

## Supplementary Information

### **An Advanced Ru-based Alkaline HER Electrocatalyst Benefiting from Volmer-step Promoting 5d and 3d Co-catalysts**

M. Ramaprakash<sup>1</sup>, Nasrin Banu G<sup>1</sup>, Bernaurdshaw Neppolian<sup>1\*</sup> and Anantharaj Sengeni<sup>2\*</sup>

<sup>1</sup> Department of Chemistry, Faculty of Engineering and Technology, SRM Institute of Science and Technology, Kattankulathur, Chennai 603203, India

<sup>2</sup> Laboratory for Electrocatalysis and Energy (LEE), Department of Chemistry, Indian Institute of Technology Kanpur, Uttar Pradesh 208016, India

\*Corresponding author e-mail: [neppolib@srmist.edu.in](mailto:neppolib@srmist.edu.in) and [ananths@iitk.ac.in](mailto:ananths@iitk.ac.in)

**Figure S1**

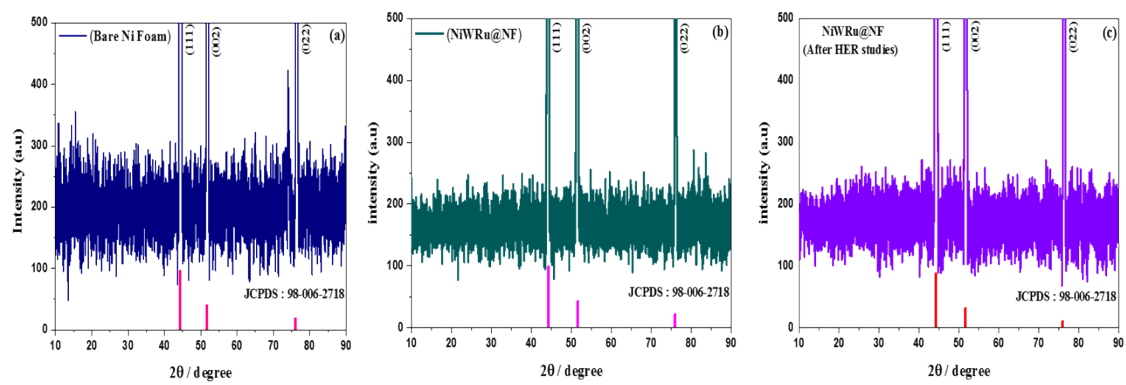


Figure S1: XRD spectra of (a) Bare Ni foam (b) electrodeposited NiWRu@NF (c) electrodeposited NiWRu@NF after chronoamperometry for HER.

