



## ELECTROOXIDATION OF METHANOL USING FLUORINE-TIN OXIDE ELECTRODE MODIFIED WITH AU–PT BIMETALLIC NANOPARTICLES DISPERSED IN MONTMORILLONITE CLAY

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### Abstract

In this research work, a new and effective catalyst was proposed for electrocatalytic oxidation of methanol. Montmorillonite (MMT) clay was used as low-cost catalyst support for gold-platinum bimetallic nanoparticles (Au-PtNPs). The morphological study of the catalyst layers was performed using Scanning spectroscopy with electron microscopy (SEM) and dispersive energy X-ray (EDX). The electrocatalytic oxidation of methanol at the surface of Au-Pt/MMT/FTO modified electrode was investigated by cyclic voltammetry and chronoamperometry techniques. The electrode proposed for oxidation of methanol molecules showed excellent electrocatalytic activity under optimized experimental conditions. Methanol electro-oxidation was also studied from a kinetic point of view, and the Tafel plots showed better kinetics are present for Montmorillonite clay methanol electrooxidation and golden nanoparticles.

**Keywords:** Electrocatalytic oxidation, methanol, montmorillonite, gold-platinum bimetallic nanoparticles

### Introduction

Recently, fossil fuel depletion, increasing energy crisis, and environmental degradation have urged scientists to develop new energy resources (Huang & Wang, 2014; Y. Wang *et al.*, 2017). Forward fuel cells with methanol (DMFCs) have received great attention as Most of the best alternative power options due to high energy efficiency, low pollution emissions and ease of use (Bianchini & Shen, 2009; Yu, Ni, & Zhai, 2018). Fuel cells are machines that directly transform the energy of a chemical reaction to high quality electrical energy (Yano, Shiraga, & Kitani, 2008). Methanol is one of the fuel candidates with the most promise. The reason is its high energy density, easy handling, high activity and nearly complete electrooxidation to the final product of CO<sub>2</sub> (Ren, Zelenay, Thomas, Davey, & Gottesfeld, 2000). To date, platinum has been widely used as a powerful anodic catalyst for electrooxidation of methanol (Ding, Ji, Wang, Pollet, & Wang, 2017). However, the high cost of platinum and The Emission Effect CO intermediates on the Pt catalyst surface are the main drawbacks, which limit its industrial applications (Xu *et al.*, 2017). Therefore, it is very important to build new low cost catalysts and better catalytic activity. Until now, several strategies have been proposed for designing the anodic materials for electrooxidation of methanol in direct methanol fuel cells. One way is the combination of Pt with a second Bimetallic metal to make a catalyst (Hosseini, Mahmoodi, & Amjadi, 2017).

By addition, the second metal, the amount of required Pt decreases and the electrocatalytic activity increases significantly Because of the synchronization results between the two metallic species (Shahrokhian & Rezaee, 2018). The use of several bimetallic catalysts such as Pt-Ag (Xie *et al.*, 2017), Pt-Ru (Calderón, Calvillo, Lázaro, Rodríguez, & Pastor, 2017), Pt-Pd (Ojani, Hasheminejad, & Raoof, 2014) and Pt-Au (Cabello *et al.*, 2017) has been reported by the researchers. Gold is a precious, inert metal with high corrosion resistance and electrical conductivity which can be used as a multi-electrolyte catalyst such as methanol,

ethanol, Formal acid, oxygen, carbon monoxide etc. Au catalyst does Do not undergo CO deactivation and its Catalytic operation and stability may be sufficient improved through modification with Pt Because of its synergistic influence between Au and Pt (Shen *et al.*, 2017; Zhang, Liu, Ma, & Ding, 2007). The other solution to minimizing fuel cell costs is to use less costly materials as alternative supports to fill the catalyst of Pt. Among different materials, conducting polymers and carbon based materials have been the subject of numerous investigations (El-Deeb, El Rouby, Abdelwahab, & Farghali, 2018; Zhao, Yang, Tian, Wang, & Zhan, 2010).

Mineral phyllosilicate which usually forms a very soft microscopic crystal. It is a member of the smectite family and its pore-like structure contains 2:1 layered clay made up of two tetrahedral silica sheets fused to a central octahedral sheet of alumina (Pinnavaia, 1983; Sarier, Onder, & Ersoy, 2010). The montmorillonite clays can exchange the cationic ions and intercalate neutral molecular species between the interlayer regions. Such ion exchange properties can be due to the electronic conductivity of the montmorillonite layers and to the intercalation into an interlayer space. Montmorillonite clays are chemically inert, environmentally friendly, inexpensive and also they are easy to obtain. Also, the montmorillonite clay layers can absorb more platinum nanoparticles and increase the surface area which makes them suitable as catalyst support for fuel cell applications (Seo, 2012). Montmorillonite clays have been utilized previously as the catalyst support in fuel cells (Gil, Gandia, & Vicente, 2000).

