Facile electrodeposited NiMoSe nanospheres for hydrogen evolution reaction

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ABSTRACT

The search for effective electrocatalysts for energy conversion is crucial for the advancement of green energy. Electrodeposition is a simple but effective method of preparing improved electrodes for use in the electrochemical sector. In the present work, we have synthesized amorphous NiMoSe nanospheres on Ni foam (NF) via a simple electrodeposition method. The synthesized NiMoSe demonstrates outstanding catalytic activity for the hydrogen evolution reaction (HER), with a small overpotential of 130 mV at a current density of 10 mA cm⁻² in 1 M KOH electrolyte and a small Tafel slope of 59 mV dec⁻¹. Furthermore, NiMoSe also shows long-term durability over 45 h.

1. Introduction

Hydrogen is recognized as the perfect energy carrier for the replacement of fossil fuels. Currently, methane reforming is used to produce hydrogen, which results in a huge emission of greenhouse gases and high energy consumption leading to global warming [1,2]. Electrolysis can be used to extract H₂ from water, resulting in a cleaner manner of manufacturing. Water splitting is made up of two half-reactions: the HER and the oxygen evolution reaction (OER) [3,4]. While HER is a relatively easy process, OER has sluggish kinetics. In general, platinum-group metals, are often used as electrocatalysts to improve the kinetics of the HER [5]. Nevertheless, their applications in large-scale commercialization suffer from supply shortages and expensive costs [6,7]. In this regard, it is extremely desirable to seek out low-cost non-noble metal-based catalysts with good electrocatalytic activity as viable HER electrocatalysts [8].

Transition metal selenides (TMSs) have demonstrated higher electron transport capabilities and improved electrochemical catalytic performances as a result of bigger atomic radii and regulated orbital occupation [9]. Moreover, TMSs show superior electrocatalytic activity than transition metal oxides due to the high conductivity of metallic Se compared to O [10,11]. As a result, the electrocatalytic community has focused a lot of attention on TMSs [12].

Herein, we presented a facile strategy for the fabrication of NiMoSe nanospheres on conductive NF substrate via electrodeposition method. The obtained trimetallic NiMoSe nanosphere electrode exhibits excellent HER catalytic properties with an overpotential of 130 mV to achieve current density of 10 mA cm⁻², a small Tafel slope of 59 mV dec⁻¹, and superior long-term stability for over 45 h in an alkaline medium. The high HER activity of NiMoSe electrode was attributed to a large number of electrochemically active surface areas and more active regions.

2. Results and discussion

The color of the NF changed from metallic to black during the electrodeposition procedure (detail process in [supporting information](#)). Fig. 1(a) depicts the XRD pattern of NiMoSe electrode. The diffraction peaks at 44.5, 51.9, and 76.4 are attributed to the (1 1 1), (2 0 0), and (2 2 0) crystal planes of NF substrate, respectively [13]. There were no new diffraction peaks seen following NiMoSe electrodeposition, indicating that the NiMoSe deposited onto NF was amorphous. Fig. S1 shows the XPS survey spectra of the NiMoSe sample in which three elements, namely Ni, Mo, and Se are identified. Besides O was also observed in the XPS survey spectrum because of surface oxidation of selenium when exposed to air. The high-resolution Ni 2p XPS spectrum (Fig. 1(b)) shows

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Fig. 1. (a) XRD pattern of NiMoSe, XPS spectra of (b) Ni 2p, (c) Mo 3d, (d) Se 3d of NiMoSe sample.

two main distinctive peaks at 856.1 and 874.1 eV, with matching satellite peaks ascribed to Ni 2p_{3/2} and Ni 2p_{1/2}, respectively [14]. As shown in Fig. 1(c) Mo 3d high-resolution spectra show two distinct peaks at 231.9 and 235.1 eV ascribed to 3d_{5/2} and 3d_{3/2}, respectively, suggesting the presence of Mo⁶⁺ species. Simultaneously, the binding energy of Mo 3d changes to the left, slightly higher than the binding energy of pure Mo element (231.1 eV), showing that electron transfer occurs between Mo and Se [15]. The core level Se 3d XPS spectrum shows two peaks at 54.7 and 59.2 eV, corresponding to Se 3d and Se-O, respectively. The Se 3d could be deconvoluted into two peaks, 3d_{3/2} and 3d_{5/2} as seen in Fig. 1(d) [14].

