Journal of Power Sources 390 (2018) 224–233

Contents lists available at ScienceDirect

Journal of Power Sources

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

Cross-linked trimetallic nanopetals for electrocatalytic water splitting

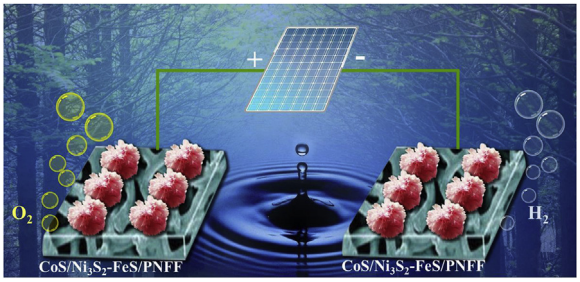
Shanqing Qu[a,1], Wei Chen[b,1], Jinsong Yu[c], Guangliang Chen[a,*], Rui Zhang[a], Sijun Chu[a], Jun Huang[b,**], Xingquan Wang[b], Chaorong Li[a], Kostya (Ken) Ostrikov[d]

[a] Key Laboratory of Advanced Textile Materials and Manufacturing Technology, Engineering Research Center for Eco-Dyeing & Finishing of Textiles, Ministry of Education, Zhejiang Sci-Tech University, Hangzhou 310018, China
[b] College of Physics and Electronic Information, Gannan Normal University, Ganzhou, Jiangxi 341000, China
[c] Department of Chemistry and Chemical Engineering, University of New Haven, 300 Boston Post Road, West Haven, CT 06516, United States
[d] School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology, Brisbane, QLD 4000, Australia

HIGHLIGHTS

- Many active sites are formed on the Ni-Fe foam treated by the air-DBD plasma.
- The sakura-like CoS/Ni_3S_2-FeS with a large surface area occurs on the PNFF.
- Ni-Fe oxides obtained by DBD plasma benefit the OER process.
- The cross-linked CoS/Ni_3S_2-FeS/PNFF exhibits a high catalytic activity for HER and OER.
- The generating efficiency of H_2 and O_2 is ultrahigh in the alkaline media.

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Bifunctional electrocatalysis
Trimetallic sulfides
Overall water splitting
Plasma treatment
Synergetic effects

ABSTRACT

A facile and effective approach for fabricating a 3D nanostructured catalyst based on nonprecious metals for water splitting is reported. The Ni-Fe foam (NFF) is pretreated by a dielectric barrier discharge (DBD) plasma under ambient conditions, resulting in numerous microtrenches on the NFF surface. Meanwhile, some NiO and Fe_2O_3 spots appear on the NFF foam upon exposure to hot filaments generated in DBD plasmas in air. Cross-linked 3D CoS/Ni_3S_2-FeS nanopetals emerge on plasma treated NFF surface (PNFF) through sulfurization of Co nanosheets electrodeposited on PNFF. The produced CoS/Ni_3S_2-FeS/PNFF nanocomposite exhibited high electrocatalytic activity and stability for the overall water splitting. Benefiting from the 3D hierarchical nanoarchitecture of CoS/Ni_3S_2-FeS/PNFF with a large surface area, fast electron transport, and low free energy for adsorption, a current density of 10 mA cm^{-2} is achieved for the HER and OER with ultralow overpotentials of 75 mV and 136 mV, respectively. The amounts of H_2 and O_2 produced at a normalized current density of 10 mA cm^{-2} in 1 M KOH are about 680 μmol h^{-1} and 1230 μmol h^{-1}, respectively. These values are very competitive compared with the state-of-the-art results reported for noble metal-free electrodes in alkaline media.

