

Short communication

Catalytic activity of platinum/tungsten oxide nanorod electrodes towards electro-oxidation of methanol

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Abstract

Tungsten oxide (WO_3) nanorods are synthesized using an Anodic alumina membrane as a template and platinum nanoparticles are supported on the nanorods. The nanorods, serving as platinum catalyst supports, are characterized by electron microscopy and by electrochemical analysis. Methanol oxidation on the prepared electrodes is studied by means of cyclic voltammetry and chronopotentiometry. A film of Pt/ WO_3 nanorods on a glassy carbon electrode exhibits good electrocatalytic activity towards the oxidation of methanol. High electrocatalytic activities and good stabilities are attributed to a synergistic effect between Pt and WO_3 that avoids poisoning of the electrodes.

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1. Introduction

Platinum supported on metal oxides has received attention in recent years, mainly because of potential application as an anode in direct methanol fuel cells [1–8]. Most often, the catalyst is dispersed on a conventional carbon support, which influences the catalytic activity through metal–support interaction. In order to achieve better dispersion of the metal, as well as to derive maximum activity from the dispersed metal sites, innovative strategies have to be adopted. One approach is to promote preferentially the oxidation of the intermediate species (partial oxidation products of methanol like CO and other partially dehydrogenated species) on other sites so that the noble metal sites are still available and free for electrochemical oxidation of the fuel [9,10]. It is essential, however, that the additional components employed for the reaction of the inhibiting intermediates should not only be contributive to the overall desired electrochemical reaction but also not render any additional impedance to the activity of the electrocatalyst and not lead to a loss of electrochemi-

cal energy converted. This means that the role of the support (mainly oxides for the preferential oxidation of partial combustion products) should be cumulative and not additive. The prospect of using tungsten oxide nanorods as supports for noble metals is examined for possible application as fuel cell anodes.

Tungsten oxide is a well-known multi-functional material, especially for fuel cell applications [11]. Tungsten oxide nanorods have been utilized as support for the following reasons. Platinum catalysts supported on tungsten oxide have been extensively studied as active catalysts for the electro-oxidation of methanol [12]. Tungsten oxide can form a hydrogen bronze (H_xWO_3) that effectively facilitates the dehydrogenation of methanol, but although these catalysts exhibit high performance, tungsten oxide undergoes dissolution in acid medium and thus suffers a reduction in electrocatalytic activity. The stability of tungsten oxide in acid medium can be improved by suitably adjusting the conditions of its preparation. Application of a tungsten oxide matrix should increase the electrochemically active surface area and facilitate charge (electron, proton) distribution [13]. Moreover, OH_{ads} groups on the tungsten oxide surface may induce oxidation of the poisoning CO intermediate [14]. The present study aims to fabricate an electrocatalytic system with optimized reactivity towards the electro-oxidation of methanol.

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Overall, the system is multi-functional in terms of promoting the oxidation of methanol.

In this communication, Pt nanoparticles supported on the surface of WO_3 nanorods are prepared and their electrocatalytic activity for methanol oxidation is compared with that of conventional electrodes. The results indicate that the Pt/ WO_3 nanorod catalysts exhibit excellent electrocatalytic activity for methanol oxidation compared with a commercial Pt/C catalyst.

2. Experimental

2.1. Materials

All the chemicals were of analytical grade. (Sisco Research Laboratories, India), phosphotungstic acid and concentrated HF (both from Merck) were used. Hexachloroplatinic acid was obtained from Aldrich. Twenty weight percent Pt/Vulcan carbons were procured from Johnson Matthey. Methanol and sulfuric acid were obtained from Fischer Chemicals. Alumina template membranes (Anodisc 47) with 200 nm diameter pores were obtained from Whatman Corp. A Nafion 5 wt.% solution was obtained from Dupont and was used as-received.

2.2. Synthesis of WO_3 nanorods

Ten grams of phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}$) was stirred in 30 ml of methanol solution. The resulting colloidal suspension was infiltrated into the membrane under vacuum by a wetting method [15]. The same procedure was repeated one to eight times. The upper surface of the membrane was then polished gently with sand paper (2500 grit) and dried at 95 °C for 1 h. The formation of WO_3 nanorods inside the alumina template (WO_3/AAO) was further achieved by programmed temperature thermal decomposition from 95 to 500 °C/min and finally calcination at 873 K for 3 h in air. The removal of the AAO template was performed by dissolution in 10% (v/v) HF. The WO_3 nanorods product was washed with a copious amount of de-ionized water, to remove the residual HF, and then dried at 393 K.

