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Short communication

Novel Pd/β-MnO$_2$ nanotubes composites as catalysts for methanol oxidation in alkaline solution

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Abstract

In this work, we demonstrated a completely new, simple and effective strategy for preparing catalysts by using β-MnO$_2$ nanotubes as the supporting materials, and the Pd nanoparticles were coated onto β-MnO$_2$ nanotubes through a simple reductive process firstly. The as-prepared materials were characterized by field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and electrochemical measurements. The results indicated that the Pd nanoparticles were homogeneously dispersed and well separated from one another on the β-MnO$_2$ nanotubes surfaces, which makes it have a potential application in catalysts. In this study, we mainly tested the electrochemical performance of Pd/β-MnO$_2$ for methanol oxidation in alkaline solution. Further research to optimize the synthesis condition, particularly to develop β-MnO$_2$ nanotubes as supporting materials of other noble metal catalysts is currently in progress.

Keywords: β-MnO$_2$ nanotubes; Pd nanoparticles; Catalyst support; Methanol oxidation

1. Introduction

There is an increasing interest in the electro-oxidation of methanol because of the development of direct methanol fuel cells (DMFCs) as power sources for electric vehicles and electronic devices. The DMFC is a promising technology as an alternative to conventional energy-generating devices due to its higher energy-conversion efficiency, low-to-zero pollutant emissions, ready availability of methanol fuel, ease in distribution, and high energy [1–7]. However, the electro-oxidation of methanol is a very complex reaction, during which many intermediate and poisoning species are involved. The electrocatalytic activity of noble metal particles for methanol oxidation is dependent on many factors such as the size and dispersion of catalysts, the properties of the supporting materials and the preparation methods. Of these, the supporting materials and their surface condition are essential for the catalysts materials to produce high catalytic activity [8–11]. It is generally accepted that the catalytic activity is not only dependent on the shape, size and distribution of the particles but also on the categories and properties of the supporting materials.

Recently, although various supporting materials such as carbon nanotubes (CNTs) [12], graphite, activated carbon fiber [13], kinds of porous carbon [14] and carbon network [15] used as potential supports for electrocatalysts have been extensively investigated, developing alternate electrode materials for better activity and stability for methanol electro-oxidation still remains challenging. In our lab, TiO$_2$ nanotube and vanadium oxide nanotubes (VOx-NTs) were also used as supporting materials and have good electrocatalytic properties. It opens a new way to find excellent catalysts substrate [16,17].

Among all the metal oxides, manganese oxide is one of the most attractive materials because of its technological importance for catalytic, molecular adsorption and electrochemical applications. However, the properties of MnO$_2$ are influenced significantly by its structure, morphology, and preparation method. Recently, tubular structure materials attracted more attention due to their high specific surface area and unique pore structure. But, preparation of MnO$_2$ nanotubes is rarely reported [18]. Moreover, to the best of our knowledge, up to now, there have been no reports of using β-MnO$_2$ nanotubes as the sup-

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porting materials of catalyst Pd nanoparticles in direct methanol fuel cells. So this research work will be of great significance.

In this work, a kind of novel Pd/β-MnO_2 nanotubes composites was synthesized successfully, and its electrocatalytic performance was evaluated by methanol oxidation in alkaline solution. The experimental results indicated that the as-obtained Pd/β-MnO_2 nanotubes catalysts have an excellent electrocatalytic activity.

2. Experimental

2.1. Preparation β-MnO_2 nanotubes

All chemicals were of analytical grade and were used without further purification. The β-MnO_2 nanotubes were prepared by hydrothermal treatment as described elsewhere [18]. The detailed process was as follows: appropriate amounts of $MnSO_4 \cdot H_2O$ and $NaClO_3$ powders were dissolved into 85 mL distilled water. 0.25 M of polyvinyl pyrrolidone (K30, polymerization degree 360) was added to the solution. After stirring for about 1 h, the resultant system was then transferred into a Teflon-lined 110 mL capacity autoclave with a stainless steel shell. The autoclave was sealed and maintained at 160 °C for 12 h. The system was then cooled to room temperature naturally. The resulting product was filtered and washed with distilled water, and then dried at 80 °C for 12 h.

