

## Noble Metal and Mn<sub>3</sub>O<sub>4</sub> Supported Carbon Nanotubes: Enhanced Catalysts for Ethanol Electrooxidation

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The carbon nanotubes (CNT) were modified by Mn<sub>3</sub>O<sub>4</sub> before deposition of metal catalysts (e.g. Pt and Pd) by improved polyol method. Crystallinity, morphology and composition of the synthesized electrocatalysts were characterized by Fourier transform infrared (FT-IR) spectroscopy, x-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive x-ray spectroscopy (EDS). It was found that the Mn<sub>3</sub>O<sub>4</sub> nanoparticles are dispersed and covered the CNT surface. The various atomic ratios of 10 wt% Pt<sub>x</sub>Pd<sub>y</sub> nanoparticles are also uniformly dispersed on Mn<sub>3</sub>O<sub>4</sub>-CNT with the particle size of 1 - 4 nm. Their electrocatalytic performances in ethanol oxidation were investigated by cyclic voltammetry (CV) and Chronoamperometry (CA). The prepared catalyst showed enhanced catalytic activity and more stability than the commercially available PtRu/Vulcan XC-72 catalyst. It is proposed that additions of metal oxides and noble metal could develop active sites for ethanol oxidation, which their catalytic performances were improved. These results imply that the prepared various atomic ratios Pt<sub>x</sub>Pd<sub>y</sub>/Mn<sub>3</sub>O<sub>4</sub>-CNT nanocomposite could be a promising electrocatalyst to enhance performance of direct ethanol fuel cell applications.

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**Keywords:** carbon nanotube(CNT); PtPd alloy; direct ethanol fuel cell; Manganese oxide

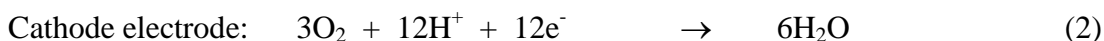
### 1. INTRODUCTION

Ethanol is used as fuel in direct ethanol fuel cells (DEFCs) reaction for numerous applications [1, 2, 3]. The ethanol is not toxic and easy to stock up and carry due to its high boiling point. It provides high energy density as using of 12 electrons transfer to complete an oxidation reaction. Moreover, it can be produced in huge quantities from raw farming products containing [3, 4, 5].

Nevertheless, the DEFCs technology has been obstructed by the slow ethanol oxidation reaction at the anode, owing to short of an active anode catalyst [2]. Moreover, small organic molecules are used as fuel can generate the poisoning species COads at anode site from surface

electro-oxidation reaction under the condition of acidic medium. Generally, Platinum (Pt) is used as catalyst in the electrochemical reaction of small organic fuel cell occurs *via* two pathway mechanisms [2, 5]. The majority desirable reaction path for direct ethanol fuel cells is *via* a dehydrogenation reaction, which does not produce carbon dioxide (CO) as oxidation reaction intermediate. The second reaction path is *via* dehydration, obtaining adsorbed CO as an intermediate. The carbon dioxide (CO<sub>2</sub>) is generated by avoiding the adsorbed CO intermediate poisoning step, by this means enhancement of the overall turnover rate occurs.

Similar to the electro-oxidation mechanism of methanol, ethanol can be described by the following equations (equation 1-3) for the electrocatalytic oxidation of ethanol at Pt catalyst surface [1, 2, 5]:



To reduce the poisoned catalyst as mentioned above and the production cost of the fuel cells, one of the key challenges is the development of catalysts with a lower content of Pt [2, 5, 6]. Binary and ternary Pt-based catalysts have been attracted our attention for choosing catalyst systems [7]. It has to be concerned some points for catalyst support selection for stabilizing the metal nanoparticles and prevention of their immediate agglomeration, a porous support can be used for metal nanoparticle preparation. These porous materials allow the high dispersion of metal nanoparticles onto their surface [8]. CNT as catalyst support for low-temperature fuel cells has attracted a lot of attention owing to their exclusive structures and properties such as high surface area, excellent electronic conductivity, strong mechanical properties and high stability [9, 10]. Although, the confront of gaining greatly dispersed metallic nanoparticles with controllable loadings on CNT still occurs. One approach to heal this problem is to transform the CNT surface before loading the metal nanoparticles. A variety of methods including oxidation in strong acids, sono-chemical and electrochemical have been used [11, 12, 13]. Moreover, carbon based materials with conductive oxides such as ITO, TiO<sub>2</sub>, WO<sub>x</sub>, IrO<sub>2</sub> and SnO<sub>2</sub> has been studied for catalyst electrode improvement [7, 11].

In this work, Pt<sub>x</sub>Pd<sub>y</sub>/Mn<sub>3</sub>O<sub>4</sub>-CNT nanocomposites were prepared by polyol method and characterized by FT-IR, XRD, TEM and EDX for determinations of functional group, crystallinity, morphology and compositions. Studies of their activity and stability for ethanol oxidation on the prepared catalysts were achieved by CV and CA.

## 2. EXPERIMENTAL

### 2.1 Materials

Multiwall carbon nanotubes (Bayer tubes C150P) are obtained from Bayer Material Science. H<sub>4</sub>Pt<sub>2</sub>Cl<sub>6</sub>·6H<sub>2</sub>O and PdCl<sub>2</sub> are purchased from Merck. Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O are obtained from Sigma-Aldrich and 10 wt% Nafion solution is brought from Fuel Cell Store. Deionized water was obtained from a Millipore Milli-Q water system.

## 2.1 Catalyst preparation

The  $\text{Mn}_3\text{O}_4$  modified CNT were prepared by improvement of modified polyol process in one-step preparation. The mass content of  $\text{Mn}_3\text{O}_4$  to CNT is 2:5 and used for all electrocatalyst preparation.

Various atomic ratios of bimetallic metal (10 wt% metal content; *e.g.* Pt and Pd) on manganese oxide ( $\text{Mn}_3\text{O}_4$ ) functionalized carbon nanotubes (CNT) were prepared with ethylene glycol as reducing agent and stabilizer. For the synthesis of Pt decorated  $\text{Mn}_3\text{O}_4$  carbon nanotubes catalyst, 40 wt% manganese oxides of manganese (II) acetate tetrahydrate and CNT were dispersed in EG 3:1 v/v ratio in ultrasonication for 30 min. The solution was refluxed at 120 °C for 1 hour. 10 wt% of  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  solution was added, and the pH of the resultant mixture was then adjusted to 11 by drop wise addition of 1 M NaOH solution. The resulting product was cooled to room temperature and the suspension was centrifuged at 9000 rpm, for 15 min. The residue was washed with DI-water until neutral pH was obtained. Finally, the product was dried overnight at 65 °C in an oven. This electrocatalyst was designated as Pt/ $\text{Mn}_3\text{O}_4$ -CNT.

The Pd/ $\text{Mn}_3\text{O}_4$ -CNT, PtPd/ $\text{Mn}_3\text{O}_4$ -CNT, PtPd<sub>3</sub>/ $\text{Mn}_3\text{O}_4$ -CNT and Pt<sub>3</sub>Pd/ $\text{Mn}_3\text{O}_4$ -CNT electrocatalysts were prepared by using similar procedures as described above. The theoretical mass of Pt and Pd metal as mono- and bi-metallic in all composite electrocatalysts were fixed at 10 wt%. with ratio 1:1, 1:3 and 3:1.

## 2.2 Catalyst characterization

Fourier transforms infrared spectroscopy (FT-IR, TENSOR-27, Bruker) was used to interpret the chemical observation and principal functional groups of the prepared electrocatalysts. XRD (Rigaku Mini Fliex II) was used in order to identify structural characteristics and the alloy formation of the prepared electrocatalysts, using the Cu K $\alpha$  ( $\lambda = 0.15418$  nm) source. The sample identification was assisted by X'Pert HighScore Plus computer software. TEM and EDX (JEM-2010, JEOL) was employed to investigate the morphologies and chemical compositions of the electrocatalysts, respectively.

