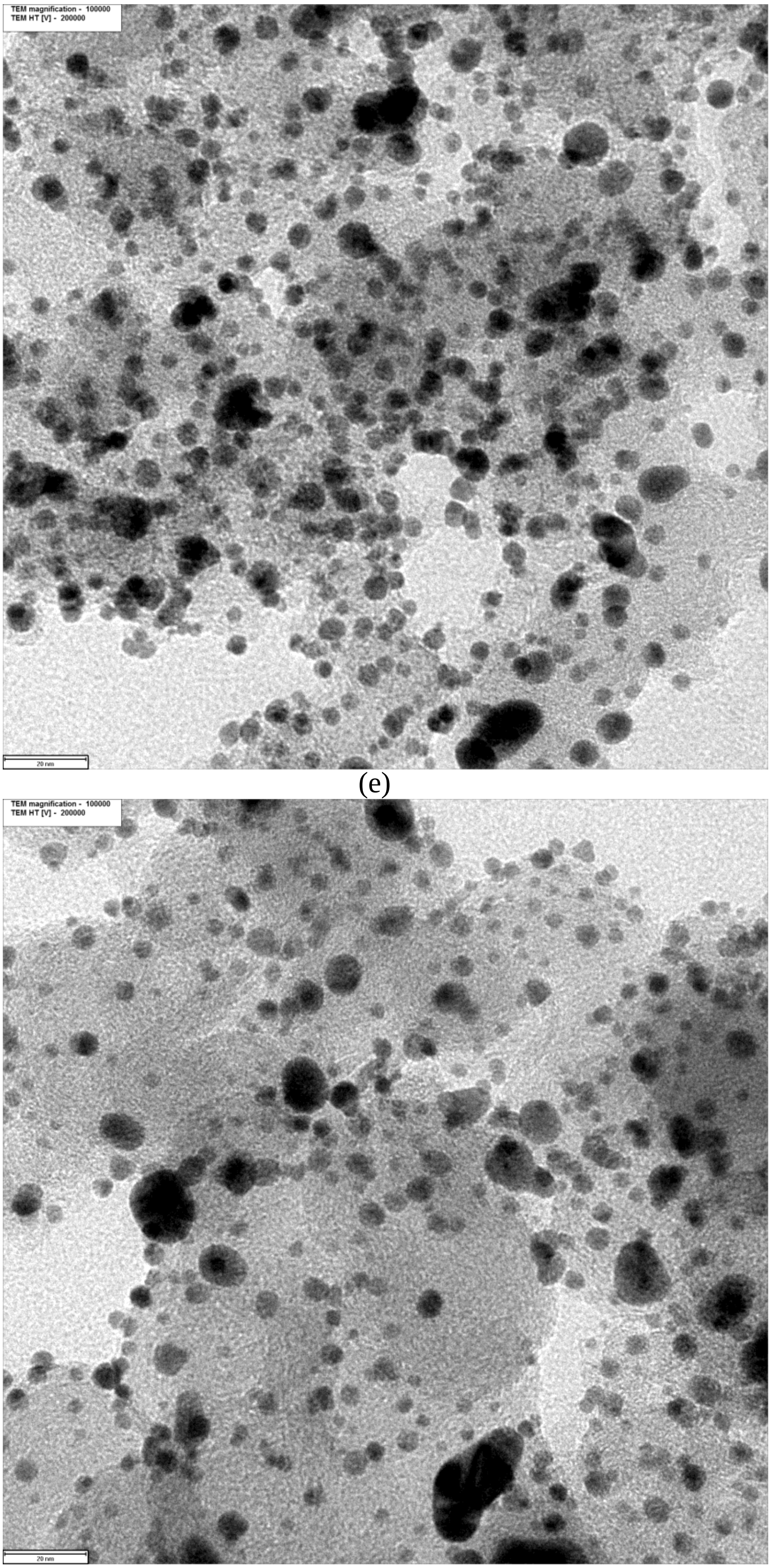
Figure A.23 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon



(c)

(d)