2.3. Preparation of Pt/ WO_3 nanorods composites

Platinum nanoclusters were loaded on the WO_3 nanorods by conventional impregnation methods [16]. The procedure was as follows: 5 ml of 73 mM aqueous hexachloroplatinic acid (H_2PtCl_6) was mixed with 100 mg of WO_3 nanorods by stirring at room temperature. The mixture was then evaporated to dryness and the resulting material was reduced in a hydrogen atmosphere at 623 K for 3 h to give Pt/ WO_3 nanorods.

2.4. Preparation of working electrode

Glassy carbon (GC) (BAS electrode, 0.07 cm²) was polished to a mirror finish with 0.05 μm alumina suspensions before each experiment and served as an underlying substrate for the working electrode. In order to prepare the composite electrode, the nanorods were dispersed ultrasonically in water at a concen-

tration of 1 mg ml⁻¹ and a 20 μl aliquot was transferred to a polished glassy carbon substrate. After evaporation of water, the resulting thin catalyst film was covered with a 5 wt.% Nafion solution. Then, the electrode was dried at 353 K and used as the working electrode.

2.5. Characterization methods

Scanning electron micrographs were obtained using a JEOL JSM-840 model, instrument operating at 15 keV. The nanorods were sonicated in acetone for 20 min and then were dropped onto cleaned silicon substrates. Imaging was performed in air using a Nanoscope IIIA atomic force microscope (Digital Instruments, St. Barbara, CA) operated in the contact mode. For transmission electron microscopic studies, nanorods dispersed in ethanol were placed on the copper grid and the images were obtained with a Phillips 420 model instrument operating at 120 keV.

2.6. Electrochemical measurements

All electrochemical studies were performed with a BAS 100 electrochemical analyzer. A conventional three-electrode cell consisting of the GC (0.07 cm²) working electrode, a Pt plate (5 cm²) as the counter electrode and an Ag/AgCl reference electrode was used for cyclic voltammetry (CV) investigations. The CV experiments were conducted using 1 M H_2SO_4 solution in the absence and presence of 1 M CH_3OH at a scan rate of 50 mV s⁻¹. All the solutions were prepared with ultra-pure water (Millipore, 18 MΩ). The electrolytes were degassed with nitrogen prior to electrochemical measurements.

3. Results and discussion

The XRD patterns for the as-synthesized tungsten oxide nanorods and platinum-loaded tungsten oxide nanorods are given in Fig. 1(a) and (b), respectively. The diffraction peaks and the peak intensities of the tungsten oxide nanorods are in good

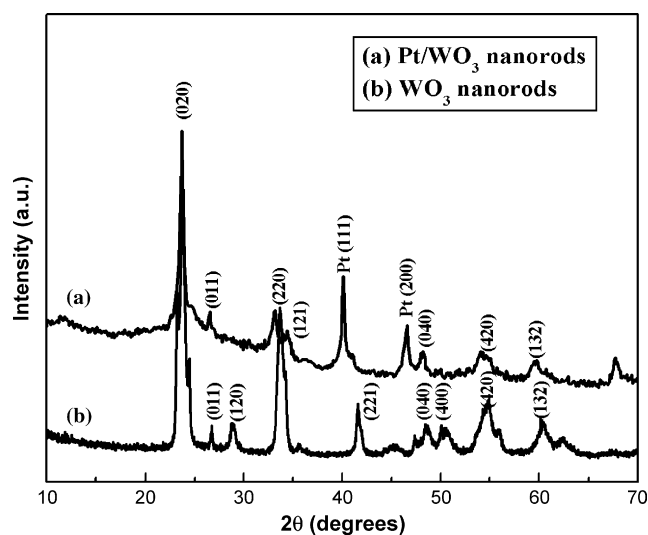


Fig. 1. XRD patterns of (a) Pt/ WO_3 nanorods and (b) WO_3 nanorods.

agreement with the diffraction peaks of the crystalline monoclinic phase of WO_3 . The presence of Pt(1 1 1), Pt(2 0 0) peaks are found in Fig. 1(b). Furthermore, the major diffraction peaks of Pt nanoparticles can be observed.