## 2.3 Electrochemical measurements

A glassy carbon electrode (GCE, 3.0 mm) was polished on the polishing cloth with alumina ( $\text{Al}_2\text{O}_3$ ) size 1.0 and 0.3  $\mu\text{m}$ , respectively. The catalyst ink was prepared as follows: 2 mg of the prepared electrocatalyst was dispersed in 1 mL mixed solution of (6.25 mL Nafion solution (5 wt%), 20 mL ethanol and 73.75 mL DI-water. After that, the catalyst was ultrasonically dispersed for 30 min. 5  $\mu\text{L}$  of the catalyst ink was gradually dropped onto the glassy carbon electrode and dried completely under the lamp.

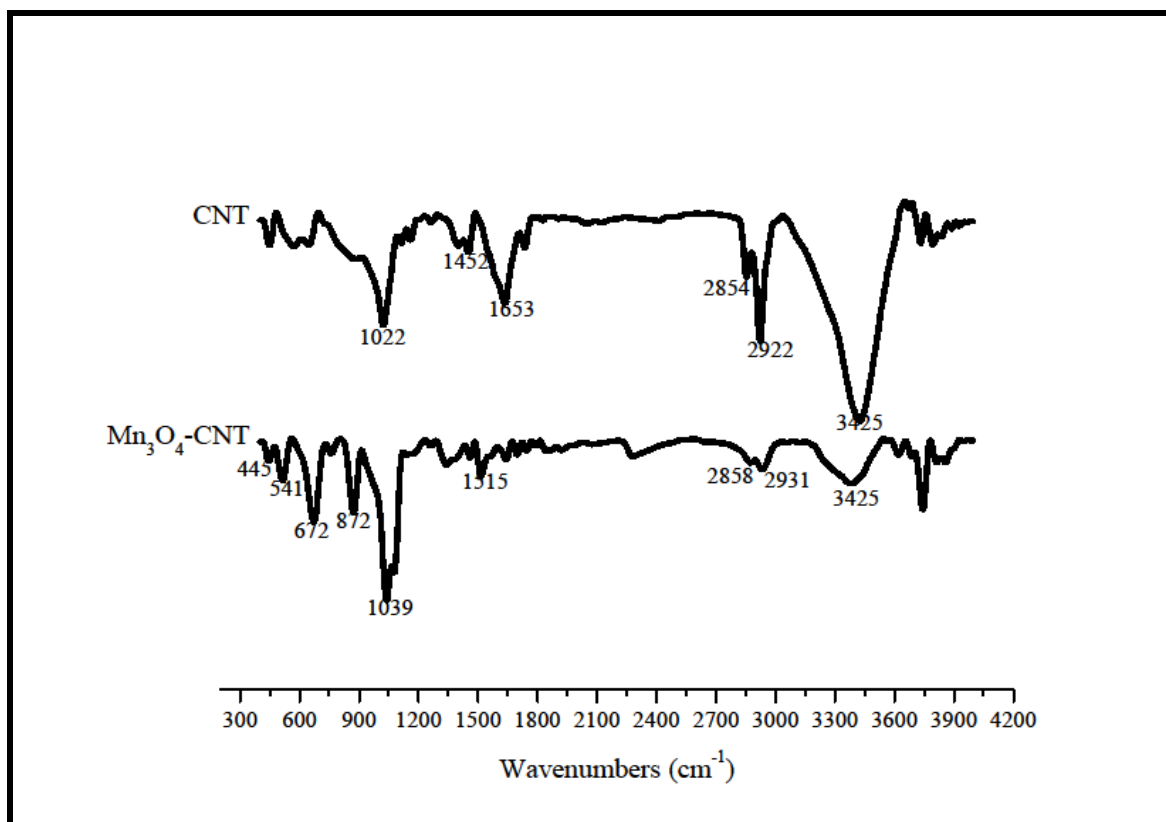
The electrochemical studies have been performed using a conventional three-electrode cell, including an Ag/AgCl (saturated KCl) electrode as the reference electrode, a Pt wire as the counter electrode. The working electrode was prepared by dropping the prepared catalysts ink on the polished glassy carbon electrode.

An eDAQ potentiostat (EChem software) was used for the electrochemical measurement. The electrochemical characterization of the catalyst electrodes was investigated in  $N_2$  saturated 0.5 M  $H_2SO_4$  solution at the potential region from -0.4 to 1.0 V at a scan rate of  $50 \text{ mVs}^{-1}$ . Also the activity of the catalyst electrodes for ethanol oxidation was measured in  $N_2$  saturated 0.5 M  $CH_3CH_2OH$  + 0.5 M  $H_2SO_4$  at the potential region from 0.0 to 1.0 V with a scan rate of  $50 \text{ mVs}^{-1}$ . Additionally, the electrochemical durability of electrocatalysts was measured by using chronoamperometer (CA) at a fixed potential of 0.25 V for 3600 second.

### 3. RESULTS AND DISCUSSION

$Mn_3O_4$  nanoparticles loaded on the CNT ( $Mn_3O_4$ -CNT) and metal nanoparticles decorated on the  $Mn_3O_4$ -CNT (Pt/ $Mn_3O_4$ -CNT, Pd/ $Mn_3O_4$ -CNT and  $Pt_xPd_y$ / $Mn_3O_4$ -CNT) were well prepared and characterized as follows:

