Contents lists available at SciVerse ScienceDirect







journal homepage: www.elsevier.com/locate/electacta

Electrochemically shape-controlled synthesis in deep eutectic solvents of Pt nanoflowers with enhanced activity for ethanol oxidation

Lu Wei^{a,b}, You-Jun Fan^{a,*}, Hong-Hui Wang^b, Na Tian^b, Zhi-You Zhou^b, Shi-Gang Sun^{b,*,1}

^a Key Laboratory for the Chemistry and Molecular Engineering of Medicinal Resources (Ministry of Education of China), College of Chemistry and Chemical Engineering, Guangxi Normal University, Guilin 541004, China

^b State Key Laboratory of Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

ARTICLE INFO

Article history: Received 30 March 2012 Received in revised form 16 May 2012 Accepted 20 May 2012 Available online 29 May 2012

Keywords: Deep eutectic solvents Pt nanoflowers Electrodeposition Shape-controlled synthesis Ethanol electrooxidation

1. Introduction

Pt nanoparticles (NPs) are of great interest in recent years due to their unique physicochemical properties and extensive applications in catalysis [1–3], sensors [4,5], and fuel cells [6]. It is known that the properties of NPs strongly depend on their shape or surface atomic arrangement, size and crystallinity. In particular, the Pt NPs with high-index planes generally exhibit much higher catalytic activity than those with low-index planes [7]. Therefore, the shape-controlled synthesis of Pt NPs has attracted enormous attention, and Pt NPs with different shapes were obtained, such as cubes [8–10], rods [11], dendritic structures [12], nanowires [13–15], nanoflowers [16–19], and polyhedra [20–24]. It is worth noting that, among various Pt NPs, very recently Pt nanoflowers have received attention because of their surface roughness, excellent electrochemical active surface area and possible high catalytic activity. For example, Mohanty et al. [16] reported a universal approach to the synthesis of star-shaped Pt nanoflowers, which is capable of catalyzing the Suzuki-Miyaura coupling reaction of phenyl boronic acid and iodobenzene in water in very high yield. In another study, Zhang et al. [17] prepared porous Pt nanoflowers with higher catalytic activity and stronger poisoning-tolerance

E-mail addresses: youjunfan@mailbox.gxnu.edu.cn (Y.-J. Fan),

ABSTRACT

The electrochemically shape-controlled synthesis in deep eutectic solvents (DESs) has been applied to produce the electrocatalyst of Pt nanoflowers. The uniform Pt nanoflowers with sharp single crystal petals and high density of atomic steps were characterized by SEM, TEM, XRD, XPS and electrochemical tests. The results illustrated that the as-prepared Pt nanoflowers exhibit higher electrocatalytic activity and stability than commercial Pt black catalyst toward ethanol electrooxidation. The growth of Pt nanoflowers in DESs by the simple electrochemical route is straightforward and controllable in terms of nanoflowers' shape and size, which can be applied in shape-controlled synthesis of other noble metal nanoparticles with high catalytic activity.

© 2012 Elsevier Ltd. All rights reserved.

for methanol electrooxidation by the electrodeposition method. However, all Pt nanoflowers mentioned above were synthesized in aqueous solution, less attention has been paid so far to study the preparation of Pt nanoflowers in non-aqueous systems.

Deep eutectic solvents (DESs), a simple eutectic-based ionic liquids, usually can be produced by using quaternary ammonium salts mixed with hydrogen-bond donors such as acids, amides and alcohols [25,26]. The properties of DESs are similar to those of ionic liquids, namely, high conductivity, viscosity, surface tensions, polarity, and thermal stability and negligible vapor pressure. Moreover, DESs have the additional advantages of nontoxicity, biodegradation, and easy preparation at low cost and with high purity. Recently, DESs have fascinated the scientific community as a promising solvent in large scale applications [27-35]. However, to the best of our knowledge, the studies on shape-controlled synthesis of metal nanomaterials in DESs are very few. Sun and co-workers reported the synthesis of star-shaped Au NPs enclosed with {331} and vicinal high-index facets in DESs by chemical reduction route, which exhibit high activity toward H₂O₂ electrocatalytic reduction [28]. Chirea and co-workers synthesized Au nanowire networks with high catalytic activity for the chemical reduction of p-nitroaniline in DESs by NaBH₄ reduction method [34]. More recently, we reported the preparation of concave tetrahexahedral Pt nanocrystals (THH Pt NCs) bounded with {910} and vicinal high-index facets in DESs by a programmed electrodeposition method, which exhibit high electrocatalytic activity and stability toward ethanol oxidation [35].

