

Short communication

TiO₂ nanotubes promoting Pt/C catalysts for ethanol electro-oxidation in acidic media

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Abstract

In this paper, TiO₂ nanotubes/Pt/C (TNT/Pt/C) catalysts for ethanol electro-oxidation were prepared by co-mixing method in solution. TEM and XRD showed that uniform anatase TiO₂ nanotubes were about 100 nm in length and 8 nm in diameter and the TGA results indicated that the amount of H₂O contained in TiO₂ nanotubes was much more than that in anatase TiO₂. The composite catalysts activities were measured by cyclic voltammetry (CV), chronoamperometry and CO stripping voltammetry at 25 °C in acidic solutions. The results demonstrated that the TNT can greatly enhance the catalytic activity of Pt for ethanol oxidation and increase the utilization rate of platinum. The CO stripping test showed that the TNT can shift the CO oxidation potential to lower direction than TiO₂ does, which is helpful for ethanol oxidation.

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Keywords: TiO₂ nanotubes/Pt/C (TNT/Pt/C); Electrocatalyst; Ethanol electro-oxidation; Direct ethanol fuel cell

1. Introduction

Direct alcohol fuel cells (DAFCs) have attracted more and more attentions due to their potential applications in transportation and portable electronic devices [1–3]. But there are still two key problems inhabiting its commercialization: the cost of precious metals employed and the low alcohol electro-oxidation kinetics caused by catalyst poisoning. To solve these problems, lots of works have been done: nanostructured conducting materials like carbon nanotubules, nanofibers and mesoporous carbon were generally used as supports for Pt catalysts to minimize the use of precious metal. And some types of electro-catalysts for alcohol oxidation reaction were proposed including platinum based alloy catalysts, e.g. PtRu [4] and PtSn [5] alloy or platinum decorated by oxides such as SnO₂ [6], RuO₂ [7] and ZrO₂ [8] to increase CO tolerance based upon the bi-functional mechanism [9] and the electronic effect [10]. Recently, more and more works have been focused on the system of combining metal oxides, C and Pt.

Titanium dioxide, which is well known for its high catalytic activity, stability in acidic or alkaline solutions and non-toxic properties, has been widely used as photocatalysts to carry out oxidation of methanol under UV excitation [11,12]. In contrast with previous work, Kamat et al. [13] found that TiO₂ can improve the performance of the Pt–Ru catalyst for methanol oxidation not only under UV excitation but also in dark because of surface area improvement or diminished poisoning effects. Recently, it had also been demonstrated that Pt–TiO₂/CNTs had higher electro-catalytic activity and CO-tolerance for ethanol oxidation in our lab [14]. Titania nanotubes (TNT) prepared from TiO₂ nanoparticles have some great potential as materials with novel properties that are not found in conventional TiO₂. It has been proved that they have larger surface area and higher photocatalytic activity than TiO₂ [15] and as support of Pd have presented excellent catalytic activity for methanol oxidation in acid solution [16].

Herein, novel titanate nanotubes were selected as the co-catalyst to promote Pt/C (E-TEK; 20 wt.% Pt on Vulcan) catalyst for ethanol electro-oxidation and compared it with Pt/C and TiO₂/Pt/C catalysts in terms of the electrochemical activity for ethanol oxidation using cyclic voltammetry (CV), chronoamperometry and CO stripping voltammetry at 25 °C in acidic solutions.