#### 3.1 Fourier transforms infrared spectroscopy (FT-IR )

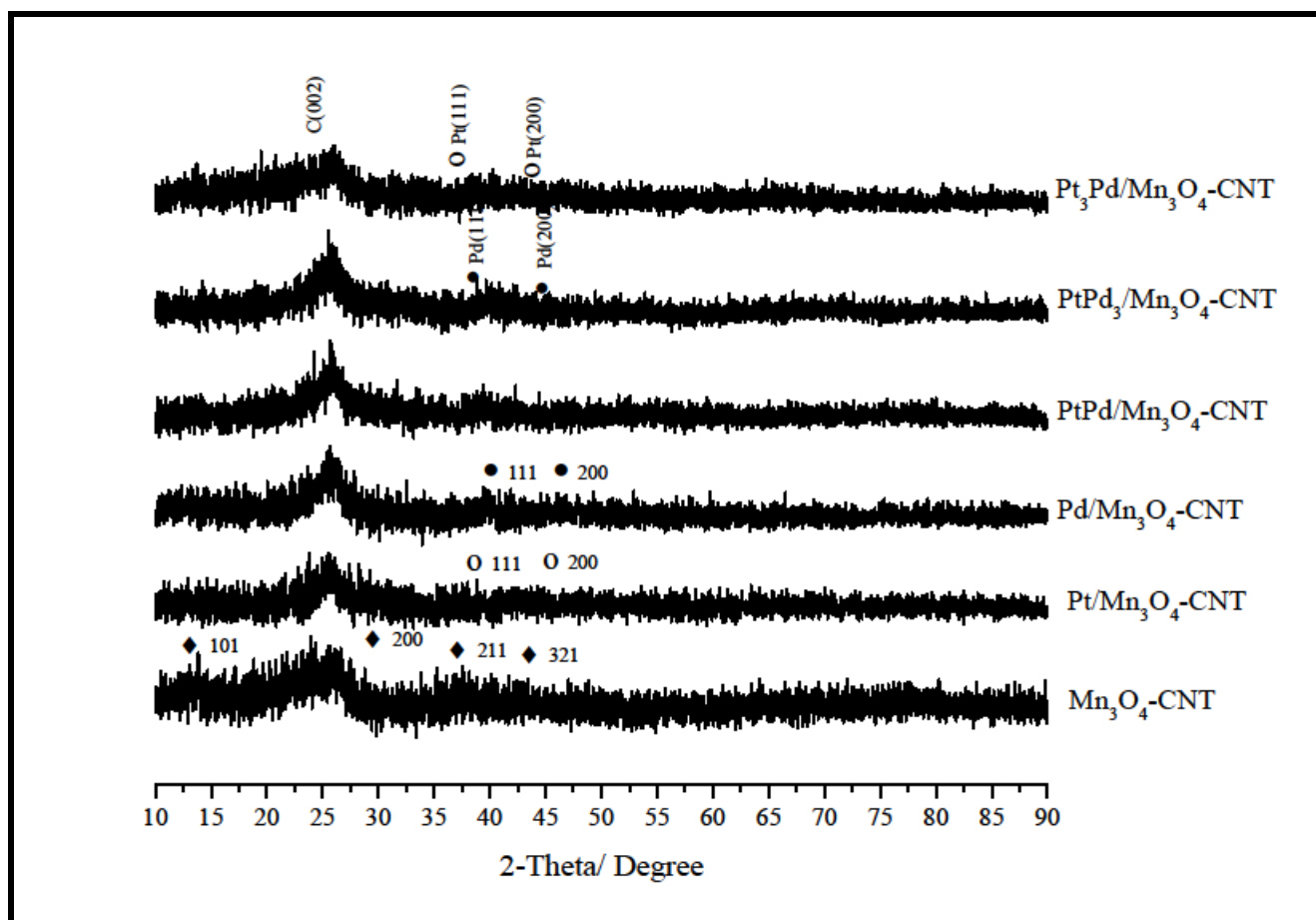


**Figure 1.** FT-IR spectra of CNT and  $Mn_3O_4$ -CNT nanocomposites.

The FT-IR spectra of CNT and synthesized  $Mn_3O_4$ -CNT nanocomposite materials in the range of  $4000-400 \text{ cm}^{-1}$  are shown in Figure 1. The broad bands observed at  $3425 \text{ cm}^{-1}$  are assigned to the intermolecular hydrogen bonding of hydroxyl groups (-OH) in CNT and  $Mn_3O_4$ -CNT. The Mn-O

stretching vibration band appears at  $672\text{ cm}^{-1}$  corresponding to a tetrahedral site. Similarly, the vibration band at  $541\text{ cm}^{-1}$  is directly related to distortion vibration of Mn-O in an octahedral site, and the absorption signal at  $445\text{ cm}^{-1}$  corresponds to the bending vibration mode of both sites [14, 15]. The absorption bands at  $1653$ ,  $1515$  and  $1452\text{ cm}^{-1}$  are spectral characteristic of C=C vibration of aromatics and C-O vibration of carboxyl group. In addition, the absorption bands at  $1039$  or  $1022\text{ cm}^{-1}$  are not only attributed to the subsistence of C-O of alkoxy groups but also assigned to Mn-O-H vibrations. Furthermore, the vibration bands at  $872$ ,  $2931$  and  $2858\text{ cm}^{-1}$  could be ascribed to the methylene ( $-\text{CH}_2$ ) and methine ( $-\text{CH}$ ) groups [16, 17, 18].

### 3.2 X-ray diffraction (XRD)



**Figure 2.** XRD patterns of  $\text{Mn}_3\text{O}_4\text{-CNT}$ ,  $\text{Pt}_x/\text{Mn}_3\text{O}_4\text{-CNT}$  and  $\text{Pd}/\text{Mn}_3\text{O}_4\text{-CNT}$  and  $\text{Pt}_x\text{Pd}_y/\text{Mn}_3\text{O}_4\text{-CNT}$  catalysts.

The phase purity and crystalline structure of the catalytic nanoparticles were characterized by XRD techniques in the  $2\theta$  range of  $10 - 90^\circ$  in Figure 2. The presence of broadening diffraction peaks at around  $26^\circ$  in all catalysts is assigned to the hexagonal graphite crystallographic planes (002) in CNT [19]. Although, all the XRD diffraction peaks of catalyst nanoparticles are undistinguished but it can be confirmed by X' Pert HighScore Plus software compared with the standard values of single

phase of CNT, Pt, Pd and  $Mn_3O_4$  (Hausmannite) as JCPDS No. 00-008-0415, No. 00-004-0802, No. 00-005-0681 and No. 00-001-1127, respectively. From the XRD pattern of  $Mn_3O_4$ -CNT, diffraction peaks at 18, 31, 36, 44, 51, 54 and 64 correspond to crystalline planes of  $Mn_3O_4$  (101), (200), (211), (220), (105) and (314), respectively. The XRD pattern of Pt/ $Mn_3O_4$ -CNT catalyst shows diffraction peaks at 39.8, 46.2 and 67.5 which can be attributed to the (111) (200) and (220) crystalline planes of the face-centered cubic (fcc) structure. For Pd/ $Mn_3O_4$ -CNT catalyst, the main diffraction peaks at 40.1 and 46.7 are assigned to (111) and (200) crystalline planes of the face-centered cubic (fcc) structure, respectively [17, 18]. The less intensity of diffracted peaks may imply the low crystallinity of the prepared catalysts. This is attributed to smaller crystallite size of mono and bi-metallic catalysts supported on  $Mn_3O_4$ -CNT [20]. Metallic particles as expected from Scherrer equation after background subtraction, the average metallic particle sizes were calculated as shown in Table 1. However, morphology and dispersion situation can also be confirmed in TEM characterization [16, 21].

**Table 1.** Summary of experimental XRD and TEM results for  $Pt_xPd_y/Mn_3O_4$ -CNT catalysts.

Catalysts	Peak	d-XRD (nm)	TEM (nm)
Pt/ $Mn_3O_4$ -CNT	220	1.56	$1.2 \pm 0.4$
Pd/ $Mn_3O_4$ -CNT	111	2.75	$3.1 \pm 0.9$
PtPd/ $Mn_3O_4$ -CNT	200	1.70	$3.2 \pm 0.8$
PtPd <sub>3</sub> / $Mn_3O_4$ -CNT	111	1.60	$2.1 \pm 0.8$
Pt <sub>3</sub> Pd/ $Mn_3O_4$ -CNT	111	2.51	$2.6 \pm 0.7$
$Mn_3O_4$ -CNT	103	3.28	$4.3 \pm 1.1$

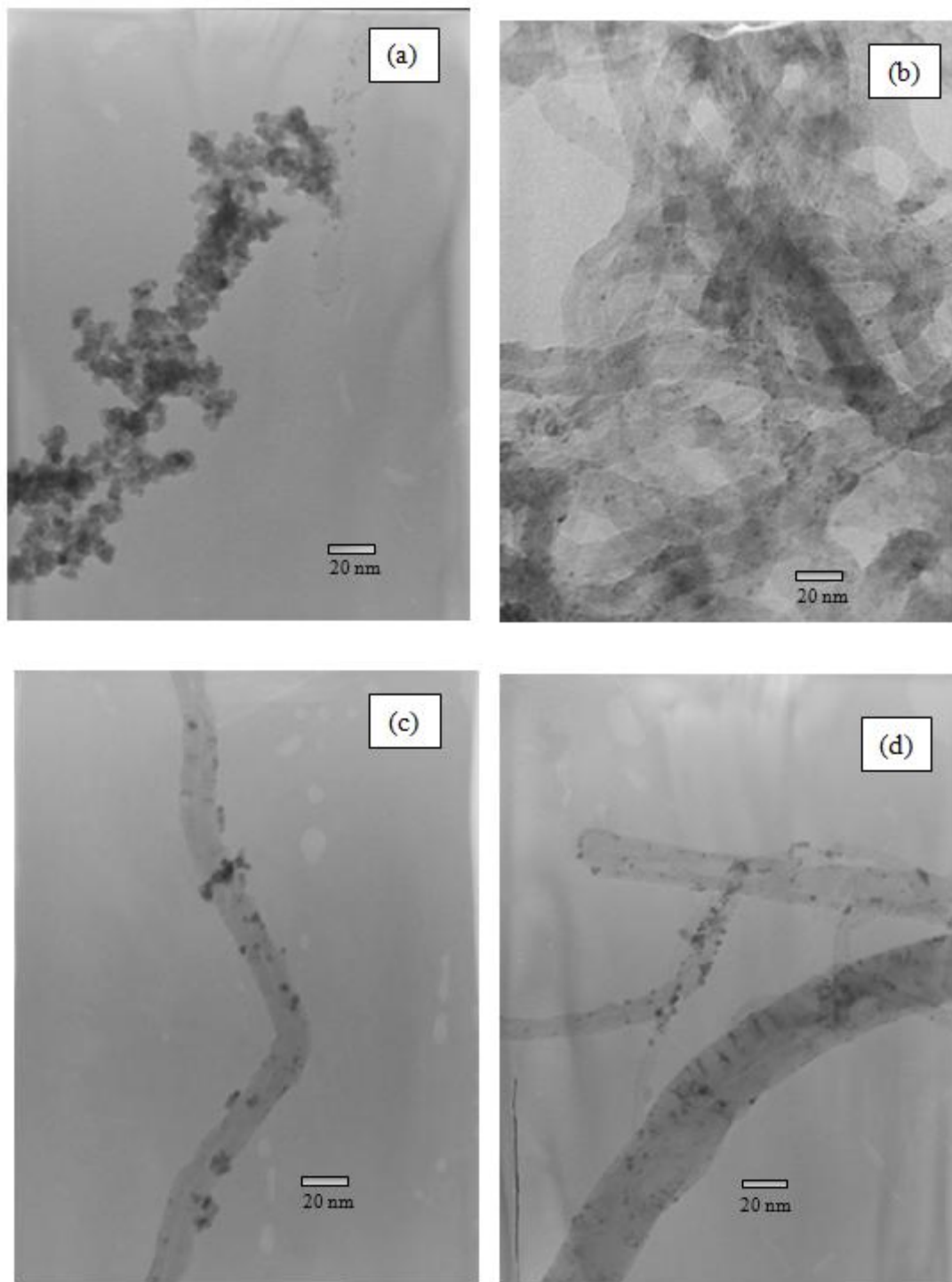
### 3.3 Transmission electron microscopy (TEM)

