

Sulfide doped cobalt oxide nanosphere as a highly efficient electrocatalyst for oxygen evolution reaction

Received Jan.8, 2019,
Accepted Feb.24, 2019,

DOI: 10.4208/jams.010819.022419a

<http://www.global-sci.org/jams/>

Qifei Guo¹, Yu Han², Rongxing He^{1,*}

Abstract. Electrochemical water splitting has been known as a promising and environmental approach to produce hydrogen by avoiding relying on fossil fuels. Unfortunately, the efficient and large-scale H₂ production is still hindered by the sluggish kinetics of the oxygen evolution reaction (OER) at the anode side of a water electrolyzer. Herein, we report a novel amorphous sulfide doped cobalt oxide (amorphous Co-S-O) nanosphere as an efficient electrocatalyst for OER. The Co-S-O electrode exhibits high HER activity and good stability.

Keywords: OER; Electrocatalyst; Sulfide Cobalt; Nanosphere;

1. Introduction

Electrochemical splitting of water provides an attractive way to produce hydrogen fuel.[1-4] The efficiency of this hydrogen generation depends enormously on the anodic oxygen evolution reaction (OER).[5] However, by the reason of multistep reaction involving four e⁻ transfers, OER has high kinetic barrier, large overpotential and low efficiency.[6] As is known to all, Pt- and Ru-based materials are the benchmark catalysts for OER, but the resource scarcity, high cost and poor stability of Pt- and Ru-based catalysts hinder their large scale application.[7-9] To meet these challenges, great effort has been given to reduce the overpotentials of OER kinetics, using cheaper earth abundant materials.[10]

Catalytic activity is of great important indicator in evaluation the efficacy of electrocatalysts. Activities are controlled by two factors: the number of active sites and more efficient mass transportation.[11] With this in mind, it is very necessary to logically design and prepare hollow structure catalysts, which maximize the specific surface area and provide abundant

active sites for OER.

Herein, we synthesized novel amorphous sulfide doped cobalt oxide (amorphous Co-S-O) nanosphere. The Co-S-O shows more remarkable OER activity than pure Co₃O₄ in 1.0 M KOH. The Co-S-O with a low overpotential of 285 mV at the current density of 10 mA cm⁻² and satisfied durability.

2. Experimental section

Firstly, Co(CH₃COO)₂•4H₂O, NaHCO₃, and polyvinylpyrrolidone were dissolved into ethylene glycol under stirring to form a clear solution, Then the solution was transferred into a Teflon-lined stainless autoclave (50 mL). Then the autoclave was sealed and placed in an oven at 200 °C for 20 h. Then, The Co₃O₄ was synthesized by calcined the pink precipitate at 300 °C for 2 h. Finally, above resultant Co₃O₄ with thioacetamide was dispersed in deionized water at 160 °C for 3 h.

3. Results and discussion

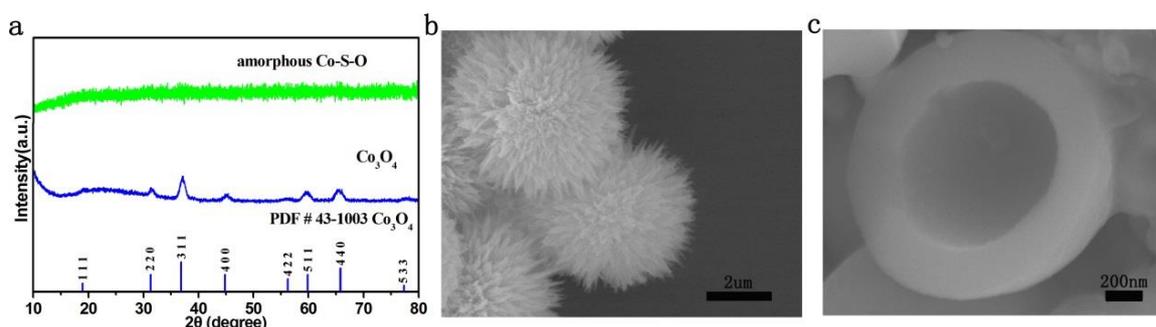


Figure 1. (a) XRD patterns of amorphous Co-S-O, and Co₃O₄ precursor; (b) The SEM images of the Co₃O₄ precursor; (c) The SEM images of the amorphous Co-S-O.

¹Key Laboratory of Luminescence and Real-Time Analytical Chemistry (Southwest University), Ministry of Education, College of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

²High School Affiliated Southwest University, Chongqing 400715, China
Corresponding author: Email: herx@swu.edu.cn.

Figure 1a shows the X-ray diffraction (XRD) patterns. The picture shows that we have successfully synthesized the precursor. For the target product, the XRD shows no obvious diffraction peaks, which indicates the amorphous nature of the

product. **Figure 1b** shows that the precursor is a burr sphere. **Figure 1c** shows that amorphous Co-S-O is a hollow sphere.

As we all know, X-ray photoelectron spectroscopy (XPS) analysis can detect the surface composition and chemical states. The XPS analyses reveal that Co-S-O include Co, S, and O elements without other impurities (**Figure 2a**). The Co 2p XPS spectrum of Co-S-O is displayed in **Figure 2b**. The Co 2p spectra peaks at 778.4 eV and 793.5 eV correspond to spin-orbit splitting values of Co 2p_{3/2}. The Co 2p spectra peaks at 781.4 eV and 797.5 eV correspond to spin-orbit splitting values of Co 2p_{1/2}. In **Figure 2c**, the two peaks at 161.5 and 162.2 eV are attributed to the S 2p_{3/2} and S 2p_{1/2} of Co-S, respectively. The peaks at 168.5 and 169.1 eV correspond to S-O bond.

