Interfacing Silicate Layer Between MoO₃ Ribbon and Pt Metalldots Boosts Methanol Oxidation Reaction

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ABSTRACT
Constructing and making highly active and stable nanostructured Pt-based catalysts with ultralow Pt loading are still electrifying for electrochemical applications such as water electrolysis and fuel cells. In this study, MoO₃ ribbons (RBs) of few micrometer in length is successfully synthesized via hydrothermal synthesis. Subsequently, 3-dimensional (3D)-silicate layer for about 10 to 15 nm is introduced via chemical deposition onto the pre-formed MoO₃ RBs; to setup the platform for Pt metalldots (MDs) deposition. In comparison with the bare MoO₃ RBs, the MoO₃-Si has served as a efficient solid-support for stabilizing and accommodating the uniform deposition of sub-2 nm Pt MDs. Such a structural design would effectively assist in improving the electronic conductivity of a fabricated MoO₃-Si-Pt catalyst towards MOR; the interfaced, porous and 3D silicate layer has assisted in an efficient mass transport and quenching the poisonous CO₃ads species leading to a significant electrocatalytic performance for MOR in alkaline medium. Uniformly decorated, sub-2 nm sized Pt MDs has synergistically oxidized the MeOH in association with the MoO₃-Si solid-support hence, synergistic catalytic activity has been achieved. Present facile approach can be extended for fabricating variety of highly efficient Metal Oxide-Metal Nanocomposite for energy harvesting applications.

Keywords : Electrocatalysis, MoO₃ Ribbon, Methanol Oxidation, Silicates Functionalization, Platinum

1. Introduction

The global ever-growing energy requirement associated with the ongoing exhaustion of fossil fuels and the diminishing ecosystem has fueled an imperative search for renewable energy sources, such as wind and solar power [1]. Nevertheless, those sustainable energy sources are subjected to the infrequent time bounded among trade and necessity. As an impact, researchers are focusing towards the technologies which could exhibit exceptionally high energy density, economic, environment-benign and safety such as energy harvesting and storage, metal-air batteries, windmills, hydrogen fuels, solar cells, water electrolysis and fuel cells [2-5]. Most of those alternative technologies are employing the electrochemical reactions, and efficiency of energy harvesting processes often suffered by the lethargic electron transfer process. In particular, direct methanol fuel cells (DMFCs), have also drawn wide consideration as power suppliers for compact/transportable electronic devices and fuel cell vehicles due to their quick start-up, less weight, high power density, and modesty, serves as one of the most challenging mysteries and has attracted tremendous research attention in the past decades [6-9]. However, prohibitive cost and poor CO-tolerance of Pt has hindered its wide application in fuel cells. Enhancing the electronic conductivity, mass activity as well as durability of Pt-based electrocatalysts becomes key factors to reduce the cost of electrode materials for methanol oxidation reaction (MOR).

In order to enhance the electro-catalytic performance and economic aspect, effective approaches were implemented such as designing innovative supporting materials, controlling the distribution, size and shape of the noble metal nanoparticles (NPs).
Especially for platinum (Pt) NPs, perfect distribution, smaller in size, chemical stability and durability should be satisfied in order to achieve an improved catalytic performance. Ultimately, a solid support with the high electrical conductivity, large surface area, strong catalyst support interaction, good hydrophilicity and high corrosion resistance in different solution pH would satisfy the criteria [10]. Furthermore, choice of solid support can not only enhance the performance, also it will reflect in maintenance life and expense of the catalyst thereby stabilize an overall performance of the fuel cell system. In this regard, several metal oxides (WO$_3$ [11], SnO$_2$ [12], Nb$_2$O$_5$ [13], TiO$_2$ [14,15], MnO$_2$ [16], MoO$_3$ [10,17,18]) and various carbon forms [19,20] were successfully used as a solid support for the Pt NPs. It is obvious that carbon as a solid support for Pt NPs is of highly attractive due to its high conductivity, high stability, and controllable structure. On the other hand, among the above-mentioned metal oxides, MoO$_3$ is one of the most important semi conductive oxide has been widely investigated for its superior gas-sensitive and lithium storage properties due to its high chemical stability [2-6]. Therefore, inclusion of MoO$_3$ in the catalyst design can boost the electronic conductivity of the Pt NPs thereby enhance the catalytic activity. In addition, limited reports are available for the MoO$_3$-Pt catalyst system employed in DMFCs. Furthermore, apart from carbon nanotubes and nanofibers, 1-dimensional (1D) supporting materials for loading the Pt NPs are rarely seen.