2.2. Fabrication of Pd/β-MnO_2 nanotubes composites

Fifty milligrams of aforementioned β-MnO_2 nanotubes was added into 0.5 mM of Pd $(NO_3)_2$ solution. After stirring for about 3 h, formaldehyde was added to the system drop wise; the reductive reaction was performed at room temperature for 12 h. The resulting product was filtered and washed with distilled water, and then dried at 50 °C for 6 h.

2.3. Fabrication of Pd/β-MnO_2 nanotubes composites-modified GC electrode

The glass carbon (GC) electrode was firstly polished with chamois leather containing Al_2O_3 slurry, and then washed with deionized water and ethanol in an ultrasonic bath. Pd/β-MnO_2 nanotubes composites were ultrasonically dispersed in 0.5% of Nafion ethanol solution. An aliquot of the Pd/β-MnO_2 nanotubes/Nafion suspension was cast on the surface of the GC electrode and allowed to dry under an infrared heat lamp. The as-obtained Pd/β-MnO_2 nanotubes-modified GC electrode was employed as the working electrode in our experiment. For comparison, Pd nanocatalyst supported onto carbon black (Vulcan-72) and their electrodes were also prepared under the same preparation conditions.

2.4. Characterization

The crystal structure of the samples was characterized by X-ray diffraction (XRD, D/max-2400 Rigaku, Japan). Morphology and microstructure of the synthesized materials was investigated by field emission scanning electron microscopy (FESEM, JSM-6700F, Japan) and transmission electron microscopy (TEM, Hitachi 600, Japan). Electrochemical measurements were performed with CHI760 electrochemical workstation (Chenhua, Shanghai), a conventional three-electrode cell configuration was used throughout this work. The working electrode is a Pd/β-MnO_2 nanotubes-modified/GC (glassy carbon electrode) electrode, platinum foil was used as counter electrode, saturated calomel electrode (SCE) was reference electrode, and all potentials were measured and reported with respect to SCE in this paper. All measurements were performed at room temperature.

3. Results and discussion

3.1. FESEM and TEM photographs of β-MnO_2 and Pd/β-MnO_2 nanotubes

The field emission scanning electron microscopy (FESEM) images in Fig. 1a show the typical morphology of the as-synthesized β-MnO_2 nanotubes. The nanotubes with the uniform diameter and length can be observed in the images, the end of β-MnO_2 nanotubes is round and opened mostly. It is clear that the nanomaterial is in the form of hollow nanotubes rather than solid nanowires or nanorods, the tube inner diameter is approximately 200 nm. The morphology of Pd/β-MnO_2 composites was observed by transmission electron microscopy (TEM). As can be seen from Fig. 1b, Pd nanoparticles are well dispersed and attached on the surface of β-MnO_2 nanotubes.

3.2. XRD analysis of β-MnO_2 and Pd/β-MnO_2

The XRD patterns of samples are displayed in Fig. 2. It is clear that the XRD diffraction peaks of the as-prepared β-MnO_2 can be assigned to β-MnO_2 with tetragonal space group $I4_1/amd$. No peaks for other types or for amorphous MnO_2 were observed in the XRD patterns of the as-synthesized MnO_2, indicating high purity and crystallinity of the final sample, which is also in accord with the results of Zheng et al. [18]. The standard XRD patterns (JCPDS card 88-2335) of pure Pd are also shown in Fig. 2. Comparing the standard spectrum with the XRD diffraction peaks of Pd/β-MnO_2 nanotubes composites, we could confirm that face-centered cubic (fcc) phase Pd was pasted onto β-MnO_2 nanotubes.