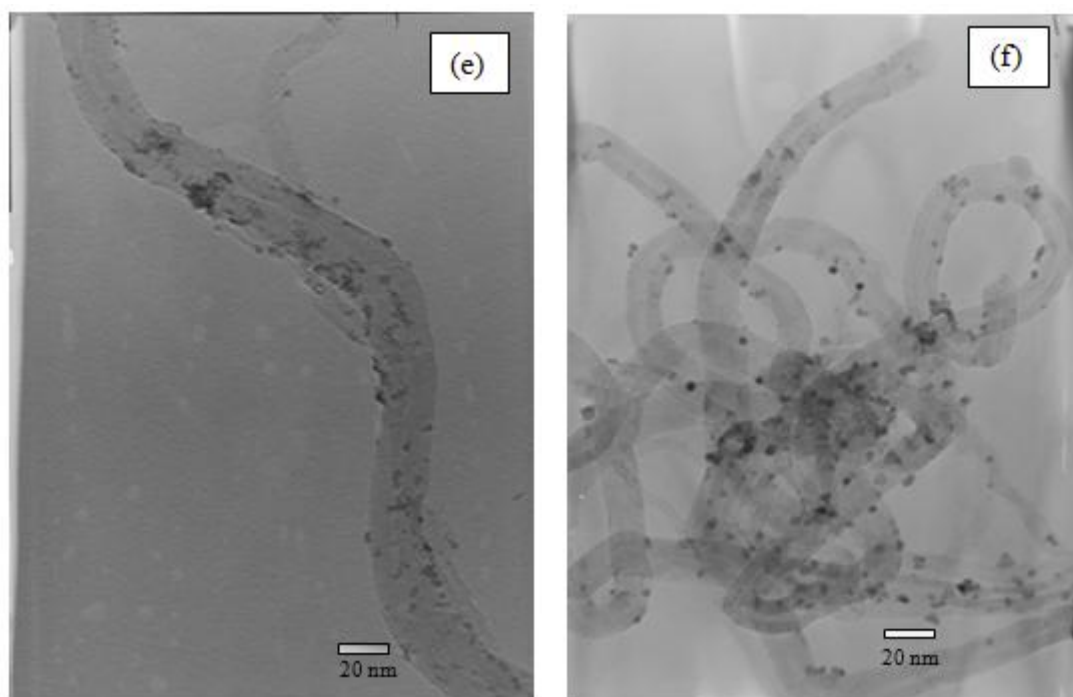
The CNT was modified with  $Mn_3O_4$  nanoparticles using ethylene glycol (EG) acting as reducing agent and stabilizer (in alkaline media) to control particles growth and prohibit agglomeration. Figure 3(a) shows the typical TEM of  $Mn_3O_4$ -CNT. It can be seen that  $Mn_3O_4$  nanoparticles reveal rather dispersed on the surface of functionalized carbon nanotubes with a size distribution of  $4.3 \pm 1.1$  nm, which are rather similar to the crystallite size calculated from XRD pattern, however some are agglomerated. It should be marked that the interaction between CNT and metal nanoparticles was strong as the metal nanoparticles could not be removed by wash and harsh stirring [15, 22].

Figure (b)-(f) shows the TEM of mono and bimetallic catalysts supported on  $Mn_3O_4$ -CNT, respectively. Approximate 100 metal nanoparticles were examined and the results are given in Table 1

and these results confirm and fairly agree with the value of the crystallite size calculated from XRD data.

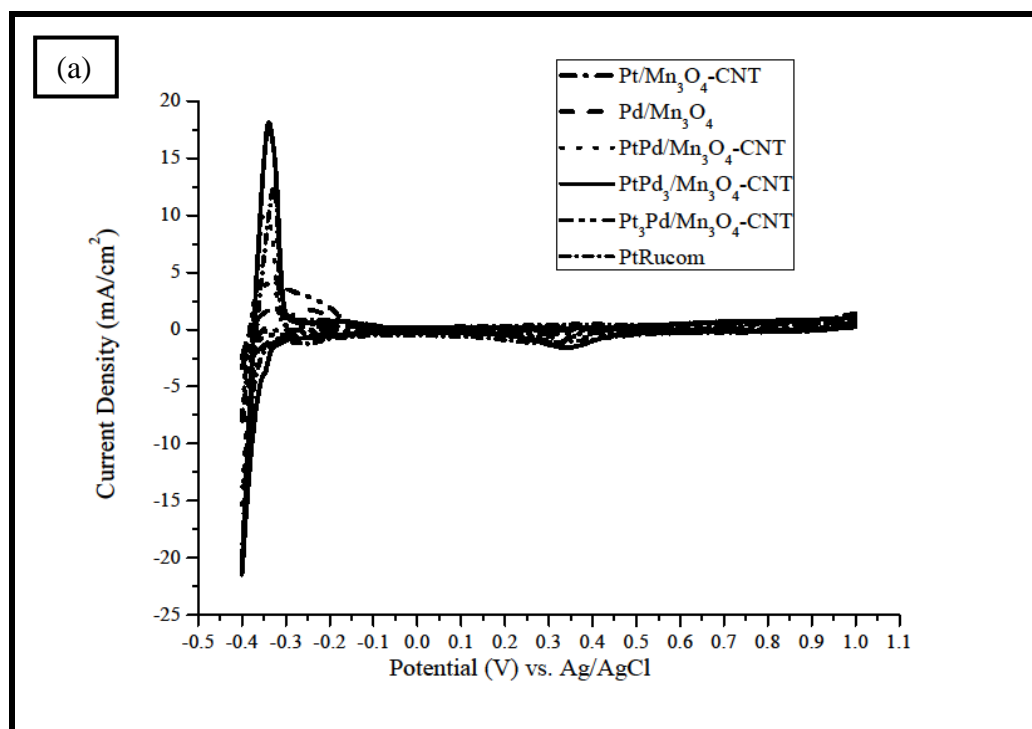
Those TEM images show the successful attachment of mono-, bi-metallic nanoparticles to the  $Mn_3O_4$ -CNT. Moreover, the EDS results (not showed here for brevity) reveals the presence of chemical compositions of the metal catalysts.



