Effect of Morphology of Co$_3$O$_4$ for Oxygen Evolution Reaction in Alkaline Water Electrolysis

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Abstract: In this paper, three different morphological Co$_3$O$_4$ electrodes for oxygen evolution reaction (OER) have been synthesized. By comparing the three morphologies of Co$_3$O$_4$, the electrocatalytic properties show that the urchin-like spheres of Co$_3$O$_4$ electrode have relative low overpotential and good electrocatalysis stability, indicating that the structure of urchin-like Co$_3$O$_4$ spheres exhibit an easy OER for water splitting.

Keywords: Co$_3$O$_4$, hydrothermal method, oxygen evolution reaction, sol-gel auto combustion 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 an 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]. Among these non-precious catalysts, cobalt is earth-abundant and both Co$_3$O$_4$ and the substituted cobaltites M$_x$Co$_3$O$_4$ (M = Ni, Fe, Cu or Zn) exhibit excellent OER activities [13-20]. Upon electrochemical oxidation, metallic Co undergoes gradually oxidation to form Co(OH)$_2$, CoO, Co$_3$O$_4$ and CoO(OH), etc [21-24]. In particular, as one of the well-known spinel electrocatalysts, Co$_3$O$_4$ 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$_3$O$_4$, increasing the effective surface area of catalysts is needed. Therefore, it was found that the morphologies of Co$_3$O$_4$ electrocatalysts play a key role in OER. In general, Co$_3$O$_4$ electrocatalysts for the OER are thin film or particle agglomerates bound together by polymers. [25-27]. Recently, one-dimensional Co$_3$O$_4$ nanowires as electrocatalyst for the OER have garnered significant attention [28, 29]. Compared with Co$_3$O$_4$ particles and thin films, the one-dimensional Co$_3$O$_4$ nanowires possess a large interfacial area, high efficient active sites, and superior mass transport property.

In this work, the urchin-like Co$_3$O$_4$ spheres have been successfully synthesized for OER via a simple and effective solution method. Simultaneously, other two morphologies of Co$_3$O$_4$ were obtained by hydrothermal process and sol-gel auto combustion method. By comparing the different morphologies of Co$_3$O$_4$, We examined their electrochemical OER activities and investigated the relationship among the catalyst activity and morphology, and surface area of Co$_3$O$_4$.

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 Co(NO$_3$)$_2$·6H$_2$O was dissolved into a 80 mL mixed solution (50 volume % ethanol: 50 volume % H$_2$O) 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 × 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$_3$O$_4$ 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 Co(NO$_3$)$_2$·6H$_2$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$_3$O$_4$ (denoted as S$_2$) was obtained by annealed at 400°C in atmosphere for 2 h.
In a typical sol-gel autocombustion method: 1 mmol of Co(NO3)2·6H2O 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 Co3O4 (denoted as S3) 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, 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 Kα radiation (λ = 1.5418 Å). 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 Co3O4 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 Co3O4 (JCPDF: 43-1003, Space group: Fd3m(227)) with lattice constants a = b = c = 8.084 Å. 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 S1. It is observed that numerous spherical urchin shape structures of Co3O4 were obtained with uniform diameters of 6 μm. Fig. (2b) shows TEM image of the sample, clearly revealing each urchin-like Co3O4 sphere has uniform...
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$_3$O$_4$. Fig. (2d) 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 S2 is also displayed in the HRTEM, the uniform 0.286 nm interplanar distance corresponds to the (220) plane of Co$_3$O$_4$. The typical thickness of these nanosheets are 150-200 nm. The typical SEM images of the S$_1$ sample are shown in Fig. (2g-I), which reveals the bulk structures of Co$_3$O$_4$.

The more detailed chemical composition and the oxidation state of the Co$_3$O$_4$ samples were further analyzed by XPS measurements. Fig. (3a) compares the XPS survey spectrum of three different morphological Co$_3$O$_4$ electrodes. Fig. (3b-c) shows the Co 2p and O 1s XPS spectrum of urchin-like Co$_3$O$_4$ spheres. As shown in Fig. (3b), two major peaks at binding energies of 780.3 and 795.4 eV corresponding to the Co 2p$_{3/2}$ and Co 2p$_{1/2}$ of Co$_3$O$_4$ 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$_3$O$_4$. The Co$_3$O$_4$ 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$_3$O$_4$ samples S$_1$ to S$_3$ have been 40.45, 19.85, and 22.25 m$^2$/g, 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$_3$O$_4$ 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$_3$O$_4$ electrodes in 1.0 M KOH at different scan rates. The current was normalized to the amount of Co$_3$O$_4$ in 1 cm$^2$ electrode. As shown in Fig. (4d), the CVs of different morphological Co$_3$O$_4$ 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).
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 S1 is 0.64 V. Before 0.64 V, no OER peak happens on the S1 electrode. In addition, the onset potential of S1 is lower 14.8 mV than that of S2, and lower 40 mV than that of S3, indicating that the urchin-like sphere of Co3O4 has a high activity for OER.

