Effect of Morphology of Co_3O_4 for Oxygen Evolution Reaction in Alkaline Water Electrolysis

Qi-Zhi Xu, Yu-Zhi Su, Hao Wu, Hui Cheng, Yun-Ping Guo, Nan Li and Zhao-Qing Liu*

School of Chemistry and Chemical Engineering/Guangzhou Key Laboratory for Environmentally Functional Materials and Technology, Guangzhou University, Guangzhou 510006, China

Abstract: In this paper, three different morphological Co_3O_4 electrodes for oxygen evolution reaction (OER) have been synthesized. By comparing the three morphologies of Co_3O_4 , the electrocatalytic properties show that the urchin-like spheres of Co_3O_4 electrode has relative low overpotential and good electrocatalysis stability, indicating that the structure of urchin-like Co_3O_4 spheres exhibit an easy OER for water splitting.

Keywords: Co_3O_4 , hydrothermal method, oxygen evolution reaction, sol-gel autocombustion method, solution method, urchin-like sphere.

1. INTRODUCTION

As a potential solution to provide a carbon-free source of hydrogen for the global energy crisis and environmental pollution, the electrochemical splitting of water has attracted great attention [1-3]. One of the critical drawbacks to making the electrochemical process viable on an industrial scale is the unavailability of cheap and highly efficient OER electrocatalysts. Currently, the commonly used catalysts for OER in electrolysis cells are still RuO_2 and IrO_2 , which are among the rarest elements on the earth [4-5]. Therefore, searching for alternative electrocatalyst which can reduce the overpotential and enhance the energy efficiency are critical to viable water electrolytic systems.

Recently, numerous efforts have been made to explore cheap and high efficient OER catalysts that have sufficient stability in prolonged exposure to oxidizing conditions [6-12]. Amongst these non-precious catalysts, cobalt is earth-abundant and both Co_3O_4 and the substituted cobaltites $\text{M}_x\text{Co}_{3-x}\text{O}_4$ ($\text{M} = \text{Ni}, \text{Fe}, \text{Cu}$ or Zn) exhibit excellent OER activities [13-20]. Upon electrochemical oxidation, metallic Co undergoes gradually oxidation to form $\text{Co}(\text{OH})_2$, CoO , Co_3O_4 and $\text{CoO}(\text{OH})$, etc [21-24]. In particular, as one of the well-known spinel electrocatalysts, Co_3O_4 has been studied as a highly efficient corrosion-stable OER catalyst in alkaline media. Worth to be mentioned, to enhance the electrochemical activity of Co_3O_4 , increasing the effective surface area of catalysts is needed. Therefore, it was found that the morphologies of Co_3O_4 electrocatalysts play a key role in OER. In general, Co_3O_4 electrocatalysts for the OER are thin film or particle agglomerates bound together by polymers. [25-27]. Recently, one-dimensional Co_3O_4 nanowires as electrocatalyst for the OER have garnered significant attention

[28, 29]. Compared with Co_3O_4 particles and thin films, the one-dimensional Co_3O_4 nanowires possess a large interfacial area, high efficient active sites, and superior mass transport property.

In this work, the urchin-like Co_3O_4 spheres have been successfully synthesized for OER *via* a simple and effective solution method. Simultaneously, other two morphologies of Co_3O_4 were obtained by hydrothermal process and sol-gel autocombustion method. By comparing the different morphologies of Co_3O_4 , We examined their electrochemical OER activities and investigated the relationship among the catalyst activity and morphology, and surface area of Co_3O_4 .

2. EXPERIMENTAL

Materials Synthesis. All the solvents and chemicals used were analytical grade and used directly without any purification. In a typical solution method: 4 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved into a 80 mL mixed solution (50 volume % ethanol: 50 volume % H_2O) at room temperature to form a clear pink solution, followed by the addition of 24 mmol of urea. And then the mixed solution was transferred to a 100 mL bottle with a cap. Firstly, the Ti foil (2 cm $\times$ 1 cm) was immersed in a 3 M HCl solution for 15 min to get rid of the possible surface oxide layer, then put into the bottle for reaction. The bottle was capped and heated at 85°C for 8 h in an electric oven. Finally, the Ti foil with grown urchin-like Co_3O_4 spheres (denoted as S_1) was obtained by annealed at 400°C in atmosphere for 2 h.