Figure S2

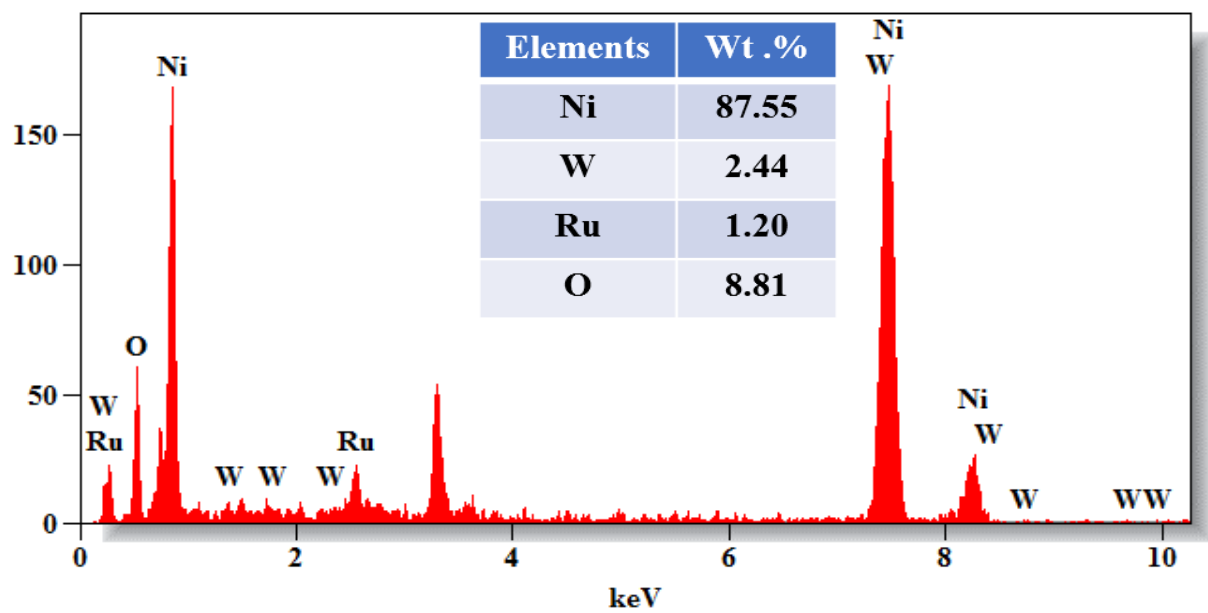


Figure S2: EDX data of electrodeposited NiWRu@NF

Figure S3

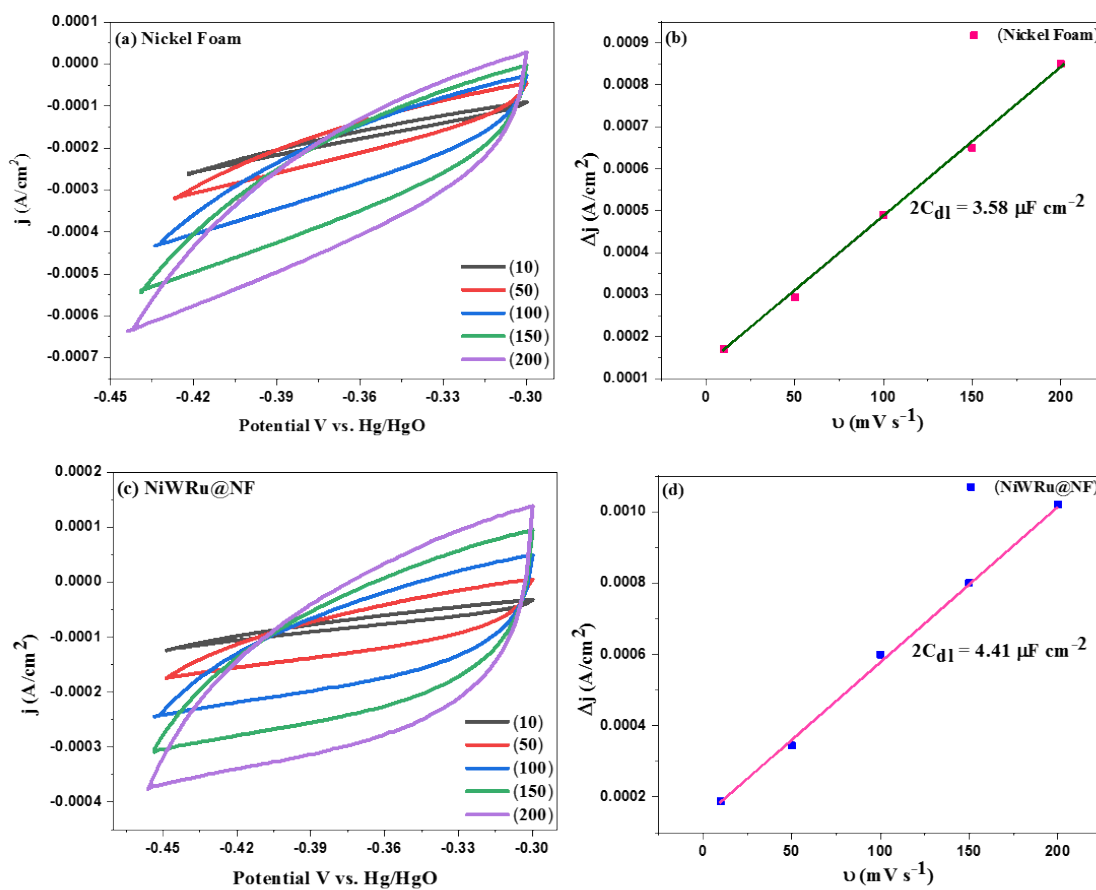


Figure S3: (a and c) CV of (a) Ni Foam and (b) NiWRu@NF with increasing scan rate. (b and d) Plot of difference in current density against scan rate showing the  $2C_{dl}$  values.