Herein, 1D MoO$_3$ ribbons (RBs) are synthesized by hydrothermal method and subjected to the encapsulation of porous 3-dimensional (3D) silicate layer for about few nanometers to prepare MoO$_3$-Si RBs. Subsequently, sub-2 nm sized Pt metaldots (MDs) are chemically loaded onto the MoO$_3$-Si RBs to derive MoO$_3$-Si/Pt RBs. Due to an interfaced 3D silicate layer, Pt MDs’ distribution is uniform, and the porous 3D silicate layer is engaged for diminishing the CO poisoning by adsorption process thereby enhanced catalytic activity has been noticed for MOR. The MoO$_3$-Si/Pt RBs’ catalytic activity has been compared with the bare MoO$_3$-Pt RBs and commercial Pt/C catalysts.

2. Experimental Section
6.1 Materials and methods
Chloroplatinic acid hexahydrate (H$_3$PtCl$_6$), ammonium heptamolybdate tetrahydrate [(NH$_4$)$_6$Mo$_7$O$_{24}$4H$_2$O], tetraethylorthosilicate (TEOS) were received from Sigma-Aldrich. The commercial Pt/C catalyst (20% Pt/C) was received from Alfa Aesar. Methanol (MeOH), ethanol (EtOH), ammonia (25%) and nitric acid (HNO$_3$) were obtained from DaeJung chemicals. Glassy carbon (GC) (3 mm diameter) and its modified forms were used as working electrodes. Pt wire was used as a counter electrode and saturated calomel electrode (SCE) was used as a reference electrode. All the electrochemical experiments were conducted in a single compartment three electrode cell using an Ivium Technologies electrochemical workstation. Nitrogen (N$_2$) was bubbled for 30 minutes prior to each experiment. FESEM images were recorded with JEOL JSM-7800F instrument. TEM, STEM and STEM-EDS images were recorded with FEI TALOS F200X instrument.

2.2. Synthesis of MoO$_3$ Ribbons
The MoO$_3$ nanowires were synthesized by a simple hydrothermal method [21]. In a typical reaction, 0.4 g of (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O and 2.4 mL of HNO$_3$ (65%) were dissolved in 13.2 mL deionized (DI) water. Contents was stirred for 15 min to get a clear solution. Then, reaction solution was transferred to a Teflon-lined autoclave with the capacity of 20 mL. Subsequently, vessel was sealed and put in a muffle furnace at 180°C. After the reaction of 24 h, autoclave was taken out and kept aside to reach the room temperature. The obtained product was purified by centrifugation process using DI water at 10,000 rpm for 15 minutes. Centrifugation process is repeated for 3 times and the obtained product was freeze dried for further use.

2.3. Synthesis of MoO$_3$-Si RBs
In a typical procedure, 100 mg of MoO$_3$ powder and 0.52 g of tri-sodium citrate (0.2 M) were mixed into the 10 mL of DI water and stirred for 15 min. Later, content was washed by centrifugation (10,000 rpm, 15 min.) using DI water. Obtained centrifugate was re-dispersed in 10 mL of DI water and the content was alkaliﬁed by adding 100 μL of NH$_3$OH solution (28%) and the content was named as “mixture A. Subsequently, “mixture B was prepared by mixing 30 mL of ethanol, 8 mL of DI water and 2 mL of NH$_3$OH solution (28%). Later, mixture A was added by dropwise manner into the mixture B under ultra-
sonication. After 10 min., 75 µL of TEOS solution was added into it and stirred overnight (12 h and 300 rpm.) The obtained product was purified by centrifugation process using DI water at 10,000 rpm for 15 minutes. Centrifugation process is repeated for 3 times and the obtained product was freeze dried for further use.

