Electrocatalytic oxidation of formaldehyde onto Pt nanoparticles modified poly (m-toluidine)/Triton X-100 film

J. Raoof¹*, S.R. Hosseini², R. Ojani¹

¹Professor, Department of Analytical Chemistry, Faculty of Chemistry, University of Mazandaran, Postal Code: 47416-95447, Babolsar, Iran
²Assistant Professor, Nanochemistry Research Laboratory, Faculty of Chemistry, University of Mazandaran, Postal Code: 47416-95447, Babolsar, Iran
*Corresponding author’s E-mail: j.raoof@umz.ac.ir(J.-B. Raoof)

Article history:
(Received: 27 May 2013, Revised: 28 January 2014, Accepted: 16 February 2014)

ABSTRACT
In this work, spherical Pt nanometer-scale particles supported on the poly (m-toluidine)/Triton X-100 film modified carbon nanotube paste electrode (Pt/PMT (TX-100)/MCNTPE) was used as a potent catalyst for electrooxidation of formaldehyde (HCHO) in both 0.5 M H₂SO₄ and 0.1 M NaOH solutions. The obtained results showed that utilization of TX-100 as an additive during the electropolymerization process enhances the electrocatalytic activity of the modified electrode towards HCHO oxidation. The onset potential of HCHO oxidation was shifted in 0.1 M NaOH to less positive values than that of the acid solution which is due to the solution pH. Then, the influences of some parameters such as potential sweep rates, switching potential, and HCHO concentration on its oxidation have been investigated to provide the first insight into the electrooxidation behavior of HCHO in the alkaline medium. Also, stability of the modified electrode was examined by potential cycling in both acidic and alkaline solutions and the obtained results showed that in 0.1 M NaOH solution, a sufficient improvement was noted. The present study shows a promising choice of the Pt/PMT (TX-100)/MCNTPE as composite catalyst for HCHO oxidation at a reasonable low overpotentials.

Keywords: Electrocatalytic oxidation; Triton X-100; Pt nanoparticles; Carbon nanotube; Formaldehyde

1. INTRODUCTION
The electrochemical oxidation of formaldehyde (HCHO) is important for full understanding of methanol oxidation in development of fuel cell technology, because it is an intermediate in methanol oxidation reaction [1]. The oxidation of HCHO is also interesting, because it is used in technologically important processes such as electroless copper plating and textile industry [2]. However, this reaction has received rather little attention and the data available in the literature are still relatively fragmented and scarce [3-7]. Fundamental research of the HCHO oxidation has been carried out on Pt electrodes regarding the reaction mechanism [8] and oscillatory phenomena [9]. The choice of a suitable supporting material for dispersion of particles is an imperative
factor that may affect the recital of supported metallic electrocatalysts owing to their interactions and surface reactivities [10, 11]. The supporting materials with high surface area are essential to reduce the metal loading under the condition of keeping the high catalytic activity. It is well known that conducting polymers (CPs) with porous structures and high surface areas have been proved to be suitable host materials for dispersion of metallic particles [12-15]. The reason for the incorporation of noble metals (e.g., Pt, Ru, Pd, etc.) particles into the porous matrixes is to increase their surface areas and thus improve their catalytic efficiency as compared with the bulk form of metal electrodes. There is also evidence in the literature to show that the poisoning of these incorporated catalytic particles by strongly adsorbed species, such as CO, is significantly less than that observed with their bulk counterparts [16, 17]. The composites of CPs with metal nanoparticles permit a facile flow of electronic charges through the polymer matrix during electrochemical processes. Recently, we have combined the advantageous features of polymer modification, dispersion of metal ions on CPs coated carbon paste electrodes by construction of Ni/P (1,5-DAN) [18], Ni/P(N-MANI) [19], Ni/POT (TX-100) [20] and Ni/CTAB-PMT [21] which can successfully catalyze the HCHO oxidation in alkaline medium. Furthermore, in our recent work, the electrocatalytic effect of Pt particles electrodeposited on the PMT (TX-100)/MCNTPE was studied for methanol oxidation [22]. The electrocatalytic oxidation behavior of HCHO in acidic media at various electrodes has been investigated extensively, but there have been only few reports about electrocatalytic oxidation behavior of HCHO in alkaline medium. Our literature survey shows that there is no available data about the electrochemical oxidation of HCHO on the Pt nanoparticles decorated poly (m-toluidine)/Triton X-100 film modified carbon nanotube paste electrode (Pt/-PMT(TX-100)/MCNTPE). The results show that utilization of TX-100 during the electrode preparation improves the electrocatalytic activity.

