Short communication

The electrochemical oxidation of methanol on a Pt/TNTs/Ti electrode enhanced by illumination

Y.Q. Wang [a,b], Z.D. Wei [a,b,*], B. Gao [a], X.Q. Qi [a,b], L. Li [a,b,*], Q. Zhang [a], M.R. Xia [a]

[a] The State Key Laboratory of Power Transmission Equipment & System Security and New Technology,
School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China
[b] School of Material Science and Engineering, Chongqing University, Chongqing 400044, China

ABSTRACT

A Pt/TNTs/Ti electrode is prepared by electrochemically depositing Pt using the modulated pulse current method onto high density, well ordered and uniformly distributed TiO_2 nanotubes (TNTs) on a Ti substrate. The results show that the performance and anti-poison ability of the Pt/TNTs/Ti electrode for methanol electro-oxidation under illumination is remarkably enhanced and is even better than the best bi-metallic Pt–Ru catalysts. CO poisoning is no longer a problem during methanol electro-oxidation with the Pt/TNTs/Ti electrode under illumination.

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1. Introduction

There is growing interest in the use of direct methanol fuel cells (DMFCs) as power sources for portable electronic devices for a variety of reasons [1]. However, two problems prevent the commercialization of DMFCs: the slow kinetics of methanol electro-oxidation due to CO poisoning, and methanol crossover from anode to cathode due to the polymer membrane presently in use [2,3].

To decrease the amount of CO poisoning during methanol oxidation, much effort has been devoted to the development of Pt-based catalysts [4–7]. The presence of a second or third foreign metal or metal oxide is expected to provide oxygen-donating species, for example, Ru, on which oxygen-donating species may form at much lower potentials than on Pt. Thus, the absorbed CO can be removed at a low potential [8,9]. Even so, methanol electro-oxidation still suffers from CO poisoning of the catalysts.

In addition to the carbon support, oxide supports are now widely used in heterogeneous catalysis and have inherently higher stability than carbon in oxidizing environments [10]. Titanium oxide has

been attractive as a support due to its stability in fuel cell operating atmospheres, low cost, commercial availability [11]. It has been reported that Pt nanoparticles supported on TiO_2 nanoparticles exhibit good catalytic activity for methanol electro-oxidation with [12] and without [13,14] illumination. The enhanced performance of a Pt–TiO_2 nanoparticle film prepared by means of the co-sputtering deposition method was thought to be due to the enhanced methanol oxidation by photogenerated holes in the TiO_2 films under illumination [12]. Obviously, there is a potential drawback of nanoparticle film of TiO_2 in a photocatalytic reaction: the photogenerated charge migration/diffusion in the TiO_2 nanoparticle film may be impeded by the non-directed 3D randomly packed particle network [15,16]. It has been observed that there is a certain amount of obstruction to electron transport at grain boundaries between individual particles [17]. The electron transport is 100–1000 times slower in mesoporous nanocrystalline TiO_2 films than in single-crystal TiO_2 [18,19]. The high rate of photogenerated electron–hole pair recombination and the poor utilization of light restrict the photocatalytic activity of TiO_2 nanoparticles (TNPs) and their practical application.

TiO_2 nanotubes (TNTs) have some great advantages over TNPs. It has been shown that TNTs have a larger effective surface area than TNPs [20]. TNTs allow more effective absorption of incident photons because of the increased light penetration depth and better scattering with a regular pore structure [21]. TNTs can therefore generate more electron–hole pairs under illumination and more oxygen-containing species •OH from H_2O oxidation by photogen-

