Short communication

Carbon nanotubes supported PtPd hollow nanospheres for formic acid electrooxidation

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ABSTRACT

Carbon nanotubes (CNTs) supported PtPd hollow nanospheres have been prepared by a replacement reaction between sacrificial cobalt nanoparticles and $PtCl_6^{2-}$, Pd^{2+} ions. The morphology, elemental composition, structure and electrocatalytic properties of the PtPd hollow nanospheres have been investigated by transmission electron microscopy, energy dispersive X-ray spectroscopy, X-ray diffraction and typical electrochemical methods, respectively. The results indicate that the CNTs supported PtPd hollow nanospheres have excellent electrochemical properties for the electrooxidation of formic acid (high electrocatalytic activity and excellent stability) due to the high surface area resulted from the hollow nanosphere structure with porous shell.

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1. Introduction

In the past decades, fuel cells become the promising power sources due to their high-energy conversion efficiency and environmental affinity. Generally, methanol is considered as one of the most promising fuels in fuel cells. But methanol has innate toxicity, sluggish anodic oxidation kinetics, and fuel crossover problem in Nafion-based membranes. Compared to methanol, although the theoretical energy density of formic acid is only about half of methanol (formic acid, 2086 Wh L^{-1}; methanol, 4690 Wh L^{-1}) [1], the direct formic acid fuel cells have the higher theoretical open circuit potential and lower fuel crossover for higher concentration of fuel [2,3] than the direct methanol fuel cells. Formic acid, as a non-explosive liquid at room temperature and non-toxic chemical, can be used in small portable fuel cell applications [4].

For formic acid electrooxidation, there are dual path mechanisms [5–11], namely the "direct pathway" and "CO pathway". In the "direct pathway", the formic acid is directly oxidized to CO_2 without the formation of carbon monoxide intermediate. In the "CO pathway", the formic acid is first oxidized to an intermediate like CO that bonds strongly to the catalyst surface and impedes the adsorption of fuel species, and then the CO-like intermediate is oxi-

dized further to CO_2. It has been reported that the electrooxidation of formic acid on Pt surfaces adopts both the "direct pathway" and the "CO pathway" [12–16]. Recently, various efforts have been made to the mitigation of the CO poisoning phenomenon to enhance the oxidation rate of formic acid on Pt catalysts, such as by alloying Pt with other metals [17–19]. In particular, the introduction of palladium in catalysts has been studied widely, such as Pt single crystals covered electrolytically by Pd [20,21], Pd "decorated" polycrystalline Pt [13], and the modification by Pd as a PtPd alloy [22].

Another effective method to enhance the electrocatalytic activity of catalysts is the core–shell construction [23–25] of the nanosized particles that exhibits different properties from their individual component or nanoparticle counterpart. Hollow metal nanostructures have been attended as the prolongation of the core–shell construction due to their high surface area, low density, economy and effective catalytic activities [26–29]. Herein, we report the PtPd hollow nanospheres for formic acid electrooxidation for the first time. PtPd hollow nanospheres were prepared by a replacement reaction between sacrificial cobalt nanoparticles and $PtCl_6^{2-}$, Pd^{2+} ions. The morphology and structure of the PtPd hollow nanospheres were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). Using the carbon nanotubes (CNTs) as the supporting material of catalyst, the electrocatalytic properties of the CNTs supported PtPd hollow nanospheres for formic acid oxidation have been investigated by typical electrochemical methods.

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2. Experimental

2.1. Materials

CNTs (20–40 nm in diameter) used in this paper were obtained from Shenzhen Nanotech Port Company (China) and purified by refluxing in concentrated nitric acid for 6 h. Nafion ethanol solution (5 wt.%) was obtained from Aldrich. All chemicals used were of analytical grade and fresh double-distilled water was used throughout.