The morphology of tungsten oxide nanorods was studied by means of SEM, AFM, and transmission electron microscopy (TEM) on a Philips CM12/STEM instrument. The SEM image presented in Fig. 2(a) shows the rod-like morphology of the product. The AFM image in Fig. 2(b) confirms the rod-like morphology at low magnification. The morphology of the nanorods can be confirmed in the TEM micrographs shown in Fig. 3(a) and (b). The dimensions of the nanorods are matched with the outer diameter of the template used. The diameter of the nanorods is found to be around 200 nm. The presence of Pt on the WO_3 nanorods can be seen in Fig. 3(b) and it is clear that the Pt is well dispersed overall of the surfaces of the nanorods. The size of the Pt nanoparticles is in the range of 3–4 nm. The optimum Pt particle size for reactions in a H_2/O_2 fuel cell is claimed to be 3 nm [17]. An EDX pattern (Fig. 4) shows the presence of Pt in the WO_3 nanorods. The complete removal of fluorine and aluminum is also confirmed.

The electrochemical behaviour of the WO_3 nanorods was studied in 1 M H_2SO_4 , as shown in Fig. 5(b). The cyclic voltammogram shows an anodic peak current at -0.07 V. This is due to the formation of tungsten bronzes by hydrogen intercalation in the tungsten trioxide. The electrochemical response due to tungsten is seen at -0.1 V in the forward scan, which matches with the peak reported in literature [18]. Further, the stability

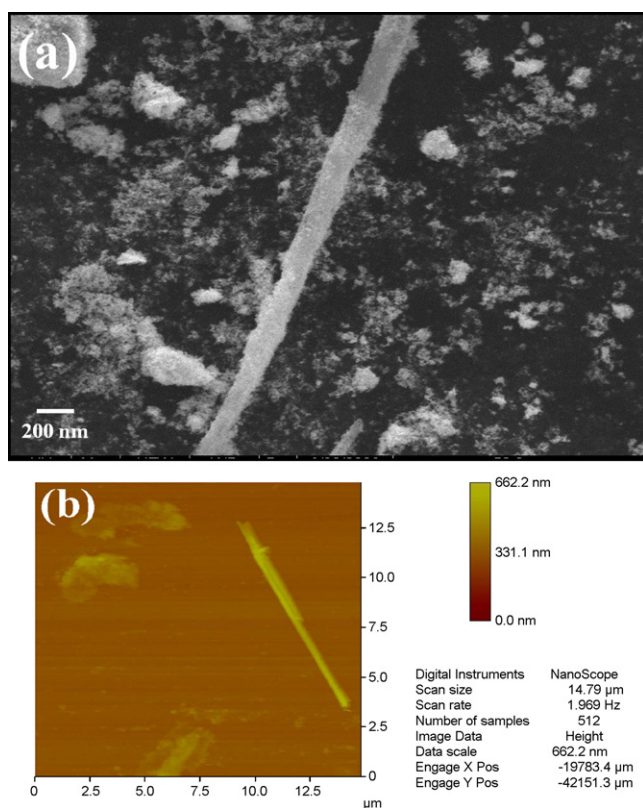


Fig. 2. (a) Scanning electron micrograph of WO_3 nanorod and (b) AFM micrograph of nanorod.