* Corresponding authors at: The State Key Laboratory of Power Transmission Equipment & System Security and New Technology, School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China.
Tel.: +86 23 60891548; fax: +86 23 65106253.
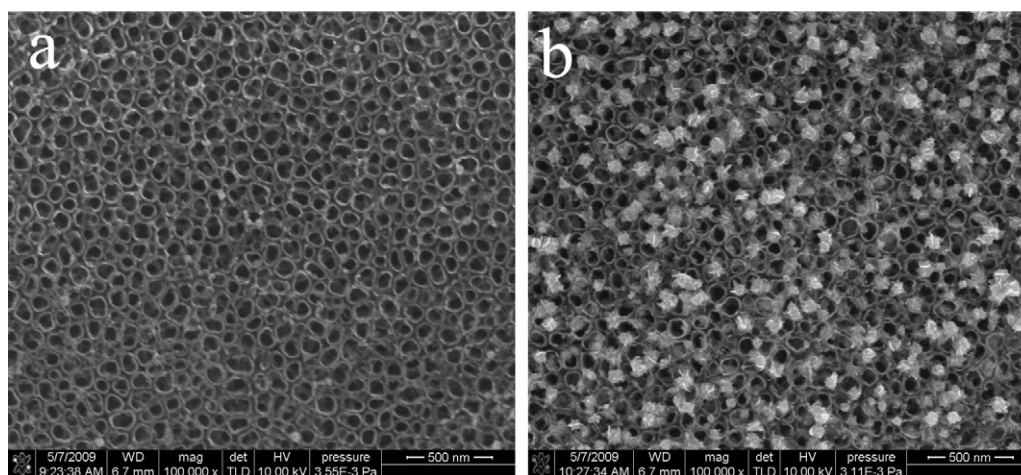*E-mail addresses:* zdwei@cqu.edu.cn (Z.D. Wei), liliraxial@cqu.edu.cn (L. Li).
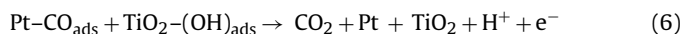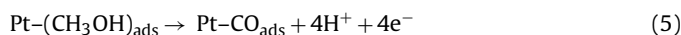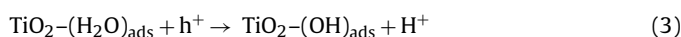
Fig. 1. FESEM images of TNT array (a) before and (b) after Pt deposition.

erated holes. In addition, the aligned crystalline straight tube walls of TNTs offer the most direct path for photogenerated electrons toward the underlying Ti metal and minimize detrimental grain boundaries, thus leading to fast and efficient charge transfer and much reduced electron–hole recombination [22,23]. Thus, in contrast to TNPs, TNTs with tubular structure combining a high surface area with minimized grain boundaries display better light absorption and higher photocatalytic activity under illumination.

On the basis of the points mentioned above, we questioned whether, under illumination, the methanol electro-oxidation could be improved with the use of a platinized TNTs/Ti electrode (Pt/TNTs/Ti) due to its increased conductance, reduced electron–hole pair recombination, and increased photogenerated oxygen-containing species $^{\bullet}OH$ via the so-called bi-functional mechanism:

$$TiO_2 + h\nu \rightarrow TiO_2 + h^+ + e^- \tag{1}$$

$$TiO_2 + H_2O \rightarrow TiO_2 - (H_2O)_{ads} \tag{2}$$

$$TiO_2 - (H_2O)_{ads} + h^+ \rightarrow TiO_2 - (OH)_{ads} + H^+ \tag{3}$$

$$Pt + CH_3OH \rightarrow Pt - (CH_3OH)_{ads} \tag{4}$$

$$Pt - (CH_3OH)_{ads} \rightarrow Pt - CO_{ads} + 4H^+ + 4e^- \tag{5}$$

$$Pt - CO_{ads} + TiO_2 - (OH)_{ads} \rightarrow CO_2 + Pt + TiO_2 + H^+ + e^- \tag{6}$$

Thus, in this paper, TNTs were prepared on a pure Ti sheet as a support for Pt catalysts, on which methanol electro-oxidation was investigated by electrochemical techniques under illumination. The results show that the performance and anti-poison ability of the Pt/TNTs/Ti electrode for methanol electro-oxidation under illumination are remarkably enhanced and are even better than the characteristics of the best bi-metallic Pt–Ru catalysts for methanol electro-oxidation. CO poisoning is not a problem for methanol electro-oxidation on Pt/TNTs/Ti electrodes under illumination.

2. Experimental

The TNTs/Ti substrate was fabricated by the electrochemical anodic oxidation technique on a pure Ti sheet (99.7% purity) in 0.5 wt% HF aqueous solution at 20 V at room temperature. The anodized titanium sheet was then annealed in air at 480 °C for 3 h and then cooled to room temperature at 5 °C min^{-1}.

