ScienceDirect

Applied Surface Science

Volume 648, 1 March 2024, 159083

Full Length Article

Economic and binder-free synthesis of $NiCo_2O_4$ nanosheets on a Flexible stainless steel mesh as a bifunctional electrode for water splitting

Pooja K. Bhoj [a], Gokul P. Kamble [a], Jyotiprakash B. Yadav [b], Tukaram D. Dongale [c], Bhaskar R. Sathe [d], Anil V. Ghule [a]

Show more

https://doi.org/10.1016/j.apsusc.2023.159083

Get rights and content

Highlights

- Economic and binder-free synthesis of bifunctional $NiCo_2O_4$@FSSM for water splitting.
- Low overpotential of 310 mV (OER) and 79 mV (HER)@ 10 mAcm^{-2}.
- OER and HER stability of $NiCo_2O_4$@FSSM examined for 43 h.
- Practical applicability of $NiCo_2O_4$@FSSM explored in the large-scale set-up.
- Scale-up showed O_2 (7.4 L) and H_2 (11.5 L) evolution in 25 h.

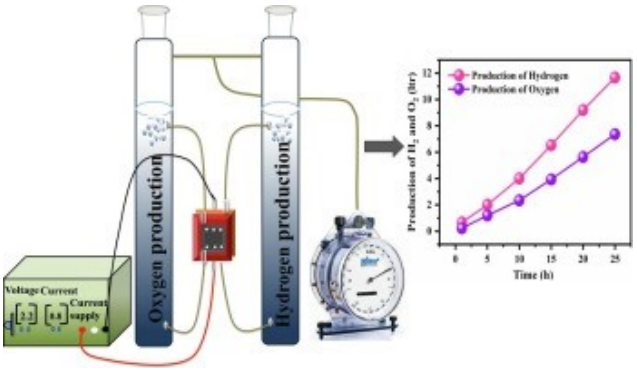
Abstract

Water as a green source of hydrogen has attracted the attention of researchers considering its

potential applications in the energy sector. Thus, developing efficient bifunctional electrocatalysts for water splitting is a potential challenge perceived by researchers exploring the development of sustainable energy technologies. With this motive, the present study focuses on the preparation of the highly active, economic, binder-free, and bifunctional $NiCo_2O_4$ nanosheets@ Flexible Stainless Steel Mesh substrate (NCO@FSSM) electrocatalyst *via* reflux condensation method for the bulk O_2 and H_2 production. The influence of reflux condensation temperatures (100, 120, 140 °C) on the morphology and electrocatalytic activity is investigated. Electrocatalytic properties for NCO@FSSM synthesized at 120 °C were noted exhibiting smaller overpotentials for oxygen evolution reaction (OER, 310 mV) and hydrogen evolution reaction (HER, 79 mV) at 10 mA cm^{-2}, which were lowest among the previously reported Ni, and Co-based electrodes. Additionally, the scale-up experiments with NCO-120@FSSM film (8 cm X 8 cm) as an anode and FSSM as a cathode and vice-versa, in a specially designed scale-up electrochemical cell revealed steady electrocatalytic performance. The real-time water splitting was studied for 25 h and was noted to produce 7.4 L of (O_2) and 11.5 L of hydrogen (H_2).

Graphical abstract

Developed bifunctional, efficient, durable, green, economical, and sustainable $NiCo_2O_4$@FSSM electrode with enhanced electrocatalytic activity for water splitting.



Download : Download high-res image (122KB)

Download : Download full-size image

Introduction

Over the years, global energy demand has rapidly increased along with the growing population, industrialization, and improvement in the standards of living, which is posing one of the biggest concerns of the twenty-first century [1]. For instance, in 2011, approximately 7 billion population in the world consumed 15 Trillion Watts (TW) of energy, which is anticipated to rise to 30 TW with a projected population of 9 billion by 2050 [1]. The statistical data explored from 2018 onwards

estimated that 79.5% of the world's energy economy is dependent on non-renewable and conventional energy sources such as fossil fuels such as coal, oil, natural gas, etc, which on combustion add to the concern, such as environmental pollution leading to global warming. To tackle this issue, efforts have been around the globe to find clean and renewable alternatives to fossil fuels [2]. Fortunately, nature offers abundant renewable energy sources, including solar, wind, tidal, biomass, etc. However, due to regional or seasonal factors, such energy sources become intermittently available, and not sufficient to overcome the further usage of fossil fuels [3]. Thus, efficient energy conversion and storage systems are required for the development of renewable energy and their technologies for widespread utilization. As a promising alternative to fossil fuels, hydrogen is considered a viable source of clean and green energy. Although the production of hydrogen from fossil fuels is feasible and affordable, it emits greenhouse gases as a byproduct causing environmental pollution and consequently adding to global warming. As a result, electrochemical water splitting has become a hot area for researchers due to its simplicity, high purity [4], and ability to scale up [5]. Moreover, the production of hydrogen from commercial electrolyzers usually operates at high cell voltage (1.8 to 2.0V), which is relatively higher than the least theoretically calculated value of 1.23V. Thus, minimizing the operating cell voltage close to the theoretical value by developing an efficient electrocatalyst is a challenge yet to be resolved [6].