3.3. Electrochemical properties of Pd/β-MnO_2 nanotubes

In order to elucidate the catalytic function of Pd/β-MnO_2 nanotubes composites in the oxidation of CH_3OH, we first investigated the voltammetric behavior of CH_3OH at the surface of β-MnO_2 nanotubes and Pd/C and Pd/β-MnO_2 nanotubes electrodes under identical conditions. As is shown in Fig. 3a, no current peaks of methanol oxidation are observed, which indicates that the β-MnO_2 nanotubes have no electrocatalytic activity for methanol oxidation. From Fig. 3b and c, in the forward scan, methanol oxidation produces a prominent symmetric anodic peak, the peak potential of 0.035 V for Pd/β-MnO_2 nan-

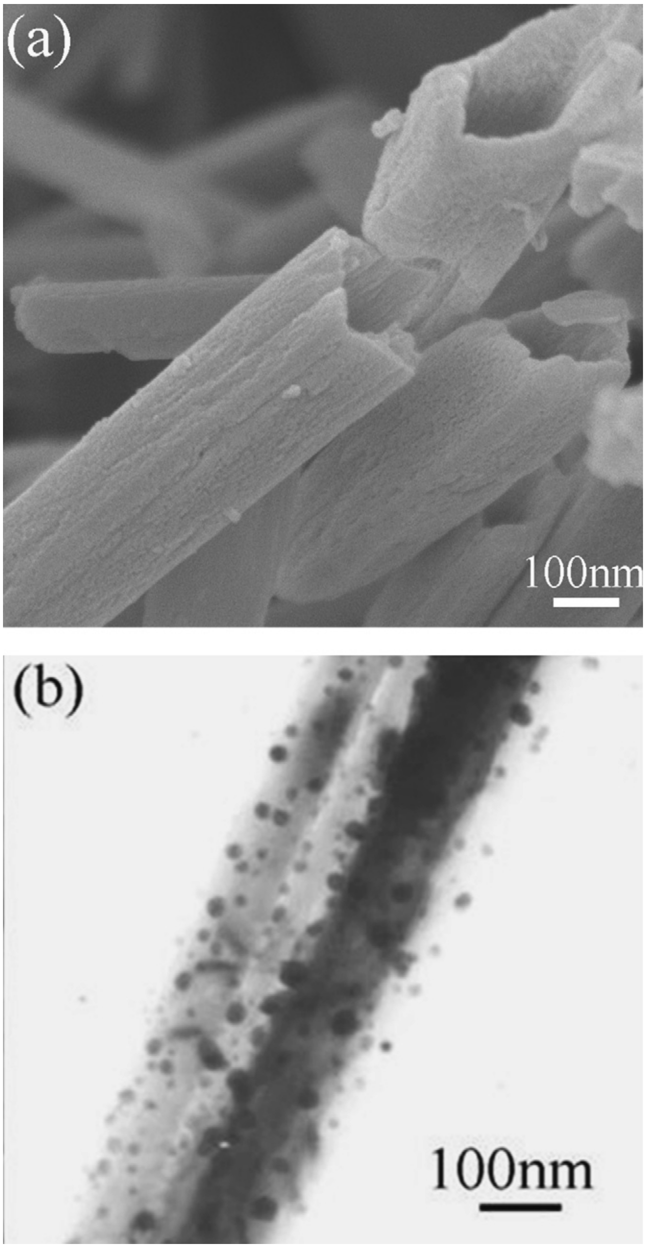

Fig. 1. FESEM and TEM images of β-MnO_2 and Pd/β-MnO_2 nanotubes (a, FESEM of β-MnO_2; b, TEM of Pd/β-MnO_2 nanotubes composites).