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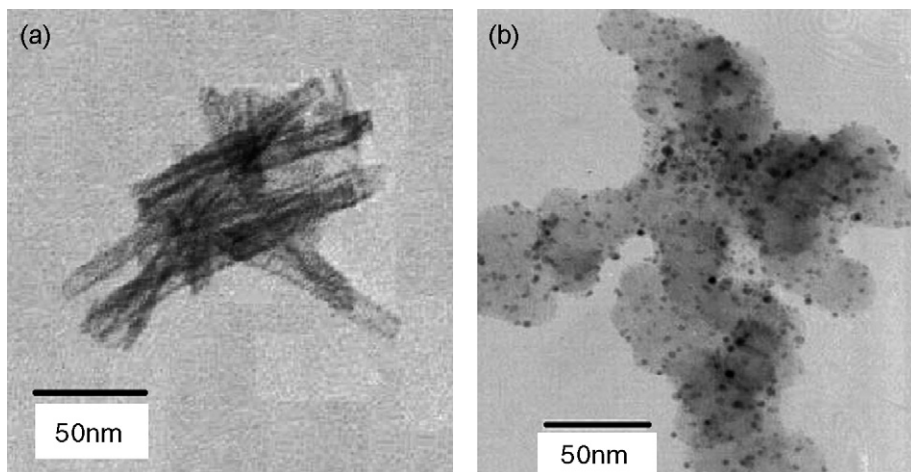


Fig. 1. TEM images of TiO₂ nanotubes (a) and Pt/C catalysts (b).

2. Experimental

The titanium dioxide powders were prepared using sol–gel method [17]. The so-prepared anatase titanium dioxide powders were put into a 250 mL Nalgene flask with 100 mL of sodium hydroxide aqueous solution with the concentration of 10 M to prepare TNT. The flask was then maintained for 24 h at 110 °C in an oil bath. The treated powders were washed well with 0.1N hydrochloric acid aqueous solution and distilled water and were subsequently separated from the washing solution by centrifugation. This operation was repeated until the washing water showed pH < 7. Then the precipitates were dried in vacuum at 80 °C for 5 h [18,19].

The surface morphology of the catalyst has been observed on transmission electron micrograph (TEM JEM-1200EX) at 100 kV acceleration voltage for conventional and X-ray diffraction (XRD) analysis was performed using the Rigaku X-ray diffractometer with Cu K α -source. The 2θ angular regions between 20° and 80° or 20° and 90° were explored at a scan rate of 6° min⁻¹ with step of 0.02°. The thermal gravity analysis (TGA) result was examined by a Universal V5.3C 2050 Instrument within the temperature range of room temperature to 800 °C with the scanning rate of 10 °C min⁻¹.

The catalysts slurry contained 16.6% anatase TNT (or TiO₂) and 83.4% Pt/C (E-TEK; 20 wt.% Pt on Vulcan) that meant the weight ratio of TNT(or TiO₂): Pt closed to 1:1, were deposited on gold electrode (1 cm in diameter) to determine their ethanol oxidation activity. The catalysts slurry was prepared by mixing Pt/C with TNT (or TiO₂) in distilled water under sonicate for 30 min, and then adding Nafion (20% Nafion and 80% ethylene glycol) solution for another 10 min. After casting, the catalysts were air-dried for 60 min at 80 °C. These as-prepared catalysts were named TNT/Pt/C (or TiO₂/Pt/C). Electrochemical measurements were carried out in a three electrode cell using a Solartron workstation at 25 °C. A gold patch (1 cm × 1 cm) coated with catalyst ink was used as working electrode. A saturated calomel electrode (SCE) and Pt gauze were used as reference and counter electrodes, respectively. All electrode potentials in this paper are referred to the SCE. A solution of 1 M

HClO₄ or 1 M C₂H₅OH + 1 M HClO₄ was used as electrolyte. All the reagents used were of analytical grade. The activation scans were performed until reproducible voltammograms were obtained. Cyclic voltammograms were recorded in the potential range of –0.2 to 1 V versus SCE at a scan rate of 50 mV s⁻¹. Only the last cycle of 50 cycles was used for comparison of the catalytic activity of the specified catalysts and the chronoamperometric curves were recorded at 0.45 V for 3600 s. The oxidation of pre-adsorbed carbon monoxide (CO) was measured by CO stripping voltammetry in 1 M HClO₄ solution at a scan rate of 10 mV s⁻¹.