2.4. Synthesis of MoO$_3$/Pt RBs and MoO$_3$–Si/Pt RBs

To begin with 100 mg of MoO$_3$ RBs or MoO$_3$–Si RBs was dispersed in 50 mL of DI water and sonicated for 15 min to obtain a homogenous solution. Subsequently, 1 mM of H$_2$PtCl$_6$ solution was added in it and stirred for another 15 min. To reduce the Pt precursor, aliquots (50 to 100 µL) of ice-cold 0.1 mM NaBH$_4$ was added and stirred for another 1 h. The resultant product, MoO$_3$/Pt RBs or MoO$_3$–Si/Pt RBs was washed and purified by centrifugation (10,000 rpm for 30 min) using DI water and freeze dried for further use.

2.5. Electrochemical studies

The electrocatalytic performance of the modified electrodes toward MOR was studied by recording cyclic voltammograms (CV) in 0.1 M KOH and 0.1 M CH$_3$OH solution scanned at 50 mV/s from –1 to 0.6 V. The stability of the catalysts was evaluated by continuous cycling test and amperometric i–t curve technique under an applied potential of –0.3 V for 1500 s.

3. Results and Discussion

3.1. Characterization of the prepared MoO$_3$/Pt RBs or MoO$_3$–Si/Pt RBs

Metal-support communication is one of the most significant factors in influencing catalysis rate of supported metal catalysts. In this regard Silica, a widely used oxide support in its spherical form, has been rarely reported as an effective support to create active metal-support interfaces for promoting catalysis. Here, by decorating Pt MDs with porous 3D silicate layer as an interface between MoO$_3$ and Pt MDs, it is identified that MoO$_3$–Si interface creates an exceptional effect to promote the MOR. To obtain the morphology information of the as prepared MoO$_3$ RBs, SEM and STEM analyses were done. Fig. 1A-C represent the SEM images of the MoO$_3$ RBs at different magnifications, suggesting the uniform size, ribbon-shaped structure and absence of spherical shaped impurities. The length of the RBs can be up to several micrometres with the diameter of about 200 nm. The TEM image (Fig. 1D) is clearly demonstrating a ribbon shape of a single MoO$_3$ ribbon. And the HAADF (Fig. 1E) and STEM-EDX image (Fig. 1F) are demonstrating the crystallinity and elemental composition of the prepared MoO$_3$ RBs, respectively.

Fig. 2A is illustrating the step by step process for applying silicate-layer coating and deposition of Pt MDs. Fig. 2B and C are the SEM images of the MoO$_3$–Si RBs at different magnifications and has exhibit visible rough and porous surface than the

![Fig. 1.](image)
smooth bare MoO₃ RBs; suggesting that the silicate coating is uniform throughout the MoO₃ RBs. In addition, MoO₃–Si RBs are completely aggregation free and easily dispersible in an aqueous medium and such property is advantageous for the secondary uniform decoration of metal NPs onto it. As a controlled experiment Si-Pt MDs is prepared and its TEM image is shown in Fig. 2D, homogeneously distrib-

Fig. 2. (A) Schematic illustration of the preparation of MoO₃–Si/Pt RBs. Comparison of SEM images of (B) MoO₃ RBs and (C) MoO₃–Si RBs; (B) before and (C) after the silicate-layer coating. (D) TEM image of Si-Pt MDs.