In a typical hydrothermal method: 1 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL deionized water under constant stirring, followed by the addition of 10 mmol of urea. The mixture was kept stirring for 30 min, and transferred to a Teflonlined autoclave (25 mL capacity). The hydrothermal reaction was conducted at 120°C for 6 h. The precipitates were collected and rinsed with deionized water and ethanol, and finally the layered Co_3O_4 (denoted as S_2) was obtained by annealed at 400°C in atmosphere for 2 h.

*Address correspondence to this author at the School of Chemistry and Chemical Engineering/Guangzhou Key Laboratory for Environmentally Functional Materials and Technology, Guangzhou University, Guangzhou 510006, China; Tel: +86 20 39366908; Fax: +86 20 39366908; E-mail: lzqgz@gzhu.edu.cn

Fig. (1). XRD patterns of Co_3O_4 samples.

In a typical sol-gel autocombustion method: 1 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 20 mL deionized water under constant stirring, followed by the addition of 2 mmol of citric acid. And the mixed solution (sol) was kept stirring and heated at 80°C till the sol was converted into gel. Ammonia solution was used to maintain the pH value of the sol at about 7-8 until the gel was formed. Then the gel was ignited at 120°C by the self-combustion process and thus obtained loose fluffy powder. Finally, the agglomerate Co_3O_4 (denoted as S_3) was obtained by sintered at 400°C in atmosphere for 2 h.

Characterizations: The as-prepared samples were characterized by using field emission scanning electron microscopy (FE-SEM, JSM-7001F) and transmission electron microscopy (TEM, 300 kV, Tecnai™ G2 F30) to analyze the surface morphology.

The crystal structure of the samples were analyzed using powder X-ray diffraction (XRD, Bruker, D8 ADVANCE) with $\text{K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The chemical state and composition of the samples were carried out by X-ray Photoelectron Spectroscopy (XPS, ESCALab250). Nitrogen adsorption/desorption measurements were conducted on an ASAP 2020M instrument. All samples were outgassed at 100°C for 300 min under flowing nitrogen before adsorption/desorption measurements.

Electrochemical measurements: All the electrochemical measurements were performed on PARSTAT 4000 electrochemical workstation in a 1.0 M KOH electrolyte with a conventional three-electrode glass cell at the room temperature. A Pt plate and a standard calomel electrode (SCE) were served as the counter electrode and the reference electrode, respectively. The samples prepared on carbon rods as working electrodes for the catalysis of the OER in 1.0 M KOH solution. The mass loading of Co_3O_4 on carbon rod is around 0.1 mg cm^{-2} .

3. RESULT AND DISCUSSION

To identify the crystal structure of the as-prepared samples, the X-ray diffraction (XRD) patterns were collected and shown in Fig. (1). All of the diffraction peaks can be perfectly indexed and assigned to the cubic phase of Co_3O_4 (JCPDF: 43-1003, Space group: $\text{Fd}3\text{m}(227)$) with lattice constants $a = b = c = 8.084 \text{ \AA}$. No other peaks could be observed from the patterns. Moreover, the intense and sharp peaks indicate that the samples are highly pure and well crystallized. Fig. (2a) shows a typical SEM image of the as-prepared S_1 . It is observed that numerous spherical urchin shape structures of Co_3O_4 were obtained with uniform diameters of $6 \mu\text{m}$. Fig. (2b) shows TEM image of the sample, clearly revealing each urchin-like Co_3O_4 sphere has uniform

Fig. (2). SEM, TEM and HRTEM images of Co_3O_4 samples: (a-c) S_1 , (d-f) S_2 , (g-i) S_3 .

Fig. (3). (a) XPS survey spectrum of Co_3O_4 samples; (b) Co 2p and (c) O 1s XPS spectrum of S1; (d) N_2 adsorption/desorption isotherms of Co_3O_4 samples.

diameters of 6 μm with numerous small nanowires radially-grown from the center. Furthermore, the high-resolution TEM (HRTEM) image in Fig. (2c), which is observed with a distinct lattice spacing of 0.286 nm, corresponding to be (220) plane of Co_3O_4 . Fig. (2d-f) shows the SEM, TEM and HRTEM images of the S_2 sample with nanosheet structure. Accordingly, as shown in Fig. (2f), the crystalline nature of S_2 is also displayed in the HRTEM, the uniform 0.286 nm interplanar distance corresponds to the (220) plane of Co_3O_4 . The typical thickness of these nanosheets are 150-200 nm. The typical SEM images of the S_3 sample are shown in Fig. (2g-i), which reveals the bulk structures of Co_3O_4 .