^{*} Corresponding authors.

sgsun@xmu.edu.cn (S.-G. Sun).

¹ ISE member.

^{0013-4686/\$ -} see front matter © 2012 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.electacta.2012.05.063



Fig. 1. Cyclic voltammogram (CV) of GC electrode in 19.3 mM H₂PtCl₆/DESs solution at 80 °C. The inset is the CV curve of GC electrode in DESs at 80 °C. Scan rate: 50 mV s⁻¹.

Herein we report a novel route of shape-controlled synthesis of Pt nanoflowers. The Pt nanoflowers with sharp single crystal petals and high density of atomic steps were successfully synthesized in DESs by simple cyclic voltammetry (CV) method. The size and shape of as-obtained Pt nanoflowers can be tuned easily by controlling the deposition conditions, such as the precursor concentration, CV number of cycle, scan rate and temperature. As compared to Pt nanoflowers with other shapes and commercial Pt black catalyst,



Fig. 2. (a) SEM image of Pt nanoflowers electrodeposited on GC by using CV method in 19.3 mM H_2 PtCl₆/DESs solution at $80 \degree$ C. Potential scan range: -1.5 to -0.2 V, scan rate: 50 mV s^{-1} , CV number of cycle: $80 \degree$ cycles. (b) TEM image of a single Pt nanoflower, the inset is the SAED pattern of the nanoflower. (c) HRTEM image of the petal marked in (b), showing the high density of atomic steps. (d) EDX image of Pt nanoflowers.



Fig. 3. SEM images of Pt nanostructures electrodeposited on GC in DESs at $80 \,^{\circ}$ C under various H₂PtCl₆ concentrations of (a) 1.93 mM, (b) 5 mM, (c) 10 mM and (d) 19.3 mM. Potential scan range: -1.5 to -0.2 V, scan rate: 50 mV s⁻¹, CV number of cycle: 80 cycles.

the Pt nanoflowers with sharp single crystal petals and high density of atomic steps show higher electrocatalytic activity and stability for ethanol oxidation. $(H_2PtCl_6.6H_2O, >99\%)$ and absolute ethanol of analytical grade, and super pure $HClO_4$ were purchased from Shanghai Chemical Reagent Ltd., China.

2.2. Preparation of DESs

2. Experimental

2.1. Chemicals

Choline chloride (HOC₂H₄N(CH₃)₃Cl, 99%), urea (NH₂CONH₂, >99%), hydrogen hexachloroplatinate(IV) hexahydrate

Choline chloride was recrystallized from absolute ethanol, filtered and dried under vacuum. Urea was recrystallized from Millipore water ($18.0 \text{ M}\Omega \text{ cm}$) provided by a Milli-Q Lab apparatus (Nihon Millipore Ltd.), filtered and dried under vacuum prior to use.



Fig. 4. SEM images of Pt nanostructures electrodeposited on GC in 19.3 mM H₂PtCl₆/DESs solution at 80 °C by using different CV number of cycle: (a) 5, (b) 10, (c) 40 and (d) 100 cycles. Potential scan range: -1.5 to -0.2 V, scan rate: 50 mV s⁻¹.



Fig. 5. SEM images of Pt nanostructures electrodeposited on GC in 19.3 mM $H_2PtCl_6/DESs$ at 80 °C by potentiostatic method at the potential of (a) -0.95, (b) -0.90 and (c) -0.80 V. The insets are the corresponding high-magnification SEM images. Scale bar of the inset is 200 nm.