The Pt particles were electrochemically deposited on the TNTs/Ti substrate according to the method described previously [24]. The electrochemical deposition of Pt on TNTs/Ti was performed on an Autolab PGSTAT 30 (Metrohm Autolab B.V.,

Netherlands) in a bath containing 10 g L^{-1} H$_2$PtCl$_6$ and 60 g L^{-1} HCl solution at room temperature. For comparison, a PtRu/C electrode was prepared by coating a catalyst ink containing a commercial catalyst of PtRu Black (Pt:Ru = 50:50 at.%; HiSPEC 6000, Johnson–Matthey, UK) and 5 wt.% Nafion on Teflon-treated carbon paper (Tony Co, Japan) coated in advance with a mixture of carbon power (Vulcon XC-72, USA) and 10% Teflon. The Pt/TNTs/Ti (area: 1 cm^{-2}; Pt loading: 0.58 mg cm^{-2}) and PtRu/C (area: 1 cm^{-2}; Pt loading: 0.66 mg cm^{-2}; Ru loading: 0.34 mg cm^{-2}) were served as the working electrode. A Pt wire was used as the counter electrode. All potentials in this report are quoted with reference to the Ag/AgCl electrode with saturated KCl (0.20 V vs SHE) unless otherwise stated. A 500-W xenon arc lamp (CHF-XM35-500W, Beijing ChangTuo, China) was used to simulate sunlight illumination. Methanol electro-oxidation was carried out in the solution containing 0.5 M H$_2$SO$_4$ and 1 M CH$_3$OH at 30 °C in a thermostat bath. The morphologies of the prepared electrodes were characterized by field emission scanning electron microscopy (FESEM) (FEI Nova 400, Peabody, MA).

3. Results and discussion

The morphology of the TNTs array before and after Pt deposition is presented in Fig. 1. It shows that the TNT arrays obtained are very dense, well ordered and uniform, with an inner diameter from 90 to 120 nm. The deposited Pt particles are located in the outside mouth of the TiO$_2$ nanotubes. The cyclic voltammogram (CV) of the Pt/TNTs/Ti electrode obtained in 0.5 M H$_2$SO$_4$ displays the typical voltammetric pattern of the active platinum in an acid electrolyte, as shown in Fig. 2a.

Linear sweeping voltammograms (LSV) and chronoamperograms (CA) of the corresponding electrodes are presented in Fig. 2. There is only a limited photogenerated current on TNTs/Ti in methanol solution after illumination. However, with the introduction of Pt, Pt/TNTs/Ti shows very good activity for methanol electro-oxidation. In particular, illumination can remarkably enhance methanol electro-oxidation on Pt/TNTs/Ti, as shown in Fig. 2b. The peak current density of methanol electro-oxidation on Pt/TNTs/Ti with illumination is about 2.6 times higher than that without illumination, as shown in the inset of Fig. 2b. The chronoamperometry results of electrodes for methanol oxidation at 0.6 V shown in Fig. 2c indicate that the current attenuation during methanol electro-oxidation on Pt–Ru, the most active binary alloy catalyst for methanol electro-oxidation so far [25], no longer appears in the case of the Pt/TNTs/Ti electrode under illumina-
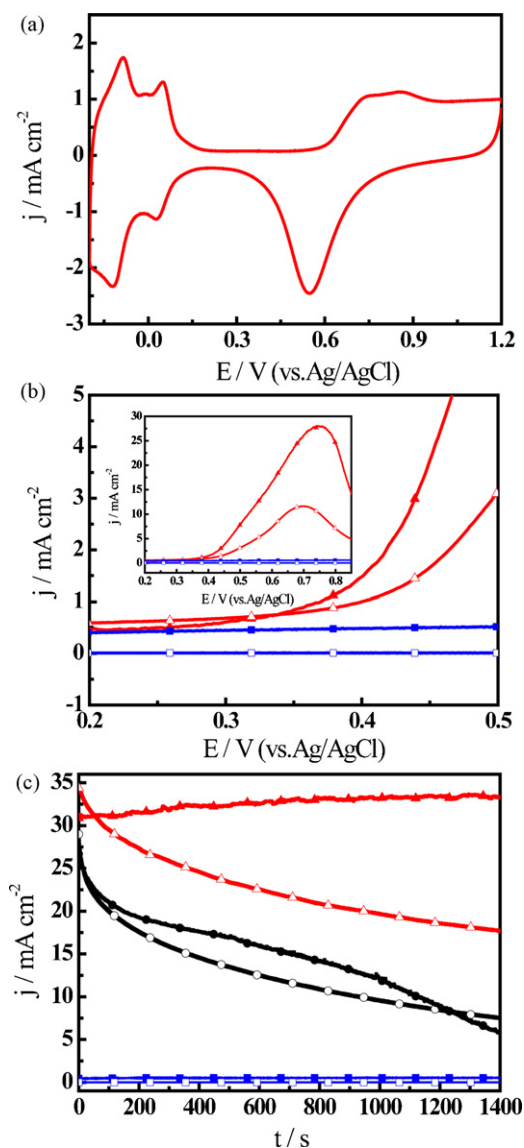
Fig. 2. (a) Cyclic voltammogram of Pt/TNTs/Ti electrode in 0.5 M H$_2$SO$_4$ at a sweep rate of 50 mV s^{-1}. (b) Linear sweep voltammograms at a sweep rate of 10 mV s^{-1}. (c) Chronoamperograms at potential of 600 mV vs Ag/AgCl. For electrodes Pt/TNTs/Ti (triangles; Pt loading: 0.58 mg cm^{-2}), for TNTs/Ti (squares) and for PtRu/C (circles; Pt loading: 0.66 mg cm^{-2}; Ru loading: 0.34 mg cm^{-2}) in 1 M CH$_3$OH + 0.5 M H$_2$SO$_4$ with illumination (filled) and without (open).