Figure S4

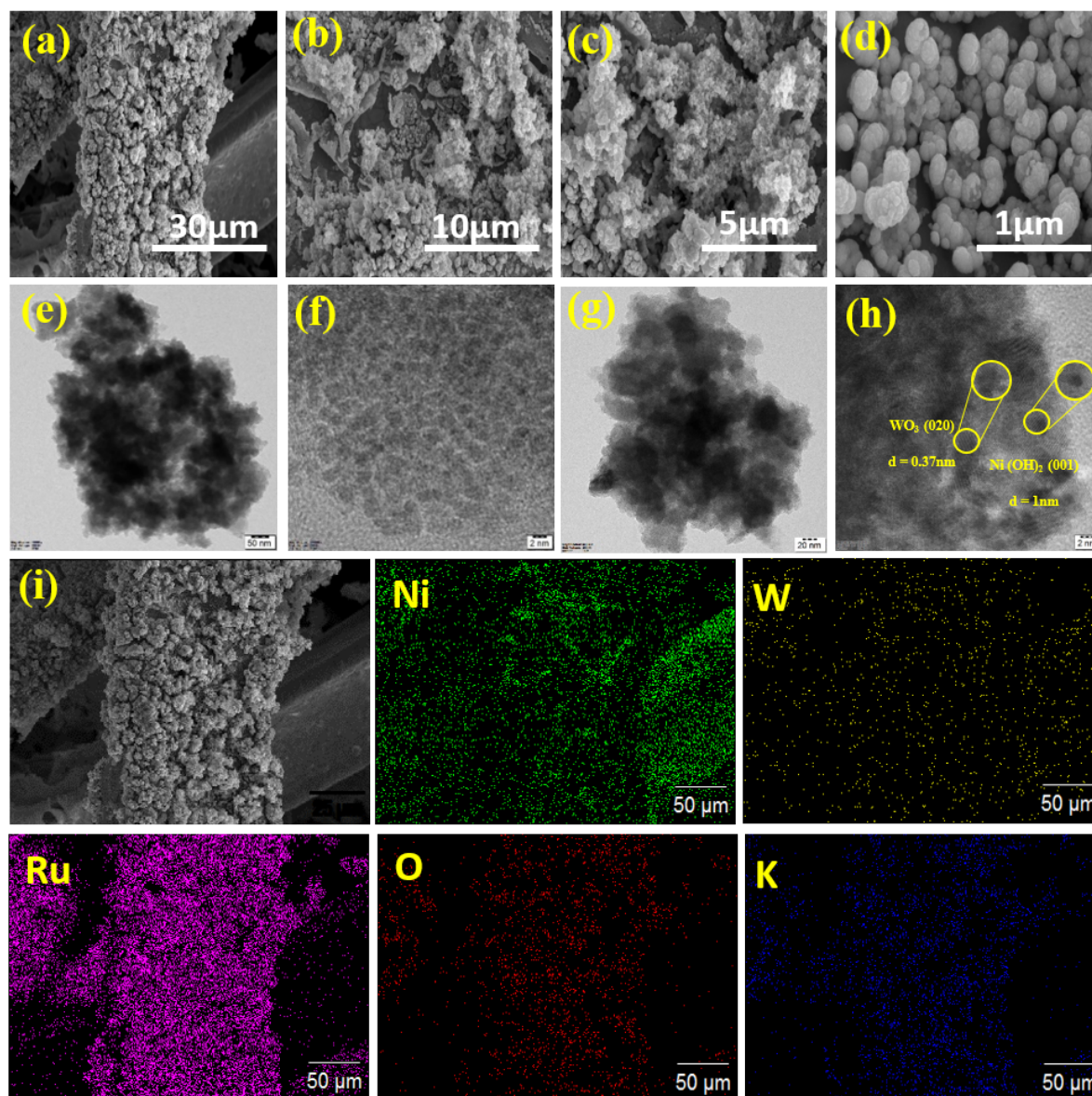


Figure S4: (a-d) SEM images, (e-g) TEM images, (h) HRTEM image and (i) SEM image and its corresponding EDS mapping of electrodeposited NiWRu@NF.