DESs were formed by stirring the above two components together, in the stated proportion (molar ratio of choline chloride/urea = 1:2), at 80 °C until a homogeneous, colorless liquid formed [25,28]. The prepared DESs, once formulated, were kept in a vacuum at 80 °C prior to use.

2.3. Synthesis of Pt nanoflowers in DESs

The electrochemical synthesis of Pt nanoflowers in DESs was carried out under an ambient environment, using a standard threeelectrode cell connected to a CHI 631 electrochemical workstation (Shanghai Chenhua Instrumental Co., Ltd., China), with a Pt wire counter electrode and a Pt quasi-reference electrode. The working electrode was a glassy carbon disk (GC, Ø 3 mm), which was polished with 5.0 μ m, 1.0 μ m, 0.3 μ m Al₂O₃ powder and washed ultrasonically in ultrapure water before each experiment. In a typical procedure, Pt nanoflowers with sharp single crystal petals and high density of atomic steps were electrodeposited directly on a GC substrate in 19.3 mM H₂PtCl₆/DESs solution at 80 °C using the CV 471

tial scan range of -1.5 to -0.2 V, scan rate of 50 mV s^{-1} and CV number of 80 cycles. Moreover, the effects of preparation conditions (such as the precursor concentration, CV number of cycle, scan rate and temperature) on the size and shape of Pt NPs were systematically investigated.

2.4. Physical characterization of Pt nanoflowers

The size and morphology of Pt nanoflowers were analyzed by scanning electron microscopy (SEM, LEO-1530) and transmission electron microscopy (TEM, FEI Tecnai-F30). The X-ray diffraction (XRD) patterns of Pt samples were recorded with an X-ray powder diffraction apparatus (Panalytical X'pert PRO) using a Cu K α source and 2θ scan rate of 6° min⁻¹. The X-ray photoelectron spectroscopy (XPS) measurements were carried out using a Physical Electronics PHI Quantum 2000 Scanning ESCA Microprobe with the Al K α X-ray source (1486.6 eV), while the chamber pressure was held below 5×10^{-9} Torr. All reported values of electron binding energy were calibrated with respect to the principal peak of C1s at 284.6 eV as an internal standard.

2.5. Electrocatalytic performance measurements

The electrocatalytic performances of Pt samples were measured in 0.1 M ethanol + 0.1 M HClO₄ solution at room temperature (25 °C). The solutions were deaerated by purging with pure N₂ gas before experiment, and a flux of N₂ was kept over the solution during measurements to prevent the interference of atmospheric oxygen. Pt black sheet and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. All potentials in the electrochemical performance tests are quoted vs. the SCE scale.

3. Results and discussion

Cyclic voltammogram (CV) of Pt electrodeposition on GC electrode in 19.3 mM $H_2PtCl_6/DESs$ solution at 80 °C is shown in Fig. 1. From this figure, in the negative-going potential scan, it can be clearly observed that two current peaks of reduction occurred at near -0.93 V and -1.29 V (vs. Pt), in comparison with the voltammogram (inset of Fig. 1) recorded on the same GC substrate in DESs. X-ray photoelectron spectra (XPS) results demonstrated that these two reduction peaks are corresponding to the electrochemical reduction of Pt(IV) to Pt(II) and Pt(II) to Pt(0), respectively (Fig. S1 and Table S1 in supplementary information). This is consistent with the electrodeposition behaviors of Pt in hydrophilic 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMIMBF₄) and hydrophobic 1-*n*-butyl-3-methylimidazolium hexafluorophosphate (BMIMPF₆) room-temperature ionic liquids [36].

