Scientific Research Publishing

Engineering, 2024, 16, 123-133
https://www.scirp.org/journal/eng
ISSN Online: 1947-394X
ISSN Print: 1947-3931

XPS Studies on Electroless As-Deposited and Annealed Ni-P Films

Towhid Adnan Chowdhury

Department of Electrical & Electronic Engineering, Ahsanullah University of Science & Technology, Dhaka, Bangladesh
Email: towhid6789@yahoo.com

How to cite this paper: Chowdhury, T.A. (2024) XPS Studies on Electroless As-Deposited and Annealed Ni-P Films. *Engineering*, **16**, 123-133.
https://doi.org/10.4236/eng.2024.165010

Received: April 11, 2024
Accepted: May 20, 2024
Published: May 23, 2024

Abstract

Electroless deposition has been used to deposit Ni-P films on glass slides using the reducing agent sodium hypophosphite. This has been done with a purpose to use Ni-P films as back contact for silicon carbide radiation detectors. By keeping deposition time, temperature, pH and concentration of the precursor solution constant, the film deposition has been done. XPS studies were done to analyze the composition and stoichiometry of Ni-P thin films.

Keywords

Ni-P, X-Ray Photoelectron Spectroscopy, Annealing, Electroless Deposition, Binding Energy, Reducing Agent

1. Introduction

Using renewable energy sources instead of fossil fuels allows to produce few greenhouse emissions, reducing environmental impact and sustaining the future social and economic social needs [1]. Production and storage are the two important steps in the exploitation of renewable technologies. Storage technologies can be electrical, chemical, electrochemical, mechanical or thermal [2]. Electrochemical techniques related to research and development for clean energy storage gained importance for their strategic value [3] and currently electrochemically generated hydrogen is one of the most encouraging energy storage mediums [4]. Though greatest amount of the hydrogen is existent in molecular forms, it can be yielded exploiting water electrolysis (WE) [5], where water breaks into H_2 and O_2. The oxygen evolution reaction (OER) occurs at the anode while the hydrogen evolution reaction (HER) occurs at the cathode.

A considerable amount of electrochemical overpotential is required to start HER in normal conditions [6]. Therefore, extremely efficient WE needs the use

of an electrocatalyst to reduce the energy barrier associated with HER. Noble metals like Pd or Pt are considered as the best electrocatalysts because of their outstanding activity in acidic environment for HER [7]. Meanwhile, their insufficient availability and high cost caused researchers to look for cost-effective substitutes. Therefore, research concentrated on the look for materials substitute to Pt [8], which is the most admired catalyst because of its robust stability and high electrocatalytic activity [9] [10]. Currently, alternative cost-effective electrocatalytic materials are unearthed and some of them have been developed to a large extent. Important examples are metal sulphides [11], phosphides [12]-[17], selenides [18], nitrides [19] carbides [19], some transition metals or alloys [20] [21] and their nanoparticles (NP) [22] [23].

Nickel phosphide is evaluated as a substitute of Pt-based electrocatalytic materials in the future. Nickel phosphides (Ni_2P) compound showed low HER overpotentials and good stability [12] [24]. Besides highly poisonous phosphine-based chemical reaction, substitute methods to prepare Ni_2P have been established. Specifically, nickel phosphide has been prepared, in the form of nanowires or NPs, via solvothermal [25] [26] or hydrothermal synthesis [27] [28], by the decomposition of metal-phosphine moieties [24], and by direct phosphorization of Ni [29] [30] [31]. Other nickel-phosphorus alloys, like Ni_3P or $Ni_{12}P_5$, are identified by stimulating electrocatalytic properties [12]. Electrodeposition or sputtering can be used to obtain nickel phosphide thin films by direct phosphorization of Ni [32] [33]. However, this synthesis process involves noxious precursors, like phosphine [34].

Nickel phosphide has a wide range of usages for electrochemical devices [35] [36] [37]. Due to high theoretical specific capacity, much work has been recently done to use nickel phosphide as anode in rechargeable lithium (Li) battery [38] [39]. Recently, the high electrochemical behaviour, great conductivity and thermal stability of transition metal phosphides have made them suitable as supercapacitors [40] [41]. Among different transition metal phosphides, nickel phosphide (NiP) is an important class.

Electroless nickel deposition is a nickel deposition method that takes place in an aqueous solution in the presence of a chemical reducing agent. It involves no external current source. The deposition having a low phosphorus content is better resistant to wear and the hardest, whereas the surface will have a better corrosion resistance if it has a high phosphorus content [42]. Electroless deposition of Ni-P films find extensive application in fields such as medical, aviation, aerospace, automobile, chemical processing, textile, oil and gas industries since they can be grown on substrates of many different materials and with complicated shapes, easily processed, and exhibit excellent resistance to corrosion, good lubricity, and high hardness [43] [44].