2. EXPERIMENTAL

2.1. Materials and instrumentation

Sulfuric acid (Fluka) and sodium hydroxide (Merck) were used for preparation of supporting electrolytes. The H₂PtCl₆·6H₂O, MT monomer (99%), HCHO, and Triton X-100 (99%) from Merck were used as received. High viscosity paraffin (density: 0.88 g cm⁻³, Fluka) was used as the pasting liquid for CNTP. MWCNTs (purity>95%, outer diameter 5-20 nm, inner diameter 2-6 nm, length 1-10 μm, number of walls 3-15, apparent density 0.15-0.35 g.cm⁻³, Nanostar Tech. Co., Tehran, Iran) and graphite powder (particle diameter: 0.10 mm, Merck) were used as the working electrode substrates. Electrochemical experiments were performed with a computer controlled potentiostat/galvanostat μ-Autolab type III modular electrochemical system (Eco Chemie BV, The Netherlands), driven with general purpose electrochemical system (GPES) soft-ware (Eco Chemie). A conventional three electrodes cell was used with Ag|AgCl|KCl (3M) as reference electrode, Pt wire as counter electrode and carbon nanotube paste as working electrode substrate.

2.2 The electrode modification

Modification of the CNTP was performed according to our previous work [22]. Briefly, electropolymerization of MT monomer by potentiodynamic method in aqueous solution containing 1.0 M H₂SO₄, 20 mM MT
and 6.0 mM TX-100 for construction of PMT (TX-100)/MCNTPE and electrodeposition of Pt particles from an aqueous sulfuric acid solution containing 4.0 mM H$_2$PtCl$_6$ by using potential cycling between 0.4 and -0.25 V for fabrication of the Pt/PMT (TX-100)/MCNTPE were performed. Table 1 summarizes the surface parameters for the modified electrode. The formation and growth of the electrodeposited Pt particles on the PMT (TX-100)/MCNTPE were checked by SEM [22]. The SEM image of the modified electrode showed Pt spherical nanometer-scale particles in different distances from each other in various sizes. The average size of the Pt particles varies from under 100 nm to slightly less than 250 nm.

**Table 1.** Surface parameters of Pt nanoparticles onto the PMT (TX-100)/MCNTPE.

<table>
<thead>
<tr>
<th>Surface parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geometric area, $A_g$/cm$^2$ ($\pi r^2$)</td>
<td>0.09</td>
</tr>
<tr>
<td>Pt loading/mg cm$^{-2}$ (0.5 $Q_{dep}/A_g$)</td>
<td>0.22</td>
</tr>
<tr>
<td>Real surface area, $A_r$/cm$^2$ ($Q_{H}/0.21$ mC cm$^{-2}$)</td>
<td>5.50</td>
</tr>
<tr>
<td>Roughness factor, RF ($A_r/A_g$)</td>
<td>61.1</td>
</tr>
<tr>
<td>Specific surface area, $S$/m$^2$ g$^{-1}$ (100 $A_r/m_{pt}$)</td>
<td>27.5</td>
</tr>
<tr>
<td>Mass activity, A g$^{-1}$ ($I_p/m_{pt}$)</td>
<td>$71^a$, $10^5^b$</td>
</tr>
</tbody>
</table>