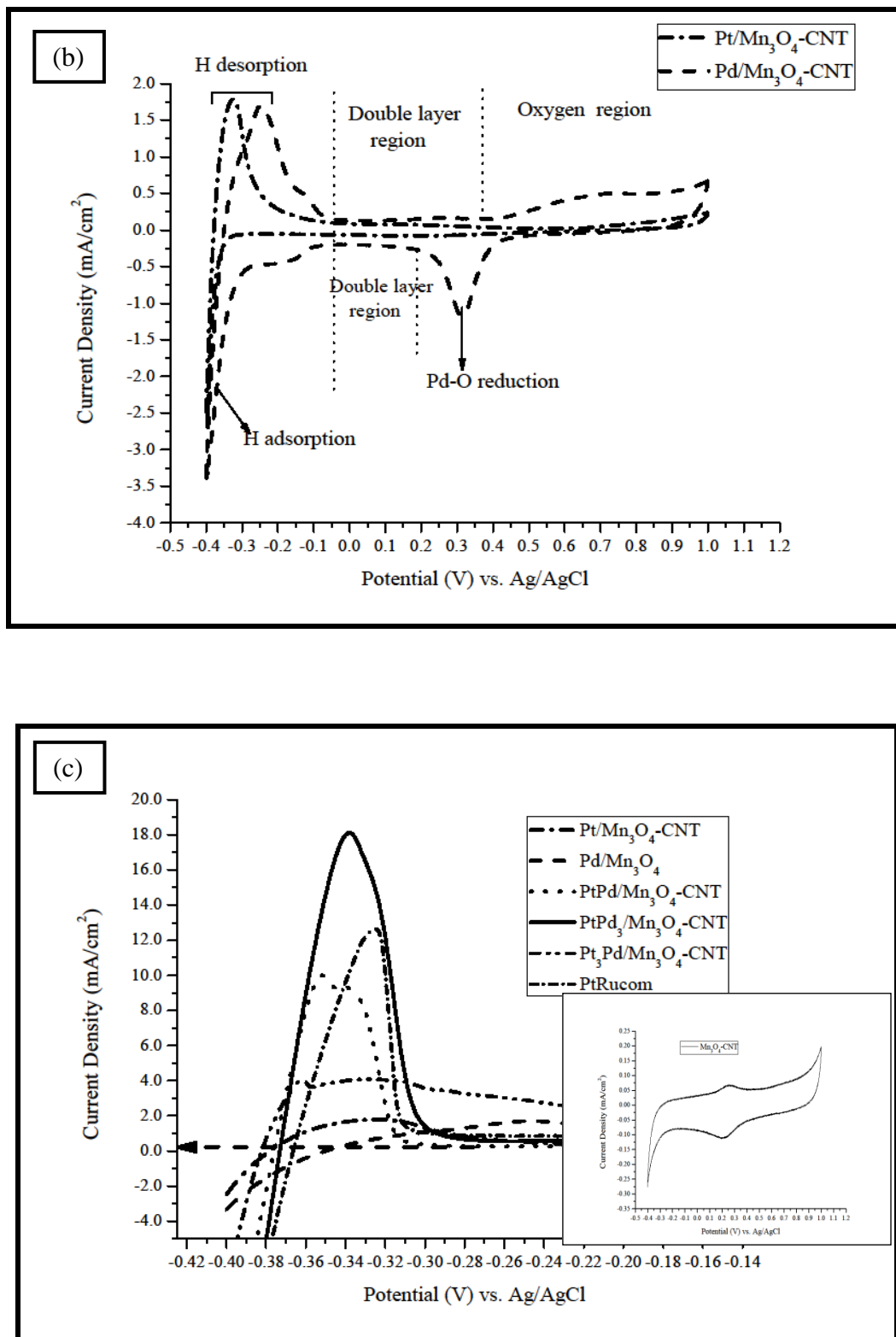


**Figure 3.** TEM images of (a)  $Mn_3O_4$ -CNT, (b)  $Pt_x/Mn_3O_4$ -CNT, (c)  $Pd/Mn_3O_4$ -CNT, (d)  $PtPd_3/Mn_3O_4$ -CNT, (e)  $PtPd/Mn_3O_4$ -CNT and (f)  $Pt_3Pd/Mn_3O_4$ -CNT.

### 3.4 Electrochemical characterization







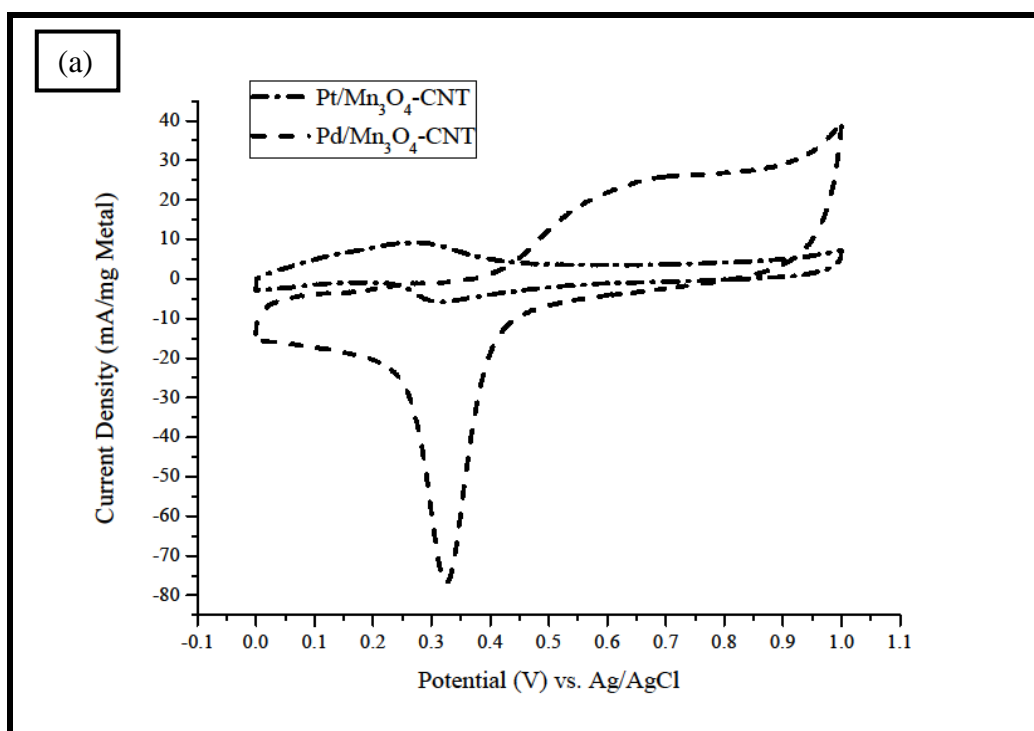
**Figure 4.** Cyclic voltammograms of (a) all catalysts and (b) Pt<sub>x</sub>/Mn<sub>3</sub>O<sub>4</sub>-CNT and Pd/Mn<sub>3</sub>O<sub>4</sub>-CNT and (c) specific area of CVs of all catalysts.

