Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 38 (2012) 3149–3153
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Selectively depositing Pt nanoparticles on pre-treated electrically conductive porous alumina and its electrochemical studies

Chunxi Hai [a,b], Takashi Shirai [a], Masayoshi Fuji [a,*], Feng Wang [b]

[a] *Ceramics Research Laboratory, Nagoya Institute of Technology, 3-101-1 Hommachi, Tajimi City, Gifu, Japan*
[b] *College of Materials Science and Engineering, Beijing University of Chemical Technology, PR China*

Received 3 October 2011; received in revised form 7 December 2011; accepted 8 December 2011
Available online 16 December 2011

Abstract

To fabricate a composite modified with uniformly dispersed metallic particles, in this paper, electrical conductive porous alumina (CPA) was firstly pre-treated with mixed acids followed by deposition of Pt nanoparticles via reductive reaction. Crystal structure of uniformly deposited Pt nanoparticles was confirmed to face centered cubic (fcc). Based on characterization results, selective surface modification was achieved by surface pre-treatment, by which various functional groups were grafted onto three-dimensional conductive networks. The electrochemical behaviors of as-fabricated composites conducted in acidic electrolyte confirmed their improved activities, which merited from novel structure of designed electrode.

Keywords: B. Composites; B. Surfaces; D. Al_2O_3; E. Electrodes

1. Introduction

Various carbon forms such as carbon black, active carbon, carbon fibers (CFs) and carbon nanotubes (CNTs) [1,2] have attracted a surge of interests in recently decades due to their outstanding properties and practical applications. So far, one of the most interesting research points is carbon-based heterogeneous composites. Basically, the commonly studied second unit includes metallic nanoparticles (Ag, Au, Ni, Cu and Pt [3–5]), polymers [6] and ceramics nanoparticles (ZrO_2, TiO_2, SiO_2, Al_2O_3, CeO_2, etc. [7–9]). Although extensive studies have been reported on exploring various carbon/ceramic composites [10–12] by various fabrication techniques (spark-plasma-sintering (SPS), hot press, etc. [15–17]), it is still a challenge to get a novel composite with good electrical conductivity and bending strength.

It is good news for researchers since the first report of binary electrically conductive porous alumina (CPA) by modified gelcasting method [13]. The mechanical strength of CPA is 20–30 MPa and the measured specific surface of CPA induced by converted nano-carbon is 196.1 m^2/g. Liu et al. reported the electrochemical activity of CPA in aggressive solution [14]. Considering its unique structure, it was interested to modify the surface of CPA by different chemicals [15–17]. As supported by these studies, it is feasible to fabricate ternary heterogenerous catalysts by deposition functional particles on the surface of CPA with suitable method. And the enhanced electrochemical activities of as-prepared composites also announced the potential application of metal/CPA as electrode in fuel cells. Herein, it is aimed to prepare a novel CPA-based composite with uniformly dispersed Pt nanoparticles. Electrochemical performance of as-prepared Pt/CPA composite was investigated in acidic electrolyte employing conventional three-electrode measuring system.

2. Materials and methods

2.1. Preparing Pt/CPA composite

Preparing technique of CPA is described in our former work [13–17]. For further investigation in this paper, as-prepared CPA was cut into small plates (10 mm × 20 mm × 2 mm). Chemicals used in this study were analytical grade without any further purification.

---

* Corresponding author. Tel.: +81 57 224 8110; fax: +81 57 224 8109.
E-mail address: fuji@nitech.ac.jp (M. Fuji).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.12.017

Firstly, CPA plates were pre-treated with concentrated mixed acid ($H_2SO_4/HNO_3 = 3:1$, v/v) as introduced in Ref. [15]. Secondly, 1.028 g of pre-treated CPA was soaked into 5 ml of H_2PtCl_6–alcohol (0.006 M) solution followed by evaporation at 60 °C for 24 h. Finally, the resulted sample was refluxed at 140 °C for 1 h in ethylene glycol (EG). As-resulted CPA deposited with Pt nanoparticles was denoted as Pt/CPA.