In the present work, nickel phosphide is investigated in the form of thin film. Electroless deposition of Ni-P thin films was obtained using the reducing agent sodium hypophosphite. Then, the resulting alloys were annealed to support P

compound formation and interdiffusion. Annealing parameters were optimized to reduce oxidation, to give the best conditions for Ni_2P formation and to reduce the formation of secondary phases. X-ray photoelectron spectroscopy (XPS) is used to identify the existence of oxides on the surface and to determine the chemical state of the elements present in the material [45] [46] [47]. In this research work, XPS is used to investigate the chemical states and surface compositions of as-deposited and annealed Ni-P film. The results would be helpful to enhance surface nature of Ni-P film.

2. Experimental Details

In the research work, the soda-lime glasses (SLG) were used as substrate. They were first cleaned by washing and scrubbing with alconox. Then sonication in acetone and methanol was done for 20 minutes. Afterwards, DI water and isopropanol was used to wash them. Then, N_2 gas was used to dry the substrates. An aqueous solution of 0.2M $NiCI_2$, 0.3 M NaH_2PO_2 and 0.2 M Na-succinate have been used for electroless deposition. To ensure a good dispersion of precursor materials, the aqueous solution was stirred for the whole duration of the experiment. The substrate temperature was controlled within ± 2˚C of 80˚C by means of a hot plate to which a thermocouple is attached. The duration of deposition was 50 minutes. Hydrochloric acid (HCl) was used to maintain the pH of the solution around 4.

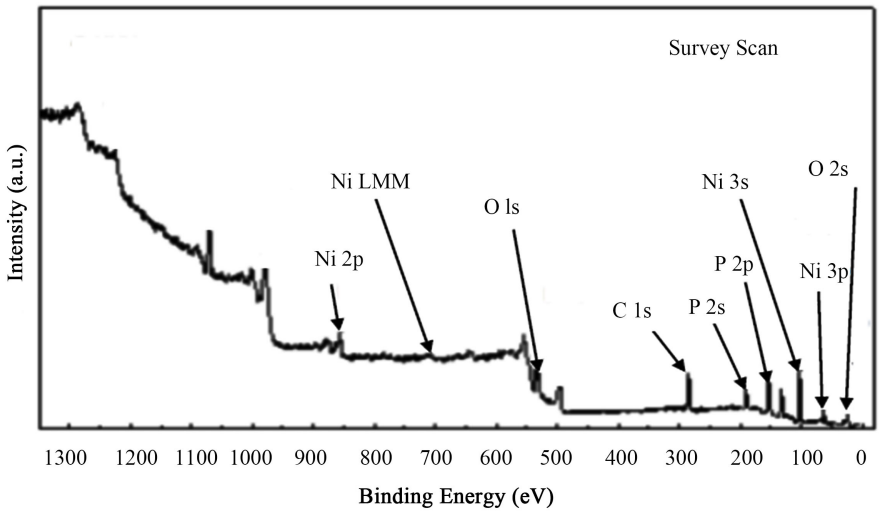
Annealing treatment was performed with the help of an MTI Corporation GSL-1100X furnace. After depositing Ni-P thin films on soda-lime glass (SLG) substrates, they were placed in a quartz boat which is centered in the quartz tube chamber inside the furnace. The system was sealed after placing the quartz tube inside the furnace. High-purity argon gas was used to vacuum purge the chamber for three cycles. The annealing process was done at 350˚C on the substrates for a duration of 60 minutes in argon atmosphere. The annealed Ni-P thin films showed a change in morphology.

XPS was done to investigate the composition of NiP thin films. Monochromatic Al Kα radiation (1486.6 eV) through a Kratos AXIS Ultra DLD XPS system was used to obtain XPS spectra. An electronic neutralization gun was used to remove the charge effect on the sample surface. The base pressure of the system was 5×10^{-10} Torr. The sample was pressed to a disc of size 1 × 13 mm at first and then fixed to the sample-holder. Afterwards, it was degassed in the load lock chamber overnight. After that, XPS study was done on it by removing it to the test chamber. The value of contaminant carbon (C 1s 284.6 eV) was used as a reference to calibrate all binding energy values.