3. Results and discussion

Fig. 1 shows transmission electron micrographs (TEM) of TNT and Pt/C (E-TEK; 20 wt.% Pt on Vulcan) catalyst. As shown in Fig. 1a, numerous tube-like structures, which are about 100 nm in length and 8 nm in diameter, were observed. Moreover, these nanotubes were very uniform. The XRD spectrum in Fig. 2a indicated that all peaks shown can be indexed to the anatase TiO₂. The raw material, nanocrystalline anatase TiO₂ (Fig. 2c) can directly convert to anatase TNT through the chem-

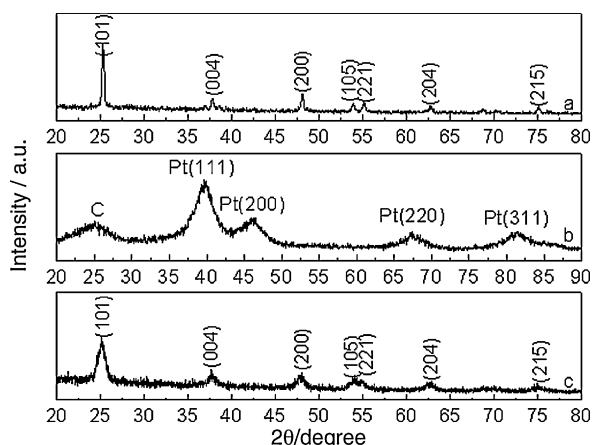


Fig. 2. XRD patterns of TiO₂ nanotubes (a), Pt/C (b) and anatase TiO₂ (c).

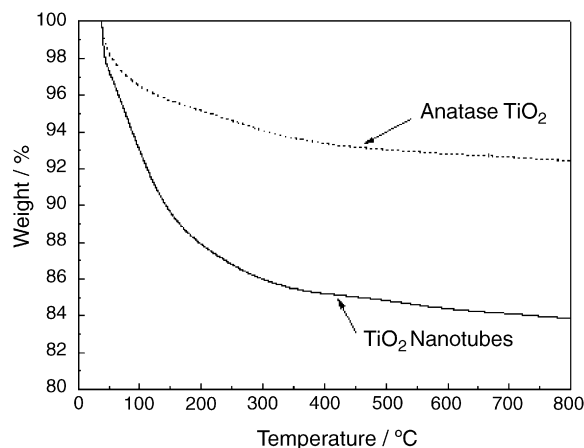


Fig. 3. TGA curves of TiO_2 nanotubes and anatase TiO_2 within the temperature range of room temperature to 800°C .

ical treatment. The TGA results for TNT and TiO_2 in Fig. 3 indicated that the amount of H_2O contained in the TNT was much more than that in anatase TiO_2 prior to undergoing chemical treatment. Fig. 1b shows that Pt/C (E-TEK; 20 wt.% Pt on Vulcan) catalyst had nice structure of the small and uniform platinum particles dispersing on carbon black (Vulcan XC-72). The characteristic XRD peaks of platinum in Fig. 2b can be indexed as the face-centered cubic phase and the particle size calculated from Pt(2 2 0) using Scherrer formula after background subtraction is 3.2 nm, which is agreed well with the results of TEM observation. This structure decides that Pt/C catalyst as commercial catalyst should have good performance for methanol or ethanol oxidation in DAFC, but the truth is not like that because the platinum can be poisoned by CO and cannot be used efficiently. Herein, the unique structure of TiO_2 nanotubes and the more H_2O contained in TNT may play an important role in increasing the utilization rate of platinum and synergetic interaction between Pt and TNT.