The objective used for this study is to improve the methanol electrooxidation efficiency by using the montmorillonite and Au–Pt bimetallic catalyst. The FTO plates were selected for the construction of the Au–Pt/MMT modified electrode because the silicate layers are very efficient adsorbents for the organic molecules. To the best of our knowledge, no report has been published to date on the electrooxidation of methanol using the Au–Pt/MMT/FTO electrode.

## Materials and Methods

### Chemicals and reagents

Methanol,  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  and  $\text{HClO}_4$  were purchased from Merck chemical company.  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  was purchased from Sigma-Aldrich and montmorillonite was obtained from Fluke. All the chemicals used in this analysis were of scientific quality and used without further washing. Both solutions were prepared with water which was deionized.

### Apparatus

The electrochemical experiments were conducted using a potentiostat/galvanostat of  $\mu$  Autolab Type III. Experiments were conducted at room temperature in a traditional tri-electrode cell. The FTO plates were purchased from Solarnix (Switzerland) and used as the working electrode. An Ag/AgCl electrode (Azar Electrode, Iran) and a platinum wire (Metrohm, The Netherlands) were used as reference and counter electrode, respectively.

The SEM images were taken using an LEO 1450 VP scanning electron microscope (Germany). The surface elemental analysis studies of the modified electrodes were performed by an Oxford-7353 energy dispersive X-ray (EDX) microanalyzer.

### Preparation of Au–Pt/MMT/FTO electrode

At first, the FTO plates were cut into  $20 \times 5 \text{ mm}^2$  pieces. The FTO pieces were then sonicated in a cleaning solution containing deionized water and soap for 10 min, isopropanol for 5 min, ethanol for 5 min and acetone for 2 min, respectively. The FTO pieces are referred to as FTO electrode. To modified the FTO electrode surface, a  $1 \text{ mg mL}^{-1}$  MMT suspension was prepared by dispersing 10 mg of MMT powder in 10 mL of deionized water for 20 min. 25  $\mu\text{L}$  of this suspension was cast onto the surface of an FTO electrode (with a surface area of  $25 \text{ cm}^2$ ) and then allowed to dry under IR lamp. The Au–Pt bimetallic nanoparticles were electrochemically deposited at the surface of MMT/FTO electrode from a 0.3 M  $\text{HClO}_4$  solution containing 1 mM  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  and 1 mM  $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ . The co-electrodeposition of Au–Pt nanoparticles was performed by cyclic voltammetry with a potential range from  $-0.4 \text{ V}$  to  $+1.2 \text{ V}$  for 15 cycles at a scan rate of  $50 \text{ mV} \cdot \text{s}^{-1}$  (Eteya, Rounaghi, & Deiminiat, 2019). The resulting modified electrode is denoted as Au–Pt/MMT/FTO electrode. A Pt/MMT/FTO electrode was prepared under the same procedure from a 0.3 M  $\text{HClO}_4$  solution containing 1 mM  $\text{H}_2\text{PtCl}_6 \cdot 3\text{H}_2\text{O}$ . Also, under the same experimental conditions a Pt / FTO electrode was created, without the MMT film covering its surface.

## Results and Discussion

### Electrode characterization

The surface morphologies of the bare and modified FTO electrodes were investigated using Electron microscopy scans (SEM) and the results are shown in Fig 1. Fig 1A, shows the SEM micrograph of the bare FTO electrode surface. A uniform and spongy surface are observed in this image, which increases the surface area of the electrode. The SEM image of the MMT/FTO modified electrode is shown in Fig. 1B. As can be seen in this Figure, the MMT has a very rough surface with irregular blocky morphology. Fig.

1C shows the SEM image of the Au–Pt/MMT/FTO electrode surface after co-deposition of Au–Pt bimetallic nanoparticles.

As is evident in this Figure, the Au–Pt nanoparticles with spherical morphology are dispersed throughout the surface of the MMT/FTO electrode and it seems that the MMT film acts as good support for Au–Pt nanoparticles deposition. For further evaluation of the surface of the Au–Pt/MMT/FTO electrode, the energy dispersive X-ray (EDX) technique was employed (Fig. 1D). The EDX spectrum confirms the presence of the Au and Pt at the surface of the Au–Pt/MMT/FTO electrode. The FTO electrode is connected to the Sn peaks. In addition, the high-intensity Si peak is due to the MMT silicate layer which indicates that the MMT film was coated on the FTO electrode surface.