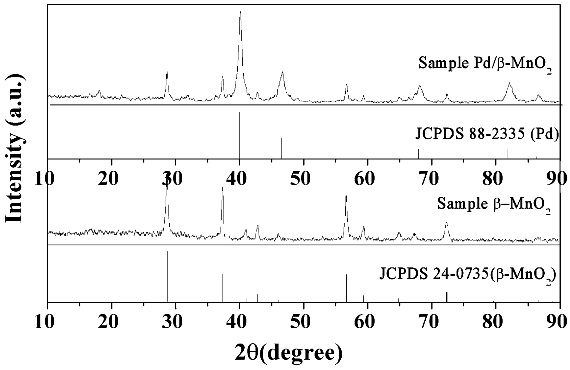

Fig. 2. XRD patterns of samples.

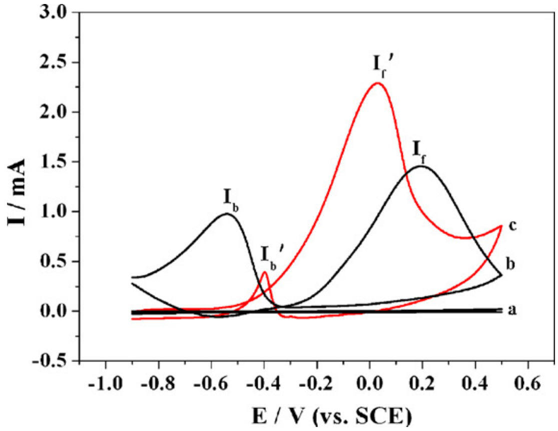

Fig. 3. Cyclic voltammograms of different electrode in 1 M CH_3OH and 0.1 M NaOH solution at 100 mV s^{-1}. (a) β-MnO_2 nanotubes/GC electrode, (b) Pd/C/GC electrode, and (c) Pd/β-MnO_2 nanotubes/GC electrode.

otubes and of 0.199 V for Pd/C electrode. In the reverse scan, there is an anodic peak which is detected in both Pd/β-MnO_2 nanotubes and Pd/C electrode, Goodenough et al. and Zhang et al. attributed this anodic peak in the reverse scan to the removal of the incompletely oxidized carbonaceous species formed in the forward scan [19,20]. Hence the ratio of the forward anodic peak current density (I_f) to the reverse anodic peak current density (I_b), I_f/I_b, can be used to describe the catalyst tolerance to carbonaceous species accumulation. A low I_f/I_b ratio indicates poor oxidation of methanol to carbon dioxide during the anodic scan and excessive accumulation of carbonaceous residues on the electrode surface. A high I_f/I_b ratio shows the reverse case [21]. From qualitative analysis of these voltammetric profiles, three aspects are immediately evident. First, the I_f'/I_b' ratio of 5.87 for Pd/β-MnO_2 nanotubes electrode is higher than that of Pd/C ($I_f/I_b = 1.49$), which indicated more intermediate carbonaceous species are oxidized to carbon dioxide in the forward scan on Pd/β-MnO_2 nanotubes electrode surface than on Pd/C electrode surface. Second, the Pd/β-MnO_2 nanotubes electrodes have a lower onset potential (ca. −0.463 V) than the one on Pd/C electrode (ca. −0.317 V), indicating better electrocatalytic activity of Pd/β-MnO_2 nanotubes electrode. Third, the current density at the Pd/β-MnO_2 nanotubes electrode is higher than that of Pd/C electrode. The above analysis results confirmed that Pd/β-MnO_2 nanotubes composites had a better electrocatalytic activity than that of Pd/C for methanol oxidation in NaOH.

The cyclic voltammograms of Pd/β-MnO_2 electrode in 1 M CH_3OH and 0.1 M NaOH solution with different scan rates are presented in Fig. 4. The relation between the peak current density obtained from forward CV scan and $v^{1/2}$ of CV is shown in the inset, and a linear relationship is also observed. It can be observed that the process of methanol oxidation may be controlled by diffusion of methanol [22]. Additionally, the peak potential (E_{pa}) (the forward scan), increase with the increase of v, and a linear relationship can be obtained between E_p and ln(v), as shown in Fig. 5. It indicates that the oxidation of methanol is an irreversible electrode process.