$^a$ in 0.5 M H$_2$SO$_4$ solution, $^b$ in 0.1 M NaOH solution

### 3. RESULTS AND DISCUSSION

#### 3.1. Electrocatalytic oxidation of formaldehyde

Previously, normal PMT films were obtained at the surface of Au and tin oxide electrodes [23, 24]. The prepared poly ($m$-toluidine) film in the presence of TX-100 (PMT (TX-100)) has higher redox current than that of PMT film. Furthermore, the PMT/TX-100 film shows larger background current which is attributed to the larger surface area [22]. The electrochemical behavior of the Pt/PMT (TX-100)/MCNTPE was studied in 0.5 M H$_2$SO$_4$ solution by using CV method (Fig. 1). As can be seen in Fig. 1A (solid line), three pair peaks (a/a’ corresponding to the hydrogen adsorption/desorption, b/b’ corresponding to the polymer oxidation/reduction and c/c’ corresponding to Pt oxide formation/reduction) are discernible. It should be noted that the reduction peak of the polymer was overlaid on the reduction peak of Pt oxide. Figure 1A (dotted line) shows a typical CV of the modified electrode during the adsorption and oxidation of formaldehyde. In aqueous solution, formaldehyde is almost completely hydrated, giving methylene glycol (gem-diol, i.e. CH$_2$(OH)$_2$) with an
equilibrium constant on the order of $10^3$. In the CV, two main peaks can be observed at 0.64 (peak I) and 1.2 V (peak II) during the forward potential sweep. The electrooxidation of formaldehyde on Pt surface in electrical double layer region also results in the formation of CO$_{ads}$ with leads to electrode poisoning. At higher potentials, a quick increase in current is observed during the forward scan. Peak I is attributed to oxidation of CO$_{ads}$ to CO$_2$, resulted from formaldehyde electrooxidation by reacting with OH$_{ads}$ formed the dissociation of water molecules on Pt surface. Peak II is also due to the oxidation of CO$_{ads}$ producing CO$_2$ and a bare Pt site, where HCHO is oxidized at the same time [7, 8, 25]. When the potential sweep is reversed, reduction of the Pt oxide occurs reactivating the electrode surface and the complete oxidation of methylene glycol occurs as indicated by the presence of an intense anodic peak (III) at 0.40 V. Also, in view of investigating the role of the PMT (TX-100) film in the electrocatalytic efficiency of the deposited Pt particles, the electrocatalytic activity of Pt particles on the other electrode was evaluated towards formaldehyde oxidation (Fig. 1A (dashed line)). The mass activity of the Pt/PMT (TX-100)/MCNTPE is about 3 times higher than that obtained in the Pt/PMT-/MCNTPE. The obtained results show that the electrocatalytic activity of the Pt/PMT (TX-100)-/MCNTPE towards formaldehyde oxidation is improved and becomes higher than that Pt/PMT/MCNTPE. The difference between electrochemical responses may be attributed to the larger $A_t$ of the Pt particles in the PMT (TX-100) film.

Fig. 1. (A) Electrochemical responses of the Pt/PMT (TX-100)/MCNTPE in 0.5 M H$_2$SO$_4$ solution in the absence (solid line) and the presence of 0.12 M HCHO (dotted line) and Pt/PMT/MCNTPE in the presence of 0.12 M HCHO (dashed line). (B) CVs of the PMT (TX-100)/MCNTPE (dotted line) and the Pt/PMT (TX-100)/MCNTPE (solid line) in 0.1 M NaOH solution. (C) Electrochemical behaviors of the Pt/PMT (TX-100)/MCNTPE (solid line) and bulk Pt electrode (dotted line) in 0.1 M NaOH + 0.12 M HCHO at $v = 0.05$ V s$^{-1}$. 
The oxidation mechanism of methylene glycol on noble metals is a dual path (Scheme 1) [1, 26-29]. In this mechanism, formaldehyde is oxidized to CO$_2$ via two parallel pathways: one through chemisorbed CO intermediate (pathway 1) and the other directly to CO$_2$ (pathway 2).

On the other hand, both forward and backward peak appear in the anodic zone, which is an indication of presence of the direct and indirect paths in the overall process (1) [30-33].

\[
\text{CH}_2\text{(OH)}_2 \rightarrow \text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \quad (1)
\]