### Electrochemical Investigations

#### Cyclic Voltammetry

Cyclic voltammetry (CV) technique has been used to examine the electrocatalytic behavior of the various modified FTO electrodes for methanol electrooxidation. Fig. 2, depicts the cyclic voltammograms (CVs) at the surface of Pt/ FTO, Pt/MMT/FTO and Au–Pt/MMT/FTO electrodes in  $0.3 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$  containing  $0.5 \text{ mol} \cdot \text{L}^{-1}$  methanol. All CVs were recorded by sweeping the potential from 0.0 to 1.0 V at a scan rate of  $50 \text{ mV} \cdot \text{s}^{-1}$ . As can be seen in this Figure, by sweeping the potential to the positive values, the oxidation peak of methanol appears around 781 mV (Krewer, Christov, Vidakovic, & Sundmacher, 2006). In the reverse scan, the reoxidation of methanol and/ or methanol residues occur on the platinum surface, and a backward peak appears (Li *et al.*, 2002). Also, an inspection of Fig. 2A shows that the Au–Pt/MMT/FTO electrode has the higher electrocatalytic activity for the oxidation of methanol which can be attributed to the existence of MMT film and Au–Pt nanoparticles on the surface of the electrode and the synergistic effect between the Au–Pt bimetallic alloy nanoparticles and MMT film.

#### Chronoamperometry

Chronoamperometry measurements were carried out for further evaluation of the electrocatalytic performance of the modified electrodes for the oxidation of methanol molecules. Fig. 3, shows the chronoamperograms of Pt/ FTO, Pt/MMT/FTO and Au–Pt/MMT/FTO electrodes at the constant potential of 0.6 V for 2000 s. As is shown in this Figure, there is a continuous decay in the current density with the time for the three studied electrodes. This behavior may be due to the formation of the intermediate species during the oxidation reaction of methanol and remaining of the adsorbed intermediates such as CO at the surface of the electrode. However, the Au–Pt/MMT/FTO electrode displays a higher current density compared to the other electrodes. This result indicates that there is a greater number of active sites on the surface of Au–Pt/MMT/FTO electrode which facilitates the electro-oxidation of the methanol molecules (Dimos & Blanchard, 2010).

#### Tafel Plots

Tafel studies were performed to investigate the electrooxidation process of methanol from a kinetic point of view. To this end, the exchange current densities ( $J_0$ ) were measured for Pt/ FTO, Pt/MMT/FTO and Au–Pt/MMT/FTO electrodes. The typical Tafel plots are shown in Fig. 4. The  $J_0$  values were calculated by using the Tafel equation ( $J$

Wang, 2006) and they were found to be:  $8.88 \times 10^{-6}$ ,  $1.08 \times 10^{-5}$  and  $2.08 \times 10^{-5}$  mA.cm<sup>-2</sup> for Pt/ FTO, Pt/MMT/FTO and Au– Pt/MMT/FTO electrodes, respectively. Comparison of the obtained values shows that the  $J_0$  value of Au–Pt/MMT/FTO electrode is higher than those of the other electrodes. These results demonstrate that the existence of MMT film and Au–Pt bimetallic nanoparticles at the surface of electrode remarkably accelerate the electrooxidation process of methanol.

### Effect of influencing parameters on the electrooxidation of methanol

#### Effect of amount of MMT clay

The experimental results show that the MMT film can increase the electrocatalytic activity of the modified electrode for the oxidation of methanol. Figure 5A illustrates the plot of the anodic peak current density of Au–Pt/MMT/FTO electrode as a function of the MMT amount. As is obvious from this Figure, the current density increases with the increment the volume of MMT dispersion up to 25 ML and then decreases. The increase of the current density can be attributed to the better exfoliation of MMT film which provides a three-dimensional matrix for deposition of the Au–Pt bimetallic nanoparticles. The decrease in the current density may be due to the formation of a compact and thick silicate layer which results in destroying the three-dimensional matrix for Au–Pt nanoparticles deposition and increasing the length of proton transfer pathway (Saghi, Rounaghi, Sarafraz-Yazdi, Razavipanah, & Moosavi, 2016). Therefore, the optimum volume of MMT dispersion was chosen 25  $\mu$ L for the modification of the electrode surface in this work.