The as-prepared TNT/Pt/C catalysts were tested for their catalytic activity in the oxidation of ethanol. In order to further investigate the role played by the TNT, TiO_2 /Pt/C and Pt/C catalyst were also tested in the same condition for comparison. Fig. 4 shows cyclic voltammetry curves recorded for the prepared and reference catalysts in the supporting electrolyte of $1\text{ M C}_2\text{H}_5\text{OH} + 1\text{ M HClO}_4$. It can be seen that TNT/Pt/C displayed a 1.87 times higher current density compared to Pt/C catalyst and 1.45 times higher than TiO_2 /Pt/C. Considering that TNT/Pt/C, TiO_2 /Pt/C and Pt/C had identical Pt loading, the TNT/Pt/C appeared significantly more active for ethanol oxidation. Furthermore, the onset potentials of TNT/Pt/C (0.43 V versus SCE) were lower than those of TiO_2 /Pt/C (0.53 V versus SCE) and Pt/C (0.52 V versus SCE) though the peak potentials (0.81 V versus SCE) were a little higher than TiO_2 /Pt/C (0.80 V versus SCE) and Pt/C catalyst (0.79 V versus SCE), this fact indicated that TNT/Pt/C catalysts have higher catalytic activity for ethanol oxidation at low potential than TiO_2 /Pt/C and Pt/C catalysts due to the addition of TNT.

Chronoamperometric curves were measured at 0.45 V for TNT/Pt/C, TiO_2 /Pt/C and Pt/C catalysts in $1\text{ M C}_2\text{H}_5\text{OH} + 1\text{ M}$

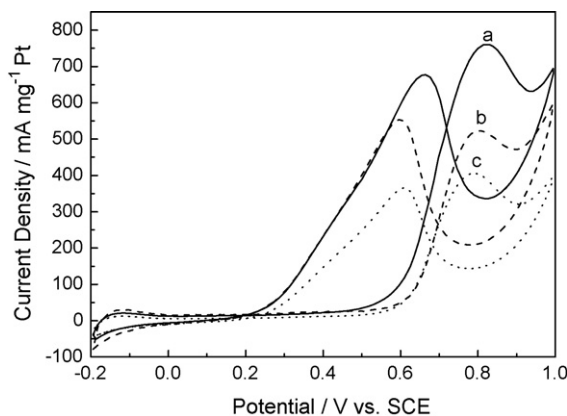


Fig. 4. Cyclic voltammogram curves for ethanol electro-oxidation at TNT/Pt/C (a), TiO_2 /Pt/C (b) and Pt/C (c) electrode in $1\text{ M C}_2\text{H}_5\text{OH} + 1\text{ M HClO}_4$ solutions with a scan rate of 50 mV s^{-1} .

HClO_4 and shown in Fig. 5. For this experiment, a potential step from the open circuit potential to 0.7 V was used. After 2 s, the potential was stepped to 0.3 V for 2 s, and then stepped to 0.45 V , and the current–time curve was recorded for 3600 s. As shown, the ethanol oxidation current density at TNT/Pt/C electrode is higher and the current density decay is much slower than that at TiO_2 /Pt/C and Pt/C electrode, though the current decay with time was observed for the three electrodes. This result illustrated that TNT/Pt/C catalysts have higher catalytic activity and better stability for ethanol oxidation than TiO_2 /Pt/C and Pt/C catalysts, which is in agreement with the results of cyclic voltammetry curves.

To understand the reason why TNT can promote the catalytic activity of Pt/C greatly, we hypothesized that TNT can prevent the catalyst from aggregation or deformation during the ethanol oxidation. Indeed the direct evidence, in Fig. 6, is shown by the increase of hydrogen desorption area. In order to get a more exact information, the electrochemical active surface (EAS) areas of the electrodes, which was proportional to the true surface area of Pt, were measured from the charge for hydrogen desorption according to Ref. [20] and the calculated results were