The more detailed chemical composition and the oxidation state of the Co_3O_4 samples were further analyzed by XPS measurements. Fig. (3a) compares the XPS survey spectrum of three different morphological Co_3O_4 electrodes. Fig. (3b-c) shows the Co 2p and O 1s XPS spectrum of urchin-like Co_3O_4 spheres. As shown in Fig. (3b), two major peaks at binding energies of 780.3 and 795.4 eV corresponding to the $\text{Co } 2p_{3/2}$ and $\text{Co } 2p_{1/2}$ of Co_3O_4 phase are observed with a spin energy separation of 15.1 eV [30]. The high-resolution spectrum for the O 1s region in Fig. (3c) exhibits two oxygen contributions, which have been denoted as O_I and O_{II} , respectively. The fitting peak of O_I at 530.0 eV is typical of metal-oxygen bonds [31]. Furthermore, the component O_{II} at 531.6 eV can be attributed to a number of oxygen defect sites in the material with small particle size

[32, 33]. On the basis of the XPS results, it can be concluded that the urchin-like spheres consist of Co_3O_4 . The Co_3O_4 samples were also investigated by nitrogen adsorption and desorption measurement at 77 K. As shown in Fig. (3d), the nitrogen adsorption-desorption curves demonstrate a Type IV isotherm [33], and the specific surface areas of Co_3O_4 samples S_1 to S_3 have been 40.45, 19.85, and 22.25 m^2g^{-1} , respectively. The BET result is consistent with the SEM observations discussed above, showing urchin-like structure with relatively high interfacial area. The structural feature gives implications of the applications in electrocatalytic field, which comes as following below.

The cyclic voltammetric (CV) curves obtained from the different morphological Co_3O_4 electrodes in the potential range of 0.0-0.7 V are shown in Fig. (4). Fig. (4a-c) shows CV behavior of the as-prepared Co_3O_4 electrodes in 1.0 M KOH at different scan rates. The current was normalized to the amount of Co_3O_4 in 1 cm^2 electrode. As shown in Fig. (4d), the CVs of different morphological Co_3O_4 electrodes exhibit an anodic peak at about 0.52 V and a corresponding cathodic peak assigned to the Co (III)/Co (IV) , which result in the emergence of the catalytic phase for the OER [14, 28]. Furthermore, the different sites Co (III) and Co (IV) derived from the oxidative process, which may form active sites to adsorb the OH^- during the OER in alkaline solution. The corresponding linear sweep voltammetry (LSV) curves of the above electrodes for the OER are shown in Fig. (5).

Fig. (4). (a-c) CVs of Co_3O_4 electrodes recorded in 1.0 M KOH at different scan rates; (d) CVs of Co_3O_4 electrodes in 1.0 M KOH at a scan rate of 2 mV/s.

The sweep rate is 1 mV/s in the potential range from 0 V to 0.9 V at the potential scanning rate of 1 mV/s in 1.0 M KOH solution. It is well known that the low value of onset potential is beneficial to OER for water splitting. The onset potential of S_1 is 0.64 V. Before 0.64 V, no OER peak happens on the S_1 electrode. In addition, the onset potential of S_1 is

lower 14.8 mV than that of S_2 , and lower 40 mV than that of S_3 , indicating that the urchin-like sphere of Co_3O_4 has a high activity for OER.