#### Effect of electrodeposition scan cycles of Au–Pt nanoparticles

To study the effect of electrodeposition scan cycles of Au–Pt nanoparticles at the surface of the electrode on the oxidation of methanol, CVs were Taken on separate scans cycles. Fig. 5B shows the changes of the oxidation Total Methanol Density molecules with the Au–Pt nanoparticles electrodeposition scan cycles in the gamut of 3 to 22 cycles. As is clear in this Figure, the oxidation Total Methanol content increases with the cycles up to 15. But at higher cycles, the current density does not change significantly. At lower cycles (lower than 15 cycles), the Au–Pt nanoparticles are almost uniformly distributed at the electrode surface which increases the active area of surface of electrode. However, the loading of Au–Pt nanoparticles over 15 cycles does not improve The catalytic activity electrode probably because of the agglomeration of Au–Pt nanoparticles during the reduction process which leads to the decrease of the electrochemically active area (Razmi, Habibi, & Heidari, 2008).

#### Effect of methanol concentration

The influence of methanol concentration on The current oxidation rate of methanol was investigated and the results are depicted in Figure 5C. According to the experimental results, the Density of anodic peak current increases with increasing the methanol concentration and 0.5 M and then remains nearly constant at higher concentrations owing to saturate the active sites in the electrode surface. Thus, the optimal methanol concentration was considered to be 0.5 M.

### Comparison of electrocatalytic efficiency of Au–Pt/MMT/FTO electrode with some of the other modified electrodes

The ratio of the forward peak current ( $I_{p,f}$ ) to the backward peak current ( $I_{p,b}$ ) was used to investigate the electrocatalytic activity of the prepared catalyst (Li *et al.*, 2013). The ratio of the forward current to the backward current ( $I_{p,f}/I_{p,b}$ ) for Au–Pt/MMT/FTO electrode and some of the other modified electrodes is compared in Table 1. As can be seen in this Table, the proposed electrode has a higher  $I_{p,f}/I_{p,b}$  value which indicates the better electrocatalytic activity of Au– Pt/MMT/FTO electrode in comparison with the other modified electrodes. This enhancement of the catalytic activity of Au–Pt/MMT/FTO electrode toward methanol electrooxidation can be explained by this fact that the use of a second metal, leads to the formation of the hydroxyl radicals through the adsorption and dissociation of water molecules with more adverse potentials which results in the increasing the electro-oxidation of the CO molecules within the surface of the proposed electrode. Also, the attendance of the alloyed metal changes The electronic architecture of the Pt nanoparticles which can help to weaken the Pt–CO bond and decrease the poisoning effect of CO intermediates. Moreover, the attendance of the MMT film at the electrode surface results in the better distribution of Au–Pt nanoparticles which produce the higher active sites at the surface of the electrode (Ghanbari *et al.*, 2017).

### Conclusions

In this study, a new anodic catalyst for electrooxidation of methanol molecules by layer modification of montmorillonite (MMT) film and Au–Pt nanoparticles was prepared on the surface of the FTO electrode. Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) spectroscopy were used to investigate the surface morphology of the Au–Pt/MMT/FTO modified electrode. The cyclic voltammetry and chronoamperometry studies showed that the Au–Pt/MMT/FTO modified electrode has a better electrocatalytic performance toward electrooxidation of methanol compared to the Pt/MMT/FTO and Pt/ FTO electrodes. This enhanced performance can be attributed to the uniform deposition on the MMT film surface of Au–Pt bimetallic nanoparticles and the synergistic effects of MMT film and gold-platinum nanoparticles. Also, the kinetic analyses indicated that the electrooxidation process of methanol molecules at the surface of Au–Pt/MMT/FTO electrode is easier from a kinetic point of view in comparison to the other electrodes which are used in this study.

### Acknowledgements

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### Figures Caption

Figure 1. The SEM images of the (A) bare FTO electrode, (B) MMT/FTO electrode, (C) Au– Pt/MMT/FTO electrode and (D) EDS analysis of Au–Pt/MMT/FTO electrode.

Figure 2. Cyclic voltammograms (CVs) of electrooxidation of methanol molecules at the surface of (a) Au–Pt/MMT/FTO electrode, (b) MMT/FTO electrode and (c) bare FTO electrode in 0.3 mol. L<sup>-1</sup> HClO<sub>4</sub>

containing 0.5 mol. L<sup>-1</sup> methanol at a scan rate of 50 mV. s<sup>-1</sup>.

Figure 3. Chronoamperograms of the (a) Au–Pt/MMT/FTO electrode (b) MMT/FTO electrode and (c) bare FTO electrode in 0.3 mol. L<sup>-1</sup> HClO<sub>4</sub> containing 0.5 mol. L<sup>-1</sup> methanol at the potential of 0.6 V.

Figure 4. Tafel plots of the (a) Au–Pt/MMT/FTO electrode (b) MMT/FTO electrode and (c) bare FTO electrode.