tion. In addition, the current for methanol electro-oxidation on the Pt/TNTs/Ti electrode under illumination not only does not show any attenuation but also increases slightly with time. As a matter of fact, the current attenuation during methanol electro-oxidation results from the reduction of active sites due to the accumulation of intermediate CO on the electrode. Therefore, more fresh active sites are created under illumination in the case of the Pt/TNTs/Ti electrode. Unfortunately, CO poisoning of Pt–Ru electrodes is still present even under illumination.

There are two anodic methanol electro-oxidation current peaks in the forward and backward scan, respectively. The forward anodic current peak is no doubt assigned to methanol electro-oxidation. The backward anodic current peak is attributed to the further oxidation of intermediates formed during the forward scan [26]. Hence, the ratio of the anodic peak current densities in the forward scan (j_f) to the backward scan (j_b) reflects the capability of electrode to remove methanol electro-oxidation intermediates [27]. Accordingly, a lower j_f/j_b value signifies poor methanol electro-oxidation
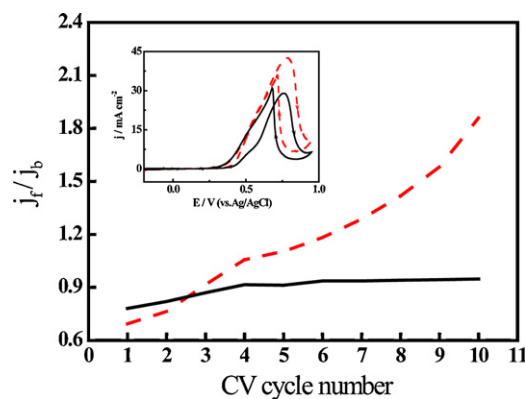
Fig. 3. The ratio of forward anode peak current density (j_f) to backward anode peak current density (j_b) of Pt/TNTs/Ti with (– – –) and without (—) illumination vs cyclic voltammogram (CV) cycle number. The insert is the 6th CV cycle for Pt/TNTs/Ti in 1 M CH$_3$OH + 0.5 M H$_2$SO$_4$.

and excessive accumulation of intermediate species on the electrode surface. The j_f/j_b ratio values for the Pt/TNTs/Ti electrode with and without illumination are given in Fig. 3. It shows that the j_f/j_b ratio values for Pt/TNTs/Ti without illumination increases with CV cycle number for the first 4 cycles, but after the 5th CV cycle, it is almost independent of CV cycle number, which may imply some balance between removal and re-occupation of intermediate species. Interestingly, with illumination the j_f/j_b values for Pt/TNT/Ti increase directly with CV cycle number, which means that more and more fresh sites are released with CV cycle number. This result is identical with that shown in Fig. 2c.

It should be noted that the thermal effect produced by illumination was deducted by keeping the electrolyte at 30 °C for all measurements.

4. Conclusions

Illumination can markedly enhance methanol electro-oxidation on a Pt catalyst supported on TiO$_2$ nanotubes. This result can be attributed to the abundance of oxygen-containing species •OH produced by H$_2$O oxidation on TiO$_2$ nanotubes under illumination.

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