2.2. *Structural characterization*

Raman spectroscopy (JEOL, NRS-3100, JASCO, Japan), X-ray diffraction (XRD, Rint, Rigaku, Japan), field-emission scanning electron microscope (FE-SEM, JEOL, JSM7000F) equipped with energy dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy (XPS, SSX-100) were employed to characterize the composite Pt/CPA.

2.3. *Electrochemical characterization*

Electrochemical performances were conducted by employing potentiostat/galvanostat system (HZ-5000, HOKUTO DENKO, Co. Japan). Conventional three-electrode measuring system was constructed. Counter electrode was Pt plate and reference electrode was Ag/AgCl (saturated by KCl solution). 40 ml of 0.5 M H_2SO_4 was used as electrolyte.

3. Results and discussion

3.1. *Physico-chemical analysis*

As shown in Fig. 1, crystal structure of carbon in CPA is detected by employing graphite as reference material. Usually, Raman shift carried out in low energy phonon spectra, normally called radical breathing mode (RBM) in the range of 150–400 cm^{-1} and the high energy modes (HEM) at ∼1600 cm^{-1} [18]. Appearance of two modes in HEM, G-band at 1580 cm^{-1} (E_{2g} derived modes) due to the in-plane vibrational movement of carbon atoms and D-band at 1350 cm^{-1} induced by disorder (converting from sp^2 to sp^3), supports the quasi-graphitic structure of nano-carbon in CPA converted by reductive sintering in Ar [13]. The intensity ratio of D-band and G-band ($R = I_D/I_G$, as shown in Table 1) is utilized to monitor the surface defects induced by different factors. By reductive sintering, well gelled polymer networks by gelcasting can be converted to inner-connected carbon paths without large defects ($R_{CPA} = 0.54$, $R_{Graphite} = 0.58$). R value increases with further surface treatment and modification, which is mainly resulted from destructed sp^2 of C–C band in nano-carbon networks by mixed acids treatment. Anchored Pt nanoparticles attributes to the biggest R value of Pt/CPA [19].

Table 1
The intensity ratio of the D and G bands (I_D/I_G) obtained from Raman spectroscopy (Fig. 1).

Samples	$R = I_D/I_G$
Graphite	0.58
CPA	0.53
Acid-CPA	0.68
Pt/CPA	0.84

X-ray diffraction (XRD) diffraction pattern of samples as shown in Fig. 2 highlights the existence of Pt nanoparticles comparing with acid-treated CPA. The broader diffraction peak in the diffract grams peak at $2\theta = 24°$ reflects the existence of nano-carbon in CPA. As displayed in XRD patterns in Fig. 2(b), deposition of platinum on the functionalized CPA is clearly evident by characteristic platinum reflections of [1 1 1], [2 0 0], [2 2 0] and [3 1 1] crystallite planes [4]. All of these crystalline planes correspond to a face centered cubic (fcc) lattice structure for the platinum crystalline. More, the particles sizes are calculated according to the scherrer equation by [2 2 0] and [2 0 0] planes. Average value of calculated particles sizes lies about 4.95 nm.

FE-SEM images of acid-treated CPA are shown in Fig. 3(a). As it displays, cross-linked high porous alumina grains with

