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# Development of pulsed deposited manganese and molybdenum oxide surfaces decorated with platinum nanoparticles and their catalytic application for formaldehyde oxidation

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## ABSTRACT

Manganese and molybdenum mixed oxides were co-deposited in a thin film form by pulsed deposition technique on a glassy carbon substrate, and this mixed oxide film was further decorated with platinum nanoparticles. Formaldehyde, being a candidate for proton exchange membrane fuel cell applications, was chosen as the test material for the catalytic activities of the developed surface in alkaline media. The synergistic effect of the mixed metal oxide deposit incorporating Pt nanoparticles was verified by using different mol ratios of the corresponding metal ions and applying pulsed deposition conditions and under optimized conditions and, resultant oxidation peak has shown a significant increase in the peak current accompanied by the small shift in the peak potential. The modified composite electrodes were characterized by SEM, EDX, XPS and EIS.

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## Introduction

Electrochemical nanotechnologies have witnessed great fundamental advances in the last two decades and hold tremendous potential for electronic, electrochromic, catalytic and analytical applications. A vast number of studies on the electrode development have been focused on metallic and

carbon based nanomaterials for sensor development, electrocatalysis, and energy storage and conversion studies [1].

Platinum is well-known to exhibit superior catalytic activity on both reactions of hydrogen evolution (HER) and oxygen reduction (ORR). Still, the necessity of cost reduction and improvement of the performance of conventional Pt-based catalysts has led to the development of multicomponent catalysis systems. Currently, nano-sized carbon based

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polymeric composites are very popular for oxygen reduction along with non-noble metal electro-catalysts [2].

Transition metal oxides, in particular, offer a wide range of applications in various fields due to their abundant sources and low cost. Molybdenum and manganese oxides have received a special attention owing to their remarkable electronic, catalytic, and electrochromic properties depending on the synthesis procedure. Electrochemical techniques present advantages over chemical synthesis being more practical and economical way for readily producing large uniform oxide thin films. In addition, the nature of the deposit can also be controlled by changing the deposition parameters and a mixed-valent metal oxide ( $\text{MeO}_x$ ) film can be produced by this means on a glassy carbon electrode (GCE) or indium tin oxide (ITO) electrodes. As consistent with the X-ray Photoelectron Spectroscopy (XPS) studies, mixed valent nature of molybdenum oxide ( $\text{MoO}_x$ ) deposit including Mo(V) and Mo(VI) has exhibited unique catalytic activity toward nitrite oxidation and ORR as well [3–5]. Further improvement in the catalytic effect can be provided by the combination of hyper d-electronic of noble metals, platinum in particular, with hypo d-electronic transition metal oxides [6].

Recent studies in this lab have revealed the synergetic effect of molybdenum [7] or manganese oxide [8] and platinum binary catalyst modified glassy carbon electrode (GCE/ $\text{MeO}_x$ /Pt) towards ORR in weakly acidic medium. Similar to mixed valent molybdenum oxides, elucidation of the ORR mechanisms of the  $\text{MnO}_x$  has revealed that the couple Mn(III)/Mn(IV) was responsible from the reaction with the  $\text{O}_2$  adsorbed on the GCE.

Electrochemical Pulsed Deposition (PD) technique is currently becoming popular as the pattern of applied potential determines the compositions and hence the morphologies of the  $\text{MeO}_x$  surfaces [9]. PD techniques favor the formation of nucleation sites and hence contribute to a high dispersion of the deposits compared to other methods. Fine nano rods of  $\text{MnO}_x$  deposited by this technique have been reported to display high electrical conductivity and excellent stability [10]. Electrode performance on both anodic and cathodic reactions can be further enhanced by decorating with metallic nanoparticles and carbon nanotubes [11].

Although there are increasing numbers of studies dealing with simultaneous anodic deposition of mixed  $\text{MeO}_x$ , no single data was observed in the literature for their co-deposition by PD technique. Present study describes a procedure for electrochemical co-deposition of  $\text{MnO}_x$ - $\text{MoO}_x$  by PD technique which was further decorated with Pt nanoparticles (GCE/ $\text{MnO}_x$ - $\text{MoO}_x$ /Pt) in pursue of any synergetic effect for electrocatalytic activity. Anodic performance of these novel electrodes was tested upon formaldehyde oxidation which constitutes an intermediate product of methanol oxidation.