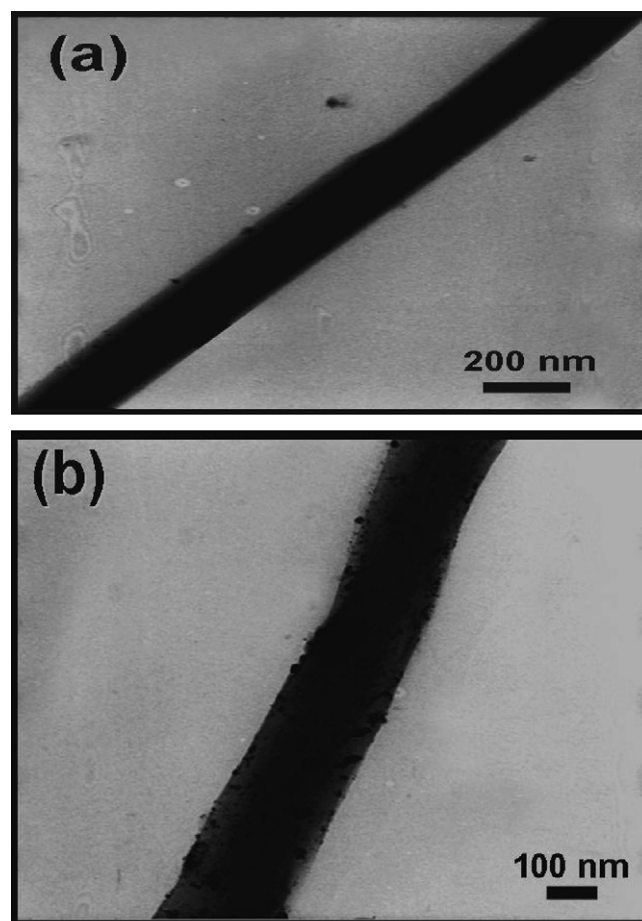


Fig. 3. TEM images of nanorods: (a) WO_3 nanorods and (b) Pt/ WO_3 nanorods.

of tungsten trioxide in a sulfuric acid medium is evaluated by undertaking repeated voltammetric cycles in 1 M H_2SO_4 . The cyclic voltammetry shows that WO_3 nanorods have higher stability compared with bulk WO_3 . There is a gradual decrease in current on cycling and this illustrates the lower stability of bulk WO_3 . After the second cycle, there is no decrease in the currents

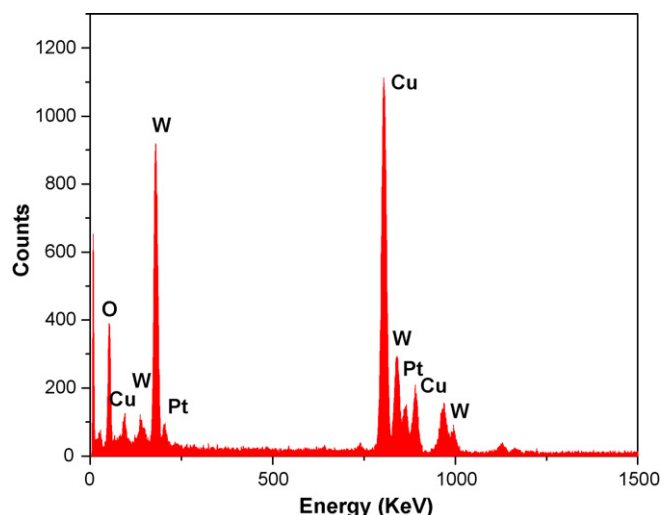


Fig. 4. EDX pattern of Pt/ WO_3 nanorod electrode.