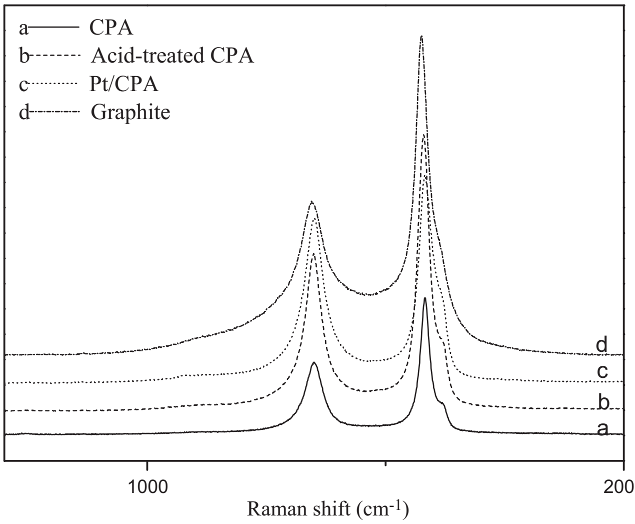

Fig. 1. Raman spectroscopy of (a) CPA, (b) acid-treated CPA, (c) Pt/CPA and (d) graphite as reference.

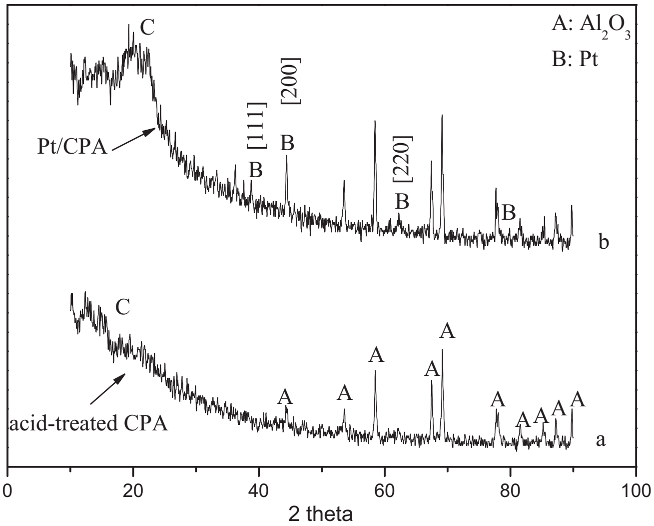

Fig. 2. X-ray diffraction patterns of (a) acid-treated CPA and (b) Pt/CPA (A means Al_2O_3 and B means Pt nanoparticles).

