

# Synthesis of NiFe/MoO<sub>3</sub>@CFP Electrocatalyst for Water Splitting via Ultrasound-Assisted Method

Yongbeom Cho<sup>1,2†</sup>, Jonguk Kwon<sup>1</sup>, and Tae-Oh Kim<sup>1,2\*</sup>

(<sup>1</sup>Dept. Environ. Eng., Kumoh Nat'l Inst. Technol.; <sup>2</sup>Dept. Energy Eng. Converg., Kumoh Nat'l Inst. Technol.)

## 1. Introduction

In the realm of electrocatalytic research, the pursuit of high-performance non-precious metal catalysts capable of facilitating both the oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) holds paramount significance<sup>1-4</sup>. In this context, we present a pioneering methodology for catalyst synthesis that integrates ultrasound-assisted synthesis with electrochemical deposition. The outcome of this approach is the creation of a NiFe-based catalyst, strategically doped with molybdenum compounds, denoted as NiFe-Mo@CFP. During the ultrasound synthesis, molybdenum compounds were harnessed as a scaffold to bolster the NiFe framework within NiFe-Mo@CFP. Notably, the formation of these compounds was facilitated by cavitation bubbles engendered by ultrasound, which exerted a pivotal role in augmenting the catalyst's operational efficiency<sup>5-7</sup>.

## 2. Materials and Methods

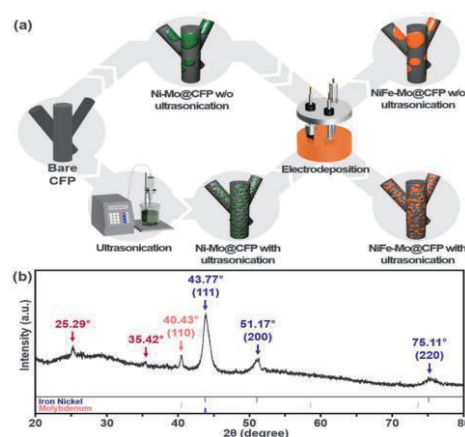
Nickel(II) acetate tetrahydrate [(CH<sub>3</sub>COO)<sub>2</sub>Ni·4H<sub>2</sub>O, JUNSEI, Tokyo, Japan], Molybdenum(V) chloride [MoCl<sub>5</sub>, Sigma-Aldrich, St. Louis, MO, USA], Iron(III) chloride hexahydrate [FeCl<sub>3</sub>·6H<sub>2</sub>O, Alfa Aesar, Ward Hill, MA, USA], Sodium hypophosphite monohydrate [NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O, DAEJUNG, Siheung, South Korea], CFP [HCP-020N, Shanghai Hesen Electronics, Shanghai, China] were used in the experiments, and all chemicals and reactants were of high purity and did not undergo any further processing. Distilled water, Ethyl alcohol [C<sub>2</sub>H<sub>5</sub>OH, SAMCHUN, Seoul, South Korea], and Isopropyl alcohol [(CH<sub>3</sub>)<sub>2</sub>CHOH, DAEJUNG, Siheung, South Korea] were used throughout the entire experiment.

Prior to ultrasonic synthesis, CFPs (0.5 cm × 2 cm) were placed in the center of a tube furnace and pyrolyzed at 600 °C for 2 h in an Ar atmosphere to improve their hydrophilicity. (CH<sub>3</sub>COO)<sub>2</sub>Ni·4H<sub>2</sub>O (0.9954 g), MoCl<sub>5</sub> (0.5760 g), and NaH<sub>2</sub>PO<sub>2</sub>·H<sub>2</sub>O (1.0299 g) were dissolved in distilled water (200 mL) to make a mixed solution, and then the pretreated

CFPs were slowly added to the solution to fully immerse them. Then, pulsed ultrasound (1 s on, 3 s off, VC750 ultrasonic processor (20 kHz; 750 W; Sonics & Materials, Newtown, CT)) of various intensities (225 W, 410 W, and 600 W) was applied to the mixture for 5 h while keeping the temperature of the solution at 105 °C to synthesize Ni-MoO<sub>3</sub>@CFP precursors (denoted as Ni-MoO<sub>3</sub>@CFP<sub>30</sub>, Ni-MoO<sub>3</sub>@CFP<sub>55</sub>, and Ni-MoO<sub>3</sub>@CFP<sub>80</sub>, respectively). After synthesis, the solution was cooled to room temperature, CFP was separated from the solution, washed with ethanol and dried at room temperature to obtain Ni-MoO<sub>3</sub>@CFP precursors. NiFe/MoO<sub>3</sub>@CFP was then synthesized by growing a NiFe layer via an electrochemical deposition process on top of the previously obtained Ni-MoO<sub>3</sub>@CFP precursor.

## 3. Results and discussion

The synthesis procedure of NiFe-Mo@CFP is depicted in the schematic diagram in Figure 1(a). The first step was the generation of Ni-Mo precursors with CFP as a support by a unique ultrasonic synthesis technique, where cavitation bubbles directly acted on the bond formation process between the surface of the carbon fiber and the Ni-Mo precursor material. The X-ray diffraction (XRD) pattern in Figure 1(b) shows the crystalline

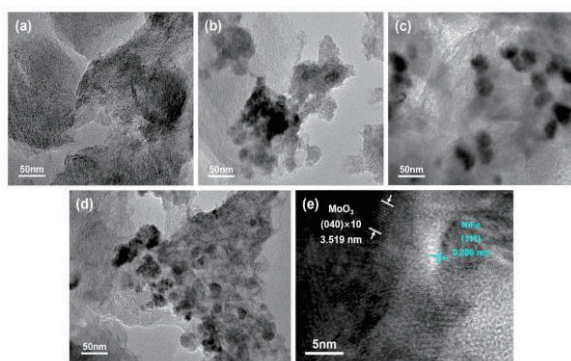


**Fig. 1** Schematic representation of the synthesis of NiFe-Mo@CFP (a) and the XRD pattern of the NiFe-Mo@CFP<sub>55</sub> catalyst (b).