The stability of OER on the Co_3O_4 electrodes was investigated with chronoamperometry. As shown in Fig. (6a), the current decay exhibits a deactivation of the electrodes. However, at the end of the test, the oxidation current on the Co_3O_4 (S_1) electrode is larger than that of the other two electrodes (S_2 and S_3). The current density of S_1 decays quickly in a short time after starting OER. Furthermore, the current density is still 0.82 mA cm^{-2} after 180 min. The current density on the S_2 and S_3 electrodes decay quickly and stabilize at 0.51 mA cm^{-2} and 0.21 mA cm^{-2} after 180 min, respectively. The current density of S_1 is higher 0.31 mA cm^{-2} than that of S_2 , and higher 0.61 mA cm^{-2} than that of S_3 , indicating that the S_1 electrode has higher activity and better stability than S_2 and S_3 electrodes for OER. Furthermore, EIS is complementary to cyclic voltammetry (CV) and charge-discharge measurements. The more vertical the slope of the straight line in the low frequency, the better performance in oxygen evolution reaction. Obviously, the slope of S_1 larger than S_2 and S_3 in Fig. (6b), indicating that the structure of Co_3O_4 with the morphology of urchin-like spheres has better performance in oxygen evolution reaction. Therefore, the improved OER performances of S_1 electrode can be attributed to following reasons: (1) the nanowires consisted of urchin-like sphere structure can facilitate the diffusion of active species and electronic transport. (2) S_1 provide a larger electrode surface areas than S_2 and S_3 .

Fig. (5). LSV curves for the OER on electrodes of Co_3O_4 recorded in 1.0 M KOH with a sweep rate of 1 mV/s at room temperature.

Fig. (6). (a) Chronoamperometric curves of Co_3O_4 electrodes recorded in 1.0 M KOH at room temperature; (b) Nyquist plots of Co_3O_4 electrodes in 1.0 M KOH.

CONCLUSIONS

In summary, on the basis of the OER activity on Co_3O_4 electrodes with various surface morphologies, it can be concluded that the onset potential of OER on the S_1 electrode is lower than that on the S_2 and S_3 , indicating that the structure of Co_3O_4 has an easier OER for water splitting. The Co_3O_4 electrode with urchin-like spheres is beneficial for the water splitting due to their high efficient activity and the ability to detach bubbles from their interfacial.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interest.

ACKNOWLEDGEMENTS

The authors acknowledge the financial support of this work by Natural Science Foundations of China (Grant No. 21306030), the Natural Science Foundations of Guangdong Province (Grant No. s2012010009719 and s201304001-5229), Scientific Research Project of Guangzhou Municipal Colleges and Universities (Grant No. 2012A064), Program Foundation of the second batch of innovation teams of Guangzhou Bureau of Education (Grant No. 13C04), and the Fresh Talent Program of Guangzhou University (Grant No. 201302).