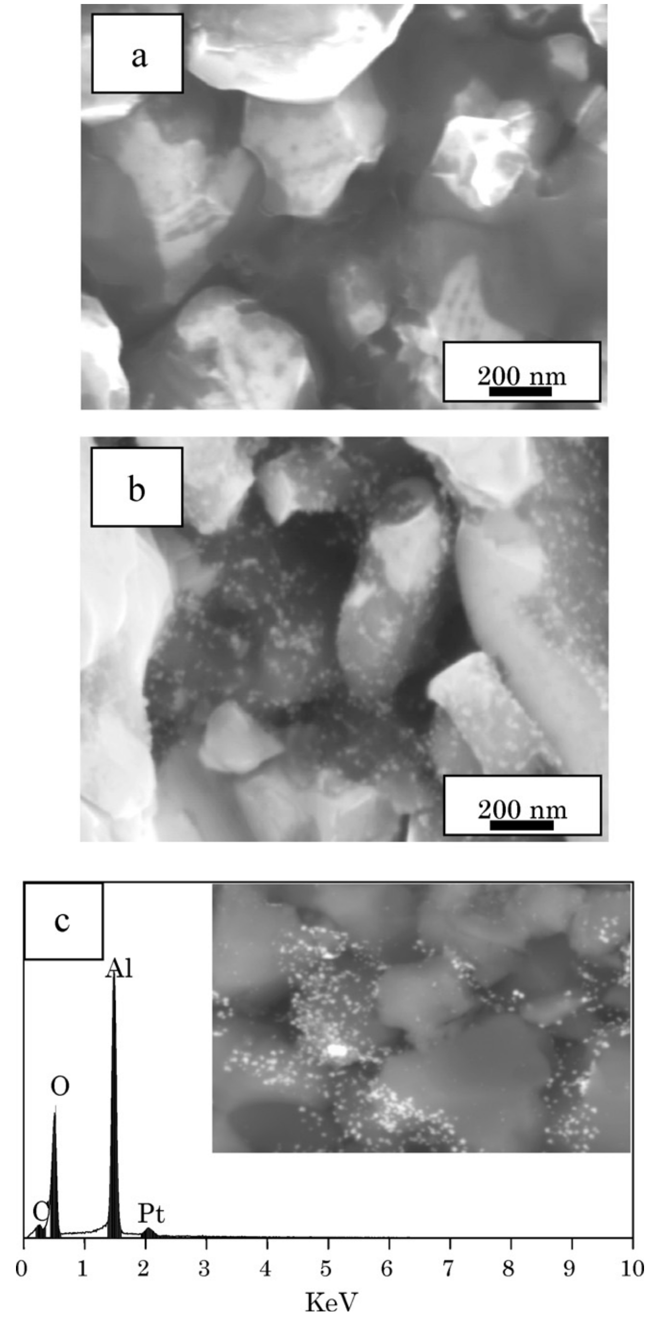

Fig. 3. FE-SEM images of (a) acid-treated CPA, (b) Pt/CPA and (c) EDS spectrum of Pt/CPA.

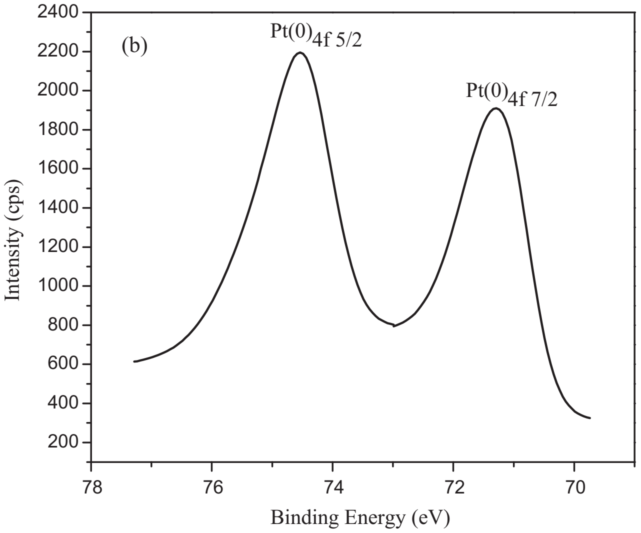

Fig. 4. X-ray photoelectron spectra of Pt 4f peak in Pt/CPA.

micro-size form physic-chemical stable matrix and three-dimensional nano-carbon networks (NCN) grow along inner-connected alumina grains resulting the electrical conductivity of CPA. NCN not only covers the Al_2O_3 grains but also connects the grain boundaries forming carbon networks. Comparing with (a), it is evidently (Fig. 3(b)) that the Pt nanoparticles are uniformly anchored onto the carbon networks with a size range of 5–10 nm in diameter (white dots). Metallic nanoparticles with little aggregation are facilitated to be deposited on nano-carbon networks than alumina grains [3–5], which merits from surface pre-treatment. The EDS analysis (Fig. 3(c)) shows that the deposited Pt content is about 7.13 wt.%. We also have measured the Pt 4f XPS spectra of Pt/CPA. As shown in Fig. 4, the double peaks of Pt $4f_{7/2}$ and Pt $4f_{5/2}$ around 71.07 and 74.4 eV [7] confirm the formation of nano-Pt (0) on CPA by reductive reaction.

Furthermore, briefly speaking, three steps were involved for making Pt/CPA. (a) Surface pre-treating, by which various surface defects on NCN with graphitic structure are available. These defects include five- or seven-membered rings in the carbon networks instead of normal ring, sp^3-hybridized defects (H or OH) and vacancies in the carbon lattice [20]. Pre-treating of CPA attributes to increased sp^3-hybridized defects (–COOH, –COH, etc.) [12]. (b) Absorption of Pt^{4+} onto substrate via electrostatic interaction and (c) chemical reduction of Pt^{4+} to Pt particles. This scheme is proposed in Fig. 5.