Scheme 1. Schematic representation of formaldehyde oxidation.
The electrochemical behaviors of the PMT (TX-100)/MCNTPE and Pt/PMT (TX-100)/MCNTPE were studied by using CV method after potential cycling (Fig. 1B). As can be seen in Fig. 1B (dotted line), the PMT (TX-100) film shows a broad redox behavior by sweeping the potential. In Fig. 1B (solid line), the CV shows characteristic electrochemical response of Pt in NaOH solutions [34, 35], this being adsorption/desorption of hydrogen in the early stages of the scan, reversible adsorption of OH\(^-\) in the middle stages of the scan and formation of oxide in the last stages of the scans. A prominent peak marks the cathodic scan, which may be due to the reduction of the Pt oxide. Figure 1C (solid line) shows a CV of the HCHO oxidation in 0.1 M NaOH solution in potential range between -0.8 and 0.8 V vs. reference electrode. Like the H\(_2\)SO\(_4\) solution, the CV has characteristic peaks of HCHO oxidation at much more favorable potentials. It is generally accepted that the oxidation of small organic compounds on metal electrodes occurs in the presence of reactive M-(OH)\(_{ads}\) species formed by hydroxyl adsorption (2) on the electrode surface.

\[
M + OH^- \leftrightarrow M-(OH)_{ads} + e^-(2)
\]

The lower onset potential in NaOH solution is attributed to the solution pH that can shuttle the electrons easily. For comparison, CV of the bulk Pt electrode in 0.1 M NaOH solution towards HCHO oxidation was also shown in Fig. 1C (dotted line). As can be seen in this figure, the modified electrodes with Pt nanoparticles show better electrocatalytic activity towards HCHO oxidation in comparison with that bulk Pt electrode.

3.2. The effect of HCHO concentration

In order to evaluate capacity of the Pt/PMT (TX-100)/MCNTPE for HCHO oxidation, the effect of concentration on the corresponding anodic peak currents in the positive going potential scan was investigated in 0.1 M NaOH solution (Fig. 2). As can be seen, the peak current increases with increasing of HCHO concentration and reaches a nearly constant value for concentrations higher than 0.12 M which caused by saturation of active sites at the electrode surface. Also, it should be noted here that in lower HCHO concentrations (e.g., ~ 0.07 M or lower), the cyclic voltammograms shapes are different from higher concentrations and resembles that of typical HCHO oxidation in alkaline media.
3.3. The effect of switching potentials on the electrooxidation of formaldehyde

In order to reveal the correlation between HCHO oxidation and Pt oxide species, the effect of upper limit potentials in cyclic potential scanning on HCHO oxidation at the Pt/PMT (TX-100)/MCNTPE was studied in 0.1 M NaOH solution (Fig. 3). The fixed lower limit is -0.8 V vs. reference electrode. As can be seen, the decrease of upper limit of potential causes an increase in the current of peak III and a positive shift of the potential. Additionally, by increasing the positive potential limit, the peaks I and II almost remain unchanged. These may be explained by the preventing of PtO formation by lowering the upper limit.
potential cycling and consequently maintaining the electrode surface relatively clean [22, 29]. Indeed, by increasing final positive potentials, conversion of Pt to PtO is accelerated and caused a decrease of oxidation current in the negative going potential sweep, which further demonstrates that HCHO can only be oxidized on clean Pt particles surfaces.

Fig. 3. The effect of upper limit potential scanning on the oxidation of 0.12 M HCHO in 0.1 M NaOH solution on the Pt/PMT (TX-100)/MCNTPE at \( \nu = 0.05 \text{ V s}^{-1} \). (1) 0.8, (2) 1.0, (3) 1.1, (4) 1.2, (5) 1.3, and (6) 1.4 V.
3.4. Effect of potential sweep rates

The effect of potential sweep rate was studied on the electrocatalytic behavior of HCHO at the Pt/PMT (TX-100)/MCNTPE. Figure 4 shows the CVs of the modified electrode at different \( \nu \) in 0.12 M HCHO + 0.1 M NaOH solution. It was found that the oxidation peak \( I \) currents are linearly proportional to \( \nu^{1/2} \), indicating a diffusion-controlled process. This phenomenon was also observed in the related literatures [26, 27, 29, 30].