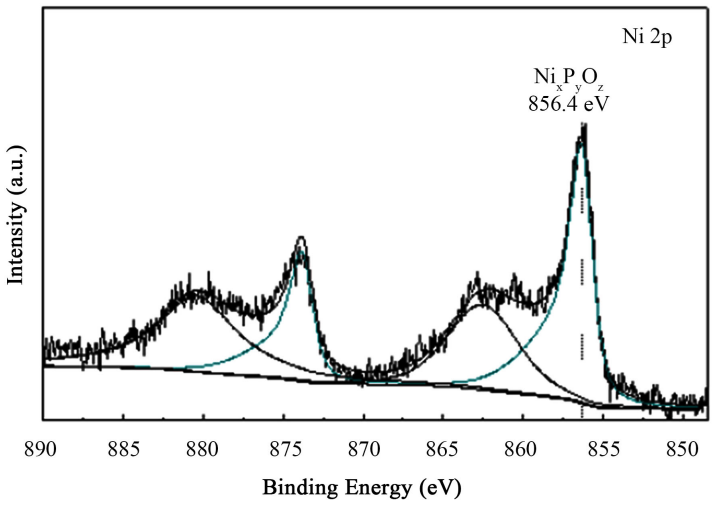
3. Results and Discussion

The composition and chemical purity of Ni-P thin films were analyzed by XPS. The typical XPS survey spectrum of as-deposited Ni-P film is showed in **Figure 1(a)**. The peaks arising from Ni 2p, 3s, 3p, Ni Auger, O 1s, C 1s, P 2s and P 2p

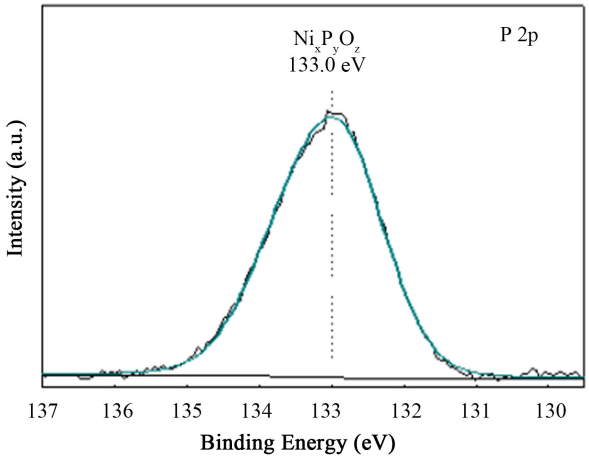
are clearly seen in the spectrum. No other impurities are observed in the spectrum. The nickel, Ni_{LMM}, Auger peak is found at 700 eV. High resolution spectra of Ni 2p core level, P 2p core level and O 1s core level are shown in **Figure 1(b)**, 1(c) and 1(d) respectively. The two peaks at 856.4 eV and 873.7 eV can be assigned to the binding energy of Ni $2p_{3/2}$ and $2p_{1/2}$. The separation of Ni 2p doublet is by 17.3 eV. These binding energy values of Ni 2p are characteristic of nickel phosphide in the oxidation state (Ni_xP_yOz; where x, y and z vary) [48]. The P peak at binding energy of 133 eV is characteristic of nickel phosphide in the oxidation state (Ni_xP_yOz; where x, y and z vary) [48]. The resolved peaks of O centered at binding energies of 531 eV and 532.5 eV (**Figure 1(d)**) corresponds to $Ni(OH)_2$ and silicon dioxide (SiO_2) respectively [49]. The peaks corresponding to silicon dioxide arise due to glass slides that were used for deposition. However, the peak of the O 1s core level is in the general XPS spectra (**Figure 1(a)**) suggest that the film was oxidized.



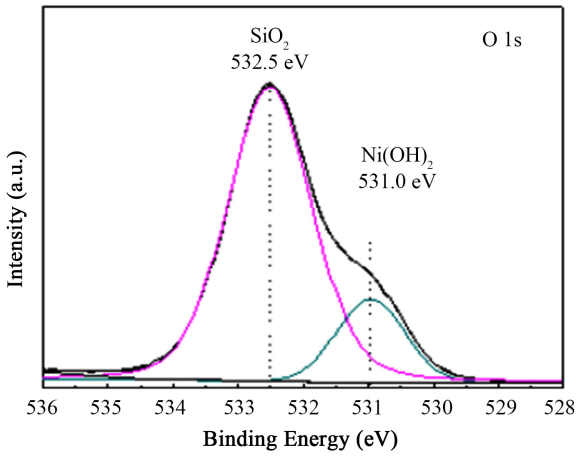
(a)



(b)



(c)