The stability of OER on the Co3O4 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 Co3O4 (S1) electrode is larger than that of the other two electrodes (S2 and S3). The current density of S1 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 S2 and S3 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 S1 is higher 0.31 mA cm⁻² than that of S2, and higher 0.61 mA cm⁻² than that of S3, indicating that the S1 electrode has higher activity and better stability than S2 and S3 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 S1 larger than S2 and S3 in Fig. (6b), indicating that the structure of Co3O4 with the morphology of urchin-like spheres has better performance in oxygen evolution reaction. Therefore, the improved OER performances of S1 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) S1 provide a larger electrode surface areas than S2 and S3.

![Fig. (4). (a-c) CVs of Co3O4 electrodes recorded in 1.0 M KOH at different scan rates; (d) CVs of Co3O4 electrodes in 1.0 M KOH at a scan rate of 2 mV/s.](image)

![Fig. (5). LSV curves for the OER on electrodes of Co3O4 recorded in 1.0 M KOH with a sweep rate of 1 mV/s at room temperature.](image)
In summary, on the basis of the OER activity on Co$_3$O$_4$ 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$_3$O$_4$ has an easier OER for water splitting. The Co$_3$O$_4$ 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.

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REFERENCES

[1] Walter, M.G.; Warren, E.L.; McKone, J.R.; Boetether, S.W.; Mi, Q.; Santori, E.A.; Lewis, N.S. Solar water splitting cells. *Chem. Rev.*, 2010, 110(11), 6446-6473.
[2] Bajdich, M.; Garcia-Mota, M.; Vojvodic, A.; Norskov, 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$_2$O$_4$ hybrid paper as an advanced electrocatalytic water-splitting material. *ACS Nano*, 2013, 7(11), 10190-10196.
[4] Petrykin, V.; Macounova, K.; Shlyakhitin, O.A.; Kril, 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.; Chamounis, 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$_3$O$_4$ 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, Z.; Zheng, Y.-R.; Yu, S.-H. Water oxidation electrocatalyzed by an efficient MnO$_x$/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.; Phiususit, D.; Yi, Y.; Lee, H.J.; Lee, J. Self-organized one-dimensional cobalt compound nanostructures from CoO$_2$ 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.; Sui, 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. Ni$_x$Co$_{3-x}$O$_4$ nanowire arrays for electrocatalytic oxygen evolution. *Adv. Mater.*, 2010, 22(17), 1926-1929.
[14] Landon, J.; Demeter, E.; Inoglu, N.; Keturakis, C.; Wachs, I.E.; Vasie, R.; Frenkel, A.I.; Katchin, J.R. Spectroscopic characterization of mixed Fe-Ni oxide electrocatalysts for the oxygen evolution reaction in alkaline electrolytes. *ACS Catal.*, 2012, 2(6), 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 oxidation of oxygen. *J. Am. Chem. Soc.*, 2013, 135(3), 12329-12337.
[17] Chi, B.; Lin, H.; Li, J. Cations distribution of Cu$_x$Co$_{3-x}$O$_4$ and its electrocatalytic activities for oxygen evolution reaction. *Int. J. Hydrogen Energy*, 2008, 33(18), 4763-4768.
[18] Wu, X.; Scott, K. Cu$_{x}$Co$_{3-x}$O$_4$ (0 ≤ 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$_2$O$_4$ 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 Zn-Co3-O4 nanoarrays with high activity for electrocatalytic oxygen evolution. Chem. Mater., 2014, 26(5), 1889-1895.

[21] García-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 TiCo3O4 electrodes. Int. J. Hydrogen Energy, 2009, 34(4), 1647-1654.

[27] Wu, L.-K.; Hu, J.-M. A silica co-electrodeposition route to nanoporous Co3O4 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 Co3O4 nanowire array electrodes. Int. J. Hydrogen Energy, 2011, 36(1), 72-78.

[29] He, J.; Meng, 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 Co3O4 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 Co3O4 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 Co3O4 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 NiCo2O4 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 NiCo3O4 spheres as efficient electrocatalysts for oxygen reduction reaction, Int. J. Hydrogen Energy, 2013, 38(16), 6657-6662.