3.2. Electrochemical measurements

Cyclic voltammetry (CV) was carried out in 0.5 M H_2SO_4 in the potential range from 1.3 to −0.3 at a scan rate of 20 mV/s. Fig. 5(I) shows the CV curves of graphite, as-received CPA, pre-treated CPA and Pt/CPA. We have reported that surface pre-treatment with mixed acids resulted in increased electro-chemical activities of pre-treated CPA comparing with commonly utilized graphite electrode [15]. Enhanced performance is attributed to grafted functional groups by covalent modification. As shown in Fig. 5(II), as-received and pre-treated CPA display electro-catalytic activities toward oxygen reductive reaction (CRR), which can be proved by similar slopes of the reductive current with decreasing potential from −0.3 V to −0.2 V. Moreover, ORR occurred at potentials of −0.1 V to +0.4 V for Pt/CPA (Fig. 5(I)). It is believed that the ORR activity of the Pt/CPA at more positive potentials is attributed to Pt (5-d orbital vacancies) nanoparticles deposition. Enhanced performance of Pt/CPA can be rapidly increased current and enlarged time window as shown in Fig. 6(I). Meng et al. [21] reported the ORR activity of Pt/C at potentials of +0.7 V. Pt/CNT/CHIT (CHIT: chitosan solution) was also

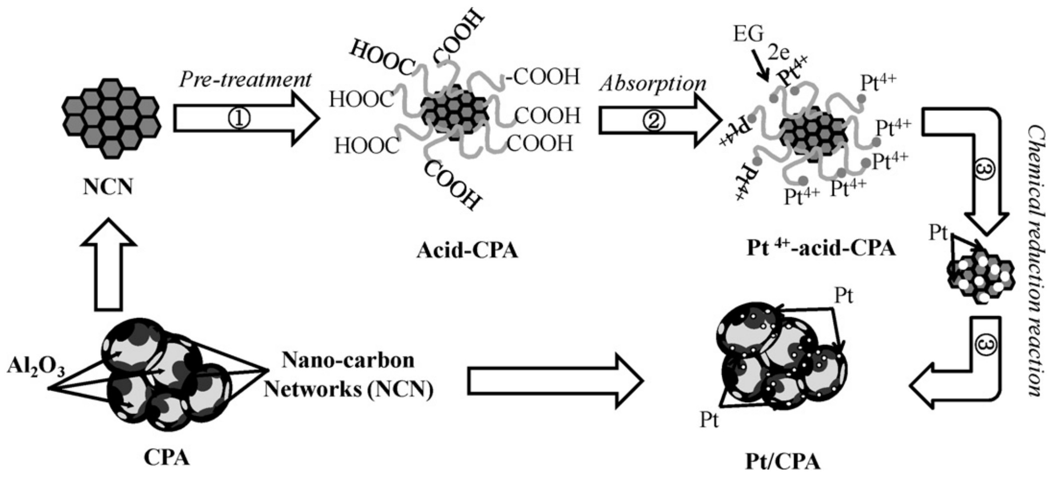

Fig. 5. Schematic representation of preparing Pt/CPA via chemical reductive reaction.