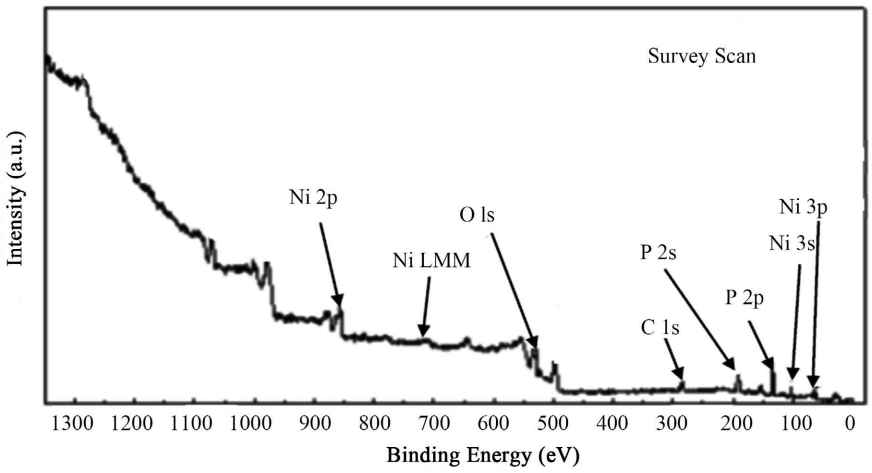


(d)

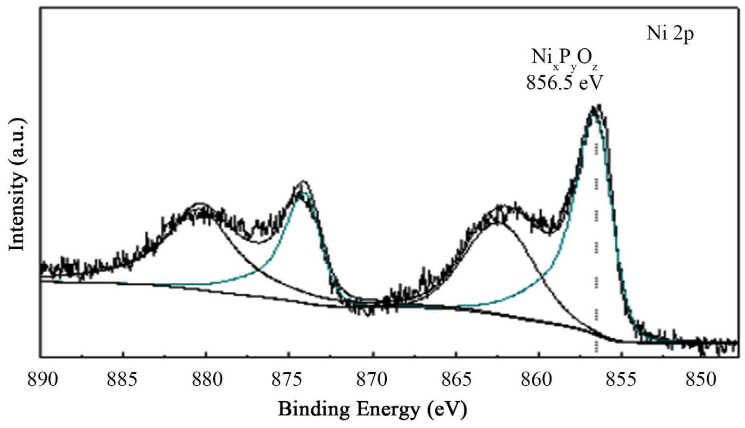
Figure 1. (a) XPS survey spectrum of as-deposited Ni-P film. (b) High resolution XPS spectra of the Ni 2p core level of as-deposited Ni-P film. (c) High resolution XPS spectra of the P 2p core level of as-deposited Ni-P film. (d) High resolution XPS spectra of the O 1s core level of as-deposited Ni-P film.

The XPS survey spectrum of annealed Ni-P thin film is showed in **Figure 2(a)**. The peaks arising from Ni 2p, 3s, 3p, Ni Auger, O 1s, C 1s, P 2s and P 2p are clearly seen in the spectrum. No other impurities are observed in the spectrum. The nickel, Ni_{LMM}, Auger peak is found at 700 eV. High resolution spectra of Ni 2p core level, P 2p core level and O 1s core level are shown in **Figure 2(b)**, **Figure 2(c)** and **Figure 2(d)** respectively. The two peaks at 856.5 eV and 873.8 eV can be assigned to the binding energy of Ni $2p_{3/2}$ and $2p_{1/2}$. The separation of Ni 2p doublet is by 17.3 eV. These binding energy values of Ni 2p are characteristic of nickel phosphide in the oxidation state (Ni_xP_yOz; where x, y and z vary) [48]. The peak has shifted about 0.1 eV to higher BE side compared with the peak before annealing. The P peak at binding energy of 133.5 eV is characteristic of nickel phosphide in the oxidation state (Ni_xP_yOz; where x, y and z vary) [48]. The oxidized NiP peak has shifted about 0.5 eV to higher BE side compared with the peak before heat treatment. The resolved peaks of O centered at binding

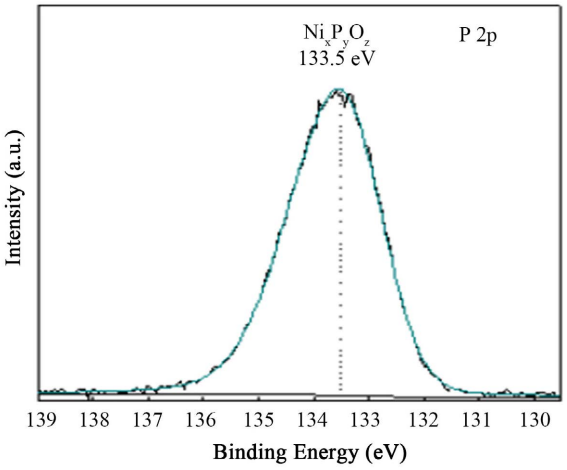
energies of 531 eV and 532.5 eV (**Figure 2(d)**) corresponds to $Ni(OH)_2$ and silicon dioxide (SiO_2) respectively [49]. The peaks corresponding to silicon dioxide arise due to glass slides that were used for deposition. However, the peak of the O 1s core level in the general XPS spectra (**Figure 2(a)**) suggests that the film was oxidized. But the intensity is lower compared to as-deposited film.