Figure S5

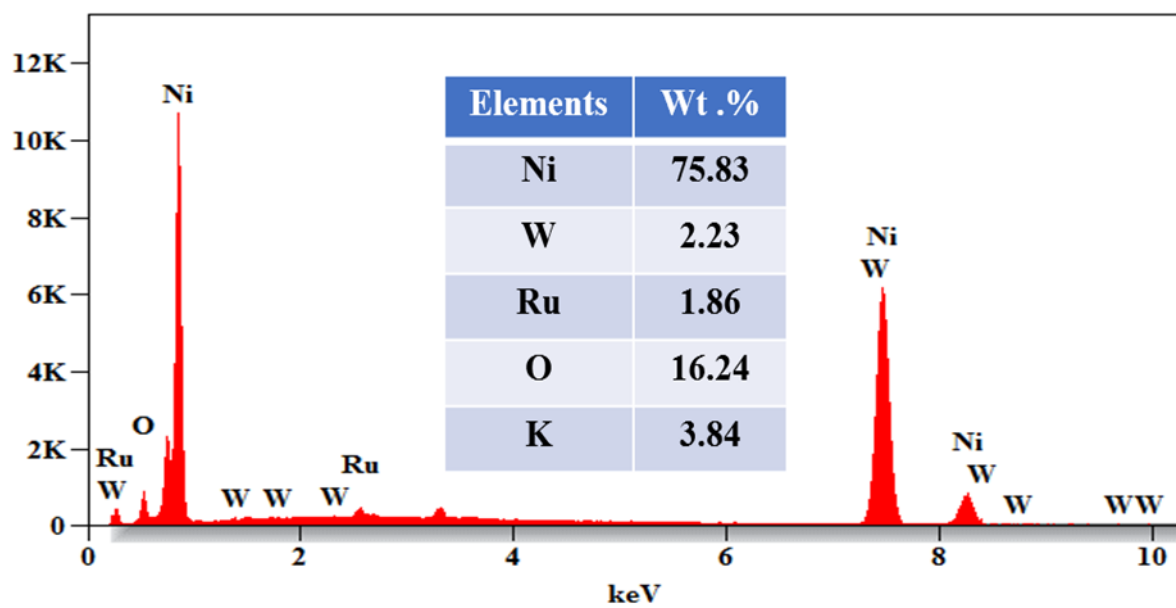


Figure S5: EDX data of electrodeposited NiWRu@NF after HER activity

Figure S6

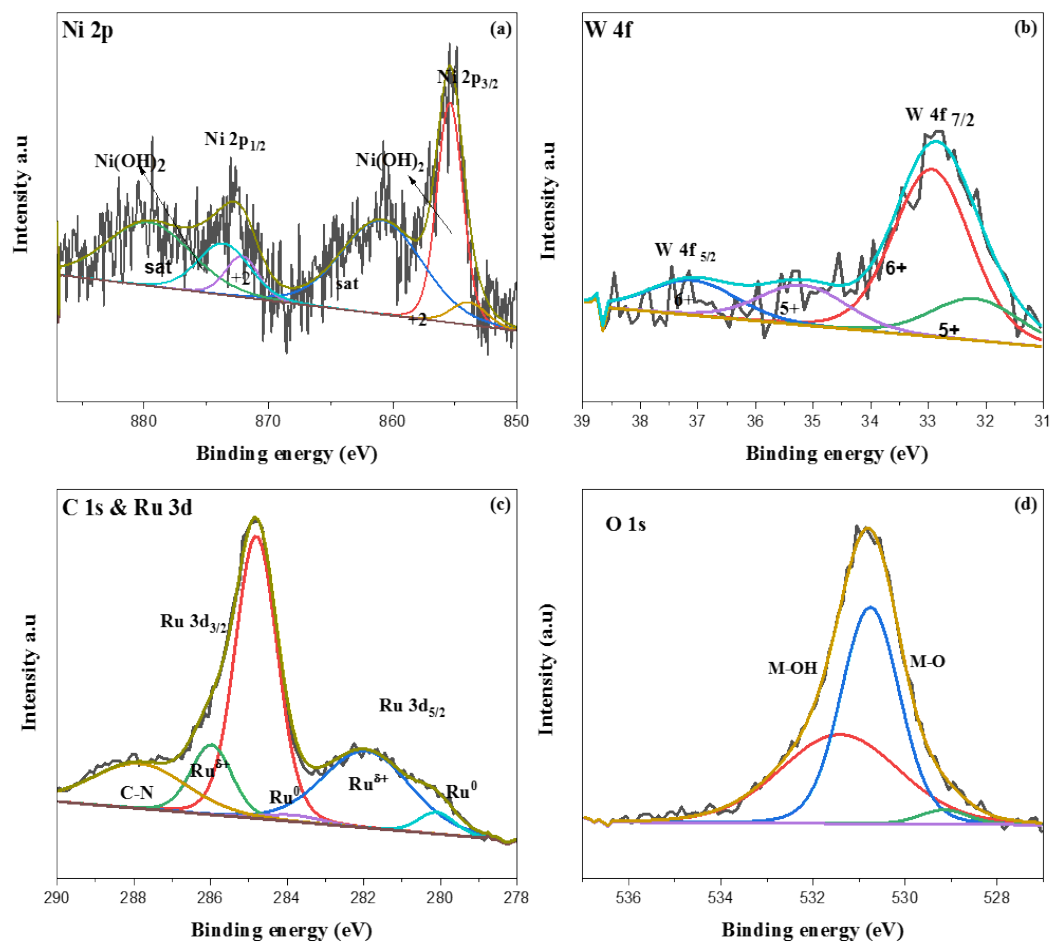


Figure S6: XPS narrow scan of (a) Ni 2p, (b) W 4d, (c) Ru 3d, (d) O1s and (e) K 2P on electrodeposited NiWRu@NF at after electrochemical studies using 1M KOH

**Table 1: Comparison of electrodeposited NiWRu@NF with recently reported HER electrocatalyst in alkaline electrolytes.**

S.No	Catalyst	Over potential mV ( $\eta$ ) at -10mA/cm <sup>2</sup>	References
1	NiWRu@NF	-48.8	This Work
2	NiCoMnFe-P	300	Ref <sup>1</sup>
3	Ni	135	Ref <sup>2</sup>
4	NiMo	-154	Ref <sup>3</sup>
5	S-NiMoO <sub>4</sub> @NiFe-LDH	-170	Ref <sup>4</sup>
6	Mo-Ni-Se@NiSe	-77	Ref <sup>5</sup>
7	Ni-Fe-Sn	-103	Ref <sup>6</sup>