In the last decade, Ir/Ru and Pt-based compounds were explored as OER and HER with great interest and were recognized as the benchmark electrocatalysts for water splitting [7]. However, their scarcity, less natural abundance, high cost, and poor stability limit their practical commercialization [8]. Thus, with the motivation to develop cost-effective alternatives as bifunctional electrocatalysts, researchers have explored the use of Fe, Co, and Ni-based borides, sulfides, selenides, and phosphides. Additionally, graphene-based materials, nitrides, cobaltites, hydroxides, and spinel oxides have also been widely investigated [9], [10], [11], [12], [13], [14]. Specifically, a brief overview of typical spinels is designated as AB_2X_4. In this spinel structure, A and B represent metals like Ni, Co, Fe, Mn, Zn, Cu, etc., whileXrepresents O, S, Se, Te, N, etc. It is important to note that metal ‘A’ and metal ‘B’ occupy the centers of tetrahedrally and octahedral coordinated locations, respectively [15], [16]. Spinels with various nanostructures, such as $CuCo_2O_4$, $ZnCo_2O_4$, $NiCo_2O_4$, $NiFe_2O_4$, and $NiMn_2O_4$, are prospective low-cost and environmentally friendly alternatives that exhibit good electrochemical performances and show a synergistic effect that increases conductivity, capacitive performance, and stability [16], [17], [18]. Among the transition-metal-based compounds, cobalt (Co)-based materials have emerged as promising electrocatalysts and significant effort has been made to create Co-based electrocatalysts with a variety of morphologies and investigating their performance in electrocatalytic activity towards HER and OER [19], [20]. In particular, it was noted that spinel $NiCo_2O_4$ with oxygen vacancy is beneficial which minimizes the obstacle for H_2O adsorption and also facilitates H_2 and O_2 desorption during the water-splitting process [21]. There are several reports on $NiCo_2O_4$ designed by ultrasonication process in powder form, hydrothermal method on Nickel foam, chemical bath method in powder form, hydrothermal method in powder form, electrodeposition method on Nickel foam, etc.[22], [23], [24], [25], [26]. Recently Sangeun Cho et. Al. reported the fabrication of mesoporous $NiCo_2O_4$

on nickel foam (NF) by using the electrodeposition technique. An electrode showed an overpotential of 315 mV at a current density of 10 mAcm^{-2} in 1 M KOH for OER [28]. Duo Cui et. al. reported the hydrothermal synthesis of $NiCo_2O_4$ on NF and presented a low overpotential of 318 mV at 10 mAcm^{-2} in 1 M KOH for OER [29]. Anna Dymerska et. al. reported the synthesis of $NiCo_2O_4$ by one-pot solvothermal method and showed the overpotential of 420 mV at 10 mAcm^{-2} in 1 M KOH for OER [23]. Leiming Tao et. al prepared $NiCo_2O_4$ on carbon fiber cloth by employing the hydrothermal method and reported 170 mV overpotential at 10 mAcm^{-2} in 1 M KOH for HER [30]. All of the above studies have only covered the electrochemical parameters, such as overpotential values, Tafel slope, etc to compare the OER and HER efficiency of the electrode. Moreover, the most widely used method includes the preparation of the catalyst in powder form and then loading onto a conductive substrate or on an electrode by using binders. Binders have a detrimental impact on electrocatalytic performance[3], and hence, the challenge is to prepare binder-free electrodes to enhance the performance as well as to avoid the detrimental impact of the binder. Furthermore, the current collector forms the important component, wherein stainless steel plates, nickel foam, carbon cloth, etc. have been widely explored as conducting substrates due to their planar surface, durability, surface area, and good electronic conductivity. However, the high cost, limited availability of surface area, and toxicity of Ni are some of the limiting aspects of their practical utility [31]. To circumvent these issues, in the present work, FSSM is employed as a current collector, which is relatively economical, has a 3D open mesh-like structure, high available surface area, and active sites. To the best of our knowledge, the use of in-situ deposited $NiCo_2O_4$ on FSSM as an electrode and its utility in the scale-up prototype device to assess the effectiveness of H_2 and O_2 evolution is reported for the first time.

Herein, we are reporting an economic approach for binder-free deposition of $NiCo_2O_4$ on low-cost FSSM substrate for the first time by employing a reflux condensation deposition technique. In this article, an effort has been made to explore the practical capability of NCO electrodes for effective electrochemical water-splitting. Additionally, the 8 cm×8 cm expanded samples were also prepared, and employed to investigate its actual oxygen and hydrogen generation capability using a scale-up electrochemical water splitting setup. It was noted that as-prepared $NiCo_2O_4$ exhibited a low overpotential of 310 and 79 mV for OER and HER respectively showing better electrocatalytic activity than previously reported $NiCo_2O_4$ electrocatalyst. It is expected that this work will pave new avenues for lowering the cost of electrode fabrication and exploring its performance for bulk H_2 and O_2 evolution in large-scale devices for practical commercialization.