Fig. 2a displays the typical SEM image of Pt nanoflowers electrodeposited on GC by using CV method in $19.3 \text{ mM H}_2\text{PtCl}_6/\text{DESs}$ solution at 80 °C. It can be seen that the Pt nanoflowers with sharp petals were homogeneously formed, and their size was about 200 nm. The crystal structure of Pt nanoflowers was further investigated by high resolution transmission electron microscopy (HRTEM). Fig. 2b shows the TEM image of a single Pt nanoflower, and the inset is the corresponding selected area electron diffraction (SAED) pattern, which indicates that the petals of as-prepared nanoflowers possess the single-crystalline structure. The HRTEM image of a petal marked in Fig. 2b is displayed in Fig. 2c. The continuous fringe pattern further verifies the single crystalline property of the petal. The lattice spacing of 0.23 nm agrees with the distance between two {1 1 1} planes of Pt. As compared to other Pt nanoflowers ers and nanothorn assemblies reported previously [16–19,37], the



Fig. 6. (a) TEM image of a single Pt nanosheet in Fig. 5b, (b and c) HRTEM images of the Pt nanosheet, (d) SAED pattern of the Pt nanosheet.

unique characteristic of as-prepared Pt nanoflowers is the formation of high density of atomic steps at the edge of the petals (Fig. 2c), which are crucial for the enhanced activity of Pt nanoflowers toward ethanol electrooxidation. The energy dispersive X-ray spectroscopy (EDX) analysis of Pt nanoflowers confirms the presence of only Pt, C and O elements (Fig. 2d), indicating no DESs residue on the surface of Pt nanoflowers.

The effect of deposition conditions, namely, the precursor concentration, CV number of cycle, scan rate and temperature on the size and morphology of Pt nanostructures electrodeposited in DESs was examined. Fig. 3 shows the SEM images of Pt nanostructures prepared by using the different concentrations of H_2PtCl_6 . We can see that, at the H₂PtCl₆ concentration of 1.93 mM, the quasispherical Pt NPs were formed (Fig. 3a), and their size ranged from 45 to 95 nm. When the H₂PtCl₆ concentration was 5 mM, the flowerlike Pt NPs without sharp petals and several cubic Pt NPs appeared (Fig. 3b). Further increasing the H₂PtCl₆ concentration to 10 mM, the sharp petals started to appear at the edge of the Pt nanoflowers (Fig. 3c). Finally, the perfect Pt nanoflowers with sharp petals were homogeneously formed at the H₂PtCl₆ concentration of 19.3 mM (Fig. 3d). The concentration dependence of the above Pt nanostructures maybe results from the high viscosity of DESs [25,26], which decreased the mass transportation of reactive species in DESs, leading to the difficult formation of Pt nanoflowers with sharp petals at the lower H₂PtCl₆ concentration.

Among all deposition conditions, the CV number of cycle exerts a leading influence on the process of particle growth. Different Pt nanostructures generated by various CV number of cycle were obtained, as shown in Fig. 4. Some irregular quasi-spherical nanoparticles with low surface coverage were produced in the lower CV number of cycle (Fig. 4a and b), which acted as the nuclei for subsequently producing Pt nanoflowers [17,19,38]. Since the nucleation process is relatively slow and irreversible, newly deposited Pt favors growing on the small Pt cores instead of generating more new nuclei [39]. Increasing the CV number of cycle would result in complex monodisperse nanoflowers with more sharp petals and larger size (Fig. 4c). Further increasing the CV number of cycle to 80 cycles, the perfect Pt nanoflowers with sharp petals were formed on the GC substrate (Fig. 3d). When the CV number of cycle was increased to 100 cycles, the aggregation phenomenon of Pt nanoflowers was observed (Fig. 4d). In addition, the scan rate plays important roles in the electrodeposition of Pt owing to its possible influence on the anisotropic growth of nanoparticles. At the lower scan rate of 1 mV s⁻¹, the rough nanosheets formed on the top of Pt nanostructures (Fig. S2 in supplementary information). Further increasing the scan rate would result in the growth of Pt nanoflowers with sharp petals. It is worthwhile noting that all electrodeposition processes discussed above were carried out at 80 °C, when the lower or higher deposition temperature was used, the sharp petals in the resultant Pt NPs were poorly developed (Fig. S3 in supplementary information). The reason for such an obvious difference in size and shape of Pt NPs prepared at different temperatures could be the variation of DESs viscosity with the temperature [25], which influences the diffusion of reactive species in DESs and thus the nucleation/growth process of Pt on GC substrate.