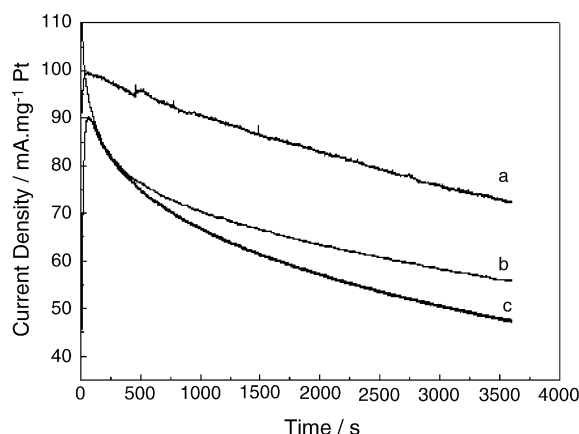
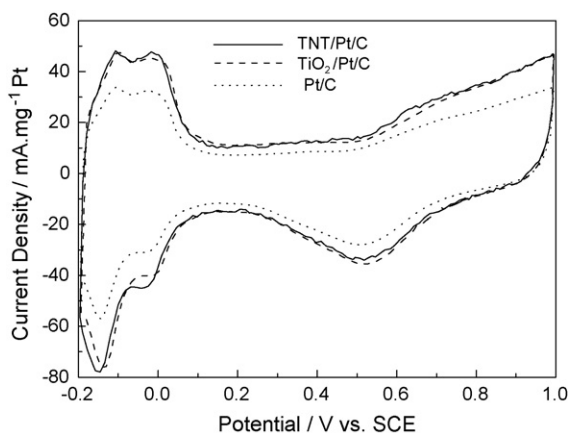


Fig. 5. Current density-time curves at 0.45 V for 3600 s at TNT/Pt/C (a), TiO_2 /Pt/C (b) and Pt/C (c) electrode in $1\text{ M C}_2\text{H}_5\text{OH} + 1\text{ M HClO}_4$ solutions.

Table 1

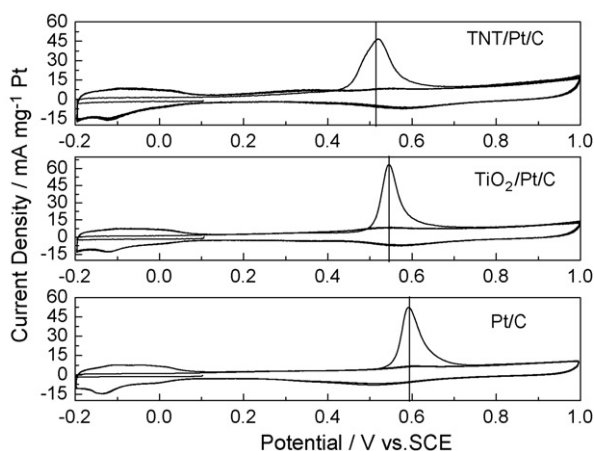
Comparison of the as-prepared catalysts and the commercial Pt/C (20 wt.% Pt, E-TEK) in terms of EAS, ethanol and CO electro-oxidation

Catalyst	Ethanol electro-oxidation			EAS, S_g ($\text{cm}^2 \text{mg Pt}$)	CO electro-oxidation	
	Peak current density (mA mg Pt^{-1})	Onset potential (V)	Peak potential (V)		Onset potential (V)	Peak potential (V)
TNT/Pt/C	761	0.43	0.81	766	0.36	0.51
TiO ₂ /Pt/C	524	0.53	0.80	764	0.46	0.54
Pt/C	407	0.52	0.79	551	0.50	0.59

Fig. 6. Cyclic voltammogram curves in 1 M HClO₄ solutions with a scan rate of 50 mV s⁻¹.

listed in Table 1. It can be seen that the EAS for TNT/Pt/C and TiO₂/Pt/C catalyst were almost the same and were 1.39 times bigger than Pt/C catalyst. These showed that both TNT and TiO₂ can enhance the true surface area of Pt, but the catalytic activity of TNT/Pt/C catalyst for ethanol electro-oxidation was much higher than that of TiO₂/Pt/C. So, it was inferred that the introduced TNT had other advantages besides preventing catalyst from aggregating.