8	Ni-Fe	-142	Ref <sup>7</sup>
9	Ni-Se	-181	Ref <sup>8</sup>
10	Ni-Se-Mo	-101	Ref <sup>9</sup>
11	Ni-Mo	-263	Ref <sup>10</sup>
12	Ni-AC composite coating	-114	Ref <sup>11</sup>
13	NF & ENF	-134	Ref <sup>12</sup>
14	CoNi/NF	-77	Ref <sup>13</sup>
15	MoO <sub>3</sub> /Ni-NiO	-62	Ref <sup>14</sup>
16	Ni-P/CeO <sub>2</sub> composite coatings	-118	Ref <sup>15</sup>
17	Ir-Ni thin film catalyst	-60	Ref <sup>16</sup>
18	Ni-Se	-65	Ref <sup>17</sup>
19	NiSe <sub>2</sub> /Ti	-96	Ref <sup>18</sup>
20	Ni-P/MoS <sub>x</sub>	-140	Ref <sup>19</sup>
21	C/Ni-NiIr	-160	Ref <sup>20</sup>
22	Ni-CNT	-82	Ref <sup>21</sup>
23	Ni-Ni(OH) <sub>2</sub>	-73	Ref <sup>22</sup>
24	W <sub>2</sub> C-Ni(OH) <sub>2</sub>	-60	Ref <sup>23</sup>
25	Co-Ni-P	-103	Ref <sup>24</sup>