REFERENCES

- [1] Walter, M.G.; Warren, E.L.; McKone, J.R.; Boettcher, S.W.; Mi, Q.; Santori, E.A.; Lewis, N.S. Solar water splitting cells. *Chem. Rev.*, **2010**, *110*(11), 6446-6473.
- [2] Bajdich, M.; García-Mota, M.; Vojvodic, A.; Nørskov, J.K.; Bell, A.T. Theoretical investigation of the activity of cobalt oxides for the electrochemical oxidation of water. *J. Am. Chem. Soc.*, **2013**, *135*(36), 13521-13530.
- [3] Chen, S.; Qiao, S.Z. Hierarchically porous nitrogen-doped graphene- NiCo_2O_4 hybrid paper as an advanced electrocatalytic water-splitting material. *ACS Nano*, **2013**, *7*(11), 10190-10196.
- [4] Petrykin, V.; Macounova, K.; Shlyakhtin, O.A.; Krtil, P. Tailoring the selectivity for electrocatalytic oxygen evolution on ruthenium oxides by zinc substitution. *Angew. Chem. Int. Ed.*, **2010**, *49*(28), 4813-4815.
- [5] Frame, F.A.; Townsend, T.K.; Chamousis, R.L.; Sabio, E.M.; Dittrich, T.; Browning, N.D.; Osterloh, F.E. Photocatalytic water oxidation with nonsensitized IrO_2 nanocrystals under visible and UV light. *J. Am. Chem. Soc.*, **2011**, *133*(19), 7264-7267.
- [6] Cheng, F.; Shen, J.; Peng, B.; Pan, Y.; Tao, Z.; Chen, J. Rapid room-temperature synthesis of nanocrystalline spinels as oxygen reduction and evolution electrocatalysts. *Nat. Chem.*, **2011**, *3*(1), 79-84.
- [7] Liang, Y.; Li, Y.; Wang, H.; Zhou, J.; Wang, J.; Regier, T.; Dai, H. Co_3O_4 nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction. *Nat. Mater.*, **2011**, *10*(10), 780-786.
- [8] Gao, M.-R.; Xu, Y.-F.; Jiang, J.; Zheng, Y.-R.; Yu, S.-H. Water oxidation electrocatalyzed by an efficient $\text{Mn}_3\text{O}_4/\text{CoSe}_2$ nanocomposite. *J. Am. Chem. Soc.*, **2012**, *134*(6), 2930-2933.
- [9] Godwin, I.J.; Lyons, M.E.G. Enhanced oxygen evolution at hydrous nickel oxide electrodes via electrochemical ageing in alkaline solution. *Electrochem. Commun.*, **2013**, *32*(7), 39-42.
- [10] Kim, J.W.; Lee, J.K.; Philusot, D.; Yi, Y.; Lee, H.J.; Lee, J. Self-organized one-dimensional cobalt compound nanostructures from CoC_2O_4 for superior oxygen evolution reaction. *J. Phys. Chem. C*, **2013**, *117*(45), 23712-23715.
- [11] Smith, R.D.L.; Prévot, M.S.; Fagan, R.D.; Zhang, Z.; Sedach, P.A.; Siu, M.K.J.; Trudel, S.; Berlinguette, C. P. Photochemical route for accessing amorphous metal oxide materials for water oxidation catalysis. *Science*, **2013**, *340*(6128), 60-63.
- [12] Chemelewski, W.D.; Lee, H.-C.; Lin, J.-F.; Bard, A.J.; Mullins, C.B. Amorphous FeOOH oxygen evolution reaction catalyst for photoelectrochemical water splitting. *J. Am. Chem. Soc.*, **2014**, *136*(7), 2843-2850.
- [13] Li, Y.; Hasin, P.; Wu, Y. $\text{Ni}_x\text{Co}_{3-x}\text{O}_4$ nanowire arrays for electrocatalytic oxygen evolution. *Adv. Mater.*, **2010**, *22*(17), 1926-1929.
- [14] Landon, J.; Demeter, E.; İnöglu, N.; Keturakis, C.; Wachs, I.E.; Vasic, R.; Frenkel, A.I.; Kitchin, J.R. Spectroscopic characterization of mixed Fe-Ni oxide electrocatalysts for the oxygen evolution reaction in alkaline electrolytes. *ACS Catal.*, **2012**, *2*(8), 1793-1801.
- [15] Kumar, B.; Saha, S.; Basu, M.; Ganguli, A.K. Enhanced hydrogen/oxygen evolution and stability of nanocrystalline (4-6 nm) copper particles. *J. Mater. Chem. A*, **2013**, *1*(11), 4728-4734.
- [16] Louie, M.W.; Bell, A.T. An investigation of thin-film Ni-Fe oxide catalysts for the electrochemical evolution of oxygen. *J. Am. Chem. Soc.*, **2013**, *135*(3), 12329-12337.
- [17] Chi, B.; Lin, H.; Li, J. Cations distribution of $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ and its electrocatalytic activities for oxygen evolution reaction. *Int. J. Hydrogen Energy*, **2008**, *33*(18), 4763-4768.
- [18] Wu, X.; Scott, K. $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$ ($0 \leq x < 1$) nanoparticles for oxygen evolution in high performance alkaline exchange membrane water electrolyzers. *J. Mater. Chem.*, **2011**, *21*(33), 12344-12351.
- [19] Chi, B.; Li, J.; Yang, X.; Lin, H.; Wang, N. Electrophoretic deposition of ZnCo_2O_4 spinel and its electrocatalytic properties for oxygen evolution reaction. *Electrochim. Acta*, **2005**, *50*(10), 2059-2064.