2.2. Preparation of the PtPd hollow nanospheres

The procedure for the preparation of PtPd hollow nanospheres is as follows: firstly, the sacrificial cobalt nanoparticles were prepared by the reduction of $CoCl_2$ (12 mL, 5 mM) aqueous solution with $NaBH_4$ as the reductant and citric acid as the stabilizer. The colour change of the solution from pink to brown indicated the formation of cobalt nanoparticles. The cobalt nanoparticle suspension was then stirred continuously for 1 h to decompose the un-reacted $NaBH_4$. Secondly, H_2PtCl_6 (38.6 mM, 0.52 mL) and $PdCl_2$ (27.9 mM, 0.72 mL) were dissolved in 50 mL double-distilled water and the mixed aqueous solution was added dropwise into the above cobalt nanoparticle suspension under vigorous magnetic stirring. Cobalt nanoparticles were oxidized immediately to cobalt ions by $PtCl_6{}^{2-}$ and Pd^{2+} in the solution and the solution colour changed gradually to black. This implied the PtPd hollow nanospheres were formed. In order to ensure the cobalt nanoparticles were oxidized completely and the PtPd hollow nanospheres were formed on the basis of the stoichiometric relationship, the reaction continued for 1 h. The obtained PtPd hollow nanospheres were marked as 1-PtPd and the morphology was investigated by TEM.

2.3. Preparation and characterization of the CNTs supported PtPd hollow nanosphere catalysts

In the above 1-PtPd suspension, a definite amount of CNTs solution (34 mg CNTs dispersed in 20 mL H_2O) was added. The mixed solution was stirred for 1 h. The products were filtered, washed several times with double-distilled water and dried in the vacuum oven at 60 °C for 8 h and labelled as 1-PtPd/CNTs catalyst. The metal content in the 1-PtPd/CNTs catalyst was determined by the inductively coupled plasma-atom emission spectroscopy (ICP-AES) and equal to about 14.2 wt.%, and the atomic ratio of Pt to Pd was 1.

The elemental composition and crystalline structure of the 1-PtPd/CNTs catalyst were investigated by energy dispersive X-ray spectroscopy (EDS, INCA) and XRD, respectively.

Electrochemical measurements were performed on an Autolab PGSTAT12 with a conventional three-electrode glass cell. A Pt wire was used as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was prepared as follows: (1) the catalyst ink was produced by dispersing 1-PtPd/CNTs catalyst in double-distilled water under ultrasonic stirring for 15 min and the concentration of the catalyst was kept at 1 mg mL^{-1}; (2) 100 μL catalyst ink was transferred to the surface of the graphite electrode (0.72 cm^2) by a micro-syringe. The quantity of the metallic PtPd in the catalyst loaded on the graphite electrode is 15 μg. After dried in air, the electrode was coated with 15 μL of 0.05 wt.% Nafion ethanol solution. All experiments were carried out at ambient temperature.

For comparison, another kind of PtPd nanocatalyst and Pt nanocatalyst were also prepared by the typical method. (1) PtPd nanoparticles: using $NaBH_4$ as the reductant, PtPd nanoparticles were obtained by adding freshly prepared $NaBH_4$ solution to the mixed solution of H_2PtCl_6 and $PdCl_2$. The obtained product was labelled as 2-PtPd. (2) Pt nanocatalyst: Pt nanoparticles were prepared by adding $NaBH_4$ solution into H_2PtCl_6 aqueous solution. According to the same procedure, the two kinds of the CNTs supported catalysts (2-PtPd/CNTs and Pt/CNTs) were also prepared and characterized. The quantity of the metallic PtPd (or Pt) in the 2-PtPd/CNTs (or Pt/CNTs) catalyst loaded on the graphite electrode is also 15 μg.