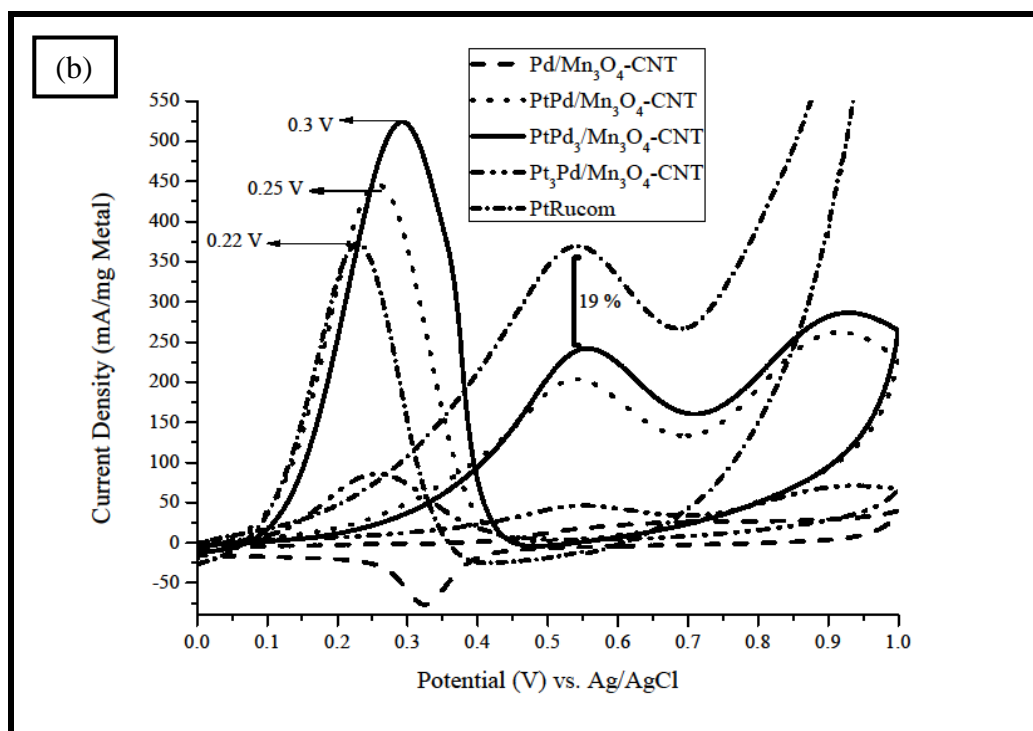
The CV of 10 wt% various atomic ratios Pt<sub>x</sub>Pd<sub>y</sub>Mn<sub>3</sub>O<sub>4</sub>-CNT and commercial PtRu/C electrocatalysts in a nitrogen saturated 0.5 M H<sub>2</sub>SO<sub>4</sub> aqueous solution at scan rate of 50 mVs<sup>-1</sup> were studied (Figure 4 (a)-(c)). The CVs visibly disclose the characteristic peaks of hydrogen

adsorption/desorption, double layer, metal oxide (of Pt, Pd) formation and metal oxides reduction on their catalyst surfaces. The peaks in the -0.4 to -0.2 V potential region of forward scan as well as reverse scan are signs of underpotential deposition of hydrogen ( $H_{\text{upd}}$ ) as a result of adsorption/desorption processes. Moreover, the peaks beyond 0.30 V during the anodic scan and 0.55 to 0.15 V in the reverse scan are characteristics of individual formation and reduction on the surfaces of the electrode indicating to the redox reactions with products of some  $\text{Pt}(\text{OH})_x \cdot n\text{H}_2\text{O}$ ,  $\text{Pd}(\text{OH})_x \cdot n\text{H}_2\text{O}$  and  $\text{Mn}(\text{OH})_2$  (where  $x = 2, 4$ ) [9, 23, 24].

On the other hand, at the voltammetric manner in the  $H_{\text{upd}}$  regions confirms possible differences in the hydrogen adsorption/desorption processes, which can be associated with the distinctions in the structural and crystallographic characteristics of dissimilar surfaces of the Pt, Pd and  $\text{Pt}_x\text{Pd}_y$  catalysts supported on the  $\text{Mn}_3\text{O}_4$  functionalized carbon nanotubes. It was stated the broad peaks might consist of (110) and (100) of hydrogen surfaces, and anions on (111) Pt surface on catalysts which designates some Pt crystallites with no specifically exposed crystal in spherical shape [24, 25]. Furthermore, the H adsorption/desorption peaks with high current densities in the  $H_{\text{upd}}$  peaks of  $\text{Mn}_3\text{O}_4$  promoted  $\text{Pt}_x\text{Pd}_y/\text{CNT}$ ,  $\text{Pt}/\text{CNT}$  and  $\text{Pd}/\text{CNT}$  as compared with commercial  $\text{PtRu}/\text{C}$  sample clearly suggests a higher amount of specifically exposed clean Pt surfaces. Therefore, proportion of Pt and Pd in bimetallic catalysts has affected to electrochemically active surface area and cooperation of Pd and  $\text{Mn}_3\text{O}_4$  that could possible to promote the electrocatalytic activity in electro-oxidation reaction.

### 3.4.1 Ethanol Electrooxidation





**Figure 5.** Cyclic voltammograms of (a)  $\text{Pt}_x/\text{Mn}_3\text{O}_4\text{-CNT}$  and  $\text{Pd}/\text{Mn}_3\text{O}_4\text{-CNT}$  and (b)  $\text{Pt}_x\text{Pd}_y/\text{Mn}_3\text{O}_4\text{-CNT}$  catalysts recorded in 0.50 M  $\text{H}_2\text{SO}_4$  aqueous solution containing 0.50 M  $\text{CH}_3\text{CH}_2\text{OH}$  at a scan rate of  $50 \text{ mVs}^{-1}$ .

Ethanol electrooxidation is a complex reaction and it can lead to poisoning of pure Pt surface due to adsorption of intermediates and poisonous species during oxidation. An entire ethanol oxidation discharges 12 electrons per molecule and the C-C bond is broken. Experimental studies have revealed that ethanol is partially oxidized to acetaldehyde and acetic acid (2 – 4 electron in oxidation reactions) instead of fully oxidized (12 electron in oxidation reactions) [12]. Consequently, the ethanol electrooxidation was considered to require more active and selective catalysts to complete the reaction.

Ethanol oxidation on our prepared catalysts was monitored by CV measurement in a nitrogen-saturated 0.5 M  $\text{CH}_3\text{CH}_2\text{OH}$  + 0.5 M  $\text{H}_2\text{SO}_4$  solution, and the results are compared with the commercial PtRu/C, shown in Figure 5. It is clear that the addition of either Pd or  $\text{Mn}_3\text{O}_4$  lead to a promoting effect in ethanol oxidation. The CVs of mono metallic catalysts,  $\text{Pt}/\text{Mn}_3\text{O}_4\text{-CNT}$  and  $\text{Pd}/\text{Mn}_3\text{O}_4\text{-CNT}$ , show diminutive oxidation and reduction peaks shown in Figure 5 as the enhancement of  $\text{Mn}_3\text{O}_4$  nanoparticles promoted Pt and Pd on functionalized carbon nanotubes catalysts, while the amount of oxygenated peak of  $\text{Mn}_3\text{O}_4\text{-OH}$  is observed at 0.33 V [12].

The  $\text{Pd}/\text{Mn}_3\text{O}_4\text{-CNT}$  clearly showed the reduction of the Pd-OHads and  $\text{Mn}(\text{OH})_2$  species and presence of reduction peaks (0.33 V) and peaks current density indicating the formation of oxygenated on Pd and  $\text{Mn}_3\text{O}_4$  species which are from the water and ethanol activations. However, more oxides or oxygenated species (oxophilicity;  $\text{M}(\text{OH})_x$  or  $\text{MO}_x$ ) result in retardation of the electrocatalytic activity for oxidation reaction of Pt base catalysts [23].

The efficiencies of the Pt and different  $\text{Pt}_x\text{Pd}_y$  bimetallic catalysts supported on high specific surfaces area  $\text{Mn}_3\text{O}_4\text{-CNT}$  and commercial PtRu/C catalysts on ethanol oxidation were compared

concerning oxidation potential, onset potential, forward and backward oxidation peak current density, the ratio of the forward peak ( $I_f$ ) to the backward peak ( $I_b$ ); these data are shown in Table 2.