1. Introduction

Facing the increasing concerns over severe environmental impacts caused by byproducts (*e.g.* CO_x, NO_x) of fossil fuel consumption, it is necessary to develop renewable and sustainable energy sources [1,2]. Hydrogen, a renewable clean and abundant energy source, is well

* Corresponding author.
** Corresponding author.
E-mail addresses: glchen@zstu.edu.cn (G. Chen), junhuang66@163.com (J. Huang).
[1] The authors contribute equally to this work.

https://doi.org/10.1016/j.jpowsour.2018.04.061
Received 25 January 2018; Received in revised form 12 April 2018; Accepted 15 April 2018

recognized as one of the most suitable candidates to replace conventional fossil fuels in the future [3–5]. Currently, electrochemical and photoelectrochemical water electrolysis remain as the two most important methods for producing ultrapure H_2. Although the photovoltaic and photoelectrochemical approaches are environmentally friendly, and the efficiency of sunlight-driven water splitting reaches 12.3% for generating H_2 [6], widespread implementation of these approaches is still impeded by the high production equipment and infrastructure costs.

Electrocatalytic water splitting into oxygen (OER) and hydrogen (HER), on the other hand, is widely considered as one of the most promising and competitive carbon emissions-free approaches [1,7,8]. However, the efficiencies of the HER and in particular, OER reactions remain insufficient due to the high activation barriers and sluggish four proton-coupled electron transfer [9]. This is why the OER is currently considered as a major bottleneck in the overall water splitting. Therefore, sustainable production of H_2 through water electrolysis demands efficient, economical and robust catalysts for both HER and OER processes [10–12]. At present, the state-of-the-art electrocatalysts for OER and HER are Ir- and Ru-based materials and Pt-group metals, respectively [13–15]. Notably, the electrodes made of noble metals normally exhibit a small overpotential, but the onset potential at high current density ($> 100\ mA\ cm^{-2}$) is still very large. In addition, high prices and limited abundance of precious metals limit their practicality for large-scale water electrolysis [2,16]. Thus, it is crucial to develop cost-efficient, nonprecious metal based bifunctional catalysts with high activity for the overall water splitting.

Driven by such needs, substantial efforts have been devoted to developing nanostructured non-noble catalysts based on transition metals, such as transition metal sulfides [17–22], nitrides [23], phosphides [24,25], selenides [5,26–28], borides [29–31] and hydroxides [32–34] for the HER or the OER. Unfortunately, their performance is still lower compared to noble metal based catalysts, mainly due to poor electrical conductivity. Another challenge related to the development of non-noble nanoparticle based electrodes is related to nanomaterial fixation using a polymer binder [35,36]. This approach not only obscures many of the active sites, but also hinders electron transport, consequently reducing the overall electrocatalytic activity towards water splitting.

Recent studies indicate that nickel/cobalt sulfide catalysts on the nickel foam are among the most viable options for water splitting in strong alkaline electrolyte solutions. For example, Feng et al. claimed that the performance for both the HER and OER in an alkaline medium can be improved if the $\{\bar{2}10\}$ high-index facets of the Ni_3S_2/NF can be exposed and accessed [13]. Wu et al. fabricated ultrasmall $Ni_xCo_{3-x}S_4$ coupled Ni_3S_2 nanosheet arrays on the nickel foam, and this catalyst delivers water-splitting current densities of 10 and 100 $mA\ cm^{-2}$ at the applied potentials of 1.53 and 1.80 V, respectively [37]. Despite these advances, the overpotentials of most of the reported bifunctional electrocatalysts are still relatively higher than those of the noble metal based catalysts. Moreover, the output efficiency of producing the H_2 and O_2 via such electrocatalysts is still unsatisfactory. Therefore, rational design of electrodes with high electrocatalytic performance is warranted, especially for applications in alkaline media.