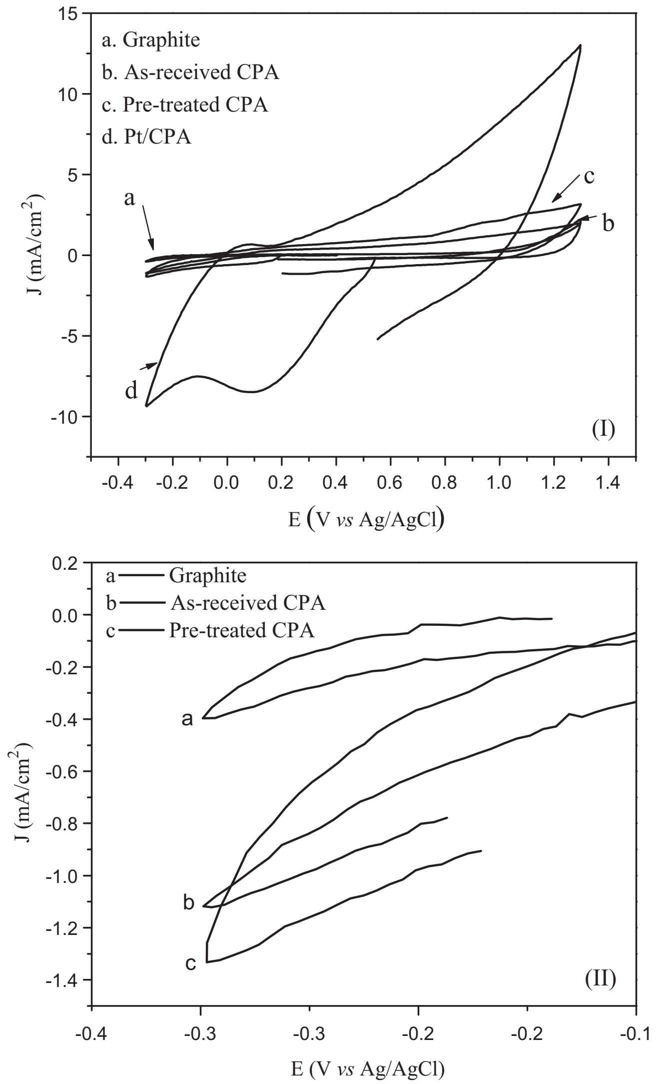

Fig. 6. Cyclic voltammetry (CV) curves of (a) graphite, (b) as-received CPA, (c) pre-treated CPA and (d) Pt/CPA with (I) all-range and (II) part-range.

claimed to be ORR activity electro-catalysts at the same measurement condition and the ORR activity occurred at +0.1 V [22]. Then, by surface modification, it was confirmed in this study that as-fabricated Pt/CPA has a potential application in fuel cells.

4. Conclusions

A novel Pt-deposited ternary composite has been fabricated using the latest discovered binary composite CPA as substrate in this work. According to the characterization results, it is facilitated to obtain a conclusion that the uniformly dispersed nano-Pt (0) particles have been successfully deposited onto substrate material CPA, whose crystal structure belongs to fcc. The enhanced electrochemical performance of Pt/CPA in acidic electrolyte is attributed to selectively deposited Pt nanoparticles.

Acknowledgements

This work was supported by Ministry of Education, Culture, Sports, Science and Technology (MEXT), Project ‘‘Cooperation for Innovative Technology and Advanced Research in Evolution Area’’. We also acknowledge the financial support from the Program of Introducing Talents of Discipline to Universities (B08003).

References

[1] Y. Kim, K. Liao, J.C. Jason, D.E. Berbreiter, J.C. Grunlan, Conductive thin films on functionalized polyethylene particles, Chem. Mater. 18 (2006) 2997–3004.
[2] P.V. Kamat, K.G. Thomas, S. Barazzouk, G. Girishkumar, K. Vinodgopal, D. Meisel, Self-assembled linear bundles of single wall carbon nanotubes and their alignment and deposition as a film in a dc field, J. Am. Chem. Soc. 126 (2004) 10757–10762.
[3] J. Xu, K. Hua, G. Sun, C. Wang, X. Lv, Y. Wang, Electrooxidation of methanol on carbon nanotubes supported Pt–Fe alloy electrode, Eletrochem. Commun. 8 (2006) 982–986.
[4] Y. Mu, H. Liang, J. Hu, L. Wan, Controllable Pt nanoparticles deposition on carbon nanotubes as an anode catalyst for direct methanol fuel cells, J. Phys. Chem. B 109 (2005) 22212–22216.

[5] A.K. Chatterjee, M. Sharon, R. Banerjee, Alkaline fuel cell: carbon nanobeads coated with metal catalyst over porous ceramics for hydrogen electrode, J. Power Sources 117 (2003) 39–44.