3. Results and discussion

3.1. Preparation and characterization of 1-PtPd catalyst

Fig. 1 shows the TEM images of the 1-PtPd catalyst. It can be observed obviously that 1-PtPd catalyst has hollow nanosphere structure, which is composed of an empty core with a PtPd shell. This result is similar with that observed in the preparation of hollow Pt nanospheres [28,29]. The diameter of the 1-PtPd nanospheres is statistically evaluated to be 15–30 nm and the thickness of the shell is about 4 nm. It should be noted that some of 1-PtPd catalysts are
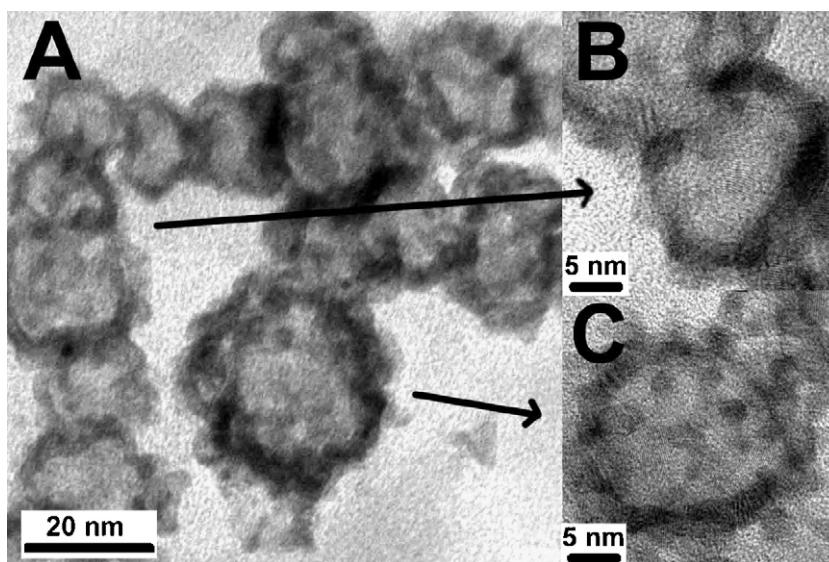

Fig. 1. TEM images of the PtPd hollow nanospheres (B) and (C), the partial region of (A) with high magnification.
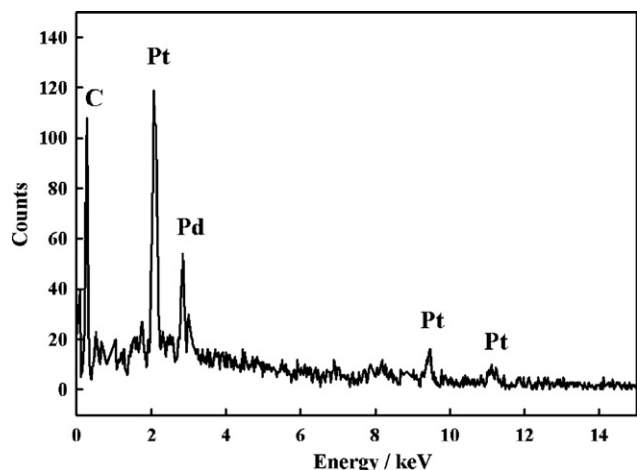
Fig. 2. EDS pattern of the PtPd hollow nanospheres supported on the carbon nanotubes.

dispersed as individual nanosphere and some connect with each other like a string of beads. The later should be due to the magnetic effect of the magnetic stirring instrument used in the preparation of 1-PtPd, because cobalt nanoparticles are magnetic. The more detail structural information is shown in Fig. 1B and C. From Fig. 1B, it is found that the connect wall is open in the string of beads. Furthermore, as observed in Pt hollow nanospheres [28,29], the shell of 1-PtPd catalysts is incomplete and porous (Fig. 1B and C), which may endow the hollow nanospheres with a high surface area and is beneficial to the electrocatalytic oxidation of formic acid. The reason of imperfectness of the shell is related to the ion migration during the formation of 1-PtPd catalysts. When the replacement reaction between cobalt and $PtCl_6^{2-}$, Pd^{2+} occurs, Co^{2+}, $PtCl_6^{2-}$ and Pd^{2+} continuously diffusing across the shell results in the porous structure of the shell.

In order to confirm the elemental composition of 1-PtPd hollow nanospheres, the EDS investigation has been carried out for the 1-PtPd/CNTs catalyst and the corresponding results are shown in Fig. 2. It indicates that Pt, Pd and C exist in the 1-PtPd/CNTs catalysts. The atomic ratio of Pt to Pd is about 1.2, which is close to the result obtained by ICP-AES. It is noted that Co element is not observed, which indicates that the sacrificial Co core is completely reacted.