E-mail: <sup>†</sup>cyb1977@kumoh.ac.kr \*tokim@kumoh.ac.kr

configuration of the NiFe-Mo@CFP\_55 catalyst. The diffraction peaks at  $43.77^\circ$ ,  $51.17^\circ$ , and  $75.11^\circ$  are the (111), (200), and (220) lattice planes of the NiFe compound with the  $(\text{Fe}_9\text{Ni}_{11})_{0.2}$  composition (ICDD no. 01-077-7968), whose composition closely matches the ratio of Ni-Fe precursors in the electrolyte used in the electrochemical deposition process. The diffraction peak at  $40.43^\circ$  is associated with (110) of bcc Mo (ICDD no.00-042-1120).

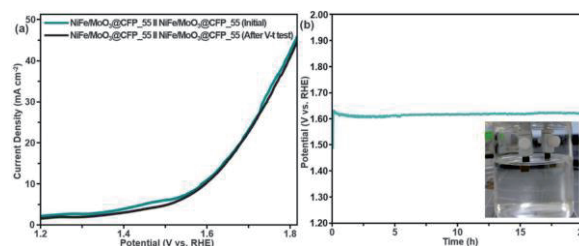
Figure 2(a-d) shows TEM images of samples with different conditions at the synthesis stage of Ni-Mo@CFP precursors, and it can be seen that the darker regions inside the crystal retain a clearer shape as the sonication intensity increases from NiFe@CFP and NiFe-Mo@CFP\_0 to NiFe-Mo@CFP\_80. The HRTEM analysis in Figure 2(e) identifies a crystal face with lattice fringes of 0.3519 nm within that region, which is consistent with the characteristics of the (040) crystal face of  $\text{MoO}_3$  identified earlier. In addition, a crystal face with lattice fringes closer to 0.21 nm was also seen in the same image, which is consistent with the (111) crystal face of the NiFe structure  $[(\text{Fe}_9\text{Ni}_{11})_{0.2}]$ . These analytical results indicate that the ultrasonic synthesis process played a key role in the modification of the CFP surface, the formation of catalyst crystals, and the bonding of CFP and catalyst, and that the synthesis conditions greatly affected the physicochemical properties of the catalyst.



**Fig. 2** TEM (a-d) and HRTEM images (e) of the catalyst samples; TEM images of (a) NiFe@CFP, (b) NiFe-Mo@CFP\_0 (CBD), (c) NiFe-Mo@CFP\_55, (d) NiFe-Mo@CFP\_80, and (e) HRTEM images of NiFe-Mo@CFP\_55, respectively.

The NiFe-Mo@CFP catalyst exhibited an exceptional diminution in overpotentials, recording values of merely 251 mV for OER and 199 mV for HER, each measured at a current density of  $20 \text{ mA cm}^{-2}$ . An intriguing revelation emerged as the same catalyst showcased a remarkable performance in effecting comprehensive water splitting when employed on both the anodic and cathodic fronts.

Impressively, a meager cell potential of 1.589 V proved sufficient to attain a current density of  $10 \text{ mA cm}^{-2}$  (Fig. 3(a)).



**Fig. 3** Total water partitioning analysis with an electrode system consisting of two NiFe/MoO<sub>3</sub>@CFP\_55 configurations without iR correction: (a) Polarization curve of the electrode system and the change in the polarization curve of the catalyst after the durability test; (b) the results of the chronopotentiometric test (V-t test) maintaining a current density of  $12 \text{ mA cm}^{-2}$  for 20 h and the reactor configuration.

## 4. Conclusions

This investigation underscores the efficacy and latent potential of an innovative catalyst synthesis methodology utilizing ultrasound, a technique that has hitherto been relatively underexplored. By demonstrating the viability of this approach, we open avenues for prospective applications in diverse domains. The NiFe-Mo@CFP catalyst's capacity to efficiently drive OER and HER processes, coupled with its proficiency in water splitting, not only highlights its intrinsic utility but also portends a promising trajectory for future electrocatalytic advancements.

## Acknowledgment

Following are results of a study on the "Leaders in Industry-university Cooperation 3.0" Project, supported by the Ministry of Education and National Research Foundation of Korea

## References

- 1) K. Zeng and D. Zhang, Prog Energy Combust Sci. **36**, 307 (2010).
- 2) C. Xiao and C. Zhao, Adv Funct Mater. **26**, 3515 (2016).
- 3) P. Zhai and B. Zhang, Nat Commun. **12** (2021).
- 4) J Liu, D Zhu, T Ling, A Vasileff and SZ Qiao, Nano Energy, **40**, 264 (2017).
- 5) J. Rooze, E. Rebrov, J. Schouten and J. Keurentjes, Ultrason Sonochem. **20**, 1 (2013).
- 6) D. Shchukin, E. Skorb, V. Belova and H. Möhwald, Adv Mater. **23**, 1922-1934 (2011).
- 7) N. Gaikwad and P. Gogate, Green Process Synth. **4** (2015).