## References

- 1) Menna M. Hasan, Aya K Gomaa, Ghada E. Khedr, Kholoud E. Salem, Basamat S Shaheen, and Nageh K. Allam, "Highly Durable Compositionally Variant Bifunctional Tetrametallic Ni-Co-Mn-Fe Phosphide Electrocatalysts Synthesized by a Facile Electrodeposition Method for High Performance Overall Water Splitting" *ACS Energy Fuels.*, 36 (2022) 14371.
- 2) Ioannis A. Poimenidis, Nikandra Papakosta, Argyro Klini, Maria Farsari, Michalis Konsolakis, Panagiotis A. Loukakos, Stavros D. Moustazis, "Electrodeposited Ni foam electrodes for increased hydrogen production in alkaline electrolysis" *Fuel.*, 342 (2023) 127798.
- 3) Fuxi Bao, Erno Kemppainen, Iris Dorbandt, Radu Bors, Fanxing Xi, Rutger Schlatmann, Roel van de Krol and Sonya Calnan, "Understanding the Hydrogen Evolution Reaction Kinetics of Electrodeposited Nickel-Molybdenum in Acidic, Near-Neutral, and Alkaline Conditions" *Chem Electro Chem.*, (2020).
- 4) Haiyan Wang, Luyao Chen, Lei Tan, Xien Liu, Yonghong Wen, Wanguo Hou, Tianrong Zhan, "Electrodeposition of NiFe-layered double hydroxide layer on sulfur modified nickel molybdate nanorods for highly efficient seawater splitting" *J. Colloid Interface Sci.*, 613 (2022) 349.
- 5) Mohammad Abedini Mohammadi, Morteza Saghafi Yazdi, Mohammad Talafi Noghani, Amirhossein Moghanian, Seied Ali Hosseini, "Synthesis and optimization of Mo-Ni-Se@NiSe core-shell nanostructures as efficient and durable electrocatalyst for hydrogen evolution reaction in alkaline media" *Int. J. Hydrogen Energy.*, 47 (2022) 34455.
- 6) Jiqiong Lian, Yihui Wu, Zongtao Lu, Qianhao Zang, "Cyclic voltammetry electrodeposition of self-standing Ni-Fe-Sn ternary alloys for accelerating alkaline hydrogen evolution" *Int. J. Hydrogen Energy.*, 48 (2023) 24295.

- 7) Zejie Zhang, Yihui Wu, Deping Zhang, “Potentiostatic electrodeposition of cost-effective and efficient Ni-Fe electrocatalysts on Ni foam for the alkaline hydrogen evolution reaction” *Int. J. Hydrogen Energy.*, 47 (2022) 1425.
- 8) Yaqian Yang, Xu Zhao, Han Mao, Rui Ning, Xiaohang Zheng, Jiehe Sui, Wei Cai, “Nickel-doped MoSe<sub>2</sub> nanosheets with Ni-Se bond for alkaline electrocatalytic hydrogen evolution” *Int. J. Hydrogen Energy.*, 45 (2020) 10724.
- 9) Ying Gao, Hanwei He, Wenyu Tan, Yizhi Peng, Xiaomei Dai, Yihui Wu, “One-step potentiostatic electrodeposition of Ni-Se-Mo film on Ni foam for alkaline hydrogen evolution reaction” *Int. J. Hydrogen Energy.*, 45 (2020) 6015.
- 10) Sandhya Shetty, M. Mohamed Jaffer Sadiq, D. Krishna Bhat, A. Chitharanjan Hegde, “Electrodeposition and characterization of Ni-Mo alloy as an electrocatalyst for alkaline water electrolysis” *J. Anal. Chem.*, 796 (2017) 57.
- 11) Shujuan Wang, Xingli Zou, Tianyu Shi, Kai Ding, Zhongya Pang, Ying Huang, Wei Tang, Qian Xu, Zhongfu Zhou, Xionggang Lu, “Facile electrodeposition of three-dimensional flower-like structure of nickel matrix composite electrodes for hydrogen evolution reaction” *Appl. Surf. Sci.*, (2019).
- 12) Ioannis A. Poimenidis, Nikandra Papakosta, Argyro Klini, Maria Farsari, Michalis Konsolakis, Panagiotis A. Loukakos, Stavros D. Moustazis, “Electrodeposited Ni foam electrodes for increased hydrogen production in alkaline electrolysis” *Fuel.*, 342 (2023) 127798.
- 13) Jingjing Bai, Qiangqiang Sun, Zenglin Wang and Chuan Zhao, “Electrodeposition of Cobalt Nickel Hydroxide Composite as a High-Efficiency Catalyst for Hydrogen Evolution Reactions” *J. Electrochem. Soc.*, 164 (2017) H587.
- 14) Xiaopeng Li, Yang Wang, Jiajun Wang, Yumin Da, Jinfeng Zhang, Lanlan Li, Cheng Zhong, Yida Deng, Xiaopeng Han and Wenbin Hu, “Sequential Electrodeposition of