Figure 5. Effect of (A) MMT clay frequency, (B) Au – Pt nanoparticles electrodeposition scan cycles, and (C) methanol concentration on methanol oxidation current density.

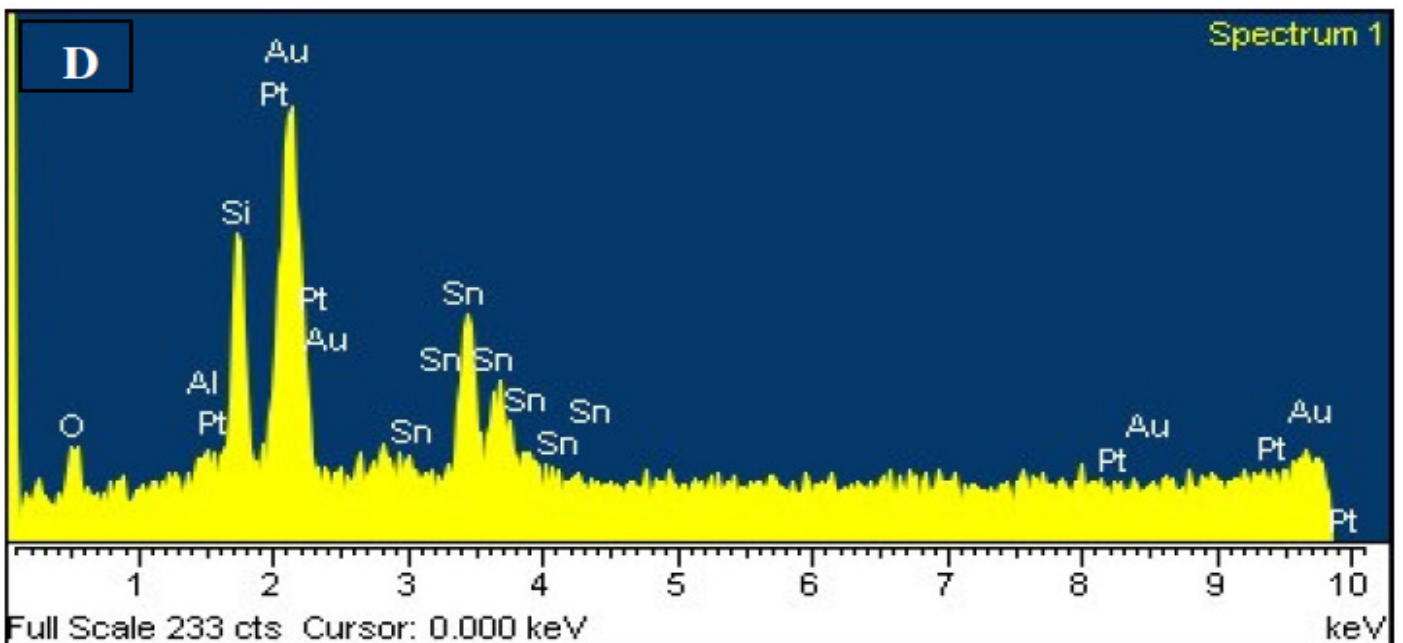
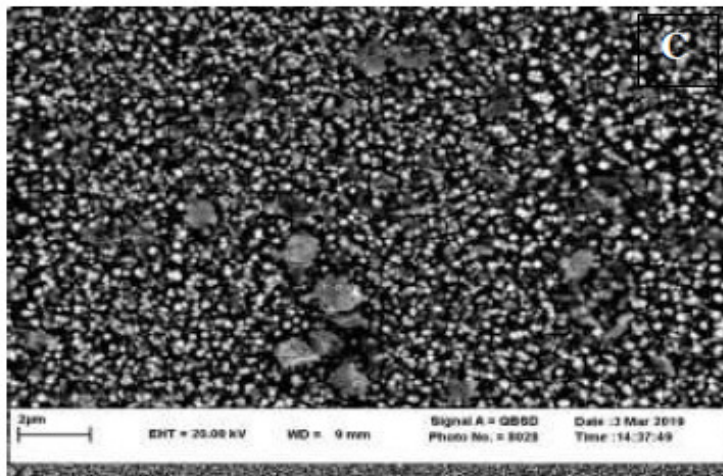
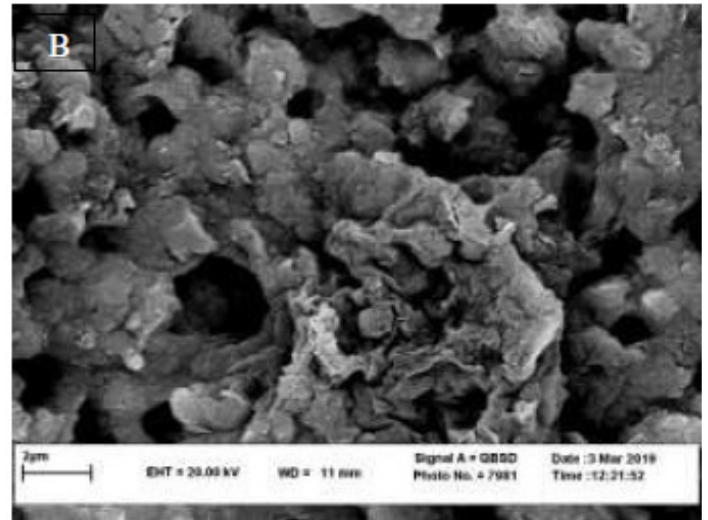
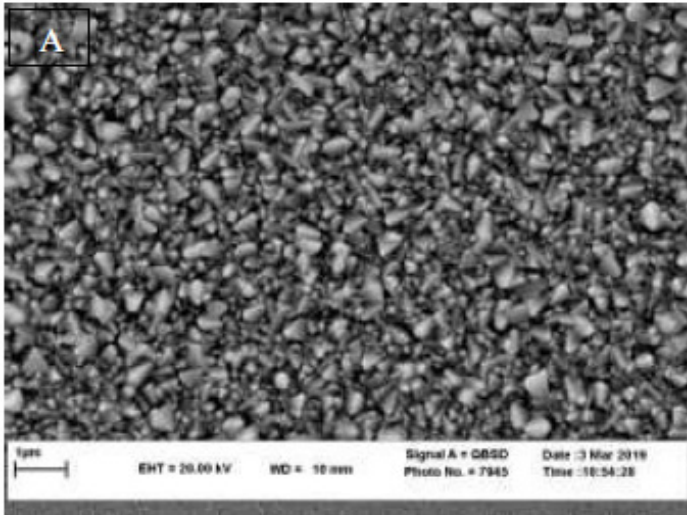