![Fig. 4. (A) CVs of the Pt/PMT (TX-100)/MCNTPE in 0.1 M NaOH + 0.12 M HCHO solution at different \( \nu \): a 0.01, b 0.02, c 0.05, d 0.10, and e 0.20 V s\(^{-1}\). (B) The dependency of the anodic peak (I) current vs. \( \nu^{1/2} \).](image)

3.5. Comparison of the electrocatalysts stability

Stability of the Pt/PMT (TX-100)/MCNTPE was examined in 0.12 M HCHO either 0.5 M H\(_2\)SO\(_4\) or 0.1 M NaOH solutions (Fig. 5). In the case of HCHO oxidation in 0.5 M H\(_2\)SO\(_4\), the peak current starts decreasing gradually with successive scans. The peak current of the 250\(^{th}\) scan is about 32% than that of the first scan. In general, the loss of the electrocatalytic activity may be due to the diffusion process occurring between the electrode surface and bulk solution. It also may be due to poisoning and the structure change of Pt nanoparticles as a result of potentials perturbation during the scanning in aqueous solutions, especially in the presence of organic compounds [36]. In 0.1 M NaOH solution, a sufficient improvement was noted. The peak current of the 250\(^{th}\) scan is about 65% for 0.1 M NaOH than that of the first scan, which ensures a higher stability than that of 0.5 M H\(_2\)SO\(_4\) solution. This stability in NaOH solution can be attributed to the less poisoning on the electrode surface. In 0.5 M H\(_2\)SO\(_4\) solution, the electrode gets accu-
mulated by CO$_{ads}$ and hence the anodic current decreases, showing a less stability. This indicates that the Pt/PMT (TX-100)/MCNTPE in 0.1 M NaOH solution has a relatively good stability. Peak potential values, type and concentration of electrolytes at some chemically modified electrodes including Pt, Pd and Au nanoparticles used for investigation of the electro-catalytic oxidation of formaldehyde were compared in Table 2. The comparison of $E_p$ values shows that Pt nanoparticles onto the modified electrode act as comparable catalyst in HCHO oxidation at favorable potentials.

![Cyclic voltammograms of the Pt/PMT (TX-100)/MCNTPE in the presence of 0.12 M HCHO in (A) 0.5 M H$_2$SO$_4$ solution and (B) 0.1 M NaOH: (solid line) 1$^{st}$ cycle; (dashed line) 10$^{th}$ cycle; (dotted line) 250$^{th}$ cycle of potential sweeping at $v = 0.05$ V s$^{-1}$.](image)
Table 2. Comparison of the electrocatalytic oxidation of formaldehyde at the surface of Pt/PMT (TX-100)/MCNTPE with some chemically modified electrodes

<table>
<thead>
<tr>
<th>Modified electrode</th>
<th>Electrolyte, C_{HCHO} (M)</th>
<th>E_P/V</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/PAANI/MWNTs/GCE</td>
<td>0.5 M H_2SO_4, 0.50</td>
<td>0.72</td>
<td>[6]</td>
</tr>
<tr>
<td>Pt-Pd/Ppy-CNT</td>
<td>0.5 M H_2SO_4, 0.50</td>
<td>0.64</td>
<td>[26]</td>
</tr>
<tr>
<td>Pt-Ppy/CNT</td>
<td>0.5 M H_2SO_4, 0.50</td>
<td>0.67</td>
<td>[26]</td>
</tr>
<tr>
<td>Pt-Pd/CNT</td>
<td>0.5 M H_2SO_4, 0.50</td>
<td>0.63</td>
<td>[27]</td>
</tr>
<tr>
<td>Single crystal disk of Pt (111)</td>
<td>0.1 M HClO_4, 0.50</td>
<td>0.70</td>
<td>[28]</td>
</tr>
<tr>
<td>Pt/Carbon-Ceramic</td>
<td>0.1 M H_2SO_4, 0.75</td>
<td>0.85</td>
<td>[29]</td>
</tr>
<tr>
<td>Pd/MWNT</td>
<td>0.1 M NaOH, 0.30</td>
<td>0.42</td>
<td>[30]</td>
</tr>
<tr>
<td>Au nanoparticles/GCE</td>
<td>1.0 M NaOH, 0.05</td>
<td>0.40</td>
<td>[31]</td>
</tr>
<tr>
<td>Pt/SWNT/PANI</td>
<td>0.5 M HClO_4, 0.50</td>
<td>0.66</td>
<td>[32]</td>
</tr>
<tr>
<td>Pt nanoparticles</td>
<td>0.05 M H_2SO_4, 0.10</td>
<td>0.40</td>
<td>[33]</td>
</tr>
<tr>
<td>Polycrystalline Pt disk</td>
<td>0.1 M H_2SO_4, 0.10</td>
<td>0.60</td>
<td>[37]</td>
</tr>
<tr>
<td>Pd/CILE</td>
<td>0.1 M NaOH, 0.30</td>
<td>0.15</td>
<td>[38]</td>
</tr>
<tr>
<td>Pt-SnO_2/Ti</td>
<td>1.0 M HClO_4, 0.50</td>
<td>0.40</td>
<td>[39]</td>
</tr>
<tr>
<td>Pt-Pd/Nf/GCE</td>
<td>0.1 M H_2SO_4, 0.001</td>
<td>0.58</td>
<td>[40]</td>
</tr>
<tr>
<td>Pt/PMT (TX-100)/MCNTPE</td>
<td>0.5 M H_2SO_4, 0.12</td>
<td>0.64</td>
<td>This work</td>
</tr>
<tr>
<td>Pt/PMT (TX-100)/MCNTPE</td>
<td>0.1 M NaOH, 0.12</td>
<td>-0.07</td>
<td>This work</td>
</tr>
</tbody>
</table>