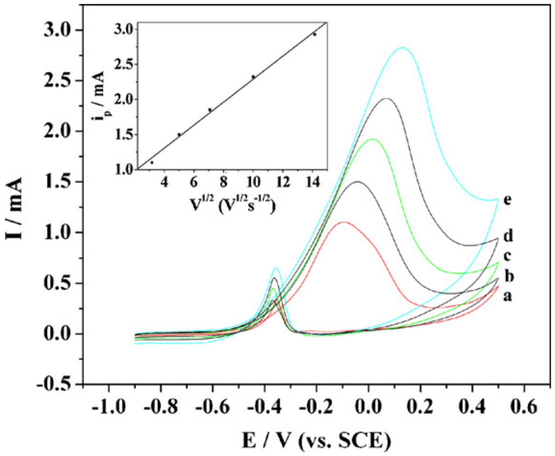

Fig. 4. *CV* curves of Pd/β-MnO_2 in 1 M CH_3OH and 0.1 M NaOH solution at (a) 10, (b) 25, (c) 50, (d) 100, and (e) 200 mV s^{-1} scan rate. Inset: the plot of peak current vs. square root of sweep rates. $C_{CH_3OH} = 1$ mol L^{-1}.

3.4. Long-term stability of Pd/β-MnO_2 nanotubes composites

The long-term stability of Pd/β-MnO_2 nanotubes composites was also investigated in 1 M CH_3OH and 0.1 M NaOH solution. The results are shown in Fig. 6. It can be observed that the peak current decreases gradually with the successive scans. After 500th scan, the peak current was still about 82% of that of the first scan. The loss may result from the consumption of 1 M CH_3OH solution during the CV scan and also due to the poisoning and structure change of Pd nanoparticles as a result of the perturbation of the potentials during the scanning in aqueous solutions, especially in the presence of the organic compound. After the long-term CV experiments, the Pd/β-MnO_2 composites-modified electrode was stored in D.I. water and measured after 1 week, the excellent catalytic activity towards methanol oxidation was still observed. It indicates that the Pd/β-MnO_2 obtained in our experiment has good long-term stability and has potential application in direct methanol fuel cells.

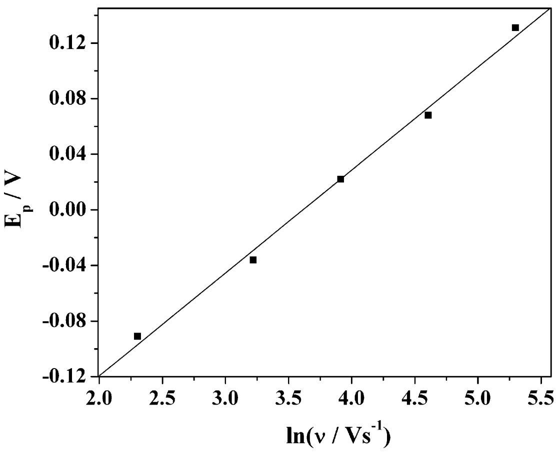

Fig. 5. The plot of E_p vs. ln(*υ*). $C_{CH_3OH} = 1$ mol L^{-1}.

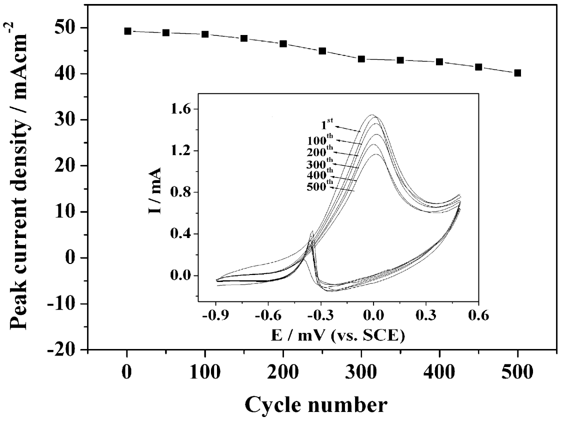

Fig. 6. Long-term stability of the Pd/β-MnO_2 nanotubes composites electrode in 1 M CH_3OH and 0.1 M NaOH solution. Inset: the different circles *CV* curves for Pd/β-MnO_2 in 1 M CH_3OH and 0.1 M NaOH solution at the same scan rate (100 mV s^{-1}).