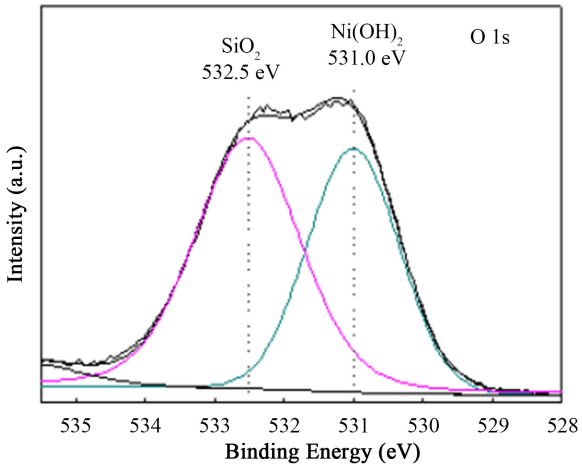
(a)



(b)



(c)



(d)

Figure 2. (a) XPS survey spectrum of annealed Ni-P film. (b) High resolution XPS spectra of the Ni 2p core level of annealed Ni-P film. (c) High resolution XPS spectra of the P 2p core level of annealed Ni-P film. (d) High resolution XPS spectra of the O 1s core level of annealed Ni-P film.

4. Conclusion

In this present research work, the electroless as-deposited and annealed Ni-P film has been analyzed using XPS study. The XPS analysis presents that film contains the elements nickel, phosphorus, oxygen, sodium and carbon. The phosphorus content is increased in the Ni-P film after annealing as observed from the survey spectrum. The P 2p binding energy corresponding to oxidized Ni-P is increased by 0.5 eV after heat treatment. These facts suggest that oxygen is transferred to phosphorus from nickel to form phosphorus oxides after annealing [45]. A chemical shift is observed for Ni (2p3/2) spectra.

Acknowledgements

The work was supported by the Advanced Support Program for Innovative Research Excellence-(ASPIRE-I), grant number 15530-E404 and Support to Promote Advancement of Research and Creativity (SPARC), grant number 15530-E413 of the University of South Carolina, Columbia, USA.

Conflicts of Interest

The author declares no conflicts of interest regarding the publication of this paper.

References

[1] Foley, A. and Olabi, A.G. (2017) Renewable Energy Technology Developments, Trends and Policy Implications That Can Underpin the Drive for Global Climate Change. *Renewable and Sustainable Energy Reviews*, **68**, 1112-1114. https://doi.org/10.1016/j.rser.2016.12.065

[2] Amrouche, S.O., Rekioua, D., Rekioua, T. and Bacha, S. (2016) Overview of Energy

Storage in Renewable Energy Systems. *International Journal of Hydrogen Energy*, **41**, 20914-20927. https://doi.org/10.1016/j.ijhydene.2016.06.243

[3] Markovic, N.M. (2013) Interfacing Electrochemistry. *Nature Materials*, **12**, 101-102. https://doi.org/10.1038/nmat3554

[4] Renssen, S. (2020) The Hydrogen Solution? *Nature Climate Change*, **10**, 799-801. https://doi.org/10.1038/s41558-020-0891-0

[5] Kelly, N.A. (2014) Hydrogen Production by Water Electrolysis. In: Basile, A. and Iulianelli, A., Eds., *Advances in Hydrogen Production, Storage and Distribution*, Elsevier, Amsterdam, 159-185. https://doi.org/10.1533/9780857097736.2.159

[6] Ezaki, H., Morinaga, M. and Watanabe, S. (1993) Hydrogen Overpotential for Transition Metals and Alloys, and Its Interpretation Using an Electronic Model. *Electrochimica Acta*, **38**, 557-564. https://doi.org/10.1016/0013-4686(93)85012-N

[7] Eftekhari, A. (2017) Electrocatalysts for Hydrogen Evolution Reaction. *International Journal of Hydrogen Energy*, **42**, 11053-11077. https://doi.org/10.1016/j.ijhydene.2017.02.125

[8] Salonen, L.M., Petrovykh, D.Y. and Kolen'ko, Y.V. (2021) Sustainable Catalysts for Water Electrolysis: Selected Strategies for Reduction and Replacement of Platinum-Group Metals. *Materials Today Sustainability*, **11-12**, Article ID: 100060. https://doi.org/10.1016/j.mtsust.2021.100060

[9] Zheng, Y., Jiao, Y., Jaroniec, M. and Qiao, S.Z. (2015) Advancing the Electrochemistry of the Hydrogen-Evolution Reaction through Combining Experiment and Theory. *Angewandte Chemie International Edition*, **54**, 52-65. https://doi.org/10.1002/anie.201407031