Fig. 3. Comparison of (A–D) TEM images, (E) STEM-HAADF image and (F–H) STEM-EDX mapping analyses of the MoO₃/Pt RBs and (I–L) TEM images, (M) STEM-HAADF image and (N–P) STEM-EDX mapping analyses of the MoO₃–Si/Pt RBs.
uted sub-2 nm sized Pt MDs are clearly observed from the image. Subsequently, to study the impact of interfacing a silicate layer between MoO$_3$ RBs and Pt MDs towards catalysis, two different materials were fabricated such as MoO$_3$/Pt RBs and MoO$_3$–Si/Pt RBs. Pt MDs were chemically deposited over MoO$_3$ RBs and MoO$_3$–Si RBs and their corresponding STEM studies are summarized in Fig. 3 and 4. As can be seen from Fig. 3A-D, Pt MDs’ deposition onto the bare MoO$_3$ is not uniform and dense, it can be attributed for the absence of silicate layer. STEM-EDX analysis (Fig. 3E-H) also revealing the less density of the Pt MDs. On contrary, from the TEM (Fig. 3I-L) and STEM-EDX (Fig. 3M-P) analyses of the MoO$_3$–Si/Pt RBs, Pt MDs growth is noticed as more uniform and denser with the size of sub 2-nm (Fig. 3K and 3P). In addition, the silicate layer thickness for about 15 nm is identified from the image (Fig. 3J). Both MoO$_3$/Pt RBs and MoO$_3$–Si/Pt RBs are highly dominated by RBs nanostructures. The surfaces of the MoO$_3$–Si/Pt RBs are much rougher than those of the bare MoO$_3$ RBs. The whole surfaces of the MoO$_3$–Si/Pt RBs are coated with silicate layer and Pt MDs. Fig. 3L is a high-resolution TEM (HRTEM) image of the surface region of the MoO$_3$–Si/Pt RBs that clearly shows their microstructures and the interface. Two different regions in terms of contrast has been noticed and the darker one corresponds to the Pt MDs due to its high electron density than the MoO$_3$–Si portion. Fig. 4 illuminates the STEM-EDS result of the MoO$_3$–Si/Pt RBs obtained by using finely focused electron probe. The sample consists of three key elements (Mo, Si, and Pt). The obvious Si and Pt signals further confirms that Si and Pt MDs are interfaced and decorated, respectively onto the MoO$_3$ RBs.

### 3.2. The growth mechanism

The growth mechanism of 1D MoO$_3$ RBs was previously investigated [21-23] by the researchers. By using the possible electroneutral and dehydration reaction, the growth process can be understood as follows;

\[
\text{Mo}_7\text{O}_{24}^6^- + 6\text{H}^+ + 11\text{H}_2\text{O} \rightarrow 7\text{MoO}_3 \cdot 2\text{H}_2\text{O} \quad (1)
\]

while increasing a temperature, MoO$_3$·2H$_2$O will drop water as defined below Eq. (2) and (3):

\[
\text{MoO}_3 \cdot 2\text{H}_2\text{O} \rightarrow \alpha\text{-MoO}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} \quad (2)
\]

\[
\alpha\text{-MoO}_3 \cdot \text{H}_2\text{O} \rightarrow \alpha\text{-MoO}_3 + \text{H}_2\text{O} \quad (3)
\]

The product obtained in the Eq. (1), MoO$_3$·2H$_2$O have the monoclinic crystal symmetry hence, ID growth is not occurred at this stage. Subsequently, after losing the H$_2$O molecules MoO$_3$·2H$_2$O has transformed (Eq. (2) and (3)) into $\alpha$-MoO$_3$ and do have Mo–O–Mo chains operating along the [001] direction. As an impact, present MoO$_3$ RBs ($\alpha$-MoO$_3$) has the high intensity of 1D growth due to the presence of two different types of the growth axes. Hence, there is a non-uniformity in the RBs size shape and aspect ratio. Furthermore, an anisotropic monocline structure of the basic element, MoO$_3$·2H$_2$O have also played a role in non-uniformity and such non-uniform ID structural growth is a common behaviour in transition-metal oxides.

Regarding the uniform and dense Pt MDs deposition onto the MoO$_3$–Si RBs, the interfaced porous and 3D silicate layer is anchoring the Pt metal precursor at the beginning during addition of the reducing
agent the metal precursors were reduced into sub-2 nm sized Pt MDs and stabilized/embedded by the silicate layer since the 3D silicate sol-gel matrices are well-known candidates for offering a stable environment for metal NPs [24-31]. In addition, porous channels of the silicate layer would enhance mass transport from a electrolyte and electronic access between bare MoO$_3$ and Pt.