As the CO species are the main poisoning intermediate during ethanol electro-oxidation, a good catalyst should possess excellent CO electro-oxidation ability, which can be verified by CO stripping test. In Fig. 7, CO stripping curves for TNT/Pt/C, TiO₂/Pt/C and Pt/C catalysts are shown. Significant difference

Fig. 7. CO stripping voltammograms in 1 M HClO₄ solutions with a scan rate of 10 mV s⁻¹.

in CO oxidation potential was observed. CO oxidation potential for TNT/Pt/C catalyst was between 0.36 and 0.66 V versus SCE, which is much lower than TiO₂/Pt/C catalyst (between 0.46 and 0.67 V versus SCE) and Pt/C (between 0.50 and 0.72 V versus SCE), although the peak current density for TNT/Pt/C catalyst has no large distinctness with TiO₂/Pt/C and Pt/C catalyst. These results demonstrated that TNT/Pt/C catalyst can oxidize CO more quickly at lower potential than TiO₂/Pt/C and Pt/C catalyst, which is helpful for releasing the active sites of Pt at low potential for further oxidation of ethanol in direct ethanol fuel cell (DEFC).

Watanabe et al. [21] have ever detected that the water molecule absorbed on PtRu alloy can be activated to form oxygen-containing species (OHads) on the Ru surface at lower potential by ATR-IRAS technique. These oxygen-containing species reacted with CO-like intermediate species on Pt surface to release the active sites for further alcohol oxidation by so-called “bi-functional mechanism”. Lamy et al. [22] presented that the rate-determining step for CO electro-oxidation at the Pt_xRu_y electrode is the formation of adsorbed OH on the Ru surface (Ru–OH bond). Rolison et al. [23,24] further found that hydrous ruthenium oxidation is very favorable for the bi-functional mechanism because of inherent surface–Ru–OH bond on RuO_xH_y. As to the system of TNT/Pt/C catalysts, Kasuga et al. [18] have presented the amount of H₂O contained in the titanium nanotubes was more than 20 times higher than that in TiO₂ prior to undergoing chemical treatment and as shown in Fig. 3. Titania nanotubes contained much more structural water in itself than TiO₂. The inherent TNT–OH bonds on TNT/Pt/C can directly donate hydroxide species to platinum sites to oxidize CO as the way hydrous ruthenium oxidation does, which in conclusion leads to the excellent catalytic activity for ethanol oxidation at TNT/Pt/C electrode. In contrast, TiO₂ must activate the H₂O in the electrolyte at a certain potential to form hydroxide species to oxidize CO for further ethanol oxidation. This was also one possible reason of the observed higher current density and dramatic difference in current decay at TNT/Pt/C electrode in Fig. 5 and the other proposed reason was the nature of hydrophilic tube-structure of TNT, which favors quicker mass diffusion in catalytic layer during the ethanol oxidation.

Additionally, tube-like structure of TiO₂ nanotubes have larger specific surface area than TiO₂ [15] and are proposed to trap more ethanol to increase the local concentration of ethanol around Pt, which can further make ethanol oxidize more easily on TNT/Pt/C catalyst. The in situ FTIR and other methods are being used to further study the reaction mechanism.

4. Conclusions

The results presented in this study indicated that the catalytic activities of Pt/C catalysts for ethanol electro-oxidation were greatly improved due to the addition of TiO₂ nanotubes, which proved that the system of Pt, C and TiO₂ nanotubes was a promising direction for developing anode catalysts of ethanol oxidation. The TEM and XRD showed that the prepared anatase TiO₂ nanotubes have uniform length and diameter distribution. The TGA results illustrated that the amount of H₂O contained in the TNT was much more than that in anatase TiO₂ prior to undergoing chemical treatment. The CV and chronoamperometric curves demonstrated that the TNT/Pt/C catalysts have higher catalytic activity and better stability for ethanol electro-oxidation. The corresponding CO stripping potential shifted to lower direction than TiO₂/Pt/C and pure Pt/C catalysts, indicating that TiO₂ nanotubes can make CO electro-oxidation easier, which is helpful for ethanol electro-oxidation and the possible mechanism was proposed.