**Table 2.** Comparison of various metal/ $Mn_3O_4$ -CNT electrocatalysts on ethanol oxidation.

Catalysts	Mole ratios	Forward anodic sweep		Reverse anodic sweep		Onset potential	$I_b/I_f$ Ratio	Stability at 3600 s
		$I_f$ (mA/mg Metal)	$E_{max}$ (V)	$I_b$ (mA/mg Metal)	$E_{max}$ (V)	E (V)		mA/mg Metal
Pt/ $Mn_3O_4$ -CNT	1	-	-	-	-	-	-	-
Pd/ $Mn_3O_4$ -CNT	1	-	-	-	-	-	-	-
PtPd/ $Mn_3O_4$ -CNT	1:1	200	0.540	450	0.259	0.125	2.25	0 at 2200 s
PtPd <sub>3</sub> / $Mn_3O_4$ -CNT	1:3	235	0.529	540	0.301	0.125	2.30	3.7
Pt <sub>3</sub> Pd/ $Mn_3O_4$ -CNT	3:1	45	0.521	84	0.285	0.125	1.88	4.4
PtRu/Vulcan	1:1	349	0.550	346	0.249	0.075	0.99	-4.3

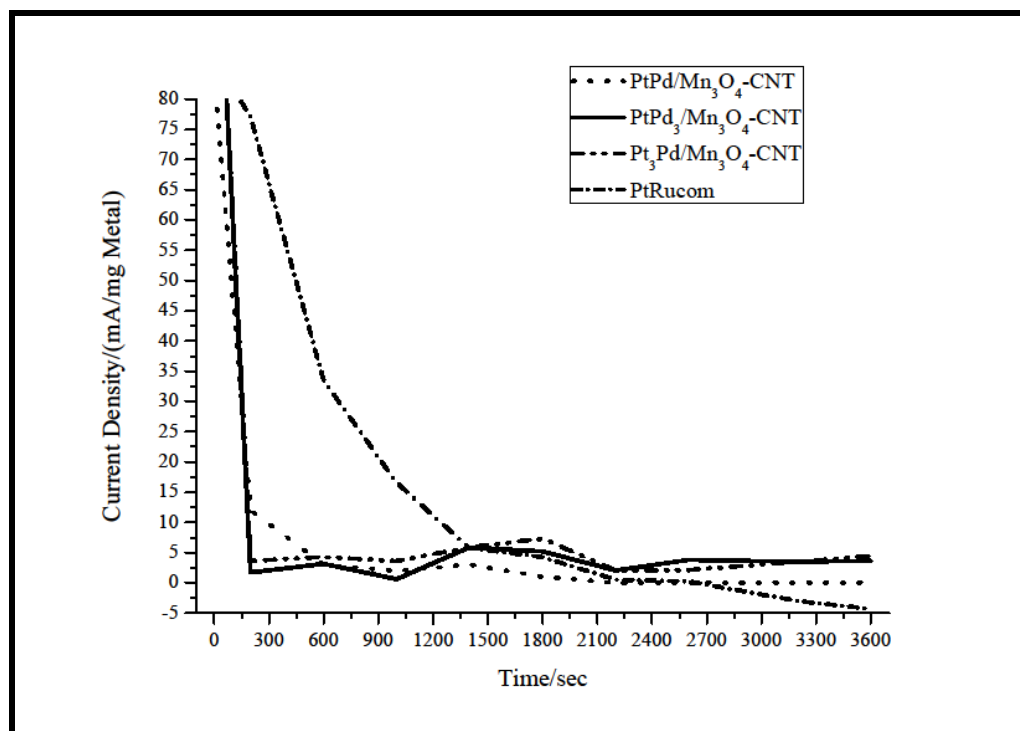
Typical voltammetry of two oxidation peaks show in all CV curves. The peak in the forward peak was related to the ethanol oxidation, and another one in the reverse peak was mainly associated with the elimination of the remaining carbonaceous species from the forward scan [25]. On the other hand, the current density during the anodic scan raise gradually at lower potentials and then increases quickly until a current peak is obtained. After backward scan, a reactivation is obtained on the electrode. The peaks at approximate 0.55 V are ascribed to ethanol oxidation, forming  $CO_2$  and adsorbed carbonaceous species (principally as CO). This adsorbed CO causes the loss of catalyst activity. The oxidation peaks of backward scan at ca. 0.30 V can attribute to oxidations of the adsorbed carbonaceous species and ethanol to  $CO_2$ . Although, the forward anodic peak current density of commercial PtRu catalysts is higher than that of synthesized PtPd<sub>3</sub>/ $Mn_3O_4$ -CNT catalysts about 19 % but reversed anodic peak is less than the prepared catalyst that implies the prepared catalysts can proficiently eliminate intermediates more than commercial PtRu/C.

However, the onset potential, the commercial PtRu catalysts is rather similar to the prepared catalysts (ca. 0.08 V). The ratio of  $I_b$  to  $I_f$  is regularly utilized to estimate the catalyst tolerance. Basically, a higher  $I_b/I_f$  value represents a relatively complete oxidation of ethanol, producing  $CO_2$ . The ratios for PtPd<sub>3</sub>/ $Mn_3O_4$ -CNT, PtPd/ $Mn_3O_4$ -CNT, Pt<sub>3</sub>Pd/ $Mn_3O_4$ -CNT and PtRu/C nanocomposites are 2.30, 2.25, 1.88 and 0.99, respectively, implying that Pt<sub>x</sub>Pd<sub>y</sub> bimetallic catalysts supported on  $Mn_3O_4$  functionalized CNT have much supplementary tolerance toward carbonaceous species poisoning and cause more complicated oxidation of ethanol [12].

### 3.4.2 Electrocatalyst stability

Chronoamperometric (CA) measurements were carried out in an electrolyte of 0.5 M  $CH_3CH_2OH$  + 0.5 M  $H_2SO_4$  with a bias potential of 0.25 V for duration 3600 s as shown in Figure 6. The current-time curves of all catalysts display quickly decay at the initial stages which are attributed

to the accumulation of poisonous intermediates, such as COads, generated from the continuous oxidation of ethanol on the catalyst surface [14,20, 26] .

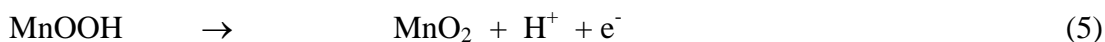
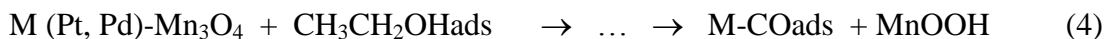


**Figure 6.** Chronoamperograms of various  $Pt_xPd_y/Mn_3O_4$ -CNT catalysts recorded in 0.50 M  $H_2SO_4$  aqueous solution containing 0.50 M  $CH_3CH_2OH$  obtained for 3600 s at 0.25 V.

After the catalytic reactions reach a steady state in which the adsorptions oxygenated species and CO-like species occur [27]. Moreover, increases in initial and limiting current densities is obviously found after the addition of Pd and  $Mn_3O_4$  in the catalysts. The current densities for the prepared catalysts are higher than that for commercial PtRu/C composites during the whole experimental range. The current density of  $Pt_3Pd/Mn_3O_4$ -CNT catalyst in ethanol oxidation is the highest when compared with the other three catalysts and also the commercial PtRu/C catalyst. This can be indicated that COads tolerance or other poisonous intermediates can be removed when Pd and  $Mn_3O_4$  were added.

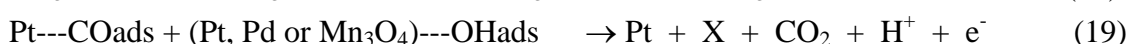
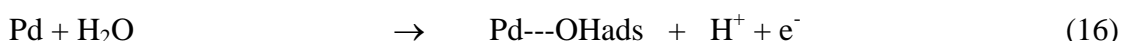
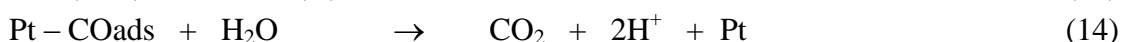
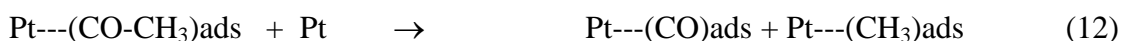
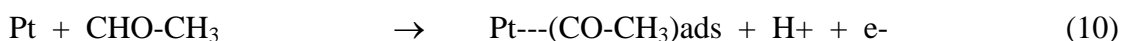
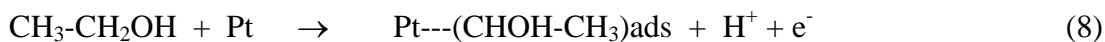
The presences of Pd and  $Mn_3O_4$  in catalysts can prove the enhancement the proton conductivity of the catalysts, which can promote the electrocatalytic oxidation of ethanol *via* dehydrogenation in ethanol oxidation [20].