Fig. 7. (a) Stable cyclic voltammograms (50 mV s⁻¹) and (b) chronoamperometric *j*–*t* curves recorded at 0.45 V (vs. SCE), for ethanol oxidation on various Pt nanoflowers and commercial Pt black catalyst in 0.1 M ethanol + 0.1 M HClO₄ solution at 25 °C.

The Pt nanoflowers of various shapes can be also obtained by adjusting the deposition potential of the potentiostatic reduction. Typical SEM images of Pt nanoflowers prepared at different potentials are shown in Fig. 5. At the deposition potential of -0.95 V, many pricks appeared and extruded from the surfaces of the studded particles (Fig. 5a). When the deposition potential was -0.90 V, the nanosheet assemblies were formed on the top of Pt nanostructures (Fig. 5b). As the deposition potential became more positive, e.g. -0.80 V, only flower-like Pt NPs with rough surface structure were observed (Fig. 5c). To further characterize the structure of Pt nanosheets in Fig. 5b, TEM measurements were carried out. A single Pt nanosheet as indicated in Fig. 6a was carefully observed by the HRTEM imaging technique. As shown in Fig. 6b, the Pt nanosheet is in fact an agglomerate of Pt nanoparticles. The lattice spacing between adjacent {111} planes is determined to be 0.23 nm, which is in agreement with the $\{111\}$ d-spacing value of face centered cubic (fcc) Pt (Fig. 6c). Interestingly, unlike the sharp petals described in Fig. 2, the high density of atomic steps cannot be observed in the Pt nanosheet. Furthermore, Fig. 6d shows the corresponding SAED pattern, where the five main diffraction rings can be indexed as the characteristic rings of Pt fcc crystal, which is fully consistent with the result of the XRD pattern (Fig. S4 in supplementary information).

The electrocatalytic performance of the perfect Pt nanoflowers with sharp petals in Fig. 2a was evaluated by CV and chronoamperometry methods in acidic solution at room temperature. Fig. 7a compares the stable cyclic voltammograms of the Pt nanostructures with different shapes and commercial Pt black catalyst (Johnson Matthey) in 0.1 M ethanol+0.1 M HClO₄ solution. The oxidation current has been normalized to the electroactive surface area, which was calculated from the electric charge of

Table 1

Comparison of peak current densities (j_p) and steady current densities (j_{1800s}) for different Pt samples toward ethanol oxidation in Fig. 7.

Sample	$j_{\mathrm{p(I)}}$ (mA cm ⁻²)	$j_{ m p(II)}\ (m mAcm^{-2})$	j _{1800 s} (mA cm ⁻²)
Pt nanoflowers in Fig. 2a	1.484	1.414	0.184
Pt nanoflowers in Fig. 5a	0.481	0.598	0.047
Pt nanoflowers in Fig. 5b	0.567	0.716	0.081
Pt nanoflowers in Fig. 5c	0.780	0.983	0.128
Pt black	0.582	0.849	0.094

hydrogen adsorption/desorption on Pt samples (Fig. S5 in supplementary information). The corresponding CV parameters are listed in Table 1. We can see that, in the positive-going potential scan, the ethanol electrooxidation on the perfect Pt nanoflowers with sharp petals gives two current peaks at near 0.56 and 0.95 V (vs. SCE), their peak current densities are 1.484 and 1.414 mA cm⁻², respectively, which are much higher than those obtained on the Pt nanoflowers with other shapes and Pt black catalyst. These results demonstrate that the electrocatalytic activity of the perfect Pt nanoflowers with sharp petals for ethanol oxidation is much higher than that of the Pt nanoflowers with other shapes and Pt black catalyst. Fig. 7b shows the current-time curves of ethanol oxidation on various Pt samples at 0.45 V (vs. SCE). It is found that the current density (t = 1800 s) of ethanol oxidation on the perfect Pt nanoflowers with sharp petals is significantly higher than that of other Pt nanoflowers and Pt black catalyst (Table 1). This further demonstrates that the electrocatalytic activity and stability of the Pt nanoflowers with sharp petals for ethanol oxidation are superior to those of other Pt nanoflowers and Pt black catalyst. The enhancement in electrocatalytic performance of the perfect Pt nanoflowers with sharp petals could be evidently attributed to their high density of atomic steps, which are beneficial for the C-C bond breaking and the oxidation of adsorbed CO in ethanol oxidation [40,41].