[6] L. He, S. Tjong, Polymer/ceramic composite hybrids containing multi-walled carbon nanotubes with high dielectric permittivity, Curr. Nanosci. 6 (2010) 40–44.

[7] J. Wang, X. Deng, J. Xi, L. Chen, W. Zhu, X. Qiu, Promoting the current for methanol electro-oxidation by mixing Pt-based catalysts with CeO_2 nanoparticles, J. Power Sources 170 (2007) 297–302.

[8] Y. Yao, G. Li, K.A. Gray, R.M. Lueptow, Single-walled carbon nanotube-facilitated dispersion of Particulate TiO_2 on ZrO_2 ceramic membrane filters, Langmuir 24 (2008) 7072–7075.

[9] K. Balani, A. Agarwal, Wetting of carbon nanotubes by aluminum oxide, Nanotechnology 19 (2008) 165701–165708.

[10] S.S. Samal, S. Bal, Carbon nanotube reinforced ceramic matrix composite—a review, J. Miner. Mater. Charact. Eng. 7 (4) (2008) 355–370.

[11] L. Gao, L. Jiang, J. Sun, Carbon nanotube–ceramic composite, J. Electroceram. 17 (2006) 51–55.

[12] Z. Xia, L. Riester, W.A. Curtin, H. Li, B.W. Sheldon, J. Laing, Direct observation of toughening mechanisms in carbon nanotube ceramic matrix composite, Acta. Mater. 52 (2004) 931–944.

[13] R.L. Menchavez, M. Fuji, M. Takahashi, Electrically conductive dense and porous alumina with in situ-synthesized nanoscale carbon networks, Adv. Mater. 20 (2008) 2345–2351.

[14] J. Liu, H. Watanabe, M. Fuji, M. Takahashi, Electrocatalytic evolution of hydrogen on porous alumina/gelcast-derived-carbon network composite electrode, Electrochem. Commun. 10 (2008) 922–925.

[15] C. Hai, H. Watanabe, T. Shirai, M. Fuji, M. Takahashi, F. Wang, Modifying the surface of the electrically conductive porous alumina, Mater. Lett. 63 (2009) 1320–1322.

[16] C. Hai, J. Liu, H. Watanabe, M. Fuji, F. Wang, M. Takahashi, Surface activation of conductive porous alumina by deposition nickel particles, J. Am. Ceram. Soc. 92 (S1) (2009) S38–S41.

[17] C. Hai, H. Watanabe, T. Shirai, M. Fuji, F. Wang, J. Liu, M. Takahashi, Chemical reductive preparation of Ni decorated conductive porous alumina composite and its electro-performance in alkaline solution, Ceram. Trans. 219 (2009) 249–254.

[18] M. Kalbac, L. Kavan, L. Dunsch, S. Dresselhaus, Development of the tangential mode in the Raman spectra of SWCNT bundles during electrochemical charging, Nano Lett. 8 (4) (2008) 1257–1264.

[19] Z.W. Zhao, Z.P. Guo, J. Ding, D. Wexler, Z.F. Ma, D.Y. Zhang, et al., Novel ionic liquid supported synthesis of platinum-based electrocatalysts on multiwalled carbon nanotubess, Electrochem. Commun. 8 (2006) 245–250.

[20] S. Banerjee, T. Hemraj-Benny, S.S. Wong, Covalent surface chemistry of single-walled carbon nanotubes, Adv. Mater. 17 (1) (2005) 17–29.

[21] H. Meng, P.K. Shen, Tungsten carbide nanocrystal promoted Pt/C electrocatalysts for oxygen reduction, J. Phys. Chem. B 109 (2005) 22705–22709.

[22] M. Yang, Y. Yang, H. Yang, G. Shen, R. Yu, Layer-by layer self-assembled multilayer films of carbon nanotubes and platinum nanoparticles with polyelectrolyte for the fabrication of biosensors, Biomaterials 27 (2006) 246–255.