Formaldehyde (FA) has been assigned as the future candidate for proton exchange membrane (PEM) fuel cells applications [12]. Depending on the electrode material, two mechanisms have been proposed for its electro-oxidation; one is the direct pathway ending up with  $\text{CO}_2$  formation and another pathway in which the intermediates passivate the active site of catalysts leading the slow reaction kinetics [13]. This reaction has been investigated at various electrode surfaces modified with Pt [14], Pd [15], Au [16],  $\text{SnO}_2$ /Pt [17], Pt/

$\text{Fe}_2\text{O}_3$  [18] and incorporating Pt and Pd metals into a polymeric composite including polypyrrole (PPy) and carbon nanotube (CNT) (PPy/CNT/Pt-Pd) electrodes [19].

Metal–metal oxide nanoparticles are particularly attractive for FA oxidation reaction probably due to their high surface area and size dependent nature [14]. Consequently, development of such catalytic surfaces is an important task for not only fuel cell technology, but also for removal of FA from waste water due to its toxicity. This study presents the early results of the catalytic behavior of mixed transition  $\text{MeO}_x$  deposits decorated with platinum nanoparticles towards formaldehyde oxidation in alkaline media.

## Experimental

### Reagents

All chemicals used were of analytical grade and used without any further purification.  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ , NaOH,  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{Na}_2\text{SO}_4$  were purchased from Merck and  $\text{K}_2\text{PtCl}_4$  was purchased from Aldrich. All solutions were prepared by using ultrapure water (with  $18.2 \text{ M}\Omega \text{ cm}$  resistivity) obtained from MilliPore Q system.

### Apparatus

Electrochemical measurements were carried out by using Autolab PGSTAT 204 and EIS measurements Autolab PGSTAT 128N voltammetric analyzer, equipped with conventional three electrode system consisting of Ag/AgCl (sat. KCl) as the reference electrode, Pt wire (99.99%) as the counter electrode and GCE (BASi, 3 mm diameter, geometric surface area  $0.0707 \text{ cm}^2$ ) as the working electrode. The SEM images were recorded by using FEI Quanta 250 SEM. XPS surface chemical analyses were performed with a Thermo Electron K-Alpha spectrometer using a monochromatic Al K X-ray source.

### Electrode modification

Under optimal conditions, 20.0 mL of the supporting electrolyte (0.1 M  $\text{Na}_2\text{SO}_4$ ) containing  $2.0 \times 10^{-3} \text{ M}$   $\text{MnSO}_4$  and  $8.0 \times 10^{-2} \text{ M}$   $\text{Na}_2\text{MoO}_4$  solution mixture was pipetted into a voltammetric cell and deaerated with  $\text{N}_2$  gas for 5 min. Freshly polished GCE was immersed into the cell and Ag/AgCl and Pt electrodes were connected to complete the three electrode system. Pulsed deposition procedure was applied by sequentially holding the potential at  $-0.25 \text{ V}$  for 5 s and then at  $1.05 \text{ V}$  for 5 s for 100 times as described in a former study [20]. The fabricated mixed metal oxide electrode, i.e. GCE/ $\text{MnO}_x$ - $\text{MoO}_x$ , was rinsed with pure water and transferred to another cell containing  $2 \times 10^{-3} \text{ M}$   $\text{PtCl}_4^{2-}$  solution for decorating the surface with platinum nanoparticles. The same PD procedure was applied for 20 cycles for fabricating the GCE/ $\text{MnO}_x$ - $\text{MoO}_x$ /Pt electrode and then, the electrode was rinsed and transferred into 0.1 M NaOH solutions spiked with FA standard solution to be 0.060 M. Cyclic voltammograms have been recorded by scanning the potential at a rate of  $50 \text{ mV s}^{-1}$  between  $-0.5$  and  $0.7 \text{ V}$ .

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