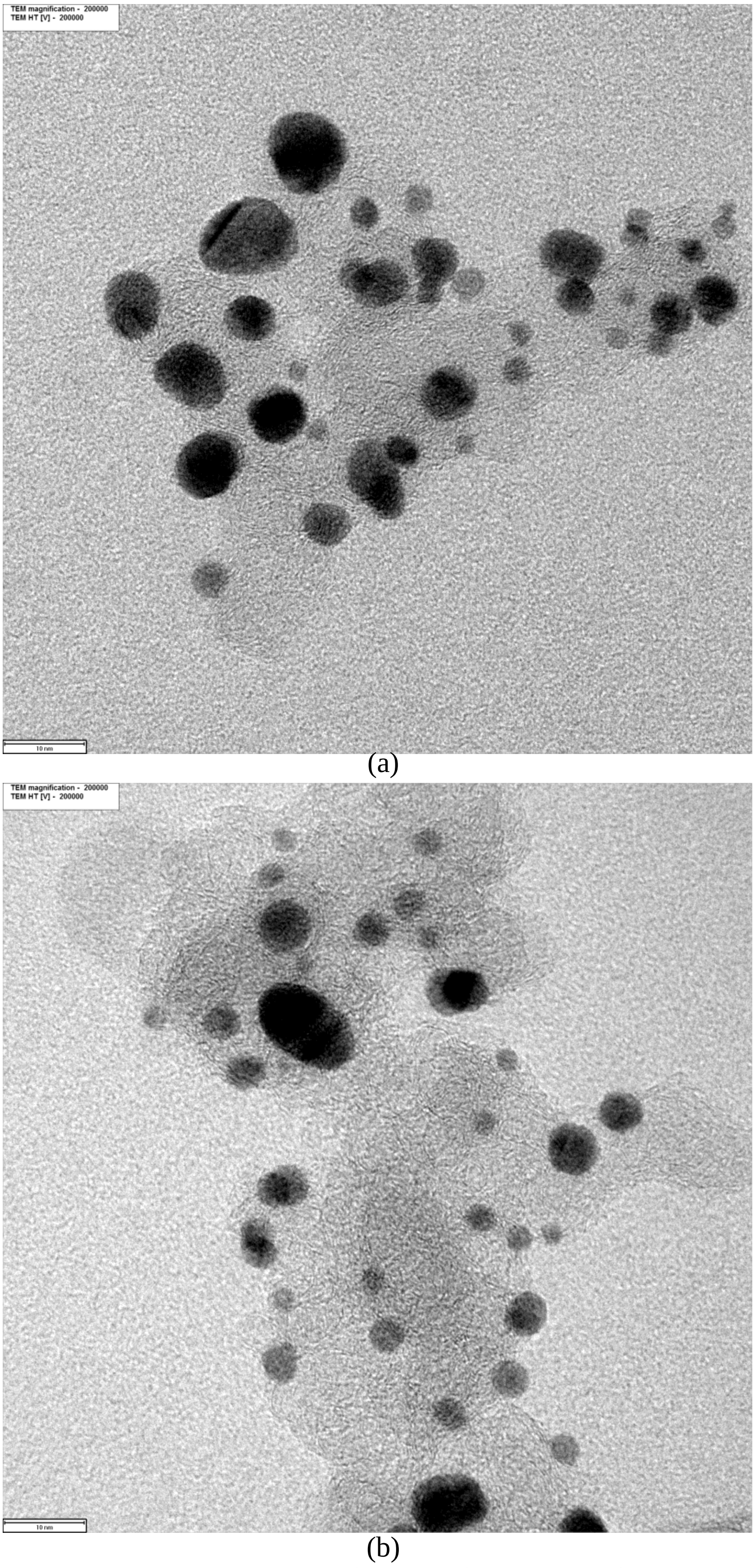
Figure A.23 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon (continue)



(e)

(f)

Figure A.23 (a)-(f) TEM image at magnification of 100,000x. of 40 wt% Au on treated carbon (continue)



(a)

(b)

Figure A.24 (a)-(b) TEM image at magnification of 200,000x. of 40 wt% on treated carbon

A.4 Electrochemical Surface Area (ESA)

The example to determine the ESA of 20 wt% Au catalyst by PVA method;

$$\text{Reduction Peak Area} = \frac{0.0055732\ \text{C/cm}^2\ \text{(G.C)}}{0.000386\ \text{C/cm}^2\text{Au}} \begin{array}{l} \longrightarrow \text{From CV result (Table A.7)} \\ \longrightarrow \text{From Literature [16]} \end{array}$$

$$= 14.44\ \text{cm}^2\text{Au}\ /\text{cm}^2\text{(G.C)}$$

Ink volume 0.2 ml contain catalyst 10 mg

Thus, Ink volume 0.0114 ml contain catalyst 0.057 mg

Since, G.C. area = 0.2827 cm^2, the amount of are catalyst on electrode per crossectional area of electrode was equal to

$$\frac{0.057\ \text{mg cat}}{0.2827\ \text{cm}^2\ \text{(G.C.)}} = 0.2016\ \text{mg cat/ cm}^2\ \text{(G.C.)}$$

There are 20 wt% of Au on catalyst, thus the amount of Au per crossectional area of electrode was

$$0.2016 \times 0.2 = 0.0403\ \text{mg Au/cm}^2\text{(G.C)}$$

Thus, $$\text{ESA} = \frac{14.44\ \text{cm}^2\text{Au/cm}^2\text{(G.C)}}{0.0403\ \text{mgAu/cm2(G.C)}}$$

$$\text{ESA} = 358.10 \frac{\text{cm}^2\text{Au/cm}^2\text{(G.C)}}{\text{mgAu/cm}^2\text{(G.C)}}$$

Table A.8 Reduction Peak Area used to determine the ESA

Catalyst	**Reduction Peak Area (C/cm^2)**		
	(set 1)	**(set 2)**	**(set 3)**
PVA method			
20%Au/ untreated C	0.0055732	0.0058280	0.0049212
20%Au/ treated C	0.0052525	0.0056989	0.0047427
30%Au/ treated C	0.0060622	0.0058588	0.0062568
40%Au/ treated C	0.0056798	0.0046540	0.0050430
Citrate method			
20%Au/ untreated C	0.0043392	0.0048039	0.0039633
20%Au/ treated C	0.0042643	0.0049486	0.0033474
30%Au/ treated C	0.0062427	0.0066683	0.0067422
40%Au/ treated C	0.0057020	0.0053630	0.0044400

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