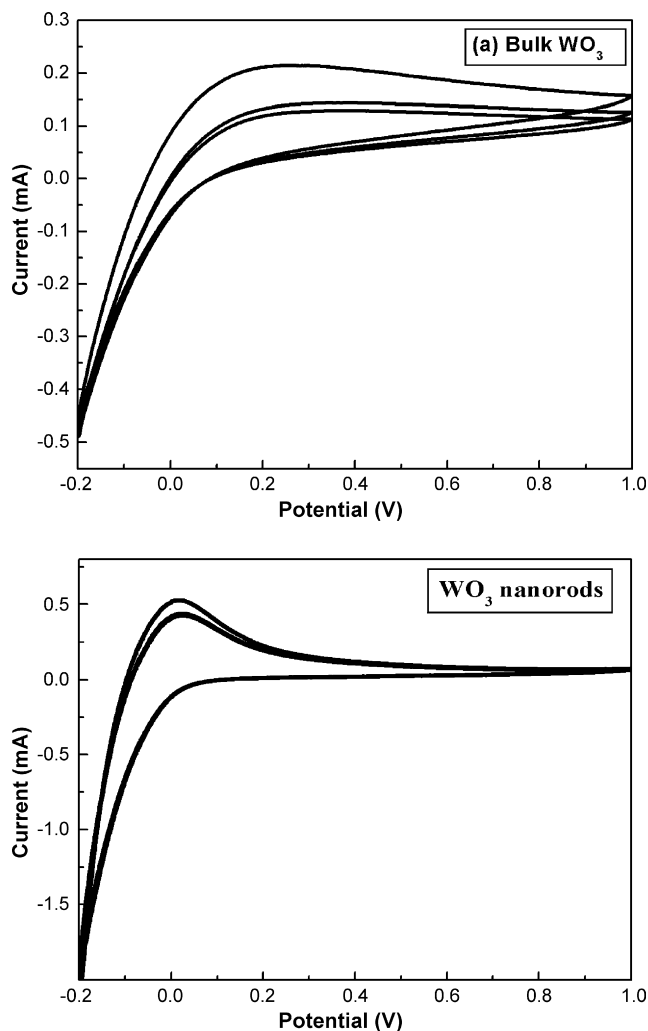


Fig. 5. Cyclic voltammogram for (a) bulk WO_3 and (b) WO_3 nanorods in 1 M H_2SO_4 at scan rate of 50 mV s^{-1} at 298 K.

produced on repeated cycling of WO_3 nanorods. This shows the good stability of WO_3 nanorods compared with bulk WO_3 in a sulfuric acid medium.

The electrochemical activity of platinum-loaded WO_3 nanorods for methanol oxidation was studied using cyclic voltammetry in the presence of 1 M H_2SO_4 and 1 M CH_3OH . Fig. 6(a) shows the electrochemical oxidation of methanol by Pt loaded on WO_3 (voltammogram obtained after the peak attaining a constant current). For comparison, methanol oxidation was also, studied with a commercial 20% Pt/C (Johnson Matthey), see Fig. 6(b). Cyclic voltammograms of WO_3 nanorods in 1 M H_2SO_4 and 1 M CH_3OH are given in Fig. 6(c). Like ruthenium WO_3 has no activity for methanol oxidation in acid solution. The unsupported WO_3 nanorods show no activity towards methanol oxidation. By contrast, two oxidation peaks are observed, with Pt/C and belong to the oxidation of methanol and the corresponding intermediates [10], see Fig. 6(c).

The methanol oxidation peak potential is lower for Pt/ WO_3 nanorods than for Pt/C, which indicates the superior performance of Pt particles supported on WO_3 nanorods. For a lower platinum loading, the WO_3 nanorods show enhanced activity

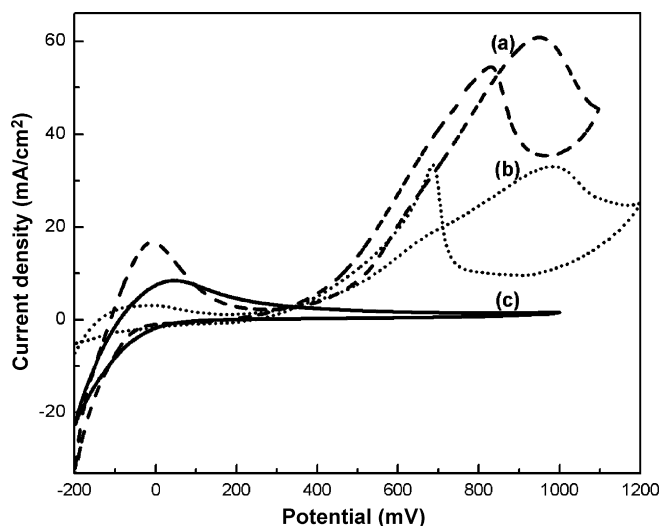
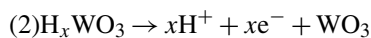
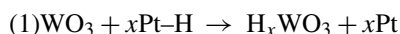


Fig. 6. Cyclic voltammograms of (a) Pt/ WO_3 nanorods, (b) Pt/C (Johnson Matthey) and (c) WO_3 nanorods in 1 M H_2SO_4 /1 M CH_3OH at 50 mV s^{-1} .

than the commercial catalyst. The specific activity (mA cm^{-2}) of the platinum supported on WO_3 nanorods is almost twice that of the commercial 20% platinum on carbon support (Table 1). The higher activity of Pt/ WO_3 can be attributed to the stabilization of Pt nanoparticles with good dispersion on the WO_3 nanorods. From the cyclic voltammogram, it can be concluded that the Pt/ WO_3 nanorods electrode is suitable for intermediate production.