The OER catalytic activity of amorphous Co-S-O and Co₃O₄ were investigated in 1 M KOH with the three electrode system. The linear sweep voltammograms (LSV) of Co-S-O exhibits the highest electrocatalytic activity with the lowest overpotential of 285 mV to reach 10 mA cm⁻², smaller than that of Co₃O₄ (320 mV) (**Figure 3a**). The Tafel slope of the Co-S-O are only about 49.67 mV dec⁻¹ (**Figure 3b**), which is much lower than that of the Co₃O₄ (72.63 mV dec⁻¹) and RuO₂ (61.05 mV dec⁻¹). amorphous Co-S-O has a low Tafel slope, which indicates that it has great reaction kinetics in the OER.

To assess the OER reaction kinetics, the electrochemical impedance spectroscopy (EIS) tests were conducted (**Figure 4a**). The Nyquist plots suggest that Co-S-O possess the smaller interfacial charge transfer resistance and faster electron transfer process than Co₃O₄. The stability of Co-S-O electrode was studied using chronoamperometry. The tested result (**Figure 4d**) at 1.52 V vs RHE suggests that the electrocatalytic activity of Co-S-O electrode can be maintained for a long time

without obvious change. The above results confirm that Co-S-O is a stable and highly active electrocatalyst for OER.

4. Conclusion

In summary, amorphous Co-S-O is demonstrated excellent electrocatalytic performance and catalytic stability for OER in alkaline medium. To approach a current density of 10 mA cm⁻², amorphous Co-S-O only needs the overpotential of 285 mV. This work breaks a new path for the single metal sulfides and opens up an avenue in designing other advanced electrocatalysts.

Acknowledgements

This work was supported by Chongqing Municipal Natural Science Foundation (cstc2018jcyjAX0625).

References

- [1]. Yu, X.-Y.; Yu, L.; Lou, X. W. D. Metal Sulfide Hollow Nanostructures for Electrochemical Energy Storage Advanced Energy Materials 2016, 6, 1501333.
- [2]. Chen, B.; Li, R.; Ma, G.; Gou, X.; Zhu, Y.; Xia, Y. Cobalt sulfide/N,S codoped porous carbon core-shell nanocomposites as superior bifunctional electrocatalysts for oxygen reduction and evolution reactions Nanoscale 2015, 7, 20674.
- [3]. Ito, Y.; Cong, W.; Fujita, T.; Tang, Z.; Chen, M. High catalytic activity of nitrogen and sulfur co-doped nanoporous graphene

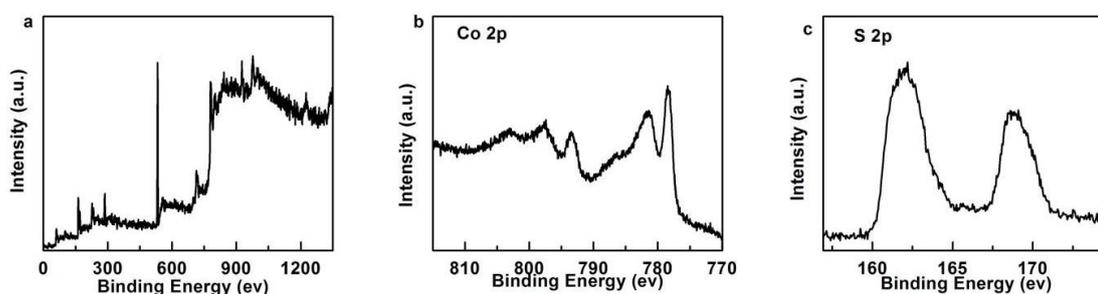


Figure 2. (a) XPS survey spectrum for amorphous Co-S-O and (b) Co 2p, (c) S 2p.

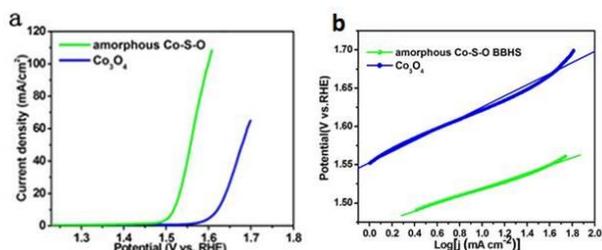


Figure 3. (a) polarization curves for OER at a scan rate of 10 mV s⁻¹ in 1.0 M KOH and (b) corresponding Tafel plots.

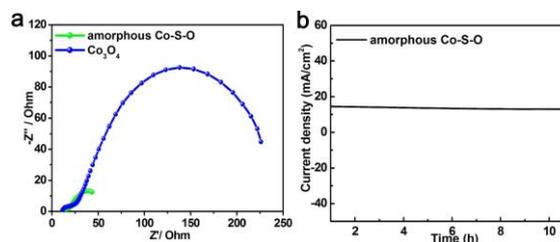


Figure 4. (a) Nyquist plots of different electrodes at an overpotential of 300 mV for HER; (b) Chronoamperometric response of amorphous Co-S-O in 1 M KOH solution at the applied potential of 1.52 V versus RHE.