Fig. 1

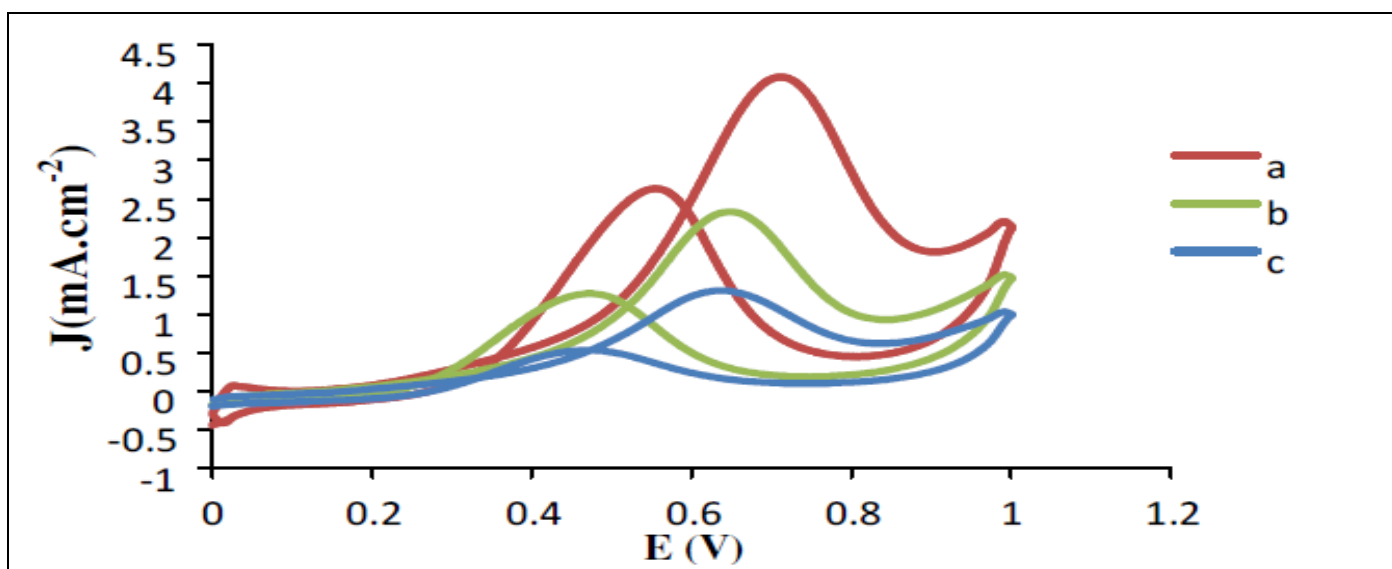


Fig. 2

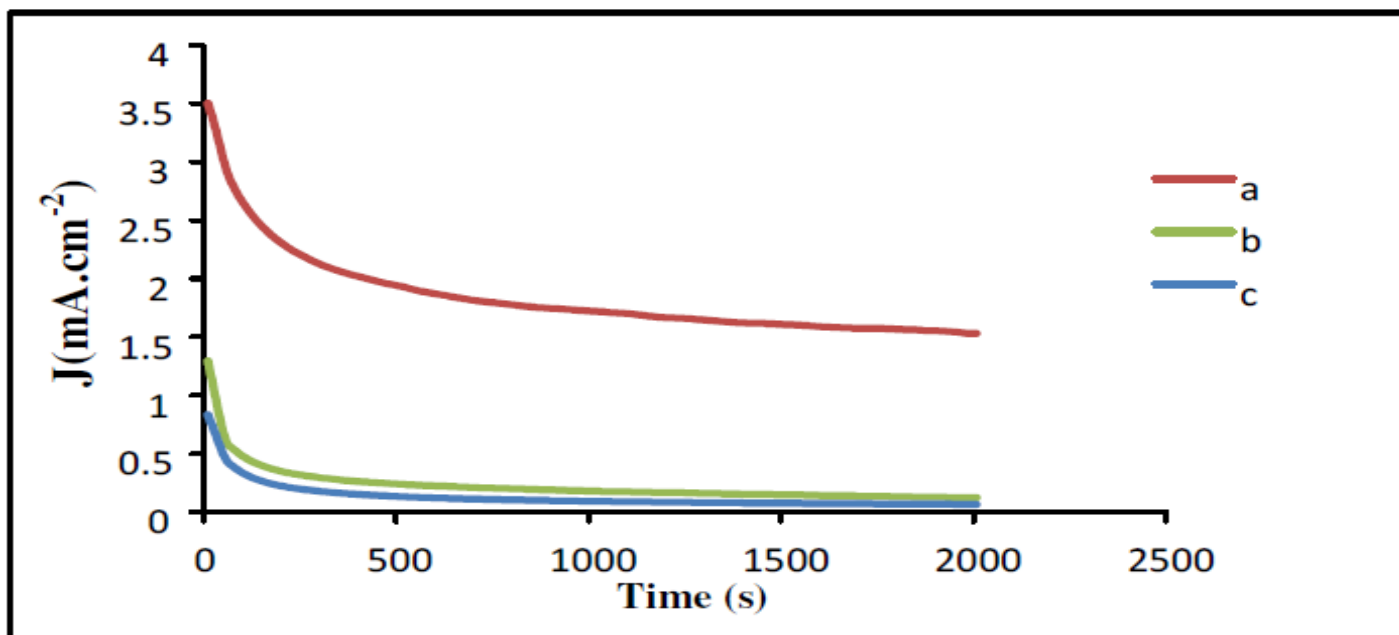


Fig. 3

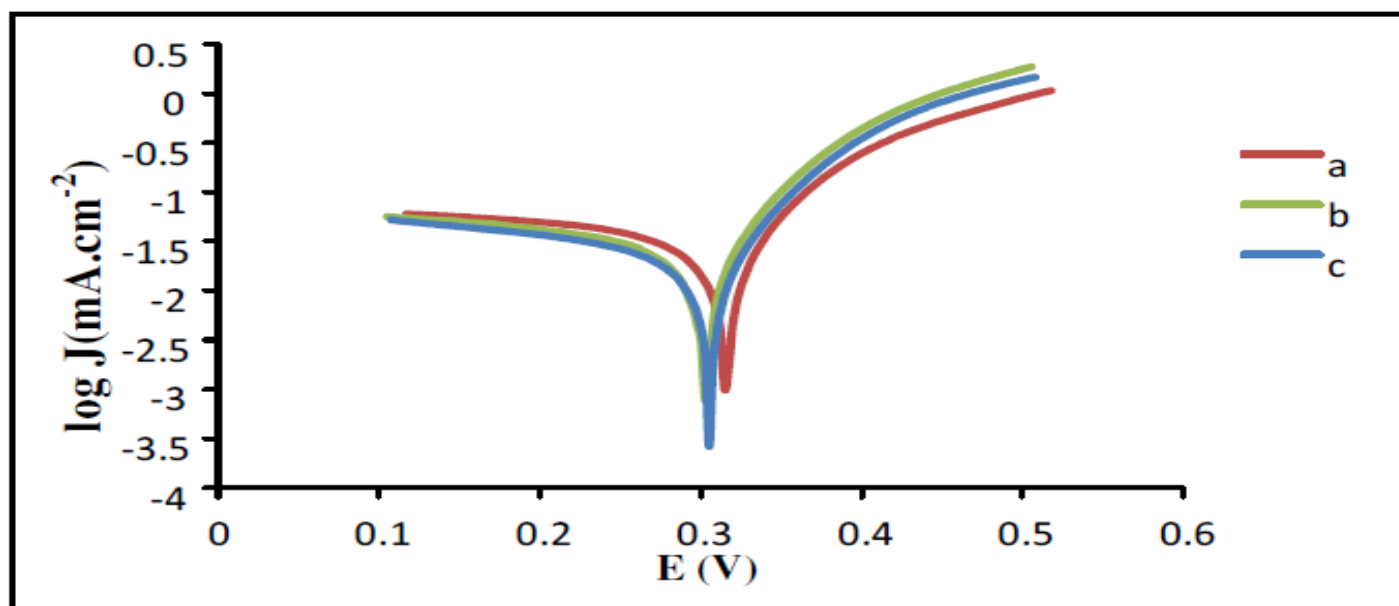


Fig. 4

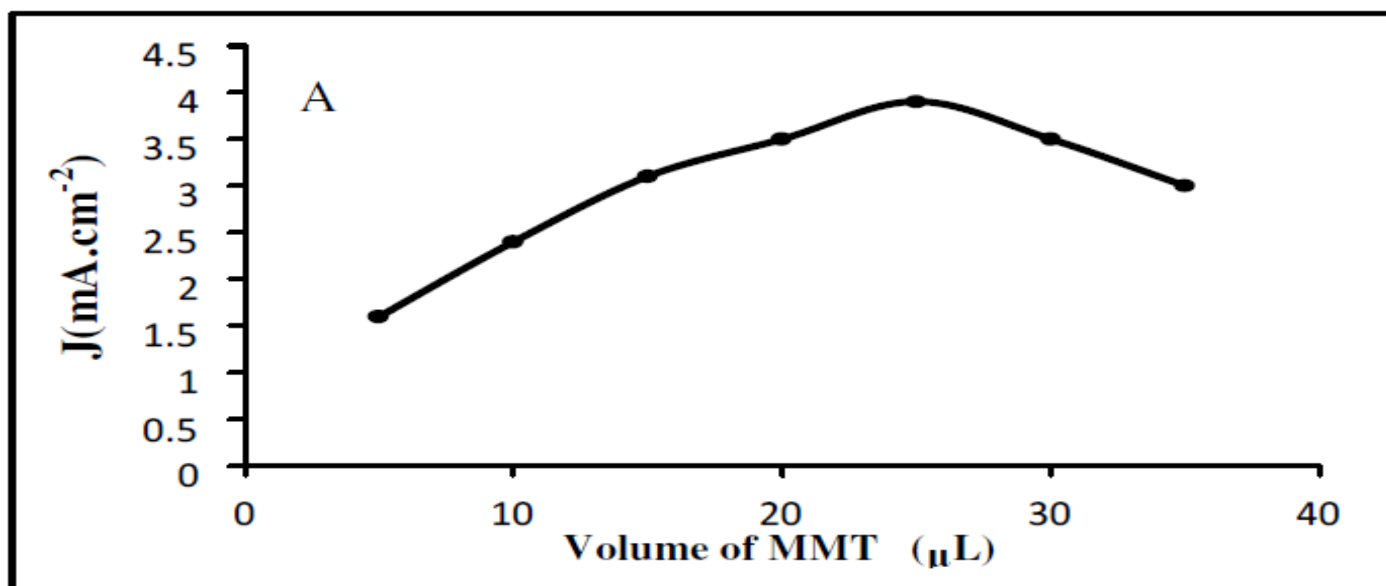


Fig. 5

**Table 1 :** Comparison of the ratio of forwarding current to backward current ( $I_{pf}/I_{pb}$ ) of Au–Pt /MMT/FTO with some other modified electrodes

No.	Modified electrode	$I_{pf}/I_{pb}$	References
1	PANI/Pt	1.41	(Yan & Jin, 2014)
2	PtNWNs/C	0.96	(S. Wang, Wang, & Guo, 2011)
3	GNP/Pt	1.21	(Huang, Chen, Sun, & Wang, 2012)
4	Pt/grapheme	1.071	(Kakaei & Zhiani, 2013)
5	Pt/T-NFs	1.01	(Zheng <i>et al.</i> , 2015)
6	Au–Pt/MMT/FTO	1.55	This work

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