On other hand, in order to investigate the effect of the hollow structure on the electrocatalytic properties of PtPd catalysts, another kind of PtPd nanocatalyst (2-PtPd) was also prepared by typical $NaBH_4$ reduction method. Fig. 3 shows the XRD results about 1-PtPd/CNTs and 2-PtPd/CNTs catalysts. The XRD diffraction patterns were collected using a fixed Cu Kα radiation. The spectra were obtained in the 2θ range from $10°$ to $90°$ at the scan rate of $0.04°/10$ s. In Fig. 3, the XRD patterns of both 1-PtPd/CNTs and 2-PtPd/CNTs catalysts are almost the same. The peak located at 2θ of about $26°$ corresponds to the CNTs [30]. Four other obvious peaks located at 2θ about $40.0°$, $46.5°$, $68.1°$ and $81.9°$ correspond to the different plane (1 1 1, 2 0 0, 2 2 0, 3 1 1) of PtPd alloy (indexed by PDF #65-6418). This implies that 1-PtPd and 2-PtPd catalysts are the bimetallic alloy and have the similar alloy degree. In addition, the crystallite size D of the prepared PtPd nanocatalysts was estimated using the Scherer equation as follows [31]:

$$D = 0.9 \frac{\lambda}{\beta \cos\theta} \tag{1}$$

where λ, β and θ are the X-ray wavelength (0.15405 nm), Bragg diffraction angle, and the full width at half-maximum of the diffraction peak, respectively. According to Fig. 3 and Eq. (1), the values of
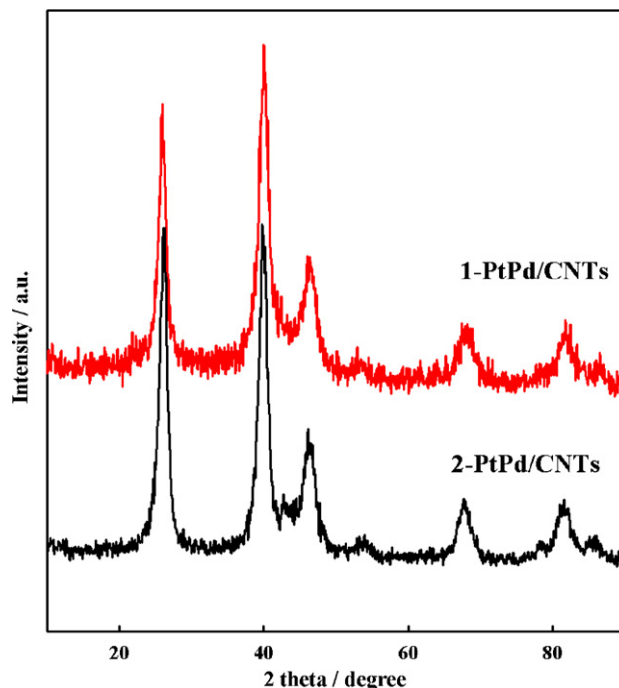

Fig. 3. XRD patterns of the 1-PtPd/CNTs and 2-PtPd/CNTs nanocatalysts.

the average crystallite sizes of 1-PtPd and 2-PtPd nanocatalysts are calculated to be about 4.7 nm and 4.6 nm, respectively. This implies that the 1-PtPd and 2-PtPd nanocatalysts have similar crystallite size. The above results indicate that the main factor affecting the electrocatalytic properties of the PtPd hollow nanospheres is the hollow structure with porous shell, not the crystallite size and alloy degree.

3.2. Electrochemical properties of the CNTs supported 1-PtPd electrode for formic acid oxidation

The electrocatalytic properties of the 1-PtPd/CNTs electrode for formic acid oxidation have been investigated in 0.5 M $HCOOH + 0.5$ M H_2SO_4 aqueous solution by cyclic voltammetry and the corresponding results are shown in Fig. 4. For comparison, the