According to Yoshiike and Kondo [19,20], water molecules are not only physisorbed but also chemisorbed on WO_3 . The oxophilic nature of WO_3 would help in adsorbing the intermediates and thereby, maintain the surface of platinum clean. This is not possible in the case of Pt supported on carbon. The advantages of using a Pt/ WO_3 electrode are:

- (i) Keeping the Pt site clean for chemisorption of methanol by the formation and oxidation of hydrogen tungsten bronzes during dehydrogenation of methanol on the surface of Pt/ WO_3 electrode, i.e.



- (ii) Oxidizing poisons such as CO, since water adsorbed on WO_3 surface can interact with CO adsorbed on Pt at the neighbouring site. Such bronzes show better catalytic activity than Pt–Ru-based electrocatalysts [13,21].

Table 1
Electrocatalytic activity of Pt/ WO_3 nanorods and Pt/C for methanol oxidation

Electrocatalyst	Pt loading ($\mu\text{g cm}^{-2}$)	Specific activity (mA cm^{-2})
Pt/C	20	29.5
Pt/ WO_3 nanorods	20	62.0

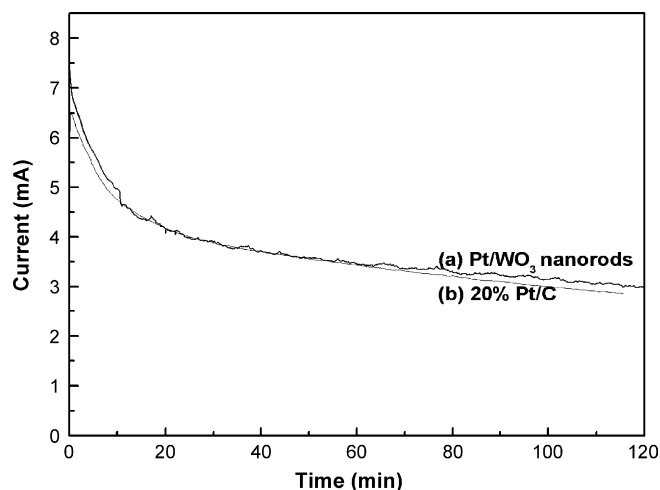


Fig. 7. Current density vs. time curves at (a) Pt/WO₃ nanorods and (b) Pt/C (Johnson Matthey) measured in 1 M H₂SO₄ + 1 M CH₃OH. Potential stepped from rest potential to 0.6 V vs. Ag/AgCl.

The stability of the electrode for methanol oxidation was evaluated by chronoamperometry. The chronopotentiometric results of methanol oxidation in 1 M H₂SO₄ and 1 M CH₃OH at 0.6 V are presented in Fig. 7. The Pt/WO₃ nanorods electrode not only exhibit higher initial activity but are also more stable than the Pt/C electrode (Fig. 7). The probable reason is the lower polarisation potential. At this potential, the leaching of W will not have a pronounced effect on the stability of the electrode for methanol oxidation [22]. Also, the oxophilic nature of WO₃ is beneficial in producing hydroxyl groups on the catalyst surface, which promotes the oxidation of adsorbed CO [14,23].

4. Conclusions

A simple template synthesis has been developed for preparing WO₃ nanorods by direct calcination of phosphotungstic acid in the channels of the alumina template. The size of the nanorods is around 200 nm, which matches with the diameter of the template used. The methanol oxidation activity of platinum supported on WO₃ nanorods has been studied and compared with that of the commercial catalyst. Pt/WO₃ nanorods exhibit higher methanol oxidation activity than the commercial Pt/C catalyst by a factor of two. Platinum supported on such nanorods is found to be stable over several cycles in an electrochemical environment.

Enhancement in the electrocatalytic activity is due to a spill-over effect in methanol oxidation. Tungsten oxide nanorods are examined for use as supports for noble metals for possible application as fuel cell anodes.

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