It has been reported that the electrocatalytic activity increases with the increase of the exchange rate of  $H^+$  ions [9], which can be promoted by the presence of  $Mn_3O_4$  because  $MnOOH$ ,  $Mn_2O_3$  and  $MnO_2$  can be generated by reactions of proton and  $Mn_3O_4$ (equation 4-7). The active  $Mn^{3+}/Mn^{2+}$  redox couples can effectively catalyze the dehydrogenation of ethanol and further promote the electrocatalytic activity, which are similar to the “hydrogen spillover effect” in Pt- $SnO_2$  system [25]. The possible mechanisms stated as follows:



where “...” stand for the processes of the C-C bond splitting

Apparently, OH<sub>ads</sub> species is necessary for removal of adsorbed CO on Pt [20, 22, 24]. Those strongly adsorbed intermediates (-CO species) such as CH<sub>3</sub>-CO and CH-CO, are also easily adsorbed on the catalyst surface in the electrooxidation. The other possible intermediate reactions can be occurred as there are some species of Pt, Pd on the surfaces of the catalysts (equation 8-19).



Both of Pd and manganese oxides provides OH<sup>-</sup> ion to oxidize the adsorbed intermediates on Pt surface [17, 28]. Moreover, the inherent Mn-OH bonds in the hydrous Mn<sub>3</sub>O<sub>4</sub> can also donate the hydroxide species to oxidize the adsorbed poisoning species. So, the Mn<sub>3</sub>O<sub>4</sub> and Pd can effectively promote the dehydrogenation of ethanol oxidation and remove the adsorbed intermediates to release the Pt active sites. Thus, the Pt<sub>x</sub>Pd<sub>y</sub>/Mn<sub>3</sub>O<sub>4</sub>-CNT exhibits enhanced electrocatalytic activity, excellent stability and anti-poisoning ability toward ethanol oxidation.

Pt-base bimetallic materials are the most commonly used as electrocatalysts in the electrochemical oxidation of small molecules because of their excellent properties in the adsorption and dissociation [28]. Nevertheless, the enhanced current in Pt-based alloys is from acetaldehyde and/or acetic acid formations than from the C-C bond cleavage. Whereas Pt is the active metal for C-C activation, these alloyed catalysts with reduced surface Pt truly lower the overall conversion to CO<sub>2</sub>. In a noble metal binary system, higher transition metal content can generate more complexes of transition metal and OH<sub>ads</sub> species, resulting in water dissociation, which assist the oxidation of small molecules, adsorbed the catalyst surfaces. Though, higher transition metal content could also diminish the occupancy of active noble metal atoms on the surface, and consequently impair the whole performance of dissociation of the adsorbed molecules.

#### 4. CONCLUSION

Preparation of Pt<sub>x</sub>Pd<sub>y</sub> bimetallic catalysts supported Mn<sub>3</sub>O<sub>4</sub> functionalized carbon nanotubes via modified polyol method was performed and the prepared catalysts were obtained uniformly dispersed. An improvement of electroactivity capability was studied by optimizing the ratio of Pt and Pd on Mn<sub>3</sub>O<sub>4</sub>-CNT for the ethanol oxidation. It was found that the presence of noble metal and Mn<sub>3</sub>O<sub>4</sub> in catalysts could enhance the electrocatalytic activity toward ethanol oxidation from CV and CA results. Therefore, it could be pointed out that the interaction between the Pt and Pd metal nanoparticles and oxygenated groups from metal oxide on the supports significantly improved the ethanol electrooxidation performance with high current densities and extended stability.

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#### References

1. C. Lamy, E. M. Belgsir and J. M. Léger, *J. Appl. Electrochem.*, 31 (2001) 799.
2. C. Lamy and C. Coutanceau, Chapter 1 Electrocatalysis of Alcohol Oxidation Reactions at Platinum Group Metals, in: *Catalysts for Alcohol-Fuelled Direct Oxidation Fuel Cells*, The Royal Society of Chemistry, United Kingdom, 2012.
3. A. O. Neto, R. R. Dias, M. M. Tusi, M. Linardi and E.V. Spinacé, *J. Power Sources*, 166 (2007) 87.
4. E. Antolini, *J. Power Sources*, 170 (2007) 1.
5. J. Friedl and U. Stimming, *Electrochim. Acta*, 101 (2013) 41.
6. A. R. Bonesi, M. S. Moreno, W. E. Triaca and A. M. C. Luna, *Int. J. Hydrogen Energy*, 35 (2010) 5999.
7. Y. -C. Chiang, W. -H. Lin and Y. -C. Chang, *Appl. Surf. Sci.*, 257 (2011) 2401.
8. C. -W. Liu, Y. -W. Chang, Y. -C. Wei and K. -W. Wang, *Electrochim. Acta*, 56 (2011) 2574.
9. S. K. Meher and G. R. Rao, *J. Phys. Chem. C*, 117 (2013) 4888.
10. M. S. Saha and A. Kundu, *J. Power Sources*, 195 (2010) 6255.
11. S. Sha rma and B. G. Pollet, *J. Power Sources*, 208 (2012) 96.
12. E. V. Spinacé, A. O. Neto, T. R. R. Vasconcelos and M. Linardi, *J. Power Sources*, 137 (2004) 17.
13. S. Yin, Q. Zhu, Y. Qiang and L. Luo, *Chin. J. Catal.*, 33 (2012) 290.
14. Z. Ji, X. Shen, G. Zhu, K. Chen, G. Fu and L. Tong, *J. Electroanal. Chem.*, 682 (2012) 95.
15. L. Laffont and P. Gibot, *Mater. Charact.*, 61 (2010) 1268.
16. K.A.M. Ahmed, Q. Zeng, K. Wu and K. Huang, *J. Solid State Chem.*, 183 (2010) 744.
17. Y. Zhao, S. Nie, H. Wang, J. Tian, Z. Ning and X. Li, *J. Power Sources*, 218 (2012) 320.
18. Z.-H. Wang, L.-X. Yuan, Q.-G. Shao, F. Huang and Y.-H. Huang, *Mater. Lett.*, 80 (2012) 110.
19. X. Yang, X. Wang, G. Zhang, J. Zheng, T. Wang, X. Liu, C. Shu, L. Jiang and C. Wang, *Int. J. Hydrogen Energy*, 37 (2012) 11167.
20. J. Cai, Y. Huang, B. Huang, S. Zheng and Y. Guo, *Int. J. Hydrogen Energy*, 39 (2014) 798.
21. Y. Zhao, W. Ran, D. -B. Xiong, L. Zhang, J. Xu and F. Gao, *Mater. Lett.*, 118 (2014) 80.
22. G. S. Gund, D. P. Dubal, B. H. Patil, S. S. Shinde and C. D. Lokhande, *Electrochim. Acta*, 92 (2013) 205.

23. J. Yin, S. Shan, M. S. Ng, L. Yang, D. Mott, W. Fang, N. Kang, J. Luo and C. -J. Zhong, *Langmuir*, 29 (2013) 9249.
24. K. V. Sankar, S. T. Senthilkumar, L. J. Berchmans, C. Sanjeeviraja and R. K. Selvan, *Appl. Surf. Sci.*, 259 (2012) 624.
25. Y. Li, W. Gao, L. Ci, C. Wang and P. M. Ajayan, *Carbon*, 48 (2010) 1124.
26. J. Ma, H. Sun, F. Su, Y. Chen, Y. Tang, T. Lu and J. Zheng, *Int. J. Hydrogen Energy*, 36 (2011) 7265.
27. Y. Huang, J. Cai and Y. Guo, *Int. J. Hydrogen Energy*, 37 (2012) 1263.
28. A. Brouzgou, A. Podias and P. Tsiakaras, *J. Appl. Electrochem.*, 43 (2013) 119.

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