Section snippets

Chemicals

All the chemicals were of analytical grade and used as received without further purification. Nickel

chloride hexahydrate ($NiCl_2{\cdot}6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), ammonium fluoride (NH_4F), and urea (NH_2CONH_2) were procured from Merck Chemicals. The flexible stainless steel 300 mesh (FSSM-300) procured from Zain Corporation India Pvt. Ltd were used as conducting substrates for in-situ deposition of $NiCo_2O_4$. Unless otherwise specified, all the solutions were prepared using double …

Structural characterizations

Investigating the electrode morphology is crucial as it influences surface area, active sites for charge storage, and the electrochemical performance for full electrolysis [28]. Fig. 2(a-c) illustrates the SEM images of NCO-100@FSSM, NCO-120@FSSM, and NCO-140@FSSM which shows the impact of varying temperatures on the electrode morphology. The SEM image of NCO-100@FSSM (Fig. 2a) shows random deposition and irregularly shaped nanosheets which are not properly grown on FSSM. Interestingly, it is…

Conclusion

In summary, the present work demonstrates the successful preparation of economic, and binder-free $NiCo_2O_4$ (NCO) nanosheets on the FSSM by the one-step reflux condensation deposition method. The electrocatalytic performance of NCO synthesized at various temperatures was studied systematically towards OER and HER. Among all the electrodes NCO-120@FSSM exhibited remarkable OER and HER activity. Interestingly, a low overpotential of 310 mV at 10 mAcm^{-2} and a small tafel slope of 98 mV dec^{-1} was…

CRediT authorship contribution statement

Pooja K. Bhoj: . **Gokul P. Kamble:** Data curation. **Jyotiprakash B. Yadav:** Data curation, Supervision, Writing – review & editing. **Tukaram D. Dongale:** Data curation, Supervision. **Bhaskar R. Sathe:** Data curation, Supervision, Writing – review & editing. **Anil V. Ghule:** ….

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.…

Acknowledgments

The author Pooja K. Bhoj is thankful to Mahatma Jyotiba Phule Research and Training Institute, Nagpur, India for the Research Fellowship MJPRF-2021 (File no. MAHAJYOTI/Nag./Fellowship/2021-22/1042 (269)). We are thankful to the Department of Chemistry, Shivaji University, Kolhapur for providing research facilities. We are also thankful to the **S**hivaji **U**niversity **G**roup for **A**dvanced

Research (**SUGAR**) for their valuable discussion.…

Recommended articles

References (50)

A. Yang *et al.*
Self-stabilization of zero-dimensional PdIr nanoalloys at two-dimensional manner for boosting their OER and HER performance
Appl. Surf. Sci. (2020)

S. Shiva Kumar *et al.*
Hydrogen production by PEM water electrolysis – A review
Mater. Sci. Energy Technol. (2019)

M. Wang *et al.*
The intensification technologies to water electrolysis for hydrogen production - A review
Renew. Sustain. Energy Rev. (2014)

W. Zhang *et al.*
Recent advances in cobalt-based electrocatalysts for hydrogen and oxygen evolution reactions
J. Alloys Compd. (2020)

J. Wang *et al.*
Earth-abundant transition-metal-based bifunctional catalysts for overall electrochemical water splitting: A review
J. Alloys Compd. (2020)

S.M. Pawar *et al.*
Nanoporous $CuCo_2O_4$ nanosheets as a highly efficient bifunctional electrode for supercapacitors and water oxidation catalysis
Appl. Surf. Sci. (2019)

R. Chen *et al.*
A flexible high-performance oxygen evolution electrode with three-dimensional $NiCo_2O_4$ core-shell nanowires
Nano Energy (2015)

D. Navadeepthy *et al.*

Boosting the kinetics of oxygen and hydrogen evolution in alkaline water splitting using nickel ferrite /N-graphene nanocomposite as a bifunctional electrocatalyst

Int. J. Hydrogen Energy. (2021)

A. Rebekah *et al.*

Zn-substituted MnCo2O4 nanostructure anchored over rGO for boosting the electrocatalytic performance towards methanol oxidation and oxygen evolution reaction (OER)

Int. J. Hydrogen Energy. (2020)

L. Fang *et al.*

Crystal-plane engineering of $NiCo_2O_4$ electrocatalysts towards efficient overall water splitting

J. Catal. (2018)

View more references

Cited by (6)

Exploring different non-iron based Co-spinel ferrites as potential electrode materials for supercapacitor applications

2024, Journal of Energy Storage

Show abstract

Tuning of physicochemical and electronic characteristics of Cu-doped NiCo<inf>2</inf>O<inf>4</inf> ternary inverse spinel oxides for effective electrocatalytic hydrogen evolution reaction

2024, International Journal of Hydrogen Energy

Show abstract

Moo<inf>3</inf>@Co<inf>2</inf>p/Nf Composite as Dual-Functional Electrocatalyst for Energy-Saving Hydrogen Production and Urea Oxidation ↗

2024, SSRN

Anchored Ru clusters on a lignin/algae carbon aerogel as an efficient bifunctional catalyst for water splitting ↗

2024, New Journal of Chemistry