[10] Gong, M., Wang, D.Y., Chen, C.C., Hwang, B.J. and Dai, H. (2016) A Mini Review on Nickel-Based Electrocatalysts for Alkaline Hydrogen Evolution Reaction. *Nano Research*, **9**, 28-46. https://doi.org/10.1007/s12274-015-0965-x

[11] Faber, M.S., Lukowski, M.A., Ding, Q., Kaiser, N.S. and Jin, S. (2014) Earth-Abundant Metal Pyrites (FeS_2, CoS_2, NiS_2, and Their Alloys) for Highly Efficient Hydrogen Evolution and Polysulfide Reduction Electrocatalysis. *The Journal of Physical Chemistry C*, **118**, 21347-21356. https://doi.org/10.1021/jp506288w

[12] Xiao, P., Chen, W. and Wang, X. (2015) A Review of Phosphide-Based Materials for Electrocatalytic Hydrogen Evolution. *Advanced Energy Materials*, **5**, Article ID: 1500985. https://doi.org/10.1002/aenm.201500985

[13] Du, H., Kong, R.M., Guo, X., Qu, F. and Li, J. (2018) Recent Progress in Transition Metal Phosphides with Enhanced Electrocatalysis for Hydrogen Evolution. *Nanoscale*, **10**, 21617-21624. https://doi.org/10.1039/C8NR07891B

[14] Wang, Y., Kong, B., Zhao, D., Wang, H. and Selomulya, C. (2017) Strategies for Developing Transition Metal Phosphides as Heterogeneous Electrocatalysts for Water Splitting. *Nano Today*, **15**, 26-55. https://doi.org/10.1016/j.nantod.2017.06.006

[15] Yu, F., Zhou, H., Huang, Y., Sun, J., Qin, F., Bao, J., Goddard, W.A., Chen, S. and Ren, Z. (2018) High-Performance Bifunctional Porous Non-Noble Metal Phosphide Catalyst for Overall Water Splitting. *Nature Communications*, **9**, Article No. 2551. https://doi.org/10.1038/s41467-018-04746-z

[16] Ray, A., Sultana, S., Paramanik, L. and Parida, K.M. (2020) Recent Advances in Phase, Size, and Morphology-Oriented Nanostructured Nickel Phosphide for Overall Water Splitting. *Journal of Materials Chemistry A*, **8**, 19196-19245. https://doi.org/10.1039/D0TA05797E

[17] Jin, M., Zhang, X., Shi, R., Lian, Q., Niu, S., Peng, O., Wang, Q. and Cheng, C. (2021) Hierarchical CoP@ Ni_2P Catalysts for PH-Universal Hydrogen Evolution at High Current Density. *Applied Catalysis B*: *Environmental*, **296**, Article ID: 120350. https://doi.org/10.1016/j.apcatb.2021.120350

[18] Wang, F., Li, Y., Shifa, T.A., Liu, K., Wang, F., Wang, Z., Xu, P., Wang, Q. and He, J. (2016) Selenium-Enriched Nickel Selenide Nanosheets as a Robust Electrocatalyst for Hydrogen Generation. *Angewandte Chemie*, **55**, 6919-6924. https://doi.org/10.1002/anie.201602802

[19] Chen, W.F., Muckermana, J.T. and Fujita, E. (2013) Recent Developments in Transition Metal Carbides and Nitrides as Hydrogen Evolution Electrocatalysts. *Chemical Communications*, **49**, 8896-8909. https://doi.org/10.1039/c3cc44076a

[20] Brown, D.E., Mahmood, M.N., Man, M.C.M. and Turner, A.K. (1984) Preparation and Characterization of Low Overvoltage Transition Metal Alloy Electrocatalysts for Hydrogen Evolution in Alkaline Solutions. *Electrochimica Acta*, **29**, 1551-1556. https://doi.org/10.1016/0013-4686(84)85008-2

[21] Safizadeh, F., Ghali, E. and Houlachi, G. (2015) Electrocatalysis Developments for Hydrogen Evolution Reaction in Alkaline Solutions—A Review. *International Journal of Hydrogen Energy*, **40**, 256-274. https://doi.org/10.1016/j.ijhydene.2014.10.109

[22] Lv, H., Xi, Z., Chen, Z., Guo, S., Yu, Y., Zhu, W., Li, Q., Zhang, X., Pan, M., Lu, G., Mu, S. and Sun, S. (2015) A New Core/Shell NiAu/Au Nanoparticle Catalyst with Pt-Like Activity for Hydrogen Evolution Reaction. *Journal of the American Chemical Society*, **137**, 5859-5862. https://doi.org/10.1021/jacs.5b01100

[23] Li, L., Zhang, G., Wang, B. Yang, T. and Yang, S. (2020) Electrochemical Formation of PtRu Bimetallic Nanoparticles for Highly Efficient and PH-Universal Hydrogen Evolution Reaction. *Journal of Materials Chemistry A*, **8**, 2090-2098. https://doi.org/10.1039/C9TA12300H