4. Conclusions

In summary, we have reported the electrochemically shapecontrolled synthesis in DESs for producing Pt nanoflowers. The Pt nanoflowers with sharp single crystal petals and high density of atomic steps were obtained in DESs by simple cyclic voltammetry. Thanks to their high density of atomic steps, the Pt nanoflowers with sharp petals exhibit higher electrocatalytic activity and stability than commercial Pt black catalyst toward ethanol oxidation. Furthermore, the size and shape of Pt nanoflowers could be easily controlled by adjusting the electrodeposition conditions. This study is of significance for shape-controlled synthesis of other noble metal NPs with high catalytic activity in DESs, as well as in potential applications of electrocatalysis, electrochemical sensors and fuel cells.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20833005, 21021002), the Opening Foundation Project of the State Key Laboratory of Physical Chemistry of Solid Surfaces (Xiamen University), Guangxi Natural Science Foundation of China (0991093, 2010GXNSFF013001) and the S&T Project of Guangxi Education Department of China (201012MS024).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/ j.electacta.2012.05.063.

References

- S.H. Joo, J.Y. Park, C.K. Tsung, Y. Yamada, P.D. Yang, G.A. Somorjai, Nature Materials 8 (2009) 126.
- [2] E. Schmidt, A. Vargas, T. Mallat, A. Baiker, Journal of the American Chemical Society 131 (2009) 12358.
- [3] E. Schmidt, W. Kleist, F. Krumeich, T. Mallat, A. Baiker, Chemistry—A European Journal 16 (2010) 2181.
- [4] J.M. Pingarrón, P. Yáñez-Sedeño, A. González-Cortés, Electrochimica Acta 53 (2008) 5848.
- [5] S. Chakraborty, C.R. Raj, Biosensors and Bioelectronics 24 (2009) 3264.
- [6] J.F. Lin, C.W. Mason, A. Adame, X. Liu, X.H. Peng, A.M. Kannan, Electrochimica Acta 55 (2010) 6496.
- [7] N. Tian, Z.Y. Zhou, S.G. Sun, Journal of Physical Chemistry C 112 (2008) 19801.
- [8] C. Susut, T.D. Nguyena, G.B. Chapmanb, Y.Y. Tong, Electrochimica Acta 53 (2008) 6135.
- [9] S.I. Lim, I. Ojea-Jiménez, M. Varon, E. Casals, J. Arbiol, V. Puntes, Nano Letters 10 (2010) 964.
- [10] C. Wang, H. Daimon, Y. Lee, J. Kim, S.H. Sun, Journal of the American Chemical Society 129 (2007) 6974.
- [11] X.Z. Gong, Y. Yang, S.M. Huang, Chemical Communications 47 (2011) 1009.
- [12] X.W. Teng, H. Yang, Nano Letters 5 (2005) 885.
 [13] D. Fenske, H. Borchert, J. Kehres, R. Kröger, J. Parisi, J. Kolny-Olesiak, Langmuir
- 24 (2008) 9011. [14] Y.J. Song, S.B. Han, K.W. Park, Materials Letters 64 (2010) 1981.
- [15] J.Y. Chen, T. Herricks, M. Geissler, Y.N. Xia, Journal of the American Chemical Society 126 (2004) 10854.
- [16] A. Mohanty, N. Garg, R.C. Jin, Angewandte Chemie International Edition 49 (2010) 4962.
- [17] H.M. Zhang, W.Q. Zhou, Y.K. Du, P. Yang, C.Y. Wang, Electrochemistry Communications 12 (2010) 882.
- [18] W. Yang, Y. Wang, J. Li, X.R. Yang, Energy and Environmental Science 3 (2010) 144.
- [19] L. Su, W.Z. Jia, L.C. Zhang, C. Beacham, H. Zhang, Y. Lei, Journal of Physical Chemistry C 114 (2010) 18121.
- [20] N. Tian, Z.Y. Zhou, S.G. Sun, Y. Ding, Z.L. Wang, Science 316 (2007) 732.
- [21] Y.N. Xia, Y.J. Xiong, B. Lim, S.E. Skrabalak, Angewandte Chemie International Edition 48 (2009) 60.