Bifunctional Catalytically Active Structures in MoO<sub>3</sub>/Ni-NiO Composite Electrocatalysts for Selective Hydrogen and Oxygen Evolution” *Adv. Mater.*, (2020) 2003414.

15) Qiongyu Zhoua, Songli Liua, Yadong Zhang, Zhiyun Zhuc, Wei Suc and Minqi Sheng, “Fabrication of porous Cu supported Ni-P/CeO<sub>2</sub> composite coatings for enhanced hydrogen evolution reaction in alkaline solution” *Ceram Int.*, 46 (2020) 20871.

16) Wangping Wu, Jianwen Liu, Näther Johannes, Lei Zhang, Yi Zhang, Tongshu Hua, Lin Liu, “Galvanostatic Electrodeposition of Thin-Film Ir-Ni Electrocatalyst on Copper Foam for HER Performance in Alkaline Electrolyte” 150 (2020) 1325.

17) S. Esmailzadeh, T. Shahrabi, Gh Barati Darband, Y. Yaghoubinezhad, “Pulse electrodeposition of nickel selenide nanostructure as a binder-free and high efficient catalyst for both electrocatalytic hydrogen and oxygen evolution reactions in alkaline solution” *Electrochim. Acta.*, 334 (2020) 135549.

18) Zonghua Pu, Yonglan Luo, Abdullah M. Asiri, and Xuping Sun, “Efficient Electrochemical Water Splitting Catalyzed by Electrodeposited Nickel Diselenide Nanoparticles Based Film” *ACS Appl Mater Interfaces.*, 8 (2016) 4718.

19) Guan-Qun Han, Xiao Li, Jing Xue, Bin Dong, Xiao Shang, Wen-Hui Hu, Yan-Ru Liu, Jing-Qi Chi, Kai-Li Yan, Yong-Ming Chai, Chen-Guang Liu, “Electrodeposited hybrid Ni-P/MoS<sub>x</sub> film as efficient electrocatalyst for hydrogen evolution in alkaline media” 42 (2017) 2952.

20) Ramazan Solmaz, “Electrochemical preparation and characterization of C/Ni-NiIr composite electrodes as novel cathode materials for alkaline water electrolysis” *Int. J. Hyrog. Energy.*, 38 (2013) 2251.

21) Gh. Barati Darband, M. Aliofkhazraei, A. Sabour Rouhaghdam, “Three-dimensional porous Ni-CNT composite nanocones as high performance electrocatalysts for hydrogen evolution reaction” *J. Anal. Chem.*, (2018).

- 22) Weiyang Zhang, Qing Yin, Yizhe Zhang, Shaoqin Peng and Yueyang Li, "Electrodeposited crystalline-amorphous Ni-Ni(OH)<sub>2</sub> electrocatalyst for efficient hydrogen evolution reaction" *J. Anal. Chem.*, 948 (2023) 169727.
- 23) Hong Chuan Fu, Xiao Hu Wang, Xiao Hui Chen, Qing Zhang, Nian Bing Li, Hong Qun Lu "Interfacial engineering of Ni(OH)<sub>2</sub> on W<sub>2</sub>C for remarkable alkaline hydrogen production" 301 (2022) 120818.
- 24) Yu Pei, Yang Yang, Fangfang Zhang, Pei Dong, Robert Baines, Yuancai Ge, Hang Chu, Pulickel M. Ajayan, Mingxin Ye and Jianfeng Shen, "Controlled Electrodeposition Synthesis of Co-Ni-P Film as a Flexible and Inexpensive Electrode for Efficient Overall Water Splitting" 37 (2017) 31887.