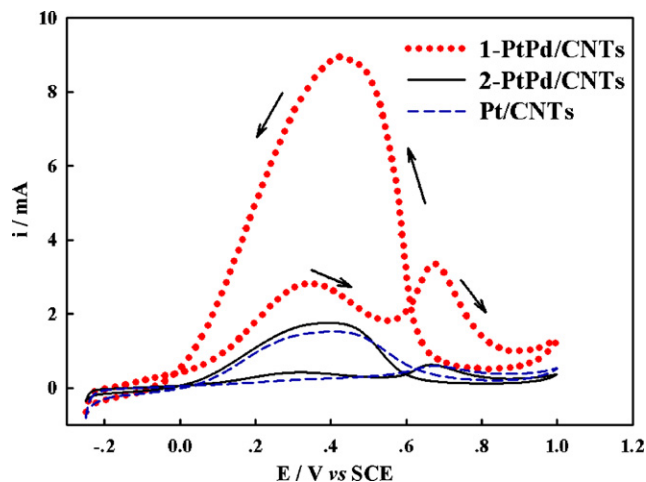**Fig. 4.** Cyclic voltammograms obtained on the 1-PtPd/CNTs, 2-PtPd/CNTs and Pt/CNTs electrodes in 0.5 M $HCOOH + 0.5$ M H_2SO_4 aqueous solutions at the scan rate of 50 mV s^{-1}. The loading mass of PtPd (or Pt), 15 μg.
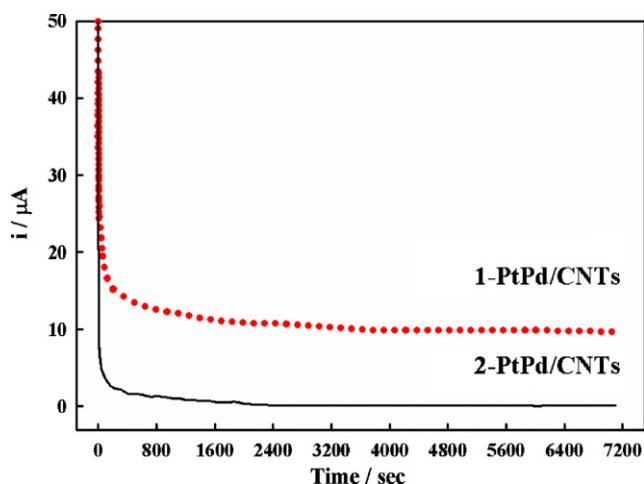
Fig. 5. Chronoamperograms obtained on the 1-PtPd/CNTs, 2-PtPd/CNTs and Pt/CNTs electrodes at 0.2 V (vs. SCE) in 0.5 M HCOOH + 0.5 M H_2SO_4 aqueous solutions. The loading mass of PtPd (or Pt), 15 μg.

Fig. 6. Cyclic voltammograms obtained on the 1-PtPd/CNTs, E-TEK PtRu/C and E-TEK Pt/C electrodes in 0.5 M HCOOH + 0.5 M H_2SO_4 aqueous solutions at the scan rate of 50 mV s^{-1}. The loading mass of PtPd (or Pt, PtRu), 15 μg.

Table 1
The specific mass activity (SA, mA mg^{-1}) of the different catalysts.

Catalyst	SA at 0.35 V (forward scan)	SA at 0.65 V (forward scan)	SA at 0.4 V (reverse scan)
1-PtPd/CNTs	200.14	237.52	633.69
E-Tek PtRu	39.77	138.45	214.25
E-Tek Pt	18.59	52.15	76.45

cyclic voltammograms of formic acid electrooxidation at the 2-PtPd/CNTs and Pt/CNTs electrodes are also presented in Fig. 4. On all electrodes with PtPd catalysts, there are two oxidation peaks on the forward branch and one anodic peak on the backward branch. The first oxidation peak of formic acid, which corresponds to the formation of CO_2 and is usually used to evaluate the electrocatalytic activity of the PtPd catalyst for formic acid oxidation, can be observed at about 0.35 V. But, there are two oxidation peaks (one on the forward branch and another on the backward branch) on the Pt/CNTs electrode. These results are in agreement with that reported in the literature [4]. Furthermore, it can be seen from Fig. 4 that the peak currents at about 0.35 V of formic acid oxidation on these catalysts have the following order: 1-PtPd/CNTs (2.82 mA)≫2-PtPd/CNTs (0.42 mA)>Pt/CNTs (0.27 mA). The value of the peak current on the 1-PtPd/CNTs electrode is 6.7 and 10.4 times as high as that on the 2-PtPd/CNTs and Pt/CNTs electrodes, respectively. The same orders are also observed for the peak currents at about 0.65 V and 0.4 V. This implies that the 1-PtPd/CNTs catalyst has highest activity for the electrooxidation of formic acid among these catalysts. The reasons may be that the 1-PtPd nanospheres have the highest specific surface area due to the hollow nanosphere structure with the porous shell (Fig. 1). This can be confirmed further from the results of the chronoamperometric investigation shown in Fig. 5. In Fig. 5, during the whole time, the current of formic acid oxidation on the 1-PtPd/CNTs electrode is much higher than that on the 2-PtPd/CNTs electrode. After the experiments run 2 h, the steady-state current of the 1-PtPd/CNTs electrode is 9.73 μA and 64.8 times as high as that of the 2-PtPd/CNTs electrode (0.15 μA). This implies that the 1-PtPd/CNTs electrode has excellent electrocatalytic stability.