- [22] T.K. Sau, A.L. Rogach, Advanced Materials 22 (2010) 1781.
- [23] T. Yu, D.Y. Kim, H. Zhang, Y.N. Xia, Angewandte Chemie International Edition 50 (2011) 2773.
- [24] X.Q. Huang, Z.P. Zhao, J.M. Fan, Y.M. Tan, N.F. Zheng, Journal of the American Chemical Society 133 (2011) 4718.
- [25] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Chemical Communications (2003) 70.
- [26] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Journal of the American Chemical Society 126 (2004) 9142.
- [27] M. Avalos, R. Babiano, P. Cintas, J.L. Jiménez, J.C. Palacios, Angewandte Chemie International Edition 45 (2006) 3904.
- [28] H.G. Liao, Y.X. Jiang, Z.Y. Zhou, S.P. Chen, S.G. Sun, Angewandte Chemie International Edition 47 (2008) 9100.
- [29] A.P. Abbott, K.E. Ttaib, G. Frisch, K.J. McKenzie, K.S. Ryder, Physical Chemistry Chemical Physics 11 (2009) 4269.
- [30] J.Y. Dong, Y.J. Hsu, D.S.H. Wong, S.Y. Lu, Journal of Physical Chemistry C 114 (2010) 8867.
- [31] F.H. Aidoudi, P.J. Byrne, P.K. Allan, S.J. Teat, P. Lightfoot, R.E. Morris, Dalton Transactions 40 (2011) 4324.
- [32] J.D. Mota-Morales, M.C. Gutiérrez, I.C. Sanchez, G. Luna-Bárcenas, F. Monte, Chemical Communications 47 (2011) 5328.
- [33] M. Steichen, M. Thomassey, S. Siebentritt, P.J. Dale, Physical Chemistry Chemical Physics 13 (2011) 4292.
- [34] M. Chirea, A. Freitas, B.S. Vasile, C. Ghitulica, C.M. Pereira, F. Silva, Langmuir 27 (2011) 3906.
- [35] L. Wei, Y.J. Fan, N. Tian, Z.Y. Zhou, X.Q. Zhao, B.W. Mao, S.G. Sun, Journal of Physical Chemistry C 116 (2012) 2040.
- [36] P. He, H.T. Liu, Z.Y. Li, J.H. Li, Journal of the Electrochemical Society 152 (2005) E146.
- [37] N. Tian, Z.Y. Zhou, S.G. Sun, L. Cui, B. Ren, Z.Q. Tian, Chemical Communications (2006) 4090.
- [38] B. Yang, S.Q. Wang, S.B. Tian, L.Z. Liu, Electrochemistry Communications 11 (2009) 1230.
- [39] T.M. Day, P.R. Unwin, N.R. Wilson, J.V. Macpherson, Journal of the American Chemical Society 127 (2005) 10639.
- [40] J. Souza-Garcia, E. Herrero, J.M. Feliu, ChemPhysChem 11 (2010) 1391.
- [41] F. Colmati, G. Tremiliosi-Filho, E.R. Gonzalez, A. Berná, E. Herrero, J.M. Feliu, Physical Chemistry Chemical Physics 11 (2009) 9114.

L. Wei et al. / Electrochimica Acta 76 (2012) 468-474