3.3. Electrocatalytic oxidation of methanol

To explore the key role of the Si-layer interfacing and the MoO$_3$–Si/Pt RBs catalyst does offer an improvement for electrocatalytic oxidation methanol over the MoO$_3$/Pt RBs and Pt/C catalysts, the MOR for the fabricated catalysts was carried out. To begin with, electrochemical characterization of the catalysts was done in a 0.5 M H$_2$SO$_4$ as shown in Fig. 5A, where one can learn the characteristic H adsorption, Pt surface oxidation, Pt surface oxides reduction and H desorption of the Pt-based catalysts [32,33]. The study usually offer the information’s about catalyst stability and electrochemically active surface area (ECSA). The ECSA measurement was carried out in 0.5 M H$_2$SO$_4$ by CVs (Fig. 5A) using the following equation

$$\text{ECSA} = \frac{Q_H}{Q_H^*}$$

where QH is the charge collected from the hydrogen adsorption region after double-layer correction and QH* is the standard value of 210 μC.cm$^{-2}$ associated with adsorption of a hydrogen monolayer at polycrystalline Pt surface [32,33]. The obtained ECSA values are summarized in the Table 1. The ECSA is determined to be $0.7789\text{ cm}^2$ for GC/MoO$_3$–Si/Pt electrode, which is remarkably higher than that of geometrical area of the GC electrode ($0.07\text{ cm}^2$). As can be seen the GC/MoO$_3$–Si/Pt electrode (Fig. 5A(b)) do exhibit the better characteristic responses of the Pt than the GC/MoO$_3$/Pt electrode (Fig. 5A(a)) and it is preliminary measure of the expected catalytic activity. The typical CV curves for MOR in alkaline media are depicted in Fig. 5B and C for the target catalyst: GC/MoO$_3$–Si/Pt electrode and target catalyst in comparison with the controlled experiments, respectively, indicating both MoO$_3$/Pt RBs and MoO$_3$–Si/Pt RBs catalysts are active for MOR in which MoO$_3$–Si/Pt RBs catalyst can reach larger current density. Controlled experiments for GC/MoO$_3$ and GC/MoO$_3$–Si electrodes does not involve in the

![Fig. 5.](image-url)
oxidation of methanol thereby confirming that Pt MDs are the key catalyst elements. To expedite the comparison, the electrochemical performances for MOR for the two catalysts are listed in Table 1. Obviously, the MoO$_3$–Si/Pt RBs is more favorable for the MOR. The onset potentials shift negatively about 63 mV and the peak current is 290 µA higher than the MoO$_3$/Pt RBs catalyst.

The negative shifting in onset potential and higher $I_f/I_b$ value of the MoO$_3$–Si/Pt catalyst is evidently observed, suggesting that the MOR is feasible MoO$_3$–Si/Pt catalyst than the MoO$_3$/Pt catalyst. The uniform and dense distribution of sub-2nm sized Pt MDs and the interfaced Si layer of the MoO$_3$–Si/Pt catalyst are favoured for the MOR and the fact for the uniform distribution of the Pt MDs is the interfaced Si layer over the MoO$_3$ RBs. The MoO$_3$–Si solid support acts as 3D constructions, leading to produce numerous pores and channels that significantly lowered the liquid sealing effect. As an impact, MeOH molecules can efficiently spread into the embedded Pt MDs and final product (CO$_2$) can easily escape from the catalyst’s interior (Fig. 6). Furthermore, to achieve maximum utilization of the available ECSA, diminishing the liquid sealing effect is the favored one. In addition, MOR performance of Pt MDs strongly depends on how MoO$_3$–Si solid support assisting in controlling the CO poisoning, it is obvious that MoO$_3$ RBs can involve in modulation of the electronic band structure of the Pt MDs thereby Pt MDs’ surface can be renewed and enhance the CO tolerance. Furthermore, poisonous CH$_3$CO$_{ad}$ intermediate species get adsorb onto the catalyst surface during the MOR in an alkaline medium, with its reaction with OH$_{ad}$ being a rate-determining step [34]. In this regard, interfaced Si layer of the catalyst can attract the OH$_{ad}$ thereby facilitating an OH$_{ad}$-rich environment. Hence an effective reaction between CH$_3$CO$_{ad}$ and OH$_{ad}$ could have occurred thus poisonous CO evolvement can be diminished.