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References

- [1] T. Zhang, Q.M. Wang, *J. Power Sources* 140 (2005) 72–80.
- [2] R. Dillon, S. Srinivasan, A.S. Aricò, V. Antonucci, *J. Power Sources* 127 (2004) 112–126.
- [3] B.D. Lee, D.H. Jung, Y.H. Ko, *J. Power Sources* 131 (2004) 207–212.
- [4] E.V. Spinacé, A.O. Neto, T.R.R. Vasconcelos, M. Linardi, *J. Power Sources* 137 (2004) 17–23.
- [5] L.H. Jiang, G.Q. Sun, Zh.H. Zhou, W.J. Zhou, Q. Xin, *Catal. Today* 93–95 (2004) 665–670.
- [6] L.H. Jiang, G.Q. Sun, Zh.H. Zhou, Sh.G. Sun, Q. Wang, Sh. Y. Yan, H.Q. Li, J. Tian, J.S. Guo, B. Zhou, Q. Xin, *J. Phys. Chem. B* 109 (2005) 8774–8778.
- [7] L. Cao, F. Scheiba, Ch. Roth, F. Schweiger, C. Cremers, U. Stimming, H. Fuess, L.Q. Chen, W.T. Zhu, X.P. Qiu, *Angew. Chem. Int. Ed.* 45 (2006) 5315–5319.
- [8] Y.X. Bai, J.J. Wu, J.Y. Xi, J.Sh. Wang, W.T. Zhu, L.Q. Chen, X.P. Qiu, *Electrochem. Commun.* 7 (2005) 1087–1090.
- [9] J.M. L'eger, S. Rousseau, C. Coutanceau, F. Hahn, C. Lamy, *Electrochim. Acta* 50 (2005) 5118–5125.
- [10] C. Lu, C. Rice, R.I. Masel, P.K. Babu, P. Waszczuk, H.S. Kim, E. Oldfield, A. Wieckowski, *J. Phys. Chem. B* 106 (2002) 9581–9589.
- [11] J. Marugán, D. Hufschmidt, M.J. López-Muñoz, V. Selzer, D. Bahnemann, *Appl. Catal. B: Environ.* 62 (2006) 201–207.
- [12] A. Yamakata, T. Ishibashi, H. Onishi, *J. Phys. Chem. B* 106 (2002) 9122–9125.
- [13] K. Drew, G. Girishkumar, K. Vinodgopal, P.V. Kamat, *J. Phys. Chem. B* 109 (2005) 11851–11857.
- [14] H.Q. Song, X.P. Qiu, F.S. Li, W.T. Zhu, L.Q. Chen, *Electrochem. Commun.* 9 (2007) 1416–1421.
- [15] M. Adachi, Y. Murata, M. Harada, *Chem. Lett.* 8 (2000) 942–944.
- [16] M. Wang, D.J. Guo, H.L. Li, *J. Electrochem. Soc.* 178 (2005) 1996–2000.
- [17] J. Hu, J.G. Deng, S.Y. He, Z.G. Chang, J.S. Zhao, J.N. Liu, *Chin. Mater. Sci. Eng.* 19 (2001) 71–73.
- [18] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Adv. Mater.* 11 (1999) 1307–1311.
- [19] T. Kasuga, M. Hiramatsu, A. Hoson, T. Sekino, K. Niihara, *Langmuir* 14 (1998) 3160–3163.
- [20] R.Zh. Yang, X.Q. Qiu, H.R. Zhang, J.Q. Li, W.T. Zhu, Zh.X. Wang, X.J. Huang, L.Q. Chen, *Carbon* 43 (2005) 11–16.
- [21] T. Yajima, N. Wakabayashi, H. Uchida, M. Watanabe, *Chem. Commun.* (2003) 828–829.
- [22] A. Kabbabi, R. Faure, R. Durand, B. Bedan, F. Hahn, J.-M. Leger, C. Lamy, *J. Electroanal. Chem.* 444 (1998) 41–53.
- [23] K.E. Swider, C.I. Merzbacher, P.L. Hagans, D.R. Rolison, *J. Non-Cryst. Solids* 225 (1998) 348–352.
- [24] D.R. Rolison, P.L. Hagans, K.E. Swider, J.W. Long, *Langmuir* 15 (1999) 774–779.