[24] Park, J., Koo, B., Yoon, K.Y., Hwang, Y., Kang, M., Park, J.G. and Hyeon, T. (2005) Generalized Synthesis of Metal Phosphide Nanorods *via* Thermal Decomposition of Continuously Delivered Metal-Phosphine Complexes Using a Syringe Pump. *Journal of the American Chemical Society*, **127**, 8433-8440. https://doi.org/10.1021/ja0427496

[25] Liu, P., Zhang, Z.X., Jun, S.W., Zhu, Y.L. and. Li, Y.X. (2019) Controlled Synthesis of Nickel Phosphide Nanoparticles with Pure-Phase Ni_2P and $Ni_{12}P_5$ for Hydrogenation of Nitrobenzene. *Reaction Kinetics*, *Mechanisms and Catalysis*, **126**, 453-461. https://doi.org/10.1007/s11144-018-1496-8

[26] Wang, X., Kolen'ko, Y.V. and Liu, L. (2015) Direct Solvothermal Phosphorization of Nickel Foam to Fabricate Integrated Ni_2P Nanorods/Ni Electrodes for Efficient Electrocatalytic Hydrogen Evolution. *Chemical Communications*, **51**, 6738-6741. https://doi.org/10.1039/C5CC00370A

[27] Liu, Z., Huang, X., Zhu, Z. and Dai, J. (2010) A Simple Mild Hydrothermal Route for the Synthesis of Nickel Phosphide Powders. *Ceramics International*, **36**, 1155-1158. https://doi.org/10.1016/j.ceramint.2009.12.015

[28] Zhang, G., Xu, Q., Liu, Y., Qin, Q., Zhang, J., Qi, K., Chen, J., Wang, Z., Zheng, K., Świerczek, K. and Zheng, W. (2020) Red Phosphorus as Self-Template to Hierarchical Nanoporous Nickel Phosphides toward Enhanced Electrocatalytic Activity for Oxygen Evolution Reaction. *Electrochimica Acta*, **332**, Article ID: 135500. https://doi.org/10.1016/j.electacta.2019.135500

[29] Xiao, J., Lv, Q., Zhang, Y., Zhang, Z. and Wang, S. (2016) One-Step Synthesis of

Nickel Phosphide Nanowire Array Supported on Nickel Foam with Enhanced Electrocatalytic Water Splitting Performance. *RSC Advances*, **6**, 107859-107864. https://doi.org/10.1039/C6RA20737E

[30] Wang, X., Kolen'ko, Y.V., Bao, X.Q., Kovnir, K. and Liu, L. (2015) One-Step Synthesis of Self-Supported Nickel Phosphide Nanosheet Array Cathodes for Efficient Electrocatalytic Hydrogen Generation. *Angewandte Chemie*, **54**, 8188-8192. https://doi.org/10.1002/anie.201502577

[31] Wang, X., Li, W., Xiong, D., Petrovykh, D.Y. and Liu, L. (2016) Bifunctional Nickel Phosphide Nanocatalysts Supported on Carbon Fiber Paper for Highly Efficient and Stable Overall Water Splitting. *Advanced Functional Materials*, **26**, 4067-4077. https://doi.org/10.1002/adfm.201505509

[32] Wang, X., Li, W., Xiong, D. and Liu, L. (2016) Fast Fabrication of Self-Supported Porous Nickel Phosphide Foam for Efficient, Durable Oxygen Evolution and Overall Water Splitting. *Journal of Materials Chemistry A*, **4**, 5639-5646. https://doi.org/10.1039/C5TA10317G

[33] Xing, J., Zou, Z., Guo, K. and Xu, C. (2018) The Effect of Phosphating Time on the Electrocatalytic Activity of Nickel Phosphide Nanorod Arrays Grown on Ni Foam. *Journal of Materials Research*, **33**, 556-567. https://doi.org/10.1557/jmr.2017.399

[34] Bains, W., Petkowski, J.J., Silva, C.S. and Seager, S. (2019) Trivalent Phosphorus and Phosphines as Components of Biochemistry in Anoxic Environments. *Astrobiology*, **19**, 885-902. https://doi.org/10.1089/ast.2018.1958

[35] Li, J., Li, J., Zhou, X., Xia, Z., Gao, W., Ma, Y. and Qu, Y. (2016) Highly Efficient and Robust Nickel Phosphides as Bifunctional Electrocatalysts for Overall Water-Splitting. *ACS Applied Materials & Interfaces*, **8**, 10826-10834. https://doi.org/10.1021/acsami.6b00731