The stability and durability of the MoO$_3$/Pt RBs, Pt/C and MoO$_3$–Si/Pt RBs catalysts toward MOR were investigated by amperometric i–t curve measurements as shown in Fig. 5D and the results are coherent with the CV data. As can be seen, initial current was higher for MoO$_3$–Si/Pt RBs catalyst associated with a slow decay in the comparison with the other catalysts. Formation of the CO$_{ad}$ and CHO$_{ad}$ intermediate species are responsible for initial fast decay during MOR. It is noteworthy to mention that in Fig. 5D(b), around 1100 s there is growth in the current followed by slow decay, and it can be attributed Pt crystallites’ growth and aggregation owing to Ostwald ripening process. Due to this process, surface renewal would occur, and it is responsible for the growth in the current. The long-term poisoning rate ($\delta$) was assessed by measuring the linear decay of the current for a period of more than 500 s from Fig. 5D by using the Eq. (5) [34].

$$\delta = \frac{100}{I_0} \times \frac{(dl/\ dt)_{t=500s}}{I_0} (% s^{-1})$$

where $(dl/\ dt)_{t=500s}$ is the slope of the linear portion of current decay and $I_0$ is the current at the start of polarization back extrapolated from the linear current decay. The poisoning rates were calculated to be 0.1430, 0.0798 and 0.0923 % s$^{-1}$ for MoO$_3$/Pt RBs, Pt/C and MoO$_3$–Si/Pt RBs catalysts, respectively.

To investigate the kinetics of MOR at MoO$_3$/Pt

Table 1. Electrochemical parameters of MOR derived at the various modified electrodes.

<table>
<thead>
<tr>
<th>Modified electrodes</th>
<th>Q (µC)</th>
<th>ECSA (cm$^2$)</th>
<th>Onset potential (V)</th>
<th>Anodic peak potential (V)</th>
<th>Specific activity (mA. cm$^{-2}$)</th>
<th>$I_f/I_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GC/MoO$_3$/Pt</td>
<td>1.64</td>
<td>0.1115</td>
<td>−0.604</td>
<td>−0.234</td>
<td>1.46</td>
<td>6.38</td>
</tr>
<tr>
<td>GC/MoO$_3$–Si/Pt</td>
<td>11.45</td>
<td>0.7789</td>
<td>−0.667</td>
<td>−0.229</td>
<td>1.75</td>
<td>7.08</td>
</tr>
</tbody>
</table>
RBs and MoO₃–Si/Pt RBs catalysts, relationships of anodic peak current (Iₚ) and peak potential (Eₚ) as a function of different scan rates (v) obtained from forward CV scans have studied and the results are summarized in Fig. 7. Relationship between log Iₚ and log v for MoO₃/Pt RBs and MoO₃–Si/Pt RBs catalysts (Fig. 7C) are demonstrating the linear relationship with the slope at 0.114 and 0.141, respectively and the slope is lying between 0 to 0.5, indicating that the system is diffusion-controlled process [32,34]. Furthermore, the linear relationship (Fig. 7D) between Ep and log (v) indicates that the MOR is an irreversible charge transfer process [32,34]. To verify the stability of the GC/MoO₃–Si/Pt electrode, 100 continuous cycles for MOR was performed as shown in Fig. 8A. After the 100 cycles, the peak current decreased by only 15.2%, which indicated that the proposed GC/MoO₃–Si/Pt electrode showed good sensitivity and stability toward the MOR.

4. Conclusions

MoO₃ has been considered as an advanced auxiliary support for Pt nanoparticle anchorage due to its excellent activity and stability. Nevertheless, its non-conduc-
tivity property still impedes its applications in electrocatalytic fields. Thus, the MoO$_3$–Si interface is fabricated and served as an efficient co-support for Pt MDs in this paper. The electrochemical measurements demonstrate that MoO$_3$–Si/Pt RBs catalyst shows higher catalytic activity, durability and stability than the as-prepared MoO$_3$/Pt RBs and commercial Pt/C catalysts. The MoO$_3$–Si solid support has active 3D constructions, to numerous pores and channels that significantly lowered the liquid sealing effect. As an impact, MeOH molecules can efficiently diffuse into the embedded Pt MDs and final product (CO$_2$) can easily escape from the catalyst’s interior thereby the diminishing CO poisoning. The remarkable enhanced performance of this MoO$_3$–Si/Pt RBs catalyst for methanol oxidation reaction can be ascribed to the abundant Pt MDs’ electrochemically active sites, uniformly dispersed Pt MDs and the strong metal-support interaction between MoO$_3$–Si and Pt MDs. These results suggest a potential usage of the MoO$_3$–Si/ Pt RBs catalyst in DMFCs.

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