The electrocatalytic properties of the 1-PtPd/CNTs catalyst were also compared with that of the commercial catalysts (E-Tek 20 wt.% Pt/C and E-Tek 20 wt.% PtRu/C catalysts) supplied by the Gruppo De Nora Company and the corresponding results are shown in Fig. 6. In order to express more clearly, the specific mass activity (mA mg^{-1}, SA), defined by peak current density (mA cm^{-2}, i_p) per unit of the metal loading mass (mg cm^{-2}, M), is used to evaluate the electrocatalytic activity of catalyst for formic acid oxidation in this work, i.e. $SA = i_p/M$ [32]. It can be seen from Fig. 6 that the 1-PtPd/CNTs catalyst is superior to the commercial E-Tek Pt/C and E-Tek PtRu/C catalysts. The related results are summarized in Table 1. From Table 1, it is noted that the 1-PtPd/CNTs electrode has the highest electrocatalytic activity toward the electrooxidation of formic acid
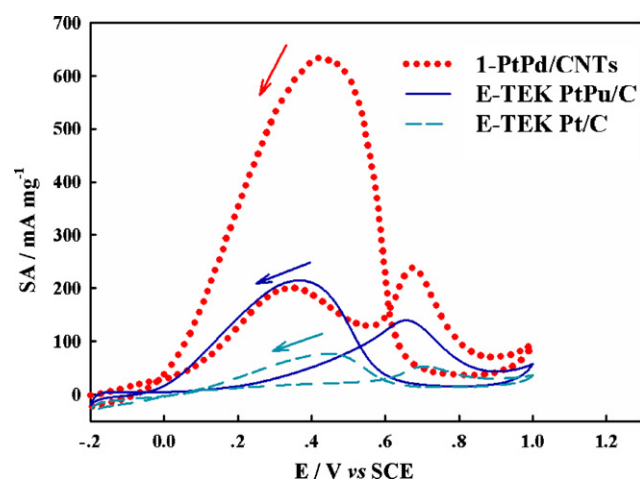
among these electrodes. The SA value at 0.35 V of the 1-PtPd/CNTs catalyst is 5.0 and 10.7 times as high as that of E-Tek PtRu/C and E-Tek Pt/C catalysts, respectively. This also implies that 1-PtPd/CNTs catalyst may have good potential application in direct formic acid fuel cell.

4. Conclusion

The bimetallic PtPd catalysts with the hollow nanosphere structure were prepared by employing cobalt metal nanoparticles as the sacrificial templates. The electrocatalytic properties of the PtPd hollow nanospheres for formic acid electrooxidation have been evaluated by the typical electrochemical methods. The results indicated that the CNTs supported PtPd hollow nanospheres had excellent electrochemical properties for the electrooxidation of formic acid (high electrocatalytic activity and excellent stability) due to the high surface area resulted from the hollow nanosphere structure with porous shell. Additionally, the electrocatalytic activity of the CNTs supported PtPd hollow nanospheres is 5.0 and 10.7 times as high as that of E-Tek PtRu/C and E-Tek Pt/C catalysts, respectively. The CNTs supported PtPd hollow nanospheres may be the good candidate as the electrocatalyst for formic acid oxidation.

References

[1] W.J. Zhou, J.Y. Lee, Electrochem. Commun. 9 (2007) 1725–1729.
[2] B.C.H. Steele, A. Heinzel, Nature 414 (2001) 345–352.
[3] Y.W. Rhee, S.Y. Ha, R.I. Masel, J. Power Sources 117 (2003) 35–38.