[36] Zhou, K., Zhou, W., Yang, L., Lu, J., Cheng, S., Mai, W., Tang, Z., Li. L. and Chen, S. (2015) Ultrahigh-Performance Pseudocapacitor Electrodes Based on Transition Metal Phosphide Nanosheets Array *via* Phosphorization: A General and Effective Approach. *Advanced Functional Materials*, **25**, 7530-7538. https://doi.org/10.1002/adfm.201503662

[37] Wu, M., Bai, J., Wang, Y., Wang, A., Lin, X., Wang, L., Shen, Y., Wang, Z., Hagfeldt, A. and Ma, T. (2012) High-Performance Phosphide/Carbon Counter Electrode for Both Iodide and Organic Redox Couples in Dye-Sensitized Solar Cells. *Journal of Materials Chemistry*, **22**, 11121-11127. https://doi.org/10.1039/c2jm30832k

[38] Lu, Y., Gua, C.D., Ge, X., Zhang, H., Huang, S., Zhao, X.Y., Wang, X.L., Tu, J.P. and Mao, S.X. (2013) Growth of Nickel Phosphide Films as Anodes for Lithium-Ion Batteries: Based on a Novel Method for Synthesis of Nickel Films using Ionic Liquids. *Electrochimica Acta*, **112**, 212-220. https://doi.org/10.1016/j.electacta.2013.09.035

[39] Fullenwarth, J., Darwiche, A., Soares, A., Donnadieu, B. and Monconduit, L. (2014) NiP_3: A Promising Negative Electrode for Li- and Na-Ion Batteries. *Journal of Materials Chemistry A*, **2**, 2050-2059. https://doi.org/10.1039/C3TA13976J

[40] Lin, Y., Sun, K., Liu, S., Chen, X., Cheng, Y., Cheong, W.C., Chen, Z., Zheng, L., Zhang, J., Li, X., Pan, Y. and Chen, C. (2019) Construction of CoP/NiCoP Nanotadpoles Heterojunction Interface for Wide PH Hydrogen Evolution Electrocatalysis and Supercapacitor. *Advanced Energy Materials*, **9**, Article ID: 1901213. https://doi.org/10.1002/aenm.201901213

[41] Zhang, N., Li, Y., Xu, J., Li, J., Wei, B., Ding, Y., Amorim, I., Thomas, R., Thalluri, S.M., Liu, Y., Yu, G. and Liu, L. (2019) High-Performance Flexible Solid-State

Asymmetric Supercapacitors Based on Bimetallic Transition Metal Phosphide Nanocrystals. *ACS Nano*, **13**, 10612-10621. https://doi.org/10.1021/acsnano.9b04810

[42] Vitry, V., Sens, A. and Delaunois, F. (2014) Comparison of Various Electroless Nickel Coatings on Steel: Structure, Hardness and Abrasion Resistance. *Materials Science Forum*, **783-786**, 1405-1413. https://doi.org/10.4028/www.scientific.net/MSF.783-786.1405

[43] Mandich, N.V. and Krulik, G.A. (1992) The Evolution of a Process: 50 Years of Electroless Nickel. *Metal Finishing*, **90**, 25-27.

[44] Karuppusamy, K. and Anantharam, R. (1992) Pit-Free Nickel Electroplating. *Metal Finishing*, **90**, 15-19.

[45] Okamoto, Y., Nitta, Y., Imanaka, T. and Teranishi, S. (1979) Surface Characterisation of Nickel Boride and Nickel Phosphide Catalysts by X-Ray Photoelectron Spectroscopy. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, **75**, 2027-2039. https://doi.org/10.1039/f19797502027

[46] Tiwari, A.P., Lee, K., Kim, K., Kim, J., Novak, T.G. and Jeon, S. (2020) Conformally Coated Nickel Phosphide on 3D, Ordered Nanoporous Nickel for Highly Active and Durable Hydrogen Evolution. *ACS Sustainable Chemistry & Engineering*, **8**, 17116-17123. https://doi.org/10.1021/acssuschemeng.0c05192

[47] Sun, T., Dong, J., Huang, Y., Ran, W., Chena, J. and Xu, L. (2018) Highly Active and Stable Electrocatalyst of Ni_2P Nanoparticles Supported on 3D Ordered Macro-/Mesoporous Co-N-Doped Carbon for Acidic Hydrogen Evolution Reaction. *Journal of Materials Chemistry A*, **6**, 12751-12758. https://doi.org/10.1039/C8TA03672A

[48] Ochs, D., Dieckhoff, S. and Cord, B. (2000) Characterization of Hard Disk Substrates (NiP/Al, Glass) Using XPS. *Surface and Interface Analysis*, **30**, 12-15. https://doi.org/10.1002/1096-9918(200008)30:1<12::AID-SIA770>3.0.CO;2-B

[49] NIST X-Ray Photoelectron Spectroscopy Database. https://srdata.nist.gov/xps/