4. CONCLUSION
Pt particles incorporated into the PMT (TX-100) films showed higher electrocatalytic activity towards HCHO oxidation than that of other Pt modified electrode. The results showed that utilization of TX-100 as an additive during the electropolymerization process and application of carbon nanotubes as incorporated materials into the carbon paste enhance the electrocatalytic activity of the modified electrode towards HCHO oxidation. The oxidation onset potentials of HCHO are about 0.3 and -0.5 V in the acidic and alkaline media, respectively, which is due to the pH of solutions. Furthermore, stability of the modified electrode was studied and it was found that the Pt/PMT (TX-100)/MCNTPE showed a higher stability in alkaline medium. Also, the linear relationship between _I_P_ and square root of the scan rates can be observed. This implies that the electrocatalytic oxidation of HCHO may be controlled by a diffusion process. In comparison with some other previous works, it seems clearly that Pt particles herein act as comparable electrocatalysts for formaldehyde oxidation at favorable potentials.
REFERENCES

اکسایش الکتروکاتالیزوری فرمالدهید بر روی پوشاش بیلی متا تولوئیدین-تربیتون X-100

اصلاح شده با نانوذرات پلاتین

چ. رنو، س. ر. حسینی، ر. اوجانی

1. استادانشکده شیمی، دانشگاه مرند، بابلسر، ایران
2. استادانشکده شیمی، دانشگاه مازندران، بابلسر، ایران

(تاریخ دریافت: 1392/3/12، تاریخ پذیرش: 1392/11/18، تاریخ پذیرش: 1392/11/27)

چکیده:
در این پژوهش نانوذرات کروی شکل پلاتین قرار گرفته بر روی الکترود نانوذگر کرین خمیر اصلاح شده با پلی-تولوئیدین (X-100 تربیتون)- تربیتون X-100 به عنوان یک الکترود بالقوه برای اکسیداسیون الکتروکاتالیزوری فرمالدهید در محلول های سولفوریک اسید 5/0 مولار و سیدیم هیدروکسید 1/0 مولار به کار گرفته شد. نتایج به دست آمده نشان داد که استفاده از تربیتون X-100 به عنوان یک افزودنی در طول فرآیند الکتروپلیمریزه شدن، فعالیت الکتروکاتالیزوری الکترود اصلاح شده در اکسایش فرمالدهید را بهبود می‌بخشد. تشکیل آغازی اکسایش فرمالدهید در محلول سیدیم هیدروکسید 1/0 مولار نسبت به محلول اسیدی به دلیل میزان pH محلول به مقدار کم مثبتتر نسبت به میزان pH محلول به مقدار کم مثبتتر در محلول اسیدی و بازی بررسی شد و نتایج به دست آمده نشان داد که در محلول سیدیم هیدروکسید 1/0 مولار یک بهبود می‌تواند بررسی شود. مطالعه حاضر انتخاب نوید بخش به عنوان یک کاتالیزور کامپوزیت برای اکسایش فرمالدهید در پتانسیل‌های Pt/PMT (TX-100)/MCNTPE مازاد کم قابل قبول را نشان می‌دهد.

j.raoof@umz.ac.ir

* مولف مسئول