[4] S.Y. Wang, N. Kristian, S.P. Jiang, X. Wang, Electrochem. Commun. 10 (2008) 961–964.
[5] X. Xia, T.J. Iwasita, J. Electrochem. Soc. 140 (1993) 2559–2565.
[6] N.M. Markovic, P.N. Rorr Jr., Surf. Sci. Rep. 45 (2002) 117–229.
[7] P. Waszczuk, T.M. Barnard, C. Rice, R.I. Masel, A. Wieckowski, Electrochem. Commun. 4 (2002) 599–603.
[8] M.F. Mrozek, H. Luo, M.J. Weaver, Langmuir 16 (2000) 8463–8469.
[9] N. Markovic, H. Gaseiger, P. Ross, X. Jian, I. Villegas, M. Weaver, Electrochem. Acta 40 (1995) 91–98.
[10] J.H. Jiang, A. Kucernak, J. Electroanal. Chem. 520 (2002) 64–70.
[11] A. Capon, R. Parsons, J. Electroanal. Chem. 44 (1973) 1–7.
[12] C. Rice, S. Ha, R.I. Masel, P. Waszczuk, A. Wieckowski, T. Barnard, J. Power Sources 111 (2002) 83–89.
[13] G.-Q. Lu, A. Crown, A. Wieckowski, J. Phys. Chem. B 103 (1999) 9700–9711.
[14] R. Parsons, T. VanderNoot, J. Electroanal. Chem. 257 (1988) 9–45.
[15] J.D. Lović, A.V. Tripković, S.Lj. Gojković, K.Dj. Popović, D.V. Tripković, P. Olszewski, A. Kowal, J. Electroanal. Chem. 581 (2005) 294–302.
[16] M. Arenz, V. Stamenkovic, T.J. Schmidt, K. Wandelt, P.N. Ross, N.M. Markovic, Phys. Chem. Chem. Phys. 5 (2003) 4242–4251.
[17] L.J. Zhang, Z.Y. Wang, D.G. Xia, J. Alloys Compd. 426 (2006) 268–271.
[18] W. Chen, J. Kim, S. Sun, S. Chen, Phys. Chem. Chem. Phys. 8 (2006) 2779–2786.
[19] Y.J. Leng, X. Wang, I.M. Hsing, J. Electroanal. Chem. 528 (2002) 145–152.
[20] M.J. Llorca, J.M. Feliu, A. Aldaz, J. Clavilier, J. Electroanal. Chem. 376 (1994) 151–160.
[21] M. Baldauf, D.M. Kolb, J. Phys. Chem. 100 (1996) 11375–11381.
[22] A. Capon, R. Parsons, J. Electroanal. Chem. 45 (1973) 205–231.
[23] J. Zeng, J. Yang, J.Y. Lee, W. Zhou, J. Phys. Chem. B 110 (48) (2006) 24606–24611.
[24] J. Trukevich, G. Kim, Science 169 (1970) 873–879.
[25] M.P. Mallin, C.J. Murphy, NanoLetters 2 (11) (2002) 1235–1237.
[26] S.-W. Kim, M. Kim, W.Y. Lee, T. Hyeon, J. Am. Chem. Soc. 124 (2002) 7642–7643.
[27] S.J. Oldenburg, G.D. Hale, J.B. Jackson, N.J. Halas, Appl. Phys. Lett. 75 (1999) 1063–1065.
[28] H.P. Liang, H.M. Zhang, J.S. Hu, Y.G. Guo, L.J. Wan, C.L. Bai, Angew. Chem. Int. Ed. 43 (2004) 1540–1543.
[29] J. Zhao, W.X. Chen, Y.F. Zheng, X. Li, J. Power Source 162 (2006) 168–172.
[30] X.F. Xie, L. Gao, Carbon 45 (2007) 2365–2373.
[31] N.S. Ramgir, Y.K. Hwang, I.S. Mulla, J.-S. Chang, Solid State Sci. 8 (2006) 359–362.
[32] B. Liu, J.H. Chen, X.X. Zhong, K.Z. Cui, H.H. Zhou, Y.F. Kuang, J. Colloid Interf. Sci. 307 (2007) 139–144.