- [20] Liu, X.; Chang, Z.; Luo, L.; Xu, T.; Lei, X.; Liu, J.; Sun, X. Hierarchical $\text{Zn}_x\text{Co}_{3-x}\text{O}_4$ nanoarrays with high activity for electrocatalytic oxygen evolution. *Chem. Mater.*, **2014**, 26(5), 1889-1895.
- [21] Garcia-Mota, M.; Bajdich, M.; Viswanathan, V.; Vojvodic, A.; Bell, A.T.; Nørskov, J.K. Importance of correlation in determining electrocatalytic oxygen evolution activity on cobalt oxides. *J. Phys. Chem. C*, **2012**, 116(39), 21077-21082.
- [22] Chou, N.H.; Ross, P.N.; Bell, A.T.; Tilley, T.D. Comparison of cobalt-based nanoparticles as electrocatalysts for water oxidation. *ChemSusChem*, **2011**, 4(11), 1566-1569.
- [23] Grewe, T.; Deng, X.; Weidenthaler, C.; Schüth, F.; Tuysüz, H. Design of ordered mesoporous composite materials and their electrocatalytic activities for water oxidation. *Chem. Mater.*, **2013**, 25(24), 4926-4935.
- [24] Alvarado, S.R.; Guo, Y.; Ruberu, T.P.A.; Bakac, A.; Vela, J. Photochemical versus thermal synthesis of cobalt oxyhydroxide nanocrystals. *J. Phys. Chem. C*, **2012**, 116(18), 10382-10389.
- [25] Cheng, S.; Liu, H.; Logan, B. Power densities using different cathode catalysts (Pt and CoTMPP) and polymer binders (Nafion and PTFE) in single chamber microbial fuel cells. *Environ. Sci. Technol.*, **2006**, 40(1), 364-369.
- [26] Palmas, S.; Ferrara, F.; Mascia, M.; Polcaro, A.M.; Ruiz, J. R.; Vacca, A.; Piccaluga, G. Modeling of oxygen evolution at teflon-bonded $\text{Ti/Co}_3\text{O}_4$ electrodes. *Int. J. Hydrogen Energy*, **2009**, 34(4), 1647-1654.
- [27] Wu, L.-K.; Hu, J.-M. A silica co-electrodeposition route to nanoporous Co_3O_4 film electrode for oxygen evolution reaction. *Electrochim. Acta*, **2014**, 116(2), 158-163.
- [28] Lu, B.; Cao, D.; Wang, P.; Wang, G.; Gao, Y. Oxygen evolution reaction on Ni-substituted Co_3O_4 nanowire array electrodes. *Int. J. Hydrogen Energy*, **2011**, 36(1), 72-78.
- [29] He, J.; Peng, Y.; Sun, Z.; Cheng, W.; Liu, Q.; Feng, Y.; Jiang, Y.; Hu, F.; Pan, Z.; Bian, Q.; Wei, S. Realizing high water splitting activity on Co_3O_4 nanowire arrays under neutral environment. *Electrochim. Acta*, **2014**, 119(5), 64-71.
- [30] Wang, L.; Liu, B.; Ran, S.; Huang, H.; Wang, X.; Liang, B.; Chen, D.; Shen, G. Nanorod-assembled Co_3O_4 hexapods with enhanced electrochemical performance for lithium-ion batteries. *J. Mater. Chem.*, **2012**, 22(44), 23541-23546.
- [31] Wu, Z.S.; Ren, W.C.; Wen, L.; Gao, L.B.; Zhao, J.P.; Chen, Z.P.; Zhou, G.M.; Li, F.; Cheng, H.M. Graphene anchored with Co_3O_4 nanoparticles as anode of lithium ion batteries with enhanced reversible capacity and cyclic performance. *ACS Nano*, **2010**, 4(6), 3187-3194.
- [32] Liu, Z.-Q.; Xiao, K.; Xu, Q.-Z.; Li, N.; Su, Y.-Z.; Wang, H.-J.; Chen, S. Fabrication of hierarchical flower-like super-structures consisting of porous NiCo_2O_4 nanosheets and their electrochemical and magnetic properties. *RSC Adv.*, **2013**, 3(13), 4372-4380.
- [33] Liu, Z.-Q.; Xu, Q.-Z.; Wang, J.-Y.; Li, N.; Guo, S.-H.; Su, Y.-Z.; Wang, H.-J.; Zhang, J.-H.; Chen, S. Facile hydrothermal synthesis of urchin-like NiCo_2O_4 spheres as efficient electrocatalysts for oxygen reduction reaction, *Int. J. Hydrogen Energy*, **2013**, 38(16), 6657-6662.