Plasma technology has recently been very effective in catalyst fabrication and performance improvement. For example, Wang et al. prepared Co_3O_4 nanosheets with oxygen vacancies [38] and CoFe LDH nanosheets with multivacancies [39] using Dielectric Barrier Discharge (DBD) plasmas in Ar gas and water vapour, respectively. The fabricated Co_3O_4 and CoFe layered double hydroxide (LDH) nanosheets exhibited high electrocatalytic activity for OER, and the Tafel slopes of Co_3O_4 and CoFe LDH nanosheets were only 68 and 36 $mV\ decade^{-1}$. Moreover, the OER activity of water-plasma exfoliated CoFe LDH nanosheets was better than RuO_2. Meanwhile, Alshareef et al. [40] fabricated bifunctional electrocatalyst made of NiCoP nanosheets on the Ni foam by processing in Ar/PH_3 plasmas, and the overpotentials of HER and OER at a current density of 10 $mA\ cm^{-2}$ were only 32 mV and 280 mV, respectively. However, the electrocatalytic stability of the nanostructured materials assembled on the surface of the metal foam appears to be weaker compared to in-situ fabricated electrocatalysts. In-situ produced bifunctional catalyst made of Ni_3S_2 particles on a NF surface [13] showed a remarkably improved stability beyond 400 h; however, electrocatalytic activity of this catalyst in HER and OER reaction was notably lower compared to the nanomaterials assembled on the NF surfaces [28,34,40]. Therefore, designing an in-situ grown electrocatalyst on the metal foam with high HER and OER performance is still a challenge. Based on the works mentioned above, the plasma technique may be an effective approach to help overcome this problem.

Herein, we process a Ni-Fe (atomic ratio: 4/1) foam (NFF) using DBD plasmas in air (for simplicity referred to as air-DBD plasma) below. This treatment resulted in many microtrenches for tuning the cross-linked 3D nanocomposite and active sites (*e.g.*, NiO, Fe_2O_3) for increasing the OER activity on the NFF surface. Briefly, hydrangea-like petals assembled with cobalt nanosheets are produced on the plasma-treated NFF (PNFF) surface using the electrodeposition method. Then, the cross-linked ternary metal sulfides (CoS/Ni_3S_2-FeS) are successful fabricated via a hydrothermal sulfidation process, and the whole procedure is presented in Fig. 1. Some roots of CoS flowers were embedded in the microtrenches and cross-linked with the in-situ fabricated Ni_3S_2-FeS nanosheets, which can greatly strengthen the electrocatalytic stability of the CoS/Ni_3S_2-FeS catalyst. The fabricated nanopetal-like M_xS catalysts exhibit excellent HER and OER perfomance and stability in 1 M KOH, with the overpotentials of 75 mV (HER) and 136 mV (OER) to deliver 10 $mA\ cm^{-2}$, outperforming most of the state-of-the-art electrocatalysts.

2. Experimental section

2.1. Chemicals and reagents

Ni-Fe foam (NFF) (thickness: 0.5 mm) was obtained from Kunshan

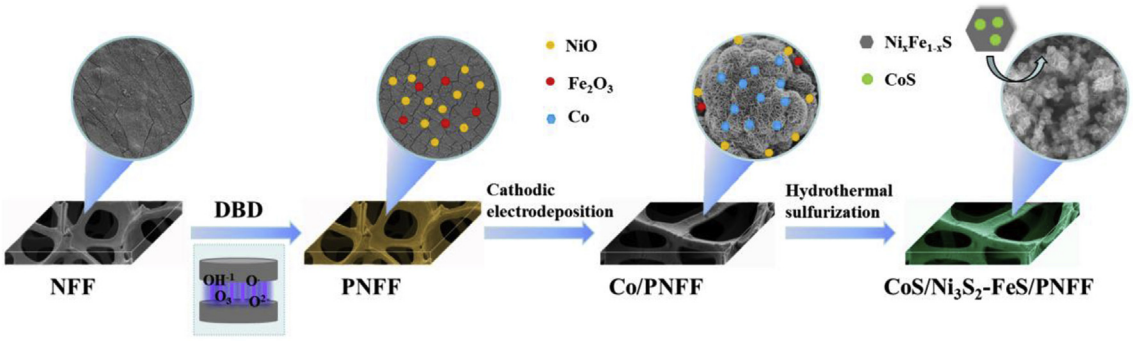


Fig. 1. Preparation of CoS/Ni_3S_2-FeS on the Ni-Fe foam.