4. Conclusion

In this work, we first proposed using β-MnO_2 nanotubes as catalyst supporting material and successfully obtained Pd/β-MnO_2 nanotubes composites via a simple and facile method. Electrochemical study indicated that Pd/β-MnO_2 nanotubes composites had a better electrocatalytic activity than that of Pd/C for methanol oxidation in NaOH solution. It implies that β-MnO_2 nanotubes may be good candidates for noble metal catalyst supports and have potential application in preparing catalysts for direct methanol fuel cells.

References

[1] N. Tian, Z.Y. Zhou, S.G. Sun, Y. Ding, Z.L. Wang, Science 316 (2007) 732.
[2] L. Li, Y. Xing, J. Phys. Chem. C. 111 (6) (2007) 2803.
[3] M. Tsuji, M. Kubokawa, R. Yano, N. Miyamae, T. Tsuji, M.-S. Jun, S. Hong, S. Lim, S.-H. Yoon, I. Mochida, Langmuir 23 (2) (2007) 387.
[4] V. Selvaraj, M. Alagar, I. Hamerton, J. Power Sources 160 (2006) 940.
[5] J. Ge, H. Liu, J. Power Sources 142 (2005) 56.
[6] T. Ito, M. Kunimatsu, Electrochem. Commun. 8 (2006) 91.
[7] N. Alexeyeva, T. Laaksonen, K. sti Kontturi, F. Mirkhalaf, D.J. Schiffrin, K. Tammeveski, Electrochem. Commun. 8 (2006) 1475.
[8] X. Li, W.X. Chen, J.Z.W. Xing, Z.D. Xu, Carbon 43 (2005) 2168.
[9] D.J. Guo, H.L. Li, J. Electroanal. Chem. 573 (2004) 197.
[10] A. Kabbabi, F. Gloaguen, F. Andolfatto, R. Durand, J. Electroanal. Chem. 373 (1994) 251.
[11] A. Gamez, D. Richard, P. Gallezot, F. Gloaguen, R. Faure, R. Durand, Electrochim. Acta 41 (1996) 307.
[12] V. Lordi, N. Yao, J. Wei, Chem. Mater. 13 (2001) 733.
[13] C.Y. Cui, X. Quan, S. Chen, H.M. Zhao, Sep. Purif. Technol. 47 (2005) 73.
[14] F. Gloaguen, J.M. Leger, C. Lamy, J. Appl. Electrochem. 27 (1997) 1052.
[15] J.S. Yu, S. Kang, S.B. Yoon, G. Chai, J. Am. Chem. Soc. 124 (2002) 9382.
[16] M. Wang, D.j. Guo, H.L. Li, J. Solid State Chem. 178 (2005) 1996.
[17] K.F. Zhang, D.J. Guo, X. Liu, J. Li, H.L. Li, Z.X. Su, J. Power Sources 162 (2006) 1077.
[18] D.S. Zheng, S.X. Sun, W.L. Fan, H.Y. Yu, C.H. Fan, G.X. Cao, Z.L. Yin, X.Y. Song, J. Phys. Chem. B 109 (2005) 16439.
[19] R. Manohara, J.B. Goodenough, J. Mater. Chem. 2 (1992) 875.
[20] L. Zhang, D. Xia, Appl. Surf. Sci. 252 (2006) 2191.
[21] G.Y. Zhao, C.L. Xu, D.J. Guo, H. Li, H.L. Li, J. Power Sources 162 (2006) 492.
[22] K. Honda, M. Yoshimura, T.N. Rao, D.A. Tryk, A. Fujishima, J. Electroanal. Chem. 514 (2001) 35.