The FE-SEM images of the NiMoSe sample at different magnifications are shown in Fig. 2(a, b). The as-deposited NiMoSe shows nanospheres decorated on NF substrate. The MoSe and NiSe samples also show same nanosphere morphology (Fig. S2(a, b)). Elemental mapping images of NiMoSe sample demonstrate a uniform distribution of Ni, Mo, and Se throughout the nanosphere as shown in Fig. 2(c).

2.1. Electrochemical performance for HER

Fig. 3(a) shows the LSV curves for HER of all samples. The NiMoSe requires a low overpotential of 130 mV to achieve a current density of 10 mA cm⁻², which is substantially lower than the MoSe (176 mV), NiSe (211 mV), and the Bare NF (229 mV). Tafel curves were plotted to reveal the reaction kinetics of the electrocatalysts, as shown in Fig. 3(b) [16]. The NiMoSe electrode possesses a much lower Tafel slope of 59 mV dec⁻¹, than that of MoSe (71 mV dec⁻¹), NiSe (97 mV dec⁻¹), and Bare NF (116 mV dec⁻¹) suggesting rapid HER kinetics of NiMoSe. Comparative plot of overpotential and Tafel values of all electrocata-

lysts is plotted in Fig. 3(c). Fig. 3(d) displays stability test of NiMoSe electrode at constant current density of 10 mA cm⁻² for 45 h. The inset in Fig. 3(d) shows negligible change in overpotential after long-term stability. The FE-SEM and XPS were studied after stability. Fig. S3 shows the nanosphere morphology of NiMoSe remains same even after 45 h of continuous gas evolution. XPS analysis of NiMoSe after HER shows the presence of Ni, Mo, and Se elements (Fig. S4).

To find out why NiMoSe has better electrocatalytic activity, the ECSA was calculated from the electrochemical double-layer capacitance (C_{dl}) using typical CV data at different scan rates in the non-faradaic zone (Fig. 4(a) and Fig. S5(a-b)) [17]. As shown in Fig. 4(b), the C_{dl} of NiMoSe is 5.30 mF cm⁻², which is more than that of MoSe (3 mF cm⁻²) and NiSe (1.98 mF cm⁻²), indicating the presence of a greater number of electrochemically active sites in the NiMoSe. From the EIS spectra of all the electrodes as shown in Fig. 4(c) it is confirmed that NiMoSe electrode has smaller charge transfer resistance than the other two electrodes. Fig. S6 displays corresponding EIS fitting circuit of NiMoSe. Mass activity and specific activity of NiMoSe are 74.2 mA mg⁻¹ and 1.94 mA cm⁻², respectively, whereas MoSe have 42.5 mA mg⁻¹ and 1.81 mA cm⁻², and NiSe have 27.81 mA mg⁻¹ and 1.34 mA cm⁻².

3. Conclusion

In summary, NiMoSe nanospheres were successfully synthesized via a simple electrodeposition technique on NF in a short time for the application of HER. Benefitting from the large electrochemically active surface area, small charge-transfer resistance the NiMoSe electrode show excellent catalytic activity for HER with a low overpotential of 130 mV to achieve a current density of 10 mA cm⁻² as well as small Tafel slope

Fig. 2. (a and b) FE-SEM images of NiMoSe, (c) Corresponding elemental mappings of Ni, Mo, Se elements.

Fig. 3. (a) HER polarization curves, (b) Tafel slopes, (c) Comparative plot of Overpotential and Tafel values, (d) Long-term stability of NiMoSe electrode (inset before and after stability LSV curve).

of 59 mV dec^{-1} . More importantly, the NiMoSe exhibits excellent stability for 45 h in 1 M KOH. As a result, electrodeposited NiMoSe may be an excellent choice for use as a platinum-free electrocatalyst in the water-splitting process.

CRediT authorship contribution statement

Komal Patil: Formal analysis, Data curation, Writing – original draft. **Pravin Babar:** Writing – original draft, Writing – review & editing, Resources. **Xue Li:** Methodology, Software. **Junsung Jang:** Software, Data curation. **Dongmyeong Kim:** Data curation, Formal

Fig. 4. (a) CV curves of NiMoSe at different scan rates, (b) Current density as a function of scan rate, (c) EIS spectra, (d) Mass and specific activities of catalysts at 350 mV overpotential.

analysis. Myeong Cheol Baek: Formal analysis, Software. Pravin Bhoite: Supervision. Jin Hyeok Kim: Funding acquisition, Project administration, Supervision.

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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matlet.2021.131409>.

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